VALUE-ADDED USE OF NON-WOOD BIOMASS COMBUSTION ASH TOWARDS PRODUCTION OF SUSTAINABLE, ECONOMICAL AND HIGH-PERFORMANCE GEOPOLYMER CONCRETE

By

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ABSTRACT

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Hydraulic cement formulations were developed with non-wood biomass ash as a primary raw material. These hydraulic cements meet the ASTM C1157 requirements for use as 'General Use' cements. Values of wheat straw, corn stalk, rice husk, and cotton gin combustion ashes as raw materials for production of hydraulic cements were demonstrated. These non-wood biomass ashes were thoroughly characterized in order to assess the contributions they can made towards an alkali aluminosilicate cement chemistry. Wheat straw, corn stalk and cotton gin ashes were found to provide notable quantities of silicon, potassium and calcium for processing of hydraulic cements. Rice husk ash has a distinct chemistry, and offers primarily reactive silica for use in production of hydraulic cements. Two abundant industrial byproducts, granulated blast furnace slag and coal fly ash, were used to supplement the chemistry of non-wood biomass ash as raw materials for production of an alkali aluminosilicate cement. Other raw materials, used in relatively small concentrations, included sources of alkalis, and additives for achieving improved dimensional stability and deicer salt scaling resistance. These raw materials were transformed into hydraulic cements using a sustainable and economical mechanochemical process. This process involves simple ball-milling of the blend of raw materials at room temperature. The raw materials formulations were refined and optimized in order to produce hydraulic cements that meet standard requirements.

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TABLE OF CONTENTS

LIST OF TABLES	ix
LIST OF FIGURES	xii
Chapter 1 Production and Characterization of Wheat Straw, Corn Stalk and Rice Hulk Ashes	1
1.1 Introduction	1
1.2 Materials and Methods	2
1.3 Characterization of Biomass Ash	5
1.3.1 Effects heat treatment conditions on the Wheat Straw Ash Properties	5
1.3.2 Elemental analysis (XRF)	6
1.3.3 Mineralogy (XRD)	8
1.3.4 Alkalinity and Total Dissolved Solids (TDS)	9
1.3.5 Thermogravimetric Analysis (TGA)	
1.3.6 Loss on Ignition (LOI)	12
1.3.7 Scanning Electron Microscopy	13
1.3.8 Alkali Solubility	16
1.3.9 Toxicity Measured Via Inductively Coupled Plasma Spectroscopy	17
Chapter 2 Development of a Sustainable Non-Wood Biomass Ash-Based Hydraulic Cement th Standard Requirements for General Use	1at Meets 20
2.1 Introduction	20
2.2 Mechanochemical Processing of Non-wood Biomass Ashe-Based Hydraulic Cements	22
2.3 Materials	24
2.4 Test Methods	26
2.5 Wheat Straw Ash-Based Hydraulic Cement Formulated with Lime Kiln Dust	28
2.5.1 Experimental Program	
2.5.2 Test Results and Discussion	29
2.6 Synthesis of Wheat Straw Ash-Based Hydraulic Cements with LKD and CaO	

2.6.1 Experimental Program	31
2.6.2 Test Results and Discussion	32
2.7 Synthesis of Wheat Straw Ash-Based Hydraulic Cement with Slag	33
2.7.1 Introduction	33
2.7.2 Experimental Program	33
2.7.3 Test Results and Discussion	34
2.8 Optimization of Wheat Straw Ash-Based Hydraulic Cement with Slag	36
2.8.1 Introduction	36
2.8.2 Optimization Experimental program	36
2.8.3 Test Results and Discussion	38
2.8.4 Optimization of the Raw Materials Formulation Through Response Surface Analysis of Results.	Test 42
2.9 Preliminary Evaluation of the Hydraulic Cement with Optimum Formulation Prepared with Difference Non-Wood Biomass Ashes	erent 48
2.9.1 Introduction	48
2.9.2 Experimental Program and Results	48
2.10 Formulation and Preliminary Evaluation of a Hydraulic Cement Formulated with Indust Produced Rice Husk Ash for Scaled-Up Production and Field Application	rially: 50
2.10.1 Introduction	50
2.10.2 Selection and Formulation of Raw Materials, and Processing of Hydraulic Cement	50
2.11 Characterization of Raw Materials and Hydraulic Cements	51
2.12 Thorough Characterization of the Preferred Hydraulic Cement Formulations Incorporating Combustion Ashes of Wheat Straw, Corn Stalk and Rick Husk	g the 57
2.12.1 Introduction	57
2.13 Dimensional Stability	57
2.13.1 Introduction	57
2.13.2 Experimental Program	58
2.13.3 Test Results and Discussion	59
2.14 Chemical Stability: Mortar Bar Expansion in Lime-Saturated Water	61
2.14.1 Experimental Program	61
2.14.2 Test Results and Discussion	63
2.15 Chemical Stability: Autoclave Expansion	66
2.15.1 Experimental Program	66

2.15.2 Test Results and Discussion	67
2.15.3 Heat of Hydration	

Chapter 3 Characterization of Concrete Materials Made with Hydraulic Cements Formulated Wood Biomass Ashes	with Non- 71
3.1 Concrete Mix Design	71
3.1.1 Introduction	71
3.1.2 Calculation of Water Film Thickness	72
3.2 Experimental Program	73
3.2.1 Test Results and Discussion	78
3.3 Concrete Compressive and Flexural Strengths Obtained with Different Non-Wood Bio Based Hydraulic Cements and Portland Cement	mass Ash- 79
3.3.1 Introduction	79
3.3.2 Experimental Program	79
3.3.3 Test Results and Discussion	82
3.4 Abrasion Resistance	
3.4.1 Introduction	84
3.4.2 Experimental Program	
3.4.3 Test Results and Discussion	
3.5 Bleeding Attributes	
3.5.1 Introduction	
3.5.2 Experimental Program	
3.5.3 Test Results and Discussion	
3.6 Sorptivity (rate of capillary water sorption)	
3.6.1 Introduction	
3.6.2 Experimental Program	
3.6.3 Test Results and Discussion	90
3.7 Acid Resistance of Non-Wood Biomass Ash-Based Hydraulic Cement Concrete	92
3.7.1 Experimental Program	92
3.7.2 Test Results and Discussion	92
3.8 Sulfate Resistances of Non-Wood Biomass Ash-Based Hydrualic Cement Concrete	94
3.8.1 Experimental Program	

3.8.2 Test Results and Discussion	95
3.9 Corrosion of Reinforcing Steel	96
3.9.1 Introduction	96
3.9.2 Experimental Program	97
3.9.3 Test Results and Discussion	
3.10 Freeze-Thaw Resistance	
3.10.1 Introduction	
3.10.2 Experimental Program	
3.10.3 Test Results and Discussion	
3.11 Deicer Salt Scaling Resistance	
3.11.1 Introduction	
3.11.2 Experimental Program	
3.11.3 Test Results and Discussion	
3.12 Fire Resistance	
3.12.1 Introduction	
3.12.2 Experimental Program	
3.12.3 Test Results and Discussion	

 Chapter 4 Design and Implementation of Scaled-Up Production of Hydraulic Cement, and Its Use in

 Industrial-Scale Concrete Production and Field Construction

 117

 4.1 Introduction

 117

 4.2 An Energy-Based Approach to Scale-Up of the Mechanochemical Process

 118

 4.3 Development of An Energy-Based Theory for Scale-Up of the Milling Process

 119

 4.3.1 Experimental Program

 123

 4.3.2 Test Results and Discussion

 124

 4.3.2.1 Particle Size Analysis

 125

 4.4 Field Evaluation and Demonstration

Chapter 5 Competitive Cost, Carbon Footprint and Energy Co	ontent Analyses of Non-Wood Biomass Ash-
Based Hydraulic Cements	
5.1 Introduction	

5.2	Cost Analysis	
5.2	2.1 Introduction	
5.2	2.2 Raw Materials Costs	
5.2	Processing Costs	
5.2	2.4 Total Initial Cost	
5.2	2.5 Carbon Footprint	
5.2	2.6 Energy Content	
Conclus	ions	139
REFEREI	NCES	

LIST OF TABLES

Table 1. Chemical properties of wheat straw ash after heat treatment. 6
Table 2. Chemical compositions (wt.%) of different non-wood biomass ashes obtained via XRF spectroscopy
Table 3. pH, TDS, and, Salinity of non-wood bottom 10
Table 4. The LOI values of non-wood biomass ashes and Class C coal fly ash13
Table 5. Alkali solubility test results for different non-wood biomass ashes. 17
Table 6. Concentrations of heavy metals and light elements in the leachates of non-wood biomass ashes.
Table 7. Standard performance specification for hydraulic cement
Table 8. Chemical compositions (wt.%) of the coal fly ash and granulated blast furnace slag used as raw materials for production of cement. 25
Table 9. The measured values of pH, conductivity, TDS, salinity and LOI for LKDs from different lime manufacture plants. 30
Table 10. Formulations of raw materials for the wheat straw ash-based hydraulic cements with different concentrations of CaO
Table 11. The raw materials formulation of the wheat straw ash based cement with slag
Table 12. Chemical composition of slag (weight %). 35
Table 13. The variables and their levels considered in the optimization experimental program37
Table 14. The raw materials formulations of the optimization experimental program
Table 15. The targeted levels of different performance attributes, and the weights associated to them44
Table 16. Optimum levels of the formulation variables. 45
Table 17. The predicted performance attributes and tht total raw materials cost of the wheat straw ash-basedhydraulic cement with optimum raw materials formulation.45
Table 18. The optimum raw materials formulation of the wheat straw ash-based hydraulic cement46
Table 19. The standard mortar mix proportions prepared with the optimized wheat straw ash-based hydraulic cement

Table 20. The mortar mix proportions prepared with different non-wood biomass ash-based hydraulic cements. 49
Table 21. Alternative hydraulic cement formulations incorporating industrially produced rick husk ash. 51
Table 22. Chemical compositions and LOI values of rice husk ash, coal fly ash, and blast furnace slag52
Table 23. Standard mortar mixtures prepared with
Table 24. Standard paste mix proportions used in drying shrinkage expansion tests on non-wood biomassash based hydraulic cement and Portland cement
Table 25. Standard mortar mix designs used in mortar bar expansion experiments
Table 26. Mortar bar expansion test results for hydraulic cements formulated wheat straw ash, corn stalk ash, and rice hulk ash, and also for Type I Portland cement (two specimens were tested for each cement).
Table 27. Autoclave expansion test results of high early strength cement based geopolymer. 68
Table 28. Designs of different concret emixtures prepared with the wheat straw ash-based hydraulic cement. 74
Table 29. Designs of concrete mixtures prepared with Type I Portland cement. 74
Table 30. Water film thickness values for different concrete mixtures prepared with wheat straw ash-based hydraulic cement. 76
Table 31. Concrete mix design. 79
Table 32. Abrasion test results. 86
Table 33. compressive strength test results for the rice husk ash (RHA)-based hydraulic cement concrete and Portland cement concrete.
Table 34. Compressive strength test results (MPa) for rice husk ash (RHA)-based hydraulic cement concrete and Portland cement concrete after different periods of sulfate attack versus the compressive strength test results produced after similar periods of storage in air
Table 35. The best cement formulation used to make specimens. 98
Table 36. The concrete mix proportions used in performance of corrosion tests. 99
Table 37. Concrete mix design. 106
Table 38. Visual appearances of concrete surfaces after exposure to different freeze-thaw cycles in the presence of deicer salt. 113
Table 39. Diameters, critical speed, and the optimum and test speeds of the laboratory- and pilot-scale ball mills used in this investigation

Table 40. Energy calculation parameters and results for the laboratory- and pilot-scale ball mills used in this investigation. 123
Table 41. The concrete mix design. 126
Table 42. Compressive strength test results for concrete specimens taken from the concrete truck 129
Table 43. Unit costs of the raw materials used in production of the non-wood biomass ashes based hydraulic cements. 132
Table 44. The non-wood biomass ash-based hydraulic cement formulation, and the corresponding raw materials and processing costs. 133
Table 45. The unit carbon footprints of the primary raw materials used in production of non-wood biomass ash-based hydraulic cements
Table 46. Calculation of the carbon footprint of the non-wood biomass ash-based class of hydraulic cements. 136
Table 47. Energy contents of supplementary raw materials. 138
Table 48. Cement formulation and the corresponding energy. 138

LIST OF FIGURES

Figure 1. The modified furnace used for combustion of biomass
Figure 2. Visual appearances of different non-wood biomasses and their combustion ashes prior to and after heat treatment
Figure 3. The kilns used for heat treatment of the ash resulting from low-temperature combustion of biomass.
Figure 4. Benchtop PH (and conductivity) meter
Figure 5. The Bruker S2 Ranger XRF spectrometer7
Figure 6. X-ray diffractometer
Figure 7. X-ray diffraction patterns for different non-wood biomass ashes
Figure 8. The pH measurement test setup10
Figure 9. The TGA test system
Figure 10. TGA/DTA test results for non-wood biomass ashes
Figure 11. The loss on ignition test setup
Figure 12. The scanning electron microscope and the sputter coater used in this investigation14
Figure 13. SEM images at different magnifications of non-wood biomass ashes
Figure 14. Test setups for measurement of alkali solubility
Figure 15. Sample preparation steps per 1316 toxicity test procedure
Figure 16. Inductively coupled plasma (Spectro Genesis) spectrometer
Figure 17. Examples of structural disordering [9]23
Figure 18. Magma-plasma model of mechanochemistry: E=exo-electrons; N=undeformed solid; D=highly deformed surface layer; P=plasma [9]24
Figure 19. Ball milling for input of mechanical energy24
Figure 20. XRD Patterns of the coal fly ash and granulated blast furnace slag used in this investigation. 26
Figure 21. Compression specimen molds and test setup27
Figure 22. Flow table test setup

Figure 23. The Vicat test apparatus
Figure 24. Heat of hydration test instrument
Figure 25. ASTM C1157 standard mortar compressive strength test results (means and standard errors) for wheat straw ash-based hydraulic cement formulations with LKDs from different lime manufacturing plants (and also with CaO)
Figure 26. Compressive strength test results obtained with wheat straw ash-based hydraulic cements with different replacement levels of lime kiln dust (LKD) with CaO
Figure 27. Compressive strength test results for wheat straw ash-based hydraulic cements formulated with 20% CaO (Mix-1) versus 25% slag and 4% CaO (Mix-2)
Figure 28. Effects of the optimization variables on the 3-day compressive strength of wheat straw ash-based hydraulic cements
Figure 29. The 3- and 7-day compressive strength test results for the wheat straw ash-based hydraulic cement formulations considered in the optimization experimental program
Figure 30. Effects of the optimization variables on the total raw materials cost of wheat straw ash-based hydraulic cements
Figure 31. The total raw materials costs of the wheat straw ash-based hydraulic cement formulations considered in the optimization experimental program
Figure 32. Effects of the optimization variables on the fresh mix flow of wheat straw ash-based hydraulic cements
Figure 33. The fresh mix flow test results of the wheat straw ash-based hydraulic cement formulations considered in the optimization experimental program
Figure 34. Response surfaces of the 3-day compressive strength for the wheat straw ash-based hydraulic cement
Figure 35. Response surfaces of the fresh mix flow for the wheat straw ash-based hydraulic cement43
Figure 36. Response surfaces of the total raw materials cost for the wheat straw ash-based hydraulic cement. 44
Figure 37. The 3- and 7-day compressive strength test results obtained with the optimized wheat straw ash- based hydraulic cement formulation versus Type I Portland cement
Figure 38. Compressive strength test results obtained with hydraulic cements formulated with different non- wood biomass ashes, and Type I Portland cement
Figure 39. XRD patterns of rice husk ash-based cement and its hydrates (Q: Quartz, P: Portlandite, and C: Calcite)
Figure 40. Typical SEM image of the rice husk ash-based hydraulic cement

Figure 41. TGA test results for rice husk ash and the hydraulic cement formulated with rice husk ash54
Figure 42. Compressive strength test results for different hydraulic cements formulated with rice husk ash, and for Portland cement
Figure 43. Mortar bar molds (a), length measurement (b), and specimens immersed in lime-saturated water (c)
Figure 44. Prismatic specimens of cements after 28 days of drying60
Figure 45. Drying shrinkage test results for different rice husk ash-based hydraulic cement formulations versus Portland cement
Figure 46. Drying shrinkage of of different wheat straw ash-based hydraulic cements versus Portland cement
Figure 47. Mortar bar expansion test specimens and experimental setups63
Figure 48. Visual appearance of prismatic specimens of hydaruic cements after 21 days of immersion in lime:saturated water: (a) Portland cement; (b) rice hulk ash-based cement; (c) wheat straw ash-based cement; and (d) corn stalk ash-based cement
Figure 49. Autoclave expansion test: (a) cement paste in prismatic molds; (b) autoclave67
Figure 50. Wheat straw ash-based hydraulic cement specimens prior to and after autoclae expansion experiments
Figure 51. The rate of heat release and the cumulative heat evolution versus time for hydraulic cements formulated with different non-wood biomass ashes
Figure 52. The excess water and paste film thickness principles
Figure 53. Particle size distributions of the wheat straw ash based cement (1), and the coarse (4) and fine (3) aggregates and standard silica sand (2) used in this study
Figure 54. (a) Limestone coarse aggregate with 19mm maximum particle size; (b) natural sand; (c) the laboratory-scale rotary drum mixe;, (d) planetary mortar mixer
Figure 55. Cylindrical concrete specimens with 75mm diameter and 150mm height made with wheat straw ash-based hydraulic cement (left) and Portland cement (right)
Figure 56. Compressive strength test results for concrete specimens prepared with Portland cement and wheat straw ash-based hydraulic cement at 3 and 7 days of age
Figure 57. Casting of flexure test specimens using concrete prepared with rice husk ash-based hydraulic cement
Figure 58. Compressive strength test specimens prepared with Portland cement or combustion ashes of different non-wood biomass, and the compression test setup

Figure 59. Flexure test specimens (after demolding) prepared with hydraulic cements formulated with the combustion ashes of different non-wood biomass
Figure 60. Flexure test setup
Figure 61. Size distribution of all granular matter used in industrial hulk ash based concrete versus the optimum modified Andreassen size distribution
Figure 62. Compressive strength test results of non-wood biomass ash based hydraulic cement and Portland cement concrete materials at 3, 7 and 28 days of age
Figure 63. A failed flexure test specimen83
Figure 64. Abrasion test system
Figure 65. The surface apperance of cocrete materials prepared with non-wood biomass ash-based hydraulic cements prior to and after abrasion testing
Figure 66. The test setup for measurement of bleed water
Figure 67. Bleeding test results for concrete materials made with Portland ceent and rice husk ash-based hydraulic cement
Figure 68. The moisture sorption test setup90
Figure 69. Capillary sorption test results concrete materials prepared with different hydraulic cements. 91
Figure 70. Initial sorption versus the square root of time
Figure 71. Concrete specimens prepared with different cement types immersed in 5% sulfuric acid solution. 92
Figure 72. Visual appearances under acid attack of Portland cement concrete versus rice husk ash-based hydraulic cement concrete
Figure 73. Rice husk ash-based hydraulic cement concrete (left) and Portland cement concrete (right) specimens fully immerse in sodium sulfate solution
Figure 74. The visual appearance of rice husk ash-based hydraulic cement concrete specimens after different periods of immersion in sodium sulfate solution
Figure 75. Corrosion test apparatus: (a) copper-copper sulfate reference electrode; (b) high impedance voltmeter
Figure 76. Schematics of the corrosion test apparatus101
Figure 77. The reinforced concrete specimens, and the setup used for their exposure to repeated cycles of wetting and drying

Figure 78. Corrosion potential data for steel bars embedded in concrete made with different hydraulic cements under exposure to repeated cycles of wetting and drying
Figure 79. Visual appearances of the reinforcing bars embedded in concrete materials prepared with different hydraulic cements after 16 weeks of exposure to repeated wet-dry cycles
Figure 80. The freeze-thaw test system: (a) freeze-thaw apparatus; (b) concrete specimens in the freeze-thaw apparatus, (c) resonant frequency test system
Figure 81. Visual appearances of concrete materials prepared with rice husk ash-based hydraulic cement and Portland cement prior to and after exposure to 100 cycles of freezing and thawing
Figure 82. Relative loss of the dynamic modulus of Portland cement and rice hulk ash cement based concrete materials versus the number of freeze-thaw cycles
Figure 83. Relative loss of the compressive strength of Portland cement and rice hulk ash cement based concrete materials versus the number of freeze-thaw cycles
Figure 84. Preparation and testing of a wheat straw ash-based hydraulic cement for evaluation of deicer salt scaling resistance
Figure 85. Exposure of concrte specimens to elevated temeprature for assessment of their fire resistance. 115
Figure 86. Visual appearance of non-wood biomass ash based concrete and Portland cement based concrete before exposure to 500°C and after exposure to 500°C temperature
Figure 87. Compressive strength test results after exposure to elevated temperatures116
Figure 88. The laboratory-sacle (a) and pilot-scale (b) ball mills used in this investigation
Figure 89. Sliding, cascading and centrifugal motions of balls in a milling far
Figure 90. Schematics of impacting balls
Figure 91. The pilot-scale ball mill, and the steel balls used in this mill
Figure 92. Particle size distributions of the hydraulic cements subjected to different periods of mechanochemical processing (milling)
Figure 93. Effects of the milling duration on the compressive strength obtained with the mechanochemically processed rice husk ash-based hydraulic ceent
Figure 94. The rice husk ash-based hydraulic cement produced at pilot scale
Figure 95. Addition of the rice husk ash-based hydraulic cement to the ready-mix concrete truck 127
Figure 96. Field pavement construction in November 2017
Figure 97. Measurement of fresh mix slump in field128

Figure 98. Placement and finishing of the rice husk ash-based hydraulic cement concrete
Figure 99. An SEM micrograph of the hydration products of the rice husk ash-based cement in the concrete used for field construction
Figure 100. CO ₂ emissions associated with production of Portland cement (U.S. DOE, 2003, Energy and Emission Reduction Opportunities for the Cement Industry, Washington DC, USA)
Figure 101. Relative contributions of different processing steps to the energy content of Portland cement [50]

Chapter 1

Production and Characterization of Wheat Straw, Corn Stalk and Rice Hulk Ashes

1.1 Introduction

The use of non-wood (e.g., wheat straw, corn stalk ash, and rice hulk ash) biomass as a sustainable fuel would benefit from development of value-added markets for the resulting combustion ash. Coal fly ash has found major applications as partial replacement for Portland cement in concrete. The high alkali content of non-wood biomass ash is an important drawback in this key application of conventional coal fly ash.

Considering the significant carbon footprint and energy content of Portland cement concrete, there is a growing trend towards use of alternative, more sustainable cementitious materials. Inorganic polymer (geopolymer) concrete is a prevalent alternative cementitious material with significant environmental and performance advantages over Portland cement concrete. Geopolymer concrete offers the potential to make value-added and large-volume use of the two key constituents (silica and alkali) of non-wood biomass ash. The work reported herein focuses on the development of new inorganic binder formulations and processing conditions which make value-added use of significant quantities of non-wood biomass ash towards development of high-performance and sustainable geopolymer concrete materials for construction applications.

Rice husk is a widely available agricultural residue in many rice producing countries. In 2014, global rice production w 744.5 million tones [1]. Rice husk is generated at about 20% of rice production rate. In most rice producing countries, much of the husk produced from processing of rice is either burnt or dumped as waste [2]. For every 1000 kg of paddy combusted in ambient condition, about 220 kg (22%) of husk is produced. When rice husk is burnt in the boilers, about

55 kgs (25%) of rice husk ash is generated. Rice husk is mostly used as fuel in boilers and in power plants. Those plants with 2-10 MW capacity range can become commercially viable, enabling more extensive use of this biomass resource. Production of 1MWh of electric energy consumes approximately 1 ton of rice husk. A combination of technical and economic factors govern the choice of rice hulk as fuel for power generation [3]. Rice husk and rice hulk ash have also been used as an alternative fuel in homes, cement and construction industries, ceramic and refractory industries, steel industry, formation of activated carbon; it is also used as a silica source, and in other applications [4].

Many biomass ashes have high silica contents, and are therefore suitable as a pozzolan for partial replacement of cement in Portland cement concrete. In this application, they would compete with coal fly ash, ground granulated blast furnace slag, rice husk ash, and silica fume. The global Portland cement production is more than 2 billion tons/yr; it is a major source of CO₂ emissions and energy use [5]. The use of pozzolans as partial replacement for Portland cement can lower the carbon footprint and energy content of Portland cement concrete. Among biomass ashes, only rice husk ash has found commercial use as a partial replacement for Portland cement. The chemical, mineralogical and variability attributes of other biomass ashes limit their potential in this application. A departure from the Portland cement chemistry, however, would enable value-added and large-volume use of non-wood and wood combustion ashes in cement production.

1.2 Materials and Methods

Wheat straw bales were obtained from farms in mid-Michigan (Lansing and Okemos). Corn stalk bales were obtained from a mid-Michigan (Muir) farm. Cotton gin was supplied by the USDA-ARS-CPPRU in Lubbock, Texas. Rice husk was obtained from Riceland Food Stuttgartm, Arkansas. Industrial rice husk ash was acquired from the Agree electric power plant in Lake Charls, LA, USA.

The collected non-wood biomass (wheat straw, corn stalk, rice husk, and cotton gin) were combusted separately in a modified furnace. Biomass was ignited, and allowed to burn by itself using the air blow supplied by a small fan over 3-4 hours. Maximum temperature of the combustion chamber reached 328°C for wheat straw. The amounts of bottom ash and fly ash produced in this furnace were 8-10% and about 0.5% by weight of biomass. Given the relatively low combustion temperature achieved in this furnace, which yielded (among other peculiarities) a relatively high loss-on-ignition, a second heat-treatment step was implemented in order to produce ashes that are more representative of those produced by biomass-burning power plants. In this second step, the bottom ash was subjected to heat treatment at 700°C for 2 hours in air in order to remove any remaining organic and volatile compounds. The visual appearances of few of the biomasses (rice husk, corn stalk and wheat straw), also their combustion ashes prior to and after heat treatment are shown in Figure 2.



Figure 1. The modified furnace used for combustion of biomass.

3

Rice hulk



Figure 2. Visual appearances of different non-wood biomasses and their combustion ashes prior to and after heat treatment.

Two types of kiln were used for heat treatment of the ash resulting from low-temperature combustion of biomass (Figure 3). The temperature and time period of heat treatment in the second step altered in order to investigate their effects on the non-wood biomass ash qualities such as pH, total dissolve solids (TDS), conductivity and salinity in solution as well as the loss on ignition (LOI). The solution used for performance of the pH, TDS, conductivity and salinity tests comprised 1 g of biomass ash and 100 mL of deionized water that was shaken for 1 hour when the tests were performed using a benchtop pH meter.



(a) Box kiln

(b) Round ceramic kiln

Figure 3. The kilns used for heat treatment of the ash resulting from low-temperature combustion of biomass.

1.3 Characterization of Biomass Ash

1.3.1 Effects heat treatment conditions on the Wheat Straw Ash Properties

The loss on ignition (LOI) as well as the pH, total dissolved solids and electrical conductivity (in solution) are presanted in Table 1 for wheat straw ashes obtained after different (second-step) heat treatment conditions. The biomass ash heat-treated in a box furnace contained more volitile organic and inorganic compounds. When an open kiln system (Amaco kiln) was used for the second-step heat treatment of ash, the measured values of LOI as well as the electrical conductivity and total dissolved solids (TDS) in solution, assessed using the instrument shown in Figure 4, decressed. For example, the TDS of wheat straw ash decressed from 4.486 ppm to 2.723 ppm. In biomass, the ash-forming matter can be present in four general forms: easily leachable salts, inorganic elements associated with the organic matter of biomass, minerals included in the fuel structure and inorganic material - typically salt. Alkaline metals are usually responsible for the pH and conductivity of ash in solution. These inorganic compounds are in the form of salts or bound in the organic matter.

Chemical Properties	Box type oven	Amaco kiln	Amaco kiln oven	
	(700 °C for 3	oven	(700 °C for 1.5	
	hr)	(700 °C for 3	hr)	
		hr)		
LOI	2.3%	1.29	1.26	
рН	11.56	11.26	11.32	
Conductivity	9.152	5.009	5.102	
(µs/cm)				
TDS (ppm)	4.486	2.456	2.723	

Table 1. Chemical properties of wheat straw ash after heat treatment.



Figure 4. Benchtop PH (and conductivity) meter.

1.3.2 Elemental analysis (XRF)

Elemental analysis was performed using the x-ray fluorescence (XRF) technique. A Bruker S2 Ranger XRF spectrometer (Figure 5) was used for elemental analysis. This equipment is capable of analyzing elements ranging from sodium (Na) to uranium. The x-ray source for this instrument is an x-ray tube with a palladium anode. It is a compact instrument with built-in vacuum pump. The evaluation method used for quantitative oxide quantitative analysis employed the Equa Oxides routine.



Figure 5. The Bruker S2 Ranger XRF spectrometer.

Table 2 presents the elemental composition of different non-wood biomass ashes. Wheat straw, corn stalk and cotton gin ashes are observed to have high contents of silica followed by potassium oxide and calcium oxide. The potassium content of these ashes, if released to the solution, could benefit the formation of hydraulic binders. The chemistry of rice husk ash is dominated by its very high silica content.

 Table 2. Chemical compositions (wt.%) of different non-wood biomass ashes obtained via XRF

 spectroscopy.

Non-Wood Biomass Ash	SiO ₂	CaO	Al ₂ O ₃	K ₂ O	MgO	P_2O_5	TiO ₂	Fe ₂ O ₃
Wheat straw ash	52.60	4.27	0.10	20.10	3.07	4.25	0.03	0.25
Corn stalk ash	51.10	11.20	6.40	15.70	3.20	2.51	0.01	3.80
Rice husk ash	90.20	0.60	0.01	2.30	0.10	1.03	0.02	0.03
Cotton gin ash	48.32	12.30	4.84	12.78	2.89	3.45	0.01	2.44

1.3.3 Mineralogy (XRD)

The mineralogy of non-wood biomass ashes was evaluated via x-ray diffraction (XRD) using a Rigaku Miniflex X-ray diffractometer equipped with Cu x-ray radiation operating at 30 kV and 15 mA (Figure 6). For the purpose of XRD analysis, samples were powderized using a pestle and mortar. The resultant powder was packed tightly and leveled in a sample holder. Peak intensities were obtained by counting with the detector every 0.05° (2 θ) /min. Powder XRD was carried out at a reflection angle range of $2\theta = 0-90^{\circ}$. Qualitative analysis of the XRD patterns led to identification of the mineral phases present in samples. The XRD analysis software (Jade 7 and Match Version 3) was used to analyze the XRD data in order to identify different phases by comparing the patterns of known compounds in a database versus those of the tested samples.



Figure 6. X-ray diffractometer.

Figure 7 shows the XRD patterns of non-wood biomass ashes. Rice huuk ash exhibits an amorphous structure with a broad peak around silica, which points at the prevalence of amorphous silica in the rice husk ash structure. Wheat straw ash exhibits a semi-crystalline structure marked by a broad peak. It also exhibits sharp peaks associated with crystalline calcite, quartz, and sylvite (KCl). Corn stalk ash exhibits a crystalline structure with peaks corresponding to quartz, calcite, sylvite and calcium silicate.



Figure 7. X-ray diffraction patterns for different non-wood biomass ashes.

Q: SiO₂ (Quartz), C: CaCO₃ (Calcite), and S: KCl (Sylvite)

1.3.4 Alkalinity and Total Dissolved Solids (TDS)

The alkalinity of non-wood biomass bottom ashes provide further insight into the active role they can play towards production of hydraulic cement. Contribution of alkalis by biomass ashes would be a favorable factor in formulation of raw materials. The chemical properties of rice hulk ash, corn stalk ash, and wheat straw ash were measured. The alkalinity of non-wood biomass ashes was measured in this experimental work through pH measurements of a solution comprising 1g of non-wood biomass ash mixed with 100 mL of deionized (DI) water, and stirred for 60 minutes. The solution was allowed to stand for 10 minutes (without stirring). Subsequently, the values of pH and total dissolved solids (TDS) of solution were measured. Figure 8 shows the pH and TDS measurement test setup. Table 3 presents the pH and TDS test data for the non-wood biomass ashes obtained after the second-step heat treatment.

All non-wood biomass ashes produced high pH levels upon addition to water. This suggests an initial fast release of alkali species deposited on the surface of the ashes, that would be followed by the diffusion-controlled release of species through the solid matrix. The main element contributing to the alkalinity of the solution appears to be potassium with some contribution from calcium, and a minor input from sodium [6, 7].



(a) Solution on shaker

(b) pH measurements

Figure 8. The pH measurement test setup.

Bottom ash	pН	TDS	
Wheat straw ash	12.30	4.32	
Corn stalk ash	11.93	4.10	
Rice hulk ash	10.02	3.28	

Table 3. pH, TDS, and, Salinity of non-wood bottom

1.3.5 Thermogravimetric Analysis (TGA)

TGA it is a method of determining the sample composition, including volatiles and inert fillers. In this test, the sample mass loss with increasing temperature is monitored, and compared with the thermal data for pure phases that are probably present in the sample. The mass loss curve obtained is transformed into the derivative form where weight losses are more visible. The TGA test system used in this investigation is sown in Figure 9.



Figure 9. The TGA test system.

The wheat straw, corn stalk, and rice husk ashes (after the second-step heat treatment) were subjected to thermogravimetric analysis. For this purpose, about 20 mg of sample was heated at a rate of 10°C/min in nitrogen environment. The TGA weight loss curves of wheat straw, corn stalk, and rice husk ashes are shown in Figure 10. The changes in sample weight reflect the material losses and the phase changes that occur at particular temperatures. The initial loss of mass around 100°C may be attributed to be to the loss of physically held water in ashes. The DTA peaks occurring between 150 and 200°C could have resulted from the decomposition of some carbonates as well as hydrates. The total mass loss when heated to 950oC varied significantly with the biomass ash type. It approached 15% and 6% for the corn stalk and the wheat straw ash considered here, and was about 2% for the rice husk ash.



Figure 10. TGA/DTA test results for non-wood biomass ashes.

1.3.6 Loss on Ignition (LOI)

LOI is the mass loss upon heating in oxygen or air up to a certain temperature. LOI is generally used to evaluate the concentration of carbon and organic matter in inorganic materials. In the presence of carbonates, depending on the maximum temperature, LOI can also reflect the concentration of carbonates in inorganic materials. The ASTM D7348 procedures were followed for measurement of LOI. Approximately 1 g of heat-treated biomass (bottom) ashes was placed in a pre-weighed crucible, and the test specimens were weighed to the nearest 0.1 mg. The specimens were then placed without cover in a furnace. Temperature was raised gradually to 500°C over a period of 1 hour. Heating was then continued to raise temperature from 500°C to 750 °C over a one-hour period. The peak temperature was maintained for an additional two-hour period [8]. Three specimens were tested for each non-wood biomass ash, and the average value of LOI was obtained. The specimens and the furnace used for measurement of LOI are shown in Figure 11.

Table 4 summarizes the LOI values measured for the non-wood biomass bottom ashes. High LOI is generally considered to indicate high carbon content. The LOI value measured for a coal fly ash classified as Class C for use as a supplementary cementitious material, is also presented in Table 4. The LOI values of the non-wood biomass ashes considered in this investigation are observed to be close to that of a coal fly ash that is suitable for use in concrete production as a supplementary cementitious material.



Figure 11. The loss on ignition test setup.

Table 4. The LOI values of non-wood biomass ashes and Class C coal fly ash.

Bottom non-wood biomass ashes	LOI,
	%
Wheat straw ash	2.32
Corn stalk ash	2.78
Rice hulk ash	1.89
Class C coal fly ash	1.73

1.3.7 Scanning Electron Microscopy

Scanning electronic microscope (SEM) inspections of different non-wood biomass ashes were carried out using a JELO-5000 SEM (Figure 12a). Samples were first coated with gold-palladium

alloy using a DESK II sputter coater (Figure 12b), and then imaged in the high-vacuum mode at an accelerating voltage of 10 or 15 kV.



(a) SEM



Figure 12. The scanning electron microscope and the sputter coater used in this investigation.

Figure 13 show SEM images of the non-wood biomass ashes at different magnifications. The ash particles are of irregular shape with curved or angular morphologies. Finer particles seem to have adhered to the coarser particles, which could have resulted from condensation on coarser particles during the ash formation process; this may have also been caused partly by the size reduction process.



(a) Rice husk ash (produced via industrial-scale combustion)



(b) Wheat straw ash



(c) Corn stalk ash

Figure 13. SEM images at different magnifications of non-wood biomass ashes.

1.3.8 Alkali Solubility

The alkali solubility of non-wood biomass ashes was assessed by first drying the ashes at 105°C. Alkali solubility was measured following Report C.D.2273 (Department of Scientific and Industrial Research of New Zealand). A sample of non-wood biomass ash (0.15 g) was added into a 300-mL nickel beaker. 200 mL of boiling 0.5M NaOH was poured into the nickel beaker, and the resulting suspension was brought back to boiling as quickly as possible. After boiling for 30 min, the suspension was cooled quickly with water, and filtered (0.2µm filter paper) via vacuum filtration. The residue was washed with cold water, and dried at 105°C over 18 hours. Weight of the undissolved material was then determined. The test setups used for measurement of alkali solubility are shown in Figure 14.



Magnetic stirrer Weighing filter paper Vacuum filtration set-up Figure 14. Test setups for measurement of alkali solubility.

The alkali solubility test results are presented in Table 5. The highest degree of alkali solubility was provided by corn stalk ash, followed closely by wheat straw ash. Rice husk ash, that was produced in an industrial-scale combustion facility, exhibited the lowest alkali solubility.

Biomass Ash	Alkali Solubility %
Rice husk ash	12.75
Wheat straw ash	27.43
Corn stalk ash	32.18

Table 5. Alkali solubility test results for different non-wood biomass ashes.

1.3.9 Toxicity Measured Via Inductively Coupled Plasma Spectroscopy

The elemental concentration of the biomass ashe leachates was investigated using the inductively coupled plasma spectroscopy technique (ICP-OES Spectrometer). The major trace elements which are present non-wood biomass ashes at detectable concentrations include Ag, As, Ba, Cu, Cr, Mn, Pb, Sr, V, Zn, which are in addition to major elements such as Si, Ca, Al, K, Na, Mg. Non-wood biomass ashes were tested in for assessment of the leaching of heavy metals in water. For this purpose, powder samples were mixed with deionized (DI) water (the leaching solution) at a solution/solid ratio of 20. The suspension was stirred for 18 hours, and the leachate was isolated via vacuum filtration. The concentration of leachate was assessed using inductively coupled plasma spectroscopy. Figure 15 shows the steps involved in preparation of samples for the performance of ICP test, and Figure 16 shows the ICP spectrometer.



Figure 15. Sample preparation steps per 1316 toxicity test procedure.



Figure 16. Inductively coupled plasma (Spectro Genesis) spectrometer.

The measured values of heavy metals concentration as well as Ca, Si, K, Na in leachates are presented in Table 6. The concentration of K (Potassium) ion in corn stalk ash is higher than in wheat straw and rice hulk ashes. The concentration of Na in cotton gin, wheat straw, and corn stalk ashes are >132.78, 0.795 and >32.073 mg/L, respectively. The heavy metals (Ag, Cd, Co, Ni) concentrations in the non-wood biomass ash leachates are minor, less than 0.009 ppm.

Table 6. Concentrations of heavy metals and light elements in the leachates of non-wood

Elements	Leachate Concentration (mg/L)					
	Wheat Straw Ash	Corn Stalk Ash	Rice Husk Ash	Cotton Gin Ash		
K	> 1980.79	> 5784.20	> 371.122	> 3250.80		
Na	0.795	> 32.073	5.292	> 132.748		
Al	< 0.049	< 0.049	< 0.049	< 0.049		
Mg	3.867	0.092	> 23.418	3.201		
Ti	< 0.002	< 0.002	< 0.002	< 0.002		
Cu	< 0.027	< 0.027	< 0.027	< 0.027		
Cd	< 0.003	< 0.003	< 0.003	< 0.003		
Со	< 0.005	< 0.005	< 0.005	< 0.005		
Ni	< 0.009	< 0.009	< 0.009	< 0.009		
Zn	< 0.009	< 0.009	1.027	< 0.009		
Ag	< 0.004	< 0.004	< 0.004	< 0.004		
Pb	< 0.025	< 0.025	< 0.025	< 0.025		
Se	< 0.051	< 0.051	< 0.051	< 0.051		
Be	< 0.000	< 0.000	< 0.000	< 0.000		
Мо	0.036	0.034	< 0.012	0.032		
Cr	< 0.004	< 0.004	0.37	11.462		

biomass ashes.
Chapter 2

Development of a Sustainable Non-Wood Biomass Ash-Based Hydraulic Cement that Meets Standard Requirements for General Use

2.1 Introduction

Efforts to develop one-part hydraulic cements based on the alkali aluminosilicate chemistry have been largely focused on the mechanical properties produced upon hydration. More efforts are needed to understand and improve the chemical composition of these cements, the effectiveness and efficiency of transforming the blends of raw materials into hydraulic cement, and thoroughly characterize these cements in order to qualify them based on the performance-based standards developed for hydraulic cements as 'General Use' cements for concrete production. The primary performance-based standard used in this work was ASTM C1157 (Standard Performance Specification for Hydraulic Cement). ASTM C1157 allows for unrestricted use of raw materials and processing methods to produce innovative hydraulic cements. Besides basic requirements, it also contains optional requirements that are not available under other specifications. The ASTM C1157 requirements are largely based on the performance limits of ASTM C150 (Standard Specification for Portland cement) and ASTM C595 (Standard Specification for Blended Hydraulic Cements). These two ASTM standards contain a combination of prescriptive and performance limits. In ASTM C1157, cements are classified into six types according to their intended use: GU ('General Use') for general construction, HE for high early strength, MS for moderate sulfate resistance, HS for high sulfate resistance, MH for moderate heat generation, and LH for low heat generation. The focus of this investigation is on development of hydraulic cements making value-added and large-volume use of wheat straw ash, rice hulk ash or corn stalk ash that meets the general use (GU) hydraulic cement requirements (Table 7).

ASTM C1157 represents a shift away from prescriptive specifications that dictate composition restrictions. Instead, the emphasis is on the ability of cement to perform. For example, in ASTM C150, the tricalcium aluminate (C₃A) content of Type II or V cement is prescriptively limited in order to control sulfate resistance. In ASTM C1157, the sulfate resistance of Type MS or HS cement is assured by actual testing for sulfate resistance per ASTM C1012. Laboratory tests, and not chemical analyses, are used as predictors for various aspects of the cement performance. Some key performance specifications considered in this project were: (i) compressive strength development with time; (ii) heat of hydration, and initial and final set times; (iii) change in length correlating with autoclave soundness (a measure of chemical stability); and (iv) expansion of mortar bar immersed in lime-saturated water (another measure of chemical stability). Scanning electron microscopy, thermogravimetry, calorimetry and x-ray diffraction techniques were employed to gain more insight into the hydration mechanisms and the microstructure of hydration products.

TABLE 1 Standard Physical Requirements							
Cement Type	Applicable Test Method	GU	HE	MS	HS	MH	LH
Fineness	C204, C430	A	A	A	A	A	A
Autoclave length change, max, %	C151	0.80	0.80	0.80	0.80	0.80	0.80
Time of setting, vicat test ^B	C191						
Initial, not less than, minutes		45	45	45	45	45	45
Initial, not more than, minutes		420	420	420	420	420	420
Air content of mortar volume, max, % ^C	C185	12	12	12	12	12	12
Compressive strength	C109/C109M						
minimum, MPa [psi] ^D							
1 day			12.0 [1740]				
3 days		13.0 [1890]	24.0 [3480]	11.0 [1600]	11.0 [1600]	5.0 [725]	
7 days		20.0 [2900]		18.0 [2610]	18.0 [2610]	11.0 [1600]	11.0 [1600]
28 days		28.0 [4060]			25.0 [3620]		21.0 [3050]
Heat of hydration	C186						
7 days, max, kJ/kg [kcal/kg]						290 [70]	250 [60]
28 days, max, kJ/kg [kcal/kg]							290 [70]
Mortar bar expansion	C1038						
14 days, % max		0.020	0.020	0.020	0.020	0.020	0.020
Sulfate expansion	C1012						
(sulfate resistance) ^E							
6 months, max, %				0.10	0.05		
1 year, max, %					0.10		
	Optio	nal Physical Requi	irements				
Option A—Air entraining ^{C,F}	C185						
Air content of							
mortar, vol %							
max		22	22	22	22	22	22
min		16	16	16	16	16	16
Option R-Low reactivity with	C227						
alkali-silica-reactive aggregates ^G							
Expansion at							
14 days, max, %		0.020	0.020	0.020	0.020	0.020	0.020
56 days, max, %		0.060	0.060	0.060	0.060	0.060	0.060
Early stiffening, final	C451	50	50	50	50	50	50
penetration, min,%							
Compressive strength, ^D 28 days, min, MPa	C109/C109M			28.0		22.0	
Drying shrinkage, %	C596	H		Н	Н	н	H

Table 7. Standard performance specification for hydraulic cement.

2.2 Mechanochemical Processing of Non-wood Biomass Ashe-Based Hydraulic Cements

Mechanochemistry refers to the chemical and physico-chemical changes of substances induced by the input of mechanical energy (e.g., via milling) [9]. Mechanical activation is a process involving an increase in the reactivity of a substance that remains chemically unchanged. The rise in reactivity associates with subtle changes in the solid structure, that occur primarily via structural disordering. Examples of structural disordering are shown in Figure 17; they can occur to different extents via input of mechanical energy. The rise in surface area and surface energy can also be categorized as examples of structural disordering that raise the reactivity of the substance.

Mechanochemical phenomena are enabled by the great quantity of energy that is set free instantaneously at the contact spot of colliding particles. This energy could produce a plasma state characterized by emission of fairly excited fragments of solid substance, electrons and photons over a short time scale (Figure 18). One can distinguish between chemical reactions that occur in the plasma and the (tribochemical) reactions taking place at the surface of particles during the significantly excited state or immediately after its expiration.

Input of mechanical energy was accomplished in this work via ball-milling at laboratory scale (Figure 19). A raw material: steel ball weight ratio of 1: 7 was used, with a milling duration of 2 hours.



Figure 17. Examples of structural disordering [9].



Figure 18. Magma-plasma model of mechanochemistry: E=exo-electrons; N=undeformed solid; D=highly deformed surface layer; P=plasma [9].





(a) Steel milling jar(b) Steel balls of different size*Figure 19. Ball milling for input of mechanical energy.*

2.3 Materials

Coal fly ash was obtained in dry condition from a power plant operated by the Lansing Board of Water and Light in Lansing, Michigan. The loss-on-ignition (LOI) of this fly ash was 1.7%, and its mean particle size was measured at 10.9 µm via laser granulometry.

The granulated blast furnace slag used in this investigation was obtained from Lafarge-Holcim. This slag has a specific gravity of 2.90 and a bulk density of 1,225 kg/m³.

Table 8 presents the chemical compositions, determined by x-ray fluorescence (XRF) spectroscopy, of the coal fly ash and granulated blast furnace slag used to prepare the hydraulic

cement. The coal fly ash used here had silica and alumina contents totaling 66.4 wt.%, with 19.3% calcium oxide content. It also incorporated some alkali metal cations. In the case of slag, silica and calcium oxides constituted about 75% of total mass, and the weight ratio of silica to calcium oxide was close to 1. The alkali metal content of this slag was relatively low (<1 wt.%).

Table 8. Chemical compositions (wt.%) of the coal fly ash and granulated blast furnace slagused as raw materials for production of cement.

	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	Na ₂ O	MgO
Coal fly ash	43.05	19.30	23.33	7.82	1.72	0.90	1.43
Granulated Blast Furnace Slag	37.53	40.78	9.54	0.47	0.21	0.25	10.85

The X-ray diffraction patterns for the coal fly ash, slag and albite used in this investigation are presented in Figure 20. The coal fly ash was found to be largely amorphous with two main crystalline mineral phases, namely quartz (SiO₂) and mullite (3Al₂O₃.2SiO₂). The crystalline phase quartz in coal fly ash is less reactive than the other ash constituents. It is, however, found to provide some chemical reactivity in an alkaline environment [10], and once finely ground, can provide nucleation sites for dispersed formation of the hydration products. The presence of quartz has been reported to enhance the rate of hydration reactions at early age [11]. The XRD pattern for the slag points at its predominantly glassy state, with peaks associated with crystalline akermanite (2CaO.MgO₃.SiO₂) identified.



Figure 20. XRD Patterns of the coal fly ash and granulated blast furnace slag used in this investigation.

Reagent grade sodium hydroxide, sodium silicate, quick lime (CaO) and sodium tetra-borate were purchased in powder form at 97-98% purity from Sigma Aldrich.

2.4 Test Methods

<u>Compressive strength</u> tests at early age were performed per ASTM C109 as the primary means of determining the quality of non-wood biomass ashes-based hydraulic cements . These tests were performaned on mortar specimens per ASTM C1600 (Figure 21a shows the molds for mortar test specimens) and concrete materials per ASTM C39. Compression tests were performed at different ages (generally 3, 7, and 28 days). Figure 21b shows the compression test setup.



(a) Molds (50x50x50mm) (b) Test setup

Figure 21. Compression specimen molds and test setup.

<u>Flow table</u> tests (ASTM C1437) were performed using the apparatus shown in Figure 22 in order to assess the fresh mix rheology, considering that ASTM C1157 requires performance of various tests on standard mortar mixtures that provide a flow of 110 ± 5 .



Figure 22. Flow table test setup

<u>Initial and final set times</u> were measured using the Vicat test apparatus (ASTM C191) shown in Figure 23.



Figure 23. The Vicat test apparatus.

The <u>heat of hydration</u> of different hydraulic cements and the control Portland cement was measured per ASTM C186 using an I-cal 2000 HPC calorimetry test equipment (Figure 24). Immediately before the test, 30 g of hydraulic cement was mixed with sufficient amount of water (depends on the w/c ratio of concrete) by hand for a fixed length of time. The paste was then placed inside the calorimeter, and heat release was monitored for 2 days.



Figure 24. Heat of hydration test instrument.

2.5 Wheat Straw Ash-Based Hydraulic Cement Formulated with Lime Kiln Dust

2.5.1 Experimental Program

Four types of lime kiln dust (LKD) were considered in this experimental work. These LKDs were characterized, and theif effects on the 3- and 7-day compressive strengths of geopolymer mortars were evaluated. The pH, total dissolved solids (TDS), conductivity and salinity of the lime kiln dusts obtained from four different lime manufacturing plants were evaluated for solutions comprising 1 wt.% LKD in deionized water (after shaking for 1 hours and resting for 10 minutes). The LKDs were also characterized per ASTM C110. In order to obtain their loss-on-ignition (LOI), there were first pre-heated at 110°C for 1 hour, and were then heated in a muffler furnace at 400°C for 30 minutes, and then at 1000°C for 30 minutes. The weight loss (after the initial pre-heating) was measured as the loss-on ignition.

The wheat straw ash-based hydraulic cements were formulated (with different LKDs) using wheat straw ash: coal fly ash: LKD: NaOH: tartaric acid at 35: 35: 25: 5: 1 weight ratios. The blends of raw materials were transformed into hydraulic cement via input of mechanical energy in a ball mill. The ball mill jar was 280 mm in diameter with 300 mm length. The steel balls used in the process comprised balls of 50 mm 35 mm: 25 mm diameter at 20: 30: 30 weight ratios. The weight ratios of steel balls to raw materials was 10. The total weight of steel balls and raw materials added to the jar for each milling process was 11 kg. The mill was operated at a rotational speed of 50 rpm over a period of two hours.

2.5.2 Test Results and Discussion

The measured values pH, conductivity, total dissolved solids (TDS), salinity and loss-on-ignition (LOI) are presented in Table 9. The pH values of these LKDs occur within the 12.42-12.94 range. The ranges covered by their conductivity, TDS, salinity and LOI are relatively broad. Their LOIs range from 16.71 to 34.26, which could be attributed to the decomposition of carbonates (rather than organic carbon) at elevated temperatures. These results point at the relatively high variability of LKDs obtained from different lime manufacturing plants.

Table 9. The measured values of pH, conductivity, TDS, salinity and LOI for LKDs from different

	Lime K	iln Dust f	rom differ	ent lime	
Chemical properties	manufacture plants				
	LKD-1	LKD-2	LKD-3	LKD-4	
рН	12.94	12.70	12.57	12.42	
Conductivity (ms/cm)	8.71	5.43	6.94	4.70	
TDS (PPT)	4.27	2.68	3.40	2.30	
Salinity (Psa)	4.90	3.00	3.85	2.56	
LOI (ASTM C110)	16.71	28.32	20.93	34.26	

lime manufacture plants.

Figure 25 presents the compressive strength test results for the wheat straw ash-based hydraulic cements formulated with the LKDs obtained from different plants. The effect of LKD types on the compressive strength of wheat straw ash-based hydraulic cement mortars are observed to vary significantly depending upon the type of LKD. For comparison purposes, lime kiln dust was replaced by reagent grade calcium oxide. This replacement is shown in Figure 25 to produce the highest compressive strengths. The formulation with the lime kiln dust LKD-1 produced the second highest levels of compressive strength. Considering that CaO is the primary chemical composition of different LKDs (per XRF data), the degree of solubility of different LKDs could be a key factor governing their performance. The strengths obtained with LKDs that produce solutions of higher alkalinities. It is worth mentioning that the 3- and 7-day strengths obtained with

cements synthesized using LKD-1 are close to (but still smaller than) the ASTM C1175 requirements of 13 and 21 MPa, respectively, for 'General Use' (GU) grade of cement.



Figure 25. ASTM C1157 standard mortar compressive strength test results (means and standard errors) for wheat straw ash-based hydraulic cement formulations with LKDs from different lime manufacturing plants (and also with CaO).

2.6 Synthesis of Wheat Straw Ash-Based Hydraulic Cements with LKD and CaO

2.6.1 Experimental Program

In this series of experiments, wheat straw ash-based hydraulic cement was synthesized with LKD-2 and CaO. Four different formulations were considered (Table 10), with different weight fractions of LKD replaced with CaO. The approach to processing of these hydraulic cements was similar to that described earlier. The hydraulic cements were characterized per ASTM C1157 using largely a mortar mix comprising cement: standard sand: water at 1: 2.75: 0.4 weight ratios, that produced similar flows of 20 cm with different cement types (ASTM C115).

Table 10. Formulations of raw materials for the wheat straw ash-based hydraulic cements with

	Weight Fraction					
	Mix-1	Mix-2	Mix-3	Mix-4		
Raw Materials	20%	15%	10%	5%		
	CaO	CaO	CaO	CaO		
Wheat straw ash	35	35	35	35		
Coal fly ash	35	35	35	35		
LKD-2	5	10	15	20		
CaO	20	15	10	5		
NaOH	5	5	5	5		
Tartaric acid	1	1	1	1		

different concentrations of CaO.

2.6.2 Test Results and Discussion

The effect of CaO content on the compressive strength of wheat straw ash-based hydraulic cement mortar at 3 and 7 days of age are presented in Figure 26. The compressive strength of mortar increased with increasing CaO content. For example, the 3-day compressive strength of mortar decreased from 13 MPa (Mix-1) to 7 MPa (Mix-4) as the CaO-to-LKD ratio decreased from 4 to 0.25. Replacement of lime kiln dust (a waste material) with calcium oxide carries penalties in terms of cost and carbon footprint. Therefore, attempts were made to further refine the wheat straw ash-based hydraulic cement formulations.



Figure 26. Compressive strength test results obtained with wheat straw ash-based hydraulic cements with different replacement levels of lime kiln dust (LKD) with CaO.

2.7 Synthesis of Wheat Straw Ash-Based Hydraulic Cement with Slag

2.7.1 Introduction

Ground granulated blast furnace slag, a byproduct of iron production, offers a desired balance of chemical composition and reactivity for use as partial replacement for Portland cement in concrete. It also offers a desired chemistry for development of calcium-rich alkali aluminosilicate hydraulic cements following the procedures followed in this project. Slag was considered as a replacement for LKD and CaO; it can contribute calcium to the solution, and can also act as a supplementary aluminosilicate precursor. The high variability of lime kiln dust was a factor that encouraged development of raw materials formulations without the use of LKD.

2.7.2 Experimental Program

A desired chemical composition could be obtained using the raw materials formulation introduced in Table 11. This formulation comprises largely of byproducts (wheat straw and coal fly ash, and slag), with minor concentrations of alkalis (sodium hydroxide and calcium oxide), and tartaric acid. The blend of raw materials was processed via ball-milling as described earlier. The standard mortar mixture prepared with this cement comprised cement: standard sand: water at 1: 2.75: 0.36 weight ratios; this mix design provided 19 cm fresh mix flow, that falls within the range required by ASTM C1157.

Materials	Weight Fraction
Wheat straw ash	35
Coal fly ash	35
Ground granulated blast furnace slag	25
NaOH	5
Additives (4% CaO and 1% Tataric acid)	5

Table 11. The raw materials formulation of the wheat straw ash based cement with slag.

2.7.3 Test Results and Discussion

Chemical analyses of blast furnace slags have generally pointed at the presence of four major oxides (lime, magnesia, silica and alumina), which make up about 95% of the slag chemistry. Minor elements that are present in blast furnace slag include sulfur, iron, manganese, alkalis, and trace amounts of several others. Free lime or free oxides of calcium and/or magnesium are also present in granulated blast furnace slag, which are dissolved in water as it percolates through the granulated slag after rapid cooling. The chemical composition of the blast furnace slag used in this investigation (Table 12) was determined using x-ray fluorescence (XRF) spectroscopy.

Slag	SiO ₂	Al ₂ O 3	CaO	Fe ₂ O 3	MgO	K ₂ O
	37.53	9.54	40.78	0.47	10.85	0.45

Table 12. Chemical composition of slag (weight %).

The 3- and 7-day compressive strength test results produced for standard mortars are presented in Figure 27. The highest compressive strengths were obtained with the formulation incorporating 25% slag and 4% CaO (Mix-2). The 3- and 7-day compressive strength test results for this formulation were 15 MPa and 24 MPa respectively, which meet the ASTM C1157 requirements for 'General Use' (GU) class of hydraulic cements.



Figure 27. Compressive strength test results for wheat straw ash-based hydraulic cements formulated with 20% CaO (Mix-1) versus 25% slag and 4% CaO (Mix-2).

2.8 Optimization of Wheat Straw Ash-Based Hydraulic Cement with Slag

2.8.1 Introduction

The non-wood biomass ashe-based hydraulic cements developed in the project were formulated with supplementary ingredients (slag, NaOH, CaO, etc.). The proportions of raw materials were selected based on chemical considerations and trial-and-adjustment experimental studies. A systematic experimental effort was undertaken in order to devise optimum formulations of raw materials. The optimization experimental program was designed using the Box-Bhenken principles.

2.8.2 Optimization Experimental program

The optimization experimental program was designed using the Box-Bhenken design procedure in the SYSTAT® statistical analysis software. Three variables were considered in this optimization program (slag, NaOH and CaO contents). The viable ranges of these variables, established empirically, are presented in Table 13. The resulting experimental program comprised 15 geopolymer binder formulations (Table 14). Only wheat straw ash was used in this optimization experimental program. All formulations were processed mechanochemically via ball milling, as described earlier. The resulting hydraulic cements were evaluated based on their 3- and 7-day compressive strengths per ASTM C1157, and also their total raw materials costs. The water/cement ratios presented in Table 14 were determined to yield the required fresh mix flow for standard mortar mixtures per ASTM C1157.

Factor	Materials	Level -	Level 0	Level 1
		1		
A	Slag wt.%	15	25	35
В	NaOH wt.%	2.5	5.0	7.5
С	CaO wt.%	2.5	5.0	7.5

Table 13. The variables and their levels considered in the optimization experimental program.

	Quantity (%)			Variables	Water/Cement		
No.	Wheat Straw	Coal Fly	Tartaric	Slag	NaOH	CaO	
	Ash	Ash	acid	%	%	%	Ratio
1	38.75	38.75	1	15	2.5	5.0	0.46
2	28.75	28.75	1	35	2.5	5.0	0.46
3	36.25	36.25	1	15	7.5	5.0	0.45
4	26.25	26.25	1	35	7.5	5.0	0.46
5	38.75	38.75	1	15	5.0	2.5	0.46
6	28.75	28.75	1	35	5.0	2.5	0.44
7	36.25	36.25	1	15	5.0	7.5	0.46
8	26.25	26.25	1	35	5.0	7.5	0.45
9	35.00	35.00	1	25	2.5	2.5	0.45
10	32.50	32.50	1	25	7.5	2.5	0.45
11	32.50	32.50	1	25	2.5	7.5	0.44
12	30.00	30.00	1	25	7.5	7.5	0.45
13	32.50	32.50	1	25	5.0	5.0	0.45
14	32.50	32.50	1	25	5.0	5.0	0.44
15	32.50	32.50	1	25	5.0	5.0	0.45

Table 14. The raw materials formulations of the optimization experimental program.

2.8.3 Test Results and Discussion

The trends in the effects of the optimization variables on the 3-day compressive strength test results are summarize in Figure 28. The 3-day compressive strength increased gradually with increasing

CaO content; it peaked at an intermediate slag content, and experienced a minor drop as the NaOH content was raised above an intermediate level. Figure 29 presents the 3- and 7-day compressive strength test results for different wheat straw ash-based hydraulic cement formulations. Higher compressive strengths were produced by Formulations 4, 11, 12, 13, 14 and 15. The compressive strengths obtained with these formulations exceeded the minimum values of 13 and 20 MPa specified by ASTM C1157 for the 'General Use' (GU) class of hydrualic cement.

The effects of different variables on the raw materials costs of the hydraulic cements are summarized in Figure 30. Slag, NaOH and CaO are the costly constituents of these formulations; the raw materials costs are thus observed to increase with increasing concentrations of these constituents. The total raw materials costs of all the formultions considered in the optimization experimental program are presented in Figure 31.

The water/cement ratios of the standard mortar mixtures made with each hydraulic cement formulation were adjusted to yield comparable fresh mix flows per ASTM C1157 (see Table 14). As a result, the fresh mixtures prepared with different hydraulic cement formulations exhibited minor variations in flowability (Figure 32 and Figure 33).



Figure 28. Effects of the optimization variables on the 3-day compressive strength of wheat straw ash-based hydraulic cements.



Figure 29. The 3- and 7-day compressive strength test results for the wheat straw ash-based hydraulic cement formulations considered in the optimization experimental program.



Figure 30. Effects of the optimization variables on the total raw materials cost of wheat straw ash-based hydraulic cements.



Figure 31. The total raw materials costs of the wheat straw ash-based hydraulic cement formulations considered in the optimization experimental program.



Figure 32. Effects of the optimization variables on the fresh mix flow of wheat straw ash-based

hydraulic cements.



Figure 33. The fresh mix flow test results of the wheat straw ash-based hydraulic cement formulations considered in the optimization experimental program.

2.8.4 Optimization of the Raw Materials Formulation Through Response Surface Analysis of Test Results.

The response surfaces obtained for the 3-day compressive strength, fresh mix flow and total raw materials costs of the alkali aluminosilicate cement formulated with wheat straw ash are presented in Figure 34, Figure 35 and Figure 36, respectively. Optimization of the formulation variables was performed using the targeted levels of 3- and 7-day compressive strength, cost and fresh mix flow introduced in Table 15; all these attributes were assigned equal weights in the optimization process. The optimum levels of the three formulation variables, derived based on the analysis of test results, are presented in Table 16. The predicted performance levels of the cement prepared with this optimum formulation are presented in Table 17.



Figure 34. Response surfaces of the 3-day compressive strength for the wheat straw ash-based

hydraulic cement.



Figure 35. Response surfaces of the fresh mix flow for the wheat straw ash-based hydraulic

cement.



Figure 36. Response surfaces of the total raw materials cost for the wheat straw ash-based hydraulic cement.

Table 15. The targeted levels of different performance attributes, and the weights associated to

them.

Response	Aim	Lower Level	Target	Upper Level	Weight
3-Day Compressive Strength, MPa	Maximize	13.0	15.0		1.0
7-Day Compressive Strength, MPa	Maximize	20.0	25.0	•	1.0
Raw Materials Cost, \$	Minimize		35.0	45.0	1.0
Fresh Mix Flow, cm	Target	19.0	21.0	24.0	1.0
	_				

		Stationary Point			
	Factor	Coded	Un-coded		
1	Slag	0.630	31.305		
2	NaOH	-0.667	3.333		
3	CaO	-0.240	4.399		

Table 16. Optimum levels of the formulation variables.

Table 17. The predicted performance attributes and tht total raw materials cost of the wheat straw ash-based hydraulic cement with optimum raw materials formulation.

Property	Optimal Response	95% Co Inte	Desirability	
		Upper	Lower	
3-Day Compressive Strength, MPa	15.000	4.496	25.504	1.000
7-Day Compressive Strength, MPa	25.009	8.873	41.144	1.000
Fresh Mix Flow, cm	19.365	19.046	19.685	0.183
Total Raw Materials Cost, \$	38.553	-	-	0.645

The optimum variables identified above yield the raw materials formulation presented in Table 18. This formulation was processed into a hydraulic cement by input of mechanical energy as described earlier. A standard mortar mixture with the proportions presented in Table 19 were prepared per ASTM C1157 with the optimized wheat straw ash-based hydraulic cement. A fresh mix flow of 19 cm was obtained for this mortar prepared at a water/cement ratio of 0.38. The 3-

and 7-day compressive strengths obtained with this cement exceeded those obtained with the Type I Portland cement (Figure 37), and easily met the ASTM C1157 requirements for the 'General Use' (GU) class of hydraulic cement.

Table 18. The optimum raw materials formulation of the wheat straw ash-based hydraulic

Materials	Proportion, wt.%
Wheat straw ash	30%
Coal Fly Ash	30%
Slag	31.305
NaOH	3.333
CaO	4.399
Tartaric acid	1

cement.

Table 19. The standard mortar mix proportions prepared with the optimized wheat straw ash-

Materials	Proportion by Weight
Wheat straw ash-based hydraulic cement	1
Standard silica sand	2.75
Water	0.38





Figure 37. The 3- and 7-day compressive strength test results obtained with the optimized wheat straw ash-based hydraulic cement formulation versus Type I Portland cement.

2.9 Preliminary Evaluation of the Hydraulic Cement with Optimum Formulation Prepared with Different Non-Wood Biomass Ashes

2.9.1 Introduction

Among the non-wood biomass ashes considered in this investigation, those resulting from combustion of wheat straw and corn stalk have similar chemistries, and rice husk ash offers a distinct chemical composition. The optimum hydraulic cement formulation developed with wheat straw ash was also prepared by replacing wheat straw ash with the combustion ashes of corn stalk and cotton stalk. The compressive strength attributes of the resulting hydraulic cements were compared with that of Type I Portland cement.

2.9.2 Experimental Program and Results

Hydraulic cements prepared mechanochemically using the raw materials formulations of Table 18, except that wheat straw ash was replaced with either corn stalk ash or cotton stalk ash. The standard mortar mix proportions prepared with the water/cement ratio adjusted to yield the fresh mix flow that occurs within the range required by ASTM C1157 are presented in

Table 20. The water requirement of the non-wood biomass ash-based hydraulic cement were comparable, and distinctly lower than that of Type I Portland cement.

The 3- and 7-day compressive strength test results obtained with different hydraulic cements are presented in Figure 38. The compressive strengths provided by the cements formulated with what straw ash and corn stalk ash are observed to exceed that provided by Type I Portland cement. The hydraulic cement formulated with cotton stalk ash, on the other hand, falls short of Type I Portland cement in terms of 3- and 7-day compressive strength. Its 3-day compressive strength fails to meet the ASTM C1157 requirement. It should be noted that cotton stalk ash was not studied extensively in this development work. The optimization experimental program needs to be repeated with each specific ash in order to derive viable formulations for their use as raw materials for production of hydraulic cements.

Table 20. The mortar mix proportions prepared with different non-wood biomass ash-based

Materials	Proportions by Weight						
	Wheat straw ash	Corn stalk ash	Cotton stalk ash	Portland cement			
Hydraulic cement	1	1	1	1			
Standard silica sand	2.75	2.75	2.75	2.75			
Water	0.38	0.40	0.37	0.46			
Fresh mix flow, cm	19	20	19	20			

hydraulic cements.



Figure 38. Compressive strength test results obtained with hydraulic cements formulated with different non-wood biomass ashes, and Type I Portland cement.

2.10 Formulation and Preliminary Evaluation of a Hydraulic Cement Formulated with Industrially Produced Rice Husk Ash for Scaled-Up Production and Field Application

2.10.1 Introduction

Rice husk ash was obtained from a power plant that uses rice husk as fossil fuel. A hydraulic cement formulation was developed with this ash, and was produced at pilot scale. This hydraulic cement was used for production of concrete at industrial scale, and implementation of field construction projects.

2.10.2 Selection and Formulation of Raw Materials, and Processing of Hydraulic Cement

Industrial rice husk ash (RHA) was obtained from the Agrilectric power plant in Lake Charles, LA, USA. Coal fly ash (Class C) was obtained from the Erickson power plant operated by the Lansing Board of Water and LIght in Lansing, MI (USA). Granulated blast furnace slag was supplied by LafargeHolcim, OH (USA). Reagent grade NaOH, Sodium metasilicate (Na₂SiO₃), Sodium Carbonate (Na₂CO₃), calcium oxide (CaO), and tartaric acid were obtained from Sigma-Aldrich. Standard silica sand was obtained from Certified Materials Testing Products, FL (USA). Rice husk ash is rich in silica (~90 wt.%), lacking adequate alumina and alkali contents for processing into an alkali aluminosilicate hydraulic cement. In order to produce a desired chemical balance for geopolymerization, coal fly ash and slag were used to supplement the chemistry of rice husk ash for achieving a desired silica-to-alumina ratio. Sodium hydroxide, sodium silicate and sodium carbonate were considered as sources of alkalis. Lime kiln dust of calcium oxide were also used as sources of calcium (to supplement that provided by slag and coal fly ash). Table 21 introduces different raw materials formulations evaluated for production of hydraulic cements making value-added and large-volume use of the industrially produced rick husk ash. These raw materials formulations were transformed into hydraulic cement mechanochemically via 2 hours of ball-milling.

Table 21. Alternative hydraulic cement formulations incorporating industrially produced rick

husk ash.

	Formulation, wt.%				
Materials					
	1	2	3	4	5
Industrial rice husk ash	35	30	30	30	30
Class C coal fly ash	35	30	30	35	35
Granulated blast furnace slag	-	30	26	20	20
LKD	25	-	-	-	-
CaO	-	5.0	4.0	5.0	4.0
NaOH	4.5	4.5	4.5	4.5	4.5
Na ₂ SiO ₃	-	-	5.0	5.0	3
Na ₂ CO ₃	-	-	-	-	3
Tartaric acid	0.5	0.5	0.5	0.5	0.5

2.11 Characterization of Raw Materials and Hydraulic Cements

The raw materials used in this investigation, and the hydraulic cement formulated with rice husk ash were characterized using the XRF, XRD, TGA, SEM, and LOI test techniques. The compressive strength development characteristics of the hydraulic cement were also evaluated per ASTM C1157.

The oxide analyses of rice husk ash (RHA), coal fly ash and slag are presented in **Error! Reference source not found.** together with their loss on ignition (LOI). The chemistry of rice husk ash is observed to be dominated by silica; its minor potassium oxide content could also be of value. Coal fly ash is rich in silica, alumina, calcium oxide and iron oxide, with minor potassium oxide and magnesium oxide contents. The blast furnace slag has relatively high calcium oxide and silica contents, with moderate alumina and magnesium oxide contents. The loss on ignition of rice husk ash (4.98%) was higher than those of coal fly ash (1.96%) and slag (0.30%).

Table 22. Chemical compositions and LOI values of rice husk ash, coal fly ash, and blast furnace

Raw materials	Chemical composition (%)					LOI (%)	
	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	
Rice husk ash	90.0	0.01	0.60	0.03	2.30	0.12	4.98
Coal fly ash	30.56	15.06	22.18	16.82	2.6	2.3	1.96
Slag	37.53	9.54	40.78	0.43	0.45	10.85	0.30

S	1	a	Q
υ	v	n	~

The XRD patterns of the investigated hardened ternary alkali aluminosilicate hydraulic cement paste cured for 28 days (Figure 39) show peaks characteristics to Portlandite (CH) at around 28, and 36 theta. Quartz and calcite are also present in the hydrated ternary alkali aluminosilicate cement paste. The XRD pattern of the non-hydrated cement shown in Figure 39 points at a less crystalline structure incorporating crystalline quartz.



Figure 39. XRD patterns of rice husk ash-based cement and its hydrates (Q: Quartz, P: Portlandite, and C: Calcite).

Figure 40 presents a typical SEM image of the rice husk ash-based hydraulic cement produced in this investigation. The hydraulic cement particles were found to be finer than the original rice husk ash particles. This could be due to the mechanochemical process adopted here for production of cement. The coal fly ash particles could still be identified among cement particles, as well as small fragments of rice husk ash and granulated blast furnace slag particles.



Figure 40. Typical SEM image of the rice husk ash-based hydraulic cement.

The thermogravimetric analysis (TGA) was performed by heating a sample in nitrogen atmosphere up to 950°C at a heating rate of 15°C/min using a TGA-4000 Perkin-Elmer instrument. The weight of sample was monitored throughout the heating process. The TGA data presented in Figure 41 indicate that rice husk ash and the hydraulic cement formulated with rice husk ash experienced 8.5% and 7% weight loss, respectively, when heated to 950°C in nitrogen. The bulk of weight loss occurred within the 450-700°C temperature range.



Figure 41. TGA test results for rice husk ash and the hydraulic cement formulated with rice husk

ash.

The hydraulic cements formulated and processed with the industrially produced rice husk ash were also characterized in order to evaluate their performance versus the ASTM C1157 requirements [12]. Most these tests were performed on mortar mixtures prepared per ASTM C109 with a standard silica sand-to-cement weight ratio of 2.75, using an adequate amount of water to produce the required fresh mix flow. The required water/cement ratios for the hydraulic cements considered in this series of tests ranged from 0.50 to 0.52 (Table 23). Portland cement was used as control in these tests. The mortar mixture was prepared by mixing the dry ingredients (hydraulic cement and standard silica sand) in a planetary mixer (Hobart Model A200F) for 2 minutes. Water was then added, and mixing was continued for 3 more minutes at medium speed. The specimens were then cast into steel molds, sealed and stored at room temperature for 24 hours. They were then demolded, and cured at 23°C and 95±5% relative humidity for different time period (3, 7 and 28 days for performance of compression tests).

	Formulation					
Material					Portland cement	
	1	2	3	4	5	
Hydraulic cement, g	330	330	330	330	330	330
Standard sand, g	908	908	908	908	908	908
Water/cement ratio	0.5	0.52	0.5	0.5	0.5	0.5
Flow, cm	19	19	19	19	19	19

Table 23. Standard mortar mixtures prepared with .
The experimental results presented in Figure 42 indicate that hydraulic cement formulations Mix-5, Mix-4 and Mix-3 produce compressive strengths that are comparable with those obtained with Type I Portland cement. The formulations designated Mix-2 and particularly Mix-1, however, fall short in terms of early-age and 28-day compressive strengths. The highest compressive strengths were provided by Mix-5 that incorporated sodium carbonate, sodium silicate and sodium hydroxide as sources of alkali and soluble silica (see Table 21). The formulations designated Mix-2 and Mix-1, that did not perform favorably, lacked sodium silicate (with only sodium hydroxide used as the source of alkali). The worst performance was exhibited by Mix-1 that incorporated lime kiln dust as replacement for slag and calcium oxide. The favorable performance of Mix-5 could be attributed to its particular combination of the soluble sodium, calcium and silicon compounds.



Figure 42. Compressive strength test results for different hydraulic cements formulated with rice husk ash, and for Portland cement.

2.12 Thorough Characterization of the Preferred Hydraulic Cement Formulations Incorporating the Combustion Ashes of Wheat Straw, Corn Stalk and Rick Husk

2.12.1 Introduction

The requirements to be met by hydraulic cements are not limited to compressive strength. Dimensional and chemical are some key ASMT C1157 performance requirements for hydraulic cements. The requirements relevant to dimensional stability relate to the drying shrinkage movements measured per ASTM C596. Measurement of mortar bar expansion per ASTM C1038 and autoclave expansion per ASTM C151 are some key considerations relevant to the chemical stability of hydraulic cements.

2.13 Dimensional Stability

2.13.1 Introduction

Measurement of drying shrinkage per ASTM C596 concerns length change of starndard mortar bars during drying. When cementitious materials are exposed to their service environment, they tend to reach equilibrium with the environment. Given the excess moisture content that is used, beyond the chemically required amount of moisture, to ensure adequate fresh mix workability, reaching equilibrium with typical ambient conditions generally involves loss of moisture. While the loss of moisture kept in the interior of larger pores does not involve volume change, shrinkage occurs upon loss of the physically adsorbed water from cured cementitious materials. The first water to be lost during drying is that held in larger capillary pores, which does not cause significant volume change. Subsequent loss of physically held water from finer pores, however, produces drying shrinkage. Excess drying shrinkage, when restrained internally (due to gradient moisture content) or externally (e.g., by bonding of pavement to sublayer), can cause cracking. If the drying shrinkage of hydraulic cement is comparable to (or preferably less than) that of Portland cement, then measures taken to control shrinkage cracking of Portland cement concrete would be adequate for concrete materials made with the new hydraulic cements. Shrinkage of concrete at early age is generally considered to be critical to the long-term durability of concrete structures [13-15]. Most of the drying shrinkage occurs during the first few months after casting of concrete. Several factors such as aggregate properties, water/cement ratio, the chemistry of cementitious materials, and the curing environment influence the shrinkage behavior of geopolymer concrete [16, 17]. Different additives such as limestone powder, Polyethylene glycol, and gypsum have been used to control drying shrinkage [18, 19]. Limestone powder which is used to reduce the heat of cement hydration and shrinkage of concrete.

2.13.2 Experimental Program

The drying shrinkage of non-wood biomass ash-based hydraulic cement was measured per ASTM C596. For this purpose, prismatic mortar bars of 25mmx25mmx279mm dimensions were prepared using a standard mortar mix (Table 24). Immediately after consolidating the mortar into molds, they were stored in a humid chamber for 24 hours at room temperature. The specimens were then demolded and cured in lime-saturated water for 48 hours. The specimens were then removed from lime-saturated water bath, and their initial length was measured using a length comparator. They were subsequently stored in air at 50±5% relative humidity for 25 days, after which the final length of specimens was measured. Figure 43 shows the molds, length measurement apparatus and the immersed specimens used in the drying shrinkage tests. Different additives such as limestone powder, polyethylene glycol, and gypsum were introduced into the formulations of hydraulic cements incorporating wheat straw or rice husk ash in order to reduce the resulting drying shrinkage.

 Table 24. Standard paste mix proportions used in drying shrinkage expansion tests on non-wood
 biomass ash based hydraulic cement and Portland cement.

	Non-wood biomass ash based hydraulic cement				
Mix Constituents	Corn stalk ash-	Wheat straw ash-	Rice husk ash-	Portland	
Mix Constituents	based hydraulic	based hydraulic	based hydraulic	1 01 11 4114	
	cement	cement	cement	cement	
Hydraulic Cement	750 g	750 g	750 g	750 g	
Silica Sand	1500 g	1500 g	1500 g	1500 g	
Water/Cement Ratio	0.45	0.40	0.50	0.45	



Figure 43. Mortar bar molds (a), length measurement (b), and specimens immersed in lime-

saturated water (c).

2.13.3 Test Results and Discussion

Figure 44 shows the visual appearances of the mortar specimens after 28 days of drying. No indications of microcracking or cracking could be detected on the specimen surfaces. The drying shrinkage test results are presented in Figure 45 and Figure 46. The alkali aluminosilicate cements

formulated with rice husk ash or what straw ash, when used without any additives for shrinkage control, are observed to produce drying shrinkage movements that are significantly higher than that obtained with Portland cement. Introduction of limestone powder at 5 wt.%, however, lowered the drying shrinkage of both the hydraulic cements formulations with wheat straw ash or rice husk ash to levels that were comparable with that of Portland cement. Polyethylene glycol (PEG), that was evaluated with the rice husk ash-based hydraulic cement, was partly effective in reducing drying shrinkage. The effectiveness of limestone powder in reducing the drying shrinkage of the resultant hydraulic cement can be attributed to its effects on the particle size distribution of cement, and the role in its surface area in nucleating hydration reactions and thus enhancing the homogeneity and refining the pore size distribution of the hydration products. PEG, on the other hand, forms hydrogen bonds with water molecules and reduces the vapor pressure [18].



Wheat straw ash

Rice hulk ash

Figure 44. Prismatic specimens of cements after 28 days of drying.



Figure 45. Drying shrinkage test results for different rice husk ash-based hydraulic cement

formulations versus Portland cement.



Figure 46. Drying shrinkage of of different wheat straw ash-based hydraulic cements versus

Portland cement.

2.14 Chemical Stability: Mortar Bar Expansion in Lime-Saturated Water

2.14.1 Experimental Program

The non-wood biomass ash-based hydraulic cements developed in the project as well as Type I Portland cement were subjected to mortar bar expansion tests per ASTM C1038. The blend of raw materials was subjected to ball-milling over two hours in order to produce the hydraulic cement.

The mortar mix design (Table 25) was prepared, with water content selected to produce a flow of 21 cm (after 25 drops per ASTM C1437). The fresh mix was molded into 25mmx25mmx279mm (1inx1in) prismatic bars (with end pins placed in bars for length measurement using a length comparator). The molds used for preparation of mortar bar specimens with end pins are presented in Figure 47a. Immediately after consolidation of the fresh standard mortars in these molds, they were stored in a humid chamber for 22.5 hours at room temperature. They were then demolded and placed in a water bath for 30 minutes prior to the initial length measurement. The specimens were then immersed in lime-saturated water, and length measurements were made at 1 and 14 days of age. The relative length changes of mortar bars were calculated to the nearest 0.001% of the effective gage length.

Mir	Hydraulic Cement Type				
	Formulated with	Formulated with	Formulated with	Portland	
Constituents	Corn Stalk Ash	Wheat Straw Ash	Rice Husk Ash	Cement	
Hydraulic	500 g	500 g	500 g	500 g	
Cement	500 g	500 g	500 g	500 g	
Standard Sand	1375 g	1375 g	1375 g	1375 g	
Water/Cement	0.45	0.45	0.55	0.47	
Ratio					

Table 25. Standard mortar mix designs used in mortar bar expansion experiments.



(a) Mortar bar mold (b) Mortar bar specimens (c) Length comparator

Figure 47. Mortar bar expansion test specimens and experimental setups.

2.14.2 Test Results and Discussion

The mortar bar expansion test results for hydraulic cements formulated with wheat straw ash, corn stalk ash, and rice husk ash are presented in Table 26. Figure 48 shows the physical appearances of mortar bar specimens made with hydraulic cements formulated with different non-wood biomass ashes after 21 days of immersion in lime-saturated water. Considering that ASTM C1157 specifies a maximum limit of 0.02% for mortar bar expansion after 14 days, the hydraulic cements developed in the project using different non-wood biomass ashes as a primary raw material easily met this requirement. The mortar bar expansions obtained with Portland cement were lower than those obtained with the hydraulic cements formulated with non-wood biomass ashes.

Table 26. Mortar bar expansion test results for hydraulic cements formulated wheat straw ash,corn stalk ash, and rice hulk ash, and also for Type I Portland cement (two specimens were

<i>Hydraulic cement type</i>	Mortar bar expansion, %		
	7 Days	14 Days	
Portland cement-1	0.0007	0.0023	
Portland cement-2	0.0007	0.0031	
Wheat straw ash based cement-1	0.0118	0.0123	
Wheat straw ash based cement-2	0.0135	0.0148	
Corn stalk ash based cement-1	0.0090	0.0090	
Corn stalk ash based cement-2	0.0160	0.0160	
Rice hulk ash based cement-1	0.0060	0.0110	
Rice hulk ash based cement-2	0.0012	0.0150	

tested for each cement).





(b)



Figure 48. Visual appearance of prismatic specimens of hydaruic cements after 21 days of immersion in lime:saturated water: (a) Portland cement; (b) rice hulk ash-based cement; (c) wheat straw ash-based cement; and (d) corn stalk ash-based cement.

2.15 Chemical Stability: Autoclave Expansion

2.15.1 Experimental Program

Autoclave expansion tests were performed on paste bar specimens prepared per ASTM C151 using the non-wood biomass ash-based hydraulic cement developed in the project. Type I Portland cement was also tested as control. The pastes prepared with Type I Portland cement, and hydraulic cements formulated with wheat straw ash, corn stalk ash and rice husk ash required water/cement ratios of 0.33, 0.28, 0.30 and 0.34, respectively, for producing the fresh mix flow required by the ASTM standard. The fresh pastes were placed in 25mmx25mmx279mm (1inx1inx11in) prismatic molds with end pins (Figure 49a). Immediately after consolidation, the paste specimens were placed in a humid chamber for 24 hours at room temperature, after which their initial lengths were measured. The specimens were then placed in an autoclave (Figure 49b), and subjected to 2.05 MPa steam pressure over 3 hours. Subsequently, the autoclave was allowed to cool down over 1.5 hours. The specimens were subsequently placed in a boiling water bath where cool water circulated the bars at a uniform rate. After 15 minutes, the specimens were removed from the water bath, and their final lengths were measured. The relative length change of specimens was calculated to the nearest 0.01% of the effective gage length.



Figure 49. Autoclave expansion test: (a) cement paste in prismatic molds; (b) autoclave.

2.15.2 Test Results and Discussion

The autoclave expansion test results for Portland cement and different non-wood biomass ashbased hydraulic cements are presented in Table 27. All the hydraulic cements considered here meet the ASTM C1157 requirement of 0.8 % maximum autoclave expansion. Figure 50 shows the physical appearances of the wheat straw ash-based cement bars before and after autoclave expansion testing. The specimens retained their integrity in this test, and no signs of microcracking or other forms of damage could be detected.

Hydraulic Cement	Autoclave Expansion	
	(%)	
Portland cement-1	0.125	
Wheat straw ash based cement-1	0.169	
Wheat straw ash based cement-2	0.192	
Rice hulk ash based cement-1	0.287	
Rice hulk ash based cement-2	0.256	
Corn stalk ash based cement-1	0.219	
Corn stalk ash based cement-2	0.208	

Table 27. Autoclave expansion test results of high early strength cement based geopolymer.



(a) Before

(b) After

Figure 50. Wheat straw ash-based hydraulic cement specimens prior to and after autoclae expansion experiments.

2.15.3 Heat of Hydration

Heat of hydration tests (that are referred to in ASTM C1157) were performed per ASTM C186 for hydraulic cements formulated with corn stalk and rice husk ashes; the water-to-cement ratios used in these mixes ranged from 0.4 to 0.5. A calorimetry test instrument was used, and the exothermic heat release was monitored over 2 days.

The heat of hydration of hydraulic cement reflects upon the intensity of exothermic reactions at each point in time. Figure 51 presents the rates of heat evolution and the cumulative heat release versus time for the hydraulic cements synthesized with corn stalk and rice hulk ashes. An exothermic peak appeared immediately when water was added to cement, which has been generally attributed to the instant absorption of solution on the surface of cement particles, dissolution of highly soluble compounds (e.g. NaOH), and hydration of CaO [20]. This observation indicates that the phenomena noted above are preceded in a continuous way with the exothermic hydration reactions without appearance of any dormant period. The hydraulic cement formulated with corn stalk ash reached the maximum value of cumulative heat release more rapidly than that formulated with rice husk ash. The total heat released peaked at 110-130 J/g, which were lower than the maximum heat release values of 290 and 250 J/g allowed by ASTM C1157 after 7 days for moderate heat of hydration (MH) and low heat of hydration (LH) hydraulic cements, respectively. ASTM C1157 does not specify a maximum value of exothermic heat release for the General Use (GU) hydraulic cement.



(a) Hydraulic cement formulated with rice husk ash



(b) Hydraulic cement formulated with corn stalk ash

Figure 51. The rate of heat release and the cumulative heat evolution versus time for hydraulic cements formulated with different non-wood biomass ashes.

Chapter 2

Characterization of Concrete Materials Made with Hydraulic Cements Formulated with Non-Wood Biomass Ashes

3.1 Concrete Mix Design

3.1.1 Introduction

The work presented in this section focused on development of mix designs for the non-wood biomass ash-based hydraulic cement concrete. The approach to mix design emphasized achievement of viable levels of excess water and paste thicknesses in order to achieve desired levels of fresh mix workability and hardened material strength.

Water plays a lubricating role in fresh concrete. All (cement and aggregate) particles in fresh mix should receive a continuous coating of water. The water film thickness formed on particles is a key factor determining the fresh mix workability [21]. In normal- and high-strength concrete materials, the available water fills the void space between particles, and also forms a continuous film on the particle surfaces (Figure 52a). An optimum water film thickness should provide adequate workability without excessively separating the particles to raise the porosity of the cementitious binder and thus lowering its strength [22-24].

Given the brittle nature of the cementitious paste, it needs to make a continuous coating on aggregates in order to render desired binding effects. The paste should fill the void space between fine and coarse aggregates before it can effectively coat the aggregate particles. The excess paste theory views the thickness of the excess paste, beyond that required for filling of voids between fine and coarse aggregates (Figure 52b), as a parameter influencing the fresh mix and the hardened material qualities.



Figure 52. The excess water and paste film thickness principles.

An experimental program was performed in order to derive the viable levels of excess water film thickness for concrete materials prepared with hydraulic cements formulated with non-wood biomass ash.

3.1.2 Calculation of Water Film Thickness

Water film thickness can be calculated by dividing the volume of water beyond that required to fill the paste voids by the surface area of particles. The solid concentration in concrete mix can be calculated by dividing the total mass of solids (cement + fine aggregate + coarse aggregate) to the total mass (cement + fine aggregate + coarse aggregate + water). The minimum voids content can then be calculated as:

Minimum voids content $(U_{min}) = 1$ – Solid concentration

The excess water ratio $(U_{w'})$ can be calculated using the following equation, where $U_{w'}$ is the excess water ratio, and U_{w} is the water ratio defined as the volume of water to the volume of solid particles.

Excess water ratio $(U_{w'}) = U_{w} - U_{min}$

The specific surface area of cement powder, fine aggregates and coarse aggregates can be calculated as follows:

Specific surface area
$$A_s = A_{CEMENT} \times R_{CEMENT} + A_{FA} \times R_{FA} + A_{CA} \times R_{CA}$$

Where A_{CEMENT}, A_{FA} and A_{CA} are the specific surface areas of the cement powder, fine aggregate and coarse aggregate, respectively, and R_{CEMENT}, R_{FA}, and, R_{CA} are the volumetric ratios of cement, fine aggregate, coarse aggregate, respectively. The specific surface area is the ratio of the surface area of solid particles to the total solid volume of the mixture.

The excess water film thickness can then be calculated as:

Excess water film thickness =
$$U_{w'}/A_s$$

3.2 Experimental Program

Concrete mixtures were prepared with different cement contents and water/cement ratios. The hydraulic cement formulated with wheat straw ash was used in this series of tests, and Type I Portland cement was used as control. The concrete mix designs considered in this experimental program are introduced in

Concrete specimens were prepared by changing cement composition of wheat straw ash based hydraulic cement and Portland cement separately. The concrete mix designs were presented in Table 28 and Table 29, respectively. The water/cement ratio of each mix was adjusted to produce similar levels of fresh mix workability defined by a slump of 100 mm.

Table 28. Designs of different concret emixtures prepared with the wheat straw ash-based

Mix	Cement	Total Aggregate	Fine Aggregate	Coarse Aggregate	Water/Cement Ratio
1	10%	90%	36%	54%	0.55
2	15%	85%	34%	51%	0.43
3	20%	80%	32%	48%	0.35
4	25%	75%	30%	45%	0.30
5	30%	70%	28%	42%	0.31
6	35%	65%	26%	39%	0.32

hydraulic cement.

Table 29. Designs of concrete mixtures prepared with Type I Portland cement.

Mix	Cement	Total Aggregate	Fine Aggregate	Coarse Aggregate	Water/Cement Ratio
1	10%	90%	36%	54%	0.55
2	15%	85%	34%	51%	0.43
3	20%	80%	32%	48%	0.35
4	25%	75%	30%	45%	0.30
5	30%	70%	28%	42%	0.31
6	35%	65%	26%	39%	0.32

The values of water film thickness were calculated for each of the mixture introduced above. For this purpose, the particle size distributions of cement, coarse aggregate and fine aggregate, presented in Figure 53 were used. Crushed limestone with 19.5 mm maximum particle size (Figure 54a) was used as coarse aggregate. Natural sand (Figure 54b) was used as fine aggregate. Coarse and fine aggregates were evaluated in oven dried condition. The calculated values of excess water film thickness are presented in Table 30 for different concrete mixtures prepared with wheat straw ash-based hydraulic cement and Portland cement.



Figure 53. Particle size distributions of the wheat straw ash based cement (1), and the coarse (4) and fine (3) aggregates and standard silica sand (2) used in this study.

Table 30. Water film thickness values for different concrete mixtures prepared with wheat straw

Mix Comont		Water film thickness, µm			
IVIIA	Cemeni	Wheat Straw Ash-Based Cement	Type I Portland Cement		
1	10%	0.43	0.40		
2	15%	0.31	0.26		
3	20%	0.20	0.18		
4	25%	0.15	0.11		
5	30%	0.09	0.06		
6	35%	0.03	0.02		

ash-based hydraulic cement.

Concrete mixtures were prepared using a rotary drum mixer of 0.035 m³ capacity (Figure 54c). Cylindrical specimens with 75mm diameter and 150 mm height were cast, cured at room temperature in sealed condition, and subjected to compression testing at 3, 7 and 28 days of age. Figure 55 shows the concrete specimens made with wheat straw ash-based hydraulic cement and Portland cement.



(a)

(b)



Figure 54. (a) Limestone coarse aggregate with 19mm maximum particle size; (b) natural sand; (c) the laboratory-scale rotary drum mixe;, (d) planetary mortar mixer.



Figure 55. Cylindrical concrete specimens with 75mm diameter and 150mm height made with wheat straw ash-based hydraulic cement (left) and Portland cement (right).

3.2.1 Test Results and Discussion

Figure 56 presents the compressive strength test results at 3 and 7 days of age. The trends in the effects of water film thickness on the compressive strength of concrete were similar for which straw ash-based hydraulic cement and Portland cement. At 3 days of age, the concrete compressive strength peaked at an excess water film thickness of about 0.1-0.15 and 0.1 micrometer for wheat straw ash-based hydraulic cement and Portland cement, respectively. At 7 days of age, compressive strength peaked at about 0.15 and 0.2 micrometer excess water film thickness for concrete materials made with wheat straw ash-based hydraulic cement and Portland cement, respectively. The optimum moisture content (excess water film thickness) seems to be smaller for wheat straw ash-based hydraulic cement when compared with Portland cement. These trends are consistent with those reported in the literature f where an excess water film thickness of about 0.09 micrometer has been found to be optimum [25]. The values of concrete compressive strength obtained with wheat straw ash-based hydraulic cement and Portland cement are comparable at 3 and 7 days of age considered here.



(a) 3 days

(b) 7 days

Figure 56. Compressive strength test results for concrete specimens prepared with Portland cement and wheat straw ash-based hydraulic cement at 3 and 7 days of age.

3.3 Concrete Compressive and Flexural Strengths Obtained with Different Non-Wood Biomass Ash-Based Hydraulic Cements and Portland Cement

3.3.1 Introduction

Concrete materials were prepared with similar mix designs at a water/cement ratio of 0.5 with Portland cement and also with hydraulic cements formulated with the combustion ashes of wheat straw, corn stalk, and rice husk. The water/cement ratio of 0.5 used here is greater than the optimum levels established in the previous section.

3.3.2 Experimental Program

The preliminary concrete mix design introduced in Table 31 was used to prepare concrete specimens with Portland cement and the hydraulic cements formulated with rice hulk ash, wheat straw ash, and corn stalk ash. The EMMA software was used for proportioning the individual granular matter, considering their particle size distributions, in order an overall particle size distribution approaching the modified Andreassen model for realizing high levels of packing density.

Materials	Quantity,
	Kg
Non-wood biomass ash based cement	2.00
Fine aggregates (Natural sand)	3.50
Coarse aggregates (19 mm)	4.50
Water/cement	0.5

Table 31. Concrete mix design.

A laboratory-scale rotary drum mixer was used to prepare homogenous fresh concrete mixtures. First, cement and sand were added to the mixer and dry-mixed for 1 minute. Subsequently, half of the mixing water was added, and mixing was continued for 1 minute. One-quarter of water was then added followed by one more minute of mixing. The remainder of water was added next, and mixing was continued for 3 more minutes. Subsequently, coarse aggregate was added followed by 2 minutes of mixing. These mixtures were cast into 75mmx150mm cylindrical molds and 75mmx75mmx275mm prismatic molds (Figure 57) for preparation of compression (ASTM C39) and flexure (ASTM C78) test specimens, respectively. Molded specimens were consolidated via external vibration at medium speed for 2 minutes. The fresh mix workability was measured using the flow table test method per ASTM C1473.





Figure 57. Casting of flexure test specimens using concrete prepared with rice husk ash-based hydraulic cement.

The compression specimens were cured for 3, 7 and 28 days in sealed condition (at 95±5% relative humidity) prior to testing using a hydraulic compression test system (Figure 58). Flexure test specimens (Figure 59) were subjected to four-point loading on a displacement-controlled (screw-driven) test system (Figure 60).



(a) Portland cement (b) Corn Stalk (c) Wheat straw (d) Rice stalk (e) Test setup
 Figure 58. Compressive strength test specimens prepared with Portland cement or combustion ashes of different non-wood biomass, and the compression test setup.



(a) Rice husk

(b) Corn stalk

Figure 59. Flexure test specimens (after demolding) prepared with hydraulic cements formulated with the combustion ashes of different non-wood biomass.



Figure 60. Flexure test setup.

3.3.3 Test Results and Discussion

Figure 61 shows the particle size distribution of all the granular matter used in concrete versus the optimum modified Andreassen optimum size distribution produced using the EMMA software (Elkem Materials). The modified Andreassen model of particle size distribution optimizes the packing density of the granular matter. The particle size distribution deviates from the modified Andreassen model, which points at the need for further optimization of the size distribution of the granular matter.



Figure 61. Size distribution of all granular matter used in industrial hulk ash based concrete versus the optimum modified Andreassen size distribution.

The compressive strength test results at different ages for concrete materials prepared with different non-wood biomass ash-based hydraulic cements and with Portland cement are summarized in Figure 62. The concrete compressive strengths obtained with the hydraulic cements formulated with non-wood biomass ashes at 3, 7 and 28 days are not notably different from those obtained with Portland cement. Given the prominent role of compressive strength as a measure of concrete quality, this finding provide support for the value of non-wood biomass ash-based hydraulic cements as replacement for Portland cement in concrete production.



Figure 62. Compressive strength test results of non-wood biomass ash based hydraulic cement and Portland cement concrete materials at 3, 7 and 28 days of age.

Figure 63 shows the typical appearance of a failed flexure test specimen. The 7-day flexural strengths obtained with wheat straw ash-based cement, and Portland cement were 4.7 and 3 MPa, respectively. These results provide further support for the competitive merits of the non-wood biomass ash-based hydraulic cements developed in the project when compared with Portland cement.



Figure 63. A failed flexure test specimen.

3.4 Abrasion Resistance

3.4.1 Introduction

Abrasive effects induce friction and rubbing that can cause significant damage to the concrete surface [26]. Abrasion resistance can be defined as the ability of a surface to resist being worn away by rubbing or friction. The abrasion resistance of concrete depends on its paste hardness, aggregate hardness, and aggregate/paste bond [27]. In general, the hardness of concrete, which is related to its strength, determines its abrasion resistance.

3.4.2 Experimental Program

ASTM C944 presents a test method for determining the abrasion resistance of concrete. Concrete specimens were prepared with Portland cement and also with hydraulic cements formulated with the combustion ashes of wheat straw, corn stalk and rice husk. The sepcimens were cured at room temperature in sealed condition for 28 days. They were then subjected to abrasion testing (Figure 64) where the specimen weight was determined (after cleaning of the surface) every two minutes up to a total abrasion test duration of six minutes.



Figure 64. Abrasion test system.

3.4.3 Test Results and Discussion

Figure 53 show the surface appearances of concrete materials prepared with non-wood biomass ash-based hydraulic cements prior to and after six minutes of abrasion testing. Abrasive effects did

not notable alter the surface appearance of concrete specimens. The weight loss test data presented in Table 32 indicate that the abrasion resistance of concrete materials prepared with non-wood biomass ash-based hydraulic cements is comparable to or somewhat better than that of Portland cement concrete. This finding provides further indications of the value of non-wood biomass ashbased hydraulic cements as sustainable replacements for Portland cement in concrete kproduction.



Rice husk

Wheat straw

Corn stalk

(a) Prior to test



(b) After abrasion testing

Figure 65. The surface apperance of cocrete materials prepared with non-wood biomass ashbased hydraulic cements prior to and after abrasion testing.

	Initial	Abrasion period			Weight
Cement Type	Weight,	2 min	4 min	5 min	Loss, g
	g				
Wheat Straw Ash-Based	1431.12	1430.23	1430.02	1428.10	3.02
Rice Husk Ash-Based	1530.06	1529.06	1528.23	1527.33	2.73
Corn Stalk Ash-Based	1797.00	1796.00	1795.50	1795.00	2.00
Portland Cement	1688.99	1687.68	1686.92	1686.03	2.96

Table 32. Abrasion test results.

3.5 Bleeding Attributes

3.5.1 Introduction

Bleeding refer to the upward movement of the water in freshly mixed concrete towards it surface, which occurs because water is typically the material of lowest density in normal-weight concrete. Bleeding raises the water content near the concrete surface. If finishing of concrete surface is completed prior to drying of bleed water, the surface concrete ends up with a higher water/cement ratio and thus compromised qualities. The bleed water can accumulate underneath the aggregates, thus compromising the aggregate-paste interface quality. Climatic conditions that accelerate moisture loss from the concrete surface (e.g., windy, sunny, low relative humidity) could cause early drying and plastic shrinkage cracking of the concrete surface. In these conditions, bleeding could actually play a beneficial role by reducing the potential for plastic shrinkage of the concrete surface that generally occurs within within few hours after placement of fresh concrete. Differences between the bleeding of concrete made with alternative types of hydraulic cement

versus Portland cement could require alteration of the common practices of concrete finishing and, and the measures taken to mitigate plastic shrinkage cracking in windy and dry climatic conditions.

3.5.2 Experimental Program

A basic concrete mix comprising cement: natural sand: crushed limestone at 20: 35: 45 weight ratios was prepared with either Portland cement or a non-wood biomass ash-based hydraulic cement formulated with rice husk ash. The ASTM C232 standard test procedure was used to measure the bleeding of concrete. For this purpose, a container was filled with fresh concrete in two layers, and vibrated for 10 seconds after placement of each layer. The container was then placed on a level platform free from vibration, and covered with a lid to prevent evaporation of water. A pipet was used to draw off the bleed water at 10-minute and 30-minute intervals until cessation of bleeding. The bleed test setup is shown in Figure 66.



Figure 66. The test setup for measurement of bleed water.

3.5.3 Test Results and Discussion

The trends in bleeding of water from concrete materials made with Portland cement and rice husk ash-based cement are shown in Figure 67. Bleeding of the rice husk ash-based hydraulic cement concrete is observed to be about 30% less than that of Portland cement concrete. The rice husk ash-based cement concrete bleeding also plateaus sooner than that of Portland cement concrete. These findings imply that the adverse effects of bleeding on the aggregate-paste interface and surface concrete qualities would be less, and the final step in finishing of the concrete surface can be implemented earlier when the rice husk ash-based hydraulic cement replaces Portland cement in concrete. On the other hand, the reduced bleeding of the rice husk ash-based cement concrete could make the concrete surface more prone to drying shrinkage cracking in windy and dry climatic conditions that increase the rate of moisture evaporation from the concrete surface within few hours after placement of fresh concrete.



Figure 67. Bleeding test results for concrete materials made with Portland ceent and rice husk ash-based hydraulic cement.

3.6 Sorptivity (rate of capillary water sorption)

3.6.1 Introduction

The durability of concrete is related to its pore system characteristics. Water is involved in most prevalent mechanisms of concrete deterioration [28]. Sorption of water by concrete, which occurs primarily via capillary action through the fine, interconnected pore system of concrete, is thus a key factor governing its durability [29, 30]. The sorption rate (sorptivity) is thus one key aspect of concrete performance.

3.6.2 Experimental Program

ASTM C1585 is a standard method for determining the rate of concrete water sorption via capillary action. Duplicated cylindrical specimens with 100 mm diameter and 50 mm height were used in this test. The sorptivity test setup is shown in Figure 68. The side surfaces of the specimen were coated with a sealant to mitigate moisture evaporation from surfaces that are not exposed to water. The top surface was covered with an impermeable plastic adhesive sheet. The bottom surface was then immersed in water (2-3 mm depth). The mass gain (with respect to the initial weight) of the specimen (due to capillary sorption of water) was measured at different time intervals per ASTM C1585; these time intervals were 1, 5, 10 and 30 minutes, and then hourly up to 6 hours. Weight measurements involved removal of the specimen from the tray, shaking off excess surface moisture, and placing it (with dry surfaces) on an electronic pan balance. The gain in mass due to the absorption of water by the concrete specimen was recorded as a function of time. Absorption is defined as the ratio of change in mass to the product of the water contact area and the density of water:

$$I_t = \frac{m_t}{ad}$$

where, I_t is absorption at time t, m_t is the change in specimen mass at time t, a is the area of the specimen exposed to water, and d is the density of water.



Figure 68. The moisture sorption test setup.

3.6.3 Test Results and Discussion

ASTM C1585 provides guidelines for analyzing the sorptivity test results for calculating the initial rate of water absorption (mm/s^{1/2}). This initial sorption rate is defined as the slope of the best linear fit to the sorption (I) curve versus the square root of time (s^{1/2}) over the first 6 hours. The secondary rate of water sorption can also be determined as the slope of the best linear fit to sorption (I) plotted against the square root of time (mm/s^{1/2}) using all the data points from1 to 7 days.

The size distribution of fine (capillary) pores in cementitious binders, the continuity of this pore system, and the hydrophilic nature of pore walls make capillary sorption the primary means of entry of moisture into concrete. The capillary sorption test results presented in Figure 69 indicate that concrete materials prepared using hydraulic cements formulated with the combustion ashes of rice husk and wheat straw exhibit lower and higher, respectively, sorptivities when compared with the concrete prepared using Portland cement. Calculation of the initial sorptivity rates (Figure 70) confirm this relative standing of the concrete materials evaluated in this series of tests. The ultimate total sorption of water trend towards similar values in the case of concrete materials prepared with Portland cement and wheat straw ash-based hydraulic cement; the total moisture sorption of concrete prepared with rice husk ash is relatively low.



Figure 69. Capillary sorption test results concrete materials prepared with different hydraulic

cements.



Figure 70. Initial sorption versus the square root of time.
3.7 Acid Resistance of Non-Wood Biomass Ash-Based Hydraulic Cement Concrete

3.7.1 Experimental Program

Acid resistance was assessed by immersing non-wood biomass ash based hydraulic cement and Portland cement concrete specimens in 5% sulfuric acid solution at 7 days of age [31]. The choice of acid and the acid concentration were made to simulate the exposure conditions of concrete in sanitary sewer pipes. The ratio of the volume of the acid solution to the volume of the specimens was 4. The solution was stirred every week, and its pH was kept below 1.0. Cubic (50mmx50mmx50mm) concrete specimens were kept fully immersed in acid solution (Figure 71) for 28 days. Acid resistance was evaluated based on visual inspection and also by measuring the change in compressive strength after acid exposure.





(a) Rice husk ash-based cement (b) Portland cement

Figure 71. Concrete specimens prepared with different cement types immersed in 5% sulfuric acid solution.

3.7.2 Test Results and Discussion

Figure 72 compares the visual appearances of normal Portland cement concrete versus rice hulk ash-based hydraulic cement concrete specimens immersed in 5% sulfuric acid solutions for up to 28 days. Portland cement concrete is observed to exhibit significant surface deterioration. The rice hulk ash-based hydraulic cement concrete, on the other hand, exhibits less visible surface deterioration. This finding could point at the stable chemistry and the superior barrier qualities of non-wood biomass ash-based hydraulic cement concrete versus Portland cement concrete. The compressive strength test results presented in Table 33 indicate that the rice husk ash-based hydraulic cement concrete retained its compressive strength under acid attack better than Portland cement concrete up to 7 days of age. Thereafter, the two concrete materials exhibited similar strength loss under acid attack.



(a) Portland cement



(b) Rice hulk ash-based hydraulic cement

1 day 3 days 7 days 14 days 21 days

Figure 72. Visual appearances under acid attack of Portland cement concrete versus rice husk

ash-based hydraulic cement concrete.

	1	<u> </u>			
Specimens in	Compressive strength, MPa				
		1		I	
acid solution	RHA (control)	RHA (acid)	Portland (control)	Portland (acid)	
1 Day	34	30	38	29	
4 Dav	35	27	41	27	
5 Day	34	29	44	27	
July		29		27	
7 Derr	20	26	47	22	
/ Day	38	20	4/	23	
14 Days	42	23	46	20	
21 Days	56	21	48	17	

 Table 33. compressive strength test results for the rice husk ash (RHA)-based hydraulic cement

 concrete and Portland cement concrete..

3.8 Sulfate Resistances of Non-Wood Biomass Ash-Based Hydrualic Cement Concrete

3.8.1 Experimental Program

Sulfate resistance of concrete specimens was evaluated by visual inspection and measuring the residual compressive strength after exposure to a sulfate solution. Test specimens were immersed in a sulfate solution comprising 5% Na₂SO₄ in water at 7 days of age (Figure 73) [32]. Average of two compression tests was taken as the compressive strength prior to and after exposure to sulfate solution. The specimens were tested in saturated surface dry condition.



Figure 73. Rice husk ash-based hydraulic cement concrete (left) and Portland cement concrete (right) specimens fully immerse in sodium sulfate solution.

3.8.2 Test Results and Discussion

Figure 74 shows the visual appearance of the non-wood biomass ash-based hydraulic cement concrete specimens after different period exposure to the sodium sulfate solution. Except for buildup of some sulfate on the surface, that could be washed away, there are only minor indications of surface deterioration over time.



Figure 74. The visual appearance of rice husk ash-based hydraulic cement concrete specimens after different periods of immersion in sodium sulfate solution.

Table 34 presents the compressive strength test results produced using non-wood biomass ashbased hydraulic cement concrete and normal Portland cement concrete after different periods of exposure to sodium sulfate solution. After 28 days of exposure, the non-wood biomass ash-based hydraulic cement concrete experienced 6% gain of compressive strength compared to 43% loss experienced by normal Portland cement concrete. The deterioration of normal Portland cement concrete under sulfate attack can be attributed to the formation of ettringite which produces harmful expansive effects [33]. In the case of non-wood biomass ash-based hydraulic cement concrete, the primary products of hydration reactions are not susceptible to sulfate attack.

Table 34. Compressive strength test results (MPa) for rice husk ash (RHA)-based hydraulic cement concrete and Portland cement concrete after different periods of sulfate attack versus the compressive strength test results produced after similar periods of storage in air.

Time	RHA Immersed in	RHA in	Portland Immersed in	Portland in
Period	Sulfate Solution	Air	Sulfate Solution	Air
3 days	46	30	32	38
7 days	47	45	30	40
14 days	46	48	28	44
a o 1			~ ~ ~	16
28 days	51	54	25	46

3.9 Corrosion of Reinforcing Steel

3.9.1 Introduction

Corrosion of the reinforcing steel embedded in concrete is an electrochemical process that requires an anode, a cathode, an electrolyte, and an electrical connection between the anode and cathode for the transfer of electrons. Coupled anodic and cathodic reactions take place on the surface of the reinforcing steel. Concrete pore water acts as the electrolyte. The body of reinforcement provides the electrical connection between the anode and cathode. Cathodes and anodes may be located on the same rebar (microcell) that are electrically connected through metallic ties. The oxidation and reduction reactions take place at the anode and cathode are called half-cell reactions. At the anode, iron is oxidized and goes into solution as ferrous ions, releasing its electrons. Depending on the availability of oxygen and the pH of the environment, different reduction reactions can take place at the cathode. In the presence of the alkaline concrete pore solution where oxygen is available, the most likely reaction that produces hydroxyl ions is as follows:

 $Fe \rightarrow Fe^{2+} + 2e$ $2H_2O + O_2 + 4e \rightarrow 4OH^ Fe^{2+} 2OH^- \rightarrow Fe(OH)_2$

The Fe^{2+} ions in solution react further with OH^- ions to form ferrous hydroxide, which can be oxidized to form hydrated ferric oxide (red brown rust). Hydrated ferric oxide can be further dehydrated to produce red rust (Fe₂O₃), and Fe₃O₄. Corrosion activity of the steel reinforcing bars can be measured by using a copper-copper sulfate reference electrode. This test method covers the estimation of the electrical corrosion potential of uncoated reinforcing steel in concrete [34]. Amoung many methods available for monitoring and measuring corrosion, the half-cell potential measurement technique is the most convenient and expedient for application to reinforcing steel in concrete. This mothod, however, only provides the probability of corrosion activity of the steel bar in concrete.

3.9.2 Experimental Program

Some non-wood biomass ashes contain relatively high contents of Cl⁻ ions, which (if released to the pore solution of concrete) accelerate the corrosion of reinforcing steel. In this study, the corrosion potential of reinforcing steel was measured per ASTM C876 in concrete materials made with biomass ash-based hydraulic cements. The formulation of raw materials (including non-wood biomass ash) used for production of hydraulic cements is presented in Table 35. The processing of raw materials was accomplished mechanochemically via ball-milling over a period of two hours.

Materials	Dosage, wt.%
Biomass ash	30.5%
Coal fly ash (Class C)	30.5%
Slag	31.3
NaOH	3.3
CaO	4.3
Tartaric acid	1%

Table 35. The best cement formulation used to make specimens.

Cylindrically shaped molds were used to make the concrete specimens with embedded steel reinforcement. The cylindrical specimens had a diameter of 100 mm with 200 mm height. S steel reinforcing bar with 16 mm diameter was placed at the center of the cylindrical concrete speciemn; Concrete mixtures were prepared using the proportions introduced in Table 36 with Portland cement, and hydraulic cements formulated with wheat straw ash or rice husk ash. The high-impedance voltmeter was consisted of two terminals, one of which was connected to the rebar in concrete, while the other was connected to a copper/copper sulfate reference cell via a porous sponge. During the measurement process, the copper/copper sulfate electrode with sponge was sled over the surface of the concrete specimen, and the measurements made using the high-impedance voltmeter were recorded on a weekly basis. The high-impedance voltmeter used in this investigation (Figure 75) was a digital voltmeter with variable input impedance ranging from 10 to 200 M Ω . At the end of the corrosion test, the actual steel mass loss of reinforcing bars was evaluated per ASTM G103.

Raw	<i>Quantity (kg/m³) for Different Hydraulic Cements</i>				
Materia l	Wheat Straw Ash	Corn Stalk Ash	Rice Husk Ash	Portland Cement	
Cement	512	512	512	512	
Coarse Agg.	800	800	800	800	
Fin Agg.	640	640	640	640	
	159	159	169	184	
Water	(water/cement=0.3	(water/cement=0.3	(water/cement=0.3	(water/cement=0.3	
	1)	1)	3)	6)	

Table 36. The concrete mix proportions used in performance of corrosion tests.



Figure 75. Corrosion test apparatus: (a) copper-copper sulfate reference electrode; (b) high impedance voltmeter.

The standard guideline on application and interpretation of the reinforcement corrosion test data is ASTM C876: Standard Test Method for Half Cell Potentials of Uncoated Reinforcing Steel in Concrete. The conditions for successful testing include the exposure and the electrical continuity of reinforcement in the test area. According to ASTM876 [35]:

- If potentials over an area are more positive than -200 mV, there is greater than 90% probability that no reinforcing steel corrosion occurs in that area at the time of measurement.
- If potentials over an area are in the range of -200 mV to -350 mV, corrosion activity of the reinforcing steel in that area is uncertain.
- If potential over an area are more negative than -350 mV, there is greater than 90 % probability that reinforcing steel corrosion occurs in that area at the time of measurement.

The half-cell potential test is a useful technique to locate likely active areas of corrosion. It is recommended that potential surveys be supplemented with tests for carbonation and soluble chloride ion content for producing more accurate results. The test apparatus contains Cu reference electrode and high impedance digital voltmeter (Schematic diagram). This method is a non-destructive electro-chemical method use to find out the probability of corrosion tendency of rebar in the concrete. This technique directly measured the potential of rebar using a high impedance voltmeter as shown in Figure 76.



Figure 76. Schematics of the corrosion test apparatus.

In order to accelerate the corrosion process of steel reinforcement in concrete, the cylindrical concrete specimens with steel reinforcement (Figure 77a) were subjected to repeated cycles of wetting and drying (Figure 77b). Corrosion measurements were made following the procedures described earlier per ASTM C878. The copper/copper sulfate electrode was moved with a sponge over the surface of the concrete specimen, and the high impedance voltmeter readings were recorded over a 16-week period of exposure to repeated wetting-drying cycles. The high-impedance voltmeter used in this investigation had variable input impedance ranging from 10 to 200 M Ω . At the conclusion of the corrosion test, the concrete specimens were split, and visual observations were made of the corrosion conditions of the embedded reinforcing bars.



(a) Reinforced concrete specimens



(b) The setup for exposure of specimens to repeated cycles of wetting(left) and drying via

radiation heating (right)

Figure 77. The reinforced concrete specimens, and the setup used for their exposure to repeated cycles of wetting and drying.

3.9.3 Test Results and Discussion

Figure 78 presents the corrosion potential data produced for the steel reinforcing bars embedded in concrete specimens prepared with Portland cement and with the non-wood biomass ashes-based hydraulic cements. The corrosion potential in Portland cement concrete was observed to be slightly greater than that in the alkali aluminosilicate cement concrete, especially after longer exposure periods. This observation points at the better protection of the embedded steel bar against corrosion provided by the non-wood biomass ash-based hydraulic cement concrete when compared with Portland cement concrete. The higher alkalinity of the alkali aluminosilicate cement and the desired barrier qualities of its hydration products could be used to explain its desired corrosion protection potential. The presence of chloride in wheat straw or corn stalk ash [6] did not cause any accelerated of corrosion, which implies that the chloride is bound in ash and/or in the hydration products of the stalk ash-based hydraulic cements, and thus cannot be released to the pore solution of concrete. The visual appearance (Figure 79) of steel bars after splitting of concrete specimens at the conclusion of the wet-dry test periods did not exhibit any obvious indication of the formation of corrosion products. It should be noted that many exposure conditions selected for acceleration of corrosion involve exposure of reinforced concrete specimens to chloride solutions. The tests conducted here, however, intended to evaluate the potential for internal release of chloride from non-wood biomass ash-based cement and its products of hydration.



Figure 78. Corrosion potential data for steel bars embedded in concrete made with different hydraulic cements under exposure to repeated cycles of wetting and drying.



(a) Rice husk ash-based hydraulic cement



(b) Portland cement



(c) Corn stalk ash-based hydraulic cement

Figure 79. Visual appearances of the reinforcing bars embedded in concrete materials prepared with different hydraulic cements after 16 weeks of exposure to repeated wet-dry cycles.

3.10 Freeze-Thaw Resistance

3.10.1 Introduction

Repeated freeze-thaw cycles in the presence of moisture is an important cause of concrete deterioration in infrastructure system exposed to colder climatic conditions. Air entrainment is an effective approach to control of freeze-thaw damage to the concrete infrastructure. However, a new hydraulic cement should provide an inherent resistance to freeze-thaw damage that is at least comparable to that of Portland cement. If this is true, then air entrainment would yield concrete materials with excellent freeze-thaw durability. An experimental program was undertaken in order to assess the inherent freeze-thaw durability of non-wood biomass ash-based hydraulic cement concrete.

3.10.2 Experimental Program

The ASTM C666 test method covers the determination of the resistance of concrete specimens to rapidly repeated cycles of freezing and thawing in water. Hydraulic cement formulated with (industrially produced) rice husk ash used to prepared concrete materials for performance of freeze-thaw tests (with both freezing and thawing performed in water). The hydraulic cement formulation comprised Class C coal fly ash: Slag: NaOH: Na₂SiO₃: CaO: Na₂CO₃: citric acid at 30: 35: 20: 3: 3: 4: 4: 0.5 weight ratios. The blend of raw materials was subjected to ball-milling over two hours in order to produce the hydraulic cement. The concrete mix design is introduced in Table 37. Cylindrical concrete specimens with 75mm diameter and 150mm height as well as 50mm cube concrete specimens were prepared. After storage at room temperature in sealed condition for 24 hours, the specimens were demolded and stored in lime-saturated water for 7 days. Subsequently, the specimens were places in the freeze-thaw test system (Figure 80a&b). Initially, and after different number of freeze-thaw cycles, the fundamental resonance frequency of the

specimens were recorded nondestructively (Figure 80c) for cylindrical specimens. Destructive compressive strength tests were also performed on cube specimens prior to and after different number of freeze-thaw cycles.

The relative dynamic modulus of elasticity was calculated as follows:

$$P_c = (n_1^2 / n^2) \ge 100$$

where, P_c = Relative dynamic modulus of elasticity after cycles of freezing and thawing

n = Fundamental resonance frequency at 0 cycles of freezing and thawing

 n_1 = Fundamental frequency after N of cycles of freezing and thawing.

	Quantity			
Materials	Rice Husk Ash-Based Hydraulic	Portland		
	Cement	Cement		
Cement	1.00	1.00		
Crushed limestone (12.5 mm max.	2.21	2.21		
Size)				
Natural sand	1.79	1.79		
Water*	0.36	0.50		

Table 37	Concrete	mix	design
<i>i uoic ji</i> .	concrete	111150	acsign.

* Water required for adequate fresh mix workability



(c)

(b)

Figure 80. The freeze-thaw test system: (a) freeze-thaw apparatus; (b) concrete specimens in the freeze-thaw apparatus, (c) resonant frequency test system.

3.10.3 Test Results and Discussion

(a)

Figure 81 shows the visual appearance of rice husk ash-based hydraulic cement concrete and Portland cement concrete specimens prior to placement in the freeze-thaw test apparatus and after exposure to 100 cycles of freezing and thawing. In order to produce adequate fresh mix workability, the rice husk ash-based hydraulic cement and Portland cement required water/cement ratios of 0.36 and 0.50, respectively. Concrete specimens prepared with the two types of hydraulic cement did not exhibit any major indication of damage associated with the deleterious expansive phenomena associated with repeated freezing of water in concrete with neither types of cement. In the case of rice husk ash-based hydraulic cement, however, more aggregates seemed to have been

exposed after 100 cycles of freezing and thawing when compared with Portland cement. This could point at the loss of the thin paste layer covering aggregates in the case of the rice husk ash-based hydraulic cement concrete after exposure to 100 freeze-thaw cycles in water.

Figure 82 presents the trends in loss of relative dynamic modulus with increasing number of freezethaw cycles for concrete materials prepared with rice husk ash-based hydraulic cement and Portland cement. The trends are observed to be similar for the two cements, indicating that the rice husk ash-based hydraulic cement performs similar to Portland cement as far as the relative loss of dynamic modulus with the number of freeze-thaw cycles is concerned.

Figure 83 shows the trends in loss of concrete compressive strength with the number of freezethaw cycles for Portland cement versus rice husk ash-based hydraulic cement. The rice husk ashbased hydraulic cement concrete is observed to experience a larger loss of compressive strength up to 20 freeze-thaw cycles, after which its compressive strength tends to be more stable. Portland cement concrete however, continues to experience a steady loss of compressive strength up to 100 freeze-thaw cycles. The trends are such that the two concrete materials could exhibit similar losses of compressive strength beyond the 100 cycles considered in this investigation. Some of these trends could also be noted, though to a lesser extent, for the effects of freeze-thaw cycles on dynamic elastic modulus.



(a) Rice husk ash-based hydraulic cement

(b) Portland cement

Figure 81. Visual appearances of concrete materials prepared with rice husk ash-based hydraulic cement and Portland cement prior to and after exposure to 100 cycles of freezing and





Figure 82. Relative loss of the dynamic modulus of Portland cement and rice hulk ash cement based concrete materials versus the number of freeze-thaw cycles.



Figure 83. Relative loss of the compressive strength of Portland cement and rice hulk ash cement based concrete materials versus the number of freeze-thaw cycles.

3.11 Deicer Salt Scaling Resistance

3.11.1 Introduction

Application of deicer salts (NaCl, CaCl₂, etc.) on concrete surfaces to mitigate ice formation induces complex physical phenomena that lead to the scaling of concrete surfaces. These aspect of concrete performance that influence its deicer salt scaling resistance, including barrier qualities and bleeding behavior, could be different for the concrete with alkali aluminosilicate hydrate binders (considered here) versus conventional concrete with binders comprising the hydration products of Portland cement. An experimental investigation was undertaken in order to investigate the deicer salt scaling resistance of non-wood biomass ash-based hydraulic cement concrete relative to Portland cement concrete.

3.11.2 Experimental Program

Concrete materials prepared with wheat straw ash-based hydraulic cement and also with control Portland cement were prepared without any additive, and also with different additives (5% PEG, 1.5mL MasterAir AE 90 air entering agent per 1 kg of cement, and 2% sodium benzoate with 0.2% triisopropnolammine). Prismatic concrete specimens with 150 mm square planar dimension and 38 mm height were prepared per ASTM C672. Figure 84a shows the mold used for preparation of the deicer salt scaling test specimens. The flat surface of specimens was covered with approximately 6 mm of a solution of calcium chloride in water (Figure 84b) that comprised 4 g of anhydrous calcium chloride in 100 mL of water. The specimens were placed in a freezing environment (Figure 84c) for 16 to 18 hours. At the end of this time, the specimens were exposed to air at 23°C and 45-55% relative humidity for 6 to 8 hours. Water was added between as necessary to maintain the proper depth of solution. This cycle was repeated on a daily basis. At the end of each cycle, the surface was flushed thoroughly, and was examined visually. Subsequently, the calcium chloride solution was re-introduced on the surface, and the freeze-thaw cycle in the presence of deicer salt was repeated.









(a) Mold

(b) Concrete specimen

(c) Frozen specimens

Figure 84. Preparation and testing of a wheat straw ash-based hydraulic cement for evaluation of deicer salt scaling resistance.

3.11.3 Test Results and Discussion

Table 38 shows the visual appearances of concrete surfaces after exposure to different numbers of freeze-thaw cycles in the presence of deicer salt. Without any additive, the wheat straw ash-based hydraulic cement concrete was susceptible to deicer salt scaling after limited number of freeze-thaw cycles. The use of air entraining agent and PEG, followed by the combination of sodiu benzonate and triisopropholaine, were highly effective in improving the deicer salt scaling

resistance of the wheat straw ash-based hydraulic cement concrete to levels that were comparable with that of Portland cement concrete. It should be noted that air entrainment of concrete is routinely practices in the case of the concrete infrastructure exposed to repeated cycles of freezing and thawing. One should make selective use of the commercially available air entraining agents to ensure their compatibility with the alkali aluminosilicate chemistry of wheat straw ash-based hydraulic cements. Sodium benzoate is also used in Portland cement concrete as a corrosion inhibitor, which acts by enhancing the barrier qualities of concrete against chloride diffusion [36, 37].

Table 38. Visual appearances of concrete surfaces after exposure to different freeze-thaw cycles

	Whea				
# of Cycle s	No Additive	0.2% Triisoproponalammin e+ 2% Benzoate	Air Entraining Agent (1.5mL/kg of cement)	5% PEG	Portland Cement Concrete
0	A	Thic y cont	3) Air Ente	2 PEG	
1	1.3		3 Air Ents	(2) PEG	
2		A PHONE REPORT	3) Air Ente	2) PEG	
3	Highly Damaged Surface		3) Air Ente	@ PEG	
4			3 Air Ente	G PEG	

in the presence of deicer salt.

3.12 Fire Resistance

3.12.1 Introduction

Fire resistance is an important advantage of concrete when compared with alternative building construction materials (wood, steel, and polymer composites). Fire attack on concrete starts with buildup of steam pressure that can cause spalling and cracking of concrete; decomposition of cement hydrates at higher temperatures can cause serious degradation of concrete. An experimental investigation was conducted in order to make an assessment of the fire resistance of concrete materials prepared with what straw ash- and corn stalk ash-based hydraulic cements relative to the fire resistance of Portland cement concrete. Fire resistance was assessed simply based on the effects of exposure to elevated temperatures on the compressive strength of concrete.

3.12.2 Experimental Program

Non-wood biomass ash-based hydraulic cement concrete and Portland cement concrete cylindrical specimens of 75 mm diameter and 150 mm height were cured for 28 days in sealed condition at room temperature. The specimens (Figure 85a) were then exposed to elevated temperatures ranging from 100 to 800°C. For this purpose, the specimens were placed inside a furnace (Figure 85b), and heated at a fixed rate of 5°C/min to reach the targeted temperature. The electrically heated furnace used here was designed for a maximum temperature of 1200°C. The highest temperature considered in this experimental program was 800°C. Concrete specimens were kept at each elevated temperature for 2 hours; afterwards, the specimens were left to cool down inside the furnace to room temperature. Compression tests were performed the day after exposure to elevated temperature.



(a) Concrete specimens

(b) Heating of specimens in a furnace

Figure 85. Exposure of concrte specimens to elevated temeprature for assessment of their fire

resistance.

3.12.3 Test Results and Discussion

The trends in the effects of elevated temperature on the visual appearance of concrete materials made with wheat straw and corn stalk ash-based hydraulic cements were similar to those of Portland cement concrete. Figure 86 shows example appearances of these three classes of concrete prior to and after exposure to 500°C. The trends in the loss of compressive strength with temperature rise were also similar for the three classes of concrete materials (Figure 87). Significant loss of compressive strength occurred at temperatures exceeding 400°C. It should be noted that the moisture content of concrete strongly influences its performance at elevated temperatures. The relatively high moisture content of the specimens considered is expected to have lowered their high-temperature stability.



(a) Before heating

(b) After heating

Figure 86. Visual appearance of non-wood biomass ash based concrete and Portland cement based concrete before exposure to 500°C and after exposure to 500°C temperature.



Figure 87. Compressive strength test results after exposure to elevated temperatures.

Chapter 3

Design and Implementation of Scaled-Up Production of Hydraulic Cement, and Its Use in Industrial-Scale Concrete Production and Field Construction

4.1 Introduction

The approach adopted here for processing of aluminosilicate-based hydraulic cements with nonwood biomass ash employs mechanochemical phenomena to: (i) incorporate alkali/alkaline earth metal cations into the aluminosilicate precursor; and (ii) simultaneously disorder the aluminosilicate structure. This approach was developed using a laboratory-scale ball mill to render mechanochemical effects. An effort was made to scale-up the mechanochemical process in order to produce adequate quantities of hydraulic cement for large-scale production of concrete to be used in field construction.

An energy calculation was made to support scale-up of the ball-milling process. This calculation considers the motion of grinding balls in ball mills with different drum diameters, and strives for achieving equivalent amounts of impact energy transferred by the grinding balls to the raw materials. The dependence of this energy upon the drum dimensions, rotational speed and time allows for deriving relationships that can guide scale-up of the mechanochemical process. The scale-up process should eventually consider both the mechanical energy applied instantaneously to the raw materials, and the cumulative amount of impact energy. Comparative experimental studies were conducted at different scales in order to validate the theoretical approach developed for scale-up of the mechanochemical process.

While sustainability considerations are increasingly emphasized in selection of construction materials and practices, cost is still the prevalent factor influencing the decisions made on selection of materials by concrete suppliers, contractors and designers, and by the owners of the concrete-

based infrastructure. In order to assess the commercial prospects of the technology, comparative sustainability and economic analyses were made of the non-wood biomass ash-based hydraulic cements versus Portland cement.

4.2 An Energy-Based Approach to Scale-Up of the Mechanochemical Process

In ball-milling, a slightly inclined or horizontal rotating cylinder is partially filled with balls, usually metal or ceramic, which grind the material to the targeted fineness by friction and impact actions of tumbling balls. Ball mills normally operate with an approximate ball charge of 30% [38]. They are characterized by a diameter and a length that is typically 1.5 to 2.5 times the diameter. The feed is input at one end of the cylinder, and the milled material is discharged at the other end. Ball mills are commonly used in the manufacture of Portland cement, and in the finer grinding stages of processing minerals.

The laboratory-scale mill used in mechanochemical processing of hydraulic cement had a diameter of 203 mm (Figure 88a). The scale-up process employed a pilot-scale ball mill with 610 mm diameter (Figure 88b).



Figure 88. The laboratory-sacle (a) and pilot-scale (b) ball mills used in this investigation.

4.3 Development of An Energy-Based Theory for Scale-Up of the Milling Process

Movement of balls in a milling jar may be sliding (Figure 89a), cascading (Figure 89b) or centrifugal (Figure 89c), depending upon the rotational speed of the jar.



Figure 89. Sliding, cascading and centrifugal motions of balls in a milling far.

The critical speed of the jar is a speed where the balls centrifuge away from the pile, and fly free, without cascading or sliding; it is primarily dependent upon the jar diameter. The critical speed (n_c, rpm) of a milling jar can be calculated in terms of its diameter (D_m, m) as follows [39].

$$n_{c} = 42.3 / \sqrt{D_{n}}$$

The optimum speed of rotation for a jar for size reduction varies from 65% to 82% of the critical speed [39]. This speed induces a cascading action that benefits size reduction. Mechanochemistry, however, requires a intense input of energy, that would be realized at rotational speeds just short of the critical speed [9]. The ball mills used in this investigation were designed for size reduction; they operated at the optimum speed for size reduction, but not for inducing mechanochemical effects. The size and speed parameters of the laboratory- and pilot-scale ball mills used in this investigation are presented in Table 39.

Table 39. Diameters, critical speed, and the optimum and test speeds of the laboratory- andpilot-scale ball mills used in this investigation.

Ball Mill	Jar	Critical Speed	Optimum Spe	ed Range, rpm	Test
Scale	Diameter, m	n _c , rpm	Min (0.65 n _c)	Max (0.82 n _c)	Speed
					n, rpm
Laboratory	0.21	86	56	71	57
Pilot	0.61	54	35	44	40

A mechanical energy-based approach was followed in this work to scale up the milling process. The scale-up of the horizontal ball mill was accomplished considering the mechanical energy applied instantaneously to the blend of raw materials, and also considering the cumulative amount of mechanical energy applied to the blend of raw materials. The impact energy of a contacting ball, E_i, was defined as:

$$E_i = \frac{1}{2}mv^2$$

where, *v* represents the relative velocity of the ball at the moment when the ball comes into contact with a ball or the drum wall, as illustrated in Figure 90.



Figure 90. Schematics of impacting balls.

The impact energy generated within a certain time has a distribution, depending on the size and operating conditions of mills. The impact energy per unit time, i.e. the power P, is defined as the total kinetic energy of contacting balls per unit time, and is calculated for the average number, k, of contact points per unit time:

$$P = \sum_{0}^{k} Ei = \sum_{0}^{k} \frac{1}{2} mv^{2}$$

In case of scale-up of the drum, it is required that the products obtained in a larger-sized mill have the same properties (traditionally size distribution) as in a smaller-sized (laboratory) mill. In order to achieve this, the amount of impact energy applied to the powder per unit mass, i.e. the specific energy, should be the same in both larger and smaller mills. It is obvious that specific energy depends on both the power and the milling time. Therefore, for calculating power, the impact energy distribution should be analyzed, leading to the determination of the operating conditions of the larger-sized mill.

The operation time for the larger-sized mill, t, can be calculated in terms of that established for the laboratory-scale mill, t₀, using the following expression (subscript 0 refers to the laboratory-scale mill):

$$t = \frac{No^{1.3}}{N} X \frac{\beta o^{-0.2}}{\beta} \frac{So^{-1.2}}{S} t_o$$
(4)

Where, t = milling time; N = ratio of the drum rotational speed to its critical speed; β = ratio of the drum depth to diameter (1.2 for the laborator-scale mill and 1.5 for the pilot-scale mill used in this investigation); S = ratio of true volume of powder to drum capacity; X = ratio of powder in the large mill to that in the small mill (10 for the mills used in this investigation).

Assuming that both the laboratory-scale and pilot-scale ball mills are operated at 70% of their critical speeds, then $(N_0/N) = 1$. For the pilot- and laboratory-scale mills considered in this investigation, the 120-minute operation time established for the laboratory-scale mill would translate into 18.2 minutes for the pilot-scale mill in order to transfer similar impact energy to the blend of raw materials for rendering mechanochemical effects.

The following equation yields the energy, E_p , that transfers from the steel balls to the blend of raw materials in a ball mill:

$$E_{p=\frac{N}{m_p}}$$

where,

$$N = 0.864 \frac{G}{\Phi} \sqrt{D\psi^3} \left[9(1 - K^4) - \frac{16\psi^4}{3} (1 - K^6) \right] kW$$

G = weight of ball, kg

D = drum diameter, m

 Ψ = Rotation rate, which is the ratio of the drum rotational speed to its critical speed

 Φ = loading rate of drum, which is the ratio of the ball volume to the drum volue

K = a parameter related to the speeding rate and the loading rate.

$$m_p$$
 = weight of powder, kg

Table 40 shows the parameters of the laboratory- and the pilot-scale ball mills, and the specific corresponding specific energies transferred to the blend of raw materials per unit time. This data indicate that the energy transferred from the steel balls to the blend of raw materials in the pilot-

scale mill is 5.8 times that in the laboratory-scale ball mill. The energy calculations summarized here are consistent with the milling time calculations presen

Table 40. Energy calculation parameters and results for the laboratory- and pilot-scale ball mills used in this investigation.

Type of Mill	Weight of Balls, kg	Rotation Rate, ψ	Loading Rate	k	Powder Weight, kg	Energy of ball N, kW	Applied Energy E _p , J/s.g
Pilot-scale	100	0.74	0.087	0.85	10	1037.07	103.71
Laboratory-scale	10	0.58	0.213	0.70	1	18.87	18.87

4.3.1 Experimental Program

Mechanochemical processing of the non-wood biomass ash-based hydraulic cement was scaled up using a medium-sized ball mill. Relatively large quantities of the rice hulk ash-based hydraulic cement were produced. Ball milling was carried out for 2 hours, and samples were collected after 30 minutes, 1 hr and 2 hrs of milling. The medium-sized ball mill (Figure 91) had a diameter of 610 mm and a length of 914 mm (with a volume of 255 liter). The laboratory-scale ball mill used for development of the technology had a volume of 5.6 liter. The steel ball sizes used in the pilotscale ball mill ranged in diameter from 10 to 50 mm, and the steel ball-to-raw materials weight ratio was 10. Mechanochemical processing of the raw materials to produce the hydraulic cement was performed at room temperature.



Figure 91. The pilot-scale ball mill, and the steel balls used in this mill.

4.3.2 Test Results and Discussion

4.3.2.1 Particle Size Analysis

Figure 92 compares the particle size distributions of the hydraulic cements produced after different durations of milling. Up to the two-hour time period considered here, increasing the milling duration reduces the resulting particle size of the hydraulic cement. The initial particle size of the rice husk ash was 100 μ m. After 30 minutes, 1 hour and 2 hours of milling, the resultant hydraulic cement mean particle size was 12, 9.5 and 6.8 μ m, respectively.



Figure 92. Particle size distributions of the hydraulic cements subjected to different periods of mechanochemical processing (milling).

4.3.2.2 Compressive Strength

The compressive strength test results, measured per ASTM C109 using 50mm cube standard mortar specimens, obtained with the rice husk ash-based hydraulic cements processed via 0.5, 1 and 2 hours of milling are presented in Figure 93. Increasing the milling period is observed to consistently increase the 3-day compressive strengths of the resulting hydraulic cements. A combination of mechanochemical effects and size reduction could explain this positive effect of increasing the milling duration. The highest 3-day compressive strength obtained with the hydraulic cement processed via 2 hours of milling was 15 MPa, that exceeds the 13 MPa ASTM C1157 requirement for the 'genera use' class of hydraulic cement.



Figure 93. Effects of the milling duration on the compressive strength obtained with the mechanochemically processed rice husk ash-based hydraulic ceent.

4.4 Field Evaluation and Demonstration

The rice hulk ash based hydraulic cement was produced at pilot scale in adequate quantities for use in a field construction project in East Lansing, Michigan. The blend of raw materials was processed mechanochemically in the pilot-scale system introduced earlier; milling was performed for 45 minutes (due to time constraints). A total of 650 kg (1443 lb) of the hydraulic cement was produced. Figure 94 shows the visual appearance of the rice hulk ash-based hydraulic cement produced at pilot scale (and stored in plastic containers).

The concrete mix proportions used in the field project are presented in Table 41. The rice husk ash-based hydraulic cement was added to a ready-mix concrete truck using a lift (Figure 95). Fine and coarse aggregates as well as water were batched into the truck using the conventional practices of the ready-mix concrete plant. The total amount of concrete produced for the performance of the field project was 4 tons. Conventional mixing methods were used to prepare the concrete mix in the ready-mix concrete truck. Field construction was performed in a relatively cold (9°C) and sunny day in November 2017.

Material	Weight Proportion
Rice hulk ash based hydraulic cement	1
Natural sand	2.07
Limestone coarse aggregate	2.50
Water	0.54

Table 41. The concrete mix design.



Figure 94. The rice husk ash-based hydraulic cement produced at pilot scale.



Figure 95. Addition of the rice husk ash-based hydraulic cement to the ready-mix concrete truck.



Figure 96. Field pavement construction in November 2017.

The ready-mixed concrete truck transported the concrete over a distance of about 20 miles. The fresh mix slump, measured in field (Figure 97), was 100 mm, and the initial set time of concrete was 90 minutes. These satisfactory properties enabled successful implementation of the field construction project.


Figure 97. Measurement of fresh mix slump in field.

Figure 98 shows construction of a sidewalk pavement using the rice husk ash-based hydraulic cement concrete. Conventional concrete placement, consolidation and finishing procedures and tools were used in construction of the sidewalk. Cylindrical (with 75 mm diameter and 150 mm height) specimens were prepared from the concrete mixed in the truck. The specimens were kept in sealed condition, demolded after 24 hours, and then kept in sealed condition at room temperature for performance of compression tests at different ages.. The compressive strength test results presented in Table 42. Compressive strength test results for concrete specimens taken from the concrete truck.Table 42 point at successful achievement of strength levels that are comparable with those provided by normal-strength Portland cement concrete.



Figure 98. Placement and finishing of the rice husk ash-based hydraulic cement concrete.

Table 42. Compressive strength test results for concrete specimens taken from the concrete

truck.

Age, days	1	3	7	28	60
Compressive Strength, MPa	6.20	20.3	26.3	41.0	48.0

Figure 99 presents a typical scanning electron microscope (SEM) image of the hydrated paste of the rice husk ash-based cement in a concrete sample obtained from the field project. The microstructure is typical of alkali aluminosilicate hydrates where the hydration products bind the non-hydrated cores of the precursor particles. Unreacted coal fly ash and slag particles could be detected, which are well-integrated by the alkali aluminosilicate hydrate gel. The rice husk ash particles could not be identified among the hydration products, which could be explained by the high reactivity of rice husk ash, and its thorough integration into the hydrated paste. Hydrates seem to form relatively dense structures.



Figure 99. An SEM micrograph of the hydration products of the rice husk ash-based cement in the concrete used for field construction.

Chapter 4

Competitive Cost, Carbon Footprint and Energy Content Analyses of Non-Wood Biomass Ash-Based Hydraulic Cements

5.1 Introduction

The non-wood biomass ash-based hydraulic cements developed in the project successfully provided performance characteristics that matched (or surpassed) those provided by the commonly used Portland cement. These hydraulic cements also met the ASTM C1157 performance requirements for the 'General Use' (GU) class of cements. In order to be commercially viable, the non-wood biomass ash-based hydraulic cements should also offer viable economic and sustainability attributes. It is worth mentioning that the chemistry and processing methods adopted in this project are inherently sustainable. A competitive assessment was made of the cost, carbon footprint and energy content of non-wood biomass ash-based hydraulic cements.

5.2 Cost Analysis

5.2.1 Introduction

A key consideration in this development effort is to produce end-products (non-wood biomass ashbased hydraulic cements) that meet relevant performance requirements at competitive cost. Initial cost is a primary factor governing successful transition of new technologies to commercial markets. Sustainability advantages and energy savings can benefit commercialization efforts as far as new products do not constitute an initial cost burden (or preferably yield initial cost savings). A comparative cost analysis was conducted on Portland cement versus the non-wood biomass ashbased hydraulic cements developed in the project.

5.2.2 Raw Materials Costs

Transportation costs were neglected in this competitive cost analysis. The unit costs of the raw materials used in the new class of hydraulic cements are presented in Table 43. Non-wood biomass ash was considered to be a landfill-bound waste that can be acquired at no cost (except for transportation, that was neglected in this comparative analysis).

Table 43. Unit costs of the raw materials used in production of the non-wood biomass ashes

Material	Cost, \$/ton
Calcium oxide [40]	90
Sodium hydroxide [41]	200
Class C fly ash [42]	30
Granulated blast furnace slag [43]	40
Non-wood biomass ash	0
Tartaric acid	800

Ł	based	hya	lraulic	cements.
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5.2.3 Processing Costs

Our experimental work as well as energy calculations indicated that the 2-hour ball milling in the laboratory-scale mill used in this investigation corresponded to about 20 minutes of pilot-scale ball milling. The pilot-scale ball mill considered in this investigation consumes about 17 kWh (5.67 kW over 20 minutes) to process one ton of processed material; the factor for conversion of power into cost was set at \$1.02 per ton (assuming that each KWh costs \$0.18).

5.2.4 Total Initial Cost

Table 44 presents the contributions of each raw material as well as mechanochemical processing to the total initial cost of a typical non-wood biomass ash-based hydraulic cement. The cost of mechanochemical processing is calculated as the current contributions of the energy costs of raw and finish grinding to the production cost of Portland cement. Raw and finish grinding consume 2.4 GJ of energy for production of 1 ton of Portland cement, which translates into \$20 per ton.

The total raw materials and processing costs of the hydraulic cement add up to \$35.05 per ton. Given the ~\$115/ton sales price of Type I Portland cement in 2018, this raw materials and processing costs for non-wood biomass ash-based hydraulic cement seem to point at the viable cost position of the new class of hydraulic cements developed in the project.

Table 44. The non-wood biomass ash-based hydraulic cement formulation, and the corresponding raw materials and processing costs.

Ingredient	Quantity, kg/ton of cement	Cost, \$ per ton of cement
Non-wood biomass ash	300	0
Class C coal fly ash	300	3.00
Calcium oxide	45	4.05
Blast furnace slag	310	9.00
Sodium hydroxide	35	7.00
Tartaric acid	5	4.00
Mechanochemical processing	2.4 GJ Energy	12
Tota	al	35.05

5.2.5 Carbon Footprint

Reduction of CO₂ emissions is an important feature of the new class of non-wood biomass ashbased hydraulic cements developed in the project. This application takes advantage of the two major constituents of biomass ash, silica and alkalis, to produce hydraulic cements with a predominantly alkali aluminosilicate chemistry (which has an inherently low carbon footprint) [44]. The energy-efficient mechanochemical approach to processing of hydraulic cements adopted in this development effort further reduce the carbon footprint of the resultant hydraulic cements.

Figure 100 presents the percent CO₂ emissions associated with the raw materials and different steps in production of Portland cement. Portland cement comprises 95% of cement is clinker and 5% of gypsum; 304 kg of clinker is thus used to produce 320 kg of Portland cement. The carbon footprint of Portland cement is estimated at 800 kg of carbon dioxide per ton of cement.



Raw material quarrying Raw material grinding Chemical reactions Kiln fuel Finish milling

Figure 100. CO₂ emissions associated with production of Portland cement (U.S. DOE, 2003, Energy and Emission Reduction Opportunities for the Cement Industry, Washington DC, USA).

The non-wood biomass ash-based geopolymer concrete developed in the project uses large biomass ash volumes as the source of silica and alkalis, and coal fly ash and slag primary as sources of alumina. Sodium hydroxide was used as sources of alkalis to supplement the alkali content of biomass ash. An environmental analysis of the material should account for the environmental implications of all these ingredients. Coal fly ash and non-wood biomass ash comprise unburnt particulate residues of coal or biomass combustion in power plants and bio refineries. These ashes are by-products of power generation; they are not synthetically processed, and thus account for minor CO₂ emissions or energy use [45]. The unit carbon footprints of the raw materials used in production of non-wood biomass ash-based hydraulic cements are presented in Table 46.

 Table 45. The unit carbon footprints of the primary raw materials used in production of nonwood biomass ash-based hydraulic cements.

Material	$Kg CO_2/ton$
Sodium hydroxide [46]	500
Calcium oxide (CaCO ₃ →CaO+CO ₂)	540
Granulated blast furnace slag [47]	60
Coal fly ash	0
Non-wood biomass ash	0

The raw materials and finish grinding operations account for 6.2% of carbon emissions in Portland cement production [48]. The grinding operation can be used, with some changes that have minor energy implications, for mechanochemical processing of the non-wood biomass ash-based hydraulic cements developed in the project. The carbon emissions associated with mechanochemical processing can thus be estimated as 6.2% of the CO2 emissions of Portland cement (~0.062x800=49.2 kg/ton of cement). The carbon footprints associated with the transportation and handling of raw materials are neglected in this analysis.

The total carbon footprint of the new class of non-wood biomass ash-based hydraulic cement is calculated in Table 46 at 109.6 kg per ton of cement. When compared with the approximate carbon footprint of Portland cement (800 kg per ton of cement in 2018), this estimate points at the potential for significant reduction of the carbon footprint of cement and concrete by transition from Portland cement to the new class of non-wood biomass ash-based hydraulic cements developed in the project.

Table 46. Calculation of the carbon footprint of the non-wood biomass ash-based class of

Ingredient	Quantity, kg/ton of	Carbon footprint, kg per ton of
	cement	cement
Non-wood biomass ash	300	0
Class C coal fly ash	300	0
Calcium oxide	45	24.3
Granulated blast furnace slag	310	18.6
Sodium hydroxide	35	17.5
Tartaric acid	5	~ 0
Mechanochemical		
processing		49.2
Tota	1	109.6

hydraulic cements.

5.2.6 Energy Content

Manufacturing of Portland cement is an energy-intensive process, accounting for 4 GJ of energy consumption per ton of cement [49]. Figure 101 shows the relative contributions of various steps in manufacturing of cement to the energy content of cement.



Finish Grinding Auxiliary Raw Grinding Clinker Burning

Figure 101. Relative contributions of different processing steps to the energy content of Portland cement [50].

The raw materials used for production of non-wood biomass ash-based hydraulic cements are predominantly industrial by-products with minor energy content (disregarding the energy used for their transportation). The sources of alkalis account for the bulk of raw materials energy contents associated with the raw materials. The unit energy content of the sources of alkalis in non-wood biomass ash-based cement raw materials are presented in Table 47. Mechanochemical processing of hydraulic cement, given the experience gained in this development work, requires the energy consumed currently in raw and finish grinding steps of Portland cement production. These two steps account for about 60% of Portland cement energy content.

Mechanochemical processing of non-wood biomass ash-based hydraulic cement thus consumes close to $0.6 \ge 4 = 2.4$ GJ energy per ton of cement. Table 48 presents the cement formulation and the contributions to energy content of raw materials and mechanochemical processing. The total

energy content of the non-wood biomass ash-based hydraulic cement developed in the project is close to 3 GJ/ton, that represents a notable reduction when compared with the 4 GJ/ton energy content of Portland cement.

Material	GJ/ton
Sodium hydroxide [51]	12
Calcium oxide [52]	3.2

Table 47. Energy contents of supplementary raw materials.

Table 18	Comont	formulation	and the	corresponding onerow
<i>Tuble</i> 40.	Cemeni	jormatation	unu ine	corresponding energy.

Ingredient	Quantity, kg/ton of cement	Energy, GJ
Non-wood biomass ash	300	-
Coal fly ash	300	-
Calcium oxide	45	0.144
Blast furnace slag	310	-
Sodium hydroxide	35	0.42
Mechanochemical processing	-	2.4
Total		2.964

Conclusions

- 1. Non-wood biomass ash can make Si, Ca, K, Al and other elements available for production of hydraulic cements based predominantly upon the alkali aluminosilicate chemistry.
- 2. Supplementing the chemistry of non-wood biomass ash with those of coal fly ash, granulated blast furnace slag and sources of alkalis can yield a balanced chemistry for production of alkali aluminosilicate cements. Minor quantities of additives would also be needed for producing cements with desired set time that yields hydration products with desired deicer salt scaling resistance and dimensional stability.
- 3. Combustion ashes of wheat straw, corn stalk and cotton gin offer similar compositional and reactivity attributes for use in production of hydraulic cements with alkali aluminosilicate chemistry. Rice husk ash, on the other hand, has a distinct chemistry that is rich in reactive silica. Hydraulic cements can be formulated with all these non-wood biomass ashes.
- 4. Mechanochemical processing is a sustainable and economical means of transforming the nonwood biomass ash and supplementary raw materials into hydraulic cements that meet standard requirements for use in concrete production.
- 5. Mechanochemically processed hydraulic cements formulated with non-wood biomass ash offer a desired balance of fresh mix rheology, set time, and hardened material mechanical properties, chemical and dimensional stability, barrier qualities, and durability characteristics. Concrete materials prepared with these hydraulic cements reflect their desired balance of qualities, and provide desired protection against corrosion of reinforcing steel, and fire resistance.

- 6. The mechanochemical approach to processing of non-wood biomass ash-based hydraulic cements is scalable. Energy-based criteria were employed to establish the scale-up the mechanochemical processing of hydraulic cements. Pilot-scale implementation of the process was successful, and yielded a hydraulic cement that offered a desired balance of qualities.
- 7. The non-wood biomass ash-based hydraulic cement processed mechanochemically at pilot scale was used successfully for industrial-scale production of concrete, which was used in field construction of a concrete pavement. Conventional concrete construction practices were found to be applicable to the non-wood biomass ash-based hydraulic cement concrete. The field performance of non-wood biomass ash-based hydraulic cement concrete under service exposures has been satisfactory.
- 8. Mechanochemically processed non-wood biomass ash-based hydraulic cements have a distinctly low carbon footprint and relatively low energy content when compared with Portland cement. The economics of non-wood biomass ash-based hydraulic cement is also favorable when compared with Portland cement.
- 9. Non-wood biomass ash-based hydraulic cements are safe, and do not release hazardous constituents to the environment.
- 10. The milling conditions established traditionally for size reduction are not necessarily optimum for rendering mechanochemical effects. There is a need to optimize milling conditions for more effective and efficient mechanochemical processing of hydraulic cements. The intensity of the energy transferred to raw materials in each instance of impact needs to be raised in mechanochemical processing of hydraulic cements.

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