HIGH RECYCLED WASTE CONTENT ALKALI-ACTIVATED BINDER AS A FULL REPLACEMENT FOR ORDINARY PORTLAND CEMENT

By

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ABSTRACT

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Aluminosilicate chemistry details the process known as geopolymerization, where alumina and silica particles are released from materials in the presence of alkali metals, reorganized and hardened into a new, amorphous material. Alkali-activated binders, following this chemistry concept, can be produced in the form of a hydraulic cement, undergoing the hardening phase of geopolymerization during hydration. Alkali-activated binders have demonstrated improved durability and strength properties compared to ordinary Portland cement (OPC). The replacement of OPC with high recycled waste content alkali-activated binders would reduce the amount of potentially harmful, stockpiled wastes globally as well as reduce the carbon footprint associated with the OPC manufacturing process. This work details the process of developing a high recycled waste content alkali-activated binder with the correct balance of strength, setting time and fresh mix workability. The results indicated that brick waste and copper tailing can both be effective aluminosilicate precursors in an alkali-activated binder at up to 20% content by total weight. An alkali-activated binder containing brick waste was produced on a pilot scale and successfully used in a concrete pavement field demonstration. The concrete used in the field, containing the alkaliactivated binder, demonstrated a favorable setting time and compressive strength compared to the requirements for a Portland cement concrete pavement.

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1. Introduction

1.1. Summary of research

The motivation for this research was to produce a more sustainable alternative to Portland cement for concrete production. The approach is based on an alternative cement chemistry which enables large-volume use of waste raw materials, and adoption of energy-efficient processing techniques. This dissertation is divided into four chapters; each chapter has been prepared as a stand-alone paper written for submission to a peer-reviewed scientific journal. For convenience, the references from each chapter have been consolidated and appear at the end of this thesis. The four main chapters of the thesis are summarized in the following.

1.1.1. Development of an Alkali-Activated Binder Incorporating Construction and DemolitionBrick Waste as an Aluminosilicate Precursor

Hydraulic cements were formulated with high contents of waste brick (activated by input of mechanical energy in the presence of sodium carbonate), coal fly ash and sodium silicate. These cements were processed using energy-efficient mechanochemical means without resorting to elevated temperatures. They were based on alkali aluminosilicate chemistry, and used sodium silicate and sodium carbonate as the primary sources of alkali metal (sodium). The hydraulic cement formulations were refined, primarily by tailoring the raw materials formulations, to achieve a desired balance of fresh mix workability, set time and hardened material strength. The experimental results indicated that the combination of mechanochemical processing and alkali aluminosilicate chemistry enable production of high-recycled-content hydraulic cements with low

energy content and carbon footprint for use in concrete construction. The experimental results generated in this project also provided insight into the structural and chemical changes brought about by input of mechanical energy onto properly selected blends of raw materials towards production of hydraulic cements.

1.1.2. Effects on the Quality of an Alkali-Activated Binder Containing Brick Waste Due to the Scale Up Process When Manufactured on a Pilot Scale

Pilot-scale mechanochemical processing conditions were devised based on theoretical considerations to input an amount of energy to raw materials that is equivalent to that input in a laboratory-scale implementation of the mechanochemical process for production of hydraulic cements. The laboratory-scale process yielded a hydraulic cement based predominantly on the alkali aluminosilicate chemistry that met standard requirements for General Use hydraulic cement. The primary raw materials used in mechanochemical processing of this cement included waste brick, coal fly ash and granulated blast furnace slag; minor quantities of dry alkaline materials were also used in the process. Deviations from the theoretically determined pilot-scale processing conditions were imposed by the limited availability of steel balls. Fundamental physico-chemical and mineralogical characterization of the hydrated cements processed at laboratory and pilot scales as well as their hydration products indicated that the scaled-up mechanochemical processing of the hydraulic cement produced similar trends towards transforming the raw materials into a hydraulic cement. The extent of this transformation in pilot-scale mechanochemical processing, however, was not as thorough as that achieved in laboratory-scale mechanochemical processing. The strength development characteristics of the cement processed at pilot scale were thus inferior to that processed at laboratory scale, considering that the cement processed at pilot scale exhibited

an improved rate of strength gain at later ages. The experience gained in this research indicates that further improvement of the pilot-scale processing conditions would be needed before the qualities of the cement processed at laboratory scale can be achieved. These improvements would involve reducing the fraction of the ball-mill jar volume filled with the raw materials and steel balls, raising the ratio of steel balls to raw materials, and/or increasing the duration of milling.

1.1.3. Alkali-Activated Binder Used as a Full Replacement for Portland Cement in a Concrete Pavement: A Field Demonstration

An alkali aluminosilicate cement formulated with high contents of waste materials was processed at pilot scale, and used for industrial-scale production of concrete and implementation of a field construction project. The concrete mix was designed with the sustainable hydraulic cement used as full replacement for Portland cement. Field construction was implemented in late October in mid-Michigan (USA). The hydraulic cement formulation was tailored towards concrete construction at colder temperatures. The sustainable hydraulic cement was found to be compatible with industrial-scale production of concrete and conventional field construction practices. Field performance of the concrete pavement was monitored over one month during which temperatures dropped below freezing, and substantial rainfall and some light snow were experienced. Concrete performed quite satisfactorily during this period, exhibiting no signs of cracking or surface damage. Compressive strength tests were performed on concrete specimens prepared in field and cured either in field or in controlled laboratory environment. The strengths achieved in both curing conditions met the 78- and 28-day compressive strength requirements for concrete materials used in pavement construction. The experience gained in this project provided support for the scalability of the hydraulic cement developed based on alkali aluminosilicate cement chemistry, and its potential for full replacement of Portland cement in concrete construction.

1.1.4. Development of an Alkali-Activated Binder Incorporating Copper Tailing Mine Waste as an Aluminosilicate Precursor

Hydraulic cements were formulated with high contents of copper tailing, coal fly ash and sodium silicate. These cements were processed using energy-efficient mechanochemical means without resorting to elevated temperatures. They were based on alkali aluminosilicate chemistry, and used sodium silicate and sodium carbonate as the primary sources of alkali metal (sodium). The hydraulic cement formulations were refined, primarily by tailoring the raw materials formulations, to achieve the immobilization of heavy metals and a desired balance of fresh mix workability and hardened material strength. The experimental results indicated that the combination of mechanochemical processing and alkali aluminosilicate chemistry enable production of high-recycled-content hydraulic cements with low energy content, low carbon footprint and the ability to immobilize heavy metals for use in concrete construction. The experimental results generated in this project also provided insight into the structural and chemical changes brought about by input of mechanical energy onto properly selected blends of raw materials towards production of hydraulic cements.

2. Development of an Alkali-Activated Binder Incorporating Construction and Demolition Brick Waste as an Aluminosilicate Precursor

2.1. Introduction

The manufacturing of Portland cement is an energy-intensive process which also involves chemical decomposition of limestone, resulting in significant emissions of carbon dioxide [1, 2]. The technical work in progress focuses on development of more sustainable hydraulic cements that suit concrete production. The work reported herein focused on formulation of high-recycled-content hydraulic cements using waste brick.

The use of waste brick as supplementary cementitious material to partially replace Portland cement (PC) clinker has been explored [3] in order to gain sustainability benefits [4, 5]. Similar efforts with other waste and natural materials have not qualitatively reduced the high carbon footprint and energy content of Portland cement. A departure from the conventional Portland cement chemistry, based primarily on calcium silicates, could enable high-impact reduction of the carbon footprint and energy content of the hydraulic cements used in concrete production [6, 7]. In recent years, the activation of fly ash, blast furnace slag, glass, and brick waste has been investigated [8-11]. Replacement of 10-35% of Portland cement with these wastes has led to improvements in the sustainability and some performance attributes of Portland cement towards a primarily alkali aluminosilicate chemistry promises to significantly raise the use of byproducts/wastes as raw materials for production of hydraulic cements of significantly improved sustainability that meet standard requirements for use in concrete production [13].

The focus of this work was on formulation of the raw materials for production of an alkali aluminosilicate cement using waste brick as an aluminosilicate precursor. Waste brick constitutes a major constituent of the construction and demolition (C&D) waste worldwide, comprising more than half of the C&D waste generated in some regions [13]. Waste brick is also produced as defective units in brick production plants. The dust generated during cutting of brick is another source of waste brick. The large landfilled quantities of waste brick rationalize efforts to develop markets for this major constituent of the C&D waste stream. The use of waste brick in cement industry would yield important cost and sustainability benefits [14].

Clay, a major source of aluminosilicates, is the primary raw material used for production of brick. During high-temperature firing of brick, a liquid phase develops, which subsequently forms a glassy phase upon cooling. It is this glassy phase that binds the crystalline and any other phases that make up brick [15]. Ground waste brick has been evaluated as a pozzolan in production of Portland cement concrete [16]. The use of ground calcined brick clay as a pozzolanic material has also been explored [17]. These effort promises to bring about improvements in the performance and sustainability of Portland cement concrete [18]. The large landfilled quantities of waste brick [19] rationalize efforts to develop markets for this constituent of the C&D waste stream.

Allahverdi and Kani [14] investigated alkali activation of construction waste brick using a mixture of sodium hydroxide and sodium silicate (with a silica modulus of 0.6). A formulation with 8% Na2O content with respect to the precursor weight produced a compressive strength of 40 MPa after 28 days of curing. The work reported herein focused on the use of waste brick and other abundant wastes of supplementary chemistry and mineralogy as raw materials (aluminosilicate precursors) in sustainable production of a hydraulic cement based on the alkali aluminosilicate chemistry.

2.2. Materials

Waste brick was collected from a waste management facility in mid-Michigan. Coal fly ash was obtained from the Erickson power plant managed by the Lansing Board of Water & Light (LBWL) in Lansing, Michigan. Ground granulated blast furnace (GGBF) slag was obtained from LafargeHolcim (Ohio, USA). Clay was acquired from three different sources: (i) Greenstripe clay from IONEMaterials; (ii) Kaolinite clay from Sigma Aldrich; and (iii) Red clay from Red Soil Dirt Clay in East Tennessee (USA). These clays were calcined at different temperatures. Sodium silicate, sodium carbonate, calcium oxide, and borax were purchased from Sigma-Aldrich in powder form. Graded silica sand (ASTM C778) was used as fine aggregate in production of standard mortar mixtures per ASTM C1157.



(a) (b) Figure 1. Brick waste (a) crushed (b) after activation

2.3. Formulation and Processing of Hydraulic Cement

Viable raw materials formulations were selected via trial-and-adjustment. Alkali aluminosilicate hydrates can assume different stoichiometric attributes, and may also be supplemented with other (e.g., calcium silicate) hydrates as inorganic binders. Reliance strictly on the chemical composition of the raw materials for their formulation (proportioning) may be misleading because some minerals within raw materials may not be made available by simple processing techniques which avoid energy-intensive and polluting processing at elevated temperatures. Table 1 presents alternative formulations of raw materials, devised initially based on chemical considerations and modified via preliminary trial-and-adjustment efforts. Screening of these raw materials formulations is a primary consideration in the work reported herein.

Processing of the blend of raw materials into hydraulic cement was accomplished in this work via mechanochemical processing without resorting to elevated temperatures. Mechanochemistry refers to chemical and physico-chemical changes of substances induced by input of mechanical energy (e.g., milling) [20]. Initially, the waste brick was milled with sodium carbonate at a 4:1 ratio and with 1% moisture added. This combination and the remaining byproduct/waste aluminosilicate precursors were milled together with sodium silicate and quick lime as alkali activators. Mechanochemical processing of raw materials was accomplished using a conventional ball mill

Figure 2). A steel ball: raw materials weight ratio of 8: 1 was used, with a milling duration of 2 hours. Minor quantities of some additives were blended with the hydraulic cement after milling.

No	Cement	Raw Material							
	Notation	Ash	Brick	Slag	Na ₂ SiO ₃	Na ₂ CO ₃	CaO	CaO Other	
1	1-AB- LBWL	45	20	20	7	5	3		
2	2-AB- LBWL	30	20	24	7	6	3	10 Greenstripe Clay	Clay calcined (12hr, 750°C)
3	3-AB- LBWL	40	20	20	7	5	3	5 Greenstripe Clay	Clay calcined (2 hr, 750°C)
4	4-AB- LBWL	40	20	20	7	5	3	5 Red Clay	Clay calcined (2 hr, 750°C)
5	5-AB- LBWL	45	20	20	7	5	3	0.5 Borax	
6	6-AB- LBWL	45	20	20	7	5	3	1 Borax	
7	7-AB- LBWL	45	20	20	7	5	3	1 Borax 1 Na ₂ SO ₄	
8	8-AB- LBWL	45	20	20	7	5	3	1 Borax 2 Na ₂ SO ₄	
9	9-AB- LBWL	48	20	20	4	5	3		
10	10-AB- LBWL	48	20	20	4	5	3	1 Borax	

Table 1. Hydraulic cement formulations



Figure 2. Laboratory-scale ball mill



Figure 3. Steel balls used in milling process

Ball Size	Diameter (cm)	Mass (g)
Small	2.50	65
Medium	3.50	200
Large	5.00	500

Table 2. Sizes of the steel balls used in the milling process

2.4. Experimental Methods

The test methods employed for characterizing the raw materials and the resulting hydraulic cements are described in the following.

2.4.1. X-Ray Fluorescence

The chemical compositions of raw materials were assessed via x-ray fluorescence (XRF) spectroscopy using a Bruker S2 Ranger XRF spectrometer. Loss on ignition (LOI) was measured following a single-step procedure per ASTM D7348.

2.4.2. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) 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. TGA was carried out using Perkin Elmer TGA 4000 at a heating rate of 15°C/min from 50 to 950°C under nitrogen atmosphere. For this purpose, about 100 mg of sample was heated at a rate of 10°C/min in nitrogen environment.

2.4.3. Fourier Transform Infrared Spectroscopy

FTIR spectroscopy was carried out using a JASCO FTIR Spectrophotometer. The wavenumber range covered 400 cm⁻¹ to 4000 cm⁻¹. The spectra were recorded after 50 scans with a spectral resolution of 4 cm⁻¹.

2.4.4. Alkalinity

The alkalinity of hydraulic cements was measured by performing pH tests per ASTM C25. In this test, 5g of cement was mixed with 45mL of deionized (DI) water, and shaken for 30 minutes. After shaking, the solution was allowed to stand still for 30 minutes before taking measurements. The solution was then shaken for 24 hours, and the measurement was repeated. The pH of solution was measured together with the total dissolved solids (TDS) and electrical conductivity. Figure 4 shows the setups used for shaking of the solution, and measurement of its pH, TDS and conductivity.



Figure 4. Shaking (left), and measurement of pH, TDS and conductivity (right)

2.4.5. Set Time

The set time of hydraulic cements was determined per ASTM C191. This test was performed using a Vicat apparatus (Figure 5). The sample was prepared with a water/cement ratio of 0.30. The hydraulic cement and any set retarder considered were mixed dry for 1 minute prior to mixing with water for two minutes. Measurements were taken every 5 minutes after the start of hydration. The final set time was recorded when the needle could not penetrate the sample beyond 25mm.



Figure 5. Vicat apparatus

2.4.6. Heat of Hydration

Heat of hydration tests were performed as per ASTM C186. Paste samples were prepared with a water/cement ratio of 0.5, using 10g of hydraulic cement and 5g of deionized water. Immediately after mixing, the paste samples were placed in the apparatus to begin measurements. A Calmetrix I-Cal 2000 HPC was used to record measurements for approximately 72 hours.

2.4.7. Compressive Strength

Hydraulic cements were characterized following the ASTM C 1157 requirements. The ASTM C109 procedures were followed to prepare mortar specimens with each hydraulic cement for performance of compressive strength tests. The standard mortar mixtures used in these tests comprised hydraulic cement: standard silica sand at 1: 2.75 weight ratio. The water/cement ratios of these mixtures were adjusted to achieve a standard flow of at least 19mm. To improve the flow, additives such as borax were mixed into the hydraulic cement. Water/cement ratios ranged from 0.49 to 0.54 for achieving the standard fresh mix workability. The mixing procedure involved 2 minutes of mixing the dry ingredients (cement, sand and additives) in a mixer at slow speed, followed by the addition of water and 3 more minutes of mixing at medium speed. The fresh mix was cast into molds and consolidated via external vibration. The specimens were moist-cured inside molds at room temperature for 24 hours. They were then demolded, and cured at room temperature in sealed condition (>95% relative humidity) until the test ages of 3 and 7 days.

2.5. Result and Discussion

2.5.1. Chemical Composition (XRF)

Table 3 presents the chemical compositions of the waste raw materials used in this investigation. The waste brick is observed to comprise largely of silica (56.90%), alumina (17.01%), iron oxide (13.02%), and potassium oxide (5.88%). All these ingredients, if made available, can contribute to the active chemistry of hydraulic cements. The coal fly ash considered here has a calcium oxide content of 22.2%, which qualifies it as an ASMT C618 Class C fly ash. The silica-to-alumina ratio in the composition of his fly ash is close to 2. In GGBF slag comprised large of calcium oxide and silica, which accounted for 78% of its weight. The alumina and magnesium oxide contents of this slag were 9.54% and 10.85%, respectively.

Table 3. Chemical compositions (wt.%) of aluminosilicate precursors obtained via X-Ray fluorescence spectroscopy

Waste Raw Material	SiO ₂	Al ₂ O ₃	CaO	SO ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	TiO ₂	P_2O_5
C&D Brick Waste	56.80	17.01	1.52	0.84	13.02	-	-	5.88	2.60	0.92
Coal fly ash	30.6	15.1	22.2	-	16.8	2.30		2.60	-	-
GGBF slag	37.5	9.54	40.8	-	0.43	10.85	-	0.45	-	-

2.5.2. Thermogravimetric Analysis

The TGA and DTA data for waste brick, sodium carbonate, and brick activated mechanochemically with sodium carbonate over different time periods are presented in Figure 6 and Figure 7, respectively. The as-received waste brick exhibits a minor weight loss with a DTE peak around 730°C, which could be a result of the presence of minor carbonates in brick. Sodium

carbonate exhibits relatively sharp peaks at about 100°C and 880°C associated with loss of adsorbed water and decomposition of carbonate, respectively. Mechanochemical activation of waste brick with sodium carbonate over 1 and 2 hours alters the TGA/DTA patterns of brick, and increases its weight loss. Considering that mechanochemical activation was performed with water added to solids a 1 wt.%, a DTA peaks appear below 100°C, with a higher temperature associated with the longer mechanochemical activation. Broad peaks also appear at about 800 and 780°C for waste bricks activated with sodium carbonate via 1 and 2 hours of milling. Activated bricks also exhibited more than 10% weight loss, compared to about 1% weight loss of the as-received waste brick. This rise in weight loss as well as the appearance of new peaks which shift with the duration of milling point at changes that occur in the primarily aluminosilicate structure of brick as a result of mechanochemical activation in the presence of sodium carbonate.



Figure 6. TGA data for brick, sodium carbonate, and activated brick



Figure 7. DTA data for brick, sodium carbonate, and activated brick

2.5.3. Fourier Transform Infrared (FTIR) Spectroscopy

Figure 8 shows the FTIR spectra of as-received brick, sodium carbonate, and brick activated mecahnochemically in the presence of sodium carbonate and 1% water over different time periods. The as-received brick shows the typical 1043 cm⁻¹ band corresponding to asymmetric Si-O-Si stretching vibration [21]. Sodium carbonate strong absorption bands at 1420 cm⁻¹ and 881 cm⁻¹, and weak bands at 2970 cm⁻¹, 1795 cm⁻¹, 701 cm⁻¹ and 694 cm⁻¹ caused by CO₃²⁻ [22]. The activated brick powder contains a small amount of moisture (1%), producing a peak at 2970 cm⁻¹ which corresponds to stretching of hydroxyl groups. The FTIR spectrum of the activated brick exhibited a shift in the carbonate peak to 1445 cm⁻¹. Similarly, the band corresponding to Si-O stretching was shifted slightly to 1070 cm⁻¹, further indicating a change in the chemical bond environment of Si-O in brick due to milling with sodium carbonate. These shifts corroborate the TGA trends, indicating that mechanical activation brings about fundamental structural and

chemical changes in the blend of raw materials considered here. Other sodium carbonate peaks could be detected in the FTIR spectra of activated bricks. In addition, the peak around 3600 cm⁻¹ to OH groups of physiosorbed water [23].



Figure 8. FTIR for as-received brick, sodium carbonate, and brick activated mechanochemically in the presence of sodium carbonate over different time periods

2.5.4. Alkalinity, Total Dissolved Solids, and Conductivity

The pH, total dissolve solids and electrical conductivity test results for as-received and activated bricks are summarized in Table 4. The values of pH, TDS and conductivity increase upon activation of brick; this trend, however, can be attributed partly to the presence of sodium carbonate in activated brick. Activation of brick could also contribute to this trend by making the brick constituents more soluble. The results obtained for the hydraulic cements developed in this investigation are presented in Table 5, with measurements taken after 24 and 48 hours. These hydraulic cements produce high pH values which is reflective of their raw materials formulations

and mechanochemical processing condition. Their total dissolved solids and conductivity in solution are also relatively high. The trends in evolution of these values with time are not consistent between different types of hydraulic cement developed here. This reflects the opposing trends of dissolution of cement constituents, and their subsequent hydration reactions and precipitation out of solution.

Table 4. pH, total dissolved solids (TDS) and electrical conductivity test results for as-received and activated waste bricks

Material	pН	TDS, ppm	Conductivity, ms/cm
As-received brick	10.49	131.5	0.260
Activated brick-Na ₂ CO ₃ -1% water-1H	11.48	1992	4.068
Brick-Na ₂ CO ₃ -1% water-2H	11.48	1776	3.622

Table 5. pH, total dissolved solids (TDS) and electrical conductivity test results for alkali activated cement formulations measured after different time periods

Material	30min			48 hrs			
	pН	TDS,	Conductivity,	pН	TDS,	Conductivity,	
		ppm	mS/cm		ppm	mS/cm	
2-AB-LBWL	13.19	388	88 0.792 13.33 3472		3472	7.085	
4-AB-LBWL	13.17	7248	14.79	13.28	6305	12.87	
6-AB-LBWL (40min	13.12	1448	2.955	13.34	7276	14.85	
Pilot-Scale Mill)							
7-AB-LBWL	13.12	4458	9.097	13.26	2251	4.593	
8-AB-LBWL	13.17	5352	10.92	13.21	7076	14.44	
10-AB-LBWL	13.15	5027	10.26	13.23	4576	9.338	

2.5.5. Set Time

Hydraulic cements based on the alkali aluminosilicate chemistry generally exhibit high initial rate of reactions and thus relatively low set time. Sodium sulphate and borax were investigated to increase the set time of hydraulic cements. The set time test results are summarized in Table 5. Formulation 1-AB-LBWL, which did not incorporate borax, produced a set time of 10 minutes when blended with 1 wt.% of sodium sulfate, and 16 minutes when blended with 1 wt.% sodium sulfate and 1 wt.% borax. The retarding effect of borax can be attributed to the formation of a dense calcium borate layer wrapping cement particles at early stages of hydration, making them less reactive temporarily. The presence of borax has some negative effect on compressive strength; the minor drop at 1 wt.% borax, however, is justified by the significant rise in set time. When sodium sulfate was milled together with other raw materials (at 1 wt.% in 7-AB-LBWL, and 2 wt.% in 8-AB-LBWL), the resulting set times were 22 and 43 minutes, respectively. These significant gains in set time, however, were accompanied with significant drops in compressive strength. Another attempt made to increase set time involve reducing the sodium silicate content of the hydraulic cement from 7% to 4%, and increasing the fly ash content instead (Formulation 10-AB-LBWL). This adjustment raised the set time significantly, and also produced high levels of compressive strength (Figure 9). The addition of 1 wt.% sodium sulfate to this formulation significantly raised its set time and also benefited its compressive strength; this adjustement, however, was not required because Formulation 10-AB-LBWL produce an desired set time of 50 minutes without the addition of sodium sulfate.

Notation	Formulation	Added During Mixing	Set Time, min
1-AB- LBWL	45% Ash, 25% Activated brick, 20% Slag, 7% Sodium silicate, 3% CaO	1% sodium sulfate	10
2-AB- LBWL	30% Ash, 26% Activated brick, 24% Slag, 10% Greenstripe clay, 7% Sodium silicate, 3% CaO	1% borax	25
4-AB- LBWL	40% Ash, 25% Activated brick, 20% Slag, 7% Sodium silicate, 5% Red clay, 3% CaO	-	27
6-AB-	45% Ash, 25% Activated brick, 20% Slag 7%	1% sodium sulphate	16
LBWL	Sodium silicate, 3% CaO, 1% Borax	1% borax, 1% sodium sulphate	30

Table 6. Set time test results for different cements measured at 0.3 water/cement ratio

17 1% sucrose 45% Ash, 25% Activated brick, 20% Slag, 7% 7-AB-Sodium silicate, 3% CaO, 1% Borax, 1% Sodium 22 _ LBWL sulphate 45% Ash, 25% Activated brick, 20% Slag, 7% 8-AB-Sodium silicate, 3% CaO, 1% Borax, 2% Sodium 43 _ LBWL sulphate 50 _ 1% sodium 85 sulphate 10-AB-48% Ash, 25% Activated brick, 20% Slag, 4% 1% CaO 35 LBWL Sodium silicate, 3% CaO, 1% Borax 1% sodium 40 carbonate 5% slag 40

Table 6. (cont'd)



Figure 9. Effects of lowering sodium silicate content and adding sodium sulfate on the compressive strength produced by the hydraulic cement

2.5.6. Compressive Strength

The compressive strength test results are presented in Table 7 together with the fresh mix flow test data for different hydraulic cement formulations. A desired balance of fresh mix workability and

hardened material strength is provided by the hydraulic cements based on the 9-AB-LBWL and 10-AB-LBWL formulations. These two formulations are very similar, except that 10-AB-LBWL incorporates 1 wt.% borax for raising the set time. Introduction of borax is observed to have minor effects on compressive strength and fresh mix flow. The distinct feature of these two formulations is their reduced sodium silicate content (4 wt.%) when compared with that in other formulations (7 wt.%). Figure 11 shows the effectiveness of reducing the sodium silicate content of the formulation, versus other measures, in raising the compressive strength obtained with the hydraulic cement. Other benefits of the reduced sodium silicate include increased set time and fresh mix flow, and favorable economics. Figure 12 shows the effectiveness of reducing the sodium silicate content are constant fresh mix workability. Increasing the dosage of sodium sulfate, which was used as a set retarder, produced lower compressive strengths. The clays considered in this investigation in as-received or calcined condition did not yield notable benefits.



(a) (b) Figure 10. Mortar cube specimen (a) before compressive strength test (b) after test

Table 7. Compressive Strength test results						
Notation	Added During Mixing	w/c	Compressive Strength, MPa	Flow, cm		

 Table 7. Compressive Strength test results

Table 7. (cont'd)

			3d	7d	28d	
	None	0.50		15.79		14
	Added 15% fly ash, using 85% of original	0.50	6.89			16
1 A D	formulation	0.50				10
LBWL	Added 15% fly ash, using 85% of original	0.50	7.74			16
	formulation and 0.5% Borax	0.50				10
	Added 15% fly ash, using 85% of original	0.50	7.32			16
	formulation and 1% Borax	0.50				10
	None	0.50	14.48	19.67		14
	10% Red clay	0.50	8.98	11.19		17
	5% Red Clay	0.50	12.37	16.80		17
	5% Red Clay and 1% Borax	0.50	12.36			17
2-AB- LBWL	1% Borax	0.50	16.0	16.83		18
	1.5% Borax	0.50	11.60			17
	5% Greenstripe clay as received	0.50	12.61			16
	5% Greenstripe clay calcined 3 hours	0.50	10.19			18
	0.2% Amine and 2% Sodium Benzonate	0.53	10.70			19
	1% Borax, 0.2% Amine and 2% Sodium	0.50	8 70			10
	Benzonate	0.50	0.79			19
3-AB-	None	0.50	14.38			14.5
LBWL	1% Borax	0.50	11.74			16
4-AB-	1% Borax			14.62		20.5
LBWL				14.02		20.3
5-AB-	None	0.49	11 /0			21.5
LBWL	None	0.47	11.47			21.3
6-AB-	None	0.54	12.58	17.80		19
LBWL	5% Na ₂ SO ₄	0.50		15.44		19
7-AB-	None		10.30	18.0		19
LBWL				10.0		17
8-AB-	None		10.10	13 70		19
LBWL				15.70		17
9-AB-	None		12.9	21.2		19
LBWL				<i>41.4</i>		17
10-AB-	None		12.47	20.89		19
LBWL				20.07		17



Figure 11. Compressive strength test results for the hydraulic cement Formulation 10-AB-LBWL with different additives



Figure 12. Water/cement ratios for achieving constant fresh mix workability with the hydraulic cement Formulation 10-AB-LBWL incorporating different additives

2.5.7. Heat of Hydration

Figure 13 and Figure 14 compare the rate of heat release and the cumulative heat released versus time, respectively, for hydraulic cement Formulations 6-AB-LBWL (with 7% sodium silicate content) and 10-AB-LBWL (with 4% sodium silicate content). Lowering the sodium silicate content is observed to reduce the initial rate of heat release, but to elongate the period of active exothermic hydration reaction. The cumulative heat released for the hydraulic cement with lower sodium silicate content exceeds that of the cement formulated with higher sodium silicate content. These trends exhibited by the cement with reduced sodium silicate content are generally preferred because it provides working time prior to setting for timely implementation of the steps involved in concrete construction.



Figure 13. Rate of heat release during hydration of different hydraulic cements



Figure 14. The cumulative heat released during hydration of different hydraulic cements

2.6. Conclusions

Hydraulic cements based on alkali aluminosilicate chemistry can be formulated with waste brick (activated mechanochemically in the presence of sodium carbonate), coal fly ash and blast furnace slag used as raw materials. These hydraulic cements used a combination of sodium silicate and calcium oxide as the primary alkali activators (and supplementary sources of silicon and calcium), and were processed using mechanochemical effects without resorting to elevated temperatures. The original formulations incorporated relatively high sodium silicate content, and provided limited set time which compromises their ability to produce concrete materials with adequate fresh mix working time to enable timely implementation of construction steps. Some generic set retarders, that are compatible with the alkali aluminosilicate cement chemistry, were found to be effective in elongating the set times without compromising the strength development ability of the hydraulic cements. Lowering the sodium silicate content, however, was found to produce the best
combination of set time and compressive strength among the measures considered in this investigation. Reduced sodium silicate contents lowered the initial rate of hydration reactions, but elongated the period of active reactions.

Structural and chemical changes brought about by input of mechanical action onto judiciously selected blends of materials can produce hydraulic cements with desired balance of qualities for use in production of concrete. There seems to be a synergy between the alkali aluminosilicate cement chemistry and mechanochemical processing for production of a new class of high-recycled-content hydraulic cements with significantly reduced energy content and carbon footprint.

3. Effects on the Quality of an Alkali-Activated Binder Containing Brick Waste Due to the Scale Up Process When Manufactured on a Pilot Scale

3.1. Introduction

Mechanochemistry [20] offers a sustainable alternative to energy-intensive processing of inorganic materials, including hydraulic cements, at elevated temperatures. Mechanochemical processing of inorganic materials can be accomplished using mills (e.g., ball mills) that are used commonly in industrial processes for size reduction [24]. Mechanochemistry refers to the chemical and physiochemical changes of substances induced by input of mechanical energy (e.g., via milling) [20]. Steel ball milling generates energy through repeated transfer of impact energy at contact areas between steel balls and raw materials.

Laboratory-scale investigations have demonstrated that ball-milling of a blend of aluminosilicate precursors and alkaline compounds can induce mechanochemical effects that transform the raw materials into hydraulic cements based on alkali aluminosilicate chemistry [25]. The work reported herein was conducted to verify the scalability of the mechanochemical approach to processing of hydraulic cements. This work involved a scale-up of the mechanochemical process from laboratory scale with about 1 kg/hr production capacity to pilot scale with about 100 kg/hr production capacity. The operation condition of the scaled-up ball mill was selected based on theoretical considerations to input similar mechanical energy to raw materials as the laboratory-scale mill. Scalability of the process was assessed by comparing the physical and mineralogical characteristics as well as the strength development attributes of the hydraulic cements produced at laboratory and pilot scales using similar raw materials.

3.2. Materials

Coal fly ash was obtained from the Erickson power plant operated by the Lansing Board of Water & Light (LBWL) in Lansing, Michigan (USA). This fly ash with the chemical composition presented in Table 8 (obtained via x-ray fluorescence spectroscopy) qualifies as ASTM C618 Class C. The waste brick used in this study was collected from a landfill in mid-Michigan (USA). The as-received brick waste was crushed to give a granular material of about 75 mm maximum particle size. Ground granulated blast furnace (GGBF) slag was obtained from LafargeHolcim in Ohio (USA). The chemical composition of this slag, obtained via x-ray fluorescence spectrostopy, is presented in Table 8. Sodium silicate was purchased from JJ Chemicals in Fort Benning, GA (USA). Sodium carbonate was purchased from Duda Energy LLC in Decatur, Alabama (USA). Calcium oxide was purchased from Pete Lien and Sons Inc in Rapid City, South Dakota (USA). Borax was purchased from Sigma-Aldrich in powder form. Graded standard silica sand (ASTM C778) was used as fine aggregate to prepare mortar mixtures. Natural sand and crushed limestone of 19 mm maximum particle size, meeting the ASTM C33 requirements, were used as fine and coarse aggregates for preparation of concrete mixtures.

Table 8. Chemical compositions of brick waste, coal fly ash and ground granulated blast furnace (GGBF) slag

Waste Raw	SiO ₂	Al ₂ O ₃	CaO	SO ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	TiO ₂	P_2O_5
Material										
C&D Brick	56.80	17.01	1.52	0.84	13.02	-	-	5.88	2.60	0.92
Waste										
Coal fly ash	30.6	15.1	22.2	-	16.8	2.30		2.60	-	-
GGBF slag	37.5	9.54	40.8	-	0.43	10.85	-	0.45	-	-

3.3. Alkali-Activated Cement Formulation and Processing Methods

For both the large and small mills, the raw materials presented in Table 9 were processed mechanochemically via ball-milling (using steel balls) to produce a hydraulic cement powder with a predominantly alkali aluminosilicate chemistry. As a first step, the brick waste was activated via milling with sodium carbonate at a waste brick: sodium carbonate 4:1 weight ratio, with 1 wt. % moisture. The remaining raw materials were then added to the mill, and further milling was performed to produce the hydraulic cement.

Coal Fly Ash	GGBF	Brick Waste	Sod. Carbonate	Sod. Silicate	Calc. Oxide	Borax	
48%	20%	20%	5%	4%	3%	1% wt of cement	

Table 9. Alkali activated cement formulation

The appropriate milling time for production of hydraulic cement was first found through trial-andadjustment studies at laboratory scale. The goal was to find the minimum milling durations that produce hydraulic cements that meet the primary ASTM C1157 requirements for the 'General Use' (GU) type of hydraulic cement. The scale-up efforts were guided by the criterion that inputs of mechanical energy at laboratory and pilot scales should be similar. For this purpose, the milling duration was expressed in terms of the milling jar rotational speed-to-critical speed ratio (N), depth-to-diameter ratio (β), powder (raw materials) volume-to-jar volume ratio (S), and x is the scale-up index defined as the mass ratio of raw materials (powder) in the pilot-scale mill to that in the laboratory-scale mill [26]. The consideration that the laboratory- and pilot-scale milling processes should input similar energy to raw materials in order to induce comparable mechanochemical effects, the required milling time (t) for the pilot-scale mill could be calculated in terms of the milling duration of the laboratory-scale mill using Equation 1 below (where the subscript 0 refers to the laboratory-scale mill) [26].

$$\frac{t}{t_0} = \left(\frac{N_0}{N}\right)^{1.3} * \left(x * \frac{\beta_0}{\beta}\right)^{-0.2} * \left(\frac{S_0}{S}\right)^{-1.2}$$
(1)

The laboratory and pilot scale mills used in this investigation are shown in Figure 15, with the corresponding dimensions presented in Table 10.





Figure 15. Small (a) and large (b) milling jars

ruble 10. Sinun und rurge mining jur dimensions						
Mill Type	Depth (cm)	Diameter (cm)	Volume (cm^3)			
Laboratory Scale	21	28	12,930			
Pilot Scale	91	61	265,940			

Table 10. Small and large milling jar dimensions

The laboratory-scale mill was operated using an 8:1 steel ball: powder weight ratio and 2 kg of powder, and required a total milling duration of 120 minutes to transform the blend of raw materials into a hydraulic cement. Using Equation 1, it was found that with an 8:1 steel ball: powder ratio, approximately 20 minutes would be required for pilot-scale transformation of raw materials into hydraulic cement. Due to limits on the availability of balls, only a 4:1 steel ball:

powder ratio could be used in pilot-scale milling. In order to accommodate this difference in ratios, the milling period was extended. Activation of brick required 20 minutes because the low amount of powder (brick alone) allowed for achieving a steel ball-to-power weight ratio of 8:1; after addition of the remaining raw materials, with a ball-to-powder weight ratio of 4: 1, an additional milling duration of 40 minutes was required (verified using a trial-and-adjustment approach which focused on production of cements with adequate strength development characteristics). The operation conditions of the laboratory- and pilot-scale mills are summarized in Table 11.

Table 11. Steel ball milling processing methods

Mill Coole	Capacity,	Brick Activation	Additional Milling Duration	Total Milling
Mill Scale	kg	Time, min	of All Raw Materials, min	Duration, min
Laboratory	2	60	60	120
Pilot	40	20	40	60

3.4. Experimental Methods

3.4.1. X-Ray Powder Diffraction (XRD) Analysis

The hydraulic cements processed at laboratory and pilot scales were subjected to x-ray powder diffraction analysis using a Rigaku Miniflex XRD instrument. The resulting XRD spectra were analyzed in order to identify the existing crystalline phases, and to assess the degree of crystallinity.

3.4.2. Particle Size Analysis

The particle size distributions of the hydraulic cements were assessed using a Horiba LA-920 laser particle size analyzer. Three replicated tests were performed for each hydraulic cements, and the mean particle size distributions were obtained.

3.4.3. Fourier Transform Infrared Spectroscopy

The samples were subjected to Fourier transform infrared (FTIR) spectroscopy using a JASCO FTIR spectrophotometer. The wavenumbers considered covered the 400 cm⁻¹ to 4000 cm⁻¹ Range. The spectra were recorded after 250 scans with a spectral resolution of 4 cm⁻¹.

3.4.4. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) data were produced for the hydraulic cements produced at laboratory and pilot scaled using a Perkin Elmer TGA 4000 instrument operated at a heating rate of 10°C/min from 50 to 950°C under a nitrogen atmosphere.

3.4.5. Heat of Hydration

Heat of hydration tests were performed per ASTM C186. Paste samples were prepared with a water/cement ratio of 0.50, and tested using a Calmetrix I-CAL 2000 HPC test instrument over 72 hours in order to record the heat of hydration.

3.4.6. Scanning Electron Microscopy (SEM) Analysis

Scanning electron microscopy (SEM) was performed using a Neoscope JCM-5000 instrument on paste specimens with water/cement ratio of 0.33 after 7 days of curing at room temperature.

3.4.7. Compressive Strength

The strength development characteristics of the hydraulic cements processed mechanochemically at laboratory and pilot scales were characterized per ASTM C 1157. The ASTM C109 procedures were followed to prepare mortar specimens for performance of compressive strength tests. The standard mortar mixtures used in these tests comprised hydraulic cement: standard silica sand at 1: 2.75 weight ratio. The water/cement ratios of these mixtures were adjusted in order to achieve a standard flow of $110 \pm 5\%$ (ASTM C1437). To improve the flow, additives such as borax and clays were introduced to the hydraulic cement during mixing. The required water/cement ratio ranged from 0.46 to 0.50. The mixing procedure comprised 2 minutes of mixing the dry ingredients (cement and sand) in a rotary mixer at slow speed, followed by the addition of water and 3 more minutes of mixing at medium speed. The fresh mix was cast into molds and consolidated via external vibration. The molded specimens were stored in sealed condition at room temperature for 24 hours. They were then demolded, and cured at room temperature in sealed condition (>95% relative humidity) until the test ages of 3 and 7 days.

3.4.8. Setting Time

Set time was measured following the ASTM C191 procedures using a Vicat apparatus. The mixture comprised 300g of hydraulic cement and 90g of water, which were mixed for approximately 2 minutes. The fresh mix was placed in the Vicat apparatus mold; a measurement was taken every 5 minutes until the initial set time was reached.

3.5. Results and Discussion

3.5.1. Alkalinity

The pH, total dissolved solids (TDS) and electrical conductivity test results obtained for solutions incorporating hydraulic cements processed at laboratory and pilot scales are presented in Table 12. Measurements were taken 30 minutes and 48 hours after addition of cement to water. The trends in TDS and conductivity indicate that the hydraulic cement processed at pilot scale are lower after 30 minutes and higher after 48 hours when compared with the cement processed at laboratory scale. The pH values, however, are higher for the cement processed at pilot scale for measurements taken at both 30 minutes and 48 hours when compared with the cement processed at laboratory scale. One purpose of mechanochemical processing is to transform alkalis and aluminosilicates into alkali aluminosilicates that can undergo timely dissolution and hydration upon addition of water. The initially slow dissolution of the cement processed at pilot scale is not necessarily a drawback since it accelerates beyond 30 minutes. The higher pH value of the cement processed at pilot scale, however, could point at the relatively low efficiency of transforming the raw materials into a hydraulic cement.

	30 min				48 Hour		
Mill Scale	пU	TDS,	Conductivity,	лU	TDS,	Conductivity,	
	рп	ppt	mS/cm		ppt	mS/cm	
Laboratory	13.15	5.027	10.26	13.23	4.576	9.338	
Pilot	13.26	3.925	8.01	13.41	7.35	15.01	

Table 12. The pH, total dissolved solids (TDS), and conductivity test results at 30 minutes and 48 hours

3.5.2. X-Ray Powder Diffraction (XRD) Analysis

The XRD patterns presented in Figure 16 and Figure 17 for the hydraulic cements processed at laboratory and pilot scales are similar, pointing at the presence of quartz as the only identifiable crystalline species, with other compounds occurring in amorphous form.



Figure 16. X-Ray powder diffraction (XRD) analysis of the laboratory scale milled cement



Figure 17. X-Ray powder diffraction (XRD) analysis of the pilot scale milled cement

3.5.3. Particle Size Analysis

The cumulative particle size distributions of hydraulic cements processed at laboratory and pilot scales are shown in Figure 18; the mean and median values of particle size for the two cements are presented in Table 13. Pilot-scale processing produced hydraulic cements with coarser particle size when compared with the laboratory-scale processing the median particle sizes of hydraulic cements processed at laboratory and pilot scales were 6.63 and 9.44 µm, respectively. This observation implies that pilot-scale milling was not as efficient as laboratory-scale milling in terms of size reduction. The initially low dissolution rate of the hydraulic cement processed at pilot scale can be explained using the coarser particle size distribution of this cement. It is worth mentioning that the particle size distribution achieved in pilot-scale processing is comparable to that of conventional Type I Portland cement. Finally, one should distinguish between the comminution and mechanochemical effects of milling; there is not necessarily a direct proportionality between these two milling effects [27].



Figure 18. Cumulative size distributions of hydraulic cements produced at laboratory and pilot scales

Table 13. Mean and median particle size values for hydraulic cements processed at laboratory and pilot scales

Particle Size	Laboratory Scale	Pilot Scale
Mean (µm)	7.62	10.59
Median (µm)	6.63	9.44

3.5.4. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of the blend of raw materials prior to milling, and for hydraulic cements processed at laboratory and pilot scales are presented in Figure 19. Milling at both laboratory and pilot scales brings about major changes in the FTIR spectra of the blend of raw materials. Milled hydraulic cements exhibited peaks at the 1000 cm⁻¹ - 1150 cm⁻¹ region, which corresponds to polymerized silica. The hydraulic cement processed at laboratory scale produced a more notable peak in this region. Both cements exhibited peaks in the 1400 cm⁻¹ - 1600 cm⁻¹ region, which points at the presence of carbonates. These carbonates could have formed via reactions involving the

carbon dioxide in air during mechanochemical processing. The peak in this region is more defined for the cement processed at pilot scale. A peak around 3600 cm⁻¹, which is more prounounced for the cement processed at laboratory scale, is indicative of the presence of hydrates (or water) which could have formed as a result of the adsorption of moisture from air and probably the consequent hydration reactions.



Figure 19. Fourier transform infrared (FTIR) spectra for the blend of raw materials prior to milling, and for hydraulic cements processed via laboratory- and pilot-scale milling

3.5.5. Thermogravimetric Analysis (TGA)

The TGA test data and the resulting differential thermal analysis (DTA) curves are presented in Figure 20 and Figure 21. Mechanochemical processing (milling) of the blend of raw materials is observed to bring about notable changes in the TGA test results. The changes in TGA test results are somewhat more pronounced after laboratory-scale milling when compared with pilot-scale milling, which confirms the observations made earlier regarding the more advanced state of mechanochemical transformation realized via laboratory-scale milling. The DTA peaks observed

at 100 - 150°C point at the presence of physically adsorbed water and some less stable hydrates. This peak is less pronounced for the cement processed at laboratory scale. It should be noted that mechanochemical activation of waste brick was performed in the presence of a minor quantity of water. This could be the reason why the blend of raw materials (prior to milling), which incorporated non-activated brick, has a smaller DTA peak in this region. One of the raw materials, borax (sodium tetraborate decahydrate) incorporates chemically bound water, and could contribute to the DTA peak at the $100 - 150^{\circ}$ C region. A second set of DTA peaks appeared within the 400 -500°C temperature range, which point at the presence of hydroxides. These hydroxides may have formed during milling due to the use of minor amount of water for mechanochemical activation of waste brick, or after milling due to hydration reactions of the resultant cement with the moisture present in air. This peak is also more pronounced for the cement subjected to laboratory-scale processing. The peaks observed at 700 - 900°C can be attributed to the presence of carbonates. At approximately 700°C all materials exhibited peaks which are likely due to the presence of sodium carbonate. This peak is more pronounced for the cement processed at laboratory scale. Additionally, between 800°C and 900°C peaks were observed for the blend of raw materials (prior to milling), and for the cement processed at pilot scale. The carbonates which produce these peaks may have formed via reactions of the raw materials constituents with the carbon dioxide present in air, which would be pronounced during milling and also upon formation of reactive compounds after milling.



Figure 20. Thermogravimetric analysis (TGA) curves for the blend of raw materials prior to milling, and for the hydraulic cements processed at laboratory and pilot scales



Figure 21. Differential thermal analysis (DTA) curves for the blend of raw materials prior to milling, and for the hydraulic cements processed at laboratory and pilot scales

3.5.6. Heat of Hydration

The heat of hydration test results are presented in Figure 22 and Figure 23. The hydraulic cement processed at pilot scale exhibited a relatively high initial rate of heat release, which could not be retained over time. For both cements, a well-defined heat release peak occurred after only few minutes; the cement processed at laboratory scale exhibited a less defined peak after about one hour. The cumulative heat release for the cement processed at pilot scale was, after 3 days, about 70% less than that processed at laboratory scale. This finding is consistent with all previous results which indicate that pilot-scale processing of the cement needs adjustment before it can produce a cement quality that, similar to the cement processed at laboratory scale, meets the ASTM C1157 strength development requirements. These adjustments relate to the fraction of the jar volume filled with raw materials and steel balls, the weight ratio of balls to raw materials, and the milling duration. It should be noted that relatively high initial rate of heat release noted for the cement processed at pilot scale, in spite of its relatively low overall reactivity, can be attributed to the greater availability of the less compounded alkalis in this cement. There is a relatively high rate of heat release associated with the rapid release of the alkali metal cations to the solution, and the subsequent alkali attack on aluminosilicate precursors.



Figure 22. The rate of heat released for hydraulic cements processed at laboratory and pilot scales



Figure 23. The cumulative heat released for hydraulic cements processed at laboratory and pilot scales

3.5.7. Scanning Electron Microscopy (SEM) Analysis

The scanning electron microscope images captured at different magnifications for the hydration products of cements processed at laboratory and pilot scales are shown in Figure 24 and Figure 25, respectively. The hydration process of the cement processed at laboratory scale seems to be more thorough, with seemingly amorphous products of hydration filling the voids and rendering binding

effects (Figure 24). These trends seem to be less advanced in the case of the hydraulic cement processed at pilot scale (Figure 25).



Figure 24. Scanning electron microscope (SEM) images at different magnifications of the hydration products of the cement processed at laboratory scale



(a) 1000x (b) 1500x (c) 2000x Figure 25. Scanning electron microscope images at different magnifications of the hydration products of the cement processed at pilot scale

3.5.8. Compressive Strength

ASTM C1157 requires standard mortar 3- and 7-day compressive strengths of 13 and 20 MPa, respectively, for 'General Use' (GU) hydraulic cements. The compressive strength test results presented in Table 14 indicated that the standard mortar made with the cement processed at laboratory scale met these requirements (within $\pm 1\%$). The cement processed at pilot scale,

however, failed to meet the ASTM C1157 requirements for General Use hydraulic cement. This was particularly true at 3 days of age, but the rate of strength gain picked up between 3 and 7 days. The flow of the fresh mortar mix prepared with the cement processed at pilot scale was somewhat higher than that prepared with the cement processed at laboratory scale. The shortfalls of the cement processed at pilot scale can be feasibly overcome by reducing the fraction of the jar filled with the raw materials and steel balls, raising the steel ball-to-raw materials weight ratio, and/or increasing the duration of pilot-scale milling. The duration of air storage of the cement processed at pilot scale. Storage of cement in bagged/sealed condition is another measure that could benefit the strength development qualities of the cement processed at pilot scale.

The compressive strength test results produced for concrete materials are summarized in Table 15. Similar to mortar mixtures, the fresh mix workability of the concrete mixtures prepared with the cement processed at pilot scale was better than that for the cement processed at laboratory scale. This allowed for lowering the water/cement ratio of the concrete prepared with the cement processed at pilot scale without compromising its fresh mix workability. In spite of this, the cement produced at pilot-scale produced concrete with significantly reduced 3-day compressive strength when compared with the cement processed at laboratory scale. The rate of concrete strength rise, however, increased between 3 and 7 days. The concrete compressive strength test results follow trends similar to those of standard mortar compressive strengths. The measures suggested for improving the pilot-scale processing of cement would thus be the same as those devised based on the standard mortar compressive strength test results.

Cement Processing	W/C	Compressive	Flow,	
Scale	w/C	3-day	7-day	cm
Laboratory-Scale	0.50	12.9	21.2	19
Pilot-Scale	0.50	6.00	14.3	20

Table 14. Compressive strength and fresh mix flow test results generated for standard mortars

Table 15. Compressive strength test results for concrete materials

Cement Processing	W/C	Compressive Strength, MPa		
Scale	w/C	3-day	7-day	
Laboratory-Scale	0.45	23.8	29.8	
Pilot-Scale	0.35	7.4	21.9	

3.5.9. Setting Time

ASTM C1157 requires initial set times occurring within the 45 to 420 minutes range for General Use hydraulic cements. The initial set time test results presented in Table 16 indicate that cements processed at both laboratory and pilot scales meet this requirement. The lower reactivity of the cement processed at pilot scale actually benefits its ability to retain the fresh mix workability by elongating its set time.

Table 16. Initial set times of cements processed at laboratory and pilot scales

Туре	Set Time, min
Small Mill	50
Big Mill	60

3.6. Conclusion

A scaled-up milling process was developed to reproduce the energy input of laboratory-scale milling that successfully produced a mechanochemically processed hydraulic cement based on the

alkali aluminosilciate chemistry that met the ASTM C1157 requirements. Some deviations from the theoretical scaled-up conditions were imposed (particularly in terms of the weight ratio of steel balls to raw materials) due to different constraints (e.g., availability of steel balls). The duration of the pilot-scale milling was adjusted to account for the deviations from the theoretical scale-up requirements. The specific hydraulic cement that was subject of pilot-scale processing comprised predominantly of waste aluminosilicate precursors (waste brick, coal fly ash, and granulated blast furnace slag). Relatively small quantities of dry alkaline materials were also used as raw materials. Waste brick required mechanochemical activation in the presence of an alkaline material and minor moisture prior to blending with other raw materials for mechanochemical production of hydraulic cement.

The trends in evolution of the physico-chemical, mineralogical and hydraulic activity of the cement produced at pilot scale were similar to those produced at laboratory scale. Laboratory-scale mechanochemical processing of the hydraulic cement, however, produced higher levels of specific surface area, solubility, reactivity, and strength development characteristics. Improvements that would benefit the qualities of the hydraulic cement processed at pilot scale include lowering the fraction of the jar volume filled with the raw materials and steel balls, raising the weight ratio of steel balls to raw materials, and increasing the milling duration.

The hydraulic cement processed at pilot scale fell significant short of the cement processed at laboratory scale in terms of 3-day strength development. At 7 days of age, however, the strength obtained with the cement processed at pilot scale was closer to (through still smaller than) that obtained with the cement at laboratory scale.

The trends in concrete strength development characteristics with cements processed at laboratory and pilot scales were similar to those achieved with the standard hydraulic cement mortar used in evaluation of the strength development attributes of hydraulic cements per ASTM C1157.

The particle size distribution of the cement processed at pilot scale was coarser than that of the cement processed at laboratory scale, and the cumulative (exothermic) release of heat of hydration was considerably smaller for the cement processed at pilot scale. These findings further indicate that the energy input of the pilot-scale milling process was not adequate to render the physico-chemical effects that effectively transform the raw materials into a hydraulic cement.

The set times of the hydraulic cements processed at laboratory and pilot scales met the ASTM C1157 requirement for 'General Use' hydraulic cements. The fresh ix workability obtained with the cement processed at pilot scale was better than that processed at laboratory scale. The water/cement ratio required for the cement processed at pilot scale is thus lower than that processed at laboratory scale. This could well be due to the smaller specific surface area and lower reactivity of the cement processed at pilot scale.

4. Alkali-Activated Binder Used as a Full Replacement for Portland Cement in a Concrete Pavement: A Field Demonstration

4.1. Introduction

The manufacturing of Portland cement is an energy-intensive process that results in a significant carbon footprint [1, 2]. Efforts have been made to replace Portland cement as the binder in concrete with the objective of mitigating the environmental impacts associated with manufacturing of Portland cement [3-5]. The alkali aluminosilicate chemistry has been an option considered for development of a sustainable class of hydraulic cements [28-33]. This cement chemistry offers several advantages over the conventional Portland cement chemistry, including enhanced durability, a reduced carbon footprint and energy content [33-36]. Fly ash, granulated blast furnace slag and metakaolin can be used as aluminosilicate precursors in the conventional approach to production of alkali aluminosilicate binders via alkali activation. The robust chemistry of alkali aluminosilicate precursors. The large-volume use of wastes as raw materials in production of alkali aluminosilicate cements should address the need to ensure consistent satisfaction of the targeted performance requirements in spite of the variability of waste raw materials [37].

Binders based on alkali aluminosilicate chemistry have been developed largely as aluminosilicate precursors that are transformed into a solid binder by the addition of highly alkaline solutions. This "two-part" approach to producing an inorganic binder deviates from the common practice of producing a solid binder using Portland cement where water (in lieu of alkaline solutions) induces

hydration reactions. In spite of this, the important sustainability and performance advantages of this class of binder has led to its growing applications in airfield [38] and highway [39, 40] pavements, and infrastructure repair [35, 41-44].

The work reported herein is part of efforts to devoted to development of hydraulic cements based on alkali aluminosilicate chemistry that can transform into a solid binder by simple addition of water and curing at room temperature. This work involved production of an alkali aluminosilicatebased hydraulic cement at pilot scale, its use for production of concrete in a ready-mix truck, and construction of a walkway using common field practices. The particular hydraulic cement considered here was formulated with waste brick as one aluminosilicate precursor. The field construction was implemented in mid-Michigan on October 18, 2017.

4.2. Materials

Waste brick, coal fly ash and ground granulated blast furnace slag were used as aluminosilicate precursors. The coal fly ash used for this investigation was obtained from the Erickson Power Plant operated by the Lansing Board of Water & Light (LBWL) in Lansing, Michigan (USA). The waste brick used for this study was obtained from a landfill in mid-Michigan (USA). As-received waste brick was crushed to produce particles of about 75 mm size. Ground ganulated blast furnace (GGBF) slag was obtained from LafargeHolcim in Ohio (USA). The alkaline constituents of raw materials included sodium carbonate, sodium silicate and calcium oxide. Sodium silicate was purchased from JJ Chemicals in Fort Benning, Georgia (USA). Sodium carbonate was purchased from Pete Lien and Sons Inc in Rapid City, South Dakota (USA). Borax was purchased from Sigma-Aldrich

in powder form. Graded standard silica sand (ASTM C778) was used as fine aggregate to prepare standard mortar mixtures. Concrete mixtures used natural sand and coarse aggregate of 19 mm maximum particle size, that were provided by High Grade Materials Co. of Lansing, Michigan (USA).

4.3. Alkali Activated Binder Formulation and Processing Methods

4.3.1. Formulation and Processing

The raw materials formulation used for processing of hydraulic cement is introduced in Table 17. These raw materials were mechanochemically processed via steel ball-milling using the pilot-scale mill shown in Figure 26. This mill measures 91cm in depth and 61cm in diameter. The steel balls (Figure 27) used in the mill were of three different sizes (Table 18). As a first step in mechanochemical processing of raw materials, brick waste, sodium carbonate and 1% moisture were milled for 20 minutes to activate the waste brick. Subsequently, the remaining raw materials (of Lansing, Michigan (USA).) were added to the mill, and milling was continued for an additional 40 minutes. This milling operation yielded 40 kg of binder. The pilot-scale mill was operated seventeen times to produce 680 kg of cement for use in the field construction project.

	$- \cdots$						
Coal Fly Ash	GGBF	Brick Waste	Sodium Carbonate	Sodium Silicate	Calcium Oxide	Borax	
48%	20%	20%	5%	4%	3%	1% wt of raw materials	

Table 17. The formulation of raw materials (proportions by weight)

50



Figure 26. The pilot-scale ball mill used for processing of the hydraulic cement



Figure 27. Steel balls of different size used in the milling process

Ball type	Mass, g	Diameter, cm
Small	65	2.5
Medium	200	3.5
Large	500	5.0

Table 18. Weights of the steel balls of different size

4.3.2. Storage of Hydraulic Cement

The hydraulic cement was produced in the period from 9/18/2017 through 10/18/2017. In order to reduce the chance of reactions between the moisture in air and he hydraulic cement during the storage time of up to 1 month, the manufactured cement was stored in a plastic container (Figure 28).



Figure 28. The type of plastic container used for storage of cement

4.3.3. Quality Control

During the pilot-scale production of hydraulic cement, samples were taken every other day (during weekdays) for the purpose of quality control through preparation of standard mortars and performance of set tome and compressive strength tests per ASTM C403 and ASTM C109. The 7-day compressive strength test results summarized in Table 19 are the mean values of compressive strengths measured for three standard cubic mortar specimens produced with the cement samples obtained on a daily basis. The compressive strength test results exhibit random variations, occurring mostly within the 11-14 MPa range at 7 days of age. These values are about 40% smaller than those obtained with similar cements processed at laboratory scale. The milling conditions at laboratory scale were more favorable, particularly as far as the weight ratio of steel balls to the raw materials is concerned. The transformation of raw materials into a hydraulic cement was thus more advanced under the laboratory-scale milling conditions considered prior to this scale-up effort. It was judged that the quality of the cement processed at pilot scale was acceptable for construction of sidewalks in the field project that was subject of this investigation. Set times were measured in outdoor conditions in preparation for the field construction work. The initial set time was measured at 60 minutes for outdoor temperatures of about 18°C. and increased to 120 minutes as the outdoor temperature dropped to about 10° C. As an adjustment for construction at lower temperatures, the sodium silicate content in the formulation of raw materials was increased from 4% to 5% in order to accelerate the setting and the early-age strength gain processes. This additional 1% sodium silicate content, however, could not be added during mechanochemical processing of the hydraulic cement. It was simply blended with the original hydraulic cement considering that the temperature during field construction was about 10°C.

Cement Sample	7-Day Compressive Strength, MPa
1	11.00
3	14.16
5	12.30
7	12.60
9	14.35
11	10.06
13	10.90

Table 19.7 day compressive strength quality control testing

4.4. Field Demonstration

4.4.1. Production of Concrete in Ready Mix Plant

The hydraulic cement was transported to a ready-mixed concrete plant operated in Lansing, Michigan (USA) by High Grande Materials Co. The concrete mix design used for the field construction work is introduced in Table 20. The ready-mix concrete truck was first loaded with about half of the required quantities of natural sand and coarse aggregate. The hydraulic cement was then added (Figure 29), followed by the remaining natural sand and coarse aggregate, and finally water and a normal dosage of an air entraining agent. The total volume of concrete prepared was close to 2 cubic meter. Mixing in the ready-mix truck followed the procedures commonly used for normal Portland cement concrete.

1 dole 20. Concrete mix design		
Material	Kg/m ³	
Alkali activated binder	445	
Natural sand	1029	
Limestone coarse aggregate	1305	
Water (w/c = 0.35)	156	

Table 20. Concrete mix design



Figure 29. Addition of the hydraulic cement to the ready-mix concrete truck

4.4.2. Field Construction and Testing

The concrete prepared in the ready-mixed concrete plant was transported over about 30 kilometer to an apartment complex in East Lansing, Michigan. Concrete was poured at about 4:45 pm at a temperature of 10-15°C in sunny condition. The slump of concrete was measured at 89 mm (Figure 30), and its initial set time at 90 minutes. The fresh concrete was placed and finished conveniently although its bulk rheology and surface characteristics could be characterized as more cohesive than a normal Portland cement concrete. Figure 31 shows different stages of construction; compatibility of the concrete produced with the new hydraulic cement with conventional field construction practices was verified through successful construction of the sidewalk.

Concrete specimens were prepared (Figure 32) using samples of fresh concrete obtained from the ready-mix truck for testing in laboratory.



Figure 30. Performing of slump test on fresh concrete







- (a) Site
- (b) Concrete discharge

(c) Pouring of concrete



(d) Leveling



(e) Bull floating



(f) Troweling





(g) Brooming (h) Finished sidewalk Figure 31. Different stages of field construction



Figure 32. Field preparation of concrete specimens for laboratory testing

4.5. Laboratory Results

Compressive strength tests were performed on the cylindrical samples taken from the field concrete mix. Half of the samples were cured in outdoor condition, and the other half in a controlled laboratory environment in sealed condition. Compressive strengths were measured at 2, 7 and 28 days of age. The Michigan Department of Transportation specifications for concrete pavements require minimum compressive strengths of 17.9 MPa and 24.1 MPa after 7 and 28 days of curing, respectively. The compressive strength results summarized in Table 21 indicate that both the outdoor and controlled curing conditions produced compressive strengths that meet the requirements for use in pavement construction.

 Table 21. Compressive strength test results at different ages for concrete specimens prepared in field and curing in different conditions

Curring Condition	Age, days		
Curing Condition	2	7	28
Outdoor	2.85 MPa	19.4 MPa	24.2 MPa
Controlled Indoor	7.31 MPa	21.0 MPa	28.9 MPa

4.6. Field Performance

The outdoor temperature during the first month after construction ranged from -6°C to 21°C; the field work was also exposed to substantial rainfall and some light snow during this period. No obvious cracking or surface deterioration was detected after one month. The surface appearances of the sidewalk after different periods of exposure to weathering effects are shown in Figure 33. The walkway surface appeared to change color over time, starting from a brown, and converting to increasingly bright grey. It should be noted that the cylindrical specimens cured outdoors

exhibited this same color change while those cured in controlled laboratory condition retained their original brown color.



(a) 2 days (b) 7 days (c) 21 days (d) 28 days Figure 33. Surface appearance of the concrete walkway after different periods of exposure to weathering effects

4.7. Conclusion

A high-recycled wastes content alkali aluminosilicate cement was manufactured at pilot scale for use in industrial-scale production of concrete and performance of a field demonstration project. The cement was used as a full replacement for Portland cement in concrete.

The cement developed in the project exhibited longer set times and lower rates of strength development at colder temperatures. The hydraulic cement formulation was tailored to suit concrete construction at colder temperatures. The tailored formulation exhibited adequate retention of fresh mix workability for industrial-scale production of concrete, its transportation to the job site, and timely implementation of field construction steps.

The concrete walkway constructed with the sustainable cement was exposed to moderate to freezing temperatures as well as substantial rainfall and some light snow during a one-month period after construction. No cracking or damage can be observed on the concrete surface.

Concrete specimens were prepared in field, and cured either in field or in controlled laboratory condition. While the colder field curing produced somewhat reduced compressive strengths, both field and laboratory curing produced 7- and 28-day compressive strengths which meet the requirements relevant to pavement applications of concrete materials.

The experience gained with pilot-scale production of cement, industrial-scale production of concrete, and field construction of a walkway point at the scalability of the high-recycled-content alkali aluminosilicate cement, and its compatibility with industrial-scale production of concrete and conventional field construction practices. The cement developed in the project offers the potential for full replacement of Portland cement in concrete construction.

5. Development of an Alkali-Activated Binder Incorporating Copper Tailing Mine Waste as an Aluminosilicate Precursor

5.1. Introduction

Environmental concerns are major issues in the mining industry. Current mining practices generate significant quantities of wastes (mine tailings), including the ore processing wastes. The toxic constituents of these wastes and their current disposal methods in tailing dams and ponds pose hazards to the environment. Contamination of the surrounding soils and groundwater supplies are examples of such hazards. When stockpiled, mine tailings can alter pH levels of soil, turning them acidic, which has strong negative impacts on the surrounding ecosystem [45]. Mine wastes have accumulated in tremendous quantities across the world. Value-added and large volume applications, which simultaneously immobilize their toxic constituents, would yield significant sustainability benefits.

Copper is a metal with vast applications that is mined worldwide and especially in the United States [46]. The United States Geological Survey (USGS) has indicated that there is a growing demand for copper; the global consumption of copper increased by 39.5% between the years 2003 and 2016 [46]. The United States Geological Survey's most recent publication indicates that 19.4 million tons of copper were produced globally, and that reserves totaled 720 million tons [46]. A past study by Robert Gordon indicated that the quality of copper ores (the percentage of usable copper) has continuously decreased over time; the ratio of waste materials per copper ore mined is thus increasing with time [47]. Today, copper ore is estimated to be composed of just 0.5 - 2% copper metal with the remains being tailings [45, 47, 48]. Based on these numbers, between 970 million and 3.88 billion tons of copper tailings were produced globally in 2016 alone. Given the

decreasing quality of copper ores, this supply of tailings will continue to rise at an increasing rate if the mining of copper continues to increase as it has for the past several decades.

Prior studies have indicated that copper tailings, when used as a partial substitution for Portland cement in concrete, provide improved strength, abrasion resistance and water impermeability [49, 50]. The hazardous heavy metals often found in copper tailings have also been found to stabilize as a result of hydration of cement in concrete [49]. A past investigation that is more relevant to this work has indicated that a geopolymer binder based on copper tailings and fly ash could achieve compressive strengths greater than 21 MPa at 7 days of age. This study also noted that the copper tailings were highly reactive and therefore made significant contributions to the strength development of concrete during the first 7 days of curing [51].

Alkali-activated cements constitute a large family of inorganic binders which solidify upon exposure of various aluminosilicate precursors to alkaline solutions. The aluminosilicate precursors commonly used in alkali-activated binders include coal fly ash, slag and kaolinite clay; mine tailings have also been used in this application [52-54]. The alkalis used for activation of these aluminosilicate precursors include sodium hydroxide and sodium silicate [52, 53]. Depending on the specifics of their formulation and curing condition, alkali-activated binders can provide competitive or superior strength, impermeability, chemical resistance, fire resistance and sustainability features when compared with Portland cement concrete [55, 56]. Alkali-activated binders have a more robust chemistry, and can be produced using broader selections of raw materials. This is an important advantage that allows for potential use of some market-limited wastes (generally as aluminosilicate precursors) in alkali-activated binders. At the same time, one should be aware of the variations in material properties resulting from the use of alternative aluminosilicate precursors in alkali-activated binders.
5.2. Materials

Coal fly ash was used as an aluminosilicate precursor in this investigation. The fly ash was obtained from the Erickson power plant operated by the Lansing Board of Water and Light (LBWL) in Lansing, Michigan. The chemical composition of this ash is presented in Table 22. This fly ash qualifies as Class C fly ash per ASTM C618

Ground granulated blast furnace slag, obtained from LafargeHolcim, Ohio, was used as another aluminosilicate precursor. Table 22 presents the chemical composition of this slag.

The copper tailing used as an aluminosilicate precursor was acquired from Montana Resources Co. in Butte, Montana. Montana Resources mines copper ore and, through a smelting and floating process, separates copper from the tailing. The copper tailing was shipped with a sandy morphology as seen in Figure 34. The crystalline structure of the copper tailing was examined with an x-ray powder diffraction (XRD) analysis and the results are presented in Figure 35. The XRD analysis indicates that the copper tailing is a crystalline material with large amounts of quartz and some calcite present. The chemical composition and the mineralogy of the copper tailing is presented in Table 22. The copper tailing was composed highly of silica oxide (SiO₂) and alumina oxide (Al₂O₃) which suggests that it could be an excellent aluminosilicate precursor.



Figure 34. Copper tailing in as-received condition



Figure 35. X-ray powder diffraction analysis of the copper tailing (Q= Quartz (SiO2), C= Calcite (CaCO3)

Waste Raw	SiO ₂	Al ₂ O ₃	CaO	SO ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	TiO ₂	P_2O_5
Material										
Copper	44.28	18.14	<2.72	0.72	3.78	-	8.67	0.81	1.73	0.87
Tailings										
Coal fly	30.6	15.1	22.2	-	16.8	2.30		2.60	-	-
ash										
Waste	61.63	1.79	20.71	0.78	4.55	1.2	5.9	1.02	0.18	0.77
Glass										

Table 22. Chemical composition of aluminosilicate sources (%)

Table 22. (cont'd)

	GGBF slag	37.5	9.54	40.8	-	0.43	10.85	_	0.45	-	-
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Waste glass was obtained from the Granger Recycling Center in Lansing, Michigan [10, 57-61]. Kaolinite [15-17], sodium silicate, sodium hydroxide, sodium carbonate, calcium oxide, borax and citric acid were purchased from Sigma-Aldrich in powder form. A polycarboxylate-based superplasticizer was purchased from Fritz-Pak Corporation (Dallas, Texas). A graded standard silica sand (ASTM C778) was used as fine aggregate for mortar samples.

5.3. Hydraulic Cement Formulations and Processing Method

Multiple cement formulations were investigated in this investigation. Each formulation was designed to maximize the contents of waste materials while producing a desired balance of set time and strength per ASTM C1157 while providing adequate moisture stability. Mechanochemical processing was used to convert the raw materials into a hydraulic cement based predominantly on alkali aluminosilicate chemistry. Mechanochemical processing refers to the use of mechanical energy to induce physio-chemical phenomena that activate and compound the raw materials [62]. Mechanical energy was input to the raw materials via ball-milling Figure 36 their blend over 2 hours with a steel ball-to-powder weight ratio of 8:1. The formulations of raw materials that were investigated are introduced in Table 23.



Figure 36. Steel ball-milling jar and apparatus

Table 23. Alternative formulations (wt.%) of raw materials used for mechanochen	nical
processing of hydraulic cements, and the additives used during mixing	

Sampla			Raw	V Materials			
Sample	Ash	Slag	Copper Tailing	Na ₂ SiO ₃	NaoH	Na ₂ CO ₃	CaO
B-11-A	45	20	20	7	5	-	3
B-12-A	45	20	20	7	-	5	3

Several different additives/supplementary materials were added in small dosages to various hydraulic cements during preparation of mortar mixtures. Some of these materials were activated prior to being added to the hydraulic cements. Kaolinite was calcined at 750°C for 12 hours. Waste glass was crushed into fine particles and mechanochemically processed with sodium carbonate with a glass: sodium carbonate weight ratio of 4:1 and with 2% moisture for 2 hours. It was determined, through multiple trials, that the mixing of sand, powder and additives for 3 minutes in a mortar mixer at medium speed was adequate for producing homogenous mixtures.

5.4. Experimental Evaluation of Hydraulic Cements

5.4.1. Alkalinity in Solution

The alkalinity levels of the hydraulic cements were measured by performing pH tests per ASTM C25. In this test, 5g of cement was mixed with 45mL of deionized (DI) water, and shaken (Figure 37) for 30 minutes. After shaking, the solution was allowed to stand still for 30 minutes before making measurements. The solution was then shaken for 24 hours, and measured again. The pH level of the solution was measured together with the total dissolved solids (TDS) and electrical conductivity. Figure 37 shows the apparatus by which these samples were stirred and Figure 38 shows the equipment utilized for the pH, TDS, and electrical conductivity measurements.



Figure 37. Shaking apparatus



Figure 38. pH, TDS and Conductivity apparatus

5.4.2. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) records the mass loss of a sample with increasing temperature at a constant rate. The results of a TGA test can help determine the physical attributes and chemical composition of a material. The rates of mass loss at different temperatures can also be found as derivatives of the mass loss test data versus temperature (DTA). TGA was executed using samples of approximately 100mg with a Perkin Elmer TGA 4000 at a heating rate of 10°C/min from 50 to 950°C under a nitrogen atmosphere.

5.4.3. Fourier Transform Infrared (FTIR) Spectroscopy

The Fourier transform infrared spectroscopy (FTIR) test was performed in order to detect the formation of chemical bonds via mechanochemical processing of raw materials. To execute an FTIR test, the cement powder was compressed into pellets (Figure 39). A pellet made of 0.125g of potassium bromide was used to establish the baseline. A pellet composed of 0.125g of potassium bromide and a small amount of the cement powder was then tested. The FTIR test was run by utilizing the JASCO Spectophotometer (Figure 40). The tests were performed using wavelengths

ranging from 400 cm⁻¹ to 4000 cm⁻¹, with the data recorded over 250 scans at a spectral resolution of 4 cm⁻¹.



Figure 39. Carver pellet press



Figure 40. JASCO FTIR Spectrophotometer

5.4.4. Compressive Strength

Mortar specimens were prepared per ASTM 1157C requirements. Immediately after mixing, the fresh mix flowability was measured on a flow table (Figure 41) per ASTM C1437-07. The fresh mix was then used to prepare 50mm cube specimens. The molded specimens were sealed and stored for 24 hours at room temperature. After 24 hours, they were demolded, sealed and allowed

to cure at room temperature for 3, 7 and 28 days. The compressive strength values were measured at these ages per ASTM 1157C.



Figure 41. Flow table

5.4.5. Measurements of Heavy Metals Concentrations in Leachated Using Inductively Coupled Plasma (ICP) Spectroscopy

Sample powders were subjected to inductively coupled plasma (ICP) analysis in order to measure the concentrations of different trace metals. This was necessary to determine whether the samples had successfully immobilized the dangerous trace metals present in the raw materials prior to milling. The samples were turned into solutions of approximately 1% - 2% HNO₃ prior to the ICP analysis. A blank sample was prepared by the same method used to prepare the unknown samples. The blank sample was run to check the cleanliness of the sample preparation procedure. A series of standard solutions with varying concentrations of multi-element standards were prepared in order to determine the concentrations in unknown sample solutions.

5.5. Results and Discussion

5.5.1. Alkalinity in Solution

The results, presented in Table 24 indicate that, after shaking for 30 minutes, the milled cement powder provided higher levels of pH, conductivity and total dissolved solids when compared with a similar blend of raw materials that was not milled. This observation points at the rise in solubility of raw materials upon milling. After 24 hours, the measurements revealed that both B-11-A samples experienced significant reductions in total dissolved solids and electrical conductivity while the B-12-A samples remained constant. The pH levels were shown to consistently exceed 13, which is ideal for alkali-activated cements.

Material		30-minute	results		esults	
	pН	TDS	Conductivity	pН	TDS	Conductivity
Copper Mine Tailing	9.06	58.12 ppm	118.3 µS/cm	9.08	57.63 ppm	117.8 µS/cm
B-11-A (blend)	13.48	24.04 ppt	49.04 mS/cm	13.54	14.33 ppt	29.23 mS/cm
B-11-A (milled)	13.60	24.52 ppt	50.04 mS/cm	13.60	21.01 ppt	42.88 mS/cm
B-12-A (blend)	13.33	14.01 ppt	28.59 mS/cm	13.46	13.88 ppt	28.21 mS/cm
B-12-A (milled)	13.37	14.49 ppt	29.57 mS/cm	13.43	14.12 ppt	28.85 mS/cm

Table 24. pH, total dissolved solids (TDS) and conductivity test results at 30 minutes and 24 hours

5.5.2. Thermogravimetric Analysis (TGA)

The TGA test results are presented in Figure 42. The DTA test data is presented in Figure 43. Several peaks can be observed in Figure 43. The copper tailing exhibits peaks at approximately 550°C and 750°C, while B-11-A and B-12-A show peaks around 100°C, 400°C and 700°C. The peaks are shifted between the copper tailing to the binder samples, indicating chemical changes

during the milling process. The peaks at 100°C indicate the presence of hydrates. The peaks at 400°C indicate chemically bound hydrates. The peaks observed at approximately 700°C indicate the presence of carbonates. The formulation B-12-A shows substantially greater mass loss at this temperature indicating that a larger amount of carbonates had formed during the milling process.



Figure 42. TGA data for hydraulic cement formulations and the copper mine tailing



5.5.3. Fourier Transform Infrared (FTIR) Spectroscopy

The samples show below, in Figure 44, observe several different peaks. The samples B-11-A and B-12-A observe larger peaks at approximately 3400 cm⁻¹, 1400 cm⁻¹ and 1050 cm⁻¹. The peaks at 3400 cm⁻¹ indicate the presence of water while the peaks at 1400 cm⁻¹ are indicative of carbonates, which both support the observed peaks on the DTA plot in Figure 43. The peaks at 1050 cm⁻¹ indicate the presence of silica. The presence of silica is expected due to the large quantity of aluminosilicate present in each formulation. The copper tailing sample observes this peak as well, which is expected because it contains 44% silica oxide content as shown in Table 22.



Figure 44. Fourier transform infrared (FTIR) spectroscopy data

5.5.4. Compressive Strength

The initial effort relies upon superplasticizer to produce hydraulic cements that met requirements relevant to fresh mix workability and set time. Superplasticizer was an effective additive in Formulations B-11-A and B-12-A. The specifics of the composition of commercially available superplasticizers, however, are protected as trade secrets; these specifics are also subject to change over time. Therefore, one cannot rely upon them as generic raw materials for formulation of a new class of hydraulic cement. The relatively high cost of commercially available superplasticizers is another concern. Efforts were thus made to find replacements for superplasticizer in formulation of hydraulic cements, considering that formulations used with superplasticizer offered 7-day compressive strength of 21 to 23 MPa. The replacements considered here included borax, citric acid, activated glass, and activated kaolinite. These replacements were considered due their potential role in improving the fresh mix workability and set time. Activated glass and activated kaolinite were particularly effective in matching these qualities offered by superplasticizer. Most

replacements were selected to lower the rate of reactions, enabling the fresh cement paste to retain its workability over longer periods. The 7-day compressive strengths obtained with activated glass and activated kaolinite were 21 MPa and 19 MPa, respectively (see Figure 45). The flow test data presented in Figure 46 confirm that the replacements considered here for superplasticizer matched its ability to improve fresh mix workability. Activated glass and activated kaolinite were used with the hydraulic cement at additive: cement weight ratio of 10: 90. Their favorable economics makes them less costly than superplasticizer, which was used at 0.5% by weight of cement. It should be noted that borax and citric acid, which were also considered as replacement for superplasticizer, were used at 1% by weight of cement.



Figure 45. 7 day compressive strength measurements of formulations with additives

The flow diameters shown in Figure 46 indicate the samples replacing the superplasticizer with activated glass and activated kaolinite both produced a material with similar or superior flowability compared to the superplasticizer sample. Borax and citric acid proved to be effective in increasing

the flowability of the samples (Figure 46), however they were found to cause significant reductions in compressive strength (Figure 45).



Figure 46. Flow diameter measurements of formulations with additives

5.5.5. Toxicity Characteristics per LEAF Procedure (ICP)

The degree of immobilization of heavy metals was evaluated using the "synthetic precipitation leaching procedure (SPLP)" suggested by USEPA (1996). The immobilization efficiency was calculated using the following equation [63]:

$$\eta(t)\% = \left(1 - \frac{C(t) \cdot V_{leach}}{q^{24h} \cdot W_{solid}}\right) \cdot 100$$
(2)

where, $\eta(t)$ % is the immobilization efficiency (%) of the hydraulic cement treated mechanically for a time interval of t(s), C(t) (mg L⁻¹) is the heavy metal concentration of leachate, V_{leach} is the

leachate volume (L), q^{24h} (mg kg⁻¹) is the initial heavy metal concentration in untreated soil (Equation (2)), and W_{solid} (kg) is the solid weight used in the test. The test results are presented in Figure 47, and the values of percent immobilization values calculated using the above equation are presented in Figure 48. Percent immobilizations achieved with B-12-A formulation Figure 48. These results point at the high degree of heavy metals immobilization provided by the binder chemistry based on alkali aluminosilicate hydrates. The Cu, Ba, Ti and Mn constituents of the copper mine tailing were 100% immobilized; the degree of immobilization of the Sr constituent of mine tailing was more than 95%. These results suggest that abundant wastes which could be hazardous could offer the potential for value-added use as aluminosilicate precursors in the approach to production of alkali aluminosilicate cements developed in this work, yielding safe cement hydrates and concrete materials which effectively immobilize the heavy metals constituents of the hazardous aluminosilicate precursor.



Figure 47. Heavy metal concentrations in the leachate of the hydrated paste B-12-A formulation at 7 days of age versus the initial concentrations in copper mine tailing



Figure 48. Percent immobilizations achieved with B-12-A formulation

5.6. Conclusion

Due to its high silica and alumina contents, copper mine tailing can be an effective aluminosilicate precursor in alkali-activated binders. The results of this investigation indicate that copper tailing can be an effective aluminosilicate precursor at quantities as high as 20% in formulation of high-recycled-content alkali aluminosilicate hydraulic cements subjected to energy-efficient mechanochemical processing. Copper mine tailing incorporates heavy metals at concentrations which mitigate its use in many applications. An experimental investigation was conducted in order to assess the potential for immobilization of the hazardous constituents of copper mine tailing by the cement hydration products. Results of the ICP spectroscopy tests performed for this purpose indicated that the heavy metals present in the copper mine tailing were substantially immobilized by the hydrated cement paste at an early age of 7 days, considering that the hydration (geopolymerization) process is not complete at this age. This finding suggests that abundant wastes which are rich in aluminosilicates could feasibly be used as aluminosilicate precursors in the

cement production process developed here in spite of their relatively high heavy metals concentrations which prevent them from use in other applications.

The use of copper mine tailing as an aluminosilicate precursor in production of cement led to increased demand on water content for achieving desired fresh mix workability. Viable solutions involving the use of generic additives such as activated kaolinite or waste glass were developed to effectively resolve this problem.

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