BENEFICIAL USE OF CARBON DIOXIDE TO TRANSFORM LANDFILLED ASH INTO A HYDRAULIC CEMENT WITH DESIRED HAZARDOUS WASTE IMMOBILIZATION QUALITIES

By

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ABSTRACT

BENEFICAL USE OF CARBON DIOXIDE TO TRANSFORM LANDFILLED COAL ASH INTO A HYDRAULIC CEMENT WITH DESIRED HAZARDOUS WASTE IMMOBILIZATION QUALITIES

Ву

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Carbon dioxide is a major greenhouse gas; power generation via combustion of fossil fuels, and production of Portland cement are among the key sources of anthropogenic CO₂ emissions. Past and ongoing combustion of coal has led to accumulation of billions of tons of coal ash in landfills. While there are concerns with the environmental impacts of the landfilled ash, this ash embodies valuable mineral resources such as aluminosilicates, calcium compounds and alkalis. The main thrust of this project was to make beneficial use of landfilled ash together with supplementary solid minerals and carbon dioxide gas to produce a hydraulic cement via sustainable processing techniques. This hydraulic cement was developed primarily for hazardous waste stabilization/solidification applications. The hydraulic cement chemistry and processing techniques were refined through an experimental investigation, and the effectiveness of this cement in immobilization of heavy metals was verified. The production process of cement utilizes significant quantities of carbon dioxide as raw materials with beneficial effects on the performance characteristics of cement hydrates.

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Chapter 1. Introduction

1.1 Motivation

The accumulation of anthropogenic greenhouse gases, predominantly CO₂, in the atmosphere is a major cause of climate change. Carbon sequestration via mineralization has been researched extensively; the high temperatures and pressures required for accelerated carbonation, however, represent serious drawbacks in mineral carbonation. Extraction, shipment and processing of minerals for carbonation, purification of carbon dioxide, and subsequent disposal of carbonated minerals are other challenges of carbon sequestration via mineralization. Mineral carbonation can emerge as a viable and high-impact means of reducing the CO₂ emissions as far as: (i) carbonation reactions add value for large-volume use of carbonated minerals; (ii) mineral carbonation can be accomplished via energy-efficient methods which do not resort to elevated temperatures and pressures; (iii) flue gases with relatively low CO₂ concentrations can be used directly or with minimal treatment for mineral carbonation; (iv) the minerals to be carbonated are abundantly available for low-cost extraction in the vicinity of major sources of carbon emission (e.g., fossil fuel-burning power plants); (v) the costs of implementing the technology at major sources of carbon emissions are rationalized by the value realized via beneficial carbonation reactions; (vi) the approach to mineral carbonation yields environmental and health benefits beyond carbon sequestration; and (vii) large volumes of carbon dioxide are converted into stable carbonates to make meaningful contributions towards reduction of carbon emissions. All these conditions are met by the approach to mineral carbonation adopted in this project.

Combustion of fossil fuels in power plants is the largest source of anthropogenic carbon dioxide emissions. Coal-burning power plants also produce significant quantities of solid wastes, including fly ash and bottom ash. The same is true in combustion of biomass and solid waste for power generation. The trends in coal ash generation and disposal rates suggest that close to 5 billion tons of coal ash have been impounded and landfilled in the vicinity of the U.S. power plants; global deposits of coal ash add up to several billions of tons, with an annual growth rate of about 0.5 billion tons. The trend towards cleaner coal combustion is actually increasing the ash generation rate per unit mass of coal combusted, and is also compromising the quality of coal ash. There are growing concerns with the environmental and health impacts of the billions of tons of coal ash that have been impounded and landfilled.

This development effort views coal ash as a mineral resource which can be beneficiated via capture of CO₂ emissions, and simultaneously compounded into a hydraulic binder with distinct qualities for solidification/stabilization of hazardous wastes, and also for construction applications. This approach relies upon: (i) a novel method of selectively incorporating carbonate anions into ash particles without resorting to elevated temperatures and pressures; (ii) alkali activation of ash parallel with incorporation of carbonate anions to produce a hydraulic binder; and (iii) effective solidification/stabilization of hazardous and radioactive wastes via integrated zeolitization and carbonation effects.

This research focused on value-added use of carbon dioxide and landfilled coal ash (with supplementary materials) to produce a hydraulic cement with desired capabilities for hazardous waste immobilization.

1.2 Summary of research

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.

1.2.1 Development of refined chemistries and processing methods for integration of carbon dioxide into a hydraulic binder for effective heavy metal immobilization

A method was developed for capture of carbon dioxide directly from combustion emissions into landfilled

coal ash, and simultaneous transformation of the carbon dioxide and ash with supplementary minerals into a hydraulic binder. In this study, several additives were investigated for raising the CO₂ uptake of landfilled ash and enhancing the end-product quality. The resultant binder meets the standard requirements for hazardous waste solidification/stabilization. The approach adopted here relies upon mechanochemical phenomena, induced by a simple milling action, to incorporate carbon dioxide into landfilled ash while concurrently transforming the raw materials (including the captured carbon dioxide) into a hydraulic binder. The CO₂ uptake in mechanochemical processing of cement was estimated as the difference in Loss Of Ignition (LOI) of cements milled in CO₂ and in air. The compressive strength achieved by hydration of cement was assessed after 7 days of curing at room temperature. The Toxicity Characteristic Leaching Procedure (TCLP) was used to evaluate the solidification/stabilization qualities of hydraulic cements. FTIR spectroscopy was used in order to get better understanding on the nature of the carbon dioxide incorporated into the hydraulic cement via mechanochemical effects. The results indicated that relatively high concentrations of carbon dioxide (up to 20 wt.%) could be incorporated into hydraulic cements with desired hazardous waste stabilization/solidification qualities. The captures carbon dioxide benefited the resultant hydraulic cement performance.

1.2.2 Carbon Dioxide Use in Beneficiation of Landfilled Coal Ash for Hazardous Waste Immobilization

Landfilled coal fly ash and supplementary minerals were processed into a hydraulic cement via input of mechanical energy at ambient temperature in the presence of carbon dioxide (considered as a gaseous raw material). An experimental program was conducted with the purpose of optimizing the raw materials formulation for achieving a desired balance of the cement CO₂ uptake, and the strength and heavy metals immobilization qualities of the cement hydration products. The optimum formulation was found to complement high levels of CO₂ uptake with desired material properties offered by the hydration products. Insight into the structure of hydration products was gained by evaluating their chemical bond structure and thermogravimetry attributes.

1.2.3 Mechanical Processing of Cements Formulated with Landfilled Ash in Different Environments

A landfilled coal fly ash was blended with different constituents for achieving a balanced chemistry that suits production of hydraulic cement and concurrent capture of carbon dioxide. The blends of raw materials were processed via input of mechanical energy into hydraulic cements. The input of mechanical energy via milling was performed in three different environments: air, N₂ and CO₂. The resultant hydraulic cements were characterized through assessment of their specific surface area, microstructure (scanning electron microscopy), chemical bond environment (FTIR), heat of hydration, and pH, total dissolved solids and electric conductivity of their solutions. Mechanical processing of the blend of raw materials was found to transform them into a hydraulic cement. The environment of mechanical processing was also found to be an important factor influencing the properties of the resultant cement.

1.2.4 Production and Characterization of a Hydraulic Cement Produced with Landfilled Coal Ashes of Different Disposal Durations, Using Carbon Dioxide As a Raw Material

The quantities of coal ash disposed of in landfills over the past decades add up to billions of tons. These large quantities of available ash can be used as sources of valuable minerals for production of hydraulic cement. In this investigation, landfilled ashes with different disposal durations were processed together with supplementary minerals into hydraulic cement via input of mechanical energy at ambient temperature in the presence of carbon dioxide or air. The carbon dioxide uptake in the process, and the strength and heavy metals stabilization qualities of the hydration products of the resultant cement were evaluated as a function of the disposal duration of the landfilled ash. Aging of the ash in landfill was noted to produce significant changes in the carbon uptake potential, strength and hazardous waste immobilization qualities of the resultant hydraulic cements.

Chapter 2. Development of refined chemistries and processing methods for integration of carbon dioxide into a hydraulic binder for effective heavy metal

2.1 Introduction

Since the beginning of the industrial age, the carbon oxide concentration in atmosphere has increased by about 30% (Huijgen and Comans 2003, Huijgen and Comans 2007). This rise in CO₂ concentration has accompanied climate warming with adverse ecological effects. Capture of carbon dioxide for value-added use in hydraulic cement is pursued here to reduce carbon emissions. The use of landfilled coal ash as the primary raw material for production of the hydraulic cement developed here offers important environmental benefits. Significant quantities of coal ash, estimated at billions of tons, have accumulated in landfills across the world. There are concerns with the environmental and health effects of landfilled coal ash. Another consequence of human's industrial activities is generation of hazardous wastes with adverse health and environmental effects. The application pursued for the hydraulic cement developed here also provides important energy and cost savings when compared with the now prevalent Portland cement.

The CO₂ capture aspect of this development effort can be viewed as a low-cost and simple variation of the methods employed for mineral CO₂ sequestration. The approach devised here employs landfilled coal ash together with supplementary minerals, which are transformed into a hydraulic binder in the presence of a dilute carbon dioxide atmosphere which represents combustion emissions. Carbon dioxide acts as a gaseous raw materials that, together with the landfilled coal ash and solid raw materials, are transformed into a hydraulic binder under input of mechanical energy in a ball-mill at ambient temperature and atmospheric pressure. Some distinguishing features of this approach when compared with methods commonly employed for mineral CO₂ sequestration (Silverstrim, Rostami et al. 1997, Dermatas and Meng 2003, Fernandez Bertos, Simons et al. 2004, Qian, Cao et al. 2006, Ahmaruzzaman 2010) are: (i) use of abundant (landfilled) industrial by-products as the primary minerals in the process; (ii) value-added use of carbon dioxide as a raw material; (iii) low-cost, energy-efficient and sustainable method of processing via simple milling action at ambient temperature and atmospheric pressure; (iv) high value of the end

product as a hydraulic binder for hazardous waste stabilization and also use construction applications; and (vi) a two-step process of transforming carbon dioxide into a stable crystalline carbonate, where the carbonate formed initially is not crystalline but transforms into a crystalline carbonate in the course of hydration of the cementitious binder.

Achievement of high CO₂ uptake was an important objective of this project. For this purpose, the raw material blend was modified by the addition of supplementary materials that have been found to raise CO₂ uptake in the conventional methods of mineral sequestration. These additives, and their mechanisms of action are: (i) sodium bicarbonate for catalytic increase of the rate and extent of carbonation (O'Connor, Dahlin et al. 2005); (ii) silicate-based additives for increasing the rate and extent of carbon dioxide sorption (Olivares-Marín, Drage et al. 2010); (iii) magnesium (and calcium) silicate for facilitating intense penetration and sorption of carbon dioxide (Kalinkin, Kalinkina et al. 2009); (iv) calcium (and magnesium) oxide for enhancing carbonation reactions; (v) amine compounds for catalytic action as CO₂ sorbents (Gray, Soong et al. 2004, Yang, Xu et al. 2008, Song, Jang et al. 2012); (vi) acetic (and other weak) acids for catalytic enhancement of the extraction of calcium ions (Huijgen and Comans 2005, Huijgen, Witkamp et al. 2006, Sipilä, Teir et al. 2008, Sanna, Dri et al. 2012, Sano, Miura et al. 2013), with subsequent use of sodium hydroxide to promote carbonation reactions; and (vii) polyethylenimine for initial adsorption of significant quantities of CO₂ (Majchrzak-Kucęba and Nowak , Yang, Xu et al. 2008). A number of these additives were evaluated for facilitating and intensifying the solid-state (mechanochemical) carbonation reactions.

2.2 Materials & Methods

2.2.1 Materials

The base formulation comprised landfilled coal fly ash, ground granulated blast furnace slag, quick lime and sodium hydroxide. Landfilled coal fly ash was obtained from a landfill in Detroit (Michigan) that stores the coal fly ash produced in a DTE Energy power plant. This ash had been disposed of in landfill for two years. Median particle sizes of this landfill coal fly ash is 14µm. The chemical composition of the ash obtained via x-ray fluorescence spectroscopy, includes: CaO (26.72 wt.%), Fe₂O₃ (21.82 wt.%), SiO₂ (19.99 wt.%), Al₂O₃ (8.89 wt.%), SO₃ (5.31 wt.%), (MgO (2.7 wt.%) Na₂O (2.7 wt.%), BaO (2.14 wt.%), TiO₂ (2.63 wt.%), K₂O (2.4 wt.%), SrO (1.64 wt.%) and P₂O₅ (1.37 wt.%).

Granulated blast furnace slag (GBFS) was supplied by Lafarge. The chemical composition of GGBF slag, obtained via x-ray fluorescence spectroscopy, includes: CaO (40.8 wt.%), SiO₂ (37.5 wt.%), Al₂O₃ (9.54 wt.%), MgO (10.9 wt.%) Fe₂O₃ (0.47 wt.%), Na₂O (0.25 wt.%) and K₂O (0.45 wt.%). Quick lime (calcium oxide) in powder foam was purchased from Sigma-Aldrich that meet analytical specification of FCC with puriss grade and density of 3.3 g/mL. Sodium hydroxide was purchased from Red Hot Devil Eye.

The base formulation was modified through the addition of various additives with the objective of achieving improvements in terms of the end product strength, CO₂ uptake, and immobilization of heavy metals. Figure 1 shows pictures of these additives that are described in the following. They were used in as-received form, except for basalt that was ground.

Dunite (a cumulate of olivine and minor crhomite (Irvine 1974)) was purchased from Persson minerals. The chemical composition of Dunite includes MgO, SiO_2 , Fe_2O_3 , CaO and Al_2O_3 . Olivine, which is the primary constituent of Dunite, comprises largely of Mg₂SiO₄ and Fe₂SiO₄.

Serpentine was supplied by Laurel Mountain Group. It is a subgroup of the Kaolinite-Serpentine group; the composition of serpentine can be espressted as [Mg, Fe, Ni, Mn, Al, Zn]₃ [Si₂O₅](OH)₄, which is a compound of six metal elements. The most common serpentite species contain large amounts of Mg. Basalt was purchased from Fisher Scientific Co LLC. Its chemical composition includes SiO₂, Al₂O₃, CaO, FeO, MgO and TiO₂. Basalt is a common extrusive volcanic rock generated from rapid cooling of lava at the surface of earth. Normally, it contains 45% to 55% silica, and its average density is close to 3.0 gm/cm³

(Kuryaeva 2004). Basalt has been categorized to different types depending on its silica, alumina and alkali contents; different levels of activity are exhibited by different types of basalt.

The celestine (or celestite) used in this study was purchased from (ebay). It is a mineral with formula (Sr,Ba)SO₄ that is generally blue in color with orthorhombic crystalline structure. Pure celestite is colorless, and the blue color is caused by its impurities.

Gypsum was purchased from Fisher Scientific Co LLC. Wollastonite, expressed by the simplified chemical

formula CaSiO₃, was supplied by Fisher Scientific Co LLC.

Clinoptilolite was purchased from Fisher Scientific Co LLC. It is a natural zeolite with a microporous arrangement silica alumina tetrahedra. the complex formula of and It has $(Na,K,Ca)_2$ - $3Al_3(Al,Si)_2Si_{13}O_{36}$ · $12H_2O$. It forms as white to reddish tabular monoclinic tectosilicate crystals with a Mohs hardness of 3.5 to 4 and a specific gravity of 2.1 to 2.2 (Sprynskyy, Buszewski et al. 2006). Talc was purchased from Sigma Aldrich. It is a mineral with pale color and waxy luster, with a chemical formula Mg₃Si₄O₁₀(OH)₂, and a hardness of 1. Talc is typically found in metamorphic rocks with abundant carbonate minerals. It is flexible, but not elastic. The carbonation reaction of talc may be expressed as Mg₃Si₄O₁₀(OH)₂+3CO₂=3MgCO₃ + 4SiO₂+H₂O (SPRINGER 1974)

Molecular sieve (13X beads -12mesh) was purchased from Sigma Aldrich. It can be expressed by the chemical formula $Na_2O:1Al_2O_3: 2.8 \pm 0.2$ SiO₂ :xH₂O.



GypsumWallastoniteClinoptiloliteTalcMolecular sievesFigure 1. Visual appearances of the additives used in this investigation.

2.2.2 Experimental method

The CO_2 uptake induced by mechanochemical processing of landfilled coal ash with supplementary minerals in carbon dioxide environment was estimated as the difference in the loss on ignition (LOI) of similar products milled in CO_2 and in air. FTIR spectroscopy was also used to better understand the nature

of the carbon dioxide incorporated into the hydraulic binder via mechanochemical means.

The compressive strength achieved by hydration of hydraulic binders was assessed following the ASTM C109 procedures. Curing was carried out at room temperature, and testing was performed at 7 and 28 days of age.

The solidification/stabilization qualities of the hydraulic binders were assessed by testing of the hydrated binder and also the hydrated binder with mixing water spiked with copper. Testing of the hydrated binder (without spiking) was performed on solid pastes cured at room temperatures until 7 and 28 days of age. The Toxicity Characteristic Leaching Procedure (TCLP) was used for this purpose. This procedure is required for regulatory purposes under the Resource Conservation and Recovery Act (RCRA) Land Disposal Restrictions (LDRs). Metal ion extractions were evaluated using the US EPA TCLP procedure. The heavy metal concentrations of leachates were determined via inductively coupled plasma (ICP) analysis. The heavy metal immobilization qualities of the hydraulic binder was assessed by spiking the mixing water with copper (30,000 ppm). Samples of the resulting pastes were prepared per ASTM C109. After curing for 7 and 28 days at room temperature, toxicity tests were performed per US EPA TCLP procedures; ICP analysis was performed to determine the leachate copper concentration.

2.3 Results and discussion

2.3.1 CO₂ uptake

In a preliminary screening process, 10 wt.% of each additive was used with the base formulation comprising 5 wt.% CaO and 5 wt.% NaOH as the main alkali activators for landfilled coal ash (90 wt.%). Table 1 presents different formulations studied and their CO₂ uptake and the coresponding pH. Additives were milled together with other raw materials over a two-hour period in the presence of carbon dioxide. CO₂ uptake was estimated as the difference in the loss on ignition (LOI) of the CO₂-milled versus air-milled hydraulic cements. The highest CO₂ uptake was achieved with the following additives (in decreasing order): Celestine (Dilmore, Howard et al. 2009), basalt, and GGBF slag. Compressive strength test results, however, indicated that celestine produced the lowest compressive strength. Hence, basalt and slag were

investigated further in order to optimize their benefits towards CO_2 uptake. Figure 2.2 presents the measured values of pH in solution and the corresponding CO_2 uptake for hydraulic cements produced via mechanochemical processing in the presence of CO_2 gas (Garrels 1983). As previous observations indicated, a high CO_2 uptake corresponds with a low alkalinity, which is expected from the incorporation of largely acidic carbonates into the alkali aluminosilicate structure.

No.	Formulation/Additive	Weigi for Pro i CO ₂	ht loss cessing n Air	%CO2 Uptak e	рН
1	Base Formulation*	13.2	9.3	3.9	12.47
2	Base Formulation with 10% GBFS	14.4	7.2	7.2	11.85
3	Base Formulation with 10% Dunite	13.8	9.7	4.1	12.48
4	Base Formulation with 10% Serpentine	14.2	11.4	2.8	12.12
5	Base Formulation with 10% Basalt	17.4	9.9	7.5	12.28
6	Base Formulation with 10% Celestine	17.0	8.9	8.1	11.18
7	Base Formulation with 10% Gypsum	14.0	11.0	3.0	12.01
8	Base Formulation with 10% Wollastonite	10.5	8.3	2.2	12.40
9	Base Formulation with 10% Clinoptilolite	15.0	12.8	2.2	12.37
10	Base Formulation with 10% Talc	12.9	9.8	3.1	11.97
11	Base Formulation with 10% MS	9.7	7.5	2.2	12.30

Table 1. Percent CO₂ uptakes in the presence of different additives.

* Landfilled Ash: CaO: NaOH at 90: 5: 5 weight ratios

Basalt was further investigated as an additive in mechanochemical processing in CO₂ environment of hydraulic cements formulated with landfilled ash. This work was performed with 4 wt.% basalt. Moisture was introduced during mechanochemical processing of raw materials in the presence of CO₂. Table 2 presents the formulations considered at this stage of investigation, together with the CO₂ uptake and the pH in solution of the resultant hydraulic cements. The presence of basalt is observed to raise the CO₂ uptake by 2.6%, with a corresponding drop in the pH of the cement in solution. The lower dosage of basalt used here produced results which were similar to those obtained with the higher dosage of basalt used in screening tests. Milling in nitrogen was performed to gain further insight into the mechanochemical phenomena that are responsible for the uptake of CO₂ and the transformation of raw materials into a hydraulic cement. The preliminary results generated in this study indicated that the hydraulic cement processed in nitrogen actually produced a lower pH in solution when compared with that processed in air. Processing in CO₂ still produced the lowest pH value.

Table 2. Effect Basalt on the CO₂ uptake and the pH in solution of the mechanochemically processed cement.

	Notation	Mater	ial Comp	osition	(Milled)	Milling Condition	% CO₂	рН
No.	Notation	Ash	Basalt	CaO	NaoH			
1	DTE 2Y-GBasalt-CaO-C	83%	4%	6%	6%	CO ₂	7.5	9.65 12.56 (air)
2	DTE 2Y -CaO-C	87%	-	6%	6%	CO ₂	4.9	11.88 12.56 (air)
3	DTE 2Y-GBasalt-CaO-N	83%	4%	6%	6%	N ₂	-	12.26

Figure 2 compares the FTIR spectra of the CO_2 -milled versus air-milled hydraulic cements. Significant enhancement of the peak intensity at 1400 cm⁻¹ was observed with milling performed in CO_2 , which points at the strong presence of carbonates. Appearance of a new peak around 2500 cm⁻¹ with CO_2 milling may also reflect the presence of carbonates. In addition, the two peaks appearing near 1600 cm⁻¹ could be due to the formation of carbonate complexes with CO_2 milling.



Figure 2. FTIR spectra of hydraulic cements with basalt incorporated into the raw materials formulation, that were processed mechanochemically in CO₂ and in air.

Table 3 introduces the formulations incorporating GBFS investigated in this work, and the CO_2 uptake and pH in solution of the resulting hydraulic cement. The highest CO_2 uptake was obtained with 20% slag. The CO_2 uptake was estimated based on the difference in LOI between binders processed in CO_2 and in air. The formulation DTE 2Y-Slag-CaO-C provided a higher CO_2 uptake, but later studies indicated that this hydraulic cement produced a relatively low compressive strength. It was also found that the compressive strength obtained this particular cement could be increased, without lowering its CO_2 uptake, by adding a relatively small dosage of sodium silicate.

		Ma	iterial C	ompo	sition (Millin			
No	Notation	Ash	Slag	Ca O	NaO H	Others	g condit ion	% CO 2	рН
1	DTE 2Y-Slag-CaO-C	70 %	20%	5%	5%	-	CO ₂	7.2	11.86 12.46 (air)
2	DTE 2Y-Slag2-CaO-C	80 %	10	5%	5%	-	CO ₂	5.9	11.21 12.4 (air)
3	DTE 2Y-Slag-CaO-sili-C	65 %	20%	5%	5%	5% Na ₂ SiO ³	CO ₂	6.0	11.92
4	DTE 2Y-Slag-CaO-basalt-C	65 %	14%	5%	5%	6% Basalt	CO ₂	5.5	12.25

Table 3. Formulations incorporating slag, and the CO₂ uptakes and pH values of the resultant binders.

FTIR spectroscopy was used to gain insight into the mechanism and extent of CO₂ uptake for the hydraulic binders formulated with slag. The relative areas under peaks provide an indication of the extent of carbonation. Figure 3 compares the FTIR spectra of slag-based formulations milled in CO₂ and in air. Similar to basalt-based hydraulic cements, the slag-based cement exhibited a significant rise in the intensity of a typical carbonate peak at 1400 cm⁻¹ after milling in CO₂. Appearance of a new peak around 2500 cm⁻¹ may also be due to the formation of carbonates. The two new peaks around 1600 cm⁻¹ could also reflect the presence of carbonate environments.



Figure 3. FTIR spectra of hydraulic binders of similar formulations with slag processed mechanochemically in CO₂ environment and in air.

With the addition of 5% sodium silicate to the formulation, compressive strength increased significantly with only a slight drop in CO₂ uptake. Figure 4 shows the FTIR spectra for cements formulated with Slag-silicate with processing performed in air and in CO₂. The area under the pead at 1400 cm⁻¹ increased, pointing at a notable CO₂ uptake. A double peak around 1600 cm⁻¹ could also be detected for the cement milled in CO₂. The FTIR spectrum of the hydrated paste made with the formulation incorporating slag processed in CO₂ points at the presence of the carbonate peak around 1400 cm⁻¹. The peak near 1064 cm⁻¹ corresponds to Si-O and Al-O stretching bands. The bands appearing around 720-730 cm⁻¹ are associated with aluminum-rich structures such as hydroxysodalite . The band at 640-630 cm⁻¹ points at the presence of zeolitic structures . In order to confirm the formation of these zeolitic structures, more



detailed studies involving x-ray diffraction spectrometry need to be carried out.

Figure 4. FTIR spectra of hydraulic cement processed mechanochemically in CO₂ environment and in air

2.3.2 Unconfined Compressive Strength

Figure 5 shows the compressive strength test data for cement formulations incorporating slag and basalt. Both these formulations showed promising CO₂ uptakes, but produced relatively low compressive strengths. This strength loss is probably due to the reduced alkalinity associated with CO₂ uptake. Steps were taken to raise strength without compromising the CO₂ uptake. Out of different approaches taken, introduction of sodium silicate seemed more promising for formulations incorporating slag. Addition of 5 wt.% sodium silicate increased the compressive strength by a factor of 2.7 at 7 days, and a factor of 4.1 at 28 days of age. Efforts were made to formulate a hybrid cement by combining basalt (4 wt.%) and slag (20 wt.%); the compressive strength produced by the resultant cement, however, was relatively low.



Figure 5. Unconfined compressive strength test results produced by hydraulic binders formulated with slag or basalt.

2.3.3 Hazardous Waste Solidification/Stabilization

The hydraulic cement with slag-silicate formulation (65% DTE -2Y ash, 20% slag, 5% NaOH 5% CaO and 5% sodium silicate), produced via mechanochemical processing in CO₂, was subjected to the TCLP procedure. Leachates of the hydrated cement milled in CO₂ were compared with those produced with the hydrated air-milled cement. Figure 2.7 presents the heavy metal concentrations in leachates of hydrated pastes of slag-silicate binders processed in air and in CO₂. Mechanochemical processing in CO₂ (versus in air) produced notable reductions in the presence of hazardous metal cations in leachates. This finding highlights the value added to the hydraulic cement by the captured CO₂. Besides reduction of the RCRA heavy metal ions (As, Ba, Cd, Cr, Pb, Se, Ag) in leachates, a reduction in Sr was also observed. Ag and Cd concentrations were below the detection limit of the instrument. The degree of immobilization was calculated for each formulation (Figure 6). The highest copper immobilization > 99.9 % was obtained with the formulation comprising 65% landfilled ash, 20% Slag, 5% NaOH, 5% CaO and 5% sodium metasilicate (processed in CO₂).

Past research on GBFS indicates that alkali activation of GBFS can form zeolitic structures that are particularly effective in immobilization of heavy metals (Malolepszy and Deja 1988, Wang and Scrivener 1995). Formation of zeolites in alkali activated slag pastes is strongly dependent on the chemical

composition of the slag, and requires a system with relatively high Al/Si ratio and a sufficiently low Ca/Si ratio (Wang 2000). The effective solidification/stabilization of heavy metals observed here can be attributed partly to immobilization in zeolite. Besides microstructure, the pH values of pastes also play an important role in the immobilization process. High pH values benefit the immobilization qualities of the paste. In an environment with high pH (>12), heavy metal hydroxides of very low solubility precipitate (Deja 2002).



Figure 6. Concentrations of different heavy metals in leachates of the hydrated solid pastes (salg-sillicate formulation) resulting from hydration of the binders processed mechanochemically in CO₂ and in air



Figure 7. Percent immobilizations achieved with different formulations of hydraulic binders processed mechanochemically in CO₂.

Chapter 3. Carbon Dioxide Use in Beneficiation of Landfilled Coal Ash for Hazardous Waste Immobilization

3.1 Introduction

Climate change and waste management are among the environmental problems threatening sustainable development (Smith, Brown et al. 2001). Cement industry has played a vital role in development of infrastructure systems which support diverse societal and economic functions that range from sewage management to transportation. Manufacturing of Portland cement, however, is a major source of CO₂ emissions; production of one ton of Portland cement releases approximately 0.8 ton of CO₂ to the atmosphere (Davidovits 1994).

One approach to CO₂ sequestration involves permanent storage of carbon dioxide in form of thermodynamically stable mineral carbonates. This process, called mineral CO₂ sequestration, offers a safe and permanent method of CO₂ disposal, since there is no possibility of an accidental release of CO₂ from the disposal site for centuries as CO₂ is chemically incorporated into the mineral and is immobilized (Oelkers, Gislason et al. 2008). Potential sequestration of carbon dioxide in basalts has also been investigated (McGrail, Schaef et al. 2006). Existing methods of mineral CO₂ sequestration, however, are costly. The end products also offer limited market value, and need to be disposed of.

Landfilled and impounded coal ash have accumulated in tremendous quantities across the globe. There are adverse environmental and health effects caused by the disposed coal ash (Lemly 2014). The work reported herein devised a process to beneficiate the landfilled/impounded coal via its reaction with carbon dioxide, producing an end product with desired qualities for stabilization of heavy metals(Kolay and Singh 2001, Dermatas and Meng 2003, Yeheyis, Shang et al. 2008, Heidrich, Feuerborn et al. 2013). This approach makes beneficial use of the landfilled/impounded ash and carbon dioxide, that are processed together with supplementary minerals to produce a hydraulic binder with desired performance, cost(Huijgen, Comans et al. 2007) and sustainability attributes for hazardous waste immobilization and potentially other applications.

The cement formulation considered here has a chemistry that employs elements of alkali-activated cements that comprise largely of alkali aluminosilicates. The cement chemistry considered here, however, is more complex, and embodies calcium silicates as well as reactive (metastable) carbonates. The raw materials used for production of this cement are landfilled coal fly ash (Majchrzak-Kucęba and Nowak 2009, Wee 2013), ground granulated blast furnace slag (Mazzotti, Abanades et al. 2005, Huijgen and Comans 2006, Huijgen 2007, Eloneva, Teir et al. 2008), quick lime (Fauth, Soong et al. 2002, Kalinkin 2009, Kalinkin, Kalinkina et al. 2009), sodium hydroxide, and sodium silicate (Pan, Chang et al. 2012). Processing of these raw materials was accomplished via input of mechanical energy in a CO_2 environment. The process yields a hydraulic cement that undergoes hydration reactions upon addition of water. In this work, an optimization experimental program was conducted based on Box-Bhernken principles(Annadurai and Sheeja 1998), with the proportions of ground granulated blast furnace slag (GGBF slag), CaO and moisture in the raw materials formulation considered as the variables to be optimized. The optimization process identifies the preferred proportions of landfilled coal ash, GGBF slag, activators and other supplementary materials in the formulation of raw materials. The properties (responses) considered in this experimental optimization program included carbon dioxide uptake(Agamuthu and Chitra 2008, Agamuthu and Chitra 2009, Anastasiadou, Christopoulos et al. 2012), compressive strength(Li and Liu 2007), cost, and heavy metal immobilization qualities (Montinaro, Concas et al., Isenburg and Moore 1992, Halim, Amal et al. 2003).

3.2 Experimental Program

3.2.1 Materials

The landfilled coal fly ash used in this work was obtained from DTE Energy. This ash was extracted from a landfill two years after disposal. The chemical composition of this landfilled ash, obtained via x-ray fluorescence spectroscopy, is presented in Table 4.

SiO ₂	CaO	Fe ₂ O ₃	Al ₂ O ₃	SO₃	Na ₂ O	MgO	BaO	TiO ₂	K ₂ O	SrO
24.9	24.4	18.1	12.78	3.74	2.3	2.6	2.68	2.13	2.37	1.42

Table 4. Chemical composition of the landfilled ash

The GGBF slag obtained from Lafarge, the chemical composition of GGBF via x-ray fluorescence spectroscopy includes: CaO (40.8 wt.%), SiO₂ (37.5 wt.%), Al₂O₃ (9.54 wt.%), MgO (10.9 wt.%), Fe₂O₃ (0.47 wt.%), Na₂O (0.25 wt.%) and K₂O (0.45 wt.%). GGBF slag was passed through No.16 sieve. Both impounded ash and GGBF slag were dried (65° C) overnight to remove any trapped moisture. The other raw materials used for production of hydraulic cements were sodium hydroxide, sodium silicate and calcium oxide, obtained from SIGMA-ALDRICH and used in as-received form.

3.2.2 Methods

The work reported herein focused on identifying an optimum formulation of raw materials that produces a desired balance of some key properties. Since carbon dioxide is used as a raw material in the process, achieving high levels of CO₂ uptake is one goal of the optimization effort. A primary application targeted for the hydraulic binders involves stabilization of hazardous wastes. High immobilization levels of heavy metals is thus another goal of the optimization efforts. Finally, mechanical properties are important considerations in most applications of hydraulic binders; achievement of high levels of compressive strength is thus another goal of the optimization effort. Finally, minimizing the total cost of raw materials is also a goal of the optimization effort.

Three key variables were selected to be optimized experimentally: slag and calcium oxide contents of the raw materials formulation, and the moisture content added (at relatively small concentrations) to the solid raw materials in the course of their processing into a hydraulic binder while simultaneously capturing carbon dioxide. The optimization experimental design and analysis were based on the Box-Behnken and the response surface principles. Design of experiments required input of viable ranges

of each variable. These ranges, established based on preliminary experiments, are presented in Table 5. Three 'responses' were used to identify the optimum formulation: (i) CO₂ uptake; (ii) heavy metal immobilization; (iii) compressive strength; and (iv) cost. The optimization process can assign different weights (importance levels) to these responses. Weights, 4, 4, 1 and 2 were assigned to CO₂ uptake, heavy metal immobilization, compressive strength and cost, respectively.

Levels	Variables								
	Slag CaO		Moisture Content						
Level -1	15%	2.5%	0%						
Level 0	20%	5%	2%						
Level 1	25%	7.5%	4%						

Table 5. Levels of the three variables used in the optimization experimental program.

The CO₂ uptake of hydraulic binders was determined via thermogravimetric/derivative thermogravimetric analysis (TG/DTG) using a Perkin Elmer TGA 400 equipment (Damartzis, Vamvuka et al. 2011, Feng, Hao et al. 2012). The TGA analysis was carried out by heating the sample to 980°C at a rate of 10°C/min under a nitrogen flow of 20 mL/min. Total mass loss and mass loss at different temperatures were evaluated in order to identify the carbonate species formed by CO₂ processing of hydraulic cements. To further confirm the data, combined mass and TGA spectroscopy experiments were also conducted.

The hydraulic cement was mixed with water (and sand in the case of mortar mixtures) at room temperature. The captured carbon dioxide was found to induce carbonation reactions that accompanied hydration reactions to produce the solid binder. The approach taken here mixes hazardous waste with hydraulic cement in order to immobilize the hazardous constituents of waste in the resultant solid binder. A 20 Quart planetary mixer (Hobart A-200) was used to mix the hydraulic cement with water (and sand). In order to assess the heavy metal immobilization qualities of the cement, it was mixed with water spiked with heavy metal cations. Mixing was performed over 3 minutes at medium speed. The resulting fresh mix was cast into 50 mm cube molds, and consolidated via external vibration. The ratio of mixed water (spiked with metal ions) to cement ranged from 0.35 to 0.45. The molded specimens were sealed, and retained at room temperature for 24 hours. This period allows for partial dissolution of the cement constituents and initial hydration/carbonation reactions. The specimens were then demolded, sealed, and stored at room temperature. Trial investigations indicated that, unlike Portland cement, this cement does not require moist curing for continued hydration (and, in this case, carbonation) reactions. This could possibly be due to the relatively low content of chemically bound water in the alkali aluminosilicate hydrates formed as a primary hydration product of this cement. Hydration of this particular binder tends to regenerate water, thus reducing or eliminating the need for external input of water. The compressive strength of cubic test specimens was measured at 7 and 28 days of age. Paste specimens as well as mortar specimens incorporating sand (at sand/cement weight ratio of 2.75) were prepared and subjected to compression testing per ASTM C109.

Specimens were prepared using water spiked with heave metal cations were prepared in 50 mm cube molds per ASTM C109. After 24 hours, the specimens were demolded and cured for 7 days at room temperature in sealed condition.

The metal ion spiked solution (Cu: 30,000 ppm, Zn: 1000 ppm, Pb: 1000 ppm and Ba: 1000 ppm) was used as the mixing water, and the cubic specimens of the hydraulic binder paste were cast per ASTM C109 (Hoang 2001, Agamuthu and Chitra 2009). After curing for 7 and 28 days, heavy metal extraction tests were performed following the TCLP procedure. The landfilled coal ash specimens were tested in this investigation for assessment of their heavy metal leachability per US EPA TCLP protocol. Prior to performing the leaching test, solid samples were crushed and passed through a sieve with 9.5 mm opening. The powder samples were then mixed with the leaching solution (pH 2.88 acetic acid) at a

solution/solid ratio of 20. The suspension was stirred for 18 hours, and the leachate was isolated through vacuum filtration. The concentrations of heavy metals in the leachate were assessed via inductively coupled plasma spectroscopy. The degree of immobilization of heavy metals was evaluated using the "synthetic precipitation leaching procedure (SPLP)" of U.S. EPA (1996). The immobilization efficiency was calculated using the following equation:

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

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 (1)), and W_{solid} (kg) is the solid weight used in test.

Fourier transform infrared (FTIR) spectroscopy (using a JASCO ATR-FTIR-4100 instrument) was used to assess the presence of bonds associated with the chemically reacted or physically adsorbed carbon dioxide in the mechanochemically processed hydraulic cement and its hydration products.

The pH, electrical conductivity and total dissolved solids (TDS) were measured for a 1% aqueous solution of the solid material using an ORION STAR A215 instrument. In this test, 1 g of the hydraulic binder (powder) was dissolved in 100g of distilled water. The solution was placed on a shaker, and the initial pH, total dissolved solids (TDS) and electrical conductivity values as well as those after 1 hour and 24 hours were measured. The particle size distribution of the hydraulic cement was measured via laser granulometry using a(Horiba LA-920 laser) particle size distribution analyzer.

3.3 Results and discussion

3.3.1 CO₂ Uptake

The CO_2 uptake of the hydraulic binders was evaluated by thermogravimetric/derivative thermogravimetric analysis. Among 13 runs, Runs # 6 provides the highest CO_2 uptakes. Figure 8 presents the TGA data for Run 6. $Ca(OH)_2$ would decomposite around 400°C, however, from derivative curve no

apparent drop close to that temperature, suggesting that all available $Ca(OH)_2$ was converted to (amorphous or crystalline) carbonates. This results in a smooth TGA curve without any trough, pointing at improved CO_2 uptake.

FTIR spectra (Figure 9) further confirmed successful carbonation of calcium hydroxide (compare Runs #6 and #7). Ca(OH)₂ appears at 3641cm⁻¹; for Run #7, almost the lowest CO₂ uptakes (spectrum b), a small peak appears that points at incomplete transfer for hydroxyl ions. CO₃²⁻ appears at 714 cm⁻¹, and between 1400 cm⁻¹ to 1500 cm⁻¹. In addition, peaks positioned at 2900 cm⁻¹, 2513 cm⁻¹ and 1900 cm⁻¹, corresponding to CaCO₃, appear in both Runs #6 and #7, with much larger peaks in Run #6 pointing at the more thorough calcium carbonate generation.



Figure 8. TGA and DTA data for Run #6.



Figure 9. FTIR spectra of the hydraulic binders formulation with slag, and processed mechanochemically in CO_2 (Runs #6 and #7).

Calcium oxide is an additive generally used with alkali aluminosilicate binders to enhance the development compressive strength when curing in performed at ambient temperature. It can also influence the CO₂ uptake of the binder subjected to mechanochemical processing in CO₂. The results presented in Figure 10, generated using the test data developed in this work, indicate that a calcium oxide concentration of 2.5% (Figure 10a) could be a viable option for achieving a relatively high CO₂ uptake. GGBF slag complements the chemistry of landfilled coal ash, and could also improve the fresh mix workability and the initial set time of the hydraulic binder. The optimum dosage of slag seems to be around 20 wt.% (Figure 10b); a further rise in slag content tends to lower the CO₂ uptake increasing with moisture content (up to a maximum of 4% considered in this investigation).



Figure 10. Effects of the calcium oxide, GGBF slag and moisture contents in formulations of raw materials on the CO₂ uptake measured via thermogravimetric analysis (TGA).

The Pearson correlation matrix, developed for the ranges of variables considered here, indicates that the correlations of the CaO, moisture and slag contents with carbon dioxide uptake are 0.083, 0.697 and -0.280, respectively. Moisture content is observed to exhibit the greatest correlation with the CO_2 uptake. The lower slag content of 15% produced adequate CO_2 uptake. The small (and negative) correlation for CaO content also suggests that the lowest CaO content of 2.5% considered here is preferred as far as the CO_2 uptake is concerned.

The results presented earlier indicated that the pH of the resultant binder (in solution) correlates well with its CO₂ uptake. Lower pH values generally correspond with higher CO₂ uptakes. Reduced pH values, on the other hand, do not favor hydration reactions of the cement chemistry considered here. The measured values of CO₂ uptake and pH presented in Table 6 confirm that the highest values of CO₂ uptake correspond to the lowest values of pH in solution. Runs #5, 6 and 10 with the highest CO₂ uptakes of about 18 wt.% produced the lowest pH values that are less than 10.

Table 6. pH values for formulations representing different runs of the optimization experimentalprogram.

Run	1	2	3	4	5	6	7	8	9	10	11	12	13
рН	11.8	10.6	12.7	10.8	10.0	9.5	12.4	11.9	9.6	9.5	12.4	12.3	11.8

3.3.2 Compressive Strength

The compressive strength test results are presented in Table 7. The early-age data (7-day paste and mortar compressive strengths) for Run #10 are missing because this formulation hardened at a very slow pace, and could not be tested at early age. The trends for the 7-day compressive strength of paste point at pronounced positive effects of the CaO content on the compressive strengths produced by the hydraulic binder, especially at higher CaO contents. Favorable values of compressive strength (Agamuthu and Chitra 2009) are obtained with CaO contents of 5 wt.% or more. The rise in the moisture content of raw materials adversely influenced the paste 7-day compressive strength produced by the hydraulic binder. The rise in CO₂ uptake with increasing moisture content, and the corresponding drop in pH value can be used to explain this trend.

Run	1	2	3	4	5	6	7	8	9	10	11	12	13
Paste (7-day)	1.70	2.24	9.06	2.66	1.8	0.96	26.64	3.02	1.42	-	2.78	10.54	3.06
Mortar (7-day)	0.59	0.54	2.86	0.51	0.71	0.57	6.56	0.87	0.32	-	5.61	9.88	0.54
Mortar (28-day)	0.24	0.30	3.66	0.38	0.38	0.36	14.02	4.42	0.80	0.16	10.64	10.54	0.88

Table 7. Compressive strength test results for paste and mortar mixtures.

3.3.3 Heavy Metal Solidification/Stabilization

The solution spiked with metal ions (Cu: 30,000 ppm, Zn: 1000 ppm, Pb: 1000 ppm and Ba: 1000 ppm) was used as the mixing water, and cubic specimens of the hydraulic binder paste were cast per ASTM C109 (Hoang 2001, Agamuthu and Chitra 2009). After curing for 7 and 28 days, heavy metal extractions were made per TCLP procedure. Inductively Coupled Plasma (ICP) spectorsopy was carried out to determine the heavy metal concentrations of the resultant leachate. The extents of heavy metal Immobilization were calculated following the procedure described earlier (Montinaro, Concas et al.).

The leaching test protocol was carried out on hardened paste specimens at 7 and 28 days of age. The percent immobilization test results are presented in Table 8. These results indicate that most hydraulic

binders considered in the optimization experimental program, which embody carbon dioxide, effectively immobilize copper. For Barium, Zinc and Lead, the degrees of immobilization generally exceeded 95%.

RUN												
Heavy Metal	1	2	3	4	5	6	7	8	9	11	12	13
Cu	99.97	99.97	99.97	99.97	99.97	98.58	99.95	99.96	99.98	99.95	99.97	99.93
Ва	93.81	97.60	98.09	97.39	94.50	96.99	98.24	97.50	97.45	98.08	98.94	97.85
Pb	96.27	96.39	96.39	96.39	96.00	94.40	96.60	96.50	96.89	96.39	96.39	96.61
Zn	98.82	99.42	99.50	99.21	99.32	95.98	99.62	98.98	96.26	99.33	99.62	98.41

Table 8. Percent immobilizations by the hydraulic binder embodying carbon dioxide.

3.3.4 Response Surface Optimization of the Hydraulic Binder Formulation

The response surfaces produced based on analysis of the data generated for the thirteen formulations are presented in Figure 11 (CO₂ uptake) and 12 (compressive strength). The weights (important factors) assigned, for the purpose of optimization) to CO₂ uptake, compressive strength, heavy metals immobilization and cost were 4, 1, 4 and 2, respectively. The optimization objective was to minimize cost and maximize heavy metals immobilization while targeting 3.5 Mpa.

The optimum values of the formulation parameters derived based on response surface analysis of the test data in light of the targeted response parameters are presented in Table 9. The predicted attributes of the hydraulic binder for the optimum formulation of raw materials are presented in Table 10.



Figure 11. Response surfaces for carbon dioxide uptake



Figure 12. Response surfaces for the (7-day mortar) compressive strength.

Factor	CaO Content	Slag Content	Moisture Content
Optimum Level (wt%)	2.5	22.6	3.9

Table 10. Tredicted attributes of the hydradic binder with optimum formalation
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Attributo	Ontimum Posnonso	95% Confide	Docirability		
Attribute	Optimum Response	Lower	Upper	Desirability	
Mortar Compressive Strength, Mpa	0.446		8.111	0.083	
CO ₂ Uptake, %	17.636	14.126	20.147	0.739	
% Immobilization of Cu	100			1.000	
% Immobilization of Ba	100			1.000	
% Immobilization of Pb	100			1.000	
% Immobilization of Zn	100			1.000	

* Overall Desirability D = 0.851
3.3.5 Experimental Evaluation of the Binder with Optimum Formulation of Raw Materials

The hydraulic binder with optimum formulation of raw materials was prepared via mechanochemical processing in CO₂. The resultant binder was tested for assessment of its CO₂ uptake, extent of heavy metal immobilization, and compressive strength. The microstructure and the crystalline structure of the hydrated binder were assessed via scanning electron microscopy and XRD spectroscopy, respectively. The results are reviewed in the following.

The optimum formulation of raw materials was subjected to mechanochemical processing over 2 hours in a pure CO₂ atmosphere. The CO₂ uptake of the binder with optimum formulation of raw materials (processed via milling in CO₂), obtained via thermogravimetric analysis (Figure 13), was 17 wt.%. This measured value of CO₂ uptake is close to the 17.6% predicted via response surface analysis of the optimization test data. When compares to air milled powder, the double peak appears on #1 represents moisture content and CO₂(g) absorption. Second peak around 400 °C, the optimal formulation has a relative small peak, which shows the high number transition for calcium hydroxide. And when temperature raises up, the optimal formulation has a larger area on DTA curve on the range of 500 to 800 °C.



Figure 13. TGA test data for the hydraulic binder with optimum formulation of raw materials subjected to mechanochemical processing in pure CO₂.

The hydraulic binder with optimum raw materials formulation was also subjected to FTIR spectroscopy in order to gain further insight into its CO₂ uptake. The optimal result shows in the Figure 14 together with those corresponding to Runs #6 and #7. Ca(OH)₂ appears at 3641cm⁻¹, in optimal formulation, this peak is in the medium of Run #6 and #7. This small peak appears that points presents the incomplete transfer for hydroxyl ions. CO₃²⁻ appears at 714 cm⁻¹, and between 1400 cm⁻¹ to 1500 cm⁻¹. In addition, peaks positioned at 2900 cm⁻¹, 2513 cm⁻¹ and 1900 cm⁻¹, corresponding to CaCO₃, optimal run shows the medium peak which further presents the carbon dioxide stabilization capability and relatively high compressive strength.



Figure 14. FTIR Spectra of hydraulic binders with optimum formulation, Run #6 and #7 subjected to mecahnochemical processing in pure CO₂ concentration.

The hydraulic binder with optimum formulation of raw materials, processed mecahnochemically in CO₂, was prepared with spiked heavy metal solutions as mixing water. After 7 days of curing at room temperature, the solid paste was subjected to TCLP procedure as described earlier. The results were used to assess the extents of immobilization of different heavy metals (Montinaro, Concas et al.). Table 11 presents the measured immobilization percentages of Cu, Pb, Ba and Zn versus the predictions of response surface analysis. More than 99.7% immobilization was achieved for all the heavy metals considered in this investigation, noting that Zn is considered here to represent heavy metals Cd and Hg.

Table 11. Immobilization degrees of different heavy metals by the hydraulic binder with optimum formulation of raw materials processed mechanochemically in CO₂.

	Cu	Pb	Ва	Zn
Predicted (%)	100	100	100	100
Experimental (%)	99.97	99.72	99.95	99.99

In order to better understand the structure of hydrated pastes, they were subjected to x-ray diffraction spectroscopy prior to and after heating at 350°C for 1 hour. Heating was performed to enhance the crystallinity of hydrates. The resulting XRD spectra are presented in Figure 15. Heating is noted to increase the degree of crystallinity, and cause appearance of new peaks. Peaks for BaCO₃ were observed,

which are anticipated to result from carbonation of the $Ba(NO_3)_2$ introduced during solidification. In addition, peaks associated with $CuCO_3$ were also observed, which point at the improved immobilization effects associated with carbonation.



Figure 15. XRD Spectra of pastes prepared with the hydraulic binder with optimum formulation of raw materials that was processed mecahnochemically in CO_2 and cured for 7 days at room temperature, with and without heating to 350°C.

Scanning electron microscopic observations (Figure 16) of the hydrated paste pointed at the formation of

a dense microstructure (which favorably affects solidification/stabilization attributes) which comprises an

amorphous binder embodying various fine crystalline species as well as some fly ash and slag particles

coated (integrated) with hydration products.



Figure 16. SEM Micrograph of the optimal formulation hydrated paste.

The compressive strength values obtained for 50 mm cube mortar specimens (ASTM C109) prepared with the spiked metal ion solution as mixing water (at water/cement ratio of 0.35) and subjected to 7 days of curing at room temperature and >95% relative humidity was 0.75 MPa compared to the predicted value of 0.446 MPa. Paste specimens of the same optimized binder produced 4.5 MPa compressive strength after 7 days of curing at room temperature. These values should be compared against those required for stabilized hazardous wastes (Hoang 2001). The U.S. EPA requires a minimum compressive strength of 0.34 MPa for solidified/stabilized hazardous wastes (USEPA OWSER Directive, No, 9437.00-2A) when compression tests are performed per ASTM C109.

Chapter 4. Mechanical Processing of Cements Formulated with Landfilled Ash in Different Environments

4.1 Introduction

Landfilled coal ash is predominantly fly ash with some bottom ash content. Coal ash is disposed of in landfills either directly or after a period of wet impoundment (Mishra and Das 2013). Significant quantities of coal ash have been accumulated in landfills over several decades. In the United States, close to 40 million tons of coal ash are disposed of in landfills annually (Zand, Tu et al. 2009). The landfilled quantities of coal ash in Europe are of the same order of magnitude as in the United States (Sushil and Batra 2006).

Coal fly ash has found applications as pozzolan (partial replacement for cement) in Portland cement concrete. Coal fly ash can also be activated with alkalis for production of geopolymer concrete, that is more sustainable than Portland cement concrete (Duxson, Provis et al. 2007), and also offers improved durability (Van Deventer, Provis et al. 2012). The need for curing of the existing classes of geopolymer concrete at elevated temperatures, however, limits their market acceptance (Palomo, Grutzeck et al. 1999, Barbosa and MacKenzie 2003). Mechanical activation of coal fly ash in the presence of alkalis can reduce the need for thermal curing of alkali activated coal ash. It has been observed that grinding of landfilled coal fly ash improves the uniaxial compressive strength of alkali-activated fly ash from 2.01 MPa (raw fly ash) to 22 MPa (activated fly ash) (Mucsi, Kumar et al. 2015). Another investigation demonstrated that, after mechanical activation of coal fly ash, NaOH-activated ash could produce a viable compressive strength of 23 MPa after 28 days of room-temperature curing (Somna, Jaturapitakkul et al. 2011). Similar results were produced in another investigation where 80% gain in the compressive strength of alkali-activated fly ash subjected to room-temperature curing was realized once the ash was subjected to mechanical activation (Temuujin, Williams et al. 2009). There is further evidence reported in the literature, suggesting that mechanical activation of fly ash via grinding significantly improves the mechanical properties of alkali-activated ash (Aydın, Karatay et al. 2010). It has been reported that the compressive strength of Cu-Ni slag geopolymer with the slag milled in CO₂ is higher than that obtained with slag milled in air, which was attributed to higher reactivity of the slag particles induced by chemisorption of carbon dioxide molecules in the form of distorted carbonate ions in the course of mechanical activation(Kalinkin,

Kumar et al. 2012, Alex, Kalinkin et al. 2013). Other investigations have confirmed that the reactivity of slag can be enhanced by grinding in a carbon dioxide atmosphere, producing higher compressive strengths upon alkali activation (Kalinkina, Gurevich et al. 2014, Kalinkina, Gurevich et al. 2015).

The work reported herein focused on the effects of mechanical activation via ball-milling, and the environment of mill (air, N_2 , CO_2) on the activity of coal fly ash as an aluminosilicate precursor in production of geopolymer (via alkali activation). N_2 was selected as an inert environment where reactions with the mill environment would not be a major factor. Air and CO_2 were considered as reactive environments that could affect the performance of the resultant (mechanically activated) coal fly ash.

4.2 Materials

The raw materials used in this process were landfilled coal ash: calcium oxide: basalt: sodium hydroxide at 82: 6: 6 weight ratios. The landfilled coal ash was obtained from DTE Energy; this ash had been landfilled for 2 years. Typical scanning electron microscope images of the landfilled coal ash are shown in Figure 17. The surface of landfilled ash is not smooth, which may due to hydration and carbonation reactions during the period of disposal in landfill. The chemical compositions of landfilled coal ash is presented in Table 12. It is worth mentioning that basalt generally comprises SiO₂, Al₂O₃, CaO, FeO, MgO and TiO₂, which are also found in the landfilled coal ash.



Figure 17. Scanning electron microscope images of the landfilled coal ash.

Table 12. Chemical composition of the landfilled coal ash (wt.%).

	SiO ₂	CaO	Fe ₂ O ₃	Al ₂ O ₃	SO ₃	MgO	Na₂O	K ₂ O	BaO	TiO ₂	SrO	P ₂ O ₅	Others
Landfilled ash	25.21	24.08	18.46	13.12	2.27	2.9	2.8	2.4	2.44	2.37	1.47	0.95	1.08

4.3 Methods

A ball mill with diameter of 140 mm and height of 140 mm, made of steel, was used at a rotational speed of 40 rpm to mill the geopolymer cement. At each time, 400 g of raw materials was milled with 4000 g of steel ball. The milling duration was 4 hours in each of the milling environments (air, N₂ and CO₂). Temperature at the mill surface were monitored using a temperature sensor with data storage capability.

The resulting geopolymer cements were evaluated via FTIR spectroscopy. For this purpose, 2 mg of cement was mixed with 200 mg of KBr, and the dry blend was formed into pellets using a high-pressure injection molding machine. A Jasco FT/IR-4100 spectrometer was used to perform these tests over a measurement range of 400 - 4000 cm⁻¹.

The pH values of cements in solution were measured by dissolving 1 g of the geopolymer cement in 100 g of distilled water. The solution was placed on a shaker, and the initial pH values as well as those aftr 1 hour and 24 hours were measured. The total dissolved content (TDS) and electric conductivity of solutions were also measured in order to gain insight into the dissolution process of the hydraulic binder.

The heat of hydration of cements was measured using the calorimetry test method (ASTM C1679), using an I-cal 2000 HPC calorimeter manufactured by Calmetrix Inc. (Boston, USA). In this test, cement was mixed with water (by hand) at water/cement weight ratio of 0.40 for 30 seconds. The fresh paste was placed inside the calorimeter, and the exothermic heat release was monitored over 24 hours.

A 20 Quart planetary mixer (Hobart A-200) was used to mix the mortar mixtures comprising cement, silica sand, water and superplasticier. Mixing was performed over 3 minutes at medium speed. The resulting fresh mix was cast into 50 mm cube molds, and consolidated via external vibration. The water/cement

and sand/cement ratios of mortar mixtures were 0.5 and 2.75, respectively; superplasticizer was used at 0.5% by weight of cement to raise the fresh mix workability. The specimens were demolded after 24 hours, sealed, and stored at $22\pm2^{\circ C}$ and $50\pm5\%$ humidity. The compressive strength of the cubic test specimens was measured at 7 and 28 days of age per ASTM C109.

4.4 Test Results and Discussion

4.4.1 Temperature of the Mill Exterior Surface

Figure 18 shows the powder temperature when geopolymer cement processing via milling was performed in CO_2 , in air and in N₂ environments. The presence of CO_2 is observed to induce an early temperature due to the frictional effects during impact of balls and particles (Takacs and McHenry 2006), and also probably the formation of carbonates as a result of exothermic mechanochemical reactions of the carbon dioxide gas with alkaline earth metal, alkali metal and other constituents of the solid raw materials. Microstructural changes under impact could also have thermal implications (Ahmadian Baghbaderani, Rahimipour et al. 2016). The peaks of powder temperature mill after about 3 hours in the presence of CO_2 , and then starts to drop gradually. However the peak powder temperature is showed after 30 min in air milling. The trends in the exterior surface temperature development of the mill with the milling duration are quite different in the presence of nitrogen. There is actually a drop in temperature during the first 20 minutes of milling, after which the temperature starts to rise slowly and seems to reach a plateau at 110 min, and then strats to drop gradurally. Compare to initial temperature, the peak temperature of powder during milling in CO₂, in air and in N₂ increase 5.8 $^{\circ}$ C, 2.3 $^{\circ}$ C and 1.8 $^{\circ}$ C. While the eventual temperature rise can be explained by the frictional impact of balls and solid raw materials, microstructural changes and mechanochemical reactions, the initial drop in temperature could result from the evaporation of the water present in solid raw materials in the N_2 environment, combined with the reduced extent of (exothermic) mechanochemical reactions due to the inert nature of N₂.

The sharp contract between the powder temperature development during milling in CO_2 versus air points at the role played by CO_2 to enhance mechanochemical effects. A host of other phenomena also occur during milling, that could be affected by the milling environment. Examples include comminution (particle size reduction) accompanied with formation of new surfaces, crystal deformation, defect formation, shear stresses buildup, reduction of crystallite size, aggregation of crystallites, local (and momentary) rise of temperature and pressure, phase transitions, amorphization, chemical bonds breakage, acceleration of diffusion processes (Ahmadian Baghbaderani, Rahimipour et al. 2016).



Figure 18. Development of the powder temperature with duration of milling in CO₂, in air and in N₂.

4.4.2 Specific Surface Area and Morphology

As shown in Figure 19, the specific surface area of the geopolymer cement milled in air is the lowest, and that milled in CO₂ atmosphere is largest (1.19 times of that milled in air). The specific surface area of the geopolymer cement milled in N₂ is close to but still lower than that milled in CO₂. These results are similar to those reported by Rakhimov (Rakhimova and Rakhimov 2014) and Kalinkina (Kalinkin, Alex et al. 2013, Kalinkina, Gurevich et al. 2014) where the specific surface area of slag geopolymer milled in CO₂ was found to be higher than that milled in air. After milling in air, a small amount of powder bonded to internal surface of the mill; this phenomenon was less pronounced when milling was performed in N₂, and it did not happen when milling was performed in CO₂. It should be noted that N₂ and CO₂ were input continuously from outside the mill; this was not the case when milling was performed in air. One may

hypothesize that the gas flow (that was absent for milling in air) would enhance the dispersion of powder and thus the efficiency of the impact energy input to the powder. This effect could be more pronounced in CO_2 with a density that is 1.5 times higher than that of N_2 . These factors could influence the rise in specific surface area when milling was performed in N_2 and especially in CO_2 .



Figure 19. Specific surface area of geopolymer cement

Scanning electron micrographs of geopolymer cements produced via milling in N₂, air and CO₂ are shown in Figure 20. These images suggest that the extent of mechanochemical reactions was probably the least when milling was performed in N₂, which could be explained by the inert nature of nitrogen that does not promote solid-gas reaction under input of impact energy. The reactive nature of air and CO₂ seem to produce morphological changes that could point at intense mecahnochemical reactions. Reactions involving carbon dioxide and the silicate constituents of raw materials could be summarized as (Montes-Hernandez, Perez-Lopez et al. 2009):

$$(Ca, Mg)SiO_3(s) + CO_2(g) \rightarrow (Ca, Mg)CO_3(s) + SiO_2(s)$$

This carbonation reaction could also destabilize the structure of silicates and promote other mechanochemical reactions.



(a) N₂





(c) CO₂

Figure 20. Scanning electron micrographs of geopolymer cement milled in different environments.

4.4.3 FTIR Spectra

The FTIR spectra of geopolymer cement before and after milling in air, N₂ and CO₂ are presented in Figure 21. Before milling, the peaks at 1460 cm⁻¹ and 880 cm⁻¹ were attributed to the presence of carbonate on the surface (Kalinkin, Kalinkina et al. 2005, Dhamal, Wadekar et al. 2013, Qu, Zhong et al. 2016) that form upon exposure of the raw materials to air. The peaks at about 3450 cm⁻¹ and 1650 cm⁻¹ can be attributed to the absorbed atmospheric water. The Si–O-Si stretching vibration produces the peak 985 and 1080 cm⁻¹, and the Si-(OH) stretching vibration produces the peak between 1094 and 1140 cm⁻¹ (Barbosa,

MacKenzie et al. 2000, Bange, Patil et al. 2008, Swedlund, Miskelly et al. 2009, Gaggiano, De Graeve et al. 2013). Peaks below 750 cm⁻¹ can be attributed to M-O vibrations, where M is Al or Ca (Puertas and Fernández-Jiménez 2003, Qu, Zhong et al. 2016). The band around 3640 cm⁻¹ detected in all samples reflects the presence of sodium hydroxide. After mechanical activation, the band at 689 cm⁻¹ is shifted to around 710 cm⁻¹, which points at the formation of new compounds via chemical reaction. The peak at 3640 cm⁻¹ after milling is smaller than that before milling, which suggests that part of sodium hydroxide has been consumed in mechanochemical reactions.

After milling in CO₂, the spectral peaks related to CO₃²⁻ of 2520 cm⁻¹, 1400 cm⁻¹ and 870 cm⁻¹ are sharper and more clear when compared with those observed after milling in air or in N₂, which can be attribute to the mechanochemical carbonation reactions during milling. After CO₂ milling, bands appeared around 1663 cm⁻¹ and 1622 cm⁻¹, and the band around 1640 cm⁻¹ disappeared; a new band at 1921 cm⁻¹ and the Si-O-Al vibration peak at 815 cm⁻¹ (Barbosa, MacKenzie et al. 2000) also appeared for the geopolymer cement processed via CO₂ milling. In the case of milling in N₂, the peaks associated with water at 1640 cm⁻¹ and 3400 cm⁻¹ are relatively weak (compared to all other spectra), pointing at the greater loss of moisture during milling in N₂. This phenomenon was relies upon earlier to explain the cooling effects observed when milling was performed in N₂.



Figure 21. FTIR spectra of blended raw materials (without milling), and geopolymer cements processed via milling for 4 hours in air, CO_2 and N_2 .

4.4.4 pH, Total Dissolved Solids and Electrical Conductivity in Solution, and Loss on Ignition

The pH value of geopolymer cement (in solution) prior to and after milling in air, N₂ and CO₂ are show in Figure 22. After milling in air and in N₂, the pH value of geopolymer cement increased from 12.31 to 12.49. This can be interpreted as a rise in the activity of the blend of raw materials after mechanichemical transformation into geopolymer cement. Mechanochemical processing in CO₂, on the other hand, reduced the pH value due to the formation of acidic carbonates. The highest pH value was obtained in N₂, which could be due to some carbonation reactions when milling was performed in air. The total dissolved solids (TDS) increased (Figure 23) upon milling of raw materials in N₂ and in air, reflecting the greater activity of the mecahnochemically processed geopolymer cement. The drop in TDS after milling in CO₂ can be attributed to the reduced solubility of the mechanochemically produced carbonates. The trends in electrical conductivity (Figure 24) are similar to those observed with pH and TDS test results, and can be explained similarly.

The LOI values (Figure 25) were highest after milling in CO_2 , and lowest after milling in N_2 . This observation could be attributed to the mecahnochemical formation of carbonated when milling was performed in air and especially in CO_2 .



Figure 22. The pH values of geopolymer cement in solution: initial, 1-hr and 24-hr values.



Figure 23. The TDS values of geopolymer cement in solution: initial, 1-hr and 24-hr values.



Figure 24. The electrical onductivity values of geopolymer cementin solution: initial, 1-hr and 24-hr values.



Figure 25. LOI values of geopolymer cement.

4.4.5 Heat of Hydration

The rate and the cumulative heat release during hydration of geopolymer cements processed mecahnochemically in air, N_2 and CO_2 are presented in Figure 26. After milling in N_2 and in air, the initial rates of heat release are higher, resulting in higher cumulative heat release. Milling in N_2 produced the highest total heat release. Both the rate and the cumulative heat release are the lowest for the geopolymer cement processed via milling in CO_2 . Geopolymer cements processed via milling in air and in N_2 exhibit only one exothermic peak after about 2 minutes, while two peaks are observed after about 3.2

and 16.5 minutes for milling in CO₂. The mechanochemical effects of milling seem to have accelerated the rate of exothermic reactions (Pacheco-Torgal, Castro-Gomes et al. 2008). This is indicative of the mechanical activation effects of milling. It has been reported (Pacheco-Torgal, Castro-Gomes et al. 2008) that the initial peak in hydration of geopolymer is related to the destruction of Ca-O, Mg-O, Si-O-Si, Al-O-Al and Al-O-Si bonds, and the second peak is due to the formation of Si-Al bonds. Higher pH values may be correlated with the higher rate of bond destruction that generates higher heats of hydration (Xie and Xi 2001, Fernández-Jiménez, Palomo et al. 2006, Petermann, Saeed et al. 2010).

Due to carbonation, the pH value of geopolymer cement milled in CO_2 is the lowest. This lowers the dissolution of iron and the formation of Si-Al bonds, thus lowering the heat of hydration. It is possible that delayed formation of Si-Al bonds produces the second exothermic peak for the cement processed in CO_2 . The pH value of the cement processed in N_2 is the highest, which can be used to explain its high rate and extent of heat release.



(a) Rate of heat release

Figure 26. Heat of hydration test results for geopolymer cements processed via milling in different environments.

Figure 26 (cont'd)



(b) Cumulative heat release

4.4.6 Compressive strength

The compressive strength test results at 7 and 28 days of age are presented in Figure 27 for mortar mixtures prepared with different cements. Cements prepared via milling in air and in nitrogen produce comparable compressive strength values. The cement processed via milling in carbon dioxide, however, produced relatively low values of compressive strength. This could be attributed to the lower pH values obtained with the cement milled in carbon dioxide. This finding implies that carbon dioxide was captured by the cement milled in CO₂, and suggests that restoring the pH value of this cement by introduction of alkaline materials either prior to or after milling could feasibly raise the compressive strength obtained with this cement.



Figure 27. Compressive strength test results at 7 and 28 days of age for mortar specimens prepared with cements processed via milling in air, CO2 and N2 atomspheres.

Chapter 5. Production and Characterization of a Hydraulic Cement Produced with Landfilled Coal Ashes of Different Disposal Durations, Using Carbon Dioxide As a Raw Material

5.1 Introduction

The accumulation of anthropogenic greenhouse gases, predominantly CO₂, in the atmosphere is a major cause of climate change (Lashof and Ahuja 1990, Smith, Brown et al. 2001). Combustion of fossil fuels in power plants is the largest source of anthropogenic carbon dioxide emissions (Worrell, Price et al. 2001). Coal-burning power plants also produce significant quantities of solid wastes, including coal ash which is largely disposed of in landfills. The historic trends in coal ash generation and disposal rates suggest that close to 5 billion tons of coal ash has been landfilled in the vicinity of the U.S. power plants; global deposits of coal ash add up to several billion tons, with an annual growth rate of about 0.5 billion tons. There are growing concerns with the environmental and health impacts of the billions of tons of landfilled coal ash (Davidovits 1994).

The research investigation reported here viewed landfilled coal ash as a mineral resource which can be used, together with carbon dioxide, as valuable raw materials in production of hydraulic cements with effective hazardous waste stabilization/solidification qualities (Yeheyis, Shang et al. 2008, Wee 2013). The approach to processing of hydraulic cements developed in this research relied upon: (i) a novel method of selectively incorporating carbonate anions into ash particles without resorting to elevated temperatures and pressures; (ii) alkali activation of ash parallel with formation of stable carbonates to produce a hydraulic binder (Juenger, Winnefeld et al. 2011); and (iii) effective solidification/stabilization of hazardous wastes via integrated zeolitization and carbonation effects (Dermatas and Meng 2003). This investigation used landfilled coal ashes obtained after different periods of disposal. Besides coal ash and carbon dioxide gas, the other raw materials used for production of hydraulic cements included ground granulated blast furnace (GGBF) slag, sodium silicate, calcium oxide and sodium hydroxide(Tsuchiai, Ishizuka et al. 1995, Monkman and Shao 2009). The fact that the coal ashes used in this investigation were disposed of in landfills indicates that they probably did not meet the requirements relevant to partial replacement of Portland cement in conventional concrete(Testing, Concrete et al.

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2005). An important aspect of this work on landfilled coal ashes concerned evolution of their properties as a function of the disposal time.

This development resorted to room-temperature meahcnoghemical (in lieu of high-temperature) processing of raw materials to produce a hydraulic cement. The same formulation of raw materials were considered, and hydraulic cements were produced with and without introduction of carbon dioxide in order to verify the value offered by carbon dioxide as a raw material for production of hydraulic cement.

5.1 Materials

Landfilled coal ashes were obtained from a DTE Energy landfill near Detroit, Michigan. The landfilled ashes were obtained from different depths to represent different periods of disposal. Table 13 introduces the nominations used for the ashes extracted from landfills after different periods of disposal. Ground granulate blast furnace (GGBF) slag was obtained from LafargeHolcim, the chemical composition of this slag, obtained via x-ray fluorescence spectroscopy, included CaO (40.8 wt.%), SiO₂ (37.5 wt.%), Al₂O₃ (9.54 wt.%), MgO (10.9 wt.%), Fe₂O₃ (0.47 wt.%), Na₂O (0.25 wt.%) and K₂O (0.45 wt.%). GGBF slag was passed through No.16 sieve. Both landfilled coal ash and GGBF slag were dried overnight in oven at 65°C to remove any trapped moisture. The other raw materials used for production of hydraulic cements were sodium hydroxide, sodium silicate and calcium oxide, obtained from SIGMA-ALDRICH and used in as-received condition.

Sample ID	Ash Type	Disposal duration, Years
DTE-Fresh	Fresh Ash	0 years
DTE-2Y	Landfilled ash	2 years
DTE-5Y	Landfilled ash	5 years
DTE-10Y	Landfilled ash	10 years

Table 13. The landfilled coal ashes obtained from the DTE Energy landfill after different disposal durations.

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5.2 Methods

The hydraulic cement formulation used in this investigation comprised 65 wt.% landfilled coal ash, 20% GGBF slag, 5% calcium oxide, 5% sodium silicate, and 5% sodium hydroxide. These raw materials were compounded to product a hydraulic cement using a ball mill in carbon dioxide environment.

The CO_2 uptake of hydraulic cements was determined via thermogravimetry analysis (TGA) using a Perkin Elmer TGA 400. The thermogravimetry analysis was carried out by heating to 960°C at a rate of 10°C/min under a nitrogen flow of 20 mL/min. The measured values of mass loss at different temperatures were used to identify the carbonate species formed as a result of processing of the hydraulic cement in a CO_2 environment. Mass spectrometry was also used in conjunction with heating for some specimens in order to verify the findings based on the trends in mass loss with temperature rise.

Cement pastes were prepared with hydraulic cements prepared in air and also in CO₂. Landfilled ashes with different disposal periods were used for production of hydraulic cements. The hydraulic cement was mixed with distilled water at room temperature. The water/cement ratios required for producing pastes of comparable fresh mix workability were 0.38 and 0.29 for hydraulic cements processed in CO₂ and in air, respectively. For the purpose of compression tests, cement pastes were placed in 50 mm cube molds and stored at room temperature in sealed condition. The specimens were demolded after 24 hours, and stored in sealed condition (>95% relative humidity) and room temperature until the test age.

The concentration of the leachate was assessed using inductively coupled plasma spectroscopy. Landfilled coal ashes with four different disposal durations, the hydraulic cements, and cement pastes at 7 days of age were evaluated. In this experiment, powdered samples were mixed with the leaching solution (pH 2.88 acetic acid) at a solution/solid ratio of 20. The suspension was stirred for 18 hours, and the leachate was isolated through vacuum filtration. The degree of immobilization of heavy metals was evaluated using the "synthetic precipitation leaching procedure (SPLP)" of USEPA (1996). The immobilization efficiency of each powdered sample was calculated using the following equation:

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

where, $\eta(t)$ % is the immobilization efficiency (%), t is time interval (sec), C(t) is the heavy metal concentration of leachate (mg L⁻), V_{leach} is the leachate volume (L), q^{24h} is the initial heavy metal concentration in untreated material (mg kg⁻¹), and W_{solid} is the solid weight used in test (kg).

Fourier transform infrared (FTIR) spectroscopy (a JASCO ATR-FTIR-4100 instrument) was used to assess the presence of bonds associated with the chemically reacted or physically adsorbed carbon dioxide in the mechanochemically processed hydraulic cement and its hydration products.

The pH, electrical conductivity and total dissolved solids (TDS) were measured using an ORION STAR A215 test instrument. In this series of tests, 1 g of the hydraulic binder (powder) is dissolved in 100 g of distilled water. The solution was placed on a shaker, and the initial pH value as well as those after 1 and 24 hours were measured. The total dissolved content (TDS) and conductivity values were also measured in order to gain insight into the dissolution process of the hydraulic binder.

The particle size distribution of the hydraulic cements was tested using a Horiba LA-920 Laser Particle Size Distribution Analyzer. In this test, two grams of the test sample was dispersed in a water-based solution of sodium hexametaphosphate ($(NaPO_3)_{13}$ ·Na₂O) in a glass vial by gently shaking the vial for 2 hours. The test instrument measures the size distribution of the dispersed particles. Finer particles tend to be more reactive, and could potentially produce improved hardened material qualities

The mineralogy of coal ash was assessed via x-ray diffraction (XRD) analysis using a Bruker D8 daVinci diffractometer equipped with Cu x-ray radiation, operating at 40 kV and 40 mA. The XRD method also allows for evaluation of the degree of crystallinity. For the purpose of XRD analysis, the powder was packed tightly into the sample cup with its surface leveled. Peak intensities were obtained by counting with Lynxeye detector every 0.05° 20. For this purpose, the sample was placed in a PVMA sample holder, and it was rotated at a rate of 5°/min. Powder XRD tests were carried out at reflection angles occurring within the 20 =10~80° range. Analysis of the XRD data yielded the degrees of crystallinity of the test samples. The presence of amorphous aluminosilicates among raw materials, which are often heterogeneous, are critical in producing mechanically strong and chemically stable alkali aluminosilicate

hydrates (Lee and Van Deventer 2003). Analysis of the XRD patterns highlights the differences between the degrees of crystallinity and the mineral compositions of different materials.

5.3 Experimental Result and Discussion

5.3.1 Visual appearance, Morphology and Microstructure

Figure 28 shows the visual appearances of the landfilled coal ashes obtained after 0, 2, 5 and 10 years of disposal. Fresh ash is observed in Figure 28 to be lighter in color than landfilled ashes. Disposal in landfill has also caused agglomeration of the ash, which could be a result of (hydration, carbonation and other) reactions under long-term exposure to moisture and air. For ashes obtained after longer disposal durations, the presence of large agglomerates necessitated their crushing with hammer. The pictures in Figure 28 were taken (for ashes with 5 and 10 years of disposal duration) after hammering the agglomerates.

Figure 29 shows typical scanning electron microscope images for a landfilled ash (collected after 2 years of disposal), and a hydraulic cement processed with this ash (and supplementary materials) via milling in carbon dioxide. The spherical ash particles can be recognized in the SEM image of Figure 29a. After processing into hydraulic cement, these spherical particles seem to be coated with products that could have resulted from the mechanochemical reactions of ash with supplementary minerals and the carbon dioxide gas during milling.



Figure 28. Coal ashes obtained from landfill after different disposal durations



(a) Landfilled ash after 2 years of disposal

(b) Hydraulic cement

Figure 29. Scanning electron microscope images of the DTE-2Y ash, and the hydraulic cement processed using this ash and supplementary raw materials via milling in carbon dioxide.

Figure 30 displays the particle size distributions of the hydraulic cements processed via milling of two-year-old landfilled ash processed via milling in air or CO_2 with supplementary minerals. The median particle sizes of these two cements are close to 10 micrometer, which is not significantly different from that of Portland cement. Milling in CO_2 produced a slightly finer particle size distribution.



Figure 30. Particle size distributions of hydraulic cements processed via milling of two-year-old landfilled ash and supplementary minerals in air and in CO₂.

5.3.2 Mineralogy and Degree of Crystallinity

The XRD technique was used to gain insight into the structure of the hydraulic cement formulated with landfilled coal ash, and processed in CO₂ or air. A landfilled ash extracted two years after disposal was used in these studies. Figure 31 presents the XRD patterns of the hydraulic cements formulated with this ash and processed and in and in CO₂. The cement processed in air has a higher content of amorphous phases when compared with that processed in carbon dioxide. As expected, milling in CO₂ raises the calcite content of the resultant cement. This observation points at capture of carbon dioxide gas during processing of cement in a carbon dioxide environment. The crystalline compounds that are prevalent in the cement processed in air include quartz and mullite.



Figure 31. XRD patterns of the hydraulic cements formulated with two-year-old landfilled coal ash and processing in carbon dioxide and in air.

5.3.3 Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectra of the hydraulic cements processed in CO₂ with coal ashes of different disposal durations are presented in Figure 32. A defined peak appeared at 3637-3641 cm⁻¹, which can be attributed to the OH baod from calcium hydroxide. The band around 1417 cm⁻¹ is due to C-O stretching vibration in CO₃²⁻ (Çelik, Damcı et al. 2008). The intensity of this peak increased depended on the age of the landfilled ash. This trend depends on the carbonation of ash over time in landfill, and also on changes under weathering effects that could make it more amenable to carbon capture during processing into a hydraulic cement. The carbonate peaks were noted at 930-730 cm⁻¹, 1833-1782 cm⁻¹ and 2646-2423 cm⁻¹, which were more pronounced with formation of carbonates. The peak at 1500 cm⁻¹ is the most obvious one pointing at the difference between ashes of different disposal periods (Lee, Kim et al. 2012). We also detected two IR bonds peaking at 2333 and 2360 cm⁻¹, for soluable CO₂ (g) in hydraulic cement (Panda, Hsieh et al. 2003). In fresh ash and also in landfilled ash with a disposal duration of five years, peaks related to CO₂ (g) were more pronounced. Small bands at 1650 and 3440 cm⁻¹ correspond to the

absorbed H₂O. The distinct band near 460 cm⁻¹ can be ascribed to the stretching vibration of the O-Si-O bond(Barbosa, MacKenzie et al. 2000); the Si-O-Si stretching vibration was detected within the 1200-950 cm⁻¹ range. The Si-O-Si bond has a more prominent stretching vibration than the O-Si-O bond. A similar trend was noted for the landfilled coal ash (Chindaprasirt, Jaturapitakkul et al. 2009). The hydraulic cement used with 10-year-old landfilled ash exhibits more intense peaks corresponding to O-Si-O and Si-O-Si bonds, pointing at the presence of large silica contents. In contrast, the cement made with the two-year-old ash exhibited a broad peak in this range, which could have resulted from the reactions of a fraction of siliceous minerals with carbon dioxide.



Figure 32. FTIR spectra of cements milled under carbon dioxide environment with landfilled ashes of different (2, 5 and 10 years) disposal durations as well as fresh ash (0 years disposal duration).

5.3.4 Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)

Figure 33 presents the TGA and DTA test results for hydraulic cements made with different coal ashes (tested up to 950°C). The total weight loss of the cement made with the fresh coal ash was 9% while those for landfilled ashes of 2, 5 and 10 years disposal duration fell within 12-15% (Figure 6a). The

cement made with the two-year-old landfilled ash exhibited the greatest weight loss. The DTA patterns presented in Figure 6b exhibit peaks at around 100, 400 and 700°C. The peak around 100°C (which covers up to 200°C) can be associated with loss of physically adsorbed water and carbon dioxide gas, and probably decomposition of some less stable hydrates. The peak around 400°C could be attributed to the decomposition of hydrates such as calcium hydroxide. Finally, the peak at 700°C corresponds to the decomposition of carbonates. Cement made with the two-year-old landfilled ash is noted to have a pronounced peak at 700°C, which supports the earlier findings that point at its high uptake of carbon dioxide gas. In the case of landfilled ash, longer disposal durations seem to reduce the carbon dioxide uptake potential of the cement production process. The carbon content of fresh ash, however, seems to be comparable to that of ten-year-old landfilled ash. These trends should be viewed cautiously in light of the variability of the landfilled ash properties, and the limited number of samples considered in this investigation.



(a) Thermogravimetric analysis (TGA)

Figure 33. TGA and DTA profiles for hydraulic cements made with fresh ash (0 years old) and landfilled ashes of different disposal durations (2, 5 and 10 years).

Figure 33 (cont'd)



(b) Differential thermal analysis (DTA)

5.3.5 Alkalinity of Coal Ashes

Figures 34a and 34b present the pH values and the total dissolved solids (in water) of hydraulic cements prepared with different (fresh and landfilled) coal ashes, respectively. Processing of cements in CO₂ (when compared with air) reduces both the pH and the total dissolved solids. These findings could be attributed to the formation of carbonates when the hydraulic cement is processed in carbon dioxide environment. The hydraulic cement made with the two-year-old landfilled ash exhibits the lowest pH value and total dissolved solids, which supports its high CO₂ uptake. The pH values seem to reflect the heavy metals immobilization qualities of these cements; higher pH values correspond to better heavy metals immobilization attributes. This could be due to a trends towards stronger formation of alkali aluminosilicate hydrates at higher pH levels. One could expect that restoration of the pH of the hydraulic cements processed in CO₂ would benefit various aspects of their performance, including hazardous waste immobilization qualities.



Figure 34. The pH values and total dissolved solids (TDS) of hydraulic cements processed with different coal ashes in air and CO₂ environments (measured after 24 hours of dissolution in water).

5.3.6 Compressive Strength

The compressive strengths for hydrated cement pastes at 7 and 28 days of age are presented in Figure 35. There is a general correlation between compressive strength and pH values. The lower pH of the hydraulic cements processed in carbon dioxide also lowers their compressive strength. This is because formation of alkali aluminosilicate hydrates takes place at high pH values. One can feasibly achieve high strength values by restoring the pH of the hydraulic cements processed in carbon dioxide environment.





Chapter 6. Conclusion

The conclusions derived based on the studies presented in each chapter of the thesis are presented in the following.

6.1 Development of refined chemistries and processing methods for integration of carbon dioxide into a hydraulic binder for effective heavy metal immobilization

- Landfilled coal ash was excavated two years after disposal, and was subjected to mechanochemical processing in the presence of diluted carbon dioxide gas and supplementary minerals. The dilute gas had a CO₂ concentraiton of 20% to simulate combustion emissions. Supplementary minerals were used to introduce additional alkali and alkaline earth metals as well as aluminosilicates for realizing a desired chemical balance for enhancing the CO₂ uptake and also the quality of the resultant hydraulic cement.
- 2. The primary application targeted for the hydraulic cement was stabilization/solidification of hazardous wastes. The selection of raw materials, the simple approach to processing and the direct use of combustion emissions (represented by the dilute CO₂ gas) were intended to lower the cost and energy content of the process.
- 3. Different formulations of raw materials were considered, and those offering a desired balance of CO₂ uptake, strength of cement hydrates, and heavy metal immobilization qualities were identified. Besides minerals supplying alkali/alkaline earth metals and silicates, which summed up to at about 15% by weight of total raw materials, granulated blast furnace slag at about 20% by weight of raw materials was found to benefit the CO₂ uptake and the performance of cement hydrates.
- 4. Comparisons were made between mechanochemical processing in air versus CO₂, which revealed the value added by capture of CO₂ towards achieving enhanced end product qualities (including heave metals immobilization). Carbon dioxide is thus a valuable (gaseous) raw material in production of the hydraulic cement.

6.2 Carbon Dioxide Use in Beneficiation of Landfilled Coal Ash for Hazardous Waste Immobilization

1. Landfilled coal ash, when blended with slag, CaO, NaOH and Na₂SiO₃, can be transformed into a hydraulic cement via input of mechanical energy.

2. When mechanical processing of raw materials into hydraulic cement is performed in a CO_2 environment, reactions of carbon dioxide with the calcium or magnesium compounds present in landfilled coal ash produce solid carbonates. The carbon dioxide uptake in this process can be over 10% by weight of solids, especially when mechanical processing is accomplished in the presence of few percent moisture by weight of solids.

3. The CO_2 uptake in the course of mechanical processing of hydraulic cement reduced the pH of the resultant cement (when dissolved in water). The drop in pH correlated with the extent of CO_2 uptake.

4. The hydraulic cement processed via input of mechanical energy in air or in CO₂ exhibited desired heavy metals immobilization qualities. Four different heavy metals (Cu, Zn, Ba, Pb) could be effectively immobilized, with more than 99.7% stabilization, in the optimal hydraulic cement formulation developed in the project. Higher CO₂ uptakes (which lowered the pH value of the resultant cement) negatively impacted the hazardous waste stabilization and the compressive strength development qualities of the hydraulic cement. Raising the concentration of alkalis in raw materials could feasibly restore these qualities of the cement processed mechanically in the presence of carbon dioxide.

6.3 Mechanical Processing of Cements Formulated with Landfilled Ash in Different Environments

- Landfilled ash, when blended with basalt, CaO and NaOH, produces a desired chemistry for production of a hydraulic cement. The blend of raw materials can be transformed into a hydraulic cement via input of mechanical energy.
- The environment in which the blend of raw materials is transformed into a hydraulic cement via input of mechanical energy influences the nature of reactions and the end product properties.
 When input of mechanical energy (via ball-milling) was done in a carbon dioxide environment,

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the temperature measured on the mill surface increased initially, and then decreased. When milling was performed in nitrogen, on the other hand, temperature at the mill surface decreased with time. This could be partly due to the exothermic reactions involving carbon dioxide during milling, that would not occur in an inert nitrogen gas environment.

- Milling in CO₂ environment transformed the calcium and magnesium silicates present in coal fly ash into carbonates. This seemed to cause release of smaller fly ash particles that are encapsulated in larger ash particles.
- 4. Input of mechanical energy activated the blend of raw materials. In an aqueous solution, the values of pH, total dissolved solids (TDS) and electric conductivity of cement increased with input of mechanical energy. These values were lowest when milling was performed in CO₂, that can be explained by the carbonation reactions that take place when processing is performed in a carbon dioxide environment. Milling in air versus nitrogen produced somewhat lower values of pH, TDS and conductivity in solution, that could be explained by some carbonation that takes place in air.
- 5. Input of mechanical energy to the blend of raw materials for their processing into a hydraulic cement accelerates the rate of reactions monitored based on the rate of heat release in calorimetry experiments. Milling in air and in nitrogen produced particularly high rates of heat release, and only one exothermic peak. Milling in CO₂, on the other hand, produced two peaks and lower rates of heat release. The cumulative heat release associated with hydration of the resultant cement was also smaller when milling was performed in CO₂.
- 6. The milling atmosphere affects the hydration heat of geopolymer cement. Due to mechano-chemical activation, the appearance of exothmic peak is more earlier that of previous test of without milling geopolymer, and the geopolymer cement which was milled in air or in N₂ have single exothmic peak, however milled in CO₂ atmosphere has double exothmic peak. Exothmic peak and total hydration heat of geopolymer which milled in N₂ is highest, that milled CO₂ is lowest. The relatively low rate and extent of heat release by the cement processed in CO₂ can be explained based on its low pH value in solution, that delays formation of Si-Al bonds.

Delayed formation of these bonds could explain the second exothermic heat release peak observed with the cement processed in CO₂. Processing in nitrogen, on the other hand, produces cements with relatively high pH values in solution. This accelerates the rate of hydration reactions and thus heat release.

- 7. The mortar compressive strengths produced with cements processed via milling in air and nitrogen were comparable. The cement milled in CO₂, however, produced relatively low compressive strengths. This was attributed to the reduced pH value of the cement milled in CO₂. The compressive strength obtained with this cement could be feasibly raised by increasing the alkali content of raw materials.
- 6.4 Production and Characterization of a Hydraulic Cement Produced with Landfilled Coal Ashes of Different Disposal Durations, Using Carbon Dioxide As a Raw Material
- Fresh as well as landfilled coal ashes with different disposal durations, when blended with GGBF slag,
 CaO, NaOH and Na₂SiO₃, can be transformed into a hydraulic cement via input of mechanical energy.
- 2. When mechanical processing of raw materials into hydraulic cement is performed in a CO₂ environment, reactions of carbon dioxide with the calcium and magnesium compounds present in landfilled coal ash produce solid carbonates. The carbon dioxide uptake is dependent upon the disposal duration of landfilled ash. This finding should be viewed cautiously considering the variability of landfilled ash properties and the limited samples evaluated in this experimental program. The landfilled ash with a disposal duration of two years produced the highest carbon dioxide uptake of about 10%. While the carbon dioxide uptake in the process decreases with increasing disposal duration of landfilled ash, even 10-year-old ash exhibits notable carbon uptake in the process.
- XRD analyses of cements produced via processing in air and in CO₂ indicated that milling in CO₂ produces a rise in carbonate minerals at the expense of non-carbonate minerals.

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- 4. In the case of cements processed in air, landfilled ashes with longer disposal durations produced hydraulic cements of lower quality. This was not the case for cement processed in carbon dioxide environment.
- 5. The CO₂ uptake in the course of mechanical processing of hydraulic cement reduced the pH of the resultant cement (when dissolved in water), which tends to compromise the structure and properties of the resultant hydrates. One could expect improved properties of cement hydrates if the pH of cement was realized by balancing its chemistry after processing in carbon dioxide environment.

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