Development of Refined Chemistries and Processing Methods for Integration of Carbon Dioxide into a Hydraulic Binder for Effective Heavy Metal Immobilization

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Abstract

A method is under developed for capture of carbon dioxide directly from combustion emissions into land filled 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 land filled ash and enhancing the end-product quality. The resultant binder meets the standard requirements for hazardous waste solidification and stabilization. The approach adopted here relies upon mechanochemical phenomena, induced by a simple milling action, to incorporate carbon dioxide into land filled 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 and 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 10wt.%) could be incorporated into hydraulic cements with desired hazardous waste stabilization and solidification qualities. The captures carbon dioxide benefited the resultant hydraulic cement performance.

Introduction

Since the beginning of the industrial age, the carbon oxide concentration in atmosphere has increased by about 30% [1,2]. 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 land filled 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 land filled 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 cements incorporating captured CO2 is the immobilization of hazardous wastes. 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 land filled 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 gaseous raw materials that, together with the land filled 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 [3-7] are:

i. Use of abundant (land filled) 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.

v. 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 CO$_2$ 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 CO$_2$ uptake in the conventional methods of mineral sequestration. These additives, and their mechanisms of action are:

a. Sodium bicarbonate for catalytic increase of the rate and extent of carbonation [8].

b. Silicate-based additives for increasing the rate and extent of carbon dioxide sorption [9].

c. Magnesium (and calcium) silicate for facilitating intense penetration and sorption of carbon dioxide [10].

d. Calcium (and magnesium) oxide for enhancing carbonation reactions.

e. Amine compounds for catalytic action as CO$_2$ sorbents [11-13].

f. Acetic (and other weak) acids for catalytic enhancement of the extraction of calcium ions [14-19], with subsequent use of sodium hydroxide to promote carbonation reactions.

g. Polyethylenimine for initial adsorption of significant quantities of CO$_2$ [13,20].

A number of these additives were evaluated for facilitating and intensifying the solid-state (mechanochemical) carbonation reactions.

Materials and Methods

Materials

The base formulation comprised land filled coal fly ash, ground granulated blast furnace slag, quick lime and sodium hydroxide. Land filled 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 are 14µm. The chemical composition of the ash obtained via x-ray fluorescence spectroscopy, includes: CaO (26.72 wt.%), Fe$_2$O$_3$ (21.82 wt.%), SiO$_2$ (19.99 wt.%), Al$_2$O$_3$ (8.89 wt.%), SO$_3$ (5.31 wt.%), MgO (2.7 wt.%), Na$_2$O (2.7 wt.%), BaO (2.14 wt.%), TiO$_2$ (2.63 wt.%), K$_2$O (2.4 wt.%), SrO (1.64 wt.%), and P$_2$O$_5$ (1.37 wt.%).

Granulated blast furnace slag (GBFS) was supplied by Lafarge. The chemical composition of GGBS slag, obtained via x-ray fluorescence spectroscopy, includes: CaO (40.8 wt.%), SiO$_2$ (37.5 wt.%), Al$_2$O$_3$ (9.54 wt.%), MgO (10.9 wt.%), Fe$_2$O$_3$ (0.47 wt.%), Na$_2$O (0.25 wt.%), and K$_2$O (0.45 wt.%). Quick lime (calcium oxide) in powder form 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, CO$_2$ 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 chromit [21]) was purchased from Persson minerals. The chemical composition of Dunite includes MgO, SiO$_2$, Fe$_2$O$_3$, CaO and Al$_2$O$_3$. Olivine, which is the primary constituent of Dunite, comprises largely of Mg$_2$SiO$_4$ and Fe$_2$SiO$_4$.

Serpentine was supplied by Laurel Mountain Group. It is a subgroup of the Kaolinite-Serpentine group; the composition of serpentine can be expressed as (Mg, Fe, Ni, Mn, Al, Zn)$_3$ (Si$_x$O$_{2x+y}$)(OH)$_y$ which is a compound of six metal elements. The most common serpentine species contain large amounts of Mg. Basalt was purchased from Fisher Scientific Co LLC. Its chemical composition includes SiO$_2$, Al$_2$O$_3$, CaO, FeO, MgO and TiO$_2$. 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 g/cm$^3$ [22]. 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)SO$_4$ 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 CaSiO$_3$, was supplied by Fisher Scientific Co LLC. Clinoptilolite was purchased from Fisher Scientific Co LLC. It is a natural zeolite with a microporous arrangement of silica and alumina tetrahedra. It has the complex formula (Na,K,Ca)$_x$-3Al$_y$(Al,Si)$_z$2Si$_4$O$_{10}$·8H$_2$O. 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 [23].

Talc was purchased from Sigma Aldrich. It is a mineral with pale color and waxy luster, with a chemical formula Mg$_3$Si$_4$O$_{10}$(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 Mg$_3$Si$_4$O$_{10}$(OH)$_2$ + 3CO$_2$ → 3MgCO$_3$ + 4SiO$_2$·2H$_2$O [24]. Molecular sieve (13X beads -12mesh) was purchased from Sigma Aldrich. It can be expressed by the chemical formula Na$_2$O:1Al$_2$O$_3$·2.8SiO$_2$·xH$_2$O.

**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 USEPA TCLP procedure. The heavy metal concentrations of leachates were determined via inductively coupled plasma (ICP) analysis.

**Results and Discussion**

**CO$_2$ uptake**

In a preliminary screening process, 10 wt. % of each additive was used with the base formulation comprising 5wt.% CaO and 5wt. % NaOH as the main alkali activators for land filled coal ash (90wt. %). Table 1 presents different formulations studied and their CO$_2$ uptake and the corresponding pH. Additives were milled together with other raw materials over a two-hour period in the presence of carbon dioxide. CO$_2$ uptake was estimated as the difference in the loss on ignition (LOI) of the CO$_2$-milled versus air-milled hydraulic cements. The highest CO$_2$ uptake was achieved with the following additives (in decreasing order): Celestine [25], 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 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 [26]. 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 (Figure 3).

**Table 1:** Percent CO$_2$ uptakes in the presence of different additives.

<table>
<thead>
<tr>
<th>No.</th>
<th>Formulation/Additive</th>
<th>Weight Loss for Processing in CO$_2$</th>
<th>%CO$_2$ Uptake</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Base Formulation*</td>
<td>13.2</td>
<td>9.3</td>
<td>3.9</td>
</tr>
<tr>
<td>2</td>
<td>Base Formulation with 10% GBFS</td>
<td>14.4</td>
<td>7.2</td>
<td>7.2</td>
</tr>
<tr>
<td>3</td>
<td>Base Formulation with 10% Dunite</td>
<td>13.8</td>
<td>9.7</td>
<td>4.1</td>
</tr>
<tr>
<td>4</td>
<td>Base Formulation with 10% Serpentine</td>
<td>14.2</td>
<td>11.4</td>
<td>2.8</td>
</tr>
<tr>
<td>5</td>
<td>Base Formulation with 10% Basalt</td>
<td>17.4</td>
<td>9.9</td>
<td>7.5</td>
</tr>
<tr>
<td>6</td>
<td>Base Formulation with 10% Celestine</td>
<td>17</td>
<td>8.9</td>
<td>8.1</td>
</tr>
</tbody>
</table>
Table 2: 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 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. Figure 4 compares the FTIR spectra of the CO₂ milled versus air-milled hydraulic cements. Significant enhancement of the peak intensity at 1400 cm⁻¹ was observed with milling performed in CO₂, which points at the strong presence of carbonates. Appearance of a new peak around 2500 cm⁻¹ with CO₂ 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 CO₂ milling.

**Effect of basalt as an additive for increasing CO₂ uptake**

Basalt was further investigated as an additive in 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 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. Figure 4 compares the FTIR spectra of the CO₂ milled versus air-milled hydraulic cements. Significant enhancement of the peak intensity at 1400 cm⁻¹ was observed with milling performed in CO₂, which points at the strong presence of carbonates. Appearance of a new peak around 2500 cm⁻¹ with CO₂ 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 CO₂ milling.
Table 2: Effect of Basalt on the CO₂ uptake and the pH in solution of the mechanochemically processed cement.

<table>
<thead>
<tr>
<th>No.</th>
<th>Notation</th>
<th>Material Composition (Milled)</th>
<th>Milling Condition</th>
<th>% CO₂</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ash</td>
<td>Basalt</td>
<td>CaO</td>
<td>NaoH</td>
</tr>
<tr>
<td>1</td>
<td>DTE 2Y-GBasalt-CaO-C</td>
<td>83%</td>
<td>4%</td>
<td>6%</td>
<td>6%</td>
</tr>
<tr>
<td>2</td>
<td>DTE 2Y-CaO-C</td>
<td>87%</td>
<td>-</td>
<td>6%</td>
<td>6%</td>
</tr>
<tr>
<td>3</td>
<td>DTE 2Y-GBasalt-CaO-N</td>
<td>83%</td>
<td>4%</td>
<td>6%</td>
<td>6%</td>
</tr>
</tbody>
</table>

Effect of granulated blast furnace (GBF) slag on CO₂ uptake

Table 3 introduces the formulations incorporating GBFS investigated in this work, and the CO₂ uptake and pH in solution of the resulting hydraulic cement. The highest CO₂ uptake was obtained with 20% slag. The CO₂ uptake was estimated based on the difference in LOI between binders processed in CO₂ and in air. The formulation DTE 2Y-Slag-CaO-C provided a higher CO₂ 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 CO₂ uptake, by adding a relatively small dosage of sodium silicate.

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

<table>
<thead>
<tr>
<th>No</th>
<th>Notation</th>
<th>Material Composition (Milled)</th>
<th>Milling Condition</th>
<th>% CO₂</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ash</td>
<td>Slag</td>
<td>CaO</td>
<td>NaoH</td>
</tr>
<tr>
<td>1</td>
<td>DTE 2Y-Slag-CaO-C</td>
<td>70%</td>
<td>20%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>2</td>
<td>DTE 2Y-Slag2-CaO-C</td>
<td>80%</td>
<td>10</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>3</td>
<td>DTE 2Y-Slag-CaO-sili-C</td>
<td>65%</td>
<td>20%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>4</td>
<td>DTE 2Y-Slag-CaO-basalt-C</td>
<td>65%</td>
<td>14%</td>
<td>5%</td>
<td>5%</td>
</tr>
</tbody>
</table>

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 5. 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.

With the addition of 5% sodium silicate to the formulation, compressive strength increased significantly with only a slight drop in CO₂ uptake. Figure 6 shows the FTIR spectra for cements formulated with Slag-silicate with processing performed in air and in CO₂. The area under the peak 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


unsaturated to Si-O and Al-O stretching bands. The bands appearing around 720-730cm⁻¹ are associated with aluminum-rich structures such as hydroxysodalite. The band at 640-630cm⁻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.

**Unconfined compressive strength**

Figure 7 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 (4wt.% and slag (20wt.%); the compressive strength produced by the resultant cement, however, was relatively low.

**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 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. The highest copper immobilization > 99.9% was obtained with the formulation comprising 65% land filled 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 [27,28]. 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 [29]. 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 [30].

**Summary and Conclusion**

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 concentration of 20% to simulate combustion emissions. The supplementary minerals were used to introduce additional alkali and alkaline earth metals as well as alumino silicates for realizing a desired chemical balance for enhancing the CO₂ uptake and also the quality of the resultant hydraulic cement. 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. Different formulations of raw materials were considered, and those offering a desired balance of CO₂ uptake and the cement hydrate strength 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. 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 heavy metals immobilization). Carbon dioxide is thus a valuable (gaseous) raw material in production of the hydraulic cement.

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References
