Mineral carbonation for carbon sequestration in cement kiln dust from waste piles

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ABSTRACT

Alkaline earth metals, such as calcium and magnesium oxides, readily react with carbon dioxide (CO_2) to produce stable carbonate minerals. Carbon sequestration through the formation of carbonate minerals is a potential means to reduce CO_2 emissions. Calcium-rich, industrial solid wastes and residues provide a potential source of highly reactive oxides, without the need for pre-processing. This paper presents the first study examining the feasibility of carbon sequestration in cement kiln dust (CKD), a byproduct generated during the manufacturing of cement. A series of column experiments were conducted on segments of intact core taken from landfilled CKD. Based on stoichiometry and measured consumption of CO_2 during the experiments, degrees of carbonation greater than 70% of the material's potential theoretical extent were achieved under ambient temperature and pressure conditions. The overall extent of carbonation/sequestration was greater in columns with lower water contents. The major sequestration product appears to be calcite; however, more detailed material characterization is need on pre- and post-carbonated samples to better elucidate carbonation pathways and products.

1. Introduction

Increased public awareness of the threats posed by global warming has led to greater concern over the impact of anthropogenic carbon emissions on the global climate. Several carbon sequestration technologies have emerged as potential means to mitigate rising concentrations of CO_2 in the atmosphere. One of these options is mineral carbonation, the reaction of alkaline earth metals with CO_2 to form relatively stable and benign carbonate minerals according to the general reaction [1]:

$$(Ca, Mg)SiO_3 + 2CO_2 + 3H_2O$$
$$\rightarrow (Ca, Mg)CO_3 + H_4SiO_4 + H_2O + CO_2 \qquad (1)$$
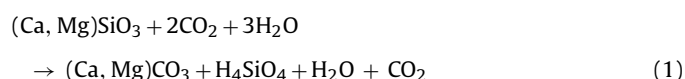
Carbonation occurs naturally through geologic processes of silicate weathering; however, the reaction rates are slow (on geologic time scales) and economic feasibility of wide-spread application is not fully known. The stability of the end-products (i.e., carbonates), however, has prompted investigations into ways to mimic and catalyze the weathering process in the laboratory. The majority of mineral carbonation research to date has examined sequestration in mined silicate minerals (e.g., serpentine, olivine) [2–8]. Mining operations and subsequent physical and chemical processing are required to produce a mineral form suitable for sequestration reactions. Both the mineral acquisition and pre-processing steps require energy inputs, reducing the overall efficiency of the process in terms of net carbon reduction. However, more readily available oxide mineral sources may be available through the reuse of industrial solid wastes and residues.

The extent of carbonation in alkaline wastes, such as coal fly ash, municipal solid waste incinerator ash, and steel slag has been investigated in preliminary experiments [4,9–13], with favorable results. In addition, the use of alkaline solid wastes for CO_2 sequestration has been acknowledged by the Department of Energy's National Energy and Technology Laboratory as a promising approach and further study is warranted [1]. The utilization of alkaline waste materials provides several advantages: (1) waste materials supply a readily available source of calcium or magnesium mineral matter without the need for pre-processing; (2) they are typically fine-grained with high reactive surface areas; (3) the environmental quality of the waste materials can be improved through pH-neutralization and mineral transformation [1,11,12]; and (4) the

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end product of the sequestration step may be amendable for beneficial re-use in products such as road base or other construction material. In addition, alkaline industrial wastes are typically generated at or near point sources of CO_2.

For a waste to be amenable for mineral carbonation it must provide alkalinity in the form of calcium or magnesium oxides. Many fine-grained industrial wastes, such as cement kiln dust (CKD), coal fly ash, and steel slag, have high mass percentages of CaO. While a majority of the research conducted on mineral carbonation of feedstocks (mined metal oxides) has focused on Mg silicates because of their availability, the carbonation of CaO is more thermodynamically favorable at ambient temperatures and pressures [1,14]. One industrial waste that has high mass fractions of CaO (20–60%) is cement kiln dust . The cement manufacturing process produces millions of tons of CKD each year, which consists of fine particles of unburned and partially burned raw materials, clinker, and some trace elements [15]. Although a fraction of CKD is used for beneficial agricultural applications, the U.S. cement industry disposes of several million tons of CKD annually in piles, quarries, and landfills [16,17]. Congress and the EPA have expressed increased concerns over the health hazards associated with the improper management of CKD [17]. Therefore, waste neutralization through sequestration may be an encouraging means to both capture carbon and mitigate the possible adverse health and environmental affects posed by improper CKD disposal. In addition to the generation of CKD, the cement industry is one of the largest CO_2 emitters in the U.S. [18] and globally [19]. Roughly half of the industry's CO_2 comes from the calcining process, while the other half is from the combustion of fossil fuels [19]. The calcining process releases CO_2 from the conversion of calcite ($CaCO_3$) to lime (CaO) and calcium silicate species at kiln temperatures in excess of 1300 °C.

In this paper, the feasibility of carbon sequestration in waste CKD under ambient pressure and temperature conditions is investigated. The aims of this study are to (1) determine if landfilled CKD will readily sequester CO_2 and (2) to measure the extent of carbonation (sequestration) under varying operating conditions (water content and CO_2 concentrations). Very few studies have been conducted that examine the sequestration of CO_2 in industrial wastes (e.g. [11,12]) and none have measured the extent of sequestration in waste cement kiln dust under ambient conditions. This paper presents the first study of the feasibility of CO_2 capture in landfilled CKD and identifies conditions that appear to improve the extent of sequestration.

2. Materials and methods

A series of column experiments were conducted using intact core segments of CKD taken from a landfilled waste pile in Alpena, Michigan (depth of sample ~25 feet). The columns were operated under varying conditions to determine the impact of humidity and CO_2 concentration on the extent of carbonation or sequestration. Humidity was added to two of the columns to assess whether added moisture impacted the extent of carbonation through gas transport limitations.

2.1. Column set-up and operation

Four segments were cut from the core (7.3 cm diameter) and fitted with PVC end caps (Table 1). High-purity carbon dioxide (CO_2) and nitrogen (N_2) (Airgas, Marquette, MI) were mixed and regulated with Dwyer gas flow meters (Models VA1043 and VA1045, Michigan City, IN) to achieve the desired input CO_2 concentration. Gas flow rates between 45 and 60 mL/min were maintained through the columns, and effluent samples were analyzed with a gas chromatograph (MTI Analytical Instruments Quad 4 Model Q30L, Fremont, CA) until full breakthrough of the input CO_2 was observed. Fig. 1 provides a schematic of the experimental set-up. The extent of carbon sequestration was measured under varied influent gas concentrations, relative humidity conditions, gas flow rates, and initial column moisture contents (Table 1). At the end of each experiment, the column was flushed with N_2 gas and CO_2 effluent concentrations were monitored to determine the amount of unsequestered CO_2 within the column tubing, end caps, pore spaces, and dissolved in the aqueous phase. After nitrogen flushing, the columns were dismantled and the final gravimetric water content of the carbonated CKD was measured. The dried content of each column was homogenized by grinding in a Bico, B100 pulverizer (Type UA, Burbank, CA) and tumbling the material for 5 min. Two 20-mL aliquots were obtained from the bulk mix of each column for compositional analyses.

2.2. Material characterization

The elemental composition of pre-carbonated CKD was analyzed with a Philips PW 2404 X-ray spectrometer (Cambridge, UK). Sample specimens were homogenized by grinding in a SPEX shatterbox (Edison, NJ). Portions of the bulk sample were ignited to a constant mass of 980 °C and then fused into glass disks with a LECO FX-503 (St. Johns, MI) automated fuser. Mineralogical composition of pre- and post-carbonated samples was assessed using powder X-ray diffraction (XRD) (Siemens D 500, Cherry Hill, NJ) equipped with a Cu X-ray tube operated at 50 kV and 27 mA medium resolution slits. Specimens were scanned from 5° to 70° 2θ, with a step-size of 0.05° and a dwell time of 2 s per step.

2.3. Extent of carbonation

The extent of mineral carbonation was determined by complementary analytical and empirical methods: (1) thermal decomposition (TGA–DTA), (2) observed mass change before and after column experiment; and (3) frontal analysis of effluent CO_2 concentrations (i.e. difference between the cumulative influent and eluted mass of CO_2 in the columns; [20]).

Thermal analysis was performed with a SDT 2960 TA-Instruments (New Castle, DE) Thermal Gravimetric Analyzer to determine carbonate content of pre- and post-carbonated CKD samples from the column experiments. Representative samples (~22 mg) were heated in corundum crucibles in a nitrogen environment from ambient to 1100 °C at 20 °C/min. Weight loss in the samples was monitored by gravimetric analysis (TGA) as a
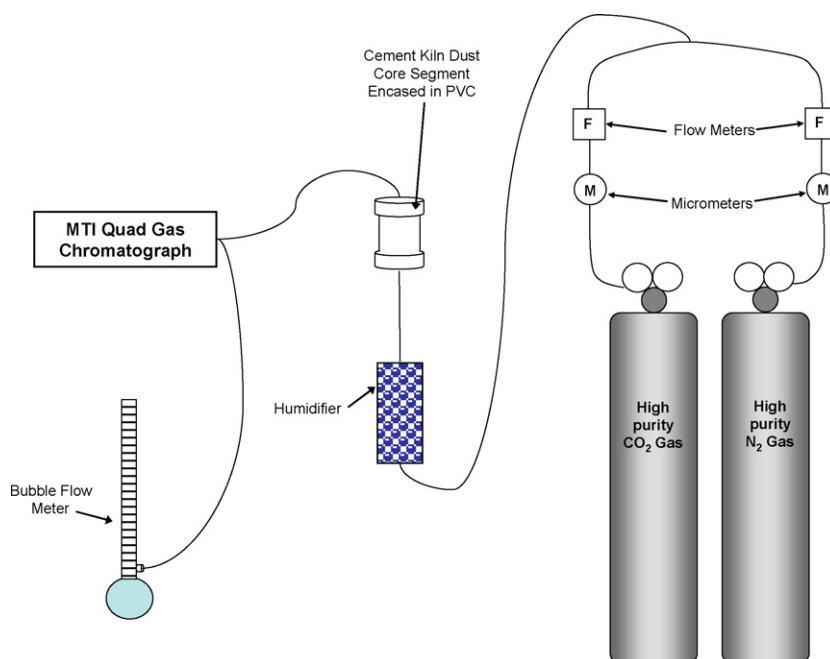
Table 1
Column and operating conditions for the four cement kiln dust columns.

Column	Length (cm)	Flow rate (mL/min)	Influent CO_2 concentration (ppm$_v$)	Influent gas humidity	Initial material dry mass (g)[a]	Initial gravimetric water content[a]	Bulk density (g/mL)
A	5.1	45	75,800	>98%	136	75%	0.60
B	5.0	45	69,900	>98%	140	45%	0.61
C	4.9	61	84,900	<1%	191	38%	0.81
D	13.6	53	35,600	<1%	424	68%	0.74

[a] Determined from forensic analysis after column dismantlement.

Fig. 1. Schematic of column set-up.

function of time. Phase change was simultaneously evaluated with differential thermal analysis (DTA) by measuring the temperature difference between the sample and inert, heat-treated corundum. Loss of calcium carbonate (i.e., CO_2) in both pre- and post-carbonated samples was observed in the temperature region of 500–800 °C. Other weight loss regions associated with the loss of moisture, ettringite (110–150 °C), and portlandite (300–500 °C) were also observed.

In addition to thermal analysis, the extent of carbonation was measured by monitoring the mass change of each column before and after CO_2 injection and through frontal analysis of measured effluent CO_2 concentrations. For those columns where dry gas was used, the recorded mass change was corrected for water vapor loss during the course of the column experiment. The loss of water mass was calculated as a function of flow rate, operation time, and the vapor pressure of water at ambient temperature and pressure conditions (21 °C, 1 atm).

2.4. Degree of sequestration

The degree of sequestration refers to the amount of CO_2 captured as carbonated mineral mass compared to the mass of CO_2 that would be consumed if all available oxides were carbonated. For this study, the degree of sequestration was determined by comparing the observed mass of CO_2 sequestered in each column via frontal analysis to the amount theoretically possible based on the elemental and phase composition of the pre-carbonated CKD. For pure oxides (e.g., CaO and Ca(OH)$_2$), the theoretical extent of carbonation is a function of basic stoichiometry:

$$CaO_{(s)} + CO_{2(aq)} \rightarrow CaCO_{3(s)} \tag{2}$$

Thus, every ton of CaO can potentially sequester up to 0.785 tons of CO_2. For waste mixtures such as CKD, the theoretical extent of carbonation can still be calculated as a function of stoichiometry, however, the extent also depends on the availability of those oxides for reaction. CKD can host a number of reaction pathways to the capture of CO_2 in addition to Eq. (2):

$$MgO + CO_2 \rightarrow MgCO_3 \tag{3}$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{4}$$

$$K_2O + CO_2 \rightarrow K_2CO_3 \tag{5}$$

$$Na_2O + CO_2 \rightarrow Na_2CO_3 \tag{6}$$

Potassium and sodium oxides can also react with CO_2 to form bicarbonates. The amount of free oxide in CKD available for reaction depends on the type of kiln, source material, fuel type used, and the manner in which CKD was recovered from the system [21–23]. Because of the wide range in CKD composition it can be difficult to specify a theoretical extent of carbonation. Nevertheless, estimates of CO_2 consumption can be made by taking into consideration the amount of calcite present in the pre-carbonated waste, along with the CaO bound in anhydrite. Similar to estimates of CO_2 consumption in mortars and concrete by Steinour [24], an estimate of the theoretical extent of carbonation in a given CKD can be calculated as follows:

$$\%CO_2 = 0.785(\%CaO - 0.56\%CaCO_3 - 0.7\%SO_3) + 1.091\%MgO$$
$$+ 0.71\%Na_2O + 0.468\%K_2O \tag{7}$$

where the $\%CO_2$ refers to the mass of CO_2 consumed in the carbonation reactions compared to the original, unreacted mass of the sample. The stoichiometric mass factors shown in Eq. (7) assume that all of the CaO (except that bound in $CaSO_4$ and $CaCO_3$) will react to form $CaCO_3$, all the MgO will react to form $MgCO_3$, and all of Na_2O and K_2O will convert to Na_2CO_3 and K_2CO_3. The mass factors for K_2O and Na_2O are doubled if bicarbonates form instead of carbonates.

3. Results and discussion

3.1. Material characterization and theoretical extent of carbonation

The elemental composition of the pre-carbonated CKD used in this study, given as weight percent of oxides, is listed in Table 2 along with the typical range in oxide composition reported for CKD [25]. The unreacted CKD is high in CaO, with moderate to low amounts of K, Mg, and Na oxides. Based on thermal analysis of pre-carbonated

Table 2
Elemental composition of pre-carbonated CKD as oxides.

Oxide	Mass Fraction (% dry wt.)	
	CKD (This study)	Typical range for CKD[a]
Na_2O	0.52	0–2
MgO	2.08	0–2
Al_2O_3	3.41	3–6
SiO_2	13.17	11–16
P_2O_5	0.05	–
SO_3	4.78	4–18
K_2O	5.84	3–13
CaO	34.5	38–50
TiO_2	0.19	–
Fe_2O_3	2.89	1–4
SrO	0.02	–
Mn_2O_3	0.04	–
LOI[b]	31.2	5–25
Oxide total	98.7	–

[a] From Corish and Coleman [25].
[b] LOI is the loss on ignition.

Fig. 3. Derivative weight loss curve from thermal gravimetric analysis (TGA) of pre- and post-carbonated CKD. The carbonated sample was taken from Column B.

samples (Figs. 2 and 3), the existing carbonate composition of the waste is relatively high (42.3%). It is possible that other carbonate species are present in the sample in addition to calcite, such as dolomite ($CaMg(CaCO_3)_2$) or ankerite ($Ca(Fe, Mg, Mn)(CO_3)_2$). However, dolomite (and ankerite) overlap severely with arcanite in XRD diffractograms (Fig. 4). Therefore, in this waste, it is difficult to definitively determine their occurrence. Assuming that the predominant carbonate phase in the unreacted CKD is calcite, only 7.8% CaO is available for carbonation, with a small fraction of that bound in anhydrite ($CaSO_4$). Gypsum ($CaSO_4 \cdot 2H_2O$) is thermodynamically stable at temperatures below 52 °C. Therefore, it is assumed that under moist conditions and at ambient temperatures and pressures

anhydrite will readily hydrate to form gypsum rather than releasing Ca for reaction with CO_2.

The major and minor mineral phases identified by powdered X-ray diffraction in the unreacted CKD were calcite ($CaCO_3$), quartz (SiO_2), anhydrite ($CaSO_4$), ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$), and arcanite ($K_2SO_4$) (Fig. 4). It is likely that the sample contains small amounts of other mineral phases, but reliable detection of minerals present in weight percents below 1% or 2% is difficult with XRD. The high percentage of calcite and the presence of ettringite indicate that the waste pile from which the CKD core was taken had
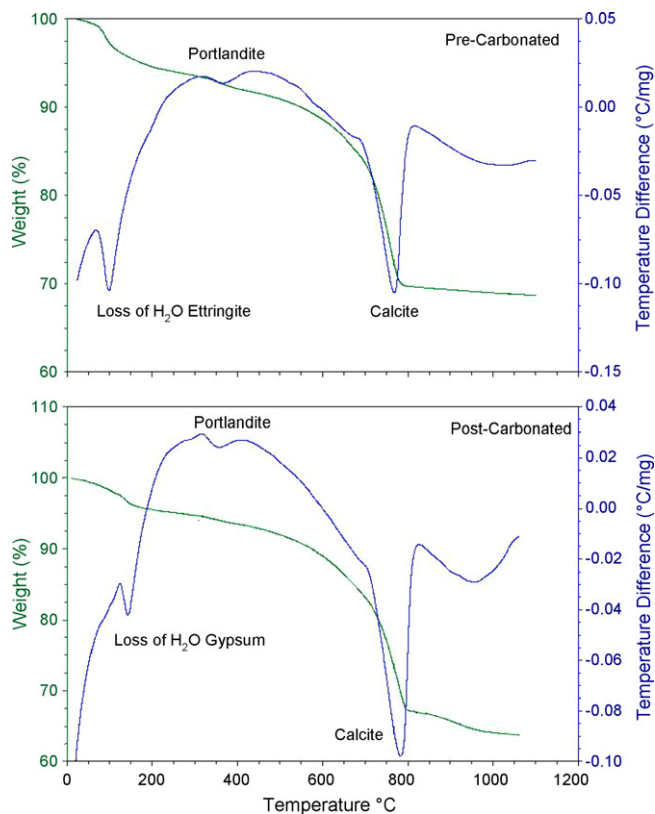
Fig. 2. Mass loss and temperature difference curves from thermal gravimetric analysis (TGA) of pre- and post-carbonated CKD. The carbonated sample was taken from Column B.
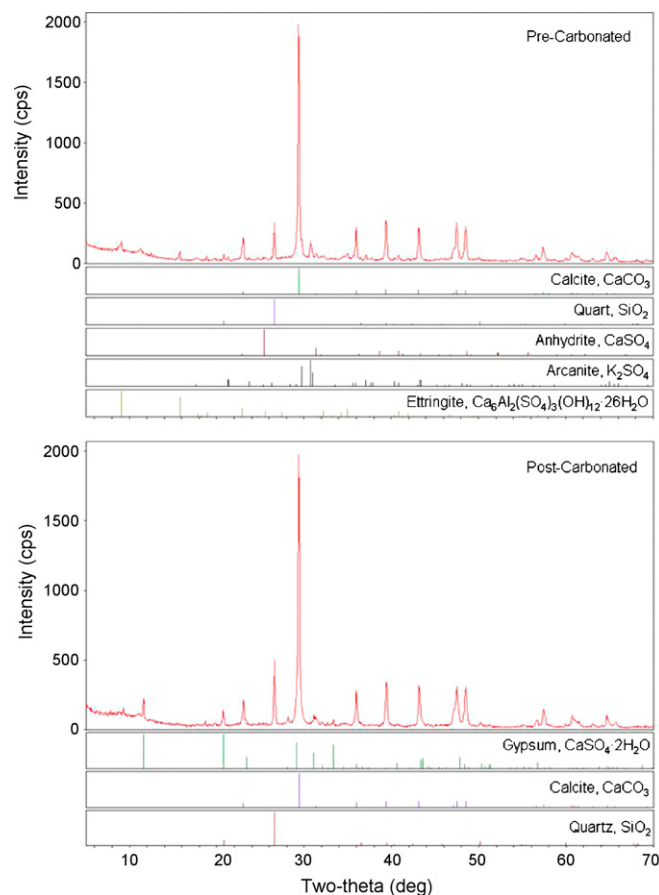
Fig. 4. Powdered X-Ray diffractograms of pre- and post-carbonated CKD samples. The carbonated sample was taken from Column B.

Table 3
Theoretical extent of sequestration possible for CKD type used in this study.

Parameter	Oxide			
	CaO	MgO	Na$_2$O	K$_2$O
Molecular weight	56.0	40.3	62.0	94.2
Weight percent of oxide	34.5%	2.1%	0.5%	5.8%
Weight percent available	7.8%	2.1%	0.5%	5.8%
Stoichiometric mass factor[a]	0.8	1.1	0.7	0.5
Percentage of CO$_2$ capture possible[b]	6.13%	2.27%	0.37%	2.73%
Percentage of total theoretical sequestration	53.3%	19.8%	3.2%	23.7%

[a] Stoichiometric mass factors assume that all of the available oxides react to form carbonates.

[b] Based on stoichiometry and the composition of the unreacted CKD. The total sequestration capacity of the waste is calculated to be 11.5% (i.e., for every 1 kg of CKD, has potential to capture 0.115 kg of CO$_2$)

been exposed to moisture and likely undergone some carbonation after its deposition. Ettringite is a common hydration product found in cements [26] and other materials high in Ca, Al, and SO$_3$, such as CKD and fly ash [27].

Based on TGA–DTA analysis (Figs. 2 and 3), the amount of ettringite in pre-carbonated samples is approximately 11.7% (2.24% SO$_3$). Based on the elemental and phase composition of the pre-carbonated CKD, the theoretical extent of carbonation (consumption of CO$_2$) can be estimated using Eq. (7). Assuming that half of the remaining SO$_3$ is bound in anhydrite and that all of the Na, K, and Mg oxides are available to react to form carbonates, the theoretical extent of carbonation for CKD used in this study is 11.5% (Table 3). This theoretical percentage is the mass of CO$_2$ that can be captured compared to the initial dry mass of material. Table 4 summarizes the expected amount of CO$_2$ sequestration for each column if all oxides available for reaction were carbonated.

3.2. Post-carbonation characterization and extent of carbonation

Post-carbonation XRD and TGA–DTA analysis was conducted on a sample taken from column B. Only three major and minor mineral phases were identified: calcite, quartz, and gypsum (Figs. 2–4). The absence of ettringite and anhydrite indicate that the assumptions of calcium availability and anhydrite conversion to gypsum were reasonable. For the CKD used in this study, CaO and K$_2$O appear to have the largest capacity for mineral carbonation (Table 3). Although no Na or K carbonate or bicarbonate species were identified with XRD analysis on the post-carbonated waste, the amount of CO$_2$ sequestered in each column suggests that calcite was not the only carbonate species formed during the experiments (Table 4). From TGA conducted on post-carbonated samples taken from column B, the derivative weight loss curve shows an increase in the area of the carbonate peak, particularly on the leading edge (Fig. 3). The decomposition of an addition, unidentified phase(s) (possibly anhydrite) was detected in the carbonated sample in the temperature region between 820 and 1000 °C (Fig. 3). More detailed quantitative analysis of pre- and post-carbonated CKD materials is needed to better quantify carbonation products. Batch scale experiments, microscopy, and additional material analysis by XRD and TGA–DTA are currently being conducted to elucidate reaction pathways and carbonation products.

The extent of sequestration in terms of total mass of CO$_2$ consumed (via frontal analysis) in each column is presented in Table 4, along with the theoretical sequestration capacity of each column calculated using Eq. (7). Thermal analysis conducted on samples taken from Column B show an increase in CO$_2$ content between unreacted and reacted CKD of 7.7% (from weight loss in TGA curve). Based on the dry mass of column material before and after carbonation, this equates to an increase in CO$_2$ content in the column of 15.84 g. The total amount of CO$_2$ sequestered via frontal analysis and observed mass change for column B was 15.3 and 14.9 g, respectively. The good agreement among the TGA, mass change, and frontal analysis results suggests that the methods used in this study for determining carbonation extent were appropriate.

3.3. Extent of sequestration as a function of operating conditions

The extent of CO$_2$ sequestration was measured in four (4) columns, operated under varied moisture and gas concentration conditions. Columns A and B were injected with humidified gas, at relatively the same influent CO$_2$ concentration (Table 1). However, the water content of Column A was elevated prior to the experiment by injecting heated, humidified N$_2$ into the column and allowing water to condense in pore spaces. Columns C and D were injected with dry gas at moderate and low concentrations of CO$_2$, respectively. The extent of sequestration in each column is presented in Fig. 3 (based on frontal analysis of column CO$_2$ effluent). The mass of CO$_2$ injected and the corresponding mass sequestered with time are normalized by the theoretical extent of sequestration for each column assuming that Na and K carbonates form (Table 4). Ideal sequestration conditions (where all CO$_2$ injected is consumed by the material until the carbonation capacity of the waste has been achieved) are also shown in Fig. 5.

The columns were operated for a period of 3.5–12 days, until full breakthrough of CO$_2$ concentration was observed. At early times, the columns follow ideal conditions, consuming all CO$_2$ that is injected. Columns A and B (humidified gas) track the idealized curve longer than Columns C and D (dry gas), however higher water contents appear to decrease the overall sequestration extent by slowing or hindering the transport of CO$_2$ to reaction sites. The shape of the normalized cumulative sequestration curves for those columns where dry gas was used deviate more from ideal conditions at early times, indicating that the absence of humidity may reduce the rate of carbonation. Or, the added humidity to the system results in increased aqueous absorption of gaseous CO$_2$ creating the appearance of higher CO$_2$ consumption and the variation in the curve shapes between dry and humidified columns. The overall extent of carbonation, however, appears to be inversely related to the water content of the columns (Fig. 6). The increase in overall carbonation

Table 4
The observed mass of CO$_2$ sequestered compared to the theoretical amount of sequestration possible, along with the extent of carbonation achieved for each column.

Column	Operation time (days)	Observed mass change[a] (g)	CO$_2$ sequestered[b] (g)	Theoretical sequestration[c] (g)	Extent of carbonation[d] (%)
A	3.4	10.8	11.8	15.7	75.0
B	4.9	14.9	15.3	16.2	94.3
C	3.3	22.5	22.3	22.0	101.2
D	12.0	29.2	34.6	49.0	70.6

[a] Observed mass changes in Columns C and D were corrected for water vapor loss due to injection of dry gas.

[b] CO$_2$ sequestered is based on frontal analysis of effluent CO$_2$ concentrations from each column.

[c] Theoretical mass of sequestration assuming that Na and K carbonates form.

[d] Extent of carbonation achieved in each column based on theoretical mass of sequestration.
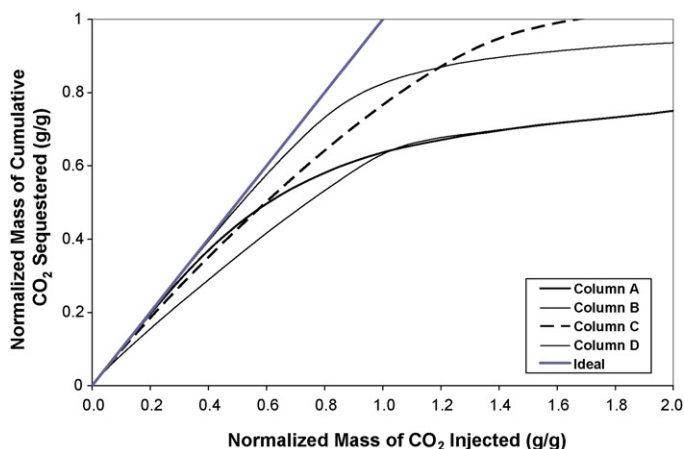
Fig. 5. Cumulative mass of CO_2 sequestered in CKD columns under varied operating conditions: normalized by theoretical extent of sequestration for each column. Under Ideal conditions, all the CO_2 injected into the column would be consumed by the waste until the carbonation capacity of the material has been achieved (blue line). Column A: humidified gas, elevated initial water content; Column B: humidified gas, normal water content; Column C: dry gas, normal water content, moderate concentration; Column D: dry gas, normal water content, low concentration. Refer to Table 1 for more detailed operating conditions.

in columns of lower water content is likely the result of greater gas pore volume and lower diffusion limitations (Table 1, Fig. 6). The significant increase in the extent of carbonation between column C and D indicates that the carbonation reaction rates may be dependent upon concentration (i.e., 1st or 2nd order) and higher concentrations may lead to faster rates and greater overall carbonation in a given period of time. However, more comprehensive column experiments are necessarily to determine if column performance is dependant on influent CO_2 concentrations.

Without more detailed characterization of pre- and post-carbonated CKD, it is difficult to determine if heterogeneity in the columns influenced their ability to sequester CO_2. Because the columns were constructed of intact core segments, extracting a pre-carbonation sample from each column for compositional analysis was not possible. It is likely that the composition of the CKD waste pile varies with depth and the core segment used in this study may have intersected layers with differing composition. Additional column studies are being conducted with fresh CKD from a number of different manufacturing facilities, kiln types, and CKD collection systems. Detailed composition analysis of pre- and post-carbonated

samples is being conducted to separate the impacts of varied material composition from operating conditions (CO_2 concentration, gas flow rate, and moisture conditions).

4. Conclusions

This paper demonstrates the feasibility of mineral carbonation in landfilled CKD. A series of column experiments were conducted in core segments of waste CKD under varied operating conditions (input CO_2 rate, gas, and water content). The results indicate:
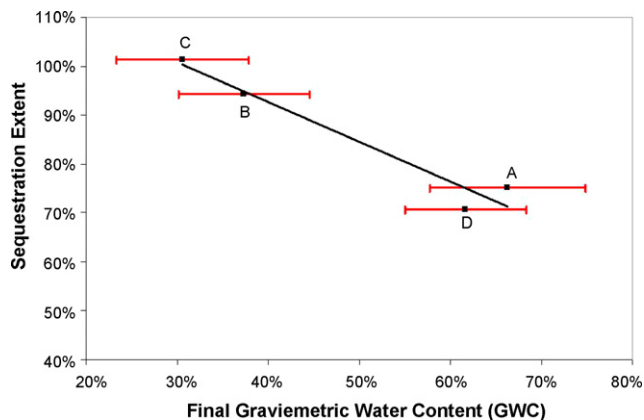
- Cement kiln dust readily sequesters CO_2 at ambient temperatures and pressures.
- The major product of carbonation appears to be calcite in both crystalline and amorphous form. However, more detailed material characterization of pre- and post-carbonated CKD are needed to better elucidate reaction pathways and products.
- Carbonation extents greater than 70% of its theoretical capacity, based on stoichiometry, can be achieved without any amendments or modifications to the waste material.
- The extent of carbonation is greater at lower gravimetric water contents due to increased access to reaction sites.
- Heterogeneity in the core segments caused variability in observed carbonation extents. Additional, more detailed experiments are needed to separate the impacts of varied material composition from operating conditions (CO_2 concentration, gas flow rate, and moisture conditions).

Fig. 6. Variation in extent of sequestration with gravimetric water content (GWC) in columns of cement kiln dust. Sequestration extent refers to the mass of CO_2 consumed compared to the amount of CO_2 sequestration theoretically possible. Error bars represent uncertainty in water content measurements due to column heterogeneity.

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