Quantification of CO₂ sequestration capacity and carbonation rate of alkaline industrial byproducts

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Abstract

CO₂ sequestration generally refers to the capture and permanent, safe storage of CO₂. This study evaluates the CO₂ sequestration potential by mineral carbonation of several alkaline industrial byproducts of high abundance, and some of them are landfilled in large part. These include cement kiln dusts, fly ashes, ground granulated blast furnace slag, and fine glass powder. Compacted cylindrical paste specimens made from each alkaline waste were subjected to a carbonation environment with tightly controlled CO₂ concentration, temperature, and relative humidity in order to characterize the CO₂ sequestration capacity, depth of carbonation, and associated material phase changes. The effect of water content and carbonation period are investigated, as is the use of binary and tertiary blends including portland cement to enhance sequestration capacity. Sequestration capacity and phase changes are characterized by thermogravimetric and X-ray diffraction analyses. Carbonation depth is measured visually using phenolphthalein indicator. Cement kiln dusts exhibit the greatest sequestration potential, with 4% CO₂ sequestration by mass.

Keywords: carbonation, CO₂ sequestration, CKD, fly ash, slag, glass powder, XRD, TGA

1. Introduction

CO₂ is one of the most abundant atmospheric gases, and is of the second highest concern among greenhouse gases. The atmospheric concentration of CO₂ has increased in recent years, approaching 400 ppm, with an annual mean growth rate of 2 ppm since 2000 [1,2,3]. Several methods of capturing and storing CO₂ have recently been investigated, including physical sequestration methods such as storage in geological formations, oceans, and below the sea bed; and chemical methods such as mineral carbonation [1,2]. Mineral carbonation has received more attention in the past since it results in virtually permanent chemical sequestration of CO₂ [4-9]. The chemistry of sequestration by mineral carbonation is well understood for natural rock minerals such as serpentine or olivine, but the slow reaction rate, large material and energy requirements, and environmental issues associated with the mining of these natural minerals hamper the practical implementation of this method [3-5].

One potential alternative to mineral carbonation with natural minerals is the use of industry-specific CO₂ sequestration methods, in which the CO₂ emissions from industrial processes are offset by sequestration using byproducts of these same processes. Many processes that result in high CO₂ emissions also produce considerable quantities of solid alkaline waste products such as combustion residues, ashes, and grinding residues [10-12]. Although some waste products such as fly ashes and ground granulated blast furnace slag (GGBFS) have been successfully implemented in the cement and concrete industry, their annual production far outweighs their consumption for beneficial uses. Other wastes are landfilled completely. The advantages of CO₂ sequestration with these waste materials are that the alkaline waste feedstock can be used beneficially, and that there is no energy requirement for mining the feedstock. A typical example of industry-specific sequestration is found in the case of portland cement production, which is

reported to be responsible for about 5-7% of the global CO₂ emissions and generates large quantities of alkaline cement kiln dust (CKD). Ideally, the CKD generated within the plant could be used to sequester a portion of the carbon dioxide generated by the plant operation.

The physiochemical properties of these alkaline waste materials affect the carbonation degree to a great extent. In general, the materials must be inorganic in nature, hydraulic or pozzolanic, carbon dioxide reactive, and should contain calcium or silicon salts [13]. The extent of carbonation, and therefore the capacity for CO₂ sequestration, is mainly dependent on the CO₂ diffusivity through the material and reactivity of the material with CO₂ [8,13]. The diffusivity is affected by the porosity and pore structure, as well as environmental conditions, while reactivity is affected by the chemical composition of the material and the degree of reactivity with water. In typical hardened cement paste, the pore structure is affected by the type and composition of the binder, water to binder ratio, degree of hydration and compaction pressure [13]. The diffusivity is also affected by temperature, relative humidity, and CO₂ concentration [13]. Several studies have reported the depth of carbonation in portland cement concrete using phenolphthalein indicator [14,15], concluding that carbonation depth increases with water/cement ratio and the age of the concrete [15]. Fick's law of diffusion proves a fair estimate of the carbonation rate in concrete, and carbonation depth can be modeled as a function of the square root of exposure time [14,15].

This paper evaluates several alkaline industrial waste materials for CO₂ sequestration. The influence of the physical and chemical properties of the waste materials on the sequestration capacity is discussed, as is the use of binary and ternary blends of alkaline wastes with ordinary portland cement (OPC) to enhance sequestration capacity. Waste materials include two CKDs, circulating fluidized bed combustion (CFBC) fly ash, class C coal fly ash (CFA), ground

granulated blast furnace slag (GGBFS), and fine glass powder (GP), which were selected for their appreciable concentrations of free alkaline earth metal oxide (CaO) or its hydroxide (Ca(OH)₂) and alkali oxide (Na₂O), which are believed to increase the CO₂ sequestration capacity considerably.

2. Materials and characterization techniques

2.1 Materials

The alkaline waste materials used for the determination of the CO₂ sequestration capacities were: two different cement kiln dusts (CKD1 and CKD2), byproducts of portland cement manufacture; ground granulated blast furnace slag (GGBFS), a byproduct of smelting operations; glass powder (GP) waste from the manufacture of safety glass beads; class C fly ash (CFA) a particulate trapped in coal power plants; and circulating fluidize combustion bed fly ash (CFBC), a combustion byproduct from circulating fluidized bed coal plants. Type I OPC was included in blended mixtures. GP mixtures also included 10% OPC by binder mass, which was required to achieve reasonable workability for molding specimens.

The oxide compositions of the six alkaline waste materials, as determined by X-ray fluorescence spectroscopy, are presented in Table 1. Calcium, magnesium, sulfur, potassium, and sodium oxides are expected to react with carbon dioxide in the presence of moisture; the summative proportion of these reactive oxides is also included in Table 1 for reference. The loss on ignition is also reported. Some of the materials contain high concentrations of calcium oxide, which can be present in the form of quick lime (QL) or calcite (CaCO₃). The former has the potential for extensive carbonation in the presence of moisture, while the latter has limited CO₂ sequestration capacity [8].

Table 1. Chemical composition of alkaline waste materials as determined by XRF

	% Composition by mass					
	CKD1	CKD2	GGBFS	CFA	GP	CFBC
SiO ₂	14.55	11.69	36.00	38.60	72.50	24.10
Al ₂ O ₃	4.46	2.20	10.53	19.19	0.40	9.93
Fe ₂ O ₃	2.11	2.93	0.67	5.70	0.20	11.90
CaO	61.15	37.05	39.80	22.75	9.70	24.40
MgO	3.84	0.87	7.93	4.48	3.30	0.94
SO ₃	10.62	7.69	2.11	2.50	---	17.0
K ₂ O	3.45	7.24	0.15	0.60	0.10	1.32
Na ₂ O	0.80	0.87	0.27	1.75	13.70	0.58
Na ₂ O eq.	3.10	6.00	0.32	---	---	---
Cl	---	0.62	---	---	---	---
Reactive Oxides	79.86	53.72	50.26	32.65	26.80	44.24
LOI (%)	23.40	29.06	3.00	0.57	---	14.70

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98 X-ray diffraction (XRD) measurements were carried out with a Bruker DX-8 diffractometer
99 using Cu-K α radiation ($\lambda=1.5418$ Å). The samples were scanned between 5 and 65° (2 θ) in
100 continuous mode with an integrated step scan of 0.02°. Calcite (CaCO₃), quartz (SiO₂), anhydrite
101 (CaSO₄) and quick lime (CaO) were identified in CKD1. CKD2 additionally contained calcite
102 and quartz, as well as sylvite (KCl) and syngenite (K₂Ca(SO₄)₂). The analytical CaO, as reported
103 in table 1, actually existed in three different forms: CaCO₃, CaSO₄ and free CaO (quick lime).
104 Though the chemical composition of CKDs shows large amounts of CaO, they were mainly
105 present in the form of calcite. Quick lime was detected at 5% and 1% by weight in CKD1 and
106 CKD2, respectively. GGBFS and GP showed typical amorphous XRD patterns with diffuse band
107 in the region 20° $\leq$ 2 θ $\leq$ 40°. CFA contained quartz, anhydrite, syngenite, gypsum, and quick lime.
108 CFBC contained large amounts of anhydrite and quartz, as well as traces of lime. Particle size
109 distributions, as determined by laser diffractive particle size analysis, are shown in Figure 2. The
110 particle morphology of each of the materials used in the study, using a scanning electron
111 microscope, is also given in Figure 3.

Figure 1. X-ray diffraction patterns of alkaline waste materials
(CC – calcite; Q – quartz; Anh – anhydrite; S – sylvite, Sg - syngenite, QL – quick lime)

Figure 2. Particle size distributions of alkaline waste materials

Figure 3. SEM micrographs of raw powders: (a) CKD1 and (b) CKD2 (c) CFBC
(d) CFA (e) GP

2.2 Experimental Methods

2.2.1 Specimen preparation

Specimens were prepared by mixing as received powder materials with a specified water content and compacting into cylindrical PVC molds (shown in Figure 4) using a constant pressure applied to a metal plunger by a hydraulic compression testing machine. Some of the mixtures, e.g., CFA with $w/p=0.3$, has good consistency and hence no compaction was needed for the preparation of the samples. Table 2 lists the details of the prepared sample sets. Additional blended mixtures containing ordinary portland cement (OPC) were also used, which are described in Table 3. A constant ratio of water/powder of 0.3 was used for blended samples.

Figure 4. Cylindrical mold and casting technique for carbonation specimens

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Table 2: Alkaline waste mixture details

Material	Water/ powder	Sample mass 19x12.5 mm (g)	Compaction force (lb)	Sample mass 19x38 mm (g)	Compaction force (lb)
CKD1	0.2	7.0	200	21.0	500
	0.3	8.0	200	24.0	500
CKD2	0.2	8.0	200	24.0	500
	0.3	8.5	200	26.5	500
CFA	0.1	10.0	500	26.0	500
	0.15	11.0	500	26.0	500
	0.2	8.5	---	20.0	500
	0.3	8.0	---	22.0	500
GGBFS	0.1	8.0	500	20.0	500
	0.15	9.0	500	20.0	500
	0.2	8.5	200	26.0	500
	0.3	8.5	---	27.0	500
GP	0.2	7.6	200	19.0	500
	0.3	8.0	200	20.0	500
CFBC	0.2	6.5	200	18.0	500
	0.3	7.0	200	19.0	500

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Table 3: Binary and ternary blended mixture details (w/p=0.3)

Mix	Composition	Sample mass 19x12.5 mm (g)	Compaction force (lb)	Sample mass 19x38 mm (g)	Compaction force (lb)
1	10% OPC 50% CKD1 40% CFA	9.0	---	25.0	---
2	10% OPC 50% CKD1 40% GGBFS	9.0	200	25.0	500
3	10% OPC 50% CKD1 40% GP	8.5	200	25.0	500
4	10% OPC 50% CKD2 40% CFA	9.0	---	25.0	---
5	10% OPC 50% CKD2 40% GGBFS	9.5	200	25.0	500
6	10% OPC 50% CKD2 40% GP	8.5	200	25.0	500
7	50% CKD1 50% CFA	9.0	---	25.0	---
8	50% CKD1 50% GGBFS	9.5	200	25.0	500

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2.2.2 Sequestration capacity

Ten 19 x 12.5mm cylindrical specimens of each mixture were prepared in order to determine the CO₂ sequestration capacity of each material. Specimens were extracted from the PVC molds immediately following compaction. Two control specimens from each mixture were soaked in isopropanol immediately after preparation in order to quench the hydration reaction. Remaining specimens were transferred to an accelerated carbonation test chamber, which consisted of a temperature and humidity controlled CO₂ incubator. The temperature, relative humidity and CO₂ concentration were maintained at 40±1°C, 65±5%, and 10±0.5%, respectively. Specimens were carbonated for 7, 14, 21, or 28 days, crushed into small cubes, and soaked in isopropanol to remove all water from the carbonated material. Specimens were then vacuum desiccated and prepared for further characterization, which included grinding into a fine powder passing a 75-µm sieve for XRD and thermogravimetric analysis (TGA). XRD was performed in the same manner as previously described in order to determine the chemical composition after carbonation. TGA was used to quantify the CO₂ sequestration. Ground specimens weighing 25±2 mg were heated to 1000°C at a rate of 10°C·min⁻¹ in a nitrogen environment with a flow rate of 40 mL·min⁻¹. Weight loss and differential weight loss curves were used to identify the phases present in each specimen.

2.2.3 Carbonation depth

Slender 19 x 38 mm cylindrical specimens were prepared in the same manner in order to determine the carbonation coefficient and observe the diffusion progress. A higher compaction force was necessary to achieve density similar to that of shorter specimens described in 2.2.2. Compacted specimens were left in the PVC mold, sealed with epoxy on one face in order to limit diffusion to a single direction, and placed in the carbonation chamber for between one and five

days. Since a high rate of carbonation was expected, the CO₂ concentration was reduced to 5±0.5%. After the desired carbonation period, specimens were removed and split lengthwise using an electric saw. The freshly cut surface was sprayed with 1% Phenolphthalein indicator; the carbonated region remained colorless (pH < 9.2) while the noncarbonated region turned purple (pH > 9.2). The carbonation depth was determined by measuring the distance to the color boundary line using a Vernier caliper, reporting the average of three measurements. Carbonation depth and the exposure period are normally correlated by the following diffusion equation.

$$X = C \sqrt{t} + a \quad \text{Eq.1}$$

Where X = Carbonation depth (cm); C = carbonation coefficient (cm $\sqrt{\text{days}}$; t = exposure period to accelerated carbonation (days); and a = empirical constant (cm).

Figure 5. Procedure for the determination of carbonation depth.

3. Results and Discussion

3.1 Sequestration capacity of

3.1.1 Alkaline wastes

Cylindrical alkaline waste specimens, prepared as described in 2.2.2 were analyzed by XRD and TGA to determine the quantity of CO₂ absorbed by the paste and the phase changes associated with the absorption. Figure 6 displays representative XRD and TGA results for CKD1 with a water/powder (w/p) ratio of 0.3, comparing 28-days carbonated specimens to control specimens and pure unreacted powder specimens. The test samples were completely carbonated at the end

of 28 days exposure period. The control specimen results indicate changes to the mineral composition when CKD1 was mixed with water, including the conversion of quick lime (QL) to calcium hydroxide (CH) and the formation of ettringite (E). The thermogravimetric derivative weight loss curve, shown in Figure 6(b), indicates the presence of ettringite, calcium hydroxide, and calcite in CKD1 control specimens, as evidenced by peaks in the derivative weight curve at 80°, 450°, and 700°C, respectively. As few as 7 days of exposure resulted in the conversion of most of the calcium hydroxide to calcite, indicating that carbonation is occurring within the specimen. Prolonged exposure resulted in a noticeable reduction in the magnitude of the ettringite peak in the derivative weight curve shown in Figure 6(b) as compared to the control specimen. Only traces of ettringite and calcium hydroxide were observed in the carbonated specimen, while the amount of calcium carbonate increased after 28 days of carbonation. Comparable results were observed for CKD2 (figures are not included), with an additional peak for Friedel's salt due to the presence of chloride.

Figure 6. (a) X-ray diffraction pattern and (b) thermogravimetric derivative weight loss for powder, control (0 day) , and 28-days carbonated CKD1 with w/p=0.3

Similarly, representative XRD and TGA results for CFA are presented in Figure 7. The main hydration products for CFA and CFBC were ettringite, with the additional presence of dolomite ((CaMgCO₃)₂) in the latter. As in CKD systems, CO₂ exposure resulted in reduced ettringite and increased calcium carbonate in CFA and CFBC. A reduction in dolomite and appearance of an additional derivative weight peak around 500°C were also observed in the latter system after carbonation. In GGBFS and GP specimens, CO₂ exposure resulted in the production of calcite.

Figure 7. (a) X-ray diffraction pattern and (b) thermogravimetric differential weight loss for powder, control, and 28-day carbonated CFA with w/p=0.3

Since carbonation is a process by which calcium containing minerals reacts with CO₂ to form calcium carbonate, the TGA and XRD analysis suggest the occurrence of several reactions as shown by Equations 2 -5 [8,13,16,17].

Eq.2 and 3 show the steps involved in the classical carbonation of Ca(OH)₂. Previous studies have shown that ettringite decomposes into gypsum (CaSO₄·2H₂O), calcium carbonate, and

aluminum hydroxide in the presence of carbon dioxide, as shown by Equation 4 [17,18]. It is therefore evident that this decomposition also occurred during the carbonation of the alkaline waste materials, resulting in additional sequestration.

The derivative TGA peak between 75 and 100 °C (Figure 7(b)) is normally attributed to the decomposition of Ettringite and C-S-H gel. Some of these waste materials, specifically calcium containing materials like class C fly ash, produce C-S-H and/or C-A-S-H in presence of water. The large derivative peak present in “0 Day” curve in Fig. 7(b) is an evidence of the presence of both of these reaction products. After 28 days of exposure to CO₂ a dramatic decrease in the peak size can be seen in this figure. The C-S-H carbonation is explained in the following reaction:

Thus carbonation of C-S-H causes de-calcification and formation of non-binding silica gel [13,17,]. A similar reaction can be expected in C-A-S-H as a result of CO₂ exposure forming silica gel, calcium carbonate and aluminum hydroxide. The exact stoichiometric coefficients of the previous reactions are not clearly defined.

The quantity of CO₂ absorbed by carbonated specimens was calculated using the TGA derivative weight loss curves. The area under the peak near 700°C, which corresponds to the loss of CO₂ during the decomposition of CaCO₃ was correlated to the weight percentage of CO₂ captured by the specimen using a calibration curve, which was determined by mixing a known proportion of pure CaCO₃ (5, 10, 15, 20, 25, 50, 75, and 100%, by mass) with ignited OPC and finding the corresponding area beneath the CaCO₃ peak on the derivative weight curve from TGA. The mass percentage of CO₂ sequestered by each specimen after 28 days is reported in Table 4.

Table 4: 28-day CO₂ sequestration by mass of alkaline waste material

Material	Water/ powder	CO ₂ sequestration (% by mass)
CKD1	0.2	3.99
	0.3	3.19
CKD2	0.2	2.51
	0.3	1.54
CFA	0.2	0.21
	0.3	0.52
GGBFS	0.2	1.32
	0.3	1.83
GP*	0.2	2.49
	0.3	2.25
CFBC	0.2	1.27
	0.3	2.50

*Glass powder waste (GP) had no binding property by itself; hence it was mixed with 10% OPC to make the sample preparation possible

258 The results presented in Table 4 indicate that CKD1 has the highest potential for CO₂
259 sequestration out of the six alkaline wastes evaluated in this study. This is likely due to the
260 presence of a higher quantity of CaO and other calcium containing minerals in CKD1. Despite
261 the formation of more reaction products in CKD1 specimens with higher w/p, higher CO₂
262 sequestration was observed in CKD1 specimens with lower w/p. This could be a result of a
263 higher water content resulting in diffusion limitations with respect to the transport of CO₂ and
264 Ca⁺ within the paste matrix [6]. Higher moisture content tends to limit the diffusion of gases
265 through the specimen; CKD2 contains hygroscopic sylvite, which can readily absorb moisture
266 from the environment and may increase the initial moisture content in CKD2 specimens, thereby
267 limiting the degree of carbonation. GGBFS, CFA, and CFBC specimens exhibited the opposite
268 trend, with increased water content resulting in additional CO₂ sequestration, as suggested by
269 previous studies [15].

The effect of the summative concentration of carbon dioxide-reactive oxides on the CO₂ sequestration capacity of the alkaline wastes is shown in Figure 8. Least-squares linear regressions are plotted on the same figure for w/p=0.3 and 0.4. Although poorly correlated (R²=0.61 and 0.44, respectively), the general trend indicates that as the reactive oxide content increases, so does the capacity for CO₂ sequestration. It is, however, apparent from the poor correlation that the sequestration capacity depends on additional factors such as the moisture content and particle size distribution of the starting material.

Figure 8. Effect of summative concentration of CO₂-reactive oxides

3.1.2 Blended alkaline wastes

The CO₂ sequestration capacity of alkaline wastes evaluated in this study is low. Binary and tertiary blends with OPC have the potential to enhance CO₂ absorption. Blended mixtures with w/p=0.3 as described in Table 3 were prepared and evaluated in the same manner as previously described in order to evaluate CO₂ sequestration capacity and associated phase changes. Representative XRD and TGA results for Mix 1 (10% OPC—50% CKD1—40% CFA) are presented in Figure 9. The powder contained predominately calcite, anhydrite, and free lime.

Several reaction products were formed in the control specimen, including ettringite and calcium hydroxide, as shown in Figure 9(a). Carbonation for 28 days resulted in the reaction of the bulk of the calcium hydroxide with CO_2 , forming calcium carbonate. These observations are confirmed by the derivative weight loss curve in Figure 9(b). The mass percentage of CO_2 sequestered by each blended specimen is reported in Table 5

Figure 9. (a) X-ray diffraction pattern and (b) thermogravimetric differential weight loss for powder, control, and 28-day carbonated blended mixture #1 with w/p=0.3

Table 5: CO₂ sequestration by mass of blended alkaline waste materials

Mix	Composition	CO ₂ sequestration (% by mass)
1	10% OPC, 50% CKD1 40% CFA	5.35
2	10% OPC 50% CKD1 40% GGBFS	6.04
3	10% OPC 50% CKD1 40% GP	3.79
4	10% OPC 50% CKD2 40% CFA	2.22
5	10% OPC 50% CKD2 40% GGBFS	2.93
6	10% OPC 50% CKD2 40% GP	3.10
7	50% CKD1 50% CFA	4.11
8	50% CKD1 50% GGBFS	4.88

The results presented in Table 5 indicate that blended Mixtures 1 and 2 have the highest potential for CO₂ sequestration out of the eight blends evaluated. This is likely due in large part to the high sequestration capacity of CKD1 by itself. Additionally, CKD can activate hydration of slag, resulting in the formation of additional reaction products such as calcium silicate hydrate (C-S-H/C-A-S-H) [19, 20]. Any calcium containing products have the capacity to absorb CO₂; as such, it stands to reason that Mixture 2 had the highest sequestration. All blended mixtures

showed increased sequestration potential over pure alkaline wastes when subjected to identical exposure conditions. The practical implication of this result is that even if wastes do not exhibit hydraulic properties, they can be blended with small quantities of cementitious materials to produce products such as bricks or floor tiles. These products can be cured in a CO₂ rich environment with several benefits, including: (1) beneficiation of an industrial byproduct, which saves landfill costs, (2) targeted, industry-specific sequestration of CO₂ through mineral carbonation, and (3) production of a stronger and more durable product through carbonation. It should be noted that mixes 7 and 8 were also performed very well despite the absence of OPC. These mixtures were prepared by blending CKD1 with class C fly ash or slag. CKD1, class C fly ash and the slag contained significant amounts of calcium, indicating the importance of high calcium content in the alkaline waste for better CO₂ absorption in the absence of OPC.

3.2 Carbonation depth

3.2.1 Pure alkaline wastes

The depth of carbonation in pastes prepared from alkaline wastes was determined at one-day increments up to 7 days of carbonation using phenolphthalein indicator and split carbonated specimens as previously described [15,21,22]. The colorless region of the specimen represents the fully carbonated region, while the purple region represents the non-carbonated region [23]. Figure 10 shows progressively deeper carbonation in CKD1 with w/p=0.3 after 3, 4, and 5 days of carbonation. Figure 11 shows the carbonation depth in CKD specimens with varying water/powder ratio after 3 days of carbonation. In CKD1 specimens, higher depth of carbonation was observed with lower water content, which logically follows similar conclusion based on the sequestration capacity of CKD specimens with varying water content. Similar results were observed for CKD2. The carbonation profiles for CKD1 and CKD2 are presented in Figure 12,

343 which displays the carbonation depth as a function of the square root of the exposure period in
344 days. The carbonation coefficients are equal to the slopes of the least squares linear regression
345 lines plotted on the same figure [7]. The carbonation coefficients for hardened CKD1, CKD2,
346 CFA, and GGBFS pastes are listed in Table 6. Progression of carbonation was much more rapid
347 in CFA and GGBFS compared to the remaining waste materials; the carbonation profile was
348 therefore obtained only for CFA with $w/p=0.15$ and GGBFS with $w/p=0.2$. CKD1 and CKD2
349 pastes exhibited lower carbonation coefficients when prepared with higher water content, which
350 may be a result of the formation of more abundant and denser reaction products with additional
351 water content, thereby reducing the porosity and diffusion potential of the paste. Additionally,
352 increased water content could result in water-filled pores, which would inhibit the diffusion of
353 CO_2 . Another possible cause of this difference could be a difference in compacted density due to
354 the use of the same compacting force with different water contents. GGBFS and CFA had
355 significantly higher carbonation coefficients, despite exhibiting lower sequestration capacity.
356 This could be due to the formation of fewer reaction products and therefore a less dense matrix
357 which allows rapid diffusion of CO_2 .

Figure 10. Carbonation depth in CKD1 specimens with w/p=0.3 (3, 4, and 5 days from left to right; NC- non-carbonated and C -carbonated regions)

Figure 11. Carbonation depth in CKD1 specimens after 3 days (left: w/p=0.2, right: w/p=0.3- NC- non-carbonated and C-carbonated regions)

Figure 12. Carbonation depth vs. square root of exposure time for (a) CKD1 and CKD2 (b) GGBFS and CFA with varying water/powder ratio

Table 6. Carbonation coefficients for CKD1, CKD2, GGBFS, and CFA

Material	Water/ powder	Carbonation coefficient
CKD1	0.2	0.42
	0.3	0.36
CKD2	0.2	0.31
	0.3	0.24
GGBFS	0.2	1.81
CFA	0.15	1.66

3.2.2 Blended alkaline wastes

The carbonation coefficient for blended mixtures, calculated in the same manner as previously described, are listed in Table 7. Mixture 6 showed the highest carbonation coefficient and therefore the most rapid carbonation progression, likely due to increased porosity or scarcity of reactive components in the mixture. Mixture 2 had the lowest coefficient and therefore the slowest carbonation progression, a result of a dense product with reduced porosity. Mixtures 1, 3, 7, and 8 exhibited nearly identical carbonation coefficients.

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Table 7: Carbonation coefficients for blended alkaline waste mixtures

Mix	Composition	Carbonation coefficient
1	10% OPC 50% CKD1 40% CFA	0.58
2	10% OPC 50% CKD1 40% GGBFS	0.36
3	10% OPC 50% CKD1 40% GP	0.57
4	10% OPC 50% CKD2 40% CFA	0.50
5	10% OPC 50% CKD2 40% GGBFS	0.63
6	10% OPC 50% CKD2 40% GP	0.71
7	50% CKD1 50% CFA	0.57
8	50% CKD1 50% GGBFS	0.56

404 4. Conclusions

405 The carbon dioxide sequestration capacity of several alkaline wastes and blends thereof were
 406 evaluated. The following conclusions can be drawn from the analysis presented here:

- 407 • CKD1 was found to have the highest CO₂ sequestration capacity, with nearly 4%
 408 absorption by mass after 28 days of exposure.
- 409 • Three main reactions are responsible for CO₂ absorption by alkaline waste materials: the
 410 conversion of calcium hydroxide to calcite, ettringite to calcium carbonate and C-S-H or
 411 C-A-S-H to calcite and silica gel.
- 412 • All of the pure alkaline wastes evaluated in this study have limited CO₂ sequestration
 413 potential.

- It appears that the chemical composition of the waste material—particularly the free calcium oxide content—is the controlling factor in determining CO₂ sequestration capacity.
- Additional factors including moisture content and particle size distribution of the waste material appear to have only secondary effect on the CO₂ sequestration capacity of the alkaline waste material.
- Carbonation depth is proportional to the square root of exposure time.
- The carbonation coefficient of alkaline waste materials appears to vary inversely with water content due to the ease of diffusion through dry or partially dry pores.
- The reduction in the carbonation coefficients of blended alkaline wastes may be due to the densification of samples due to the formation of more reaction products, and the subsequent reduction in the porosity
- The CO₂ sequestration capacity can easily be improved by the use of blended alkaline wastes and portland cement, due in part to the formation of C-S-H, which has additional carbonation capacity

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