

An Investigation of CO₂ Sequestration Through Mineralization

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ABSTRACT

Global climate change, greenhouse gas (GHG) emission reduction, capture, and sequestration are important topics that require critical new technologies for several decades as humankind strives to meet the needs of today in a sustainable manner. Mineralization of carbon dioxide (CO₂) into carbonate compounds can be a final resting place for CO₂ gas. High-surface area calcium and alkali rich by-product materials which include sources of cement-kiln dust, blast furnace slag, fly ash, lime-kiln dust, recycled concrete fines were used to sequester CO₂ from ambient atmospheric gas, CO₂ gas, and coal-combustion flue gas. A process is described that utilizes a foam generator with a foaming agent and various CO₂ containing gases to produce a lightweight adequate strength, material with readily available increased surface area from by-product materials, and the available CO₂ for rapid carbonation. The carbonated product is then crushed into a carbonate-rich aggregate suitable for a variety of construction uses.

INTRODUCTION

The topic of climate change relates to several global factors including increased CO₂ emissions generated as a result of human activities. World population growth, deforestation, and industrialization have combined to increase the overall background CO₂ emission levels on the planet Earth. The environmental significance of these increased CO₂ levels is still being debated in the technical and political arenas with respect to environmental impacts over geologic time. Major sources of greenhouse gases are: CO₂, CH₄, N₂O, HFCs, PFCs, and SF₆. According to the April 3, 2006 edition of Time magazine, CO₂ concentrations have increased from 180 ppm (i.e., 180 tons per million tons) in the ice age to 280 ppm up to 150 years ago, and to 380 ppm today [Kluger 2006] [Naik 2006].

Global climate change, greenhouse gas (GHG) emissions reduction, and CO₂ capture and sequestration are important topics that promise to require technologies as humankind strives to meet the needs of today in a sustainable manner with increased population growth, consumption of manufactured products, and modernization of industries world-wide. A multi-faceted approach needs to be developed that would include continuously increasing efficiency in fossil fuel combustion systems, replacement of fossil fuel systems with renewable or nuclear energy sources, existing forest preservation, reforestation, algae farming, deep geologic injection and mineralization [Naik 2006] [NRG Energy 2006] [Ramme 2008] [Druckenmiller 2006] [Druckenmiller 2006] [Naik 2002] [Malhotra 2006] [Malhotra 1999] [Ramme 2004].

Due to economies of scale with efficiency improvements, and capturing CO₂ from large emitters, they are potentially the most economical investments [Saxena 2006]. Increased

efficiency of fossil fuel combustion, replacement of aging lower efficiency facilities, and switching to alternative energy sources offer the most immediate and significant potential reduction of CO₂ emissions from industrial sources. [Pacala 2004] “Forests play a dual role in climate change by acting both as a source of greenhouse gas emissions, particularly emissions of carbon dioxide (CO₂) during decay, and as a storehouse of carbon in trees, also called a carbon-sink. By avoiding or reducing the CO₂ emissions that result from the destruction of the forests and enhancing their ability to absorb and store CO₂, forest conservation and management projects work to reduce net CO₂ emissions; thereby, mitigating effects of climate change” [The Nature Conservancy 2004].

Approximately 7% of GHG emissions can be attributed to the production of portland cement world-wide. The portland cement and concrete industries are thus provided with an opportunity and a challenge for decreasing its impact on GHG emissions. “The 1992 Earth Summit in Rio de Janeiro defined sustainable development as economic activity that is in harmony with the earth’s ecosystems. The goal of sustainable development of the cement and concrete industries is, therefore, very important, and it can be reached if we make a serious effort for complete utilization of the cementitious and pozzolanic by-products produced by thermal power plants and metallurgical industries” [Mehta 1998].

This study tests the hypothesis of utilizing high surface area calcium and alkali-rich by-product materials such as, cement-kiln dust (CKD), blast furnace slag (SLG), Class C fly ash (CFA), lime-kiln dust (LKD), and recycled concrete fines to sequester CO₂ from ambient air, concentrated CO₂, and power plant flue gas. The carbonation rate and mass of CO₂ sequestered in the various foamed by-product materials were measured and reported. The hardened materials are crushed into an aggregate to continue accelerating the carbonation process and produce a useful end product [Ramme 2008].

LITERATURE REVIEW

A literature review was conducted. Rather than compiling an exhaustive annotated bibliography of the available literature here, readers are referred to a recent publication [Ramme 2008].

PROCESS DESCRIPTION

This process utilizes a foam generator with a foaming agent and CO₂ containing gases to produce a material with increased surface area, and the available CO₂ for rapid carbonation. The hardened, carbonated materials are then crushed into a carbonate-rich aggregate suitable for a variety of uses. Such aggregates can also be made with reduced densities for lightweight construction materials.

Laboratory analyses were used to identify the various elements present in the high surface area alkali-rich by-product materials that included cement-kiln dust, blast furnace slag, fly ash, lime-kiln dust, and recycled concrete fines to identify those available for hydration, and possible formation of carbonates. A phenolphthalein indicator was utilized to identify the degree of carbonation achieved over time. Following tests for compressive strength, the hardened and carbonated test cylinders were crushed into a carbonate-rich aggregate. The actual CO₂ captured was measured by gravimetric testing [Ramme 2008].

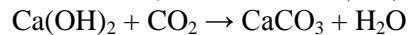
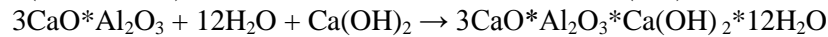
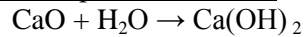
RESEARCH SIGNIFICANCE

The results of this study provide information on capturing CO₂ with the use of various by-product materials for the production of aggregates and construction materials. Natural aggregate sources can thus be preserved for use by future generations. The aggregate materials produced have potential for use in a wide-range of geotechnical and product applications including additives to paint, rooting media for green roofs, geotechnical applications, thermal insulating applications, reduced density applications, and for the production of ready-mixed concrete and many other varieties of cement-based products.

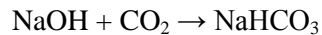
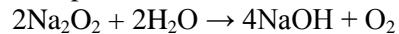
CHEMISTRY OF CARBONATE FORMATION

The following equations represent the primary alkaline compounds that occur during hydration of cement-kiln dust, blast furnace slag, fly ash, lime-kiln dust, and recycled concrete materials which react with CO₂ and consume hydroxides, such as Ca(OH)₂, and thus sequester CO₂.

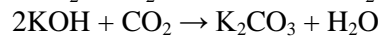
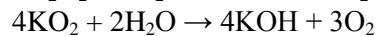
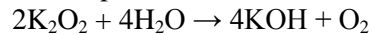
Calcium Compound Reactions



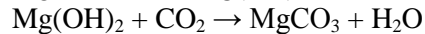
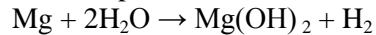
Sodium Compound Reactions



Potassium Compound Reactions



Magnesium Compound Reactions



TESTING MATERIALS AND EQUIPMENT

The following key materials and equipment were used for this project:

- 1) A Mini (½ inch, 1.27-cm) Open Air-Foam-Generating System foam generator which consisted of a regulator, diaphragm pump, and foam mixing nozzle for use with its proprietary foaming agent was manufactured and supplied by Elastizell for this project.
- 2) Commercial, bottled, compressed air, and compressed pure-CO₂ gas were used. Bottled compressed simulated flue gas was obtained from We Energies Pleasant Prairie Power Plant and it contained: 11.72% CO₂, 232.3 ppm NO_x, and 293.7 ppm SO_x.
- 3) Drinking water was used for preparation of the low-strength slurry mixtures.
- 4) A modified sodium gluconate chemical admixture retarder was used to reduce the flash set characteristics and extend the set time of the mixtures utilizing Class C fly ash.
- 5) A double roller crusher used for recycling rock cores at a crushed stone quarry in Waukesha, Wisconsin was used for crushing the broken test cylinder pieces into a crushed aggregate after strength and carbonation testing. A mineral oxides analysis, and selected physical analyses of the various by-products, are included in Table 1.

Table 1. Mineral oxides analysis and selected physical properties of by-product materials (%).

Mineral Analysis*	Cement Kiln Dust (CKD)	Lime Kiln Dust (LKD)	Recycled Concrete Fines (RCF)	Class C Fly Ash (CFA)	Blast Furnace Slag (SLG)
SiO ₂	14.47	9.5	35.5	39.2	39.2
Al ₂ O ₃	5.1	4.8	3.9	21.0	10.4
Fe ₂ O ₃	2.0	1.1	1.8	5.5	0.7
CaO	49.8	32.7	20.3	22.5	38.2
MgO	2.2	24.9	8.4	4.0	11.0
K ₂ O	3.8	0.8	0.5	0.7	0.4
Na ₂ O	NA	NA	4.7	3.0	0.0
SO ₃	12.3	0.5	0.3	1.4	1.2
TiO ₂	0.0	0.0	0.0	1.4	0.4
LOI 750°C**	9.4	22.5	21.9	1.2	-0.5
LOI 1000°C**	10.5	24.9	24.5	1.4	-1.5
SUM	100.0	100.0	100.0	100.0	100.0
Available Alkali	6.8	4.0	0.2	2.6	0.5
Physical Analysis					
Specific Gravity	2.98	2.80	2.38	2.61	2.97
Fineness % Pssing #325 Sieve (45 mucious)	93.7	48.5	13.3	84.7	97.9

* ASTM D 4326-2004, “Standard Test Method for Major and Minor Elements in Coal and Coke Ash by X-Ray Fluorescence.”

** ASTM C 311-2005, Standard Test Methods for Sampling and Testing Class C Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete.”

MINERALS BY X-RAY DIFFRACTION AND SCANNING ELECTRON MICROSCOPE (SEM) IMAGES

The five finely divided mineral by-products were analyzed by X-ray diffraction to identify the various mineral compounds found in each by-product material. Calcium found in mineral forms that are already combined with carbon or sulfur such as calcite (CaCO₃), dolomite (Ca Mg (CO₃)₂), gypsum (CaSO₄ + 2H₂O), or bassanite (CaSO₄ + 0.5H₂O) are not likely to combine with CO₂ to form additional carbonate mineral compounds. Lime (CaO) and periclase (MgO) that have not combined with carbon or sulfur are likely to capture CO₂ and form carbonate mineral compounds. SEM images were taken of the five by-product materials at UW – Milwaukee, CKD and LKD particles appear similar in shape, surface texture, and size. The Class C fly ash particles are spherical in shape and finer with a large quantity of particles under 5 microns in size. The recycled concrete particles appear much larger in size with relic cementitious coatings on the aggregate particles. The quenched slag particles are angular crystals in shape with a well-graded distribution of sizes approaching a maximum of about 20 microns. Detailed results for each by-product material are included in a recent publication [Ramme 2008].

ACTUAL MIXTURE PROPORTIONS AND MORTAR DATA

The amount of ingredients used, for each 1.8 cu ft (0.051 cu m) batch of foamed mortar slurry produced are shown in Table 2. The wet cylinder weight was targeted at 4.8 pounds +/- one pound (2.2 kg +/- 0.45 kg) for consistency of density. Additional quantities of carbon dioxide-based foam were required to obtain the desired range of density due to the instability of the foam after formation. Figure 1 shows the depth of carbonation measured on split 4 in (100 mm) diameter by 8 in (200 mm) long cylinders for each of the five types of foamed mortar materials produced with air. Figures 2 and 3 shows depth of carbonation for each of the five by-product material cylinders when produced with integral foamed flue gas and CO₂ respectively.

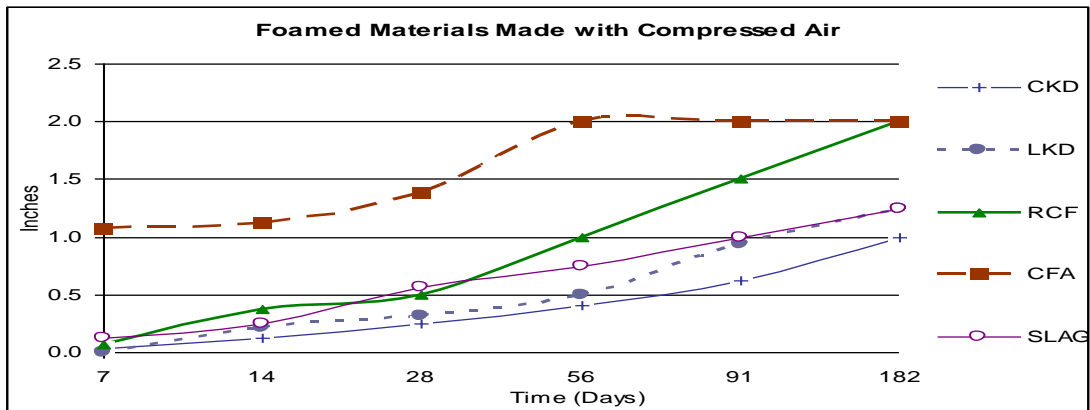


Figure 1. Foamed Materials Made With Compressed Air–Carbonation Depth Versus Time (1.00 in = 2.54 cm).

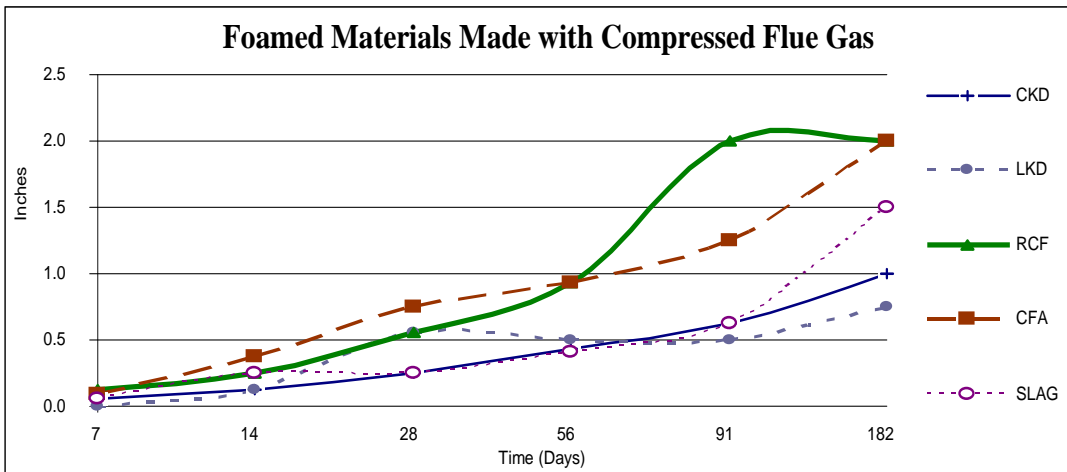


Figure 2. Foamed materials made with compressed flue gas carbonation depth versus time (1.00 in = 2.54 cm).

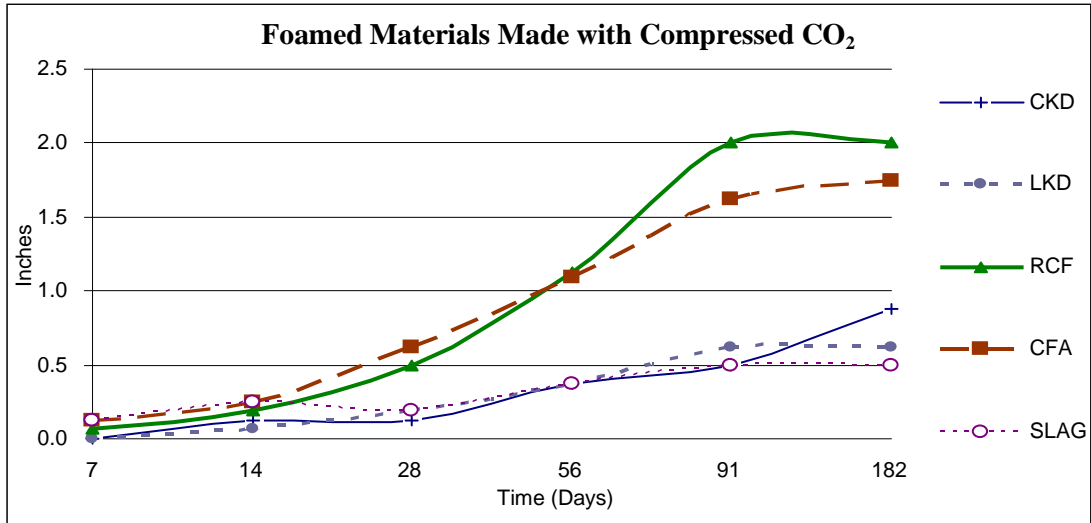


Figure 3. Foamed materials made with compressed CO₂ gas - carbonation depth versus time (1.00 in = 2.54 cm).

Figure 4 provides a comparison of the measured CO₂ contained in the five by-product-based mortar materials made using compressed air gas, in the foaming process, and the change in CO₂ content by percent mass times the carbonated volume over time. Similarly, Figure 5 provides a comparison for compressed flue gas; and Figure 6 provides a comparison for compressed CO₂.

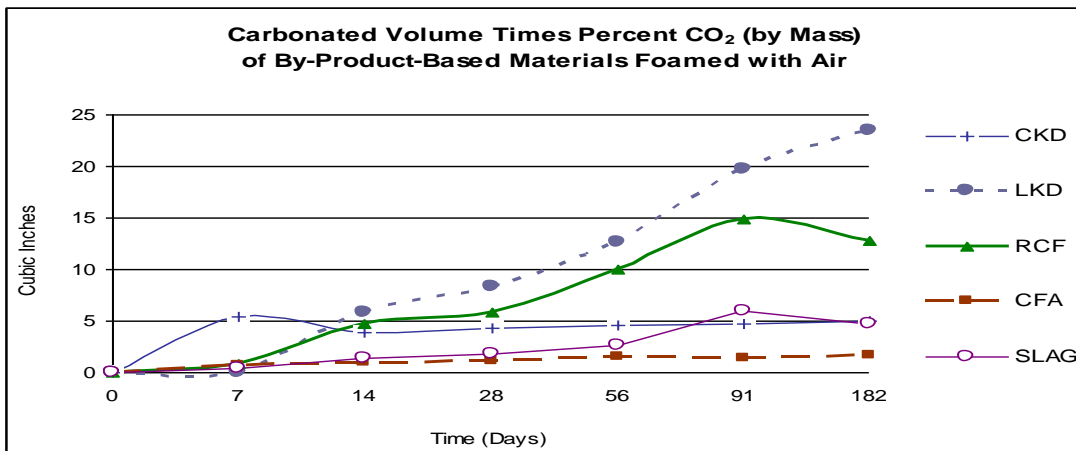


Figure 4. CO₂ sequestration with compressed air in various by-product-based materials versus time (1.00 in = 2.54 cm).

QUANTIFICATION OF CO₂ MINERALIZATION

A portion of the carbonated cylinder from each type of mortar material, was sealed in a plastic food-grade bag for testing per ASTM C 25, "Standard Test Method for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime," for carbon dioxide content. Immediately after compression testing and carbonation testing, samples were vacuum-sealed in the plastic bags. The samples were filed to the full depth of carbonation, and the filings were collected for further preparation by grinding in a mortar and pestle. The ASTM C 25

gravimetric test method was used for quantifying the amount of carbon dioxide contained within a mineral sample. The samples were decomposed with hydrochloric acid and the liberated CO₂ was passed through a series of scrubbers to remove water and sulfides. The CO₂ was absorbed with Ascarite, a special sodium hydroxide absorbent, and the gain in weight of the absorption tube was determined and calculated as percent CO₂. Detailed results for each by-product materials are included in a prior publication [Ramme 2008].

Table 2. Mixture proportions and fresh mortar data for 1.8 ft³ (0.051 M³) batches.

	CKD + Air	CKD + Flue Gas	CKD + CO ₂	LKD + Air	LKD + Flue Gas	LKD + CO ₂	RCF + Air	RCF + Flue Gas	RCF + CO ₂	CFA + Air	CFA + Flue Gas	CFA + CO ₂	Slag + Air	Slag + Flue Gas	Slag + CO ₂
Mineral (lb)	85	85	83.2	105	105	105	84	84	84	105	105	113	107	107	107
Foam (gallon)	3	4	25	6	4	15	9	9	14	3.4	4	6	6.5	7	15
Water (lb)	64	64	64	44	44	44	25	25	30	44	44	44	43	43	43
Retarder (ml)	0	0	0	0	0	0	91	91	136	179	179	179	0	0	0
Class C ² Fly Ash (lb)	0	0	0	0	0	0	53	53	53	0	0	0	0	0	0
Flow ³ (in)	10	11	14	9	11.5	19	7	5.5	12.5	19	24	20	7.5	7	14
Temp. Rise (°F)	34	37	32	20	13	20	23	28	20	11	14	12	10	9	10
Wet Cylinder Wt. (lb)	4.8	4.7	5.2	4.0	5.0	5.7	5.0	5.0	5.1	4.5	4.5	4.9	4.9	4.9	4.9

Notes:

- 1) 1.00 lb = 0.4536 kg, 1°F = 1.8°C + 32, 1 ml = 0.0338 fl oz
- 2) Standard Specification for Coal Fly Ash, ASTM C 618-2003.
- 3) Flow Consistency of Controlled Low Strength Materials, ASTM D 6103-2004.

CO₂ CONTENT (BY MASS) DATA ANALYSIS

The percentage of CO₂ content for each by-product-based set of mortar mixtures was analyzed with the Student's t distribution method of analysis. Confidence intervals were determined based on the 18 data points and 17 degrees of freedom available for each by-product-based material. Table 3 shows the mean, standard deviation and confidence intervals for percent CO₂ by mass at 95% and 99%. A trend line and equation were also developed for each mineral by-product and CO₂-containing gas combination using linear regression analysis [Ramme 2008]. An example of the linear equation and trend line developed for each of the fifteen materials is shown in Figure 7. These equations could be used to predict the

amount of CO₂ contained in these by-product-based materials at a point in time when subjected to the same curing conditions.

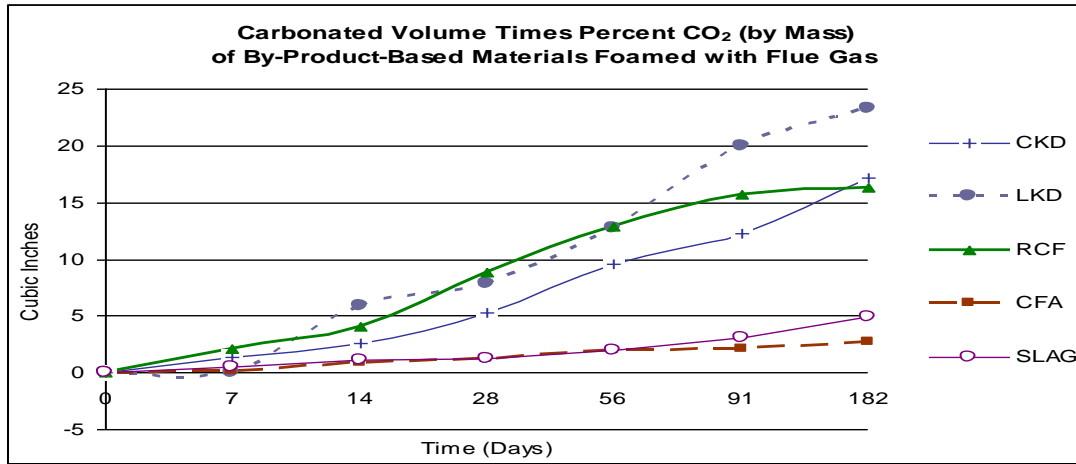


Figure 5. CO₂ sequestration with compressed flue gas in various by-product based materials versus time (1.00 in = 2.54 cm).

Table 3. Confidence intervals for percent CO₂ using student's t distribution.

Material	Mean (%) X	Standard Deviation (%) S	95% Confidence Interval	99% Confidence Interval
CKD	18.65	3.21	17.06 – 20.24	16.46 – 20.84
LKD	24.06	1.59	23.27 – 24.85	22.97 – 25.15
CFA	1.93	0.62	1.62 – 2.24	1.51 – 2.35
RCF	13.16	2.01	12.16 – 14.16	11.79 – 14.53
SLAG	4.65	1.36	3.97 – 5.33	3.72 – 5.58

Notes: Number of Samples, n = 18
 Degrees of Freedom, (n - 1) = 17
 t = 2.110 at 95% Confidence
 t = 2.898 at 99% Confidence
 Confidence Interval = $\bar{X} \pm t (S/ \sqrt{n})$

COMPRESSIVE STRENGTH AND AGGREGATE TESTING

Four-inch (100 mm) diameter by eight-inch (200 mm) long specimens were cast, cured, and tested in a compression testing machine located in the University of Wisconsin - Milwaukee Concrete Laboratory. The compressive strength of the five by-product-based materials used with each of three gases was determined at the ages of 7, 14, 28, 56, 91, and 182 days. The average compressive strength was obtained for the three cylinders tested in compression for each of the 15 test mixture materials (five by-products and three types of gases) at each test age. The by-product-based materials tested were low-strength compared to a typical structural-grade concrete and fall in the range of CLSM, with a required compressive strength of 1200 psi (8.3 MPa).

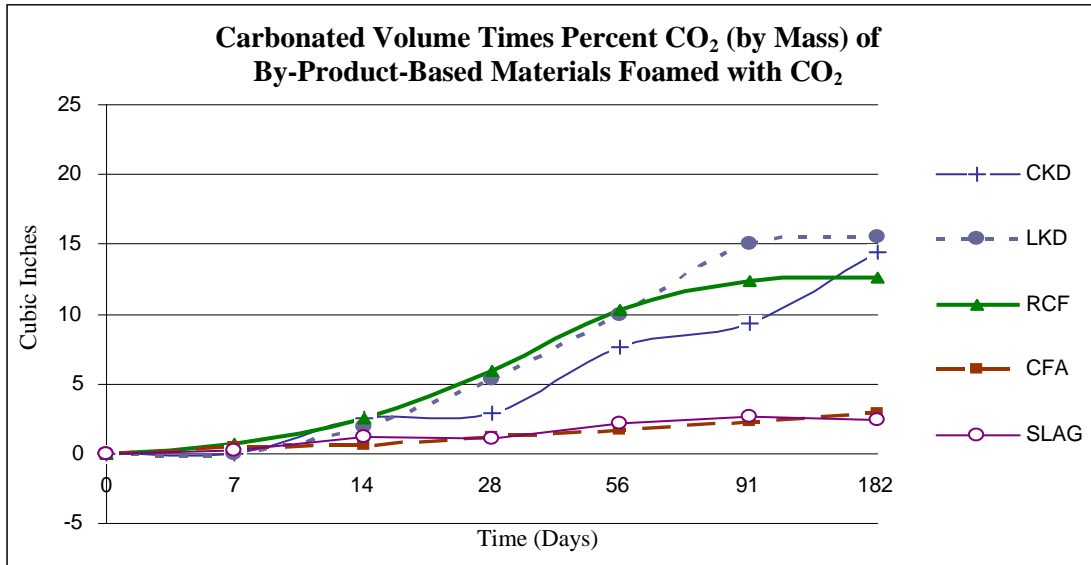


Figure 6. CO₂ sequestration with compressed CO₂ gas in various by-product-based materials versus time (1.00 in = 2.54 cm).

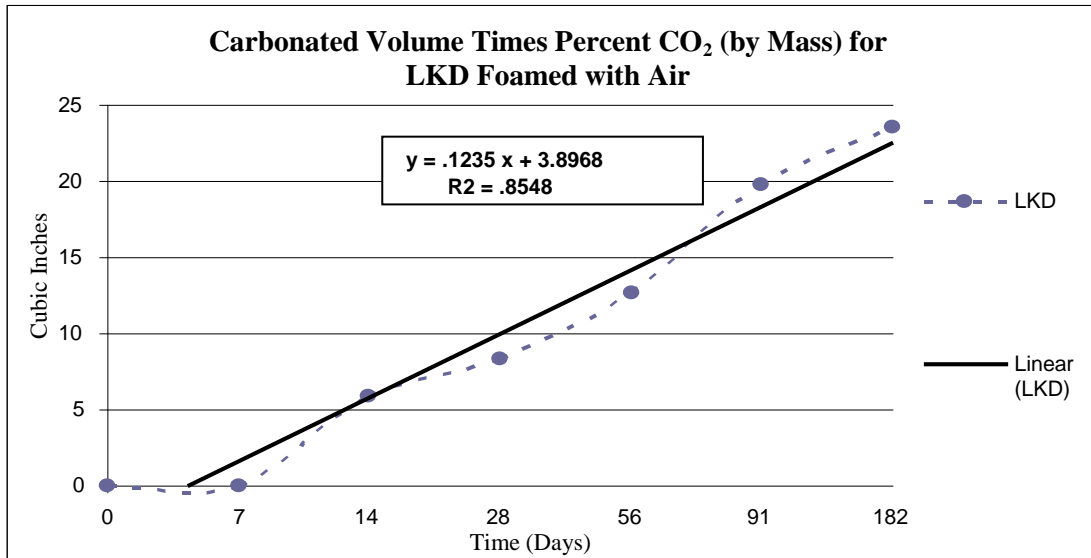


Figure 7. Carbonated volume times percent CO₂ by mass equation - LKD foamed with air mixture (1.00 in = 2.54 cm).

The hardened and carbonated materials were crushed to form aggregates. Values for physical properties are compared to published values for natural crushed gravel, two sources of pumice, and a source of manufactured expanded shale aggregate. It should be noted that these by-product-based aggregates are unique, and do not necessarily mirror the properties of natural or lightweight aggregates. An attempt was not made to optimize grain size distribution but rather to show the as-crushed condition for each of the new aggregate materials. Specific gradations could be managed with conventional commercial aggregate screening plant equipment. Detailed compressive strength and aggregate results for each by-product material are included in a recent publication [Ramme 2008].

CONCLUSIONS

The carbonated aggregates produced do not compare exactly to natural or commercial materials presently on the market. However, the desirable engineering properties for these carbonated and selected commercial materials are similar. In some cases, the crushing of the low-density and low-strength materials provided a higher percentage of fines than normally desired within construction-grade aggregates. This may present an opportunity for using this process to manufacture a lightweight fine aggregate for specialized applications. In reviewing and analyzing the research data presented in this report, the following conclusions can be drawn for this specific set of by-product materials tested and used in this study.

- 1) Essentially, all of the compressed gases used (air, flue gas, or carbon dioxide) in the production of foam based mortar materials had similar effects on the rate of carbonation for each of the specific by-product-based materials tested. Therefore, the chemical make-up of the by-product-based materials had a greater influence on the rate of carbonation than the concentration of CO₂ in the various compressed gases used.
- 2) The complications and associated expense of using compressed flue gas or carbon dioxide do not appear warranted at this time in production of by-product-based mineralized aggregates. However, the use of residual heat contained within flue gas from power plants or kilns to assist with curing in winter climates may be a valuable and sustainable resource to employ.
- 3) The phenolphthalein colormetric test was valuable in demonstrating where carbonation occurred (within the no-color zone), and in measuring the rate of carbonation at different ages in the hardened cylinders of each industrial by-product-based foamed mixture. The carbonated zone could then be used for analysis of actual CO₂ content with the ASTM C 25-2006, "Standard Test Method for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime."
- 4) The trend lines and equations developed using linear regression for the measured rates of carbonation growth for each of the 15 mineral by-product and CO₂ containing gas combinations. These equations can be used for each specific by-product and CO₂ containing gas combination to predict the depth of carbonation at up to the six month age for these same temperature and humidity curing conditions [Ramme 2008].
- 5) Aggregates typically make-up approximately 80% or more of concrete based products. The production and incorporation of carbonated by-product based aggregates has the potential to significantly increase the percent green content of concrete and geotechnical construction materials.

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