Preliminary Method to Determine CO_2 Sequestration in Cementitious Units

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INTRODUCTION

Given heightened attention to the interrelationship between industrial manufacturing and carbon dioxide (CO_2) emissions, there is a market-driven interest across all industries to identify means of reducing their carbon footprint through various adsorptive, absorptive, and source-reduction techniques. In construction, despite being the most frequently used material globally, portland cement is assumed to emit approximately 1 lb. (450 g) of CO_2 for each 1 lb. (450 g) of cement produced for construction (EPA (2010)); thus creating the perception that cement-based products are environmentally unfriendly. The fallacy of partial data snippets such as this is they do not consider the use phase of a cement-based material where the concrete will re-capture (sequester) a portion of the CO_2 that was released during the calcination phase of cement production. Historically, quantifying the sequestered carbon dioxide in concrete has been inconsistent and error prone; originally due to technological limitations and more recently due to a lack of understanding as to how latent CO_2 within the constituent materials of a concrete material can influence the measured results. For example, thermogravimetric analysis can be used to measure the amount of carbon dioxide within concrete. It cannot, however, accurately differentiate between the carbon dioxide sequestered by the concrete post-production and the carbon dioxide already present within the constituent materials prior to production. In the scenario where the aggregates used to produce the concrete are, for example, limestone based, significant errors can result.

While the topic of concrete sequestration has been studied for years (Andrade (1997)), the focus has historically been on the impact such carbonation has on the corrosion of reinforcing steel rather than the environmental benefits of recapturing carbon dioxide. Only more recently (Tavares (2015)) has attention been redirected toward attempting to quantify the environmental reduction of CO_2 via hydraulic cement-based materials (ASTM C219 (2014)) through various adsorptive, absorptive, and source-reduction mechanisms. Unfortunately, not all previously conducted research on this topic accounted for, and subsequently differentiated, the total CO_2 initially contained within the raw materials comprising various types of concretes (ASTM C125 (2015)); thus prompting this investigation.

The procedure presented here applies generically to virtually all near zero-slump manufactured concrete products produced to comply with ASTM C90, ASTM C936, ASTM C1364, ASTM C1372, ASTM C1670, as well as similar dry-cast concrete products. In this study "near zero slump" is used as a physical measurement (slump) of the same mix once subtracting the effects of water reducing agents. The preliminary analytical reporting protocol (herein referred as "protocol") is a proposed method to improve the accuracy of reported CO_2 sequestration, thus providing better guidance to the production industry supplying the design and construction industries as well as for decision and policy-makers.

BASELINE MEASUREMENTS OF CONSTITUENT MATERIALS

In order to understand and quantify the mineral composition of a manufactured concrete product, one needs to have a quantitative understanding of the constituent materials used in its production. Therefore, this investigation began with conducting visual and chemical baseline assessments of reference materials commonly present in the production of manufactured concrete products. One of the observations noted within virtually all images of naturally sourced raw materials is the presence of aggregate particles much smaller than 100 mesh (0.150 mm), which given their relative size and surface area have often been considered to be a significant contributor to the latent CO_2 content of constituent materials. As such, historical analytical techniques used to assess carbon sequestration of concrete mixes often pre-screened materials to remove these fine (minus 100 mesh) aggregate particles under the assumption that aggregate and other raw materials possibly containing latent CO_2 are separated simply by fine screening. Nevertheless, very fine raw

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materials, including aggregate, silt, clay, and pigment fines, along with their associated soluble-to-colloidal constituents, are finding their way into the cementitious paste and inadvertently altering the measured CO_2 content of the sample being analyzed.

One source of CO_2 includes Type II alkaline materials, which are partially soluble depending upon temperature (Lide, (2003)). The migration of these solubilized as well as colloidal portions of the constituent materials into the cement paste during mixing is not captured by pre-production aggregate screening. In addition, delivered powdered cement is known to contain some latent CO_2, which obviously is not separated by any aggregate pre-screening method.

Further, the manufacturing process itself can introduce CO_2 measurement variability by further breaking down particles within the mix resulting in a higher concentration of fines. Physically, the shearing and abrasion forces to which materials are exposed is known to break down agglomerated and weaker raw material particles. This disintegration occurs during processing in the mixer as well as during product forming during the material feeding and vibration stages of production. Further, the alkaline nature of cementitious mixtures, potentially accentuated by the presence of some additives and admixtures, can further break down the weaker mineral and chemical bonds of natural agglomerates within the mix. The net result of the disintegration and deagglomeration of the larger constituent particles increases the percentage of fine constituents available to the paste during the production process, particularly during the "wet" or "green" production phases. Awareness of aggregate disintegration has been known for some time (Hool, (1924)). Indeed, contemporary aggregate evaluation protocols (ASTM C33 (2013)) include methods to numerically determine an aggregate's propensity to break down under abrasion and impact using the "Los Angeles Machine" (Hewlett, (2008)). Even these testing protocols, however, do not include the added destabilizing effects that manifest from strong alkaline conditions and admixture presence.

In practice it is not unusual to find a 30% (or more) increase in fines (minus 100 mesh (0.150 mm)) when comparing an aggregate wet sieve analysis before and after unit production. Hence, the assumption that aggregate gradation pre-production is representative of the aggregate gradation within the mix post-production is often flawed. By assuming the simple act of pre-screening aggregates can adequately capture and segregate embodied sources of latent CO_2 will likely result in significant measurement errors. Thus, a more comprehensive CO_2 analytical protocol incorporating time-proven geochemical, lithogeochemical, and mineral and rock sample preparation as presented herein is needed. Though thorough investigations of such phenomena are outside the scope of this work, an overview of typical cause and effect relationships follows.

As with any analytical test method, calibration is critical to producing meaningful and accurate results. Further, as measurement sensitivity increases, such as in the case of determination of sequestered CO_2, identifying reference materials capable of being dispensed, often times in very small quantities, with the same content percentage and weight control as when utilized in much larger quantities becomes increasingly difficult, particularly when sourcing reliable, certified carbon dioxide standard reference materials. Both ASTM C25 (ASTM C25 (2011)) and ASTM C114 (ASTM C114 (2015)) acknowledge the absence of laboratory reportable bias and reference material precision regarding CO_2 analyses. Nevertheless, coarse calcium carbonate crystalline minerals (Figures 1, 2, 3, 4) have been shown to offer reliable stability whether dispensed in large quantities or small, provided they are carefully reduced in sample size (Bugbee, (1984), Smith, (1978)) and protected from sporadic laboratory corrosive atmospheres and temperatures.

Figure 1 – Trilling Crystals of Aragonite; Morocco. Field of View is Approximately 10 inches (25 cm)

Figure 2 – Dogtooth Spar Crystals of Calcite, Texas. Field of View is Approximately 10 inches (25 cm)

Figure 3 – Psuedo-Hexagonal Crystals of Aragonite, Spain. Field of View is Approximately 3 inches (8 cm)

Figure 4 – Crystalline Iceland Spar Calcite; Mexico. Field of View is Approximately 5 inches (13 cm)

One key advantage of using pure, geologically-sourced, coarse crystalline minerals carefully comminuted as a means of calibrating both analytical test methods and instrumentation includes their natural stability compared to hydrated Type I/II alkaline reference materials. Further, it was also determined that the use of large-scale crystal forms of reference materials (Figures 1 through 4) are more dependably identified compared to their microscopic counterparts. For instance, during analyses using X-ray diffraction there was a sample lot initially identified, labeled and sold as cryptocrystalline, massive aragonite. However upon subsequent investigation it was determined to actually be calcite and therefore rejected from this study. Calcite and aragonite are known to have different densities as described below (Lide, (2003), Fleischer et al (1984), (O'Neil (2001)).

There are other reasons to confirm not only the chemical composition of calibration materials but also their crystalline structure. Even when each sample is carefully analyzed and found to be pure with the exception of trace constituents, there exist statistically significant density differences among and between the crystalline categories that eventually manifest during subsequent measurement and analysis. For instance, calcite, which has a typical density of 2.71g/cc (1.57 oz./in.^{3}), has a different lattice structure as well as density than aragonite, which ranges from 2.83-2.94g/cc (1.64-1.70 oz./in.^{3}), even though they reportedly have proportionately identical ratios of calcium oxide (56.03%) to carbonate (43.97%) (O'Neil (2001), Lide (2003), Fleischer et al (1984)). When comparing inter-crystalline (calcite to aragonite) polymorphs, however, the actual mineral proportions were found to vary. As an example, the concentration of carbonate in calcite was determined to be 43.80% when assessing crystalline dogtooth spar as compared to aragonite's 42.22% concentration of carbonate in the trilling crystals form. Similar variations were seen intra-crystalline (aragonite-to-aragonite and calcite-to-calcite). As there are hundreds of forms of calcium carbonate, it became evident that a precise mineral composition analysis was necessary for each reference material used in this investigation.

In addition to natural variations of constituent materials, sample preparation has long been a source of measurement uncertainty reported by researchers as a result of possible crystalline changes during sample preparation, such as during crushing and pulverizing samples to a minus 200 mesh (0.074 mm) dry pulp (ASTM C50 (2013), Activation Laboratories (2015)). Crystalline changes in assessed samples, for example aragonite changing crystalline structure to calcite, were not seen in this investigation when carefully limiting the temperature to below 200 °F (93 °C) during sample preparation, as confirmed by X-ray diffraction analyses (ASTM C1271 (2012)).

In summary, given that trigonal calcite has two polymorph crystalline forms, aragonite and vaterite (O'Neil (2001), Lide (2003), Fleischer et al (1984), and Gaines, (1997)), each having different densities despite identical calcium oxide to carbonate proportions, researchers and analysts require some degree of latitude when assessing CO_2 content, particularly when measuring a complicated matrix of constituent materials as in the case of concrete. (Taylor (1997)). Therefore, despite the best efforts of all involved, carbon dioxide analyses will always have inherent uncertainties due to a variety of crystalline and chemical variables. This approximates to at least a 4% range or about +/-2%, discounting statistical as well as practical analytical variables.

ASSESSING CARBON SEQUESTRATION

Results of multiple analyses utilizing routine petrographic examination (ASTM C856 (2014)), X-ray diffraction, electron microprobe, thermogravimetric (ASTM E2105 (2010)), thermogravimetric infrared spectrometer, acid digestion/volumetric capture (Furman (1975)), hot acid digestion infrared spectrometer, inductively coupled plasma, scanning electron microscope (ASTM C1723 (2010)), and energy dispersive spectroscopy apparatus from laboratories across North America were compared as part of this investigation. It is not unusual, however for laboratories involved with the higher precision and accuracy demanded of concrete sequestration-related CO_2 analyses to find themselves repeating the initial testing using more controlled calibration and assessment procedures for the reasons previously outlined.

It has been observed that a concrete product contains only a relatively small percentage of cement, which in turn may contain a smaller percentage of CO_2, which in turn may have but a small percent change due to sequestration of CO_2. Furthermore, the sensitivity of the measurements and analyses can be highly dependent on the efforts behind identifying and controlling impacting variables. Mathematically, a laboratory could be faced with analytical procedures that require a precision capable of assessing mass differences that are only a small fraction of a percent of the mass of the original batch of concrete. As a further complication, a representative sampling of powdered concrete pulp might only be an analytical specimen/aliquot of 2 to 0.5 grams (0.071 to 0.018 oz.), compounding the need for precision at each stage of analyses.

Figure 5 illustrates under electron micrograph magnification a typical example of the aggregate, paste, and aggregate-paste interface within a concrete masonry unit following 28 days of curing. Samples were also subjected to Energy Dispersive Spectroscopy (EDS) analyses to confirm a) carbon dioxide sequestration at the cement paste locations; and b) similar chemical reactions are not occurring with the aggregate. Cement grains and flocs need to be hydrated before they can emit secondary cement reactions, and once hydrated can culminate in byproducts such as CaO and CaOH. This confirms the long-standing assumption that the hydrated cement – and not the aggregate – is providing the primary mechanism for post-production CO_2 sequestration. However, as a further complication not all cement within a manufactured concrete product hydrates as illustrated in Figure 6. The dark regions in Figure 6 show hydrated cement where carbon dioxide sequestration takes place. The white areas represent unhydrated materials as well as open voids within the matrix. It should be noted that hydration continues indefinitely providing the unhydrated cement eventually has access to moisture. Within the ranges of atmospheric conditions during processing and curing found today, carbon dioxide sequestration is primarily reacting at the highest alkalinity sites, so long as the CO_2 has access to these locations within the matrix of the product.

OVERALL PROTOCOL

Through several phases of refinement, this investigation identified and developed the following procedure for accurately and repeatedly assessing carbon sequestration following production of a manufactured concrete product.

Step 1: Procure reference materials. Ensure reference materials are stable and reliable for analytical calibration.

Step 2: Procure sample(s) of manufactured product(s) as well as samples of each constituent raw material used in production (water, cement, aggregate(s), etc.). Product sample(s) should be obtained providing for sufficient time to prepare the sample while accounting for curing time if a specific curing duration is desired (e.g., 28 days of curing).

Step 3: Submit product and material sample(s) to a third-party laboratory. Minerals should be analyzed with registered, or similarly credentialed, chemists/assayers. Ensure samples are appropriately labeled.

Step 4: Clean or sand-flush laboratory sample preparation equipment to mitigate sample contamination.

Step 5: Perform primary crushing, and if necessary secondary crushing, of sample(s). Separate samples using riffle-type divider.

Step 6: Comminute dried splits of sample(s) to minus 200 mesh (0.074 mm) pulp. Monitor sample temperature and maintain temperature below 200 °F (93 °C).

Step 7: Recombine minus 200 mesh pulp. For independent verification, split sample and distribute to selected analytical laboratories while maintaining at least one reference sample.

Step 8: Calibrate measurement equipment using provided reference sample(s). Analyze sample(s) for sequestered CO_2.

Step 9: To ensure repeatability of measurement, sequestration analysis should be repeated four times for a total of five tests on each sample(s) to be analyzed.

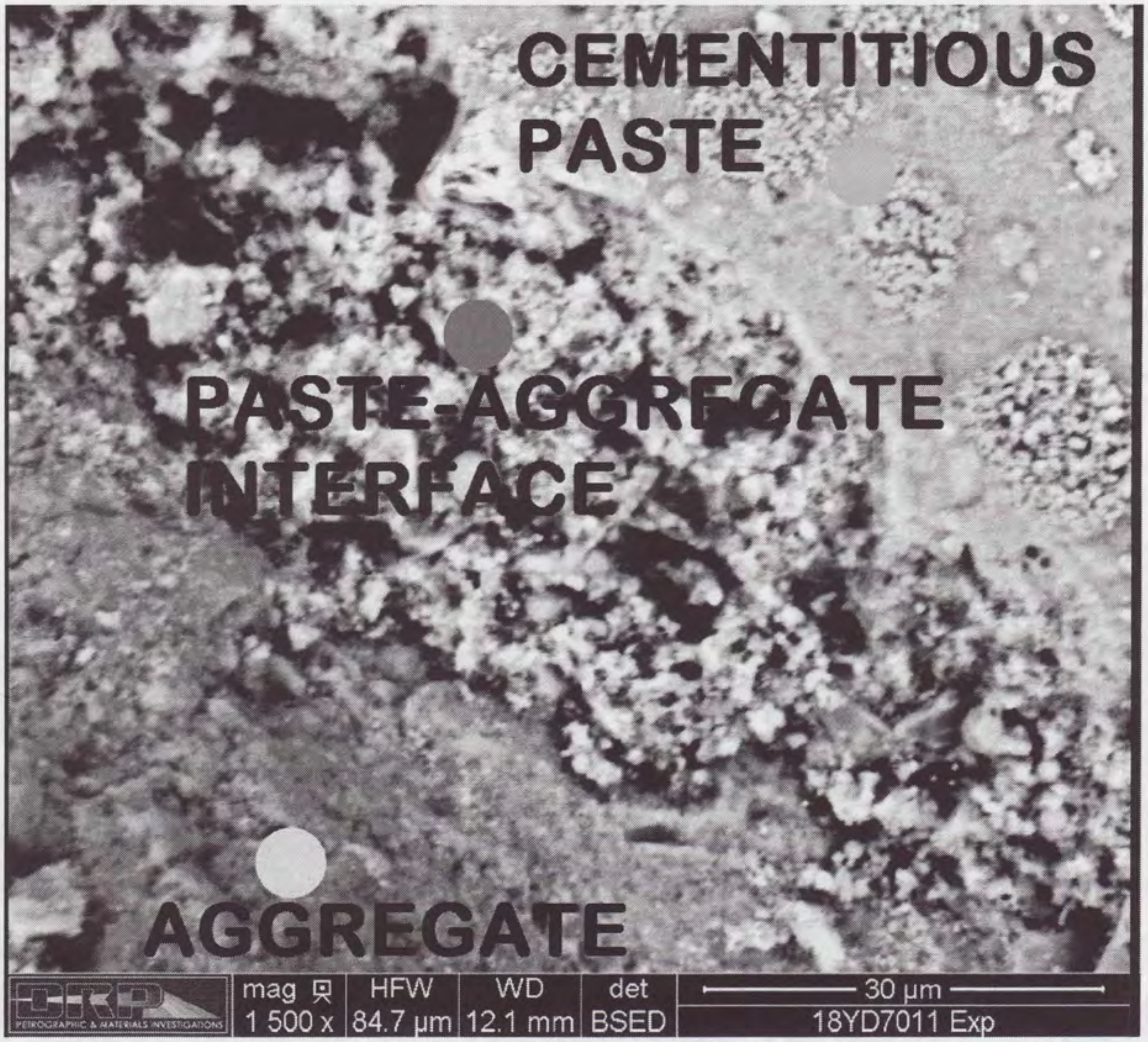

Figure 5 – Electron Micrograph of a Concrete Masonry Unit Following 28 Days of Curing

CALCULATIONS

The calculations for percent sequestered CO_2 of the cement within 28 day-old product unit(s) first requires determinations of pre-production CO_2 of raw materials (n1, n2, n3, …) used within the respective mix. The increments used are pounds, lbs.:

(Raw Material lbs.)(% CO_2) = Raw Materials CO_2, lbs. (n1, n2, n3 …) (1)

The CO_2 present within each raw material before processing is added to give total raw materials CO_2 lbs. within the mix.

Raw Materials CO_2, lbs. $\sum$ (n1, n2, n3 …) = Total Raw Materials CO_2, lbs. (2)

The total mix mass is next calculated by adding the individual raw materials' weights reported from the target batch weights or from production records in lbs.:

Raw Materials, lbs. $\sum$ (n1, n2, n3 …) = Total Mass Mix, lbs. (3)

The total CO_2 present within the 28 day-old product unit(s) is also calculated:
(Total Mix Mass, lbs.)(28 day-old % CO_2) = 28 Day-old Total Product Units CO_2, lbs. (4)

Next the total net amount of CO_2 sequestered within the 28 day-old total product units is calculated by subtracting the total raw materials CO_2 present before processing:

(28 Day-old Total Product Units CO_2, lbs.) – (Total Raw Materials CO_2, lbs.) = Net CO_2 Sequestered, lbs. (5)

Finally, the % CO_2 sequestered of portland cement and other hydraulic cement(s) is calculated:

(Net CO_2 Sequestered, lbs.) / (Hydraulic Cement(s), lbs.) = % CO_2 Sequestered, Hydraulic Cement(s) (6)

Additional calculations may be provided to highlight mix characteristics:

Cementitious, lbs.) / (Total Aggregate, lbs.) = % Cementitious / Aggregate (7)

(Cementitious, lbs.) / (Total Mix Mass, lbs.) = % Cementitious / Total Mix Mass (8)

Non-reportable numbers have no significant digit limits so as to maintain internal precision and accuracy. Reportable numbers are both a maximum of 5 significant digits, and are double underlined in examples 1 and 2 below.

Equations (1) to (8) are incorporated within the hypothetical examples below.

Following the Calculations below, see hypothetical Examples 1 & 2, the results of which are tallied in Table 3 and further graphically displayed in Figure 7. Carbonate-based aggregates for instance would be expected to give far different results than those shown in the Examples, Graph, Tables, and tally.

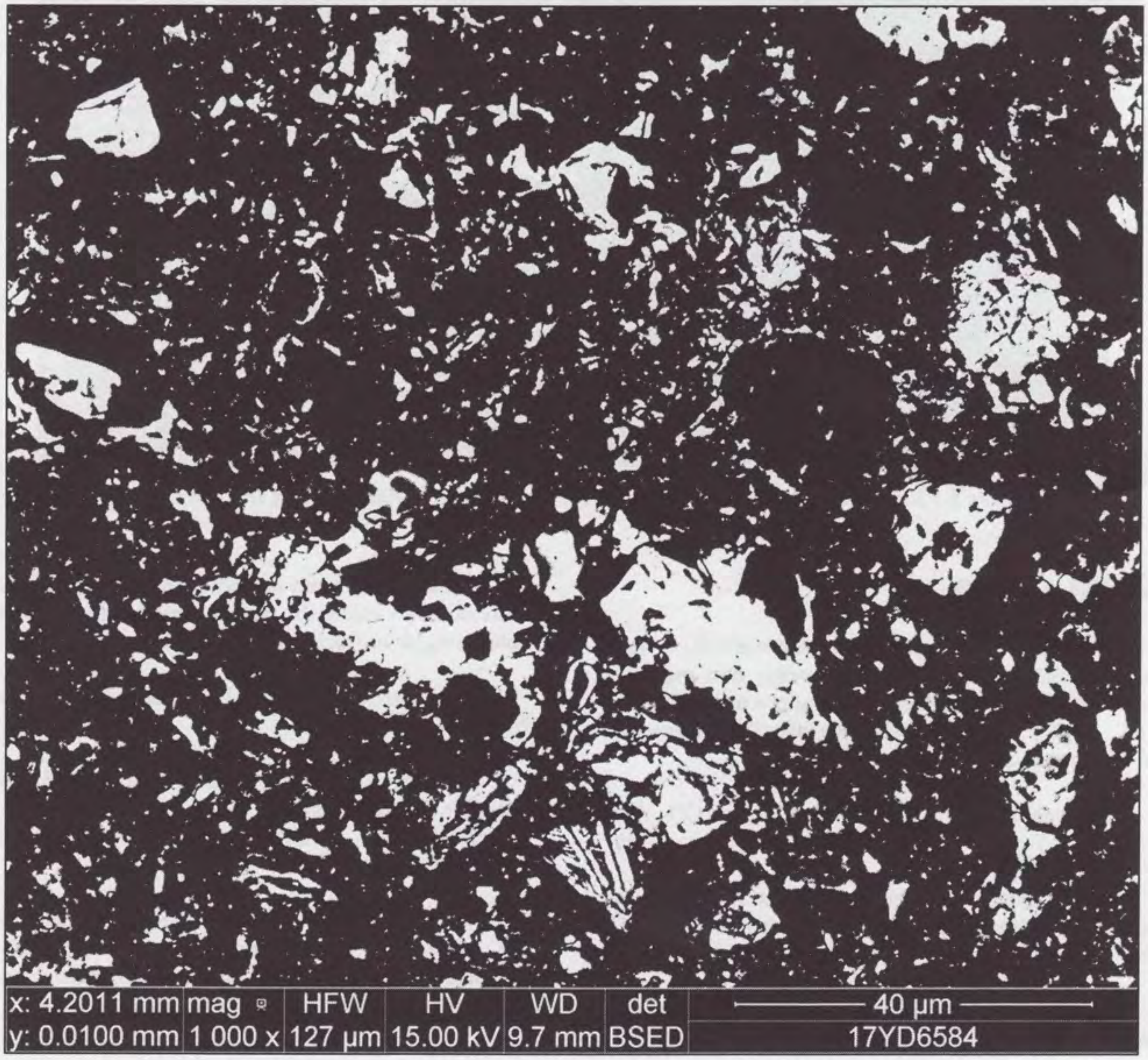

Figure 6 - Electron Micrograph of a Concrete Paver (Approx. 1 yr. Old) Incorporating Contrast Imagery. Notice the Amount of Both Unhydrated Material as Well as Open Voids Represented by the White Areas

BATCH SAMPLE CALCULATIONS

The following discussion provides example calculations illustrating how the sequestered carbon dioxide in a manufactured concrete product is determined using the protocol described herein. Both examples are for illustrative purposes only as results will vary depending upon the constitute materials used and their relative proportion. Carbonate-based aggregates, for instance, would be expected to give widely different results than those shown in these examples.

Example 1 – Mix Design A

The mix design shown in Table 1 is to be assessed for the carbon dioxide sequestration following 28 days of post-production curing. Prior to analysis, the latent CO_2 in each of the constituent materials is measured with the results shown in Table 1.

Using the protocol previously outlined, a 28-day sample of the manufactured concrete product from example 2 below is tested for its total CO_2 content, and is assumed to contain 0.8894% CO_2 from the laboratory test results. Extrapolating this sequestered carbon dioxide to the total batch mass, the total embodied CO_2 would be:

$$\begin{aligned}\text{Total } CO_2 \text{ Content} &= (0.008894)(5350 \text{ lbs.}) \\ &= 47.5829 \text{ lbs.} \\ \text{SI: Total } CO_2 \text{ Content} &= (0.008894)(2426.7 \text{ kg}) \\ &= 21.5831 \text{ kg}\end{aligned}$$

Knowing, however, that the constituent materials contained 19.4105 lbs. (8.8045 kg) of latent carbon dioxide, the net amount of CO_2 sequestered would be:

$$\begin{aligned}\text{Net } CO_2 \text{ Content} &= 47.5829 \text{ lbs.} - 19.4105 \text{ lbs.} \\ &= 28.1724 \text{ lbs.} \\ \text{SI: Net } CO_2 \text{ Content} &= 21.5831 \text{ kg} - 8.8045 \text{ kg} \\ &= 12.7786 \text{ kg}\end{aligned}$$

Expressed as a percentage of the portland cement used in the batch, the net CO_2 sequestered in this example following 28 days of curing is:

$$\text{Net } CO_2 \text{ Sequestered by Mass of Cement} = \frac{28.1724 \text{ lbs.}}{575.0 \text{ lbs.}} = 4.900\%$$

Example 2 – Production Record of Intended Mix Design A

For this example, the total CO_2 sequestered within each constituent material as well as that sequestered post-production is shown in Table 2.

From Table 2: 4924 lbs. Total Mix Mass
SI: (2233 kg) Total Mix Mass

Laboratory results: 0.8894% CO_2 28 Day-old Product

(4924 lbs.)(0.008894 CO_2) = 44.0206 lbs. Total CO_2 28 Day-old Product
SI: (2233 kg) (0.008894 CO_2) = 19.9674 kg Total CO_2 28 Day-old Product

44.0206 lbs. CO_2 - 17.9674 lbs. CO_2 = 26.0531 lbs. Net CO_2 Sequestered
SI: 19.9674 kg CO_2 - 8.1499 kg CO_2 = 11.8175 kg Net CO_2 Sequestered

26.0531 lbs. CO_2 Net / 528.0 lbs. portland cement = 4.9343%; 4.93% Net CO_2 Sequestered, Portland Cement
SI: 11.8175 kg CO_2 Net / 239.5 kg portland cement = 4.9343%; 4.93% Net CO_2 Sequestered, Portland Cement

528.0 lbs. portland cement / 3868 lbs. Total Aggregate = 13.65% Cement / Aggregate
SI: 239.5 kg portland cement / 1754 kg Total Aggregate = 13.65% Cement / Aggregate

528.0 lbs. portland cement / 4924 lbs. Total Mix Mass = 10.72% Cement / Total Mix Mass
SI: 239.5 kg portland cement / 2233 kg Total Mix Mass = 10.72% Cement / Total Mix Mass

Table 1. Sample Calculations for Mix Design A

Constituent Material	Mass of Constituent Material, lbs. (kg)	Percentage of Latent CO_2 Embodied in Constituent Material	Mass of CO_2 Embodied in Constituent Material, lbs. (kg)
Sand	3000 lbs. (1361 kg)	0.30037%	9.01107 lbs. (4.087 kg)
Gravel	1200 lbs. (544.3 kg)	0.06441%	0.77287 lbs. (0.3506kg)
Water	430.0 lbs. (195.0 kg)	0.01139%	0.04898 lbs. (0.02222 kg)
Fly Ash	145.0 lbs. (65.77 kg)	0.074%	0.1073 lbs. (0.04867 kg)
Portland Cement	575.0 lbs. (260.8 kg)	1.647%	9.4702 lbs. (4.296 kg)
TOTAL	**5350 lbs. (2426.7 kg)**		**19.4105 lbs. (8.8045 kg)**

Table 2. Sample Calculations for Production Record of Intended Mix A

Constituent Material	Mass of Constituent Material, lbs. (kg)	Percentage of Latent CO_2 Embodied in Constituent Material	Mass of CO_2 Embodied in Constituent Material, lb (kg)
Sand & Gravel	3868 lbs. (1754 kg)	0.236%	9.12848 lbs. (4.141 kg)
Water	396.0 lbs. (179.6 kg)	0.01139%	0.04510 lbs. (0.02046 kg)
Fly Ash	132.0 lbs. (59.874 kg)	0.074%	0.09768 lbs. (0.04431 kg)
Portland Cement	528.0 lbs. (239.5 kg)	1.647%	8.69616 lbs. (3.9445 kg)
TOTAL	**4924 lbs. (2233 kg)**		**17.9674 lbs. (8.1499 kg)**

Table 3. Preliminary CO_2 Content Within 28 Day Old Units*

Product	Mass	%
Sequestration from Atmosphere	26.05 lbs. (11.82 kg)	59.2%
Sand & Gravel	9.13 lbs. (4.14 kg)	20.7%
Water	0.05 lbs. (0.02 kg)	0.1%
Fly Ash	0.10 lbs. (0.04 kg)	0.2%
Portland Cement	8.70 lbs. (3.94 kg)	19.8%
TOTAL	44.02 lbs. (19.97 kg)	**100%**

*Extracted from Example 2. This is a generic representation only. Note: pie chart below (Figure 7) and this table are examples only. Actual values may differ significantly.

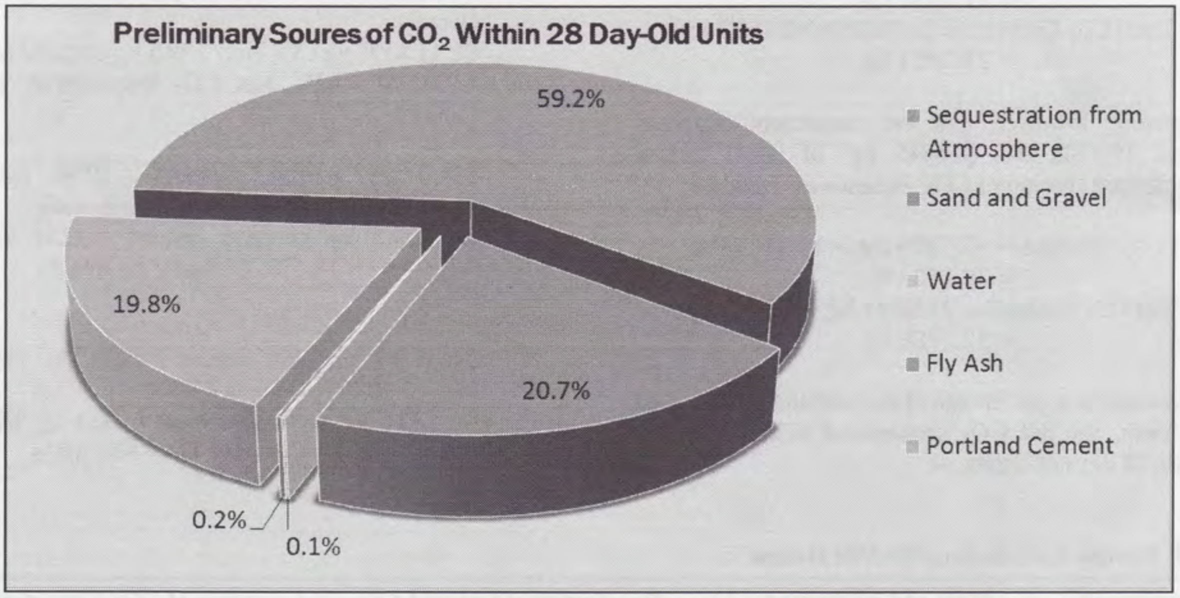

Figure 7 – Pie Chart of Preliminary CO_2 Sources, Pre- and Post- Manufacturing (See Table 3)

CONCLUSIONS

The proposed preliminary method to determine CO_2 sequestration in cementitious units described herein has to date proven to be both precise (as repeatable) as well as accurate. Because analyses for CO_2 sequestration by any method require great sensitivity, the attention to detail is above routine work. Just as important the subtraction of the raw material CO_2 contribution from the 28-day product CO_2 is a more accurate representation of the net sequestered CO_2. The use of stable, reliable calibration materials is critical, as one would typically assume, especially for highly sensitive analytical methods. Numerous cross-checks both intra-laboratory as well as inter-laboratory have been performed supporting this protocol.

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Dedicated to the memory of Eric Hoffman Ph.D., P.Geo., one of the co-contributors to this work.

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NOTATION

g = grams
kg = kilograms
lbs. = pounds