Field demonstration of the Reversa™ mineral carbonation process using coal and natural gas flue gas streams at the National Carbon Capture Center, AL

Authors of Report:
Dale Prentice ([1],[2]), Stephen Raab ([3]) and Gaurav Sant ([1],[2],[4],[5])

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[1] Laboratory for the Chemistry of Construction Materials (LC^2), Department of Civil and Environmental Engineering, University of California, Los Angeles, CA 90095, USA
[2] Institute for Carbon Management (ICM), University of California, Los Angeles, CA 90095, USA
[3] CarbonBuilt Inc., 570 Westwood Plaza, Los Angeles, CA 90095
[4] Department of Materials Science and Engineering, University of California, Los Angeles, CA 90095, USA
[5] California Nanosystems Institute (CNSI), University of California, Los Angeles, CA 90095, USA

Executive summary:
Concrete, a mixture composed of a cementation agent, mineral aggregates, and water has the potential to serve as a gigaton-scale sink for carbon dioxide (CO_2). This could make concrete the world's largest CO_2 utilization opportunity. CarbonBuilt's Reversa^{TM} process, developed at UCLA's Institute for Carbon Management exploits simple acid-base chemistry to mineralize CO_2-dilute flue gas emissions into mineral carbonate-based cementation agents at ambient pressure, at flue gas temperatures, and without a need for carbon capture. The approach leverages innovations in the use of portlandite ($Ca(OH)_2$: calcium hydroxide, or slaked lime) which carbonates readily, and produces limestone ($CaCO_3$: calcium carbonate) – a potent cementation agent – upon its carbonation. Within the scope of a project sponsored by the US Department of Energy's Office of Fossil Energy, the Reversa technology was upscaled and demonstrated using a modularized pilot-plant at the National Carbon Capture Center (Wilsonville, AL) using coal- (~12 vol. % CO_2) and natural gas (~4 vol. % CO_2) flue gas streams. The field demonstration led to the production of over 5,150 concrete masonry units (CMUs, also known as concrete blocks) and achieved: (1) a CO_2 utilization efficiency in excess of 75%, and (2) achieve CO_2 uptake greater than 0.5 % of concrete (mass basis) and, (3) ensuring compliance of carbonated blocks with industry standard specifications (ASTM C90). Importantly, based on rigorous 3rd-party validation, the CMUs produced were confirmed to be compliant with all relevant industry specifications (ASTM C90). The success of this demonstration suggests that the pioneering Reversa technology is ready for commercialization.

1 Introduction

Anthropogenic sources of carbon dioxide are generated from a number of sources, but key among these are ordinary Portland cement (OPC) production and combustion of fossil fuels [1]. Cement production is the largest global CO_2 source from the mineral decomposition of carbonates [1]. This is due to the clinkering process whereby limestone (mainly consisting of $CaCO_3$) is decomposed into CaO and CO_2, and combined with silica rich clays at high temperatures to form clinkers (i.e. the four key minerals that comprise cement) [2]. The high temperature range of 1400 – 1550 °C required for this process accounts for up to 60% of the generated CO_2 from cement production [3]. Combination of the limestone decomposition and thermal requirements of the clinkering process causes cement production to contribute 8-9% of annual global CO_2 emissions [1,2,4–6]. Combustion of fossil fuels (coal, oil, and gas) was shown to contribute a much larger portion of global CO_2 emissions. As of 2018, combustion of fossil fuels accounted for 65% of global CO_2, where 41% was derived from stationary sources for electricity and heat generation and the other 24% was related to transport [7]. To reduce these contributions, key steps forward in CO_2 utilization technologies are required. Therefore, a CO_2 mineralization technology (CO_2 mineralization concrete) to reduce the OPC content in concrete, while utilizing flue gas emissions from fossil fuel combustion has been developed to address both areas simultaneously.

This Reversa technology utilizes low-carbon cementation agents produced by *in situ* CO_2 mineralization ("mineral carbonation reactions") to offer a promising alternative to OPC [8–12]. CO_2 mineralization relies upon the reaction of dissolved CO_2 with inorganic alkaline reactants to precipitate mineral carbonates (e.g., $CaCO_3$), which bind proximate particles and achieve cementation [9,12–14]. Herein, a concrete *green body*, that is composed of a mixture of binder, water, and mineral aggregates, is exposed to CO_2 borne in industrial flue gas streams. This manner of CO_2 mineralization allows the production of construction components that feature equivalent engineering attributes as their OPC based counterparts while featuring a much smaller embodied carbon intensity (eCI).

The reliability of the Reversa technology has proved effective for the production of concrete masonry units (CMUs) at bench scale, where the units exceeded the required 13.8 MPa compressive strength requirements [14,16]. The results detailed herein will demonstrate the applicability of this technology at an industrial scale. In total, 6 production runs were completed at the National Carbon Capture Center (NCCC), Wilsonville, AL, using coal fired and natural gas (NG) flue gas as the CO_2 source. This was the second site demonstration performed using this technology following 12 successful production runs at the Integrated Test Center (ITC), Gillette, WY. Over the course of the production runs at NCCC, the CO_2 utilization as a function of time, 18-h CO_2 uptake, electricity usage, and 28-d net area compressive strength recorded for each run. Collection of this data will be used to determine the success of the demonstration goals: (1) achieving in excess of 75% CO_2 utilization efficiency, (2) achieve CO_2 uptake greater than 0.5 % of concrete (mass basis) and (3) ensuring compliance of carbonated blocks with industry standard specifications (ASTM C90[19]).

2 Materials and methods

The field demonstration at NCCC required the CMUs to be produced off-site at the Blair Block concrete plant, where the CMUs were transported to NCCC, then loaded into a custom-built carbonation chamber. A mixture of inorganic reactants (e.g., the *binder*), inert aggregates (concrete sand, #8 aggregate and washed fines), and water was used to produce "dry-cast" formulations suitable for the fabrication of concrete masonry units (CMUs; "concrete blocks"). The binder used consisted of commercially available portlandite ($Ca(OH)_2$) powder (Standard Hydrated Lime, Mississippi Lime Co.), ASTM C150-compliant ordinary portland cement (Type III OPC),[17] and an ASTM C618-compliant class C fly ash [18].

Blair Block produced structural hollow concrete masonry units (CMU) [16]. The overall dimensions of the blocks were 200 mm x 200 mm x 400 mm ($w \times h \times L$) with face-shell and web thicknesses of 32 mm and 25 mm, respectively. After forming, the fresh concrete blocks were pre-cured to gain sufficient strength (compressive strength σ_c = 6 ± 1MPa) to enable transport, handling and loading into the carbonation reactor.

The curing chamber at the NCCC, consisted of a modified open-sided 40' shipping container with steel racks (40 in. wide x 98 in. deep x 76 in. tall), each capable of holding 108 blocks (around 1.73 metric tons of carbonated concrete), comprising a total of 864 blocks (13.82 metric tons) of carbonated concrete per production batch.

Two process cycles were used to complete the carbonation process: 1) carbonation cycle where conditioned flue gas was introduced to the curing chamber, and 2) purge cycle to remove the flue gas from the chamber. During the carbonation cycle, the inlet flue gas stream of [CO_2] = 12.2 ± 1 v/v% for coal flue gas and 3.9 ± 1 v/v% for NG flue gas) were used. The total curing cycle was set at 24 hours including 6-h pre-curing and 18-h carbonation to match commercial block production cycle time under ambient pressure and sub-boiling temperature (<75 °C).

CO_2 utilization as a function of time was calculated based on the change of CO_2 mass fraction of the outlet flue gas as compared to the inlet flue gas over time. Over the course of an 18-h production run, this value can be averaged to provide the 18-h CO_2 uptake value. Electricity usage of the chiller and process skid (heater, fans, and control HMI) was recorded to detail the energy usage of the process.

The performance of carbonated concrete masonry units produced during system operations was assessed against the relevant industry standard for conventional concrete masonry units (ASTM C90[19]) by a certified testing lab (BASF Corporation, Construction Chemicals Division). The net area compressive strength of the CMUs was measured as per ASTM C140 after 28 days of age.

Analysis of the heavy metal and sulfur uptake during the carbonation process was analyzed using X-ray fluorescence (XRF) spectroscopy and acid-dissolution followed by inductively coupled plasma optical emission spectrometry (ICP-OES). These methods were employed to calculate the elemental composition of the pre-carbonated and carbonated concrete blocks. A toxicity

characteristic leaching procedure (TCLP) was also conducted to further confirm the low possibility of toxic materials leaching from the concrete.

Embodied carbon intensity was calculated via the sum of the equivalent CO_2 for producing the raw materials, transport, energy used in the block making process, energy for the carbonation process and finally a reduction based on the CO_2 uptake.

3 Test plan for NCCC demo

The main objectives of the pilot-scale demonstration of the carbonated concrete mineralization system at NCCC site in Wilsonville, AL are as follows (and Table 1):

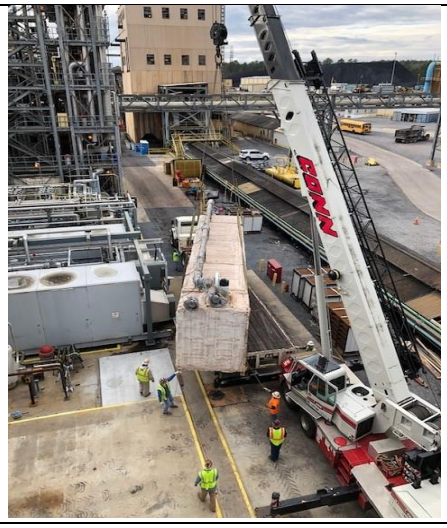
- Refine the process following our recent ITC demonstration to optimize system performance and system energy input. This considers the effect of temperature and relative humidity (RH) of the carbonation process.
- Demonstrate robustness with respect to flue gas CO_2 concentration (coal: ~12 vol% and NG: ~4 vol%) and environmental conditions.
- Develop a code compliance report in collaboration with the International Code Council's Evaluation Service (ICC-ES)

Table 1: Test plan and operational procedures for Reversa demonstration at the NCCC site. Each batch underwent 18 hours of carbonation.

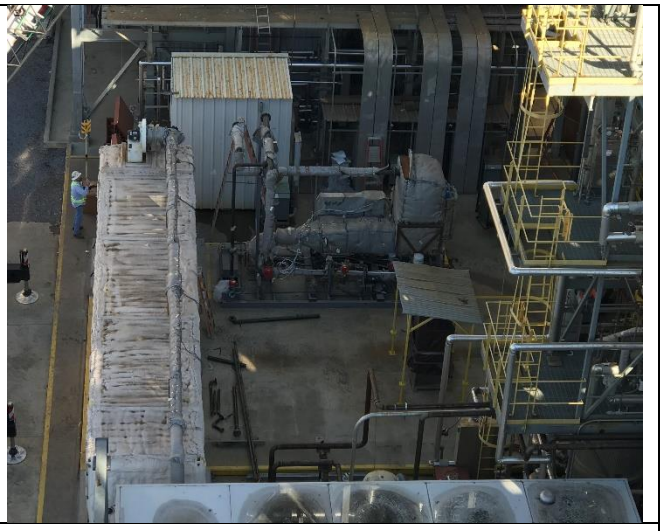
Batch #	Flue gas source (CO_2 %)	Carbonation duration	Milestone description
N1	Coal (~12 vol%)	18 hours	**Objective: Baseline without gas processing** • Effect of highest relative humidity (RH) on CO_2 uptake without any gas processing
N2	Coal (~12 vol%)		**Objective: System process** • Effect of RH control on CO_2 uptake • Effect of RH control on system energy demand
N3	Coal (~12 vol%)		
N4	NG (~4 vol%)		**Objective: CO_2 concentration** • Effect of CO_2 dilution on CO_2 uptake and product performance • Control of space velocity of curing chamber
N5	NG (~4 vol%)		
N6	Coal (~12 vol%)		**Objective: Material formulation** • Effect of cement formulation on product performance and CO_2 uptake

4 System installation

Following completion of the first field demonstration at Wyoming ITC, the system was delivered to NCCC site at the end of November 2020 for the second field demonstration. Installation of the Reversa system was completed by January 31st, 2021. Figure 1 presents photographs of the system in various stages of installation.



(a)



(b)

Figure 1: Photographs of **(a)** delivery of curing chamber, and **(b)** the CO_2 mineralization curing chamber and process skid installed onto their foundations.

Once the system was installed and the pre-startup safety review (PSSR) meeting was completed, commissioning of the equipment began. Commissioning consisted of applying improvements to the system based on the NCCC HAZOP and, instrument and sensor installation. Calibration of the equipment and alterations to the equipment configuration was required to address differences in the site pressure operating conditions compared to those encountered at the ITC.

5 Results

The pilot scale demonstration of the Reversa system at the NCCC host site was completed by the end of March 2021. In total, 6 operational runs were completed fulfilling an operational duration of nearly 120 hours. Around 89 tonnes of concrete blocks were produced while achieving 0.77 tonnes of CO_2 uptake.

Figure 2a) and b) display the CO_2 conversion performance of a representative carbonated concrete batch using coal (N3) and NG (N5) flue gas, respectively. The cumulative CO_2 input was computed from the system inlet flow rate and CO_2 concentration. The CO_2 uptake was determined in two ways: (1) from the difference in CO_2 mass flow rates between the system inlet and system exhaust, and (2) from the difference in chamber inlet and outlet mass CO_2 mass flow rates. The CO_2 utilization efficiency was calculated as the CO_2 uptake into the carbonated

concrete blocks divided by the CO_2 input into the system. Each batch demonstrated CO_2 uptake trends similar to that of Figure 2a) and b), with some variations due to changes in system inlet flow rates, mixture compositions, and the specific processing conditions that were applied. Both the coal and NG flue gas systems exhibited an initial peak within the first 2 hours of operation followed by a steady reduction of CO_2 utilization efficiency thereafter.

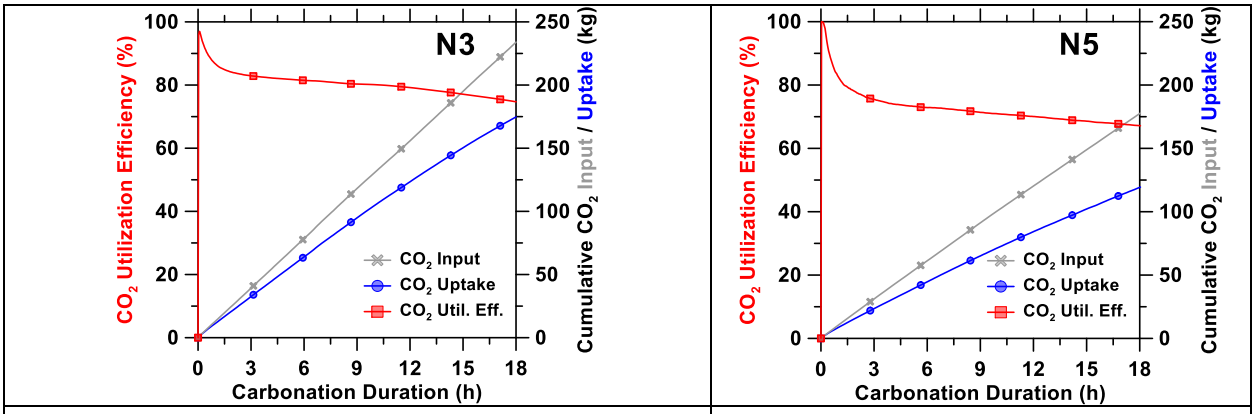


Figure 2: Representative plot of cumulative CO_2 input into the system, cumulative CO_2 uptake into the blocks, and CO_2 utilization efficiency as a function of 18-h carbonation duration in Batch **a)** N3 – coal flue gas, and **b)** N5 NG flue gas.

The Reversa system's performance fulfilled our design specifications including (1) achieving CO_2 utilization efficiency > 75 % (mass basis) as shown in Figure 3a), (2) achieve CO_2 uptake greater than 0.5 % of concrete (mass basis) and, (3) ensuring compliance of carbonated blocks with industry standard specifications (ASTM C90). For the NCCC runs, the CO2 uptake ranged between 0.75 % to 1.5 % mass solid during only 18-h carbonation duration at ambient pressure and at sub-boiling temperature (<75 °C). Importantly, these performance metrics were met using a "direct CO_2 utilization" process, i.e., without any need for flue-gas pretreatment (e.g., clean-up, enrichment). Thereafter, the CO_2 borne in the flue gas was utilized at sub-boiling temperature, at near-ambient pressure. The process conditions were optimized to a) minimize the process's carbon (energy use) footprint, and b) to achieve production price parity with traditional cement-based concrete blocks. It is evident to observe that optimization of the gas processing performed at NCCC caused a vast reduction in energy usage when compared to the previous demonstration at the ITC as shown in Figure 3b). Such optimizations were accomplished without sacrificing CO_2 uptake performance (see Figure 3c)) and optimizing the carbonation step.

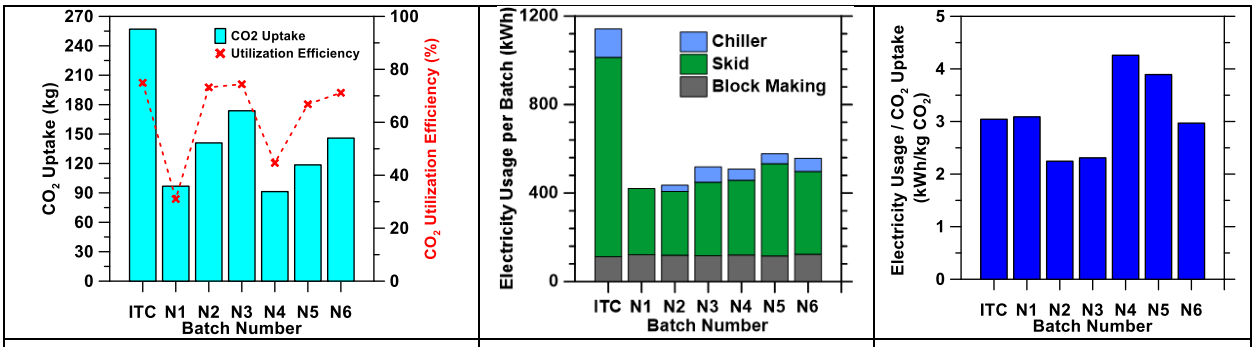


Figure 3: The trends in batch-wise **(a)** CO_2 uptake and CO_2 utilization efficiency over the 18-h carbonation duration, **(b)** electricity usage per batch, and **(c)** total energy usage per unit of CO_2 uptake.

The compressive strength was measured for each batch, with the average compressive strength of the coal and NG flue gas determined to be 20.12 ± 1.31 and 20.87 ± 0.86 MPa, respectively (Figure 4). This compressive strength of the carbonated concrete blocks easily fulfilled the compressive strength specified by ASTM C90 (i.e., 13.8 MPa).

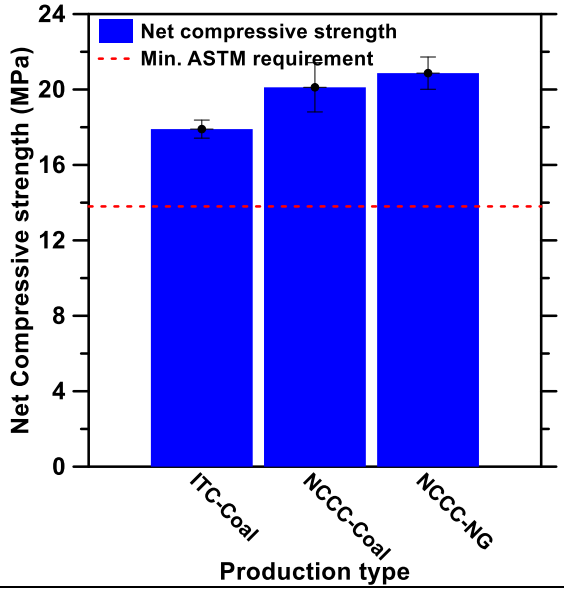


Figure 4: Net area compressive strength of the coal and NG flue gas concrete blocks.

As the Reversa process utilizes the CO_2 emissions from coal combustion, there may be a possibility of heavy metal and sulfur uptake during the carbonation process. This may lead to the formation of secondary products from the contact of flue gas with the concrete.

Based on XRF analysis of the pre-carbonated and carbonated concrete blocks, no uptake of heavy metals was determined for both the coal and NG flue gas units. XRF performed on the blocks determined that all the heavy metals of interest from a TCLP test (arsenic, barium, cadmium,

chromium, lead, mercury, selenium, and silver) were undetectable. The low heavy metal content was also confirmed via acid-dissolution followed by ICP analysis. Figure 5a) and b) show that heavy metal content was < 0.01 wt.% of the carbonated and non-carbonated units for coal and NG exposure. This is a promising sign for the technology as it does not show any uptake of harmful heavy metal contaminants. Accompanying the elemental analysis, a TCLP analysis was conducted via the NCCC staff to assess the leachability of the carbonated concrete blocks. All heavy metals were undetected in the analysis except for the presence of Ba (2.3 mg/L) in the coal flue gas units, which was far below the TCLP standard requirement of 100 mg/L.

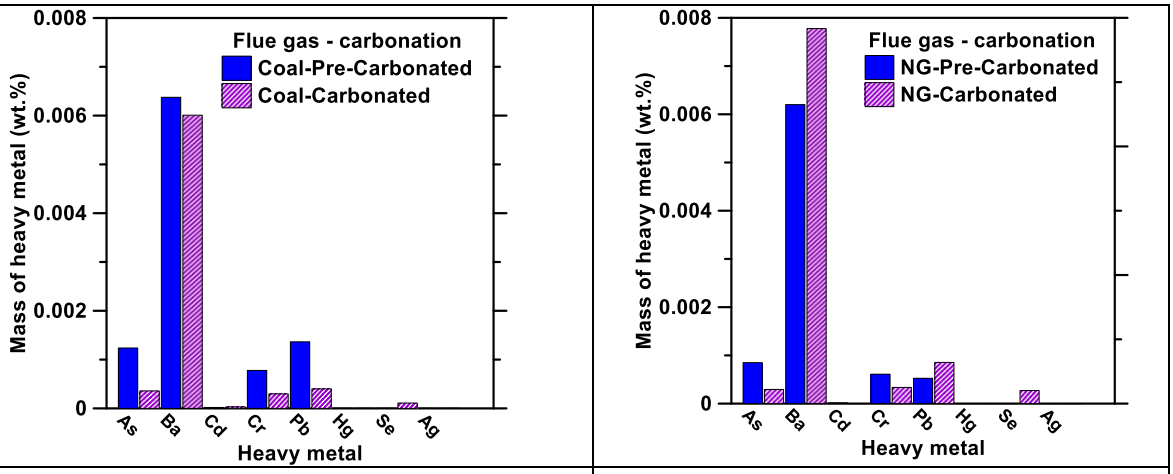


Figure 5: The calculated weight percentage of heavy metals as determined by acid-dissolution followed by ICP analysis of the carbonated and non-carbonated concrete blocks considering **(a)** coal flue gas exposure and **(b)** NG flue gas exposure.

XRF analysis determined sulfur content of the concrete blocks to be approximately 0.35 wt.% for carbonated and non-carbonated concrete blocks as shown in Figure 6. Variation in sulfur content is minimal and differences shown are within standard deviation of each result. This indicates that sulfur uptake was negligible during the carbonation process. Furthermore, low sulfur uptake was expected as coal flue gas inlet contained < 1.05 ppm of SO_3. NG flue gas is expected to have a lower SO_3 content however, no instrumentation was available to account for SO_3 content in the NG flue gas stream.

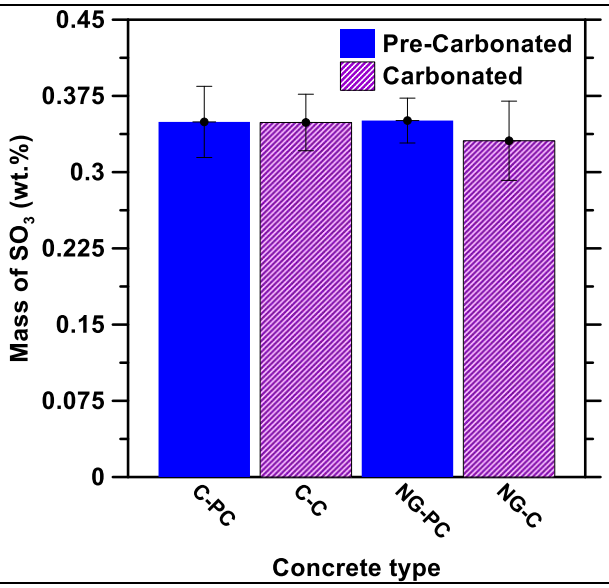


Figure 6: SO_3 content of CMU's pre-carbonated ('-PC') and carbonated ('-C') of coal ('C-') and NG ('NG-') flue gas blocks

In addition, compared to traditional concrete products and production practices, this carbonated concrete offers a greatly reduced embodied carbon intensity (eCI, kg CO_2e/m^3), as shown in Figure 7. This reduction in carbon intensity is achieved while the compressive strength is approximately 40% greater than the requirements. This large eCI offset is largely due to the replacement of the cement by portlandite which emits approximately 50% less CO_2 during production. This is due to the lower kiln temperature of ~800 °C required to produce the CaO prior to hydration for portlandite production, compared to the 1400-1500 °C kiln temperature required to form cement. The CO_2 uptake from the process also adds to the net reduction of eCI during the carbonation process of portlandite. An eCI penalty for the Reversa process is observed due to the energy required for gas processing during the carbonation cycle. However, due to the carbon avoidance and CO_2 uptake, the overall eCI of these carbonated concrete blocks was determined to be up to 50 % lower than traditional cement-based concrete blocks.

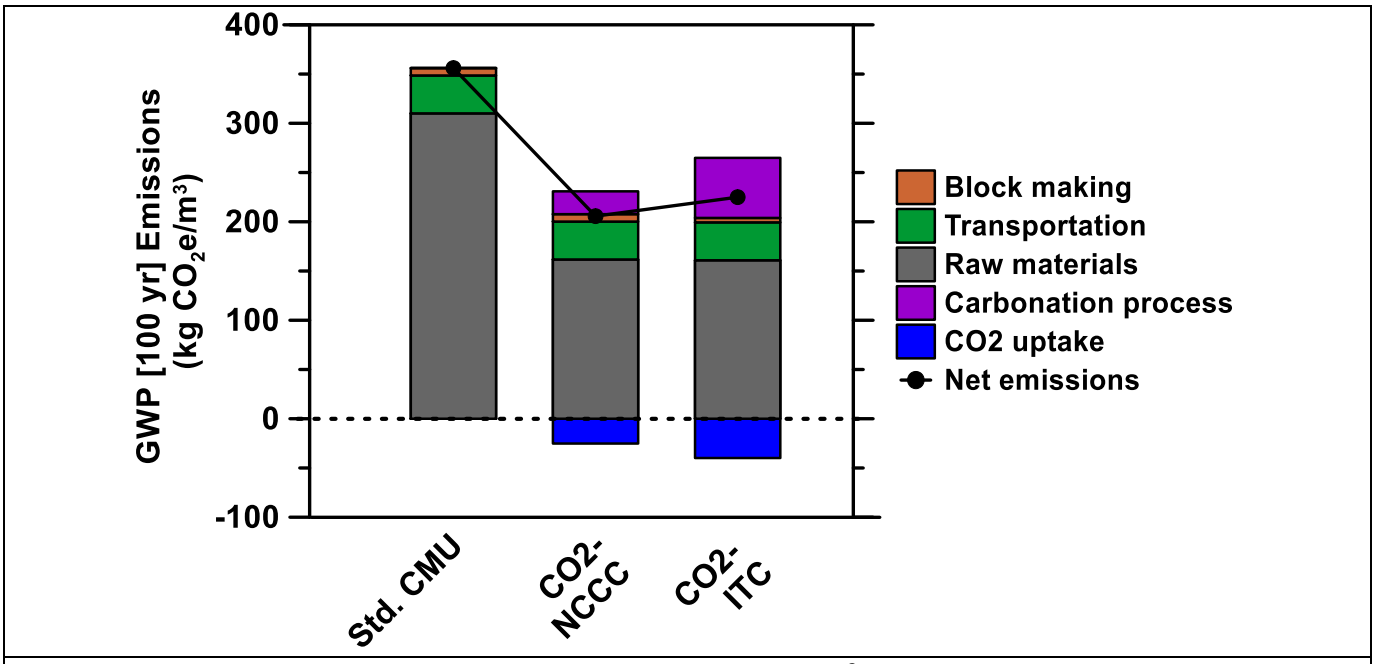


Figure 7: The global warming potential (GWP, kg CO_2e/m^3 concrete) for carbonated concrete (estimated) and conventional OPC-concrete masonry, based on an industry-averaged environmental product declaration (EPD).

6 Conclusion

The system's performance fulfilled all design specifications: (1) achieving in excess of 75% CO_2 utilization efficiency, (2) achieve CO_2 uptake greater than 0.5 % of concrete (mass basis) and (3) ensuring compliance of carbonated blocks with industry standard specifications (ASTM C90[19]). Furthermore, the Reversa process conditions were optimized to reduce the energy input as compared to conventional cement-based concrete block. The Reversa process addresses the largest opportunity for CO_2 utilization (i.e., construction materials) by exploiting chemical reactions that do not require extrinsic energy inputs (i.e., thermodynamically downhill) even while using CO_2-dilute feedstocks (flue gases). The blocks produced via Reversa processing and formulation achieved price parity to traditional cement-based concrete blocks. The cost analysis for the NCCC demo indicated that reducing cement content and use of low-cost supplementary cementitious materials in the Reversa process. This offset the increased processing cost which enabled achieving cost equivalence to traditionally produced concrete blocks at the demonstration block producer plant (Blair Block).

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