Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com

Valorization of waste concrete through CO_2 mineral carbonation: Optimizing parameters and improving reactivity using concrete separation

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A R T I C L E I N F O

Article history:
Received 5 January 2017
Received in revised form 1 August 2017
Accepted 2 August 2017
Available online xxx

Keywords:
Waste concrete
Flue gas composition
Aqueous mineral carbonation
Response methodology surface
Parameters influence

A B S T R A C T

The use of CO_2 mineral carbonation represents an attractive approach to recycling waste concrete. In this study, the effect of gas pressure, Liquid/Solid (L/S) ratio (w/w), Gas/Liquid (G/L) ratio (v/v) and reaction time for CO_2 sequestration were investigated. While carbonation of such matrix is already described, this study opens new insights in concrete carbonation. To increase the reactivity potential of concrete, the fine fraction (<500 µm), which contains mostly cement paste, was separated from the inert coarse aggregates. Separation was conducted by crushing and sieving. The ground fine concrete fraction showed enhanced reactivity with 75% of CO_2 removed (corresponding to 0.057 g CO_2 removed/sample) compared to that of raw concrete, with 54% of CO_2 removed (corresponding to 0.034 g CO_2 removed/sample). Tests were conducted under 144 psi of gas pressure (9.93 Bars) at ambient temperature for 10 min. On the other hand, the resulting aggregates fraction have an improved potential recycling value. The new proposed approach allows better carbonation efficiency and increases the overall valuation of waste concrete.

Abbreviations

$CO_{2\,c}$	CO_2 converted
$CO_{2\,r}$	CO_2 removed (sum of CO_2 dissolved and CO_2 converted)
G/L	gas/liquid
L/S	liquid/solid

1. Introduction

Carbon dioxide (CO_2) sequestration is an important challenge that involves various technologies known as Carbon Capture, Utilization and Storage (CCUS). Among them, mineral carbonation (MC) is an attractive method that allows for safe and permanent CO_2 storage. The approach mimics the natural silicate weathering process involving the reaction between CO_2 and divalent cations (Ca^{2+} or Mg^{2+}) to form metal carbonates (Huijgen and Comans, 2003).

An example of carbonation reactions involving CaO and MgO are presented in the following equations (1) and (2):

$$CaO_{(s)} + CO_{2\,(g)} \rightarrow CaCO_{3\,(s)}\ (\Delta \mathrm{rH298} = -179\ \mathrm{KJ/mol}) \tag{1}$$

$$MgO_{(s)} + CO_{2(g)} \rightarrow MgCO_{3(g)}\ (\Delta \mathrm{rH298} = -118\ \mathrm{KJ/mol}) \tag{2}$$

MC can be performed under dry, wet or aqueous conditions with various type of feedstocks. Among them, several industrial wastes such as; steelmaking slags, cement kiln dust, waste cement, asbestos tailings, nickel tailings, red mud, municipal solid waste incinerator (MSWI) bottom ash, MSWI fly ash/air pollution control (APC) residue, coal fly ash, oil shale ash and alkaline paper mill waste can be used (Bobicki et al., 2012).

Construction and demolition (C&D) wastes are increasingly considered to be a valuable source of building materials for the construction industry (Kuosa, 2012). Of the total C&D waste generated, it is reported that 40% is concrete (De Belie et al., 2007). As a result, the waste concrete obtained after C&D activities is potentially reusable in the production of fresh concrete (Corinaldesi and Moriconi, 2009). In general, only coarse aggregates can be used in producing concrete because finer particles have a larger absorption capacity, which leads to a higher water demand for the new concrete (Domone and Illston, 2010). Therefore, the fine fraction of concrete could be managed rather than continuing the normal practice of disposal (Martins et al., 2013). Instead, MC could be an alternative or complementary solution for recycling waste concrete.

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https://doi.org/10.1016/j.jclepro.2017.08.015
0959-6526/© 2017.

Cementitious materials are interesting for MC due to the presence of reactive phases, especially portlandite ($Ca(OH)_2$) and calcium silicate hydrate (C-S-H) (Thouvenot et al., 2013). Table 1 summarizes the main carbonation processes and cementitious material uses that have been reviewed, along with the results. In most cases, previous research has focused on the curing process of concrete and the use of cement kiln dust (CKD). Otherwise, the use of cement waste in an indirect MC process with the goal of producing pure calcium carbonate (PCC).

As shown in Table 1, chemical additives, high pressure gas, high temperatures, long reaction durations and concentrated CO_2 have been employed to achieve reasonable CO_2 sequestration results within cementitious materials. However, these methods may represent significant energy and economic constraints when applied in practice. In this way, the use of moderate pressure and temperature

Table 1
Summary of mineral carbonation processes using cementitious materials as feedstock (L/S – liquid/solid, amb. – ambient).

Author	Type process	Material	Duration	T (°C)	Gas comp.	Pressure (Bar)	Ratio L/S	Gas Flow	Results	Remarks
(Shuto et al., 2015)	- Discontinuous - Indirect	Waste cement	Calcium Extraction: 40 min $CaCO_3$ Precipitation: 30 min	amb.	100% CO_2	–	–	–	Carbonates purity>94%	- Calcium extraction with HNO_3 - Carbonates precipitation with NaOH
(Shao et al., 2014)	- Discontinuous - Indirect	Cement	2 h	amb.	99.50% CO_2	1.5	0.36	–	CO_2 absorption: 12%/cement weight	Concrete curing process
(Mun and Cho, 2013)	- Discontinuous - Indirect	Waste cement	Calcium Extraction: 1 h $CaCO_3$ Precipitation: 1 h	amb.	100% CO_2	amb.	10	1.5 mL/min	0.06 g CO_2/g cement	Calcium extraction with: EDTA and CH_3COOH.
(Uliasz-Bocheńczyk and Pomykała, 2011)	- Discontinuous - Indirect	Cement	14 days	20–25	100% CO_2	9 à 10	–	–	Absorption: 0.31 gCO_2/g cement	Relative Humidity: 40%
(Gunning et al., 2010)	- Discontinuous - Direct	Cement	72 h	25	100% CO_2	80	0.26	–	CO_2 absorption: 30%/cement weight	Relative Humidity: 75%
(Kashef-Haghighi and Ghoshal, 2009)	- Continuous - Direct	Cement	Concrete hydration: 180 min Carbonation.: 16 min	25	20% CO_2, 40% N_2	0.2 (CO_2 Pressure)	–	1.17 L/min	Carbonation efficiency: 18%	Concrete curing process
(Huntzinger et al., 2009)	- Discontinuous - Direct	Cement Kiln Dust (CKD)	8 h	amb.	5 à 15% CO_2	amb.	0.3	–	Carbonation efficiency: 75–80%	–
(Shao et al., 2006)	- Discontinuous - Direct	Cement	2 h	amb.	100% CO_2	5	0.15	–	CO_2 absorption: 9%–16% per cement weight	Concrete curing process

Table 1 (*Continued*)

Author	Type process	Material	Duration	T (°C)	Gas comp.	Pressure (Bar)	Ratio L/S	Gas Flow	Results	Remarks
(Katsuyama et al., 2005)	- Discontinuous - Indirect	Waste cement	Calcium Extraction: 0–120 min Precipitation:0–30 min	50–30	100% CO_2	30–1	Ratio S/L: 0.29–2.9		Purity $CaCO_3$>98%	
(Short et al., 2001)	- Discontinuous - Direct	Cement	24 h	60	100% CO_2	93	0.6	–	Carbonation efficiency: 16.2%	–
(Teramura et al., 2000)	- Discontinuous - Direct	Waste cement	0.8–100 h	20	0.03–100% CO_2	1–4	0.25–0.5	–	Carbonation efficiency: 1.6–16.5%	–

conditions was also studied. Baciocchi et al. (2010) investigated the carbonation of steel slags under less extreme pressure (3 Bar) and temperature (50 °C) conditions for a reaction duration of 2 h using 100% CO_2. In this process, they demonstrated the possibility of achieving reasonable results (0.13 g CO_2/g sample) under moderate conditions. Additionally, Huntzinger et al. (2009) studied the mineral carbonation of CKD under ambient temperature and atmospheric pressure. Nevertheless, the best results were obtained with reaction duration of 8 h, which would not be viable when applied in practice. While these results are encouraging with respect to the feasibility of the carbonation process under moderate conditions, the aforementioned studies used pure CO_2, which requires an additional step for capturing flue gas. Technical feasibility of MC relies in simplicity and low cost operations. Thus, the use of diluted sources such as industrial flue gases under mild conditions is preferable.

Our previous work demonstrated that waste concrete obtained from the C&D activities is quite reactive when used in direct aqueous MC, under moderate temperature and pressure and the use of simulated flue gas (18% CO_2) (Ben Ghacham et al., 2015). In continuity with the precedent work, this study investigate the effects of the different factors that influence the reactivity of concrete under the conditions previously tested. We also developed a novel approach that enhance the level of reactivity towards an improved recycling scenario.

2. Materials and methods

2.1. Methodology

Experiments were conducted by the aqueous route using a Mini bench top reactor (model 4560, Parr Instrument Company), as illustrated in Fig. 1. In this process, the feedstock material was mixed with distilled water to obtain the required Liquid/Solid (L/S) ratio. Next, the gas representing a cement plant flue gas (18.2% vol. CO_2 and 4.0% vol. O_2), balanced with N_2, was introduced in the reactor. At the end of the reaction, the concentration of the exiting gas was determined using an infrared CO_2 analyzer (Quantek Instruments). Then, the slurry was filtered using 934-AH filters (porosity: 1.5 µm), and the liquid phase was analyzed for the Cinorg concentration (Shimadzu TOC-VCPH, equipped with NDIR detection) and its chemical composition after acidification (at 5% HNO_3) with ICP-AES analysis. Afterwards, the solid phase was oven-dried at 60 °C for 24 h, and then, its carbon content was determined by CHNS (Leco).

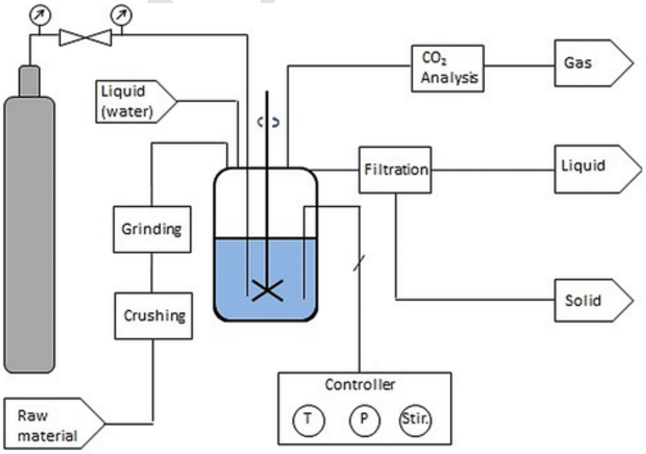

Fig. 1. Experimental presentation of aqueous mineral carbonation (Pasquier et al., 2014).

Thermogravimetry analysis (TGA) was conducted for a few samples of raw concrete and carbonated residue to obtain results. TGA tests were carried out using a Perkin Elmer Diamond instrument. Heat was increased at a rate of 10 °C/min, reaching 1000 °C. The initial weight of the samples was between 30 and 40 mg.

In the first part of the study, an experimental design was used for the Response Surface Methodology (RSM), using the Design Expert 9.0.3 (Stat-ease, Inc. Minneapolis, USA) software. This class of response surface design offers an advantage in that it requires fewer runs compared to a central composite circumscribed (CCC) design or central composite inscribed (CCI) design (Yetilmezsoy et al., 2009).

We intended to conduct the experiment under moderate conditions composed of a low gas pressure range, an ambient temperature and a short reaction duration. The factors that were evaluated consisted of the following: gas pressure (120–280 psi/8.25–19.30 Bar), liquid/

solid (L/S) ratio (w/w) (2.5:1–10:1), the gas/liquid (G/L) ratio (v/v) (1:1–3:1) and the reaction time (10–30 min). Because the goal of the study was to enhance the CO_2 removal capacity per sample mass unit, the chosen response was the amount of CO_2 removed according to the following equation: (converted + dissolved)/sample (w/w).

The aim of the second part of the study was to enhance the reactivity of the concrete by recovery, using the hardened cement paste fraction. In general, the fresh concrete formula contains 6–16% by volume of cement, 12–20% of water, 20–30% of fine aggregates and 40–55% of coarse aggregates. During hardening, chemical hydration reactions between cement and water will produce hardened cement that binds the aggregates together. Generally, coarse aggregates are crushed rocks or gravel obtained from local sources (Domone and Illston, 2010). While these components could be inert in mineral carbonation, there are reports in the literature indicating that during several mechanical stages in the concrete recycling process, the amount of mortar attached to the coarse aggregates is reduced. In this case, the cement paste would accumulate in the fine fraction of the concrete (De Juan and Gutiérrez, 2009; Gokce et al., 2011; Silva et al., 2014).

Therefore, in this study, the coarse aggregates were separated by crushing and sieving the samples prior to carbonation. The crushing was performed by adjusting the operating distance of the jaw crusher (C-RC-335). Then, separation was conducted using two sieves in succession. The first sieve contained a 2-mm mesh that allowed the separation of the coarse aggregates. The second sieve, composed of a 500-μm mesh, further separated the fine fraction of the concrete. The fine fraction was then tested with and without grinding to compare the level of reactivity. The grinding was conducted using a vibratory disc mill (Retsch RS200).

The third part of the study consisted of conducting tests to estimate the enhancement of the material reactivity. This was accomplished by bringing the same slurry in contact with successive batches of gas (of 10 min). The first method involved applying successive batches of gas without renewing the water. The second method involved renewing the liquid phase after each batch of gas was applied, while the third method included both water renewal and grinding the material between successive applications of gas.

2.2. Material

The waste concrete samples were recovered from an eco-center located in Québec City. Two batches of concrete were selected and used in the study. The first batch (Concrete 1) was used for the Box-Benkhen runs, and the second batch (Concrete 2) was used for the concrete separation. After the samples were grinded, they were analyzed for their chemical composition. In addition, a portion of the samples for analyzed for their mineralogical composition using X-ray powder diffraction (XRD).

Table 2 shows the chemical composition of the different concrete fractions. The results indicate that the samples are rich in CaO. The samples contained in Concrete 1, total Concrete 2 (TC) and the fine concrete fraction (FC) were analyzed for their mineralogical composition using XRD (Siemens D5000 X-Ray Diffractometer with copper anode X-ray tube) (2θ between 0 and 65). The results are shown in Fig. 2. For each of the two batches of concrete, the dominant mineral phases included calcite, quartz and other natural minerals, such as albite and microcline, which were likely derived from the aggregates contained in the concrete structure. Unfortunately, the C-S-H phases generally present in the composition of the concrete were not observed; this is probably due to their amorphous nature.

Table 2
Chemical composition of the samples.

	CaO (%)	FeO (%)	MgO (%)	SiO_2 (%)	Al_2O_3 (%)	LOI (%)	Ct (%)	Weight (%)
Concrete 1	26.77	2.1	0.63	45.2	8.1	17.2	4.00	
Total concrete 2 (TC)	29.22	1.69	2.11	37.95	6.35	27.62	4.75	100
Coarse aggregates (CA) (>2 mm)	38.42	1.17	1.29	20.66	2.65	35.63	7.8	62.63
Fine aggregates (FA) (2 mm > FA> 500 μm)	29.33	1.41	1.55	38.43	6.52	25.4	5.57	30.01
Fine concrete fraction (FC) (<500 μm)	30.84	2.08	2.02	40.54	8.29	17.29	3.04	6.14

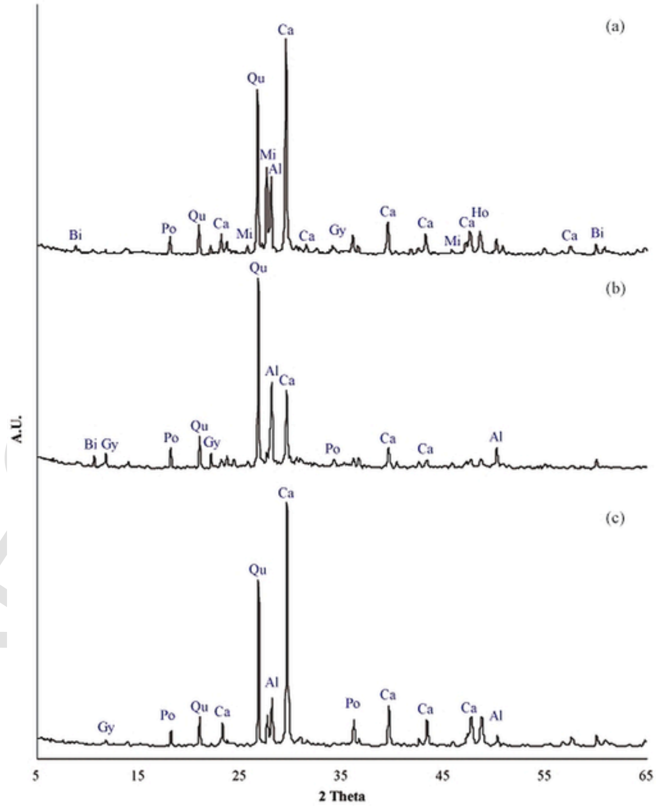

Fig. 2. XRD pattern of (a) concrete (Batch 1), (b) concrete powder and (c) total concrete (Batch 2) consisting of Bi (Biotite), Gy (Gypsum), Po (Portlandite), Qu (Quartz), Al (Albite), Mi (Microcline), Ca (Calcite) and Ho (Hornblende).

2.3. Calculations

The formula used in this study is the same as that used in our previous work (Ben Ghacham et al., 2015):

- CO_2 removal (%)

As the composition of CO_2 in the gas before and after the reaction is known, the percentage of CO_2 removed is calculated as follows:

$$\% \ CO_2 \text{ removal} = \frac{mass\ CO_{2(i)} - mass\ CO_{2(f)}}{mass\ CO_{2(i)}} * 100 \tag{3}$$

The mass of CO_2 in the gas is calculated using the ideal gas law.

- Calcium initially present as calcium carbonate in raw samples (g)

$$\text{Initial carbonated calcium mass} = n\ Cinorg\,(i) * M\ Ca \tag{4}$$

$$\text{With the number of moles C inorg} = \left(\left(\frac{\%\ Cinorg\,(i) * sample\ mass}{100}\right) / MCi\right)$$

% C inorg (i): percentage of initial inorganic carbon present in the raw sample that was analyzed with CHNS

M: molar mass (g/mol)

- Mass of CO_2 converted into carbonate (g)

$$\text{Converted } CO_2 \text{ mass} = \left(\frac{C\ inorg\ formed\ mass}{M\ C}\right) * M\ CO_2 \tag{5}$$

- Theoretical carbonation capacity (g CO_2/g sample)

$$\text{Theoretical carbonation capacity} = \left(\frac{calcium\ mass\ per\ g\ of\ sample}{MCa}\right) * MCO_2 \tag{6}$$

This calculation excluded calcium that was initially carbonated for concrete samples.

- Carbonation efficiency:

$$\%\ \text{Efficiency} = \frac{\left(CO_2\ converted\ mass / sample\ mass\right) * 100}{Theoretical\ carbonation\ capacity}$$

- Mass calcium converted into carbonate (g)

$$\text{converted calcium mass} = n\,(Cinorg\ converted) * M\ Ca \tag{8}$$

3. Results and discussion

3.1. Box-Benkhen statistical analysis

Table 3 shows the experiment matrix and response in terms of the amount CO_2 removed/sample obtained. The best response (0.078 g CO_2 removed/g sample) was obtained using the following parameters: 20 min of reaction time, 280 psi (19.30 Bar) of total gas pressure, a L/S ratio of 10:1 and a G/L ratio of 2:1. Conversely, the lowest response (0.010 g of CO_2 removed/g of sample) was obtained using the following parameters: 20 min of reaction time, 100 psi (6.89 Bar) of total gas pressure, a L/S ratio of 2.5:1 and a G/L ratio of 1:1. The differences between these results show that increasing the gas pressure, L/S and G/L ratios had a positive effect on the amount of CO_2 removed/sample (g/g).

Table 3
Design matrix for the experimental factors.

Run	Time (min)	Pressure (psi)	L/S (w/w)	G/L (v/v)	Response: CO_2 removed/sample (w/w)
1	20 (0)	120 (−1)	10 (+1)	2	0.044
2	20 (0)	200 (0)	2.5 (−1)	3	0.031
3	20 (0)	280 (+1)	4 (0)	3	0.038
4	20 (0)	120 (−1)	4 (0)	1	0.012
5	20 (0)	200 (0)	4 (0)	2	0.029
6	10 (−1)	120 (−1)	4 (0)	2	0.020
7	10 (−1)	200 (0)	4 (0)	3	0.033
8	20 (0)	200 (0)	10 (+1)	1	0.042
9	20 (0)	280 (+1)	2.5 (−1)	2	0.027
10	10 (−1)	280 (+1)	4 (0)	2	0.034
11	30 (+1)	200 (0)	2.5 (−1)	2	0.021
12	20 (0)	200 (0)	4 (0)	2	0.027
13	20 (0)	200 (0)	4 (0)	2	0.040
14	20 (0)	200 (0)	10 (+1)	3	0.056
15	20 (0)	120 (−1)	2.5 (−1)	2	0.012
16	10 (−1)	200 (0)	10 (+1)	2	0.058
17	20 (0)	120 (−1)	4 (0)	3	0.039
18	10 (−1)	200 (0)	2.5 (−1)	2	0.023
19	20 (0)	280 (+1)	10 (+1)	2	0.078
20	30 (+1)	120 (−1)	4 (0)	2	0.022
21	10 (−1)	200 (0)	4 (0)	1	0.021
22	30 (+1)	200 (0)	10 (+1)	2	0.057
23	20 (0)	200 (0)	2.5 (−1)	1	0.010
24	30 (+1)	200 (0)	4 (0)	3	0.043
25	20 (0)	280 (+1)	4 (0)	1	0.026
26	30 (+1)	280 (+1)	4 (0)	2	0.041
27	20 (0)	200 (0)	4 (0)	2	0.038
28	20 (0)	200 (0)	4 (0)	2	0.039
29	30 (+1)	200 (0)	4 (0)	1	0.017

The statistical analysis obtained using ANOVA (Table 4) indicated that gas pressure and the L/S and G/L ratios were significant factors. Fig. 3 illustrates the positive effect of gas pressure and the L/S and G/L ratios on the amount of CO_2 removed/sample. According to Henry's law, the partial pressure of CO_2 would increase the dissolution of CO_2 in the aqueous phase, thereby increasing the reaction efficiency. In addition, the response improved with an increase in the L/S ratio within the range tested, while an increase in the slurry dilution increased the dissolution and precipitation of the CO_2 per unit of mass of the initial material within the range tested. Indeed, the ratio of 10:1 appears to be the better value, and the enhancement of the G/L ratio increased the reaction efficiency. This observation might be explained by the greater quantity of gas introduced in the reactor. In fact, under the same conditions, in terms of gas pressure and temperature, an increase in the volume of gas would likely improve the dissolution of the gas and therefore the reaction efficiency.

To yield the maximum amount of CO_2 removed/sample, the parameters were optimized by increasing the response and decreasing the gas pressure. As such, the optimized reaction conditions proposed by the software were: reaction duration of 10 min, total gas pressure of 144 psi (10.68 Bar), L/S ratio of 10:1 and G/L ratio of 2.43:1. The predicted response was: 0.042 CO_2 removed/sample (w/w). The result of the experiment was 0.037 CO_2 removed/sample (w/w) (corresponding to 0.031 g CO_2 converted/sample).

Geochemical simulations were conducted using the PHREEQC software to predict the potentially precipitated phases under these conditions. Due to the lack of data concerning the molar ratio of the mineral phases present in the concrete, a molar ratio range of 0.002–0.007 was selected for both C-S-H 1.6 ($Ca_{1.6}SiO_{3.6}$: $2.58H_2O$) and ($Ca(OH)_2$), representing the cementitious reactive phases. Simulation results using portlandite ($Ca(OH)_2$) as the main mineral phase indicated that the potentially precipitated phases are mainly calcite

Table 4
ANOVA results for Response Surface Quadratic model.

Source	Degree of freedom	Sum of square	F value	p-value Pr > F	Conclusion
Model	14	0.005	20.85	5.64 E−07	significant
A- Time	1	5.22E-05	2.89	0.11	not significant
B- Pressure	1	0.0007	40.03	1.97E-5	significant
C- L/S	1	0.0029	163.92	4.05E-09	significant
D- G/L	1	0.00091	50.46	5.31E-06	significant
AB	1	1.03E-05	0.57	0.46	not significant
AC	1	3.23E-05	1.79	0.20	not significant
AD	1	7.08E-05	3.03	0.067	not significant
BC	1	1.64E-05	0.91	0.35	not significant
BD	1	7.63E-06	0.42	0.52	not significant
DC	1	3.84E-06	0.21	0.65	not significant
Aˆ2	1	3.06E-05	1.69	0.21	not significant
Bˆ2	1	5.08E-05	2.81	0.11	not significant
Cˆ2	1	0.00015	8.53	0.001	significant
Dˆ2	1	0.00018	9.96	0.007	not significant
Residual	14	0.000252			
Lack of Fit	10	0.0001	0.28	0.95	not significant
Pure Error	4	0.000148			
Cor Total	28	0.0055			

$\mathbf{R}^2$ = 0.95; predicted $\mathbf{R}^2$ = 0.85; adjusted $\mathbf{R}^2$ = 0.91; adequation precision = 17.50.

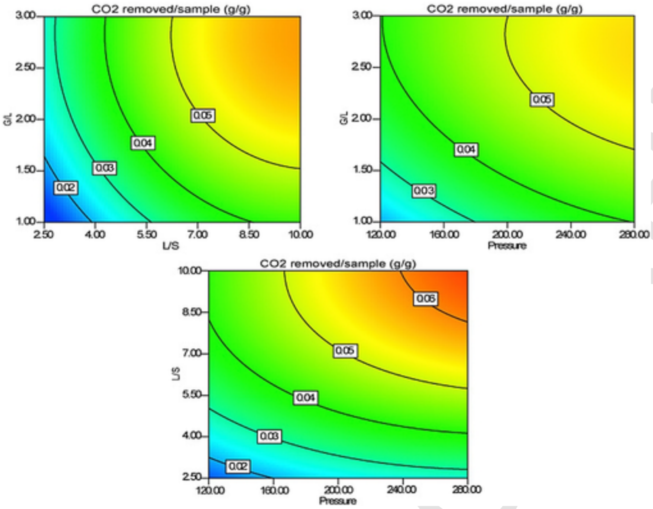

Fig. 3. Effects of different factors on the response CO_2 removed/sample using a response surface contour plot.

and aragonite with saturation indices (SIs) of between 0.94-3.21 and 0.77–3.07, respectively. For simulations conducted with C-S-H, calcite, aragonite and $CaCO_3.H_2O$ (s) were the favored forms to precipitate thermodynamically (with SIs between 1.64 and 3.99 for calcite and 1.47–3.8 for aragonite).

XRD analysis of the reaction residue was completed. However, because the calcite signature was initially high in the raw material, the enhancement of the peak intensity was not clearly observed from the reacted residue. To obtain more relevant data, a thermal analysis (TGA) of the solid material was completed before and after the reaction, the results of which are presented in the Fig. 4. The results showed a different trend for the samples in terms of weight loss (%). The data interpretation, based on Lee et al. (2009), summarizes the temperature ranges that correspond to the amount thermal decomposition from the different mineral phases present in the hydrated cement paste. Fig. 4 highlights the differences between the reacted and unreacted samples. The level of dehydration in phases of C-S-H and calcium hydroxide is higher in raw concrete. However, it may be that the decomposition curve between 640 and 830 °C is greater for the carbonated sample. Indeed, Lee et al. (2009) found that the peak temperature for $CaCO_3$ decomposition is in the range of 640–800 °C, while Bye (1999) noted that the peak temperature for calcite decomposition is between 802 and 882.85 °C. In light of these observations, the weight loss (%) between 640 °C and 830 °C for the reacted sample could be related to the $CaCO_3$ decomposition, which corresponds to both the $CaCO_3$ initially present in the raw concrete and that was formed during the mineral carbonation reaction of the concrete. The resulting mass loss from the carbonated residue (corresponding to the calcium carbonate decomposition) is 2.64%, which represents 0.0264 g of CO_2 when converted into carbonates/g sample. The difference compared the carbon analysis using CHNS could be attributed to the sum of experimental errors and analysis sensitivity.

These results suggest that the C-S-H and portlandite ($Ca(OH)_2$) phases present in the initial material reacted during the MC and were thus transformed into calcium carbonate.

3.2. Concrete separation and reactivity of the fine fraction of concrete in mineral carbonation

In this section, the fine concrete powder (<500 μm) contained in the concrete matrix was separated according to the steps illustrated in Fig. 5.

Tests were conducted using the following: grinded total concrete (TC), grinded fine concrete fraction (GFC) and non-grinded fine concrete fraction (NGFC). The mean size of TC, NGFC and GFC are 33.31 μm 253.25 μm and 32.60 μm, respectively.

To evaluate the reactivity of the coarse aggregates (CA) in the same experimental conditions, samples of pure CA were selected, crushed and grinded as previously discussed. Tests with only water (DW) were also conducted to represent a blank reaction. Tests were performed under optimal conditions consisting of the following: L/S ratio of 10:1, total gas pressure of 144 psi and a reaction time of 10 min. The results are shown in the Fig. 6.

The GFC material demonstrated the highest amount of CO_2 removed of 74.79% and a CO_2 removed/sample ratio of 0.057. In contrast, the amount of CO_2 removed from the TC and NGFC samples was 54.16% and 59.55%, corresponding to 0.034 and 0.043 g CO_2 removed/g sample, respectively. Finally, CO_2 removed from the CA and DW samples were similar at 34.6% and 27.25%, respectively.

To compare these results, a bivarious analysis coupled with a simple regression was performed following a Tukey-Kramer honest significant difference (HSD) analysis (average-to-average method) using JMP software. This method allows one to compare differences in terms of CO_2 removal and CO_2 converted/sample between all the samples. The results are presented in Tables 5 and 6.

The results from the GFC sample are significantly higher than from the TC samples. The presence of a higher quantity of coarse aggregates per unit mass for the TC has an influence on the material reactivity compared to the fine concrete fraction.

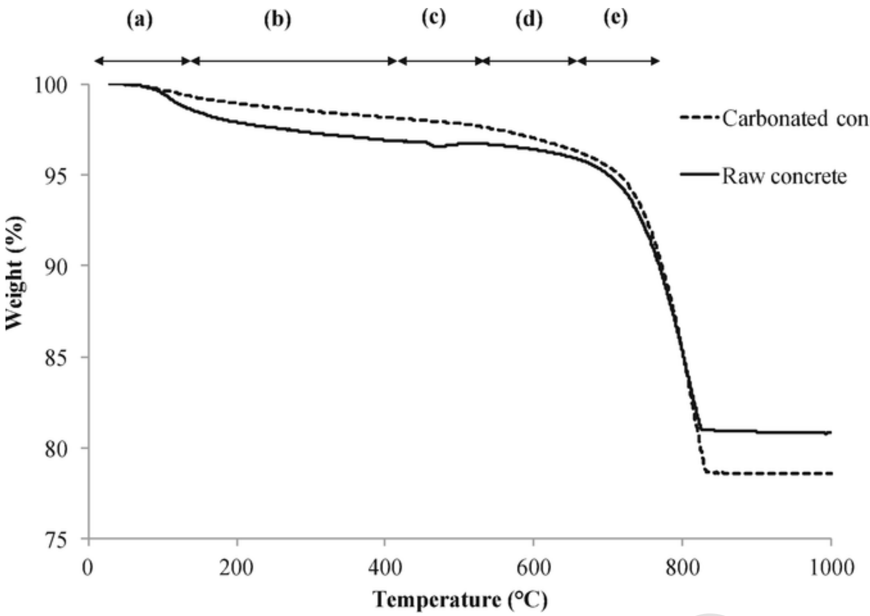

Fig. 4. TGA decomposition data for raw and carbonated concrete. (**(a)** 20–120 °C: evaporation of free water and dehydration of C-S-H and ettringite, **(b)** 230–400 °C: dehydration of C-S-H and dehydration of Calcium Hydroxide, **(c)** 400–530 °C: dehydration of C-S-H and dehydration of Calcium Hydroxide, **(d)** 530–640 °C: dehydration of C-S-H and decomposition of poorly crystallized $CaCO_3$, **(e)** 640–800 °C: dehydration of C-S-H and decomposition of $CaCO_3$).

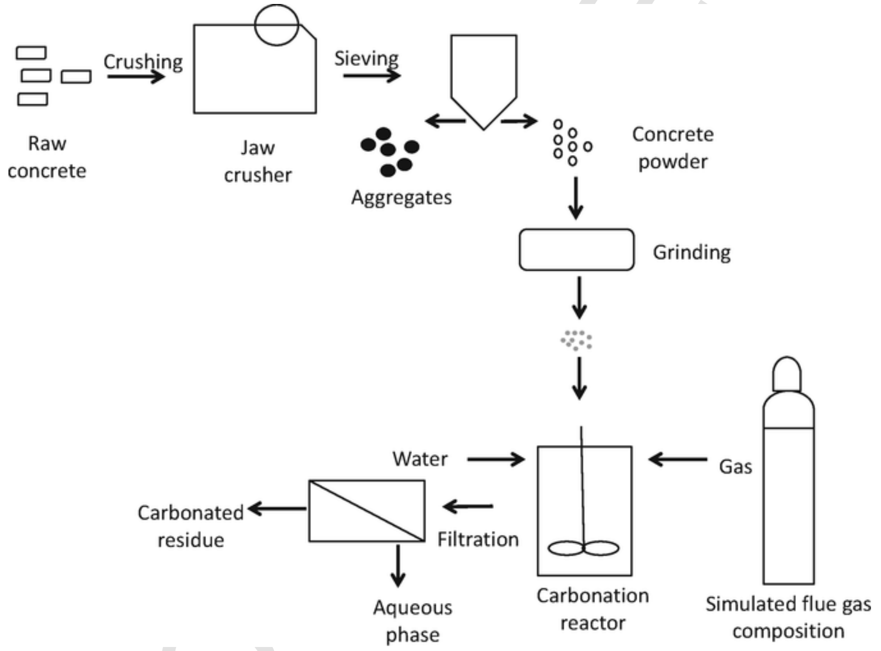

Fig. 5. Concrete separation and carbonation process.

According to the chemical composition, coarse aggregates >2 mm represent 7.8% of the total carbon. On the other hand, in Fig. 2 (b), the peak of calcite present in the TC is higher than in the fine concrete fraction. The difference in the calcite intensity peak (between the total concrete and the finer concrete fraction) and the higher initial carbon content in the coarse aggregates suggests that the coarse aggregates present in the concrete composition have a mostly calcareous nature. Further, the calcium content in the CA is high, but is not reactive for MC, as it is already in a carbonated form. Additionally, the amount of reactive calcium content would be greater in the FC compared to the TC. Therefore, as initially expected, the cement paste is mainly present in the fine concrete fraction. In comparing the NGFC and TC samples, both the amount of CO_2 removed and CO_2 converted/sample are not significantly different. In comparing the GFC and NGFC in terms of CO_2 removed (%), the following p-value was obtained: 0.07 (not significantly different). For the CO_2 converted/sample, a small difference was identified in which a p-value of 0.05 was obtained. From these data, it is possible to determine the relative differences in their reactivity. This observation may be due to the higher specific area (due to the differences in term of granulome-

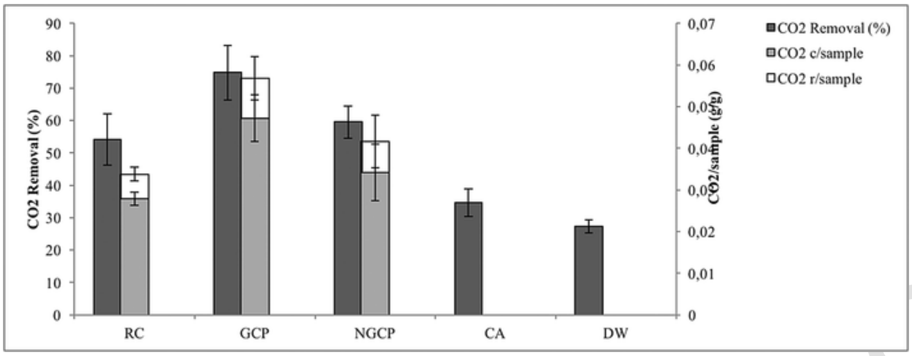

Fig. 6. CO_2 removal with raw concrete, concrete powder, aggregates and distilled water.

Table 5
Statistical comparison based on results of % CO_2 removed.

Material 1	Material 2	P-Value
GFC	DW	<0.001
GFC	CA	<0.001
NGFC	DW	0.0005
TC	DW	0.0020
NGFC	CA	0.0035
GFC	TC	0.0126
TC	CA	0.0176
GFC	NGFC	0.0680
CA	DW	0.5874
NGFC	TC	0.8064

Table 6
Statistical Comparison based on CO_2c/sample.

Material 1	Material 2	P-Value
GFC	TC	0.0089
GFC	NGFC	0.0495
NGFC	TC	0.3505

try) present in the GFC compared to NGFC, which influences the dissolution of the reactive elements (calcium essentially). In summary, the GFC presented a higher level of reactivity compared to other samples, except compared to the NGFC. In addition, a conversion ratio of 0.047 CO_2 converted/sample obtained with the GFC corresponds to a 36.15% efficiency rate (based on a theoretical carbonation capacity of 0.13). However, even if the level of reactivity is lower for the NGFC, its use could avoid the grinding process, an energy-intensive step as reported by Huijgen et al. (2006).

3.3. Experiments with successive batches of gas

The results from the application of successive batches of gas to the same slurry are shown in Figs. 7–9. Fig. 7 (a) shows a decrease in CO_2 removed (%) between batch 1 and batch 3, from 71.17% to 14.62%, respectively. The total amount of CO_2 removed from the introduced CO_2 mass (with 3 batches of gas) is 41.5% which corresponds to 0.051 g CO_2 converted/sample (Fig. 7 (b)).

However, for the second and third methods, an increase in CO_2 removal was observed, especially for the third batch (Figs. 8 and 9), including batches in which water was renewed between batches. This outcome is due to further dissolution of the gas in the fresh water. This stands in contrast to the saturation state in the first methodology in which increased dissolution was not possible. In fact, for the amount of CO_2 dissolved/sample, an increase was observed from 0.009 for a simple batch to 0.013 when successive batches of gas were applied without water renewal, to 0.018 when water was renewed, and to 0.027 for the process that involved water renewal and grinding residue.

Globally, the maximum amount of CO_2 removal (%) of 55.57% is obtained using the method of water renewal and residue grinding between successive applications of batches of gas (Fig. 9). This corresponds to 0.054 g CO_2 converted/sample. In these methods, there is a

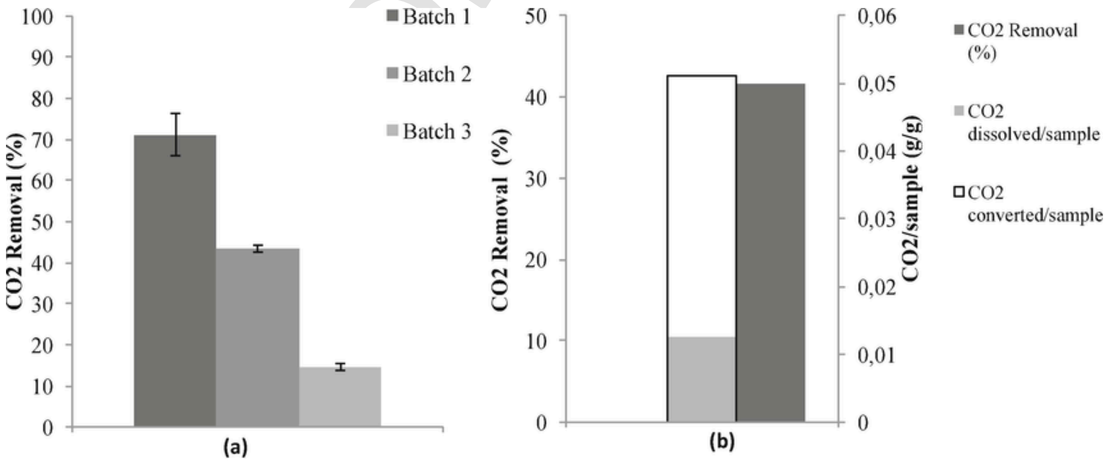

Fig. 7. Experiment results for successive batches of gas without water renewal **(a)** CO_2 Removal (%); **(b)** Total CO_2 Removal (%), CO_2 converted/sample and CO_2 dissolved/sample.

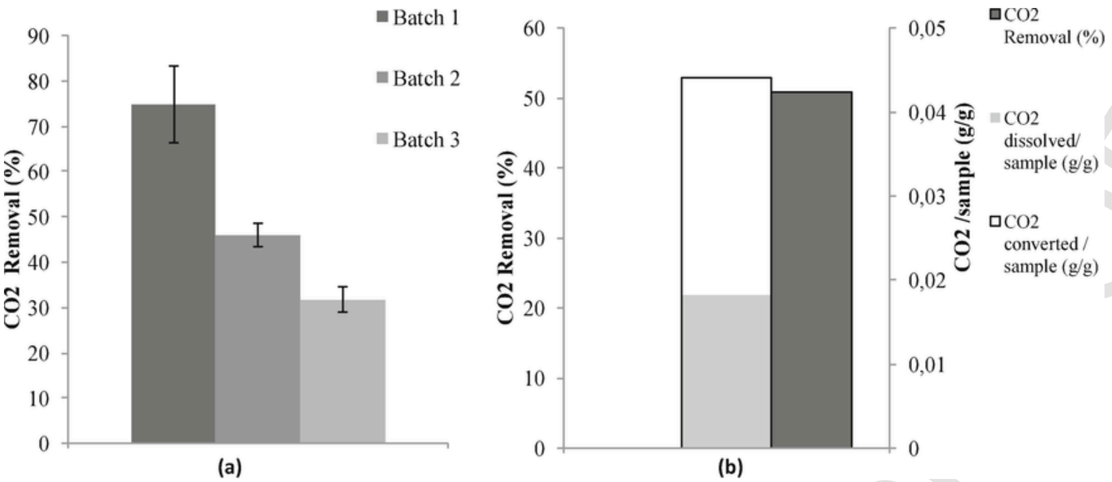

Fig. 8. Experiment results for successive batches with water renewal. **(a)** CO_2 Removal (%); **(b)** Total CO_2 Removal (%), CO_2 converted/sample and CO_2 dissolved/sample.

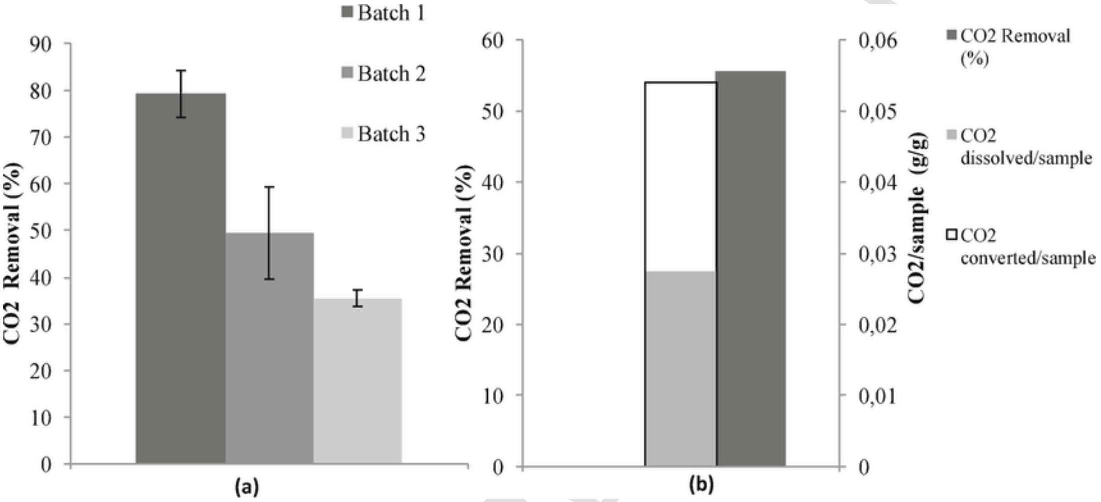

Fig. 9. Experiment results for successive batches of gas with water renewal and material grinding between batches. **(a)** CO_2 Removal (%); **(b)** Total CO_2 Removal (%), CO_2 converted/sample and CO_2 dissolved/sample.

slight overall increase in the amount of CO_2 converted/sample compared to a simple batch.

As considered previously (Table 1), few studies have examined the possibility of using waste concrete as a feedstock material in MC. While Shuto et al. (2015) and Katsuyama et al. (2005) focused on carbonate purity as a result of indirect processes, the sequestration capacity of waste concrete was not discussed. Indeed, the amount of energy required by indirect processes would be more significant compared to a simple and direct process.

However, Mun and Cho (2013) were able to obtain 0.06 g CO_2/g waste cement from an indirect process that included the use of chemical additives (EDTA and acetic acid) as well as pure CO_2 over the course of 2 h. Therefore, the present result shows a comparable sequestration rate of 0.047 g CO_2 converted/g sample achieved using the grinded fine fraction of concrete after a reaction time of 10 min using a simple batch. Additionally, a rate of 0.051 g CO_2 converted/g sample resulted when applying three successive batches of gas. Therefore, this study demonstrates that it is possible to obtain a relatively significant sequestration rate by using a direct process and flue gas composition.

Moreover, the process involving the separation of coarse aggregates from the fine fraction of concrete represents two advantages. First, the fine fraction contains more cement paste in its composition, which would cause increased reactivity during MC. Second, the process allows for the recovery of coarse aggregates, which helps limit the amount of natural aggregate that must be extracted for new concrete. According to previous research, this has significant benefits because the process of extracting and crushing natural aggregates requires a large amount of energy and is responsible of increased CO_2 emissions (Gokce et al., 2011).

4. Conclusion

In the first section of this study, an experimental design using the Box-Benkhen methodology demonstrated that increasing the total gas pressure, the G/L and the L/S ratios improved the efficiency of MC. In the second section, the separation of the larger-sized aggregates present in the concrete matrix enhanced the reactivity of the material, in particular with the smaller particles obtained after grinding. Moreover, the NGFC showed good results and could also be used as feedstock material in MC, eliminating the grinding step. In overall, 75%

of the CO2 contacted with the fine concrete fraction is removed from the gas phase within 10 min at ambient temperature and 144 PSI (9.93 Bars). It corresponds to a conversion of 0.057gCO2 per g of concrete.

Besides increasing the carbonation efficiency, the proposed methodology is integrated into the actual practice regarding concrete recycling. Thus, the process allows removing the coarse aggregates present in the concrete. This material could be easily reused in construction. While the environmental benefit is increased, only the reactive fraction is used in MC, decreasing the mass of solid material transported. Nevertheless, the low sequestration potential of waste concrete remains a potential major barrier for an application, and a more detailed technical and economic study should be performed.

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