

CO₂ Uptake of Cement Exposed to As-Captured Flue Gas

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Abstract: Carbonation curing of Portland cement and cement bonded cellulose fiberboard in a cement kiln flue gas was studied. The purpose was to examine if the as-captured flue gas without carbon separation can be used to accelerate the hydration of cement at the same time to sequester carbon dioxide from flue gas. A multiple injection process was developed to incorporate a gas of low CO₂ concentration. The process took place in a chamber under a pressure of 0.5 MPa and at an ambient temperature. On exposure to a cement kiln flue gas of 13% CO₂ concentration for five hours, the cement compacts could uptake 6.8% carbon dioxide by weight of cement and gain a compressive strength of 7.4 MPa; while for cement fiberboard, they were 7.0% and 10.2 MPa respectively. Their microstructure development was examined and compared with carbonation in pure gas.

1. Introduction

Portland cement has the ability to convert carbon dioxide to a stable calcium carbonate. At full conversion, cement can uptake 50% CO₂ [1]. This carbonation process can take place in hardened concrete and will reduce pH of pore solution, eventually leading to a carbonation corrosion of steels in reinforced concrete. Considerable research has been conducted to understand the mechanism of carbonation corrosion and to develop mitigation technologies [2]. However, for applications without reinforcing steel, early age carbonation curing makes concrete products perform better in achieving strength, durability and dimensional stability due to the near-complete depletion of calcium hydroxide. The rapid carbonation reaction of calcium silicate binders with carbon dioxide accelerates the hydration and shortens the time required for production [3, 4].

This well-known phenomenon has gained renewed interests recently in global CO₂ sequestration activities. CO₂ sequestration has become an important component in greenhouse gas mitigation exercise. The proposed approaches include the geologic storage in aquifers and depleted oil wells, and the mineral sequestration using magnesium silicates [5]. Compared to those approaches, carbonation process of Portland cement based building products can integrate CO₂ sequestration into a commercial concrete production and demonstrate environmental,

technical and economical benefits. Moreover, carbonation of cement can directly use the as-captured flue gas without separation, leading to a tremendous energy savings since the cost for capturing and separating CO₂ from flue gas can be as high as up to \$45 per ton of carbon dioxide.

This paper is to present a study on an early age carbonation curing of cement compacts as well as cement bonded cellulose fiberboards in an as-captured cement kiln flue gas without separation. Their carbon uptake, strength gain and microstructure development in a process of five hours were examined. Parallel study was carried out with pure carbon dioxide to investigate the effect of CO₂ concentration on performance of carbonated products.

2. Experimental Procedure

Type 10 CSA Portland cement was used with composition of CaO=63.1%, SiO₂=19.8%, Al₂O₃=4.9%, MgO=2%, blaine number = 373 m²/kg, and initial CO₂ content = 0.54%. Cellulose fibers were craft fibers with diameter of about 30 microns, length of 3 mm and density of 1.5, for a cellulose fiberboard (CFB) of a fiber weight ratio (W_f) of 12%. Both paste and CFB plate specimens (127 x 76 x 13 mm) were press-formed at a compact pressure of 0.7 MPa with water to cement ratio (w/c) of 0.15 for paste and 0.25 for CFB. The sample preparation of CFB was a simulated Hatschek process which employed slurry and dewatering method to disperse fibers. The compacts were then placed in a pressure vessel right after their compact forming for a carbonation curing at a gas pressure of 0.5 MPa and an ambient temperature. Compressive strength tests were performed immediately after 5 hours carbonation as well as 28 days after subsequent hydration in a sealed plastic bag to determine the short term and long term strength (f_c). Cement compacts and fiberboard compacts cured in sealed plastic bags without carbonation were also tested at 5 hours and 28 days as hydration reference. For comparison, two-hour carbonation curing of compacts in pure gas (99% purity) was conducted. For each batch, three plate samples were carbonated. After 3-point flexural tests, the plates broke into two halves; three one-half samples were tested immediately after carbonation and the other three were tested after 28 days subsequent hydration in plastic bags. Material compositions and process parameters are shown in Table 1.

Table 1: Material compositions and process parameters

Batch	Product	CO ₂ concentration	W/C	W_f (%)	Time (hour)	Cycle
B1	Paste	13%	0.15	0	5	7
B2	CFB	13%	0.25	12	5	7
B3	Paste	99%	0.15	0	2	1
B4	CFB	99%	0.25	12	2	1

The carbonation curing set-up is shown in Figure 1. Two types of carbon dioxide gases were used: a cement kiln flue gas with 13% CO₂ concentration and a pure gas with a purity of 99%. A pressure vessel of 5.5-litre in volume was equipped with a pressure transducer to record the pressure drop over time and with a type-T thermocouple to measure the reaction temperature in cement. A carbon dioxide meter was used to measure the CO₂ concentration at the time when the gas was injected and at the time when it's released. The pressure vessel was placed on an electrical scale and the mass change of the closed-loop system was measured. The pressure, temperature and mass curves were recorded by a data acquisition system (Measurement Groups Inc.).

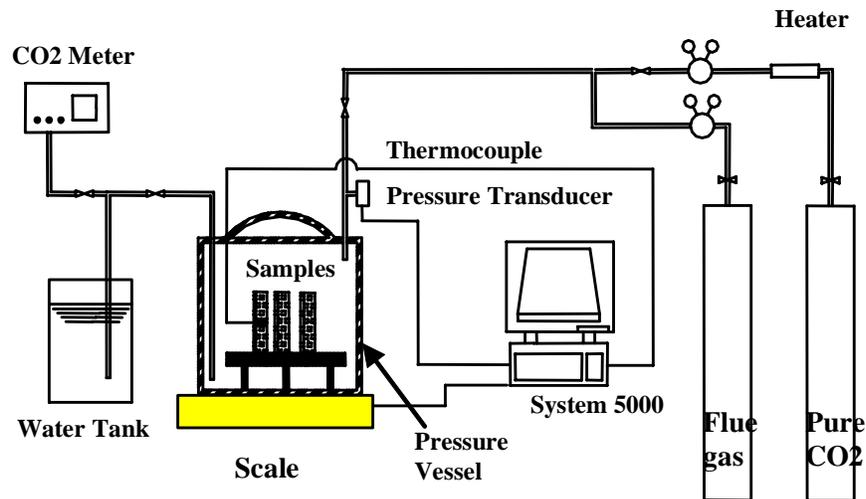


Figure 1: Setup for carbonation curing

Because of the low CO₂ concentration in flue gas, a multiple injection – release process was developed to promote maximum CO₂ uptake in 5 hours. The process was divided into 7 periods, each taking 35, 45, 35, 45, 35, 45 and 35 minutes respectively. In each period, the flue gas was injected to a pressure of 0.5 MPa, the concentration was measured and the gas supply valve was then closed. After the designated time of each period, the gas was released and the CO₂ concentration was measured again. The cycle was repeated for each period for total of 7 cycles in 5 hours. For comparison, pure gas carbonation was also conducted using identical compacts. It was done in the chamber at a gas pressure of 0.5 MPa for 2 hours continuous carbonation at a constant pressure such that carbon dioxide is frequently replenished.

CO₂ uptake is characterized as percent mass gain which was obtained based on the difference between the mass measured before carbonation and the mass after carbonation, taking dry cement binder as reference:

$$\% \text{Mass gain} = \frac{(Mass)_{aft,CO_2} - (Mass)_{bef,CO_2} + (Mass)_{lost\ water}}{(Mass)_{dry\ binder}} \quad (1)$$

Water evaporation due to exothermic reaction was observed. The evaporated water was condensed on the wall of vessel and collected by an absorbent paper after the curing. The collected water was added to the initial mass in Eq (1). The percent mass gain was also verified using an infrared based CO₂ analyzer (Eltra SC800). The analyzer comprises an induction oven allowing the thermal decomposition of carbonates at 1000°C and an infrared sensor quantifying the fused carbon.

3. Results and Discussion

3.1 Carbon uptake and strength gain

Typical pressure and temperature curves of cement paste compacts exposed to flue gas in a multiple injection and release process are shown in Figure 2. The pressure drop was indicative of CO₂ uptake. It was clear that cement was still carbon reactive in the end of 5-hour carbonation process. The maximum reaction temperature was about 40 °C. The pressure and temperature curves of same cement compacts carbonated in pure gas are shown in Figure 3. While pressure was maintained constant, temperature rise was rapid with the peak of 95 °C reached in 10 minutes and temperature drop was also steep, indicating the slowdown of the reaction.

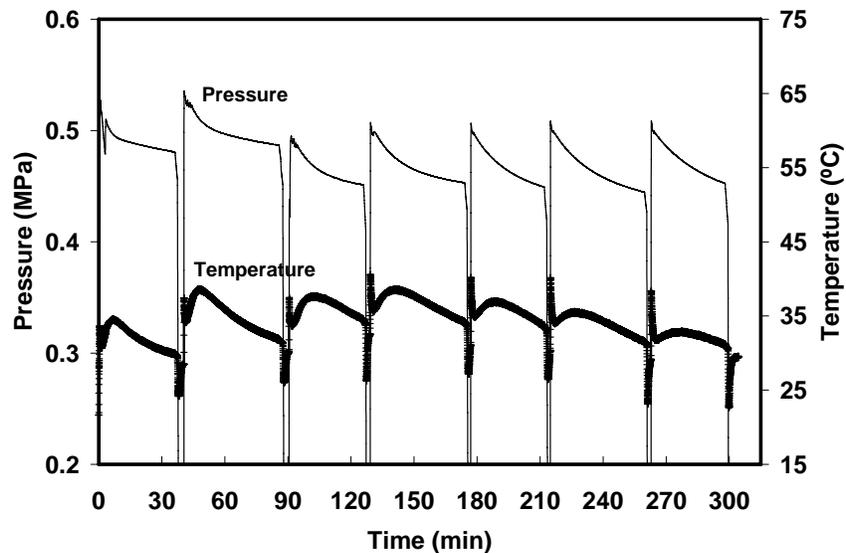


Figure 2: Pressure (P) and Temperature (T) curves of cement in flue gas

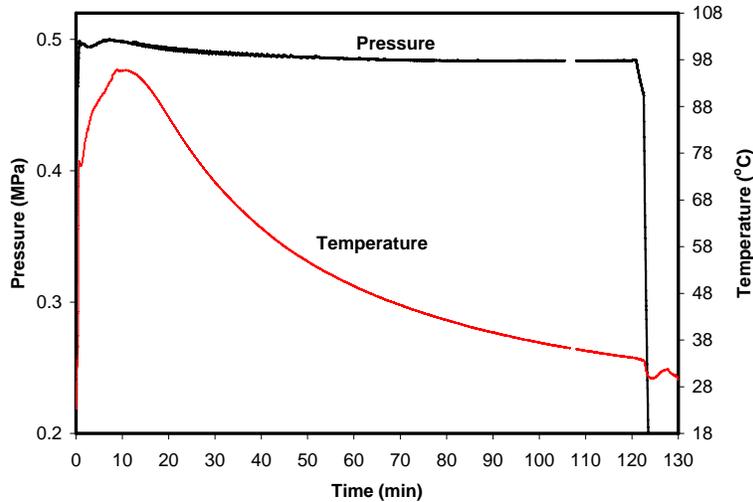


Figure 3: Pressure (P) and Temperature (T) curves of cement in pure CO₂

Experimental results are summarized in Table 2. B1 and B2 are carbonated in flue gas, and B3 and B4 in pure gas. Mass gain calculated by Eq. (1) shows flue gas carbonation in 5 hours takes only half of the carbon as pure gas does in 2 hours, while the corresponding water loss in flue gas carbonation was about a quarter of pure gas. This suggests that reaction of cement with flue gas was slower. It was possibly attributed to the lack of carbon dioxide in the gas and the interference of non-CO₂ gas components. However the strength gain immediately after the carbonation in different concentration was in the same order of magnitude. Cement compacts gained 7.4 MPa in 5 hours flue gas and 8.1 MPa in 2 hours pure gas. Similarly cellulose fiberboard obtained 10.2 MPa after 5 hours in flue gas and 10.5 MPa after 2 hours in pure gas. In other words, flue gas carbonation can achieve the same strength gain as pure gas, regardless of its lower carbon uptake.

Table 2: Experimental results on carbon uptake and strength gain

Batch	Product	Mass Gain, %	Water Loss, %	Carbonation Strength (MPa)		Hydration strength (MPa)	
				2hr/5hr	28-day	5-hr	28-day
B1	Paste	6.8	13.5	7.4(5h)	11.0	0.4	10.2
B2	CFB	7.0	14.7	10.2(5h)	15.7	3.1	15.6
B3	Paste	13.5	55.5	8.1(2h)	8.4	0.4	10.2
B4	CFB	18.9	59.5	10.5(2h)	12.0	3.1	15.6

Strengths of specimens hydrated 5 hours in sealed bags were also tested to investigate the contribution of carbonation to the early age strength.

They are also summarized in Table 2. The 5-hour hydration strengths were mainly generated by compaction. If this strength is subtracted from carbonation strengths, it is clear that the contribution to the strength gain by carbonation is about 7 MPa in both 5 hours flue gas carbonation and 2 hours pure gas carbonation. The 28-day strengths of carbonated specimens as well as hydrated references are also shown in Table 2. Apparently specimens carbonated in flue gas gained more strength in subsequent hydration than those in pure gas. This was because flue gas carbonation created much less water evaporation than pure gas, leaving more water for subsequent hydration and leading to a 28-day strength comparable to reference hydration strength. The rapid reaction by pure gas promoted more carbon uptake, created higher water loss, and eventually resulted in a lower 28-day strength.

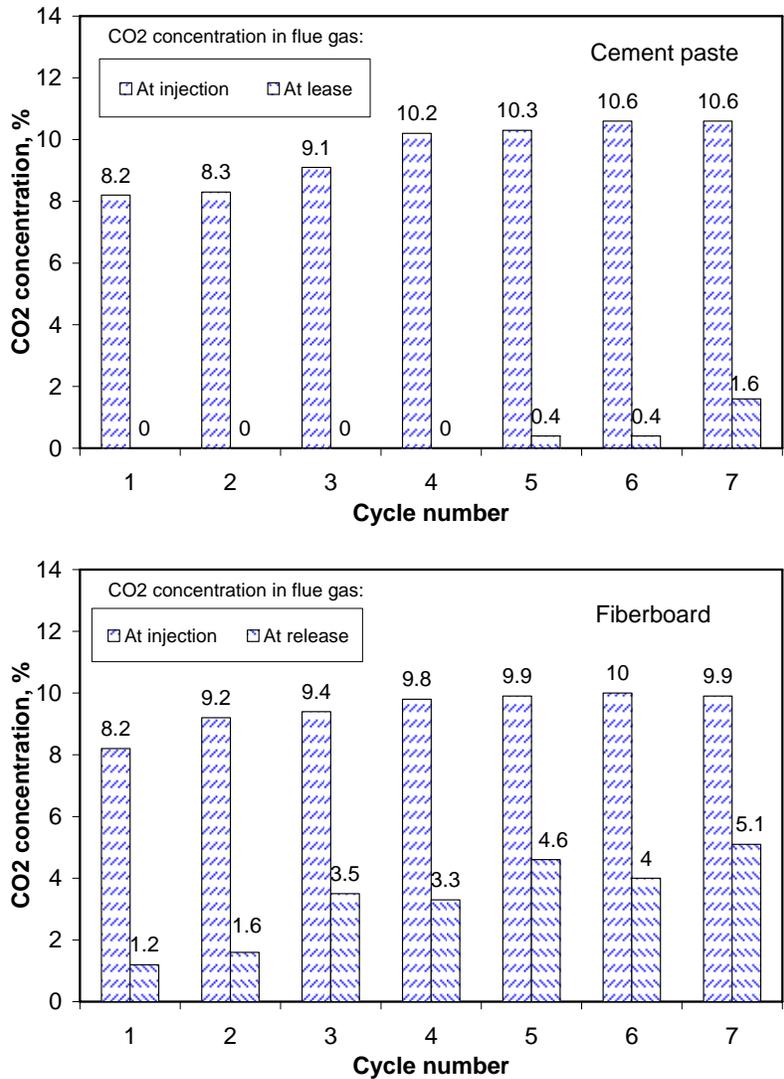


Figure 4: CO₂ concentration change in flue gas

Figure 4 compares CO₂ concentration of the flue gas at injection and at release for each designated cycle. The concentration change indicates the CO₂ uptake. For cement paste, the CO₂ concentration of the released gas was zero in first four cycles and was reduced by 85% in the end of 5 hours process. It implies that cement paste has the capacity to absorb all the carbon dioxide in flue gas in two hours. For fiberboard, although the efficiency was not as high, it still sequestered 85% CO₂ in first cycle to 52% in the last cycle. Clearly the uptake is dependent on the cement content in the products and the CO₂ concentration in gas. In this process, cement based products have served as carbon dioxide filter, making the released gas much cleaner.

The concentration change can be used to quantify the mass of CO₂ taken by cement in each cycle based on ideal gas law:

$$m_{CO_2} = \frac{44V}{R} \left(\frac{P_i C_{CO_2,i}}{T_i} - \frac{P_f C_{CO_2,f}}{T_f} \right) \quad (2)$$

The same ideal gas law can also be used to estimate the amount of CO₂ taken by cement according to the pressure drop, using the pressure curve shown in Figure 1:

$$m_{CO_2} = \frac{44V}{R} \left(\frac{P_i}{T_i} - \frac{P_f}{T_f} \right) \quad (3)$$

In Eqs. (2) and (3), V=volume of the gas (=5.25 liter), R=gas constant (=0.082 atm liter/(mol K)), P=gas pressure (atm), C_{CO₂}=CO₂ concentration in gas, T=gas temperature (K), i=initial value at injection in each cycle, f=final value at release in each cycle.

Table 3: Comparison of CO₂ uptake from flue gas by different methods

Product	Uptake Eq(1) (%)	Uptake Eq(2) (%)	Uptake Eq(3) (%)	Uptake mass curve (%)	Uptake IR, % surface	Uptake IR,% core	Uptake IR,% ave.
Paste	6.8	6.4	5.1	6.7	8.7	3.7	6.2
CFB	7.0	6.3	6.2	6.9	10.2	3.7	6.9

CO₂ uptakes from flue gas by cement paste and fiberboard determined by different methods are summarized in Table 3. Uptake due to mass gain by Eq (1) serves as reference. Cumulative CO₂ uptake based on reduction in CO₂ concentration (Eq. 2) and based on pressure drop (Eq. 3) are slightly lower than that by direct mass gain, but in the order of magnitude. CO₂

content was also detected using infrared (IR) based carbon analyzer, which is a point based analysis. The results are also compared in Table 3. Surfaces of samples were more carbonated than the cores in flue gas carbonation. Nevertheless their averages are surprisingly close to the mass gain by Eq. (1).

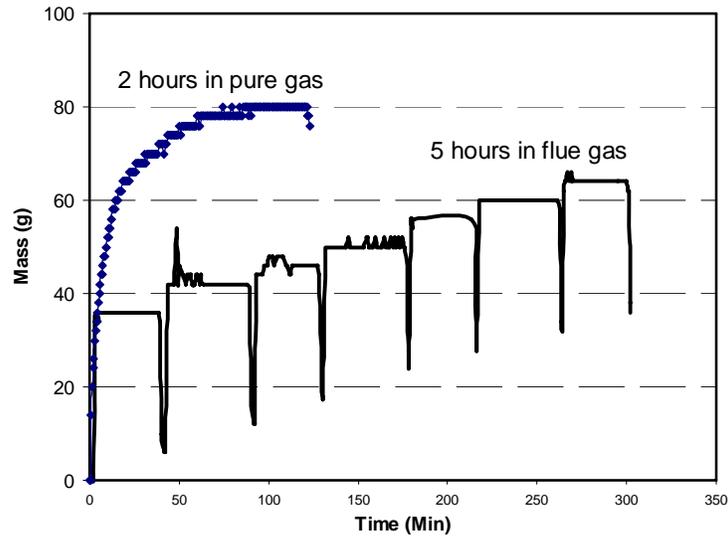


Figure 5: Comparison of mass curves of cement pastes

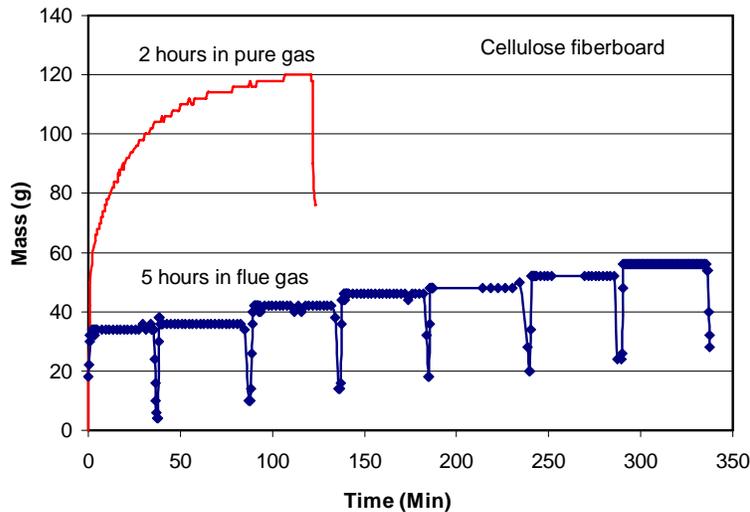


Figure 6: Comparison of mass curves of cellulose fiberboards

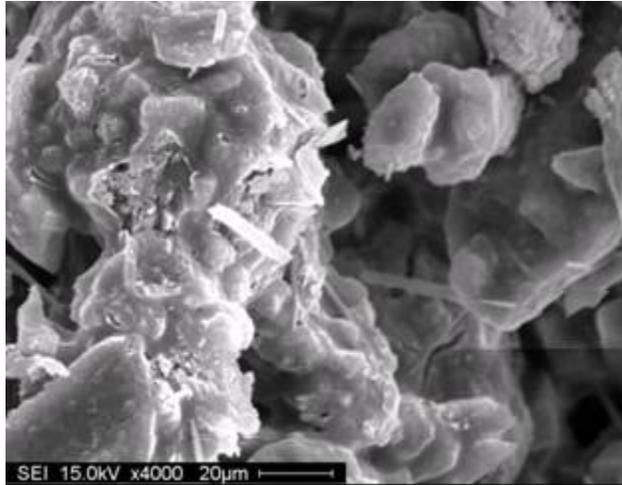
Reactivity of cement with carbon dioxide was also studied through the mass curve which was recorded as a function of time. They are displayed in Figure 5 for cement pastes and in Figure 6 for fiberboards with comparisons of flue gas with pure gas. The residual mass corresponding

to the last point of each curve represents the mass of carbon dioxide taken by the samples in a closed loop system. They are 36 g for cement paste in flue gas, 77 g for cement paste in pure gas, 25 g for fiberboard in flue gas and 78 g for fiberboard in pure gas. These absolute mass increases are based on three plate samples. Their percent uptakes compare very well with weight gain by Eq. (1) in Table 3. The mass curves provide an insight on the kinetics of reaction. In pure gas, 75% reaction was completed in less than 15 minutes and reaction rate was significantly reduced after 60 minutes. In contrary, flue gas reaction was much slower, but more progressive, and showed potential to continue after 5 hours.

3.2 Microstructure of carbonated products

Microstructure of carbonated cement pastes and fiberboards were examined under scanning electron microscope. Figure 7 compares the micrographs of cement pastes hydrated in water, carbonated in flue gas and carbonated in pure gas. Because of the low compact force (0.7 MPa) and low water/cement ratio (0.15), the hydrated cement was porous and had very low strength. Same compacts, carbonated in carbon dioxide, gained however higher strength and more densified structures. It is interesting to note that carbonation products produced in flue gas are much smaller than that in pure gas; the former being composed of grains of sub-microns while the latter composed of crystals of a few microns grown from substrates of sub-microns. This explains how the pure gas carbonation doubled the uptake by flue gas. However the large crystals did not improve the long term strength because of the lack of moisture due to the significant water loss in pure gas reaction. Cement particles were almost totally covered by carbonation products which made diffusion of the gas, and thus its related carbonation, more difficult to proceed after certain time. It was especially significant in pure gas carbonation where a plateau on mass curve was reached at about one hour of reaction and was suggestive of the termination of reaction.

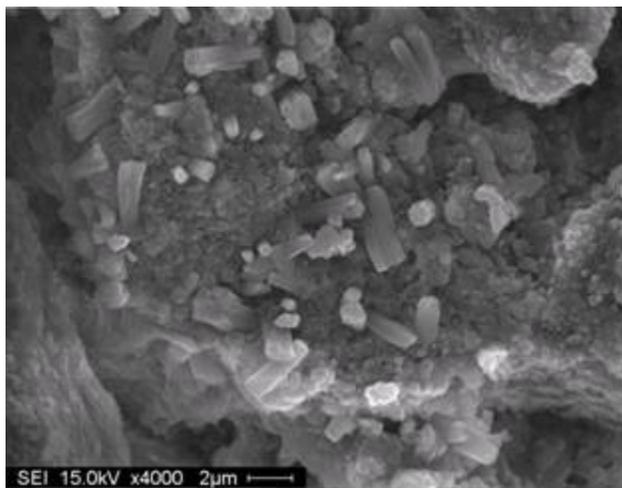
Similar phenomenon was observed in cellulose fiberboard. The comparison is given in Figure 8, with the micrographs taken from fiber surfaces. There was no considerable difference in fiber morphology created by flue gas and pure gas carbonation. The extensive CO₂ uptake in pure gas suggested that the carbonation products on fiber surface could be thicker and denser, and could even penetrated into the hollow fibers, making more deposits inside fibers.



(a) Hydrated cement paste

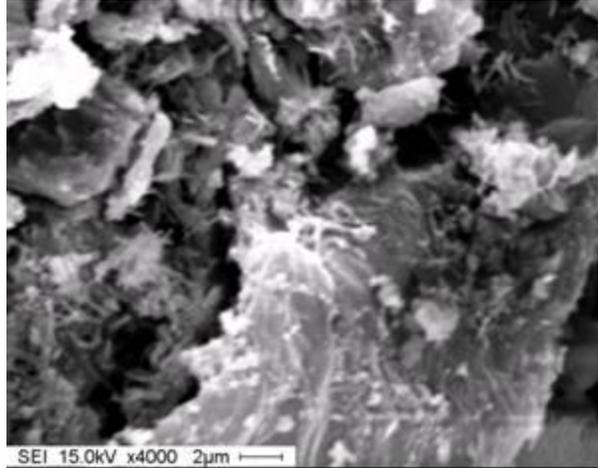


(b) Carbonated cement paste in flue gas

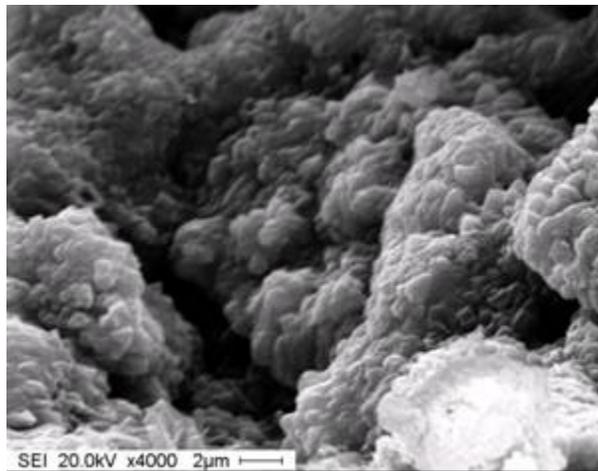


(c) Carbonated cement paste in pure gas

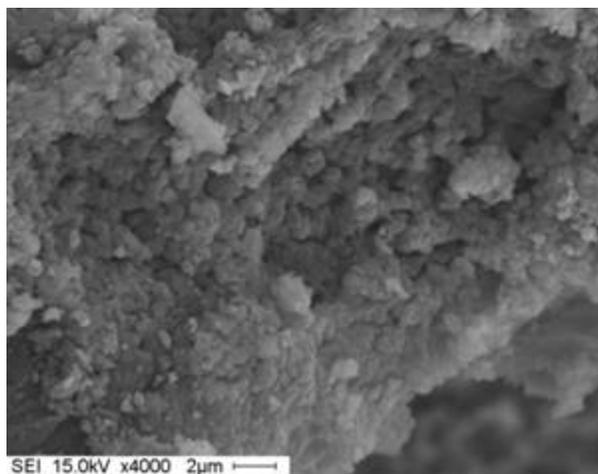
Figure 7: SEM micrographs of cement pastes



(a) Hydrated fiberboard



(b) Carbonated fiberboard in flue gas



(c) Carbonated fiberboard in pure gas

Figure 8: SEM micrographs of cellulose fiberboard

4. Conclusions

Carbonation curing of cement based products using as-captured flue gas without separation was studied. It seemed that flue gas CO₂ could be used to accelerate hydration in a similar way as pure gas, at the same time to be stored in concrete product as stable carbonates for carbon sequestration and emission reduction. The challenge for using as-received flue gas was the low CO₂ concentration. Since there was not enough carbon dioxide, a multiple injection approach had to be employed to promote carbonation reaction and CO₂ uptake. Five hours carbonation in flue gas could absorb about 7% carbon dioxide based on cement binder. It was accomplished at 0.5 MPa gas pressure, in 7 cycles and with an efficiency of 85% of flue gas CO₂ sequestration. The efficiency is apparently dependent on the cement content and carbon concentration. The early age strength produced was comparable to that by pure gas carbonation. Since flue gas carbonation was a slow reaction, it generated less heat, evaporated less water and eventually resulted in an ultimate strength higher than the same product cured by pure gas. CO₂ uptake in flue gas could still be improved by extending the curing time or shortening each cycle to a dynamic system. Compared to other proposed CO₂ sequestration methods, this carbonation approach can be integrated into a commercial production, is profit oriented and can have environmental and technical benefits. The production can be carried out anywhere in the world, and is best suited to the place where the flue gas is produced.

5 References

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