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**CAPTURE OF GREEN-HOUSE CARBON DIOXIDE
IN PORTLAND CEMENT**

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Abstract

A novel process has been developed to sequester green-house carbon dioxide produced by the cement industry in precast cement products. Typically, 10 - 24 wt. % of CO₂ produced by calcination of calcium carbonate during clinkering of the cement may be captured. The carbonation process also cures the cement paste within minutes into hard bodies. The process maintains high pH conditions during curing to allow conventional steel reinforcement of concrete. The process will save time and money to the cement industry, and at the same time, help them to comply with the Clean Air Act by sequestering the green-house carbon dioxide.

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I. INTRODUCTION

Increasing levels of "greenhouse" gases has raised serious concern regarding possibilities of global climatic change. Carbon dioxide (CO₂) is the single largest greenhouse gas, which accounts for 55% of the total volume of greenhouse gases produced annually. Utility industries followed by cement industries are responsible for this production. This project dealt with sequestering CO₂ released during production of cement in products made of cement itself, so that the entire industry can be partially self-sufficient in reducing its emissions of CO₂.

I.1. Contribution of Green House CO₂ by the Cement Industry:

Cement industry contributes CO₂ to greenhouse gases in two different ways. Approximately 64% of the cement is calcium oxide, which is obtained by calcining calcium carbonate (CaCO₃) in the form of lime stone. This calcining follows the reaction,

Calcium oxide becomes a component of the cement and CO₂ is released to the atmosphere. The other source of CO₂ during production of cement is due to the use of fuel for power production needed for calcining and clinkering. It is estimated that these two sources emit nearly equal amount of CO₂. For each ton of cement produced, approximately 0.5 ton of CO₂ is produced by each of these two sources and hence the total CO₂ production is 1 ton [Source: Portland Cement Association].

FIGURE 1: World carbon dioxide production due to cement manufacturing [1].

Fig. 1 shows the projection of world CO₂ production by the cement industry. Though cement industry contributed only 5% of the total CO₂ produced, its share will keep increasing because of the population rise and hence the increase of activities in the construction sector where cement is the major ingredient. In particular, the rapid population growth in China and India will require increase of cement production, and as a result, the cement production will also rise. This rise is responsible for the projected increased share of CO₂ production by the cement industry [1] as shown in Fig. 1. It is estimated that by the year 2015, ~3500 million tons of CO₂ will be produced annually, which is 3.5 times that of the current cement

production rate. This lion's share of CO₂ production by the cement industry clearly indicates that sequestering this CO₂ may help reduce the greenhouse gases significantly.

In the United States, reduction of CO₂ emissions may have regulatory importance also. The Clean Air Act of 1990 will require that the emissions of greenhouse gases be reduced by the turn of the century to their 1990 levels. To comply with this act, every industry may require new technologies to reduce emissions. The method investigated here may provide a novel process to reduce CO₂ emissions in the cement industry and thereby comply with the Clean Air Act.

II. Carbonation of cement as a method of sequestering greenhouse CO₂

It is well known that certain lime based products harden by aging due to carbonation. Greek and Roman lime mortars made of Ca(OH)₂ have been shown to slowly form CaCO₃ and strengthen by carbonation when exposed to atmospheric CO₂. Berger et al. [2], Young et al. [3] and Goodbrake et al. [4, 5] extended these studies to investigate the effect of CO₂ and water on cement. These authors worked with laboratory synthesized calcium trisilicate, 3CaO.SiO₂ (C₃S)* and calcium disilicates, 2CaO.SiO₂ (C₂S)*, which are the major binding phases of the cement. They showed that, if these binders are cured in the presence of humid CO₂ environment, they rapidly develop strength and sequester large amount of CO₂.

Berger et al. [2] and Young et al. [3] suggested that the sequestration of CO₂ in Portland cement is a result of the chemical reactions given in Eq. (1-4) given below. These reactions are written in cement chemistry notations, i.e., H = H₂O, C = CaO, C = CO₂, S = SiO₂, C_nS = β -dicalcium silicate (C₂S) for n = 2, and tricalcium silicate (C₃S) for n = 3.

where, $w = y - n + x$,

where $x > n$ and $y > y$.

* Cement chemistry notation

These equations suggest that the two main cement phases, i. e. the dicalcium silicate and the tricalcium silicate are responsible for sequestration of CO₂ by forming calcium carbonate in the process. They further suggest that progressive carbonation of the C-S-H would lead eventually to silica gel ($x = 0$). Eq. 2 now becomes

where $S H_z$ is the silica gel. These reactions were investigated by Goodbrake et al. [3] in laboratory synthesized C₂S and C₃S. We exploited this mechanism to sequester CO₂ in commercial Portland cement for rapid setting.

II.1. Characterization of Portland cement and the CO₂ Budget

Six types of Portland cements are commercially sold. They are called Type I-V and the last one is called White cement. Their composition, particle size and formation methods are vary in each type. We used Commercial Portland cement (CAS # 65997 - 15 - 1), which was Type I cement in this study. Type I cement is used mostly in building industry. This cement was characterized in the laboratory, before its use.

Table 1 gives the chemical composition of the Portland cement Type I. As one can see, the content of C₂S and C₃S in this cement is high and should be responsible for the sequestration of CO₂ in a significant amount.

The mineral phases of the cement powder are shown in the XRD output in Fig. 2.

TABLE 1 : Composition of Portland cement Type I. [5]

Chemical composition of cement		Potential compound composition	
Oxide	(%)	Chemical phase	(%)
SiO ₂	20.9	C ₃ S	55
Al ₂ O ₃	5.2	C ₂ S	19
Fe ₂ O ₃	2.3	C ₂ A	10
CaO	64.4	C ₄ AF	7
SO ₃	2.9	Other	9

T

FIGURE 2. X-ray diffraction output of Portland cement Type I.

In Fig. 2, C₃S and β-C₂S phases are dominant. There is no evidence of any CaCO₃, but one can see a peak of gypsum, which might have been due to the SO₃ content in the powder. As we shall see later, this gypsum

forms an entirely new room temperature setting cement called ettringite. Though this is a minor phase, it has been noted in the literature [6] that this phase is affected by carbonation. Thus the net effect of carbonation is due to carbonation of C_3S and β - C_2S phases and also that of the ettringite phase. However, the minor phase of ettringite will not affect the overall budget of the CO_2 intake, though it may affect the strength characteristics of the carbonated cement slightly. In this initial study, we will ignore this phase in calculating the CO_2 budget in Portland cement.

TABLE 2. CO_2 budget in Portland cement

Cement type	CaO content (wt.%)	CO_2 release due to calcination of $CaCO_3$ (wt.%)	Theoretical intake (wt.%)
I	64.4	50.6	41.5
II	63.6	49.97	41.76
III	64.9	50.99	42.07
IV	62.3	48.95	41.23
V	64.4	50.6	44
White	65	51.07	42.6

Table 2 gives the CO₂ budget in various types of the Portland cement, estimated on the basis of the reactions given by Equations 1-4. Based on the numbers in this Table, one may conclude that, overall the total CO₂ release during manufacture of the cements and the theoretical upper limits for sequestration are nearly the same for all the cement types. Further, the theoretical intake ranges between 92 -95% of the release of CO₂ due to calcination of calcium carbonate. This implies that, independent of which type of cement is in use, sequestration of CO₂ in Portland cement may be equally effective for curtailment of green-house CO₂.

II.2 Method of estimation of CO₂ captured

If sequestration of CO₂ results in the formation of CaCO₃, then it should be possible to decompose CaCO₃ at ~ 900 °C into CaO and CO₂ [6] and estimate the amount of CO₂ that has escaped from the material. Berger et al [2] calcined the trisilicate and disilicate samples at 980 °C to estimate the intake of CO₂. The commercial cement used in our study contains, in addition to the disilicate and trisilicates, other components such as calcium aluminate, and therefore it is necessary to ensure that any other high temperature reactions do not interfere with this estimate. To investigate this, differential thermal analysis (DTA) of the sample was done.

DTA studies involve monitoring the weight of the sample as it is heated from the room temperature to a desired higher temperature. The rate of loss in weight due to evolution of gases such as CO₂ is detected by

dips in the endotherms plotted as a function of the temperature. From this study, one can identify exact temperatures at which such evolutions occur.

The DTA output of the carbonated cement samples is shown in Fig. 3. As one may notice there are four dips at elevated temperatures. These are given in Table 3 along with the transformations occurring in the material at these temperatures. These transformations suggest that to estimate the content of CO_2 in the cement, we can fire the specimens at temperatures $>825^\circ\text{C}$ and find the weight loss occurring between 540°C and that temperature.

TABLE 3 Phase evolution in carbonated cement at high temperatures.

Temperature ($^\circ\text{C}$)	Phase evolution	Reference
~125	Ettringite ($\text{C}_6\text{AS}_3\text{H}_n$) seems to form in the cement due to gypsum	5
~175	gypsum decomposition	5
540	decomposition of $\text{Ca}(\text{OH})_2$	5
825	decomposition of CaCO_3 and evolution of CO_2 and formation of CaO	6

FIGURE 2 Differential thermal analysis of cement cured in CO₂.

The analysis suggests that it is possible to estimate the amount of CO₂ captured by measuring the weight loss of the cement between 540 °C and 900 °C. We used this method to estimate CO₂ capture in our work.

III. STUDIES OF CEMENT PASTE CURED IN CO₂ ENVIRONMENT

To study the effect of the carbonation on setting of cement paste, we investigated carbonation effects on a mixture of Portland cement and silica sand with proportion of the sand varying from 0 to 70%. In this range, samples could be made by pressure-moulding the paste of the mixtures in a cylindrical die at a pressure of 2000 psi using a press in a uniaxial mode parallel to the cylindrical axis. The pressure was held for 10s. The ratio of water to the mixture of the powder was 0.125. During pressing, some water squeezed out of the samples. The samples were made in disk shapes, with a typical thickness of 0.25" and a diameter of 1".

The curing arrangement contained two identical desiccators, one for air curing and the other for CO₂ curing. The desiccator for CO₂ curing had an inlet and an outlet for the gas to enter and exit. Both desiccators were air tight and had water at the bottom so that inner atmosphere remained humid. The CO₂ was bubbled through water which was stored at the bottom of the desiccator, so that the samples were exposed to moist CO₂. Samples were placed on wire shelves of both the desiccators just above the water level, so that the specimens had no direct contact with the water. To accelerate the evaporation of this water, an infra-red lamp was kept shining above the transparent covers of both the desiccators. The samples were protected from the direct radiation by an opaque cover, so that excessive drying of the samples did not occur during curing.

After curing them for a 30 minute duration in CO₂, the samples were dried at ~75 °C. The second set of samples were cured in air also for this duration. However, in this short duration, the samples cured in air did not set. The exact dimensions of CO₂ cured samples were measured and then they were tested immediately on an Instron machine in a compressive mode .

The parameter, which describes the relevant mechanical property from practical point of view for the use of cement concrete is the compression strength. This parameter reflects the load bearing ability of cement. The data on the carbonated samples is given in Table 4.

TABLE 4: Strength and porosity data on carbonated samples

Samples	Compressive strength (psi)	CO ₂ intake (% of sample weight)
Cement only	4780	10
Cement concrete (50% sand)	2612	8

The data showed that setting and the strength enhancement in carbonated environment is more rapid than in air. Considering that the ASTM requirements for 28 day set Portland cement is 4000 psi, this strength may be obtained in a very short duration of 30 minutes by carbonating the cement paste. Extended studies showed further that During the first day carbonated samples gained a strength more than twice the strength of air cured samples.

To estimate the intake of CO₂, the carbonated samples were weighed on an analytical balance and were heated to different temperature

intervals suggested by the DTA result. The percentage weight losses at each of these temperatures are given in Table 5.

TABLE 5 Weight loss due to decomposition of various components in the carbonated concrete

Temperature range	28 °C-125 °C	125 °C-540 °C	540 °C-980 °C
% wt loss	2.111	2.346	3.389

The data in Table 5 show that the amount of CO₂ absorbed is ~3.4%. Considering the fact that the samples contain 50% Portland cement and 50% sand, this means that ~ 6.8% CO₂ can be absorbed in cement. It is also interesting to note that at 540 °C, due to decomposition of Ca(OH)₂ into CaO and H₂O, the % weight loss is ~ 2.3%. It may be possible to react CO₂ with this Ca(OH)₂ and produce CaCO₃ and sequester more CO₂. Such conversions have not been attempted in this project.

To confirm the conversions of dicalcium and tricalcium silicates due to carbonation of the cement according to the Equations 1-4 in the last Section, X - ray diffraction studies were done. Fig. 4 gives the X- ray diffraction output before the samples were fired to 980 °C and after they were fired. The relevant peaks were identified and are labeled in the Figure.

The diffraction output before firing shows clear peaks of C₃S , β C₂S, silica and CaCO₃. On the other hand, after firing, one can see that the

peak of CaCO_3 has disappeared and now we see peaks of CaO . Neither the peaks of CaO nor CaCO_3 exist in the output of the original cement shown in Fig. 2. The yield of CaO in Fig. 4 (b) may be due to decomposition of either CaCO_3 or Ca(OH)_2 or both. However, due to the absence of the peak of CaCO_3 , one can conclude that the weight loss at 980°C is certainly due to evolution of CO_2 .

FIGURE 4. X-ray diffraction output of cement cured in CO_2 . (a) sample as prepared, and (b) sample fired at 880°C .

The results presented above imply that the effect of CO_2 is significant at the initial stage. Efforts must be concentrated to exploit this feature of curing cements, so that the CO_2 can be captured to the maximum extent,

and simultaneously, curing time can be reduced. Reduction of curing time may provide considerable savings to the industry involved in the prefabricated products of concrete.

One may see two difficulties in effectively achieving this. The permeation of CO₂ through thicker structures may be difficult, unless forced circulation is used. Also, often when the samples are wet, the water envelop formed on the particles of the cement prohibits them from reacting with CO₂. If these difficulties are overcome, we believe that we will have a useful method to utilize CO₂ from flu gas.

III. *IN SITU* CARBONATION OF PORTLAND CEMENT USING AMMONIUM CARBONATE AS A VEHICLE OF CO₂

III.1 Ammonium carbonate as a vehicle of CO₂

Ammonium carbonate is a crystalline chemical, which is unstable and decomposes easily at even a slightly elevated temperatures. It is soluble in water and for hydration setting of cement, it may be used as a vehicle of carbon dioxide. With the exothermic reaction of the setting of cement, (NH₄)₂CO₃ decomposes into CO₂ and NH₃ and provides the necessary CO₂ to the setting cement. The amount of water to be added to the cement powder is governed by the workability of the paste. Too much of water makes the paste too dilute and it does not set into required shapes. Also excess water makes the samples porous. In Type I Portland cement, we found that the workable ratio of cement to water is 5:1, even though this ratio automatically puts a limit on the amount of CO₂ which can be made available to the setting cement.

For saturated solution of (NH₄)₂CO₃ equal amount of this material and water were mixed. To form a supersaturated solution, we put in 28 g of (NH₄)₂CO₃ crystals to 20 g of water, and 100 g of the cement powder was stirred into this solution. When the slurry becomes warm, it was poured into cylindrical moulds of radii 2.55.cms and heights ranging from 1.5 to 2.cms, and samples were moulded at a pressure of 2,000 psi. Mixing and moulding lasted for ~15 m. During this time ammonia was being released from the samples indicating decomposition of the carbonates into CO₂ and NH₃. The samples were immediately transferred into a desiccator containing saturated solution of (NH₄)₂CO₃ for further curing.

To make the concrete samples, cement powder was mixed with silica sand in the desired ratios. The ratio of the concrete : water : $(\text{NH}_4)_2\text{CO}_3$ was maintained at 100 : 20 : 28. Samples made this way were subjected to the various tests given below.

III.2. Identification of minimum time of setting

During setting, it is expected that due to the exothermic reaction, the temperature of the solution will increase. A thermometer was used to monitor this temperature during setting. Fig. 5 shows the temperature build up in the paste during first few minutes of setting. After a slow rise of the temperature for first 12 minutes, the temperature was 52°C within next three minutes. It subsequently dropped equally fast and was 22°C in next 5 m. We believe that initial rise in temperature releases CO_2 from the solution. Capture of this CO_2 sets the cement faster, which raises the temperature further. The process continues till all $(\text{NH}_4)_2\text{CO}_3$ decomposes and most of the CO_2 is captured in first 15 m. After this period, the cement returns to its normal setting rate and the temperature falls due to dissipation of the heat energy. This implies that most of the setting of the cement occurs in first 15 m. Thus further curing does not increase the setting rate considerably. This was confirmed by direct measurements as follows.

III.2. Estimation of CO_2 captured:

Samples of cement were fabricated and cured in the desiccator with the solution of $(\text{NH}_4)_2\text{CO}_3$ for different time periods. At the end of each period, samples were dried and then were heated to 950°C to drive away

Fig. 1 : Temperature rise during carbonation and setting of cement

FIGURE. 5 : Temperature rise during carbonation and setting of cement

Fig. 2 : Time dependence of carbonation

FIGURE. 6. Time dependence of carbonation

all CO₂ from the samples. This allowed us to estimate the amount of CO₂ captured in the specimens by the procedure described in Section II. The results are given in Fig. 6.

Each data point in Fig. 6 is an average of readings on four samples. The time needed to press these samples and to place them in the desiccator varied between 5 m to 10 m, with an approximate average of 7 m. Thus the curing time on each sample was this initial time plus the time shown on the x-axis.

The amount of CO₂ captured appears to be a logarithmic function of time. Initially, the capture occurs at a fast rate, but subsides in approximately 15 m of total curing. This is consistent with our earlier interpretation of the data in Fig. 4. Initially, CO₂ is captured from the solution that was added to the cement during setting. However, the solution in the desiccator is at the room temperature and the sample has cooled down during transfer to the desiccator. In such environment, the rate of carbonation is low and hence the curve in Fig. 5 tapers off. This implies that one could consider about 15 m curing time for most of the carbonation to occur. We decided to cure the samples for 30 m for practical reasons in our future study.

III.3 Carbonation in concretes:

Cement is mostly used as the binding phase in concrete. Therefore it is necessary to study carbonation of concrete. For this reason, we prepared samples of concrete by mixing cement and silica sand in various

proportions and carbonated them according the procedure given above. In each case the amount of CO₂ captured was estimated. The results are given in Fig. 7.

FIGURE. 7 : . CO₂ capture as a function of wt% of cement in concrete

The results show that the dependence of the amount of CO₂ captured is again a function of the cement content. The fact that it is not a linear function indicates that there are other factors influencing the carbonation. We believe that the porosity might be affecting the carbonation of the concrete. At small content of the cement in concrete, the porosity is expected to be higher. This will result in an exposure of more surface area of the cement component to the CO₂. This will result in higher CO₂ capture at lower concentration of the cement component.

At 30% of the cement content, 24% CO₂ is captured. It is 56% of the CO₂ produced during calcining of CaCO₃ for producing that cement. At

higher content of the cement in the concrete, this percentage is reduced to ~9% at 100% of the cement. This variation is also shown in Fig. 6

IV.4. Microstructure of the carbonated cement

Fig. 8 presents the scanning electron micrographs of the fractured surfaces of the uncarbonated and carbonated cement. As one may see, the structures in the two cases are different. In the case of uncarbonated samples, except for very fine needle like structures, the major phase is noncrystalline. The fine needles are likely to be those of ettringite. On the other hand, the micrograph of the carbonated sample shows prismatic structures of aragonite (CaCO_3) formed out of the β -dicalcium silicate and tricalcium silicates after carbonation. These observations are consistent with those made by Young et al. [3] on synthesized dicalcium and tricalcium silicates. In addition to these, one may also notice that the crystals are coated by a layer of spheroidal structure. Such spherical structures are found every where in the material. Typical size of these structures is less than a micron. We have not identified these structures as yet. They do not appear in the carbonated dicalcium and tricalcium silicates studied by Young et al., which implies, they might have been formed out of alumina or sulfur present in the Portland cement.

IV.5. Effect of carbonation on reinforcement of steel

Finally we addressed the issue of effect of carbonation of cement on the reinforcement of steel. It has been reported [1] that one of the problem of carbonation of cement is the deterioration of the bond

FIGURE 8. Microstructure of the cement,
(a) uncarbonated, (b) carbonated.

between the cement matrix and the reinforcement steel. Carbonation reduces the pH of the setting cement. Lower pH is detrimental to the development of the protective corrosion layer on the surface of the steel, which in turn does not allow good bonds between the steel and the cement matrix. We confirmed this by incorporating low carbon steel wires in the cement matrix and carbonating the samples externally by putting them in a carbonation chamber. The bonding was found to be poor. On the other hand, when the wires were put in the the paste which was prepared with ammonium carbonate solution, and set, the wires were bonded well in the cement matrix and could not be separated. When the sasmples were fractured with an impact force, the matrix cracked, but the wires bonded in the matrix.

The reason for this bonding is clear. During carbonation, ammonia is released, which maintained high pH of the paste. Direct measurement showed a pH of 12, which is nearly the same or slightly higher than that of setting cement in water. Thus use of ammonium carbonate as a vehicle helps to maintain the pH high during setting, which in turn helps good bonding between the reinforcement of steel to the matrix.

V. DISCUSSIONS AND RECOMMENDATIONS

The investigations reported here show that carbonation of Portland cement can reduce the setting time of the cement considerably. In particular, using ammonium carbonate, one can capture significant amount of CO₂ in cement, which can reduce the CO₂ emissions in cement industry. The setting time is less than half an hour, which can save considerable time and money to an industry involved in the production of precast components of cement. Use of ammonium carbonate also provides a compatible process to reinforce cement structures with conventional reinforcement steel.

V.1 Recycling of ammonia during carbonation

The evolution of ammonia may be of some environmental concern during carbonation of the cement. However, ammonium carbonate may be formed by resynthesis of the evolved ammonia with green-house carbon dioxide. Preliminary studies on such resynthesis show that this is possible. Thus, it may be recycled in the process, which not only avoids its evolution in the open atmosphere, but also makes the entire process economical. This is shown in the schematics in Fig. 9.

The work done in this project shows the feasibility of sequestering green-house carbon dioxide at the bench scale. It is highly recommended that a working model be attempted to demonstrate the feasibility of the schematic model shown in Fig. 6 and develop a pilot scale production facility to assess the economic feasibility.

FIGURE. 9

Proposed CO₂ cycle in the cement industry.

V.2 Coclusions and future directions

No process, designed to reduce environmental pollution, becomes commercially viable, unless it is also economical. The work conducted in this project developed a process to sequester green-house carbon dioxide in Portland cement, which not only reduces the green house gases produced by the cement industry, but also reduces the cost of the production of construction products. Therefore it should be a commercially viable process.

The process needs some fine tuning. It is necessary to understand the details of the microstructure of the carbonated cement, sto gain complete confidence in the carbonated cement and also to optimize the

process and the properties of the cement. It is also necessary to develop a working model of the cyclic process shown in Fig. IV.1. Such a model will attract industrial interest. That will help development of collaborative projects with the cement industry and the technology transfer for the overall economy of the industry and for a better environment.

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