

Carbon dioxide sequestration in concrete in different curing environments

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ABSTRACT: This paper summarizes the results of an investigation on carbon dioxide (CO₂) sequestration in concrete. Concrete mixtures were not air entrained. Concrete mixtures were made containing Class C fly ash at 0%, 18%, and 35% of total cementitious materials. Effects of three different curing environments on properties of concrete were studied: (1) moist-curing room with 100% relative humidity (RH) and 0.15% CO₂ concentration; (2) drying room with 50% RH and 0.15% CO₂; and (3) CO₂ chamber with 50% RH and 5% CO₂. Concrete specimens were tested for compressive strength, splitting tensile strength, flexural strength, depth of carbonation, and abrasion resistance. Among the three curing environments, the rate of carbonation of concrete was the highest in the CO₂ chamber. In spite of the lack of moist-curing due to the 50% RH environment in the CO₂ chamber, the specimens carbonated in the CO₂ chamber generally showed approximately the same strength as the specimens cured in the moist-curing room. The abrasion resistance of carbonated specimens was lower than that of moist-cured specimens. The specimens cured in the drying room without enough moisture or carbonation showed the lowest strength and abrasion resistance.

1 INTRODUCTION

Carbon dioxide (CO₂) emissions are one of the most serious concerns among all greenhouse gas emissions. CO₂ emissions can be affected by combustion of organic materials (e.g., wood, coal, oil, and other fuels), or by human and animal metabolism (respiration) in which oxygen is utilized and CO₂ is given off as an end product [Riddick 1967]. Also, dead animals, plants, and other organic matter generate CO₂. Oil- or coal-burning power plants and cement-producing industries account for a large amount of CO₂ emissions.

Since about the year 1750 to 1950, the CO₂ concentration on the earth increased from about 275 ppm to 310 ppm. In last 50 years, the CO₂ concentration has increased from approximately 310 ppm to 375 ppm [US-EPA]. According to the statistics of the year 1998, 3.1% of the total CO₂ emissions were from the cement manufacturing industry [World Resource Institute]. Approximately 88% of the CO₂ emitted by the cement and concrete industries is produced by cement production, 1% is produced by concrete production, 9% by its use in

construction, and 3% by demolition and waste handling [Jahren 2004].

There exists an urgent need for a reduction in CO₂ emissions and/or recycling of CO₂. An effective method for the reduction of CO₂ in the environment is to sequester it in lime- or cement-based products (e.g., concrete).

The sequestration of CO₂ from the environment in lime- or cement-based products can be accomplished via the process of carbonation. For a long time, carbonation has been considered a reaction that deteriorates the durability of concrete. Carbonation affects the surface hardness and strength of concrete. Carbonation occurs in the pores near the surface of concrete and progresses towards the inside of a concrete element, and is dependent upon the pore structure of the concrete, the relative humidity and CO₂ concentration in the environment, the availability of Ca(OH)₂ and water, and the replacement of cement with mineral additives [Lea 1971].

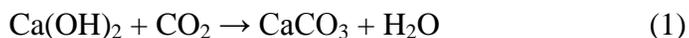
2 LITERATURE REVIEW

2.1 Carbonation of concrete

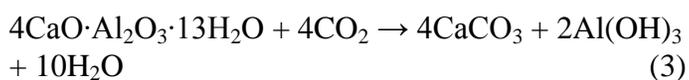
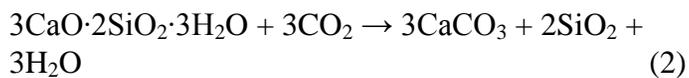
Carbonation is known to improve surface hardness, strength, and durability of cement-based products by pore refinement of the cement paste matrix. Carbonation can be helpful in non-reinforced cement-based products. However, for reinforced cement-based products, as the pH of carbonated cement paste reduces due to carbonation, reinforcing steel loses its passivity and becomes vulnerable to corrosion [Concrete Experts International 2004].

Carbonation in cement-based products can be defined as a reaction between the CO₂ dissolved in water and the cement hydration product Ca(OH)₂ in the pore water [Chi et al. 2002]. This reaction produces calcium carbonate (CaCO₃) and water. Calcium silicate hydrates and calcium aluminate hydrates also react with CO₂ in the presence of moisture to produce calcium carbonate and hydrates of silicates and aluminates and water [Montemor et al. 2002, Neville 1995, Malhotra & Ramezani-pour 1994, St. John et al. 1998]. Montemor et al. [2002], has explained the sequence of the carbonation mechanism as follows:

- CO₂ diffusion through the cement paste matrix;
- CO₂ dissolution in the pore solution and reaction with calcium hydroxide:



- Reaction with silicates and aluminates:



CO₂ diffuses through the pores depending upon the pore structure and the degree of saturation of the pores in the cement paste matrix. CO₂ in gaseous phase does not react with cement hydration products; it has to dissolve in the pore water first to form carbonic acid (H₂CO₃). Of the hydrates in the cement paste, the one which reacts with CO₂ most readily is Ca(OH)₂. Other hydrates also react with dissolved CO₂, and hydrated silica, alumina, and ferric oxide are produced [Montemor et al. 2002, Neville 1995]. When all Ca(OH)₂ becomes carbonated, the pH value of the pore solution is reduced from 12.5 to 8.3 [Concrete Experts International 2004, Neville 1995].

CaCO₃ produced by the process of carbonation precipitates inside the pores of the cement paste matrix. This results in pore refinement of the carbonated cement paste matrix. Pore refinement leads to increased surface hardness, reduced permeability of the carbonated portion of the cement-paste matrix, and increased compressive strength of the cement-based product.

Due to pore refinement, however, it becomes difficult for CO₂ to diffuse further in the cement paste matrix, which results in reduced rate of carbonation of cement-based products.

The compressive strength and flexural strength of concrete specimens cured in a high-CO₂ environment may increase up to 100% higher than the specimens cured in a CO₂-free environment [Lea 1971].

2.2 Factors affecting carbonation

The rate of carbonation is the highest when the relative humidity of the surrounding environment is 50% to 70% [Neville 1995, Atis 2004]. Concrete with high internal moisture shows a much lower rate of carbonation because the diffusion of CO₂ becomes difficult when pores are saturated with water. Carbonation rate also reduces at a lower internal moisture level due to insufficient water in the pores [St. John et al. 1998].

When fly ash is used as a partial cement replacement material in cement-based products, the initial amount of CaO available for hydration decreases, and a lower amount of Ca(OH)₂ is produced [Montemor et al. 2002]. The silica from fly ash reacts with Ca(OH)₂ [Neville 1995] and less Ca(OH)₂ remains in concrete. At early ages of concrete containing fly ash, less CO₂ is required to consume Ca(OH)₂ to produce CaCO₃; and, the expected reactions of fly ash with Ca(OH)₂ do not occur because of less availability of Ca(OH)₂ for the hydration of fly ash [Montemor et al. 2002, Neville 1995]. A low degree of hydration of fly ash results in increased porosity [Montemor et al. 2002].

Sagüés et al. [1997] found that the depth of carbonation increased as the water-cementitious materials ratio (W/Cm) increased from 0.37 to 0.50. They also found that at a given W/Cm, the depth of carbonation increased as the cement replacement by fly ash increased from 20 to 50%. Collepardi et al. [2004] concluded that at a given W/Cm, the rate of carbonation increased when the cement replacement rate with fly ash increased beyond 15%.

Concrete containing fly ash, if not cured sufficiently, may have a higher degree of carbonation. Good quality fly ash concrete can show the same trend of carbonation as concrete made without fly ash [Malhotra & Ramezani-pour 1994].

2.3 Accelerated carbonation

The use of accelerated carbonation of concrete to project the long-term effects of natural carbonation on concrete has become a common practice in conducting research. Using accelerated carbonation, carbonation rates of concrete up to 3000 times higher than that could occur in the normal atmosphere, can be achieved [Andrade 1997]. Accelerated carbonation of concrete can be achieved by curing the concrete specimens in favorable environmental conditions for carbonation, i.e. a high CO₂ concentration and a certain level of relative humidity. The temperature of the curing environment is also a factor to be considered for accelerated carbonation.

3 MATERIALS, CO₂ CHAMBER, AND TESTS

3.1 Portland cement

ASTM Type I portland cement was used in this research. The strength of cement mortar (ASTM C 109) was 17.5, 26.1, 32.1, and 42.2 MPa at 1, 3, 7, and 28 days, respectively. The oxides composition of the cement was 20.5% SiO₂, 4.7% Al₂O₃, 2.7% Fe₂O₃, 64.9% CaO, 2.5% MgO, 2.5% SO₃, 0.26% TiO₂, 0.11% P₂O₅, 0.16% Na₂O, and 0.58% K₂O.

3.2 Fly ash

ASTM Class C fly ash obtained from Green Bay, Wisconsin was used for this research. The fly ash had the following properties: strength activity index (ASTM C 311) of 98% and 99% of Control mortar at 7 and 28 days, respectively; water requirement of 91% of Control; and density of 2.86 g/cm³. The oxides composition of fly ash was 39.1% SiO₂, 18.6% Al₂O₃, 5.6% Fe₂O₃, 21.3% CaO, 5.0% MgO, 1.6% SO₃, 1.7% Na₂O, and 0.8% K₂O.

3.3 Fine aggregate

The fine aggregate used for this research was river sand. The fine aggregate had specific gravity of 2.66, absorption of 1.4%, and bulk density of 1,790 kg/m³.

3.4 Coarse aggregate

The coarse aggregate used for this research was crushed stone having a nominal maximum size of 19 mm. The coarse aggregate had specific gravity of 2.66, absorption of 0.4%, and bulk density of 1550 kg/m³.

3.5 CO₂ chamber

To enable accelerated carbonation of concrete specimens, a CO₂ chamber was constructed. CO₂ concentration of 5 ± 1.25%, relative humidity of 50 ± 4%, and temperature of 21 ± 1.5°C were maintained in the chamber. A fan was provided in the chamber to circulate the CO₂ within the chamber. Specimen racks made of steel bars were provided on all four walls.

3.6 Types of tests and specimens

Fresh concrete was tested for the following properties: slump (ASTM C 143), density (ASTM C 138), and air content (ASTM C 231).

Hardened concrete specimens were tested for compressive strength (ASTM C 39 using 100 × 200 mm cylinders), splitting tensile strength (ASTM C 496 using 100 × 200 mm cylinders), flexural strength (ASTM C 78 using 100 × 75 × 300 mm beams), depth of carbonation (RILEM CPC-18 using split halves obtained from splitting tensile tests), and abrasion resistance (ASTM C 944 using 45-mm thick disks saw-cut from the top of 150 × 300 mm cylinders).

For measurement of depth of carbonation, a pH-indicator solution (made of 1% phenolphthalein in a 70% ethyl alcohol solution) was sprayed on the fractured surface of concrete specimens. After spraying this solution, the area that turned pink was considered non-carbonated, and the area that did not show discoloration was considered carbonated.

The top surfaces of abrasion specimens were abraded with rotating cutters for six minutes under a load of 197 N.

For each test type, three specimens were tested at each test age.

4 MIXTURE PROPORTIONS, RESULTS, AND DISCUSSION

4.1 Mixture proportions

Nine concrete mixtures were produced in the laboratory. Class C fly ash was used as a partial

replacement of cement. For 1 kg of cement being replaced, 1.25 kg of fly ash was added. The concrete mixtures were not air entrained.

Approximately 24 hours after casting, specimens were removed from molds. Immediately, they were put in one of three curing environments.

The concrete mixtures were designated as shown in Table 1, based on the type of curing environment and the amount of fly ash.

Table 2 shows mixture proportions and fresh properties of concrete.

Table 1. Mixture designations.

Fly ash / cement- itious materials (%)	Curing condition		
	Moist-curing room 100% RH & 0.15% CO ₂	Drying room 50% RH & 0.15% CO ₂	CO ₂ chamber 50% RH & 5% CO ₂
	Mixture designation		
0	F0-M	F0-D	F0-C
18	F18-M	F18-D	F18-C
35	F35-M	F35-D	F35-C

4.2 Compressive strength

Figures 1, 2, and 3 show the test results for compressive strength, splitting tensile strength, and flexural strength of concrete, respectively.

As shown in Figure 1, the concrete specimens cured in the drying room developed the lowest compressive strength. In the drying room, there was little or no gain in compressive strength after the 28-day age, and the concrete containing 35% fly ash showed the lowest compressive strength. On the other hand, the CO₂ chamber was as effective as the moist-curing room in developing the compressive strength of concrete containing 0% to 35% fly ash.

In Figure 2, the concrete specimens cured in the drying room developed the lowest splitting tensile strength, except the 3-day splitting tensile strength of those containing 0% to 18% fly ash. In the drying room, the concrete containing 35% fly ash showed the lowest splitting tensile strength. The CO₂ chamber was as effective as the moist-curing room in developing the splitting tensile strength of concrete containing 0% to 35% fly ash.

As shown in Figure 3, the development patterns of flexural strength of the concrete cured in the three curing environments were similar to those of splitting tensile strength.

Table 2. Mixture proportions and fresh properties of concrete.

Mixture designation	F0-M	F0-D	F0-C	F18-M	F18-D	F18-C	F35-M	F35-D	F35-C
Cement (kg/m ³)	297	301	298	253	253	252	211	210	209
Fly ash (kg/m ³)	0	0	0	56	56	56	113	113	112
Sand, SSD (kg/m ³)	884	899	893	902	902	899	904	902	899
Coarse aggregate, 19-mm max., SSD (kg/m ³)	1040	1060	1050	1050	1050	1040	1050	1050	1040
Water (kg/m ³)	157	157	154	160	160	160	153	152	152
Water-cementitious materials ratio, W/Cm	0.53	0.52	0.52	0.52	0.52	0.52	0.47	0.47	0.47
Slump (mm)	75	70	50	70	65	75	75	90	95
Air content (%)	2.2	2.6	1.7	1.5	1.5	1.2	1.2	1.4	1.6
Density (kg/m ³)	2380	2410	2400	2420	2420	2410	2430	2430	2420

SSD: Saturated surface dry.

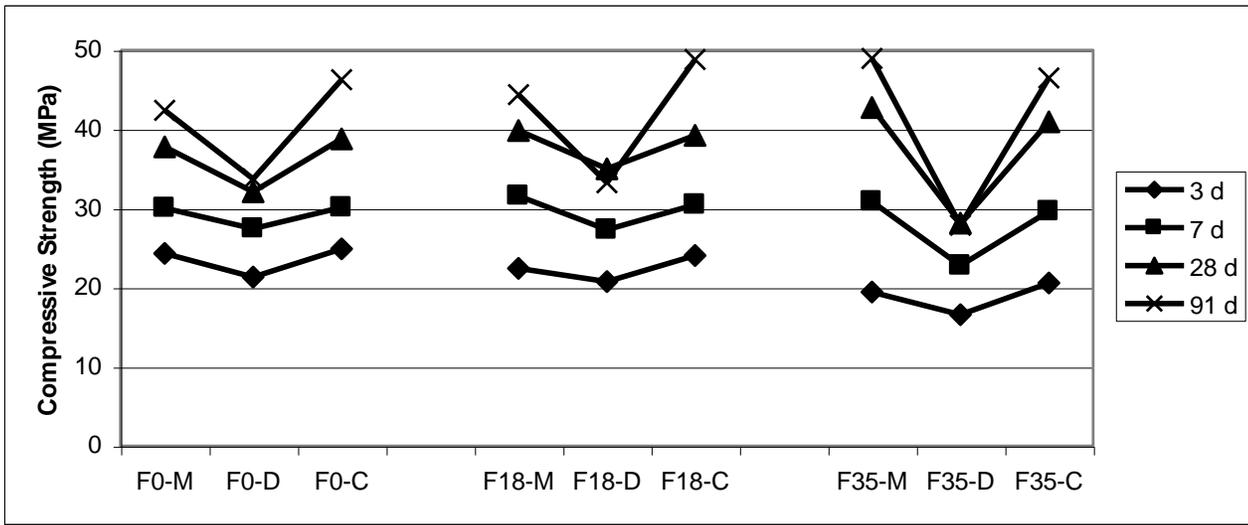


Figure 1. Compressive strength of concrete.

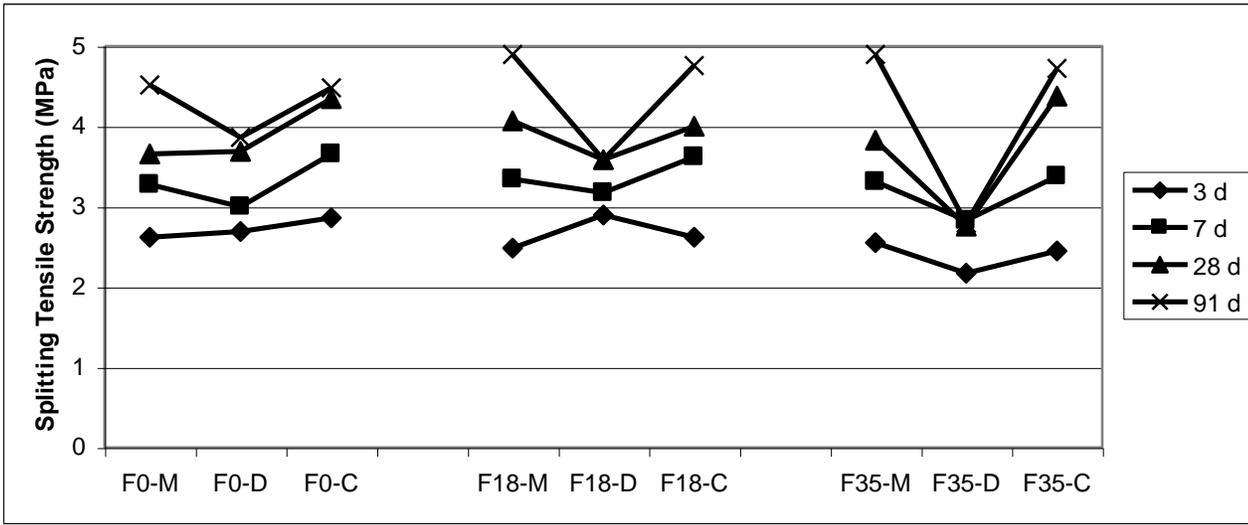


Figure 2. Splitting tensile strength of concrete.

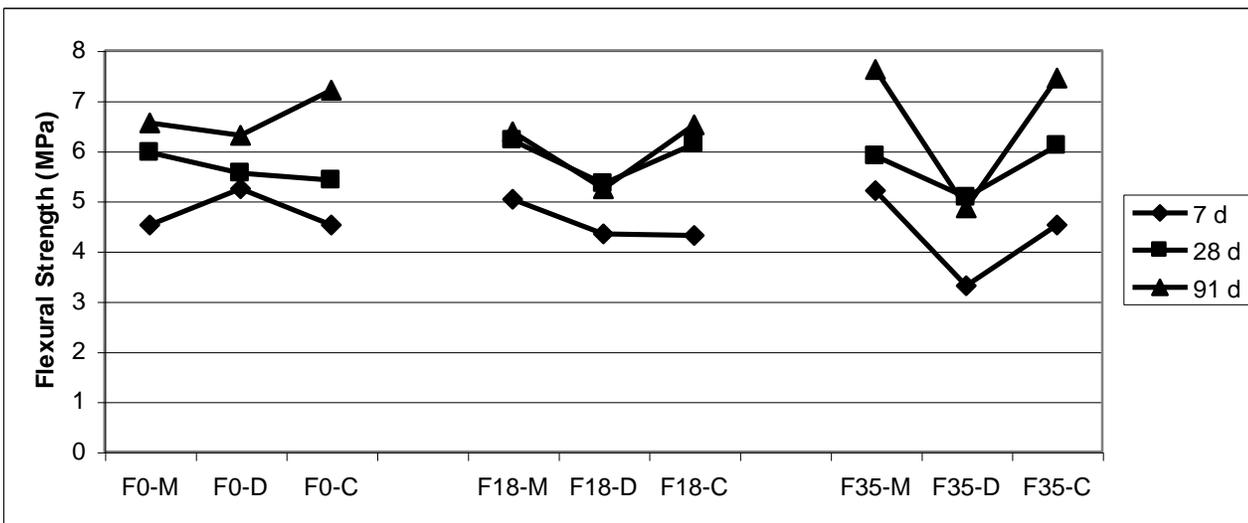


Figure 3. Flexural strength of concrete.

4.3 Depth of carbonation

Table 3 shows the test results for depth of carbonation of concrete. Figure 4 shows a photograph of concrete specimens that were tested for depth of carbonation.

Table 3. Depth of carbonation of concrete (mm).

Mixture designation	Age (days)			
	3	7	28	91
F0-M	0	0	0	0
F0-D	0	0	3	6
F0-C	3.5	7.5	12	22
F18-M	0	0	0	0
F18-D	0	1	5.5	6.5
F18-C	3	7	13.5	22.5
F35-M	0	0	0	0
F35-D	0	2	6	7.5
F35-C	4	7.5	16	24



Figure 4. Depth of carbonation of concrete mixtures containing 35% fly ash, measured at 28 days.

Concrete made with or without fly ash, cured in the moist-curing room (100% RH and 0.15% CO₂) did not show carbonation at 3, 7, 28, and 91 days.

In the drying room (50% RH and 0.15% CO₂), concrete carbonated to some extent. Concrete cured in the CO₂ chamber showed much higher carbonation than the concrete cured in the drying room. In general, in the drying room and CO₂ chamber, the depth of carbonation increased slightly as the amount of fly ash increased (F0-D to F18-D to F35-D; and F0-C to F18-C to F35-C).

4.4 Abrasion resistance

Table 4 shows the test results for mass loss of concrete due to abrasion.

Table 4. Mass loss of concrete due to abrasion (g).

Mixture designation	Age (days)	
	28	91
F0-M	3.1	3
F0-D	15.7	17.5
F0-C	11.7	9.9
F18-M	4	3.9
F18-D	8.6	12.4
F18-C	7.9	7.8
F35-M	4	2.1
F35-D	12.8	20
F35-C	10.5	9.7

The concrete cured in the moist-curing room showed the least mass loss upon abrasion. The concrete cured in the drying room showed the highest abrasion mass-loss, which worsened with age (2.2 to 5.1 times the abrasion mass-loss of moist-cured concrete at 28 days, and 3.2 to 9.5 times the abrasion mass-loss of moist-cured concrete at 91 days). The abrasion mass-loss of the concrete cured in the CO₂ chamber was lower than that of the concrete cured in the drying room, but much higher than that of moist-cured concrete (2.0 to 3.8 times at 28 days, and 2.0 to 4.6 times at 91 days).

In both the moist-curing room and the CO₂ chamber, the abrasion resistance concrete improved with age.

In all three curing environments, the abrasion mass-loss of concrete containing no fly ash was comparable to that of concrete containing 35% fly ash.

5 CONCLUSIONS

The following conclusions may be drawn based on the analysis of the test results of concrete:

- 1 Compared to moist-cured concrete, the concrete cured in the CO₂ chamber showed approximately the same strength and a lower abrasion resistance (higher mass-loss).
- 2 The concrete cured in the drying room without enough carbonation showed the lowest strength and abrasion resistance (highest mass-loss).

3 Sufficient initial curing before exposure to an accelerated carbonation condition might have resulted in improved abrasion resistance of carbonated concrete.

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