

CO₂ Sequestration in Foamed Controlled Low Strength Materials

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ABSTRACT

This project consisted of performance testing and evaluation of foamed Controlled Low-Strength Materials (CLSM) produced using a commercial foam generator. The CLSM consisted of a ASTM Class C fly ash, water, and foam. The CLSM was produced using the foam generator with one of three different types of compressed gases: compressed air; carbon dioxide; and, a mixed gas. One of the goals of this project was to determine the feasibility of using flue gas to generate a low-density CLSM with sufficient strength to be used as lightweight aggregates. The hypothesis of the project was that the use of the flue gas will promote carbonation of the sample, thereby increasing the compressive strength and binding the carbon dioxide in the carbonation reaction. The carbonation reaction of the CLSM would also have the potential to reduce carbon dioxide emissions at a coal-fired power plant.

Keywords: carbon dioxide sequestration, carbonation, carbon dioxide emission, concretes, foamed Controlled Low-Strength Materials.

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).

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 deteriorating reaction for the durability of concrete. Carbonation is also known to have effects on the surface hardness and strength of concrete. Carbonation occurs in the pores near the surface of concrete and progresses towards the center of the concrete element. It is dependent upon the pore structure of the concrete, relative humidity and CO₂ concentration in the environment, availability of Ca(OH)₂ and water, and replacement of cement with mineral additives.

The carbonation of cement-based products is of importance as it has various effects on physical properties and durability of cement-based products. Carbonation is known to improve surface hardness, strength, and durability of the cement-based products by pore refinement of the cement paste matrix. Carbonation is helpful in non-reinforced cement-based products. However, for reinforced cement-based products, as pH of carbonated cement paste reduces, reinforcing steel loses its passivity and becomes vulnerable to corrosion (Concrete Experts International, 2004). Improved pore structure of the carbonated portion of the concrete increases the strength of concrete. The compressive strength and flexural strength of concrete specimens cured in high-CO₂ environment may increase up to 100 % higher than the specimens cured in a CO₂-free environment (Lea, 1971). Atis (Atis, 2004) reported lower depths of carbonation at higher strength levels. Higher depth of carbonation of concrete with higher porosity was also reported.

Neville (Neville, 1995) mentioned “the fundamental factor controlling carbonation is the diffusivity of the hardened cement paste, which is a function of the pore system of the hardened cement paste during the period when the diffusion of CO₂ takes place.” The rate of carbonation is the highest when the relative humidity of the surrounding environment is 50 % to 70 % (Neville, 1995, Atis, 2004). It has also been reported that a lower water to binder ratio and a prolonged curing period in water resulted in a slower rate of carbonation (Sulapha et al., 2003).

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). Silica from fly ash also reacts with Ca(OH)₂ (Neville, 1995). 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, 1994).

There are certain issues involved with accelerated carbonation, which need to be taken into consideration for more precise interpretation of experimental results of the tests performed on concrete exposed to accelerated carbonation conditions. Using too high CO₂ concentrations, during accelerated carbonation of the concrete, may greatly increase internal humidity of concrete, because of water being produced rapidly due to high rate of carbonation (Moreno, 1999). We Energies (Naik et al., 2006) has proposed a method to sequester CO₂ through the production of a lightweight cellular Controlled Low-Strength Materials (CLSM), while at the same time increasing the compressive strength of the CLSM.

This project consisted of performance testing and evaluation of foamed Controlled Low-Strength Materials (CLSM). Foam was produced using a commercial foam-generator. The CLSM consisted of a Class C fly ash, water, and foam. The CLSM was produced using one of three different types of compressed gases: compressed air; carbon dioxide; and, a mixed gas. This mixed gas was used to simulate a typical flue-gas generated from the combustion

of coal at a typical coal-burning power plant. One of the goals of this project was to determine the feasibility of using flue-gas to generate a low-density CLSM with sufficient strength to be used as lightweight aggregates. The hypothesis of the project was that the use of the flue-gas will promote carbonation of the sample thereby increasing the compressive strength and binding the carbon dioxide in the carbonation-reaction products.

MATERIALS AND TEST PROCEDURES

Materials used in this project consisted of one source of Class C fly ash, water, Elastizell foam concentrate, and three types of compressed gas. Material characterization of the fly ash was not part of the scope of this project.

The simulated flue gas consisted of a mixture of carbon dioxide, sulfur dioxide, nitrogen, and nitrous oxide. The carbon dioxide concentration in the simulated flue gas was 11.4%. The compressed air and simulated flue gas was provided by We Energies, Milwaukee, Wisconsin. Compressed carbon dioxide gas was provided by UWM-CBU.

The foam generator used for the project was supplied by We Energies. The generator was a Mini (1/2") Open Air-Foam-Generating System (MiniOAS) manufactured by the Elastizell that consisted of a regulator, diaphragm pump, and foam mixing nozzle. Two pressure regulators were used for the compressed gas supply, one at the compressed gas tank, and the second at the foam generator. Gas from the tank was regulated to a pressure of 1.2 MPa prior to introduction in the foam generator.

Manufacturing of CLSM Mixtures

CLSM was mixed using a rotating-drum mixer with a volume of 0.25 m³ (for final CLSM mixtures) at the facilities of the UWM Center for By-Products Utilization. All CLSM ingredients were manually weighed and loaded in the mixer. The required amounts of the fly ash and water were loaded into the mixer and mixed for three minutes. If during the mixing process, ash agglomerated and adhered to the inside surface of the mixer, the mixer was briefly stopped, material was scraped from the mixer surface and then restarted for the remaining time. The desired volume of the foam was then added to the CLSM with the mixer running. The amount of foam was specified as a volume for each mixture. Since the rate of foam generation was determined, the amount of foam was timed to obtain the specified volume. The foam was then mixed into the CLSM.

CLSM Specimen Preparation and Testing

Fresh CLSM properties such as unit weight (ASTM D 6023) was measured and recorded. CLSM temperature was also measured and recorded. 15 cm. diameters by 30 cm. long cylindrical test specimens were prepared from each mixture for compressive strength (ASTM D 4832) and carbonation testing (RILEM CPC18). Compressive strength of the final CLSM mixtures was evaluated at the specified ages of 1, 3, 7, 28, 56, 91, 182, and 365 days. All test specimens were cast in accordance with ASTM D 4832. Three CLSM test specimens were tested at each test age. These specimens were typically cured for one day in their molds in the UWM-CBU laboratory at about 21°± 3°C. The test specimens were then demolded and placed in a curing room maintained at 50% R.H. and 23°± 1°C temperature until the time of test. Initial humidity of the curing room increased to approximately 75% for the first 7 to 14 days after the specimens were placed in it due to evaporation of water from the foamed test specimens.

Carbonation Evaluation

In order to evaluate the effects of the different types of gases used in the foamed-CLSM, carbonation of the mixtures were tested in accordance with RILEM test procedure CPC18, Measurement of Hardened Concrete Carbonation Depth (Materials and Structures, Vol. 21, No. 6, November-December 1988). In accordance with this test procedure, a phenolphthalein indicator solution is sprayed on to the broken section of a test cylinder. A solution of 1% phenolphthalein in 70% ethyl alcohol was used. The cylinders used for the carbonation measurement were first tested for splitting-tensile strength. The splitting-tensile strength test was performed in accordance with ASTM C 496, modified for the CLSM test specimens by reducing the loading rate to approximately 227-272 kg/min. The broken surface of the cylinder was lightly brushed (with a horse-hair brush to avoid damaging the surface of the CLSM) to remove loose particles, and then sprayed with the indicator solution. Typically, the indicator solution was applied approximately two to three minutes after completion of the test for splitting-tensile strength. Carbonated areas of the test specimens remained colorless, while non-carbonated areas turned pinkish-red. Measurements for the depth of carbonation were taken after one to two minutes of application of the indicator solution.

Measurement of Carbonation

Carbonation of the CLSM mixtures was evaluated at the specified ages of 1, 3, 7, 28, 56, 91, 182, and 365 days. One test specimen was tested for the splitting-tensile strength at each test age, and the broken surface tested for carbonation. Fig. 1 shows a test cylinder, after a splitting tensile strength test, with the split surface treated with the indicator solution. One of the broken sections was then split in half at approximately mid-height of the cylinder and again treated with the phenolphthalein indicator solution. The depth of carbonation was measured at the top and bottom of the test cylinder, as well as on the two sides of the broken surface of the specimens tested in splitting tension. The average depth of carbonation was recorded, and the overall percentage of carbonation of the sample was calculated based on the cross-sectional area of the split test cylinder. Carbonation visible in the interior section of the test specimen was also recorded. Fig. 2 shows a typical measurement for the carbonation depth.

MIXTURE PROPORTIONS

CLSM Mixture Proportions

Three different types of CLSM mixtures were prepared and tested in the UWM-CBU Laboratory. One mixture of CLSM was made for each source of the compressed gas: air, simulated flue gas, and carbon dioxide. The CLSM mixture proportions were specified by We Energies prior to the start of the project. The basic mixture proportions specified by We Energies were:

- Foam: 370370 cm³/m³ of CLSM
- Fly Ash (ASTM C 618, Class C): 756 kg/m³
- Water: 341 kg/m³

CLSM Trial Mixture Proportions

Foamed-CLSM mixtures were first produced in the UWM-CBU Laboratory in batches of approximately one cubic foot to establish initial fresh foamed-CLSM density, as well as to establish mixture proportions based on yield of the test batches. These trial mixtures were

also produced to confirm and adjust the density of the CLSM. CLSM produced with compressed air had a low density, but setting time was very short, within one to two minutes after the addition of the compressed-air-foam into the CLSM mixture.

CLSM Final Mixtures Proportions

CLSM final mixture proportions and fresh properties for foamed-CLSM are given in Tables 1 to 3. Similar to the trial mixtures, the CLSM produced with compressed air exhibited extremely short setting time after the foam was added to the mixture. Due to insufficient consolidation of the test cylinders for Mixtures FS-1 and FS-1A (CLSM was just poured into the cylinder molds), three batches of mixtures were required (Table 1) for the compressed-air-CLSM. The CLSM mixture went through its final set while CLSM was being placed in the test cylinders. Mixture FS-1B was produced to obtain additional test specimens. Fresh density of the CLSM was $1.11 (\pm 0.02) \text{ g/cm}^3$. The hardened density of the CLSM after approximately 182 days of curing at 50 to 75% R.H. was less than 0.90 g/cm^3 .

Fresh foamed-CLSM properties of the final mixtures using carbon dioxide is shown in Table 3. Fresh density of CLSM ranged from 1.0 to 1.1 g/cm^3 . To obtain a fresh density of CLSM made with carbon dioxide similar to mixtures using either compressed air or the simulated flue gas, the foam required was approximately eight times the volume of the foam required for compressed air or the simulated flue gas.

DISCUSSION OF RESULTS

CLSM Compressive Strength

CLSM has a maximum compressive strength specified by ACI Committee 229 1.5 to 8 MPa at the age of 28 days. A desirable compressive strength level of CLSM at the 28-day age, for applications where the CLSM is used as a fill material and required to be removed at a later age, by the use of hand shovels, is usually specified to be less than 0.7 MPa. The CLSM produced in this project was not intended as a back fill material, but rather as a potential source of lightweight aggregates (fine and/or coarse).

The compressive strength data for all the CLSM mixtures are presented in Tables 4 to 6. Compressive strength of the CLSM mixtures using foam generated with compressed air (Mixtures FS-1/1A and FS-1B) increased from 0.8 MPa at the age of one day, to 2.1 MPa at the age of 182 days. Compressive strength for the CLSM using the simulated flue gas is given in Table 5. A comparison of the compressive strength of the three types of foamed-CLSM is shown in Fig. 3.



Figure 1. Test Cylinder Treated with Indicator Solution



Figure 2. Measurement of Carbonation (in cm)

Table 2. Final Foamed-CLSM Mixture Proportions, Gas Source: Simulated Flue Gas

Mixture Number	FS-2	FS-2A
Fly Ash, Dry Wt., kg/m ³	730	764
Foam Generated, cm ³ /m ³	359259	374074
Foam Generated, kg/m ³	16.02	16.73
Water, kg/m ³	329.3	343.5
Air Temperature (°C)	18	20
Foamed-CLSM Temperature (°C)	22	19
Fresh Foamed-CLSM Density (g/cm ³)	1.07	1.13
Hardened Foamed-CLSM Density (182-day age) (g/cm ³)	0.92	

Table 1. Final Foamed-CLSM Mixture Proportions, Gas Source: Compressed Air*

Mixture Number	FS-1*	FS-1A*	FS-1B
Fly Ash, Dry Wt., kg/m ³	765	750	733
Foam Generated, cm ³ /m ³	381481	374074	366667
Foam Generated, kg/m ³	16	15	15
Water, kg/m ³	347	338	336
Air Temperature (°C)	19	19	19
Foamed-CLSM Temperature (°C)	19	18	22
Fresh Foamed-CLSM Density (g/cm ³)	1.13	1.11	1.10
Hardened Foamed-CLSM Density (182-day age) (g/cm ³)	0.90		

*Approximately half of the test specimens cast from these mixtures were discarded due to insufficient consolidation.

Table 3. Final Foamed-CLSM Mixture Proportions, Gas Source: Carbon Dioxide

Mixture Number	FS-3	FS-3A
Fly Ash, Dry Wt., kg/m ³	688	641
Foam Generated, cm ³ /m ³	3148148	3037037
Foam Generated, kg/m ³	213.58	207.65
Water, kg/m ³	231.4	216.5
Air Temperature (°C)	17	16
Foamed-CLSM Temperature (°C)	37	39
Fresh Foamed-CLSM Density (g/cm ³)	1.13	1.05
Hardened Foamed-CLSM Density (182-day age) (g/cm ³)	0.78	

CARBONATION TESTING

Carbonation of CLSM Mixtures

The carbonation measurements obtained from the CLSM specimens are shown in Tables 7 to 9. Fig. 4 shows the comparison of carbonation for all three types of CLSM. Carbonation of the foamed-CLSM specimens that used compressed air increased from no indication of carbonation at the age of one day, to complete carbonation at the age of 182 days. Carbonation of CLSM that used the simulated flue gas exhibited a similar carbonation pattern increasing from zero at the age of one day to 100% carbonation at the age of 182 days. The CLSM that used the carbon dioxide started carbonation more quickly. Approximately two percent of the specimen was carbonated at the age of one day to over 89% at the age of 91 days. These results illustrate that using carbon dioxide in CLSM has a greater effect on the rate of carbonation than either the compressed air or the simulated flue gas. This comparison is more clearly visible in Fig. 4. The rate of carbonation is approximately the same for CLSM using the compressed air or simulated flue gas. Assuming the same rate of carbonation for the CLSM with carbon dioxide, complete carbonation can be estimated at the age of less than 120 days.

CONCLUSIONS AND RECOMMENDATIONS

The CLSM that used the carbon dioxide started carbonation more quickly. The results illustrate that using carbon dioxide in CLSM has a greater effect on the rate of carbonation than either the compressed air or the simulated flue gas.

Based on the testing performed for this project, a number of recommendations can be made. Additional laboratory work is recommended to modify the mixtures with the compressed air and the simulated flue gas to slow the setting of the CLSM, particularly for the CLSM using foam generated with the compressed air.

The phenolphthalein indicator method used for this testing gives an indication of the carbonation based on pH of the CLSM. The initial pH of concrete is approximately 12.6 to 13.5, while the pH of carbonated concrete is approximately 9. The color change for the indicator solution changes to pink at pH above approximately 9.5. The pink color indicates the presence of calcium hydroxide, but does not indicate an absence of carbonation. Since it was expected that the incorporation of the simulated flue gas or the carbon dioxide would increase the rate of carbonation internally, a new test method should be used to monitor the actual pH changes in the CLSM. This would probably give a better indication of the internal carbonation.

The foam generated with carbon dioxide quickly dissipated in the CLSM mixtures. Using warm water with the foam concentrate solution seemed to slightly improve the retention of air in the CLSM. A specific attempt was not made to warm the carbon dioxide gas itself prior to its introduction in the foam generator other than using a longer length of a heated-hose from the supply tank. Warmed carbon dioxide should be investigated to determine if this would improve the retention of air in the CLSM mixtures.

The reaction for the carbonation of the CLSM should be more closely evaluated to better determine the amount of carbon dioxide that could be absorbed from the simulated flue gas.

Table 4. Compressive Strength of Foamed-CLSM, Gas Source: Compressed Air

Compressive Strength, MPa		
Test Age, days	Mixture Number	
	FS-1 / FS-1A	FS-1B
	Average	Average
1	0.83	--
3	0.76	--
7	1.14	--
28	1.38	--
56	--	1.97
91	--	1.03
182	--	2.14
365	--	--

Table 6. Compressive Strength of Foamed-CLSM, Gas Source: Carbon Dioxide

Compressive Strength, MPa		
Test Age, days	Mixture Number	
	FS-3	FS-3A
	Average	Average
1	0.62	--
3	0.83	--
7	1.07	--
28	1.34	1.07
56	--	1.03
91	--	--
182	--	--
365	--	--

Table 5. Compressive Strength of Foamed-CLSM, Gas Source: Simulated Flue Gas

Compressive Strength, MPa		
Test Age, days	Mixture Number	
	FS-2	FS-2A
	Average	Average
1	0.59	--
3	1.14	--
7	1.59	--
28	1.76	--
56	--	2.55
91	--	2.83
182	--	3.24
365	--	--

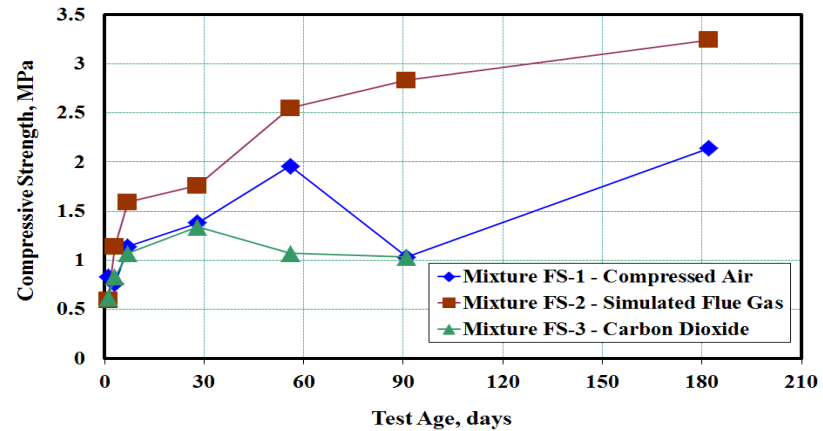


Figure 3. Compressive Strength of Foamed-CLSM Mixtures

Table 7 - Foamed-CLSM Carbonation, Gas Source: Compressed Air

Carbonation Depth				
Test Age, days	Mixture Number			
	FS-1 / FS-1A		FS-1B	
	Average, mm	% Carbonation	Average, mm	% Carbonation
1	0	0	--	--
3	1	2	--	--
7	4.5	8.9	--	--
28	10	19.1	--	--
56	--	--	25	44.4
91	--	--	30	62
182	--	--	Full-Depth	100%

Table 8 - Foamed-CLSM Mixture Carbonation, Gas Source: Simulated Flue Gas

Carbonation Depth				
Test Age, days	Mixture Number			
	FS-2		FS-2A	
	Average, mm	% Carbonation	Average, mm	% Carbonation
1	0	0	--	--
3	3	5.9	--	--
7	4	7.9	--	--
56	--	--	19	35.7
91	--	--	28	52.4
182	--	--	Full-Depth	100%

Table 9 - Foamed-CLSM Mixture Carbonation, Gas Source: Carbon Dioxide

Carbonation Depth				
Test Age, days	Mixture Number			
	FS-3		FS-3A	
	Average, mm	% Carbonation	Average, mm	% Carbonation
1	2	2.3	--	--
3	2	4	--	--
7	4	7	--	--
28	12	22.7	--	--
56	--	--	37	61.8
91	--	--	62	89.8

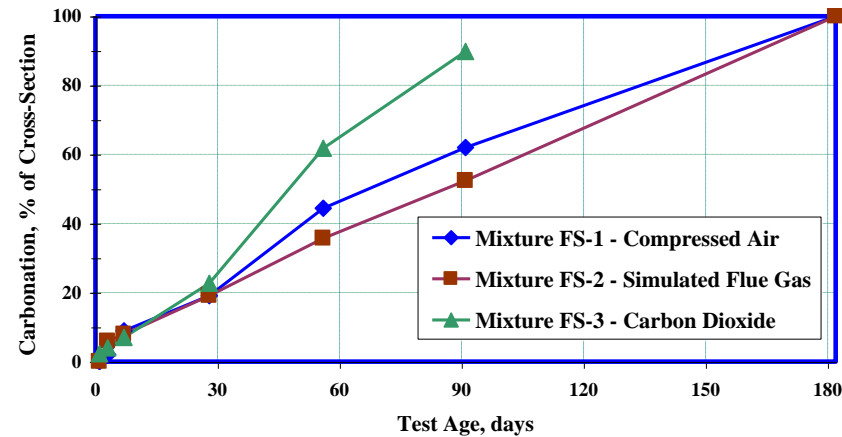


Fig. 4 – Carbonation of Foamed-CLSM Mixtures in 6-in. Dia. by 30-cm Long Cylinders

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