

# **Center for By-Products Utilization**

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and Fethullah Canpolat**

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## **ABSTRACT**

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 with 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 a lightweight aggregate. 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. The carbonation-reaction of the CLSM would also have the potential to reduce carbon dioxide emissions at a coal-fired power plant. The use of a foam generator was intended to have two effects on the CLSM produced, to lower the density of the material, and to distribute the selected gas throughout the CLSM. The distributed gas bubbles would then provide a source for the carbonation reaction within the CLSM. 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. Detailed results are presented.

**Keywords:** carbon dioxide sequestration, carbonation, carbon dioxide emission, compressive strength, concretes, fly ash, foamed Controlled Low-Strength Materials

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## INTRODUCTION

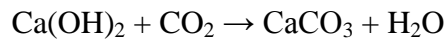
Carbon dioxide (CO<sub>2</sub>) emissions are one of the most serious concerns among all greenhouse gas emissions. CO<sub>2</sub> emissions can be affected by combustion of organic materials (e.g., wood, coal, oil, and other fuels), or by human and animal metabolism (respiration) in which oxygen is utilized and CO<sub>2</sub> is given off as an end-product [1].

The sequestration of CO<sub>2</sub> 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, and is dependent upon the pore structure of the concrete, relative humidity and CO<sub>2</sub> concentration in the environment, availability of Ca(OH)<sub>2</sub> and water, and replacement of cement with mineral additives.

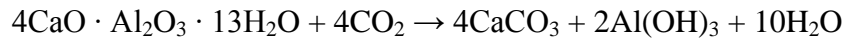
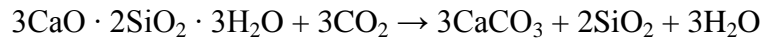
The carbonation of cement-based products is of great importance as it has various effects on physical properties and durability of cement-based products. Carbonation is known to improve surface hardness, strength, and durability of the cement-based products by pore refinement of the cement paste matrix. 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 [2].

Carbonation in cement-based products can be defined as a reaction between the CO<sub>2</sub> and the cement hydration product Ca(OH)<sub>2</sub> dissolved in the pore water [3]. Calcium silicate hydrates and calcium aluminate hydrates also react with CO<sub>2</sub> in the presence of moisture to produce calcium carbonate [4, 5, 7, 8] and hydrates of silicates and aluminates. Montemor et al., has explained the sequence of the carbonation mechanism as follows [4]:

- (1) CO<sub>2</sub> diffusion through the cement paste matrix.
- (2) CO<sub>2</sub> dissolution in the pore solution and reaction with calcium hydroxide.



- (3) Reaction with silicates and aluminates.



CO<sub>2</sub> diffuses through the pores depending upon the pore structure and degree of saturation of the pores in the cement paste matrix. CO<sub>2</sub> in gaseous phase does not react with cement hydration products; it has to dissolve in the pore water first. Of the hydrates in the cement paste, the one which reacts with CO<sub>2</sub> most readily is Ca(OH)<sub>2</sub>. This reaction produces calcium carbonate (CaCO<sub>3</sub>) and water. Other hydrates also react with dissolved CO<sub>2</sub>; and hydrated silica, alumina, and ferric oxide are produced [4, 5]. When all Ca(OH)<sub>2</sub> becomes carbonated, the pH value of the pore solution is reduced from 12.5 to 8.3 [2, 5]. CaCO<sub>3</sub> 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.

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- $\text{CO}_2$  environment may increase up to 100 % higher than the specimens cured in a  $\text{CO}_2$ -free environment [6]. Lea [6] has also reported a considerable increase in tensile strength of lime mortar and cement mortar specimens cured in high  $\text{CO}_2$  environment compared to the specimens cured in  $\text{CO}_2$ -free air.

The process of carbonation and the rate of carbonation penetration in a concrete product, depend greatly on the dimensions of the concrete product, pore structure of concrete, availability of  $\text{Ca}(\text{OH})_2$ , moisture content of the concrete product, relative humidity and  $\text{CO}_2$  concentration of the surrounding environment, and use of mineral admixtures in concrete [6]. Atis [9] reported lower depths of carbonation at higher strength levels. He also reported higher depth of carbonation of concrete with higher porosity.

Neville [5] 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  $\text{CO}_2$  takes place.” Pore structure has a direct effect on the permeability of concrete. The permeability of concrete to air and water mainly depends on the type and amount of cementitious materials, the degree of hydration, the water to cementitious materials ratio, type, size and grading of aggregates, the degree of compaction, and curing conditions [10]. Sulapha et al. [11] found that a lower water to binder ratio and a prolonged curing age in water resulted in a slower rate of carbonation.

The rate of carbonation is the highest when the relative humidity of the surrounding environment is 50 % to 70 % [5, 9]. Concrete with high internal moisture shows a much lower rate of carbonation because the diffusion of  $\text{CO}_2$  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 [8]. Besides relative humidity, the  $\text{CO}_2$  concentration in the surrounding environment of the concrete is also a very important factor that affects the rate of carbonation. Verbeck [12] concluded that carbonation proceeds slowly and produces little shrinkage at relative humidities of 100 % and 25 %; and he found maximum carbonation shrinkage at 50 % relative humidity. He also concluded that besides relative humidity, the specimen size and the  $\text{CO}_2$  concentration in the curing environment also have significant influence on the carbonation and carbonation shrinkage. He found out that prior carbonation improved the volume stability of mortars to subsequent moisture changes [12].

When fly ash is used as a partial cement replacement material in cement-based products, the initial amount of  $\text{CaO}$  available for hydration decreases, and a lower amount of  $\text{Ca(OH)}_2$  is produced [4]. Silica from fly ash reacts with  $\text{Ca(OH)}_2$  [5] and less  $\text{Ca(OH)}_2$  remains in concrete. At early ages of concrete containing fly ash, less  $\text{CO}_2$  is required to consume  $\text{Ca(OH)}_2$  to produce  $\text{CaCO}_3$ ; and, the expected reactions of fly ash with  $\text{Ca(OH)}_2$  do not occur because of less availability of  $\text{Ca(OH)}_2$  for the hydration of fly ash [4, 5]. Low degree of hydration of fly ash results in increased porosity [4].

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 [7].



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 [13]. Accelerated carbonation of concrete can be achieved by curing the concrete specimens in favorable environmental conditions for carbonation, i.e. a high CO<sub>2</sub> concentration and a certain level of relative humidity. The temperature of the curing environment is also a factor to be considered for accelerated carbonation.

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 CO<sub>2</sub> concentrations during accelerated carbonation of concrete, may greatly increase internal humidity of concrete, because of water being produced rapidly due to high rate of carbonation [14]. Due to high saturation of pores in concrete, it may become difficult for CO<sub>2</sub> to diffuse further in the pore network and may result in a reduced penetration rate of carbonation. Even the products of accelerated carbonation of cement may differ from those produced under natural carbonation. For example, the calcium carbonate crystals produced during accelerated carbonation process may be smaller than the calcium carbonate crystals being produced under natural carbonation process [13]. Also the maturity of concrete specimens under accelerated carbonation conditions is lower than that of the naturally carbonated specimens that show similar degrees of carbonation under natural carbonation conditions [7]. Concrete with a lower level of maturity may show a higher rate of carbonation. Fly ash concrete exposed to accelerated carbonation conditions may

show a higher rate of carbonation as the pozzolanic reactions of fly ash may be hindered by high rate of carbonation.

We Energies has proposed a method to sequester CO<sub>2</sub> through the production of a lightweight cellular Controlled Low-Strength Materials (CLSM), while at the same time increasing the compressive strength of the CLSM.

Sometimes, foam is added to CLSM to reduce the density of CLSM. We Energies' proposed method is to replace the normal air used in producing the foam with CO<sub>2</sub> and flue gas generated from electric power plants. The CO<sub>2</sub> in the flue gas should react with hydration products in the CLSM and in turn sequester the CO<sub>2</sub>. Typically, carbonation occurs at the surface, where the material is exposed to a source of CO<sub>2</sub>, for example from air, and slowly penetrates further in depth.

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 with 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 a lightweight aggregate. 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.

### **Fly Ash**

One source of fly ash was used throughout this project. Fly ash was from We Energies Oak Creek Power Plant throughout the project. This selection was made by We Energies to represent a typical ASTM C 618 Class C fly ash available from We Energies. Material characteristics of the fly ash reported in this project was provided by We Energies. They are given in Tables 1 and 2.

### **Foam Concentrate**

A foam concentrate solution was used for generating foam for this project. The foam concentrate was obtained from Elastizell Corporation of America, Dexter, MI. Prior to mixing the CLSM, the foam concentrate was diluted with water at a ratio of 40 parts of water to one part of foam concentrate by volume. Temperature of the water used to mix the foam concentrate was increased when carbon dioxide was used to generate the foam.

### **Compressed Gas**

Three types of compressed gas were used to generate the foam used for this project, compressed air, carbon dioxide, and a gas used to simulate flue gas from a coal burning electric power plant. 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. Compressed carbon dioxide gas was provided by UWM-CBU.

### **Foam Generator**

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 (Fig. 1). 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 175 psi prior to introduction in the foam generator. When using carbon dioxide, a rubber hose extension, approximately six feet long, was used to somewhat warm the carbon dioxide gas before introduction into the foam generator. Without the additional length of hose, the foam generator began to freeze and leak gas. The regulator on the foam generator was adjusted to 100 psi. The intake hose from the diaphragm pump was placed in the foam concentrate solution which was diluted using the ratio specified by the manufacturer of 40 parts of water to one part of foam concentrate by volume. The valve on the foam nozzle was opened and foam was generated until it reached a uniform quality (within approximately 5 to 10 seconds). The valve on the nozzle was then closed until foam was to be added to the CLSM mixture. For each type of gas used, the density of the foam and the rate of foam production were calculated. Characteristics of the foam generated is given in Table 3.

### **Manufacturing of CLSM Mixtures**

CLSM was mixed using a rotating-drum mixer with a volume of nine cubic feet (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 (Fig. 2), the amount of foam was timed to obtain the specified volume. Fig. 3 shows the foam being mixed into the CLSM. When the foam had uniformly mixed into the CLSM, the CLSM was discharged on to a pan for tests of unit weight and temperature, and for casting of test specimens. Depending upon the type of gas used to generate the foam, the amount of foam was either added all at once, or periodically during the mixing of the CLSM when carbon dioxide was used to generate foam. Due to the number of test specimens required for the specified tests, two replicate mixtures were prepared for each of the final mixtures for each type of gas.

### **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. 6-inch diameter by 12-inch 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 were 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  $70^{\circ} \pm 5^{\circ}\text{F}$ . The test specimens were then demolded and placed in

a curing room maintained at 50% R.H. and  $73^{\circ}\pm 3^{\circ}\text{F}$  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. 126, November-December 1988). In accordance with this test procedure, a phenolphthalein indicator solution is sprayed on to a broken section of 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 (Fig. 5). The splitting-tensile strength test was performed per ASTM C 496 modified for the CLSM test specimens by reducing the loading rate to approximately 500-600 lb/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 remain colorless, while non-carbonated areas turn 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 splitting-tensile strength at each test age, and the broken surface tested for carbonation. Fig. 5 shows a test cylinder 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, and 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 6-in. diameter by 12-in. long test cylinder. Carbonation visible in the interior section of the test specimen was also recorded. Fig. 6 shows a typical measurement for 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 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: 10 ft<sup>3</sup>/yd<sup>3</sup> of CLSM
- Fly Ash (ASTM C 618, Class C): 1275 lb/yd<sup>3</sup>
- Water: 575 lb/yd<sup>3</sup>

### **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. The trial mixture proportions and fresh CLSM properties of the CLSM produced with compressed air are shown in Table 4. 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.

Details of the properties of the trial CLSM mixtures using the simulated flue gas source are given in Table 5. This mixture also exhibited a very fast short time of set; however, it was slower than the mixture containing compressed air.

Mixture proportions and fresh CLSM properties of trial mixtures using carbon dioxide are given in Table 6. Carbon dioxide, when introduced into the mixer, appeared to retard the setting of the CLSM significantly compared to CLSM that used compressed air or the simulated flue gas. The air that was introduced with the foam also quickly dissipated from the CLSM. After a series of trial mixtures, the desired density of the CLSM was achieved by extended mixing time and periodic addition of the foam containing carbon dioxide. CLSM was mixed for a total of approximately 20 to 25 minutes before the air content of the CLSM became stable enough to produce test specimens. The voids observed in a broken section of CLSM that used carbon dioxide appeared to be much larger than the voids observed in CLSM that used either



compressed air or the simulated flue gas. Trial mixture proportions of the CLSM mixtures using all types of gases were submitted to We Energies for approval prior to finalizing the mixture proportions for production of test specimens.

### **CLSM Final Mixtures Proportions**

CLSM final mixture proportions and fresh properties for foamed-CLSM are given in Tables 7 to 9. 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 7) for the compressed-air-CLSM. The CLSM mixture went through its final set while CLSM was being placed in the test cylinders. Subsequent mixtures using compressed air used an ASTM designated vibratory table to further consolidate the test cylinders when the consistency of the CLSM became less flowable (i.e., more stiff). Mixture FS-1B was produced to obtain additional test specimens. Fresh density of the CLSM was  $69.5 (\pm 1) \text{ lb/ft}^3$ . The hardened density of the CLSM after approximately 182 days of curing at 50 to 75% R.H. was less than  $56.3 \text{ lb/ft}^3$ .

CLSM produced with the simulated flue gas also exhibited a very short setting time after the foam was added to the mixture. The quantity of the foam added to the mixture and the fresh CLSM density (Table 8) were similar to the foamed-CLSM made with compressed air. Fresh density of the CLSM ranged from  $66.6$  to  $70.8 \text{ lb/ft}^3$ . The hardened density of the CLSM after approximately 182 days of curing at 50 to 75% R.H. was again less than  $57.6 \text{ lb/ft}^3$ .

Fresh foamed-CLSM properties of the final mixtures using carbon dioxide is shown in Table 9. Fresh density of CLSM using carbon dioxide ranged from 65.7 to 70.6 lb/ft<sup>3</sup>. 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. The foam was added in several parts, more foam was added each time when the CLSM appeared to be beginning to stiffen. The water was also reduced to partially account for the large volume of foam being added to the mixture. The test cylinders appeared to accumulate froth on the top of the cylinders while in the molds. This indicates that some of the air incorporated into the CLSM had migrated to the surface. The density of the hardened CLSM after approximately 182 days of curing at 50 to 75% R.H. was 47.8 lb/ft<sup>3</sup>, which was less than the CLSM produced with the other two gases.

## **DISCUSSION OF RESULTS**

### **CLSM Compressive Strength**

CLSM has a maximum compressive strength specified by ACI Committee 229 as 1,200 psi 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 100 psi. The CLSM produced in this project is 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 10 - 12. Compressive strength of the CLSM mixtures using foam generated with compressed air

(Mixtures FS-1/1A and FS-1B) increased from 120 psi at the age of one day, to 310 psi at 182 days. Compressive strength for the CLSM using the simulated flue gas is given in Table 11. The compressive strength of these mixtures was lower, 85 psi, compared to the compressed air CLSM at the age of one day, but increased to 470 psi at the age of 182 days. The compressive strengths developed by CLSM mixtures using carbon dioxide (Table 12), at the age of one day was 90 psi; and it achieved a compressive strength of only 150 psi at the age of 91 days. For this CLSM mixture, compressive strength up to the age of 28 days was 195 psi, but compressive strength tested at the 56 and 91-day age were lower (probably because the actual batch of CLSM was different).

A comparison of the compressive strength of the three types of foamed-CLSM is shown in Fig. 7. This figure shows that the compressive strength developed by the foamed-CLSM using the simulated flue gas was higher than the CLSM using the other two gas sources beginning at the age of 3 days. This trend continued through the later ages. The mixture of the simulated flue gas provided a much better strength gain, especially when compared to carbon dioxide alone at later ages.

## **CARBONATION TESTING**

### **Carbonation of CLSM Mixtures**

The carbonation measurements obtained from the CLSM specimens are shown in Tables 13 - 15 and Fig. 8. The carbonation of the CLSM mixtures shown in Table 13 is for CLSM using compressed air, Table 14 for CLSM using simulated flue gas, and Table 15 for CLSM with carbon dioxide. Fig. 3 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. 8. 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. 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.

Based on the testing performed for this project to date, 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 (RILEM test procedure CPC18) used for this testing work 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 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.

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## **List of Tables**

**Table 1** - Physical Properties of Oak Creek Fly Ash

**Table 2** - Chemical Analysis of Oak Creek Fly Ash

**Table 3** - Characteristics of Foam Generated

**Table 4** - Foamed-CLSM Trial Mixture Proportions, Gas Source: Compressed Air

**Table 5** - Foamed-CLSM Trial Mixture Proportions, Gas Source: Simulated Flue Gas

**Table 6** - Foamed-CLSM Trial Mixture Proportions, Gas Source: Carbon Dioxide

**Table 7** - Final Foamed-CLSM Mixture Proportions, Gas Source: Compressed Air

**Table 8** - Final Foamed-CLSM Mixture Proportions, Gas Source: Simulated Flue Gas

**Table 9** - Final Foamed-CLSM Mixture Proportions, Gas Source: Carbon Dioxide

**Table 10** - Compressive Strength of Foamed-CLSM, Gas Source: Compressed Air

**Table 11** - Compressive Strength of Foamed-CLSM, Gas Source: Simulated Flue Gas

**Table 12** - Compressive Strength of Foamed-CLSM, Gas Source: Carbon Dioxide

**Table 13** - Foamed-CLSM Mixture Carbonation, Gas Source: Compressed Air

**Table 14** - Foamed-CLSM Mixture Carbonation, Gas Source: Simulated Flue Gas

**Table 15** - Foamed-CLSM Mixture Carbonation, Gas Source: Carbon Dioxide

## **List of Figures**

**Fig. 1** - Foam Generator

**Fig. 2** - Determining the Foam Generation Rate

**Fig. 3** - Mixing Foam in CLSM

**Fig. 4** - Testing of CLSM for Splitting-Tensile Strength

**Fig. 5** - Test Cylinder Treated with Indicator Solution

**Fig. 6** - Measurement of Carbonation (in cm)

**Fig. 7** - Compressive Strength of Foamed-CLSM Mixtures

**Fig. 8** - Carbonation of Foamed-CLSM Mixtures

**Table 1 - Physical Properties of Oak Creek Fly Ash**

Analysis Parameter	Material	ASTM C 618 Requirements		
	Oak Creek Fly Ash	Class N	Class C	Class F
Moisture Content, (%)	0.02	3.0 max.	3.0 max.	3.0 max.
Retained on No. 325 Sieve (%)	10.6	--	34 max.	34 max.
Strength Activity Index with Cement (% of Control)	7-day	100.4	75 min.	75 min.
	28-day	104.6	75 min.	75 min.
Water Requirement, (% of Control)	93.0	115 max.	105 max.	105 max.
Autoclave Expansion, (%)	0.07	0.8 max.	0.8 max.	0.8 max.
Density	2.68	--	--	--

**Table 2 - Chemical Analysis of Oak Creek Fly Ash**

Chemical Composition	Oak Creek Fly Ash, %	ASTM C 618 Limits, %		
		Class N	Class C	Class F
Silicon Dioxide, SiO <sub>2</sub>	35.2	-	-	-
Aluminum Oxide, Al <sub>2</sub> O <sub>3</sub>	19.4	-	-	-
Iron Oxide, Fe <sub>2</sub> O <sub>3</sub>	5.9	-	-	-
Total, SiO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub>	60.5	70.0 min.	50.0 min.	70.0 min.
Sulfur Trioxide, SO <sub>3</sub>	1.5	5.0 max.	5.0 max.	5.0 max.
Calcium Oxide, CaO	25.1	-	-	-
Magnesium Oxide, MgO	6.4	-	-	-
Titanium Dioxide, TiO <sub>2</sub>	1.4	-	-	-
Potassium Oxide, K <sub>2</sub> O	0.4	-	-	-
Sodium Oxide, Na <sub>2</sub> O	2.2	-	-	-
Loss on Ignition	0.2	10.0 max.*	6.0 max.*	6.0 max.*
Available Alkali (equivalent % of Na <sub>2</sub> O)	1.4	1.5 max.**	1.5 max.**	1.5 max.**

\* Under certain circumstances, up to 12.0% max. LOI may be allowed.

\*\* Optional. Required for ASR Minimization.

**Table 3 - Characteristics of Foam Generated\***

Property	Gas Source						
	Compressed Air	Simulated Flue Gas		Carbon Dioxide			
	Trial Number	Trial Number		Trial Number			
	1	1	2	1	2	3	4
Foam Generation Rate (ft <sup>3</sup> /min)	8.4	--	8.4	6.0	4.8	5.3	5.4
Foam Density (lb/ft <sup>3</sup> )	2.6	--	2.8	4.1	--	4.5	4.2
Comments	Foam appeared to consist of very fine bubbles. Stable foam, did not appear to break down.	No foam was generated. Gas in partially filled tank consumed while adjusting pressures of regulators.	Foam appeared to break down slightly over time.	Foam broke down entirely within 5-10 minutes. Regulator with 18-inch braided s.s. hose connected directly to foam generator. Frost on foam generator and regulator after use.	Foam solution mixed with hot (87°F) water). Foam appeared to be more stable than in Trial 1. Used 6-ft. hose extension between regulator fitting and foam generator.	Foam solution mixed with cold (45°F) water). Foam volume and density determined 2 minutes after generating.	Foam solution mixed with warm (87°F) water). Foam volume and density determined 2 minutes after generating.

\* Regulator pressure on the gas tank adjusted for 175 psi feed to foam generator. Regulator on foam generator set at 100 psi. (Two pressure regulators used.)

**Table 4 - Foamed-CLSM Trial Mixture Proportions, Gas Source: Compressed Air**

Mixture Number		WEFS-1
Date		11/5/03
Fly Ash, Dry Wt., lb/yd <sup>3</sup>		1210
Foam Generated, ft <sup>3</sup> /yd <sup>3</sup>		9.6
Foam Generated, lb/yd <sup>3</sup>		24.4
Water, lb/yd <sup>3</sup>		545
Flow, in.		6-1/4
Fresh Foamed-CLSM Density (lb/ft <sup>3</sup> )		65.9
Compressive Strength, psi	1-day	115

**Table 5 - Foamed-CLSM Trial Mixture Proportions, Gas Source: Simulated Flue Gas**

Mixture Number		WEFS-2
Date		11/12/03
Fly Ash, Dry Wt., lb/yd <sup>3</sup>		1230
Foam Generated, ft <sup>3</sup> /yd <sup>3</sup>		9.8
Foam Generated, lb/yd <sup>3</sup>		26.1
Water, lb/yd <sup>3</sup>		555
Flow, in.		8-1/2
Fresh Foamed-CLSM Density (lb/ft <sup>3</sup> )		67.2
Compressive Strength, psi	1-day	185

**Table 6 - Foamed-CLSM Trial Mixture Proportions, Gas Source: Carbon Dioxide**

Mixture Number	WEFS-3	WEFS-4	WEFS-5	WEFS-6	WEFS-7	WEFS-8
Date	12/3/03	12/3/03	12/8/03	12/8/03	12/8/03	12/18/03
Fly Ash, Dry Wt., lb/yd <sup>3</sup>	1930	1890	1690	1605	1555	1475
Foam Generated, ft <sup>3</sup> /yd <sup>3</sup>	15.3	16.6	55.0	80.5	149.3	118
Foam Generated, lb/yd <sup>3</sup>	12.8	13.1	45.0	65.8	122.9	101.3
Foam Concentrate/Water Temperature, °F	45	82	67	67	67	95
Water, lb/yd <sup>3</sup>	870	853	762	724	527	505
Water Temperature, °F	45	45	67	67	67	108
Fresh Foamed-CLSM Density (lb/ft <sup>3</sup> )	104.2	102.0	92.8	88.4	81.4	77.6
Hardened Foamed- CLSM Density (lb/ft <sup>3</sup> )	104.5	103.9	93.3	90.0	86.1	--
Compressive Strength, psi	450 (6-days)	455 (6-days)	255 (1-day)	145 (1-day)	50 (1-day)	--
Comments	All foam added to mixture after ash mixed with water.	All foam added to mixture after ash mixed with water.	Foam added to mixture in three parts.	Foam added in four parts. Total mixing time = 22.33 min. Foam added at 4-min., 5-min., 9-min., 16-min., and 22 min. after start of mixing	Foam added to mixture in 7 parts. Total mixing time = 25 minutes.	Foam added in 4 parts. Mixture used hot water for both mixing water and generating foam.

**Table 7 - Final Foamed-CLSM Mixture Proportions, Gas Source: Compressed Air\***

Mixture Number	FS-1*	FS-1A*	FS-1B
Date	11/17/03	11/17/03	11/24/03
Fly Ash, Dry Wt., lb/yd <sup>3</sup>	1290	1265	1235
Foam Generated, ft <sup>3</sup> /yd <sup>3</sup>	10.3	10.1	9.9
Foam Generated, lb/yd <sup>3</sup>	26.4	25.8	25.2
Water, lb/yd <sup>3</sup>	585	570	566
Air Temperature (°F)	68	68	68
Foamed-CLSM Temperature (°F)	66	65	72
Fresh Foamed-CLSM Density (lb/ft <sup>3</sup> )	70.6	69.6	68.4
Hardened Foamed-CLSM Density (182-day age) (lb/ft <sup>3</sup> )	56.3		

\*Approximately half of the test specimens cast from these mixtures were discarded due to insufficient consolidation. CLSM stiffened while material was being placed in cylinders.

**Table 8 - Final Foamed-CLSM Mixture Proportions, Gas Source: Simulated Flue Gas**

Mixture Number	FS-2	FS-2A
Date	11/19/03	12/1/03
Fly Ash, Dry Wt., lb/yd <sup>3</sup>	1230	1287
Foam Generated, ft <sup>3</sup> /yd <sup>3</sup>	9.7	10.1
Foam Generated, lb/yd <sup>3</sup>	27	28.2
Water, lb/yd <sup>3</sup>	555	579
Air Temperature (°F)	65	68
Foamed-CLSM Temperature (°F)	72	67
Fresh Foamed-CLSM Density (lb/ft <sup>3</sup> )	66.6	70.8
Hardened Foamed-CLSM Density (182-day age) (lb/ft <sup>3</sup> )	57.6	

**Table 9 - Final Foamed-CLSM Mixture Proportions, Gas Source: Carbon Dioxide**

Mixture Number	FS-3	FS-3A
Date	1/6/04	1/20/04
Fly Ash, Dry Wt., lb/yd <sup>3</sup>	1160	1080
Foam Generated, ft <sup>3</sup> /yd <sup>3</sup>	85	82
Foam Generated, lb/yd <sup>3</sup>	360	350
Water, lb/yd <sup>3</sup>	390	365
Air Temperature (°F)	62	60
Foamed-CLSM Temperature (°F)	98	102
Fresh Foamed-CLSM Density (lb/ft <sup>3</sup> )	70.6	65.7
Hardened Foamed-CLSM Density (182-day age) (lb/ft <sup>3</sup> )	48.7	

**Table 10 - Compressive Strength of Foamed-CLSM, Gas Source: Compressed Air**

Compressive Strength, psi		
Test Age, days	Mixture Number	
	FS-1 / FS-1A	FS-1B
	Average	Average
1	120	--
3	110	--
7	165	--
28	200	--
56	--	285
91	--	150
182	--	310
365	--	

**Table 11 - Compressive Strength of Foamed-CLSM, Gas Source: Simulated Flue Gas**

Compressive Strength, psi		
Test Age, days	Mixture Number	
	FS-2	FS-2A
	Average	Average
1	85	--
3	165	--
7	230	--
28	255	--
56	--	370
91	--	410
182	--	470
365	--	



**Table 12 - Compressive Strength of Foamed-CLSM, Gas Source: Carbon Dioxide**

Compressive Strength, psi		
Test Age, days	Mixture Number	
	FS-3	FS-3A
	Average	Average
1	90	--
3	120	--
7	155	--
28	195	155
56	--	150
91	--	
182	--	
365	--	

**Table 13 - Foamed-CLSM Carbonation, Gas Source: Compressed Air**

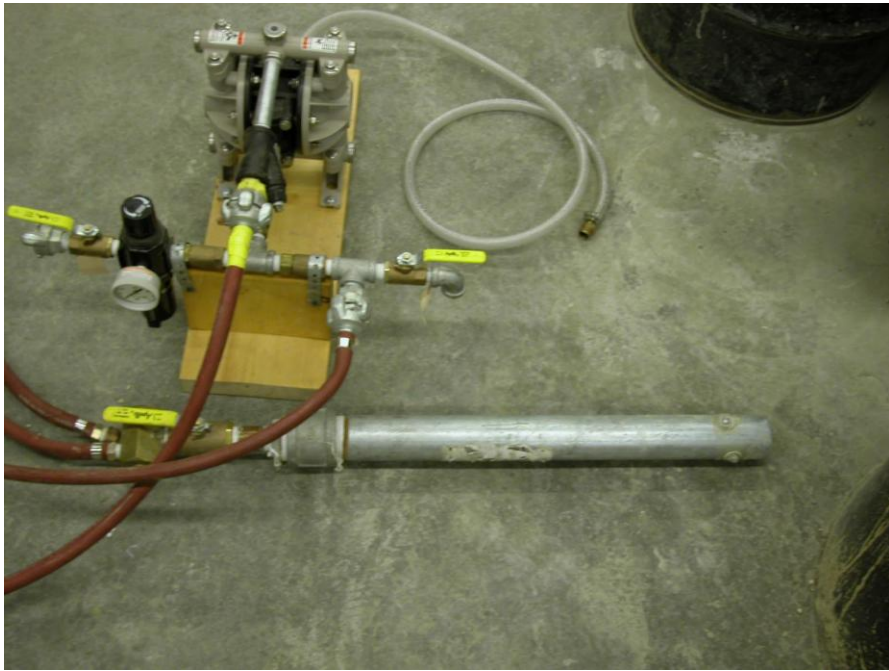
Carbonation Depth						
Test Age, days	Mixture Number					
	FS-1 / FS-1A			FS-1B		
	Average at top, sides, bottom, mm	Average, mm	% Carbonation	Average at top, sides, bottom, mm	Average, mm	% Carbonation
1	0	0	0	--	--	--
	0			--		
	0			--		
3	1	1	2.0	--	--	--
	1			--		
	1			--		
7	4.5	4.5	8.9	--	--	--
	4.5			--		
	4.5			--		
28	10	10	19.1	--	--	--
	10			--		
	10			--		
56	--	--	--	25	25	44.4
	--			25		
	--			25		
91	--	--	--	30	30	62.0
	--			30		
	--			30		
182	--	--	--	N/A	Full-Depth	100%
	--			N/A		
	--			N/A		
365	--	--	--			
	--					
	--					

**Table 14 - Foamed-CLSM Mixture Carbonation, Gas Source: Simulated Flue Gas**

Carbonation Depth						
Test Age, days	Mixture Number					
	FS-2			FS-2A		
	Average at top, sides, bottom, mm	Average, mm	% Carbonation	Average at top, sides, bottom, mm	Average, mm	% Carbonation
1	0	0	0	--	--	--
	0			--		
	0			--		
3	3	3	5.9	--	--	--
	3			--		
	3			--		
7	4	4	7.9	--	--	--
	4			--		
	4			--		
28	10	10	19.1	--	--	--
	10			--		
	10			--		
56	--	--	--	17	19	35.7
	--			20		
	--			20		
91	--	--	--	24	28	52.4
	--			32		
	--			27		
182	--	--	--	N/A	Full-Depth	100%
	--			N/A		
	--			N/A		
365	--	--	--	--		
	--			--		
	--			--		

**Table 15 - Foamed-CLSM Mixture Carbonation, Gas Source: Carbon Dioxide**

Carbonation Depth						
Test Age, days	Mixture Number					
	FS-3			FS-3A		
	Average at top, sides, bottom, mm	Average, mm	% Carbonation	Average at top, sides, bottom, mm	Average, mm	% Carbonation
1	7	2	2.3	--	--	--
	0			--		
	0			--		
3	2	2	4.0	--	--	--
	2			--		
	2			--		
7	6.5	4	7.0	--	--	--
	3			--		
	3			--		
28	14	12	22.7	--	--	--
	12			--		
	10			--		
56	--	--	--	37	37	61.8
	--			37		
	--			37		
91	--	--	--	84	62	89.8
	--			62		
	--			40		
182	--	--	--	--	--	--
	--			--		
	--			--		
365	--	--	--	--	--	--
	--			--		
	--			--		



**Fig. 1 – Foam Generator**



**Fig. 2 – Determining the Foam Generation Rate**

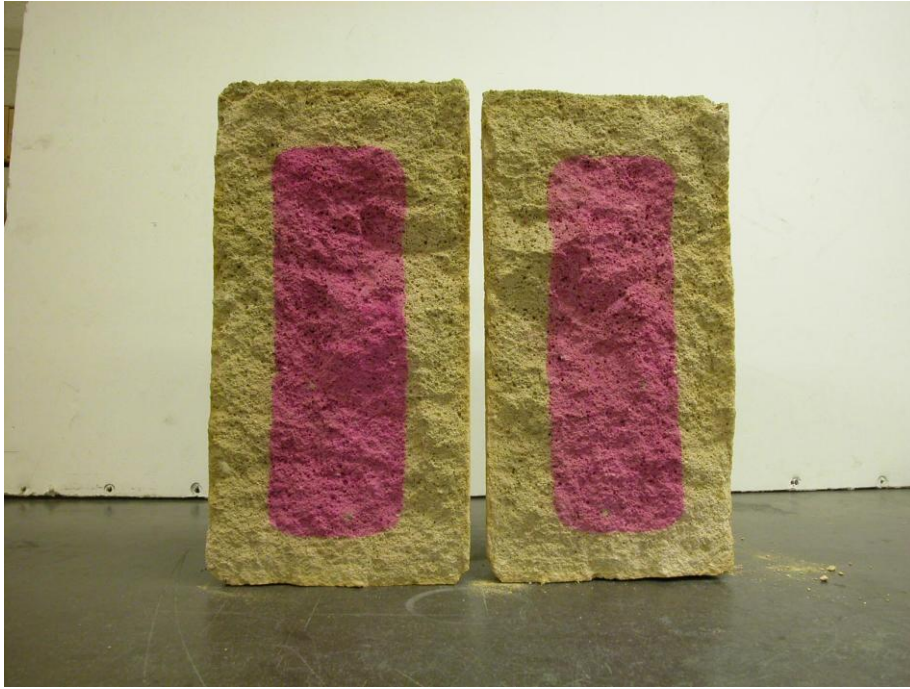


**Fig. 3 – Mixing Foam in CLSM**

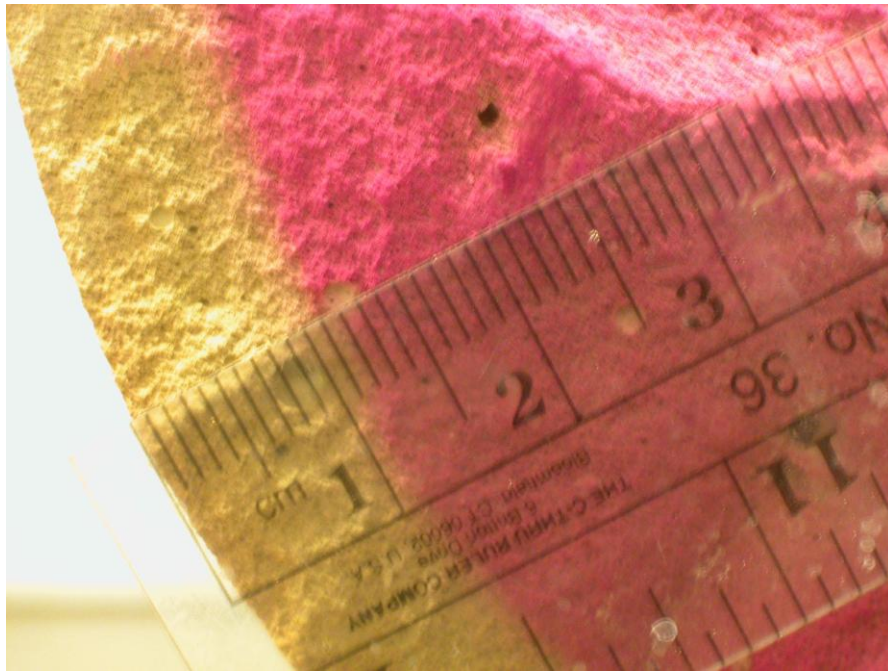


**Fig. 4 – Testing of CLSM for Splitting-Tensile Strength**





**Fig. 5 – Test Cylinder Treated with Indicator Solution**



**Fig. 6 – Measurement of Carbonation (in cm)**

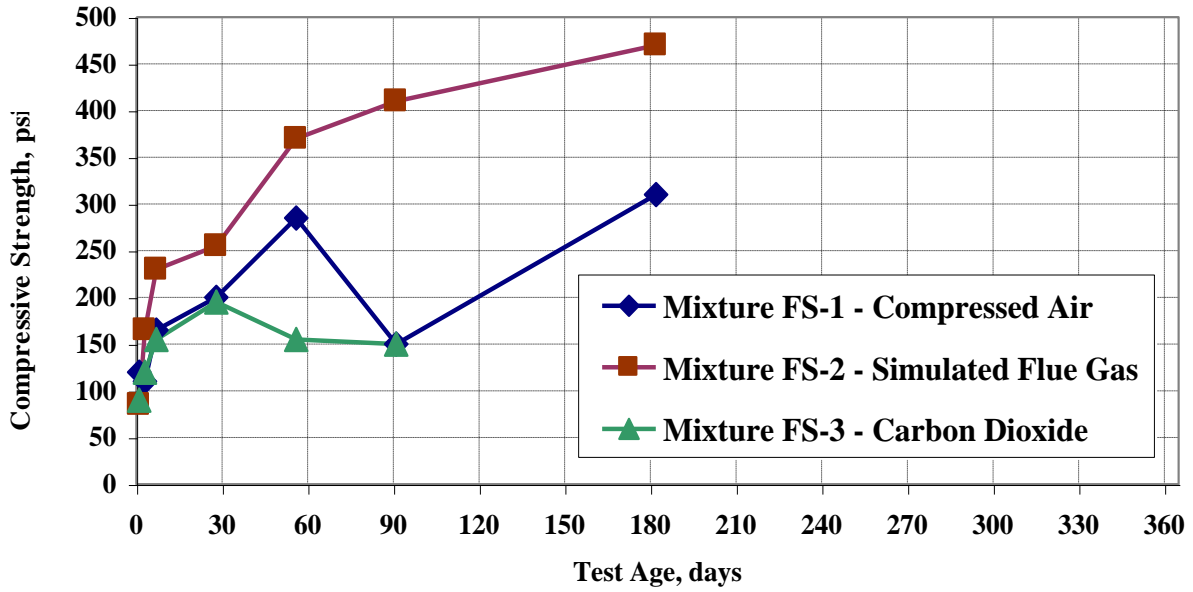


Fig. 7 - Compressive Strength of Foamed-CLSM Mixtures

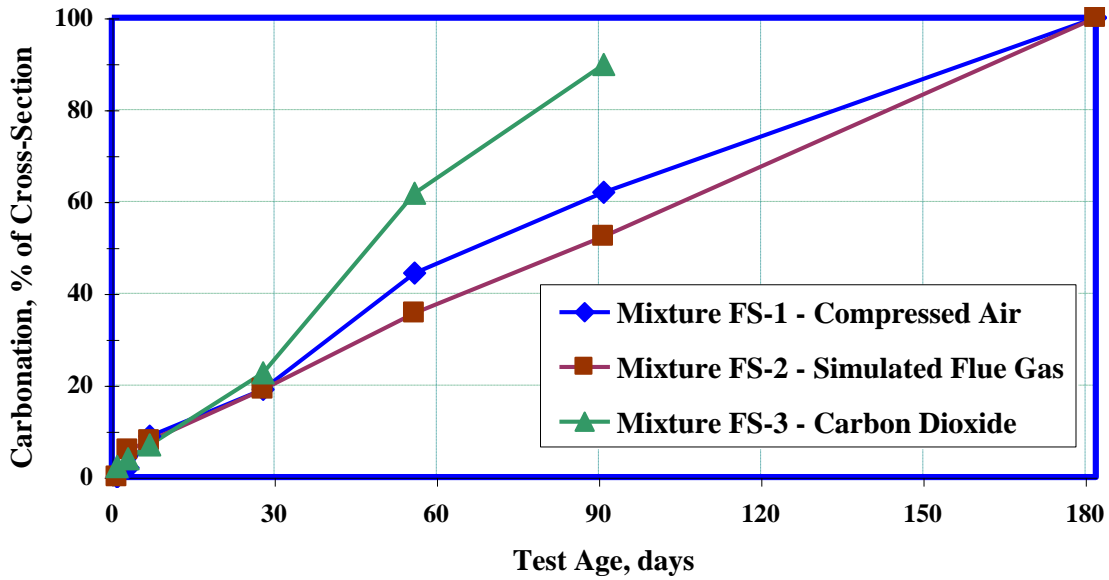


Fig. 8 – Carbonation of Foamed-CLSM Mixtures in 6-in. Dia. by 12-in. Long Cylinders