EFFECTS OF SUPERCRITICAL CARBON DIOXIDE ON WELL CEMENTS

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ABSTRACT

Due to the widespread manifestation of large scale miscible CO_2 enhanced recovery projects, particularly in West Texas and Gulf Coast regions, considerable concern has developed regarding the performance and/or durability of hydrated cement located across producing and injection intervals in CO_2 related wells.

It is known that carbonation affects the microstructure of cement affecting both porosity and compressive strength. The CO_2 reactivity of a cement is characterized not only by its chemical composition, but also by the properties of the CO_2 medium itself, that is, partial pressure, temperature and relative humidity. However, a clear understanding of this phenomenon and its effects on portland cement is still not completely substantiated, giving rise to contradictory opinions in this particular area of research.

This lead to the need and development of a laboratory program for examining the effects of supercritical CO_2 on preset cement, as well as the influence of carbonation on the early stages of the cement hydration process. This article presents the findings of a comprehensive study which show that after prolonged exposure to CO_2 under supercritical conditions, the hydration products formed in the hydration of common portland cement undergo decomposition into calcium carbonate and a siliceous residue. Cement samples exposed to the lower extremes (temperature and pressure) of a supercritical CO_2 environment exhibited greater reactivity under dynamic conditions as compared to static conditions, while increasing CO_2 pressure increased the degree of reaction regardless of the carbonation conditions employed.

INTRODUCTION

Carbonation reactions involving cementitious materials have been of interest for many years. Previous research[1-3] has focused on the carbonation of the hydration products of portland cement mortars, compacted pastes of pure hydraulic calcium silicates and aluminates and non-hydraulic calcium silicate mortars and powders. Workers in this area of research have reported a wide variety of observations, noting phenomena ranging from a mere self-inhibited reacted skin layer to the complete decomposition of calcium silicate hydrate gel, the main binding component in hydrated cement, into calcium carbonate and an amorphous silica. However, little data has been generated which is relative to cementing compositions typically used for well completions in the oil and gas industry and/or the carbonation conditions associated with CO_2 enhanced recovery projects.

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At the critical temperature and pressure of carbon dioixde, 31°C (87.8°F) and an absolute pressure of 7.3 MPa (1,071 psi), the liquid and vapor states become indistinguishable. Above these conditions, the fluid state that exists may be defined as a gas -- or supercritical fluid. It is this supercritical state that has provoked concern regarding the service life of the cement used in the oil and gas industry since these are conditions associated with: 1) the continuous injection of relatively dry liquid CO_2, as well as alternate gas-water injection, into potential pay zones, 2) the recovery of CO_2 saturated formation fluids and gases along the producing intervals of both recovery and source (naturally produced CO_2) wells, and 3) the separation and preparation (for recycling) of CO_2 from produced fluids at the surface plant.

The effect of CO_2 on cement has generally been considered to be the same as any other weak acid (with available moisture); that is it should attack the alkaline constituents (lime) in set cement and have minimal effect on the calcium silicates. The present investigation revealed that the calcium silicate hydrate phases resulting from the normal hydration of portland well cementing compositions will undergo a type of pseudomorphosis[1] into any of three calcium carbonate phases (vaterite, aragonite, and calcite) and an amorphous silica similar to common silica gel when exposed to a CO_2-rich environment. Under exposure conditions in which samples had completely decomposed into calcium carbonate and amorphous silica, in most cases no detrimental effects to the physico-mechanical properties of the set cement were noted. The degree to which this conversion ultimately occurs becomes a crucial effect recognizing the necessity of frequent chemical (acid) treatments in well maintenance programs. It is shown that by decreasing the water to cement ratio (for reduced permeability in set cement) and substituting or adding reactive siliceous materials for converting undesirable free lime (calcium hydroxide), as well as providing water gap (void) filling properties, the rate at which carbonation progresses in set cement can be decreased. However, complete resistance to the effects of supercritical CO_2 could be obtained only through the use of a totally synthetic cementing formulation.

It is the intent of this paper to describe the factors which influence the rate at which this conversion phenomenon occurs and to elucidate the aggressivity of supercritical CO_2 towards a variety of well cementing formulations and to afford a scientific awareness into the designing and appraising of a CO_2 - serviceable cementing composition.

SCOPE AND PROGRAM

Previous investigations into the carbonation of cement have centered around less severe testing conditions stemming primarily from construction and commercial interests. Most of these studies have been concerned with the accelerated curing (as compared to normal hydration) of freshly prepared cementitious systems having low water to solids ratios (ranging from 0.05 to 0.30) under CO_2 exposure pressures ranging from atmospheric to as high as 5.6 MPa (850 psi),[2,3] others have dealt with the postcarbonation (after normal curing) of hydrated cement, examining the effects on the physical and mechanical properties of set cement samples.

From these, it is known that while the ultimate effect of carbonation is dependent on the chemical nature of the cement hydration products, the actual progress of carbonation is influenced more by the porosity and water content of

the exposed cement surface. Under low pressure static conditions, a large porosity is advantageous to the diffusion of CO_2 and while some water is necessary to initiate a reaction, excessive moisture in the exposure medium becomes detrimental to the carbonation reaction due to the blockage of the sample pores.

In brief, the carbonation mechanism can be described as follows:

1. CO_2 diffuses into the capillary pores of the cement which contain, to some extent, a water film resulting from internal condensation and/or diffusion of environmental fluids.

2. CO_2 dissolves in the water film to form carbonic acid by:

   a) $H_2O + CO_2 \quad HCO_3^- + H^+$

   b) $HCO_3^- \quad CO_3^{2-} + H^+$

3. The resulting carbonic acid reacts with the free lime in the cement affording a continuous supply of fresh water, thus additional carbonic acid by:

   $$Ca(OH)_2 + 2H^+ + CO_3^{2-} \quad CaCO_3 + 2H_2O$$

While the formation of both carbonic acid and calcium carbonate are strongly exothermic, any heat applied to the system will favor vaporization of moisture from within the sample saturating the CO_2 atmosphere. Data clearly shows that as the carbonation pressures are increased, this excessive moisture becomes less significant as the enhanced penetration of CO_2 into a sample becomes the controlling influence.

In view of these discussions, the present investigation was undertaken to determine the reactivity of various portland and special well cementing compositions under the more stringent conditions associated with full-scale CO_2 production and injection projects. To establish a working knowledge in this particular area of research, a recently proposed carbon dioxide flooding program served as the groundwork for this study. From this, the following test criteria were derived:

Case A: CO_2 source well,
total depth - 2987 m (9,800 ft),
bottom hole temperature - 82°C (180°F),
reservoir pressure - 17.2 MPa (2,500 psi).

Case B: CO_2 injection well,
total depth - 2530 m (8,300 ft),
bottom hole temperature at injection interval 41°C (105°F),

Case C: Production (oil, gas and water) unit,
total depth - 1600 m (5,250 ft),
bottom hole temperature - 41°C (105°F),
reservoir pressure - 20.7 MPa (3,000 psi).

Due to the comprehensive nature of this study, the program was divided into two major categories: 1) the postcarbonation of cement samples that had been

allowed to hydrate under normal conditions for extended periods, and 2) the influence of carbonation on cement hydration immediately after slurry preparation. These categories were then divided into static test conditions and dynamic test conditions. Data were compiled on the basis of cement performance with respect to changes in both physical and chemical properties.

EXPERIMENTAL

Equipment

Postcarbonation System: To study the effects of postcarbonation (after normal hydration) of cement samples under both static and dynamic supercritical CO_2 conditions, it was necessary to utilize the apparatus shown in Figure 1. This in-house system consists primarily of a conventional 1200 cc autoclave pressure-vessel assembly (for housing samples) plumbed with a pneumatic hydraulic pump for intensification of standard CO_2 cylinder pressure (approximately 6.2 MPa (900 psi)). The addition fo a dry-ice container and/or the aid of a refrigerated (ethylene-glycol) water bath proved beneficial in the prevention of gas-locking. Utilizing a cylinder with an internal dip-tube permits transfer of liquid CO_2 to the low pressure side of the pump. The high pressure side of the pump is regulated with an in-line relief valve which maintains constant pressure as CO_2 is supplied to the pressure-vessel; installation of an exit relief valve set at a lower pressure enables a continuous flow of CO_2 under high pressure and temperature. In conjunction with this system, a device, as illustrated in Figure 2, can be utilized for agitation of the carbon dioxide environment (CO_2 and water) around the core by means of a rotating cage while simultaneously measuring changes in the cement core's permeability under supercritical conditions. Afterwards, the core sample can be removed, examined and the compressive strength determined.

Stirring Autoclave: In order to simulate downhole exposure conditions (CO_2 production) during the initial stages of curing, a device, as shown in Figure 3, which was originally fabricated for measuring static gel strength development after slurry placement, was plumbed in such a manner to permit CO_2 percolation of freshly prepared cement slurries while under pressure and temperature. A low friction magnetic drive allows the slurry to be stirred while monitoring consistency as a measurement of the torque required to rotate the paddle. The equipment is designed to operate at a maximum temperature of 204°C (400°F) and 69 MPa (10,000 psi).[4]

Ultrasonic Analyzer: Continuous monitoring of strength development while under the influence of constant CO_2 pressure was provided by a nondestructive ultrasonic analyzer system (Figure 4). The system consists basically of three components: a microprocessor unit, a high pressure-high temperature autoclave and a digital plotter. The analyzer measures the transit time (reciprocal of velocity) of an ultrasonic wave pulse through a cement slurry and converts it (through empirically developed correlations) to apparent compressive strength.[5]

Testing Procedures

A preliminary study was conducted under static supercritical conditions using gaseous CO_2 and two common cementing compositions, specifically a neat API Class H cement slurry mixed at a water to cement ratio (w/c) of 0.40 and a pozzolan (siliceous material)-Class H cementing mixture containing two percent

bentonite mixed at a w/c of 0.57. The latter was chosen to establish the fundamental chemical resistant properties afforded by the familiar silica-lime reaction. Where applicable, cement slurries were mixed according to API specifications, (35 seconds on Waring Blender at high speed).[6] The cementing compositions used herein are summarized in Table I.

For this first series of tests, standard 5.08 cm cubical specimens were precured for three days at 82°C (180°F) and 6.5 MPa (950 psi) pressure under normal conditions. The samples were then placed in the pressure-vessel assemblies and covered with deionized water in such a manner so as to leave approximately three inches of void in the closed vessel. This allowed the units to be filled with sufficient gaseous CO_2 to saturate and blanket the water medium to create a carbonic acid environment. Exposure tests were conducted for periods of two, three and four weeks under the initial curing temperature and pressure. Afterwards, the samples were removed and examined for changes in physical and chemical properties as compared to control samples cured under normal conditions for the same durations.

The next series of tests was conducted under slightly different conditions. In these tests, a wider variety of cementing compositions was examined and an exposure temperature and pressure of 41°C (105°F) and 19.3 MPa (2,800 psi) for one and six week periods. As before, samples were precured for three days under normal conditions at the appropriate temperature and pressure. In this series of tests, the pressure-vessels were filled completely with pure liquid CO_2 so as to facilitate the immediate intensification of the surroundings to 19.3 MPa (2,800 psi) CO_2 pressure. Once heat was applied to the vessels and the temperature exceeded 31°C (87.8°F), a supercritical environment would persist.

Under the initial investigation it was also desired to examine the effects of CO_2 contamination during and after placement of a cement slurry acorss a producing carbon dioxide zone. This particular phase of the program was studied using two techniques.

Utilization of the stirring autoclave unit allowed for consecutive injection (percolation) of 12 gram CO_2 cartridges until the desired carbon dioxide concentration had been reached. During and after injection, continuous monitoring of viscosity and temperature changes caused by the formation of carbonic acid and precipitation of calcium carbonate could be maintained with a dual-pen chart recorder. Once viscosity and temperature had stabilized, the slurries were removed and placed in the ultrasonic analyzer autoclaves in order to monitor the compressive strength development.

A second technique employed was to pour the cementing compositions directly into 5.08 cm cubical curing molds, place into 1200 cc pressure vessels and then immediately intensify to 19.3 MPa (2,800 psi) with pure dry liquid CO_2. Once pressurized, the vessels were heated to 41°C (105°F) forcing the carbon dioxide environment into a supercritical state. Preliminary tests were conducted for a one week period.

As a supplement to the latter, freshly prepared cement slurries were also poured directly into the ultrasonic curing chambers. Afterwards, slurries could be either prepressurized with water and allowed to cure at the appropriate temperature for a period of twenty-four hours prior to replacement of water with

gaseous CO_2 or immediately placed under CO_2 pressure. In either case, continuous monitoring of strength development was provided.

Due to pursuant inquiries relative to approaching remedial cementing operations on potential CO_2 injection well candidates at the time of this investigation, the scope of the program was shifted exclusively towards the postcarbonation (static and dynamic conditions) of cement samples that had been precured under normal conditions for different lengths of time.

Measurements

Where applicable, compressive strengths were determined with a universal testing machine with a 27,215 Kg (60,000 lb) load capacity according to the latest edition of ASTM Designation C109.[7]

In the initial investigation, a core micro-permeameter was utilized for determining air permeabilities while a conventional cement permeameter was used for determining permeability to water. Where core samples were not precast, cores were taken from the specimen cubes in a manner that would allow one of the carbonated sides to function as a flow surface. The water permeabilities were calculated according to Darcy's equation:[8]

$$k = \frac{1{,}000\ QL\mu}{A\Delta p} \tag{1}$$

When determining gas permeabilities, a modification of Equation 1 was used in the calculations:

$$k = \frac{cQL}{A} \tag{2}$$

Equation 2 was derived from the horizontal gas flow equation:

$$k = \frac{2{,}000\ L_p Q_\mu}{A(p_1^2 - p_2^2)} \tag{3}$$

By means of Equation 2, calculations could readily be made since the micropermeameter had been calibrated to display "c", which is approximately the inverse of the differential pressure shown in Equation 3.

A CuKα radiation diffractometer was used for quantitative x-ray diffraction analysis (XRDA) on select regions of samples as to degree of reactivity. Samples were ground to less than 5 μm in size with a vibrating shatterbox using trichlorotrifluoroethane as a grinding aid. Peaks were scanned at ½° 2θ/minute and the appropriate background corrections made.

Specimens were also examined through the use of a binocular polarizing microscope and a scanning electron microscope (SEM) which incorporated an energy dispersive x-ray analyzer (EDX) and a multi-channel analyzer.

RESULTS AND DISCUSSION

Characteristics of Reaction

The carbonation mechanism under consideration in this study is of a vigorous nature in portland cement and is not confined to the conversion of calcium hydroxide alone, but also includes the removal of calcium ions (Ca^{2+}) from the calcium silicate hydrate phases:

$$C_3S + xH_2O \quad CSH^a + yCa(OH)_2$$

$$\beta\text{-}\ C_2S + xH_2O \quad CSH^a + yCa(OH)_2$$

$$Ca(OH)_2 + 2H^+ + CO_3^{2-} \quad CaCO_3 + 2H_2O$$

$$C_xSH_y + (x\text{-}x')CO_2 \quad C_{x'}SH_{y'} + (x\text{-}x')CaCO_3 + (y\text{-}y')\ H_2O\ ^9$$

a calcium silicate hydrate (tobormorite gel) has an approximate composition of $C_5S_6H_5$.

The latter reaction results in the production of a highly polymerized silica gel (SiO_2-gel); this is characterized by the rearrangement of the silica tetrahedra into a tridimensional array. Previous work[10], utilizing infrared spectroscopy, indicates that this reaction is preferential to the $Ca(OH)_2$-CO_2 reaction. It is not clear whether this phenomenon is due to kinetics (large surface of the C-S-H gel) or whether chemical thermodynamics is the controlling factor.

In the intermediate carbonation of freshly prepared portland cement slurries (Tables II, III, and Figure 5), this reaction also tends to dampen the compressive strength development evidently due to a lowered calcium to silica ratio. Up to a certain point during the percolation of these slurries, the lowered calcium content causes significant gelation as a result in the shift from an electropositive dispersion to one that is neutral, or slightly negative. Beyond this point, thinning occurs and at extremely high levels of carbonation (electronegative dispersion) the silicate hydrations are accelerated according to:

$$C_nS + (n\text{-}x)CO_2 + yH_2O \quad C_xSH_y + (n\text{-}x)CaCO_3\ ^{11}$$

The aggressivity of CO_2 on portland cement is dependent on several factors. First, one must consider not only the properties of the CO_2 medium (partial pressure, temperature and relative humidity) but also the composition and properties of the cementing composition in concern. Secondly, the specific conditions under which the cement specimens are initially cured, namely temperature and pressure, cannot be overemphasized as these determine the resulting microstructure of the particular cementing composition in question. Finally, in attempting to evaluate a cementing composition's performance in this type of environment, one

has to realize that the degree of aggressivity is dependent not only on the exposure duration, but whether or not static or dynamic conditions are being employed.

As regards depth of CO_2 reaction (penetration) in the initial series of tests (Tables IV thru VI), the main influence is exerted by the CO_2 partial pressure and temperature and only in the second place by the moisture content of the environment, as these tests were conducted under static conditions. This is evidenced by Figures 6 and 7. Based on the carbonation periods studied, the reaction is confined mainly to the outer 0.32 cm (1/8") to 0.64 cm (1/4") of the specimens. It is known that the formation of both carbonic acid and calcium carbonate results in the liberation of 160 Kcal of heat per mole, respectively[3,12]. Under low pressure static conditions, this water vapor can saturate the CO_2 atmosphere and become trapped in the pores on the surface of the specimen causing the enhanced formation of a $CaCO_3$ rich impermeable layer on the exterior of the specimen preventing any further penetration. This also appeared to be the case even in the samples carbonated immediately after slurry preparation as the inner portions of the specimens had undergone considerably less carbonation than the exterior. In contrast, under more stringent conditions (124°C (255°F), and 44.8 MPa (6,500 psi)), complete conversion of specimens into calcium carbonate and silica-gel was observed (Tables VII, VIII and Figure 8). At lower pressures, specimens showed a higher degree of reactivity when carbonated under dynamic conditions (Figure 9).

Presently, the effects of CO_2 on some of the more specialized cementing compositions, such as high aluminate cement, epoxy sealants and synthetic silicate formulations, are still not clear. Test results have indicated such phenomenon as: 1) cracking, apparently due to internal stress forces, in cases of high aluminate cements and silicate formulations, and 2) leaching of solvent from the matrix of some epoxy systems.

In the cases involving high aluminate cement, this "cracking" might be caused by internal stress forces associated with the conversion of the initially formed metastable hexagonal hydrates (CaH_{10}, C_2AH_{19}) to the stable cubic hydrate (C_3AH_6). Research[13,14] into the stability of the calcium aluminate hydrates has shown that this conversion will eventually take place with all set aluminate cements and that the rate of conversion is temperature dependent. It is known that the rate of conversion increases with rising temperature and sufficient moisture, and that a loss in strength is associated with this conversion. In addition, the conversion of the hexagonal hydrates involves a density change from 2.0 g/cm^3 to 2.5 g/cm^3, giving rise to a considerable reduction in hydrate volume. Thus, this results in an increase in the internal porosity of the set cement matrix which is usually accompanied by an increased permeability. When using high water/cement ratios (> 0.40), this increase in porosity is sufficient to cause a large drop in compressive strength.

As is evidenced by the x-ray diffraction data (Table III), aqueous suspension of the hexagonal hydrates react with CO_2 to form calcium aluminum oxide carbonate hydrate ($Ca_4Al_2(CO_9)\cdot 11\ H_2O$). It has been suggested that this compound may be responsible for the "dusting" phenomenon that occurs upon dry curing[14]. Basically, as the cement matures, alumina gel and calcium carbonate are formed from aluminate carbonates.

Morphology of Reaction Products

Conventional microscopic examination, with the aid of polished etched sections (Figure 10) and a rhodamine-B dye treatment using a polarizing light source, confirmed a fairly symmetrical migration of calcium carbonate formation in specimens containing portland cement. The penetration depth was examined with the latter technique by applying a solution of 0.1 percent rhodamine-B in ethanol to a fresh cut surface. This cationic dye tends to enhance the somewhat natural fluorescent properties of the calcium carbonate phase.

SEM analysis reveals that during the course of carbonation a pseudomorphosis of the microstructure occurs converting a majority of the C-S-H crystals into vaterite, aragonite, and eventually into stable calcite and SiO_2-gel (Figure 11). However, in comparison to the morphology of the uncarbonated control specimens, there appears to be no substantial change in the "binding framework"[1] of the tobermorite crystals. The latter appear to be plate-shaped and interlinked (Figure 12) while the calcite crystallites appear poorly developed and intimately dispersed in the microstructure (Figure 13).

Compressive Strength Development

Compressive strength development was interpreted by comparison to control specimens cured under the same temperature and pressure using conventional methods. Results of this examination have been summarized in Tables II, IV and VII. Due to the variety of test procedures used, data has been organized according to the relative carbonation techniques used.

In the initial series of tests, in which all specimens were precured for three days, the supercritical CO_2 environment appears to have minimal effects on compressive strength development regardless of the exposure duration. As previously mentioned, the calcium carbonate formation was limited to the outermost region in all samples tested, owing to the relatively small change, if any, in compressive strength observed.

The most significant changes were observed in the preliminary study which involved the neat Class H cementing composition, higher exposure temperature and the submersion of the test specimens in deionized water. This occurrence might be explained by a thermal cracking phenomenon, resulting to a small extent in the failure of the contact areas of the individual crystals. However, this apparently does not substantially affect the actual physical properties of the composition with continued carbonation as can be seen by the 21 and 28 day exposure results. In tests where samples had been carbonated under high temperature-high pressure conditions, there usually resulted an increase in compressive strength even after samples had completely converted. Earlier research[1] involving the effects of CO_2 on porous concrete has indicated that even after long-term carbonation (365 days), specimens showed large increases in compressive strength after noting significant decreases in strength earlier in the carbonation period.

Permeability Data

In most cases, which involved the majority of the conventional cementing compositions, no detectable changes in water permeability were noted. Both the control specimen and the carbonated specimen showed no measurable permeability at the end of the test period. The exceptions to this were in the cases involving the high aluminate cement, the epoxy sealant, the inorganic polymer corrosion resistant cement and a couple of isolated cases involving a 50-50 pozzolan-Class

H Cement composition and a foamed Class C Cement. In these cases, an increase in permeability was observed. The reasons for this phenomenon are unclear. The previously mentioned exothermal reactions may cause superficial stresses and/or cracking which, when dealing with high porosity cementing compositions, can eventually penetrate the entire matrix (Figure 14). Thus, an apparent increase in permeability results.

In reference to air permeability, it was difficult to establish any trends as data were erratic and difficult to reproduce. Examination of the samples after drying revealed that a considerable amount of cracking had occurred around the ends of several of the samples. Most of the conventional cementing compositions exhibited permeabilities in the range of 0.1 to 0.5 millidarcies in the controlled environment.

To date, an acceptable method for obtaining reliable permeability data for cement samples has not been attained. Ideally, a test specimen must be free of moisture when conducting a gas permeability test. When moist samples are subjected to gas flow, rapid changes in permeability occur due to a drying effect of the gas. Because of this, core samples are normally dried in an oven at approximately 60°C (140°F) for a two to four hour period prior to conducting tests. Although completely dry cement samples are not really representative of down-hole conditions, these conditions should be somewhat representative of the state at which maximum permeability would exist.

Since it is generally accepted that wet cement is less permeable to gas due to a blocking effect[15], results obtained using water should represent the more severe conditions when dealing with specimens bearing moisture.

CONCLUSIONS

A comprehensive study was made to determine the effects of supercritical carbon dioxide on a variety of well cementing compositions. Under the conditions associated with most CO_2 injection and production wells (shallow depths, low temperatures and pressures, unconsolidated formations, etc.) the recommended cementing composition is a 50-50 pozzolan-portland cement mixture which, in slurry form, is densified by deletion of the normally incorporated bentonite (gel). The reaction of pozzolan with the soluble compounds formed in the hydration of portland cement makes the pozzolan-portland cement composition less susceptible to the leaching action of carbonic acid and maintains a low permeability over a longer period of time as compared to compositions formulated exclusively with portland cement. In addition, due to the specific gravity of pozzolan, a lighter slurry is produced which is beneficial across formations which are easily fractured due to excessive hydrostatic pressure. At higher temperatures (above 132°C (270°F)) and pressure, strength stability can be maintained with the addition of silica flour or sand at a concentration of seventeen percent by weight of blend.

Laboratory data collected from this study supports the following:

1. Under supercritical conditions, the rate of carbonation is influenced mainly by the CO_2 partial pressure and temperature and only in second place by the moisture content of the environment, while the degree of aggressivity is dependent on the composition and properties of the cementing composition under consideration.

2. Based upon the cementing compositions and carbonation durations investigated, calcium carbonate formation and migration in preset samples is primarily limited to the outer region of precured cementing compositions when exposed to low-temperature and low-pressure supercritical CO_2 conditions, while complete conversion of the C-S-H and $Ca(OH)_2$ to calcium carbonate and silica gel is noted at the higher temperatures and pressures.

3. Cement samples exposed to the lower temperature and pressure conditions exhibit greater reactivity under dynamic conditions as compared to static conditions, while increasing CO_2 pressure increased the degree of reactivity regardless of the carbonation conditions employed.

4. Immediate carbonation of freshly prepared conventional cement slurries causes a reduction in the calcium to silica ratio, thus, a reduction in compressive strength.

5. Based upon the carbonation durations investigated, compressive strength development and permeability are not significantly affected in cementing compositions that have been cured for three to five days prior to CO_2 exposure. In most cases, marked increases in strength are noted. However, the degree to which this "conversion" ultimately occurs is critical if subsequently exposed to acid.

6. CO_2 exposure of precured samples of the more specialized cementing compositions, such as high aluminate cement, epoxy sealants and various synthetic formulations showed marked to complete inhibition of calcium carbonate formation. However, such phenomena as cracking, surface spalling and leaching of solvent (in the case of some epoxy systems) were noted.

In view of these findings, the recommended cementing composition in conjunction with good cementing practices can provide a successful approach to the cementing of CO_2 enhanced recovery projects.

NOMENCLATURE

Chemical

A	Al_2O_3
C	CaO
H	H_2O
S	SiO_2

Equations

A	cross-sectional area of sample, sq cm
c	inverse of differential pressure, atm
k	permeability, md
L	length of sample, cm
p	atmospheric pressure, atm
Δp	difference in inlet and outlet pressures, atm
p_1	inlet pressure, atm
p_2	outlet pressure, atm
Q	flow rate at atmospheric pressure, cc/sec
μ	viscosity of flowing fluid at room temperature, cp

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Table 1
Compositions Tested

Composition No.	Formulation
	Initial Testing
1	Class H Cement, w/c - 0.38
2	50-50 pozzolan - Class H Cement + 2% gel, w/c = 0.57
3	Class C Cement + 1.25% dispersant, w/c = 0.42
4	Class B Cement + 10% salt + 1.0% dispersant, w/c = 0.56
5	Calcium Aluminate Cement, w/c = 0.43
6	50-50 pozzolan - Class B Cement + 2% gel + 18% salt + 1.0% dispersant, w/c = 0.57
7	Calcium Aluminate Cement, w/c = 0.53
8	Class C Cement + 1.0% fluid loss additive + 0.5% dispersant, w/c = 0.56
9	50-50 pozzolan - Class H Cement + 2% total gel + 12.5% salt, w/c = 0.57
10	Epoxy Sealant + 59.24 wt. percent silica flour
11	Inorganic Polymer Corrosion Resistant Cement
12	Foamed Class C Cement + 2% $CaCl_2$, w/c = 0.56 (9.5 lb/gal)
13	Class C Cement, w/c = 0.53
14	50-50 pozzolan - Class H Cement (no gel), w/c = 0.44
	High-Temperature, High-Pressure Testing
1	50-50 pozzolan - Class C Cement (no gel), w/c = 0.47
2	50-50 pozzolan - Class C Cement (no gel) + 17% silica sand + 0.2% fluid loss additive, w/c = 0.47
3	50-50 pozzolan - Class H Cement (no gel) + 17% silica flour + 0.2% fluid loss additive, w/c = 0.47
4	50-50 pozzolan - Class H Cement (no gel) + 17% silica sand + 0.2% fluid loss additive, w/c = 0.47
5	Class H Cement + 35% silica flour + 0.75% dispersant + 18% salt, w/c = 0.48

Table 2
Compressive Strength and Permeability Data for Carbonated Well Cements

Initial Testing - CO_2 Percolated

Slurry No.	Curing Temp (°C)	Curing Pressure (MPa)	Percent CO_2 Injected	7 Day Compressive Strength[1] (MPa)	Permeability	
					Water (md)	Air (md)
1	41	19.3	Control	36.2	NMF_2	0.10
			2	33.8	NMF	0.10
			4	32.7	NMF	0.14
3	41	19.3	Control	29.3	NMF	0.90
			2	33.8	NMF	0.51
			3	33.8	NMF	0.27
6	41	19.3	Control	22.1	NMF	----[3]
			2	21.2	NMF	----[3]
			4	19.6	NMF	----[3]
			6	24.1	NMF	----[3]
			10	19.0	NMF	----[3]
7	41	19.3	Control	13.8	0.005	3.24
			2	12.5	0.021	3.83
			4	10.3	0.528	5.24
			6	11.2	0.024	0.45
			10	11.2	0.051	0.59

[1] Compressive strength as interpreted from ultrasonic analyzer plot.
[2] No measurable flow.
[3] This sample had a microcrack; k_{air} value was invalid.

Table 3
X-Ray Diffraction Analysis[1]

(Reference Table 2)

	Amount Determined									
Phases Detected	**1(0)[2]**	**1(4)**	**3(0)**	**3(4)**	**3(10)**	**6(0)**	**6(3)**	**7(0)**	**7(4)**	**7(10)**
Amorphous[3]	lg	lg	sm-mod	sm	sm	lg	lg	lg	lg	lg
Unhydrated[4]	mod	mod	sm	----	----	sm	sm	sm	sm	sm
Portlandite	mod	mod	----	----	----	mod	mod	v sm	----	----
Ettringite	sm	sm	----	----	----	sm	sm	sm	sm	sm
Calcite	v sm	sm	v sm	----	----	sm	sm	sm-mod	sm-mod	mod
$Ca_4Al_2(CO_8)\cdot 11H_2O$[5]	----	sm	----	sm-mod	sm-mod	----	----	sm-mod	sm-mod	sm-mod
Gibbsite	----	----	sm	sm-mod	sm-mod	----	----	----	----	----
$Ca_3Al_2(OH)_{12}$[5]	----	----	maj	maj	maj	----	----	----	----	----
Quartz	----	----	----	----	----	----	----	sm	sm	sm

[1] XRD analysis conducted on outer 0.32 cm (⅛ in.) - 0.62 cm (¼ in.) region of 5.08 cm (2 in.) specimen cube.
[2] Value in parentheses indicates the percent CO_2 injected.
[3] Amorphous designation is associated with any noncrystalline material which is associated with the transitional period of the cement hydration process or the initial starting materials (e.g., pozzolan, epoxy, etc.).
[4] Unhydrated compounds vary according to the starting materials. Portland cements show varying amounts of C_3S, C_2S and C_4AF, while high calcium aluminate cements indicate C_4AF and various spinel compounds.
[5] Chemical formulas have been used where mineral names were not available. Appropriate chemical formulas corresponding to the aforementioned minerals are as follows: Calcite - $CaCO_3$; Ettringite - $Ca_3Al_2O_6{\cdot}3\,CaSO_4{\cdot}3l\,H_2O$; Gibbsite - $Al(OH)_3$; Portlandite - $Ca(OH)_2$; Quartz - SiO_2.

CODING

maj = major
lg = large
mod-lg = moderate-large
mod = moderate
sm-mod = small-moderate
sm = small
v sm = very small

Table 4
Compressive Strength and Permeability Data for Carbonated Well Cements

Initial Testing - Static Conditions

Composition No.	Curing Temp (°C)	Curing Pressure (MPa)	Carbonation Time (Days)	Sample	Compressive Strength (MPa)
TEST SERIES A (Preliminary Investigation): Precured [1] Samples Submerged in Deionized Water with Gaseous CO_2 Cap					
1	82	6.5	14	Control	49.5
				CO_2	24.8
			21	Control	60.8
				CO_2	38.3
			28	Control	47.4
				CO_2	51.7
2	82	6.5	14	Control	16.9
				CO_2	19.7
			28	Control	15.3
				CO_2	19.4

Composition No.	Curing Temp (°C)	Curing Pressure (MPa)	Carbonation Time (Days)	Sample	Compressive Strength (MPa)	Permeability Water (md)	Permeability Air (md)
TEST SERIES B: Precured[1] Samples Submerged in Dry Liquid CO_2							
3	41	19.3	7	Control	39.5	NMF_2	0.18
				CO_2	51.2	NMF	1.38
4	41	19.3	7	Control	36.3	NMF	----[3]
				CO_2	39.4	NMF	1.70
5	41	19.3	7	Control	26.9	NMF	0.57
				CO_2	32.8	1.800	0.56
6	41	19.3	7	Control	10.6	NMF	0.08
				CO_2	18.0	NMF	3.10
7	41	19.3	7	Control	15.3	0.005	1.24
				CO_2	13.4	1.600	4.59
TEST SERIES C: Precured[1] Samples Submerged in Dry Liquid CO_2							
3	41	19.3	42	Control	46.7	NMF	0.14
				CO_2	----	NMF	0.04
8	41	19.3	42	Control	32.5	NMF	0.12
				CO_2	30.7	NMF	0.01
9	41	19.3	42	Control	38.2	NMF	0.92
				CO_2	23.2	NMF	0.05
7	41	19.3	42	Control	15.3	NMF	----[3]
				CO_2	11.0	0.321	1.10
10	41	19.3	42	Control	40.0	NMF	0.003
				CO_2	43.9	NMF	0.01
11	41	19.3	42	Control	21.0	2.619	11.90
				CO_2	20.2	NMF	0.91
TEST SERIES D: Precured[1] Samples Submerged in Brine Water with Liquid CO_2 Cap							
7	41	19.3	7	Control	15.3	0.005	1.24
				CO_2	8.6	0.024	1.88
12	41	19.3	7	Control	6.2	0.124	1.22
				CO_2	4.7	0.022	----[3]
13	41	19.3	7	Control	33.2	NMF	----[3]
				CO_2	28.6	NMF	0.71
14	41	19.3	7	Control	24.2	NMF	0.40
				CO_2	25.3	NMF	2.09
2	41	19.3	7	Control	16.6	NMF	0.48
				CO_2	15.4	0.021	0.47
1	41	19.3	7	Control	46.5	NMF	0.10
				CO_2	45.1	NMF	0.42
TEST SERIES E: Slurry Samples Cured in Dry CO_2							
3	41	19.3	7	Control	39.5	NMF	0.18
				CO_2	22.8	NMF	----[3]
7	41	19.3	7	Control	15.3	0.05	1.24
				CO_2	7.7	0.074	1.14
14	41	19.3	7	Control	24.2	NMF	0.40
				CO_2	17.1	NMF	0.38
1	41	19.3	7	Control	46.5	NMF	0.10
				CO_2	41.4	NMF	----[3]

[1] Cured for 3 days at appropriate temperature and pressure under normal conditions.
[2] NMF = No Measurable Flow.
[3] This sample had a microcrack; k_{air} value was invalid.

Table 5
X-Ray Diffraction Analysis

(Reference - Table 4)
Preliminary Investigation

Slurry No.	Carbonation Time (Days)	Area Examined	Sample	Phases Detected		
				Major	Minor	Trace[1]
1	14	Exterior[2]	Control CO_2	hydrated cement calcite	portlandite hydrated cement	calcite aragonite-vaterite-portlandite
1	14	Interior[3]	Control CO_2	hydrated cement hydrated cement	portlandite portlandite	calcite calcite
1	28	Exterior	Control CO_2	hydrated cement calcite	portlandite hydrated cement	calcite aragonite-vaterite-portlandite
1	28	Interior	Control CO_2	hydrated cement hydrated cement	portlandite portlandite	calcite calcite
1	28	Exterior Crystalline Growth	CO_2	calcite		aragonite
2	14	Exterior	Control CO_2	hydrated cement aragonite	portlandite hydrated cement	calcite calcite
2	14	Interior	Control CO_2	hydrated cement hydrated cement	portlandite portlandite	calcite calcite
2	28	Exterior	Control CO_2	hydrated cement calcite	portlandite hydrated cement	calcite portlandite-aragonite-vaterite
2	28	Interior	Control CO_2	hydrated cement hydrated cement	portlandite portlandite	calcite calcite

[1] Compounds listed in approximate order of concentration (larger to smaller).
[2] Exterior = outer 0.32 (⅛ in.) - 0.64 cm (¼ in.) region of 5.08 cm (2 in.) specimen cube.
[3] Interior = central 2.54 cm (1 in.) region of 5.08 (2 in.) specimen cube.

Table 6
X-Ray Diffraction Analysis[1]

(Reference Table 4)

Phases Detected	Amount Determined									
	3	4	5	6	7	8	9	7	10	11
Amorphous[2]	lg	lg	mod	lg	mod	mod-lg	lg	mod	lg	mod-lg
Unhydrated[3]	sm-mod	mod	sm	sm-mod	sm	sm	sm	----	----	----
Portlandite	mod-lg	mod-lg	----	sm	----	sm	v sm	----	----	----
Ettringite	v sm	sm	----	sm	----	----	----	----	----	----
Calcite	sm-mod	mod	sm-mod	lg	sm-mod	lg	lg	mod	----	----
Aragonite	----	----	sm	----	sm	sm	sm	sm	----	----
Vaterite	v sm	v sm	sm	v sm	sm	mod	v sm	sm	----	----
$Ca_3Al_2(OH)_{12}$[4]	----	----	maj	----	maj	----	----	maj	----	----
Hydrocalumite	----	sm	----	sm	----	----	v sm	----	----	----
Gibbsite	----	----	mod	----	mod	----	----	mod	----	----
Quartz	----	----	----	sm	----	----	sm	----	maj	maj
Sodium Bicarbonate	----	----	----	----	----	----	----	----	----	sm

Phases Detected	Amount Determined													
	7	7 Control	12	12 Control	13	13 Control	14	14 Control	2	2 Control	3	7	14	1
Amorphous[2]	mod	sm-mod	lg	lg	lg	lg	lg	lg	lg	lg	lg	lg	lg	lg
Unhydrated[3]	sm	sm	sm	mod	sm	mod	sm	mod	sm	mod	sm	mod-lg	sm-mod	mod-lg
Portlandite	----	----	mod	lg	mod-lg	mod-lg	sm	mod	sm	sm	mod-lg	----	----	mod
Ettringite	----	----	v sm	sm	sm	sm	sm	sm	sm	sm	sm	----	sm	sm
Calcite	sm	v sm	lg	sm	sm-mod	sm	sm-mod	sm	mod	sm	mod	sm-mod	maj	----
Aragonite	sm	----	----	----	----	----	----	----	----	----	----	v sm	sm	----
Vaterite	sm	----	sm	sm	----	sm	----	----	----	----	----	v sm	----	----
$Ca_3Al_2(OH)_{12}$[4]	maj	maj	----	----	----	----	----	----	----	----	----	mod	----	----
Hydrocalumite	sm	sm	----	----	----	----	sm	sm	sm	----	----	sm	----	----
Gibbsite	sm	sm	----	----	----	----	----	----	----	----	----	mod	----	----
Quartz	----	----	----	----	----	----	sm	----	sm	sm	----	----	sm	----
Sodium Bicarbonate	----	----	----	----	----	----	----	----	----	----	----	----	----	----

[1] XRD analysis conducted on outer 0.32 cm (⅛ in.) - 0.64 cm (¼ in.) region of 5.08 cm (2 in.) specimen cube.
[2] Amorphous designation is associated with any noncrystalline material which is associated with the transitional period of the cement hydration process or the initial starting materials (e.g., pozzolan, epoxy, etc.)
[3] Unhydrated compounds vary according to the starting materials. Portland cements show varying amounts of C_3S, C_2S and C_4AF, while high calcium aluminate cements indicate C_4AF and various spinel compounds.
[4] Chemical formulas have been used where mineral names were not available. Appropriate chemical formulas corresponding to the aforementioned minerals are as follows: Aragonite - $CaCO_3$; Calcite - $CaCO_3$; Ettringite - $Ca_3Al_2O_6{\cdot}3\ CaSO_4{\cdot}3I\ H_2O$; Gibbsite - $Al(OH)_3$; Hydrocalumite - $Ca_{18}Al_8(OH)_{54}CO_3{\cdot}2I\ H_2O$; Portlandite - $Ca(OH)_2$; Quartz - SiO_2; Vaterite - $CaCO_3$.

CODING

maj = major
lg = large
mod-lg = moderate-large
mod = moderate
sm-mod = small-moderate
sm = small
v sm = very small

Table 7
High-Temperature, High-Pressure Testing

(Static and Dynamic Conditions)[1]

Composition No.	Curing Temp (°C)	Curing Pressure (MPa)	Carbonation Time (Days)	Compressive Strength (MPa)	
				Control	CO_2
1	82	19.3	60 (S)[2]	28.6	27.0
2	124	19.3	14 (D)[3]	28.3	28.4
	124	44.8	35 (S)	31.4	42.2
3	124	44.8	35 (S)	47.2	52.9
4	124	44.8	21 (S)	42.0	63.8
5	124	44.8	28 (S)	58.3	64.6

[1] All samples precured 5 days prior to exposure.
[2] S = Static Conditions.
[3] D = Dynamic Conditions.

Table 8
X-Ray Diffraction Analysis[1]

High-Temperature, High-Pressure Testing
(Reference - Table 5)

Phases Detected	Composition No. 1[2]		Composition No. 2[3]		Composition No. 4[4]	
	Brown	Gray	Exterior	Interior	Brown	Gray
Quartz	small	small	mod-large	mod-large	large	mod-large
Calcite	large	mod-large	mod-large	mod	mod	small
Aragonite	small	mod	mod	mod	mod	v small
Vaterite	trace	---	mod	mod	---	---
Tobermorite	---	---	---	---	---	mod
C_4AF (tetracalcium aluminoferrite)	small	small	small	small	small	small

[1] All samples contained large amounts of amorphous material.
[2] Conversion ratio (based on 5.08 cm cubical specimen) - 0.50; brown = reacted, gray = unreacted.
[3] Conversion ratio (based on 5.08 cm cubical specimen) 1.00; fully converted.
[4] Conversion ratio (based on 5.08 cm × 5.08 cm cylinder) - 0.95; brown = reacted, gray = unreacted.

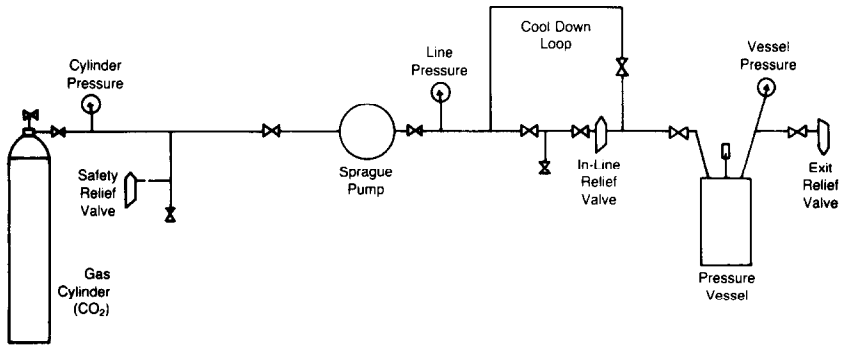


Figure 1 - Apparatus for static and dynamic carbon dioxide testing at high temperature and pressure

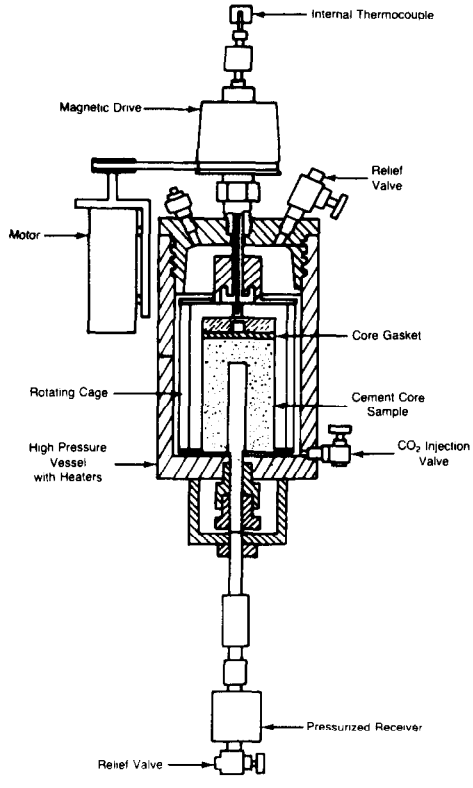


Figure 2 - Schematic of auxiliary dynamic CO_2 exposure apparatus

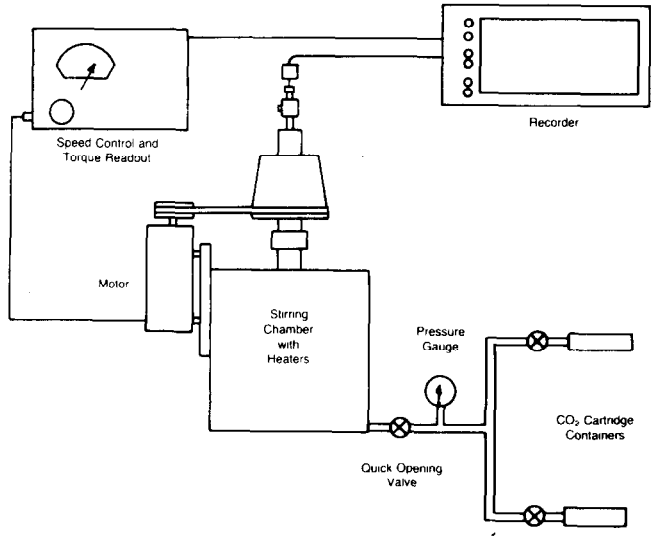


Figure 3 - Schematic of equipment used for CO_2 injection and measuring slurry consistency

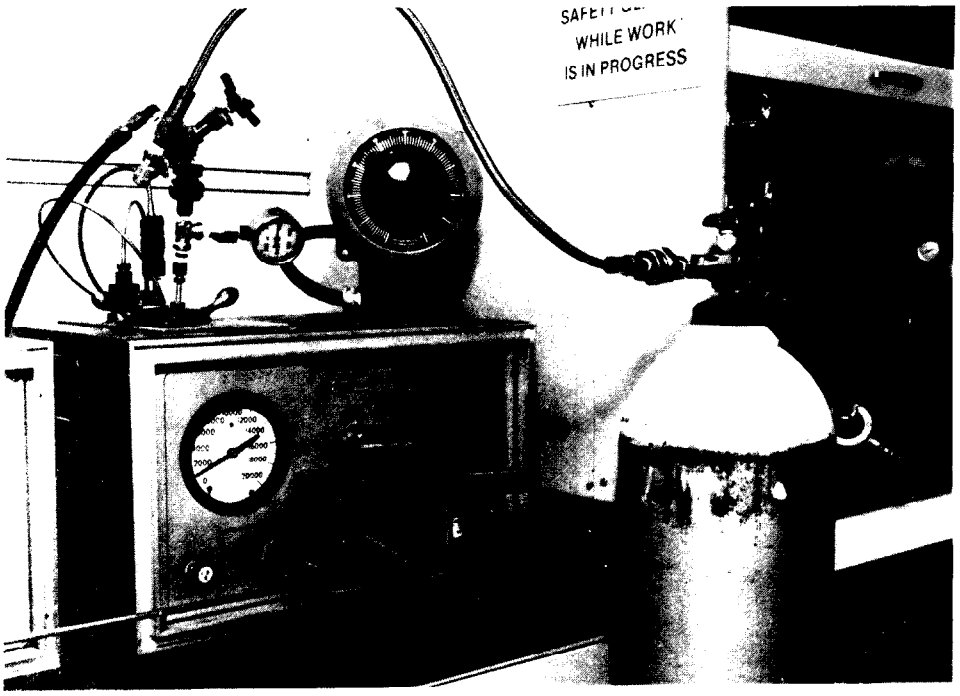


Figure 4 - Ultrasonic analyzer for monitoring influence of CO_2 on compressive strength

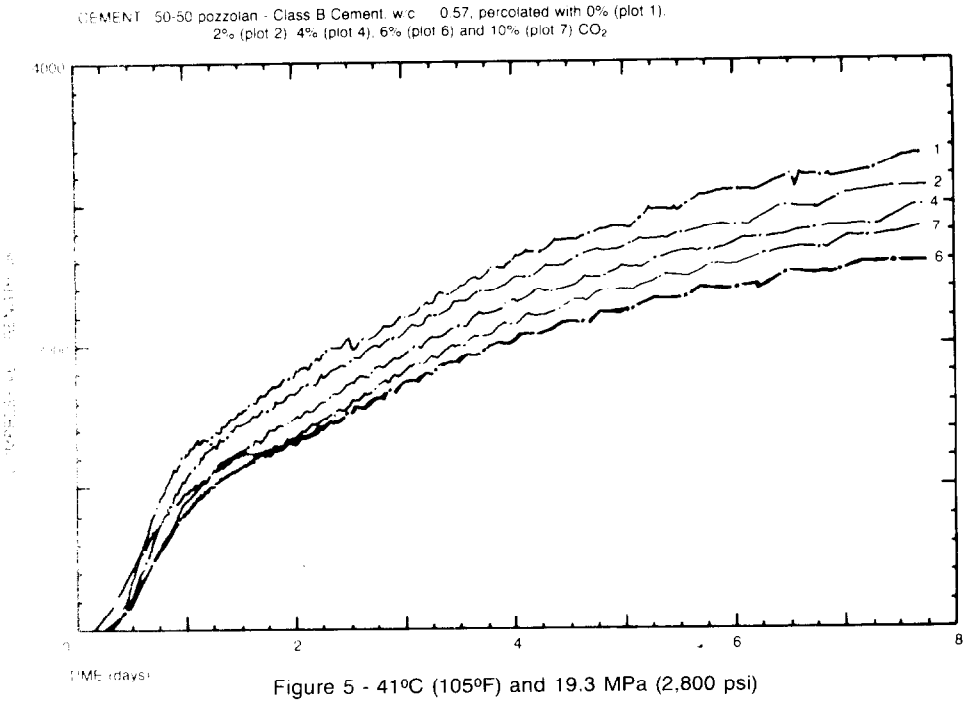
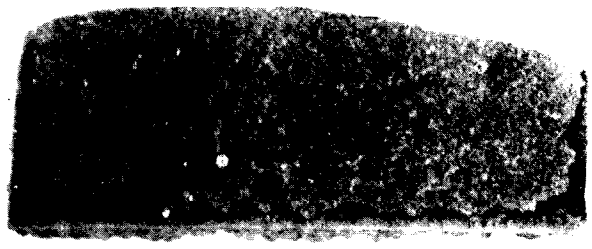


Figure 5 - 41°C (105°F) and 19.3 MPa (2,800 psi)



Cross-sectional area of a neat Class H cement cube after 28 days of carbonation in water at 82°C (180°F) and 6.5 MPa (950 psi) CO_2 pressure cap.

Calcite crystalline growth on exterior of a neat Class H cement specimen after 14 days of carbonation in water at 82°C (180°F) and 6.5 MPa (950 psi) CO_2 pressure cap.

Figure 6

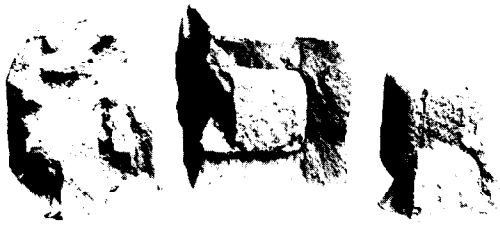


Figure 7 - 50-50 pozzolan - Class C cement (no gel), w/c = 0.47, 2 month exposure at 82°C (180°F) and 19.3 MPa (2,800 psi)

Figure 8 - Lone Star Class H cement + 18% sand, w/c = 0.48, 1 month exposure at 124°C (255°F) and 44.8 MPa (6,500psi). Water sample shown is by-product of reaction

Figure 9 - 50-50 pozzolan - Class C cement (no gel) + 17% SSA-2, w/c = 0.47, 2 weeks dynamic exposure at 124°C (255°F) and 19.3 MPa (2,800 psi)

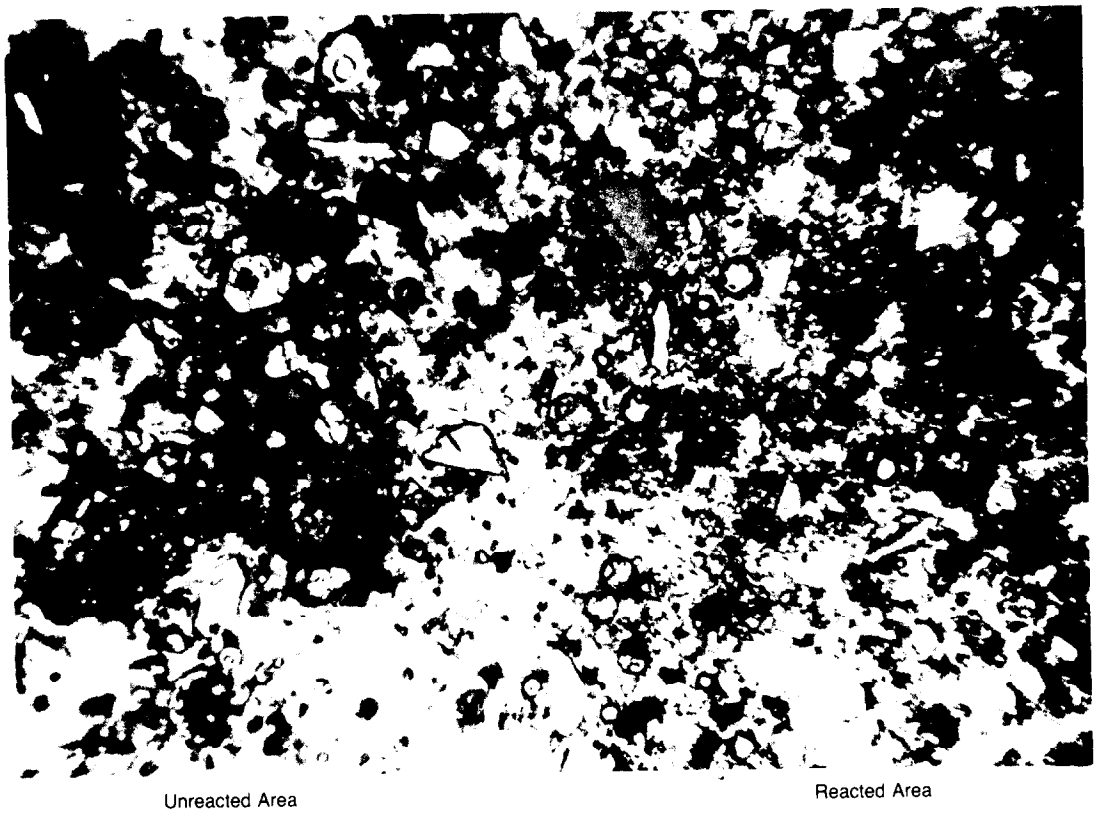


Figure 10 - Polished etched section microscopy

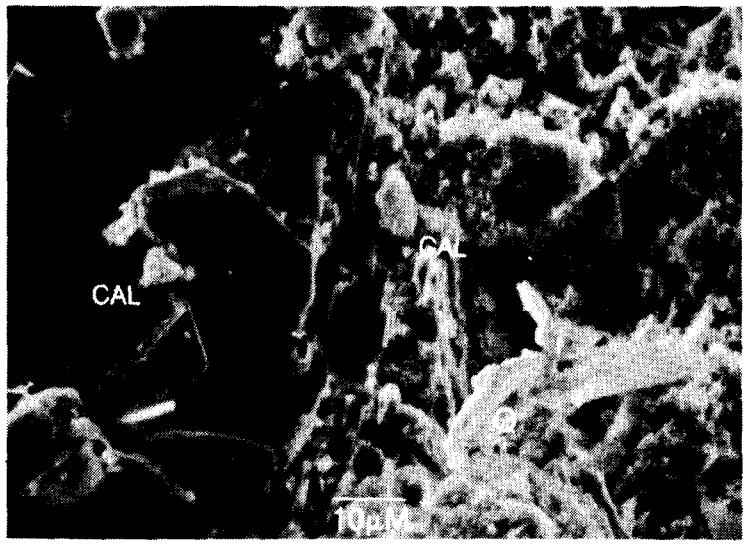


Figure 11 - Microstructure of a neat Class H cement after 21 days of carbonation in water at 82°C (180°F) and 6.5 MPa (950 psi) CO_2 pressure cap.

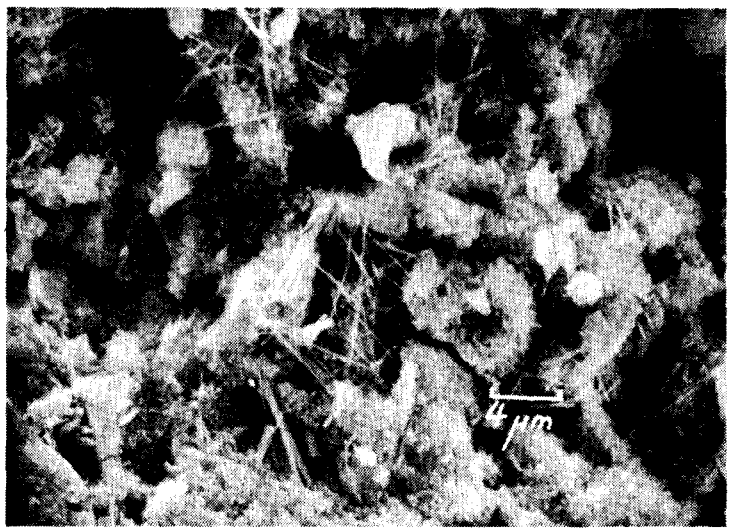


Figure 12 - Microstructure of a neat Class H cement cured under normal conditions. This photograph reveals the interlinked CSH crystals and ettringite spicules.

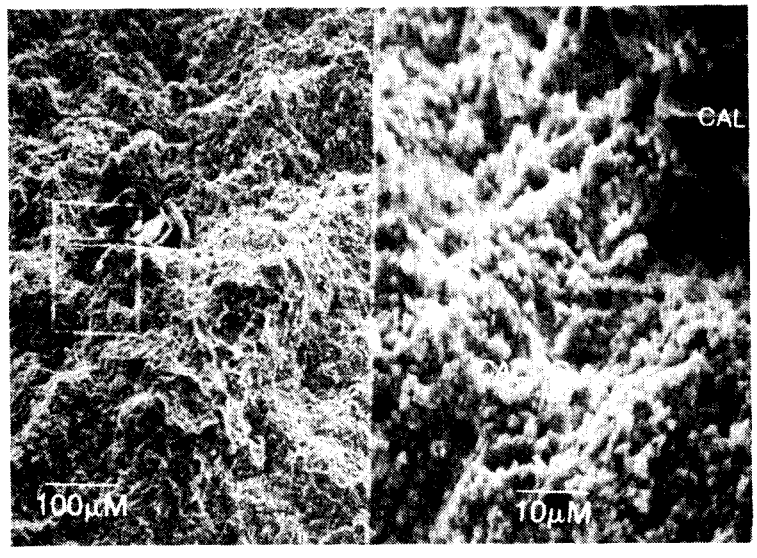


Figure 13 - Microstructure of a carbonated neat Class H surface revealing growth of calcite crystallites. Sample carbonated at 82°C (180°F) and 6.5 MPa (950 psi) CO_2 pressure cap.

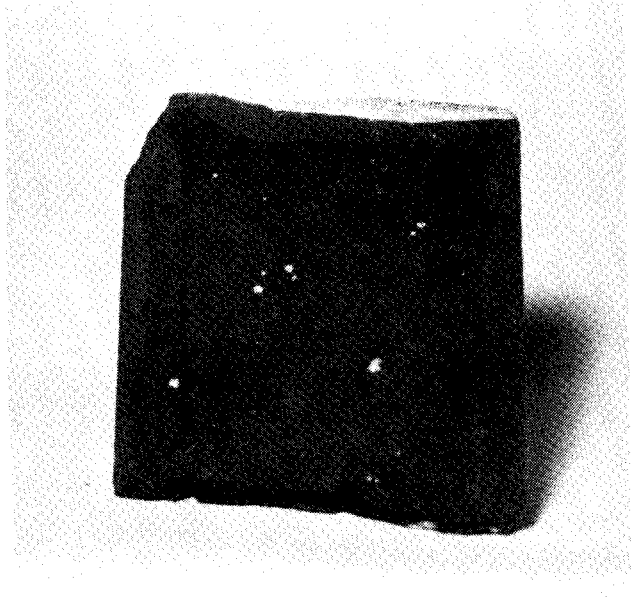


Figure 14 - High calcium aluminate cement specimen after 42 days of carbonation at 82°C (180°F) and 19.3 MPa (2,800 psi) dry liquid CO_2.