LIGHTWEIGHT CO₂-RESISTANT CEMENTS FOR GEOTHERMAL WELL COMPLETIONS

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ABSTRACT

Materials formed by acid-base reactions between calcium aluminate compounds and phosphate-containing solutions yield high strength, low permeability and CO₂-resistant cements when cured in geothermal environments. The cementing formulations are pumpable at temperatures up to 150°C, thereby making their use for well completions technically feasible. When this cementing matrix was exposed in an autoclave containing CO₂-saturated brine for 120 days, <0.4 wt% CaCO₃ was produced. A conventional portland cement-based well completion material will form ~10 wt% CaCO₃ after only 7 days exposure. The addition of hollow aluminoisicate microspheres to the uncured matrix constituents yields slurries with densities as low as ~1.2 g/cm³ which cure to produce materials with properties meeting the criteria for well cementing. These formulations also exhibit low rates of carbonation. Laboratory characterization is nearing completion. Engineering scale-up is underway, and plans for field testing in a variety of geothermal fluids are being made.

1. INTRODUCTION

The quality of the cementing phase of a geothermal well completion often establishes the life expectancy of the well. Improperly designed cement jobs can result in blow-outs and casing corrosion or collapse. In addition to the need for cements which, upon curing, yield the necessary physical, mechanical and chemical characteristics, their slurry precursors must have rheological properties that permit placement. Low slurry densities (~1.2 g/cm³) are desirable to minimize the frequency of lost circulation episodes when attempts are made to cement in weak unconsolidated rock zones with very fragile gradients.

As drilling environments become more hostile, the need for lightweight, carbon dioxide (CO₂)-resistant cements becomes more critical. It is well known that alkali metal catalyzed reactions between CO₂-containing brines and the calcium silicate hydrate (CSH) compounds and calcium hydroxide in conventional well cements result in rapid deterioration at pressures, temperatures and CO₂ concentrations typical of geothermal wells (Milestone et al, 1987). In these cases, reactions between Na₂ and K in the brines with CSH phases produce substituted CSH compounds such as pectolite and reyrite, both of which are susceptible to carbonation. The attack of portland cement by CO₂ is described in the following equations (Schumberger Dowell, 1993):

\[
\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \quad (1)
\]

\[
\text{Ca(OH)}_2 + \text{H}^+ + \text{HCO}_3^- \rightarrow \text{CaCO}_3 + 2\text{H}_2\text{O} \quad (2)
\]

\[
\text{C-S-H} + \text{H}^+ + \text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{amorphous silica gel} \quad (3)
\]

In Equation 1, ~1% of the dissolved CO₂ reacts with water to form carbonic acid. The free carbonic acid reacts with free calcium hydroxide (Equation 2) and calcium silicate hydrates (Equation 3) in the cement matrix. As CO₂ laden water continues to invade the cement matrix, more equilibria are established.

\[
\text{CO}_2 + \text{H}_2\text{O} + \text{CaCO}_3 \leftrightarrow \text{Ca}([\text{HCO}_3^-])_2 \quad (4)
\]

\[
\text{Ca(HCO}_3^-)_2 + \text{Ca(OH)}_2 \leftrightarrow 2\text{CaCO}_3 + 2\text{H}_2\text{O} \quad (5)
\]

Additional CO₂ reacts with the calcium carbonate to form water-soluble calcium bicarbonate (Equation 4). Finally, dissolved calcium bicarbonate reacts with more calcium hydroxide, forming calcium carbonate and "fresh water" (Equation 5). The fresh water can then dissolve more calcium bicarbonate. As long as a continuous supply of CO₂ laden water exists, the above-described process will continue. Cementitious material is leached from the cement matrix, increasing the permeability and porosity and decreasing the strength. The eventual result is lost casing protection and lost zonal isolation. Cement failures attributed to CO₂ are occurring in less than 5 yr. and in one case, resulted in a collapsed well casing within 90 days.

As a result of this rapidly expanding problem which if unsolved could seriously constrain the development of the World's geothermal resources. Brookhaven National Laboratory (BNL) under the sponsorship of the U.S. Department of Energy, initiated work in 1989 to develop non-portland based cementing materials. The following performance criteria were established: 1) slurry density, <1.3 g/cm³, 2) pumpability, 4 hr at 100°C, 3) compressive strength, >5 MPa at 24 hr age, 4) bond strength to steel, >0.07 MPa, 5) carbonation rate, <5% CaCO₃, after 1 yr in brine at 300°C containing 500 ppm CO₂, and 6) water permeability, <0.1 Darcy.

The work focused on the identification of pathways leading to the formation of chemically bonded cements (CBC) by acid-base reactions. The CBCs were prepared from two chemical components, the basicity (a proton accepting cation-leachable powder), and the acidity (a proton-donating liquid). The powder may be either a metal oxide (MO) as a single component system, or an acid-decomposable binary or ternary system such as MO+xAl₂O₃, MOₓSiO₂ or MO+xAl₂O₃γSiO₂. The cementitious products formed are salt complexes which hinder the partially reacted powder particles into a coherent mass. Such cement forming reactions may be represented by the generic equations given below.

Metal oxide-acid reaction

\[
\text{MO} + \text{H}_2\text{A} \rightarrow \text{MA} + \text{H}_2\text{O} \quad (6)
\]

base acid salt matrix
Metal aluminate of silicate-acid reaction

\[ \text{MO} + \text{SiO}_2 + \text{H}_2\text{O} \rightarrow \text{MA} + \text{xSiO}_2 + \text{H}_2\text{O} \]  
(base acid) silica gel

\[ \text{MO} \times \text{Al}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{MA} \times \text{xAl}_2\text{O}_3 + \text{H}_2\text{O} \]  
(base acid) alumina gel

where M represents the cations and A is the acid anion. Both M and A are taken as being nominally divalent for convenience of representation.

The ongoing work is organized into five phases: 1) fundamental cement research, 2) mix design, 3) property characterization, 4) placement technology, and 5) downhole testing. The results to date indicate that the properties needed for a superior well cement can be attained. In this paper, the results from Phase 1-4 laboratory evaluations on CBCs produced by reactions between several calcium aluminate cements, polycrystalline compounds and lightweight fillers are summarized. A successful development will decrease the cost of well completions due to reductions in lost circulation control episodes, increase the life expectancy of wells, and reduce environmental concerns regarding blow-outs. It will also permit development of higher temperature, higher CO₂ content brine resources which are not currently exploitable due to cement deterioration concerns.

2. EXPERIMENTAL PROCEDURES

2.1 Materials

Four commercially available calcium aluminate cements (CAC): Recon (RE), Luminite (LU), Secar 80 (80), and Secar 41 (41) were used as the base solid reactants. The first two were supplied by the Lehigh Portland Cement Company, the others by the Lafarge Calcium Aluminate Company. Prior to use, chemical characterizations of the CACs were performed using XRD analysis over the range 0.444 to 0.229 nm. These data which have been published (Sugama and Carciello, 1993), indicated that the 41 CAC powder contained two major components; monocalcium aluminate (CA) and gehlenite (C₂A₅S). Please note that the chemical notations are abbreviated. C₆CaO₂₅Al₄O₉ and S₅SiO₂₃. The LU and RE-type reactants contained these compounds plus monocalcium di-aluminate (CA₂), while the 80 had CA and CA₂, as major components and C₂A₅S as a minor one.

An ammonium polyphosphate fertilizer solution, known commercially as Poly-N (fertilizer grade: 11-37-0, Arcadian Corporation) was generally employed as the acid liquid reactant. Sodium hexametaphosphate [Na₅P₃O₁₀] was supplied by Albright and Wilson Americas, was utilized in some later tests. In the latter, the (Na₅P₃O₁₀) was dissolved in water to make solutions varying between 30 and 40 w/o.

Five commercial inorganic and organic microspheres were evaluated as lightweight fillers for CBCs. These were Q-Cel 650 (Q-C), and Extennodes (EX). Both supplied by the PQ Corporation: Macrolite (MA) and glass bubbles (GL) from the 3M Corporation; and Dualite 6071Æ (DU), supplied by Pierce and Stevens Corporation. All except the MA are categorized as hollow microspheres. Physical and chemical property data for each of these fillers are given in Table 1.

2.2 Sample Preparation

Neat calcium phosphate cement (CPC) pastes were prepared by thoroughly hand-mixing 60 wt% CAC powders and 40 wt% Poly-N solution at room temperature for ~3 min. The slurries were then cast in 30 mm-diam x 70 mm-long cylindrical molds and cured for 20 hr in an autoclave at 250°C.

Lightweight specimens (LCPC) were made by first drying mixing the CAC powder with the filler. Either Poly-N or [Na₅P₃O₁₀] was added. After casting and curing at room temperature for 2 hr, autoclave curing was accomplished for 20 hr at 200°F or 300°C. Compared to the CPC slurries which had a density of 1.98 g/cc, the LCPC slurries ranged from 1.02 to 1.55 g/cc.

2.3 Measurements

Differential scanning calorimetry (DSC) was used to determine the extent and onset temperature of the exothermic acid-base reaction between the CAC and the Poly-N. The phase compositions and transformations of CPC after exposures to hot 0.05 M Na₂CO₃ solutions were explored by X-ray powder diffraction (XRD). Quantitative data on the amount of CaCO₃ formed in the CPC bodies were obtained from thermogravimetric analysis (TGA) by the weight loss at which thermal decomposition of CaCO₃ occurs over the range 600°C to 770°C. Compressive strength tests were performed on neat CPC specimens having a diameter of 30 mm and a length of 40 mm: the result given is the average value of three specimens.

The characteristics of the microspheres used to produce LCPCs, namely bulk density, particle size and chemical composition, were measured using helium comparison pycnometer, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), respectively. XRD and Fourier transform infrared (FT-IR) spectroscopy were used to determine the phase compositions and transformations of the LCPCs after hydrothermal exposure. Image analyses using SEM coupled with energy dispersion X-ray spectrometry (EDX) were made of the LCPC fracture surfaces to determine their microstructure and the chemical components in the matrix and at the critical contact zones between the CPC and the microspheres.

3. RESULTS

3.1 Calcium Phosphate Cement Pastes

In initial tests, Differential Scanning Calorimetry (DSC) was used to estimate the reactivity of the CAC reactants with Poly-N. Heating at a constant rate of 10°C/min in a N₂ environment was used. The data showed that the magnitude of reactivity of CAC with Poly-N depends mainly on the proportion of CA, to CA + C₂A₅S. Powders containing a high ratio retard setting, while those with a low ratio accelerate it. Based upon these results the reactivities of the four CAC powders are as follows: 41>80>RE>80.

Compressive strength results for each of the CAC formulations after exposure to a 0.05M Na₂CO₃ solution at 250°C are given in Figure 1 (Sugama and Carciello, 1991). The data for the RE, LU, and #80-induced specimens show that strength increases during the first 7 days of exposure, and then decreases with time to 28 day; beyond this time, strength seems to level off. In contrast, there was no improvement in strength after 7 days exposure of the #41 specimens. This one had the highest initial strength in the test series. The retrogression of strength for this specimen occurred for 28 days, and thereafter, showed no significant change in strength. The ultimate development of strength in CPC specimens was due to the combined structure of crystalline HOPAP (hydroxyapatite) and γ-Al(OH)₃ (Boehmite) phases, together with the amorphous NH₄CaPO₄·xH₂O and Al₁₂O₃ gel phases which bind the partially reacted and non-reactive CAC particles into a coherent mass. The excessive in-situ growth of crystalline phases in the amorphous bodies led to the decrease in strength. Thus, we believe that the increased strength for 7 day-exposed RE, LU, and #80 specimens is related directly to the growth of crystalline phases. Assuming that the reductions in strength result from the formation of crystalline phases in the amorphous bodies, the absence of significant changes in strength for the specimens after exposure for 28 days is due to the ending of the hydrothermal phase conversion.
HOAp and Al₂O₃ gel → γ-AlOOH phase transitions were completed at the exposure age of 28 days. The strengths of the 120day-exposed CPC specimens fell into the following order; RE > #41 > LU > #80. The exposed RE specimens had an excellent strength of > 80 MPa. All of the strengths greatly exceeded the API criterion of 5 MPa.

In conjunction with the compressive strength determinations, analyses were performed to measure the rate of carbonation and the phases formed. TGA was used for the former, XRD for the latter. Carbonation data are summarized in Figure 2. As noted, a small amount of CaCO₃, 0.1 to 0.2 wt%, was already present in the unexposed control specimens, the origin of which was the CAC base constituent. The data indicate that the rate of carbonation for CPC specimens depends primarily on the species of the CAC reactants. The rates for LU and #41 specimens tended to increase monotonously with increased exposure time; after 120 days these specimens contained only 0.2 wt% CaCO₃, while 0.5 wt% CaCO₃, was detected in the RE samples. By comparison, a higher rate of carbonation occurred in the #80 specimens. The rate of carbonation for this specimen increased with exposure time; after 28, 91, and 120 days the amount of CaCO₃ was 0.9, 1.3, and 1.7 wt%, respectively. However, the concentration at 120 days was considerably lower than that for 200°C-autoclaved neat CAC paste.

<table>
<thead>
<tr>
<th>Microsphere (Symbol)</th>
<th>Type</th>
<th>Density \text{g/cm}^3</th>
<th>Particle Size \text{μm}</th>
<th>Chemical Composition of Shell Surfaces, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Si</td>
</tr>
<tr>
<td>Q-sol 650 (Q-C)</td>
<td>Borosilicate Glass</td>
<td>0.05</td>
<td>6-95</td>
<td>11.0</td>
</tr>
<tr>
<td>Extendospheres (EX)</td>
<td>Aluminosilicate</td>
<td>0.67</td>
<td>75-200</td>
<td>13.1</td>
</tr>
<tr>
<td>Macroline (MA)</td>
<td>Nepheline Syenite Ceramic</td>
<td>125</td>
<td>300-450</td>
<td>64</td>
</tr>
<tr>
<td>Glass Bubbles (GL)</td>
<td>Soda Lime Borosilicate Glass</td>
<td>0.38</td>
<td>5-45</td>
<td>116</td>
</tr>
<tr>
<td>Dualite (DU)</td>
<td>Acrylonitrile Copolymer w/ C₃ A₄ O₅ Coating</td>
<td>0.13</td>
<td>25-100</td>
<td>50.9</td>
</tr>
</tbody>
</table>

exposed for 7 days to the Na₂CO₃ solution at 25°C (1.7 wt% vs. 6.2 wt%). These results, and data from earlier exothermal reactions suggested that the carbonation rate for CPC specimens probably is associated with the magnitude in reactivity of CAC with Poly-N. The specimens made with the #41 and LU reactants with a high reactivity, had a low rate of carbonation, while the RE reactants with a moderate reactivity, had a moderate rate of carbonation. In contrast, #80 reactant with the lowest reactivity showed the highest rate of carbonation in this test series.

For comparative purposes, a conventional class G cement paste was also exposed to the hot Na₂CO₃ environment. In this case, the CaCO₃ concentration was 9.5 wt% after 7 days.

In addition to strength, low permeability and CO₂ resistance, well cementing materials must exhibit good adherence to the casing string and the borehole rock formation. If so, the cement not only serves to mechanically support the casing and resist blow-outs, but also protects the casing from external corrosion sources. In order to evaluate the ability of CPCs to meet this design criterion, their bonding characteristics at 200°C with cold-rolled steel (CRS) and stainless steel substrates were measured. For comparison purposes, similar measurements were performed for a conventional class G cement (CGC) which is generally used for well completions.

The compatibility of CPCs with a variety of commercial inorganic and organic microspheres was then studied (Sugama and Wetzl, 1992). These hollow fillers were evaluated mainly on the reactivity of the slurries and the compressive strengths of hydrate-thermally cured specimens. The mechanical behavior of the lightweight specimens (LCPC) was then correlated with the phase compositions, transformations and morphological features of the composite cement matrices, and with the chemical elements and microstructural developments at the contact points near the microsphere particles. The latter analyses provided us with information on the possible interaction mechanism between the CPC and the microspheres.

3.2 Lightweight CPC Composites

The compressive strength data for LCPC specimens a, a function of slurry density, are shown in Figure 3. The specimens were autoclaved for 20 hr at 200° or 300°C prior to test. Specimens containing the aluminosilicate microspheres (EX) exhibited the highest strengths for both curing temperatures. Specimens with a slurry density of 1.2 g/cc had a strength of 8.5 MPa. At 300°C, this decreased to ~4.5 MPa. The strengths increased with slurry

Table 1. Properties of Microspheres

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autoclaved for 20 hr at 200°C or 300°C prior to test. Specimens containing the aluminosilicate microspheres (EX) exhibited the highest strengths for both curing temperatures. Specimens with a slurry density of 1.2 g/cc had a strength of 8.5 MPa. At 300°C, images of EX-containing LCPCs revealed that failure occurred through two different modes, one of which was an adhesive mode in which separation occurred at the critical boundary regions between the CPC and the microspheres, leaving either matrix craters or smooth microspheres without any CPC coverage on the fractured matrix surface. The other mode of failure was a cohesive one, occurring through the microsphere shell. Based upon these analyses, we propose that the strength reduction with temperature results from the strong chemical affinity between the EX microsphere’s surfaces and the CPC matrix. This not only leads to the formation of intermediate layers, which improve the interfacial bond strength between them, but also decreases the effective thickness of the hollow microsphere shell. The latter effect might cause the distribution of mechanically weak microspheres in the matrix phase. Since cohesive failure of the microsphere was observed on all four fracture surfaces, the retrogression of strength may be related to the high extent of microporous-CPC interaction, rather than to the development of a porous microstructure brought about by the in situ conversion of amorphous ammonium calcium orthophosphate salt (AmCOP) and Al₂O₃·nH₂O into crystalline HOAp and Boehmite, respectively.

Tests to measure the carbonation rate of LCPCs are in progress. In this work, samples prepared from slurries consisting of 40 wt% CAC powder, 20 wt% aluminosilicate microspheres and 40 wt% (NaPO₃)₄ were exposed for 10 days in 0.05M Na₂CO₃ solutions at 100°C, 200°C, and 300°C. After the 300°C exposure, samples produced using a 40 wt% (NaPO₃)₄ solution exhibited -0.2 wt% CaCO₃. The compressive strength and water permeability was 9.4 MPa and

<table>
<thead>
<tr>
<th>Cement</th>
<th>Metal Substrates</th>
<th>Shear Bond Strength (MPa)</th>
<th>Phase Composition at Interfaces</th>
<th>Major</th>
<th>Minor</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPC</td>
<td>CRS</td>
<td>0.75</td>
<td>Na-zolite, HOAp***</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CPC</td>
<td>SS</td>
<td>0.47</td>
<td>Na-zolite 8-ALOOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CGC</td>
<td>CRS</td>
<td>1.65</td>
<td>Fe₂O₃, Xonolite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CGC</td>
<td>S</td>
<td>1.43</td>
<td>Xonolite, Fe₂O₃</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* CPC: calcium phosphate cement
** CGC: class G Cement
** CRS: AISI 1008 cold-rolled steel
** SS: AISI 304 stainless steel
*** HOAp: hydroxyapatite
5.1x10^{-3} m Darcy, respectively. Samples prepared using a 30 wt% (NaPO_4) solution had -0.35 wt% CaCO_3. Lower strength (6 MPa), and higher permeability (4.1x10^{-2} m Darcy), (Sugama and Carciello. 1994). These tests are continuing.

The pumpability of a cement slurry is an extremely important criterion for its use as a well completion material. In ongoing studies, set retarders and CAC compositional changes are being evaluated as methods for extending pumping times at elevated temperature. The goal is -4 hr at 100°C. In these studies, 1.3 g/cc slurries consisting of CAC, [NaPO_4], and aluminosilicate (EX)-shelled hollow microspheres were used. Two factors were found to control the thickening time. One is the chemical composition of the CAC. The second is the rate of reaction between the microspheres and the [NaPO_4]. For the former, CAC reagents having a high ratio of Ca/Al+Ca+AS retard the hydrothermal acid-base reaction, whereas CACs with a low ratio accelerate this reaction, thereby shortening the thickening time. In the second case, Na ions dissociated from the [NaPO_4] react with the microsphere shells to form X type zeolite. Improved zeolite formation results in a decrease in the thickening time. Thickening times of >20 min at 100°C and -80 min at 150°C have been measured. Further increases by the addition of retarders are anticipated.

Segregation of low density fillers during mixing with cement can be a problem during the placement of large quantities of conventional lightweight well completion formulations. Ideally, a slurry mixture which undergoes some degree of interaction between the constituents would not segregate. CPC displays this characteristic as a result of chemical interactions between the microspheres and Na ions originating from the [NaPO_4]. No segregation of the formulation occurred after storage for 24 hr at 25°C.

4. CONCLUSIONS

Materials that yield a cementing matrix produced by acid-base reactions between calcium aluminate cements and phosphate-containing compounds can be mixed with lightweight fillers to produce pumpable slurries with densities as low as -1.1 g/cc. Upon curing for 20 hr in hydrothermal environments up to 300°C, high strength, durable and CO_2-resistant cement pastes are produced. Four different commercially available calcium aluminate cements were used as base reactants, and it was determined that the reactivity and resistance to carbonation were dependent upon the chemical composition of the base ingredient. The presence of monocalcium aluminate (CA) and gehlenite (CaAS) accelerated the setting of the cement and reduced carbonation. All of the cement pastes exhibited compressive strengths >58 MPa after hydrothermal curing at 250°C for 20 hr. Subsequent exposure to a 0.05 M Na_2CO_3 solution at 250°C for 120 days indicated strength changes over the first 28 days due to the growth of crystalline phases, after which the compressive strength remained constant. Measurements of the CaCO_3 concentrations produced during the 120 days indicated values of <0.4 wt% for all of the cements except the one rich in CA (#80). A conventional Portland cement-based well completion material will form -10 wt% CaCO_3 after only 7 days exposure to the same environment.

The susceptibility of the various CPC matrices to carbonation was in the following order, #80 > RE > LU > 41. However, although #80-derived CPC specimens exposed for 120 days had the highest CaCO_3 concentration of ~1.7%, this value was considerably lower than that of autoclaved neat calcium aluminate and APi class G and H cement pastes. The loss in compressive strength for all the CPC specimens occurred in the first 30 days of exposure, but beyond this time, there was little change. Thus, this retrogression of strength is more likely to be associated with the phase transformation of amorphous ammonium calcium orthophosphate salt and Al_2O_3·9H_2O gel into crystalline HOAp and γ-AlOOH, respectively, rather than the detriment of cement bodies caused by CaCO_3.

The incorporation of inorganic and organic microsphere fillers into CPC produces a lightweight, moderate strength and highly durable cement. An aluminosilicate-based hollow microsphere (EX), with a density of 0.67 g/cc and a particle size of 75 to 200 µm, produced the most suitable results, a low slurry density of ~1.3 g/cc and a compressive strength greater than 6.89 MPa. The slurry did not

Figure 3. Compressive strengths of LCPC specimens as a function of slurry density (a) 200°C-autoclaved (b) 300°C-autoclaved (ao;Q-C, -EX, □: MA, x: GL, o:DU).
segregate after storage for 24 hr at 25°C due to chemical interactions between the microspheres and the cementing matrix formulation. Upon curing, this microsphere-filled lightweight CPC exhibited the following characteristics: 1) after autoclaving at 200°C, amorphous ammonium calcium orthophosphate (AmCOP) salt and $\text{Al}_2\text{O}_3\times\text{H}_2\text{O}$ gel phases, formed by the reaction between calcium aluminate cement and an $\text{NH}_4\text{H}_2\text{PO}_4$-based fertilizer, were primarily responsible for the development of strength, and 2) at a hydrothermal temperature of 300°C, the microsphere shell moderately reacted with the CPC to form an intermediate reaction product, epistilbite (EP), while crystalline hydroxyapatite (HOAp) and Boehmite were yielded by the phase transformations of AmCOP and $\text{Al}_2\text{O}_3\times\text{H}_2\text{O}$, respectively.

Only short term data on the carbonation resistance of LCPCs containing aluminosilicate microspheres are currently available. After exposure to 0.05M CaCO$_3$ solutions for 10 days at temperatures between 100°F and 300°F, <0.4 wt%CaCO$_3$ was produced. Acceptable compressive strengths and water permeabilities were also produced. Longer term exposure data are needed before field testing can commence.

The use of hollow acrylonitrile microspheres covered with a calcite sizing layer results in CBCs with slurry densities as low as 1.1g/cc which when cured yield properties which appear suitable for use in wells at 200°C. At this temperature the compressive strength is 3.7 MPa and the water permeability 0.05 m Darcy. Unfortunately, hydrothermal decomposition of the microspheres occurs at ~300°C, thereby eliminating higher temperature applications.

5. REFERENCES


