LIGHTWEIGHT CO_2-RESISTANT CEMENTS FOR GEOTHERMAL WELL COMPLETIONS

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ABSTRACT

Materials formed hy acid-base reactions between calcium aluminate compounds and phosphate-containing solutions yield high strength, low permcability and CO_2-resistant cements when cured in hydrothermal environments. The cementing formulations are pumpable at temperatures up to 150°C. thercby making their use for well completions technically feasihle. When this cementing matrix was exposed in an autoclave containing Na_2CO_3-saturated brine for 120 days, <0.4 wt% CaCO, was produced. A conventional portland cement-based well completion material will form –10 wt% CaCO, after only 7 days exposure. The addition of hollow aluminosilicate microspheres to the uncured matrix constituents yields slurries with densities as low as –1.2 gicc which cure to produce materials with properties meeting the criteria for well cementing. These formulations also exhibit low rates of carbonation. Lahoratory 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 thc 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/cc) are desirable to minimize the freyuency 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 (CO_2)-resistant cements becomes more critical. It is well known that alkali metal catalyzed reactions hetween CO_2-containing brines and the calcium silicate hydrate (CSH) compounds and calcium hydroxide in conventional well cements result in rapid deterioration at pressures, temperatures and CO_2 concentrations typical of geothermal wells (Milestone et al, 1987). In these cases, reactions between Na and K in the brines with CSH phases produce substituted CSH compounds such as pectolite and reyerite. both of which are susceptible to carbonation. The attack of portland cement by CO, is described in the following equations (Schumberger Dowell, 1993):

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO^-_3 \quad (1)$$

$$Ca(OH)_2 + H^+ + HCO^-_3 \rightarrow CaCO_3 + 2H_2O \quad (2)$$

$$C\text{-}S\text{-}H + H^+ + HCO^-_3 \rightarrow CaCO_3 + \text{amorphous silica gel} \quad (3)$$

In Equation 1, ~1% of the dissolved CO, 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 CO_2 laden water continues to invade the cement matrix, more equilibria are established.

$$CO_2 + H_2O + CaCO_3 \leftrightarrow Ca(HCO_3)_2 \quad (4)$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \leftrightarrow 2CaCO_3 + 2H_2O \quad (5)$$

Additional CO_2 reacts with the calcium carbonate to form water-soluble calcium bicarbonate (Equation 4). Finally. dissolved calcium bicarbonate racts 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 CO, 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 CO_2 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/cc, 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% CaCO, after 1 yr in brine at 300°C containing 500 ppm CO_2, and 6) water permeability, <0.1 m Darcy.

The work focused on the identification of pathways leading to the formation of chemically bonded cements (CBC) by acid-base reactions. Thc 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 $MO{\cdot}xAl_2O_3$, $MO{\cdot}xSiO_2$ or $MO{\cdot}xAl_2O_3{\cdot}ySiO_2$. The cementitious products formed are salt complexes which hind 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

$$MO + H_2A \rightarrow MA + H_2O \quad (6)$$

base acid salt matrix

Metal aluminate or silicate-acid reaction

$$\underset{\text{base}}{MO{\cdot}xSiO_2} + \underset{\text{acid}}{H_2A} \rightarrow MA + \underset{\text{silica gel}}{xSiO_2} + H_2O, \quad (7)$$

$$\underset{\text{base}}{MO{\cdot}xAl_2O_3} + \underset{\text{acid}}{H_2A} \rightarrow MA + \underset{\text{alumina gel}}{xAl_2O_3} + H_2O, \quad (8)$$

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, polyphosphate 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 hlow-outs. It will also permit development of higher temperature, higher CO_2 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): Refcon (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 Aluminates Company. Prior to use. chemical characterizations of the CACs were performed using XRD analysis over the range 0.444 to 0.249 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 (C_2AS). Please note that the chemical notations are abbreviated. C=CaO, A=Al_2O_3 and S=SiO_2. The LU and RE-type reactants contained these compounds plus monocalcium dialuminate (CA_2), while the #80 had CA and CA, as major components and C_2AS 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 $[NaPO_3]_n$, supplied by Albright and Wilson Americas, was utilized in some later tests. In the latter, the $(NaPO_3)_n$ was dissolved in water to make solutions varying between 30 and 40 wt%.

Five commercial inorganic and organic microspheres were evaluated as lightweight fillers for CBCs. These were Q-Cel *650* (Q-C), and Extendospheres (EX). both supplied by the PQ Corporation: Macrolite (MA) and glass bubbles (GL) from the 3M Corporation; and Dualite M6017AE (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 tillers 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 dry mixing the CAC powder with the filler. Either Poly-N or $[NaPO_3]_n$ was added. After casting and curing at room temperature for 2 hr. autoclave curing was accomplished for 20 hr at 200° or 300°C. Compared to the CPC **sluny** 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 exothermal acid-base reaction between the CAC and the Poly-N. The phase compositions and transformations of CPC after exposures to hot 0.05 M Na_2CO_3 solutions were explored by X-ray powder diffraction (XRD). Quantitative data on the amount of $CaCO_3$ formed in the CPC bodies were obtained from thermogravimetric analysis (TCA) by the weight loss at which thermal decomposition of $CaCO_3$ occurs over the range 600° to 770°C. Compressive strength tests were performed on neat CPC specimens having a diameter of 30 mm and a length of 60 mm: the result given is the average value of three specimens.

The charactcristics of the microspheres used to produce LCPCs, namely bulk density, particle size and chemical composition. were measured using helium comparison pycnometry. 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 N_2 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 + C_2AS. 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>LU>RE>#80.

Compressive strength results for each of the CAC formulations after exposure to a 0.05M Na_2CO_3 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 HOAp (hydroxyapatite) and γ-A100H (Boehmite) phases, together with the amorphous $NH_4CaPO_4{\cdot}xH_2O$ and Al_2O_3 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 ofthe hydrothermal phase conversion

→ HOAp and Al_2O_3 gel → γ-AlOOH phase transitions were completed at the exposure age of 28 days. The strengths of the 120 day-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 $CaCO_3$, 0.1 to 0.2 wt%, was already present in the unexposed control specimens, the origin of which was the CAC hase 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% $CaCO_3$, while 0.5 wt% $CaCO_3$ was detected in the RE samples. By comparison, a higher rate of carbonation occurredin the #80 specimens. The rate of carhonation for this specimen increased with exposure time; after 28, 91, and 120 days the amount of $CaCO_3$ 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 pastes exposed for 7 days to the Na_2CO_3 solution at 250°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 Na_2CO_3 environment. In this case, the $CaCO_3$ concentration was 9.5 wt% after 7 days.

In addition to strength. low permeability and CO_2 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.

Evaluations of the shear bond strength and the interfacial phase compositions were made. For the latter, analyses of both the interfacial-failed cement and metal sides wen: performed after completion of the shear hond tests. The results from these examinations, given in Table 2, indicate that the bond strength is dependent upon the cement type and the metal composition. The CGC exhibited better bonding than the CPC. Both cements had higher hond strengths to CRS than with SS. Studies of the phase compositions at the interfaces indicated that the high shear strengths at the CGC/metal joints were due to strong mechanical bonding between the rough Fe_2O_3 layer formedas a corrosion product and the xonotlite phase formed by hydrothermal reactions with the CGC pastes. In contrast, no significant amount of Fe_2O_3 was found at the CPC/metal interfaces.

The interfacial contact layer between the CPC and the metals consisted of δ-AlOOH and Na-zeolite phases separated from the major phase HOAp component of the matrix. Therefore, this phase segregation at the interface probably is the reason for the lower bond strength with CPC/metal systems. However. it should also he noted that the lowest bond strength measured was 0.47 MPa, almost 7 times the API criterion of 0.07 MPa.

Table 1. Properties of Microspheres

Microsphere (Symbol)	Type	Density g/cm³	Particle Size μm	Chemical Composition of Shell Surfaces, %								
				Si	Al	B	C	K	O	Fe	Ca	Na
Q-cel 650 (Q-C)	Borosilicate Glass	0.05	6-95	11.0	-	21.3	15.2	2.3	37.3	-	-	12
Extendospheres (EX)	Aluminosilicate	0.67	75-200	13.1	10.1	-	37.8	2.0	36.5		-	0
Macrolite (MA)	Nepheline Syenite Ceramic	125	300-450	64	19.7		30.8	18	368	2.3		2
Glass Bubbles (GL)	Soda Lime Borosilicate Glass	038	5-45	116		169	251	24	717		1.9	9
Dualite (DU)	Acrylonitrile Copolymer w / $CaCO_3$ Coating	013	25-100				50 9		331	50	110	

3.2 Lightweight CPC Composites

The compatibility of CPCs with a vanety of commercial inorganic and organic microspheres was then studied (Sugama and Wetzel, 1992). These hollow fillers were evaluated mainly on the relationship between the densities of the slurries and the compressive strengths of hydi-othermally 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 zones near the microsphere particles. The latter analyses provided us with information on the possible interaction mechanism between the CPC and the microspheres.

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 bad a strength of 8.5 MPa. At 300°C, this decreased to –4.5 MPa. The strengths increased with slurry

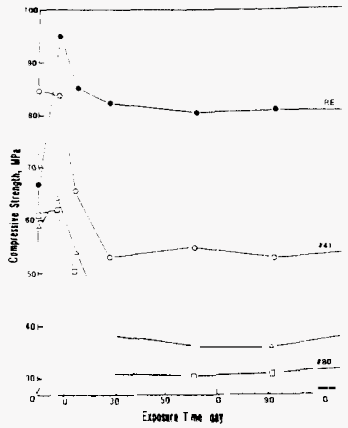

Figure 1. Changes in compressive strcngth of various CPC specimens as a function of exposure time to a 250°C-Na_2CO_3 solution.

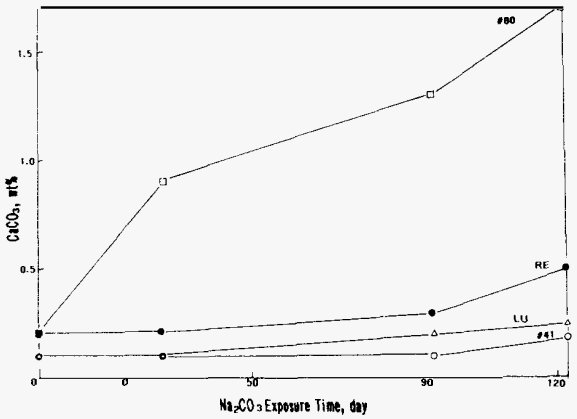

Figure 2. Concentrations of $CaCO_3$ formed in various calcium aluminate derived CPCs after exposure for up to 120 days to Na_2CO_3 solution at 250°C.

autoclaved for 20 hr at 200° or 300°C prior to test. Specimens containing the aluminosilicate microspheres (EX) exhibited the highest strengths for hoth curing temperatures. Specimens with a slurry density **of** 1.2 g/cc had a strength of 8.5 MPa. At 300°C, this decreasec! to −4.5 MPa. The strengths increased with sluny density. For the middle-range density **of** ~ 1.35 g/cc, LCPC strengths were in this order: EX > Q-C = GL > DU > **MA.** The poor performance of the MA filler **was** attributed to physical incompatibility; the spheres mixed poorly with the cement and separated quickly. floating to the top. This created non-uniform, weak specimens that performed poorly at both temperatures. In comparison with specimens autoclaved at 200°C, the hydrothermal treatment at 300°C resulted in a loss **of** strength, with the rates **of** reduction in strength for DU- and MA-filled CPC specimens being lower than those for the other microsphere-filled specimens. The mechanical strengths of the specimens made with the borosilicate-hased glass fillers such as Q-C and GL were especially poor, exhibiting values hetween −1.0 and −3.0 MPa.

Table 2. Bond Strengths and Phase Compositions at Cement/Metal Interfaces

Cement*	Metal Substrates**	Sheer Bond Strength (MPa)	Phase Composition at Interfaces Major	Minor
CPC	CRS	0 75	δ-A100H	Na-zeolite. HOAP***
CPC	SS	0 47	Na-zeolite δ-AL00H	HOAP
CGC	CRS	1.65	Fe_2O_3, Xonotlite	
CGC	S	1 43	Xonotlite	Fe_2O_3

* CPC: calcium phosophate cement
CGC: class G Cement
** CRS: AISI 1008 cold-rolled steel
SS: AISI 304 stainless steel
*** **HOAP:** hydroxyapatite

SEM coupled with EDX. XRD and FT-IR analyses wcrc used to investigate the causes !or the strength changes, and to identify phase compositions and transformations. These results which were published hy Sugama and Wetzel (1992), in.licated that the factors governing the development an2 loss of strength were 1) phase composition and transformation of the matrix, 2) interfacial reaction products formed hy interactions between the microspheres and the CPC. 3) changes in microstructure developed at the microsphere-CPC interfaces and in the matrix phase. and 4) the susceptibility *o!'* the microspheres to hydrothermal and thermal decomposition. SEM images of EX-containing LCPCs revcalcd 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 microsphcrcs without any CPC coverage on the fractured matrix surlace. 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 hond 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 micmspherc-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 $Al_2O_3 \cdot xH_2O$ into crystalline HOAp and Boehmite, respectively.

Tests to measure thc carhonation 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% $(NaPO_3)_n$ wcrc exposed for 10 days in 0.05M Na_2CO_3 solutions at 100°, 200°, and 300°. After the 300° exposure, samplcs produced using a 40 wt% $(NaPO_3)_n$ solution exhibited −0.2 wt% $CaCO_3$. The compressive strength and water permeability was **9.4** MPa and

$5.1x10^{-3}$ m Darcy, respectively. Samples prepared using a 30 wt% $(NaPO_3)_n$ 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 –4hr at 100°C. In these studies, **1.3** g/cc slurries consisting of **CAC.** $[NaPO_3]_n$, 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 $[NaPO_3]_n$. For the former. **CAC** reactants having a high ratio of $CA_2/[CA+C_2AS]$ 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,], react with the microsphere shells to form **X** type zeolite. Improved zeolite formation results in a decrease in the thickening time. Thickening times of >120 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 hetween the constituents would not segregate. CPC displays this characteristic as a result of chemical interactions between the microspheres and Na ions originating from the $[NaPO_3]_n$. 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 gchlenite (C_2AS) accelerated the setting of the cement and reduced carhonation. All of the cement pastes exhibited compressive strengths >58 MPa after hydrothermal curing at **250°C** for 20 hr. Suhsequcnt 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, 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, hut 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 $Al_2O_3 \cdot xH_2O$ 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 filers 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 200μm, produced the most suitable results, a low slurry density of –1.3 g/cc and a compressive strength greater than 6.89 MPa. The sluny did not

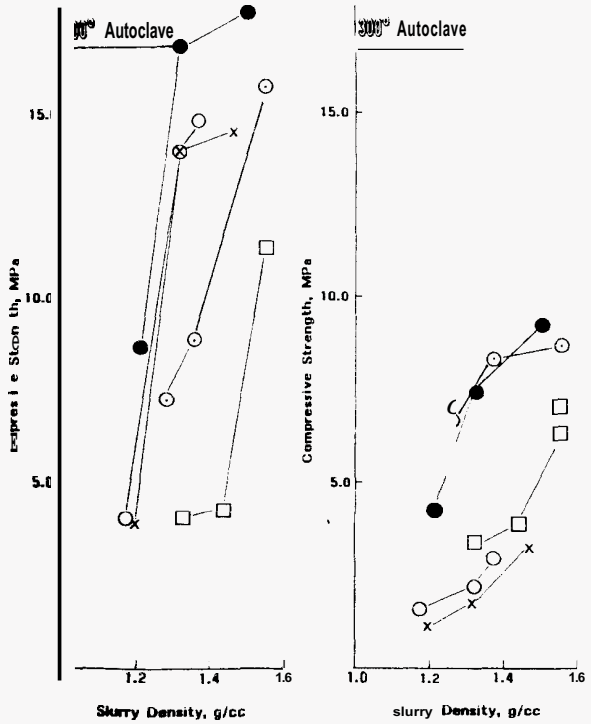

Figure 3.Compressive strengths of LCPC specimens as a function of slurry density (a) 200°C-autoclaved (b) 300°C-autoclaved (o:Q-C, ·:EX, □: MA, x: GL, o:DU).

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 $Al_2O_3 \cdot xH_2O$ gel phases, formed by the reaction between calcium aluminate cement and an $NH_4H_2PO_4$-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 $Al_2O_3 \cdot xH_2O$, respectively.

Only short term data on the carbonation resistance of LCPCs containing aluminosiliate microspheres are currently available. After exposure to 0.05M $CaCO_3$ solutions for 10 days at temperatures between 100° and 300°C, <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.

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