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MULLITE MICROSPHERE-FILLED LIGHTWEIGHT CALCIUM PHOSPHATE CEMENT SLURRIES FOR GEOTHERMAL WELLS: SETTING AND PROPERTIES

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ABSTRACT

The chemical factors affecting the setting properties of microsphere-filled lightweight calcium phosphate cement (LCPC) slurries, ranging in density from 1.32 to 1.12 g/cc, at high hydrothermal temperature were investigated. The LCPC slurries consisted of calcium aluminate cement (CAC) as the base reactant, a $-(-NaPO_3-)-_n$ solution as the acid reactant, and mullite-shelled hollow microspheres as the lightweight additive. Two major aspects were studied; one was the importance of the chemical constituents of CAC, and the other was the rate of the hydrothermal reaction between the mullite shell and the Na ions dissociated from $-(-NaPO_3-)-_n$. For the former, the use of CAC having C_2AS and CA phases as the major chemical components shortened the thickening time of LCPC slurries, whereas CACs with CA, CA_2, and α-Al_2O_3 phase components extended the thickening time. For the hydrothermal reaction, an excess of zeolite X type formed by the uptake of Na by mullite microspheres reduced the thickening time.

Introduction

When cementing materials are used to complete geothermal wells at high temperature, the criteria of their performance involves the following seven important properties, 1) a cement slurry with low density, 2) a certain thickening time of slurry, 3) a low rate of wet carbonation, 4) a low permeability to water, 5) high compressive strength, 6) good adherence to steel and cement, and 7) mitigation of corrosion of steel casing. In our ongoing research efforts to develop and formulate material systems to meet all these criteria, we previously reported that microsphere-filled calcium phosphate cements have a high potential as alkali carbonation-resistance lightweight cementing materials[1,2]. The lightweight calcium phosphate cements (LCAC) can be prepared by exposing a low-density cement slurry (1.28 g/cc) consisting of calcium aluminate cements (CAC), NH_4, or alkali-containing polybasic phosphate, and mullite-shelled hollow microspheres to hydrothermal environments. The LCPC specimens after exposure for up to 10 days to 0.05 M Na_2CO_3-laden water at 200°C had a compressive strength of > 9.0 MPa, water permeability of < 0.1 millidarcy, and low rate of alkali carbonation of < 0.5 wt%. Furthermore, our most recent studies on the interfaces between hydrothermal cements and steels suggested that the calcium phosphate cement (CPC) paste mitigates the corrosion of the steel in contact with the cement layers, while also adhering satisfactorily to the steel surfaces. Thus, the LCPCs are very attractive for use as practical cementing materials to support the casing steel pipe in geothermal wells where the temperatures may rise to 200°C.

The capability of LCPC slurries to maintain pumpability at high temperatures around 150°C has not yet been satisfactorily established. Unlike ordinary portland cements formed by the hydrolysis-hydration reaction, the CPCs were synthesized through the acid-base reactions between the CAC as the base reactant, and NH_4 or alkali metals-containing phosphate compounds as acid reactants. Thus, the chemical components in the CAC reactants played an essential role in retarding and accelerating the setting of the CPC slurry; CAC with a low ratio of CaO/Al_2O_3 mole fraction retard its setting, whereas a high CaO/Al_2O_3 ratio promoted the rate of setting[3].

Based upon this information, we had two major objectives in this work: one objective was to investigate the thickening characteristics of fast- and slow-setting LCPC slurries at hydrothermal temperatures of 125° and 150°C; the second aspect was to determine the compressive strength and water permeability of the LCPC specimens after exposing them for 24 hr in autoclave at 200°C, and to identify the reaction compounds formed by the hydrothermal reaction between the phosphate-based solution and the CAC powders or the mullite-shelled hollow microspheres.

Experimental

Materials

Two commercial calcium aluminate cements (CAC), Refcon (RE) supplied by the Lehigh Portland Cement Company, and Secar 80 (#80) obtained from the Lafarge Calcium Aluminates, were used as the base solid reactants. The X-ray powder diffraction (XRD) data for these CACs showed that the chemical components of RE consisted of three major phases, monocalcium aluminate, $CaO\cdot Al_2O_3$, (CA), gehlenite, $2CaO\cdot Al_2O_3\cdot SiO_2$, ($C_2AS$), and monocalcium dialuminate, $CaO\cdot 2Al_2O_3$, (CA_2). In contrast, #80 had CA, CA_2, and α-Al_2O_3 (corundum) as its major components, and C_2AS as a minor one.

The polybasic sodium phosphate reagent, $-(-NaPO_3-)-_n$, was dissolved in water to make a 30 wt% $-(-NaPO_3-)-_n$ solution as the acid liquid reactant (pH 6.15). Commercial mullite ($3Al_2O_3\cdot 2SiO_2$)-shelled hollow microspheres, called as Extendospheres (EX, PQ Corp), were incorporated into the cement slurry as the lightweight filler. These microspheres had a density of 0.67 g/cm^3 and a particle size from 75 to 200 μm.

Table 1 shows the formulation of lightweight CPC (LCPC) slurries used in this study, and their densities and consistencies at 25°C. For the viscosity of the slurry, the bearden units of consistency (Bc), obtained on a pressurized

Table 1
Density and Consistency of Microsphere-Filled Lightweight CPC Slurries

Specimen No.	Formulation	Density of slurry, g/cc	Consistency of slurry at 25°C, Bc
1	33wt%RE -19wt%EX-48wt%[30wt%-(-NaPO$_3$-)-$_n$]	1.32	28
2	33wt%#80-19wt%EX-48wt%[30wt%--(-NaPO$_3$-)-$_n$]	1.30	27
3	26wt%#80-18wt%EX-56wt%[30wt%--(-NaPO$_3$-)-$_n$]	1.24	28
4	17wt%#80-15wt%EX-68wt%[30wt%--(-NaPO$_3$-)-$_n$]	1.19	27
5	13wt%#80-14wt%EX-73wt%[30wt%--(-NaPO$_3$-)-$_n$]	1.12	27

consistometer, are dimensionless units. The densities of these slurries ranged from 1.32 to 1.12 g/cc, while all their consistencies were ≈ 27 Bc. The LCPC slurries were cast into cylindrical molds of 30 mm-diam. x 65 mm-long to measure compressive strength, and into discs of 30 mm-diam. x 39 mm-long for determining the water permeability. The molds and discs were then exposed in an autoclave at 200°C for 24 hrs under a pressure of 1.1 MPa.

Measurement

The consistency of the slurries at high temperatures was measured in accordance with API Schedule 29 L7 and 30 L7 Specifications[4]. The former schedule corresponds to a simulated 4270 m-depth well at 126°C under a pressure of 92.4 MPa, and the latter simulated a 4880 m-depth well at 150°C under a pressure of 111.0 MPa. The test was completed when the consistency (Bc value) of the slurry exceeded 70.

The phase compositions formed in neat CPC and LCPC specimens were explored using XRD. A Ruska liquid permeameter was used to determine the water permeability of the LCPC specimens; this measurement was made by measuring the amount of water which passed through the discs under a pressure gradient of 2 atm. Compressive strength also was tested on LCPC specimens; the results given are the average values from three specimens.

Results and Discussion

In preparing the microsphere-filled lightweight cement slurries with a density of < 1.30 g/cc, one of the important considerations is that the lightweight microspheres must be uniformly distributed in the slurry phase; there must not be any segregation of the microspheres from the slurry. To obtain this information, we visually observed the condition of LCPC slurries placed in the glass tube. There were no visible signs of segregation for all the LCPC slurries left for 24 hr at 25°C.

The thickening time was recorded as the elapsed time before the consistency reached a Bc value of 70. Table 2 lists the thickening times for the slurries. The use of the RE reactant (specimen No.1) in the slurry systems corresponded to an averaged thickening time of only ≈ 40 min at 125°C. A further increase in temperature to 150°C reduced this time to only ≈ 15 min. In contrast, the thickening times at 125°C for all the #80-related slurries were > 120 min, excepting specimen No.5. We were particularly interested in why specimen No.5, with the lowest density of slurry and the lowest weight fraction of #80/[EX + -(-NaPO$_3$-)-$_n$] had a shorter thickening time than the other #80 slurries. In fact,

Table 2
Thickening Times of Slurry Specimens at 125° and 150°C

Specimen No.	API Schedule 29 L7 at 125°C, thickening time, min	API Schedule 30 L7 at 150°C, thickening time, min
1	≈ 40	≈ 15
2	> 120	≈ 100
3	> 120	≈ 90
4	> 120	≈ 80
5	≈ 100	≈ 60

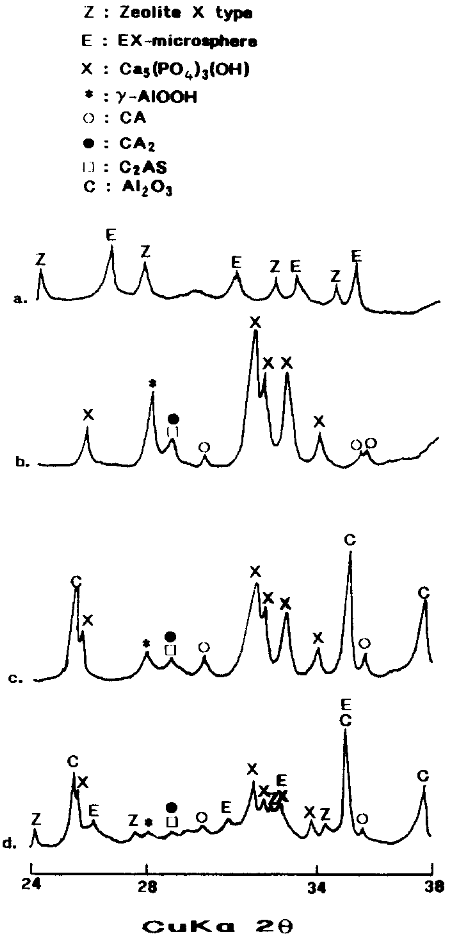

Fig. 1 XRD patterns for EX--(-$NaPO_3$-)-$_n$ (a), RE--(-$NaPO_3$-)-$_n$ (b), #80--(-$NaPO_3$-)-$_n$ (c), and EX-#80--(-$NaPO_3$-)-$_n$ (d) systems after exposure for 24 hr in autoclave at 200°C.

the increase in temperature to 150°C clearly verified that thickening times tended to be reduced with a decreasing ratio of #80/[EX + $-(-NaPO_3-)-_n$], from ≈ 100 min for specimen No.2, to ≈ 60 min for specimen No.5. Thus, it is possible to assume that the $-(-NaPO_3-)-_n$ reactant not only chemically reacts with the #80 reactant, but also has a strong affinity with EX.

To ascertain what sort of reaction products were formed by reaction between EX and the $-(-NaPO_3-)-_n$ solution, and to identify the phase composition developed in the LCPC bodies, we inspected four samples autoclaved at 200°C by XRD tracing, ranging from 0.37 to 0.24 nm; the samples were 17 wt% EX-83 wt% [30 wt% $-(-NaPO_3-)-_n$ solution], 60 wt% RE-40 wt% [30 wt% $-(-NaPO_3-)-_n$ solution], 60 wt% #80-40 wt% [30 wt% $-(-NaPO_3-)-_n$ solution], and specimen No.3. Figure 1 shows the results from these samples. The diffraction pattern (a) of the EX-mixed $-(-NaPO_3-)-_n$ sample without the CAC reactant demonstrated that the hydrothermal reaction product was the zeolite X type, $Na_{14}Al_{12}Si_{13}O_{23}\cdot 3H_2O$, while the unreactive mullite microspheres, denoted as E, still remain. Thus, it is apparent that Na ions, dissociated from $-(-NaPO_3-)-_n$, favorably react with the mullite ($3Al_2O_3\cdot 2SiO_2$) microspheres to form zeolite X type under the hydrothermal conditions at 200°C. The spacing pattern (b) of RE-associated CPC pastes is indicative of the presence of hydroxyapatite, $Ca_5(PO_4)_3(OH)$, (HOAp), and boehmite, γ-AlOOH as the reaction products, with some unreactive RE components, such as CA, CA_2, and C_2AS. The reaction products similar to that of the RE-CPC paste can be seen in the #80-CPC pastes (c). This XRD pattern also suggested that the reactivity of the α-Al_2O_3 in #80 reactant with the $-(-NaPO_3-)-_n$ is very poor because of the remain of strong α-Al_2O_3-related d-spacings. As expected, specimen No.3 (d) prepared by mixing the #80, microspheres, and $-(-NaPO_3-)-_n$, was characterized by having the multiple phases consisting of HOAp as the major component, and zeolite X type and γ-AlOOH as the minor ones, with remaining unreactive microspheres and #80 reactants in the LCPC bodies. Consequently, we believe that zeolite X type, formed by the hydrothermal reaction of mullite with $-(-NaPO_3-)-_n$, is the reason why the slurries with a low ratio of CAC/[EX + $-(-NaPO_3-)-_n$] have a short thickening time.

Table 3
Changes in Compressive Strength and Water Permeability as a Function of Density of Slurries

Specimens, No.	Density of slurry, g/cc	Compressive strength, MPa	Water permeability, millidarcy
1	1.32	11.51	1.8×10^{-2}
2	1.30	12.10	1.6×10^{-2}
3	1.24	9.00	1.2×10^{-1}
4	1.19	5.86	3.3×10^{-1}
5	1.12	4.66	5.9×10^{-1}

Table 3 shows the changes in compressive strength and water permeability as a function of the density of slurry for LCPC specimens after exposure for 24 hr in autoclave at 200°C. A given data indicates that the properties depend primarily on the density of the slurries; the compressive strength decreased with a lowering of density, from ≈ 12.00 MPa for ≈ 1.31 g/cc slurry, to 4.66 MPa for 1.12 g/cc slurry. The value of water permeability increased with the decreasing slurry density.

Conclusion

When the lightweight calcium phosphate cement (LCPC) slurries (density of < ≈ 1.30 g/cc) consisting of mullite-shelled hollow microspheres as the lightweight additive, calcium aluminate cements (CAC), and polybasic sodium phosphate $-(-NaPO_3-)-_n$, are applied in geothermal wells at elevated temperature, the thickening time of the slurries depended on the two factors; one reflected the CAC species, such as the base reactants, and the other was the rate of hydrothermal reaction between the microspheres and the $-(-NaPO_3-)-_n$ solution. For the former, CAC reactants having CA, CA_2, and α-Al_2O_3 phases as the major chemical components retarded the hydrothermal acid-base reaction, whereas CACs with C_2AS and CA phase components accelerated this reaction, thereby shortening the thickening time of the slurry. The Na ions dissociated from the $-(-NaPO_3-)-_n$ favorably reacted with the mullite shells to form zeolite X type. However, a well-formed zeolite caused a decrease in the thickening time of slurry.

Nevertheless, after a 24-hour exposure in an autoclave at 200°C, the #80 CAC-related LCPC slurries with densities of 1.19 g/cc displayed excellent properties, involving thickening times of > 120 min at 125°C and ≈ 80 min at 150°C, compressive strength of 5.86 MPa, and water permeability of 3.3×10^{-1} millidarcy. The major contributors to the development of such a compressive strength were the combined phases of hydroxyapatite, $Ca_5(PO_4)_3(OH)$, and zeolite X type, reaction products formed as the matrix layers in the LCPC bodies and as the intermediate layers at interfaces between matrix and mullite.

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