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TREATED CERAMIC MICROSPHERE-CEMENT LIGHTWEIGHT COMPOSITES FOR GEOTHERMAL CEMENTING SYSTEMS

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ABSTRACT

The compressive strength and water permeability of high-temperature lightweight cementing materials containing sillimanite-based hollow microspheres as a filler can be improved by treating the surfaces of the microspheres with a Ca(OH)2-saturated solution at temperatures up to 200°C. The precipitation of an epitaxial layer formed by an interaction between a hot calcium hydroxide solution and the surface of the sphere plays an essential role in developing favorable bonding characteristics at the interfaces and in promoting the hydration of the cement matrix. The properties of the composites include a slurry density of <1.2 g/cc at 25°C, a 300°C-24 hour compressive strength of >1015 psi (7.0 MPa), a water permeability of <10^-4 Darcy, and a bulk density of <1.0 g/cc. It was observed that tobermorite-truscottite transformation and anorthite formation during autoclave exposure for 180 days in brine at 300°C results in slight strength reductions and increased water permeability.

INTRODUCTION

Work to develop high-temperature low-density cement slurries is in progress at Brookhaven National Laboratory (BNL). If successful, the work will reduce lost-circulation problems caused by the high hydrostatic pressures that are required to pump normal-density (1.7 to 1.9 g/cc) slurries.

Two methods for reducing slurry density have been applied in geothermal wells. One method is to introduce air bubbles into an ordinary cement slurry that has an adequate cement-to-silica ratio (Sugama and others, 1986). The resulting small, fine foam bubbles which are dispersed uniformly within the slurries are thought to promote stronger cement walls around the bubbles and so provide a set cement of increased integrity. Discrete bubbles under high pressure conditions are chemically and physically stabilized as microscopic cells within the cement slurry until the cement sets; this produces a hardened foam cement with adequate compressive strength and low permeability to water and gas.

A second method is to incorporate pressure-resistant hollow microspheres into cement slurries (Martin, 1983). In addition to producing a lightweight slurry, the relatively high bridging ability of the hollow beads enhances its effectiveness in controlling lost-circulation problems. However, results from BNL preliminary studies on the preparation of microsphere-filled lightweight cement systems suggested that the inclusion of the microspheres as a filler was not sufficient to yield the properties needed for geothermal cements. For instance, when a slurry with a density of 1.16 g/cc was autoclaved for 24 hour at a temperature of 300°C and a hydrostatic pressure of 1500 psi (10.3 MPa), the compressive strength of the set cement paste was only 610 psi (4.2 MPa). The low strength was presumed to be due to poor bonding at the cement-microsphere interface, and a low degree of hydration in the cement matrixes. Therefore, modification of the microsphere surfaces was deemed necessary to produce a high-quality high temperature lightweight cementing material that could meet the criteria. These included a slurry density of <1.2 g/cc at 25°C, a 300°C-24 hour compressive strength of >1000 psi (6.9 MPa), water permeability of <10^-6 Darcy, and a bulk density of <1.10 g/cc.

It was anticipated that if the surface of the spheroidal-shaped filler was covered with a reactive calcium-based hydrate layer, the addition of the modified spheres to a cement paste would yield a higher strength lightweight cementing material with low water permeability. As a result, the surfaces of spheres were treated with a saturated solution of calcium hydroxide at temperatures up to 300°C to determine if a highly reactive surface could be produced.

A major part of the study was focused upon determination of the mechanical, physical, and microstructural characteristics of lightweight cement systems prepared by incorporating ceramic spheres that were treated with a hot alkali solution. These data were then correlated indirectly with the phases formed in the matrices of the bulk cement pastes as a function of autoclave exposure time at 300°C. In addition, the resultant hydrothermal reaction products, surface chemical
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states, and microstructural features of the treated sphere fillers which are responsible for the strength development and water permeability improvement of the set lightweight cements, were explored. Techniques such as scanning electron microscopy (SEM) associated with energy-dispersive x-ray spectrometry (EDX), x-ray photoelectron spectroscopy (XPS), and x-ray powder diffraction (XRD) were used.

Materials

The lightweight filler used consisted of pressure-resistant hollow microspheres, having an average particle size of approximately 125μm and a bulk density of 0.4 g/cc, supplied by Fillite U.S.A., Inc. An API class H cement, supplied by the Lehigh Portland Cement Co., was used as the matrix. A typical analysis of the cement was: 64.4 wt% CaO, 22.4 wt% SiO₂, 4.29 wt% Al₂O₃, 4.92 wt% Fe₂O₃, 0.8 wt% MgO, and 2.2 wt% SO₃. To prevent retrogression of strength at high temperatures, silica flour having a particle size of <44μm was added to the cement.

The surface modification of the microspheres was accomplished as follows. The microspheres were first rinsed with deionized (D.I.) water to remove any contamination and then exposed for approximately 20 hour in a saturated solution of calcium hydroxide [Ca(OH)₂] at temperatures up to 300°C. Then the microspheres were again washed in D.I. water and subsequently dried in an oven at 110°C. Microspheres treated with only the D.I. water at temperatures up to 300°C were employed as controls.

Microsphere-filled lightweight cements, used to determine compressive strength and to explore cement-microsphere interfaces, were prepared in the following way. The lightweight cement slurries, consisting of 30 wt% class H cement, 10 wt% silica flour, 25 wt% microspheres, and 35 wt% water, were poured into glass test tubes, 3.5-cm diam by 7.0-cm long. The slurry-filled test tubes then were autoclaved for 24 hour at 300°C.

RESULTS AND DISCUSSION

Surface and Subsurface Characteristics of Modified Spheres

The chemical constituents of the shell material responsible for the high shear strength and high pressure resistance of the microspheres were identified by XRD analysis in the diffraction range from 0.553 to 0.206 nm. The XRD pattern showed the presence of two major silicon compounds. One was sillimanite Al₂(SiO₅), (Joint Committee Standards) which was characterized by two prominent lines at 0.337 and 0.22 nm, medium intensities at 0.341, 0.269, and 0.253 nm, and relatively weak diffractions at 0.535, 0.288, 0.242, 0.229, and 0.211 nm. Another strong line at 0.334 nm indicated the presence of quartz as a second major component. Thus, the shell structure of the hollow microspheres appeared to be an assemblage of hybrid phases of sillimanite and silica glass.
Comparing micrographs 1-B and 1-A, it is apparent that the originally smooth surface of the "as-received" spheres was transformed into a geometrically reticulated network by exposure to D.I. water at 200°C. This morphological transformation reveals the characteristics of the underlying structure and indicates that the thin overlay can be removed by hot D.I. water. It should be noted that D.I. treatment at 100°C is too low to remove the film, suggesting that the glass and carbon adhere tightly to the underlying materials. The typical network structure of lath-like crystals in the underlying material beneath the thin film must be associated with the formation of sillimanite, Al(AlSiO₅), as the major phase of the shell structure. Referring to the EDX data in Figure 1-B, the conspicuous growth of the Si peak suggests that the underlying crystalline materials contain a large amount of silicon compounds. No significant changes in peak intensity were observed for elements such as Al, K, Ti, and Fe.

Figure 2 shows an XPS wide scan for the 200°C D.I.-treated sphere surface. Compared with the untreated surface, the scan is characterized by intense Al, Si, and O signals, the appearance of identical K and Fe peaks, and a considerable reduction in C peak intensity. The probable reason for the latter is the elimination of carbon contamination by the hot D.I. water treatment.

Of particular interest are the morphological transformations which occur on the sphere surfaces modified by the Ca(OH)₂-saturated solution at 200°C (Figure 1-C). The SEM image exhibits a morphological peculiar surface that consists of a layer of elongated crystals, providing evidence of epitaxial growth of certain hydration products. The epitaxy is topographically identical to the formation of a continuous layer overlaid on the sphere surface. The continuous epitaxy film seems to form a shell structure that encapsulates the sphere particle. The EDX spectrum for this hydration shell reveals noteworthy reductions in the intensities of the Si, K, Ti, and Fe peaks, a Ca signal, and an unchanged Al peak (Figure 1-C). The presence of the Ca peak relates directly to the reaction products at the interface between the Ca(OH)₂ and the chemical constituents of the sphere surface, and the Ca(OH)₂ precipitated on the sphere. The reduction in the peaks for Si, K, Ti, and Fe elements may indicate that the sphere was covered by calcium hydration products to a depth of at least 1μm. The essentially constant Al intensity for both the Ca(OH)₂- and the D.I.-treated spheres verifies that a relatively large amount of Al is present in the epitaxy layers.

Generally, direct phase data for the outermost surface sites of spheres are very difficult to obtain using x-ray diffraction analysis because of the limited amount of material available. However, XPS high-resolution spectrum analysis is very useful for precise phase identifications.
Let us consider in detail the XPS data from the Ca-based hydrates formed on the Ca(OH)$_2$-treated sphere surfaces. The consequent spectrum for the calcium 2p3/2 core level in the BE range of 343.1 to 350.6 eV is illustrated in Figure 3. This spectrum was reconstructed from the four major peaks which represent the presence of four distinct calcium species. The lowest BE at 346.7 eV is due to unreacted and residual Ca(OH)$_2$. The calcium in CaO-SiO$_2$-H$_2$O is readily identifiable from the secondary low BE level (No. 2) at 347.6 eV. The principal line arising at 348.4 eV (No. 3) is possibly associated with the presence of the calcium aluminate silicate hydrate (CaO-Al$_2$O$_3$-SiO$_2$-H$_2$O) system. However, the phase present at the 349.1 eV peak is unknown. Nevertheless, the main conversion product precipitated by the chemical interaction between the Ca ions from the Ca(OH)$_2$ and the sphere surfaces under the hydrothermal environment is likely to be associated with the formation of the CaO-Al$_2$O$_3$-SiO$_2$-H$_2$O system, rather than the CaO-SiO$_2$-H$_2$O system.

![Figure 3. Calcium 2p3/2 and 2p1/2 spectra of 200°C Ca(OH)$_2$-treated sphere surface: (1) Ca(OH)$_2$ at 346.7 eV, (2) CaO-SiO$_2$-H$_2$O system at 347.6 eV, (3) CaO-Al$_2$O$_3$-SiO$_2$-H$_2$O system at 348.4 eV, and (4) unknown at 349.1 eV.](image)

From our observations we can reasonably draw the following empirical evidence for the interaction at the interface between the sphere surface and the Ca(OH)$_2$ solution, and for the formation of its reaction products at the interface. When the sillimanite-based microspheres are exposed to the alkaline Ca(OH)$_2$-saturated solution at 200°C, more silicate and aluminate is dissolved from the sphere surface as an essential first step in the chemical reaction. This dissolution significantly promotes the precipitation of epitaxial CaO-Al$_2$O$_3$-SiO$_2$-H$_2$O formations, produced by the chemical reactions between the dissociated Si and Al with the abundant Ca ions released from the Ca(OH)$_2$ solution. With increased hydration, the precipitated layer is overlapped by these epitaxial hydration products. While the epitaxies grow in vicinity of the sphere surface, the unreactive Ca(OH)$_2$ also precipitates in the contact layer formed at the interfacial regions between the spheres and the reaction products. Finally, the continuous contact layer forms a spherical shell structure to fully encapsulate the sphere.

Properties and Phase Assemblages

To evaluate the ability of treated sphere surfaces to enhance the compressive strength of sphere-filled lightweight cement systems, cement slurries were prepared consisting of 30 wt% class "H" cement, 10 wt% silica flour, 25 wt% microspheres, and 35 wt% water. The slurry density for all specimens ranged from 1.16 to 1.20 g/cc. These lightweight slurries were autoclaved for 24 hour at 300°C.

Table 1 summarizes the slurry density measurements, and the densities, compressive strengths, and water permeabilities of the cured specimens. Each value represents the average of three measurements. As expected, the control specimens had a low compressive strength (600 psi) (4.2 MPa). This was greatly improved by treatment of the spheres with either D.I. water or Ca(OH)$_2$. The strength of the specimens made with D.I.-treated spheres appears to depend on the temperature of the treatment. For example, the strength developed in the 100°C D.I.-treated specimens was considerably lower than those at 200° and 300°C. This reduced level of improvement might be associated with the presence of a larger amount of a carbon contaminant on the sphere surface, suggesting that such a contaminant cannot be removed by D.I. water. The strengths for the Ca(OH)$_2$ sphere-filled specimens appear to be less dependent on the temperature of the treatment. Here, a maximum strength of 1440 psi (9.92 MPa) was obtained for the 200°C Ca(OH)$_2$-treated specimens. This value corresponds to an improvement in strength of approximately 2.4 times above the controls and 1.3 times greater than the 300°C D.I.-treated specimens. It should also be noted that the incorporation of spheres treated with the Ca(OH)$_2$ solution at the high temperature of 300°C results in a reduction in strength. Therefore, a temperature of up to 200°C should be used. As expected, an increase in compressive strength results in a reduction in water permeability. Notably, the water permeability value for the 200°C Ca(OH)$_2$-treated sphere specimens was two orders of magnitude less than that for the untreated specimens.
Table 2 summarizes the compressive strength and water permeability of the cured cements, and the phases formed after prolonged exposures to brine at 300°C in an autoclave. The results indicate that the compressive strength increases with exposure time up to 10 days. At this age, a maximum strength of 1541 psi (10.62 MPa) was developed. Continued autoclave exposure seems to result in strength reductions. The strength of 1168 psi (8.05 MPa) which was obtained after a 180 day exposure was approximately 24% less than that obtained after 10 days. Exposure tests are still above the acceptance criteria.

<table>
<thead>
<tr>
<th>Treatment of microspheres</th>
<th>Compressive strength, Mpa (psi)</th>
<th>Water permeability, 10^-6</th>
<th>Hydrated phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>1.16 (8.05)</td>
<td>1.76 x 10^-5</td>
<td>-</td>
</tr>
<tr>
<td>100°C O.I.-treated</td>
<td>1.16 (8.05)</td>
<td>1.64 x 10^-6</td>
<td>-</td>
</tr>
<tr>
<td>300°C O.I.-treated</td>
<td>1.17 (8.06)</td>
<td>1.44 x 10^-6</td>
<td>-</td>
</tr>
<tr>
<td>100°C(OH)4-treated</td>
<td>1.19 (8.11)</td>
<td>1.23 x 10^-6</td>
<td>-</td>
</tr>
<tr>
<td>300°C(OH)4-treated</td>
<td>1.20 (8.15)</td>
<td>1.04 x 10^-6</td>
<td>-</td>
</tr>
</tbody>
</table>

The water permeability exhibited an initial decrease reaching a minimum after 10 days. It then gradually increased. However, after 180 days, both the strength and permeability were still above the acceptance criteria.

The results from XRD analyses of the cement paste matrices revealed dramatic changes in the phases of the CaO-SiO2-H2O (C-S-H) compounds formed as a function of the autoclave exposure time. The major hydration product formed within the first 10 days was 11 A tobermorite [Ca6Si12O30(OH)12]·2H2O. Truscottite [Ca9Si6P4O14(OH)8]·2H2O in conjunction with a minor amount of tobermorite was present as the major crystalline product after a 30-day exposure to the hydrothermal environment. This transformation of tobermorite into truscottite can be deduced from the pronounced diminution of the line intensity at 3.34 Å spacing which ascribes to the presence of unreactive silica. This means that the silica remaining in the samples is very reactive and forms tobermorite. This transformation of tobermorite into truscottite is likely to occur progressively during exposure periods of approximately 30 days. However, in our studies, the reaction was still incomplete after that time. The formation of truscottite in the cement paste results in a strength decrease and enhanced water permeability. Truscottite, therefore, is a low-strength binder. In contrast, a well-formed tobermorite crystal would yield improvements in strength and a decrease in permeability.

Particular interest was given to identification of the phases present in the cement matrix after a 180-day exposure. The data indicated that prolonged autoclave time tended to favor the formation of two major hydration compounds, truscottite and triclinic anorthite, CaAl2Si2O8. The latter can be detected by the growth of new peaks at 3.21, 3.19, and 4.04 Å spacings (Joint Committee Standards). Since the wall material used was composed of sillimanite, Al2(AlSiO5), it is therefore reasonable to assume that the anorthite resulted from a hydrothermal reaction between the CaO-SiO2 species in the matrix and the sillimanite shell. Thus, the strength retrogression and permeability increase which gradually occurred during the 180-day exposure at 300°C are believed to be due to the transformation from tobermorite to truscottite and the new interfacial reaction product identified to be anorthite.

CONCLUSIONS

Characterizations of pressure-resistant hollow microsphere shell [as a sillimanite, Al2(AlSiO5)] surfaces that were treated with a Ca(OH)2-saturated solution at temperatures up to 200°C were performed. It was found that the epitaxial layers precipitated by interactions between hot alkali and the sphere surface play an important role in developing cement paste-to-sphere interfacial bonds and in enhancing the extent of hydration of the cement matrix. The major constituents of this epitaxy seem to be CaO-Al2O3-SiO2-H2O and CaO-SiO2-H2O systems.

For autoclaved cement-treated sphere composite systems, the major factors controlling both the compressive strength and water permeability were found to be not only dependent on the bonding characteristics at the matrix/sphere joints, but also on the phase species in the cement paste matrix. A well-crystallized tobermorite formed in the cement matrix after exposure for 10 days in an autoclave at 300°C was responsible for the development of 1450 psi (10.0 MPa) compressive strength and a water permeability of 1.76 x 10^-6.
Darcy. Increasing the autoclave exposure time to 180 days leads to a tobermorite-truscottite transformation and the formation of anorthite. This results in a decrease in compressive strength and increased water permeability. However, after 180 days both the strength and permeability values were still above the acceptance criteria for geothermal well cements. Longer term autoclave exposures at 300°C and downhole field tests at 320°C are currently in progress.

REFERENCES


