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Sodium Metasilicate-Modified Lightweight High Alumina Cements for Use as Geothermal Well-Cementing Materials

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In studying the use of sodium metasilicate (SMS)-modified high alumina cements containing mullite-shelled microspheres as lightweight geothermal cementitious materials, we found that the following were the most advantageous characteristics of the slurries and of the 200 and 300°C autoclaved cements: (1) the slurries have a low density of <1.25 g/cc, (2) the incorporation of SMS retarded the setting of the cements, (3) sodium calcium silicate hydrate and boehmite were formed in the matrix phase by hydrothermal reactions between the cement and SMS, and (4) there was a favorable reaction between the mullite shell layer in the hollow microspheres and the SMS to form analcime and boehmite phases. For characteristics (3) and (4), the pronounced development of these phases at 300°C generated a dense microstructure in the cements and was reflected on a reduced water permeability and a low rate of porosity. ADVANCED CEMENT BASED MATERIALS 1996, 3, 45–53

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One of the important considerations in designing a geothermal well-cementing slurry is density. Slurries of normal density, 1.9 to 2.0 g/cc, used for completing geothermal wells frequently create lost circulation zones, which are caused by the formation of voids in the underlying rocks during drilling operations. Such undesirable voids and fractures are formed by the significant hydrostatic pressures required to pump the very dense cement slurries. To solve this problem, cement slurries of low density are needed.

We previously prepared several lightweight cementitious materials by incorporating air bubbles and organic- or inorganic-shelled hollow microspheres into the binders, such as an API Class H cement, calcium aluminate cement, and calcium phosphate cement at temperatures up to 300°C [1–3]. An aluminosilicate (mullite, $3Al_2O_3 \cdot 2SiO_2$)-shelled microsphere, with a bulk density of 0.67 g/cm^3 and particle size of 75 to 200 μm, was identified as one of candidates for producing a cement slurry with a low density of <1.3 g/cc and the capability of developing a compressive strength greater than ≈5.0 MPa. However, it was necessary to incorporate a large number of microspheres (volume fraction of ≈75%) into the binder phases to formulate a slurry with such a low density. Thus, if the shell surfaces of hollow microspheres are hydrated by a chemical reagent used in forming the cement matrices, it is possible to assume that the hydrated compounds growing on the microsphere's surfaces will interlock together with the cement hydrates. The development of such interlocking structures at the cement-microsphere interfaces may contribute to improving the adherence of the microspheres to the cement.

Alkaline activators have been used to stimulate the latent pozzolanic properties of industrial byproduct materials, such as fly ash and sludge [4–8]. One of the major chemical components of their byproducts was aluminosilicate compounds that are similar to those of the chemical compounds forming on the microsphere shells. The reaction between alkalis and aluminosilicates causes the formation of hydroaluminosilicate phases that can be classified as zeolite. This information strongly suggested that the addition of alkaline activators to the microsphere-incorporated lightweight slurry would promote the hydration reactions at the surfaces of the microsphere. In this study, we used sodium metasilicate (SMS), $\text{-(-}Na_2O \cdot SiO_2\text{-)-}_n$, as the activators.

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TABLE 1. Changes in the density, porosity, and compressive strength of SMS-modified #80 cement pastes as a function of hydrothermal temperatures and SMS concentration

Autoclave (°C)	SMS (wt%)	Density (g/cc)	Porosity (%)	Compressive strength (MPa)
200	0	3.11	52.3	25.8
200	5	3.28	47.3	20.1
200	10	3.36	42.6	17.4
200	20	3.40	39.8	13.2
300	0	3.30	51.1	18.3
300	5	3.44	42.9	10.6
300	10	3.60	37.9	9.1
300	20	3.66	35.2	8.8

SMS = sodium metasilicate.

On the other hand, a high alumina cement (HAC) was employed as the cement binders.

Accordingly, emphasis in this study was directed toward the following three objectives: (1) the characterization of SMS-modified HAC pastes at hydrothermal temperatures of 200 and 300°C, (2) the effect of SMS on the maintenance of pumpability of a microsphere-filled cement slurry with a low density, and (3) the phase compositions and microstructure developed in the autoclaved lightweight cements. All the information obtained from our third objective was integrated and correlated with the changes in compressive strength and water permeability for the hardened lightweight cement specimens as a function of hydrothermal temperatures and slurry densities.

Experimental

Materials

The calcium aluminate cement was Secar 80 (#80) obtained from the Lafarge Calcium Aluminates. The X-ray powder diffraction (XRD) data for #80 cement showed that its chemical composition consisted of monocalcium aluminate, $CaO \cdot Al_2O_3$, (CA), calcium dialuminate, $CaO \cdot 2Al_2O_3$, (CA_2), and corundum, α-Al_2O_3 phases. However, no attempt was made to obtain the compositions of these phases. The SMS (supplied by Petratch Systems Silanes & Silicones) was dissolved in water to make a 5, 10, or 20 wt% solution as the alkaline activator. Commercial mullite ($3Al_2O_3 \cdot 2SiO_2$)-shelled hollow microspheres (Extendospheres EX, PQ Corp) were used as the lightweight filler. The microspheres had averaged bulk density of 0.67 g/cm^3 and a particle size from 75 to 200 μm.

Measurement

The consistency of the low-density slurries was measured in accordance with API schedule 4G Specification. This schedule corresponds to a simulated 1830 m depth well at 50°C under a pressure of 26.9 MPa. The test was completed when the consistency (Bc value) of the slurry exceeded 70. The porosity, density, and volume of neat SMS-modified cement pastes and microsphere-filled lightweight cements was determined by helium comparison pyconometry. A Ruska liquid permeameter was used to determine the water permeability of the specimens; this measurement was made by measuring the amount of water that passed through the discs under a pressure gradient of 2 atm. The phase composition formed in the neat SMS-modified cement pastes and the SMS-activated lightweight cements containing microspheres at the hydrothermal temperatures of 200 and 300°C were explored by XRD. Correspondingly, the microstructure developed in the neat cements, and the interfacial contact regions between the cements and the microspheres was explored using scanning electron microscopy (SEM) coupled with energy-dispersive X-ray analysis (EDX) operated at 17 KV and 10 nA.

Results and Discussion

SMS-Modified HAC Pastes

To determine the changes in compressive strength, porosity, and density of SMS-modified #80 cement pastes by varying the hydrothermal temperatures and the concentration of SMS, we prepared the neat cement pastes by mixing 60 wt% #80 and 40 wt% SMS solution and

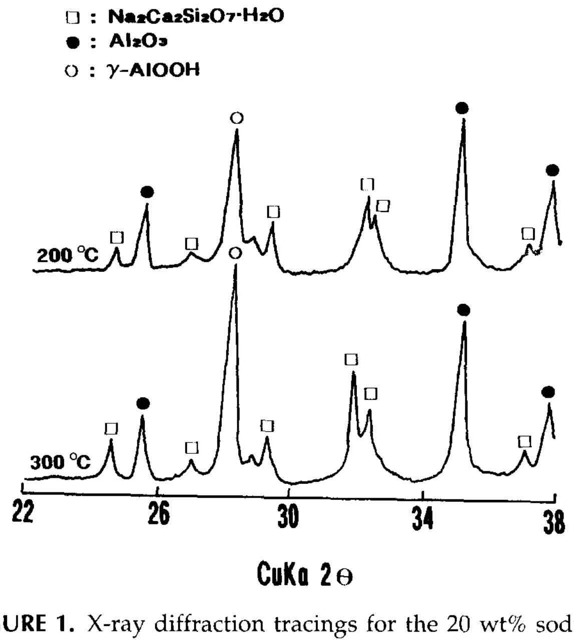

FIGURE 1. X-ray diffraction tracings for the 20 wt% sodium metasilicate-modified high alumina cement pastes after exposure in autoclave at 200 and 300°C.

then exposing them for 24 h in an autoclave at 200 and 300°C. The results from these neat cement pastes are given in Table 1. The data showed that the density of autoclaved cement pastes tends to increase with an increased concentration of SMS at both temperatures. As expected, pastes with a high density correspondingly had a low porosity. Moreover, the hydrothermal temperature at 300°C led to the formation of a dense structure with a lower porosity compared with the 200°C autoclaved pastes. The two factors, the elevated temperature and a high concentration of SMS, contributed significantly to the increased density and decreased porosity of the pastes, suggesting that some degree of shrinkage may occur. These factors were not responsible for the increase in compressive strength. In fact, the incorporation of 20 wt% SMS resulted in an ≈50% loss in compressive strength compared with that of unmodified neat pastes. In addition, the strengths of 300°C autoclaved pastes were much lower than those of the 200°C ones. However, there was no evidence whether the loss of strength was due to the in situ phase transformation or the development of crack caused by shrinkage, or both.

To better understand and rationalize these findings, our attention focused on identifying and exploring the phase composition assembled and the microstructure developed in the 20 wt% SMS-modified cement pastes after exposure in an autoclave at 200 and 300°C by XRD and SEM-EDX. Although some degree of shrinkage or expansion may occur for the autoclaved pastes, no attempt was made to determine these physical factors. Figure 1 shows the XRD patterns for 200 and 300°C autoclaved pastes in the diffraction ranges from 0.404 to 0.237 nm. At 200°C, the XRD tracing indicated the presence of three different phases: sodium calcium silicate hydrate ($Na_2Ca_2Si_2O_7 \cdot H_2O$) and boehmite (γ-AlOOH) as the hydrothermal reaction products and corundum (α-Al_2O_3) as the nonreacted chemical component of

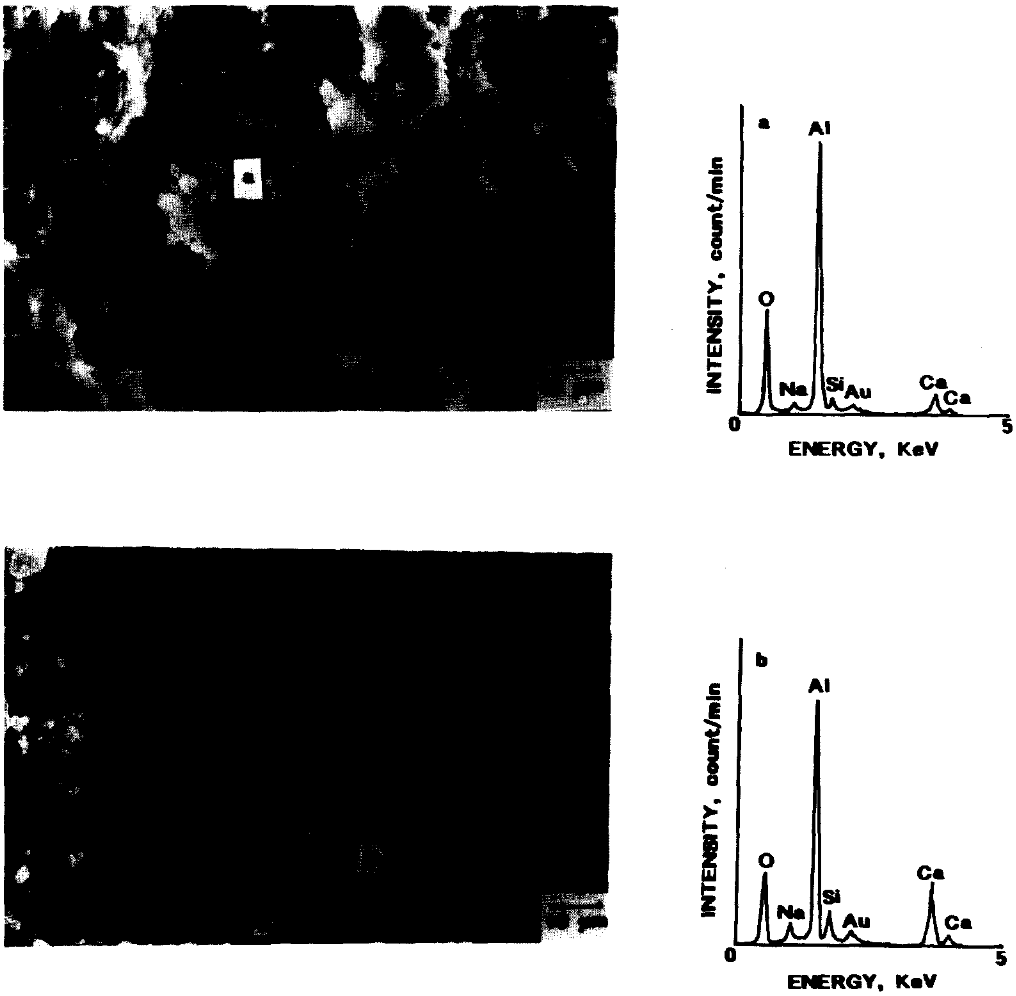

FIGURE 2. SEM micrographs coupled with energy-dispersive X-ray spectra for the fractured surfaces of 20 wt% sodium metasilicate-modified cement pastes after exposure in autoclave at 200°C (top) and 300°C (bottom). (Au is due to the sputtered gold film.)

TABLE 2. Formulation of microsphere-incorporated cement slurries with a low density of ≈1.24 g/cc as a function of concentration of SMS

Specimen	Formulation
1	45 wt% #80 – 23 wt% EX – 32 wt% solution (0 wt% SMS)
2	42 wt% #80 – 22 wt% EX – 36 wt% solution (5 wt% SMS)
3	42 wt% #80 – 21 wt% EX – 37 wt% solution (10 wt% SMS)
4	41 wt% #80 – 20 wt% EX – 39 wt% solution (20 wt% SMS)

SMS = sodium metasilicate.

#80. The signal intensities of $Na_2Ca_2Si_2O_7 \cdot H_2O$ and γ-AlOOH phases increased with an increasing temperature to 300°C, thereby reflecting the formation of a well-crystallized reaction product.

This information was supported by comparing the SEM micrographs, together with the EDX spectrum of fractured surfaces from the 200 and 300°C autoclaved paste specimens. The resulting SEM-EDX data are given in Figure 2. The SEM image clearly verifies that hydrothermal treatment of the paste at 300°C (Figure 2, bottom) contributes to the development of a smooth fracture surface as compared with the rough surface of the 200°C treated specimens (Figure 2, top). The former mode of the fracture surfaces seems to represent the formation of a relatively dense structure; contrarily, the treatment at 200°C causes the development of porous microstructure, reflecting a low density. No feature of crack generated by the changes in volume of the autoclaved specimens was observed in the SEM image at 300°C. Also, the SEM image taken from the 200°C specimens was characterized by a random distribution of clusters ranging from 40 to 10 μm. The EDX spectrum of a cluster denoted as site "a" represents its chemical composition, with Al and O as the major elements, while appreciable amounts of Na, Si, Au, and Ca elements were also detected. From the prominent peaks of Al and O, these clusters are probably either corundum and boehmite. On the other hand, the EDX spectrum from site "b" of the 300°C specimens was notable for the growth in the peak intensity of Na, Si, and Ca, while the Al and O signals still remained as the major elements. The origin of Na, Si, and Ca may be the $Na_2Ca_2Si_2O_7 \cdot H_2O$ that is formed as the hydrothermal reaction product. Thus, a possible explanation for the increased density of 300°C autoclaved specimens is that the in situ growth of these reaction products has the effect of filling the interstices and voids present in the cement body. However, although the density of these

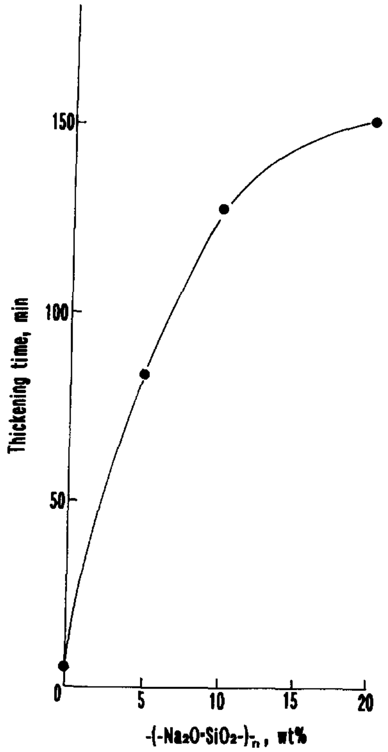

FIGURE 3. Changes in thickening time of lightweight cement slurry as a function of concentration of sodium metasilicate.

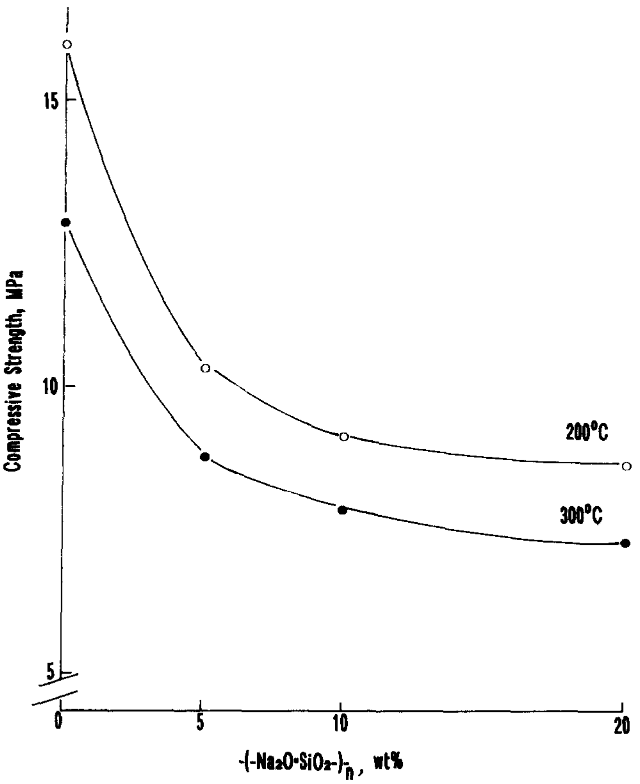

FIGURE 4. Compressive strength versus sodium metasilicate content for 200 and 300°C autoclaved lightweight high alumina cement specimens.

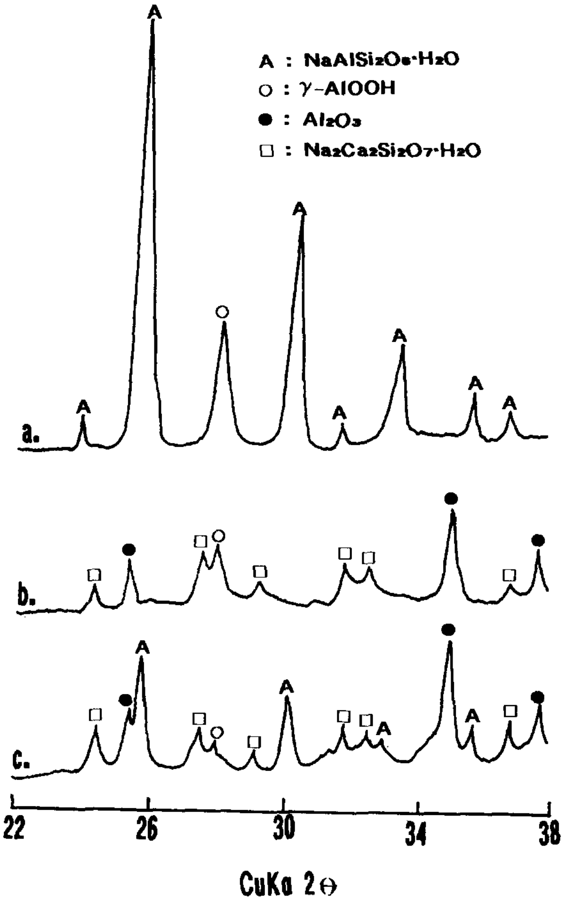

FIGURE 5. X-ray diffraction patterns for the sodium metasilicate-treated microsphere in autoclave at 200°C (a), and the fractured surfaces of 200 (b) and 300°C autoclaved (c) lightweight high alumina cement specimens.

specimens was increased, excessive growth of these reaction products caused a retrogression of compressive strength, thereby suggesting that the loss of strength is dependent on the in situ phase transformation but may be independent of the development of cracks generated by the changes in volume of autoclaved specimens.

Microsphere-Filled Lightweight Cements

Table 2 gives the formulation of the lightweight slurries consisting of the microsphere, #80 cement, and SMS solution. All of the formulations were designed to have slurry density of ≈1.24 g/cc. Based upon this formulation, Figure 3 shows the changes in thickening time at the isothermal temperature of 50°C for the slurries as a function of the concentration of SMS. The thickening time of ≈5 min for the lightweight high alumina cement (LHAC) slurries unmodified with the SMS was too short to maintain the pumpability of slurry at this temperature. This suggests that in the absence of set-retarding additives, LHAC slurries will be very difficult to apply in the geothermal wells. However, the modification of LHAC by SMS retarded its setting. In fact, the thickening time of LHAC slurries was increasingly prolonged with increasing concentrations of SMS. The incorporation of 20 wt% SMS into the LHAC resulted in a thickening time of ≈150 min, corresponding to an extension of more than 140 min, compared with the thickening time of the unmodified LHAC. Although there is no evidence about its retarding mechanism, it is apparent that SMS is able to retard markedly the hydrothermal setting of cements. Figure 4 shows the changes in compressive strength of the 200 and 300°C autoclaved LHAC specimens as a function of the concentration of SMS. Compressive strength tests were performed on autoclaved LHAC specimens with a diameter of 30 mm and a length of 60 mm; the result given is the average value of three specimens. The variations in value of strength ranged from +0.2 to −0.2 MPa. The strengths of the specimens depended mainly on the amount of SMS and the temperature of autoclave; the loss of strength occurred as the concentration of SMS and the hydrothermal temperature were increased.

To elucidate the reasons for the loss of strength, the phase compositions and microstructure developed in lightweight cements consisting of 41 wt% #80, 20 wt% EX, and 39 wt% (20 wt% SMS), after exposure for 24 h in autoclave at 200 and 300°C, were investigated by XRD and SEM-EDX. In addition, we also prepared the 200°C autoclaved reference specimen consisting of a 60 wt% (20 wt% SMS solution) and 40 wt% microspheres in the absence of #80. The XRD results from these powder samples are depicted in Figure 5. For the SMS-treated microspheres, as the reference specimen, the XRD pattern (Figure 5a) demonstrated that the hydrothermal reaction between SMS and the microspheres at 200°C led to the formation of two well-crystallized reaction products, analcime ($NaAlSi_2O_6 \cdot H_2O$), which is a naturally occurring zeolite, and γ-AlOOH. Thus, the mullite layers, which are the major chemical component of the shell of hollow microspheres, hydrothermally reacted with the SMS and were converted into analcime and boehmite. Of further interest in the hydrothermal interaction between SMS and the microspheres was the morphological alteration of microsphere's surfaces. As seen in Figure 6, SEM images of the surfaces of these microspheres treated hydrothermally with SMS reactant showed a peculiar structure being covered with the crystalline reaction products generated during autoclaving at 200°C. The EDX spectrum (site "c") taken from reaction products surrounding the microspheres had an intense signal of Si, moderate line intensities for Al and O, and weak Na and K peaks. Relating this finding to the XRD data, we inferred that the contributors to these elements (excepting K, which comes from

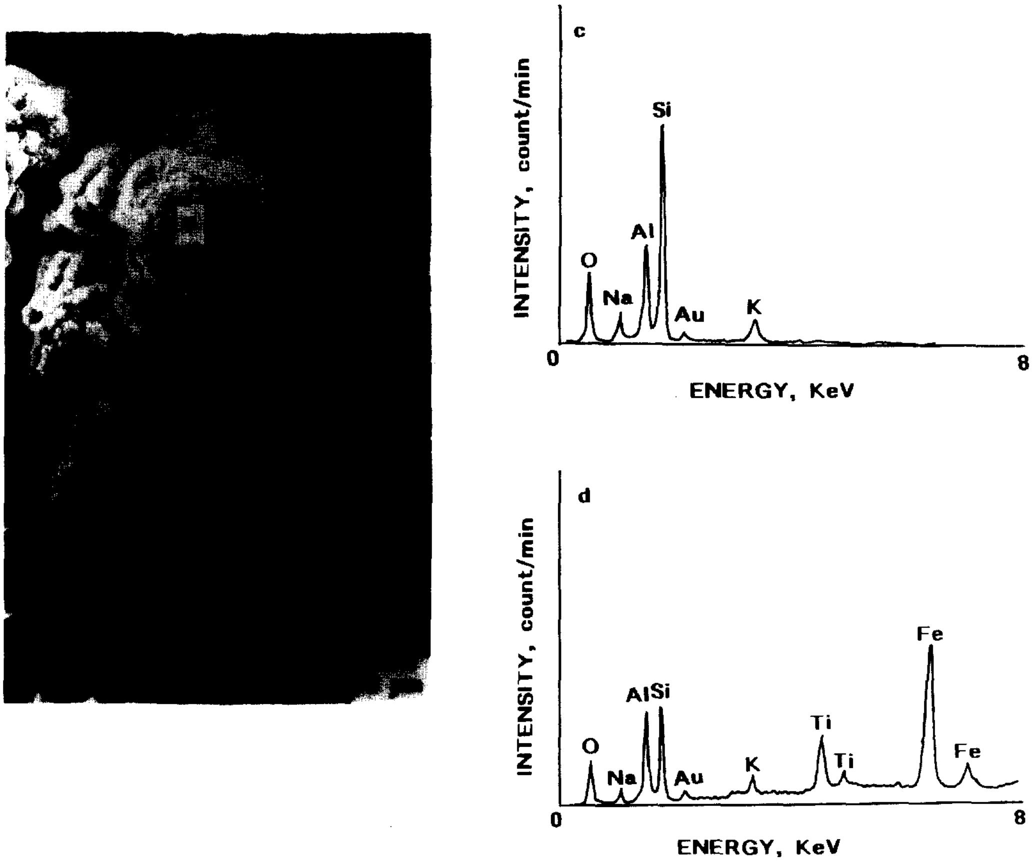

FIGURE 6. SEM image of microsphere surfaces treated with 20 wt% sodium metasilicate solution and autoclaved at 200°C.

the underlying microsphere) are the two reaction compounds, analcime and boehmite. As is evident from the EDX spectrum at site "d," the chemical composition of the underlying microsphere surfaces not only includes Al, Si, and O, reflecting the mullite, but also has the additional elements, such as K, Ti, and Fe. As described in our previous paper [2], the detected Ti and Fe elements belong to an unreactive mullite shell.

The diffraction pattern (Figure 5b) of the 200°C autoclaved specimens is similar to that of the neat cement paste (Figure 1) autoclaved at the same temperature. No d spacings attributed to analcime were found in these specimens. Supporting this information, SEM-EDX data taken at the critical interfacial regions between the cement matrix and microsphere are shown in Figure 7. The SEM micrograph (bottom of Figure 7) is an enlargement of a portion of the interfacial area identified as A in the top micrograph. The high-resolution image of the area marked as site "e" disclosed an interlocked structure of rectangular-shaped crystals deposited on the microsphere surfaces. From the EDX analysis, these crystals can be identified as aluminum hydroxide compound, belonging to a possible γ-AlOOH. Thus, this aluminum compound, as the reaction product, appears to form preferentially in the interfacial contact zones with the microsphere's surfaces, rather than the $Na_2Ca_2Si_2O_7 \cdot H_2O$ phase. The increase in temperature to 300°C led to the incorporation of analcime as an addition phase into the hybrid hydrate phases, such as $Na_2Ca_2Si_2O_7 \cdot H_2O$ and γ-AlOOH reaction products, that are formed in the 200°C autoclave lightweight cement bodies (Figure 5c). Because analcime is generated by the interaction of Na in SMS with the mullite shells, we believe that an elevated hydrothermal temperature to 300°C promotes the formation of analcime in the lightweight cement composites. However, such an uptake of Na by the mullite seems to inhibit the hydrothermal reaction between HAC and SMS. In fact, XRD pattern showed a marked decrease in intensity of HAC-SMS reaction product-related d spacings, especially γ-AlOOH, compared with those of the 200°C autoclaved LHAC specimens and the SMS-modified HAC pastes at 300°C (see Figure 1). Nevertheless, the development of a well-formed intermediate layer was observed from the interfacial areas of specimens autoclaved at 300°C (Figure 8). The EDX spectrum from this layer indicated the presence of strong signals from Al and Si elements and lesser signals from Na, O, and Ca. Thus, the major components of this intermediate layer that links directly between matrix and microspheres

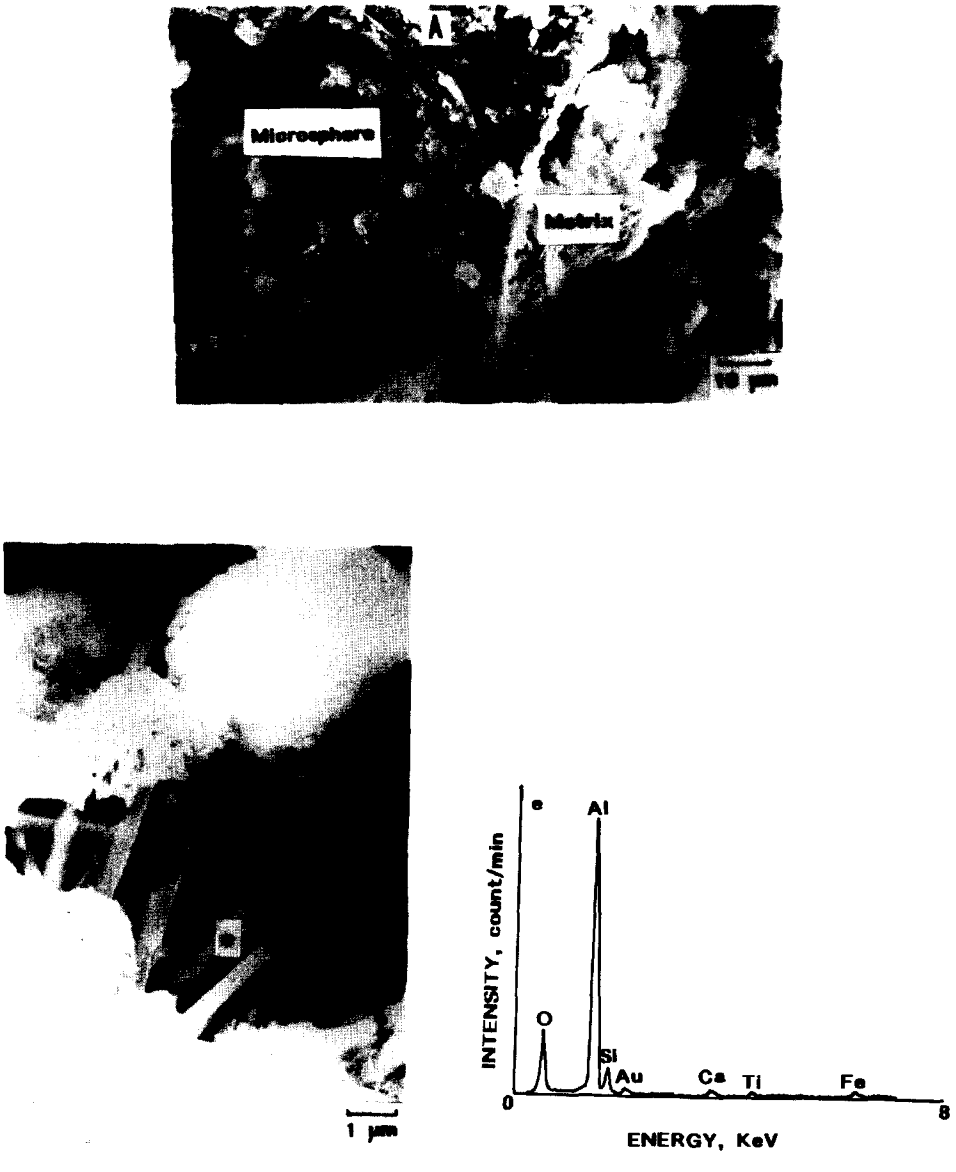

FIGURE 7. Development of microstructure at the interfacial region between the cement matrix and microspheres for 200°C autoclaved lightweight high alumina cement specimens.

seems to consist of analcime and some γ-AlOOH. Furthermore, the SEM image suggested that morphologically this layer has a highly dense structure compared with the porous structure formed by agglomerating rectangular crystals for 200°C autoclaved specimens. The creation of such a dense intermediate layer in the interfacial transition zones may be responsible for improving the cement-microsphere interfacial bonds. In addition, we determined the changes in volume of 0, 5, 10, and 20 wt% SMS-modified LHAC specimens during autoclaving for 24 h at 200 and 300°C. The results from these specimens are shown in Table 3. The volumes for all the LHAC specimens made at 25°C conspicuously decreased when they were exposed in autoclave at 200°C. Increasing the temperature to 300°C caused a further decrease in volume. The changes in volume of the specimens also depended on the concentration of SMS; namely, the use of a high concentration of SMS corresponded to a high rate of decrease in volume. As described earlier, the compressive strength of the 300°C autoclave specimens was lower than that of the specimens at 200°C. Hence, although the interfacial bonds were improved at 300°C, the lowering of compressive strength might be due to the following three factors: (1) the mullite ($3Al_2O_3 \cdot 2SiO_2$) $\rightarrow$ $Na_2Ca_2Si_2O_7 \cdot H_2O$ and γ-AlOOH phase transformation occurring at the shell surfaces of the microspheres, (2) the well-formed γ-AlOOH and $Na_2Ca_2Si_2O_7 \cdot H_2O$ reaction products formed in the cement matrix, and (3) the decrease in volume of the specimens. The first factor may cause reduced thickness of the shells, thereby resulting in the decrease in the inherent strength of the shell structure of the microsphere itself.

We also report the changes in compressive strength

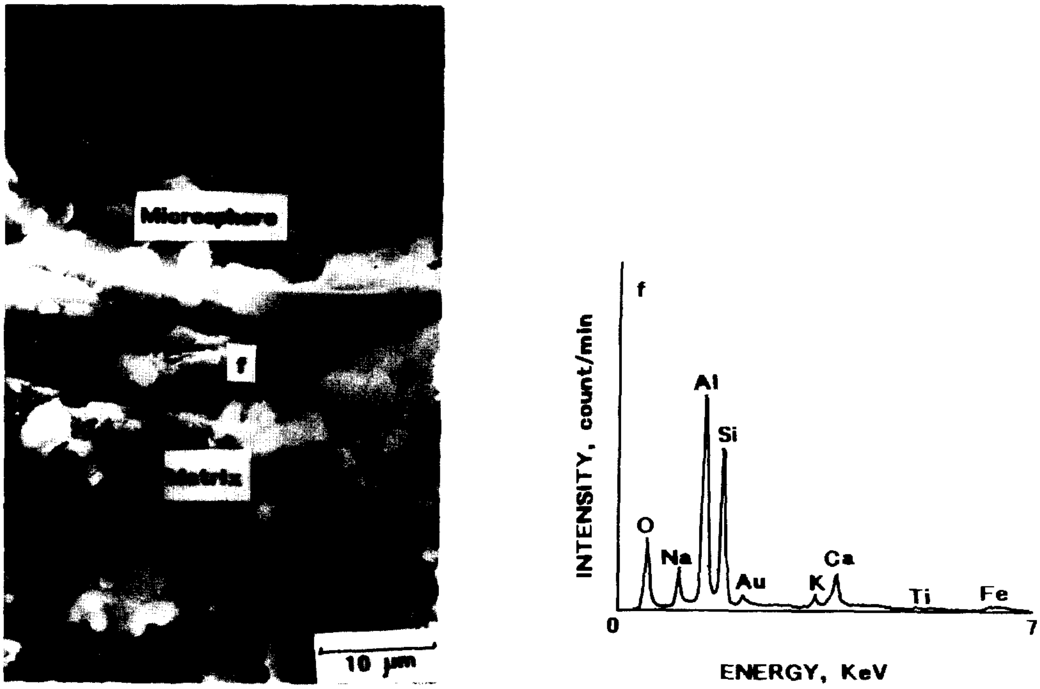

FIGURE 8. SEM image of the microstructure developed at the critical interfacial regions between the microspheres and matrix in 300°C autoclaved lightweight high alumina cement specimens.

and water permeability for the 20 wt% SMS-modified LHAC specimens after exposure for 24 h in autoclave at 200 and 300°C as a function of the density of slurry (ranging from 1.24 to 1.11 g/cc; Table 4). A decrease in the density of slurry appears to markedly lower the strength and increase the rate of water transportation. For instance, the specimens derived from the lowest density slurry (1.11 g/cc) at 200 and 300°C had compressive strengths of 3.12 and 2.25 MPa and water permeability of 6.60 and 5.57 mdarcy, respectively. These compressive strength values corresponded to a reduction of ≈64% and ≈70% compared with those of 200 and 300°C autoclaved specimens with a 1.24 g/cc density of slurry, whereas water permeability was increased more than four times over that of the 1.24 g/cc specimens. However, all of the 300°C autoclaved specimens had a lower permeability than the 200°C specimens, suggesting that this phenomenon is due mainly to the creation of the dense matrix and intermediate layers formed at the interfacial transition zones between the cement and the microsphere.

Conclusions

Slurries of SMS-modified LHAC with a low density of <1.25 g/cc were evaluated for use as lightweight cementitious materials in geothermal wells at hydrothermal temperatures up to 300°C. The incorporation of SMS significantly retarded the thickening time of the LHAC slurry, thereby providing an adequate time to maintain the pumpability of slurries. When the LHAC slurries consisting of #80 cement, SMS solution, and

TABLE 3. Changes in volume of 0, 5, 10, and 20 wt% SMS-modified LHAC specimens after exposure for 24 h in autoclave at 200 and 300°C

SMS (wt%)	Changes in volume (%)	
	200°C	300°C
0	−26.3	−30.6
5	−29.7	−33.2
10	−32.5	−37.4
20	−33.1	−38.9

SMS = sodium metasilicate; LHAC = lightweight high alumina cement.

TABLE 4. Compressive strength and water permeability of lightweight cement specimens derived from slurries with low density

Density of slurry (g/cc)	Compressive strength (MPa)		Water permeability (mdarcy)	
	200°C	300°C	200°C	300°C
1.24	8.72	7.35	1.41	0.82
1.18	6.25	4.79	4.84	3.73
1.11	3.12	2.25	6.60	5.57

mullite-shelled microsphere were exposed in an autoclave at elevated temperatures, the SMS reacted with both the #80 cement and the microspheres. The hydrothermal reaction between CA or CA_2 in #80 cement and $\text{-(-}Na_2O \cdot SiO_2\text{-)-}_n$ in SMS led to the formation of sodium calcium silicate hydrate ($Na_2Ca_2Si_2O_7 \cdot H_2O$) and boehmite ($\gamma$-AlOOH) as the reaction products. At 300°C, these phases were converted into well-crystallized ones, reflecting the increase in density and lowering of porosity of the matrix layers. SMS also favorably reacted with the mullite ($3Al_2O_3 \cdot 2SiO_2$) shells of the microspheres to yield analcime and boehmite. These reaction products formed a dense intermediate layer that enhanced the degree of crosslinking between the cement matrix and microspheres, thereby improving the cement-microsphere interfacial bonds. However, although the well-formed phases significantly contributed to the increase in density, low value of porosity, and decreased water permeability for the autoclaved LHAC specimens, they did not improve the compressive strength.

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