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Bentonite-based ammonium polyphosphate cementitious lost-circulation control materials

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Bentonite-based cementitious materials have been formulated and evaluated in terms of their properties for use as cementitious lost-circulation control materials in geothermal wells at temperatures up to 300° C. The formulation which appears to have the highest potential as a new cementitious lost-circulation control material is composed of bentonite, ammonium polyphosphate, borax, magnesium oxide, and water. The appropriate combination of these ingredients results in the formation of slurries with viscosities and thickening times adequate to allow placement. After curing at elevated hydrothermal temperatures, the cement produced was characterized by a compressive strength >500 psi (>3.45 MPa) at 2 h age, a permeability to water $<2.0 \times 10^{-4}$ Darcy, and a linear expansion $>15\%$. The reaction compound responsible for the strength development at 300° C was found to be an assemblage of interlocking crystals composed of a grown thin-plate crystal. It was inferred that this microcrystalline cluster is associated with montmorillonite and ammonium polyphosphate-based complex formations.

1. Introduction

Major interruptions in the circulation of drilling mud during the drilling of geothermal wells often result from fluid loss into horizontal and vertical loss zones. These zones consist of porous sand and gravel, natural fractures, induced fractures, and cavernous zones. Although the magnitude of the mud losses vary depending upon the type, severity, location and temperature of the zones, there is no doubt that lost circulation contributes significantly to the cost of drilling geothermal wells.

Operators prefer to solve these problems by using cementitious lost-circulation materials (CLCM) which are easily stored at the drilling site [1]. Favoured materials are those that can be added directly to the drilling fluid and then circulated to the formation where the loss of fluid occurs.

For consideration as a CLCM, the slurry must be pumpable, have an adequate and predictable thickening time at the anticipated temperature, and be relatively low in cost. Once the slurry materials are pumped into the lost circulation zones, the thin mud build-up in the zones should set as rapidly as possible. CLCMs exhibiting extended setting times at the downhole temperature are particularly susceptible to being washed away by the movement of formation water and well-bore fluids around the slurry. In addition, the mechanical strength of the hardened CLCM plugs is a critical parameter for geothermal drilling. After curing, the CLCM plug must be capable of withstanding well-bore differential pressure across the plug. The difference between the hydrostatic fluid head of the drilling fluid and the formation pore pressure is more than 500 psi (3.45 MPa) for many geothermal formations, which are typically underpressured [2]. Thus, materials exhibiting a compressive strength of at least 500 psi (3.45 MPa) and a net expansion upon curing are needed to provide an effective seal. Furthermore, since the temperature profile and the bottom hole temperature play key roles in establishing the pumpability and setting time, and since these temperatures vary from well to well, the formulations must be properly designed with retarding or accelerating admixtures.

It has been reported [3] that for use in oil wells, a CLCM must reduce the permeability of porous formations to the range of 10 to 100 Darcys. On the basis of this value, we have assumed that for geothermal applications, the hardened CLCM plugs should possess a permeability by water of $< 1 \times 10^{-2}$ Darcy.

For many years, bentonite has been used as viscosity and thixotropic control additives in water-based drilling mud fluids for oil and geothermal wells. It has been estimated [4] that the best bentonite contains about 60 to 70% sodium (Na) montmorillonite. The remaining 40% might be calcium (Ca) montmorillonite or other low-yielding clays, such as kaolinite. An ideal montmorillonite may be defined as having the unit cell composition shown below [5], in which the superscripts IV and VI in the formula denote the respective tetrahedral layer cations, and M^+ represents a univalent or equivalent compensating cation.

$$[(Si_8)^{IV} \cdot (Al_{3.33}Mg_{0.67})^{VI} \cdot O_{20}(OH)_4]0.67\,M^+$$

As already established by Hoffmann [6], Marshall [7] and Hendricks [8], the structure of montmorillonite consisting of a $[Al_2(OH)_4]n^{2n+}$ sheet layer

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sandwiched between two $(Si_2O_5)n^{2n-}$ sheet layers is composed of superposed lamellae, which have an edge absorption at a diffuse negative silica sheet with various cations balancing unsaturated oxygen ions at edges in the crystal lattice of the lamellae. This negative charge arising on this layer as the result of the substitution is balanced by chemisorption of cations such as H^+, Na^+, K^+, Ca^{2+}, Mg^{2+} and Al^{3+} compensating ions located between the sheets together with molecules of water. These intersheet cations are readily ion-exchangeable. As is expected from their large ion-exchange capacity, montmorillonite clays are much more affected by their cations, though the same principles apply.

Wyoming bentonite, which is believed to have been formed by the weathering of volcanic ash in an ancient sea with little subsequent leaching, is well known to have Na^+ ions as the principal compensating cations. Na^+-montmorillonite can be readily dispersed to form a more thixotropic gel than Ca^{2+}- or H^+-montmorillonites [10].

On the basis of the above information, the goal of the current BNL work is to develop Wyoming bentonite-based cementitious materials for use as expansive high strength and low permeability CLCM plugs in geothermal formations. A cement having a compressive strength > 500 psi (3.45 MPa) after 2 h exposure in an autoclave at an elevated temperature is desired. The *in situ* conversion of bentonite into a cement is achieved by the addition of magnesium oxide (MgO) powder and ammonium polyphosphate (AmPP) solutions to bentonite powders. As reported in a previous paper [11], neat paste containing the proper proportions of MgO and AmPP exhibited high early mechanical strength. It was also found that the inclusion of sodium tetraborate decahydrate (borax) as a retarding admixture for the magnesium polyphosphate cement was very effective.

Accordingly, the studies reported in the present paper were focused on optimization of bentonite-based magnesium polyphosphate cementitious systems and an evaluation of their applicability as a CLCM. In addition, the reaction products formed during autoclave exposure at hydrothermal temperatures up to 300° C were also determined using X-ray powder diffraction, energy-dispersive X-ray, and scanning electron microscopy.

2. Experimental details

The montmorillonite used was a Wyoming bentonite, supplied by NL Baroid, Inc., with a typical X-ray analysis as follows: 85% montmorillonite, 5% quartz, 5% feldspars, 2% cristobalite, 2% illite, and 1% calcite and gypsum. MgO of a size < 200 mesh, having a surface area of 1 to 5 $m^2 g^{-1}$, was supplied by Martin Marietta Chemicals. An ammonium polyphosphate (AmPP) solution containing ~44% water, known commercially as Poly-N and supplied by the Allied Chemical Company, was employed as a cement-forming liquid. Sodium tetraborate decahydrate, $Na_2B_4O_7 \cdot 10H_2O$ (Borax 10 mol), which was evaluated as a retarding agent, was obtained from the United States Borax and Chemical Corporation. Distilled water was added to the AmPP solution to reduce the viscosity of the solution to ~22 cP. The ratio by weight of AmPP to water was 100/11.1. A quantity of borax sufficient to yield a concentration of 45% by weight of the total AmPP solution mass was added to the diluted AmPP solution, and then stirred for 3 h at 30° C until completely dissolved. To prepare the bentonite-based magnesium polyphosphate cementitious materials, the mix powders consisting of 100 to 75% bentonite and 0 to 25% MgO were incorporated directly into the AmPP mixture and subsequently mixed for ~3 min in a Hamilton–Beach mixer. The viscosities of the prepared slurry samples were measured using a Fann Direct Indicating Viscometer, and were found to range from 600 to 200 cP. The range of mix formulations used preliminarily in this study is given in Table I.

TABLE I Mix formulations used in this study

Bentonite (%)	MgO (%)	AmPP (%)	Borax 10 mol (% by weight of AmPP solution mass)
33 to 45	0 to 10	55	0 to 70

On the assumption that the plugging materials will have to be placed into water-filled fractures, all the slurries were slowly poured into water-filled glass test tubes, 3.5 cm diameter by 10.0 cm long and 3.0 cm diameter by 3.9 cm long. The samples were maintained at room temperature until the slurry settled completely to the bottom of the aqueous media. After settling, the slurry-filled tubes were exposed in an autoclave for 2 h to temperatures up to 300° C. The hardened specimens were subsequently removed from the glass moulds, and compressive strength and water permeability measurements were made at a temperature of 24° C. The compressive strength tests were performed on autoclaved specimens having a diameter of 3.5 cm and a length of 7.0 cm. Measurements were performed in triplicate and the average values are shown as the results. A Ruska liquid permeameter was used for determining the water permeability of discs 3.0 cm in diameter and ~3.9 cm thick. The permeability measurements were made by determining the amount of water that is passed through the discs under a pressure gradient of 2 atm.

3. Results and discussion

3.1. Slurry properties

The viscosity of the CLCM slurry is of primary importance in establishing the pumpability of the material. Results from viscosity measurements for bentonite-MgO-AmPP slurries containing various borax concentrations are shown in Table II. All

TABLE II Effect of borax 10 mol additions on the viscosity of 40% bentonite–5% MgO–55% AmPP slurry formulations

Borax (% by weight of AmPP total mass)	Viscosity at 24° C (cP)
0	570
10	420
20	390
30	360
50	330
70	280

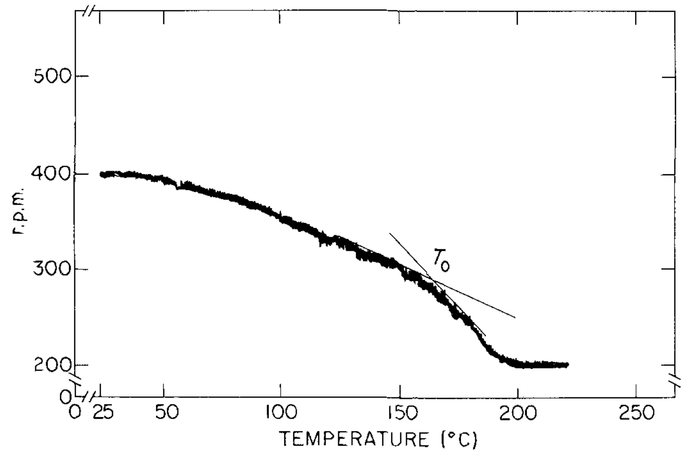


Figure 1 Typical stirrer speed curve which depicts changes in slurry viscosity as a function of temperature.

measurements were made using a Model 35A Fann Direct Indicating Viscometer.

The viscosity–borax concentration relation indicates that the viscosity of the slurry is significantly decreased by increasing concentrations of borax. The viscosity of the slurry containing 70% borax by weight of the total AmPP solution was 280 cP, compared to a value of 570 cP for the slurry without borax. The reason for this effect is not yet known, but it is speculated that the borax may act to wet the bentonite grain surfaces. The borax may also increase the diffusion rate of bentonite grains in the AmPP aqueous media. The increased diffusion rate could enhance the rate of the interfacial interactions occurring between the bentonite, MgO and AmPP phases, thereby increasing the mechanical strength of the solidified bentonite specimens.

The effect of borax used as a retarding admixture to extend the thickening time at an isothermal temperature and to increase the gel temperature of the slurry was also investigated. A slurry consisting of 43% bentonite, 2% MgO and 55% AmPP was employed in this test series. In these studies, borax concentrations ranging from 0 to 70% by total mass of AmPP solution were added to the basic slurry system.

Preliminary measurements of the gel and thickening temperatures for bentonite–borax slurry samples were obtained using a 7.5 cm diameter by 23.8 cm long stirred autoclave. Tests were conducted according to the following procedures: approximately 800 g of the mixed slurry was placed in the autoclave which was then pressurized to 1500 psi (10.34 MPa) before raising the autoclave temperature. The stirrer was then started at a speed of 400 r.p.m. and the speed was monitored as the temperature increased. A typical stirrer speed–temperature curve is given in Fig. 1. As seen in the figure, initially there is a slight increase in motor speed since the slurry viscosity decreases with increasing temperature. However, when the slurry starts to gel, the motor speed decreases rapidly. The thickening temperature, T_0, of the samples can be estimated from the curves by finding the intersection point of two linear extrapolations. When compared with that obtained from a visual observation of a coagulated specimen after autoclaving, a statistical error of this estimation value ranged from -5 to $+5$° C.

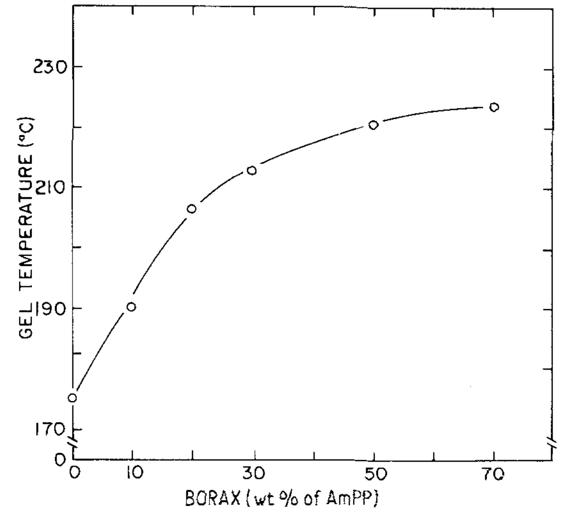


Figure 2 Borax concentration against gel temperature of slurry.

As shown in Fig. 2, the T_0 values obtained in this manner were then plotted against the borax concentration in the slurry. The resulting data indicate that borax is a very effective set-retarding admixture, and the degree of set-retardation correlates directly with the concentration. Without borax, the slurry gels at an autoclave temperature of 175° C, and with 70% borax, the gel temperature is extended to ~225° C.

In contrast, the addition of MgO powder, which is leachable and releases a divalent magnesium cation in an aqueous medium, accelerates the setting of the slurry. In these studies, a slurry formulation containing 50% borax by weight of the total mass of AmPP was used. The concentration of MgO in the slurry systems ranged from 0 to 5%. The thickening times for these slurries at isothermal temperatures between 50 and 250° C were determined from stirrer speed–elapsed time curves. These results are presented in Fig. 3. As is evident from the figure, the actual degree of acceleration relates directly to the MgO content. Samples without MgO had a thickening time of ~30 min at 250° C, ~80 min at 200° C, and ~240 min at 150° C. The inclusion of 1% MgO in the slurry resulted in considerably reduced thickening times. However, at temperatures < 150° C the time was too long to permit attainment of adequate mechanical strength at an autoclaving age of 2 h. This problem can be easily solved by the addition of greater amounts of MgO. A 5% MgO concentration is likely to be the maximum amount suitable for applications

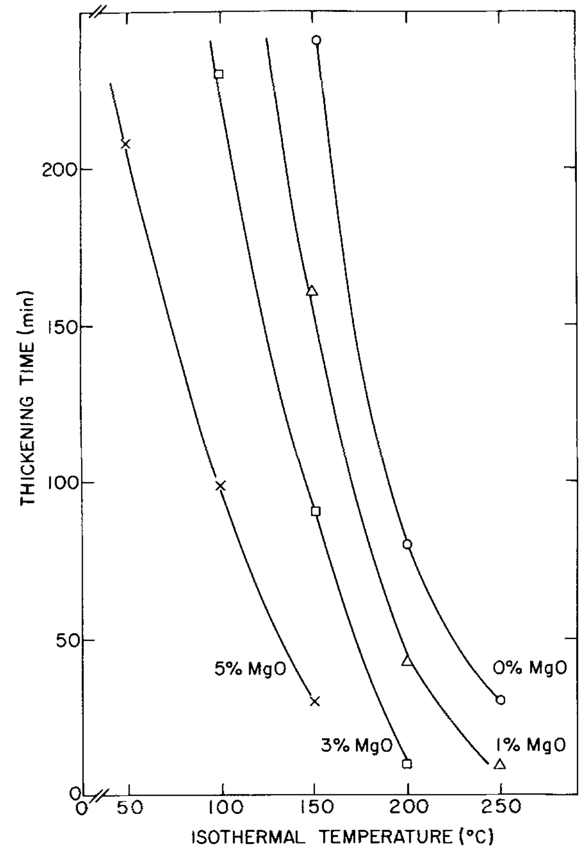


Figure 3 Effect of MgO concentration on the thickening time of slurry.

at temperatures ranging from 50 to 150° C since larger amounts cause a very rapid stiffening which gives the appearance of a quick set.

From these data, it appears that MgO cation exchangeable admixtures can be used to accelerate the setting rate of bentonite–AmPP slurries in a controllable way.

3.2. Properties of hardened cement

Important mechanical and physical properties of cementitious materials designed for CLCM applications include compressive strength, water permeability, and volume changes. Therefore, these properties were determined for solidified cement specimens after 2 h exposure in an autoclave at 300° C. These properties as a function of borax concentrations are given in Table III. For samples without borax, the 2 h compressive strength for 3.5 cm diameter by 7.0 cm long specimens was ~290 psi (2.00 MPa). Strength increases are evident as the borax concentration was increased from 10 to 50% where the maximum strength of 670 psi (4.62 MPa) was obtained. A further increase in concentration up to 70% resulted in a reduction in the 2 h strength to a level of 560 psi (3.86 MPa).

The water permeability of the specimens was measured by forcing pressurized water through 3.0 cm diameter by ~3.9 cm thick samples. The water permeability at pressures up to 2 atm was computed by using the following formula

$$K_a = \mu VL/AP \qquad (1)$$

where K_a is the permeability in Darcys of the sample (intrinsic permeability), V (cc sec^{-1}) is the rate of flow at the fluid viscosity μ (cP), and L and A are the thickness (cm) and the cross-sectional area (cm^2) of the sample under the hydrostatic pressure P (atm). A constant of 7.09×10^{-2}, was calculated from a driving pressure of 2.0 atm, a surface area of 7.065 cm^2, and a viscosity at 20° C of 1.002 cP. Hence, the intrinsic permeability K_a is defined by $K_a = 7.09 \times 10^{-2}\, VL$ (Darcy).

Test results from these cylindrical specimens (Table III) indicate trends in agreement with those for the compressive strength. The permeability value was lowered by increasing the borax content up to 50%, going from 4.43×10^{-4} Darcys for specimens without borax to 1.18×10^{-4} Darcys for those containing a 50% concentration. Further increases in borax content increased the permeability.

The borax is also very effective as a foaming agent. As noted in Table III, the linear expansion increased dramatically with the amount of borax up to a concentration of 50%. The control specimen expanded ~7% at an exposure age of 2 h. By contrast, the addition of a 50% concentration of borax resulted in a value of 15.48%, slightly higher than that at 70%. This large expansion should help to produce an effective seal after placement. From these data, it appears that the presence of borax 10 mol in bentonite-based polyphosphate cementitious material systems has a significant effect on the early age properties of the cements upon exposure to brine at 300° C.

Experiments were also conducted to determine if other borate compounds would yield similar or improved results compared to those using the borax

TABLE III 2 h compressive strength, water permeability and dimensional characteristics of autoclaved specimens as a function of borax concentration

Borax 10 mol (%)	2 h compressive strength [psi (MPa)]	Water permeability $\times 10^{-4}$ (Darcys)	Swelling* (change in length, %)
0	290 (2.00)	4.43	7.03
10	350 (2.41)	3.51	8.11
20	420 (2.89)	–	10.52
30	550 (3.79)	1.83	12.91
50	670 (4.62)	1.18	15.48
70	560 (3.86)	1.25	15.30

$*\dfrac{L_a - L_i}{L_i} \times 100$

L_a = length after autoclave exposure.
L_i = initial length.

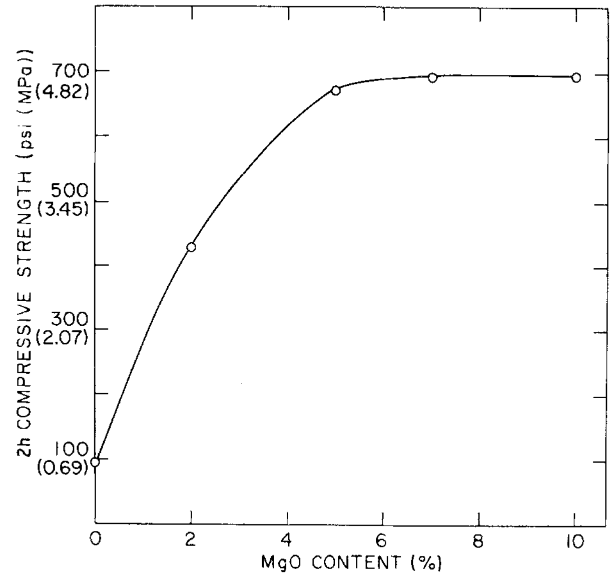


Figure 4 Effect of MgO additions on the strength of cured CLCM slurry.

10 mol. In these studies, various borate compounds (see Table IV) were added to a 40% bentonite–5% MgO–55% AmPP system, and then the samples were exposed to the autoclave at 300° C for 2 h. The ability of borate compounds to improve the mechanical strength was then evaluated on the basis of compressive strength data from these autoclaved specimens. In a preliminary examination, it was found that the degree of solubility in the AmPP solution for each of the borate admixtures is entirely different. Hence, the quantity of admixture that can be mixed with the AmPP solution to prepare a pumpable bentonite cement slurry with a viscosity in the range of 330 to 182 cP depends on the type of admixture. Sodium tetraborate decahydrate was the most soluble. A concentration of 50% by weight of the AmPP solution could be added to the slurry while maintaining the viscosity at a pumpable 330 cP. The addition of the large amount of retarder while maintaining a pumpable slurry viscosity would be expected to yield a longer working time at elevated hydrothermal temperatures. The test results from these specimens are given in Table IV. The data for the 2 h compressive strength of autoclaved specimens indicate that the bentonite specimens made with 50% borax 10 mol had the highest strength of 670 psi (4.62 MPa). All of the other borate compounds yielded samples with strengths < 400 psi (< 2.76 MPa). From the above results, it was found that borax 10 mol retarder is the most effective admixture to develop high-strength bentonite cements at elevated temperatures.

The mechanical strength enhancement is due not only to the addition of borax admixture, but also to the presence of MgO in the slurry systems. Fig. 4 shows the 2 h compressive strength of the specimens plotted against MgO concentrations in the range 0 to 10%. As seen in the figure for MgO concentrations between 0 and 7%, the strength increases with MgO content. Values ranged from 99 psi (0.68 MPa) for hardened specimens without MgO to 690 psi (4.75 MPa) when the concentration was 7%. This is an improvement by a factor of ~7. MgO additions beyond 7% did not affect the strength. These data verify that the inclusion of a small quantity of MgO in the slurry greatly accelerates the rate of *in situ* conversion of the slurry into a cement.

3.3. Reaction compound identification

An attempt was made to determine the reaction compounds responsible for the development of the mechanical strength of the autoclaved bentonite–AmPP–borax systems with and without MgO. Analytical techniques employed were X-ray powder diffraction (XRD) with Cu*Kα* radiation, and energy dispersive X-ray (EDX) spectrometry coupled with scanning electron microscopy (SEM). Five different formulations: bentonite–H_2O; bentonite–borax–H_2O; bentonite–AmPP–H_2O; bentonite–AmPP–borax–H_2O; and bentonite–AmPP–borax–MgO–H_2O were used in this analytical work. In these formulations, the bentonite–AmPP and bentonite–borax ratios by weight were held constant at 1/0.5 and 1/0.7, respectively. Samples were prepared by pouring thoroughly mixed slurries into 12 mm diameter by 75 mm long test tubes, and then exposing them in an autoclave for 2 h at 300° C. After autoclaving, the samples were dried in a vacuum oven at 110° C for 24 h to remove any moisture from the cementitious materials. Small pieces of dried materials were then ground to a size < 0.044 mm for subsequent XRD analysis. The micromorphology of fractured surfaces and the chemical states present were determined using combined SEM–EDX techniques. The actual reaction products in the samples were speculated by detecting the nearly

TABLE IV Effect of various borate compounds on early compressive strength of bentonite conversion cements

Chemical name	Formula	Content* (%)	Viscosity of slurry at 24° C (cP)	2 h compressive strength of specimens hardened at 300° C [psi (MPa)]
Boric acid	H_3BO_3	20	231	95 (0.66)
Sodium tetraborate anhydrous (anhydrous borax)	$Na_2B_4O_7$	10	281	360 (2.48)
Sodium tetraborate pentahydrate (borax 5 mol)	$Na_2B_4O_7 \cdot 5H_2O$	20	182	220 (1.52)
Sodium tetraborate decahydrate (borax 10 mol)	$Na_2B_4O_7 \cdot 10H_2O$	50	330	670 (4.62)
Boric anhydride	B_2O_3	5	289	80 (0.55)
Disodium octaborate tetrahydrate (polybor)	$Na_2B_8O_{13} \cdot 4H_2O$	20	248	190 (1.31)

*By weight of total AmPP solution mass.

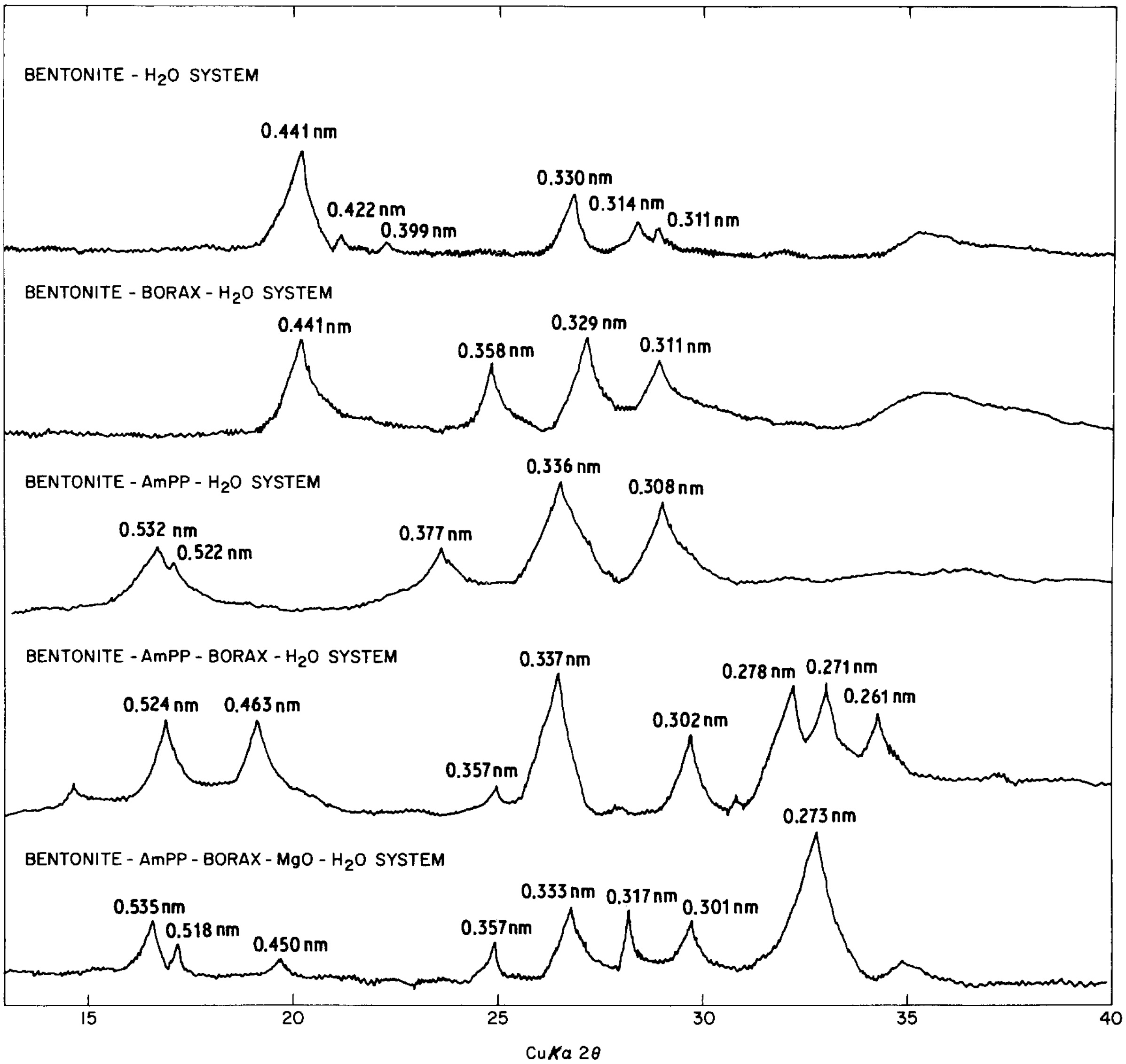
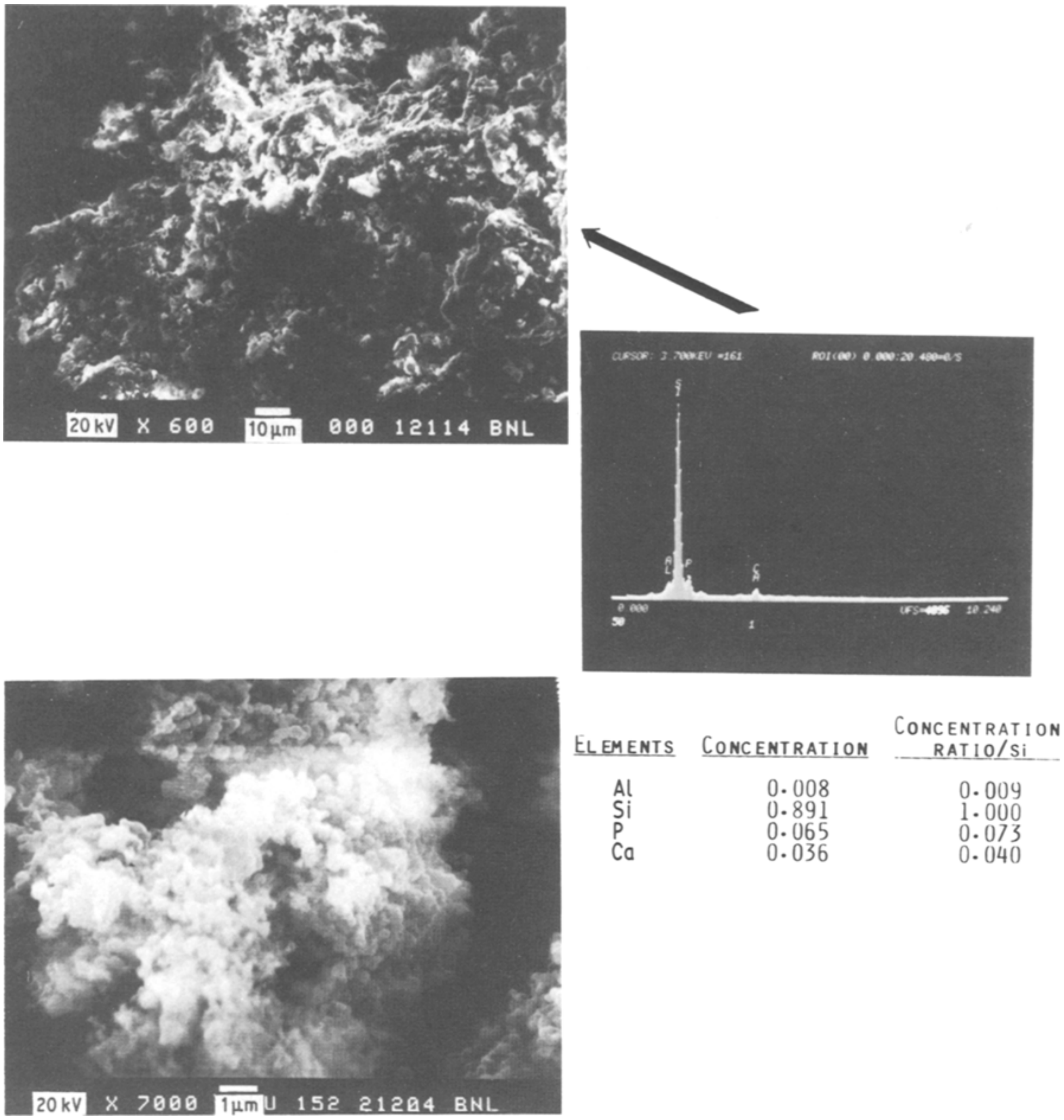


Figure 5 X-ray diffraction tracings for bentonite-based materials autoclaved for 2 h at 300° C.

identical spacings and by comparing the concentration of chemical elements for each of these formulations. XRD tracings were recorded for the diffraction range 0.680 to 0.225 nm, and the results are given in Fig. 5. SEM images, EDX spectra, and the concentration distribution of elements derived from the quantitative analysis of EDX peak counts for the representative samples are illustrated in Figs. 6–8.

For the hydrated bentonite (bentonite–H_2O) system, the XRD pattern indicates the formation of montmorillonite crystals which are characterized by the strong lines at ~0.441 and 0.330 nm, medium intensities at 0.314 and 0.311 nm, and weak diffractions at 0.422 and 0.399 nm. The bentonite hydrated with borax reagent exhibited a new line at 0.358 nm over this diffraction range. The montmorillonite crystal is composed of superposed lamellae, which bear a diffuse negative charge due to different substitutions in the crystal lattice of the lamellae. Thus, this newly produced spacing may be due to the Na-saturated montmorillonite hydrate formed by reactions between the negatively charged silicate plates and Na^+ ions liberated from the borax ($Na_2B_4O_7 \cdot 10H_2O$) in the aqueous media. The polar Na^+ ions which penetrate between the lamellae act to promote cohesion between lamellae. The pattern for the bentonite–AmPP–H_2O system seems to demonstrate that the phases consist of unreacted ammonium phosphate hydrate which is the predominating chemical constituent of AmPP and the montmorillonite. The former can be ascribed to the spacing at 0.532, 0.522, and 0.377 nm. It is not clear if the cause of the disappearance of the bentonite line at 0.441 nm is due to the transformation of montmorillonite as a result of reaction with AmPP.

A micrograph and EDX peak counts of the fractured surfaces of this system are presented in Fig. 6. As discussed in earlier papers [12, 13] SEM images indicate that the microstructure of hydrated montmorillonite is formed of units called aggregates, with sizes often ranging between 0.1 and 1.0 μm. An aggregate is likely to be made up of a number of structure units or primary particles. EDX spectrometry coupled with SEM has a high potential for the quantitative analysis of any selected elements which exist at solid composite materials subsurfaces. This feature can greatly enhance the results, as well as facilitate the interpretation of SEM studies. The EDX spectra for the bentonite–AmPP–H_2O system are also shown in Fig. 6. As indicated, the predominant element, which is represented by the highest peak intensity, is silicon.

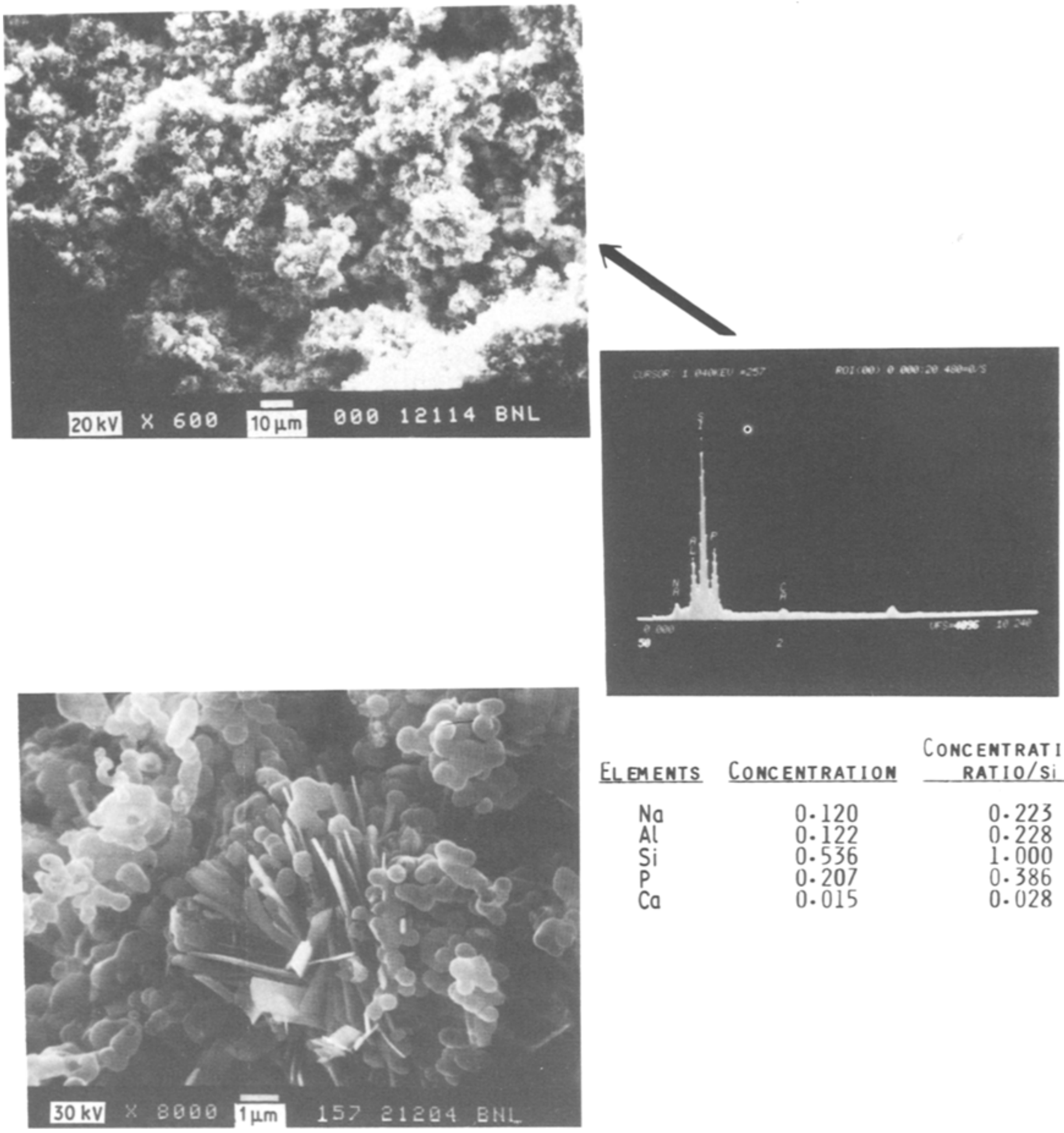


ELEMENTS	CONCENTRATION	CONCENTRATION RATIO/Si
Al	0·008	0·009
Si	0·891	1·000
P	0·065	0·073
Ca	0·036	0·040

Figure 6 Scanning electron microscopy images and energy dispersive X-ray spectra obtained from fractured surfaces of autoclaved bentonite–AmPP–H_2O systems.

Other elements present, but with low peak intensities, are aluminium, phosphorous and calcium. To obtain quantitative data, the concentration distributions of some main elements were computed from the ratios of the peak counts. The resultant chemical constituents for the bentonite–AmPP–H_2O systems are composed of 89.1% Si, 6.5% P, 3.6% Ca, and 0.8% Al. The notable calcium atom peak suggests that the bentonite used contained a relatively large amount of calcium montmorillonite rather than sodium montmorillonite. The incorporation of borax reagent with the bentonite–AmPP–H_2O system resulted in the occurrence of new XRD spacings at 0.463, 0.278, 0.271, and 0.261 nm. Fig. 7 shows the nature of the microtexture of a fractured surface of this material. Its surface morphology represents two discriminable hydration layers; one is that of thin plate-like crystals and the other is the aggregate-like layers. The latter are associated with sodium- and calcium-saturated montmorillonite.

The transformation in bentonite–AmPP mix phases caused by the addition of borax was investigated by comparing the element to silicon concentration ratios in the bentonite–AmPP–H_2O system with and without borax. Large changes in the concentration ratios, as shown in Fig. 7, were detected for the aluminium and phosphorous atom peaks. The aluminium and phosphorous to silicon concentration ratios for the borax-containing system are considerably higher than those for the system without borax. This suggests that the conformation of montmorillonite consisting of $[Al_2(OH)_4]_n^{2n+}$ sheet layers sandwiched between two $(Si_2O_5)_n^{2n-}$ sheet layers was geometrically transformed by the hydrothermal reaction with the mixture of AmPP and borax. In this connection, the increase in phosphorous atom concentration results in the replacement of some silicon atoms of montmorillonite with the phosphorous atom of AmPP brought about by the breaking of a crystal lattice of superposed lamellae. The transformed structure is more likely to be associated with the presence of the newly formed crystal rather than the agglomerated montmorillonite crystals. Thus, it was found that the borax reagent

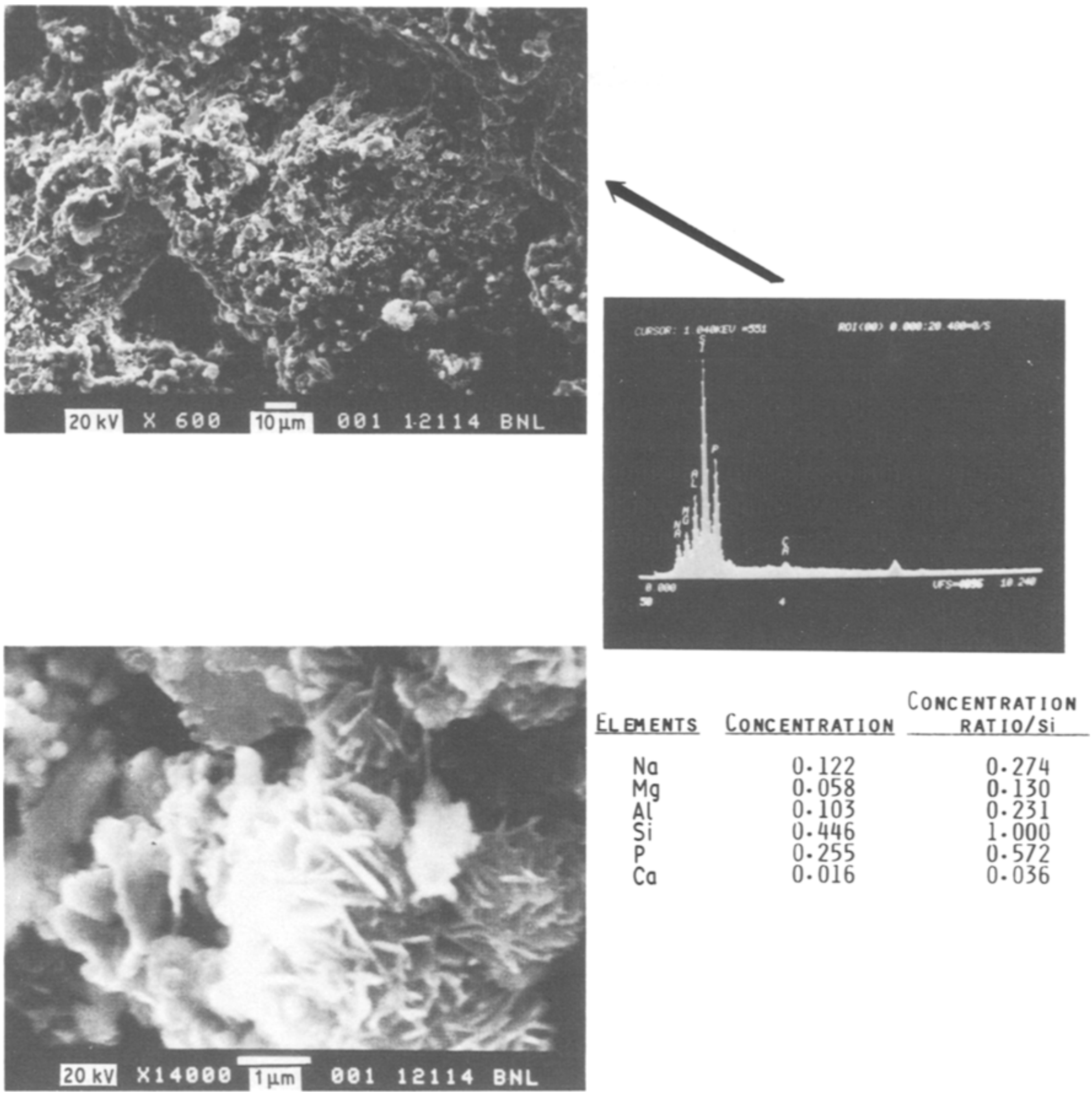


Elements	Concentration	Concentration ratio/Si
Na	0·120	0·223
Al	0·122	0·228
Si	0·536	1·000
P	0·207	0·386
Ca	0·015	0·028

Figure 7 Micrograph of energy dispersive X-ray analysis of fractured surface of bentonite–AmPP–borax–O systems.

significantly acts to promote the hydrothermal reaction between the bentonite and AmPP. From the above speculations, the plate-like crystal features observed on SEM may represent the montmorillonite–AmPP–borax complex hydration compounds. Consequently, the recorded new X-ray diffraction lines may assign to a complexed crystal formation. However, the chemical structure and formulation of this complex are not clear.

The pattern for the bentonite–AmPP–borax–MgO–H_2O system exhibited a strong line at 0.273 nm, medium intensities at 0.301, 0.317, 0.333, and 0.535 nm, and weak peaks at 0.357, 0.450, and 0.518 nm. By comparison with the four tracings described above, the reduction in peak intensities of 0.301, 0.333, and 0.535 nm, which represent the unreactive montmorillonite and ammonium phosphate hydrates, suggests that a large amount of these unreactive materials are transformed into new complex compounds in the presence of MgO. As shown in Fig. 8, the reaction products formed in the autoclave processing are well crystallized. The SEM image shows that the morphological features of the crystalline reaction products are characterized by being representative of scroll-tubular and interlocking plate crystals. Micrographs also indicated that all of the aggregate-like montmorillonite crystals were converted into assemblages of interlocking crystals composed of a grown thin-plate crystal. Thus, the addition of MgO to the bentonite–AmPP–borax-H_2O system seems to result in significant enhancement in dense agglomeration of microcrystalline clusters. The strength development is known to be directly related to the crystalline formation, orientation, and space-filling properties of the reaction products. Growth of the crystal leads to improvements in the mechanical strength of the cement. It appears from the quantitative analysis of EDX peaks that the major chemical constituents of these well-crystallized phases are silicon and phosphorous. Although the concentration ratios of sodium, aluminium, and calcium to silicon are almost the same as those computed for the bentonite–AmPP–borax–H_2O system, the phosphorous to silicon ratio was increased significantly by the addition of MgO.



ELEMENTS	CONCENTRATION	CONCENTRATION RATIO/Si
Na	0.122	0.274
Mg	0.058	0.130
Al	0.103	0.231
Si	0.446	1.000
P	0.255	0.572
Ca	0.016	0.036

Figure 8 Micromorphological features and X-ray spectra of well-crystallized bentonite–AmPP–borax–MgO–H_2O systems.

Therefore, it is speculated that the interlocking crystal associated with the spacing at 0.273 and 0.317 nm results in the formation of a complex that is responsible for the strength development of autoclaved cements.

4. Conclusions

From the results described above and the subsequent discussions, it appears that bentonite-based cementitious materials are potentially useful as CLCMs. The optimum formulation consists of 35% bentonite, 43% AmPP (49.5% water), 22% borax 10 mol, and MgO at concentrations ranging from 0 to 12.5% by weight of the total bentonite mass. In these formulations, the borax is used as a retarding admixture to extend the thickening time of the CLCM slurry at elevated hydrothermal temperatures, as well as to increase the diffusion rate of bentonite grains in the AmPP aqueous media. Since the MgO admixture accelerates the setting rate of the slurries significantly, the CLCM system without the MgO could be used when the bottom hole temperature is in the range of 200 to 250° C. At temperatures ranging from 50 to 100° C, it is necessary to add 12.5% MgO in order to achieve compressive strength of > 500 psi (> 3.45 MPa) at an age of 2 h. This suggests that a slurry system containing a large amount of MgO is very attractive as an alternative material for utilization under circumstances where a very rapid set is required. The cured cements formed by the *in situ* conversion of slurries in the autoclave had adequate compressive strengths at 2 h age, very low water permeability, and a high degree of expansion. Although the predominant reason for the development of mechanical strength is the presence of MgO, it was found that the borax also contributes to strength development. The borax is also very effective as a foaming agent which leads to a large expansion of the CLCM during curing.

SEM images of fractured surfaces of the bentonite–AmPP–borax–H_2O system revealed two discriminable layers, aggregate-like montmorillonite hydrate and thin-plate-like crystals. It was speculated from XRD and EDX analyses that the latter represent the montmorillonite–AmPP–borax complex hydration products. The addition of MgO to the bentonite–AmPP–borax–H_2O system results in dense agglomeration of the microcrystalline clusters. This assemblage of interlocking crystals composed of a grown thin-plate crystal is due to the formation of a complex containing an abundant amount of silicon and phosphorous. The formation of this well-crystallized complex seems to be primarily responsible for the strength development of the cement upon curing.

References

1. T. E. HINKEBEIN, V. L. BEHR and S. L. WILDE, "Static slot testing of conventional lost circulation materials", Sandia National Laboratories, SAND 82-1080, January (1983).
2. M. E. CHENEVERT, "Fundamentals of drilling", Short Course, Sandia National Laboratories, Albuquerque, July 25–26 (1979).
3. J. U. MESSENGER, in "Lost Circulation" (Penn Well Publishing, 1981) p. 1.
4. P. L. MOORE, "Drilling Practices Manual" (The Petroleum Publishing Co. Tulsa, 1974) p. 80.
5. D. H. SOLOMON and D. G. HAWTHORNE, "Chemistry of Pigments and Fillers" (Wiley, New York, 1983) p. 14.
6. U. HOFFMANN, K. ENDELL and D. WILM, *Z. Krist.* **A86** (1933) 340.
7. C. E. MARSHALL, *ibid.* **A91** (1935) 433.
8. S. B. HENDRICKS, *J. Geology* **50** (1942) 276.
9. D. H. SOLOMON and D. G. HAWTHORNE, "Chemistry of Pigments and Fillers" (Wiley, New York, 1983) p. 15.
10. P. C. CARMAN, "Chemical Constitution and Properties of Engineering Materials" (Edward Arnold, London, 1949) p. 389.
11. T. SUGAMA and L. E. KUKACKA, *Cem. Concr. Res.* **13** (1983) 499.
12. A. M. SICAND, J. MERING and I. P. BONNET, *Bull. Soc. Min. Cryst.* **74** (1951) 439.
13. A. BLUMSTEIN, *J. Polym. Sci.* **3** (1965) 2653.

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