

Fig.8-TEM micrographs of natural bentonite (a) and PCE/ bentonite complex(b).

over, T_{max} (the temperature when the rate of weight loss reaches a maximum) of natural bentonite was observed to be at approximately 668 °C (1234.4 °F), in contrast, T_{max} of PCE/ bentonite is 657 °C (1214.6 °F) and the intensity of the peak also decreased, which means the dehydroxylation process was altered by changes in the bonding nature of the interlayer water, possibly caused by the intercalation of PCE molecules. This was supported by the results obtained from FTIR and XRD studies.

TEM observation

In order to find further evidence of the basal spacing enlarging, the microstructure of natural bentonite and PCE/bentonite complex were evaluated by using TEM, which permits the direct observation of microstructural features of clays.

In comparison with natural bentonite, it proved to be difficult to obtain detailed TEM micrographs since the high vacuum of TEM and the high-energy beam can remove the water or surfactant molecules that makes the layer structures collapse and prohibits the structures from being readily observed. Therefore, one must take photographs as soon as possible to obtain clear, accurate images during the period of TEM viewing, especially at high magnifications. In the PCE/bentonite complex, layer spacing of 1.42 nm was in good agreement with the XRD results, but in some areas, the layer spacing remained about 1.24 nm similar to natural bentonite. This suggests that not all the interlayers were intercalated by copolymers, resulting from irregular intercalation or structure collapse mentioned above. Meanwhile, a characteristic swelling of bentonite containing termination as shown by the arrow in **Fig.8b** also was observed. This suggested that the swelling of silicate layers maybe augmented by defect in the clay structure.²⁰

Adsorption amount of PCE with different molecular structure onto bentonite

Based on the reported intercalation of PCE molecules into bentonite interlayers, PCEs with different carboxyl density and side chain length were synthesized to investigate if it is possible to decrease the sensitivity of PCE to bentonite by changing its molecular structure. The molecular structure of PCE was shown in **Table 3**.

The variation in adsorption amount of PCE is shown in **Fig.9**. For ester-based PCE (**Fig.9a**), adsorption amount of PCE decreased with increasing carboxyl density, and when n_{MAA}/n_{MPEG} increased to 0.96 (M400-3), 2.40 (M1000-3), respectively, the decreasing trend

Sample/Item		Mxxx-1	Mxxx-2	Mxxx-3	Mxxx-4	Mxxx-5	Mxxx-6
$m_{MAA}/(m_{MAA+}m_{MPEG})$		6.44%	12.10%	17.11%	21.58%	25.60%	29.22%
n _{MAA} /n _{MPEG}	M400	0.32	0.64	0.96	1.28	1.6	1.92
	M1000	0.80	1.60	2.40	3.20	4.00	4.80
Sample/Item		Txxx-1	Txxx-2	Txxx-3	Txxx-4	Txxx-5	Txxx-6
m _{AA} / (m _{AA+} m _{TPEG)}		4.58%	6.72%	8.76%	10.71%	12.59%	14.38%
n _{AA} /n _{TPEG}	T1200	0.80	1.20	1.60	2.00	2.40	2.80
	T2400	1.60	2.40	3.20	4.00	4.80	5.60
	T4000	2.67	4.00	5.33	6.67	8.00	9.33

Table 3-Molecular structure of PCE

Note: Mxxx-y is ester-based PCE, and Txxx-y is ether-based PCE.



Fig.9-Comparison of adsorption amount of polycarboxylate with different molecular structure onto bentonite (a:esterbased, b-ether-based)

of adsorption amount slowed down. The affinity between anionic bentonite and anionic PCE was mainly realized by intercalation of EO side chains into bentonite interlayers. When the carboxyl density of PCE main chain increased, the repelling force between adsorbate molecules and adsorbent particles increased correspondingly. The intercalation of side chains into bentonite interlayer became more difficult and the adsorption amount decreased. When molecular weight of side chain increased from 400 to 1000 with a certain carboxyl density, the adsorption amount had a little reduction (shown in **Fig.9a**). That was because the enlargement of side chain size was unfavorable for the intercalation.

For ether-based PCE (**Fig.9b**), the variation in adsorption amount of PCE with carboxyl density and side chain increasing was similar to ester-based PCE. However, adsorption amount of ether-based PCE onto bentonite was much less than that of ester-based PCE. The adsorption amount of ether-based PCE ranged from 15 to 30 mg/g with comparison to 75-120 mg/g for ester-based PCE in our experiment. The ester-based PCE was synthesized with methoxy polyethylene glycol methacrylate (MPEG) as macromonomer and methacrylic acid as comonomer, and the ether-based PCE was synthesized with isoamyl alcohol polyoxyethylene ethers (TPEG) as macromonomer and methacrylic acid as comonomer. The methyl groups in ester-based PCE has strong shielding effect on negatively charged carboxyl groups. Otherwise, the carboxyl groups in ether-based PCE will play effective electrostatic repulsion between the polymer and bentonite particles, resulting in the reduction in adsorption amount.

Mortar test

The variation in cement mortar with 2%bwoc bentonite with PCE above was shown in **Fig.10** (water/cement ratio-0.49, sand/cement ratio-2.07, PCE dosage-0.40%bwoc). For ester-based PCE, the fluidity increased initially, and then decreased with increasing carboxyl density. However, the effect of side chain size with same carboxyl density on fluidity didn't show regular trend. For chain Mw of 400, maximum flow observed with Mxxx-5, whereas for chain Mw of 1000, Mxxx-3 exhibited maximum flow. For etherbased PCE, mortar fluidity increased with increasing carboxyl density with same side chain length. That is because the increase of carboxyl density lowered the harmful loss caused by bentonite and cement particles were dispersed well. In addition, mortar fluidity increased with increasing side chain length with same carboxyl density. With side chain length increasing, adsorption amount of PCE onto bentonite decreased, meanwhile, the steric hindrance of PCE molecules on cement particle surface decreased the agglomeration trend and improved the fluidity of cement mortar.

Effect of PVA dosage on the fluidity of cement mortar with 2%bwoc was shown in **Fig.11** (water/cement ratio-0.36, sand/cement ratio-2.07, PCE dosage-0.50% bwoc). Without PVA, mortar almost had no fluidity, which is ascribed to the large amount of consumption of PCE by bentonite resulting in inadequate dispersion of cement particles. When PVA dosage increased from 0.25% bwoc to 1.00% bwoc, the mortar fluidity increased from 130 mm (5.118 in.) to 310 mm (12.205 in.). PVA adsorbed onto bentonite with PCE competitively, and that decreased the PCE adsorption amount, weakening the consumption of PCE caused by bentonite. As a result, the insensitivity of cement dispersion with PCE was enhanced.



Fig.10-Effect of PCE on the fluidity of cement mortar with bentonite.

CONCLUSION

(1) A large amount of PCE was found to be adsorbed onto bentonite ranging from 157 mg/g to 230 mg/g. The interlayers of bentonite are intercalated by PCE molecules with surface adsorption to a certain extent indicated by characterizing PCE/bentonite complex.

(2) PVA adsorbs onto bentonite competitively with PCE which decreases the adsorption amount of PCE drastically.

(3) Cement mortar experimental data indicates ether-based PCE has better clay tolerance than ester-based PCE. Increasing side chain length and carboxyl density in main chain are favorable for weakening the sensibility of PCE to bentonite. PVA as sacrificial agent can enhance the dispersibility of PCE for cement with clay.



Fig.11-Effect of PVA dosage on the fluidity of cement mortar with bentonite.

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Effect of the Stereochemistry of Polyols on the Hydration of Cement: Influence of Aluminate and Sulfate Phases

by Camille Nalet and André Nonat

The difference in the retarding effects induced by sugar alcohols on the hydration of pure tricalcium silicate and white cement pastes is investigated. The polyols studied which are stereoisomers (D-glucitol, D-galactitol and D-mannitol) generate a lower retarding effect on the hydration of white cement than on the hydration of pure tricalcium silicate. The presence of aluminate and sulfate phases in white cement pastes is shown to reduce the retarding effect induced by the molecules. Moreover, these alditols strongly complex aluminate in solution and adsorb on hydrating cement. The interactions of polyols with the anhydrous and/or hydrated aluminate phases and their effects on the hydration kinetics of white cement are discussed.

Keywords: adsorption; aluminate; cement; complexation; hydration; kinetics; polyols; reactivity; stereochemistry.

INTRODUCTION

Portland cement is composed of silicate (C_3S , C_2S), aluminate (C_3A , C_4AF) and sulfate ($CaSO_4$, xH_2O) phases which interact between each other during hydration and make its study complicated. The generalized use of chemical admixtures confers to concrete specific properties either related to its fresh state (rheology modifiers, set accelerators or retarders...) or longer term properties (strength enhancers, durability improvers...).¹ Although used since decades those additives are often considered from a performance point of view^{2,3} but their interactions with mineral surfaces are hardly resolved and understood.

Hence, this study is focused on the understanding of the interactions of hexitols with white cement paste and their effects on its kinetic of hydration. Here, we compare the effect of the conformation of D-glucitol, D-galactitol and D-mannitol on the hydration kinetics of pure tricalcium silicate (C_3S) and of white cement. Then, the interactions of the hexitols with the anhydrous and/or hydrated aluminate phases present during cement hydration are assessed.

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	White cement	Tricalcium silicate	Tricalcium aluminate-Gypsum-Hemihydrate	
Specific surface area (m ² /g)	0.40 ª	0.49 ^b	0.34 ^b	
Mono. Alite (%)	66.10	-	-	
Tric. Alite (%)	0.00	100.00	-	
Belite (%)	24.20	-	-	
Ferrite (%)	0.40	-	-	
Cub. Aluminate (%)	2.00	-	80.00	
Ortho. Aluminate (%)	0.70	-		
Lime (%)	0.30	-	-	
Gypsum (%)	0.20	-	5.00	
Hemihydrate (%)	0.70	-	15.00	
Anhydrite (%)	1.00	-	-	
Calcite (%)	2.40	-	-	
Portlandite (%)	1.80	-	-	
Quartz (%)	0.10	-	_	

Table 1-Physical and chemical compositions of the cement phases.

– = not measured items.

^a Blaine method,

^b Calculated from particle size distribution assuming that the density of particles is homogeneous with the size, that the particles are spherical and considering the different densities (C_3S : 3210 kg/m² and C_3A = 3030 kg/m²).

RESEARCH SIGNIFICANCE

With the diversity of existing cements and the increasing levels of Supplementary Cementitious Materials of Portland cement in modern concrete, the current limited knowledge on the interactions between chemical admixtures and mineral phases and their influence on the hydration mechanisms of cement phases represents a real limitation in the development of new products with improved properties. This study intends to contribute to fill this knowledge gap by focusing on the effects and interactions of hexitols with hydrating cement phases.

EXPERIMENTAL PROCEDURE

Materials

A batch of white cement, a C₃A-gypsum-hemihydrate mixture and triclinic C₃S were used, **Table 1**. The molecules studied were D-glucitol (\geq 98%), D-galactitol (\geq 99%) and D-mannitol (\geq 98%) which were in a powder form. The preparation of all pastes, suspensions and solutions was made with water which was both distilled and deionised. Calcium oxide used in different experiments was obtained after decarbonation of calcium carbonate (98.5-100%) at 1000 °C [1830 °F] for 24 h. All the saturated lime solutions were obtained by equilibrating water at 25 °C [77 °F] with an excess of calcium oxide.

Methods

Isothermal calorimetry - The kinetics of hydration of different cement phases in presence of sugar alcohols were monitored by isothermal calorimetry at 23 °C [73 °F]. The mixing