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Effect of dispersants on the hydrate morphologies of spinel-containing calcium aluminate cement and on the properties of refractory castables

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Abstract

This research studied the effects of several dispersants on the morphologies of cement hydrates and properties of refractory castables. The results showed that the cement hydrate morphologies were closely related to the types of dispersants used. With naphthalene sulfonate formaldehyde condensate (FDN) and sodium tripolyphosphate (STPP) as dispersants, the cement hydrate of C_3AH_6 obtained anomalistic shapes, and the AH_3 particles showed a diameter of not more than 1 μm. When propionic acid (PA) was added, C_3AH_6 formed inerratic cubical grains, whereas AH_3 changed from particles to long column agglomerates; the ratio of the long radius increased with increasing PA concentrations. The addition of PA as dispersant generated $CaCH_3CH_2CO_2^+$, which resulted in a decrease in Ca^{2+} concentration. Also, the relatively higher apparent porosity satisfied the space requirement for the growth of C_3AH_6, eventually resulting in larger inerratic cubical grains. The H^+ hydrolyzed from PA accelerated the growth on the (100) and (110) crystal planes of AH_3; thus, gibbsite stretched along the *c*-axis. The maximum values of CCS and CMOR for refractory castables prepared with PA as dispersant were 5.6 MPa and 46.6 MPa, respectively, which were higher than those for refractory castables with FDN and STPP. The observed excellent performance in strength might be related to the bridging effect resulting from the long-column AH_3.

Keywords: Dispersants; Spinel-containing calcium aluminate cement; Hydrate morphologies; Long-column AH_3

1. Introduction

The use of spinel-containing calcium aluminate cement (CMA) as a new binder in castables opens a commercial way to produce microcrystalline spinel simultaneously with calcium aluminate inside the same clinker on an industrial scale. Microstructure analysis of this cement revealed that submicron-sized spinel grains were distributed homogenously within the phase of calcium aluminate. The presence of in situ spinel in CMA has been found to significantly improve volume stability at high temperature, slag resistance, and high hot sagging under load as it is used as binder of refractory castables [1–3]. Therefore, this cement has been increasingly used in refractory manufacturing, such as in the lining of steel ladles, in continuous casting tundishes, and in degasser snorkels and lancers [4].

For calcium aluminate cement (CAC)-bonded refractory castables, the use of a suitable dispersant is well known to effectively reduce the water requirement, as well as to optimize the workability and installation performance of the refractory castables, especially low cement castables (LCCs) and ultra-low cement castables (ULCCs); thus, dispersants play a very important role in LCCs and ULCCs. However, most of the investigations in this field thus far have focused on the effects of accelerators/retarders on the development of hydrated products in consolidated cement-containing materials [5–7]. Few researches have investigated the influence of dispersants on the microstructure and properties of refractory castables. Although several recent studies have shown the importance of dispersants in the development of high-performance refractory

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castables, the mutable and dynamic nature of cement particles in aqueous medium makes it difficult to understand the effect of dispersants on the properties of refractory castables. Pan [8] found that the dispersibility, air entrainment, and retarding properties of dispersants mainly affected the microstructures of cement hydration products. Oliveira [9] investigated the effect of citrate and polymethacrylate salts on the setting behavior of ULC refractory castables and reported that sodium citrate could induce the earlier setting of ULC refractory castables due to the formation of a gelled phase between the citrate anions and the ions in cement particles. Hafiane [10] and Smith [11] found that acetic acid was an efficient dispersant for aluminous cement paste, retarding or accelerating the precipitation of the hydrated phase.

When CMA is mixed with water, the anhydrous phases begin to quickly dissolve, generating a saturated solution of Ca_2^+ and $Al(OH)_4^-$ ions [12,13]. The dissociation process continues until the concentrations of these ions in the aqueous solution reach a certain saturation level, at which point the ions tend to precipitate through a nucleation and growth mechanism to form hydrated phases, resulting in an interlocked network that is responsible for setting and providing the prefiring strength [14]. The authors' previous work showed that the phase distribution and particle size of $MgAl_2O_4$ within CA/CA_2 phases have a great influence on the rheological behavior and hydration kinetics of the CMA cements [15–16]. Recently, researchers also realized that the additives including dispersants have a great influence on the properties of CMA-bonded refractory castables. For example, using the raw materials of Egyptian dolomite and active alumina, Khalil [1] prepared CMA and found that addition of Li_2CO_3, acting as a strength modifier, will enhance the strength of CMA-bonded castables obviously due to the adjustable hydration process of CMA. Wöhrmeyer et al. [17] found that polycarboxylate ether (PCE), as the dispersant, can deflocculate the castables efficiently, and the mixing water requirement can be reduced significantly. Compared with CAC-bonded castables, the hot modulus of rupture (HMOR) and slag resistance of CMA-bonded castable can be respectively enhanced by about 20% and 50%.

The above investigation revealed that some of the possible interactions certainly take place between the dispersants and CMA particles in an aqueous medium [18]. Therefore, the purpose of this work is to investigate the interactions of dispersants with CMA particles and their impact on the properties of refractory castables. Three dispersants, namely, propionic acid (PA), naphthalene sulfonate formaldehyde condensate (FDN), and sodium tripolyphosphate (STPP), were studied regarding their influence on the hydrate morphologies of CMA and the mechanical strength of refractory castables; particular attention was given to the effect of PA on the properties of refractory castables.

2. Experimental procedure

The raw materials used to prepare the suspensions and high-alumina castables were tabular alumina (98.9 wt% Al_2O_3; Zhejiang Zili Co. Ltd., China) of various particle sizes (mesh #4-300), reactive alumina (99.23 wt% Al_2O_3, D50 = 4.1 μm; Zhejiang Zili Co. Ltd., China), and CMA (D50 = 13.6 μm, 77.0 wt% MA, 19.1 wt% CA, 3.9 wt% CA_2). The dispersants used were propionic acid (PA), naphthalene sulfonate formaldehyde condensate (FDN), and sodium tripolyphosphate (STPP). Table 1 shows the physical chemistry characterization of the different additives.

Table 1
Physical chemistry characteristics of dispersants.

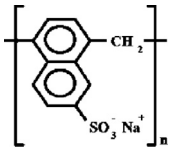
Dispersant	Chemical formula	Molecular weight (g/mol)	Density (g/cm^3)	PH (10 g/L)
PA	$C_3H_6O_2$	74	0.99	5
STPP	$Na_5P_3O_{10}$	367.8	2.6	8
FDN		–	1.6	8

Table 2
Composition of the refractory castables evaluated in the present study.

Raw materials (wt%)	Tyler mesh # range	Content (wt%)
Tabular alumina	4–200	70
	≤200	2
	≤300	5
Reactive alumina	≤1000	7
CMA	≤300	16
Dispersant	–	–
Water	–	6.5%

Refractory castables were prepared with a fixed water content of 6.5 wt% based on dry solids.

Suspensions were prepared with a fixed water/cement ratio (0.5) to evaluate the phase compositions and microstructures with different dispersants. A fixed amount of dispersant was first mixed with the cement powders; distilled water was then gradually added into the mixture with the use of a laboratory mixer. Suspension specimens were cured at 30 °C for 24 h and then dried at 110 °C for 24 h. Suspensions were prepared with different dispersants for rheologic tests; the experiments were carried out by using a rheometer (Physica MCR301, Anton Paar) at 20 °C. The phase compositions of the suspension specimens were evaluated by X-ray diffraction (X'Pert Pro, Philips), and the microstructures were studied with FESEM (Nova 400 Nano SEM; FEI) and EDS (INCA, IE350 penta FET X-3; Oxford Instruments).

The high-alumina refractory castable samples were prepared with tabular alumina as aggregates and α-Al_2O_3 and cement as the matrix constituents (as shown in Table 2). For such LCCs, in which the water content is minimized, and to obtain the maximum density, the particle size distribution has been optimized based on the packing model proposed by Andreassen:

$$\mathrm{CPET} = \left(D/D_L\right)^q \quad (1)$$