

Effects of Different Dispersants on the Change of Chemical Bond of Colloidal Silica

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ABSTRACT

This work studied the relationships between dispersant and the change of chemical bonds of the particles of colloidal silica. Two different dispersants (sodium tripolyphosphate (STP), polycarboxylate (FS10)) have been added to colloidal silica-bonded alumina castables to influence their green strength. The results show that STP or FS10 have a positive effect on the green strength improvement of colloidal silica-bonded alumina castables. The results of Fourier transform infrared spectroscopy (FTIR) indicated that the addition of STP promotes the condensation reaction between the particles of colloidal silica, and the introduction of the cations (Na^+) results in the condensation reaction of colloidal silica, forming a three dimensional network structure, thus increasing green strength of the castables. The reaction between FS10 and the solid particles of colloidal silica could promote the formation of an organic-inorganic interpenetrating network structure, which lead to the green strength improvement.

1 INTRODUCTION

Colloidal silica bonded castable has advantages on drying, sintering properties, volume stability and high temperature strength^[1-5]. However, the low green mechanical strength of colloidal silica-bonded refractory castables may cause severe damage during demoulding and transportation, thereby narrowing the range of application of these materials. Aiming to minimize the above drawbacks, many publications are focused on studying the impact of additives.

Others usually use dispersant to improve the fluidity of castable, while we are concerned about the impact of dispersant on the chemical bond changes of the colloidal silica and the demoulding strength of silica-bonded castables. In this context, the impact of dispersant (phosphate, polycarboxylate) on the chemical bond changes during the dehydration condensation reaction of the colloidal silica were investigated.

2 EXPERIMENTAL

2.1 Experimental Materials

The colloidal silica bonded castables were composed of

colloidal silica (solid content of 30%), tabular corundum (6-3 mm, 3-1 mm, 1-0 mm), tabular corundum powder 325 mesh (≤ 0.045 mm), calcined alumina (CL370, $D_{50}=2.6$ μm), and the castables with sodium tripolyphosphate and polycarboxylate FS10 as dispersant. The chemical compositions of the raw materials are shown in Tables 1 and 2. And the formulation of the castables with colloidal silica is shown in Table 3.

Table 1 Chemical compositions of tabular corundum and calcined alumina (wt.%)

Raw materials	Al ₂ O ₃	SiO ₂	R ₂ O	CaO	Fe ₂ O ₃	MgO
tabular corundum	99.5	≤ 0.09	≤ 0.40	—	≤ 0.02	—
calcined alumina	99.8	≤ 0.03	≤ 0.01	≤ 0.02	≤ 0.03	≤ 0.01

Table 2 Chemical composition (wt.%) and performance parameters of colloidal silica

SiO ₂	R ₂ O	PH	Density /g·cm ⁻³	Viscosity /mPa·s
30	≤ 0.1	8.9	1.2	5.9

Table 3 Formulation of castables with colloidal silica

tabular corundum				CL	colloidal silica
6-3mm	3-1mm	1-0mm	325 mesh	370	
20	30	20	24	6	6.6
dispersant		Proportion of dispersant			
STP		0、0.05、0.1、0.15、0.2			
FS10		0、0.03、0.05、0.1			

2.2 Experimental Procedure

The castable mixtures were dry-mixed for 1 min, followed by 2-min wet mixing with colloidal silica in a laboratory mixer. After that, the castables were cast into the moulds of 40 mm×40

mm×160 mm under vibration. After curing at 30 °C for 24 h, the samples were de-molded, and green strength of the samples was tested.

In order to study the effect of dispersants on the formation of chemical bonds in colloidal silica, colloidal silica and dispersants were all kept at 30 °C for 24 h. Then the mixture with colloidal silica and dispersant was agitated with a magnetic stirrer for 4 min, and then placed into the incubator cured for 24 h at 30 °C. Then, these samples were freeze vacuum dried immediately. Fourier transform infrared spectroscopy (FT-IR) spectra of the samples were collected with a sample/KBr mixture micropellets using the Thermo Scientific Nicolet IS 50 FT-IR spectrometer between 4000-400 cm^{-1} . Background and sample spectra were obtained from 32 scans each with a nominal resolution of 4 cm^{-1} .

3 RESULTS AND DISCUSSIONS

3.1 Demoulding Strength

Fig. 1 shows the cold modulus of rupture (CMOR) of colloidal silica bonded castables after curing for 24 h at 30 °C. As shown in Fig. 1, with STP as dispersant, the CMOR of CS + STP is significantly improved compared to the CS ones. When the amount of STP is 0.1%, the CMOR (0.8MPa) is maximum. Therefore, the addition of STP can enhance the green mechanical strength of colloidal silica-bonded alumina castables.

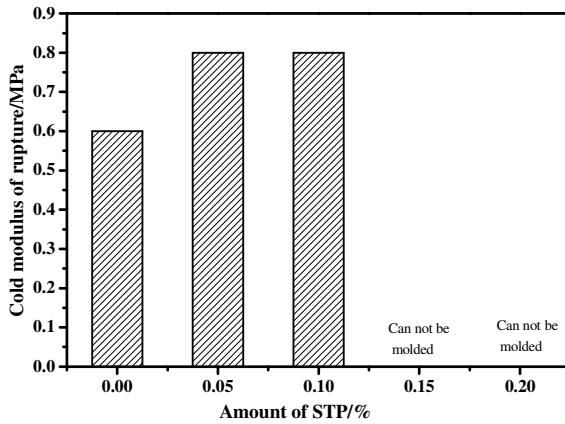


Fig. 1 CMOR of alumina castables bonded colloidal silica with STP as dispersant

Fig. 2 shows the change of CMOR of colloidal silica bonded castables. As shown in Fig. 2, the CMOR of castable without dispersant is 0.6 MPa. In comparison, the CMOR of castable with FS10 (0.05%) is 0.71 MPa. The results show that STP has a positive effect on the green strength improvement of colloidal silica-bonded alumina castables.

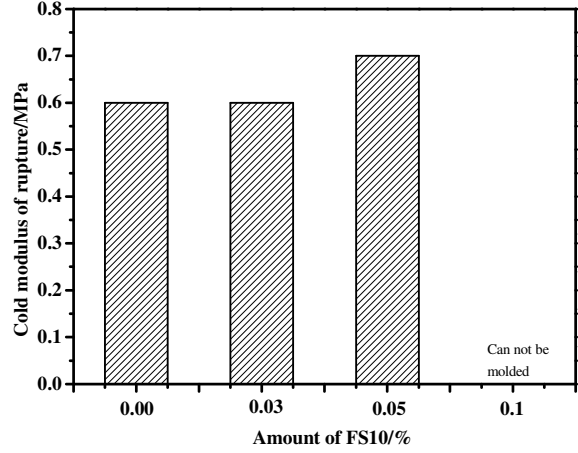


Fig. 2 CMOR of alumina castables bonded colloidal silica with FS10 as dispersant

3.2 Fourier Transform Infrared Spectroscopy (FT-IR)

The FTIR spectra of colloidal silica and colloidal silica with STP are shown in Fig. 3. For colloidal silica, the stretching and bending vibration modes of surface hydroxyl moieties were detected at 3448 cm^{-1} and 1637 cm^{-1} [8], respectively. The siliconoxygen bond stretching mode was detected at 1115 cm^{-1} , while at 799 cm^{-1} , 474 cm^{-1} and 976 cm^{-1} are related to the symmetrical stretching vibration of Si-O-Si, the bending vibration of Si-O-Si, and the Si-OH vibration[9], respectively.

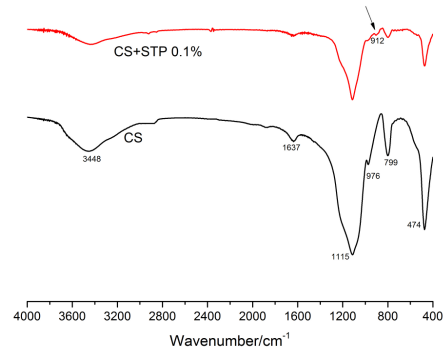


Fig. 3. The FTIR spectra of colloidal silica and colloidal silica with STP

Fig. 3 also exhibits a weak vibration peaks at 912 cm^{-1} when STP is added into the colloidal silica. After the addition of STP, the dispersion of the particles is achieved by the electrostatic repulsion generated by the molecules adsorbed on the surface of the particles[6]. The new vibration at 912 cm^{-1} may be assigned to Si-O-Na[10]. When STP contacts with the water in the colloidal silica, Na^+ ions are dissolved first, and then react with the Si-OH on the surface of colloidal silica particles to form new chemical bonds. Moreover, the electronegativities of Na and H are 0.9 and 2.1, respectively. When the hydrogen

atom with higher electronegativity in Si-OH is substituted by Na atom with lower electronegativity, the original electrons near the hydrogen atom shift to the oxygen atom. As a result, the electron cloud densities of the oxygen atom increases, and the length of the Si-O bond becomes longer. Consequently, the force constant of chemical bond of the Si-O decreases. So the replacement of H⁺ in Si-O-H by Na⁺ would lower the frequency to 912 cm⁻¹.

Therefore, the new chemical bonds (Si-O-Na) of the SiO₂ sol particles form a three dimensional network structure^[10], and then coalesce the particles in the castable matrix, thus increasing demoulding strength of the castable (as seen in Fig. 1).

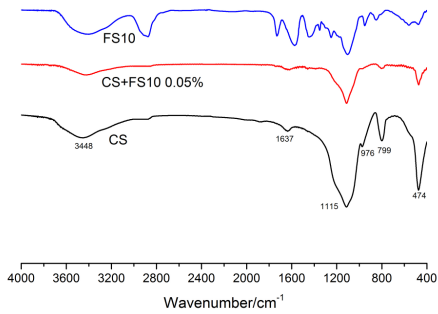


Fig. 4. The FTIR spectra of colloidal silica, colloidal silica with FS10 and FS10

The FTIR spectra of colloidal silica, colloidal silica with STP and FS10 are shown in Fig. 4. These peaks at 3448 cm⁻¹ and 1637 cm⁻¹ are respectively assigned to O-H stretching vibration and H-O-H bending vibration^[8]. The FT-IR spectrum of colloidal silica shows the most intense peak at 1115 cm⁻¹, assigned to Si-O-Si asymmetrical stretching vibration; the peak at 799 cm⁻¹ is assigned to the symmetrical stretching vibration of Si-O-Si, and the peak at 474 cm⁻¹ corresponding to the bending vibration^[9].

However, the vibration peak of Si-OH at 976 cm⁻¹ disappears after adding FS10, and the significant decrease in the intensity of the hydroxyl stretching vibration peaks at 3444 cm⁻¹ compared to colloidal silica suggested that Si-OH bases in the system has decreased significantly. The most possible reason for the decrease of Si-OH bases is hydrolysis of FS10 in the colloidal silica which has induced the Si-O-C breaking into Si-OH bases. Therefore, the formation of Si-O-Si bonding has indicated that dehydration between Si-OH bases has occurred between colloidal silica particles and hydrolysate, or among hydrolysate themselves. These series of reactions involved in colloidal silica particles would promote the three dimensional

network structure formation, and as a result, an inorganic-organic composite network structure formed, as shown in Fig. 5. This type of network structure is beneficial to green mechanical strength enhancement (as seen in Fig. 2).

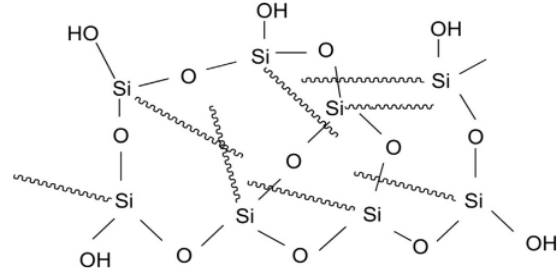


Fig. 5 Inorganic-organic composite network structure of colloidal silica doped with FS10

4 CONCLUSIONS

As clearly indicated by the experimental results, the appropriate addition of STP or FS10 improved the green mechanical strength of alumina castables. In the mixture of STP and colloidal silica, the new vibration peaks appear at 912 cm⁻¹ of the FT-IR spectrum, possibly because the hydrogen atom with higher electronegativity in Si-OH is substituted by Na atom with lower electronegativity. The effect of FS10 may be attributed to the accelerated setting process of colloidal silica via its hydration. The hydrolysate of FS10 can bridge silica particles together and promote the formation of an inorganic-organic composite network structure in the early stage at lower temperatures. Furthermore, the addition of FS10 is also beneficial for the rheological performance of colloidal silica-bonded alumina castables, which is also helpful to achieve better mechanical strength. As a result, the green mechanical strength of alumina castables bonded by colloidal silica was enhanced.

ACKNOWLEDGEMENT

The authors would like to thank the National Natural Science Foundation of China (51572244, 51372230, 51672255, 51402089, U1604252) for the financial support.

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