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The mechanochemical process and properties of Portland cement with the addition of new alkanolamines

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ABSTRACT

Grinding aids have been researched and used for decades to reduce energy consumption in the process of cement production. In this work, the effects of new alkanolamines, such as N,N-bis(2-hydroxyethyl)isopropanolamine (DEIPA), N,N-bis(2-hydroxypropyl)-2-aminoethanol (EDIPA) and N,N,N′,N′-tetrakis(2-hydroxyethyl)ethylenediamine (THEED), on the grinding, flowability and physical properties of Portland cement were investigated. The results indicated that DEIPA and EDIPA could significantly decrease the sieve residues (45 μm), and improve the flowability of the cement powder. They could decrease the compressibility and the magnitude of the pressure drop of the cement at a definite normal stress, thereby preventing cement particles from agglomerating. Notably, DEIPA and EDIPA increased both the early (3-day) and late (28-day) compressive strengths. DEIPA can be used as an accelerator to shorten the setting time. THEED just provides a greater contribution to the late compressive strength.

1. Introduction

Since 1824, cement has been one of the most important, irreplaceable and traditional building materials. The world cement production reached 4.18 billion tons in 2014. However, large amounts of CO_2 are released and limestone and energy are consumed during the cement manufacturing process. Approximately 0.98 tons of CO_2 is released during the manufacturing of 1 tons of clinker, the primary component of cement. Approximately 40% of the total electric energy (110 kW h/ton cement) is consumed for final cement clinker grinding [1–3]. Hence, the cement industry is facing severe challenges with respect to global warming and the present energy crisis.

Increasing amounts of chemical additives have been used in the process of cement grinding [4–6]. In the process of comminution and mixing, positive and negative charges are created on the newly fractured surfaces, leading to the agglomeration of particles due to van der Waals forces and electrostatic attraction. At the same time, coatings form on the surface of grinding media, which reduces the grinding efficiency [7,8]. On the one hand, chemical additives are generally adsorbed on the particle surfaces to decrease the hardness of the particle surfaces and better disperse fine particles by neutralizing charges and screening attractive forces [9,10]. On the other hand, some chemical additives can significantly affect the physical and mechanical properties of cement because of their physical and chemical interactions with hydrates and/or unhydrated phases rather than increasing the fineness of the particles [11–13]. The chemical additives used include alkylamines, alcohols, water-soluble polymers and inorganic salts. With developments in science and technology, alkanolamines have been synthesized and applied in the process of cement grinding. At present, the most widely used alkanolamines contain triethanolamine (TEA) and triisopropanolamine (TIPA). However, TEA increases only the early compressive strength, particularly before 3 days, and even decreases the strength in later stages [14]. TIPA improves only the late strength significantly [14–16]. Subsequently, new alkanolamines, such as DEIPA, EDIPA [17] and THEED [18] were developed.

The primary objective of this work is to investigate the effects of new alkanolamines on the grinding efficiency, flowability, phase structure, and physical and mechanical properties of Portland cement. The effects of DEIPA, EDIPA and THEED on the grinding efficiency were examined in terms of sieve residues (45 μm sieve size), specific surface area and particle size distribution. The changes in the angles of repose, the basic flowability energy (BFE) and specific energy (SE) were also examined to evaluate fluidity of the ground cement. The compressivity and air permeability of ground cement were measured to evaluate agglomeration during storage. The quantity of water required for normal consistency, setting time and strength were measured to evaluate the physical and mechanical properties of the ground cement.

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2. Materials and methods

2.1. Materials

2.1.1. Raw materials

The clinker and gypsum used in this work were obtained from a Chinese cement company. The chemical and mineralogical compositions of the clinker are shown in Table 1. TEA and TIPA were obtained from Jiaxing Jinyan and Fushun Jiahua, respectively, with purities of 85%. DEIPA, EDIPA and THEED were synthesized in the laboratory, and their molecular structures are shown in Fig. 1.

2.1.2. Sample preparation

Mixtures of clinker, gypsum and different amounts of the alkanolamines were ground using a laboratory batch ball mill with dimensions of 500 mm × 500 mm. The dosages of DEIPA, EDIPA or THEED were 0.01%, 0.015%, 0.03% and 0.05% by weight of the mixture of the clinker and gypsum. The dosage of TEA or TIPA was 0.015% as a reference. First, 4 kg of a mixture of 95% clinker and 5% gypsum was weighed and placed into the ball mill. Then, one of the chemical additives was added to the ball mill prior to initiating grinding of the mixture. Finally, the mixture was ground for 15, 20, 25, 30 and 35 min to prepare cement powder.

2.2. Characterization methods

2.2.1. Sieve residue of the cement

To investigate the effect of alkanolamines on the fineness of the cement, the sieve residue was measured using a negative pressure sieve analyzer with a sieve size of 45 μm and a pressure in the range of 4000–6000 Pa, according to the Chinese standard GB/T1345-2005.

2.2.2. Specific surface area of the cement

The specific surface area of the cement was measured using the Blaine method in accordance with the Chinese standard GB/T8074-2008.

2.2.3. Particle size distribution

The particle size distribution was measured by laser diffractometry in a Microtrac S3500SI.

2.2.4. Flowability of the cement

The angle of repose of the powder was measured using the injection method in FT-104B according to the Chinese standard GB11986–89. Two-hundred grams of cement was weighed and then dropped onto the experimental desk through a funnel to form a cone. The radius (R) and height (H) of the cone were measured. Finally, the angle of repose (α) was calculated according to Eq. (1).

$$\tan\alpha = \frac{H}{R} \tag{1}$$

Table 1
The chemical compositions for the clinker and gypsum and mineral compositions calculated by Bogue for the clinker.

Clinker	Loss	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O
Chemical composition	0.46	65.70	21.60	5.51	3.39	1.65	0.41	–	–
Mineral	C_3S	C_2S	C_3A	C_4AF	f-CaO	KH	n	p	
composition	60.76	16.96	7.24	10.67	0.42	0.91	2.58	1.42	

Note: KH represents lime saturation factor, n represent silica ratio, P represent alumina ratio.

2.2.5. BFE, SE, compressibility and air permeability of the cement

BFE, SE, density and the value of the pressure drop of air through the ground powder were measured at a definite normal stress using a multifunctional powder tester in FT-4 (Freeman Technology). The compressibility was calculated according to Eq. (2), where ρ_0 is the density at a stress of 0 kPa and ρ_p is the density at a definite normal stress.

$$\text{Compressibility} = \frac{\rho_p - \rho_0}{\rho_0} \times 100\% \tag{2}$$

2.2.6. X-ray powder diffraction

The phase composition was investigated using a Rigaku SmartLab 3000A diffractometer with Cu K_α radiation ($\lambda = 0.154$ nm). The X-ray tube was operated at 35 kV and 30 mA. The optical configuration included a fixed divergence slit (1/2°) and a D/teX Ultra detector. The measurements were performed using a θ–θ reflection geometry. Data were collected from 10° to 70° in continuous mode.

2.2.7. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FT-IR) was also used to analyze the phase compositions by studying the molecular vibrations for cement. FT-IR spectra were recorded on a Thermo Scientific Nicolet IS5 spectrometer over the range of 400 to 4000 cm^{-1}. KBr was used as a reference. The ratio of KBr to cement was 1:50. The cement and KBr were mixed and then pressed into a solid pellet before being measured.

2.2.8. Physical properties

The setting times and normal consistency of the cement paste were determined in accordance with the Chinese standard GB/T1346 using a Vicat apparatus. Cement paste was prepared from cement and water. The ratio of water to cement was 0.5.

2.2.9. Mechanical properties

The compressive and flexural strengths of mortars were measured according to the Chinese standard GB/T17671-1999. Mortars were prepared with Chinese standard sand, cement and water. A cement powder/sand/water weight ratio of 1:3.0:0.5 was employed.

3. Results and discussion

3.1. Effect of new alkanolamines on the fineness of the cement

The sieve residues (45 μm) are shown in Fig. 2 for cements without and with different alkanolamines ground for 15, 20, 25, 30 and 35 min. The sieve residues decreased with time for all samples. The new alkanolamines (DEIPA, EDIPA and THEED), particularly DEIPA and EDIPA, decreased the sieve residues for the cement under the same grinding conditions. The sieve residues decreased with increasing dosages of the alkanolamines at the same grinding time for DEIPA and EDIPA. Compared to DEIPA and EDIPA, THEED showed a slight effect on the sieve residue. The differences in sieve residues between the blank cement and cements containing EDIPA increased with increased grinding time. EDIPA had a greater effect on the grinding process at the later stages. Compared with TEA, the effects of THEED on the sieve residue were much less at the later age.

The specific surface area was also used to characterize the fineness of cement. The specific surface areas are shown in Fig. 3 for the cements without and with 0.015% alkanolamines. The specific surface area increased with grinding time for all samples. The specific surface area was lower for the cement containing DEIPA or EDIPA while it was higher for the cement containing THEED, compared to the blank cement ground for a given time.

In the initial stage of grinding, particles are shattered and new cracks, active sites and electrostatic charges occur on the fractured