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Effect of clinker grinding aids on flow of cement-based materials

Joseph J. Assaad [a,*], Camille A. Issa [b,1]

[a] Holderchem Building Chemicals, P.O. Box 40206, Lebanon
[b] Lebanese American University, P.O. Box 36, Lebanon

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ABSTRACT

Grinding aids (GAs) are increasingly used during cement production to reduce energy consumption and/or optimize clinker factor. This paper seeks to assess the effect of such additions on variations in flow of cement pastes, including static yield stress (τ_0) and viscosity (η). Grinding tests were performed at fixed specific energy consumption (Ec) or Blaine cement fineness. For fixed Ec, tests have showed that the increase in cement fineness resulting from the addition of higher GA concentration leads to reduced flow and increased τ_0 and η values. Conversely, cement ground for fixed Blaine fineness exhibited an improvement in flowability together with reduction in τ_0 and η values. This was related to a dispersion effect of cement agglomerates in the presence of GA molecules. Special emphasis is placed throughout this paper regarding the effect of GAs on ASTM C465 requirements.

1. Introduction

Grinding aids (GAs) are incorporated during comminution of clinker to reduce electrostatic forces and minimize agglomeration of cement grains [1–3]. Their chemical basis mostly includes ethanolamines such as monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA) as well as glycols such as propylene glycol (PG), monoethylene glycol (MEG), and diethylene glycol (DEG). Because of their highly organic polar nature, GAs are preferentially adsorbed on surfaces formed by the fracture of electrovalent bonds (Ca–O and Si–O), thus reducing surface energy forces. Such additions are commonly used to increase cement fineness and compressive strength for given specific energy consumption (Ec) [1,2]. This could be particularly the case when producing cement possessing increased Blaine fineness necessary for high early strength requirements (i.e., ASTM C150 Type III cement [4]). Nevertheless, with today's constraints regarding the reduction of usable energy, GAs are more and more used to reduce Ec for given fineness, thereby leading to savings in electrical energy and improved mill productivity [1,3,5]. Typical GA dosage rates used during grinding of clinker vary from 0.01% to 0.15% of the manufactured cement mass.

After the grinding process, GAs may not preserve their original molecule structures; however, they do remain adsorbed onto the cement particles to entail variations of cement properties whether in the fresh or hardened states. The setting and hardening properties of cement containing GAs are well documented in literature. For instance, Ramachandran reported that TEA retards hydration of C_3S and β-C_2S together with some changes in morphology and microstructure of the hydration products [6]. The hydration of C_3A was accelerated in the presence of TEA due to the accelerated formation of hexagonal aluminate hydrate and its transformation to a cubic form [6]. Heren and Olmez found that the addition of increased ethanolamine concentrations alters cement hydration and leads to retardation in setting times in the order of TEA > DEA > MEA [7].

Triisopropanolamine (TIPA), which is an amino-alcohol and belongs to the group of alkanolamines, was found to change hydration reactions and particularly increase cement strengths. Perez et al. reported that TIPA remains in the interstitial paste solution (not adsorbed to the cement surface, as the TEA) and forms iron complexes to accelerate hydration of C_3S and C_4AF [8]. Besides the enhancement of alite and felite hydration, Ichikawa et al. presented evidence that TIPA also promotes the hydration of limestone and densifies the interfacial transition zone (ITZ) between hydrated cement paste and sand or aggregate particles [9]. Sandberg and Doncaster reported that the strength increase resulting from the presence of TIPA is not solely dependent on an ITZ mechanism [10]. The strength gain observed in hydrated cement pastes suggested that TIPA is capable to enhance mechanical properties without any paste-aggregate ITZ, regardless of the cement type and age of testing [10].

2. Context and objectives of this project

Limited data exits in literature pertaining to the effect of GAs on flow of cement-based materials. In fact, current literature has extensively

* Corresponding author. Tel.: +961 3 437786; fax: +961 5 921118.
E-mail address: joseph.assaad@lau.edu.lb (J.J. Assaad).
[1] Tel.: +961 3 022682; fax: +961 9 547254.

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treated different aspects of cement rheology as well as the factors and mechanisms governing the aptitude to flow [11,12]; however, refrained to consider the effect of GAs added during cement production. Aiad et al. were among the few researchers who studied the direct effect of GAs on the rheology of cement pastes [13]. The authors found that viscosity is highly dependent on the type and dosage rate of ethanolamine used, whereby a decrease in viscosity was noticed following the sequence of TEA > poly-TEA > MEA. This was related to the number of O–H groups in the ethanolamine molecules that are adsorbed on the surface of cement grains, causing different repulsive forces and leading to variations in fluidity levels. However, it is important to note that the tests carried out by Aiad et al. [13] cannot be conclusive as the ethanolamines were added as post-additions to the cement (i.e., not during the grinding process) and at concentrations varying from 0.1% to 2% of cement weight (i.e., substantially higher than in real situations).

In dry cement, Jolicoeur et al. reported that PG resulted in improved fluidity due to the repulsive forces created between the powder particles [14]. This was affected by the additive molecular weight following the sequence of trimer (TPG), dimer (DPG), and monomer (PG). At increased concentrations, however, it is hypothesized that the GA polymers adsorbed onto the surface tend to make the clinker grains sticky, thus causing agglomeration of the system [14,15]. Anna et al. compared the Z-potential of clinker containing TEA with others ground with polycarboxylate (PC) or poly-naphthalene sulfonate (PNS) concrete superplasticizers [16]. The authors found that the TEA fluidifying mechanism for the dry cement system lies between the steric hindrance associated with PC polymers and electrostatic interaction of PNS with the positive charges of cement grains [16]. While characterizing GAs and their impact on cement performance, Katsioti et al. noted an improvement in workability of cement pastes containing TIPA [17]. This was related to the breaking down of cement agglomerates and balance modification between inter-particle forces.

Besides the lack of documentation in literature, the variations in flow and rheology of cement-based materials due to the incorporation of GAs are not abided by any standard specification or testing protocol. For example, the NCHRP report 607 neglected the effect of such additions on the rheology of cementitious materials, and recommended only some chemical and physical tests to be performed [18]. ASTM C465 [19] defined acceptance criteria for GAs based on a series of chemical and physical tests (no rheological tests are specified) for determining whether such additions dramatically affect cement properties prescribed in ASTM C150 [4]. The most relevant physical requirement of ASTM C465 includes the water demand needed to achieve normal consistency for cement containing GA, which should not increase by more than 1% from that required by the corresponding control cement. The setting times of cement ground with GA should not vary by more than 1 h or 50%, whichever is lesser, from those obtained by the control cement [19]. ASTM C465 specifies that the mortar compressive strength should not decrease by more than 5% from the value resulting from a similar mortar made with the corresponding control cement [19].

The first objective of this paper is to assess the effect of GAs on variations in flow, including static yield stress and viscosity, of cement pastes prepared with different water-to-cement ratios (w/c). Grinding tests were performed in two ways, i.e. fixed Ec or Blaine cement fineness. Commercially available amine and glycol-based GAs were used at various concentrations. The second objective of this paper is to provide a discussion pertaining to the effect of GAs on ASTM C465 requirements, and corresponding variations in rheology. Relevant parameters including water demand, setting time, and compressive strength were evaluated. Such data can be of particular interest to cement manufacturers and concrete technologists as well as standardizing committees dealing with specifications for GAs.

3. Experimental investigation

3.1. Materials

Industrial clinker used for the production of ASTM C150 Type I cement [4], ground granulated blast furnace slag meeting the requirements of ASTM C989 Grade 80, and gypsum materials were employed in this study. Their chemical compositions are presented in Table 1. The $(C_3S + C_2S)/(C_3A + C_4AF)$ ratio of clinker used is equal to 3.14, indicating high grindability requiring relatively reduced amount of energy for given cement fineness [20]. The relative hardness of the clinker, slag, and gypsum determined according to the Mohs hardness scale were around 5.5, 6, and 2, respectively.

Two commercially available GAs were tested. The amine-based GA is commonly used as a grinding aid and strength enhancer in the cement industry. It had 68% active chemicals when determined by the Karl Fischer method and specific gravity of 1.09. The Thin-Layer Chromatography analysis of this GA revealed the presence of TIPA (C_3H_9NO) and TEA ($C_6H_{15}NO_3$) in the proportions of around 58 to 42%, respectively, of the total active chemicals. Its pH was found equal to 7.2, indicating that this GA has been acidified (given that the pH of TIPA and TEA are generally in the order of 10.5 ± 1). This GA is completely soluble in water and has a brown color, viscosity of 125 cP, and ammonia-like odor.

The second GA used in this study is glycol-based composed of DEG ($C_4H_{10}O_3$) and MEG ($C_2H_6O_2$). It is commonly referred to as grinding aid and pack-set inhibitor in the cement industry. Its active chemicals determined by the Karl Fischer method, pH, and specific gravity were equal to 72%, 7.8, and 1.107, respectively. It is highly soluble in water, odorless, and has a brown color and viscosity of 85 cP.

3.2. Production of cement used for testing

A 50-liter grinding mill connected to an electric counter for monitoring Ec was used (Fig. 1). The Ec in kWh/ton was determined as (Tc × 1000) / (mass of ground mix in kg × MF), where Tc refers to the amount of electricity in kWh measured from the electric counter, and MF is the constant mill factor taken equal to 3 by the grinding mill manufacturer. The mill's drum diameter, width, and rotational speed were 400 mm, 400 mm, and 50 rpm, respectively. It contained a total of 80 kg steel balls among which 36 kg has 20-mm diameter and 44 kg has 30-mm diameter. Prior to grinding, the clinker, gypsum, and slag materials were crushed and sieved so that all particles are smaller than 10 mm. The gypsum and slag were dried to constant mass at 45 and 105 °C, respectively, prior to use. All grinding tests were conducted using 7 kg of a mix composed by 90% clinker, 5% gypsum, and 5% slag.

First, a mix ground without GA at 42 kWh/ton was tested and considered in this project as being the reference or control cement. Then,

Table 1
Chemical compositions of clinker, slag, and gypsum.

	SiO_2, %	Al_2O_3, %	Fe_2O_3, %	CaO, %	MgO, %	SO_3, %
Clinker	20.6	6.35	4.5	64.1	1.86	0.22
	C_3S = 54.6%; C_2S = 17.4%; C_3A = 9.2%; C_4AF = 13.7%; Loss on ignition = 1.15%; Na_2O_{eq} = 0.39%; Free lime = 0.26%; Specific gravity = 3.14					
Slag	34.5	12.1	0.75	41.2	9.05	2.4
	Loss on ignition = 0.21%; Moisture content = 0.04%; Na_2O_{eq} = 0.66%; Slag activity index with cement at 28 days = 86.4%; Specific gravity = 2.94					
Gypsum	2.7	0.55	0.4	31.5	1.5	43.2
	Free water (T < 45 °C) = 0.03%; Combined water (T < 230 °C) = 15.6%; Carbon dioxide = 3.7%					