Hindawi Publishing Corporation
Advances in Materials Science and Engineering
Volume 2015, Article ID 938176, 12 pages
http://dx.doi.org/10.1155/2015/938176

Research Article

Industrial versus Laboratory Clinker Processing Using Grinding Aids (Scale Effect)

Joseph Jean Assaad

Holderchem Building Chemicals, P.O. Box 40206, Baabda, Lebanon

Correspondence should be addressed to Joseph Jean Assaad; jassaad@ndu.edu.lb

Received 14 September 2015; Accepted 11 November 2015

Academic Editor: Luigi Nicolais

The evaluation of grinding aid (GA) effect on clinker processing in laboratory grinding mills is relatively simple. Yet, the results obtained cannot be directly transposed to industrial mills, given the fundamentally different operational modes and grinding parameters. This paper seeks to evaluate the scale effect by comparing the results obtained from a closed-circuit tube mill operating at 90 ton/hr to those determined using a 50-liter laboratory mill. Tests results have shown that the decrease in specific energy consumption (Ec) due to glycol or amine-based GA can be evaluated under laboratory conditions. However, such tests underestimate the actual performance that could be achieved in real-scale mills; the Ec reduction due to GA is around twofold higher when grinding is performed in real-scale mill. Compared to industrial tests, the cement particle size distribution curves widened and shifted towards higher diameters when grinding was performed under laboratory conditions, particularly with GA additions. This led to remarkable changes in water demand, setting time, and 1- and 28-day compressive strengths.

1. Introduction

Grinding aids (GAs) are incorporated during clinker processing to reduce electrostatic forces and agglomeration of cement grains. Their chemical basis mostly includes ethanolamines such as triethanolamine (TEA) and triisopropanolamine (TIPA) as well as glycols such as diethylene glycol (DEG) and propylene glycol (PG) [1–3]. The practical consequences of such additions to the cement industry can broadly be divided into two aspects including an increase in cement Blaine fineness and compressive strength for given specific energy consumption (Ec) and/or savings in electrical energy and Ec together with improved mill productivity for given fineness. The former direction is relevant when producing cement possessing increased fineness necessary for high early strength requirements (i.e., ASTM C150 Type III [4]), while the latter is more and more demanded with today's constraints regarding the reduction of usable energy [5]. It is to be noted that GAs blended with TIPA molecules are known by their capability to promote cement hydration reactions, thereby leading to increased compressive strengths [2, 6–8].

The evaluation of GA effect on clinker processing in laboratory grinding mills is relatively simple; it provides a preliminary assessment of GA effects on cement fineness and properties. Yet, the results obtained cannot be directly transposed to industrial mills, given the fundamentally different operational modes and grinding parameters such as comminution forces, screening, ventilation, and clinker temperature [9, 10]. For instance, the clinker processing in real-scale mills is a continuing process, whereby the grinding forces are applied to the coarse particles while the fine ones are discharged as soon as they have been reduced to the required cut size. All particles larger than the cut size would be sent to a reject stream, therefore creating a so-called circulating load (CL). The CL is defined as the average number of times that the material circulates through the grinding system before becoming the product [11].

Unlike industrial mills, laboratory grinding mills operated over given time interval do not account for CL, therefore leading to different cement particle size distribution (PSD) curves [11, 12]. This consequently alters cement properties such as water demand, rheology, and hydration processes such as heat release, setting time, volume change, and strength development [13, 14]. It is to be noted that the Blaine measurement cannot effectively represent the entire PSD, given the fact that two cements with different ratios of fine-to-coarse particles and described by different PSD can possess the same Blaine value [15, 16].

The differences in PSD curves determined under laboratory and industrial mill conditions were noticed by several researchers in the cement and mineral grinding industries [8, 10, 12]; the laboratory tests yielded significantly wider PSD curves than those experienced in practice. ASTM C465 Standard Specification for GAs related such changes to cement flowability and mill retention time (MRT) during grinding [17]. The MRT can be defined as the average time necessary for the bulk material to pass through the tube mill [18]. Hence, to properly evaluate GA effect on cement properties, the standard recommends the realization of full-scale tests over enough time to ensure reaching equilibrium conditions and stable CL [17].

In the literature, limited attempts have been made to quantify the scale effect (i.e., industrial versus laboratory mill) that could result from GA additions on cement fineness and properties. This research project was initiated following an industrial grinding test undertaken to validate the effect of glycol and amine-based GAs on Ec and cement performance. It presents data collected over 2 consecutive days of clinker grinding in real-scale closed-circuit tube mill operating at around 90 ton/hr. Results obtained were compared with those determined using a 50-liter laboratory grinding mill. This paper can be of particular interest to cement manufacturers, GA suppliers, and researchers dealing with processing and testing procedures of cement and clinker materials.

2. Materials Used and Testing Methods

2.1. Materials. Industrial clinker used for the production of ASTM C150 Type I cement [4], natural pozzolan meeting the requirements of ASTM C618 Class N [19], and gypsum materials were employed. Their ratio in the cement produced was maintained at 86.5%, 8.5%, and 5%, respectively. The materials chemical composition and PSD are presented in Table 1.

Two commercially available GAs were tested in this study. The glycol-based GA is composed by DEG and PG chemicals; it is referred to as grinding aid and pack-set inhibitor in the cement industry. Its active chemicals determined by Karl Fischer method, specific gravity, and pH were 64%, 1.08, and 7.8, respectively. The second GA is amine-based; it is commonly used as grinding aid and strength enhancer in the cement industry. Its main components include TIPA and TEA; the active chemicals, specific gravity, and pH were 60%, 1.09, and 7.2, respectively.

2.2. Testing Methods. The cement fineness characteristics were evaluated using the Blaine measurement, sieve residue, and PSD curve. The Blaine was determined using the air permeability apparatus as per ASTM C204 Test Method [20], while the 45 and 90 μm residues referred to as R-45 and R-90, respectively, were determined using a mechanical shaker. A laser particle size diffraction analyzer (Analysette 22 NanoTec Plus) capable of measuring particle sizes varying from 0.01 to 2000 μm was used for cement particle measurements. The apparatus complies with ISO 13320 technical requirements, with reproducibility (d_{50}) less than 1%. The equipment generates high-speed data processing at 5000 cycles per second within an entire measuring time less than 2 minutes and yields high-accuracy measurements that deviate by not more than ±0.4% from standard samples.

Table 1: Chemical composition and grading of clinker, pozzolan, and gypsum.

	Clinker	Pozzolan	Gypsum
SiO_2, %	20.6	73.2	2.7
Al_2O_3, %	6.32	15.3	0.53
Fe_2O_3, %	4.3	4.4	0.39
CaO, %	64.2	2.8	32.5
MgO, %	1.86	2.25	1.5
SO_3, %	0.22	0.13	43.1
Percent retained on			
9.51 mm	1.2	3	0
4.76 mm	7.3	5.6	0.6
2.38 mm	3.7	6.2	3.5
1.19 mm	26	12.3	16.8
0.595 mm	11.5	13	24.4
0.297 mm	26.5	25.6	22.1
0.149 mm	14	20.5	14.5
0.074 mm	7.8	8.8	16
Pan	2	5	2.1

The cement PSD curves were deducted by fitting the laser diffraction data into the Rosin-Rammler-Sperling-Bennett (RRSB) function given as [21]

$$Q(x) = 1 - \exp\left[-\left(\frac{x}{d_0}\right)^n\right]. \quad (1)$$

x refers to the measured particle size in μm, $Q(x)$ is the cumulative fraction passing function, n is the slope of size distribution reflecting the narrowness or wideness of PSD (the higher n means a narrower PSD), and d_0 indicates the powder fineness in μm that corresponds to 63.2% cumulative passing value on the distribution curve. The resulting correlation coefficients (R^2) of the regression lines built throughout this project between $\ln(x)$ and $\ln[\ln(1/1 - Q(x))]$ varied between 0.92 and 0.96.

The water demand required to achieve normal consistency was determined by mixing 650 g of ground cement with a measured quantity of water, as per ASTM C187 Test Method [22]. Using the same cement paste produced for normal consistency, the Vicat initial and final setting times were then determined as per ASTM C191 Test Method [23]. The compressive strength was determined as per ASTM C109 Test Method [24]. Tests were performed using mortars prepared with 450 g of ground cement, 1350 g of normalized sand (EN 196-1), and fixed w/c of 0.485. The cubes were demolded the second day from casting and stored side by side in saturated limewater until the testing time of 1 and 28 days.

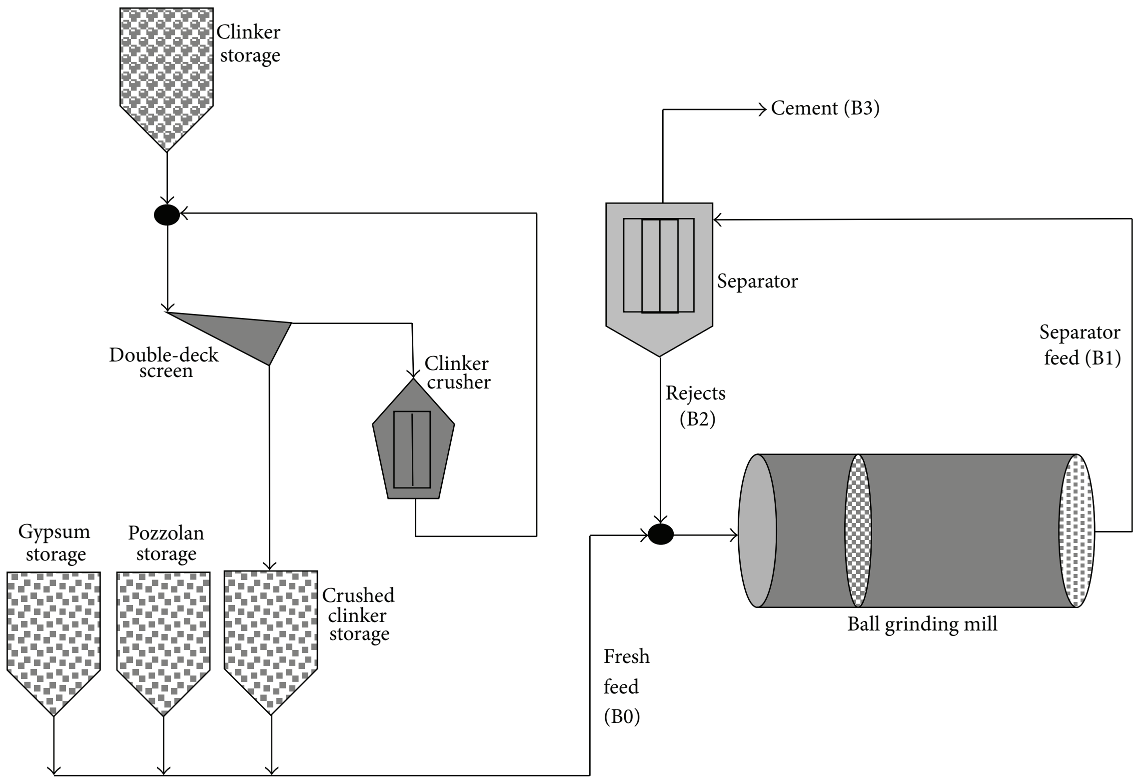

Figure 1: Various stages during industrial closed-circuit grinding tube mill.

Table 2: Design parameters for the tube ball mill and separator.

Tube ball mill	Compartment 1	Compartment 2	Rotor separator	
Internal diameter, m	3.6	3.7	Rotor diameter, m	2
Internal length, m	3.6	8.4	Rotor height, m	1.06
Filling degree, %	29.5	34	Motor power, kW	110
Charge weight, ton	43	138	Rotor speed, rpm	260
Ball size, mm	20 to 50	15 to 20	Fan power, kW	280
Mill motor power, kW	3200		Air flow, m^3/min	1500
Mill speed, rpm	17			
Fan motor power, kW	150			
Production rate, ton/hr	90 (design value)			

3. Test Results and Discussion

3.1. Data Obtained from Industrial Tube Mill

3.1.1. Description of Mill Employed. Industrial closed-circuit tube (or ball) mill schematically presented in Figure 1 was used for cement production. The clinker initially passes through a double-deck screen, where all particles larger than 10 mm are sent to a precrusher. A measured fresh feed mixture (B0) of precrushed clinker, gypsum, and pozzolan is introduced in the mill. After grinding, an elevator conveys the entire ground material (B1) to a rotor separator where it is divided into two fractions. The coarse fraction constitutes the separator rejects (B2) that is sent back to the mill for an additional cycle of grinding, whereas the fine fraction becomes the final product (B3). During steady-state operation, the mill productivity is equal to B0 (or B3), since neither accumulation nor generation of new material takes place inside the mill. The CL is calculated as $B1/B3 = (B0+B2)/B0$. The design parameters of the industrial tube mill and rotor separator are given in Table 2.

3.1.2. Control of Grinding Mill Parameters. The industrial mill was operating without any GA. The first stage of testing consisted in ensuring uniformity of grinding parameters and sampling cement at regular time intervals for use as control mixtures. This stage was pursued over 3 hours; the data collected are summarized in Table 3. The fresh feed rate (B0), mill sound, mill motor power consumption, separator motor power, separator air flow rate, rejects (B2), and CL were equal

Table 3: Data collected over time during industrial grinding without or with GA.

Day/time, hr:min	GA, g/ton	Feed (B0), ton/hr	Mill sound, dB	Mill motor power, %	Rotor motor, kW	Air flow rate, m^3/min	Rejects (B2), ton/hr	CL	Blaine, cm^2/g
1/0:00	**0**	**90.5**	**82**	**79.3**	**108.4**	**1366**	**38.8**	**1.43**	**3820**
1/1:00	**0**	**91**	**83.3**	**79.1**	**105.6**	**1380**	**40.7**	**1.45**	**3840**
1/2:00	**0**	**90.5**	**81.9**	**79.3**	**108**	**1365**	**38.9**	**1.43**	**3885**
1/3:00	**0**	**91.5**	**82.7**	**79.3**	**108.3**	**1294**	**39.6**	**1.43**	**3850**
1/3:30	530	105.5	85.4	75.8	126.2	1423	97	1.92	4020
1/4:00	530	107	90	75	135.3	1325	86.6	1.81	3745
1/5:00	530	108.2	87.7	76.7	134	1290	97.5	1.90	3770
1/6:00	530	114	86.9	81.7	142.6	1264	87.8	1.77	3820
1/7:00	530	110.4	84	80.4	136.5	1255	83	1.75	3905
1/8:00	**530**	**111.6**	**83.4**	**78.8**	**138.8**	**1268**	**86.6**	**1.78**	**3790**
1/9:00	**530**	**110**	**82.1**	**79.1**	**140.2**	**1290**	**90.3**	**1.82**	**3880**
1/10:00	**530**	**109.3**	**82.9**	**79.2**	**135.7**	**1302**	**91.2**	**1.83**	**3820**
1/11:00	**530**	**110.5**	**83.3**	**79**	**141.9**	**1277**	**88**	**1.80**	**3745**
2/0:00	460	97.6	86.1	74	113.5	1310	54.7	1.56	3660
2/0:30	460	99	85	75.9	113.8	1406	72	1.73	3835
2/1:00	460	100.6	85.7	76.1	122	1415	69.5	1.69	4105
2/2:00	460	104	78.3	80.4	120.7	1340	63.7	1.61	4000
2/3:00	460	103.1	81.3	78.5	121	1303	63.5	1.62	3860
2/4:00	**460**	**103.6**	**80.7**	**78.8**	**128.1**	**1304**	**60.4**	**1.58**	**3825**
2/5:00	**460**	**104.2**	**82**	**79.6**	**130**	**1283**	**66**	**1.63**	**3905**
2/6:00	**460**	**105.3**	**77.6**	**81**	**126.5**	**1294**	**65.8**	**1.62**	**3880**
2/7:00	**460**	**104.4**	**79.5**	**78.8**	**126**	**1291**	**63.9**	**1.61**	**3845**

Values in bold correspond to stable mill conditions.
Glycol-based GA was used in the first testing day, while amine-based one was used in the second day.

to 91 ± 0.5 ton/hr, 82.5 ± 1 dB, 79.2% ± 0.1%, 107.6 ± 2 kW, 1350 ± 50 m^3/min, 39.5 ± 1 ton/hr, and 1.44 ± 0.01, respectively. The product's temperature leaving the mill (B1) hovered around 97 ± 3°C, and Blaine fineness was within 3850 ± 35 cm^2/g. The resulting Ec calculated as the ratio between the consumed mill motor power and B0 was around 27.91 ± 0.2 kWh/ton.

Then, sprinkling of glycol-based GA over the fresh feed introduced in the mill started at a rate of 530 g/ton using an automatic dispenser. The grinding parameters were adjusted over time to maximize mill productivity under stable conditions while achieving similar Blaine fineness as the control mix (i.e., Blaine of 3850 ± 75 cm^2/g). For instance, the mill sound is an indicator of filling state in mill compartments during operation [10, 25]; an emptier mill will produce a louder sound, whereas the increased amounts of clinker will dampen the clanking noise and result in lower decibel (dB) values. Hence, this index sharply increased to around 90 dB during the first hour of GA addition, thus reflecting improved clinker processing and reduced MRT (Table 3). The decrease in motor power consumption from 79% to 74.1% of ultimate capacity is another indicator of improved clinker processing. The mill sound and power consumption were readjusted to around 83 ± 0.9 dB and 79% ± 0.2%, respectively, by increasing gradually B0 to 110.4 ± 1.1 ton/hr (Table 3). Further increases in B0 would not be desirable as this may abuse the mill motor capacity (an 80% threshold value was placed by the cement company). The corresponding Ec decreased from 27.91 kWh/ton when grinding was performed without GA to 22.92 kWh/ton; this can be directly attributed to the organic GA molecules adsorbed on clinker surfaces, thus reducing cement agglomeration with direct consequences on B0 and Ec [2, 3, 8].

The separator's rotor speed (or motor power) and air flow rate are crucial parameters for controlling cement fineness and residue [10, 11, 25, 26]. Hence, increasing the rotor speed will elevate the product's fineness and increase the rejects (B2), since more particles will be returned back to mill. Conversely, higher air flow inside the separator would carry particles of larger size into the fine stream, therefore decreasing cement fineness with reduced B2. Around 4 hours was necessary to regulate B0, rotor motor power, and air flow rate in order to obtain stable mill conditions delivering cement fineness close to that of the control mix. The B2 varied between 83 and 97 ton/hr during the first 4 hours and thereafter stabilized at around 89.3 ± 3.5 ton/hr. The corresponding CL ranged from 1.75 to 1.92 and stabilized at around 1.81 ± 0.3.

The increase in CL due to GA additions is a common phenomenon in the cement grinding industry, mostly attributed to a decrease in MRT and improved cement flowability [11, 18, 26]. In other words, the use of GA makes coarser the product that leaves the mill (B1), thereby requiring increased number

TABLE 4: Ec and cement properties after reaching stable conditions in industrial mill grinding.

	Control cement	Cement with glycol-based GA at 530 g/ton	Cement with amine-based GA at 460 g/ton
Ec, kWh/ton	27.91 (0.56%)	22.92 (1.09%)	24.39 (0.79%)
Blaine, cm^2/g	3850 (0.71%)	3810 (1.48%)	3865 (0.92%)
R-90, %	2.76 (5.52%)	0.9 (5.55%)	1.17 (9.89%)
R-45, %	16.07 (5.45%)	13.87 (3.78%)	14.57 (3.43%)
n	0.946 (0.69%)	1.052 (0.14%)	1.041 (0.47%)
d_0, μm	19.2 (4.42%)	16.76 (3.28%)	17.56 (4.77%)
Water demand, %	28.7 (0.35%)	28.5 (1.75%)	28.8 (0.8%)
Final setting, min	220 (2.73%)	266 (2.86%)	245 (7.04%)
1-day compression, MPa	14.46 (3.81%)	12.26 (1.69%)	14.83 (5.06%)
28-day compression, MPa	52.13 (1.93%)	54.67 (2.65%)	56.8 (6.33%)

The COV values are given between parentheses.

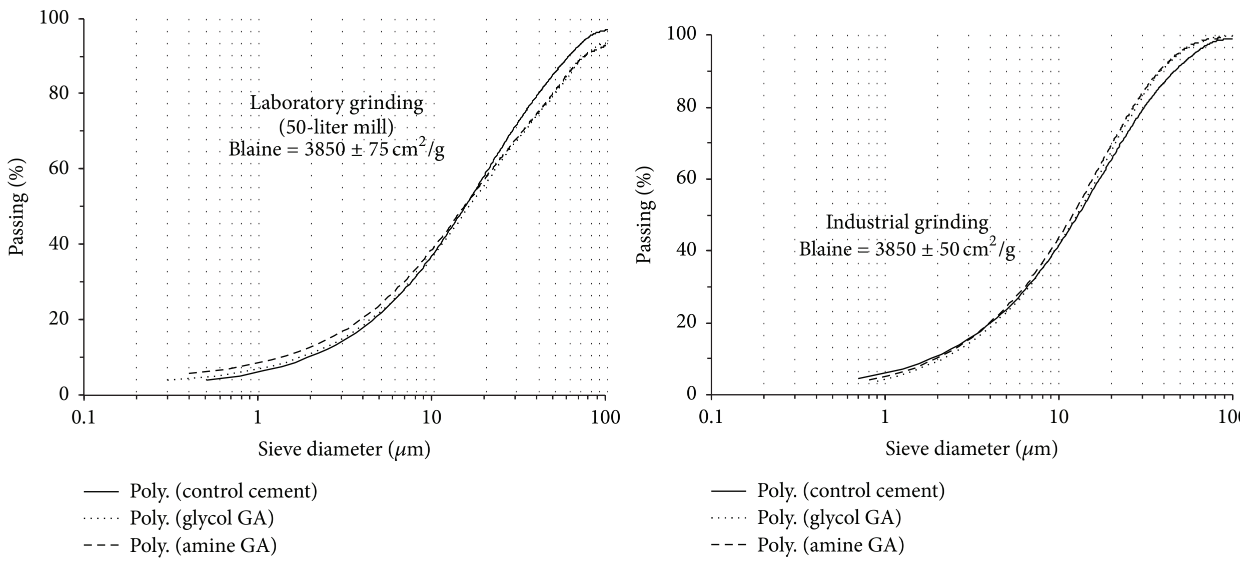

FIGURE 2: PSD curves obtained under industrial and laboratory grinding conditions of control cement and those containing GAs.

of passages through the system to reach the targeted fineness level. After reaching stable mill conditions, the grinding tests were pursued for 4 additional hours, whereby samples of cement were taken at regular time intervals. The product's temperature leaving the mill (B1) hovered around 102 ± 4°C.

The dispensing of glycol-based GA was stopped overnight, and industrial testing resumed the second day using the amine-based one. Again, after assuring stability of mill conditions, dispensing of the amine-based GA started at relatively reduced rate of 460 g/ton (this was due to economic reasons established by the cement company). As earlier, the tube mill and separator parameters were adjusted to ensure stable grinding conditions delivering cement fineness close to that determined on the control mix (Table 3). After around 4 hours of grinding, the B0 reached 104.38 ± 1 ton/hr, while mill sound, motor power consumption, separator motor power, separator air flow, B2, and CL were equal to 79.9 ± 1.5 dB, 79.6% ± 1.4%, 127.6 ± 2.4 kW, 1293 ± 11 m^3/min, 64 ± 4 ton/hr, and 1.61 ± 0.3, respectively. The Ec that resulted from the amine-based GA was 24.39 kWh/ton. It is to be noted that the air speed within the tube mill varied from around 1.58 m/s when grinding was realized without GA to 1.73 and 1.71 m/s when the glycol- and amine-based GAs were used, respectively.

3.1.3. Effect of GAs on Cement Fineness and Properties: Industrial Grinding. Table 4 summarizes the properties of control cement and those containing GAs that resulted from industrial grinding after reaching stable conditions (the Ec values are also given). It is to be noted that the data reported in Table 4 are averages of 3 to 4 measurements collected after reaching stable mill conditions. The coefficient of variation (COV) for each measurement determined as the ratio between standard deviation and mean values, multiplied by 100, is given.

The PSD curves of cement mixtures sampled after reaching stable mill conditions are plotted in Figure 2 (this figure also plots the various PSD curves determined under laboratory conditions that will be discussed later in text). Although the Blaine values are quite close to each other and varied within 3850 ± 50 cm^2/g, it is clear that GA additions affected PSD curves including a reduction in the percentage of very fine particles smaller than around 5 μm as well as those retained on coarser sieve diameters. For example, the R-90 decreased from 2.76% for the control mix to 0.9% and 1.17% with the addition of glycol- and amine-based GA, respectively. This resulted in narrower PSD curves together with their shifting towards smaller diameters. Hence, n increased from 0.946 for the control cement to 1.052 and 1.041 when grinding was performed using the glycol- and amine-based GA, respectively. The corresponding d_0 decreased from 19.2 to 16.76 and 17.56 μm, respectively. The narrowing of PSD curves due to GAs is well proven in the cement industry; it is related to an improvement in cement flowability [12, 27].

The water demand necessary to achieve normal consistency of various sampled mixtures remained almost invariable at 28.65% ± 0.15% (Table 4). Nevertheless, the setting time remarkably increased from 220 min for the control cement to 266 min when the glycol-based GA was used. For given Blaine fineness, this can be attributed to a combination of different phenomena including the reduction of cement particles finer than around 5 μm that mainly influence the setting [14]. Additionally, the adsorption of glycol monolayers onto cement grains can partly block hydration reactions, just like what happens with the use of water reducers in concrete mixtures [3, 8]. Because of similar reasons, the 1-day compressive strength decreased from 14.46 MPa for the control mortar to 12.26 MPa for that prepared using cement containing glycol GA (Table 4).

The setting time that resulted from cement containing amine-based GA was relatively lower than the one obtained using glycol GA (i.e., 245 versus 266 min, resp.). This can be attributed to the TIPA existing in the former GA; those molecules are known by their capacity to promote cement hydration reactions with consequently reduced setting times [2, 6, 7]. The resulting 1-day compressive strength slightly increased to 14.83 MPa.

The 28-day compressive strength increased from 52.13 MPa for the control mortar to 54.67 MPa for the one made using cement ground with glycol-based GA. This strength improvement can be related to enhanced cement PSD possessing increased amount of fraction grains varying from around 5 to 25 μm [14]. The increase in 28-day compressive strength was more accentuated (i.e., 56.8 MPa) when the amine-based GA was used. Concurrent to the enhancement in PSD, the remarkable increase in compression up to 56.8 MPa can be related to the TIPA molecules that improve cement hydration reactions and lead to increased strengths [2, 6, 7, 28].

3.2. Grinding Tests Performed under Laboratory Conditions

3.2.1. Description of Laboratory Mill. A 50-liter laboratory grinding mill having a drum diameter, length, and rotational speed of 400 mm, 400 mm, and 50 rpm, respectively, was used in this testing program (Figure 3). The mill was connected to an electric counter for monitoring Ec in kWh/ton determined as (Tc × 1000)/(mass of ground mix in kg × mill factor), where Tc refers to the amount of electricity in kWh consumed during the grinding time interval and mill factor equal to 3 as per the manufacturer calibration procedure. A total of 80 kg steel balls (36 kg of 20 mm diameter and 44 kg of 30 mm diameter) were used for grinding, thus making a filling degree equal to 34.2%. The mill operated in a room where ambient temperature and relative humidity were 23 ± 2°C and 55 ± 5%, respectively.

FIGURE 3: Photo of the 50-liter laboratory grinding mill.

3.2.2. Approach Used for Clinker Grinding. Initially, a control mix was prepared by grinding 6 kg of materials without any GA until achieving a Blaine fineness similar to that obtained from industrial testing, that is, 3850 ± 75 cm^2/g. The percentages of clinker, pozzolan, and gypsum in the ground mix were maintained similar to those used in industrial tests. The approach consists in grinding the materials for a certain elapsed time, stopping the mill, and sampling around 100 grams to check whether the Blaine became close to the targeted value. If not, additional grinding is performed. The control mix was found to require an Ec of 43.27 kWh/ton (i.e., grinding time of 29.5 min).

Two other grinding tests were then realized by sprinkling the preselected glycol- and amine-based GA concentrations of 530 or 460 g/ton onto the 6 kg feed materials. Grinding stopped when the cement mixtures reached Blaine fineness equivalent to the control mix. The temperature of cement obtained right after the end of grinding hovered around 32 to 36°C. It is to be noted that each test was repeated twice to evaluate the COV of various measurements, as summarized in Table 5.

3.2.3. Effect of GAs on Cement Fineness and Properties: Laboratory Grinding. As expected, the addition of GA led to reduced Ec, given the decrease in cement agglomeration, that is, from 43.27 kW/ton for the control mix to 39.23 and 40.33 kWh/ton for those containing glycol- and amine-based GA, respectively.

The GA addition was associated with an increase in R-45 and R-90 values (Table 5), given the reduced Ec applied

Table 5: Ec and cement properties following laboratory grinding.

	Control cement		Cement with glycol-based GA at 530 g/ton		Cement with amine-based GA at 460 g/ton	
Test number	1	2	1	2	1	2
Ec, kWh/ton	43.27	43.27	39.6	38.87	40.33	40.33
	43.27 (0%)		39.23 (1.31%)		40.33 (0%)	
Blaine, cm^2/g	3870	3825	3810	3775	3880	3790
	3848 (0.82%)		3792 (0.65%)		3835 (1.66%)	
R-90, %	5.8	5.3	6.7	7.4	5.7	6.4
	5.55 (6.37%)		7.05 (7.02%)		6.05 (8.2%)	
R-45, %	18.3	17.7	23	23.3	19.6	22
	18 (2.36%)		23.15 (0.91%)		20.8 (8.16%)	
n	0.893	0.888	0.782	0.81	0.748	0.771
	0.891 (0.39%)		0.796 (2.48%)		0.759 (2.14%)	
d_0, μm	23.5	25.1	27.8	26.92	29	25.8
	24.3 (4.65%)		27.35 (2.32%)		27.4 (8.26%)	
Water demand, %	27.7	27.8	27.9	27.5	27.7	27.3
	27.75 (0.25%)		27.7 (1.02%)		27.5 (1.03%)	
Final setting, min	210	215	225	215	205	190
	212.5 (1.7%)		220 (3.21%)		197.5 (5.37%)	
1-day compression, MPa	14.3	14.7	16.3	15.9	17	15.8
	14.5 (1.95%)		16.1 (1.75%)		16.4 (5.17%)	
28-day compression, MPa	46.4	44.8	42	44.2	54.3	49.2
	45.6 (2.48%)		43.1 (3.61%)		51.7 (6.97%)	

The mean of two values is considered for analysis. The COV is given between parentheses.

during processing [8]. For example, the R-45 increased from 18% for the control cement to 23.15% and 20.8% when the glycol- and amine-based GA was used, respectively. Nevertheless, a certain amount of fine material was produced during grinding of mixtures containing GA due to reduced level of agglomeration, thus widening the PSD curves while maintaining similar Blaine fineness (refer to Figure 2). Hence, the n parameter decreased from 0.891 for the control cement to 0.796 and 0.759 for those prepared with glycol- and amine-based GA, respectively. The corresponding d_0 increased from 24.3 to 27.35 and 27.4 μm, respectively.

Compared to the control mix, the incorporation of GA did not remarkably alter water demand and setting time; those measurements varied within 27.6% ± 0.15% and 210 ± 15 min, respectively (Table 5). Nevertheless, remarkable increase in early strength occurred when both GAs were used (i.e., 14.5 MPa for the control mortar compared to 16.1 and 16.4 MPa for glycol and amine GA, resp.). The increase in 1-day compression could mostly be attributed to an increase in the amount of fine cement particles, as a consequence of GA additions [6, 7].

The 28-day compression was differently affected by GA additions, as compared to the control mortar that exhibited strength of 45.6 MPa (i.e., values of 43.1 and 51.7 MPa were measured for mortars made using cement containing glycol and amine GA, resp.). The decrease in 28-day compression that resulted from glycol-based GA could be related to increased percentage of cement particles coarser than 25 μm, especially knowing that glycol chemicals added at relatively low to moderate rates do not affect the development of compressive strength [7, 8, 14]. Conversely, the increase in compressive encountered with the use of amine-based GA can be attributed to the presence of TIPA molecules, thus promoting cement hydration reactions and resulting in higher late-age strengths [2, 6, 7].

3.3. *Comparison of Data Obtained from Industrial versus Laboratory Tests*

3.3.1. Effect of GAs on Mill Performance. The variations in Ec due to GA additions that resulted from industrial and laboratory grinding are plotted in Figure 4. Compared to industrial tests, excessively high Ec was required to secure a cement Blaine of 3850 ± 75 cm^2/g when grinding was realized in the laboratory mill. For instance, the Ec of 27.9 kWh/ton needed for industrial grinding of the control mix increased to 43.27 kWh/ton in laboratory grinding. The addition of glycol- and amine-based GA led to reduced Ec to 39.23 and 40.33 kWh/ton, respectively, albeit still substantially higher than those registered from industrial grinding. The significantly reduced absolute Ec values that resulted from industrial grinding could be related to a combination of phenomena including improved grinding energy due to the presence of 2 compartments with different ball sizes and

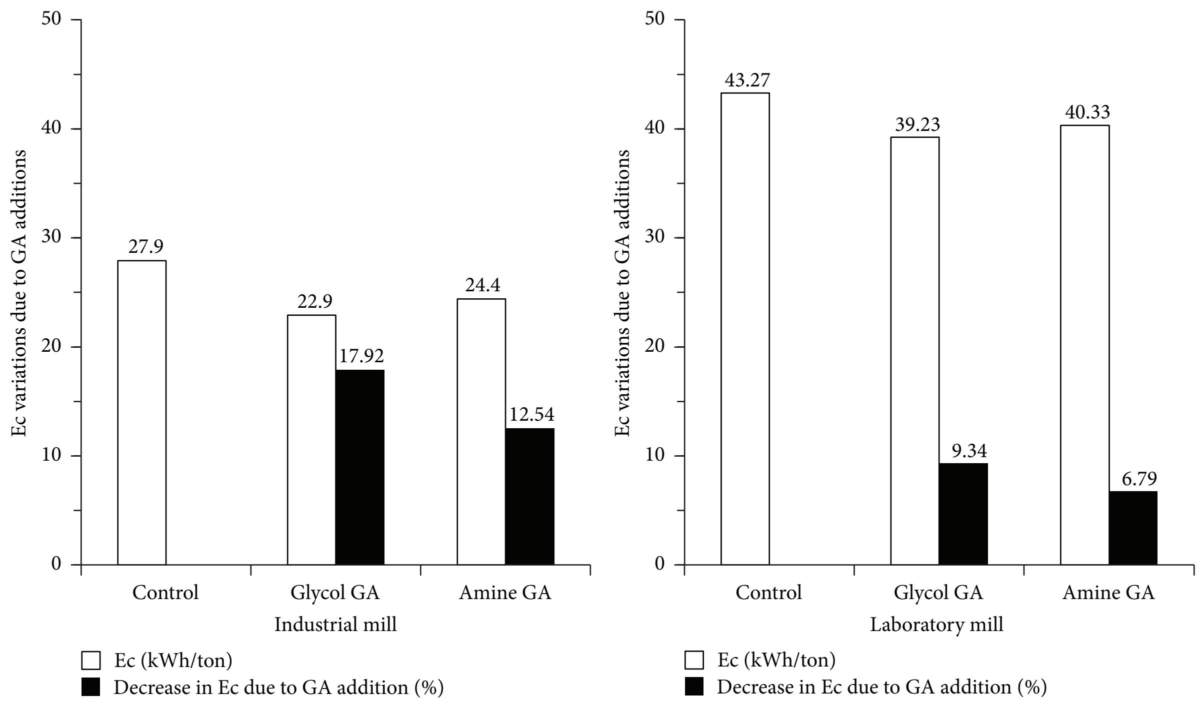

FIGURE 4: Ec and its rate of decrease due to GA additions during industrial and laboratory grinding.

enhanced screening efficiency associated with the CL [9, 10, 25, 29].

Regardless of the grinding conditions (i.e., industrial versus laboratory), the use of glycol-based GA showed enhanced reduction in Ec as compared to the amine-based one (Figure 4). Yet, it is important to note that the decrease in Ec due to GA is around twofold higher when grinding was performed in industrial mill, as compared to laboratory mill. For example, the decrease in Ec varied from 17.92% to 12.54% when industrial grinding was realized using the glycol- or amine-based GA, respectively. Such variation was from 9.34% to 6.79% in the laboratory mill, respectively. Among the most influential parameters that may lead to increased Ec variations in industrial mills could be the ventilation system that helps optimizing the MRT at which the product passes through the tube as a result of reduced cement agglomeration [11, 18]. In other words, this suggests that the assessment of GA influence on Ec under laboratory conditions is adequate for comparison purposes of various GAs within each other; however, such tests underestimate the actual performance that could be achieved in real-scale mills.

3.3.2. Comparison of Cement Fineness. The variations in R-45, d_0, and n determined on control cement and those containing glycol- and amine-based GA following industrial or laboratory grinding are plotted in Figure 5. Compared to data obtained from industrial tests, it is clear that laboratory grinding widens the cement PSD curve and shifts it towards higher diameters. For example, the n parameter of the control cement decreased from 0.946 to 0.891 when grinding was realized in industrial or laboratory conditions, respectively. The corresponding d_0 increased from 19.2 to 24.3 μm, respectively. Additionally, it is important to note that the widening of PSD and shifting towards larger diameters were particularly accentuated with GA additions during laboratory grinding, that is, unlike the steeper trend that resulted from industrial tests. For instance, n of 1.052 obtained from industrial test realized with glycol-based GA dropped considerably to 0.796 with laboratory grinding, while the corresponding d_0 increased from 16.8 to 27.35 μm, respectively.

The remarkable changes in cement PSD curves generated during industrial and laboratory grinding are well documented in the literature. For example, Katsioti et al. [27] reported that GAs added during clinker processing in industrial mills lead to narrow PSD, given the reduced percentage of very fine particles lower than around 1 μm. Conversely, when grinding is realized in laboratory mills, the percentage of such fine particles increases due to reduced cement agglomeration resulting from the presence of GAs [8, 12]. This phenomenon is mostly attributed to different mill operational modes (i.e., mainly the CL) that directly influence amount of fine particles including the overall PSD curves.

3.3.3. Comparison of Cement Properties. The comparison between industrial and laboratory grinding following GA addition on water demand, setting time, and compressive strength is plotted in Figure 6. Generally speaking, laboratory grinding led to reduced water demand (i.e., 27.6% ± 0.15% compared to 28.65% ± 0.15% in industrial grinding), which could be related to enhanced packing density resulting from increased PSD wideness (i.e., lower n factor) [8, 13]. The setting time remained almost unchanged at 220 ± 10 min, with the exception of two cement mixtures including the one industrially ground with glycol-based GA (i.e., 265 min)

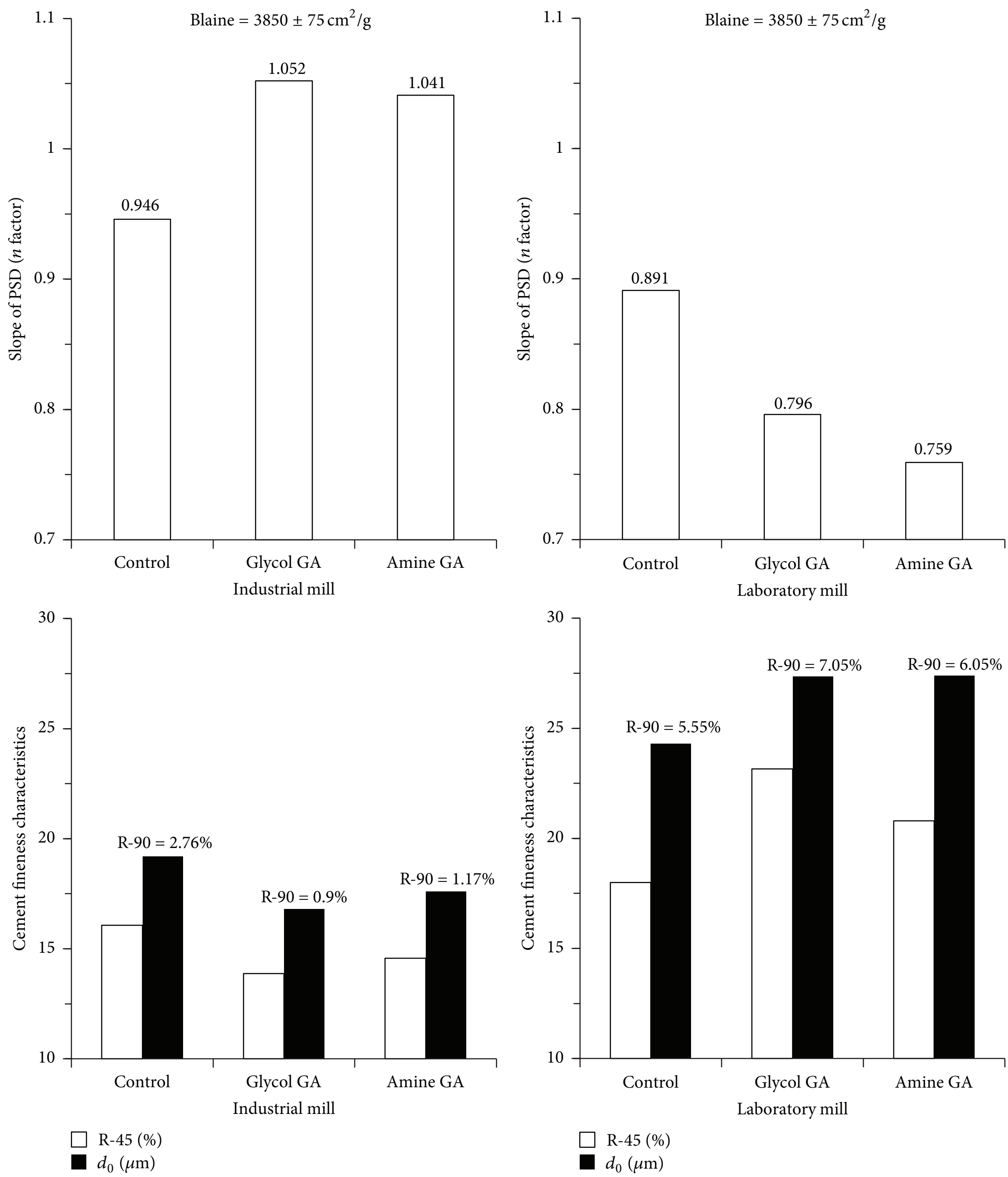

Figure 5: Comparison of cement fineness characteristics that resulted from industrial and laboratory grinding mills due to GA additions.

and the one ground in laboratory using the amine-based GA (i.e., 197.5 min). In the former case, the excessive lengthening in setting can be attributed to the couple effect of reduced fine particles as well as adsorption of glycol molecules onto cement grains that could retard hydration reactions over time [8]. Conversely, the reduced setting encountered in the latter case could be associated with increased fine cement particles generated during laboratory grinding and acceleration of hydration reactions due to the TIPA molecules [2, 6].

The early- and late-age compressive strengths are differently affected by the grinding method; hence, the highest 1-day strengths were achieved from laboratory grinding, while the highest 28-day values were obtained from industrial grinding. For instance, the 1-day compression for the mortar containing cement ground with glycol-based GA varied from 12.26 MPa in industrial grinding to 16.1 MPa in laboratory grinding. The corresponding 28-day compression varied from 54.67 to 43.1 MPa, respectively. As already noted, this

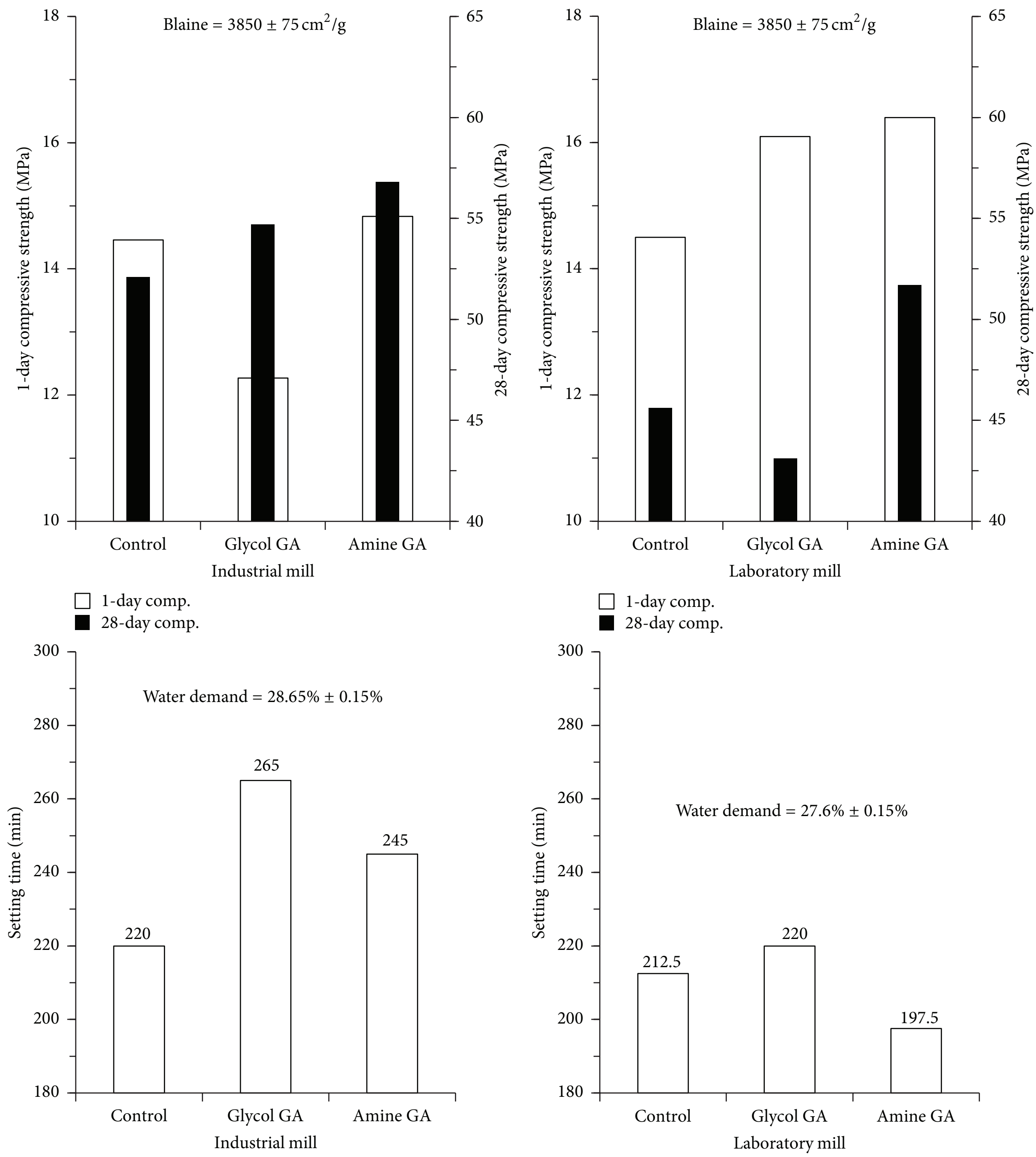

Figure 6: Comparison of cement properties that resulted from industrial and laboratory grinding mills due to GA additions.

can be related to variations in the fine-to-coarse cement particles generated from each grinding method and their influence on cement hydration reactions and strength development over time.

4. Summary and Conclusions

This research project was initiated following an industrial test undertaken to validate the effect of glycol- and amine-based GAs on mill performance and cement properties. It mainly seeks to evaluate the scale effect by comparing the results obtained from the closed-circuit tube mill operating at around 90 ton/hr to those determined using a 50-liter laboratory mill. Grinding was realized for fixed Blaine fineness of $3850 \pm 75\,cm^2/g$.

Compared to laboratory tests, remarkably reduced Ec was required during industrial grinding, given the adapted operational mode for enhanced clinker processing such as the presence of 2 compartments and improved screening associated with the rotor separator, ventilation, and CL.

The use of glycol-based GA led to reduced Ec, as compared to the amine one albeit such reduction was around twofold higher when grinding was performed in industrial mill, as compared to laboratory mill. This suggests that the assessment of GA influence on Ec under laboratory conditions is adequate for comparison purposes of various GAs; however, such tests underestimate the actual performance that could be achieved in real-scale mills.

Compared to industrial tests, the cement PSD curves widened and shifted towards higher diameters when grinding was performed under laboratory conditions. The PSD widening was particularly accentuated with GA additions, unlike the steeper trend that resulted from industrial tests. Cement mixtures ground in laboratory exhibited slightly reduced water demand, compared to those ground in industrial scale. The setting time remained almost unchanged at 230 ± 15 min, with the exception of the cement industrially ground with glycol GA (i.e., 265 min) and the one ground in laboratory using amine GA (i.e., 197.5 min). On the other hand, the highest 1-day compressive strength was achieved from laboratory grinding, while the highest 28-day strength was obtained from industrial grinding. The changes in cement properties with grinding method were attributed to variations in fine-to-coarse cement particles associated with interferences of glycol and TIPA molecules with hydration reactions developed over time.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

The author wishes to acknowledge the support provided by Holderchem Building Chemicals, Baabda, Lebanon.

References

[1] I. Teoreanu and G. Guslicov, "Mechanisms and effects of additives from the dihydroxy-compound class on Portland cement grinding," *Cement and Concrete Research*, vol. 29, no. 1, pp. 9–15, 1999.

[2] J. P. Perez, A. Nonat, S. Pourchet, M. Garrault, and C. Canevet, "Why TIPA leads to an increase in the mechanical properties of mortars whereas TEA does not," *ACI Materials Journal*, vol. 217, pp. 583–594, 2003.

[3] J. J. Assaad, "Quantifying the effect of clinker grinding aids under laboratory conditions," *Minerals Engineering*, vol. 81, pp. 40–51, 2015.

[4] ASTM C150, "Standard specification for cement," ASTM C150-12, ASTM International, West Conshohocken, Pa, USA, 2012.

[5] J. J. Assaad, S. E. Asseily, and J. Harb, "Effect of specific energy consumption on fineness of portland cement incorporating amine or glycol-based grinding aids," *Materials and Structures*, vol. 42, no. 8, pp. 1077–1087, 2009.

[6] P. J. Sandberg and F. Doncaster, "On the mechanism of strength enhancement of cement paste and mortar with triisopropanolamine," *Cement and Concrete Research*, vol. 34, no. 6, pp. 973–976, 2004.

[7] J. J. Assaad, S. E. Asseily, and J. Harb, "Use of cement grinding aids to optimise clinker factor," *Advances in Cement Research*, vol. 22, no. 1, pp. 29–36, 2010.

[8] J. J. Assaad and C. A. Issa, "Effect of clinker grinding aids on flow of cement-based materials," *Cement and Concrete Research*, vol. 63, pp. 1–11, 2014.

[9] H. Benzer, L. Ergun, A. J. Lynch et al., "Modelling cement grinding circuits," *Minerals Engineering*, vol. 14, no. 11, pp. 1469–1482, 2001.

[10] G. G. Mejeoumov, *Improved cement quality and grinding efficiency by means of closed mill circuit modeling [Ph.D. thesis]*, Texas A&M University, College Station, Tex, USA, 2007.

[11] J. Bhatty, F. Miller, and S. Kosmatka, *Innovations in Portland Cement Manufacturing*, CD-ROM: SP400, Portland Cement Association, Skokie, Ill, USA, 2004.

[12] B. Fidan, *A comparative analysis of the recent cement grinding systems with particle-based influences on cement properties [Ph.D. thesis]*, Middle East Technical University (METU), Ankara, Turkey, 2011.

[13] Y. M. Zhang and T. J. Napier-Munn, "Effects of particle size distribution, surface area and chemical composition on Portland cement strength," *Powder Technology*, vol. 83, no. 3, pp. 245–252, 1995.

[14] D. P. Bentz, E. J. Garboczi, C. J. Haecker, and O. M. Jensen, "Effects of cement particle size distribution on performance properties of Portland cement-based materials," *Cement and Concrete Research*, vol. 29, no. 10, pp. 1663–1671, 1999.

[15] C. Ferraris, V. Hackley, A. Avilés, and C. Buchanan, "Analysis of the ASTM Round-Robin test on particle size distribution of portland cement: phase I," National Institute of Standards and Technology Report 6883, Technology Administration, US Department of Commerce, Washington, DC, USA, 2002.

[16] G. Delagrammatikas and S. Tsimas, "Grinding process simulation based on Rosin-Rammler equation," *Chemical Engineering Communications*, vol. 191, no. 10, pp. 1362–1378, 2004.

[17] ASTM C465, "Standard specification for processing additions for use in the manufacture of hydraulic cements," ASTM C465-10, ASTM International, West Conshohocken, Pa, USA, 2010.

[18] L. Sottili and D. Padovani, "Effect of grinding aids in the cement industry," in *Proceedings of the Petrochem Conference*, p. 16, Saint Petersburg, Russia, April 2002.

[19] ASTM C618-12a, "Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete," ASTM C618-12, ASTM International, 2012.

[20] ASTM, "Standard test methods for fineness of hydraulic cement by air-permeability apparatus," Document no. ASTM C204-11, ASTM International, 2011.

[21] H. G. Merkus, *Particle Size Measurements: Fundamentals, Practice, Quality*, Technology and Engineering, Springer, 2009.

[22] ASTM, "Standard test method for amount of water required for normal consistency of hydraulic cement paste," Document no. ASTM C187-11e1, ASTM International, 2011.

[23] ASTM C191, "Standard test methods for time of setting of hydraulic cement by Vicat needle," ASTM C191-08, ASTM International, West Conshohocken, Pa, USA, 2008.

[24] ASTM C109, "Standard test method for compressive strength of hydraulic cement mortars (using 2-in. or [50-mm] cube

specimens)," ASTM C109-12, ASTM International, West Conshohocken, Pa, USA, 2012.

[25] R. Schnatz, "Optimization of continuous ball mills used for finish-grinding of cement by varying the L/D ratio, ball charge filling ratio, ball size and residence time," *International Journal of Mineral Processing*, vol. 74, supplement, pp. S55–S63, 2004.

[26] M. Fuerstenau and K. Han, *Principles of Mineral Processing*, Society for Mining, Metallurgy, and Exploration, Littleton, Mass, USA, 2003.

[27] M. Katsioti, P. E. Tsakiridis, P. Giannatos, Z. Tsibouki, and J. Marinos, "Characterization of various cement grinding aids and their impact on grindability and cement performance," *Construction and Building Materials*, vol. 23, no. 5, pp. 1954–1959, 2009.

[28] T. S. Sverak, C. G. J. Baker, and O. Kozdas, "Efficiency of grinding stabilizers in cement clinker processing," *Minerals Engineering*, vol. 43-44, pp. 52–57, 2013.

[29] P. Alsop, *Cement Plant Operations Handbook for Dry Process Plants*, Tradeship Publications, Portsmouth, UK, 2001.