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The effects of fatty acids on the particle size distribution of the Portland cement

Ali Tugrul Albayrak · Muzaffer Yasar · M. Ali Gurkaynak · Ismet Gurgey

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Abstract The cement has to be ground fine enough and have the optimum particle size distribution (PSD) to meet the requirements such as strength properties and setting times in current standards. As it takes quite a long time to determine especially the late strength, grinding has to be based on the cement fineness and the PSD. In this study, the effects of fatty acids were investigated on the PSD of Portland cement. Experimental results showed that the fineness of the cement was decreased for that replaced with 0.025 wt.% lauric acid (LA), myristic acid (MA) and sunflower oil acid (SO), then increased for the other additions. The fineness measurements revealed that the cement grains aggregated for an amount of 0.025 % (w) during the grinding. Also, when the PSD of the ground cement is examined, the relationship between the saturated and the unsaturated components is evident that milling the cement clinker together with 0.1% (w) LA and 0.1 wt.% MA gave the finer cement from that with 0.1 wt.% SO.

Introduction

The greater the surface of the hydraulically active components, and therefore the higher the Blaine surface, the faster does the cement harden. Nevertheless, the Blaine value only gives an indication and not an absolute value, as it does not adequately reflect the PSD which is an important parameter for the grinding process and affects many properties of cement, such as compressive strength, fluidity, porosity, bleeding characteristics, hydration of cement, packing density and water demand. With regard to the strengths, the fraction of the cement between 0 and 7 μm is responsible for high early strengths, whereas the fraction between 0 and 25 μm contributes to strengths at all ages, especially the late ones and cement particles above 40 μm hydrate very slowly and their contribution to cement hardening is certainly of minor importance [1].

When cement clinker is ground using grinding aids, a narrower particle size range is generated as compared with cement without grinding agents, as the percentage of very fine particles, which only influence the setting time, is reduced. There are so many advantages of using grinding aids. For example, these are greater specific surface area, improved cement granulometry, lower grinding media consumption, higher separator efficiency and decrease of mill internal temperature [2]. Among these studies, the literature provides ample information about the effect of PSD on the properties of the cement.

Huiwen et al. [3] investigated the influences of different granulated blast furnace slag (GGBS) ground in a ball mill on cement properties and it was found that the PSD of GGBS processed by a ball mill is the widest. Also the additions change the early strength of the samples which are related to the surface area and PSD of GGBS. Seung et al. [4] searched that the effect of PSD of fly ash-cement system on the fluidity of the cement pastes using class F fly ash (63.0 SiO_2, 24.8 Al_2O_3, 4.6 Fe_2O_3, 2.3 CaO, 0.9 MgO, 1.0

A. T. Albayrak · M. Yasar (✉) · M. A. Gurkaynak · I. Gurgey
Department of Chemical Engineering, University of Istanbul, Avcilar, Istanbul 34320, Turkey
e-mail: yasar@istanbul.edu.tr

TiO_2, 1.2 Na_2O, 0.7 K_2O, 0.3 SO_3, 0.7 C, loss on ignition 1.1, based on the % weight) and show that the fluidity increases as the PSD becomes wider. The addition of transition metal oxides in cement raw meals influences the clinker porosity and the number of pores. For example, the Portland cement clinker containing MnO and Cr_2O_3 have increased porosity and larger pores [5]. On another work [6], it is reported that the highest values of the bleeding rate and capacity were exhibited by the mixes in which the slag with the medium range of PSD was included. Frigione and Marra [7] have demonstrated that the volume of hydrated product, therefore the mechanical strength, increases when the granulometric range decreases. Aiqin et al. [8, 9] reported that the more narrow the particle size distribution of cement, the faster the rate of hydration of cement is and that the wider the PSD, the higher is the packing density and the lower the water demand is.

In our previous work [10], the effects of SO, LA and MA on the surface area of the cement and the compressive strength of the concrete were examined. In this study, experimental results provided insight into the question of the optimum dosage of fatty acids as grinding aids.

In the current work, the objectives were to gain additional insight into the effects of fatty acids on the PSD of Portland cement.

Experimental

Materials

SO, LA and MA were supplied from Alemdar Chemical Industry, Gebze, Turkey. The chemical composition of the cement clinker, the shape and the dimensions of the box mill and the properties of the balls were also given in previous work [10].

Methods

The experiments were performed as described elsewhere [10]. To summarize, the total weight of a 2,000 g of the mixture was used for each experimental run. The balls occupied 17% of the space volume of the box mill. The speed and the grinding run time were 47 rpm, and 45 minutes, respectively. Determination of fineness was determined as the % retained by sieving a sample of 10 g cement ground on 0.045, 0.090 and 0.200 mm screen opening according to ASTM C430-96 [10, 11]. The density was found by multi pycnometer (Model MVP_1) according to ASTM C 188-95 [10, 12]. The specific surface was found by Blaine Star type ZZB/PC-MT according to ASTM C 204 [10, 13]. Determination of the consistency was performed by vicat apparatus with a cylindrical plunger according to ASTM C 187-98 [10, 14]. Determination of the initial and the final setting times was carried out by settling a needle in place of plunger according to ASTM C 191-01a [10, 15]. The PSD analyses were made using a Malvern Mastersizer instrument [4]. All analytical tests were carried out at the Akcansa Cement Factory Laboratories, Istanbul. The reproducibility of experimental points was checked separately at all experimental runs. The deviations of the experimental points were not statistically significant.

Results and discussions

Mechanism of agglomeration phenomena

Caking of material on liners and grinding media may be due to various causes. Their interactions giving rise to this undesirable phenomenon have not yet been fully explained. The main causal factors are static electricity, surface energy forces, adsorption and mechanical impact. According to static electricity theory, because of very fine particles in a mill become charged, and, if different materials are being ground, one part becomes positively charged and the other negatively. These opposite charges attract each other and the particles agglomerate. In the surface energy forces theory, atoms on the surface of a solid may not be completely saturated as to their valencies and form non-homogeneous fields on their surface. This unbalanced condition causes agglomeration in the mill. In the case of adsorption theory, individual particles adsorb a surface film of air. Presumably this film tends to prevent the particles from combining. However, if this film is removed in some way, the particles may then be free to combine more readily. Mechanical impact theory states that the grinding balls strike each other with such impact that the particles of material are rammed together and tamped upon the uneven ball surface. Because of the many causes and their interaction, it is not possible to lay down generally valid rules for the prevention of build-up. Therefore, grinding aids are used to prevent ball coating, agglomeration and consequently mill efficiency is increased. The majority of grinding aids are substances which become strongly adsorbed by the ground particles, so that surface energy requirements are satisfied and no bonds remain to attract other particles and cause agglomeration. By elimination of the surface energy forces which normally cause interparticle attraction, grinding aids improve cement flowability after grinding. The supplement of a grinding aid such fatty acids in the mill triggers spreading of the feed particles away from each other and revealing more surface area to the grinding media. Therefore, a supplementary grinding aid must be used to reduce agglomeration and ball coating in the mill. In our study the agglomerate phenomenon has taken place only in the added amount (0.025%) regardless of unsaturated fatty acid and saturated fatty acid. The simple explanation is that at this relatively low grinding aid concentration, there is not enough grinding material to prevent ball coating, agglomeration. Despite a voluminous literature on the subject, there is no accepted scientific method to choose such aids; there is not even agreement on the mechanisms by which they work [16–19].

Interpretation of the results

In the cement production, particle size is important in terms of energy efficiency and costs. Concerning economic evaluation of grinding aids, the clearest advantage resulting from the use of that lies in the increase in the plant output, which then provides a quite easily computable energy saving. The goal of these grinding experiments was to determine the effect of the fatty acids as grinding aids on the PSD of the Portland cement and also to provide a comparison at Portland cement behavior when mixed with different amount of grinding aids. Figure 1 shows relationship between the additive amounts and the fineness (residue %) for 45 μm screen opening. The fineness of the cement without the grinding agent is 12.2 wt.%. All of the grinding aids used give a maximum at a ratio of 0.025 wt. %. For an addition of 0.1 wt.% LA, MA and SO, the % residue is more and more increased, successively. It is clear that the particles of the cement with LA are finer than that of the other cement samples. At 0.5 wt.%, all of the additives used make the cement grains finer, especially for MA and LA. It is readily seen from Fig. 1 that SO is less efficient in the grinding of the cement clinker according to the other aids. The maxima exhibited by the cement at the 0.025 wt.% addition of SO, LA and MA grinding aids are indicative of agglomeration of the cement grains. Clearly the global fineness of Portland cement are influenced by the grinding aids. The fineness of the Portland cement was similar at 0.5-wt.% addition for LA and MA.

Figure 2 demonstrates the % mass residue on 0.090 mm screen opening, depending on the supplements. At the replacement of 0.025 wt.% LA and MA, the mass fraction retained on 90-μm-size mesh is almost the same, whereas higher for the same quantity of SO. For the cement substituted with 0.1 wt.% LA, MA and SA, the fraction is increasingly changed, respectively. Figure 2 showed that as the amount of addition increased, the fineness of the cement increased. The cement particles for an amount of 0.5 wt.% addition are finer than for the 0.025 and 0.1 wt.% additions, particularly for MA.

Figure 3 indicates the fraction on the 200-μm-size mesh and is similar to Fig. 1 and Fig. 2. There is a maximum at 0.025 wt.% LA and MA, except for the same replacement ratio of SO. The fraction of the coarse cement particles at 0.1 wt.% SO is more than

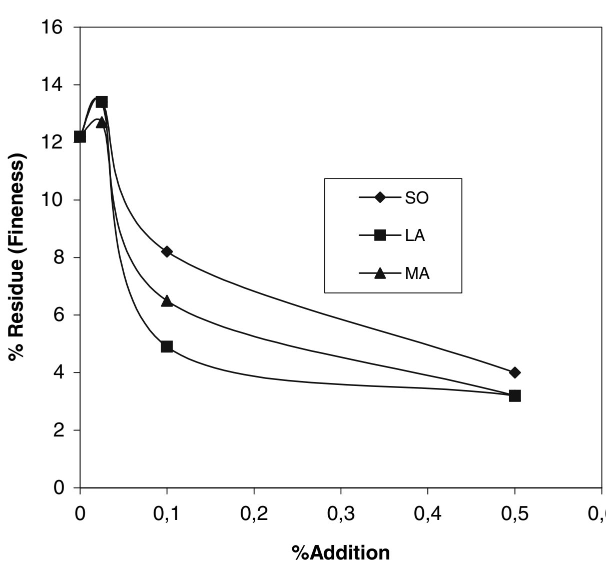

Fig. 1 The fraction retained on 0.045 mm screen opening

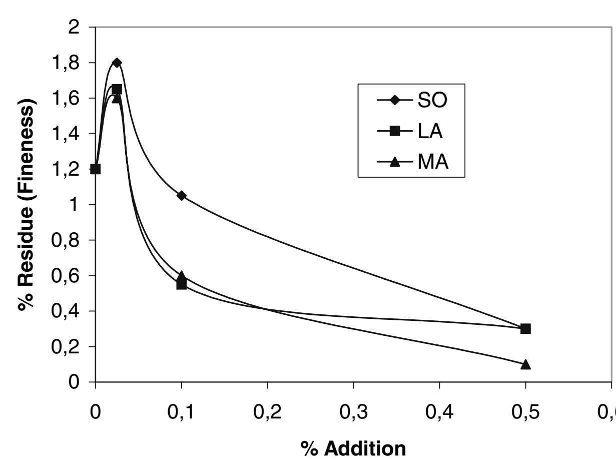

Fig. 2 The fraction retained on 0.090 mm screen opening

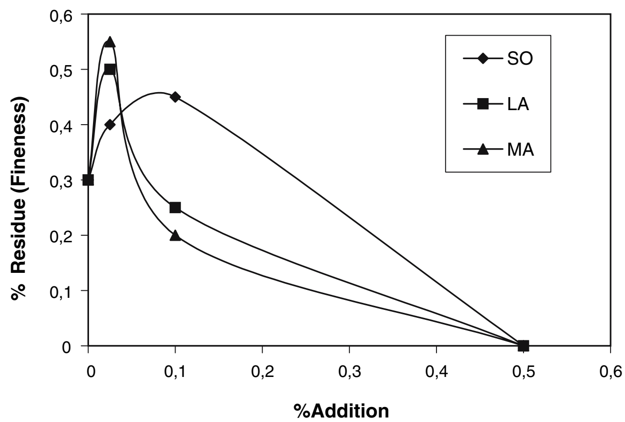

Fig. 3 The fraction retained on 0.200 mm screen opening

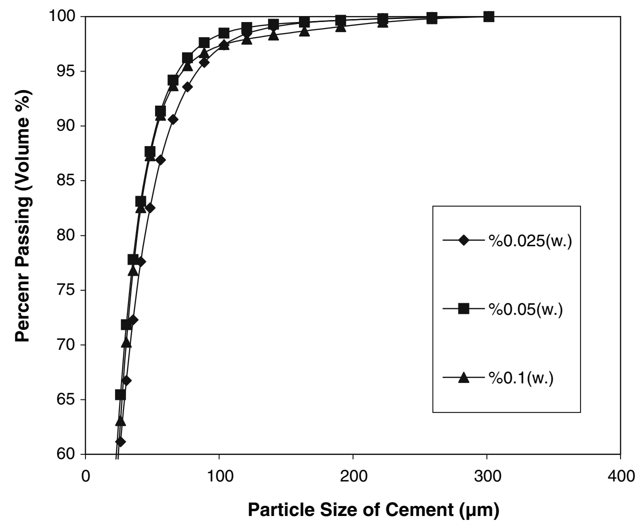

Fig. 4 The PSD of cement with SO

that of the other two additives and also the SO addition gives a maximum. The fine cement fractions at 0.5 wt.% are so extreme that almost all of the cement particles are below 200-μm-size mesh.

It is seen from Figs. 1–3 [18] that the cement grains agglomerate or cake at 0.025 wt.% addition and for a supplement of 0.1 wt.%, the cement replaced with SO gives the coarser cement than that with LA and MA. It can be concluded that 0.025 wt.% addition is not enough to overcome interparticle attraction and accordingly the agglomeration has occurred only in the added amount regardless of unsaturated fatty acid and saturated fatty acid. Consequently, in our previous paper [10], the 7-day and the 28-day compressive strength values for 0.025 %wt. quantity are lower as compared with the cement which is free of grinding aid. At 0.5 wt.%, the grinding becomes easy due to the increase of cracks which there always exists in cement clinker depending on the increasing additive content.

Figures 4–6 show the granulometric ranges for every addition. In Fig. 4, for 0.025 and 0.05 wt.% SO, the number of the cement particles below 120.67 μm is approximately the same. However, it is seemed that the percent below 120.67 μm changed decreasingly due to the increasing admixture. As a result of this data, as the additive increases from 0.025 wt.% to 0.1 wt.%, the number of the fines decreases. That's, the cement replaced with 0.1 wt.% SO has coarser particles than that with 0.05 wt.% SO.

Figure 5 indicates the variation of the particle size range with LA addition. Respectively, for the cement substituted with 0.025, 0.05 and 0.1 wt.% LA, the percent in volume under 120.67 μm gradually increases. It is seen that as the admixture increases from 0.025 to 0.1 wt.% the fine cement fraction increase.

Figure 6 exhibits the PSD of cement with MA for each individual addition. It is certain from the graphic that the cement substituted with 0.025 wt.% MA has a coarser fraction than that with 0.05 wt.% for the particles under 120.67 μm. For an admixture of 0.1 wt.%, the cement particles are finer than for the other two additions.

Increasing the additive content doesn't always rise the compressive strength. With respect to our previous research [10], the strength values for 0.5-wt.% additive are still lower than that with 0.1 wt.%. This may be that because the supplementary agents affect the chemical and mechanical properties of the cement, negatively. Besides, in our past examination [10], we concluded that the compressive strength values of the samples with LA and MA are much more higher than for SO containing significant quantities of unsaturated oil, which includes double bonds, since LA and MA contains single bond in their structure. Also, as complementary of these results, it can be observed from Figs. 4–6 that %100 of the total cement particles in

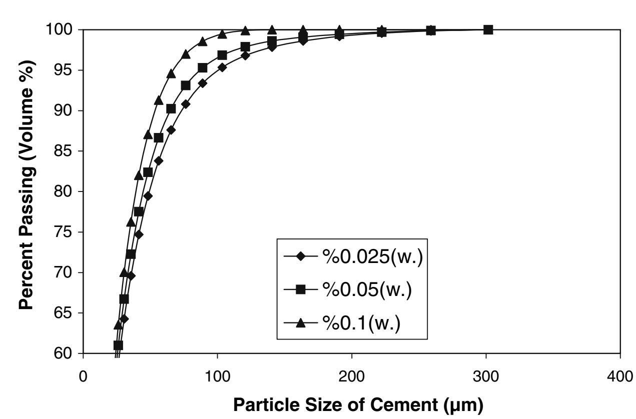

Fig. 5 The PSD of cement with LA

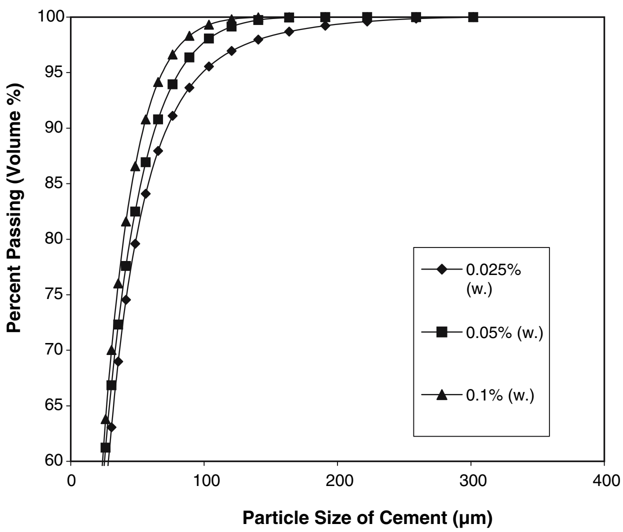

Fig. 6 The PSD of cement with MA

volume for the ground cement substituted with 0.1 wt% LA and MA is below 140.58 μm and 163.77 μm, respectively, while for 0.1 wt.% SO below 301.68 μm. It is clear that the cement replaced with the saturated components has shorter particle size range.

Conclusions

1. The cement particles with LA and MA are finer, while those with SO are coarser. Accordingly, SO agglomerates the cement grains.
2. The PSD of the cement narrows when the addition of LA and MA into cement clinker is increased, except for SO. That's, as the addition of SO is increased, the granulometric range widens.
3. MA and LA contributes more to compressive strengths at all ages than SO. Because the cement including MA and LA has finer cement particles and narrower PSD. But this contribution is not very important. The greatest effect on the strengths is that MA and LA don't have the double bonds in the structure of those acids.

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