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Discussion

A discussion of the paper "Determination of grinding aids in Portland cement by pyrolysis-gas chromatography-mass spectrometry" by A.A. Jeknavorian, E.F. Barry, and F. Serafin[1]

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Drs. Jeknavorian, Barry, and Serafin have reported an interesting study for determining grinding aids in Portland cement by pyrolysis-gas chromatography-mass spectrometry, which, when coupled with in situ pretreatment (derivitisation) of the cement with N,O-bis (trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS), improved the recovery rate of various common grinding aids. The recovery rate was found to be highly dependent on both the clinker-gypsum grinding process and the binding capacity of the particular grinding aids [1]. In practice, as the authors pointed out [1], it is not easy in practice to analyse cements quantitatively for their grinding aid content, as required by a number of national standards like ASTM C 465 [2].

Grinding aids are substances that assist particle comminution during the grinding of materials. In clinker-gypsum grinding for producing Portland cement, grinding aids often are added in small amounts ~0.01–0.10% by weight of the cement produced, so that the desired surface area can be achieved in less time without the cement properties being affected significantly from the engineering viewpoint. The mill retention times for the materials being ground into the finished cements are reduced, as a result of which much electrical and mechanical energy expended during normal grinding is saved.

The different clinker minerals have different grindabilities. The relative ease of grinding them tends to be in the following order: gypsum $>>> C_3S > C_3A \sim C_4AF > C_2S$.

Gypsum is a much softer material than the main Portland clinker phases. The measured surface areas of finished cements are average effects of all their mineralogical constituents in the quantities present. For example, in a Portland cement ground to $\sim$300 m^2/kg, the actual surface area for the gypsum component is likely to be $\sim$1200 m^2/kg or more. It is important to remember that none of the clinker phases is pure [3]. Hence, the actual grindabilities of the individual clinker phases are unique to the particular cement manufacturing plant. Surface area, with all the ramifications of the relative grindabilities of the particular clinker phases in a given Portland cement, is only one of numerous parameters that cement manufacturers have to control to satisfy the requirements of the relevant standards.

Many materials, organic, inorganic, and mixed organic-inorganic substances, have been used as grinding aids in the manufacture of Portland cements. The most commonly used grinding aids are organic from the categories of amines and their salts, polyols, alcohols, lignosulfonates, and fatty acids and their salts [4,5]. Most grinding aids are polar compounds, but nonpolar compounds also have been used, although in general terms they are significantly less effective. Harmful materials should not be utilised for health and safety reasons.

The mechanism of grinding aid action is not known with certainty, but it appears to be based on the decrease in resistance to comminution—the Rehbinder effect [6]—and the prevention of agglomeration. The Rehbinder effect is based on the Griffith's theory [7], which postulates that brittle materials contain microcracks or, more generally, flaws that create discontinuities in the crystal structures of the materials concerned. Under fairly strong impacts, the microcracks propagate through the material as far as to cause its fracture. The same action can create other microcracks where internal flaws exist. During grinding, however, mechanical stresses act discontinuously. Hence, during the active periods, the propagation of the existing cracks and the formation of new ones take place. During the periods of inactivity, the microcracks can rejoin, due to the attraction of the unsaturated valency forces that exist on the walls forming the cracks themselves. Grinding aids appear to be sorbed into the microcracks, thus eliminating or reducing local valency forces and preventing microcracks from rejoining. As

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[1] Cem Concr Res 28 (1998) 1335–1345.

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a result, there is less resistance to the comminution of the grains, which thereby is achieved more speedily [4,5].

From this it appears that the grinding aids function by interacting with the surfaces of the anhydrous phases during comminution by effectively forming a film that prevents agglomeration. Polar compounds tend to make better grinding aids, because the electrostatic charges help to keep the particles apart and thus improve the flow properties of the cement. Nonpolar compounds tend to be less effective, because they do not interact so well during shear with the unsatisfied surface forces that are generated. Traditionally it has been common practice in many cement manufacturing plants for relatively small amounts of coal (essentially nonpolar) to be ground up inside the clinker-gypsum grinding mills to remove residual agglomerates when cleaning out the mills during routine maintenance.

Although grinding aids are known to modify the particle size distribution of cements, in general they are normally perceived as having little influence on the engineering properties of the hardened cements. This situation arises because of the low concentrations of these additives with respect to the cement weight. Certainly, at concentrations above 0.1% wt, grinding aids can increasingly affect in a negative manner important cement properties such as setting, compressive strength development, and the propensity to bleed. In some cements, such as Class G and H oilwell cements, grinding aids are still not officially permitted for use during manufacture [8,9]. Tests need to be undertaken for such cements in trials with approved grinding aids to determine the suitability of the latter.

The experimental work undertaken by the authors [1] is a valuable study in an area where there has been criticism of the difficulties of determining grinding aid concentrations in finished cements. This has led to situations where grinding aids have not always been recommended for use in clinker-gypsum grinding when their presence could be beneficial to both the cement manufacturer and the customer. I would agree with the authors [1] that different mechanisms are likely to be operative in the determinations where recovery rates for estimating grinding aid levels are low, such as salt or complex formation and partial thermal degradation from the milling process and/or the pyrolysis procedure. Higher grinding temperatures, longer grinding times, more intense grinding conditions, and the binding capacity of the different grinding aids (related to their hydroxy and/or amino group functions), all tending to cause lower recovery rates, are compatible with the occurrence of such mechanisms.

References

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