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Differential comminution of gypsum in cements ground in different mills

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Abstract

Identical mixes containing fixed amounts of ordinary Portland cement clinker and gypsum were ground in two types of industrial cement mills—viz. ball mill (BM) and vertical roller mill (VRM)—to identical Blaine fineness to examine the effect of any possible differential comminution of gypsum on cement setting times. The present investigation demonstrates that during comminution of cements, the degree of crystallinity of gypsum, as determined by X-ray diffraction (XRD), changes with used grinding mills and this causes changes in setting times of similar cements even when ground to identical Blaine fineness.

Keywords: Gypsum; X-ray diffraction analysis; Setting; Blaine fineness

1. Introduction

A number of researchers have shown that comminution of gypsum plays an important role in determining the cement properties, particularly setting times. In 1984, Kanare and Gartner [1] presented a critical review of a number of research papers dealing primarily with the phenomenon of optimum sulphate levels in Portland cement. Bensted [2] and Goswami et al. [3] studied the effect of comminution on early hydration of Portland cement. Soroka and Abayneh [4] determined the effect of gypsum contents and fineness on mechanical properties of cement. Theisen [5] examined the relationship between gypsum dehydration and strength development in Portland cement. Although, the effect of gypsum comminution on cement properties are generally regarded to be due to the morphological changes in the calcium sulphate. Kanare and Gartner [1] and Menetrier et al. [6] failed to find discrete particles of any form of calcium sulphate in commercial cement and in an integrated mixture of gypsum and C_3S, respectively. This suggests the possibility of loss of crystallinity of calcium sulphate phase during comminution. Goswami et al. [7] examined the degree of crystallinity of gypsum by X-ray diffraction (XRD) in laboratory ground cements.

In the present investigation, the variation in setting times of industrial Portland cements of identical Blaine fineness and gypsum contents was examined in respect to the loss of crystallinity of gypsum during comminution in two types of mills.

2. Materials examined and experimental procedures

An industrial Portland cement clinker containing: – 19.7% SiO_2, 5.9% Al_2O_3, 3.7% Fe_2O_3, 62.9% CaO, 5.1% MgO, 0.45% SO_3, 0.98% K_2O and 0.07% Na_2O having C_3S, C_2S, C_3A, C_4AF and free CaO 60.1%, 11.2%, 9.3%, 11.2% and 0.6%, respectively, and a by-product gypsum with 42.4% SO_3 were used as the base materials. The mix was ground in three different occasions to three different Blaine fineness, but keeping almost identical gypsum contents (4.5%). In each occasion, the mix was ground both in a cement ball mill (BM) and a vertical roller mill (VRM).

Setting times of the cement samples were determined according to the Indian standard 4031-1988. XRD patterns of the samples covering dÅ from 8.85 to 2.564 were obtained using Ni-filtered CuKα radiation at 30 kV, 20

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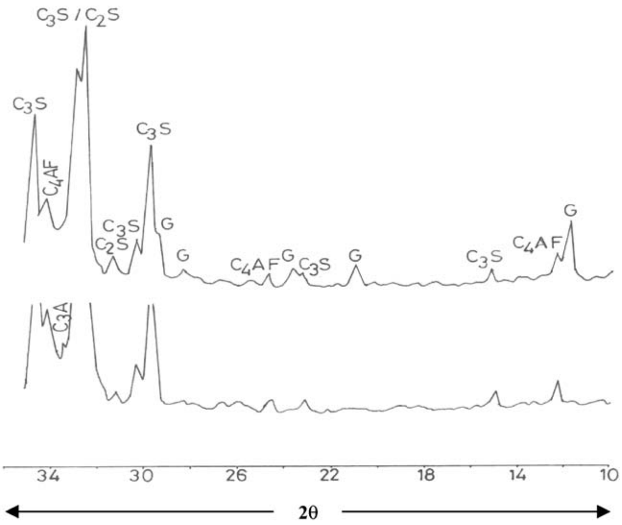

Fig. 1. XRD patterns (CuKα) of the cement samples (3.1 and 3.2).

mA. Although the XRD spectra covered gypsum peaks at 2θ = 11.7 (7.56 Å), 20.8 (4.27 Å), 23.5 (3.79 Å), 28.2 (3.163 Å) and 29.2 (3.059 Å) in all cases, gypsum recorded maximum XRD intensity at dÅ 7.56, 2θ = 11.7 (Fig. 1), and accordingly, relative crystallinity of gypsum was determined by recording XRD pulse counts for gypsum at 2θ = 11.7 (dÅ = 7.56) after background correction.

Combined DTA/TG of the sample was conducted in the Netzsch Simultan Thermo Analyse, Model 429 with Potentiometric Recorder up to 1000 °C. The rate of heating was kept constant at 10 °C/min. The weight of the sample taken for analysis in all cases was 100 mg.

3. Results

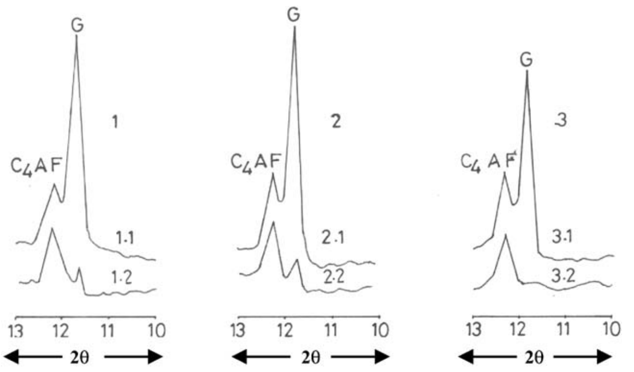

Fig. 2. XRD peak intensities (CuKα) of gypsum (G) ground in different mills in identical cement fineness. (1, 2 and 3) Cements with fineness (Blaine) of 408, 380 and 367 m^2/kg, respectively. (1.1, 2.1 and 3.1) VRM ground cements. (1.2, 2.2 and 3.2) BM ground cements.

In Table 1, Blaine fineness, SO_3% and setting times of the cement compositions ground in three different occasions are recorded. It is observed that there was very little difference in SO_3 contents of the VRM and BM ground cements. Blaine fineness of the VRM and BM cements in every occasion was almost identical. However, there were very significant differences between the setting times of the VRM and BM cements in every occasion. It is of interest that in every occasion, the VRM cement recorded much lower setting times than the BM cement. While the initial setting time (IST) and final setting time (FST) of the VRM products were within 90 to 150 and 125 to 180 min, respectively, those of the BM products were within 365 to 420 and 420 to 450 min, respectively.

The XRD patterns of the examined cement samples recorded no other Ca-sulphate phase except gypsum (Fig. 1). It was also found that although XRD intensities for common cement phases (C_3S, C_2S, C_3A and C_4AF) were almost identical in all the cement samples, gypsum recorded much variation. In fact, the cement sample no. 3.2 (Table 1) recorded neither gypsum nor any other Ca-sulphate phase (Fig. 1); XRD pulse counts for gypsum (at 2θ = 11.7) and the

Table 1
XRD pulse counts for gypsum at 2θ = 11.7 (CuKα) and corresponding cement properties (gypsum = 4.5%)

Cement	Mill	Blaine fineness (m^2/kg)	SO_3%	Setting times (min)		XRD pulse[a] counts for gypsum
				IST	FST	
1.1	VRM	408	2.6	90	125	2340
1.2	BM	406	2.2	365	420	116
2.1	VRM	382	2.5	90	180	2175
2.2	BM	380	2.2	405	435	637
3.1	VRM	367	2.4	105	150	1528
3.2	BM	369	2.3	420	450	Nil

[a] At 2θ = 11.7, after background deduction.

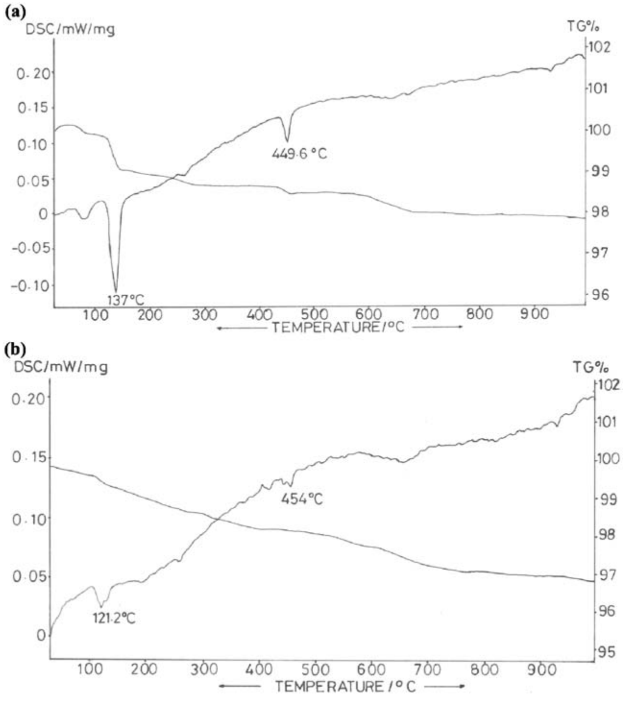

Fig. 3. (a) DTA/TG curves of cement sample 3.1. (b) DTA/TG curves of cement sample 3.2.

corresponding XRD peaks are shown in Table 1 and Fig. 2, respectively. It is found that although SO_3 contents in all the cement samples are almost identical, their gypsum XRD pulse counts were quite different and they were invariably significantly less in the BM products than in the VRM products.

DTA of the cement samples recorded endothermic peaks for gypsum at around 140 °C with corresponding weight loss in TG (Fig. 3). The VRM ground sample (sample no. 3.1, Fig. 3a) recorded very sharp DTA peaks for gypsum (137 °C) and $Ca(OH)_2$ (450 °C) with corresponding weight loss. However, in the case of the BM ground samples (sample no. 3.2, Fig. 3b), DTA peaks were not sharp and TG recorded continuous weight loss. Neither anhydrite nor hemihydrate was recorded by the combined DTA/TG of the samples. On the other hand, the absence of sharpness in DTA peaks and the occurrence of continuous loss in weight particularly in the BM ground samples suggest the formation of some amorphous phase.

4. Discussion

From Table 1, it is evident that the BM cements invariably recorded both IST and FST higher than the VRM cements, although both were produced from the same clinker incorporating the similar amount of gypsum and grinding to the same Blaine fineness. Only significant difference between the two products was found to be their gypsum content as determined by the XRD (Table 1) and combined DTA/TG (Fig. 3). In all cases, XRD intensity for gypsum (Table 1) in the VRM product was significantly higher than that for gypsum in the BM product. As the SO_3 content of both the products were similar and the XRD spectra did not record any other crystalline Ca-sulphate phase (Fig. 1), it is evident that the BM product contained a significant portion of Ca-sulphate in amorphous form. Repeated XRD examination of the cement samples established that there was no "Orientation effect" on the gypsum crystals of the examined samples. Gypsum recorded maximum XRD intensity at $2\theta = 11.7$ and none of the other lines for gypsum appeared in the spectrum, when the line at $2\theta = 11.7$ was absent. This suggested that gypsum in the examined samples was proportionate to the peak at $2\theta = 11.7$.

Similarly, combined DTA/TG did not record any crystalline Ca-sulphate phase other than gypsum (Fig. 3). On the other hand, continuous weight loss in TG without any sudden loss at a particular point also suggested the presence of some amorphous phase.

Effect of grinding on amorphism was reported by Juhasz and Opoczky [9]. In a similar study on amorphism of silica, Anderson [8] showed that on grinding silica material, an amorphous layer forms around the original crystal. It is conceivable that with the increase of fineness, relative volume of amorphous layer increases, although the thickness of the layer remains the same. For example, Anderson [8] calculated that with a constant 0.03 μm thickness of amorphous layer, volumes of amorphous material would be 1.8% and 93% of 10.0 and 0.1 μm spheres, respectively. That the very fine crystalline phase coated with amorphous phase fails to respond to XRD is demonstrated in the present study also by the fact that although the BM sample no. 3.2 recorded gypsum, peak in the DTA curve (Fig. 3b), XRD spectrum of the same did not record any gypsum. Absence of any other crystalline Ca-sulphate phase like anhydrite and hemihydrate in the examined materials suggests that there was practically no effect of grinding temperature on the transformation of gypsum phase and subsequently on the setting times. Thus, it is conceivable that only the differential amorphism of gypsum caused during grinding was solely responsible for variation in setting times.

Earlier, Goswami et al. [7] conducted experimental cement grinding in controlled laboratory conditions and demonstrated that with the increase of grinding time, amorphism of gypsum also increased, which in turn by enhancing the reactivity of Ca-sulphate with the cement phases, increased the ettringite contents of the cement paste and consequently caused retardation of the setting times. Some recent studies on materials grinding have discredited the hypothesis of amorphisation during grinding. However, the present investigation shows that even in identical Blaine fineness, grinding in BM produces fine gypsum, wherein the ratio of amorphous coating to inner gypsum crystal is higher than that produced in VRM grinding cements, and this difference in amorphism leads to higher setting times in BM cements than in otherwise similar VRM cements.

References

[1] M. Kanare, E.M. Gartner, Optimum sulphate in Portland cement, Cem. Res. Prog. (1984) 213–251 (Chapter 13).

[2] J. Bensted, Effects of the clinker–gypsum grinding temperature upon early hydration of Portland cement, Cem. Concr. Res. 12 (3) (1982) 341–348.

[3] G. Goswami, B.N. Mohapatra, J.D. Panda, Gypsum dehydration during comminution and its effect on cement properties, J. Am. Ceram. Soc. 73 (3) (1990) 721–723.

[4] I. Soroka, M. Abayneh, Effect of gypsum on properties and internal structure of Portland cement paste, Cem. Concr. Res. 16 (4) (1986) 495–504.

[5] K. Theisen, Relationship between gypsum dehydration strength development in Portland cement, Zem.-Kalk-Gips 36 (10) (1983) 571–577.

[6] D. Menetrier, I. Jawed, J. Skalny, Effect of gypsum on C_3S hydration, Cem. Concr. Res. 10 (5) (1980) 697–702.

[7] G. Goswami, B.N. Mohapatra, P.K. Panigrahy, J.D. Panda, Application of X-ray diffractometry in comminution of gypsum, 10th Int. Cong. Chem. Cem., 1997 (P.3V008).

[8] P.L. Anderson, Free silica analysis of environmental samples—A critical literature review, Am. Ind. Hyg. Assoc. J. 36 (1975) 767.

[9] Z.A. Juhasz, L. Opoczky, Mechanical Activation of Minerals by Grinding, Pulverizing and Morphology of Particles, Ellis Horwood, Chichester, England, 1990.