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The influence of grinding mechanism on the liberation characteristics of clinker minerals

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Abstract

This study deals with the characterization of narrowly sized fractions of clinker ground by ball mill and high-pressure grinding rolls. Chemical, physical and mineralogical characterizations were made by using XRF, laser sizing, Blaine, BET, SEM, and image analysis techniques. The emphasis was given to the preferential liberation of the constituent clinker phases. High-pressure grinding rolls gave higher degrees of liberation of mineral phases arising from the intergranular breakage along the grain boundaries compared to ball mill grinding. This is expected to influence the downstream service properties of cement.

Keywords: Grinding; Image analysis; Liberation; Clinker

1. Introduction

The service properties of cement are affected not only by its chemical and mineralogical composition but also by its fineness and particle size distribution. Hence, a considerable number of studies were made to investigate the effect of particle size, particle size distribution, individual mineral grain size of the constituent minerals, and surface area upon the main quality parameters of cement such as strength development, water demand, setting time and heat of hydration [1–6].

Cement minerals, mainly alite, belite, celite and ferrite, must be exposed to water molecules for hydration to take place. The degree to which individual grains of these minerals are exposed depends to a great extent upon the surface of the individual grains relative to the surface of particles in which they are contained. Hence, the concept of "liberation" from the mineral-processing field must be introduced into the cement field.

High compression applications are finding widespread use in cement grinding because of their ability to improve specific energy consumption by up to 40%. Although HPGR technology is widely used in the cement industry, the possibility of preferential liberation of clinker minerals as recognised and beneficially applied in the mineral processing industry has not received much attention. In broad terms, if the same ore is subjected to comminution by two different methods such that particle size distribution is similar, yet subsequent downstream treatment demonstrates substantial differences, then there is reason to believe that preferential liberation has occurred. The benefits of high-pressure rolls grinding in increased gold [7] and copper leachability [8] and process enhancement of diamond [9], iron [10] and cassiterite [11] concentration due to the improved

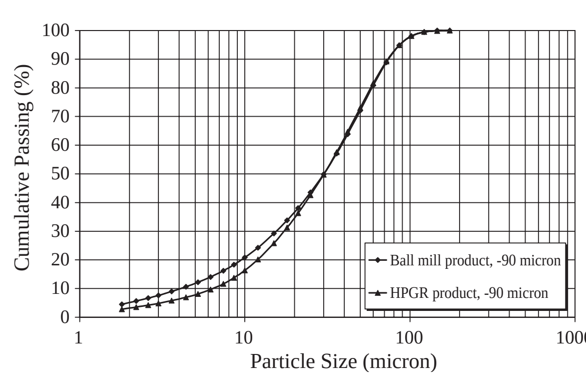

Fig. 1. −90 μm particle size distributions of ball mill and HPGR products.

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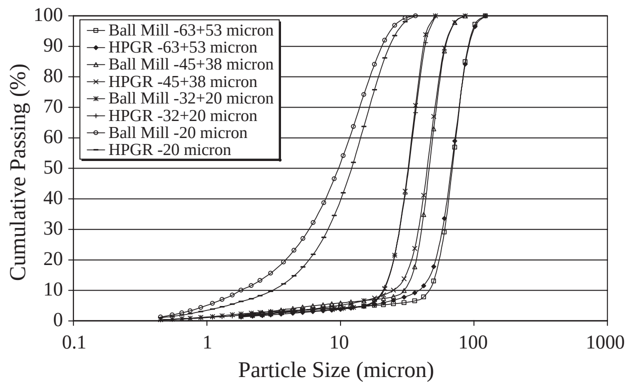

Fig. 2. Particle size distributions of narrow size fractions in the two grinding modes.

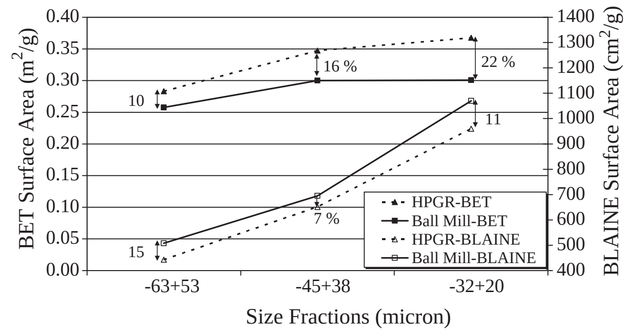

Fig. 3. Specific surface area of size fractions.

liberation have been reported in literature. Although high-pressure grinding rolls (HPGR) have much wider use in cement grinding compared to mineral industries, there has been very little quantitative research work comparing liberation effect of different milling modes [12] but none on the influence of liberation effect upon the service properties of cement.

With this fact in mind, it was decided to carry out comparative test work to ascertain if the two most used different milling techniques in cement grinding, namely, ball milling and HPGR, had any substantial differences on properties, particularly on preferential liberation, of the cement minerals, and consequently, their downstream effects on product service properties. In this article, mainly characterization of differently ground particles is presented. For the results to be comparable and to eliminate the effect of gypsum addition on the characterization, the work was carried out on closely sized fractions of differently ground clinker. The effects of changes in clinker minerals' characteristics due to different grinding modes upon the downstream service properties, after the addition of adequate amount of gypsum, will be the subject of another publication.

2. Experimental work

Clinker ground in an HPGR equipment was sampled in an industrial cement plant, and after deagglomeration, −90 μm fraction was separated by sieving to be used for the experiments. The HPGR feed was simultaneously sampled and ground in a laboratory ball mill to give approximately the same percentage of −90 μm as compared to the industrial HPGR product whose particle size distributions determined by laser sizing are given in Fig. 1. As clearly seen in the figure, the HPGR product shows a narrower distribution being pronounced below the 20 μm size range.

Minus 90 μm clinker products were sieved to the same narrow size fractions to prepare pairs of samples having the same sieve size, but differing in the mode of comminution by which they were produced. The choice of narrow size fractions for the study was to facilitate the image analysis particularly for the determination of liberation degrees. The fractions prepared were −63+53 μm, −45+38 μm, −32+20 μm and −20 μm. Particle size distributions of these closely sized fractions, determined by laser sizing, which did not show any noticeable difference depending on the mode of grinding as seen in Fig. 2 except −20 μm fractions which, as expected, show considerable difference due to the wide size range and also greater fines content produced by ball milling.

To check if chemical compositions varied according to particle size and the mode of comminution applied, XRF analyses were performed.

Specific surface areas of samples were determined by Blaine and by BET (based on N_2 adsorption) techniques to see if there were any differences in the pairs of samples having the same size arising from the different modes of grinding. Size fractions were also examined under SEM, and the photographs

Table 1
Chemical composition of ball mill and HPGR products

	Ball mill			HPGR		
	−63+53 μm	−45+38 μm	−32+20 μm	−63+53 μm	−45+38 μm	−32+20 μm
SiO_2	21.12	21.46	21.81	21.34	21.56	22.18
Al_2O_3	5.66	5.36	4.73	5.41	5.15	4.46
Fe_2O_3	3.61	3.36	3.40	3.41	3.17	3.11
CaO	66.51	66.84	66.62	67.17	67.47	67.22
MgO	1.27	1.25	1.24	1.25	1.24	1.22
SO_3	0.47	0.47	0.44	0.46	0.46	0.43
Na_2O	0.08	0.08	0.16	0.09	0.08	0.16
K_2O	0.61	0.58	0.62	0.54	0.52	0.56
TiO_2	0.20	0.20	0.22	0.20	0.20	0.22
Free lime	1.57	1.07	0.24	0.85	0.44	0.17
LOI	0.50	0.50	0.10	0.84	0.88	0.10

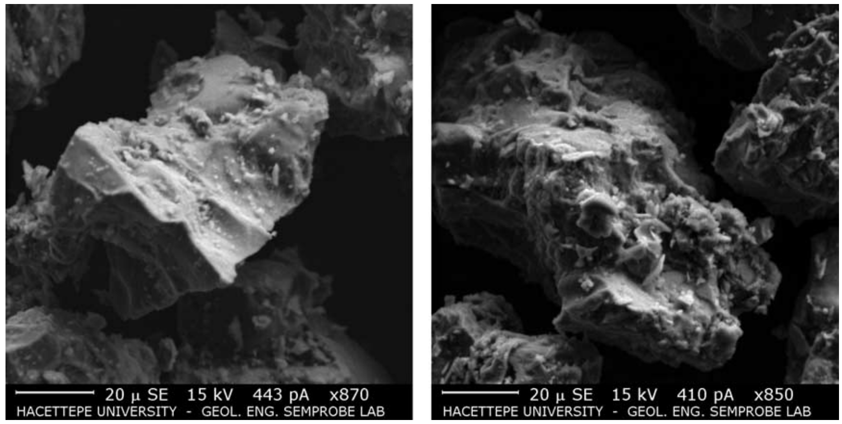

Fig. 4. SEM photographs of −63+53 μm fractions, left: ball mill product; right: HPGR product.

taken to see the differences in the surface texture and shape of the particles.

Mineralogical characterization of the samples was made by image analysis. It was soon evident that etching was required to differentiate the clinker minerals, particularly the silicates, under the microscope. A number of etching solutions was tried and nital (HNO_3–ethyl alcohol) [13] was selected as the proper etchant. The apparatus used was Clemex Vision PE 3.5, and specimens were prepared by impregnation of size fractions in epoxy resin. After cutting and polishing by using alcohol instead of water, etching was carried out. From the etched images, alite (C_3S), belite (C_2S), and the liquid phase were analyzed. Total amount of minerals, crystal sizes, amount of embedded belite grains within alite, and most importantly,

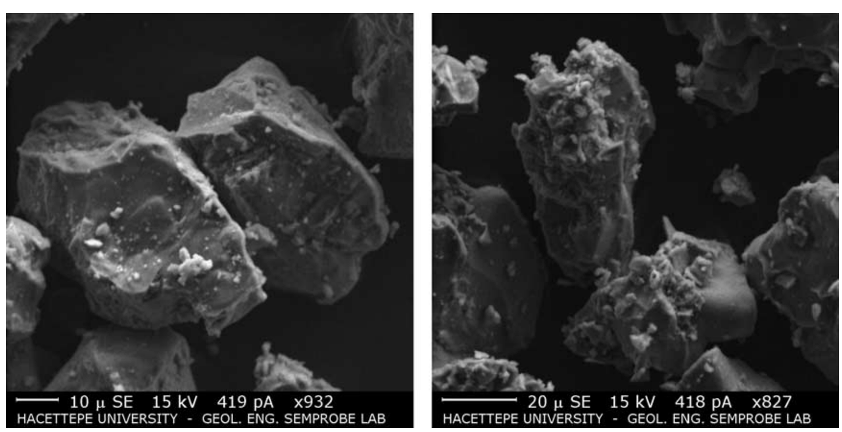

Fig. 5. SEM photographs of −45+38 μm fractions, left: ball mill product; right: HPGR product.

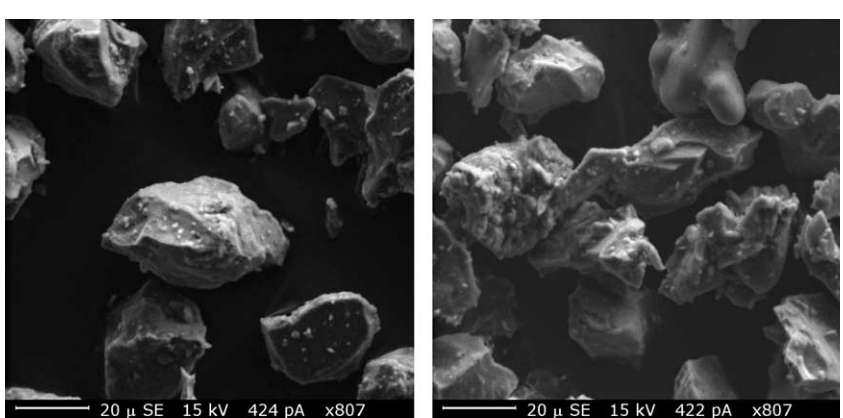

Fig. 6. SEM photographs of −32+20 μm fractions, left: ball mill product; right: HPGR product.

Table 2
Mineralogical compositions of main mineral phases in size fractions of grinding modes

Size fractions (μm)	HPGR (%)			Ball mill (%)		
	Alite	Belite	Liquid phase	Alite	Belite	Liquid phase
−63+53	72.7	2.9	24.4	73.1	3.7	23.1
−45+38	77.9	4.5	17.5	76.4	2.8	20.8
−32+20	86.0	3.7	10.3	84.0	2.0	13.9

liberation degree of each mineral in different size fractions were quantified.

3. Results and discussions

In order to interpret the data obtained from the tests on a sound base, the chemical composition of different size fractions should be similar. Although the analyses of Al_2O_3 and particularly free lime revealed a certain decrease as the size got smaller, and additionally, free lime revealed some change due to the mode of grinding, it can be accepted that all fractions have similar compositions as seen from the XRF results given in Table 1.

The results of Blaine and BET specific surface area measurements are presented in Fig. 3. It is clear that Blaine specific surface areas for the same size fractions exhibit some differences due to differing modes of comminution, the ball mill fractions giving higher values. This can be due to the better packing, i.e., smaller voidage, of the particles with comparatively smoother surfaces exhibiting higher resistance to air flow measured in Blaine determination. The BET values for the same size fractions show more considerable differences; this time, the HPGR products giving higher specific surface areas. It may be suggested that the relatively rough surfaces and some extra cracks give rise to a greater BET specific surface areas for particles ground under high compression.

Comparison of the SEM photographs included as examples provides considerable insight into the surface details in support of the above given argument. The photographs in Figs. 4–6 reveal that there is a clear difference in surface texture due to the different modes of grinding. HPGR milled particles have rougher surface texture showing more cracks indicating preferential breakage along the grain boundaries as well as generation of fissures on the surface of the particles due to the high loads applied.

Image analysis was carried out on the polished and etched samples of the same clinker size fractions. The algorithms, defining the images of the samples most properly, were integrated into Clemex software and the measurements such as the amount and crystal sizes of the main clinker phases, C_2S grains embedded in C_3S, and more importantly, degrees of mineral liberation were made.

Table 2 gives the mineralogical composition of the size fractions studied. There are considerable variations in the amounts of all phases depending on the particle size. As clearly illustrated in the table, the amount of alite increases and the amount of liquid phase decreases as the particle size gets finer. The amount of belite is surprisingly low in all size fractions, however; this is possible as also reported by other researchers [6].

Crystal sizes of alite and belite, which were expressed as the longest dimension (the measured diameter equal to the maximum value of Feret's diameter), depending on the particle size classes and the mode of grinding, are presented in Table 3. As expected, they get smaller with the decrease in particle size, and belite crystals are much smaller than alite crystals. There seems to be no appreciable difference due to the mode of

Table 3
Size and shape characteristics of alite and belite crystals

	Alite crystals		Belite crystals	
	HPGR	Ball mill	HPGR	Ball mill
−63+53 μm				
Length (μm)	Mean: 25.9	Mean: 25.8	Mean: 10.4	Mean: 9.8
	Maximum: 95.3	Maximum: 86.0	Maximum: 43.0	Maximum: 58.9
	Minimum: 10.6	Minimum: 9.3	Minimum: 2.6	Minimum: 2.5
Sphericity	0.53	0.56	0.79	0.81
Aspect ratio	1.76	1.79	1.54	1.52
−45+38 μm				
Length (μm)	Mean: 17.9	Mean: 18.2	Mean: 5.3	Mean: 4.9
	Maximum: 57.2	Maximum: 58.9	Maximum: 34.8	Maximum: 22.7
	Minimum: 6.6	Minimum: 6.7	Minimum: 1.4	Minimum: 1.2
Sphericity	0.35	0.39	0.81	0.78
Aspect ratio	1.85	1.84	1.54	1.66
−32+20 μm				
Length (μm)	Mean : 16.6	Mean: 16.1	Mean: 5.1	Mean: 4.7
	Maximum: 70.9	Maximum: 50.4	Maximum: 25.2	Maximum: 16.9
	Minimum: 4.2	Minimum: 3.9	Minimum: 1.2	Minimum: 1.1
Sphericity	0.49	0.50	0.84	0.85
Aspect ratio	1.76	1.82	1.46	1.50

Table 4
Amount of C_2S spots embedded in C_3S crystals

Size fraction μm	HPGR		Ball mill	
	C_3S area (%)	C_2S spots area (%)	C_3S area (%)	C_2S spots area (%)
−63+53	95.29	4.71	93.77	6.23
−45+38	97.16	2.84	95.67	4.33
−32+20	97.25	2.75	96.61	3.38

grinding. Sphericity and aspect ratio of crystals are also given in the table.

Quantification of C_2S spots within C_3S was rather difficult particularly in the −32+20 μm size fraction. Therefore, the results presented in Table 4 should be viewed on a qualitative basis. It is clear from the studies that the amount of C_2S grains varies with the particle size as well as with the mode of grinding. The variation with the latter is a clear reflection of the preferential fracture along the grain boundaries between alite and embedded belite because of the high loads applied in HPGR. In ball milling, however, the repeated collisions of balls result in predominantly transgranular fracture. An image of −45+38 μm BM fraction is given as an example in Fig. 7.

Our greatest interest in this work was obviously the comparison of grinding mechanisms in terms of mineral liberation. Liberation is well known to be the key to success in mineral processing and in the authors' opinion must be introduced to the cement field also. The degree of liberation is expressed by the percentage of a mineral that exists as free particles to the total of that mineral. In an individual clinker particle, major or minor phases can be seen together, mostly C_3S and C_2S within interstitial, expressing a locked type of mineral. When water gets in contact with a clinker/cement particle, it penetrates to a certain depth. The microcracks in the particles can lead to an increase in this penetration by providing a physical path. Consequently, it might be expected that such a phenomenon can affect the service properties of the cement particles with different surface properties, particularly with different liberation characteristics.

As for the liberation studies, firstly, liberation classes were defined. If one particle consisted of only one mineral, it was called a free particle. If two minerals existed in one particle, it was termed a binary particle. A ternary particle was the one having three minerals together.

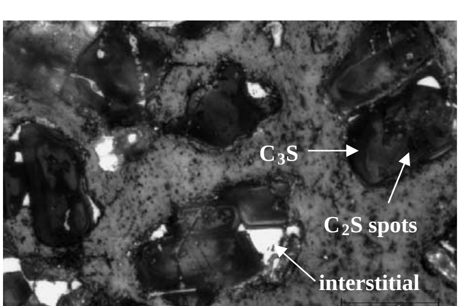

Fig. 7. An etched image of −45+38 μm size fraction of ball mill product.

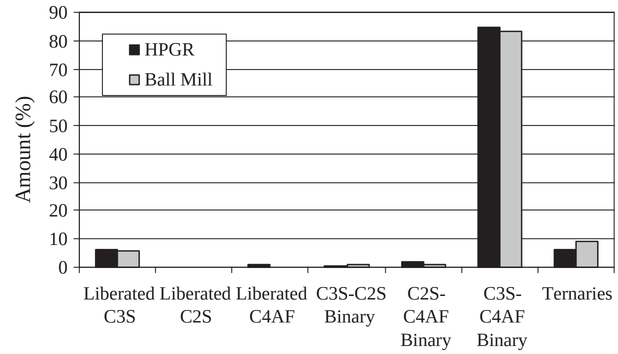

Fig. 8. Liberation classes of −63+53 μm size fraction.

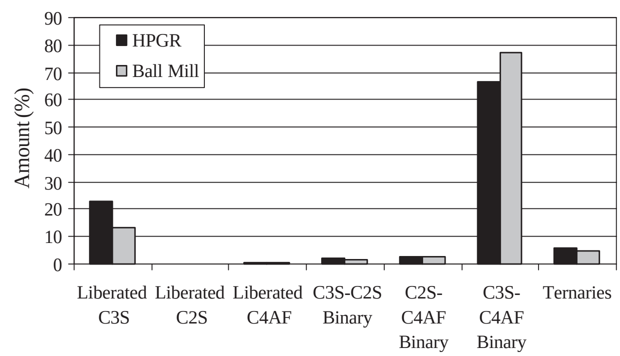

Fig. 9. Liberation classes of −45+38 μm size fraction.

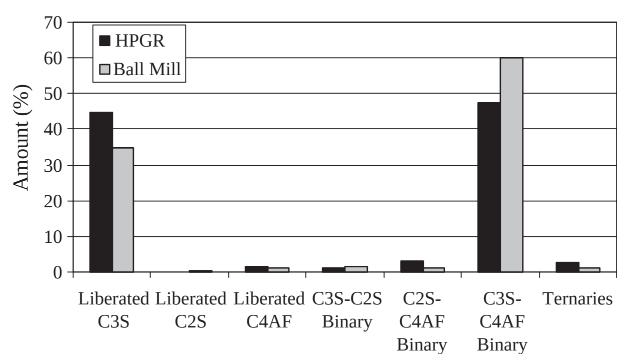

Fig. 10. Liberation classes of −32+20 μm size fraction.

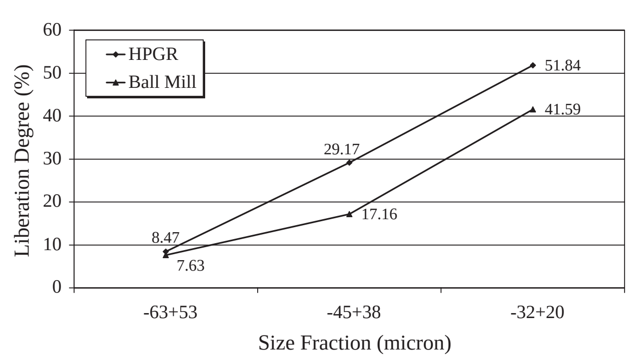

Fig. 11. Liberation degree of C_3S.

The results were obtained by counting 800–1500 particles in each size fraction and the liberation classes are given in Figs. 8–10.

The samples are mostly composed of C_3S, in amounts of approximately 70–85%, and C_2S generally occurred as nests within C_4AF and embedded spots in C_3S. It is interesting to see clearly in Figs. 9 and 10 that the amount of liberated C_3S particles of HPGR product is higher in each size fraction studied in comparison to the ball mill product. The calculated liberation degrees of size fractions are given in Fig. 11 comparatively.

4. Conclusions

Based on the findings, the following conclusions can be drawn:

– HPGR products have narrower particle size distributions compared to BM products. They have larger BET and smaller Blaine specific surface areas in the same size fraction.
– The harder component C_2S seems to fracture along the weak boundaries with C_3S when HPGR is used; and this is probably why; the amount of C_2S spots embedded in C_3S is less in HPGR products.
– Average crystal sizes of alite and belite show no variation in the narrow size fractions due to the grinding modes applied. They get smaller as the size fractions get finer.
– Ball mill ground products exhibit smoother breakage surfaces compared to HPGR products.
– Mineralogical composition of the size fractions indicates variations depending on the fineness.
– Most importantly, HPGR grinding causes breakage along grain boundaries resulting in better liberation of constituent minerals compared to BM grinding as confirmed by quantitative determination of the degree of liberation by the image analysis of the closely sized fractions of products. This is expected to affect the service properties of cement ground under differing modes.

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