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The influence of grinding technique on the liberation of clinker minerals and cement properties

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Abstract

This paper describes a study of the relationship between the physical, chemical and mineralogical parameters of cement products obtained by different grinding mechanisms namely high pressure grinding rolls (HPGR) and ball milling, and their effects upon the properties of cements prepared from the ground clinker. Samples were prepared as narrow size fractions and also as distribution samples. Characterization parameters were ascertained by using XRF, laser sizing, Blaine and BET surface area and image analysis methods. HPGR grinding resulted in higher degrees of liberation of clinker phases arising from the intergranular breakage along the grain boundaries compared to ball mill grinding. As for service properties, water demand of HPGR products was higher than ball mill products resulting from high micro fissured structure. Despite high liberation of particularly alite mineral in HPGR grinding, the compressive strength of ball mill products was slightly higher than HPGR products for narrow size samples. Finally, particle size distribution effect on strength was more obvious for distribution samples; generally ball milling gave higher strength values.

Keywords: Clinker; Grinding; Image Analysis; Liberation; Compressive strength

1. Introduction

Besides ball mill, different types of mills which have different grinding mechanisms such as high pressure grinding rolls (HPGR), vertical mill and Horomill are being used in cement industry. Particularly HPGR has a great acceptance in cement industry for almost 20 years because of its ability to reduce specific energy consumption up to 40%. In recent years HPGR is also being used in the mineral industry as it improves liberation of constituent minerals giving rise to mineral recovery in addition to the energy savings. Liberation improvement with HPGR grinding and its effect on downstream processes with some types of ores such as copper, gold, diamond and iron are reported in literature [1–4].

Not only are the fineness and particle size distribution parameters effective on service properties of cement, but also the chemical, mineralogical and micro structural parameters have an important role, particularly on strength development. Many research studies investigating these parameters separately or in combination have been completed up to date [5–9]. According to

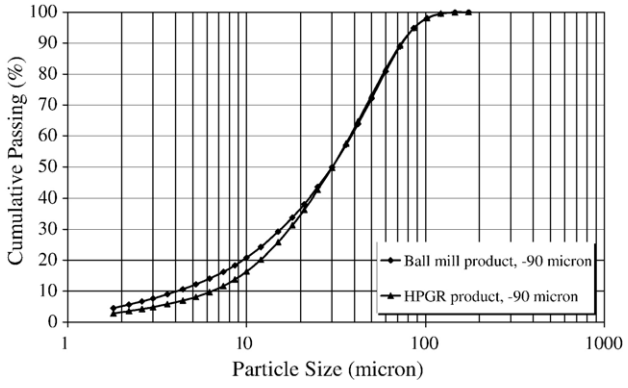

Fig. 1. −90 μm particle size distributions of ball mill and HPGR products.

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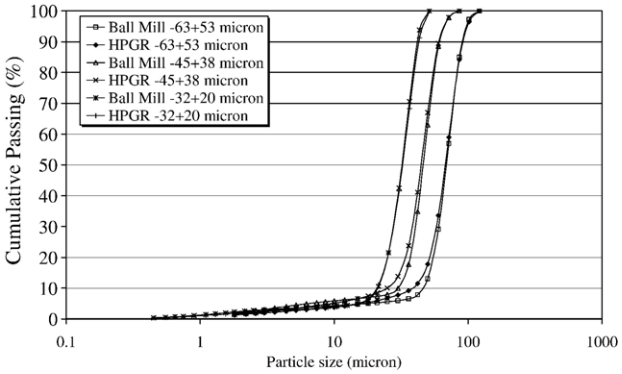

Fig. 2. Particle size distributions of narrow size fractions in two grinding modes.

literature; mineralogical and microstructure properties are mostly examined on coarse clinker particles and obtained results such as amount and dimension of mineral phases, porosity and some operational parameters of clinker manufacturing are usually dealt with clinker grindability [10,11]. Clinker or cement microstructure data could also help to predict cement service properties, particularly strength. But the combined effect of these micro structural parameters on strength should be considered otherwise the correlation may be low if these parameters are evaluated in isolation against compressive strength [12]. It is apparent that several factors may play different roles together on service properties.

Essentially microscopic analysis can be applied to cement powder, but few studies have appeared probably because of technical difficulties such as etching and processing of micron size material. In these studies only morphological parameters including shape properties were examined by SEM because of complex composition of cement [13,14]. If image analysis is performed, complexity of cement should be more considered because of the difficulties in differentiating the major and minor

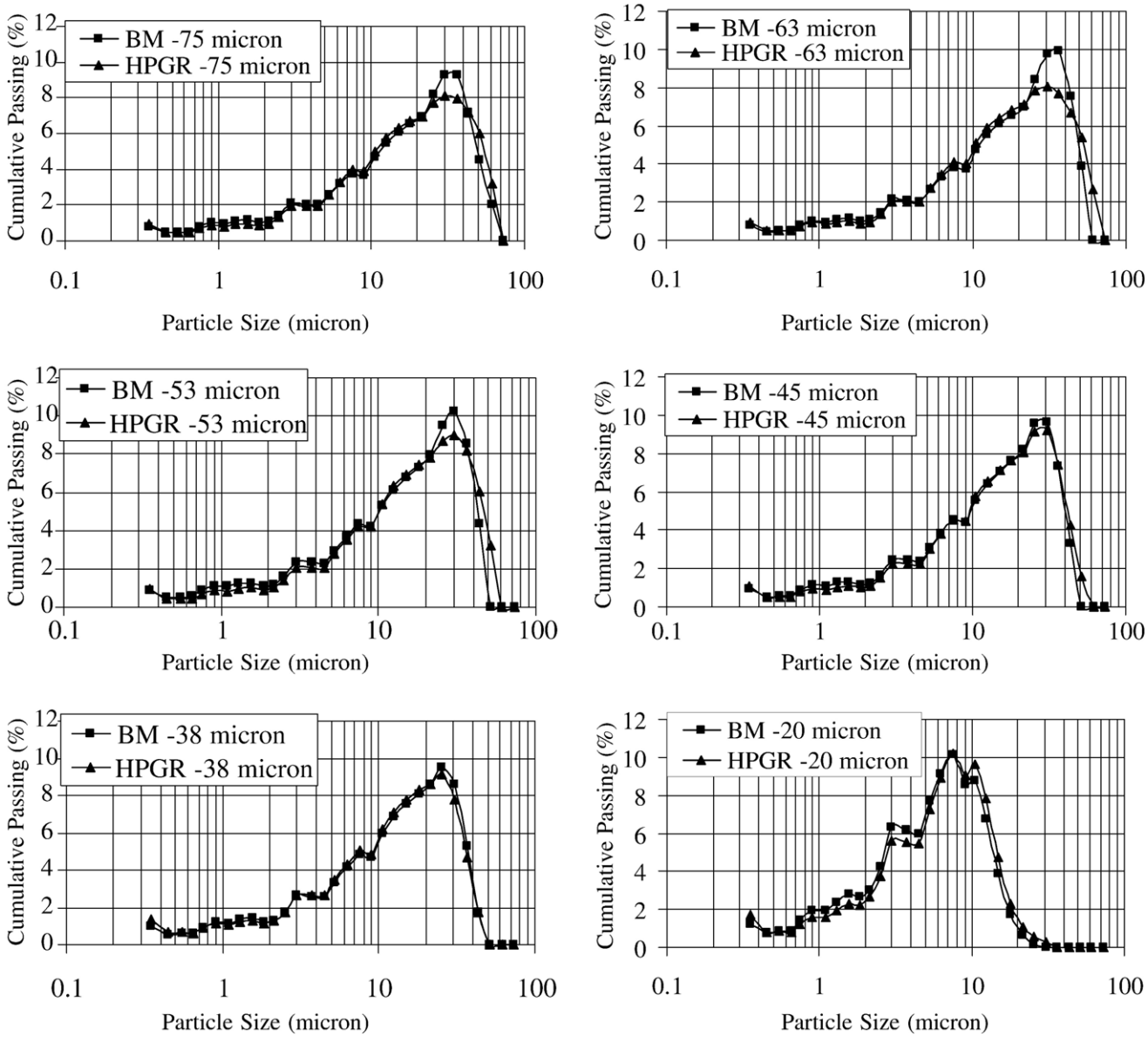

Fig. 3. Particle size distributions of samples in two grinding modes.

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

phases. Since the reflectivity and color differences are not exactly certain between the phases, it is necessary to expand their contrast by outer influence i.e. by etching [15].

It is well known that the properties of cement products of HPGR and ball mill show considerable differences since breakage mechanisms are quite different. This difference is reflected in particle size distribution and particle geometry. Consequently some service properties such as water demand, reactivity of C_3A and C_3S phases and setting can be changed as well [6,16]. There are a few studies examining microstructure properties of chemically identical cement products of HPGR and ball milling [17] but, no study has been encountered which interprets differences of microstructure due to different grinding modes and their combined effects on quality parameters. With this aim, some chemical, physical and mineralogical differences of HPGR and ball mill cement products were characterized and the effects of these on service properties were ascertained.

2. Experimental work

Samples were collected from HPGR feed and product clinker (with no gypsum) streams in an industrial cement plant in two different sampling periods. In the first sampling period HPGR feed clinker was ground in a laboratory ball mill to give approximately the same percentage of −90 μm as compared to the industrial HPGR product for both sampling periods. Clinker as sampled from the plant was ground in a laboratory ball mill having a diameter of 700 mm and a length of 500 mm. The filling ratio (approx. 20%) and ball size distributions were similar to the industrial applications; to simulate the breakage mechanisms in the 1st and 2nd compartments, 30 kg of clinker was ground in two steps. In the first step a coarse ball size distribution (80 mm–40 mm) was used while a finer ball size distribution was selected (30 mm–15 mm) for the finish grinding. The reason for obtaining the products having same percentage of −90 μm was to eliminate a possible scattering in chemical compositions of same narrow size fractions. As can be seen from the Fig. 1, −90 μm particle size distributions of both grinding modes are similar down to 20 μm. Since ball mill grinding was not a continuous process, avoidance of very fine particles was impossible, but the difference was not too much (Fig. 1). Ball mill grinding was carried out by using a laboratory scale mill, since it was impossible to get clinker only samples from an industrial ball mill because of gypsum addition during the grinding process. Gypsum in clinker was not preferred for liberation analysis since it makes the mineralogy complex. As the HPGR product could be obtained without gypsum, it was not added in ball mill grinding step in order to facilitate and simplify segmenting the images of narrow size fractions during image

Table 2
Chemical composition of ball mill and HPGR distribution products

%	HPGR				Ball mill			
	−75 μm	−53 μm	−38 μm	−20 μm	−75 μm	−53 μm	−38 μm	−20 μm
SiO_2	20.82	20.86	20.78	19.59	20.88	21.06	20.98	20.19
Al_2O_3	5.28	5.14	5.02	4.91	5.43	5.41	5.31	5.34
Fe_2O_3	3.18	3.14	3.08	3.06	3.37	3.33	3.30	3.47
CaO	67.12	67.15	67.11	66.69	66.89	66.97	66.8	66.28
MgO	0.97	0.99	0.94	0.96	1.00	1.01	1.02	0.98
SO_3	0.35	0.36	0.37	0.47	0.34	0.36	0.37	0.51
Na_2O	0.51	0.50	0.48	0.52	0.59	0.54	0.55	0.52
K_2O	0.66	0.66	0.67	0.80	0.67	0.67	0.67	0.82
LOI	1.12	1.20	1.30	2.80	0.66	0.80	0.86	1.82

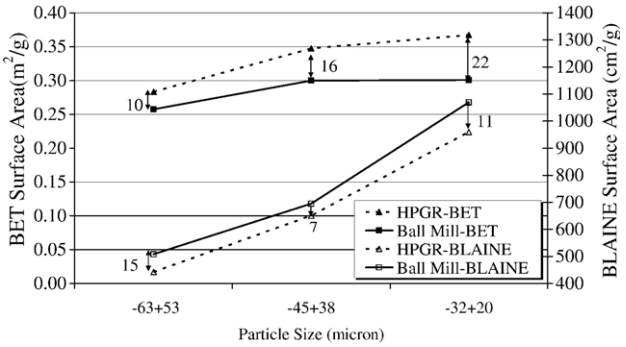

Fig. 4. Specific surface area of narrow size fractions.

analysis. But service properties were ascertained after adding adequate amount of identically sized gypsum. −90 μm products of both grinding modes were sieved into same narrow size fractions to perform image analysis study, particularly for liberation test. Particle size distribution of −63+53 μm, −45+38 μm and −32+20 μm narrow fractions determined by laser sizing are given in Fig. 2.

In the second sampling period samples were prepared similarly but this time as distribution samples such as −75 μm, −63 μm, −53 μm, −45 μm, −38 μm and −20 μm material. Products of both grinding modes were sieved in the same size classes and attention was paid to get comparable size distributions to eliminate the impact of size distribution difference on cement service properties. By choosing this type of sample preparation, it was expected to see the effects of certain size ranges on service properties, particularly on strength. Particle size distributions determined by laser sizing are given in Fig. 3.

Chemical characterization of narrow size and distribution samples was performed by XRF analyses to check if any variation occurred due to particle size and mode of grinding.

As HPGR was reported to cause some extra cracks in particle structure, it was expected to see this effect firstly on specific surface area values. Blaine and BET (N_2 adsorption) methods were used for specific area determinations.

Mineralogical study was carried out only for narrow size fractions of both grinding modes to facilitate the determination of

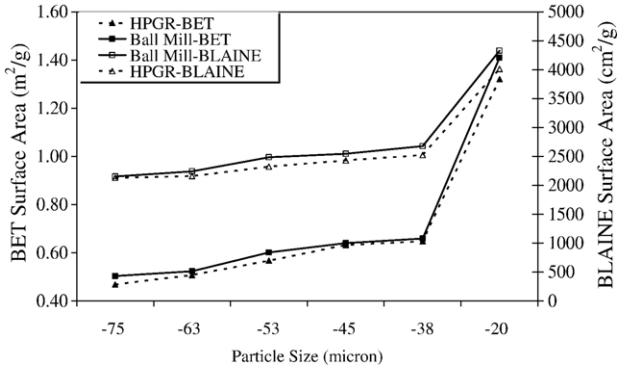

Fig. 5. Specific surface area of distribution samples.

Table 3
Mineralogical compositions of the main mineral phases in similar size fractions of different 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. By using Clemex Vision PE 3.5 apparatus and its software, image analysis was applied on polished and etched samples. It was obvious that etching was required for differentiating clinker minerals, particularly the calcium silicates. By using nital (HNO_3: ethyl alcohol, 1:1000) as a proper etchant, alite (C_3S), belite (C_2S) and liquid phase was analyzed. In order to obtain reliable results, approximately 80 image fields including 790–1575 particles from every fraction were randomly chosen and proper algorithms best defining the image was integrated into software. Some mineralogical properties such as total amount of minerals, distribution of liberation classes and shape characteristics of particles were quantified.

Cement quality properties such as water demand, setting time, soundness and compressive strength tests were performed according to Turkish standards [18,19] for narrow size and distribution samples of HPGR and ball mill products to see the effect of grinding mechanism and mineralogical differences. Five percent of gypsum was added to all samples as set regulator. Constant *w/c* ratio was used for the strength tests to get comparable results as defined in standards [18]. Strength values were measured by using four prism samples formed from 2 different molds of the same mortar to provide reproducibility.

3. Results and discussions

The goal was to compare service properties of products of different grinding modes, so it was expected that the chemical compositions of size fractions should be similar. As can be seen from Table 1, chemical compositions of main oxides of the narrow size fractions are similar, except for free lime, indicating that the examined properties will be comparative.

Similar results were seen in the chemical compositions of distribution samples. The values in Table 2 showed no appreciable differences due to particle size and mode of grinding.

Figs. 4 and 5 present the specific surface area measurements of narrow size fractions and distribution samples of both grinding modes respectively. It is clear that surface area differences are more evident in narrow fractions, particularly for BET measurements of HPGR products. This is probably due to the formation of rough surfaces and extra cracks produced under high compression. But in Blaine measurements, ball mill fractions gave higher surface areas resulting from probably better packing, i.e. smaller voidage between the particles causing higher resistance of air flow measured.

As for Blaine measurements of distribution samples, specific surface areas of ball mill fractions have higher values of about 7%.

Table 4
Distributions of liberation classes in HPGR and ball mill products

Liberation classes	HPGR (%)			Ball Mill (%)		
	−63+53 μm	−45+38 μm	−32+20 μm	−63+53 μm	−45+38 μm	−32+20 μm
Free alite	6.16	22.73	44.59	5.58	13.12	34.98
Free belite	0.02	0.17	0.13	0.02	0.06	0.28
Free liquid phase	0.74	0.31	1.40	0.14	0.71	1.05
Alite-belite binary	0.39	2.10	0.98	0.74	1.64	1.34
Belite-liquid phase binary	1.70	2.52	3.15	1.07	2.61	1.03
Alite-liquid phase binary	84.85	66.56	47.22	83.41	76.99	60.04
Ternaries	6.14	5.61	2.52	9.04	4.88	1.27

While BET values of HPGR products were much higher in narrow size fractions, that difference closed up in distribution samples because of existing fine particles. It indicates that HPGR mechanism produces much fissured particles and it was supported by SEM photographs as presented in a previous study [20].

As clearly illustrated in Table 3, distribution of mineral phases in different grinding modes show differences due to particle size. Amount of C_3S increases and the amount of liquid phase decreases as the particle size gets finer indicating that the grindability of C_3S is much easier than C_2S.

The greatest interest in this study was obviously to determine if there were any differences between grinding mechanisms in terms of mineral liberation; and their influences on main cement service properties. Clinker minerals, mostly C_3S and C_2S can be seen together within liquid phase, expressing a locked type of mineral. It is known that hydration takes place firstly on the surfaces of phases and water penetrates into a certain depth. In the authors' mind amount of free surfaces and/or micro cracks produced within these phases by virtue of high compression might affect the service properties. Consequently, liberation analysis was performed to determine the liberation states of mineral phases. Firstly, liberation classes were defined as free, binary and ternary. Results are given in Table 4 for ball mill and HPGR products respectively. It is clearly seen from the table that alite was generally locked within liquid phase and amount of its liberation was increased as the particle size got finer. It is also seen that the amount of free alite particles of HPGR was higher in each size fraction compared to the ball mill products. Another observation from the images was the nests of belite within liquid phase and embedded spots in alite.

Breakage mechanism in ball mill grinding is known to be more repeated random fracturing across mineral grains. But the stress in high compression is much intensive along grain boundaries. This may be regarded as an answer of high liberation in HPGR products. Also it was thought that transgranular fracture in ball milling might have an effect on shape of particles. As can be seen in Table 5 the average perimeter of clinker particles are a little higher in ball milled particles becoming more pronounced in coarse size fraction (−63+53 μm) as expected. Other shape properties related to alite and belite minerals such as size of crystals, sphericity, aspect ratio and embedding amount of belite within alite will not be mentioned here since they were reported earlier [20].

Service properties such as water demand, setting time, soundness and compressive strength were studied for the samples, including 5% percent of gypsum, in comparison with image analysis results.

The results for closely sized fractions given in Table 6 show that HPGR products consume more water than ball mill products to attain normal consistency. This is due to the fissured structure of HPGR products as indicated by BET test results also. Setting test was performed on closely sized samples but, because of absence of fine fraction, setting times were so long and no appreciable difference was recorded. It was also reported in the literature that the amount of coarse material may cause bleeding and have practically no effect on hydration [21].

The results of setting time, water demand and soundness tests for distribution samples are given in Tables 7 and 8. It can be said that difference in grinding modes had no effect on setting times since particle size distributions were so similar. Fineness may have an influence on setting as can be seen particularly in the −20 μm fractions. When fineness increases, the surface area contacting with water increases and the rate of hydration reactions accelerates. As it was in narrow fractions, same trend in water demand values are seen; water consumption was changed due to both particle size and grinding mode. But it should be noted that when particle size gets finer it needs more water to facilitate the movement of particles on each other. Soundness results were in standard limits [18] and showed no variation.

Table 5
Shape properties of clinker particles in HPGR and ball mill products

Size fractions μm	Average perimeter, μm	
	HPGR	Ball mill
−63+53	74.33	96.92
−45+38	66.36	68.99
−32+20	62.82	62.08

Table 6
Water demand of size fractions (%)

Size fractions μm	Ball mill	HPGR
−63+53 μm	35.0	39.0
−45+38 μm	36.4	38.5
−32+20 μm	33.0	35.0

Table 7
Setting time, water demand and soundness properties of HPGR products

μm	Setting time, minutes		Water demand, %	Soundness, mm
	Initial	Final		
−75	230	255	30.0	1
−63	195	275	30.6	0
−53	200	260	32.4	1
−45	215	270	34.4	0
−38	190	275	33.2	0
−20	170	220	40.0	0

Compressive strength tests were performed on narrowly sized fractions on 2nd, 7th and 28th days to see if any relationship existed between liberation and strength development. HPGR products were expected to give better strength values by virtue of having more liberated alite surfaces. Contrary to our expectations, although no big differences were observed, ball mill fractions gave slightly higher strength values in all ages particularly for −32+20 μm fraction as shown in Fig. 6.

Standard compressive test results of HPGR and ball mill distribution samples for 2nd, 7th and 28th days were given in Fig. 7 comparatively. It is seen that ball milling resulted in better strength development in all of its size distributions for all ages except −20 μm fraction. It is known that ball milling produces more fine particles in the fine tail of the distribution which was the case in our experiment. These very fine particles in the −20 μm sample of ball mill may have quickly hydrated because of high surface area in the certain parts of the cast, which would have caused some weak zones in whole. Therefore, these zones may have resulted in poor strength development.

Although the products of HPGR and ball mill have similar particle size distribution and chemical compositions, ball mill products gave higher strength values. Similar results were reported in literature by Müller-Pfeiffer and Clemens [22] who stated that in spite of the same component materials, the compressive strength of ball mill product had been higher than those of the products that had been preground in the HPGR and vertical grinding mill and then finish ground in ball mill. This situation was interpreted that every clinker mineral phase might be distributed in different amounts to all size classes due to different grinding mechanism. It is proved in this study that every size class had different mineralogy as it is indicated in Table 3. Also it is known that these

Table 8
Setting time, water demand and soundness properties of ball mill products

μm	Setting time, minutes		Water demand, %	Soundness, mm
	Initial	Final		
−75	185	275	29.2	0
−63	180	265	29.6	0
−53	185	275	30.0	1
−45	200	265	31.6	0
−38	200	255	33.0	0
−20	175	235	42.0	0

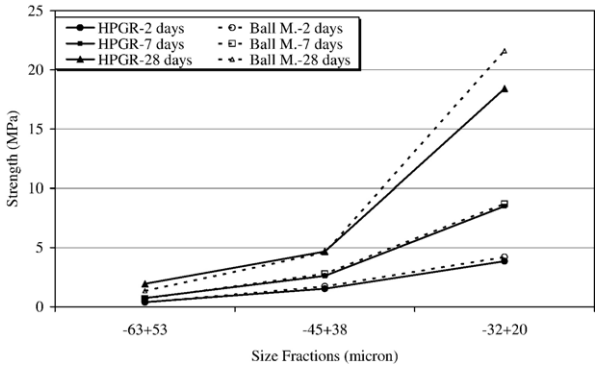

Fig. 6. Strength development of narrow size fractions in 2nd, 7th and 28th days.

clinker phases have different grindabilities and different contributions on strength development.

4. Conclusions

In view of investigating different grinding mechanisms in terms characterization and downstream service properties, following conclusions can be deduced:

- Despite having no variation in chemical compositions, mineralogical compositions of the narrow size fractions indicate variations depending on the fineness.
- High compression grinding resulted in micro fissured structure of particles; hence higher BET results have been obtained.
- HPGR grinding gave better liberation of particularly alite mineral compared to ball milling due to intergranular breakage along grain boundaries.
- Water demand of HPGR products was higher than ball mill products resulting from rough surfaces and fissured structure.
- No appreciable difference was observed in setting times and soundness results of fractions due to different grinding modes.
- In narrow size fractions, compressive strength values of ball mill products were slightly higher than HPGR products.
- In distribution samples, probably the lower specimen compaction of the HPGR samples might have affected the strength adversely. Compressive strength was much more in

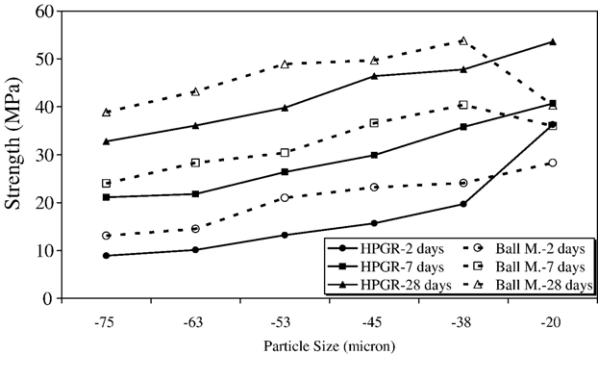

Fig. 7. Strength development of distribution size fractions in 2nd, 7th and 28th days.

favor of ball milling except for −20 μm sample. Strength of −20 μm sample of ball mill was poor probably due to some weak zones resulted from rapid hydration of very fines in certain parts of the cast.

- Finally; particle size distribution, particularly minus 30 μm fraction, had most important impact on service properties.

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