COMMINUTION AND MECHANICAL ACTIVATION OF PORTLAND CEMENT IN DIFFERENT MILL TYPES

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The experiments of comminution (grinding-mechanical activation) were performed in laboratorial ball mill, vibro mill with balls and vibro mill with rings, using portland cement from the regular production. A noticeable mechanical activation was registered in vibro mill with rings (as confirmed by XRD analysis). In all three mill types, mechanical properties of ground cement were improved due to an increase of specific area to approximately the same value (400 $m^2 kg^{-1}$). The highest compressive and bending strengths were achieved in Portland cement comminuted in vibro mill with rings (55MPa and 9MPa, in comparison with the original PC values 43 MPa and 7.5 MPa respectively), as registered after 28 day solidification period. Thereby, the compressive strength was about 10 % higher and bending strength about 3.5 % higher then in the cement treated in mill with balls until the same specific area was reached.

INTRODUCTION

Over the last few years, comminution and mechanical activation of the silicate systems are the subject of large interest and extensive investigation [1,2]. It has been shown that comminution in special mill types (in energy grinding intensive mills) and induced mechanical activation cause certain microstructural defects and power amorphization, thus influencing the diffusion process and reactions in a solid state, which are important for obtaining inorganic bonding agents [3, 4, 5]. It has also been shown that it is possible to influence, by mechanical activation, the kinetics of the clinker mineral hydration and consequently, the kinetics of binding and solidification of Portland cement based products [6]. In this paper, the investigational results on influence of the mill type, the comminution conditions and induced mechanical activation of Portland cement on its microstructural properties, binding and solidification processes, influencing the final mechanical strength of products based on cement, are presented.

EXPERIMENTAL PART

The experiments of comminution were carried out in three mill types: laboratorial mill with balls, vibrational mill with balls ("Siebtechnic GmbH") and vibrational mill with rings ("KHD Humboldt AG"). The sample of Portland cement (PC) was obtained from the cement factory "Novi Popovac". Characteristics of the starting sample are presented in table 1.

Table 1. Characteristics of starting Portland cement.

component	composition (wt.%)	other	
SiO_2	19.59	humidity, at 105 °C (wt.%)	0.80
Al_2O_3	5.22	specific area ($m^2 kg^{-1}$)	288
Fe_2O_3	2.59	saturation degree	94.97
CaO	62.64	silicate modul	2.50
MgO	2.62	aluminate modul	2.01
SO_3	2.49	hydraulic modul	2.28
insoluble residue	0.46		
LOI	2.60		
total	98.21		
free CaO	1.26		

As can be seen from table 1, investigated Portland cement was of customary chemical composition and corresponding modules.

Portland cement was composed of Portland cement clinker (95 wt.%) and anhydrite (5 wt.%), ground together.

By preliminary investigations, the time necessary to comminute Portland cement to achieve the specific area of 400 m^2 kg^{-1}, was determined. The times required to achieve this specific area in different mill types were as follows:

laboratorial mill with balls:	30 min, (PC MB)
vibration mill with balls:	19 min, (PC VMB)
vibrational mill with rings:	3 min, (PC VMR)

Based on obtained results, vibrational mill with rings appears to be the most efficient. The Portland cement sample were then analyzed by the X-ray diffractometer (XRD) and further used for determination of the physico-mechanical properties. The same investigations were performed upon mechanically untreated Portland cement.

XRD analyses were performed using Phillips diffractometer PW-1710. Specific area was determined by a standard Blain method. Mechanical characteristics were determined by Yugoslav (JUS) method, standard for this purpose.

RESULTS AND DISCUSSION

The results of the XRD analyses of the clinker minerals of starting Portland cements are presented in table 2. Figure 1 shows the intensity of the highest diffractional peaks and *d*-value for the starting sample and the same sample treated in different mills.

On the basis of the data from table 2 and figure 1 it can be seen that the most important changes of clinker minerals (C_3S, C_2S and C_3A) and anhydrite occurred during grinding in vibrational mills with rings: diffractional peak intensities for C_3S were reduced from 277 to 166, for C_2S from 185 to 149 and for C_3A, from 83 to 71 and for anhydrite, from 32 to 16 cts; in other two mills, these decreases were considerably smaller. The decrease is an indication for defects in the crystal lattice and amorphization of powder. Evidently, these phenomena are best expressed in the Portland cement sample comminuted in vibro mill with rings (table 2, figure 1).

For these reasons, mechanical activation contributes to faster hydration reactions of the clinker minerals during setting. This is confirmed by shorten setting time for Portland cement ground in vibro mill with rings in comparison with starting cement or cement ground in ball mill (table 3). In fact, beginning of setting for Portland cement ground in vibro mill with rings is two times faster then for the starting Portland cement. At the same time, water consumption for cement ground in vibro mill with rings is reduced by 8.5 % and 14 % in comparison with starting Portland cement and Portland cement ground in ball mill, respectively.

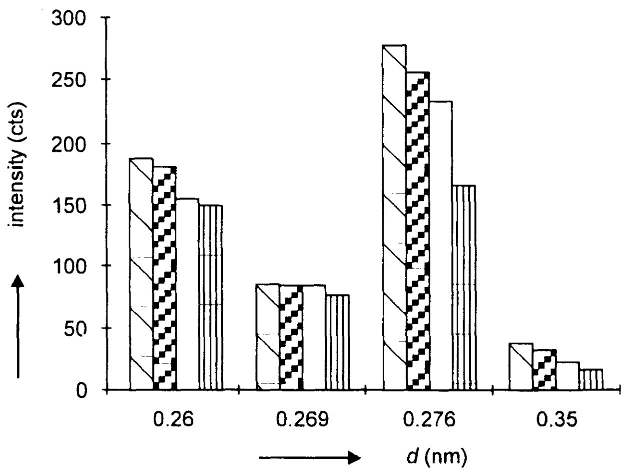

Figure 1. The integral intensities of diffraction lines characteristics for clinker minerals for starting sample and the same sample after treatment in different mills.
▧ - PC, ▩ - PC MB, □ - PC VMB, ▥ - PC VMR

Table 2. Peak intensities (XRD) for Portland cements treated in different mill types.

sample	intensity (cts)			
	C_2S d = 0.26 nm	C_3A d = 0.269 nm	C_3S d = 0.276 nm	Anhydrite d = 0.35 nm
starting PC	185	83	277	32
PC treated for 30 min in ball mill(PC MB)	164	82	237	28
PC treated for 19 min in vibro mill with balls (PC VMB)	154	81	225	19
PC treated for 3 min in vibro mill with rings (PC VMR)	149	71	166	16

Cement notation is used throughout: C = CaO, S = SiO_2, A = Al_2O_3.

Table 3. Physico-mechanical properties of Portland cement, before and after mechanical activation.

sample	grinding time (min)	screen oversize at (0.09 mm) (wt.%)	specific area ($m^2\,kg^{-1}$)	water consumption (wt.%)
starting PC sample	0	4.4	290	27.00
PC sample treated in ball mill (PC MB)	30	1.6	400	28.75
PC sample treated in vibro mill with balls (PC VMB)	19	0.6	390	25.10
PC sample treated in vibro mill with rings (PC VMR)	3	0.6	420	24.70

sample	setting time (hours) (min)		bending strength after day (MPa)			compressive strength after day (MPa)		
	initial	final	3	7	28	3	7	28
starting PC sample	2 - 10	3 - 15	5.7	6.9	7.5	25.6	31.2	43.0
PC sample treated in ball mill (PC MB)	2 - 10	3 - 50	6.9	7.3	8.7	38.0	41.7	50.0
PC sample treated in vibro mill with balls (PC VMB)	1 - 15	2 - 50	6.2	7.6	8.2	28.8	39.2	51.1
PC sample treated in vibro mill rings (PC VMR)	1 - 00	3 - 00	6.2	8.0	9.0	33.0	40.8	55.2

In table 3, the comparative results on physico mechanical properties of starting Portland cement and Portland cement treated in different mill types, are presented.

It is quite obvious that comminution in each of the three mill types for the times required to attain the same specific area of about 400 $m^2\,kg^{-1}$ improved mechanical properties of cement in comparison with the starting samples. After 28 day setting, compresive strength increased by 16.0 %, 18.8 % and 28.4 % for Portland cements ground in ball mill (30 min), vibro mill with balls (19 min) and vibro mill with rings (3 min), respectively, in comparison with compresive strength of starting Portland cement samples.

Additional comminution of investigated sample in ball mill (30 min) also improved its mechanical properties (compressive and bending strength, table 3). This improvement can be dominantly contributed to increase of the specific area (from 290 to 400 $m^2\,kg^{-1}$), since the results of XRD analysis (table 2 and figure 1) did not indicate the important presence of the structural changes in the cement sample during comminution. Compressive and bending strength of the cement sample ground in vibro mill with rings (3 mins) until the specific area of 400 $m^2\,kg^{-1}$ were higher in comparison with the values achieved in ball mill (table 3). Under these conditions, however, XRD analysis confirmed the presence of the important microstructural defects (figure 1). As can be seen from table 3, bending strength of the sample ground in vibro mill with rings measured after 28 days was 3.5 % higher, while the compressive strength was 10 % higher, in comparison with the sample ground in ball mill.

CONCLUSION

By grinding Portland cement samples in different mill types for different times (ball mill - 30 min, vibro mill with balls - 20 min, vibro mill with rings - 3 min), the samples of approximately the same specific surfaces (400 $m^2\,kg^{-1}$) were obtained. Independent of the type of mill, this additional comminuting improved compressive strength and bending strength , also contributing to the appearance of structural defects and amorphization. Structural changes were particularly well expressed in the sample ground (for 3 min) in vibro mill with rings, but very small in the sample ground in conventional ball mill (for 30 min), as confirmed by lower intensities of diffractional peaks characteristic for clinker minerals. Well expressed structural changes in the sample ground in vibro mill with rings were accompanied by raised activity of this cement in hydration reactions during setting. For these reasons, the beginning of binding was almost twice faster in comparison with the starting sample or the sample ground in ball mill. At the same time, water consumption was for about 8.5 % lower in comparison with cement ground in ball mill. Compressive strength and bending strength were highest for the sample ground in vibro mill with rings: they were higher for 10 % and 3.5 %, respectively, in comparison with the values for the sample ground in ball mill, after 28 day setting.

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MLETÍ A MECHANICKÁ AKTIVACE PORTLANDSKÉHO CEMENTU V RŮZNÝCH TYPECH MLÝNŮ

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Byly provedeny laboratorní zkoušky aktivačního mletí cementu z běžné výroby v laboratorním kulovém mlýnu, vibračním mlýnu s koulemi, a ve vibračním mlýnu s kroužky. Významné mechanické aktivace (potvrzené analýzou XRD) bylo dosaženo mletím ve vibračním mlýnu s kroužky. U všech tří druhů mlýnů bylo dosaženo zlepšení mechanických vlastností přemletého cementu v důsledku zvýšení specifického povrchu na přibližně stejnou hodnotu 400 $m^2\ kg^{-1}$. Nejvyšší pevnosti v tlaku a v tahu za ohybu po 28 dnech byly dosaženy u cementu přemletého ve vibračním mlýnu s kroužky (55 MPa a 9 MPa proti hodnotám 43 MPa a 7,5 MPa původního cementu). Přemletím cementu ve vibračním mlýnu s kroužky, ve srovnání s přemletím ve vibračním mlýnu s koulemi na stejný specifický povrch, se pevnost v tlaku zvýšila o cca. 10 % a pevnost v tahu za ohybu o cca. 3,5 %.