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EVALUATION OF THE GRINDABILITY OF RECYCLED GLASS IN THE PRODUCTION OF BLENDED CEMENTS

OCENA SPOSOBNOSTI DROBLJENJA RECIKLIRANEGA STEKLA PRI PROIZVODNJI MEŠANIH CEMENTOV

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The replacement of primary raw materials in cement production is a current topic. Potentially usable raw materials include recycled glass. The disadvantage of glass is its tendency to aggregate. The conventional method for the production of blended cement is separate grinding and then homogenizing the components. However, in this case aggregated fine glass in the cement composites acts only physically and mechanically as a filler rather than as an active pozzolan. An interesting option to prevent the formation of aggregates formed from glass is co-grinding. This procedure is not very common in practice. Various ingredients of blended cements have widely different grindabilities, and it is therefore better to grind them separately. The aim is to compare the co-grinding and separate grinding of a combination of Portland clinker and recycled glass. The grindability was tested on clinker, glass, and blended cements prepared by co-grinding and by separate grinding. The results of the experiment show that by co-grinding the components of blended cement with the addition of 20 % of recycled glass as a pozzolan, a synergy effect caused by the various mechanical properties of the components occurs. The aggregation of grains is less significant than during separate grinding and it leads to a better grinding effect. This knowledge can by utilized in the design and processing of new blended cements. Also, co-milling the glass-cement system can eliminate the stage of homogenization, and, therefore save energy.

Keywords: grindability, Portland clinker, recycled glass

Tema članka je nadomeščanje primarnih surovin pri proizvodnji cementa. Potencialno uporabno surovino predstavlja reciklirano steklo. Pomanjkljivost stekla je, da ima nagnjenost k sprijemanju. Običajna metoda proizvodnje mešanega cementa je ločeno drobljenje in homogenizacija sestavin. V tem primeru drobnozrnato steklo v cementnih mešanicah deluje samo fizikalno in mehansko kot polnilo in ne kot aktiven pozolan. Dodatno mletje je pomembno za preprečevanje nastanka skupkov stekla. Vendar pa ta postopek ni tako pogost v praksi. Različne sestavine cementne mešanice se različno drobijo in je zato bolje, da se jih drobi ločeno. Namen študije je primerjati dodatno mletje in ločeno mletje kombinacije Portland klinkerja in recikliranega stekla. Mletje je bilo preizkušeno na klinkerju, steklu in mešanici cementov, pripravljenih z dodatnim mletjem in z ločenim mletjem. Rezultati preizkusov so pokazali, da se pri istočasnem mletju mešanic cementov z dodatkom 20 % recikliranega stekla kot pozolana, pojavi sinergijski pojav zaradi različnih mehanskih lastnosti sestavin. Združevanje zrn je manj izrazito kot pa pri ločenem mletju in povzroči boljši učinek mletja. To dejstvo je mogoče uporabiti pri načrtovanju in izdelavi novih mešanic cementov. Torej se lahko z istočasnim mletjem sistema steklo-cement, odpravi fazo homogenizacije in s tem prihrani energijo.

Ključne besede: sposobnost mletja, portlandski klinker, reciklirano steklo

1 INTRODUCTION

Secondary raw materials represent an ever more frequent replacement for primary raw materials in the production of building materials. The area of cement production is no exception. In current practice, blended cements are applied increasingly more often. In these cements, the Portland clinker is replaced by hydraulically active compounds or agents with pozzolanic properties.[1–3] Glass is chemically and mineralogically very close to traditional pozzolans. Therefore, various types of recycled glass may be potentially interesting raw materials for the production of blended cements. Various authors have described the behavior of finely ground glass in cement composites.[4,5] However, due to a considerable ability to agglomerate, the recycled glass used as an additive for the cement composite is not reactive enough and acts only physically-mechanically as a filler.[4] The common production process for blended cements is separate grinding of the individual components and their subsequent homogenization. This procedure is common in the production of blast-furnace slag cements. In this case the procedure is advantageous because Portland cement clinker and blast-furnace slag have very different grindabilities and it is therefore preferable to grind them separately, and subsequently to homogenize.[6] As noted above, fine glass powder exhibits a significant ability for aggregation, which greatly complicates the homogenization with Portland cement. Therefore, the traditional approach of separate grinding and subsequent homogenization seems to be less suitable in the case of a glass-cement system. An interesting option to prevent the formation of agglomerates with pure glass is co-grinding of the glass and clinker. The content of SiO_2 in recycled glass is only in amorphous form and the hardness is 7 on the Mohs scale. The standard alite clinker contains four main minerals, and their weighted average hardness is between 6 and 7 on the Mohs scale.[7] However, the recycled glass is much more fragile, which means the grindability of both components could be very similar. Various authors have chosen different methods to assess grindability. Most methods are based on an evaluation of the ratio of the energy consumption and refinement of the material.[8–12] An interesting approach is to evaluate the grindability by using particle size distribution curves.[6] The aim was to assess whether in the case of a cement-glass system, co-grinding of the component is more advantageous than separate grinding with subsequent homogenization. The selected approach was to monitor and compare the grindability of the individual components as well as the mix. The method of monitoring the impact of the constant grinding time on the particle size distribution curves and specific surface area was chosen for the experiment.

2 MATERIALS AND METHODS

For monitoring the grindability, recycled glass and Portland cement were used. The chemical composition of the recycled glass was determined by traditional chemical analysis. The modified Chapelle test method[13] was used for the pozzolanic activity determination. The modified Chapelle test consists of the reaction of pozzolan and freshly annealed CaO in an aquatic environment at 93 °C for 24 h. The reaction takes place in a tightly sealed stainless-steel vessel and the suspension is stirred by an electromagnetic stirrer. The result is expressed as the amount of $Ca(OH)_2$ bound in mg per 1 g of pozzolan. The density of the recycled glass was determined by automatic pycnometer Micromeritics AccuPyc II 1340. For the measurement of the specific surface according to Blaine, an automatic PC-Blaine-Star device was used to measure the cell capacity of 7.95 cm^3. The determination was performed three times to eliminate errors. The morphology of the particles was determined by scanning electron microscope (SEM). A Tescan MIRA 3 XMU SEM with a secondary-electron detector was used. The Portland cement was prepared in a laboratory ball mill by co-grinding of the Portland clinker from cement plant Hranice and the chemo-gypsum Pregips in the ratio 95/5. Milling was carried out to the same specific surface area that was measured on the recycled glass. The chemical composition, the density, the specific surface area, and morphology of the particles were also determined. The blended cement was prepared by co-milling Portland clinker, gypsum and recycled glass in the ratio 76/4/20. Milling was carried out to the same specific surface area that was measured on the recycled glass. As in the previous case, chemical composition, density, specific surface area and morphology of the particles were also determined. The milling in this phase of the experiment was always carried out at a total dose of 5 kg in a Brio OM 20 ball mill at a speed of 40 min^{-1}. The grinding of the recycled glass, the Portland cement and the blended cement for determining the grindability was performed in a Fritsch Pulverisette 6 planetary mill at 500 min^{-1}. A steel vessel of 500 mL and 25 steel grinding balls of 20 mm diameter and a mass of 180 g of material were always used. The grinding times were (1, 2, 3 and 5) min. Then, the particle size distribution was performed on each of these samples using a Matest Air jet sieve. The sieves mesh size were (0.010, 0.020, 0.041, 0.063, 0.090 and 0.125) mm. The Blaine specific surface area and morphology of the particles by SEM were determined on all the samples ground for 5 min. A simple calculation using weighted-average values of the surface areas separately milled components was made to facilitate the grindability comparison, Equation (1):

$$S_{BC} = 0.8 \cdot S_{PC} + 0.2 \cdot S_{GR} \quad (1)$$

Where S_{BC} is the theoretical specific surface area of the blended cement, S_{PC} is the specific surface area of the Portland cement and S_{RG} is the specific surface area of the recycled glass. Subsequently, a sample of the blended cement was prepared by homogenization of the separately ground components in the same proportions. Homogenization of the sample was performed using a laboratory homogenizer for 1 h. On the resulting samples the specific surface area according to Blaine was determined. The results were compared with the calculation.

3 RESULTS

Chemical compositions of the clinker and gypsum are summarized in **Tables 1** and **2**.

Table 1: Partial chemical composition of clinker
Tabela 1: Parcialna kemijska sestava klinkerja

Component	SiO_2	CaO	Al_2O_3	Fe_2O_3	SO_3	Others
Content (%)	20.29	65.33	5.21	5.04	0.79	3.34

Table 2: Partial chemical composition of gypsum
Tabela 2: Parcialna kemijska sestava mavca

Component	$CaSO_4 \cdot 2H_2O$	H_2O	$CaSO_4$	Others
Content (%)	84.00	11.00	2.40	2.60

The chemical composition of the selected clinker is typical for Portland clinkers. In the case of gypsum, it is highly pure with a relatively high humidity; therefore, it should be dried for the cement preparation to reduce the humidity to under 5 % according to ČSN 721206.

Chemical composition of the recycled glass is summarized in **Table 3** and its pozzolanic activity is indicated in **Table 4**.

Table 3: Partial chemical composition of the recycled glass
Tabela 3: Parcialna kemijska sestava reciklliranega stekla

Component	SiO_2	CaO	Al_2O_3	K_2O	Na_2O	Others
Content (%)	69.25	8.09	0.83	0.41	16.44	4.98

Table 4: Pozzolanic activity of recycled glass with different specific surface area
Tabela 4: Pozolanska aktivnost recikliranega stekla z različno specifično površino

Specific surface area (m^2 kg^{-1})	244
Pozzolanic activity (mg $Ca(OH)_2$/g pozzolan)	1112

The chemical and mineralogical compositions of the recycled glass resemble a classic pozzolan. The sample of recycled glass with a specific surface area of 244 m^2 kg^{-1} reached a pozzolanic activity of 1112 mg $Ca(OH)_2$/1 g in a modified Chapelle test.

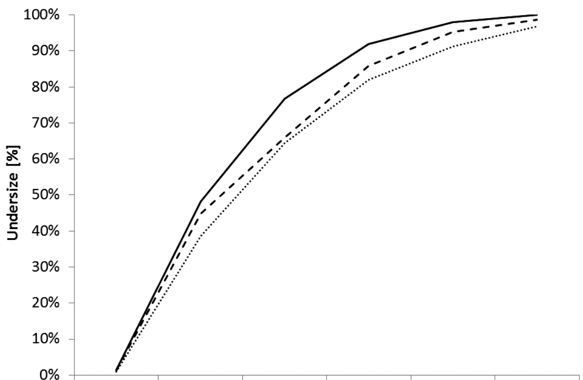
An overview of the properties of the raw materials on the grindability are included in **Table 5**. All the pre-grinding was made on a ball mill to ensure roughly the same surface area as the recycled glass.

Table 5: Overview of input materials
Tabela 5: Pregled vhodnih materialov

Material	Components	(%)	Preground	Density (kg/m^3)	Specific surface area (m^2 kg^{-1})
Portland cement	Clinker	95	Yes	3081	250
	Gypsum	5			
Glass	Glass	100	No	2458	244
Blended cement	Clinker	76	Yes	2952	247
	Gypsum	4			
	Glass	20			

All the input materials were then ground in a planetary mill for (1, 2, 3 and 5) min with a rotational speed of 500 min^{-1}. Each sample was then examined with a sieve analysis. The results are summarized in **Figures 1** to **5**.

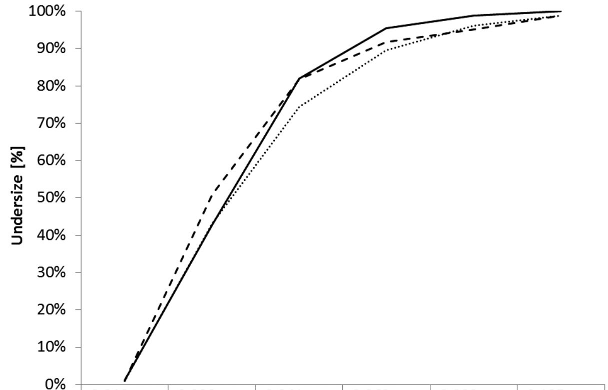
From the size distribution curves of the input materials it is evident that although the specific surface area is similar, the recycled glass is much coarser. This is caused by the different shapes of the grains in the recy-



	0,010 mm	0,020 mm	0,041 mm	0,063 mm	0,090 mm	0,125 mm
Cement	1,563%	48,264%	76,722%	91,933%	97,983%	100,000%
glass	0,904%	38,668%	64,453%	81,909%	91,301%	96,851%
Mix	1,321%	44,769%	65,940%	85,943%	95,325%	98,620%

Particle size [mm]

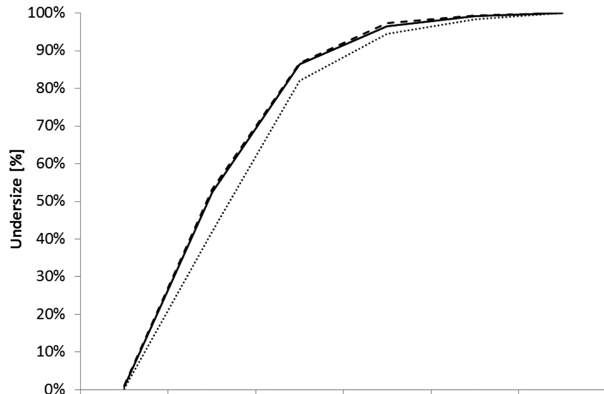
Figure 1: Size distribution of input materials
Slika 1: Razporeditev velikosti vhodnih materialov



	0,010 mm	0,020 mm	0,041 mm	0,063 mm	0,090 mm	0,125 mm
Cement	1,145%	42,811%	81,973%	95,398%	98,893%	100,000%
glass	0,914%	43,098%	74,352%	89,521%	96,210%	98,808%
Mix	0,992%	50,892%	81,726%	91,726%	95,057%	98,848%

Particle size[mm]

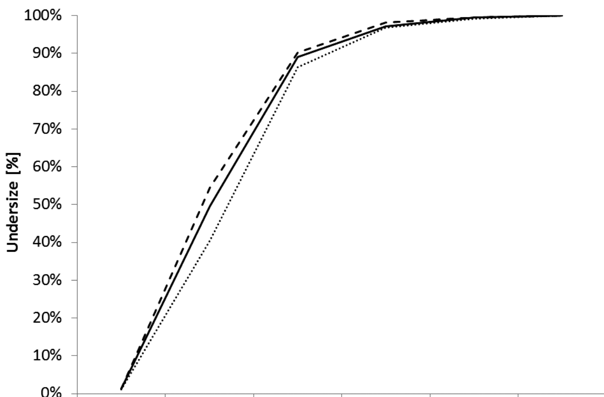
Figure 2: Size distribution after 1 min
Slika 2: Razporeditev velikosti po1 min



	0,010 mm	0,020 mm	0,041 mm	0,063 mm	0,090 mm	0,125 mm
Cement	0,744%	52,399%	86,351%	96,571%	99,165%	100,000%
glass	0,291%	42,079%	82,028%	94,548%	98,319%	100,000%
Mix	1,227%	53,358%	86,755%	97,285%	99,305%	100,000%

Particle size [mm]

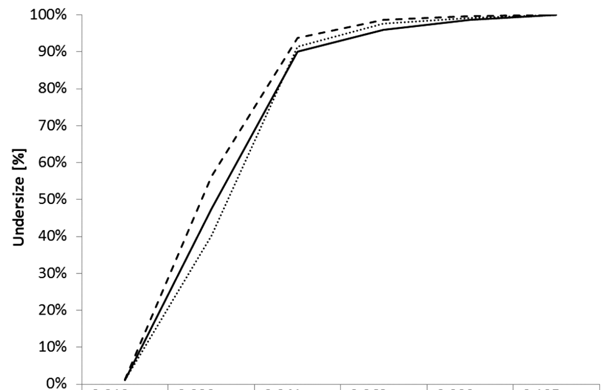
Figure 3: Size distribution after 2 min
Slika 3: Razporeditev velikosti po 2 min



	0,010 mm	0,020 mm	0,041 mm	0,063 mm	0,090 mm	0,125 mm
Cement	1,346%	49,473%	89,088%	97,110%	99,450%	100,000%
glass	1,137%	40,432%	86,370%	96,803%	99,250%	100,000%
Mix	1,320%	54,526%	90,185%	98,156%	99,570%	100,000%

Particle size [mm]

Figure 4: Size distribution after 3 min
Slika 4: Razporeditev velikosti po 3 min



	0,010 mm	0,020 mm	0,041 mm	0,063 mm	0,090 mm	0,125 mm
—— Cement	1,159%	47,595%	90,130%	95,902%	98,660%	100,000%
······ glass	1,090%	40,251%	91,360%	97,677%	99,115%	100,000%
– – Mix	1,206%	56,368%	93,742%	98,615%	99,700%	100,000%

Particle size [mm]

Figure 5: Size distribution after 5 min
Slika 5: Razporeditev velikosti po 5 min

cled glass, Portland cement and blended cement, as seen in **Figures 6** to **8**. The curves of the particle size distribution of the grinded materials indicate that the grindability of the recycled glass and the Portland cement is similar for selected time intervals. However, by co-grinding these materials, the grinding effect was stronger.

The images taken by scanning electron microscopy before and after the grinding of the components are

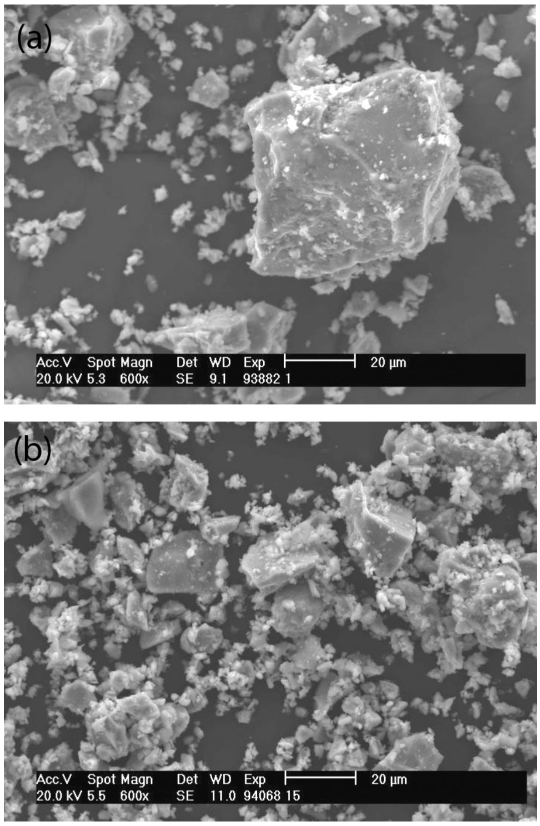


Figure 7: SEM image of PC: a) before and b) after grinding
Slika 7: SEM-posnetek PC: a) pred in b) po mletju

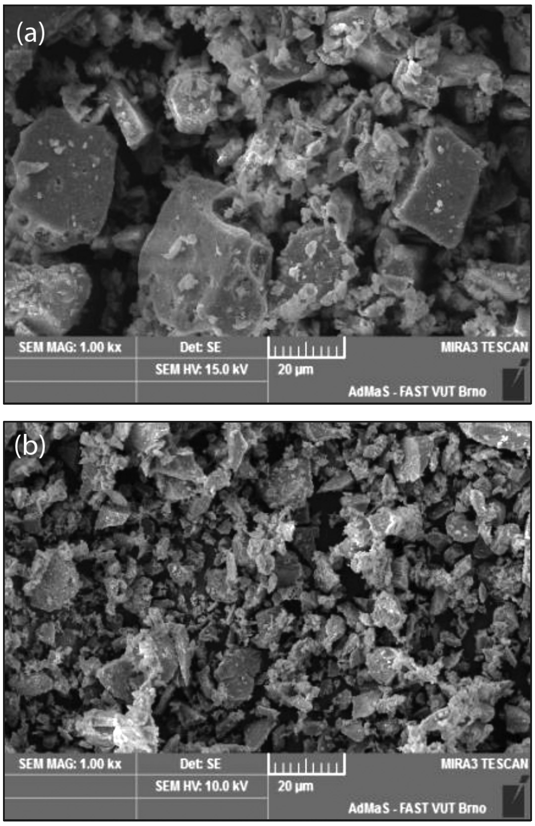


Figure 6: SEM image of BC: a) before and b) after grinding
Slika 6: SEM-posnetek BC: a) pred in b) po mletju

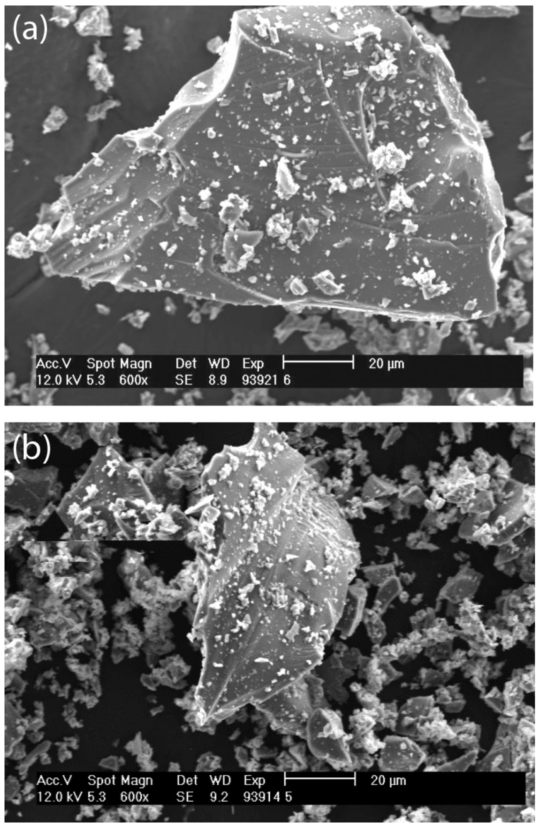


Figure 8: SEM image of RG: a) before and b) after grinding
Slika 8: SEM-posnetek RG: a) pred in b) po mletju

shown in **Figures 6** to **8**. BC is an abbreviation for blended cement, PC for Portland cement and RG for recycled glass.

The Blaine specific surface area was determined on all the samples ground for 5 min. The results of the measurement and the calculated specific surface area are summarized in **Table 6**.

$$S_{BC} = 0.8 \cdot S_{PC} + 0.2 \cdot S_{GR}$$

$$S_{BC} = 0.8 \cdot 500 + 0.2 \cdot 517 = 503.4$$

Table 6: Change of specific surface area before and after 5 min of grinding
Tabela 6: Sprememba specifične površine, pred in po 5 min mletju

Component	Cement	Glass	Blended c (together)	Blended c (separate)	Blended c (calculation)
Specific surface area before g (m^2/kg)	250	244	247	–	–
Specific surface area after g (m^2/kg)	500	517	532	504	503.4

Specific surface area of separate grinded blended cement corresponds with the calculation. In the case of co-grinded blended cement the specific surface area is considerably higher.

4 DISCUSSION

The chemical and mineralogical compositions of the recycled glass resemble a classic pozzolan. The sample of recycled glass with a specific surface area of 244 m^2 kg^{-1} reached a pozzolanic activity of 1112 mg $Ca(OH)_2$/1 g in a modified Chapelle test. The pozzolan activity of the chosen recycled material can be rated as high, because classic pozzolans such as fly ash reach values of 700 mg to 850 mg.[14] Therefore, it can be stated that this is a promising pozzolanic material. The chemical composition of the selected clinker is typical for Portland clinkers with a large amount of tricalcium silicate.[7] In the case of gypsum, it is a highly pure by-product gypsum from the production of titanium dioxide.

The grain morphology of the Portland cement and glass, which were adjusted to the same initial surface area and were used as the input for the grindability tests, are significantly different. Unlike Portland cement, recycled glass consists of grains with a substantially sharp-edged morphology. This grain shape can be explained by the high fragility and amorphous structure of the glass.[15] From the measured values of the balances of the raw materials on the sieves, the statement can be made that with a low surface area and larger grain size, Portland cement is milled the best. Glass is indeed fragile, but has a higher tendency to aggregate the particles.[15,16] This phenomenon can affect the outcome of the determination of the particle size distribution during the early stages of grinding. As shown in **Figures 2** to **5**, with increasing surface area, blended cement is ground more intensively than recycled glass or Portland cement. Increased efficiency co-milling is caused by the different mechanical properties of the clinker and the glass.[7,15] When recycled glass is milled separately, it preserves the delicate character and this leads to its rapid disintegration. Nevertheless, the distinctive ability of aggregation and agglomeration negatively affects the final particle size distribution, as evidenced in **Figure 8**. In the case of clinker, the ability to aggregate and agglomerate is lower.[17] Because of the chemical and mineralogical compositions of the grains they are more able to compensate for the impacts of the grinding elements. This affects the particle size distribution. The co-milling of cement and recycled glass leads to a better milling effect, since the above-described phenomena are compensated, plus the clinker grains are functioning as an additional grinding medium. This is reflected not only in the resulting particle size distribution obtained on specific surfaces, but also in a better homogeneity of mixed cement. The synergistic effect of co-milling in the case of cement glass was proved by the simple calculation model of weighted averages for the results of the separately ground materials' surface areas. The result of the calculation, 503.4 m^2 kg^{-1}, correlated well with the experimentally measured value of the specific surface area of the blended cement composed of separately milled components, i.e., 504 m^2 kg^{-1}. By joint grinding of the blended cement in same grinding conditions, a much larger specific surface area has been achieved, i.e., 532 m^2 kg^{-1}.

5 CONCLUSION

The pozzolanic activity of the fine recycled glass is relatively high. It reaches higher levels of pozzolanic activity than traditional ash, and on a significantly lower surface area. The distribution of particles of recycled glass and Portland cement measured by sieve analysis with separate grinding is similar. The synergistic effect of co-milling was demonstrated in comparison with a blended cement prepared by the homogenization of separately ground materials. This phenomenon is caused by the fact that the negatives associated with separate grinding of the individual materials are suppressed. Another advantage of co-milling the glass-cement system is energy saving, by eliminating the stage of homogenization. Based on the results obtained, recycled glass appears as a potentially useful pozzolan for the preparation of blended cements by co-milling with cement.

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5 REFERENCES

[1] C. Meyer, Y. Xi, Use of recycled glass and fly ash for precast concrete, Journal of Materials in Civil Engineering, 11 (**1999**), 89–90, doi:10.1061/(ASCE)0899-1561(1999)11:2(89)

[2] D. Gazdič, Slag-Sulphate Binder Preparation, Advanced Materials Research, 818 (**2013**), 68–71, doi:10.4028/www.scientific.net/amr.818.68

[3] M. Keppert, P. Reiterman, Z. Pavlík, M. Pavlíková, M. Jerman, R. Černý, Municipal solid waste incineration ashes and their potential for partial replacement of Portland cement and fine aggregates in concrete, Cement Wapno Beton, 15/77 (**2010**) 4,187–193

[4] T. Melichar, J. Přikryl, P. Matulová, Substituce pojiva v cementových kompozitech jemně mletou recyklovanou sklovinou s ohledem na životní prostředí, Beton TKS, 9 (**2009**) 3, 50–55

[5] A. Khmiri, B. Samet, M. Chaabouni, A cross mixture design to optimise the formulation of a ground waste glass blended cement, Construction and Building Materials, 28 (**2012**) 1, 680–686, doi:10.1016/j.conbuildmat.2011.10.032

[6] M. Öner, A study of intergrinding and separate grinding of blast furnace slag cement, J. Cement and Concrete Research, 30 (**2000**), 473–480, doi:10.1016/S0008-8846(00)00197-6

[7] P. C. Hewlett, Lea's Chemistry of Cement and Concrete, 4 (**2003**), Elsevier

[8] F. C. Bond, Crushing and grinding calculations Part I, British Chemical Engineering, 6 (**1961**), 378-–385

[9] F. C. Bond, Crushing and grinding calculations Part II, British Chemical Engineering, 6 (**1961**), 543–634

[10] G. Mucsi, Fast test method for the determination of the grindability of fine materials, Chemical Engineering Research & Design, 18 (**2008**), 395–400, doi:10.1016/j.cherd.2007.10.015

[11] N. Magdalinovic, Calculation of energy required for grinding in a ball mill, Int J Miner Process, 25 (**1989**), 41–46, doi:10.1016/0301-7516(89)90055-0

[12] R. F. Yap, J. L. Sepulveda, R. Jauregui, Design And Installation Of Comminution Circuits, Chapter 12 – Determination of the bond work index using an ordinary laboratory batch ball mill (2008)

[13] R. Largent, Estimation de l'activité pouzzolanique. Bull. Liaison Labo. P. et Ch., 93, (**1978**), 61–65

[14] J. Pokorný, M. Pavlíková, E. Navrátilová, P. Rovnaníková, Z. Pavnlík, R. Černý, Application of a-SiO_2 Rich Additives in Cement Paste, Applied Mechanics and Materials, 749 (**2015**), 362–367, doi:10.4028/www.scientific.net/AMM.749.362

[15] E. Le Bourhis, Glass: Mechanics and Technology, Wiley VCH, 2007

[16] W. Pietsch, Agglomeration Processes: Phenomena, Technologies, Equipment, Wiley VCH, 2008

[17] S. Sohoni, R. Sridhar, G. Mandal, The effect of grinding aids on the fine grinding of limestone, quartz and Portland cement clinker, Powder technology, 67 (**1991**), 3, 277–286, doi:10.1016/0032-5910(91)80109-V