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The Improvement of the Pozzolanic Properties of Recycled Glass during the Production of Blended Portland Cements

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Abstract

The replacement of primary raw materials in cement production is a relevant topic today. One potentially usable raw material is recycled glass. The disadvantage of glass is its tendency towards aggregation. Due to this phenomenon fine glass incement composites work only physically and mechanically as filler rather than as an active pozzolan. The possibilities of improving the pozzolanic properties of recycled glass by means of new milling techniques were examined in this paper. Next to the pozzolanic activity of recycled glass, the advancement of the hydration process of the binder and the effect on the physical and mechanical properties were also monitored. A combination of a ball mill and a nontraditional high-speed pin mill DESI 11 was selected for sample preparation. Portland clinker and recycled glass mixed at a ratio of 80: 20 wt. % were used for the preparation of the blended cement. The pozzolanic activity of the pure recycled glass was evaluated using a modified Chapelle test. The hydration process of glass grains in the cement composite was observed using an SEM with an EDX probe. The effect of the grinding technology on the cement rheology and on the compressive and flexural strength was also assessed. The results of the experiment show that the improvement of the pozzolanic properties of recycled glass by using it as the basis of blended cement is possible. The synergistic effect of the co-grinding of the components was observed. The glass particles were better distributed in the composite and could react with Portland cement hydration products. It positively influenced the values of the material's physical and mechanical parameters.

Keywords: Blended cement; recycled glass; pozzolanic activity; high-speed grinding

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1. Introduction

The cement industry is a manufacturing industry that significantly impacts the environment. However, it is also a very important processor of waste for re-use in manufacturing. The actual issue is the problem of CO_2 emissions during the production of cement-based materials. At present, this issue is particularly important because of global climate changes and is being addressed in the Kyoto Protocol. In addition, the energy-climate package "20-20-20", approved by the European Parliament and the Council in 2008 and legitimized in June 2009, concerns an issue closely related to the long-term basic research objectives of the EU countries in the area of reducing the energy intensity of building structures, the use of renewable sources of raw materials and advanced building materials with a high utility value [1]. Potential ways of reducing emissions are being seriously addressed in the lime and cement industry, which produce a significant amount of CO_2 during the thermal decomposition of limestone as well as from fuel combustion. There is approximately 75% of $CaCO_3$ in the raw meal in a standard case of cement production. Thus, approximately half a ton of CO_2 per each ton of Portland cement is released when Portland clinker is burnt. A further reduction in CO_2 emissions can be achieved by blended cement production. Latent hydraulic, pozzolanic, as well as various inert substances are widely used as more eco-friendly substitutions of clinker. The ratio of CO_2 emissions can be reduced by 10 to 15% per unit in this case [2]. When searching for potential new substitute materials it is recommended to focus on substances that will act in the cement both physico-mechanically as filler and physico-chemically as a pozzolan. One such promising raw material is recycled glass. Glass is chemically and mineralogically very close to traditional pozzolans. There are relatively many sources of this material, mainly packaging glass or glass from dismantled CRT screens [3]. Various authors have described the behavior of ground glass in cement composites [4, 5]. The traditional approach to the production of blended cement is separate grinding and subsequent homogenization of all ingredients. However, this procedure seems to be less suitable in the case of a glass-cement system. Because recycled glass is prone to agglomeration during the milling process, the pozzolanic properties of the glass particles are insufficient and glass acts in this system only physico-mechanically as a filler [4, 5]. An interesting option to prevent the formation of agglomerates in pure glass is co-grinding of the glass and clinker. Both substances have very similar hardness and there is a synergistic effect of the co-milling as well. [6, 19]. Another interesting option could be the utilization of mechanical or mechanochemical activation of the glass. The effects of mechanical activation have been described for model materials such as dolomite [7] or clay minerals [8, 9, 10], or, for example, for silica [11] or sand [12]. One of the trends in the area of milling and mechanical activation that have been intensively explored recently is high-energy milling (HEM). High speed grinding (HSG) represents one type of HEM. HSG involves delivering large amounts of energy using very short and intense power pulses. A high-speed pin mill with two counter-rotating rotors, known as a disintegrator, is one of the types of mills suitable for HSG [13]. The use of a combination of both methods may lead to an increased reactivity of glass particles during the hydration of blended cement. The aim of this work was to describe and assess the effects of a traditional and HSG milling technique on the pozzolanic properties of glass particles and on the physico-mechanical properties of the cement pastes as well as the cement composites made from the blended cement.

2. Materials and methods

The first step in the research was an analysis of the pure glass and the impact of the milling techniques on its properties. Recycled glass from the Czech producer RECIFA was used for examining the impact of the milling technique in question on the material properties. The glass was analyzed before milling had begun; its chemical composition was determined by traditional chemical analysis. Density was determined by a Micromeritics AccuPyc II 1340 automatic pycnometer. Blaine specific surface area was measured using a PC-Blaine-Star automatic device with a measurement cell capacity of 7.95 cubic centimeters. The measurement was performed three times to eliminate errors, and the resultant value was the average of the three readings. The modified Chapelle test method [14] was used for the determination of pozzolanic activity. The modified Chapelle test involves the reaction of a 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 the pozzolan.

Samples with approximately the same specific surface area of 320 and 350 m^2/kg were prepared using two milling techniques. The laboratory ball mill OM BRIO 20 represented the traditional milling technique. The mill rotation frequency was 45 rpm at a total dose of 5 kg. The disintegrator DESI 11 represented an HSG mill. It is a high speed pin mill with two counter-rotating rotors. The total installed output of the mill is 4.1 kW. Rotor rotation frequency is up to 12000 rpm and maximum speed of impact is 240 $m.s^{-1}$. The material is fed by a continuous feeder and enters the grinding chamber through the middle of the left rotor. The construction of the mill allows for a choice of working tools. For the evaluation of the milling process, CR type rotors were used. The rotors were designed and manufactured by the company FF servis s.r.o. The left rotor has two rows of pins and the right rotor has three rows. The pins were cubic. All of the ground samples were analyzed by the same method as the raw glass. Next step was the preparation of the blended cement for the assessment of its physico-mechanical properties. It was prepared from two components at the ratio of 80 wt % of Portland cement to 20 wt % of recycled glass. Portland cement was prepared also in a laboratory from a Portland cement clinker at a dose of 95 wt % and from gypsum PREGIPS at a dose of 5 wt %. All the components were homogenized in a laboratory homogenizer. The blended cement thus produced was used in the preparation of two samples by means of the two different milling technologies mentioned above. Both samples were ground to the same specific surface area of 375 m^2/kg according to Blaine. This value was similar to the surface area of the reference which was CEM I 42.5 R from the cement plant Hranice. The water/cement ratio, initial and final setting time of each sample were determined according to CSN EN 196-3 [15]. The viscosity test was carried out on a Reostar viscometer. The tests were performed at 100 rpm, a coolant temperature of 20 °C, at time 0 to 90 minutes. The water/cement ratio of 0.5 was selected for this test. This value is higher than the common ratio of 0.3 given in literature [16]. However, this value was chosen so as to amplify the rheological differences among the samples. All the mechanical tests were conducted according to CSN EN 196-1 [17]. Increases in compressive strength at the age of 1, 3, 7, 28 and 56 days were observed on these samples. The homogeneity of the components in the blended cement and the hydration of the glass particles in the cement paste after 28 days were examined using an electron microscope (SEM) Tescan MIRA 3 XMU with an EDX probe.

3. Results

3.1. Properties of the raw recycled glass

Table 1 below shows the results for the chemical composition of the recycled glass. Only important oxides are listed there.

Table 1.The chemical composition of the recycled glass

Components	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	Others
Content [%]	69.25	0.83	8.09	16.44	0.41	4.98

The specific surface area and density are then presented in Table 2.

Table 2. Density and specific surface area of the recycled glass

Density [kg/m^3]	2460
Specific surface area [m^2/kg]	244

The chemical and physical properties are typical for conventional packaging glass. The specific surface area of the recycled glass is high enough for easy dosage into a cement mill.

3.2. Pozzolanic activity of the recycled glass

Table 3 shows the results of the pozzolanic activity tests performed on the samples with the specific surface area of 320 and 350 m^2/kg prepared by two different milling techniques.

Table 3. Pozzolanic activity of the samples ground by different milling techniques

Sample description	Sample identification	Specific surface area [m^2/kg]	Pozzolanic activity [mg $Ca(OH)_2$/g of pozzolan]
Raw recycled glass	RG	244	1112
Ball mill	BM 320	321	1237
Ball mill	BM 350	350	1294
DESI 11	HSG 320	319	1246
DESI 11	HSG 350	353	1307

The pozzolanic activity of the industrially produced recycled glass is relatively high. The difference in the results of the pozzolanic activity is observable in the case of the samples having the same surface area, but which were prepared by a different grinding technology.

3.3. Technological properties of the blended cement

3.3.1. Specific surface area, water cement ratio and the setting time

The laboratory-prepared blended cement with 20 wt % of recycled glass was used in all of the technological tests and standard CEM I 42.5 R was used as a reference. The results of the specific surface area according to Blaine and water cement ratio, initial and final setting time according to CSN EN 196-3+A1 are presented in the Table 4.

Table 4. Specific surface area, water cement ratio and the setting time of the cement samples

	DESI 11 HSG 375	Ball mill BM 375	CEM 42.5 R REF
Specific surface area [m^2/kg]	374	376	377
W/C ratio	0.280	0.275	0.290
Initial setting time (min)	160	160	155
Final setting (min)	200	215	210

The HSG 375 sample achieved a higher w/c ratio than the sample BM 375 with a very similar specific surface area but ground by the traditional technology. Setting time was very similar in all cases including the reference.

3.3.2. Rheological properties

The results of the cement paste viscosity tests of all three the samples are presented in Fig. 1.

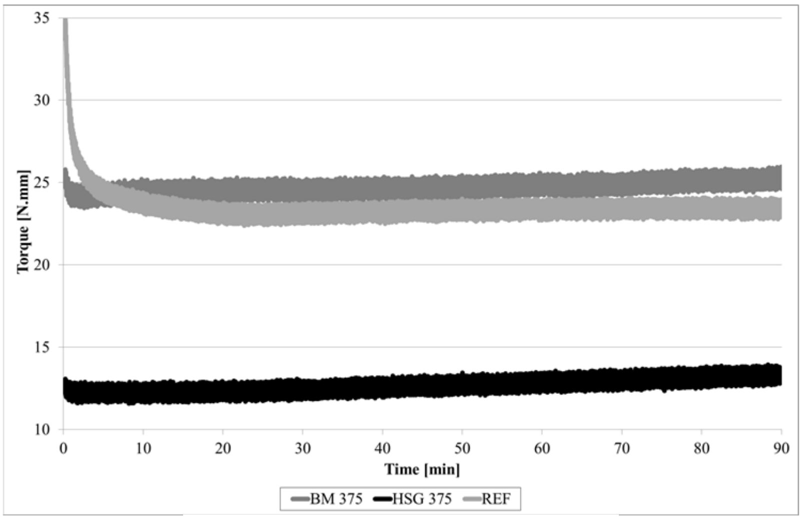

Fig. 1. Viscosity measurement of all samples

Whereas sample BM 375 was rheologically very similar to the reference, sample HSG 375 achieved significantly lower viscosity. The torque measured in this sample was approximately two times lower than in the case of BM 375 and the reference as well.

3.3.3. Mechanical properties

The bulk density, compressive strength and bending strength tests were carried out on all three samples in the age of 1, 3, 7, 28, and 56 days, see Table 5 and 6.

Table 5. Bending strength

Sample	Bulk Density [kg/m^3]	Bending strength [N/mm^2]				
		1day	3 days	7 days	28 days	56 days
HSG 375	2260	3.8	5.5	6.9	8.4	9.3
BM 375	2210	1.9	5.3	7.0	9.1	9.3
REF	2200	2.7	6.5	7.9	9.3	9.7

Table 6. Compressive strength

Sample	Bulk Density [kg/m^3]	Compressive strength [N/mm^2]				
		1day	3 days	7 days	28 days	56 days
HSG 375	2260	11.4	19.3	28.2	43.6	43.7
BM 375	2210	5.4	18.5	29.6	40.2	42.7
REF	2200	7.7	29.0	41.1	48.8	49.9

Higher strengths at the early age were achieved in the samples which were milled in the high speed mill. The first day strengths were also higher than in the case of the pure Portland cement. However, the compressive strength of sample HSG 375 after fifty-six days was only slightly higher than the result achieved by sample BM 375.

3.4. Homogeneity of the blended cement particles and glass particles hydration

The effectiveness of the co-grinding of all components in the mill is illustrated in Figure 2. It is visible that the glass particles covered the clinker particle and formed a composite agglomerate. An EDX probe was used for the identification of the glass particles. The beginning of the glass particle hydration is demonstrated in Figure 3. The presence of the hydration products (CSH gel) is visible in the contact zone between the glass particle and the cement hydration products.

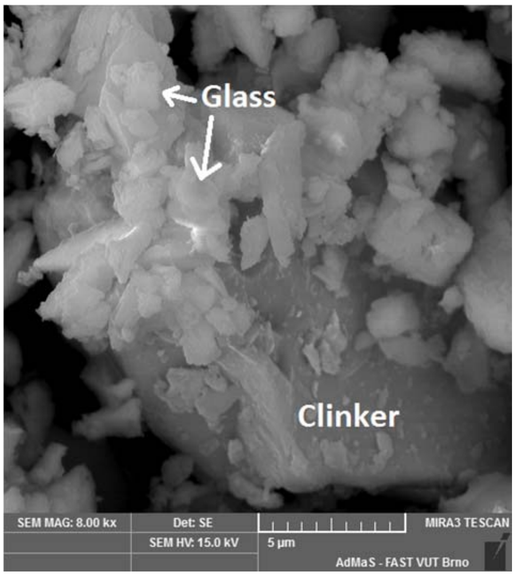

Fig. 2. Glass and clinker particles in the blended cement (HSG 375)

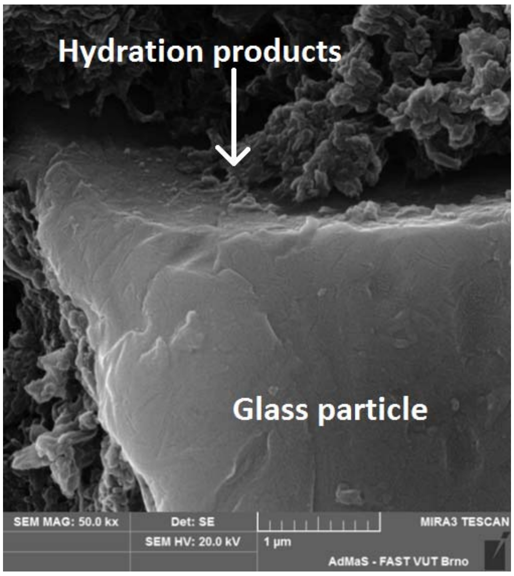

Fig. 3. Hydration of the glass particles after 28 days. (HSG 375)

4. Discussion

The results indicate that the selected industrial recycled glass could be a promising material for the production of blended cements. This material contains a large amount of SiO_2, up to 70%. Moreover it is produced as a powder of a relatively high specific surface area of 240 m^2/kg according to Blaine, which is very a useful form for the cement industry. In this powder SiO_2 was predominantly in the amorphous form, which was shown by very a high pozzolanic activity, 1112 mg of $Ca(OH)_2$/g of pozzolan. The pozzolanic activity of the chosen recycled material can be rated as high, because traditional pozzolanas such as fly ash are reaching values of 700 to 850 mg $Ca(OH)_2$/g of pozzolan [18]. The pozzolanic activity was of course increased by milling as reactivity depends fundamentally on the reaction surface area. However, there was a difference in the results of the pozzolanic activity between the samples which had the same surface area but which were prepared by a different grinding technology. In both tested specific surface areas the pozzolanic activity was higher in the cases where the HSG technology was used. This effect can be explained by the mechanical activation of the glass particles as has been described by various authors [7, 8, 9, 12]. The pozzolanic activity of sample HSG 350 achieved 1307 mg $Ca(OH)_2$/g of pozzolan, which is approximately two times higher than in the case of traditional fly ash. Moreover, standard blended cements are usually milled to a specific surface area of 370 to 400 m^2/kg so an even higher value of pozzolanic activity can be expected in practice. Because recycled glass has a considerable tendency towards agglomeration during the milling process, the co-grinding of all components was chosen to prevent the formation of pure-glass agglomerates in the blended cement. The synergistic effect of co-milling described in [19] was confirmed by the SEM with EDX. Figure 2 shows that the glass particles covered the clinker particle and formed a composite agglomerate. It can be expected hydration water would enter this type of aggregate easily. Contact zone between glass and clinker particles would be larger and the glass grains would start to react with $Ca(OH)_2$. The beginning of this phenomenon was observed in the sample after 28 days by SEM. Of course the process of glass hydration is slower than in the case of clinker and would more clearly observable in a long-term hydration period. The selected grinding technology had only a small impact on the water/cement ratio of the blended cements. The achieved values were similar. However, the cement prepared by HSG achieved a slightly higher value due to different particle shapes [6, 19]. The setting time was similar in the cases of BM 375 and the reference. Nevertheless, the final setting of HSG 375 was shorter. This was in accordance with the results of the first day strength results. Bending and compressive strength at the early age was significantly higher in the disintegrator type cement than in the case of the ball mill type cement, however, the final strength was in essence similar. This phenomenon could be caused by mechanical activation of the binder. [8, 9, 10, 12]. It can be assumed the DESI 11 mill mechanically activated the surfaces of all grains and increased the hydration reaction rate at the early age. Very interesting is to compare the results of the blended cement with the reference pure Portland cement. However, over a long-term period the hydration water had enough time to wet the internal parts of the grains and the hydration reaction could start in the whole volume of the cement. The most interesting are the results of the rheology of the cement pastes. Sample BM 375, prepared in a laboratory ball mill, was rheologically very similar to the reference, produced in an industrial ball mill. Compared to that, sample HSG 375 achieved a significantly lower viscosity. The torque measured in this sample was approximately two times lower than in the previous two cases. It is difficult to explain this phenomenon to a satisfactory degree. However, the reason for this behavior would be in the air content of the cement after milling. HSG is an entirely different milling technology. The material is dosed into the mill in an air stream and the particles spend only a few seconds inside the milling chamber, keeping in very fast motion. In the end, the cement looked more “fluffed” than after the traditional milling process. This could help to reduce the viscosity of the cement paste. It seems to be an advantage of this technology because the same rheology of the cement paste could be achieved at a lower water/cement ratio.

5. Conclusion

The replacement of primary raw materials as well as the reduction of CO_2 emissions in cement production is a frequently discussed topic today. One raw material showing great promise in this field is recycled glass. Glass is chemically and mineralogically very close to traditional pozzolans. The pozzolanic activity of fine recycled glass is relatively high. It reaches higher levels of pozzolanic activity than traditional ash, and on a significantly lower surface area. Pozzolanic activity can be increased not only by milling but also by mechanical activation in HSG mills. Concerning glass-based blended cements discussed here, co-grinding prevented the formation of the pure glass agglomerates and the glass could then function in the cement paste as an active ingredient; not only as filler. Finally, the mechanical activation of the blended cement in an HSG mill increased the hydration rate at the early age and did not have a negative influence on the final properties. In conclusion, it can be said that the utilization of this waste material in combination with the technology of milling can help to reduce CO_2 emissions and save natural raw material resources.

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