CHARACTERIZATION AND POZZOLANIC ACTIVITY OF WASTE EXPANDED PERLITE

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Abstract
This paper deals with characterization of multiple waste expanded perlites (WEP) from local central European sources with an emphasis on their suitability for use in cement composites. Influence of the milling time on their properties was studied. Both raw and milled WEP samples were thoroughly characterized in terms of their physical properties, composition, particle size, specific surface area, and pozzolanic activity. The findings affirm their potential as supplementary cementitious materials.

Keywords
Cement, supplementary cementitious materials, waste perlite, pozzolanic activity

1 INTRODUCTION

The use of supplementary cementitious materials (SMCs) has long been established as one of the leading approaches to reduce the carbon footprint and to increase the sustainability of current cement production. Their use allows for both the reduction of clinker content in cement and the improvement of the long-term properties of cement composites [1]. Especially with the recent emphasis in the cement industry on reducing its environmental impact, as outlined in the CEMBUREAU Roadmap [2], the clinker content in cement has been steadily decreasing [1], increasing the importance of the use of SMCs in blended cements. With the vast amount of research already done on the use of various SMCs, they represent one of the most cost-effective ways of achieving these goals, while also contributing to the circular economy ideal by utilizing waste by-products of other industries [3], [4].

Due to the uncertain future of traditional SMCs such as fly ash (FA) and ground granulated blast furnace slag (GGBFS) associated with the phase-out of coal power plants and the high price and decreasing quantities of GGBFS, alternative SMCs are needed [3]. One of the promising materials is waste expanded perlite (WEP) [5], [6], with more than 4.2 million tonnes of perlite produced worldwide in 2020 [7]. During expanded perlite production, a large amount of very light fine particulates with high specific surface area and small particle size is produced (often more than 200%). The utilization of these fines is very limited and their storage and landfilling are complicated by the dusting of the material, which is related to their low density [8].

Due to the amorphous structure and the high amount of reactive SiO_2, WEP shows high pozzolanic activity, which can be further increased by milling. The pozzolanic activity of expanded perlite of appropriate granulometry and quality can reach levels comparable to those of silica fume [9]. However, as with all waste materials, small differences in composition and physical properties can significantly affect their performance in cement composites. Therefore, the choice of material and appropriate processing is critical.

In this study, WEP from multiple local Central European sources was thoroughly characterized with respect to its physical properties, chemical and mineralogical composition and its suitability for use as SMCs in cement composites was assessed. The influence of further milling on physical properties and pozzolanic activity of WEP was also investigated.

2 METHODOLOGY

Waste expanded perlite samples were characterized in terms of bulk density, poured bulk density, tapped bulk density and the water absorption. Chemical composition was determined using an energy-dispersive X-ray fluorescence (XRF) spectrometer (Vanta). Elements with atomic number ranging from magnesium to uranium

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were analysed. Elements lighter than magnesium are included as light elements (LE). Due to the nature of the samples, the chemical composition was interpreted in terms of oxide composition.

X-ray diffraction analysis was used to evaluate the mineralogical composition of WEP samples. The analyses were performed using a Bruker D8 Advance diffractometer with a Cu anode (λKα=1.54184 Å) with an input current of 30 mA and variable divergence apertures at θ/2θ reflective Bragg-Brentano parafocusing geometry. The determination of amorphous phase content was carried out using 20 wt. % Y_2O_3 addition as an internal standard.

Particle size distribution of WEP samples in the as-received state was determined using sieve analysis. All waste expanded perlite samples were milled for 30, 60, 120 and 300 s in a vibration mill using a steel mill jar. The weight of the milled perlite was kept constant for all samples. The particle size distribution of the milled samples was determined by laser diffractometry (Helos KR, Sympatec). The specific surface area was determined using Nitrogen adsorption Quantachrome Nova with a BET method.

The pozzolanic activity of the samples was determined by a modified Chapelle test according to the NF P18-513 standard, Annex A [10]. The test was performed by mixing 0.4 g of pozzolan sample, 0.8 g of CaO and 100 ml of deionized CO_2-free water. The suspension was stirred and kept at 85 ± 5 °C for 16 h. After cooling the flask to laboratory temperature, 24 g of sucrose was added. After stirring for 30 min, the suspension was filtered using a Büchner funnel. 10 ml of filtrate was titrated with 0.15 M HCl solution. Blank samples were prepared in the same manner without the addition of pozzolan.

3 RESULTS

The following tables and figures show the determined results of the WEP samples, including oxide composition, mineralogical composition, particle size distribution and pozzolanic activity. The WEP samples used for the determination of properties were selected based on the available supply of raw perlite used in the factory in Šenov u Nového Jičína, Czech Republic, which produces expanded perlite for Czech and Polish market.

Tab. 1 Oxide composition of WEP samples.

Sample	SiO_2	Al_2O_3	K_2O	Fe_2O_3	CaO	TiO_2	MnO_2	LE
Z2SK [wt %]	78.52	11.75	6.43	2.27	0.85	0.16	0.07	0.74
Z3SK [wt %]	77.66	11.88	6.50	2.15	0.88	0.16	0.07	0.00
Z3HU [wt %]	77.54	11.87	4.76	1.46	0.63	0.06	0.03	3.65

Tab. 2 Mineralogical composition of WEP samples.

Sample	Amorphous phase	Quartz	Illite	Anorthite sodian	Albite
Z2SK [wt %]	97.1	0.1	0.1	2.7	-
Z3SK [wt %]	95.9	0.2	0.2	3.7	-
Z3HU [wt %]	98.0	0.3	-	-	1.7

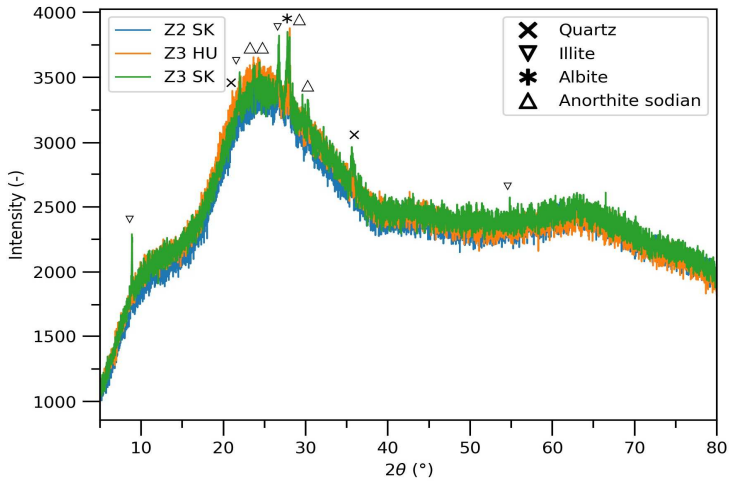

Fig. 1 X-ray diffraction of WEP samples.

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Tab. 3 Properties of unmilled WEP samples.

Sample	Bulk density [kg·m^{-3}]	Poured bulk density [kg·m^{-3}]	Tapped bulk density [kg·m^{-3}]	Water absorption [wt. %]
Z2SK	290	100	120	250
Z3SK	400	180	230	150
Z3HU	280	70	100	240

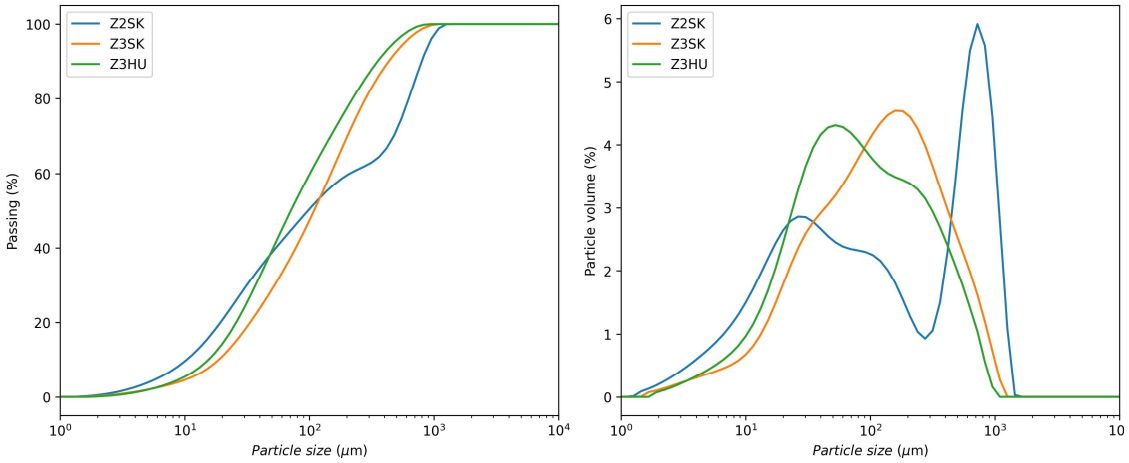

Fig. 2 Cumulative (left) and differential (right) particle size distribution curves of WEP.

Tab. 4 Particle size distribution of WEP samples with different milling times.

Sample	milling time [s]	D50 [μm]	D90 [μm]
Z2SK	0	112.02	914.364
	30	5.7	20.07
	60	3.44	10.81
	120	1.79	5.94
	300	1.31	3.87
Z3SK	0	125.18	496.688
	30	6.34	24.61
	60	5.31	24.27
	120	1.83	7.32
	300	1.18	3.65
Z3HU	0	81.58	404.593
	30	5.25	11.93
	60	3.32	9.45
	120	2.25	7.18
	300	1.76	5.7

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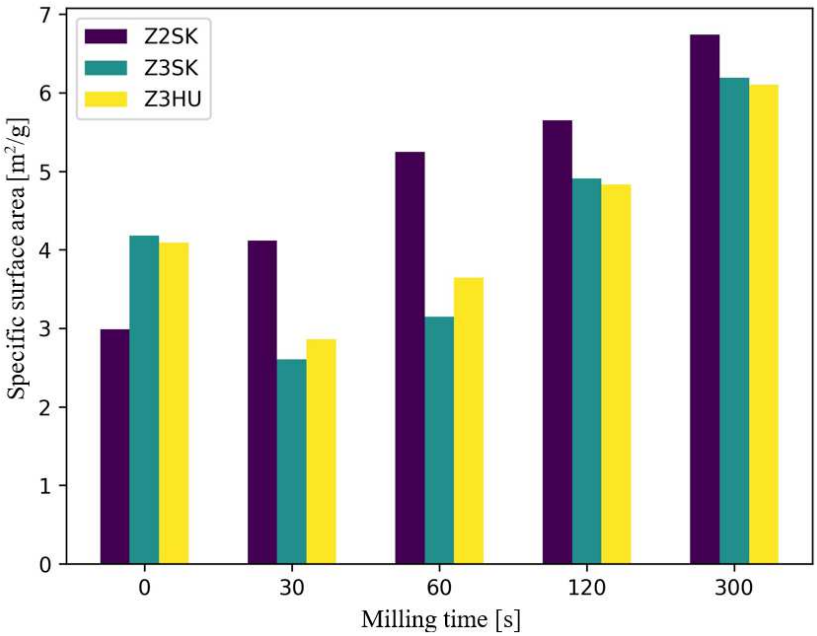

Fig. 3 Dependence of specific surface area of WEPs on milling duration.

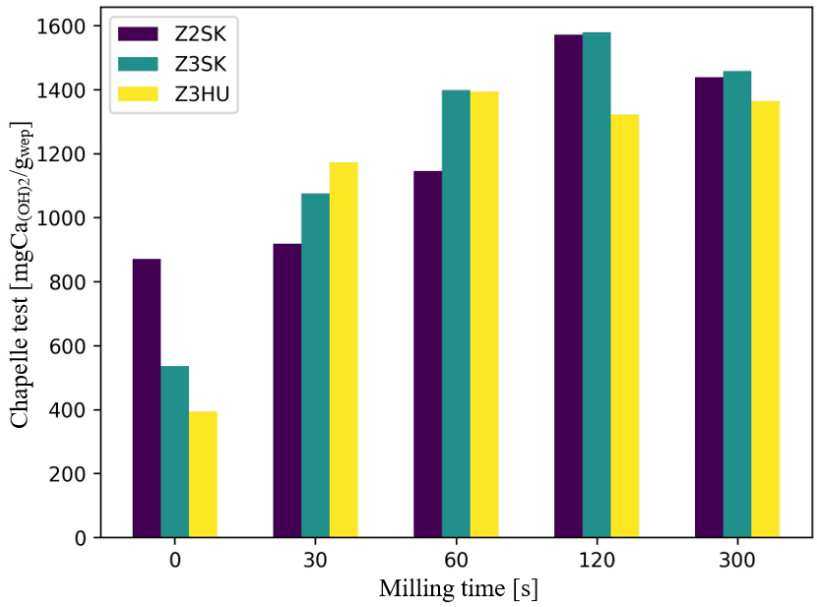

Fig. 4 Dependence of Pozzolan activity determined by Chapelle test of WEPs on milling duration.

4 DISCUSSION

The oxide composition of WEP samples is shown in Tab. 1. The main oxides, accounting for roughly 90 wt. % of all samples, are SiO_2 and Al_2O_3. Z2SK and Z3SK samples have very similar oxide compositions. However, sample Z3HU contains less K2O, with a corresponding increase in light elements present in the sample, which are not detectable by the used XRF method.

The mineralogical compositions are given in Tab. 2 and the corresponding X-ray diffractograms are shown in Fig. 1. The XRD patterns of all samples show an amorphous halo centered around 25°, which is typical for expanded perlite [11]. This is caused by the very high amorphous phase content in all samples, accounting for more than 95 wt. %. This is an important fact for the potential use as SMCs. With the limited content of crystalline phases, most of the SiO_2 is expected to be in a reactive form capable of pozzolanic reaction during cement

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hardening. Crystalline phases such as quartz, anortite and albite are present and they should not have any negative effect on the behaviour of WEP in cement paste and, consequently, on the properties of cement composites. A small amount of illite was detected in two WEP samples. Clay minerals can have a negative effect on concrete, causing a decrease in workability due to high water absorption and reduction of compressive strength caused by their ability to reduce the bond strength between cement paste and coarse aggregate particles. Therefore, monitoring clay mineral content is critical when dealing with uncalcined SMCs. Only trace amounts of illite were detected in the analyzed WEP samples, with levels orders of magnitude lower than those where these negative effects become noticeable [12]. This further suggests that the analysed WEPs are suitable for use as SMCs without the necessity of calcination.

Physical characteristics of the unmilled WEP samples are listed in Tab. 3. From the results, it can be seen that the Z3SK sample has the densest structure with the highest bulk density, while the Z2SK and Z3HU WEP samples have very similar characteristics. Water absorption is inversely proportional to the density of the samples, with the two lighter perlites achieving approximately 100% higher water absorption values compared to the Z3SK sample. The Z2SK and Z3HU samples showed similar characteristics in all bulk density measurement values. The Z3SK sample showed higher values, which corresponds to lower water absorption.

The cumulative curve and differential particle size distribution determined by sieve analysis of WEP samples are shown in Fig. 2. The Z2SK sample has the widest particle size distribution, including both very fine fractions as well as containing a significant portion of particles with sizes larger than 500 μm, which corresponds to the lowest d10 and highest d90 values of the three, respectively. Z2SK WEP is also the only WEP with a bimodal particle size distribution. Due to all WEP samples containing a significant number of particles larger than 100 μm, none of the WEP samples is suitable for use as SMCs in the as-received state.

Tab. 4 lists relevant D_{10} D_{50} and D_{90} values describing the particle size distributions of the three perlite samples with different milling times. The dependence of specific surface area determined with the BET method is shown in Fig. 3. Z2SK WEP has a lower initial surface area than the other two WEP samples and an increase can be seen with the milling process. The increase is faster at the initial milling stage and slows down with prolonged milling times as the efficiency of the milling process decreases with decreasing particle size. For the samples Z3SK and Z3HU, different behaviour can be observed. Both WEP samples have higher specific surface area above 4 m^2/g due to their highly porous structure. At short milling times, the specific surface area decreased significantly despite the decrease in particle size. This is caused by the destruction of the porous structure during the milling process.

The influence of milling on the pozzolanic activity of the WEP is shown in Fig. 4. The highest pozzolanic activity of the as-received WEP samples was measured for the Z2SK sample. This is not a surprising finding, considering the fact that the oxide and mineralogical composition of all samples was found to be very similar, with a similar content of amorphous phase above 95 wt. %. From the determined particle size distributions, Z2SK perlite contains significantly more particles under 30 μm, which is a typical range in which pozzolan materials [13] achieve sufficient reactivity. However, with milling, the pozzolanic activity increases slower than in the other WEP samples. Comparable pozzolanic activity was only achieved after two minutes of milling time for the WEP samples, indicating that the particle size and specific surface area were affected by the destruction of the microporous structure of WEP. Specific surface area is thus not a good indicator of expected pozzolan reactivity. Similar results were found by Cordeiro [14] for rice husk ash, which is another pozzolanic material with a porous structure. Internal porosity is likely less capable of pozzolanic reactions and the rate of pozzolanic reaction is more influenced by the mechanically activated defective surfaces created during the milling process than by the total expanded perlite surface area available for the reaction [15]. All WEP samples showed the same behaviour, whereby no further increase in pozzolan activity was observed after reaching the optimal milling time. Optimal milling time was similar for all samples.

5 CONCLUSION

Three waste expanded perlite samples were characterized in terms of their physical properties and composition. All samples contained a very high amount of amorphous phase, with other constituents comprising less than 5 wt.% of the total sample weight . The analysed WEP samples had very similar chemical and mineralogical compositions. No constituents preventing their use in blended cements were present in significant quantities. The biggest differences were observed in their particle size distribution, which, due to the highly porous structure of WEP, significantly influences properties such as bulk density and water absorption. Pozzolanic activity of the unmilled WEP was primarily affected by the content of very fine particles. A poor correlation was found between specific surface area and pozzolanic activity due to the porous structure of WEP. Pozzolanic activity as high as 1500, as determined by the modified Chapelle test, could be achieved by appropriate milling. The similar phase composition and behaviour during milling could allow for their combined use, increasing the potential production capacity of blended Portland cements. Overall, the analysed WEPs have shown to be very promising pozzolanic

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materials and could be used in blended Portland cements with the only necessary pre-treatment being milling to achieve optimal granulometry and reactivity.

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