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MICROSCOPIC AND PHASE ANALYSIS OF CEMENT PASTE CONTAINING WASTE MICRONIZED MARBLE POWDER

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Abstract. The article focuses on the impact of waste marble powder on resulting cement composites. We investigate of influence waste marble powder on the hydration process and hence the resulting phase composition. The hydration process was investigated using calorimetry and phase composition of the resulting composite by electron microscopy. The results are compared with a reference sample composed of Portland cement.

Keywords: Micronized marble powder, marble sludge, cement composites, calorimetry, elemental analysis.

1. Introduction

The great demand for marble in export markets has led to increased his production. An important factor is the amount of mined stone, regardless of the quantity of waste. Production lines for mining and stone processing produce two types of waste. The first one is in the form of crushed stone that arises by removing marble blocks from the line due to their bad shape or when the blocks are broken or cracked. The production of this waste is great, but its application is so effective in the form of aggregates and gravel to the concrete that it does not create any ecological risks. The second form of waste is marble sludge and dust, which occurs during the mining, crushing and cutting of marble blocks or during the final grinding and polishing process. The amount of waste produced is estimated, for example, for the Egypt region at one million tonnes per year [1]. The amount of waste produced is not only associated with less advanced countries such as the Middle East but also with Europe, where, for example, in Portugal, the amount of waste generated is estimated at 600 thousand tonnes per year [2]. An approximately 10 to 20% of the waste is further processed and used [3]. The most common use is in road infrastructure, as asphalt filler or underlayer [4]. The remaining unused waste is stored in the vicinity of the factories, regardless of their possible use, thus causing serious environmental problems. For these reasons, it is important to create an application of these wastes, which would result in improved safety and health protection by lowering dust particles in the air, lowering the cost of storage, transport, and waste handling, and generating potential revenue [5]. One option is to use waste as a partial substitute for Portland cement, where recycling material could have a positive effect on resulting properties of cement composites. The resulting properties of the cement matrix are directly dependent on the composition. The resulting cement matrix is composed of a plurality of phases. The largest proportion of the phases has the C-S-H gel (hydrosilicate), which is furthermore formed by tobermorite, afwillite, xonotlite and other still unknown phases. Furthermore, hydroaluminate, gypsum, ettringite, ferrite hydrate and portlandite (CH crystals) appear in the cement matrix [6]. They are several works that solve the possibility of replacing cement with marble sludge, and the result is two contradictory findings. The first statement is described in a study by Demirel [7] at the Firat Technical University in Turkey. He found using an electron beam microscope that when the marble sludge was added to the cement composite, the CH crystal size was changed. Mixtures without marble sludge had a form of large CH crystals. While in a mixture with marble sludge had very small CH crystals and it was produced across all the matrix. This effect is explained by the fact that fine sludge grains act in the cement composite as nucleation centers for the growth of CH crystals and accelerate the hydration of silicate and aluminate phases [8]. The second claim is described in the work of Aliabdo et al. [9]. They examined the morphology of the internal structures of the cement slurry with and without marble sludge by using a scanning electron microscope and they found that, is not distinctly different from each other, meaning that the marble sludge has no noticeable role during the hydration process and therefore only acts as an inert filler in the new product. With the development of the technique, new possibilities arise to confirm or rebut possible claims about the inclusion of marble sludge during hydration. One possibility is the treatment of marble sludge using high-speed milling [10], where the resulting micronized marble powder has a higher density and therefore a higher reactivity [11]. This recycling method has already been successfully used

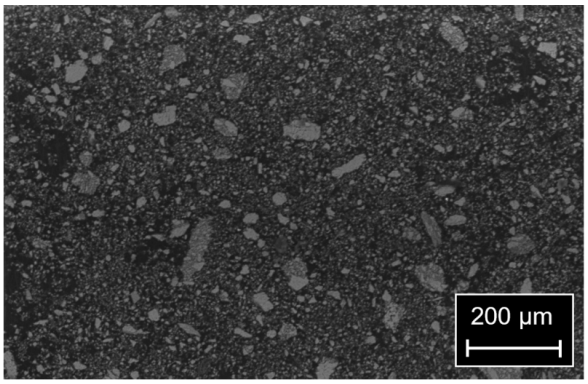

FIGURE 1. The image of micronized marble powder, magnified 100×, BSE detector.

for concrete recycling [12].

2. Materials and samples

Portland cement CEM I 42.5 R was chosen as reference material from Českomoravský beton, a.s. with a factory in Radotín. It is a cement used for high strength concrete and mortars and plasters. The main ingredient is Portland clinker with a proportion of 95 to 100 wt. %. The remaining amount of weight is the complementary components. The marble sludge that was created during the cutting and polishing of limestone marble was chosen for investigating the possibility of replacing cement with micronized mechanically activated marble powder. The marble sludge comes from an industrial area located on the West Bank. The marble sludge was lumpy and contained big grains. The marble sludge was micronized on high-speed mills in collaboration with LAVARIS for improved workability, improved marble sludge properties, and increased surface area. The high-speed mill type SBD 600 with a power of 2×30kW with patented cutting edges was used for this purpose. Two grinding modes and two types of grinding elements were used. In the first case, it was used element in the form of patented 400 mm diameter pins, and in the second case patented teeth with a diameter of 150 mm. In both cases, the grinding speed was set to 300 m/s. The result of high-speed grinding was micronized marble powder. Two sets of samples were created for research. The first set was used for calorimetry testing, consisting of cement pastes with varying amounts of micronized marble powder. Mixture M0 served as a reference and contained only cement. Mixtures M5 to M50 contained Portland cement and micronized marble powder in 5, 10, 15 and 50 wt. % (Table 1). The water ratio, i.e., the weight of water to the total dry mass mixture, was 0.45. The second set was used for electron microscopy testing. Two microscopic samples were created for the examination of the materials at the nano/micro level. The first sample was made by mixing micronized marble with epoxy resin and served to examine the size and shape of the grains and to analyze the recyclate itself. The second sample was made of a hardened cement paste which was made up of 50 wt. % Portland cement and 50 wt. % recycled micronized marble powder. It was sample M50 from calorimetric measurements. Before creating the cuts, it was necessary to fill the pore space with a suitable substance so as not to release the grains of materials during the preparation of the samples. The vacuum impregnation method for epoxy resin samples (Epofix Kit) was used for this purpose. The polished sections were prepared on Struers' Tegramin machine. The samples were ground and polished in several steps to achieve the best surface quality of the samples. A different preparation procedure was performed for each sample due to different material. The first sample, the recycled micronized marble powder is homogeneous and does not react with water, so it is possible to use silica paper and water-based lubricant. In the first step, silica paper with a grain size of 220 grains/cm^2 was used to remove the greatest unevenness after cutting. In the following steps, finer silica paper was used: 500 grains/cm^2, 1200 grains/cm^2, 2000 grains/cm^2 and 4000 grains/cm^2. Each step lasted 2 minutes, and the pressure on the sample was 5 N. In the last step the samples were polished by hand using a 1/4 microns emulsion containing the nanodiamonds for 1 minute. The second sample is made up of several phases, so we used diamond plates that do not affect this inhomogeneity and does not occur relief in the grinding and polishing process. Also, the cement reacts with water, so an alcohol-based lubricant has been used. MD-Piano 500 was used in the first step (corresponding 500 grain / cm^2 silica paper roughness), and the next steps were MD-Piano 1200, MD-Piano 2000 and MD-Piano 4000. The grinding and polishing time was several hours because polishing and grinding were performed without pressure. Finally, both samples were sputtered with a carbon layer at 30 nm to improve the required surface conductivity of the sample and improve the quality of the analysis.

3. Experimental methods and results

The development of hydration heat was measured to measure the effect of micronized marble powder on the hydration process of Portland cement. Measurement of the development of the hydration heat was performed on a TAM Air Calorimeter. TAM Air is an isothermal calorimeter for accurately determining the heat flow (production and consumption) and the amount of heat produced. A total of 10 chambers were used for the measurements (two chambers for each mixture). The mixtures were tested for 7-day measurement of the development of heat flow at a constant temperature of 20 °C. The mixtures were stored in plastic closable containers which were described, weighed and eventually compacted before insertion into the calorimeter. Each container contained approximately 25-38 g of the mixture. The output from the calorimetric measurement was the heat flow in W.

Mixtures	Replacing cement	Cement (CEM I 42.5 R) [g]	Micronized marble powder [g]	Water [g]
M0	0 wt. %	80	0	36
M5	5 wt. %	76	4	36
M10	10 wt. %	72	8	36
M15	15 wt. %	68	12	36
M50	50 wt. %	40	40	36

Table 1. Composition of the individual set/mixtures.

Element	Weight Wt. [%]	Wt. standard deviation [%]	Atomic [%]
C	16.93	0.33	30.06
O	32.29	0.50	43.04
Mg	0.32	0.10	0.04
Ca	50.47	0.41	26.86
Total	100.00		100.00

Table 2. Evaluation of elemental analysis.

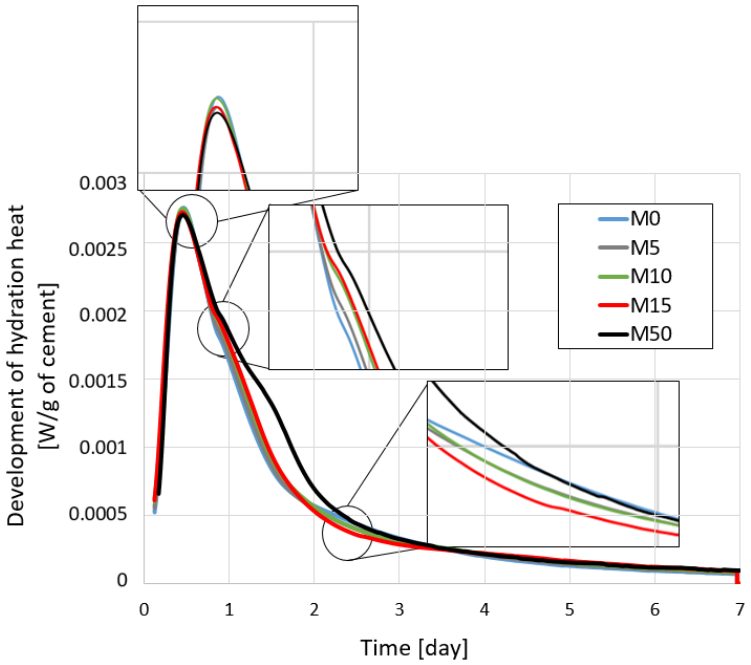

Figure 2. Curve of heat evolution for tested materials.

The results from the calorimetric measurement were converted to 1 g of cement based on the masses of the mixtures in the container. The FEG SEM Merlin ZEISS scanning electron microscope was used for microscopic structural and elemental analysis, which is located in the Laboratory of Electron Microscopy and Microanalysis at the University Center of Energy Efficient Buildings. Qualitative and quantitative analysis of the chemical composition of the samples was performed using an X-ray microanalysis, namely an Energy Spectrometer (EDS) by Oxford Instruments. The point ID method was used in the first sample, where only selected areas (areas with marble limestone) were tested. The second sample was examined using line scans. The method best describes the possible effect of micronized marble powder on the final product. The microscope setting was such that the accelerating voltage was 10 kV, the current 1 nA, the working table distance 8.5 mm, the measuring time of one point 50 μs and the resolution 1024 px. The composition of the recycled micronized marble powder can be determined from the results from the microscopic elemental analysis. Figure 1. shows the areas under investigation, and the results from the microscopic elemental analysis are presented in Table 2. The results are slightly distorted due to the need for sputtering the samples with a 30 nm carbon layer. It can be stated that about 99% of the waste material is made up of $CaCO_3$ (calcite) and the remaining 1% is of minor constituents, the most important of which is $MgCO_3$. From the pictures taken during the microscopic analysis, it is clear that the grains consist

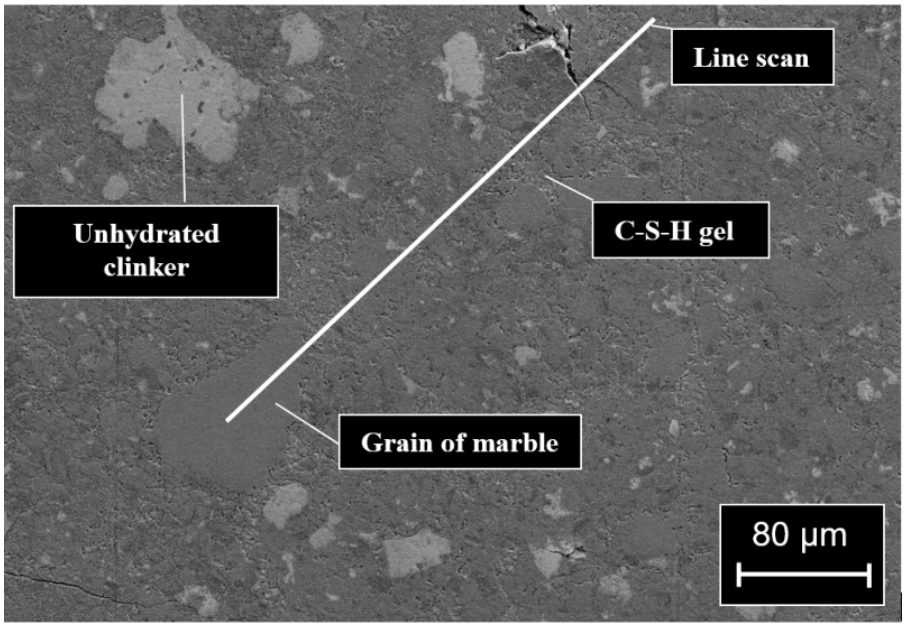

FIGURE 3. The image of cement paste containing micronized marble powder, magnified 500×.

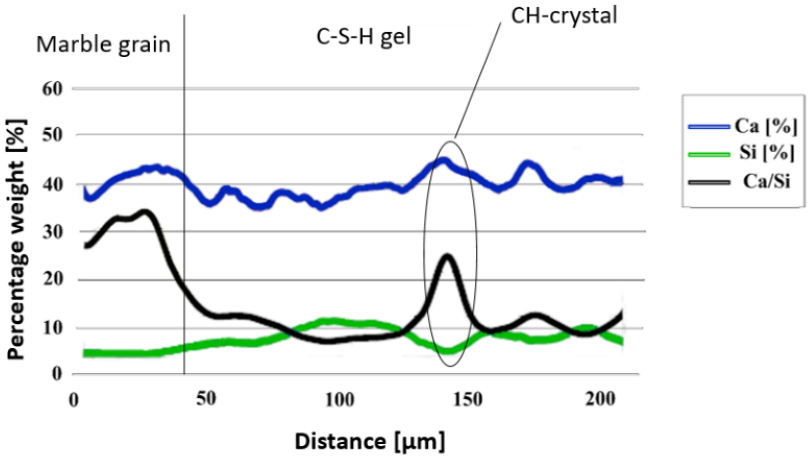

FIGURE 4. Concentration of calcium and silicon in line scan.

of one phase, they have a sharp and oblong shape. The calorimetric measurement (Figure 2.) shows the effect of micronized marble powder on the developing of hydration heat of the mixture. Thanks to the conversion of the heat flow to 1 g of cement, the differences in the hydration process were highlighted. For mixtures with micronized marble powder, it can be observed that after 20 hours of mixing, there was a slight increase in the heat flow, probably due to the hydration of C_3S. The difference in heat flow is apparent up to approximately three days (M50). Further, the course of heat flow is similar, i.e., micronized marble powder has no significant effect on C_2S hydration. This effect can be caused either by marble powder or the addition of finely ground particles. For this reason, we have proceeded to microscopic elemental analysis. Figure 3 shows the examined area for which four line scans were created. A backscatter electron detector was used to display the phase contrast information. The result was similar for each scan, so one was chosen as representative, on which the results were described (Figure 3). Figure 4 shows the weight distribution of calcium and silicon and also their ratio (Ca / Si). Emphasis was placed on these elements because CEM I 42.5 R Radotin has a high content of C_3S (tricalcium silicate) and C_2S (dicalcium silicate) and low content of C_3A (tricalcium aluminate) and C_4AF (tetracalciumaluminoferite), i.e., the resulting product is mainly composed of these elements. At the point of occurrence of the C-S-H gel, that is, the phases resulting from the hydration and hydrolysis of C_3S and C_2S, the amount of calcium and silicon affect the resulting phases, where the greatest proportion of calcium has xonotlite and the smallest afwillit. Overall, the identification and precise composition and structure of hydro silicates (hydro silicate gels) is difficult and therefore only the Ca/Si ratio is indicated. The resulting C-S-H gel can be chemically described

as follows:

$$xCaO \cdot ySiO_2 \cdot zH_2O, \quad (1)$$

where the high density C-S-H gel is in range: $x = 0.5 - 1.5$, $y = 1$, $z = 0.5 - 2.5$, and low density C-S-H gel $x = 1.5 - 2$, $y = 1$, $z = 1 - 4$. If we look at the weight of calcium (Figure 4), we see that there is a greater concentration of calcium at the site of the grain. A large amount of calcium in the grain is due to its composition because it is mostly composed of calcium, i.e., $CaCO_3$. Ca/Si ratio is increased up to a distance of about 50 microns from the grain, mainly due to the reduction in the amount of silicon, followed by a further 30 microns of gradual normalization of the values. From the results, it can be stated that another phase is preferred in the vicinity of the grains. This phase could be a low-density C-S-H gel.

4. Conclusions

This work focuses on the effect of micronized marble powder as a partial substitute for Portland cement. The resulting cement pastes contained Portland cement and micronized marble powder in 5, 10, 15 and 50 wt. %. Based on the results, it can be concluded that:

- The high-speed milling process generates grains that are angular and oblong.
- Calorimetry results showed that after 20 hours of mixing, there was a slight increase in heat flow caused by C_3S hydration, the heat flow was the same, so the marble powder did not have a significant effect on the hydration of C_2S.
- From the results of the elemental analysis, it can be stated that the creation of one phase is preferred in the vicinity of the grains. This effect is probably because around the grain of marble is less free water needed to hydration of the cement. This phase could be a low-density C-S-H gel.

The results of the work are in contradiction with the statement of Demirel [7] and Aliabdo [9], because marble powder during the hydration process is not completely inert, and smaller CH crystals do not appear in the surroundings of grains. In the future, the research will focus on confirming the theory of creating a low-density C-S-H gel around the grain of marble. For this reason, further work will be devoted to micromechanics around marble grains using nanoindentation.

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