Edyta Spychał, Anna Kotwa
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ASSESSMENT OF THE POSSIBILITY OF USING CHALCEDONITE POWDER AS A COMPONENT OF MORTARS

OCENA MOŻLIWOŚCI ZASTOSOWANIA MĄCZKI CHALCEDONITOWEJ JAKO SKŁADNIKA ZAPRAW BUDOWLANYCH

Edyta Spychał*, Anna Kotwa
Kielce University of Technology, Poland

Abstract

The article presents the results of the assessment of the possibility of using chalcedonite powder as a partial replacement for cement in mortars. Portland cement CEM I 42.5 R was used as a binder, which was replaced in the amount of 5%, 20%, 35% and 50% with chalcedonite powder. The experimental tests concerned the determination of the technological and mechanical properties of mortars: consistency, air content, compressive and bending strength, supplemented by X-ray diffraction analysis and calorimetric measurements of the pastes. The research results indicate that chalcedonite powder can be used in the production of mortars. The best mechanical properties of tested mortars were obtained in the case of replacing cement with the addition of powder in the amount of 5% and 20%.

Keywords: chalcedonite powder, cement mortar, additive, consistency, bending and compressive strength, calorimetrics measurements, XRD method

Streszczenie

W artykule dokonano oceny możliwości wykorzystania mączki chalcedonitowej jako częściowego zamiennika cementu w zaprawach budowlanych. Jako spoiwo zastosowano cement portlandzki CEM I 42,5 R, który zastępowano w ilości 5%, 20%, 35% oraz 50% mączką chalcedonitową. Badania doświadczalne dotyczyły określenia właściwości technologicznych i mechanicznych zapraw: konsystencji, zawartości powietrza, wytrzymałości na ściskanie i zginanie, uzupełnionych o rentgenowską analizę dyfrakcyjną oraz badania kalorymetryczne zaczynów. Wyniki badań wskazują, że mączka chalcedonitowa może być stosowana do produkcji zapraw budowlanych. Najlepsze właściwości mechaniczne badanych zapraw uzyskano w przypadku zastąpienia cementu dodatkiem mączki w ilości 5% i 20%.

Słowa kluczowe: mączka chalcedonitowa, zaprawa cementowa, dodatek, konsystencja, wytrzymałość na zginanie i ściskanie, pomiary kalorymetryczne, metoda XRD

1. INTRODUCTION

Chalcedonite is a sedimentary siliceous rock. It may be found in the deposits of Dęborzynek, Gapinin, Lubocz and Teofilów, in the region of Tomaszów Mazowiecki and Nowe Miasto. Chalcedonite, due to its very small area of occurrence, is one of the unique rocks in Poland and in Europe. The Teofilów deposit is the only one documented and currently exploited. The main component of the rock is chalcedony, other compounds are: quartz, opal, iron hydroxides, pyrite, manganese compounds and clay minerals. In chemical terms chalcedonite is a homogeneous material, consisting of silica in amount of about 94% by weight [1, 2]. Directions of use of chalcedonite in the form of sand

*Kielce University of Technology, Poland e-mail: espychal@tu.kielce.pl

and broken aggregate of fractions 0.8-2.0 mm and 16.0-32.0 mm have yet been varied. It has been classified, among others, as an aggregate for the foundation of road with small and very small traffic. It was used as a raw material for the production of powders for scrubbing and liquids for washing car chassis. Chalcedonite can be used as a sorbent in drinking water treatment [1, 3]. In the form of chalcedonite powder, this material was used in the alkali-silica reaction tests [4], as a partial replacement for fine aggregate in concrete [5], sand-lime products [6] or as a partial replacement for binder in lime mortars [7].

Carbon dioxide emissions accompannying production of cement clinker, the depletion of natural resources causes the search of alternative ingredients that may be a partial substitute for the basic raw materials used in the production of mortars and concretes. For both economical and ecological reasons as well as development of new technologies the need to look for a substitute for cement is constantly growing. Mineral addditives with pozzolanic properties used for the production of mortars and concretes are among others fly ash, silica fume, metakaolin, zeolites [8-11]. An alternative to commonly used mineral additives are stone powders, which are waste generated during the process of mechanical treatment or dedusting of mineral aggregates. Due to the fact that the chemical and mineral composition of these dusts is the same as the parent rock, they can be used in the production of construction products, being a partial substitute for a binder or fine aggregate [5, 6, 11-16]. The research carried out so far concentrated on the use of basalt [12-14, 17], marble [11, 18, 19], granite dust [13-15], melaphyre powder [20]. A commonly used material is limestone dust [12, 14, 20]. On the basis of the reserach to date, it has been found that these waste materials contribute to the improvement of rheological and mechanical properties, can increase durability of mortar and concrete. The possibilities of using stone dust in the production of mortars and concretes are wide, but varied, which is influenced by the grain size of material, its origin or the method of processing (drying, grinding) [12, 14].

The aim of the research presented in the article was to rate the possibility of using chalcedonite powder as the component of mortar by partially changing cement with waste material. The assessment was carried out on the basis of the technological and mechanical properties of the mortars, supplemented with calorimetric measurements and XRD X-ray diffraction pastes. This article is a continuation of the issues raised by the authors in the publication [21].

2. MATERIALS AND METHODS

Four series of mortars and pastes were prepared, in which Portland cement was substituted with chalcedonite powder in the amounts of 5% (CH5), 20% (CH20), 35% (CH35) and 50% (CH50) and reference sample – without additive (CH0). The industrial ordinary Portland cement CEM I 42.5 R was used in research. The chemical composition of cement and chalcedonite powder were given in Table 1.

Fine aggregate fraction 0-2 mm and tap water were used in the experiments. The mortar mix proportion were detailed in Table 2.

Table 1. Chemical composition of cement and chalcedonite powder [%]

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Cl	P_2O_5	TiO_2	Fe_2O_3	ZrO_2	BaO	F
Cement	19.49	4.75	3.25	62.3	2.08	3.0	0,55	0.79	0.06	–	–	–	–	–	–
Chalcedonite powder	91.8	3.04	1.28	0.45	0.15	0.05	0.42	0.09	–	0.04	0.11	1.28	0.01	0.04	0.06

Table 2. Composition of tested mortars [g]

Series of mortar	Cement	Chalcedonite powder	Fine aggregate	Water
CH0	450.0	0	1350.0	225.0
CH5	427.5	22.5	1350.0	225.0
CH20	360.0	90.0	1350.0	225.0
CH35	292.5	157.5	1350.0	225.0
CH50	225.0	225.0	1350.0	225.0

Additive in the form of chalcedonite powder, which was applied in these research, came from the mine of chalcedonite broken aggregates in Inowłódz. It was a final waste lying on the piles. In order to receive more homogeneous material, with a smaller granulation, it has also undergone 4 hours of grinding in a ball mill. Cement (C symbol), chalcedonite powder before (CHP symbol) and after grinding (CHPG symbol) were examined for particle size distribution with a laser diffractometer HELOS KR producted by Sympatec GmbH (Fig. 1).

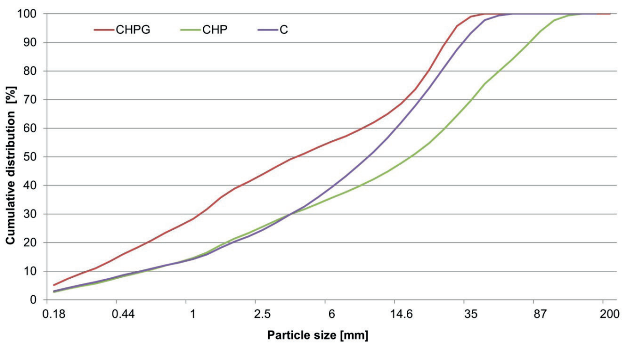

Fig. 1. Particle size distribution of cement and chalcedonite powder

Chalcedonite powder before grinding (CHP) has the particle size ranging from 0 to 175 µm, but chalcedonite powder after grinding (CHPG) has the particle size ranging from 0 to 51 µm, which gives a grain size smaller than cement (C). In the case of the CHPG sample, 50% of the grain size are grains up to 4.2 µm, while the CHP sample contains about 50% of grains with dimensions up to 17.4 µm.

The measurements of standard consistency were done according to PN-EN 1015-3 (as a flow) [22] and PN-B-04500 (as a cone penetration) [23] standards.

The air content was determined in accordance with PN-EN 1015-7 standard [24].

The research of mechanical properties were carried out on 40 x 40 x 160 mm mortars bars according to the PN-EN 196-1 standard [25] (after demoulding, were stored in tap water at 20 ±2°C). Each value was the average of three measurements of bending strength and the average of six measurements of compressive strength. The samples were tested after 28 and 90 days.

The hydration kinetics was carried out by calorimetry operating under non-isothermal and non-adiabatic conditions, using the calorymeter BT 2.15 produced by SETARAM. Tests were made on 7.5 g samples (pastes – Table 3) – 5 g of binder (cement or cement and chalcedonite powder) and 2.5 g of distilled water at constant water to binder ratio = 0.5, in the temparature of 20°C. The samples were placed each time in plastic bags, which were put in the measuring cell of the calorimeter. Results were read every 30 seconds for a period of 48 hours.

Table 3. Composition of tested pastes

Series of pastes	Cement [g]	Chalcedonite powder [g]	Water [ml]
CH0	5.00	0.00	2.5
CH5	4.75	0.25	2.5
CH20	4.00	1.00	2.5
CH35	3.25	1.75	2.5
CH50	2.50	2.50	2.5

Additionally, on the basis of calorimetric measurements (diagrams of total heat evolved), the hydration degree of the pastes was calculated, using the formula [26]:

$$SH = \left(\frac{x_1}{x_2}\right) \cdot 100 \qquad (1)$$

where:
SH – hydration degree;
x_1 – value measured after the period of hydration;
x_2 – value measured after full hydration or after a certain period of time taken as a refernce.

In the article, the measurements of the heat of hydration of CH0 paste after 48 hours were adopted as the value of x_2.

XRD images were obtained in a X-ray Diffractometer Empyrean produced by PANalytical. The research of X-Ray diffraction analysis were carried out on pastes after 2 days of maturing (the composition of the pastes was the same as in the calorimetric tests).

3. TEST RESULTS AND DISCUSSION

The results of mortar consistency tests were shown in Table 4. Replacing the cement in 5% (CH5) with chalcedonite powder increased the flow from 155 mm (CH0) to 160 mm (CH50), what can be explained by the lubricating effect of this material, which can be related to the physical interaction of this dust grains [27]. In other cases, an increase in the amount of chalcedonite powder resulted in a decrease in the flow (from 155 to maximum 142 mm – by about 9%). In the case of the consistency test using the cone penetration method, the addition of chalcedonite powder reduced the tested parameter (from 5.1 cm maximum to 4.2 cm). The highest reduction was observed in CH50 mortar containing 50% addition (by about 17.6%).

Table 4. Consistency and air content of the tested mortars

Sample of mortar	Flow [mm]	Cone Penetration [cm]	Air content [%]
CH0	155	5.1	9.0
CH5	160	4.6	11.0
CH20	147	4.5	11.5
CH35	145	4.4	16.0
CH50	142	4.2	19.5

Air content (Table 4) for the reference mortar (CH0) was 9%. The greater the amount of the additive, the greater the air entrainment of the mortars. The content of chalcedonite powder in the amount of 5% to 20% by weight in relation to cement caused a slight increase in the air content (from 9% to 11.5%). The air content was more than twice as high in CH50 mortar than in reference mortar (CH0). This may be retalted to the properties of chalcedonite. According to the publication [3], the porosity of chalcedonite ranges from 14-35%.

In Tables 5 and 6 were presented the results of determining the bending and compressive strength for the mortars modified with chalcedonite powder. These measurements were compared with the values of the reference mortar CH0 (without additive).

Comparing the results of the bending strength of the reference mortar and chalcedonite powder modified mortars, it can be seen that its increase causes a reduction in the mortar strength after 28 and 90 days. The smallest changes in mechanical properties were noted in the case of CH5 and CH20 mortars (9-17% relative to the CH0 sample). Chalcedonite powder addition of 5% and 20% caused slight increase of compressive strength of mortars after 28 days of hardening, in comparison with the reference mortar. Compressive strength of CH5 mortar after 90 days of research was similiar to the result for CH0 mortar. However, the higher addition brings the strength reduction. The findings from the tests performed after 28 and 90 days were also least favourable for the CH50 sample. CH35 and CH50 mortars with the smallest bending and compressive strength were characterized by a much higer air content compared to the others, which had an impact on their mechanical properties. The strength of the mortars (CH5 and CH20) may be due to the filling effect (sealing the structure) and the pozzolanic properties of this additive.

On the basis of calorimetric research shown in Figures 2 and 3 it may be stated, that chalcedonite powder delays the process of cement hydration. The total heat released by tested pastes after 12, 24, 36, 48 h of hydration and hydration degree of each pastes are given in Table 7.

Table 5. Bending strength of mortars

Sample of mortar	Bending strength after 28 days [MPa]	Standard deviation of bending strength [MPa]	Bending strength after 90 days [MPa]	Standard deviation of bending strength [MPa]
CH0	2.3	0.14	2.4	0.43
CH5	2.1	0.00	2.1	0.05
CH20	2.0	0.05	2.0	0.05
CH35	1.6	0.00	1.6	0.08
CH50	0.2	0.05	0.2	0.05

Table 6. Compressive strength of mortars

Sample of mortar	Compressive strength after 28 days [MPa]	Standard deviation of compressive strength [MPa]	Compressive strength after 90 days [MPa]	Standard deviation of compressive strength [MPa]
CH0	60.8	2.91	70.3	3.62
CH5	65.3	2.53	72.1	3.49
CH20	62.3	2.57	62.6	2.52
CH35	41.5	2.20	43.3	0.76
CH50	26.5	1.75	26.0	1.91

Table 7. Heat of hydration of tested pastes

Sample of pastes	Heat after hours of hydration [J/g]				Degree of hydration			
	12 h	24 h	36 h	48 h	12 h	24 h	36 h	48 h
CH0	134.91	239.75	287.52	317.50	42.49	75.51	90.56	100.00
CH5	132.61	235.85	281.62	307.83	41.77	74.28	88.70	96.95
CH20	112.61	203.04	240.97	263.23	35.47	63.95	75.90	82.91
CH35	110.90	185.62	216.90	234.19	34.93	58.46	68.31	73.76
CH50	90.19	149.87	175.62	191.12	28.41	47.20	55.31	60.20

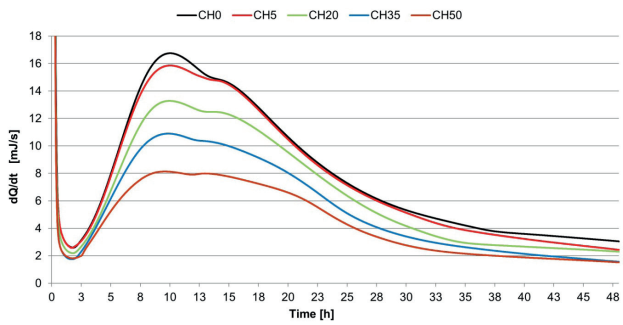

Fig. 2. The heat evolution curves as a function of time for tested pastes

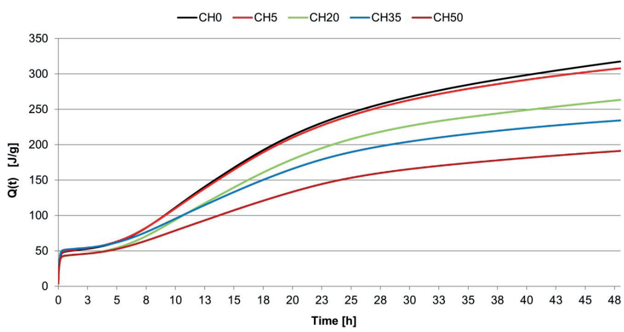

Fig. 3. Total heat evolved as a function of time for tested pastes

The hardening heat of individual pastes is differential – it's maximum for CH0 paste and significantly lower in the case of CH50 paste. The microcalorimetric curves for paste containing 5% chalcedonite powder show that both the total amount of evolved heat and the rate of heat evolution over time do not differ significantly, as compared to a base paste CH0 without chalcedonite powder. It may be noticed, that the addition in the amount of 5% acts as a cement substitute. The increase of chalcedonite powder content effects in „dilution" of active material with the additive and increase in the effective water-cement ratio [28]. It can be seen that the addition affects the reduction of the thermal effect after 12, 24, 36 and 48 hours for pastes in which the cement was replaced with 20, 35 and 50 % chalcedonite powder (for the reference sample). In the case of CH0÷CH35 pastes, two maxima (between 8 and 18 hours) are clearly visible in Figure 2 (the amount of heat released varies). In the case of the CH50 paste, both maxima are at a similar level. It can be noted that the biggest heat emission from the hydration process was obtained with the CH0 and CH5 samples, and in the case of these pastes, the biggest compressive strength were achived after 28 and 90 days. The highest degree of hydration after 48 hours was recorded for the CH0 paste, and the lowest for the CH50 sample. The degree of hydration for CH50 paste was about 40% less than the degree of hydration for CH0.

XRD patterns of reference sample (CH0) and pastes containing 5, 20, 35 and 50% chalcedonite powder replacing after 2 days of hydration are presented in Figure 4. There have been shown the peaks characteristic of the cement phases, non-hydrated clinker phases [29] and the peaks of mineral contained in the chalcedonite powder such as quartz [1-5].

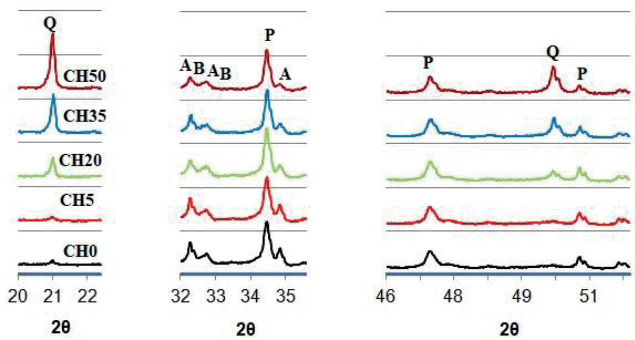

Fig. 4. XRD patterns of tested pastes (denotation: Q – quartz, A – alite, B – belite, P – portlandite)

The most intense peaks for all pastes were recorded for portlandite and quartz. Portlandite intensity was the biggest for CH0, CH5 and CH20 samples, but quartz intensity was the biggest for CH50 sample (due to the highest chalcedonite powder content).

4. CONCLUSIONS

The test results reveal that partial replacement of cement with chalcedonite powder has a noticeable effect on the technological and mechanical properties of mortars:

1. The 5% addition of this dust has a positive effect on the consistency of the mortar. Chalcedonite powder in an amount greater than 5% in relation to the weight of cement contributed to the reduction of the flow of the mortar, which may result in a necessity of superplasticizer application (especially when replacing cement with 35 and 50% of chalcedonite powder).
2. With a share of chalcedonite powder as a cement substitute with 5% and 20% by weight, the compressive strength slightly increases after 28 days in relation to mortar without addition. More of the additive reduces the compressive strength.
3. Chalcedonite powder affects the delay of hydration process. This effect is rising with the increase of addition amount.

The results of these research point the fact, that the chalcedonite powder may be a good component of mortars in the amount to 20% (based on the weight of cement). Partial replacement of cement by chalcedonite powder can be profitable from an economic and ecological point of view.

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