

# Kinetics of hydration process and rheology of cement pastes containing mechanically activated chalcedonite powder

Edyta Spychał<sup>1</sup> Martin Vyšvařil<sup>2</sup>

<sup>1</sup> Faculty of Civil Engineering and Architecture, Kielce University of Technology, Poland

<sup>2</sup> Faculty of Civil Engineering, Brno University of Technology, Czechia

**Abstract.** Reducing the amount of Portland clinker in the cement composition is one of the key aspects of the carbon dioxide emission reduction strategy. One solution is to use waste materials for this purpose, for example stone fine powder, especially limestone, basalt, granite, melaphyre powder. There is relatively little information about the use of chalcedonite powder as an addition in cement or cement composites. Any precise information about impact on particle size of this material on changes in the properties of cement pastes is lacking. The research in the article focuses on the impact of the particle size and amount of chalcedony powder on the hydration processes and rheological properties of cement pastes. The addition was used at 10 %, 20 %, and 30 % by weight of the cement, with grain sizes up of 10  $\mu\text{m}$ , 20  $\mu\text{m}$  and 36  $\mu\text{m}$ . The hydration kinetics of the pastes was assessed based on calorimetric measurements, supplemented by DTA-TG analysis and mechanical properties test. Additionally the rheological properties were determined. The study demonstrated that chalcedony powder affects the tested parameters to varying degrees. In rheological research, the cement paste containing the largest grain size (CHP36) chalcedonite powder showed the most similar properties to the CEM cement paste (without the addition). In turn, the pastes modified with chalcedonite powder, in which the cement was replaced by 10 % of the additive, exhibited the highest amount of cumulative heat. In terms of 28-days compressive strength, the materials containing CHP20 powder demonstrated the most similar properties to the reference paste, without the addition.

**Key words:** carbon dioxide emissions; cement paste; chalcedonite powder; waste; particle size; hydration processes; rheology

## 1. INTRODUCTION

Currently, material modifications in the production of cement, mortar, and concrete are closely linked to global industrialization, climate change, natural resource management, and government regulations [1-3]. The main challenge in the cement industry is the need to reduce greenhouse gas emissions associated with cement clinker production. Proposed solutions involve introducing changes to production processes in cement plants, for example, through the use of alternative fuels, technologies of CO<sub>2</sub> capturing, high-performance classifiers, more efficient grinding technologies, as well as modifications to the composition of the binders themselves [1,3-5]. The use of cements with additions and low-clinker cements is a solution that allows for reducing the clinker content in cement compositions [4,5]. Additionally, the process of mechanical activation of cement components may have a beneficial effect on accelerating the hydration process, increasing the pozzolanic activity of non-clinker cement components, or improving mechanical properties [6,7]. In addition to commonly used mineral additives, other

alternative materials are being sought that will be characterized by low energy consumption in production processes and will also allow for the efficient use of waste. Stone powders are natural mineral materials, usually subjected only to mechanical processing, allowing for the production of materials with varying grain sizes depending on the needs [8-11]. Information on the effects of limestone, basalt, granite, marble and melaphyre powders, in particular, can be found in the literature [8-16]. Chalcedonite has so far been used mainly as a partial substitute for addition and fine aggregate in ordinary concretes [17], a component of reactive powder concrete [18], a partial substitute for binders in pastes and mortars [19-21]. It is also used in other industries such an ingredient in biodegradable polymer composites [22,23]. However, there is relatively little information on its effect on the properties of pastes, mortars, and concretes, in which it acts as a partial cement substitute. Literature analysis indicates that it affects among others on consistency, rheological properties, cement hydration process, and mechanical properties [17-21]. Studies conducted to date have focused solely on assessing the effect of chalcedonite powder or chalcedonite sand on selected properties of cement

composites. The effect of its grain size on the standard or functional properties of the materials has not been analyzed. The authors of the article [18] applied the chalcedonite fillers of fraction 0/250  $\mu\text{m}$  and 250/500  $\mu\text{m}$ . They demonstrated, that chalcedonite-based concrete with smaller amount of cement had decline compressive strength and frost resistance. On the other hand the strength values were enough high to note this concrete such as high-performance concrete. Chalcedonite dust with maximum grain size 72  $\mu\text{m}$  in the research [17] was used to check the impact on concrete parameters resulting from the designed concrete classes C30/37, C35/45 and C40/50. Chalcedonite powder influenced on the average compressive strength reduction of 10 %, but all series of concretes modified

## 2. MATERIALS AND METHODOLOGY OF RESEARCH

### 2.1. Materials

#### 2.1.1. Materials characterization

The ingredients used in these research included industry ordinary Portland cement CEM I 42.5R NA, chalcedonite powder and water. Chalcedonite waste was produced from chalcedonite rock. Deposits of this rock are located in Poland, in Inowłódz, near Tomaszów Mazowiecki. The material used for this research was only prepared in mechanical industry processing, characterized by different grain sizes with maximum 10  $\mu\text{m}$ , 20  $\mu\text{m}$  and 36  $\mu\text{m}$  (name of additions: CHP10,

Material	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	MnO	P <sub>2</sub> O <sub>5</sub>	L.O.I.
CEM I	20.49	3.98	4.19	65.54	0.73	2.90	0.56	0.37	0.31	0.09	0.28	0.56
CHP10	98.90	0.90	0.04	0.05	0.02	-	0.03	0.04	0.02	0.00	0.00	0.00
CHP20	99.00	0.80	0.04	0.04	0.03	-	0.03	0.04	0.02	0.00	0.00	0.00
CHP36	98.89	0.88	0.05	0.06	0.02	-	0.03	0.04	0.02	0.00	0.00	0.01

chalcedonite powder achieved the assumed strength classes. Analyzing the rheological properties of cement pastes with 10 % and 20 % chalcedonite powder with grain size of up to 10  $\mu\text{m}$ , it can be seen that the use of this addition increased the yield stress and consistency coefficient, decreased the mini-slump flow in comparison to the paste without the addition [20]. Based on literature studies, it can be concluded that chalcedonite powder affected the tested physico-mechanical properties to varying degrees. Due to its grain size, this addition reduced consistency (reduce flow, cone penetration and mini slump cone), which is also noticeable by increasing the consistency coefficient. Calorimetric measurements showed lower heat release dynamics for pastes modified with chalcedonite powder. The effect on the compressive strength of the tested materials was varied.

This article focuses on determining the effect of both the quantity and grain size of chalcedonite powder on cement hydration processes and the rheological properties of pastes, partially replacing cement with chalcedonite powder. For this purpose, calorimetric and thermogravimetric studies were performed, supplemented by an assessment of the mechanical properties of the pastes. The yield stress, consistency coefficient, and thixotropy were assessed using rheological tests, which were supplemented by an examination of the pastes' consistency. The effect of the additive on cement hydration processes was also determined. Based on this, the interaction between cement and chalcedonite powder and its effect on the kinetics of reactions occurring in the cement paste was determined. This information is important from both a scientific and practical perspective. This knowledge is essential for a comprehensive analysis and determination of the potential use of chalcedonite powder in cementitious composites.

**TABLE 1.** Chemical composition of materials, [%]

CHP20, CHP36). The chemical composition of cement and chalcedonite dust was introduced in Table 1. It was measured with an Axios X-ray fluorescence (XRF) spectrometer Malvern Panalytical Ltd. Percentage quantity of all components of cement is typical for this binder. As one can note (Table 1) all three types of chalcedonite powder have similar compositions, characterized by quantity over 98 % of SiO<sub>2</sub>. The mechanical properties of cement were assessed. The research was performed according to PN-EN 196-1. 2-days and 28-days flexural strength of cement was 5.13 MPa and 8.60 MPa, but 2-days and 28-days compressive strength was 22.43 MPa and 48.54 MPa.

#### 2.1.2. Methods for determining physical properties of materials

The specific density of materials was determined using the pycnometric method according to PN-EN 1097-7 and the specific surface area using Blaine method according to PN-EN 196-6. Granulometry of ingredients was measured using a laser particle sizer (HELOS KR, company Sympatec GmbH). Granulation of all additions was smaller than that of the cement (Table 2, Figure 1). The specific density of cement was 3.11 g/cm<sup>3</sup>, of CHP10 was 2.66 g / cm<sup>3</sup> and of CHP20 and CHP36 was 2.67 g / cm<sup>3</sup>. The specific surface of cement was 2990 cm<sup>2</sup> / g. CHP36 had the smallest specific surface equal to 7910 cm<sup>2</sup> / g (comparing only the addition with different grain sizes). The remaining waste powders (CHP10 and CHP20) were characterized by a specific surface area equal to 16590 cm<sup>2</sup> / g and 12950 cm<sup>2</sup> / g.

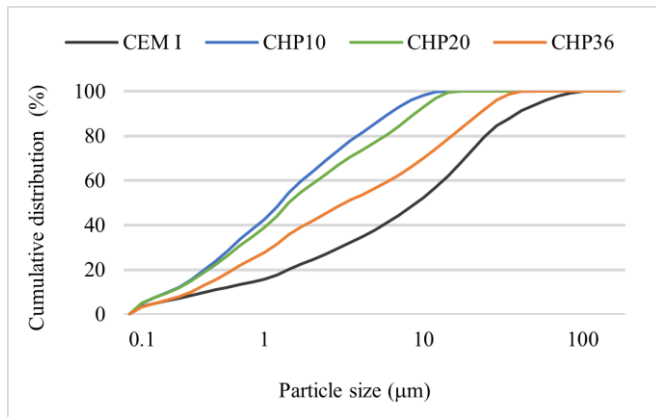


FIGURE 1. Particle size distribution of ingredients

TABLE 2. Information of median diameter of selected particles of cement and chalcidonite powder

	CEM I	CHP10	CHP20	CHP36
$d_{10}$ ( $\mu\text{m}$ )	0.45	0.27	0.27	0.36
$d_{50}$ ( $\mu\text{m}$ )	9.25	1.29	1.49	3.34
$d_{90}$ ( $\mu\text{m}$ )	39.92	6.24	9.04	22.83

### 2.1.3. Method for determining pozzolanic activity of chalcidonite powder

Additionally, the pozzolanic activity of additions was determined by chemical method - Chapelle test [24,25]. It should be noted that according to the Chapelle method, a material is considered to be pozzolanic active if its reactivity after 1 day of measurement is at least 650 mg  $\text{Ca}(\text{OH})_2$  / g. According to this research, each chalcidonite powder exhibited pozzolanic activity after just 1 day (Table 3). The smaller the granulometry (Fig.1), the higher the activity of the addition.

TABLE 3. Pozzolanic activity of chalcidonite powder, (mg  $\text{Ca}(\text{OH})_2$  g<sup>-1</sup>)

Type of CHP	After 1 day	After 3 days
CHP10	832	1414
CHP20	1166	1419
CHP36	727	1371

### 2.1.4. Pastes preparation

Ten types of pastes were prepared for testing. Base paste CEM, consisting only of cement and water and 9 pastes in which cement was replaced in amounts 10 %, 20 % and 30 % by weight with the chalcidonite powder of various grain sizes: CHP10, CHP20, CHP36. The water to binder ratio was constant for all pastes and was 0.5. Composition of all binders used for research was shown in Table 4. The pastes for rheological and consistency tests contained 90 g of binder and 45 g of water. The samples for calorimetric measurements consisted of 4 g of binder and 2 g of water. The pastes for strength tests and DTA/TG analysis each contained 160 g of binder and 80 g of water. Before each test the dry ingredients were pre-mixed and then the specified amount of water was added.

TABLE 4. Percent composition of binders

Type of paste	CEM [%]	CHP10 [%]	CHP20 [%]	CHP36 [%]
CEM	100	-	-	-
CH10_10	90	10	-	-
CH10_20	80	20	-	-
CH10_30	70	30	-	-
CH20_10	90	-	10	-
CH20_20	80	-	20	-
CH20_30	70	-	30	-
CH36_10	90	-	-	10
CH36_20	80	-	-	20
CH36_30	70	-	-	30

## 2.2. Methodology of research

On Figure 2 all types of tests were introduced. As it can be seen, the research consisted of two main parts – the assessment of the properties of the pastes in the plastic state and the evaluation of the setting and hardening processes at different stages of material curing.

The rheological properties of the pastes were compared. Each time ingredients were mixed, the sample was placed into the cylinder of testing (rheometer Discovery HR-1, company TA Instruments), and the remaining part was used to the test of consistency. The hybrid rheometer was equipped in a Peltier Concentric Cylinder system with a DIN rotor (standard DIN cylinder system 5.917 mm). The temperature during the measurements was 20 °C. Determined, among others yield stress ( $\tau_0$ ), consistency coefficient (K) and fluidity index (n) in accordance with the Herschel-Bulkley model [26]. Thixotropy of the samples was determined using the TRIOS software taking into account the hysteresis area between ascending and descending flow curves. For each type of pastes, 3 results were compiled, introducing the measurements taken after 5, 30 and 60 min.

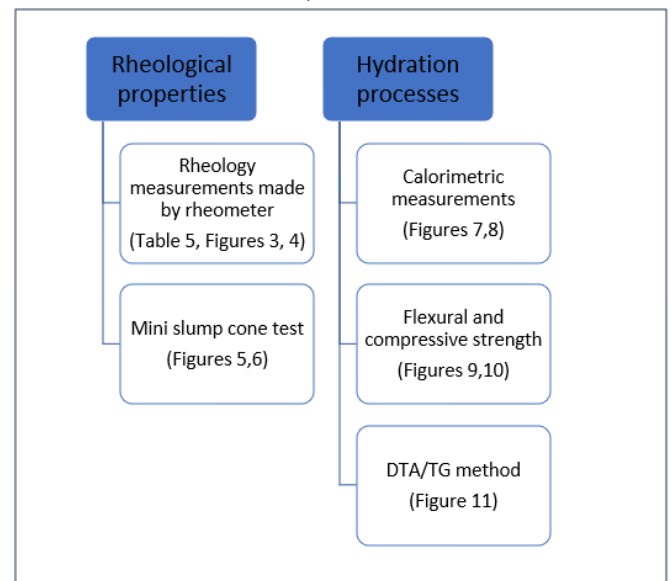


FIGURE 2. Diagram of the research methods

The shear rate changed in range firstly from  $1 \text{ s}^{-1}$  to  $100 \text{ s}^{-1}$  and secondly from  $100 \text{ s}^{-1}$  to  $1 \text{ s}^{-1}$ . The mixing method of pastes was as follows: 1 min mixing manually  $\rightarrow$  2 min break  $\rightarrow$  1 min mixing manually  $\rightarrow$  1 minute break and measurement. In the consistency test – mini slump cone test [27], the flow diameter (average of 4 measurements) and the high of sample (average of 3 measurements) were determined. Measurements were made using an electronic caliper.

The heat of hydration was measured in TAM Air 8-channel isothermal microcalorimeter (TA Instruments company). Each time dry ingredients and water were stored in ampoules in calorimeter for 24 h in order to achieve thermal equilibrium and then they were mixed and the measurement was started. The hydration processes of pastes monitored for 72 hours.

Mechanical properties of pastes was determined after 3 and 28 days of curing. All of ingredients were mixed manually for 1 min. For this purpose, samples of moulds with dimensions of  $20 \text{ mm} \times 20 \text{ mm} \times 100 \text{ mm}$  were formed. After forming, the samples were stored for 24 h in air-dry conditions (protected with foil against excessive water evaporation), and then seasoned for 2 or 27 days in containers, in water. Flexural strength research was determined using a three-point flexural test. The cross-section of the bending surface had the dimensions of  $20 \times 20 \text{ mm}$ , but the spacing between the supports was equal  $70 \text{ mm}$ ). The compressive strength test was performed on halves of the beams, where the compressed surface was a square with a cross-section  $20 \times 20 \text{ mm}$ . The flexural strength was determined as the average of 3 measurements for each type of paste and the compressive strength was calculated as the average of 6 results. All tests were performed at a temperature  $20 \pm 2 \text{ }^\circ\text{C}$ . After testing the mechanical properties, samples were taken for DTA/TG measurements (STA 2500 Regulus thermogravimeter, company NETZSCH GmbH & Co.). Each hardened paste was manually ground in a mortar and the hydration process was stopped using acetone. 8-10 drops of acetone were added and each sample was dried for 15 minutes in a stream of cool air. During thermal analysis, the pastes were placed in a nitrogen stream and heated to a temperature of  $1000 \text{ }^\circ\text{C}$  at a rate of  $10 \text{ }^\circ\text{C} / \text{min}$ . The analyzed sample mass was  $300 \text{ mg}$ . The resulting data were evaluated using Proteus software, version 6.1.0.

### 3. RESULTS AND DISCUSSION

#### 3.1. Rheological properties

The results for the rheological parameters were introduced in Table 5, Figure 3 and 4. The results of rheological measurements indicated that the addition of chalcidonite waste powder impacted on a much higher increase in rheological parameters, especially yield stress and consistency coefficient, within 1 hour compared to cement paste without addition (Fig. 3). The change in these parameters was visible, taking into account both the amount and the grain sizes of the addition (Fig. 4). The increase in the amount of addition and the reduction in its grain size resulted in an increase in  $\tau_0$  and K parameters. These results are related to the grain size and therefore the specific surface area of the waste material. The exception are 2 pastes modified with

CHP10 powder in the amount of 10 % and 30 %, in the case of which the consistency index decreased over time. The addition of the finest CHP10 to the cement paste can enhance the time growth of the inter-slip structure (flocculation + nucleation/ionic effects)  $\Rightarrow \tau_0$  increases, but at the same time it can improve lubrication during flow (better particle packing + surface charge at high pH)  $\Rightarrow$  viscosity decreases [28]; this is also clearly visible in the flow curves in Fig. 4. For CH10, the curve rises steeply at low shear rates (high viscosity) and after exceeding  $30 \text{ s}^{-1}$ , the steepness of the flow curve decreases significantly (viscosity decreased at higher speeds = easier flow, greater lubrication). With repeated shear forces, particle packing can be further improved (reduction of viscosity, increase of the yield point over time). In coarser chalcidonite powder case, contrary, frictional/hydrodynamic dissipation and poorer lubrication may prevail  $\Rightarrow$  viscosity increases, while the colloidal network is weaker/diluted  $\Rightarrow \tau_0$  decreases [29].

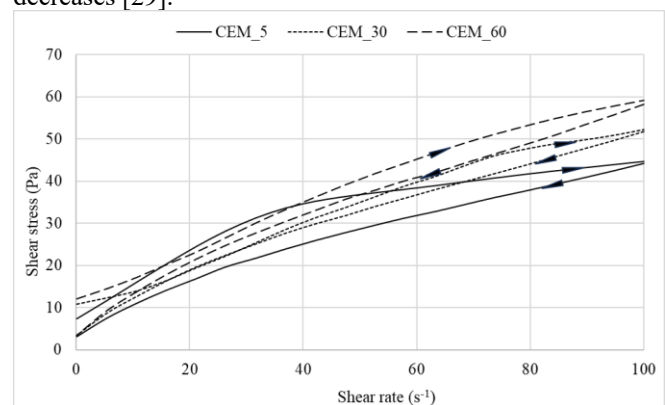


FIGURE 3. Results of shear stress for cement pastes after 5,30,60 minutes of measurements

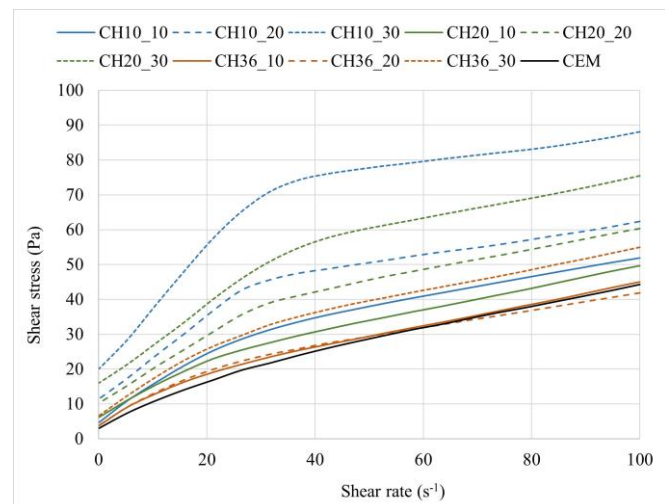


FIGURE 4. Selected results of shear stress for pastes after 5 minutes

Changes in rheological properties during the first 60 minutes are greater for each of the pastes containing chalcidonite powder compared to the behavior of the paste without the additive (Figure 3 and 4). An increase in the consistency index translates to an increase in the viscosity of the pastes, which is visible for samples modified with chalcidonite powder. This means that these pastes will be more resistant to

segregation than pastes without the addition of chalcidone [30]. On the other hand, the yield stress of the pastes with CHP20 and CHP36 powder decreased over time. The exception are the pastes with CHP10 powder, for which this phenomenon did not occur in every case. Adding 10 % or 30 % of CHP10 powder to the paste causes the yield stress to increase over time. For all pastes with chalcidone powder an increase in pseudoplasticity was noted, because the parameter  $n$  was decreased. The paste CH36 containing chalcidone powder CHP36 had the closest properties result to cement paste CEM. The decrease in the thixotropy of pastes over time was related to ongoing hydration reactions in the cement, particularly the formation of primary ettringite [31]. During the shear force on cement pastes, the surfaces of the cement grains that have not yet reacted are exposed. Their subsequent hydration (or other reaction) caused the paste structure to thicken (hence the largest changes in thixotropy occur between 5 and 30 minutes). The greatest differences in thixotropy were seen between measurements after 5 and 30 minutes. In each case, a significant reduction in thixotropic properties was noted.

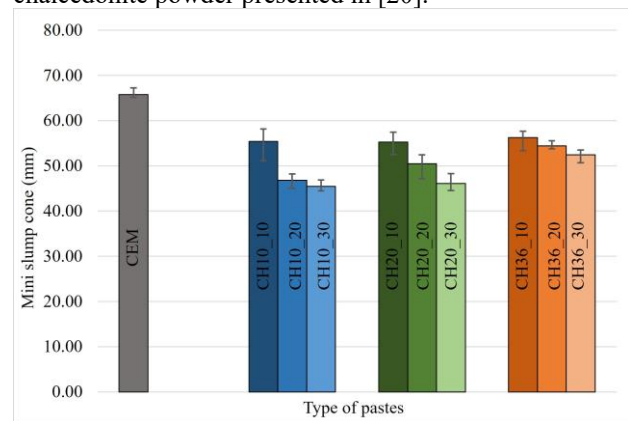
**TABLE 5.** Rheological parameters of tested pastes

Type of Paste	t [min]	$\tau_0$ [Pa]	K [Pa·s]	n [-]	R <sup>2</sup> [-]	Thixotropy [Pa·s <sup>-1</sup> ]
CEM	5	2.18	1.90	0.67	0.99941	611
	30	2.68	2.06	0.69	0.99952	208
	60	2.61	2.25	0.69	0.99929	350
CH10_10	5	1.75	5.01	0.50	0.99470	245
	30	2.59	4.88	0.52	0.99704	132
	60	3.17	4.58	0.55	0.99811	-22
CH10_20	5	4.93	9.22	0.40	0.96922	947
	30	5.46	9.60	0.38	0.97221	169
	60	4.26	10.55	0.36	0.97431	224
CH10_30	5	6.93	18.13	0.33	0.94347	1347
	30	9.68	17.88	0.32	0.94813	372
	60	11.36	15.93	0.35	0.96423	360
CH20_10	5	4.97	2.71	0.61	0.99792	821
	30	3.41	4.01	0.52	0.99820	186
	60	3.00	4.56	0.48	0.99714	125
CH20_20	5	6.47	5.08	0.51	0.98847	845
	30	4.18	6.92	0.44	0.98785	194
	60	4.05	6.71	0.44	0.98887	220
CH20_30	5	10.21	6.89	0.49	0.97768	1100
	30	8.59	8.77	0.44	0.97464	326
	60	7.88	9.06	0.43	0.97775	377
CH36_10	5	3.29	2.20	0.63	0.99873	707
	30	2.68	2.82	0.60	0.99913	224
	60	2.74	3.21	0.56	0.99880	103
CH36_20	5	2.28	3.35	0.53	0.99758	487
	30	1.88	3.98	0.52	0.99803	131
	60	1.92	4.04	0.53	0.99792	115
CH36_30	5	4.05	4.34	0.53	0.99550	662
	30	3.12	5.95	0.47	0.99346	160
	60	2.98	6.43	0.46	0.99433	127

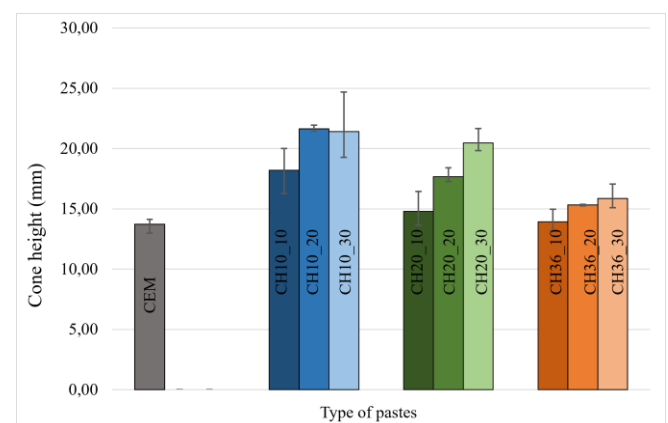
### 3.2. Consistency test

All modified pastes had smaller flow diameter and smaller height of cone than base cement paste (Fig. 5 and 6). Average mini slump cone of cement paste was 65.78 mm, average cone height was 13.72 mm. Average mini slump cone of paste with CHP10 was in range 45.44÷55.40 mm, for paste with CHP20 in range 46.12÷55.29 mm, for paste with CHP36

52.43÷54.43mm. Average height of cone for paste with CHP10 was in range 18.20÷21.63 mm, for paste with CHP20 in range 14.80÷20.47 mm, for paste with CHP36 13.91÷15.87 mm. The consistency of modified pastes decreased by a maximum of 31 % compared to the sample without the addition. In each case, increasing the amount of addition resulted in a decrease in flow and an increase in the cone height. This is due to the smaller grain size and the higher specific surface of additives compared with parameters of cement. The biggest changes were noted for pastes with CHP10, the smallest - for samples with CHP36. When comparing pastes containing chalcidone powder with one type of granulometry but different amount of additive, it can be seen that the larger the amount, the lower the consistency and the higher the H parameter. Pastes containing 10 % of additive, regardless of grain composition, were characterized by a similar flow. Paste CH36\_10 containing 10 % of CHP36 chalcidone powder had the closest properties to cement paste without addition. The effect of chalcidone powder on the consistency of the pastes is consistent with the results of the consistency coefficient from rheological measurements. It can be seen that both the increase in the addition and the degree of fineness was noticeable in the increase in the consistency coefficient and in the reduction in the mini slump cone. The results of consistency test (the impact of chalcidone powder on pastes flow) presented in the article are consistent with the results of pastes containing CHP10 chalcidone powder presented in [20].



**FIGURE 5.** Results of flow for all tested pastes



**FIGURE 6.** Results of cone height for all tested pastes

### 3.3. Calorimetric measurements

The hydration heat evolution of the base cement paste CEM and modified pastes CH10, CH20, CH36 was presented in Figure 7. On the other hand the cumulative heat for all pastes was shown in the Figure 8. As research shown, addition of chalcedonite powder resulted in the noticeable decrease of amount of heat evolution and also contributed to a decrease in the amount of accumulated heat. These changes were more noticeable the larger the amount of additive and the smaller its grain size (larger specific surface). The most similar heat release pattern when comparing the reference CEM and modified pastes was achieved by pastes with 10 % powder in CHP10 and CHP20. The use of chalcedonite powder in each case (regardless of its grain size and quantity) resulted in a reduction in the occurrence of the main peak maximum on the hydration heat release rate curve. For all pastes the second maximum was recorded after approximately 6-8 hours of hydration, what is related to the hydration of  $C_3S$ . It is associated with the nucleation and growth of C-S-H and portlandite [32]. The third peak is assigned to  $C_3A$  hydration after sulfate depletion (sulfate depletion point) and hydration of  $C_4AF$ . The fourth maximum is associated with monosulfate formation and sometimes  $C_2S$  hydration may also contribute to this peak [32-34]. In some mixtures CH20\_20 and CH20\_30 were prominent, in CH36 it is shifted to later times (around 20 hours) and less prominent. The analysis of the calorimetric curve of the CH36\_30 paste shows that the thermal effect is much more extended in time compared to other pastes. The induction period of the pastes modified with chalcedonite powder was slightly extended. The cement paste without any addition had the highest amount of accumulated heat equaling 246 J / g. The highest cumulative amount of heat evolution of pastes with addition was recorded in the case of the pastes modified with 10 % chalcedonite powder equal to about 233 J/g, and the lowest for the paste equal to 189 J / g. The cumulative amount of heat evolution decreased by a maximum of approximately 23 % - comparing all tested pastes. The biggest differences compared to the base paste CEM in the amount of accumulated heat were recorded for pastes with chalcedonite powder in the amount 30 % (regardless of the grain size of addition).

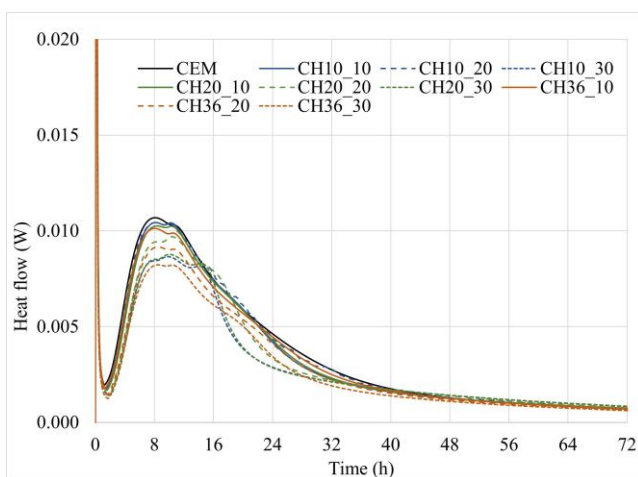


FIGURE 7. Calorimetric curves of all tested pastes

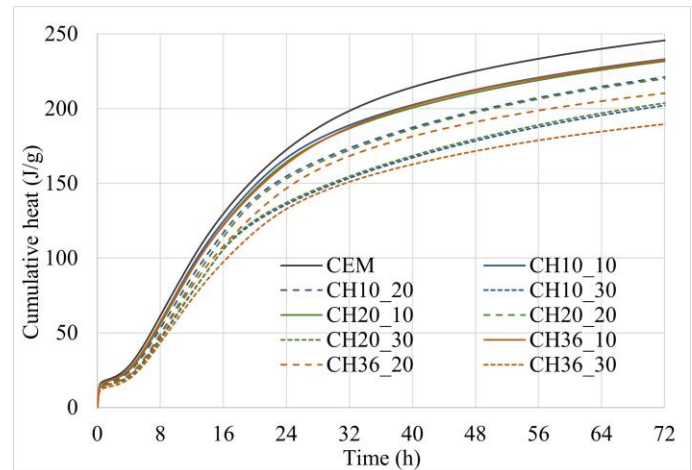


FIGURE 8. Curves of cumulative heat for all tested pastes

### 3.4. Flexural and compressive strength

Figures 9 and 10 presented increase in flexural and compressive strength after 3 and 28 days of curing. Each figure shows bars illustrating the average of strength after 3 and 28 days. The highest flexural strength after 3 days was recorded for the cement paste without the addition (4.91 MPa). Slightly lower results were achieved by pastes with 10 % chalcedonite powder, the smallest - pastes with CHP10, CHP20 and CHP36 in amount 30 %. The biggest flexural strength after 28 days was found in the cement paste without the addition CEM (8.01 MPa). Pastes CH20\_10 and CH36\_10 with chalcedonite powder in the amount of 10 % had the highest 28-days flexural strength among others modified pastes. It was noticed that increasing the amount of addition caused a decrease in flexural strength. On the other hand, the influence of grain size is not so clear. After 28 days, the flexural strength of the pastes containing chalcedonite powder was lower by 7÷29 % than paste CEM. The biggest increase in flexural strength over time was achieved by the pastes with chalcedonite powder CHP36. Pastes with CHP20 and CHP36 powder were characterized by similar results, comparing the amount of these material. Pastes CH20 and CH36 with 10 % and 20 % chalcedonite waste had higher flexural strength than samples CH10. The difference was only visible in the case of the paste CHP10\_30. Paste with chalcedonite CHP10 in the amount of 30 % (CH10\_30) had close 28-days flexural strength to paste CH20\_30 and CH36\_30.

The compressive strength of the cement paste without addition after 3 and 28 days of curing was equal to 13.14 MPa and 22.02 MPa. The samples CH10\_10 and CH20\_10 were characterized by the biggest compressive strength after 3 days equal to 15.28 MPa and 15.00 MPa. On the other hand, the use of CHP20 chalcedonite powder in the amount of 10 % (CH20\_10) resulted in an increase in compressive strength compared to the base cement paste (CEM) both after 3 and 28 days. Similarly to the flexural strength research, the bigger the amount of addition within one type of grain size, the smaller the compressive strength. After 28 days, the compressive strength of the pastes containing chalcedonite powder was lower by maximum 34 % than base cement paste without addition. The greatest increase in compressive strength over

time was recorded for pastes containing CHP20 and CHP36. The most optimal solution, from the 28-days compressive strength point of view, seemed to be the use of CHP20 and CHP36 chalcidonite powder in the amount of 10 % (22.90 MPa, 21.02 MPa).

Taking into account calorimetric measurements and the 3-day compressive strength results, it can be seen that both increasing the amount of addition and increasing the specific surface area resulted in a decrease in the accumulated heat and a decrease in compressive strength compared to the reference sample. Only in the case of pastes containing 10% addition there was an increase in compressive strength observed, which may be due to the sealing of the material structure resulting from the addition of chalcidonite powder.

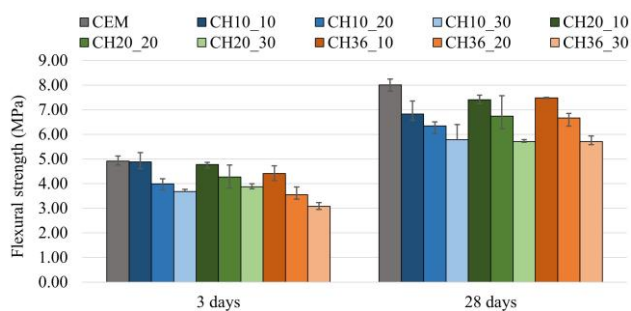


FIGURE 9. Results of flexural strength for all tested pastes

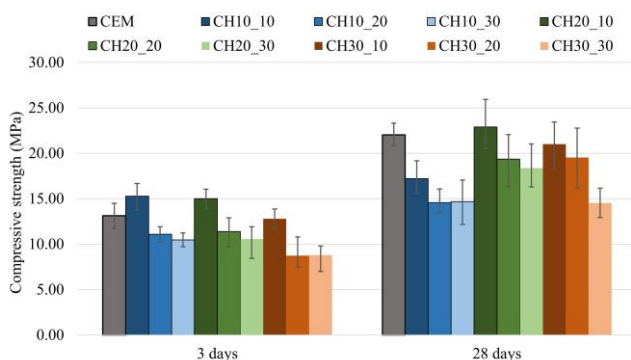


FIGURE 10. Results of compressive strength for all tested pastes

### 3.5. DTA-TG results

The thermogravimetric results were carried out for the series of CEM paste and all pastes CH10, CH20 and CH36. Data showing amount of chemically bound water  $H_2O$ , portlandite  $Ca(OH)_2$  and calcium carbonate  $CaCO_3$  was plotted in Figure 11. When analyzing the changes in the pastes over 28 days, an increase in chemically bound water and portlandite was noticeable for each of the pastes. On the other hand, the calcium carbonate content decreased over time. It can be seen that with the passage of time the amount of chemical bound water was increasing, which corresponded to a larger amount of C-S-H phase. These results reflected well with the results obtained from the mechanical properties research, especially with compressive strength. The portlandite content in the reference sample CEM I was increasing as the hydration time progresses (from 13.90 % to 17.48 %). The differences in the amount of  $Ca(OH)_2$  after

3 days of curing between the reference sample CEM and the other pastes might be due to the reduced amount of Portland clinker. The amount of portlandite with the addition of chalcidonite powder was increasing between days 3 and 28, but it wasn't as large as in the case of cement paste without the waste powder. Analyzing the obtained results, it can be seen that the increase in the amount of the addition had a bigger impact on the change of amount of portlandite than on the change in the amount of chemically bound water. Replacing some of the cement with an addition resulted in a reduction in portlandite. The greater the amount of chalcidonite powder, the lower the amount of  $Ca(OH)_2$ . The effect of grain size is not as noticeable as the effect of the amount of addition in terms of changes in the amount of chemically bound water and portlandite.

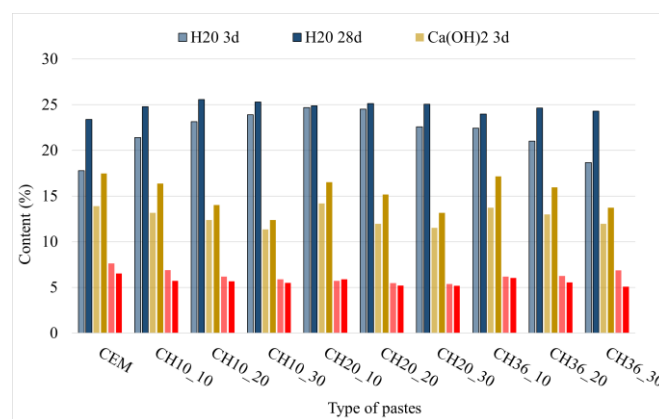


FIGURE 11. Results of DTA/TG analysis

#### 4. CONCLUSIONS

This article shows an original research to the assessment of selected properties of cement pastes modified with dust of chalcidonite powder. The variable factors in the studies were the quantity and grain size of the addition. The focus was on rheological studies and the processes of setting and hardening of pastes. These properties as important to selecting cement for a specific application.

As shown, the amount of the chalcidonite powder and its grain size influence both the rheological properties and the hydration kinetics as well as hardening processes after a longer curing time.

1. The amount and grain size of chalcidonite powder influenced the consistency of the tested pastes. The larger the amount of addition and the smaller its grain size, the smaller the flow of the paste. 10 % replacement of cement with an addition regardless of grain size had the least impact on the change in consistency. Further increase in the amount of chalcidonite powder caused a decrease in the flow. In practical application, obtaining the consistency of the grout modified with chalcidonite powder similar to the consistency of the cement grout without the additive would be possible if a plasticizing admixture was used.

2. Yield stress and consistency coefficient of the cement paste without addition are similar throughout the entire measurement period. Adding chalcidonite powder to cement and its grain size significantly effect on the rheology of the tested pastes. An increase in the amount of chalcidonite powder causes an increase in consistency coefficient. This parameter increases within an hour of the measurement. An increase in the amount of chalcidonite powder added and an increase in grain size causes an initial increase in the yield stress, which decreases after measurements taken after 30 and 60 minutes, which is most noticeable for pastes with chalcidonite powder CHP20 and CHP36.

3. In the case of the tested pastes, the amount of heat released decreases with increasing amounts of mineral addition. This effect is also visible with decreasing grain size of the chalcidonite powder. The total heat of hydration in the case of pastes containing chalcidonite powder is lower than in the base paste (without the addition).

4. Taking into account the compressive strength results after 3 and 28 days of curing, it seems most advantageous to replace cement in the amount of 10 % with chalcidonite powder with a grain size of 20  $\mu\text{m}$  or 36  $\mu\text{m}$ , what was consistent with research results of DTA/TG. It is planned to carry out long-term tests (determining mechanical properties after at least 90 days) in order to check the puzzolan activity of the addition after a longer maturation period.

Chalcidonite powder can be an alternative to commonly used addition in cement production, reducing carbon footprint of binders. The choice of an addition should be preceded by a thorough analysis of the properties of the obtained materials. It would be justified to adjust the appropriate cement-chalcidonite powder proportions to the appropriate applications of this binder in construction, taking into account both rheological properties and the evaluation of the setting and hardening processes.

Further research is planned to be conducted in which chalcidonite powder will be used as a binder component in mortars (masonry or plastering). It will be important to select, among other things, the appropriate amount and grain size of chalcidonite powder in order to obtain optimal standard properties (consistency, compressive strength, adhesion) and application properties.

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