



Phase development of lime-based plasters blended with waste calcined shale

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Abstract

Restoration of historical buildings requires an application of suitable and convenient materials which are compatible with historical legacy. On the other hand, the used materials have to show adequate durability and fulfil current tendencies of environmental-friendliness policy. Most historical buildings have their facades made of lime-based, or more precisely, blended-lime-based plasters. Metakaolin belongs to one of the most common representatives of pozzolanic admixtures used in this field. It is an artificial product, which arises by the calcination of kaolinitic clay or claystone at temperatures of about 550–900 °C. Like every other production process, a remarkable amount of waste rises also in the case of metakaolin. This study is aimed at the utilization of this waste, specifically the waste calcined shale (WCS). It is composed of not properly burned particles with varying compositions. Contrary to metakaolin, it contains a lower amount of amorphous phase and a higher amount of kaolinite and mullite. WCS was used in the production of lime-based plasters with a dosage of up to 50%. During the hardening, the carbonation process takes place in combination with the pozzolanic reactions. It gives rise to a higher amount of amorphous structures, about 15% in the case of pure lime contrary to up to 45% (in the highest dosage of WCS) and other crystal phases such as calcium-aluminate-carbonate hydrates. Obtained phase analyses are supported by the determination of SEM analysis and mechanical properties, which are also measured depending on time.

Keywords Lime-based plasters · Waste calcined shale · Thermal analysis · Phase development · Mechanical properties

Introduction

Historic buildings are the great pride of any city. Every visitor loves to gaze at a beautifully preserved piece of history that will transport them back in time, at least for a while. Nevertheless, to preserve this cultural heritage, it needs to be reconstructed in a proper and gentle way. The first element that everyone sees is the plaster of the building. However, plaster has not only a decorative function but also a protective one. It is in direct contact with the outside environment, with all the vagaries of the weather, and protects the main structure of the building from them. Due to the lack of original drawings, it is often very difficult to identify the original plaster material and choose an adequate replacement.

Another problem is the fact that, due to more advanced technologies, today's lime in plaster has completely different properties from the lime of the past. The hardening product of this lime is calcium carbonate, which easily breaks down when exposed to acid exhaust gases [1] and thus is much more susceptible to impurities in the surrounding air. It also causes lower strength than hydraulic and pozzolanic hardening products. Scientists in the 1920s found that the strength of such plaster could be improved by adding Portland cement. However, cultural heritage authorities do not agree with this method. One reason for this may be that it is not the material that was originally used in the plaster. The properties of such facades are also an issue. The adhesion of Portland cement-based plasters is insufficient, their thermal conductivity is usually higher and their open porosity is lower than that of lime-based plasters [2–5]. Therefore, it is necessary to investigate what admixtures could be added to the plasters and to find the most similar ones that preserve or even improve the properties of the reconstructed plasters with respect to the historical context.

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Since ancient Rome, pozzolanic materials have been used in construction practice. Such materials are able to react with calcium hydroxide and form hydration products similar to the hydration of cement (i.e. calcium–aluminum–silicate–hydrates C–A–S–H). They are usually of an aluminosilicate or calcium–aluminosilicate nature and historic examples of these materials were volcanic dust, tuff, or spongilite, which were used as admixtures in plasters [2, 4, 6]. Another pozzolanic material that was widely added to lime plasters was finely ground brick powder. Historic buildings with this type of facade can be found all over the world, in addition to Rome, in Turkey, India and Arab countries [7, 8]. Since such plasters solidified in water and proposed higher mechanical strengths, they were used for the construction of aqueducts, bridges, and baths and as a base for mosaics in ancient Rome [9, 10]. The properties of lime-brick mortars and plasters were also discussed in the eighteenth and nineteenth centuries in England and France by Loriot et al. [11]. In 1828, Vicat described three methods of firing clay minerals used to create artificial pozzolans [12]. There are many scientific papers dealing with the testing of lime plasters with metakaolin. These articles often focus on mechanical properties, as these are the most important in practice [5, 13–18]. Furthermore, fundamental hydric properties [4, 15, 16], thermal properties [4] and chloride binding [19–21] have been analysed. In the previous research performed by Vejmelková et al. [18], the properties of lime plaster, commercial plaster and plaster with added metakaolin and calcined shale were compared. Plasters with pozzolanic admixture had about 5% lower bulk density and 10% lower matrix density, and conversely 10% higher open porosity than pure lime plaster. The addition of metakaolin significantly improved compressive strength, which was 5.5 times higher than lime plaster. The compressive strength of plaster with alternative admixture surpassed even one the commercial plaster [22]. Another study showed that plasters with metakaolin and calcined shale had better mechanical properties than plasters with brick dust. The higher compressive and tensile strength is probably due to the formation of calcium silicate and calcium aluminate hydrates during the hardening process [23].

Every industry process gives rise to waste materials. A remarkable amount of waste rises also in the case of metakaolin and calcined shale production. This study is aimed at the utilization of such waste; specifically, the waste calcined shale (WCS) is studied. It is composed of not properly burned particles with varying compositions. Contrary to metakaolin, it has a lower amount of amorphous phase and contains a higher amount of kaolinite and mullite. WCS is not nearly as thoroughly studied, despite having promising properties close to those of metakaolin. Of course, another advantage of the WCS is that it is a waste material

that unnecessarily ends up in landfills, although it has great potential for further use in building materials.

This article is focused primarily on the phase development of lime-based plasters with up to 50% of WCS. In addition to phase development (investigated by XRD, DSC and SEM analysis), also basic physical and mechanical properties were determined in time up to 180 days.

Experimental

Characterization properties

Phase analysis was performed by XRD method using a PANalytical Aeris diffractometer equipped with a conventional X-ray tube (CoK α radiation, 40 kV, 30 mA, line focus). Determination of amorphous and not identified phases was done by utilization of internal standards; namely, ZnO was used. For the quantitative analysis of XRD patterns, HighScore and Profex software were used [24].

In order to investigate the transformation of amorphous structures in more detail, simultaneous thermal analysis (STA) consisting of differential scanning calorimetry (DSC) and thermogravimetry (TG) measurements was carried out using a LABSYS EVO DTA/DSC device (SETARAM Inc.). The heating rate was 5 °C min⁻¹ in an argon atmosphere with a flow rate of 40 mL min⁻¹.

Structural changes were also observed using a scanning electron microscope (SEM). Microscopic images were taken with a Phenom XL electron microscope desktop device equipped with a BSE detector and CeB6 source. The voltage was set at 15 kV, and the magnification was from 500 \times to 1000 \times . The sample was placed on a double-sided carbon tape glued on an aluminium substrate. A thin layer of gold was sputtered onto the sample before it was placed in the microscope.

For the assessment of the WCS pozzolanic activity, isothermal calorimetry was employed. The used device was the TAM Air calorimeter (TA Instruments), where three sets of experiments were measured: 75% of used lime Ca(OH)₂ was mixed with 25% of either WCS, conventional metakaolin or fine silica sand. Used w/b ratio was 0.3 and for accelerating the pozzolana reaction temperature was set to 40 °C.

Physical properties

Bulk density was measured using the gravimetric method. Specifically, specimens for further investigation of mechanical properties were primarily measured and weighted, and then, the bulk density was counted.

Compressive strength and bending strength were determined according to the standards [25] on the same beams. Three prismatic samples with dimensions of

160×40×40 mm were produced. The bending strength was measured using an MTS 100 loading device. The arrangement of the measurement was a three-point bending test with a span length of 100 mm. The resulting fragments of the original beams were then inserted into the EU40 loading device between two 40×40 mm steel plates, and the compressive strength was measured on them. After the destructive experiments, fragments of the specimens were gathered, and their matrix density was determined by a helium pycnometer. Namely, the device Pycnomatic ATC from Thermo Fisher Scientific Inc was used. Finally, the value of porosity was counted from known bulk density and matrix density.

Studied materials

Studied materials were primarily characterized, their chemical composition is presented in Table 1, the particle size distribution curves of fine components can be found in Fig. 1, while Fig. 2 proposes the results of STA.

For the production of the tested plasters, lime hydrate CL 90-S, produced by LB Cemix, s.r.o (Czech Republic), was chosen as a reference binder. This product is prepared by firing pure limestone (min. 97.5% of CaCO_3), which is subsequently crushed and hydrated to reach the required

parameters. From the mineralogical point of view, used lime contained 85% of Portlandite and 14% amorphous and not identified phases. Only a trace amount of calcite (1%) was identified.

Waste calcined shale (WCS) was used as a pozzolanic substitute. Shale is a fine-grained, clastic sedimentary rock composed of clay minerals and other tiny fragments such as quartz and calcite. By its calcination, artificially created pozzolana-like metakaolin can be produced. Shale is fired in rotary kilns at a temperature of 500–750 °C and then ground into a fine powder (D_{50} —12.5 μm) [26]. However, as with all production, also in the case of shale calcination, some waste material is generated. Namely, it is imperfectly burned powder, which contains a higher amount of raw phases (e.g. kaolinite) as well as over-burned components (such as mullite). Imperfectly burnt shale or let's say waste calcined shale is unnecessarily discarded, even though it still has very good pozzolanic properties. In this research, WCS from company České lupkové závody a.s. was used. From the chemical point of view, it was aluminium silicates. Regarding the phases, it contained 30% kaolinite, 11% mullite, 10% mica and 40% amorphous phase. A low amount of quartz, illite and orthoclase was identified as well. Compared to lime, its particle size distribution is slightly finer and narrower, which proposes a good opportunity for lime substitution.

Table 1 Composition of raw materials

Materials	CaO	Al ₂ O ₃	MgO	SiO ₂	Fe ₂ O ₃	TiO ₂	K ₂ O	SO ₃
Lime hydrate (L)	94.43	3.04	1.65	0.50	0.16	0.01	–	–
Waste calcined shale (WCS)	0.90	41.04	1.08	49.58	2.76	2.38	1.03	0.81

Fig. 1 Granulometry of lime and waste calcined shale (WCS). (Color figure online)

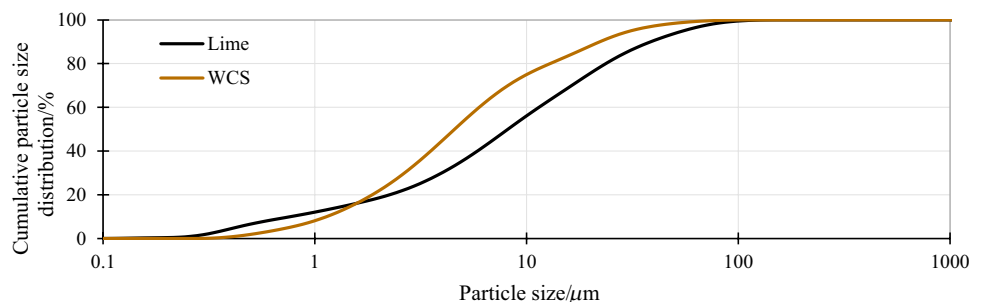


Fig. 2 STA of lime and waste calcined shale (WCS). (Color figure online)

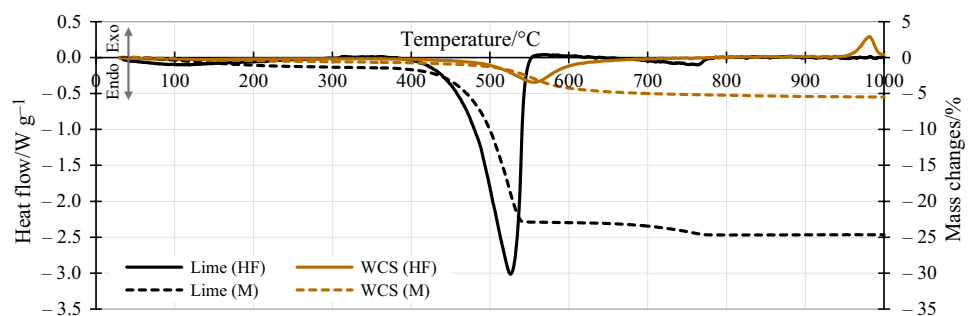


Fig. 3 Isothermal calorimetry—assessment of WCS pozzolanic activity. (Color figure online)

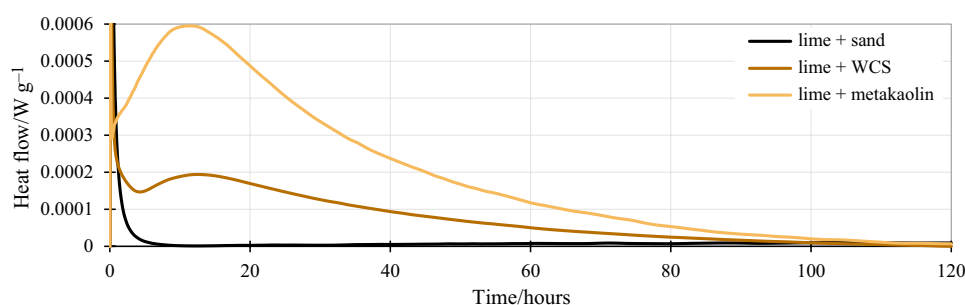


Table 2 Compositions of lime-based pastes

Mixture	WCS dosage	Lime/kg	WCS/kg	Water/L
HP-R	0%	3.750	–	3.45
HP-S-10	10%	3.375	0.375	3.38
HP-S-20	20%	3.000	0.750	3.25
HP-S-30	30%	2.625	1.125	2.98
HP-S-50	50%	1.875	1.875	2.75

Because the main idea of this paper was to use WCS as a pozzolana admixture in lime-based plasters, it seemed to be essential to assess the pozzolanic activity of the waste. Due to the higher kaolinite content, conventional methods (such as the Frattini test or lime-saturation test) could lead to misleading information as clay minerals in their nature have high ionic exchange capacity, meaning they can fix Ca^{2+} themselves [27]. On that account, isothermal calorimetry was used to measure the reaction heat evolved during the pozzolanic reaction of the WCS with lime and based on its value assessed pozzolanic activity. Measure heat flows are delineated in Fig. 3. It is visible, that in the case of lime with nonreactive silica sand, only the first peak attributed to the wetting and dissolving heat was observed. Contrary, in the case of lime with WCS, the ongoing pozzolanic reaction was proved due to the presence of the second peak. The counted value of reaction heat was 31.2 J g^{-1} . In accordance with the mentioned lower reactivity of WCS, the reaction peak was in the case of conventional metakaolin remarkably higher, as well as the reaction heat, which reached 84.1 J g^{-1} .

For the need of this study, two sets of mixtures were produced. The first one was used for the evaluation of the phase development of blended plasters (namely XRD, STA and SEM analysis), and the composition is summarized in Table 2. This set contained only lime, WS and water. The lime was continuously replaced by waste calcined shale in a ratio of 10–50%. The composition of the second set is presented in Table 3; these samples were used for the measurement of the physical properties of designed plasters. In this case, three gradings of silica sand were employed, specifically ST 03/08, ST 06/12 and ST 10/40 from Sklopísek Střeleč, a.s. were used. Regarding the water dosage, it

Table 3 Compositions of lime-based plasters

Mixture	WCS dosage	Lime/kg	WCS/kg	Aggregate/kg	Water/L
HP-R	0%	3.750	–	11.250	3.94
HP-S-10	10%	3.375	0.375	11.250	3.56
HP-S-20	20%	3.000	0.750	11.250	3.14
HP-S-30	30%	2.625	1.125	11.250	2.90
HP-S-50	50%	1.875	1.875	11.250	2.55

was regulated in order to achieve equal consistency of the designed mixtures; the desired value was the flow of 160/160 of the fresh blend (Fig. 4a). The more pozzolanic WCS mixtures contained, the less water had to be added to reach the latter goal. The samples (Fig. 4b) were produced, cured and examined in a climate-controlled laboratory with an air temperature of 19–21 °C and relative humidity of 50%. The experiments were carried in the age of 7, 28, 90 and 180 days (Fig. 4c).

Results and discussion

XRD analysis

The summary of phase analysis measured with the help of XRD is summarized in Fig. 5. Pure lime at the age of 7 days showed only a low carbonation degree, as it still contained a substantial amount of Portlandite $\text{Ca}(\text{OH})_2$. Over time this phase was continuously disappearing, while the amount of calcite CaCO_3 increased substantially. It can be noted that the rate of Portlandite decrease at the age of 28 days was somehow lowered afterwards. This can be attributed especially to the lower humidity of plaster together with lower concentration of CO_2 . The decrease in CO_2 presence is caused by a decreasing permeability of the matrix (decreasing porosity), which consequently causes a lower penetration of air CO_2 into the system [28]. On the other hand, the crystallization of calcite CaCO_3 is more fluent.

The replacement of lime by WCS significantly modified the composition of the studied plasters. This is caused by the pozzolanic reaction, which was ongoing simultaneously

with the carbonation. These reactions gave rise to calcium-aluminate-carbonate-hydrates (CA \hat{C} H), strätlingite and especially to the rise of amorphous phases. These should be composed of so-called calcium-aluminium-silicate-hydrates (CASH) or calcium-silicate-hydrates (CSH). Not surprisingly, the higher content of WCS was used, the higher content of hydrated phases was observed. Regarding the other components, unreacted phases of WSA are presented in the unvarying amount; specifically, kaolinite, mullite and mica are observed in a similar quantity during the time.

In order to assess the ratio between the carbonation and pozzolanic reaction, Fig. 6 is delineated considering the amount of Portlandite. These calculations covered several steps. Firstly, the mass of Portlandite in the fresh mixture

was calculated from the known content of this phase in the lime, the ratio of raw materials and the amount of water adopted from the STA (specifically, from TG summarized in Fig. 8). Afterwards, the amount of Portlandite which was necessary for the crystallization of Calcite (amount based on XRD) was counted employing the known chemical reaction of the carbonation. From this value, the carbonation degree was determined as the ratio of carbonated Portlandite to its mass in the fresh mixture. Afterwards, the amount of Portlandite acting in the pozzolanic reaction was counted as a difference between the original amount in the fresh mixture and the sum of carbonated Portlandite and the one remaining in the phase composition obtained by XRD. Again, the Pozzolana reaction degree was related to its original dosage

Fig. 4 Studied materials: **a** measurement of consistency (flow), **b** prepared samples, **c** measurement of bending strength. (Color figure online)

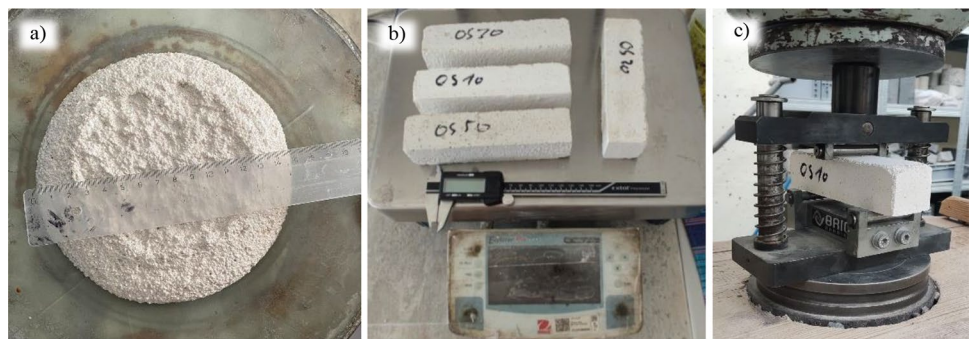


Fig. 5 Phase composition of pastes measured by XRD. (Color figure online)

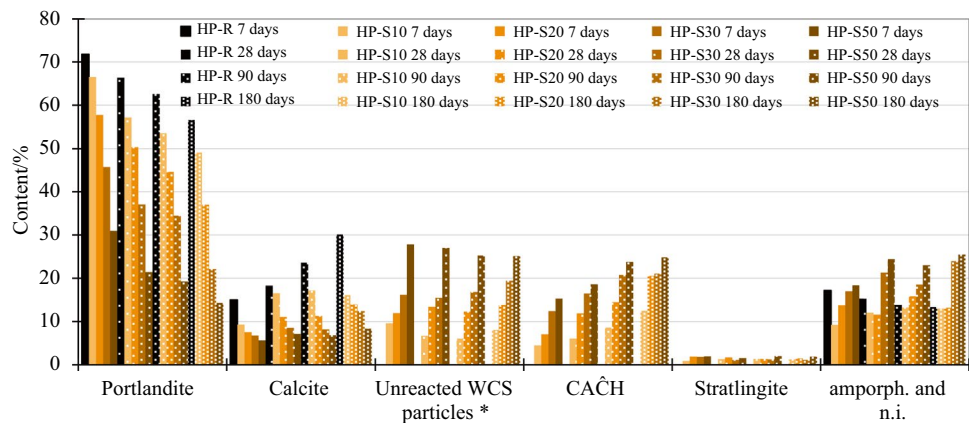
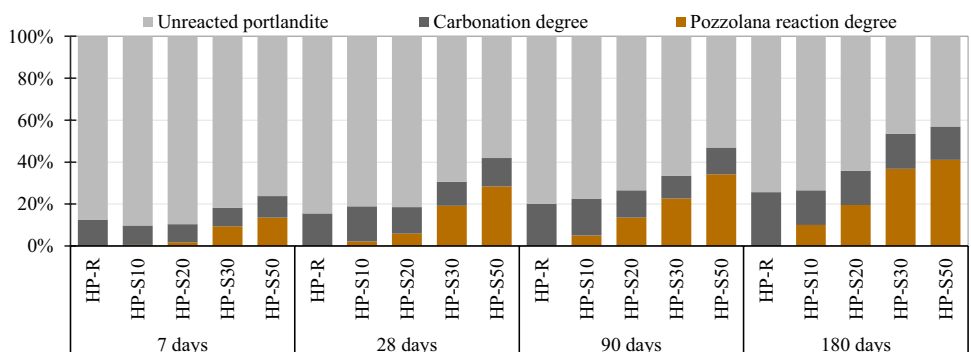


Fig. 6 Reactions equilibrium based on Portlandite consumption. (Color figure online)



in the fresh mixture. Despite the simplification of reaction kinetics, the results proved that in accordance with the raw-material dosage, the higher the content of WCS, the stronger the pozzolanic reaction was. Nevertheless, from Fig. 6, it can be seen that the carbonation is somehow slowed down when pozzolana is used. The carbonation rate of the reference plaster was always significantly higher compared to blended plasters. At a lower percentage of WCS (up to 20%), the pozzolanic reaction was only marginal and it gave importance after a longer time (more than 90 days). Contrary, the higher percentage of WCS caused a significant pozzolanic reactivity, and these reactions were distinctively dominant during the time. It could be assumed that the pozzolanic reaction would be finished in a shorter time because of a depletion of free water. However, according to the results, it still continued. This can be explained by ongoing carbonization, where a noticeable amount of water is released. Moreover, due to the substantial amount of unreacted Portlandite, it can be assumed that both reactions will further continue up to the depletion of reactive pozzolana.

STA analysis

Results of DSC are summarized in Fig. 7, while the content of particular components derived from the TG are presented in Fig. 8. For the determination of mass changes (for water, and recalculated for Portlandite and calcite content), the tangential approach was used. When focused firstly on the reference plaster HP-R (Fig. 7a), it showed a common performance. The first peak at 7 days at about 90 °C can be attributed to the free water content. It is visible that this peak disappeared at further ages, as the water evaporated. After 180 days of curing the water content decreased by 44% compared to the data at 7 days. The biggest peak at the temperature range from 400 to 570 °C corresponded to the Portlandite $\text{Ca}(\text{OH})_2$ decomposition. Again, its heights continuously decreased. This time it was caused by the carbonation of this mineral. After 180 days the content fell down by 21% compared to 7 days. The last distinctive peak from about 600 to 880 °C was attributed to the CaCO_3 (concerning the results of XRD in Fig. 5 probably in the form of calcite). The rise of this phase in time was indisputable; its content grew by 76% during that time.

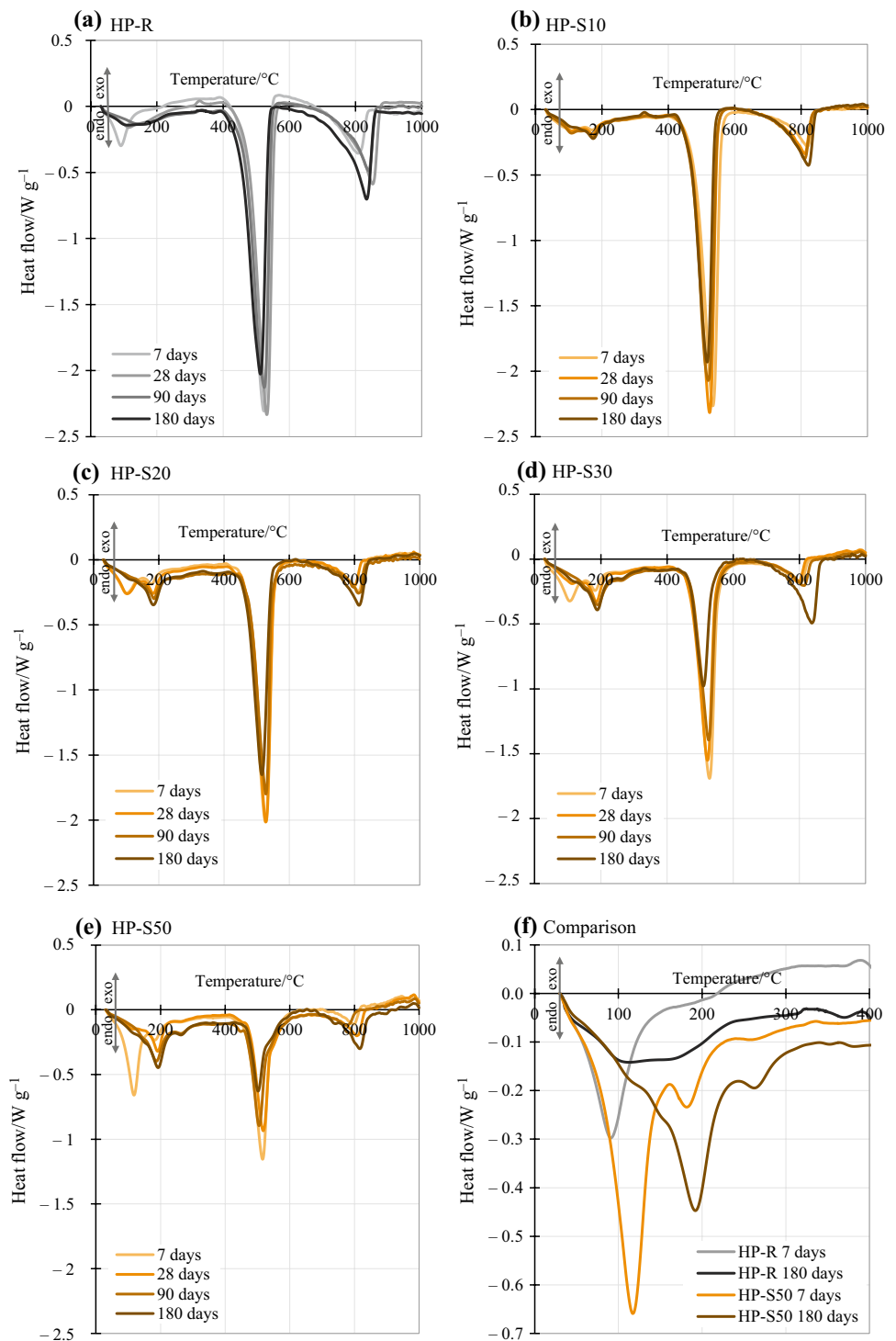
WCS caused the modification of STA curves primarily in the lower temperatures, as the hydration products usually decompose up to about 400 °C. Naturally, the higher content of WCS was used, the more altered curves were observed. For better comparison, in Fig. 7f), there is delineated the difference between the reference plaster HP-R and HP-S50, the one with the highest percentage of WCS. Both materials showed at the age of 7 days the first significant peak at 90 °C HP-R and 117 °C for HP-S50 which corresponded with free water content. Afterwards, the distinctive difference

between the two binders can be observed. Pure lime plaster did not show any noticeable peaks. Contrarily, the curve of blended plaster with WCS was remarkably lower; thus, the endothermic reactions were more profound in this case. This can be attributed to the amorphous CSH or CASH, which dehydrates in this wider temperature range. Moreover, there were two remarkable peaks observed for HP-S50. At the temperature of about 190 °C, there is a significant peak which can be attributed to the crystal phase of calcium-aluminate-carbonate-hydrates $\text{CA}\ddot{\text{C}}\text{H}$ [29]. In accordance with XRD analysis (Fig. 5), its magnitude rose with the WCS content as well as over time. The second one at 268 °C was relatively small at the age of 7 days, but after 180 days, it became clearly recognizable. When concerning the decomposition temperature of phases identified by XRD (Fig. 5), this peak can signify the Strätlingite C_2ASH_8 dehydration [30]. The overall water content in plasters derived from TG can be found in Fig. 8. Contrary to pure lime the amounts of water in the case of blended plasters went significantly up during the time; for the plaster HP-S50 even by 34%. It was caused by the ongoing pozzolanic reaction. When focused on the further performance at higher temperatures, the peak of Portlandite decomposition was the most distinctive in all cases of studied plasters. Nevertheless, as the ratio of WCS utilization grew, the intensity of this peak became lower. In the case of HP-S50 with the highest replacement level, this peak was visibly modified by another reaction. This was caused by kaolinite decarboxylation which takes place at a temperature range of 530–630 °C [31]. Because of this permeation of peaks corresponding to Portlandite and Kaolinite decomposition the values of Portlandite content for HP-S50 are not covered in Fig. 8. The last peak denoting calcite CaCO_3 decomposition was again observed in all cases of studied plasters. It can be summarized that its intensity decreased with the WCS replacement level and increased over time.

SEM analysis

Images of the reference pure lime plasters (HP-R) and the blended plaster with 50% of WCS (HP-S50) are shown in Figs. 9 and 10, respectively. There are always four images: two at the age of 7 days and two after 180 days. For the lower magnification (1000×) samples were embedded in an epoxy resin. This was done in order to be able to observe the overall structure of the plaster including higher water content. Both plasters performed similarly; at the age of 7 days, there is a significant amount of water, while at the age of 180 days, there is visible primarily the crystal structure. When comparing particular plasters, the blended plaster with WCS (HP-S50) showed a more heterogeneous composition. Especially at the age of 7 days, there were observed marginal differences between the structure of the studied plasters. The

Fig. 7 DSC of studied pastes: **a** HP-R, **b** HP-S10, **c** HP-S20, **d** HP-S30, **e** HP-S50, **f** comparison. (Color figure online)



blended plaster HP-S50 contained a higher amount of fine-grained crystals.

Regarding the particular components, they were observed at higher magnification ($5000\times$). Because it was aimed at phase analysis, samples were dried in the oven for 24 h at $50\text{ }^{\circ}\text{C}$. The identification of phases was done with the help of spectral analysis and the known morphology of observed

crystals. At the age of 7 days, the structure of the reference plaster contained primarily $\text{Ca}(\text{OH})_2$, but also carbonation products CaCO_3 were observed. On the other hand, after 180 days, the carbonation product CaCO_3 became dominant, and the structure seemed to be less porous. When focused on blended plaster HP-S50, the first noticeable difference is the presence of spherical aluminosilicate. They originated in

Fig. 8 Content of particular phases based on the TG changes. (Color figure online)

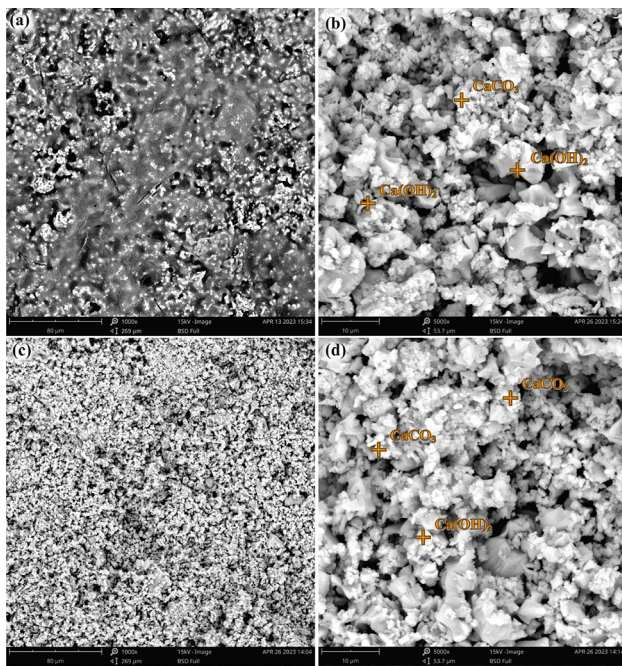
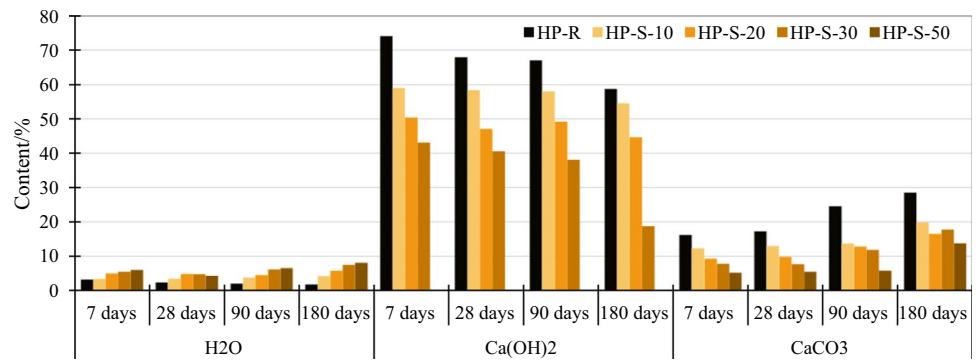


Fig. 9 SEM images of reference lime paste HP-R: **a** at 7 days—magnification 1000 \times , **b** at 7 days—magnification 5000 \times , **c** at 180 days—magnification 1000 \times , **d** at 180 days—magnification 5000 \times . (Color figure online)

WCS, specifically, they had been created during the calcination of claystone [31]. These remained unchanged during the time, but after 180 days they were slightly covered by other created products. CaCO_3 , Ca(OH)_2 and C-A-S-H were identified with the help of spectral analysis. From that point of view, it seems that the amorphous phases were composed mainly of C-A-S-H as no C-S-H was identified.

Physical properties

In Table 4, there are summarized results of the bulk density and the matrix density of studied plasters in time up to 180 days. It can be seen that the bulk density increased with the amount of pozzolanic admixture. The difference between

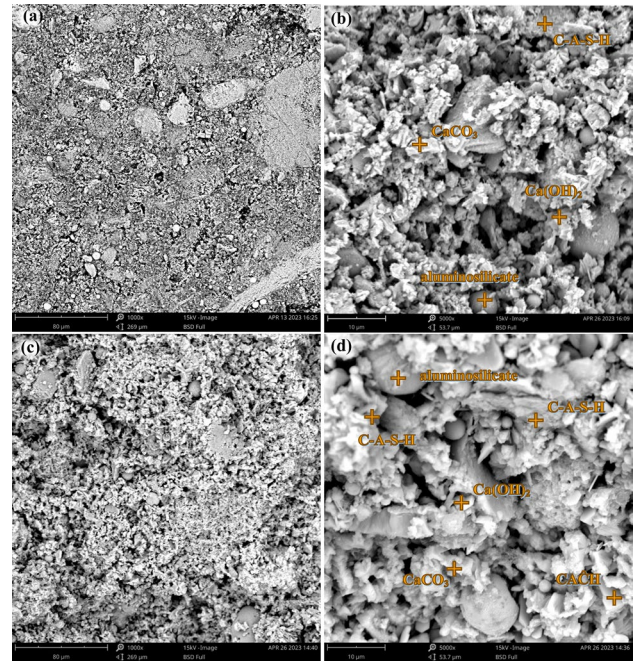


Fig. 10 SEM images of blended plaster HP-S50 with 50% of CSW: **a** at 7 days—magnification 1000 \times , **b** at 7 days—magnification 5000 \times , **c** at 180 days—magnification 1000 \times , **d** at 180 days—magnification 5000 \times . (Color figure online)

the reference sample and the one with 50% of pozzolanic substitution was 12–22%. Also in time, the bulk densities went up. The highest difference was observed in the case of the reference plasters HP-R, whose value increased by 15% (comparing 7 and 180 days). Contrary, plasters with WCS showed slower growth, as the values went up only by about 5–7%.

Regarding the matrix densities, the pure lime plaster reached relatively higher values. When lime was replaced by a low amount of WCS it caused its significant drop (by 4–9% for HP-S10), while with increasing pozzolana content, the values of matrix density went continuously up (up to max increase by 5% for HP-S50). In terms of time, the matrix density grew in all cases of studied plasters. The

Table 4 Basic physical properties of studied plasters

Plaster	Bulk density/kg m ⁻³				Matrix density/kg m ⁻³			
	7 days	28 days	90 days	180 days	7 days	28 days	90 days	180 days
HP-R	1457 ± 58	1544 ± 63	1604 ± 49	1673 ± 38	2302 ± 32	2382 ± 23	2454 ± 18	2537 ± 67
HP-S10	1668 ± 61	1695 ± 73	1757 ± 57	1790 ± 44	2207 ± 49	2249 ± 51	2309 ± 43	2319 ± 45
HP-S20	1736 ± 56	1743 ± 64	1769 ± 59	1822 ± 48	2312 ± 54	2328 ± 57	2335 ± 42	2392 ± 51
HP-S30	1747 ± 71	1773 ± 75	1807 ± 63	1867 ± 58	2358 ± 21	2396 ± 63	2401 ± 60	2467 ± 35
HP-S50	1777 ± 68	1787 ± 63	1813 ± 52	1875 ± 54	2416 ± 32	2425 ± 69	2434 ± 62	2506 ± 28

Fig. 11 Porosity of studied plasters. (Color figure online)

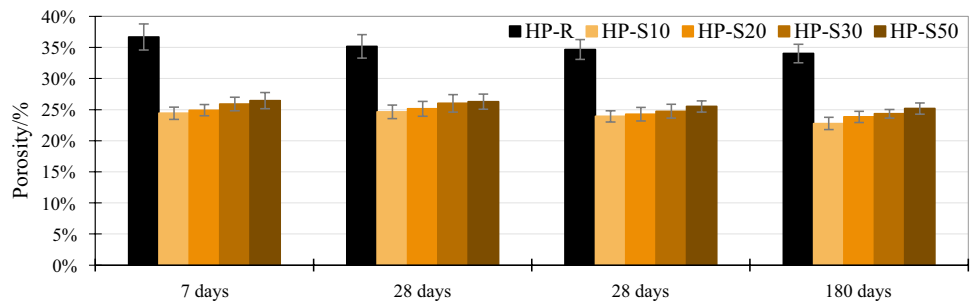
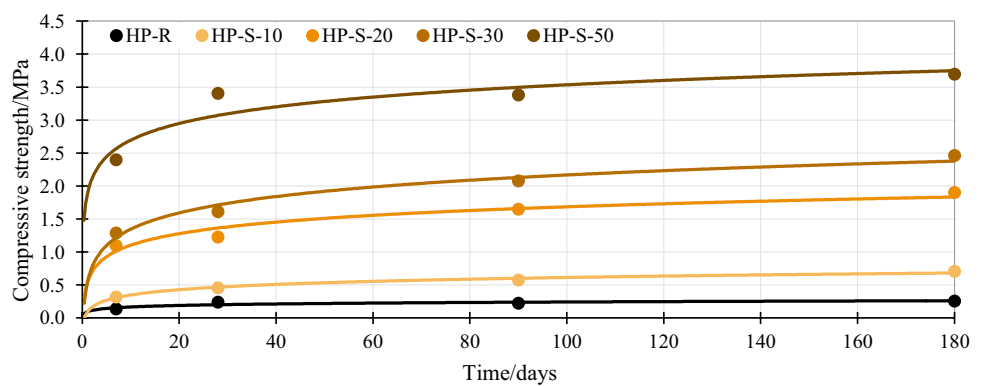


Table 5 Mechanical strengths of studied plasters

Plaster	Compressive strength/MPa				Bending strength/MPa			
	7 days	28 days	90 days	180 days	7 days	28 days	90 days	180 days
HP-R	0.14 ± 0.01	0.24 ± 0.01	0.22 ± 0.02	0.26 ± 0.01	0.17 ± 0.08	0.26 ± 0.06	0.20 ± 0.03	0.32 ± 0.04
HP-S10	0.32 ± 0.02	0.46 ± 0.04	0.57 ± 0.04	0.71 ± 0.04	0.18 ± 0.07	0.30 ± 0.06	0.40 ± 0.05	0.44 ± 0.06
HP-S20	1.09 ± 0.07	1.23 ± 0.06	1.65 ± 0.08	1.90 ± 0.09	0.27 ± 0.07	0.51 ± 0.03	0.71 ± 0.04	0.94 ± 0.03
HP-S30	1.29 ± 0.06	1.61 ± 0.07	2.08 ± 0.09	2.46 ± 0.30	0.36 ± 0.08	0.62 ± 0.04	0.97 ± 0.05	1.04 ± 0.04
HP-S50	2.40 ± 0.10	3.41 ± 0.13	3.38 ± 0.16	3.70 ± 0.11	0.75 ± 0.04	1.14 ± 0.07	1.29 ± 0.02	1.25 ± 0.03

Fig. 12 Development of compressive strength in time. (Color figure online)



biggest growth was observed in the case of the reference plaster HP-R, whose values went up by 10%, while for the blended plasters with WCS, the increase was in the range of 3–5%. This can be explained primarily by the ongoing

carbonation when the denser calcite CaCO₃ (specific gravity 2.71 g cm⁻³) was formed from Portlandite Ca(OH)₂ (specific gravity 2.23 g cm⁻³).

The results of porosity are summarized in Fig. 11. This time, the application of WCS caused a distinctive decrease in all cases. Blended plasters showed on average about 29% lower porosity than the reference lime plaster. This can be attributed to two aspects. Firstly, the particles of WCS were slightly finer (Fig. 1.) and thus can fill or complement the inter-grains space. The second reason can be found in the pozzolanic reaction, which gave rise to other products filling the pores. Over time, the porosity of plasters went down. A slightly higher decrease was observed in the case of the pure lime plaster HP-R, namely by 7%, while in the case of blended plaster, the fall was within the range of 4–7%.

In Table 5, it can be seen at a glance that the addition of the WCS led to a significant increase in mechanical strength. Due to the additional pozzolanic reaction, which led to the filling pores by further reaction products, all mixtures with the alternative admixture achieved significantly higher strengths than the reference plaster HP-R. It is very positive that even the mixture with the highest proportion of pozzolanic admixture achieved the highest compressive strength, and despite the 50% replacement level, the WCS did not overdose. Quite the opposite, this mixture reached the best performance. The compressive strength of HP-50 showed almost 18 times higher already after 7 days. In the case of bending strength, the improvement was not so huge, but also this property was remarkably increased; specifically by three times compared to the reference HP-R.

Regarding the development of mechanical properties in time, with the ongoing reactions (carbonation and pozzolana reactions), both compressive and bending strength increased with continuing time. But indisputably, the rate of mechanical strength increased during time slowed down. When measured data of the compressive strengths f_c were delineated depending on time t (Fig. 12), and considering the general rate equation more precisely its integrated form (1), the coefficient of compressive strength development k was determined as an identifier for strength rate development. In addition to the mathematical base of such an assumption, the logarithmic function seemed to be in suitable correlation with measured data. The results of these k values are summarized in Table 6 as well as the values of the initial or more precisely counted value of

compressive strength at one day f_{c0} . It is visible that the pozzolana additive has a significant impact on the rate of strength development, as the k values went up by an order of magnitude.

$$\frac{df_c}{dt} = \frac{k}{t} \rightarrow f_c = f_{c0} + k \cdot \ln(t) \quad (1)$$

Conclusions

This paper was aimed at the study of the phase development of lime-based plasters. As the alternative pozzolana admixture, waste calcined shale was used. Shale is a sedimentary rock composed of clay minerals, and it is used for the production of materials alike metakaolin. Waste calcined shale is arising during production, and despite its somewhat worse composition, further application seemed to be possible. Raw materials, hydrated lime and WCS were primarily characterized, and afterwards, blended binders with a replacement level of up to 50% were designed. For the phase development, the lime-WCS-based pastes were produced, and XRD, DSC and SEM analyses were performed. Thereupon, the blended plasters with lime-WCS binders were made and examined from the point of view of their basic physical and mechanical properties. As the aim of the presented study was the development of blended plasters in time, all characteristics were measured at different ages, specifically at the ages of 7, 28, 90 and 180 days. The main findings can be summarized as follows:

- Due to the pozzolanic reaction, the phase composition of the hardened binder was modified. Calcium-aluminate-carbonate-hydrates, strätlingite and amorphous calcium-aluminate-silicate-hydrates were formed.
- Pozzolanic reaction kept going also after 180 days. In the case of the highest replacement level at the latter time, 41% of the Portlandite underwent this hydration reaction, 16% belonged to the carbonation process, and the rest 43% remained still unreacted.
- Products of the pozzolanic reaction caused a significant fall in the porosity of blended plasters with WCS. However, over time the decrease in porosity, or more precisely the continuing filling of pores, was less profound compared to the reference pure lime plaster.
- Regarding the mechanical properties, the WCS application led to a distinctive improvement. Not only the values of the compressive strength and bending strength were substantially increased, but also the rate of their development was positively affected.

Table 6 Coefficients of compressive strength development

Plaster	Coefficient of compressive strength development $k/$ –	Initial compressive strength f_{c0}/MPa
HP-R	0.033	0.092
HP-S10	0.115	0.083
HP-S20	0.253	0.521
HP-S30	0.357	0.523
HP-S50	0.364	1.857

- Based on the presented observation, the plaster with 50% WCS was found to be the most promising for further application, and the utilization of studied waste material was proved to be not only possible but even beneficial.

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