Use of Zeolite Dust in Lime Mortars

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Summary

Fine grained waste zeolite in the form of a zeolite dust or a finely ground zeolite can be used as an active pozzolanic admixture to lime mortars. Lime mortars containing various content of fine grained zeolite were prepared and tested. Development of compressive strength, shrinkage and weight loss of lime mortars stored in different conditions was then evaluated. X ray powder diffraction of lime-zeolite pastes was also used to evaluate lime-pozzolan reaction. The results confirmed that fine grained zeolite can be usefully used as pozzolanic addition to lime mortars. Positive effect of pozzolan on the compressive strength of mortars is effective when mortars are stored in humid atmosphere where favorable conditions for lime-pozzolan reaction are. However, compressive strength of mortars stored in open air at RH 65% cannot fully develop and after some time it even decreases.

Keywords: Lime, zeolite, paste, mortar, compressive strength, relative humidity, carbonation

Introduction

Lime mortars are widely used in the conservation and repair of historic structures because historians accentuate the need to use materials and techniques that should be comparable with the properties and the appearance of the original structure (Maravelaki-Kalaitzaki et al., 2003; Makýš et al., 2006). However, properties of air lime mortars are not convenient for use in constructions that are in contact with water or moisture, the compressive strength gain of the mortars is slow due to slow process of carbonation and also their final strength is sometimes not sufficient. Therefore, use of mortars with hydraulic properties is often preferred. One possibility how to obtain hydraulic properties of lime is use of pozzolanic admixtures to air lime. In this paper we focus on study of zeolite as a possible admixture that is possessing pozzolanic properties.

Natural zeolites are crystalline, hydrated aluminosilicates with three-dimensional structure containing alkali and alkaline earth cations. Their structure allows dehydration, ion exchange and absorption of molecules of different sizes. There exist large number of zeolite minerals (about fifty) with slightly different structure and Si/Al ratio, where the clinoptilolite, mordenite, erionite and chabazite are probably the most frequently found. Natural zeolites can be generally found in rocks near active or extinct volcanoes. Zeolites can be used as mineral admixture for example in concrete where it can prevent bleeding and segregation, decrease permeability, improve durability and increase strength of concrete (Feng et al., 2005). Pozzolanic reaction of ground natural zeolites with variable Si/Al ratios was studied by Mertens et al., 2009. The authors mentioned that it is difficult to draw general conclusions or to predict the reactivity of a potential pozzolan. They found that finer grained zeolite yield higher short-term pozzolanic activity but they also found that cation content has an effect on both the long- and short-term reactivity. Also Jana, 2007 studied the use of zeolite in concrete. He found that zeolite only moderately improved strength at 10% addition and reduced strength at 20–30% addition to concrete. But he reported improvement in resistance to chloride permeability, alkali-silica reaction and sulfate attack.

Two different, combined and competitive chemical reactions are responsible for hardening of lime-pozzolan based binders (Cizer, 2009; Cizer et al., 2010). They are: a) lime-pozzolan reaction of calcium hydroxide with active silica or alumina of the pozzolan and water; b) carbonation reaction of calcium hydroxide. All types of chemical reactions affect pore structure and compressive strength of mortars.

Raw materials used

Test samples were made from material as follows:

a) Natural quartz sand (standard siliceous sand with continuous grading**,** CEN EN 196-1);
b) Hydrated calcium lime powder (non/hydraulic dry hydrated lime EN 459-1 CL90-S);
c) Ground natural zeolite from pure zeolite deposits produced by ZEOCEM, a.s. Bystré, Slovakia. The product designated as ZEOCEM Micro 50 contains prevailingly particles with size up to 50 μm with the median size of about 10 μm.

Main mineral is clinoptilolite. Effective pore diameter in the zeolite rock is 0.4 nm, volume of hollow spaces of the rock varies from 24 to 32%. (Note: In next the research we intend to use waste zeolite dust, e.g. ZeoBau Grit).

Chemical composition of used materials is given in Table 1.

Experimental methods

Mortars made from lime (M1) and lime-zeolite mixtures (MZ2; UZ 50; MZ3) together with a paste (Z/L=50/50) composed from equal content of lime and zeolite were prepared. Composition of prepared mixtures is given in Table 2. (Composition of mortars MZ2 and UZ 50 was almost identical with only a slight difference in water content, and also the lime used was from different producers. All mortars were prepared with about the same consistency – which was determined by a flow table test method. Cylindrical test specimens with diameter and length of 30 mm were then prepared in cylindrical molds. Test specimens were demoulded after 4 days and stored for extra 2 days in a chamber with humid atmosphere at RH = 95–100%. Prepared mortar specimens were then divided into three groups and each was cured/stored in different conditions:

I. Specimens of the first group were left to harden in an open air in a chamber with RH about 65%; where carbonation of mortars by CO_2 from the air could take place.
II. Specimens of the second group were stored in enclosed chambers at RH 95-100% - without access of CO_2 from the air. These mortars thus could not carbonate.
III. These specimens were originally stored for 3 months at RH 95–100% and subsequently they were stored in an open air with RH 65% and access of CO_2 from air.

For shrinkage testing the prisms were prepared from mortars with size of 40x40x160 mm. Test prisms were fitted with glass contacts at their ends.

Samples from a lime-pozzolan paste (Z/L=50/50) were prepared in the shape of small thin slabs with thickness of 15 mm. The samples were then stored in two types of environment: I.) – in an open air at RH 65% – where the paste could dry and carbonate; and II.) - in a closed box at RH 95–100%.

Compressive strength, shrinkage and weight

Table 1. Chemical composition of zeolite and hydrated lime (in wt. %)

Tabela 1. Skład chemiczny zeolitu i wapna hydratyzowanego

	SiO_2	Al_2O_3	Fe_2O_3 (total)	CaO	MgO	TiO_2	K_2O	Na_2O	SO_3	Ignit. loss	CO_2
Zeolite Micro-50	70.2	12.4	1.52	3.28	0.62	0.19	3.46	0.63	0.03	7.45	0.02
Hydrated lime CL90-S (1)	2.00	0.82	0.32	70.4	1.63	–	0.31	0.03	0.17	24.2	3.28

Table 2. Average mineralogical composition of the ground zeolite given by the producer

Tabela 2. Średni skład mineralogiczny proszku zeolitowego podany przez producenta

Mineral type	Content [%]
Clinoptilolite	84
Cristobalite	8
Feldspar (plagioclase)	3–4
Clayish mica	4
Quartz	traces

Table 3. Composition of mortars and pastes and consistency of fresh mortars determined by flow table test

Tabela 3. Skład zapraw i past oraz konsystencja świeżych zapraw określona przez test płynięcia

Sample type	Mixture designation	Zeolite admixture		Lime CL90-S	Sand	Water	Water/Lime	Water/Binder(1)	Flow value
			[g]	[g]	[g]	[ml]	[–]	[–]	[mm]
Mortar	M1	None	0	350[a]	1350	320	0.91	0.91	152
Mortar	MZ2	Micro-50	175	175[a]	1350	334	1.91	0.95	156
Mortar	UZ50	Micro-50	175	175[b]	1350	320	1.83	0.91	152
Mortar	MZ3	Micro-50	350	350[a]	1350	530	1.51	0.76	150
Paste	Z/L=50/50	Micro-50	150	150	–	250	1.67	0.83	–

1) “Binder” – here a mixture composed of lime and zeolite

changes were determined in the predetermined time on mortar specimens. Chosen samples of raw materials, mortars and pastes were analyzed by X-ray diffraction (XRD) using D2 PHASER diffractometer (Bruker) equipped with Cu anode. Hydration of moist samples for XRD analysis was stopped by ethylalkohol and subsequently the samples were dried at 40^0C; dry samples were analyzed without drying.

Results and discussion

Compressive strengths development of mortars stored under different conditions are given in Figures 1 and 2. Figure 1 shows that compressive strength of mortars MZ2 and MZ3 containing lime-zeolite binder continuously increased during their storage in the humid atmosphere (at RH 100%). Compressive strengths values of the mortars were 6.9 MPa and 8.6 MPa after 28 days. After 550 days the strengths of the mortars reached 8.8 MPa and 9.6 MPa, respectively. However, compressive strengths of mortars that were stored at RH 65% with the access of air were lower. At these storing conditions the mortars obtained maximum compressive strengths values during the first 28 days (3.3 MPa and 6.7 MPa) – but these compressive strength values were lower than those of mortars stored at RH 100%. In later time period the compressive strength values decreased and then remained at almost constant values of about 2.6 MPa and 4.7 MPa for MZ2 and MZ3 mortars.

Results shown in Figure 1 also confirmed that lime mortar M1 did not harden in humid atmosphere (RH 100%) without access of carbon dioxide from air. Compressive strength of mortar M1 after 28 days of storing at RH 65% was also relatively low – but it continued rising during the first year due to carbonation. After 1 year the compressive strength of this mortar reached 2.9 MPa, which was even a higher value than that of lime-pozzolan mortar MZ2-65 with compressive strength of about 2.6 MPa. Mortars M1-65 of this age carbonated through their entire volume.

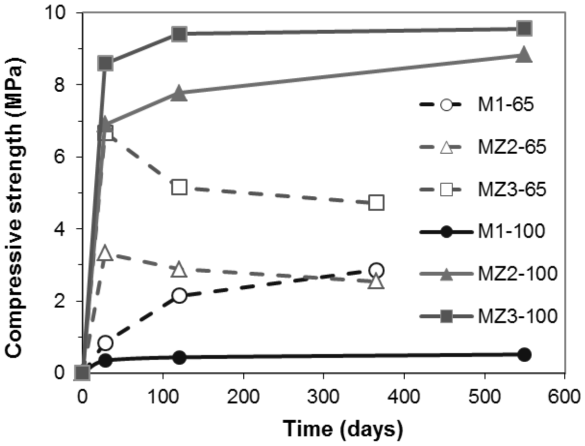

Fig. 1. Compressive strength of mortars M1, MZ2 and MZ3 stored at RH 100% and RH 65%

Rys. 1. Wytrzymałość na ściskanie zapraw M1, MZ2 i MZ3 przechowywanych w wilgotności względnej 100% i 60%

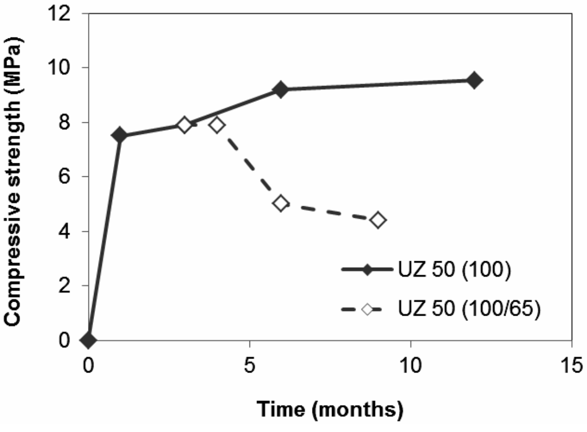

Fig. 2. Compressive strength of mortars UZ 50 stored permanently at RH 100% and mortars stored first 3 moths ina humid atmosphere and then at RH 65%

Rys. 2. Wytrzymałość na ściskanie zapraw UZ 50 przechowywanych stale w wilgotności względnej 100% i zapraw przechowywanych przez pierwsze 3 miesiące w wilgotnej atmosferze, a następnie w wilgotności względnej 65%

Results in Figure 2 again show a continuous rise of compressive strength of lime-pozzolan mortar UZ 50 during storage in wet conditions (RH 100%), but as soon as the storing conditions changed and humidity dropped to RH 65% with the access of air – the compressive strength began decline and then probably stabilize at much lower values.

We can conclude that pozzolanic reaction between calcium hydroxide and zeolite took place in wet mortars especially during the first 3 months of

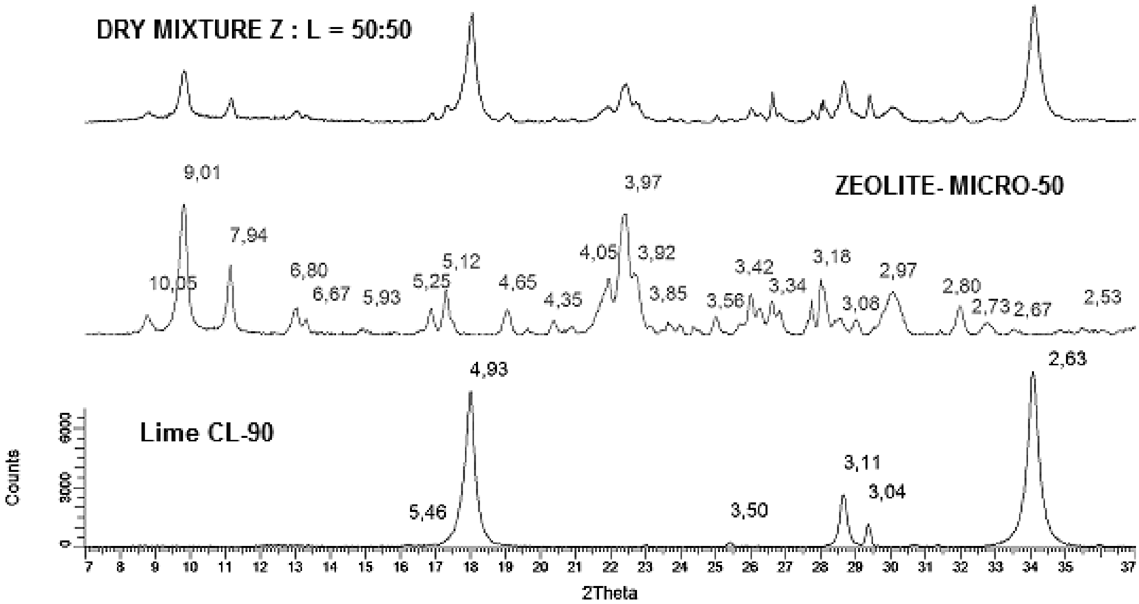

Fig. 3. X-ray diffraction patterns of raw materials (zeolite and lime) and also dry mixture of lime and zeolite in weight proportion 50 : 50)

Rys. 3. Wzory dyfrakcji promieniowania rentgenowskiego materiału surowego (zeolit i wapno) jak również suchej mieszanki wapna i zeolitu w proporcji 50:50

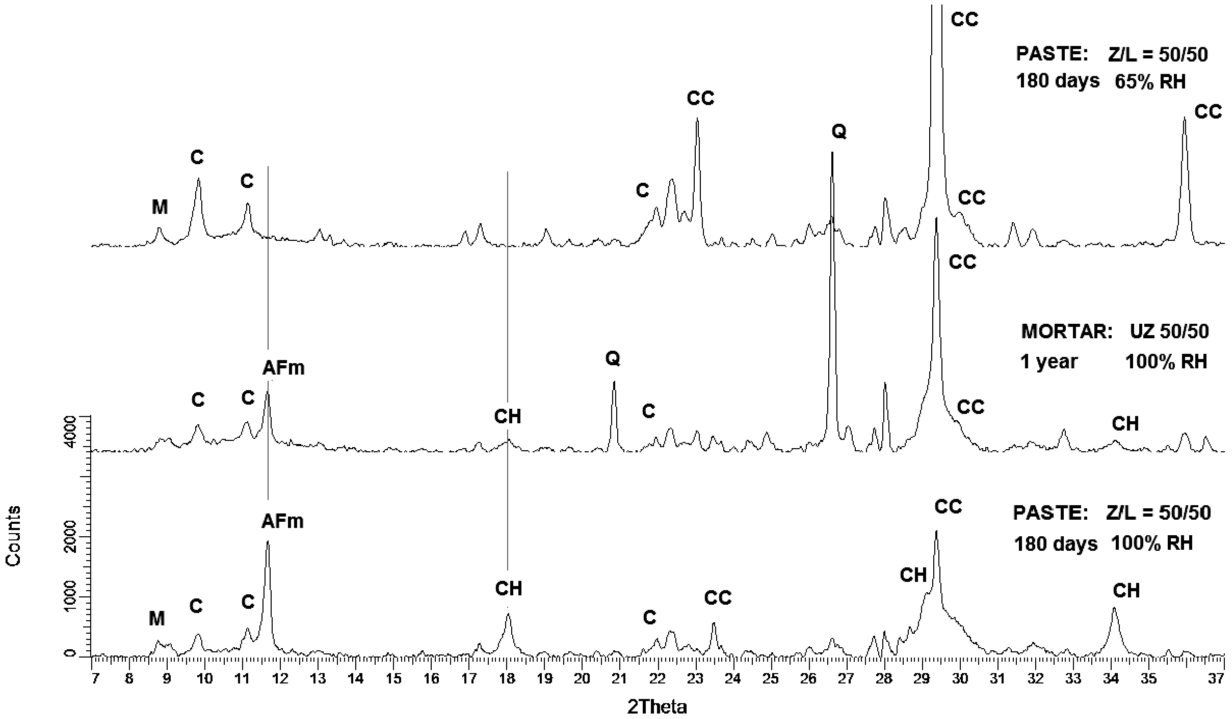

Fig. 4. X-ray diffraction patterns of lime-zeolite pastes and a mortar stored in different environment. (M-mica; C–clinoptilolite; Q-quartz; CC-calcite; AFm-phases – prevailingly $C_3A{\cdot}CaCO_3{\cdot}11H_2O$; CH – calcium hydroxide/portlandite)

Rys. 4. Wzory dyfrakcji promieniowania rentgenowskiego zapraw wapienno-zeolitowych oraz zapraw przechowywanych w różnych środowiskach. (M-mika; C-klinoptylolit; Q-kwarc; CC-kalcyt; Fazy AFm-dominacja $C_3A{\cdot}CaCO_3{\cdot}11H_2O$; CH-wodorotlenek wapnia/portlandyt) hardening. Results of XRD analyses of the lime-pozzolan paste Z/L=50/50 after 180 days of hardening at RH 100% showed significant content of unreacted portlandite (calcium hydroxide) left in the paste and presence of a new phase belonging to the AFm group (namely calcium carbolaluminate hydrate $3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}11H_2O$) – which was the result of pozzolanic reaction between calcium hydroxide and aluminates in the zeolite. Supposed presence of amorphous calcium silicate hydrates could not be detected by XRD method. Similar results were obtained by XRD analysis of a separated binder from mortar UZ 50/50 that was stored 1 year at RH 100%. In this case the amount of both mentioned phases – those of unreacted portlandite and AFm product - was lower.

On the other hand, the calcite content – indicating some carbonation of the mortar – was higher. However, results of XRD analyses of the lime-pozzolan paste Z/L=50/50 after 180 days of storage at RH 65% showed significant differences. Sample of this paste did not contain either portlandite or AFm phase; however there was a very strong peak corresponding to calcite. These results confirmed that storage of mortars at RH 65% conditions resulted in total carbonation of samples, where calcium aluminate phases could not develop, or the phases were decomposed by the action of CO_2 during carbonation.

Another factor that prevents lime-pozzolan reaction is drying of mortars. Figures 5 and 6 show shrinkage of lime-zeolite mortars stored at RH 65% after previous 3 months storage in humid atmosphere. It is obvious that the moist mortar rapidly loses water and shrinks after it is placed into RH 65% environment. The process is equilibrated in about 3 moths (prism samples).

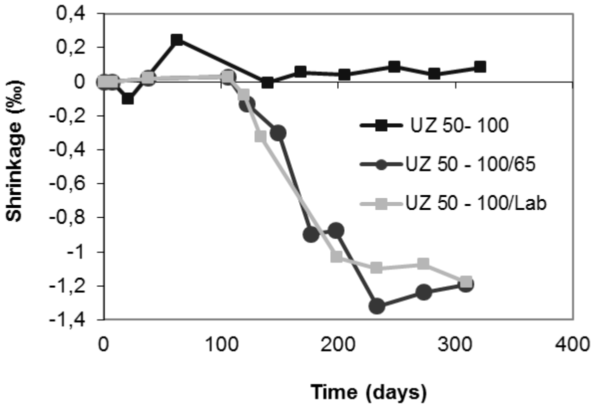

Fig. 5. Shrinkage of lime-zeolite mortars stored in different environments: (i) permanently at RH 100%; (ii) 3 moths at RH 100% and then at RH 65%; (iii) 3 moths at RH 100% and then in laboratory atmosphere

Rys. 5. Kurczenie się zapraw wapno-zeolit przechowywanych w różnych warunkach: (i) stale w wilgotności względnej 100%; (ii) 3 miesiące w wilgotności względnej 100% a następnie w 65%; (iii) 3 miesiące w wilgotności względnej 100%, a następnie w laboratorium

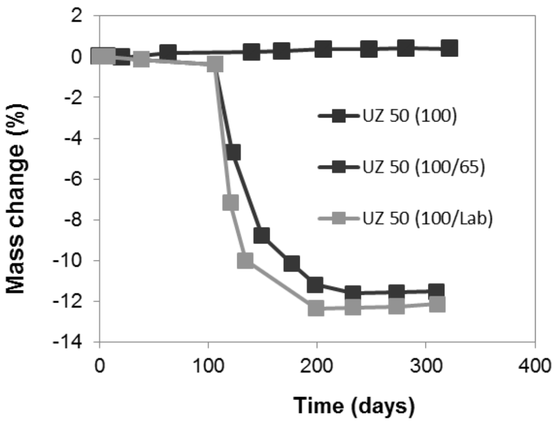

Fig. 6. Mass change of lime-zeolite mortars stored: (i) permanently at RH 100%; (ii) 3 moths at RH 100% and then at RH 65%; (iii) 3 moths at RH 100% and then in laboratory atmosphere

Rys. 6. Zmiana masy zaprawy wapno-zeolit: (i) stale przechowywanej w wilgotności względnej 100%; (ii) 3 miesiące w wilgotności względnej 100%, a następnie w 65%; (iii) 3 miesiące w wilgotności względnej 100%, a następnie w laboratorium

It can be therefore concluded that lime-zeolite mortars stored at RH 65% rapidly loose water and also carbonate. Processes, drying and carbonation limit process of lime-pozzolan reaction.

Conclusions

Properties of lime-pozzolan mortars can be very significantly affected by their storage conditions.

- Lime mortars containing zeolite obtained higher compressive strength than lime mortars in humid conditions. Compressive strength of lime-zeolite mortars continuously increased during their storage humid environment and after about 1 year it reached about 9 MPa. At these conditions pozzolanic reaction between lime and zeolite could take place. Process of lime-pozzolanic reaction was confirmed by XRD analysis. Lime mortars are not able to harden in humid conditions.
- Storing of lime-zeolite mortars at RH 65% in the presence of carbon dioxide from air resulted in lower final strength and the strength even started to decrease after 1 moth. Storing of mortars at these conditions is also accompanied by significant loss of mass due to drying and shrinkage of mortars. These results confirm that drying and carbonation prevents the course of lime-pozzolan reaction and it limits achievement of better properties of these mortars. However, these conditions are favorable for carbonation and hardening of lime mortars.
- Lime-zeolite mixtures cannot be effectively used without precise knowledge about their storage/use conditions. Mortars of this composition are not suitable for use in dry conditions. Their use at such conditions cannot be recommended. Their use in humid environment should be reconsidered.

Acknowledgements

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Wykorzystanie pyłu zeolitowego w zaprawach wapiennych

Drobnoziarnisty zeolit odpadowy w formie pyłu zeolitowego lub proszku zeolitowego może zostać użyty jako pucolanowa domieszka do zapraw wapiennych. Zaprawy wapienne zawierające różne ilości drobnoziarnistego zeolitu zostały przygotowane i przetestowane. Następnie określono wytrzymałość na ściskanie, kurczenie się oraz utrata masy zaprawy wapiennej składowanej w różnych warunkach. Widmo rentgenowskie proszkowe zostało również zastosowane w celu oznaczenia reakcji wapno-pucolana. Wyniki potwierdziły, że drobnoziarnisty zeolit może być z powodzeniem użyty jako pucolanowy dodatek do zaprawy wapiennej. Pozytywny efekt pucolanu na wytrzymałość na ściskanie jest skuteczny gdy zaprawa jest składowana w wilgotnej atmosferze gdzie występują dogodne warunki dla reakcji wapno-pucolana. Jednakże, wytrzymałość na ściskanie zaprawy wapiennej przetrzymywanej na otwartym powietrzu o wilgotności względnej 65% nie może się w pełni rozwinąć i po pewnym czasie wytrzymałość ta nawet maleje.

Słowa kluczowe: wapno, zeolit, zaprawa, naprężenia, wilgotność względna, uwęglenie