Possibilities of Utilization Zeolite in Concrete

M. Sedlmajer, J. Zach, J. Hroudová, P. Rovnaníková

***Abstract*—**There are several possibilities of reducing the required amount of cement in concrete production. Natural zeolite is one of the raw materials which can partly substitute Portland cement. The effort to reduce the amount of Portland cement used in concrete production is brings both economical as well as ecological benefits.

The paper presents the properties of concrete containing natural zeolite as an active admixture in the concrete which partly substitutes Portland cement. The properties discussed here bring information about the basic mechanical properties and frost resistance of concrete containing zeolite. The properties of concretes with the admixture of zeolite are compared with a reference concrete with no content of zeolite. The properties of the individual concretes are observed for 360 days.

***Keywords*—**Concrete, zeolite, compressive strength, modulus of elasticity, durability.

I. Introduction

CONCRETE is one of the most frequently used materials today and the idea of modern construction without its use is impossible. It brings many advantages but also certain restrictions. However, the positives outweigh the negatives. In terms of composition, the most demanding component in concrete is cement which has the highest manufacturing energy consumption and its production brings significant CO_2 emissions in global terms. Depending on the production technology, the CO_2 emission may range from 0.73 to 0.99 t of CO_2 for 1 t of cement [2]. For this reason there is an effort to reduce the need for Portland cement.

In cement production, many mineral raw materials are used which enter the concrete composition during cement manufacturing and are a part of composite cements. Their amount is limited in composite cements by definition in the EN 197-1 [1] for cements CEM II through CEM V. Alternative raw materials are also suitable for use in the design of concrete where they enter the production of concrete as reactive admixtures and their amount can be different from the content in composite concretes. One of the reasons for why their use is beneficial is the possible partial substitution of the energy-consuming and environmentally damaging cement. Next, these admixtures have a positive influence on the properties of hardened concretes, mainly when they are admixtures with latent hydraulic or pozzolanic properties which brings at the presence of $Ca(OH)_2$ the formation of hydration products similar to those produced during cement hydration. One of these materials can be zeolite which exhibits pozzolanic properties [3], [4]. These materials alter the properties of the resulting concrete.

Natural zeolites are microporous crystalline aluminosilicates composed of TO_4 tetrahedra (T = Si, Al) with oxygen atoms connecting neighbouring tetrahedra. They are products of the transformation of glass mainly of volcanic origin, x-ray amorphous clay, aluminosilicate gels, plagioclase, nepheline, biogeneous SiO_2 or clay minerals. The determining factors for the formation of the individual species of zeolite are temperature, pressure, reaction time and the Si/Al ratio, Ca^{2+}, Na^{+}, K^{+} and partial H_2O pressure. This general formula applies to natural zeolites

$$(Na,K,Li)_x(Ca,Mg,Ba,Sr)_y\left[Al(\rangle\rangle Fe)_{x+2y}\cdot Si_{n-x-2y}O_{2n}\right]\cdot mH_2O \qquad (1)$$

The increase in the Si/Al ratio brings a significant change in properties such as hydrothermal stability or hydrophobicity. Zeolites are therefore a large group occurring naturally but can also be synthesises. One of the natural zeolites is clinoptilolite which forms monoclinic platy crystals, has 10-membered and 8-membered rings connected by channels and its Si/Al ratio is higher than 2 and lower than 5. Clinoptilite is a zeolite of the heulandite group and is microcrystalline. This group has a high content of Si ions, is porous and, due to its layered structure, is very reactive [4]. The structure is such that it forms a microporous structure with cage-like formations (diameter less than 2 nm) joined into channels. The resulting empty spaces are filled with water molecules and metal cations which compensate the substitution of Si^{4+} for Al^{3+} in the structure.

The reactivity (pozzolanic activity) of zeolites with calcium hydroxide depends on the type of zeolite, its structure, specific surface area and the presence of secondary minerals. It is especially the large specific surface area open for reaction and the open structure of zeolites which contribute to the increased reactivity. Chemical composition of zeolites, i.e. Si/Al ratio and the content of exchangeable cations influence both short-term as well as long-term reactivity. Zeolites with an increasing Si/Al ratio exhibit a higher long-term pozzolanic activity and better mechanical properties compared with zeolites with lower silicon content. Zeolites containing alkali metals as exchangeable cations change the composition of the pore solution in a cement paste and increase the rate of the pozzolanic reaction in comparison with zeolites which contain Ca^{2+} as exchangeable cations [5].

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II. Test Mixtures and Production of Test Samples

The concept of the composition of the individual concrete mixes was based on a gradual increase in the substitution of Portland cement with natural zeolite. The observed properties of concretes with admixture of zeolite are compared with the reference concrete where only Portland cement is used. The concrete was designed as an aerated one with Portland cement (CEM I 42.5 R), three fractions of aggregate with maximum grain size 16 mm, aeration (SIKA LPS-V) and superplasticising admixture (SIKA Viscocrete 1035). The dosage of zeolite, which contained 45 % clinoptilolite and 35 % of amorphous phase, ranged from 7.5 % to 30 % of the mass of the cement. Table I shows the composition of the individual mixtures.

TABLE I
Mix Proportion of Concrete

		C	CZ7	CZ15	CZ22	CZ30
Zeolite	[%]	-	7.5	15	22.5	30
Zeolite	[kg/m^3]	-	29	58	88	117
Cement	[kg/m^3]	389	360	331	301	272
Water	[kg/m^3]	140	155	162	168	182
Plasticizer	[kg/m^3]	4	4	4	4	4
Air-entraining agent	[kg/m^3]	0.64	0.64	0.64	0.64	0.64
Aggregate 0/4 mm	[kg/m^3]	889	889	889	889	889
Aggregate 4/8 mm	[kg/m^3]	210	210	210	210	210
Aggregate 8/16 mm	[kg/m^3]	679	679	679	679	679

In order to ensure ideal conditions for the curing of the concrete, which has a dramatic effect on the final properties of concrete, the specimens made from the individual concretes were permanently submerged under water

The finely milled zeolite Zeobau 200, which was used in the production of the concretes being studied, is a clinoptilolite. The zeolite was subjected to the determination of specific surface area which was 1362 m^2/kg and density which was 2279 kg/m^3. Next, particle size distribution was determined using a laser analyser (Fig. 1). The figure shows the particle size distribution curve and a passing curve for the individual grades. The medium grain size d_{50} is 27.6 µm

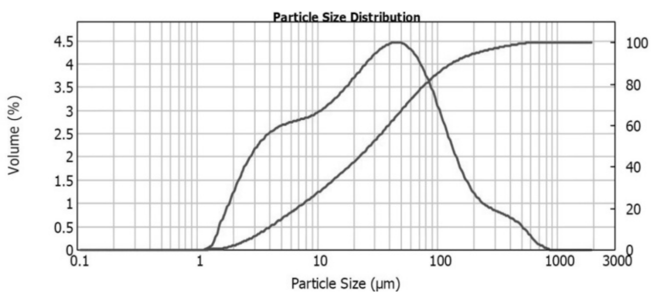

Fig. 1 Particle size distribution of zeolite

Fig. 2 captures a view of the structure of the zeolite taken by a scanning electron microscope. Table III shows its chemical composition.

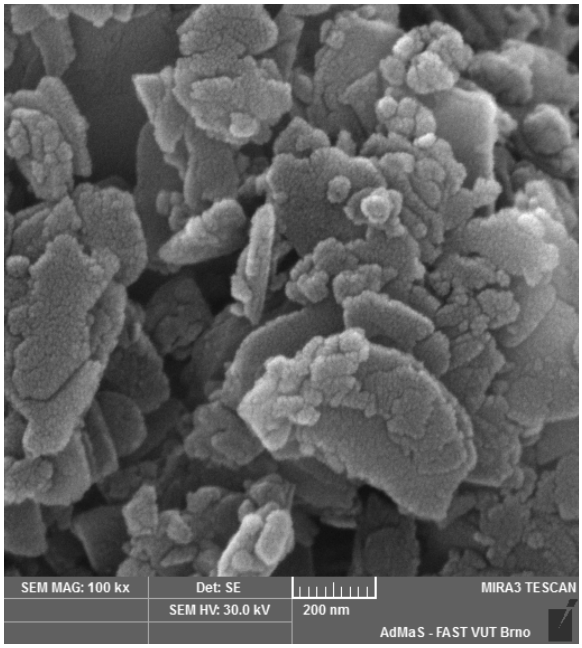

Fig. 2 A view of the structure of the zeolite

TABLE II
Mineralogical Composition of Zeolite

Mineral		Volume
Clinoptilolite	[%]	44.5
Mordenite	[%]	-
Silica	[%]	3.5
Cristobalite	[%]	9.2
Albite	[%]	2.6
Illit + mica	[%]	5.6
Orthoclase	[%]	-
Kaolinite	[%]	-
Sanidine	[%]	-
Amorphous phase	[%]	34.5

The consistency of fresh concrete was determined using the slump test [6] and the air content using the pressure method [7]. The air content in fresh concrete was between 4.1 and 6.4 % and is listed in Table III together with the slump test. Given the pore structure and the properties of zeolite, the dosage was increased together with increasing amount of zeolite in the concrete maintaining a constant amount of superplastifying admixture.

TABLE III
Properties of Concrete in Fresh State

Mixture	Air content [%]	Slump test [mm]
C	4.1	140
CZ7	4.5	140
CZ15	5.8	140
CZ22	5.6	100
CZ30	6.4	100

III. Results of Test Measurements

Compressive strength was tested on the hardened concrete [8] after 7, 28, 90 and 360 days of curing under water. The determination of compressive strength reveals the positive influence of zeolite which is clearly manifested after 90 and 360 days of curing. In the instance of the substitution of cement with zeolite in the 30 % dose, a significant increase of compressive strength after 28 and 90 days can be seen. It is therefore apparent that in case of zeolite, pozzolanic reaction is slower than the hydration reaction of Portland cement. A similar phenomenon is also known with other admixtures used in concrete, e.g. fly ash. As expected, the greatest strength after 28 days is exhibited by the reference concrete (62.4 (N/mm^2), where only Portland cement with no zeolite is used. After 90 days, the strength of the concrete with zeolite CZ7 admixture is higher than the strength of the reference sample. A greater substitution of cement with zeolite results in a minor decrease in strength after 90 days. Compressive strength values after 360 days increases as expected in all the concretes. Concretes with the maximum zeolite content approach the compressive strength of the reference concrete but only at a higher age. Therefore, should the mechanical properties of a concrete containing zeolite be compared with traditional concrete containing only Portland cement, it is advisable to do so at an age later than 28 days. This has been concluded from the observation of compressive strength during the period of 1 year.

The increase in strength over time is determined by the pozzolanic reaction where when $Ca(OH)_2$ is present, compounds are formed similar to those produced during the hydration of cement. This conclusion is shared by other authors also [11]-[13].

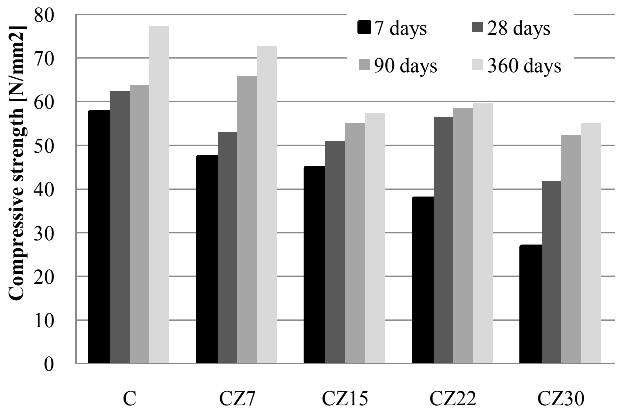

Fig. 3 Compressive strength after 7, 28, 90 and 360 days

The decrease in compressive strength with an increasing amount of zeolite is influenced also by the amount of water. The required amount of water in the mixture rises along with the increasing amount of zeolite. The decrease in compressive strength with an increasing dose of zeolite is indicated by the bulk density of the concretes since the bulk density drops with a greater amount of zeolite. The difference in bulk density of the reference concrete (C) compared to the concrete with 30 % of zeolite (CZ30) is around 150 kg/m^3.

Next, modulus of elasticity [9] after 28, 90 and 360 days was determined. Modulus of elasticity is defined as a ratio of change in stress and a corresponding change in flexural relative strain. As seen in Fig. 4, the modulus gradually increases as concrete ages. All the tested concretes saw an increase of modulus of elasticity over time. As the amount of zeolite in the concretes increased, modulus of elasticity decreased. This phenomenon was expected since modulus of elasticity corresponds to compressive strength.

Concrete CZ30, where 30% of Portland cement was substituted by zeolite, exceeded 30 000 N/mm^2 after 360 days. In comparison with the reference concrete, which had the highest modulus of elasticity after 360 days (40 000 N/mm^2), the difference is 25%. Concretes closest to the reference concrete is the one where 7.5% of Portland cement was substituted by zeolite, where modulus of elasticity was 38 kN/mm^2, and the one with 15% of zeolite where modulus of elasticity is 35 000 kN/mm^2.

Concerning the durability of the concrete against frost and chemicals, the hardened concrete was subjected to the test: Resistance of cement concrete surface to water and defrosting chemicals. It is a Czech testing standard [10]. The principle lies in the action of freeze-thaw cycles (1 cycle). The device cools the surface of the specimen from 20 °C to -15 °C for 45 – 50 min. The specimen must then be warmed up after the same time interval. The specimens are put in bowls inside the testing chamber of the device in which there is a solution of a thawing agent (3% solution of sodium chloride NaCl) and which contain the disintegrations from the test surfaces. The specimen must be submerged in 5 ± 1 mm standing upright. The resistance of the cement concrete surface to water and defrosting chemicals is determined by the mass of the flaked-off material to a unit of the surface area; the flakes are separated after every 25th cycle.

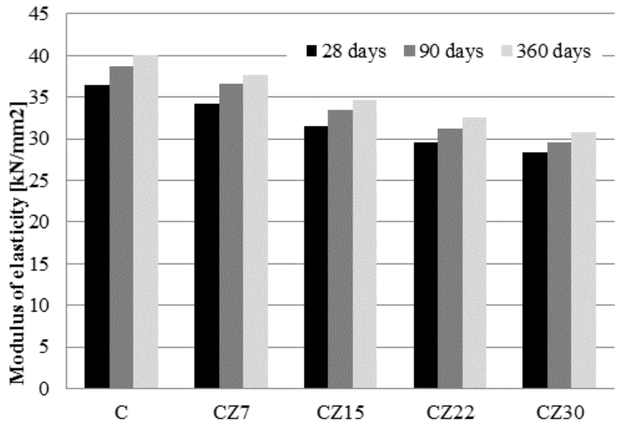

Fig. 4 Modulus of elasticity after 7, 28, 90 and 360 days

The results of the test of Resistance of cement concrete surface to water and defrosting chemicals are shown in Fig. 4. The flakes from the surface of the concrete specimens 150 x 150 mm are recalculated to the area of 1 m^2. In order for the concrete to qualify as satisfactory, maximum disintegration must be within 1000 g/ m^2 of the surface area of the concrete.

As can be seen, minimal flaking was seen in the reference concrete with no zeolite admixture. In concretes where zeolite was used as a substitute for Portland cement in the amount up to 22.5% the flaked-off material was 400 g/m^2. The concrete containing 30% of zeolite exhibited flaking of 940 g/m^2. This value is still lower than the maximum acceptable limit of 1000 g/m^2. It can therefore be stated that these concretes have performed satisfactorily in this test. Testing for resistance of the cement concrete surface to water and defrosting chemicals is aimed at assessing the suitability of a concrete for application in road structures and structures exposed during the winter season to temperatures below 0°C and which come in contact with thawing agents for removing ice and snow. These concretes can therefore be considered suitable for these purposes.

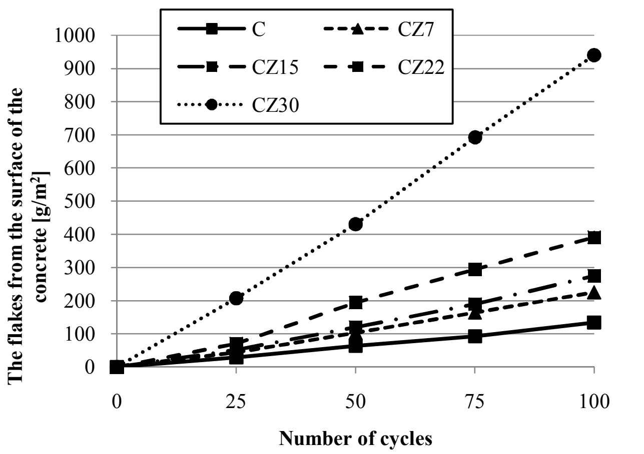

Fig. 5 Resistance of cement concrete surface to water and defrosting chemicals

IV. Conclusion

The paper lists some properties of concrete in which cement was substituted by a natural raw material, i.e. finely milled zeolite (clinoptilolite) with substitution of up to 30% of the mass of the cement. The use of zeolite in concrete as a partial cement substitute appears to be appropriate. Zeolite as a silicate material is entirely compatible with other concrete components. Given the structure of zeolite, one must bear in mind the need for a greater content of water in the mixture which is also visible in the composition of the concretes. If the composition of concrete with the original water content is kept, e.g. by a change or a greater amount of the plasticising agent, very good properties can be attained even at higher content of zeolite while decreasing the need of Portland cement. Worse mechanical properties with a higher portion of zeolite are believed to be due to the greater content of water in the mixtures. Another possible option could be to adapt the granulometry of the zeolite being used, especially as far as very fine grades are concerned. This step could lead to the reduction of the amount of water necessary in the concrete production.

When substituting cement with zeolite by up to 22%, after 90 and 360 days of curing compressive strength values were reached comparable to those of the concrete with Portland cement only. A smaller amount of Portland cement and the use of zeolite can thus result in similar properties as those of concretes with Portland cement only.

From this perspective, zeolite can be considered an active admixture which over time contributes to the formation of microstructure and to the improvement of required resulting properties of hardened concrete. For this reason, finely milled natural zeolite appears to be a suitable raw material in the production of concrete with which it is possible to partially substitute Portland cement.

Acknowledgment

This paper has been worked out under the project No. LO1408 "AdMaS UP - Advanced Materials, Structures and Technologies", supported by Ministry of Education, Youth and Sports under the „National Sustainability Programme I".

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