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A. Woszuk, J. Kukiełka, W. Franus [*]
Politechnika Lubelska, Wydział Budownictwa i Architektury
Katedra Dróg i Mostów,
[*]Katedra Geotechniki,

THE EFFECT OF ZEOLITE ADDITION AT A TEMPERATURE COMPACTION OF ASPHALT MIXES

The beginnings of warm mix asphalt are connected with the use of foamed asphalt in the ‘60s of the last century. Asphalt foaming occurs by contact with water or water steam that can be entered mechanically or under pressure. The foaming effect can be also obtained by the adding of zeolite to the asphalt mixture which causes the lower viscosity of the asphalt, better workability and adhesiveness of the mixture to the aggregate in lower temperatures. Presently, synthetic zeolites Aspha-Min and Advera are used for reducing the processing temperature. In this work, natural zeolite clinoptilolite (Sokirnica Mine, Ukraine) and synthetic zeolite Na-P1 were used as additives for the warm mix asphalt production. Investigation of the adsorbed water release in the function of time and temperature constituted the basis for estimating the amount of zeolite additive. It was assumed that the amount of released water with respect of asphalt should be 2,5%. The samples of asphalt with appropriate amount of zeolite were thickened in Marshall’s rammer in the temperatures of 140, 120 and 100 ^{0}C. The free spaces, modulus of elasticity in and water resistance were determined for each sample. Obtained results indicate that physico-mechanical properties of the samples with addition of zeolites were improved while the thickening temperature were reduced of 20 ^{0}C.

Key words: asphalt, zeolite, viscosity, workability, adhesiveness.

Перші згадки про теплі асфальтові суміші пов’язані з використанням спіненого асфальту в 60-ті роки минулого століття. Спінювання асфальту відбувається у разі контакту з водою або водяною парою, які можуть бути введені механічно або під тиском. Ефект спінювання можна також отримати додаванням цеоліту в асфальтові суміші, що зумовлює нижчу в'язкість асфальту, кращу легкоукладальність та адгезійну здатність суміші до заповнювачів за низьких температур. Нині синтетичні цеоліти Aspha-Min і Advera використовують для зниження температури обробки. Природний цеоліт – клиноптилоліт (Сокирницьке родовище, Україна) і синтетичний цеоліт Na-P1 у роботі використані як добавки для виробництва теплих асфальтових сумішей. Дослідження виділення адсорбованої води як функції часу і температури становлять основу для оцінки кількості добавки цеоліту. Передбачалося, що кількість видаленої води відносно асфальту має становити 2,5 %. Зразки асфальту з відповідною кількістю цеоліту ущільнено у приладі Маршалла за температури 140, 120 та 100 ^{0}C. Модуль еластичності та водонепроникність визначали для кожного зразка. Отримані результати показують, що фізико-механічні властивості зразків з добавкою цеоліту покращились, тоді як температура загущення знизилась на 20 ^{0}C.

Ключові слова: асфальт, в'язкість, легкоукладальність, адгезія.

Introduction

The production temperature of the traditional asphalt mixes (hot-mix) is 140–200°C, depending on the type of asphalt t[14]. A warm mix asphalt (WMA), also requires high temperatures to liquefy bitumen, surroundings of the aggregate, and to condense; however, it reduces the temperature of technological process by 20-40°C[17]. Thus energy consumption decreases, comfort and safety improve [15]. Furthermore, the lower temperature production also means slower ageing of the binding agent and better mixture workability.

Currently, there are over 20 known technologies that reduce the temperature of the production and compaction of asphalt mix [17]. The origins of WMA application was the use of foaming processesbitumen. The first attempts in this direction were carried out in 1956, in the USA [4].Asphal foaming occurs as a result of contact with water or steam which can be placed mechanically or under pressure. The foaming of the binder temporally increases its volume and lowers viscosity, which improves coating and workability of the mineral mix, but its duration is limited. Asphalt foaming effect can also be obtained by adding minerals from the group of zeolites.

Zeolites are mainly a group of skeletal aluminosilicates with various structure in which the voids are referred to as chambers and channels. In these voids, apart from the exchangeable cations, there are also specifically bound water molecules (so-called zeolite water). While heating this type of a mineral to a temperature of about 400^0C, zeolite water is brought from their structure continuously, without changing the shape of the crystals.

Such a specific internal structure associated with the porous structure of zeolites and water gives them a lot of physical and chemical characteristics that are extremely beneficial for all kinds of industrial applications [7, 6,20, 3]. The sizes of channels in zeolite fall within the range of from about 3 Å to 30 Å and are large enough for not only the individual atoms to diffuse and penetrate their interiors, but also for small molecule chemical compounds. Therefore, a group of these minerals can be called nanoporous materials .

Previous studies of asphalt mix with the addition of zeolite focused on two patented technologies: Aspha-Min and Advera. The use of zeolite in asphalt mix brings a number of technological, economical and environmental benefits. Synthetic zeolite in Aspha-Min technology comprises about 21% by weight of water, which is releasedin the temperature range 85-182°C. As a result of adding zeolite to the mineral mix simultaneously with the asphalt, the water collected in the pores of the zeolite begins to release. The process of zeolite water vaporization leads to the expansion of the binder volume, the effect of which is foamed bitumen and reduced viscosity. It facilitates better coatings of the bitumen on aggregates at lower temperatures [8]. This phenomenon continues for 2-3 hours, thus the effect of increased workability lasts during the production process, transport and the laying of the asphalt mix [5].

Added zeolite in the asphalt mix recipe replaces the filler and in research should be perceived , as a filler [10, 9, 21]. In technology Aspha-Min zeolite is dosed in an amount of 0.3 % by total weight of the mix [8,1]. Studies of viscosity with the addition of various zeolites indicate also the possibility of natural zeolite use [2] in the production of AC.

The use of zeolite in Aspha-Min technology allows for lowering the temperature to 30°C of AC production, which results in energy savings of 9 kWh per 1 mg of a produced mix. Temperature reduction of 10°C involves decreasing by half the emissions of fumes and aerosols [10]. In addition to the environmental benefits, the reduced emission of fumes and aerosols enhances the comfort of people employed in the production and incorporation of asphalt mix. Better working conditions reflect into higher productivity and quality of performed work. The production of WMA with the addition of zeolite also retains water and frost resistance [9]. The parameter which is slightly lower, after the addition of zeolite is resistance to permanent deformation [8, 9]. The use of modified asphalt significantly improves the results of rutting [9]. The addition of the zeolite improves also the compactibility of WMA compared to conventional mixtures for both of the samples taken in the vibratory compactor[8] and in the gyratory compactor[18]. Lower temperature also positively affects the ageing of the asphalt binder, which prevents resilience the layer of recycled materials (RAP). Research on the life cycle of asphalt pavement, WMA with the addition of zeolite, showed overall decrease in the extraction of aggregates, gas emission and energy consumption by 13-14 % after the addition of 15 % RAP [16].

Due to the fact that in the above described technologies, there is no information on detailed crystalline structure of the mineral zeolite selected for research, which has a direct effect on the properties of the zeolite, two types of zeolite were selected for survey in the present study: natural zeolite represented by the most commonly found in nature mineral of this group - clinoptilolite, and synthetic zeolite Na- P1 obtained on the basis of the synthetic reaction of fly ash [19]. The effect of various % additives of the above mentioned types of zeolite on the compactibility of asphalt mixes at different temperatures, for samples taken in Marshall's compactor and gyratory compactor, were tested. The optimum modifier additive was determined on the basis of the content of voids in relation to the reference asphalt mix. In order to verify the properties of WMA samples (with the addition of zeolite), made in Marshall compactor, the stiffness modulus was examined in Nottingham Asphalt Test (NAT) and their water resistance was specified.

Materials

Two types of zeolites were selected to tests. Mineral composition was determined by X-ray diffractometry (XRD). The first zeolite was represented by natural clinoptilolite, and the second by a synthetic zeolite Na-P1. Diffractograms of the mineral composition of the two materials are shown in Figure 1. The presence of zeolite phases was identified on the basis of its characteristic interplanar distance d_{hkl} for clinoptilolite peaks in = 8.95, 7.94, 3.96, 3.90 Å, and for Na-P1 (d_{hkl} = 7.10, 5.01; 4.10, 3.18 Å). The mineral composition of the clinoptilolite material was completed by small amounts of opal CT, quartz and potassium feldspars. In the case of synthetic material, it includes mullite, quartz and unreacted aluminosilicate enamel sections. In both cases, the content of zeolite phases was about 80% vol.

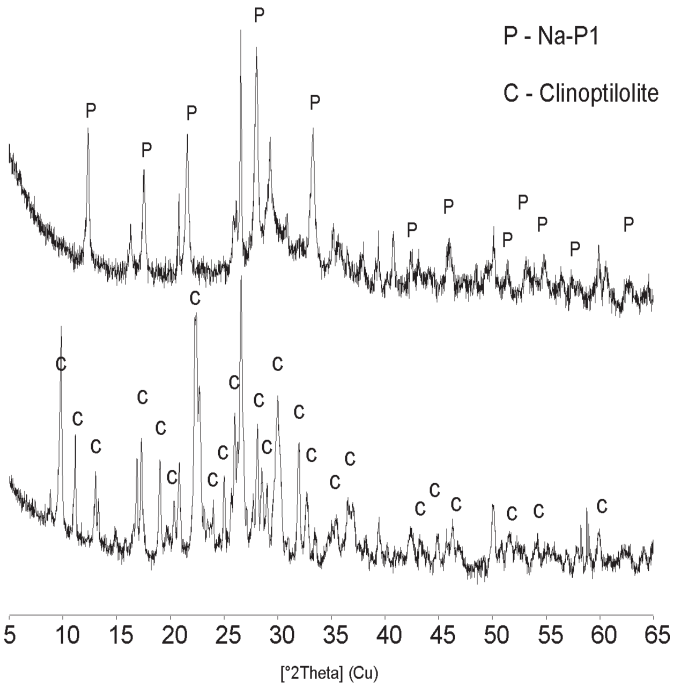

Fig. 1. XRD patterns of mineral composition of zeolite materials

Morphologically clinoptilolite is in the form of tiles with sizes of 20-30 microns, occasionally in a scanning electron microscope SEM, their hexagonal shape is visible(Fig. 2A). In contrast, zeolite type Na-P1 forms lamellar aggregates with sizes ranging from 1 to 3 microns. (Fig 2B).

The chemical composition of the tested zeolites determined by means of XRF is presented in Table 1. All tested zeolites contain a lot of oxides, but they are mainly composed of SiO_2 and Al_2O_3. Clionoptilolite contains 68,02 % of SiO_2 and 12,92 % of Al_2O_3, Na-P1 37,93 % and 18,83 % of SiO_2 and Al_2O_3 respectively. These proportions are connected with the Si/Al ratio, on the basis of which, a surface charge and surface properties can be estimated. Si/Al ratio for clinoptilolite is 4,64, for Na-P – 1,78. Other oxides, such as CaO, K_2O, Na_2O, MgO, and Fe_2O_3 are present in smaller quantities.

Fig. 2. SEM images of tested zeolites. Magnification12 000X. 1A – clinoptilolite; 1B Na-P1

Table 1

Chemical composition of tested zeolites

Component	Clinoptilolite, %	Na-P1, %
SiO_2	**68,02**	**37,93**
Al_2O_3	**12,92**	**18,83**
Na_2O	0,69	6,57
MgO	0,75	1,15
P_2O_5	0,16	0,31
SO_3	0,09	0,25
K_2O	3,36	1,00
CaO	3,71	14,41
TiO_2	0,20	0,83
MnO	0,06	0,08
Fe_2O_3	2,11	5,09

The distribution of grain size of both zeolite materials selected for testing is shown in Figure 3. Grain size distribution curve of zeolite Na-P1 represents the modal distribution of the particles of the zeolite with a maximum of 25 microns. In the case of natural zeolite, there is a bimodal distribution with the first maximum of 25 micron diameter, and the second for particle size of 300 microns.

Clear differences are also evident in the textural properties of both materials (Table 2). Zeolite material type Na-P1 has nearly fourfold higher specific surface area of 86.8 m^2/g than clinoptilolite 18.3 m^2/g. Synthetic zeolite also has a higher proportion of mesopores in relation to the natural. Practically all textural parameters are much higher for Na-P1 relative to the clinoptilolite.

Zeolite type Na-P1 is also characterized by a greater density 2.319g/cm^3 than clinoptilolite 2.135g/cm^3.

The result of the compaction in Marshall compactor

Conditions for sample preparation in Marshall compactor were established on the basis of standard [12] and the Technical Requirements [11]. Before preparing the first sample, a mold was heated to compaction temperature.

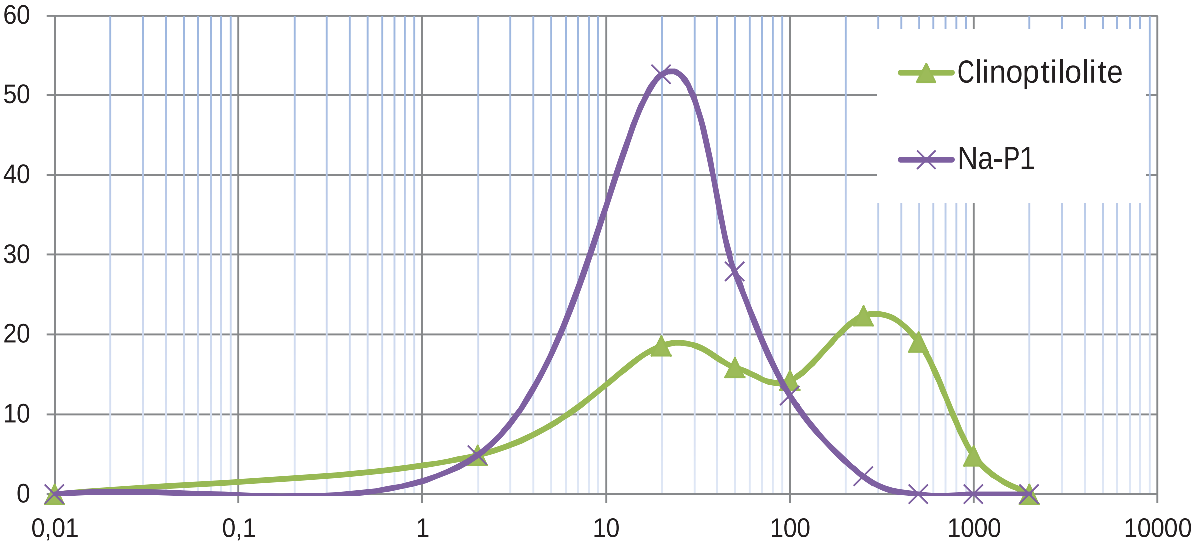

Fig. 3. Particle size distribution of tested zeolites

Table 2

Textural parameters of investigated zeolites

Material	$S_{BET}m^2/g$	$V_{mic}cm^3/g$	$S_{mic}m^2/g$	$V_{mes}cm^3/g$	$S_{mes}m^2/g$	$D_p nm$
clinoptilolite	18,3	0,05	7,68	0,0046	10,65	10,5
Na-P1	86,8	0,32	32,84	0,0143	54,01	11,6

Where: S_{BET} – specific surface area, V_{mic}/V_{mes}– volume of micropores/volume of mesopores, S_{mic}/S_{mes} – surface of micropores/surface of mesopores, D_p – average diameter of pores

The mass needed to perform a single sample was calculated on the basis of bulk density and tested through the execution of the test concentration. The consolidation temperature of the reference mixture was adopted on the basis of the type of asphalt - 140^0C ± 5^0C [11]. The samples were made by using the 75 blows from each side.

Taking into account the recommended procedure of the quantities of water necessary to foam bitumen (preferably about 2.5%), 1% addition of zeolite by total weight of the mixwas pre-fixed. This volume is appropriate for asphalt content in AC of 4.5%. The dosage of the water-soaked zeolite, depending on the origin was different and dependent on the absorbency. The addition of natural zeolite with its water content of 50% should be 0.2% (m / m), whereas synthetic zeolite with water absorption 160% - 0.07% (m / m) relative to the asphalt mixture (Table 3).

Table 3

Zeolite addition based on the optimum water content to foaming bitumen

Type of zeolit	Soaked [%]		Not soaked [%]
	clinoptilolite (C)	zeolite Na-P1 (P1)	(C) and (P1)
Moisture zeolite	50	160	10
addition of zeolite	0,20	0,07	1,13
The content of zeolite compared to asphalt	**5,00**	**1,75**	**25,0**
The content of zeolite compared to asphalt	**2,50**	**2,63**	**2,50**

The composition of the mineral mixture without zeolite was determined by the typical method of boundary curves (table 4, Figure 4). The design recipe is for the bonding layer of asphalt concrete, KR 3-6 (AC 16 B). Graining of aggregate was examined by screening.

Table 4

Mineral aggregate composition

Sievesize [mm]	Passing a sieve [%]	Grading limitcurve	
31,5	100,0		
22,4	100	100	
16	99	90	100
11,2	80	70	90
8	58	55	85
5,6	51	-	-
4	44	-	-
2	29	25	50
0,125	6	4	12
0,063	5	4	10

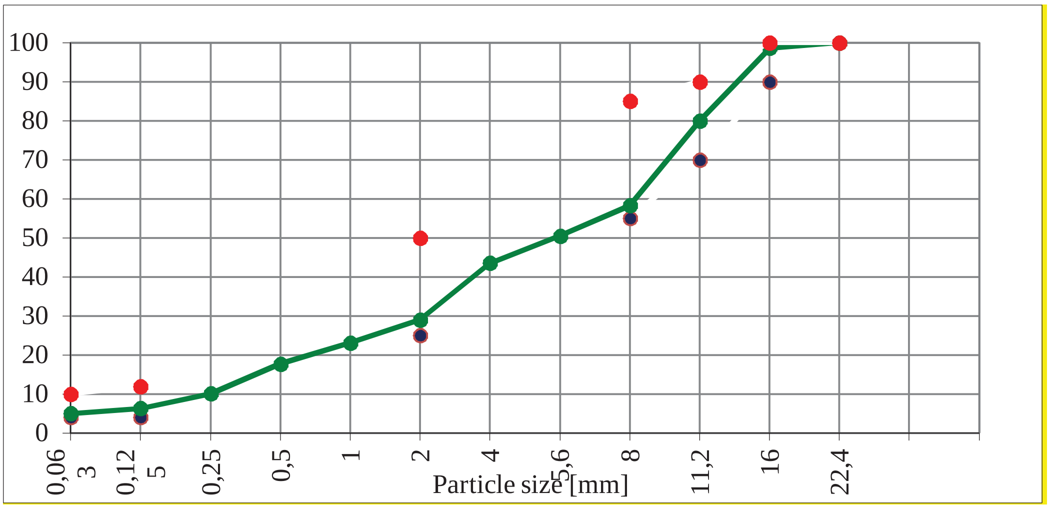

Fig.4 Gradation curve

The amount of asphalt is assumed to be minimal, according to WT 2, taking into account the density of the mineral mix. The adopted composition of mineral mixture and the composition of the mineral-asphalt mixture are shown in Table 5.

Table 5

Designed mix

Component mix	Content of the mix[%]	
	MM	AC
Filler	3	2,9 – zeolit*
Fine aggregate uncrushed 0/2	12	11,4
Graded aggregate crushed 0/4	22	21,1
Coarse aggregate2/8	18	17,2
Coarse aggregate8/11	24	23
Coarse aggregate11/16	20	19,1
Asphalt 35/50	4,5	4,5
Zeolite		0,07 to 1,13

* The amount of filler is reduced by% addition of zeolite.

Marshall samples were made from AC 16 W 35/50 mixture with the addition of natural and synthetic zeolite, soaked and not soaked, and the obtained results are shown in Figure 5.

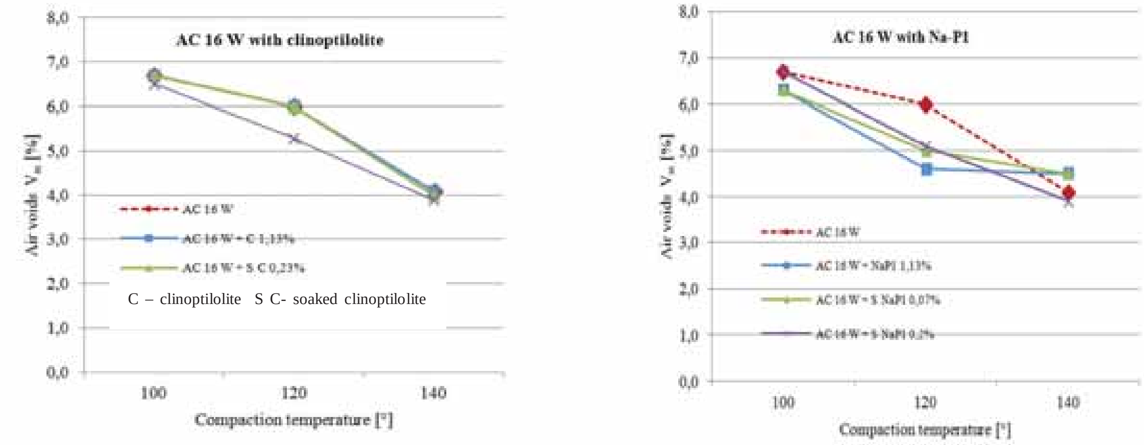

Fig. 5. Air voids of the different mixes studied

A marked difference in the resulting free space can be observed, depending on the type of zeolite. The decrease in the temperature relative to the reference mixture of 20^0C, was obtained for the synthetic not soaked zeolite, dosed at 1.13% (Figure 5).

The resilence modulus test was made in NAT on the samples. After the test the samples were saturated with water and next one freeze-thaw cycle was made, in accordance with the procedure described in WT 2010 [11]. On the conditioned samples, resilience modulus in NAT was again made. Water resistance was determined on the basis of the indirect tensile stiffness modulus ratio (ITSMR) defined as:

$$ITSMR = \frac{S_2}{S_1}$$

S_2 – average stiffness modulus in NAT obtained on samples with conditioning,
S_1 – average stiffness modulus in NAT obtained on samples without conditioning.
The test results are shown in Figures 6 and 7.

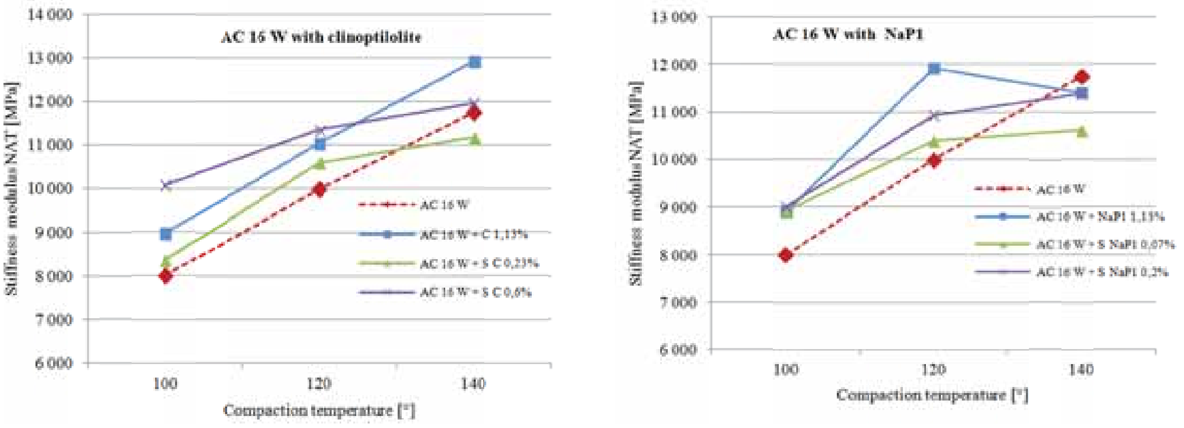

Fig. 6. Results of the stiffness modulus test of the different mixes studied

The values of NAT resilience modules obtained at temperatures less than 140^0C with addition of zeolite are higher than the reference samples. The best results on samples compacted at a temperature of 120^0C was achieved with1.13% addition of a non-soaked synthetic zeolite and 0.6% of natural soaked zeolite.

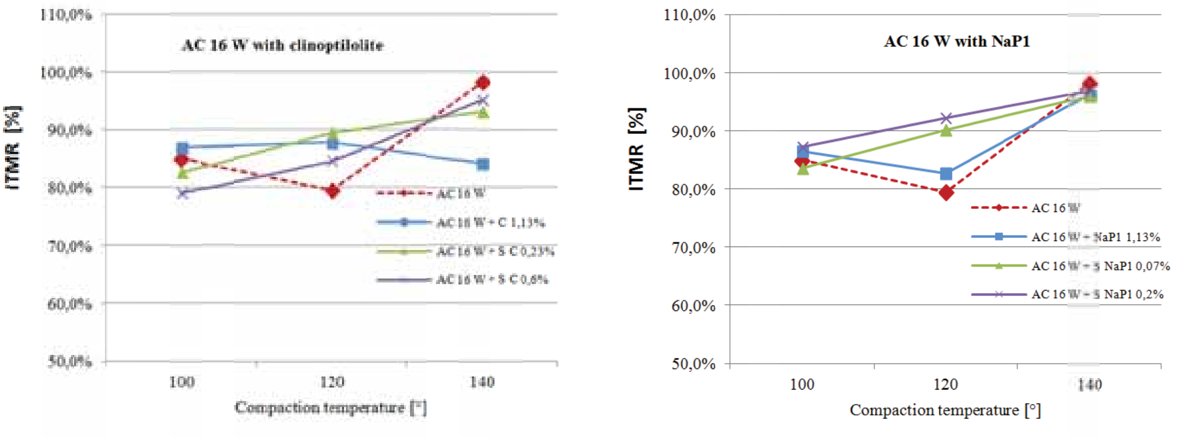

Fig. 7. Results of the water resistance test ITSMR of the different mixes

Water resistance of various samples containing zeolite at temperatures of 100^0C and 140^0C is similar to the reference samples. Clear differences occur at 120^0C, in which the addition of zeolite, regardless of the amount, increases the ITMR ration in relation to tests on reference samples.

The results of compaction in the gyratorycompactor.

The conditions of AC compaction with the addition of zeolites made in the gyratorycompactorwere established on the basis of a standard [13]. Before testing, a mold with a diameter of 100 mm was put in the oven at compation temperature for 2 hours. The hot mixture to the compaction was thermostated in a mold for 30-45 minutes. Sample weight was calculated assuming 0% of freeair voids. The angle of the piston in gyratory compactor was $1{,}25^0$, vertical pressure 600 kPa, the speed of rotation of the longitudinal axis - 30 revolutions/minute, the number of turns – 100. The compaction temperature of the reference mixture was assumed on the basis of the type of asphalt - 160^0C [13]. Samples with various additives of zeolites were compacted at 145^0C and 130^0C respectively. The analysis of air voids, defined on the basis of geometric bulk density after 100 gyrator turnovers, confirms the possibility of lowering the compaction temperature of asphalt mix by the addition of zeolites (Fig. 8 and 9).

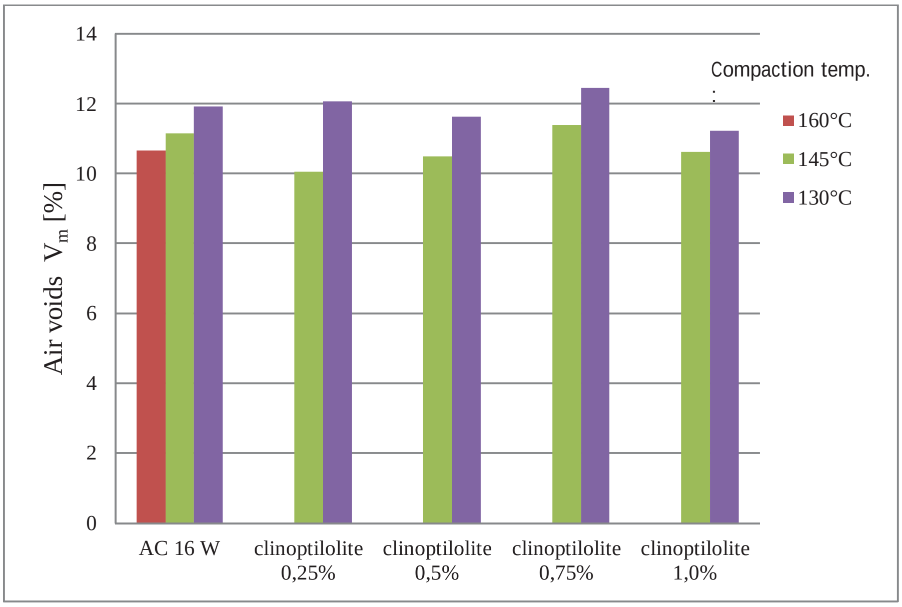

Fig. 8 Compactibility AC with the clinoptilolite

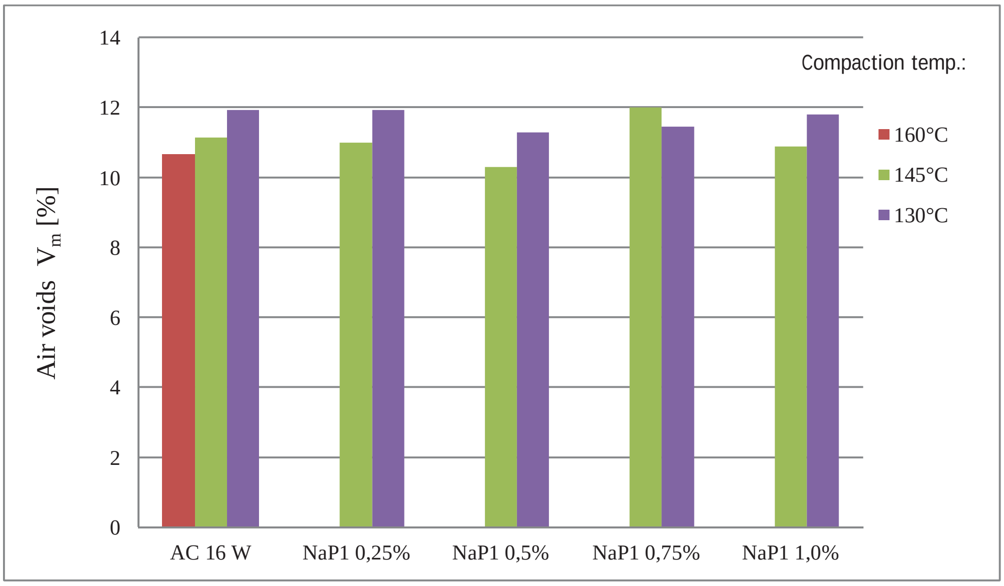

Fig. 9. Compactibility AC with zeolite material type Na-P1

The content of airvoids in the compacted samples at 145^0C with an optimal amount of zeolite is less than the reference asphalt mix compacted at 160^0C. In temperature compaction 130^0C, the results are comparable to the reference samples tested at 145^0C. For zeolite Na-P1, the best results were achieved for 0.5% additionin relation to the weight of asphalt mix. The optimum amount of clinoptilolite is 0.5 or 1.0%, depending on the compaction temperature .

Conclusions

The addition of zeolite to the WMA can reduce the compaction temperature to 120^0C. On the basis of the resultstaken on the Marshall samples, the optimal additionof the zeolite Na-P1 non-soaked is 1.13% and clinoptilolite soaked with water 0.6%. Samples compacted at 120^0C have a higher water resistance after optimal zeolite addition. Resilience modules tested on these samples in the NAT are comparable to the results achieved for the reference samples compacted at 140^0C.

The gyratory compactor has shown a possibility of decreasing the temperature of compaction to 120^0C using 1% of clinoptilolite or 0.5% Na-P1 zeolite. The optimal amount of zeolite in WMA dependent on the amount of released water adsorbed form zeolite in a function of time and temperature.

Acknowledgement

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