Effect of zeolite properties on asphalt foaming

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HIGHLIGHTS

- Synthetic zeolites from fly ashes can be used in asphalt foaming technology.
- The efficiency of asphalt foaming depends on the type of zeolite structure/property.
- DTA/TG assesses amount and timing of water release from zeolite during foaming process.

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ABSTRACT

This study includes investigation of two zeolite additives to non-modified asphalt binder and associated foaming phenomena. Two zeolites differ in their crystalline structures, i.e. one was Na-P1 synthetic zeolite and second was clinoptilolite natural zeolite. Prior to asphalt foaming these materials were additionally soaked with water which resulted in total of four base materials for laboratory investigation. The amount of zeolite dosed to the asphalt binder was 5% with respect to asphalt mass. The foaming effect was examined in terms of dynamic viscosity and further analyzed as a function of physical and chemical properties of both zeolites. In conclusion it was noted that the foaming effect strongly depends on the amount of water in zeolite structure, mode of its release with time, type of exchangeable cations as well as silicone to aluminum ratio in zeolites and finally their texture properties.

In order to mitigate these adverse effects, modern asphalt technology has been working on environment-friendly technologies. Over the last 20 years, several dozens of WMA (Warm Mix Asphalt) technologies were developed, allowing decrease in mixing and compaction temperatures by approx. 20–40 °C [2–4]. Temperature level decrease has resulted in significant reduction in the emission of harmful compounds [5–8]. Further, due to better workability WMA can contain higher RAP (Reclaimed Asphalt Pavement) content [9–13] as well as contain CRM (Crum Rubber Modifier) and recycled Asphalt Shingles (RAS) additives [14–16]. The construction of road surfaces using WMA technology also includes lower energy use and asphalt surface construction costs [17–22]. However, the range and the extent of observed benefits depends on the implemented WMA technology. The most common WMA technology utilizes asphalt foaming by adding a small amount of water into the hot binder or directly to the aggregate and asphalt mixer [23–28]. Several asphalt foaming technologies have been developed, which could be generally categorized as two groups [2].

- water-based,  
- water-storing additives, e.g. zeolites.

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Zeolites are a group of aluminosilicates with diversified frameworks. The Structure Commission of the International Zeolite Association (IZA-SC) assigns a 3-letter framework type code to each zeolite unique structure (e.g. for clinoptilolite it is HEU, for Na-A zeolite it is LTA). This code is a part of the official International Union of Pure and Applied Chemistry (IUPAC) nomenclature for microporous materials [29].

Crystalline zeolite structure includes empty spaces in the form of chambers and channels which provides zeolites with unique properties that are particularly advantageous for a number of industrial applications, including WMA [30–32]. Channel dimensions of the zeolites are on the order of 3 Å up to 30 Å which makes them sufficiently large so that not only single atoms but also small chemical compound particles can diffuse and penetrate inside them. One particular distinctive property of minerals from this group includes presence of water particles in their composition, so-called ‘zeolite water’. When heating material up to approximately 400 °C, zeolite water is released from the mineral structure in a continuous manner without changes in the crystalline volume. Consequently, during cooling a mineral in the humid environment, water particles are continuously absorbed by its structure.

Genetically, the zeolite material group includes natural and synthetic zeolites. At this moment, natural zeolite group includes approximately 100 different minerals. However, only some of them exist in the form of accumulations of so-called deposits that are economically feasible in terms of mining and processing. The most common zeolites creating deposits include: clinoptilolite, phillip-site, chabazite and mordenite [33]. In the second genetic group, synthetic zeolites are artificially created with strictly defined structure parameters which is dictated by a particular industrial application (e.g. selective molecular sieves). The most common zeolites obtained in the industrial synthesis processes include minerals of Na-X, Na-Y, Na-A, ZSM-5 type. Synthetic zeolites are obtained from the chemical reagents, mineral materials such as clay minerals and silica-group minerals as well as from some waste by-products of coal processing (such as fly-ashes) [34,35]. Up to date the WMA technologies include the use of synthetic zeolites manufactured using chemical reagents [6,36–38], synthetic zeolites from fly ashes [39], and natural zeolites such as clinoptilolite [38–42]. Studies available in the literature have examined the effect of zeolite additives on asphalt properties [43–46] as well as on the properties of WMA produced at lowered temperatures [9,47–50].

Regardless of the genetic group, zeolites allow for asphalt foaming due to the incremental release of water stored in their internal structure. Discharge of zeolite water from the crystalline structure is a long-term process. Therefore it is feasible to improve WMA workability during production, construction and compaction [5]. Study by Lai et al. focused on examining in details this phenomenon [51]. That study analyzed the release of zeolite water from the zeolite with LTA structure as a function of time and temperature. It was noted that zeolite gradually released water with time up to stabilization that occurred after 20–40 min. Stabilization time was highly depended on temperature and it was observed that the higher the temperature, the more water was released from zeolite structure within analyzed temperature range (from 76.6 °C to 121.16 °C).

Optimal amount of water needed for asphalt foaming spans between 2 and 4% with regards to the asphalt mass [52–54]. With insufficient amount of water the foaming is ineffective, whereas with the excessive water there is a significant risk of adhesion failure between asphalt and aggregate [55]. Therefore when using asphalt foaming technology with zeolites, it is necessary to recognize the topology of zeolite structure, the amount of zeolite water and its character, as well as water release characteristics as a function of time and temperature. In terms of the environment protection, it is desirable that the amount of water released from zeolite would be as high as possible, and temperature of its release as low as possible.

In the recent years there has been a number of studies assessing the effect of zeolites on asphalt and mix asphalt properties but only one has focused on zeolite properties. In that study [39], optimal amount of zeolite was assessed using compactability experiments in the gyratory compactor. In addition to optimal zeolite content, the results from the physical and chemical tests showed that synthetic zeolites with NaP1 structure type are feasible for WMA technology. However, that study [39] did not explain the mechanism of asphalt foaming with zeolite water. Other available studies in the literature do not contain any results allowing to associate the asphalt foaming effect with the type of zeolite structure. Thus it seems worthwhile to study the hypothesis that foaming efficiency is the results of zeolite water release determined by the zeolite structure. Having considered that, the aim of this study was to analyze the effect of Na-P1 (synthetic) and clinoptilolite (natural) zeolite type on asphalt foaming efficiency and attempt to explain the mechanism of this process through the topology of zeolite structures. The first part of this study presents a comprehensive property evaluation of both zeolites together with the base asphalt. Then foaming effect is assessed for all four zeolite-modified asphalts in terms of the complex shear modulus and dynamic viscosity. Final part includes discussion and identifies potential links between zeolite topology and foaming potential.

2. Materials and methods
2.1. Base materials

Zeolites used in this study represent two significantly different framework topologies (see Fig. 1). According to standard nomenclature [29] Na-P1 (synthetic zeolite) represents gismondine-like framework (GIS). In this structure, 8-membered channels of 3.1 × 4.5 Å and 2.8 × 4.8 Å are formed by two 4-membered rings. On the other hand, natural clinoptilolite characterizes heulandite topology (HEU) with two-dimensional channel system formed by 8-membered rings (4.1 × 4.1 Å) and 10-membered rings (5.5 × 3.1 Å) [56].

The Na-P1 was obtained in the conversion of F-class fly ash and aqueous solution of sodium hydroxide. The preparation of the zeolite was performed using patented semi-industrial scale device for zeolite synthesis. In that process, 20 kg of fly ash and 12 kg NaOH were mixed with 90 dm³ of H₂O. The substrates were subjected to hydrothermal synthesis at the temperature of 80 °C and duration 36 h [34,58–60].

Natural zeolite clinoptilolite (ZN-C) originated from Ukrainian deposit (Sokyrntysya) in a form of zeolitic tuff [61].

The foaming effect was studied using 35/50 asphalt binder. 35/50 parameter refers to European classification of asphalt binders that is based on penetration testing according to EN 12591:2010. Typical elemental composition and fraction composition for this asphalt are presented in Table 1. Chemical composition was determined using ED-XRF method (Energy Dispersive X-ray Fluorescence Spectroscopy, spectrometer Epsilon 3X). Fractional composition was determined using TLC-FID chromatography (Thin-Layer Chromatography Flame Ionization Detection) that identifies four typical asphalt groups – namely saturate, aromatic, resin and asphaltene (SARA) [62]. The TLC-FID chromatogram is presented in Fig. 2. Gaestel Index (I₇) calculated from the SARA results is equal to 0.37 which indicates colloidal microstructure of this base binder.
2.2. Asphalt modification with zeolites

The asphalt binder was modified with zeolites in the air-dry condition as well as after soaking with water. Zeolites were mixed with water in the following proportions (in relation to dry mass, water:zeolite): 3:1 for Na-P1 and 1:3 for clinoptilolite. In order to compare the effect of different zeolite structural types on asphalt properties, the study assumed a fixed concentration of 5% of zeolite material with respect to the asphalt mass. This is an optimal value due to the lowest acceptable asphalt viscosity determined from the previous study [41]. The basic properties of asphalt with zeolite additives are presented in Table 2.

Based on Table 2, it can be concluded that modification with zeolite minerals did not significantly affect the standard properties of base asphalt. The results of penetration tests indicate a relatively small binder hardening effect after adding Na-P1 zeolite. The breaking point also decreased insignificantly by – 3.5 °C after using natural zeolite modified with water (CLIN + W). The addition of zeolites modified with water decreased IP index from 0.58 to –0.73. Lower IP index indicates the increase of thermal susceptibility of modified asphalt that can potentially lead to deterioration of low-temperature properties [63,64].

2.3. Characterization of zeolites

Particle size distribution (PSD) were measured using laser diffraction method on Mastersizer 3000 with Hydro G dispersion unit with the measuring range of 0.02 μm to 2 mm. Mie theory was applied for PSD determination with parameters of 1.52 for light refractive index and 0.1 for absorption coefficient. Measurements were carried out with the pump and stirrer speeds of 1750 and 700 rpm, respectively.

In order to characterize textural parameters (specific surface area, pore volume, etc.) of the zeolites nitrogen adsorption/desorption isotherms were measured at –194.85 °C using Accelerated Surface Area and Porosimetry System ASAP 2020 M. Specific surface area was determined using Braunauer-Emmett-Teller’s multilayer adsorption theory (BET) at p/p0 between 0.06 and 0.3 (p, p0 – equilibrium pressure and saturation pressure of nitrogen). The volume of pores (V) was determined from the volume of adsorbed nitrogen at pressure p/p0 = 0.98. Pore diameters (Dp) were calculated according to the equation Dp = 4V/SBET.

Mineral composition of zeolites were determined using X-ray Diffraction method (XRD) using X’pert PROMP diffractometer with PW 3050/60 goniometer, Cu lamp and graphite monochromator. The analysis was performed with the angle range of 5° to 65° (2θ). The method allows to determine interstitial spacing d_{hal} characteristic for a particular crystal structure on the basis of the Bragg’s law.

The morphology and chemical composition in microarea of main mineral phases were assessed using Scanning Electron Microscope (SEM) FEI Quanta 250 FEG equipped with EDS system (Energy Dispersive Spectrometer). In the SEM method a sample surface is scanned by a focused beam of electrons which interact with atoms present in the sample. As a result, various signals are produced giving information about the morphology and chemical composition.

The amount and temperature range of water release from zeolites’ structure were analyzed using thermal analysis. Differential Thermal Analysis/Thermogravimetric curves (DTA/TG) were recorded using derivatograph STA 449 F3 Jupiter Netzsch between Fig. 1. Structure of analyzed zeolite materials: a) NaP1 (synthetic zeolite), b) clinoptilolite (natural zeolite) [57].

Table 1
Chemical composition and fraction composition SARA of 35/50 asphalt binder.

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Hydro carbon matrix</th>
<th>S</th>
<th>Ca</th>
<th>V</th>
<th>Fe</th>
<th>Ni</th>
<th>Sn</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content [%]</td>
<td>96.176</td>
<td>3.726</td>
<td>0.001</td>
<td>0.029</td>
<td>0.006</td>
<td>0.007</td>
<td>0.007</td>
<td>0.034</td>
<td>0.011</td>
<td>0.004</td>
</tr>
<tr>
<td>SARA fraction composition</td>
<td>Saturate</td>
<td>Aromatic</td>
<td>Resin</td>
<td>Asphaltene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Content [%]</td>
<td>4</td>
<td>29</td>
<td>44</td>
<td>23</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. Chromatogram for 35/50 asphalt binder.
25 and 800 °C in the air atmosphere with the heating rate of 10 °C/min. DTA curve reflects endothermic and exothermic processes taking place in the sample during heating such as dehydration, dehydroxylation, thermal decomposition of minerals, and structure destruction. Finally, TG curve corresponds to the sample mass loss resulting from these phenomena as a function of time.

2.4. Testing of asphalt samples

2.4.1. Complex shear modulus |G′| The rheological properties of asphalt samples were performed using Dynamic Shear Rheometer (DSR). The loading history was set as a frequency sweep repeated at 13 temperatures with 6 °C incremental step. For temperatures between 10 °C and 46 °C specimen diameter of 8 mm with 2 mm gap size was used, whereas for temperatures between 46 °C and 82 °C larger geometry was used, i.e. diameter of 25 mm with 1 mm gap size. Frequency range for each test temperature was between 0.16 Hz and 15.85 Hz which corresponds to angular frequency of between 1 and 100 rad/s. 11 equidistant frequencies were used in the logarithmic scale at each test temperature [65,66].

For all frequency-temperature combinations, complex shear modulus |G′| and corresponding phase angle were measured. Assuming that asphalt samples behave as a linear viscoelastic material and that time-temperature superposition can be applied, |G′| results were processed into mastercurves at the reference temperature, Mastercurves were constructed by shifting first individual isothersms using Williams–Landel–Ferry (WLF) equation and then the Christensen-Anderson (CA) model parameters were fitted to the shifted raw data. WLF equation can be formulated as follows [67]:

\[
\log \alpha = -\frac{C_1(T - T_{ref})}{C_2 + |T - T_{ref}|}
\]  
(1)

where:
- \(C_1, C_2\) – fitting coefficients
- \(T\) – temperature level,
- \(T_{ref}\) – reference temperature,
- \(\alpha\) – shift factor for data at temperature \(T\).

CA model for the asphalt mastercurve [68]:

\[
|G'(\omega)| = G_0 \left[1 + \left(\frac{\omega}{\omega_c}\right)^{\nu}\right]^\eta
\]

(2)

in which:
- \(G_0\) – glassy modulus [Pa] (one of the fitting parameters),
- \(\omega\), \(\omega_c\) – model parameters.

All fitting parameters were estimated using the Method of Least Squares (MLS), i.e. best-fit parameters were selected by minimizing the squared sum of residuals between measured and fitted |G′| values.

2.4.2. Dynamic viscosity Dynamic viscosity tests were performed using Brookfield’s viscometer at two temperatures corresponding to temperatures occurring during the process of pavement construction, i.e.:

- 135 °C – experienced during paving and compaction,
- 160 °C – during production in the asphalt plant.

The data post-processing involved calculating the ratio of shear stress caused by rotating spindle submerged in asphalt and its rotation speed. After preparing the asphalt samples modified with zeolites, the sample was placed for 15 min in a dryer with the air temperature of 145 °C. The viscosity tests were performed on separate samples at each individual temperature. Viscosity measurements were taken at the following time intervals: 15, 30, 45 and 60 min, counted from the moment of placing the asphalt specimen in Brookfield’s viscometer.

3. Results and discussion

3.1. Zeolite properties

PSD and SEM photographs of the studied materials are presented in Fig. 3. Na-P1 exhibited monomodal PSD where approximately 25 μm covering 55% of the volume. On the contrary, PSD of clinoptilolite was heterogenous with peaks at 25 and 300 μm covering 19% and 23% of the volume, respectively. In terms of morphologic shape, clinoptilolite is formed by 20–30 μm sized tiles and their hexagonal shape can be noted in the SEM images. On the other hand, NaP1 type zeolite forms small tile conglomerate with the size on the order of 2 and 3 μm. It can be concluded that SEM images confirmed PSD measurements and both methods clearly demonstrated a high volume of smaller particles in synthetic zeolite with a significant volume of particles located in the relatively narrow band.

Mineral composition of both zeolites is shown in Fig. 4. Both diffractograms confirm the main mineral substrates of analyzed samples, i.e. clinoptilolite and NaP1phases. Clinoptilolite was recognized by characteristic interplanar distance, \(d_{\text{calc}} = 8.95; 7.94; 3.96; 3.90 \, \AA\) whereas NaP1by \(d_{\text{calc}} = 7.10; 5.01; 4.10; 3.18 \, \AA\). Mineral composition of the natural zeolite comprised small amounts of CF opal, quartz and potassium feldspars, whereas in a case of...
synthetic zeolite additional minerals were quartz and unreacted portions of aluminosilicate glass.

DTA/TG thermal curves of modified asphalts with zeolites are presented in Fig. 5. Observations can be divided into two temperature regions: up to 250 °C that is of particular interest for asphalt foaming efficiency and above that region. In the first region, there is an apparent endothermic effect, i.e. heat collection from the surroundings. This effect is more intense for NaP1 zeolite. Maximum for NaP1 zeolite occurs at the temperature of 120 °C whereas for the natural zeolite at 190 °C. Both discussed effects are accompanied by the distinct mass reduction (TG curve). In a case of NaP1 zeolite, it amounts to 20.4%, whereas in a case of clinoptilolite to 7.7%. In the second region of interest (above 250 °C) both zeolite materials demonstrate a poor endothermic effect with the maximum at approximately 450 °C accompanied by a small mass decrease of 2.34% for NaP1 zeolite and 4.14% for clinoptilolite which is caused by OH group dehydroxylation. In the range between 450 °C and 800 °C, thermal curves of both zeolites show exothermic effect. The maximum of this effect for NaP1 falls between 580 and 620 °C and at approximately 640 °C for clinoptilolite. These effects are accompanied by a small mass decrease of 6.32% for NaP1 zeolite and 5.94% for clinoptilolite, respectively which is related to recrystallization and collapse as well as disintegration of zeolite framework structure.

As could be expected from the PSD/SEM measurements, the synthetic zeolite exhibits significantly more developed specific surface area expressed by $S_{\text{BET}}$ parameter which was equal to 94 m$^2$/g for Na-P1 and 18 m$^2$/g for clinoptilolite. Na-P1 zeolite has a substantial contribution of mesopores which is reflected in the mesopore surface and volume levels (86 m$^2$/g and 0.23 cm$^3$/g, respectively) that are 10 times higher than corresponding values for the natural zeolite (8 m$^2$/g and 0.05 cm$^3$/g). In terms of micropores, both zeolites produced similar surface and volume levels (about 11 m$^2$/g and 0.005 cm$^3$/g, respectively). Finally, considering the average pore diameters, clinoptilolite showed slightly less narrow pores (10 nm for Na-P1 whereas 9 nm for clinoptilolite).

In the final evaluation of zeolite properties, SEM-EDS device was used to evaluate chemical composition of their microareas (Fig. 6). In order to perform such an assessment, the silicon to aluminum ratio (Si/Al) is often calculated. The Si/Al parameter allows to classify zeolites into high-silicon (Si/Al = 10–100), medium-silicon (Si/Al = 2–5) and low-silicon (Si/Al = 1–1.5) materials. In this study, clinoptilolite had higher Si/Al (7.07) as compared to NaP1 zeolite (2.30). SEM-EDS results also showed that both zeolites differ in terms of ion-exchangeable cations which compensate the negative charge of crystalline network. Divalent Ca$^{2+}$ and Mg$^{2+}$ cations dominate in clinoptilolite structure whereas the main ion-exchangeable cation in NaP1 zeolite includes Na$^+$. 

![Fig. 3. SEM images (magnification 30 000x) and particle size distributions of clinoptilolite and Na-P1.](image)

![Fig. 4. Diffractograms of mineral composition for clinoptilolite and NaP1 zeolites.](image)

![Fig. 5. Derivatograms of clinoptilolite and NaP1 zeolites.](image)
3.2. Rheological properties of modified asphalts

3.2.1. Complex shear modulus $|G'|$

Table 3 shows CA model parameters for 35/50 asphalt binder as well as for its modifications with zeolite materials. It can be noted that individual parameter values do not vary significantly among different materials. The most significant discrepancy includes $|G'|$ modulus decrease for the zeolite-modified asphalt samples which generally has a positive effect on the thermal stress accumulation during the cooling process.

3.2.2. Dynamic viscosity

Dynamic viscosity was used as the main parameter to assess the effectiveness and feasibility of different zeolites to asphalt foaming. The results of viscosity evaluation are presented in Figs. 7–9. Overall observation indicates that viscosity of the asphalt modified with NaP1 zeolite and clinoptilolite in the dry condition was higher than viscosity of the asphalt binder in both test temperatures. It is the effect of introducing non-dissolved solid body into the asphalt binder. Application of zeolite soaked with water positively affected asphalt viscosity resulting in its decrease compared to zeolite materials without extra water. It is particularly prominent at $135^\circ C$ whereas at $160^\circ C$ viscosity levels were similar for samples with and without extra water. Based on the analysis of normalized viscosity (see Fig. 9) it is possible to observe a high effect of temperature on viscosity results and differences in terms of zeolite structure’s effect. Substantial differences in viscosity were obtained at $135^\circ C$ regardless of zeolite type and presence of extra water.

Samples with NaP1 zeolite were characterized by the highest viscosity among all tested materials. One can deduce this is the effect of sixfold greater mesopore volume for this material as compared to clinoptilolite. As a result, the synthetic zeolite absorbs asphalt binder particles to a higher degree. At the same time the largest viscosity decrease with time was observed also for asphalt modified with NaP1 zeolite: 6.3% at $135^\circ C$ and 6.7% at $160^\circ C$. The viscosity decrease occurred after 45 min from adding zeolite material to the base binder which translates to 30th minute of the test shows in Figs. 7–9. Any shift from horizontal trend observed after 30 min in Fig. 9 can be contributed to the measurement errors and natural variability of material response. Thus it can be concluded that the values recorded at the subsequent time intervals did not show further decrease in viscosity. Similar observation was made for both zeolites used in this study. At the same time, one should note that the zeolite has a solid body structure (powder) and it does not dissolve into the asphalt binder which has a negative effect on the result of viscosity tests. In a case of other liquid modifiers (e.g. Fischer-Tropsch wax) they can create a homogeneous fluid with the binder.

Zeolite structure type, its textural properties, type of exchangeable cations compensating the negative charge of zeolite's crystalline framework affect the amount and method of zeolite water release. When zeolite structure intensively releases water (both in terms of released amount as well as release temperature), there is a sharp endothermic effect occurring in DTA curve. In a case when zeolite releases water slowly/gradually, this endothermic effect occurs in a broad temperature range without a clear maximum. Therefore Na-P1 structure determines more effective asphalt foaming than clinoptilolite manifested by a greater decrease in asphalt viscosity. The amount of absorbed water and intensity of its release can be associated with mesopore sizes in the zeolite structure. The structure of mesoporous zeolite is capable to absorb the highest amount of water which directly translates to the amount of water released at the technological temperatures of the asphalt mix. The amount and temperature range of zeolite water release should be also associated with the crystallochemical character of analyzed zeolites. Clinoptilolite is considered to be a high-silicon zeolite which directly affects the course of dehydration process. Similar relation is found in a case of zeolites in which divalent cations (Ca$^{2+}$ and Mg$^{2+}$) prevail in ion-exchange space.

Table 3

Rheological parameters for 35/50 asphalt binder and its modifications with zeolites.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Model parameters CA</th>
<th>Model parameters WLF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Complex dynamic modulus</td>
<td>Crossover frequency</td>
</tr>
<tr>
<td></td>
<td>$</td>
<td>G'</td>
</tr>
<tr>
<td>35/50</td>
<td>2.01E+07</td>
<td>596.83</td>
</tr>
<tr>
<td>CLIN</td>
<td>1.52E+07</td>
<td>510.89</td>
</tr>
<tr>
<td>CLIN + W</td>
<td>1.81E+07</td>
<td>590.23</td>
</tr>
<tr>
<td>NaP1</td>
<td>1.49E+07</td>
<td>469.51</td>
</tr>
<tr>
<td>NaP1 + W</td>
<td>1.45E+07</td>
<td>525.21</td>
</tr>
</tbody>
</table>

Fig. 6. SEM-EDS for clinoptilolite and NaP1 zeolites.
which is the case for clinoptilolite. NaP1 zeolite is considered to be a medium-silicon zeolite. Sodium is its main ion-exchange cation and as a result water release process occurs at as early as 120 °C and it is characterized by the narrow endothermic peak.

4. Conclusions and recommendations

Modern synthesis technologies allow to engineer synthetic zeolites with desirable structures and properties required by specific...
industrial applications. Therefore it is important to recognize zeolite properties that determine their applicability in lowering the asphalt mix production and paving temperatures. Initial studies concerning zeolite application in the WMA technologies focused on the zeolites with LTA code typically obtained from the chemical reagents. In the recent years some studies focused on the natural zeolites as well as on the synthetic zeolites produced using by-products of carbon combustion. Some studies went even further to examine natural and synthetic zeolites soaked additionally with extra water.

Based on analysis presented in this study, it is possible to conclude that the amount and mode of zeolite water release are affected by the zeolite structure type, its textural properties and crystallochemical character. The character and intensity of zeolite water release can be observed in the thermal curves. Zeolite materials for which rapid endothermic effect occurs at lower temperatures allows for more effective asphalt foaming. Another important criterion in terms of asphalt foaming process includes Si/Al ratio in the zeolite framework. The higher the Si/Al ratio, the higher the zeolite water binding force resulting in slower release. Moreover, divalent cations are more hydrated by water particles than monovalent cations. Meso pores specific surface area and volume are another significant parameters determining applicability of zeolite as WMA additive. These characteristics determine higher amount of water-binding sites per mass unit which translates to the higher amount of water which can be introduced into zeolite structure. Due to zeolite modification with water it is possible to decrease the amount of dosed zeolite which translated to economic efficiency of WMA production process.

Changes of the PI index for the asphalt with zeolites modified with water indicate the potential deterioration of thermal susceptibility of modified asphalt. In order to further explore this PI trend, further research effort on the low temperature properties should be performed. Dynamic viscosity tests allow to assess the effect of particular zeolite structure on asphalt foaming effect. Regardless of the zeolite type, decrease in viscosity occurred after 45 min from introducing the zeolite to asphalt binder however it is more desirable to release water gradually with a proper amount allowing effective binder foaming. Results presented in this study could define yet another fundamental study to determine the minimum batch conditioning prior to the preparation of samples using discussed technologies. Finally, in order to further investigate different zeolite structures and their feasibility to asphalt foaming, a similar study is planned in the near future with a larger number of synthetic zeolites. It is planned that future study will also include the assessment of the resistance of zeolite-modified asphalts to the environmental factors.

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