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Study of the Simultaneous Utilization of Mechanical Water Foaming and Zeolites and Their Effects on the Properties of Warm Mix Asphalt Concrete

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Abstract: The paper aimed at assessing the feasibility of using natural zeolites as a mineral filler substitute for asphalt mixtures produced at around 120 °C temperatures with a water foamed binder and compacted at 100 °C. The tests utilized the AC 16 asphalt concrete mixture intended for the binder and base course with the mineral filler fraction amounting to 4% by wt. comprising limestone dust and zeolites (when added). A reference hot mix and warm mix with foamed bitumen were compared to two mixes with zeolites, with one containing 0.4% of a water-modified (20% moisture content) zeolite and the second containing 1.0% of natural air-dried zeolite. The investigations included: assessment of compactability using a gyratory compactor, air void content, indirect tensile strength before and after conditioning with one freeze-thaw cycle, and the resulting resistance to moisture and frost damage. The mixtures with zeolites exhibited decreased compactability when compared to reference mixes, which the Marshall samples confirmed. The mechanical properties have also deteriorated in zeolite-bearing mixtures, which was partially accounted to the decreased compaction level. It was concluded that the temperature of the mixture production was too low for the zeolite water to significantly improve the compactability of the asphalt mixture and its mechanical parameters.

Keywords: WMA; asphalt concrete; natural zeolite; foamed bitumen; moisture susceptibility

1. Introduction

The production of traditional hot mix asphalts (HMA) is very energy consuming, mainly because of the high production temperatures, which typically range from 160 to 190 °C. The actual production temperature depends chiefly on the type of used asphalt and its viscosity at high temperatures, which is decisive in terms of coating the mix's components. As such, paving with asphalt mixtures is a source of emission of greenhouse gases and other substances with a negative impact on the environment. Human labor conditions at HMA paving over long periods of time are also a concern. Due to the above, the production of HMA's is not considered to be indifferent to the environment, but these effects can be reduced with the use of adequate technical measures. Therefore, actions are taken to change the asphalt production technologies to make them more environmentally friendly and contributing to worker safety. The effect of these activities is the development of new technologies of producing warm mix asphalts (WMA) and research on the half-warm mix asphalts (HWMA) [1–5].

Currently, the greatest technological developments are seen in the field of warm mix asphalt, in which mainly Fischer-Tropsch synthetic waxes or Montan-type waxes and chemical state-of-the-art warm mix additives are used. The use of a water foamed binder is another popular method of achieving

this goal. In this scope, it is possible to distinguish two main technology groups: foaming using water injected directly into the binder (mechanical foaming) and by the use of zeolites or other similarly acting granular materials (e.g., mesoporous silica [6]) added to mineral-bitumen mixes as a mean for introducing foaming water.

The bitumen foaming technique for producing bitumen-aggregate mixtures was at first used for producing road paving mixes at ambient temperatures with low-quality aggregates and recycled road base material, but now it is also used in WMA and HWMA techniques [7]. The investigations of bitumen water-foaming for production of WMA came in the late 1990's and early 2000's with the emergence of other warm mix techniques [8]. The sudden expansion of water contacting hot bitumen results in the formation of bitumen foam with greatly increased volume and surface area, decreased viscosity, and enhanced coating abilities. These effects in conjunction with adequate aggregate temperature permit the production of high-quality asphalt mixtures at lowered temperatures [4,5,9–11].

Zeolites are crystalline, hydrated aluminosilicates of alkali elements (Na, K, less often Li), alkali soils (Ca, Mg, Ba, more rarely Sr), or other monovalent or polyvalent metals. These materials are micro-porous solids with exchangeable cations and zeolite water in the crystalline network channels. The zeolite voids are sufficiently big to enable diffusory permeation of not only single atoms, but whole chemical compound particles without changing the volume of the crystal structure, which makes zeolites a medium for certain chemical compounds and it enables their use, e.g., for absorbing unwanted chemical reaction products [12–14]. Zeolites possess unique absorptive properties, which are mainly related to their porous structure that allows for water release and absorption. Water desorption is a function of time and temperature. Thanks to their properties, zeolites became widely used in the global economy, not only as WMA additives, but also, among others, in the cement concrete technology [15–17], as sorbents in the environmental protection and household chemical products technologies [18–21] and as catalysts in the chemical and oil industry [22].

The naturally occurring zeolites include several dozen various mineral variants, among which the most common and used are: clinoptilolite, modenite, analcime, or chabasite. Many other variants are only known from singular aggregations [23]. Due to the high demand for zeolites, they are also produced on an industrial scale through synthesis. Thus far, over 400 zeolites were obtained this way [24].

A specific feature of zeolites is the occurrence of the so-called “zeolite water”, which is continuously released into the environment, along with their heating up to approx. 400 °C. This fully reversible process, does not cause changes in the volume of zeolite crystal structure. The potential occurrence of this phenomenon was observed in terms of the possibility of improving the workability of asphalt mixtures. Zeolites are currently a popular WMA additive, which are usually used as a replacement for a fraction of the filler aggregates. The technology of producing asphalt mixes with zeolites does not differ from traditional technologies [25], which is why its implementation is possible without incurring substantial financial expenses. The mixing temperature causes the gradual release and vaporisation of the zeolite's pore water, thereby causing asphalt foaming. At the same time, zeolites do not change the properties of the bitumen binder.

The research that was conducted by Lai et al. [26] showed that the the *Advera* synthetic zeolite gradually releases water over time, whereas the stabilisation of this process takes place after 20–40 min. More zeolite water is released along with increasing temperature. The improvement of the asphalt mixture's workability takes place after a minimum of 20 min. from the introduction of zeolites to the mixture. The optimal temperature that is required for effective asphalt foaming amounts to 110–120 °C [26].

The analysis of the results presented in A. Wozuk's paper [27] on compactability testing in the gyratory compactor indicates that the optimal content of the NaP1 synthetic zeolite amounted to 0.5% by wt. of mineral mix and 0.4% in the case of water modified zeolite. The optimal quantity was 1.0% by wt. of mineral mix and 0.4% for water-soaked mineral in relation to the weight of the mineral mix when using the clinoptilolite natural zeolite.

Analysis of the possibility of simultaneous use of bitumen mechanical foaming (using water injection) and zeolites were not found in the literature, therefore the purpose of this paper was to evaluate the feasibility of the simultaneous use of the mechanical water-foaming and the utilization of zeolites in the production of WMA asphalt concrete mixtures at ca. 120 °C. The investigations included an assessment of the compactability and basic mechanical properties (indirect tensile strength, resistance to moisture, and frost damage) of an AC 16 mix designed to withstand a medium traffic load (up to 7.3×10^6 100 kN equivalent single axle loads in the design period).

2. Aims and Design of Experiment

2.1. Purpose and Scope of Research

The research subject was to test the feasibility and effects of using the natural zeolite additive for asphalt mixtures produced and then compacted in lowered temperatures along with the mechanical bitumen water foaming method. The main purpose of laboratory testing was to determine the impact of the zeolite additive on selected physical and mechanical properties of the WMA and water foamed asphalt mixtures as well as on its compaction.

The utilization of natural zeolite was evaluated while using the AC 16 asphalt concrete mix based on limestone and quartzite aggregates, with the use of the reference mixes that are produced in the hot mix asphalt technology HMA_{Ref} and warm-mix method with foamed bitumen only WMA_{Ref} . The only differences concerned the production temperatures (HMA_{Ref} : ca. 160 °C, WMA mixes: ca. 120 °C), compaction temperatures, dosed binder form (liquid in the HMA_{Ref} mix and water foamed in the WMA mixes), and additives in the composition of the asphalt concrete. Table 1 presents the materials used in the formulation of the asphalt concrete mixes. In the case of zeolite dosage, the mixture composition was corrected by lowering the mineral filler content in the mineral mix by the quantity of the incorporated zeolite additive. The laboratory testing utilised zeolite in two forms: dry (unmodified) and modified with water (up to 20% moisture content).

Table 1. The framework composition of the evaluated AC 16 mixture.

AC Constituents	Material Type	
Natural Aggregates	Filler aggregate (limestone)	
	Fine natural aggregate 0/2 mm (limestone)	
	Continuously graded natural aggregate 0/4 mm (limestone)	
	Coarse aggregate 2/5 mm (quartzite)	
	Coarse aggregate 5/8 mm (quartzite)	
Bituminous Binder	Paving Bitumen 35/50	Liquid (unfoamed) Foamed (water injection)
	Adhesion Promoter (Wetfix BE)	
Additives	Natural Zeolite	Saturated with water up to 20% (wt.) Dry (air-dried at room temp, RH = 60%)

The analysis covered the following mixes:

- HMA_{Ref} - reference Mix Produced as Hot Mix Asphalt Using the 35/50 Asphalt with 0.3% (by wt.) of Adhesion Promoter,
- WMA_{Ref} - reference mix produced at lowered temperature with water foamed asphalt produced from 35/50 binder, with 0.6% (by wt.) of adhesion promoter,
- $WMA_{nz,0.4\%S}$ - mix produced at lowered temperature with water foamed asphalt produced from 35/50 binder, with 0.6% (by wt.) of adhesion promoter, including natural zeolite in the amount of 0.4% of the mix weight, soaked to 20% moisture content,
- $WMA_{nz,1.0\%D}$ - 35/50 binder, with 0.6% (by wt.) of adhesion promoter, including natural zeolite in the amount of 1.0% of the mix weight and 7.4% moisture content.

As specified before, it was decided to evaluate the impact of dosing of natural zeolite in two variants: dry (at its natural moisture content in air-dry conditions, *D*—dry) and soaked in water (up to 20% moisture content by weight, *S*—saturated). The quantity of water soaked zeolite amounted to 0.4% (by wt.) of the mineral mix, whereas the dry zeolite was used in the quantity of 1.0% (by wt.). These values were chosen based on the analysis of technical literature [27]. The degree of saturation was chosen in this way, so that the total quantity of water delivered to the asphalt mixture by means of zeolite was in both cases comparable. Table 2 presents adequate calculations.

Table 2. The calculation of total added moisture in the investigated mixtures.

Mix Type	Binder Content in the Mix	Foaming Water Content	Zeolite Water Content	Zeolite Content	Calculation of Total Added Moisture in the Mix
<i>HMA</i> _{Ref}	4.5%	-	-	-	-
<i>WMA</i> _{Ref}	4.5%	3.0%	-	-	$4.5\% \times 3.0\% = 0.135\%$
<i>WMA</i> _{nz,0.4%<i>S</i>}	4.5%	3.0%	20%	0.4%	$0.135\% + 0.4\% \times 20\%$ $= 0.135\% + 0.08\% =$ 0.215%
<i>WMA</i> _{nz,1.0%<i>D</i>}	4.5%	3.0%	7.4%	1.0%	$0.135\% + 1.0\% \times 7.4\%$ $= 0.135\% + 0.074\% =$ 0.209%

It was first necessary to determine the impact of using the adhesion promoter on the properties of the binder and asphalt foam due to the use of various contents of the adhesion promoter and foamed bitumen binder in the analysed mixes. The testing of asphalt concrete was conducted during the second stage of works.

2.2. Evaluation of the Properties of Bituminous Binders

The purpose of the first stage was to determine the impact of the Wetfix BE [28,29] adhesion promoter (referred to as WBE) on the basic properties of the 35/50 penetration paving bitumen prior to foaming, the impact of this additive on the foaming process, and to determine the optimal foaming water content for this binder. The investigated 35/50 binder is commonly used in central and eastern Europe for producing asphalt concrete mixtures that are intended for road pavements with medium traffic ($0.5 \times 10^6 \leq \text{ESAL}_{100 \text{ kN}} \leq 7.3 \times 10^6$).

The liquid adhesion promoter was dosed in the following quantities: 0.3%, 0.6%, and 0.9% (by wt.). The quantitative range of using the surfactant additive was formulated based on the high silicon dioxide content ($\text{SiO}_2 > 60\%$) in the aggregate and on the lowered technological temperatures used in WMA mixes with foamed asphalt. Increased amounts of surface active chemical agents are also recommended due to the necessity of ensuring the asphalt pavement's water and frost resistance, exploitational durability, and ensuring adequate foaming performance.

The 35/50 road paving bitumen was subjected to the determination of the effects of WBE adhesion promoter on the basic parameters describing its consistency, thermal sensitivity and low temperature performance based on the following laboratory testing:

- penetration at 25 °C (Pen_{25}) acc. to EN 1426:2015-08 [30], 10 replicates
- softening point acc. to the "Ring and Ball" method ($T_{R\&B}$) acc. to EN 1427:2015-08 [31], four replicates
- Fraass breaking point (T_{Fraass}) acc. to EN 12593:2015-08 [32], three replicates.

Based on the obtained results, the following parameters were determined by using analytical methods:

- penetration index *PI* based on EN 12591:2010 [33]
- temperature plasticity range (*PR*) acc. to EN 14023:2011 [34]

All of the binders were also subject to measurements of the following asphalt foam's physical parameters in accordance to procedures presented in [1,35–39]

- ER_m —maximum expansion ratios
- HL —half-life.

The bitumen foam parameters were measured at five different foaming water contents (FWC) ranging from 1.5% to 3.5%. The measurements were conducted four times for each of the FWC's. The adhesion promoter used in the testing was mixed with the binder directly in the Wirtgen WLB 10S device prior to the foaming process, which ensures the binder's homogenisation. The foaming conditions (air and water pressure, bitumen temperature) were in accordance with [38,40,41]. All of the test samples were prepared according to EN 12594:2014-12 [42].

Based on the aforementioned comprehensive test results and author's prior experiences, the WBE additive content was determined for producing HMA and WMA mixes with foamed asphalt.

2.3. Evaluation Of The Properties of Foamed Warm Mix Asphalt with Zeolites

All of the experiments utilized the same AC 16 asphalt concrete mix designed with a maximum aggregate size of 16 mm intended for binding and base courses of pavements with medium design traffic. The mix was designed in accordance to EN 13108-1:2008 [43] and Polish technical requirements WT-2 [44].

The 35/50 penetration paving bitumen was used in all of the asphalt mixtures. It was necessary to use an adhesion promoter (WBE) due to the fact that the designed mineral mix composition featured quartzite aggregates, where content in relation to the binder's weight amounted to 0.3% in the HMA_{Ref} reference mix and 0.6% in the WMA mixes in relation to the binder's weight, which was determined based on previous experiences [45,46] and the test results included in the latter part of the paper.

The scope of the laboratory works included testing of the following physical and mechanical properties of the AC 16 asphalt concrete mixes:

- density ρ_{mv} acc. to EN 12697-5:2010 [47],
- bulk density ρ_{bssd} acc. to EN 12697-6:2012 [48],
- air void content V_a acc. to EN 12697-8:2005 [49],
- indirect tensile strength ITS_{dry} in air-dried conditions, indirect tensile strength $ITS_{freeze-thaw}$ after conditioning with a single freeze-thaw cycle, and
- water and frost resistance $ITSR$ acc. to EN 12697-12:2008 [50] and acc. to WT-2 (Appendix no. 1) [44]—the procedure was specified in detail in paper [4] (procedure B, Section 2.3).

In addition, the compaction performance of the asphalt mixtures was analysed while using a gyratory compactor (Controls S.p.A., Milan, Italy) acc. to EN 12697-31 [51].

3. Materials

3.1. Natural Aggregates

Natural aggregates were chosen based on EN 13043 [43] and domestic requirements (WT-1 [52], WT-2 [44]), as intended for the binding layer and the subbase of pavement with a medium traffic load, in order to develop the reference composition of the AC 16 asphalt concrete mix.

Table 3 and Figure 1 present the results of air-jet sieving of the filler aggregate in acc. to EN 933-10 [53] and the remaining aggregate gradation determined by the sieving method acc. to EN 933-1 [54].

Table 3. Results of sieve analysis of mineral aggregates used in AC 16 asphalt mixes.

Particle Size # (mm)	Component					
	Filler	0/2 mm	0/4 mm	2/5 mm	5/8 mm	8/16 mm
16	0	0	0	0	0	6.8
11.2	0	0	0	0	0	42.3
8	0	0	0	0	8.2	40.8
5.6	0	0	2.4	11.0	64.5	7.0
4	0	0.1	13.3	31.9	16.5	0.5
2	0	9.2	29.0	45.9	6.8	0.2
1	0	25.9	20.6	8.4	1.2	0
0.5	0	19.8	11.1	0.7	0.3	0
0.25	0.8	16.7	6.7	0.1	0.2	0
0.125	2.3	16.4	3.8	0.2	0.3	0.1
0.063	4.8	8.3	2.7	0.4	0.5	0.2
<0.063	92.1	3.5	10.4	1.4	1.5	2.0
Sum	100	100	100	100	100	100

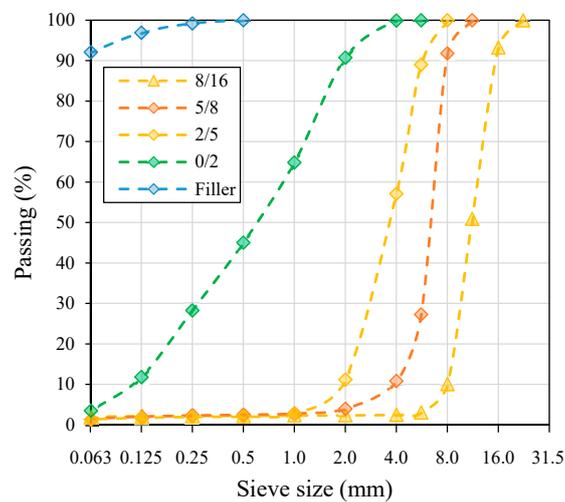


Figure 1. Grading curves of the mineral aggregates used in asphalt concrete (AC 16) mixtures.

3.2. Bitumen Binder and Surfactant

All of the asphalt concrete mixes utilised the 35/50 road paving bitumen, which, in accordance with the requirements of WT-2 [44], is recommended for the binding layer and subbase of pavement with a medium traffic load. As mentioned, the AC 16 mix utilised acidic aggregates (quartzites), it was therefore necessary to use a surface active agent (adhesion promoter) to improve the aggregate’s wettability with the bitumen binder and, thus, provide adequate bitumen-aggregate adhesion. The WBE adhesion promoter was used for this purpose and its content in relation to the bitumen weight amounted to 0.3% for the reference hot mix asphalt (HMA_{Ref}) and 0.6% for the warm mix asphalts.

3.3. Zeolites

The ZeoBau natural zeolite (0–50 μm) was utilized in the laboratory tests. After milling to adequate granulation and drying to remove excess water, this mineral presents a form of grey powder, as presented in Figure 2. Figure 3 presents its microscopic image with grains mostly not exceeding 50 μm , which corresponds to the results of the granulometric analysis conducted while using the air-jet sieving method acc. to EN 933-10 [53], as presented in Figure 4.



Figure 2. Macroscopic image of the ZeoBau 0–50 μm natural zeolite.

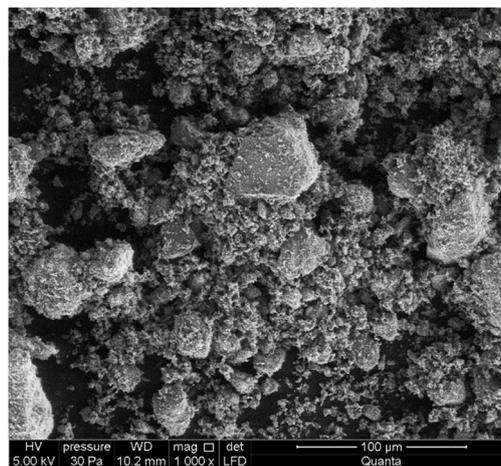


Figure 3. Scanning electron microscope image of the natural zeolite (Quanta FEG 250 SEM).

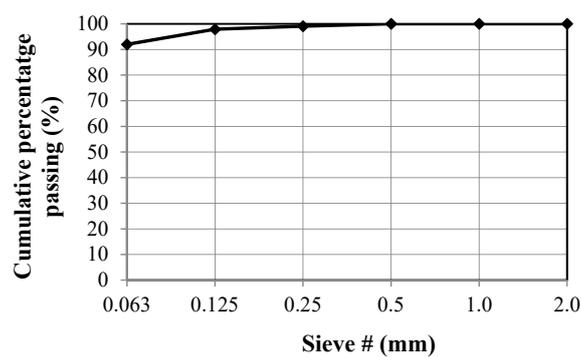


Figure 4. Grading curve of the ZeoBau 0–50 μm natural zeolite.

Figure 5 and Table 4 present the results of the natural zeolite's EDX (energy dispersive X-ray spectroscopy) analysis using the standardless ZAF quantification method in the Quanta FEG 250 Scanning Electron Microscope (FEI / Thermo Fisher, Hillsboro, OR, USA). The dominant elements of natural zeolite are O, Si, and Al, which correspond to the chemical composition specified by the manufacturer. The analysed sample demonstrated additional presence of potassium, calcium, iron, and trace amounts of magnesium and sodium.

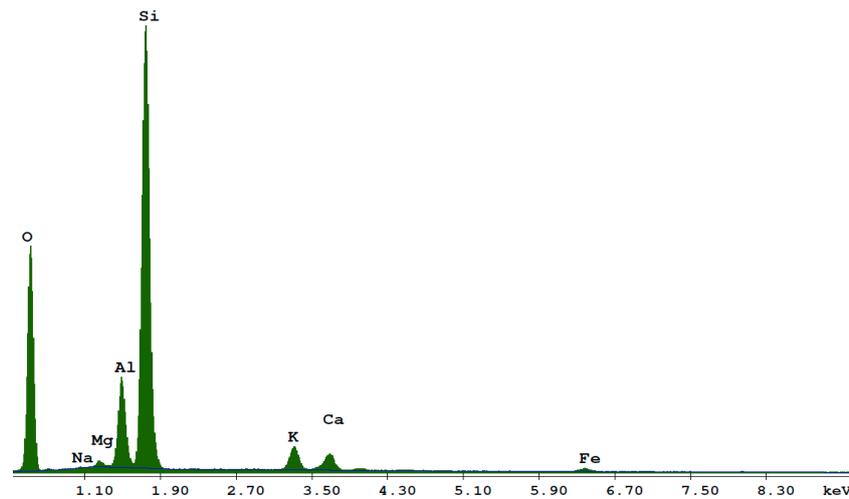


Figure 5. The EDX spectrum of the investigated zeolite sample.

Table 4. The results of EDX analysis using standardless ZAF quantification method of the natural zeolite using the Quanta FEG 250 SEM.

Elem.	wt. %	at. %	k-Ratio	Z	A	F
O K	41.18	56.15	0.1245	1.0310	0.2931	1.0005
Na K	0.07	0.06	0.0003	0.9649	0.4611	1.0059
Mg K	0.55	0.49	0.0034	0.9891	0.6209	1.0119
Al. K	7.68	6.21	0.0564	0.9600	0.7513	1.0183
Si K	42.02	32.64	0.3230	0.9880	0.7772	1.0010
K K	4.00	2.23	0.0333	0.9374	0.8848	1.0043
Ca K	2.92	1.59	0.0254	0.9596	0.9063	1.0007
Fe K	1.59	0.62	0.0137	0.8718	0.9928	1.0000

3.4. Asphalt Concrete Mix

As mentioned before, the investigated asphalt concrete mixes were designed with identical compositions, with changes only in the amounts of the filler and zeolites added. Table 5 provides the framework composition of all the mineral mixtures (mm) and asphalt mixtures (am).

Table 5. Framework composition of the investigated AC 16 asphalt mixes.

Component	Percentage (wt. %)					
	Asphalt Concrete Mixture Type					
	HMA_{Ref}	WMA_{Ref}	$WMA_{nz,0.4\%S}$		$WMA_{nz,1.0\%D}$	
	mm	am	mm	am	mm	am
Filler aggregate	4	3.8	3.6	3.4	3	2.9
Fine natural aggregate 0/2 mm	15	14.3	15	14.3	15	14.3
Continuously graded natural aggregate 0/4 mm	15	14.3	15	14.3	15	14.3
Coarse aggregate 2/5 mm	12	11.5	12	11.5	12	11.5
Coarse aggregate 5/8 mm	12	11.5	12	11.5	12	11.5
Coarse aggregate 8/16 mm	42	40.1	42	40.1	42	40.1
Zeolite	-	-	0.4	0.4	1	0.9
Paving bitumen 35/50	-	4.5 ^{(a),(b)}	-	4.5 ^(b)	-	4.5 ^(b)
Total		100	100	100	100	100

Surface active agent (Wetfix BE) added in the amount: ^(a) 0.3% (by wt.) to HMA_{Ref} ^(b) 0.6% (by wt.) to WMA_{Ref} , $WMA_{nz,0.4\%S}$ and $WMA_{nz,1.0\%D}$.

Table 6 presents the digest of sieving analysis, i.e., filler, (<0.063 mm), sand (from 0.063 to 2 mm), and coarse fraction (>2 mm) content, as well as the density of the designed mineral asphalt mixtures. Figure 6 represents the final grading of the mineral mix along with the boundary grading points.

Table 6. The digest of sieving analysis of the designed asphalt concrete mixtures.

Feature	Asphalt Concrete Mixture Type			
	HMA_{Ref}	WMA_{Ref}	$WMA_{nz,0.4\%S}$	$WMA_{nz,1.0\%D}$
Fraction > 2 mm (%)	71.3		71.3	71.3
Fraction from 0.063 mm to 2 mm (%)	21.7		21.7	21.7
Fraction < 0.063 mm mm (%)	7.0		7.0	7.0
Density ρ_a (Mg/m ³)	2.697		2.695	2.692

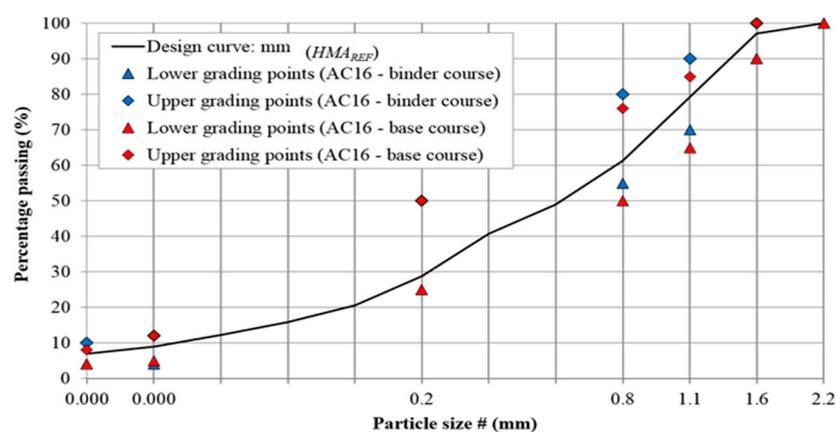


Figure 6. Grading curve of the AC 16 mineral mix with boundary points in accordance to WT-2 [44].

The aforementioned results indicate that the presence of zeolite in the mineral mixes did not cause changes in their granulometry in comparison to reference mixes and only the mineral mixes' density (ρ_a) has slightly changed.

All of the utilised mineral materials met the requirements stated in relevant technical documents [44,52] concerning their use in pavements' binding and base courses.

The design and production of asphalt mixtures featured the use of recommendations specified in relevant technical documents [55]. Prior to the production of asphalt mixtures, the coarse and fine aggregates were heated for 4 h at a temperature of 170 °C (HMA) or 130 °C (WMAs). The adhesion promoter was added to the asphalt before producing the asphalt mixture and its uniform mixing with the binder was ensured. Zeolites were added in adequate proportions to the filler aggregate and then mechanically mixed for 2 h. This "mixed filler" was added to the mix without pre-heating.

The following technological temperatures were used during the production and compaction of asphalt mixtures:

- reference hot-mix HMA_{Ref} (road paving bitumen: 35/50 + 0.3% WBE):
 - bitumen temperature 35/50: 170 °C,
 - temperature of produced mineral-bitumen mix: 160 °C–170 °C,
 - specimen compaction temperature: 140 °C–145 °C,
- reference warm-mix WMA_{Ref} (road paving bitumen: 35/50 + 0.6%WBE):
 - bitumen temperature prior to foaming: 155 °C,
 - temperature of produced mineral-bitumen mix: 120 °C–125 °C,
 - specimen compaction temperature: ca. 100 °C.

- warm mixes WMA_{Ref} , $WMA_{nz,0.4\%S}$ and $WMA_{nz,1.0\%D}$ (road paving bitumen: 35/50 + 0.6%WBE):
 - bitumen temperature prior to foaming: 155 °C,
 - temperature of produced mineral-bitumen mix: 120 °C–125 °C,
 - specimen compaction temperature: ca. 100 °C.

4. Results and Discussions

4.1. Bituminous Binder Properties Prior to Foaming

Tables 7 and 8 present the basic properties of the 35/50 penetration binder with the addition of the WBE adhesion promoter in concentrations from 0.0% to 0.9%.

Table 7. Basic properties of 35/50 asphalt binders with variable amounts of surfactant.

Variable	WBE Percentage (%)	Descriptive Statistics					
		Valid N	Mean	Min.	Max.	Std. Dev.	CV (%)
Penetration in 25 °C (Pen_{25}) (0.1 mm)	0.0	10	36.6	35.0	38.0	1.17	3.21
	0.3	10	40.8	38.3	43.6	1.59	3.90
	0.6	10	41.5	40.3	43.2	0.95	2.30
	0.9	10	42.9	40.2	45.2	1.82	4.25
Softening point ($T_{R\&B}$) (°C)	0.0	4	54.3	53.8	54.6	0.36	0.66
	0.3	4	53.9	53.8	54.1	0.13	0.23
	0.6	4	53.7	53.6	53.8	0.08	0.15
	0.9	4	53.4	53.3	53.6	0.13	0.24
Fraass breaking point (T_{Fraass}) (°C)	0.0	3	−13.7	−14.0	−13.0	0.58	4.22
	0.3	3	−13.3	−15.0	−12.0	1.53	11.46
	0.6	3	−12.7	−13.0	−12.0	0.58	4.56
	0.9	3	−12.3	−13.0	−11.0	1.16	9.36

Table 8. Calculated penetration index (PI) and temperature plasticity range (PR) of 35/50 asphalt binders with variable amounts of surfactant.

WBE Percentage (%)	PI	PR (°C)
0.0	−0.9	68.0
0.3	−0.7	67.2
0.6	−0.7	66.4
0.9	−0.7	65.7

The use of the WBE additive caused an increase in penetration from 36.6 (0.1 mm) at the WBE's concentration of 0.0% to 42.9 (0.1 mm) at the WBE's concentration of 0.9% in the bitumen binder. In the case of the softening and breaking points, a slight impact of using the WBE additive at 0.3% and 0.6% to the 35/50 binder was noted. The difference in results for the first feature did not exceed 1 °C, whereas it amounted to 1.4 °C for T_{Fraass} .

When evaluating the calculated penetration indexes that enable initial asphalt classification in terms of their temperature sensitivity, it was observed that these values increased as a result of adding the surface active agent. These amounted to −0.9 for pure asphalt, whereas the bitumen with the adhesion promoter in concentrations of 0.3%, 0.6%, and 0.9% obtained a PI values of −0.7.

In road construction, the usually used of bitumens range in PI from −2.0 to +2.0, but it is recommended to use the asphalts with the PI from −1.0 to +1.0 [56]. Based on the obtained values of this parameter, the tested binders can be classified as rheological sol-gel with the penetration index from −2 to +2. The introduction of the adhesion promoter resulted in a slight decrease of the temperature plasticity range of the base road paving bitumen. The PR value was decreased from the initial 68.0 °C to 65.7 °C at the 0.9% concentration of the additive.

It can be observed that the highest coefficient of variance was recorded for T_{Fraass} (11.2%) and the lowest for $T_{R\&B}$ (average value of 0.32%) when analysing the descriptive statistics. On the other hand, the Pen_{25} parameter had an average value of 3.41%.

An analysis of variance was carried out in the statistical evaluation of the impact of the WBE additive content on the basic parameters of bitumen binders, the results of which are presented in Table 9.

Table 9. Results of analysis of variance (one-way ANOVA) assessing the effects of WBE content on the basic properties of the tested bituminous binders.

Variable	Effect	SS	Df	MS	F	p-Value
Penetration in 25 °C Pen_{25}	Intercept	52,141.68	1	52,141.68	23,150.84	<0.001
	WBE percentage	23.34	2	11.67	5.18	0.012466
	Error	60.81	27	2.25		
Softening point $T_{R\&B}$	Intercept	34,582.80	1	34,582.80	2,706,480	<0.001
	WBE percentage	0.50	2	0.25	20	0.000522
	Error	0.12	9	0.01		
Fraass breaking point T_{Fraass}	Intercept	1469.444	1	1469.444	1102.083	<0.001
	WBE percentage	1.556	2	0.778	0.583	0.586816
	Error	8.000	6	1.333		

Df—degrees of freedom, SS—Sum of Squares, MS—Mean squares.

It is possible to state that the WBE adhesion promoter had a statistically significant impact on the Pen_{25} and $T_{R\&B}$ parameters, because the p -value < 0.05 was achieved, after the analysis of the obtained p -values for the F statistic (Table 9), with the assumed significance level of $\alpha = 0.05$. Statistically significant impact of the WBE was not proven only in the case of the last feature (T_{Fraass}).

4.2. Foamed Bitumen Binder Properties

Table 10 presents the characteristics of the foamed reference 35/50 penetration grade road paving bitumen. The analysed binder was characterised by the lowest expansion ratio at low foaming water contents, which increased along with the FWC increase. In the case of the bitumen foam half-life, this dependency was inverted, and the HL value proportionally decreased to the increase in the foamed water content. At the the lowest FWC = 1.5% the recorded bitumen foam characteristics amounted to $ERm = 7.3$ and $HL = 38.3$ s, while, at the highest FWC = 3.5%, the expansion ratio was more than doubled (16.3) and half-life was almost halved (20.3 s).

Table 10. Foaming performance of the reference 35/50 penetration bitumen.

FWC	Valid N	ERm (–)					HL (s)				
		Mean	Min.	Max.	Std. Dev.	CV (%)	Mean	Min.	Max.	Std. Dev.	CV (%)
1.5%	4	7.3	7.0	8.0	0.50	6.90	38.3	37.0	40.0	1.50	3.92
2.0%	4	9.5	9.0	10.0	0.58	6.08	32.8	31.0	34.0	1.26	3.84
2.5%	4	11.8	11.0	13.0	0.96	8.15	27.5	26.0	29.0	1.29	4.69
3.0%	4	14.3	13.0	16.0	1.26	8.83	24.5	23.0	26.0	1.29	5.27
3.5%	4	16.3	15.0	18.0	1.26	7.74	20.3	19.0	21.0	0.96	4.73

To evaluate the impact of the WBE adhesion promoter on the foaming properties of the 35/50 bituminous binder, its foaming performance was evaluated at different levels of foaming water content and WBE content while using response surface method with first order and interaction terms. Figure 7a,b present the response surfaces derived for ERm maximum expansion and the HL half-life as a function of foaming water content and the WBE additive content. Tables 11 and 12 present the statistical evaluation of these models' parameters.

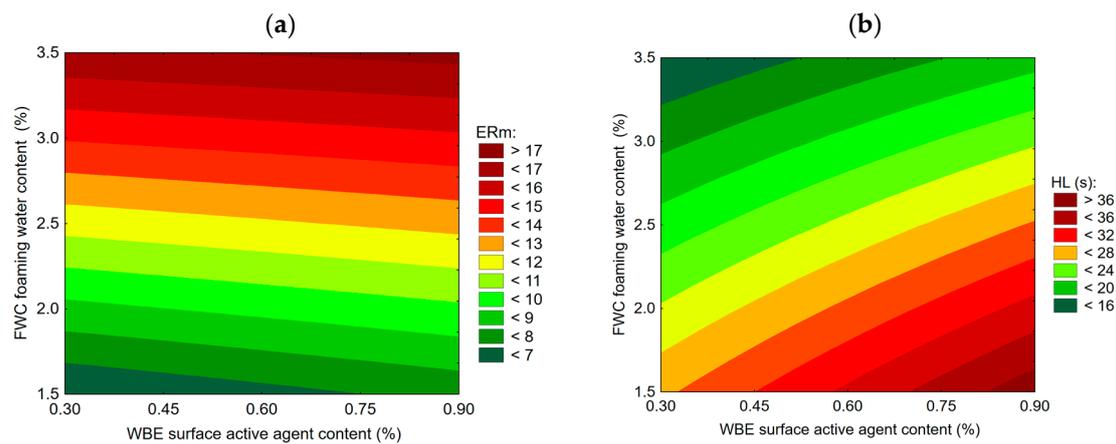


Figure 7. The foaming performance of 35/50 penetration bitumen as a function of foaming water and WBE contents: expansion ratio (a), half-life (b).

Table 11. Statistical analysis of the model predicting ERm of 35/50 foamed bitumen based on the foaming water content, WBE content, and their interaction.

Variable	Estimate	Std. Error	T Value	Pr(> t)
Intercept	−2.78393	1.82614	−1.5245	0.13042
WBE	3.32847	2.89098	1.1513	0.25222
FWC	5.41563	0.70269	7.7069	0.00000
WBE * FWC	−0.72934	1.11274	−0.6554	0.51364

Regression Summary: ERm (35/50 + WBE)

Multiple R^2 : 0.8333, Adjusted R^2 : 0.8285 F -statistic: 173.3 on 3 and 104 DF, p -value: $< 2.2 \times 10^{-16}$

Table 12. Statistical analysis of the model predicting HL of 35/50 foamed bitumen based on the foaming water content, WBE content and their interaction.

Variable	Estimate	Std. Error	T Value	Pr (> t)
Intercept	31.7447	4.3541	7.2907	0.00000
WBE	22.1424	6.8931	3.2123	0.00175
FWC	−5.8413	1.6755	−3.4864	0.00071
WBE*FWC	−3.8837	2.6531	−1.4638	0.14626

Regression Summary: HL (35/50 + WBE)

Multiple R^2 : 0.7364, Adjusted R^2 : 0.7288 F -statistic: 96.86 on 3 and 104 DF, p -value: $< 2.2 \times 10^{-16}$

The results of foaming of the 35/50 asphalt with the WBE adhesion promoter additive that are presented in Figure 7a indicate a very limited impact of the adhesion promoter content on the maximum expansion, which is, therefore, mainly affected by the foaming water content (Table 11). In the case of the bitumen foam half-life, it was, however, demonstrated that increasing the WBE content caused a significant increase in the foam's half-life (Figure 7b, Table 12). It can be concluded that adding WBE agent resulted in minor decrease of maximum expansion and a significant increase in half-life.

When comparing the results of the reference binder and the 35/50 bitumen with the initial addition of 0.3% of WBE, the adhesion promoter had minor impact on expansion and it significantly shortened the bitumen foam half-life.

Figure 8a,b present the results of evaluation and optimisation of the tested binders' composition in the function of the WBE additive content and the foaming water content, based on their foaming performance. Two independent methods were used to simultaneously evaluate the foaming

performance (ERm and HL)—the desirability function (Figure 8a) and the method of designating the intersection of the ERm and HL foaming characteristics (Figure 8b), as specified in publications [40,41,57].

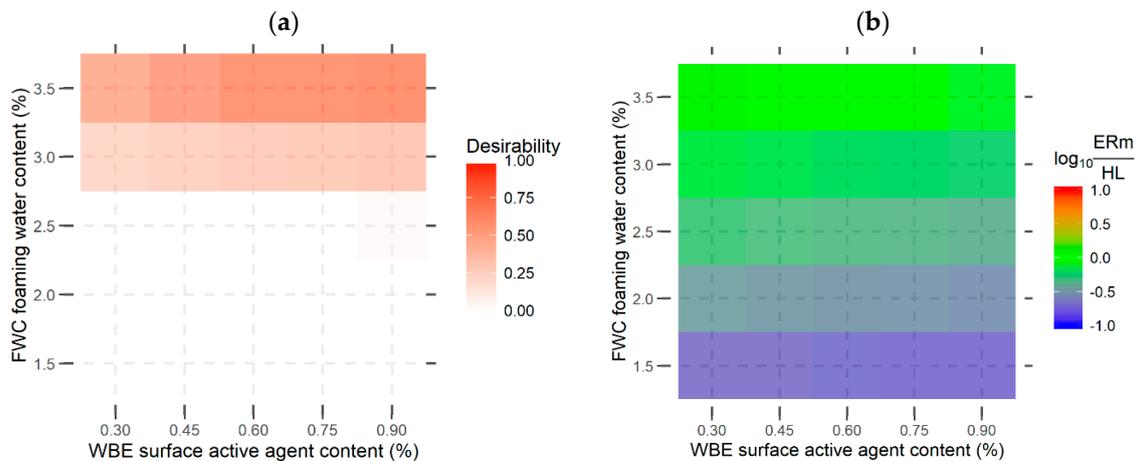


Figure 8. Evaluation of the foaming features of the 35/50 asphalt with the WBE additive: (a) desirability function, (b) the \log_{10} of the ratio of foam's maximum expansion and half-life.

The applied desirability function assigned a certain value of desirability D to each experiment point (defined by a combination of the foaming water content and WBE content). The desirability is only assigned a positive non-zero value when all of the specified boundary conditions were simultaneously met (i.e., $ERm \geq 12$ and $HL \geq 10$ s). The desired ERm and HL levels were based on previous experiences and literature [40,41,57,58]. The desirability function applied in this case is assigned with the following values:

- 0: if $ERm < 12$ or $HL < 10$ s,
- 0 to 1: if $20 > ERm \geq 12$ or $16 > HL \geq 10$ s,
- 1: if $ERm \geq 20$ s and $HL \geq 16$ s.

The second method that was employed for evaluating the foaming was based on designating the intersection of the ERm and HL foaming features (numeric equality of ERm and HL), and mathematically was performed by calculating the $\log_{10}(\frac{ERm}{HL})$, which was equal to:

- 0: for $ERm = HL$ (when ERm and HL are equal, i.e., they intersect),
- 1: for $ERm = 10 \cdot HL$,
- -1: for $10 \cdot ERm = HL$.

The applied method that was based on presenting the common logarithm from the ERm 's and HL 's ratio on the chart was found to be convenient for representing the ratio of the two features on a plane with the use of a colour scale.

The values of the desirability function D that are presented in Figure 8a indicate that meeting the boundary foaming parameters requires the 35/50 binder with the WBE additive to be foamed with at least 3% of foaming water content. The additive content had minor impact on the quality of the asphalt foam evaluated using the desirability function due to the minor impact of the WBE additive content on the maximum expansion (and its relatively low values). The intersection of binder foaming characteristics (ERm and HL) occurred at ca. FWC = 3.5% and the WBE additive content = 0.30–0.45 (Figure 8b).

When considering the prior experiences and the aforementioned results of bitumen binder testing, further laboratory testing (for WMA asphalts with foamed asphalt) featured the use of a binder with 0.6% of the surfactant content, characterised by $ER = 14.1$, $HL = 20.5$ s at FWC = 3.0%.

4.3. AC 16 Mixes' Compactability Test Results

It was decided to firstly conduct the compactability testing in the gyratory compactor acc. to EN 12697-31 in order to determine the usefulness of the natural zeolite additive for the AC 16 asphalt concrete mix produced with water foamed asphalt and with lowered process temperatures [51].

Figure 9 and Table 13 present the compactability of the tested HMA_{ref} and WMA_{ref} reference mixes as well as the ones including 0.4% soaked natural zeolites (with 20% moisture content by wt.) and 1% of zeolites in a air-dry state, $WMA_{nz,0.4\%S}$ and $WMA_{nz,1.0\%D}$, respectively.

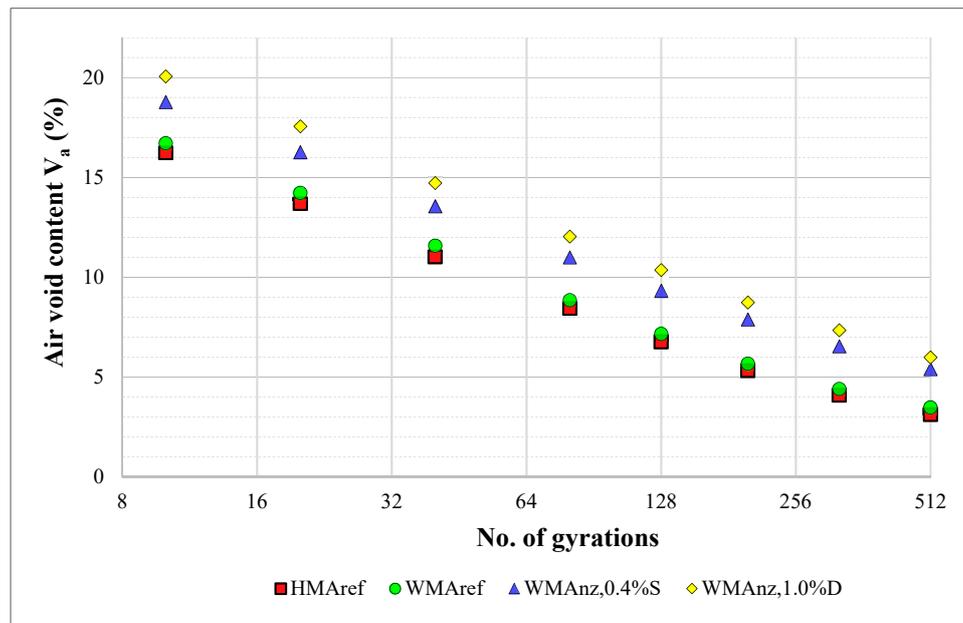


Figure 9. Results of the compactability analysis of the AC 16 mixes compacted in the gyratory compactor; mean values of the samples' air voids content V_a .

Table 13. Results of the compactability analysis of the AC 16 mixes compacted in the gyratory compactor; mean values of the samples' air voids content V_a .

No. of Gyrations	Air Void Content V_a (%)			
	HMA_{ref}	WMA_{ref}	$WMA_{nz,0.4\%S}$	$WMA_{nz,1.0\%D}$
10	16.23	16.71	18.77	20.06
20	13.69	14.22	16.26	17.56
40	11.02	11.58	13.55	14.72
80	8.44	8.85	10.99	12.04
128	6.76	7.16	9.33	10.36
200	5.33	5.67	7.88	8.74
320	4.09	4.41	6.54	7.35
512	3.12	3.48	5.40	5.99

When analysing the presented compactability curves, it is possible to state that both reference mixes were characterised by similar compactability. The introduction of zeolites into the mixtures with foamed bitumen had a substantial impact on their compaction process, resulting in an increased air void content during the whole compaction process, on average by approximately 2.1 to 3.1% in the case of soaked and air-dry zeolites, respectively. It was also found that the water-soaked zeolites added in smaller amounts resulted in more efficient compaction when compared to the 1.0% addition of air-dry zeolites.

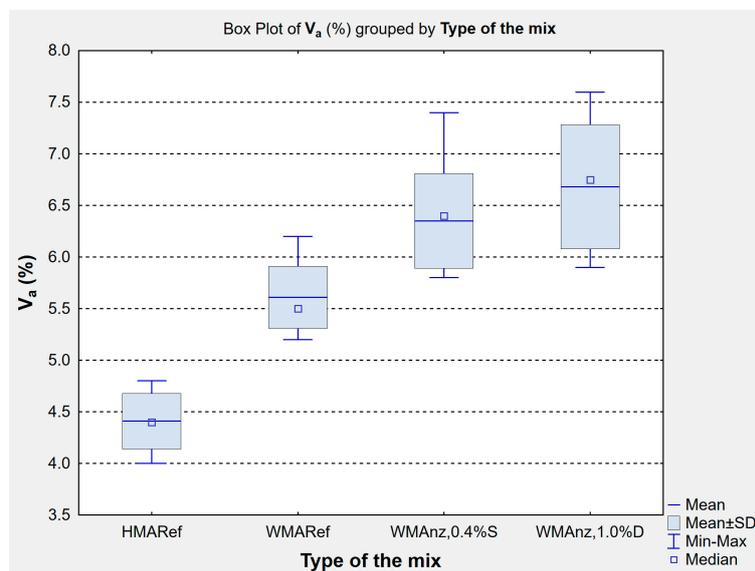
There are at least two possible explanations for these effects. On one hand, the temperatures of WMA mixes' production and compaction (approx. 120 °C and approx. 100 °C, respectively) were not high enough to cause zeolite water to release at sufficient rate. Thereby, the additional effects of asphalt foaming due to adding zeolite could be insignificant and, furthermore, the forming asphalt mastic became stiffened due to adding zeolite, which is confirmed by other researchers' studies [27]. On the other hand, the observed phenomenon could be also related to the reported findings [58] about the negative impact of higher foamed water contents on the asphalt mixture workability—the addition of zeolites has substantially increased the quantity of water delivered to the asphalt mix.

4.4. Results of Volumetric and Mechanical Tests Performed on the AC 16 Mixtures

4.4.1. Air Void Content (V_a), Indirect Tensile Strength (ITS_s , $ITS_{freeze-thaw}$), Water and Frost Resistance ($ITSR$)

The obtained volumetric and mechanical properties of the investigated asphalt mixtures are presented as bar charts that are supplemented with error bars denoting standard deviations of the respective means.

Figure 10 presents the results of air void content measured in Marshall compacted samples.

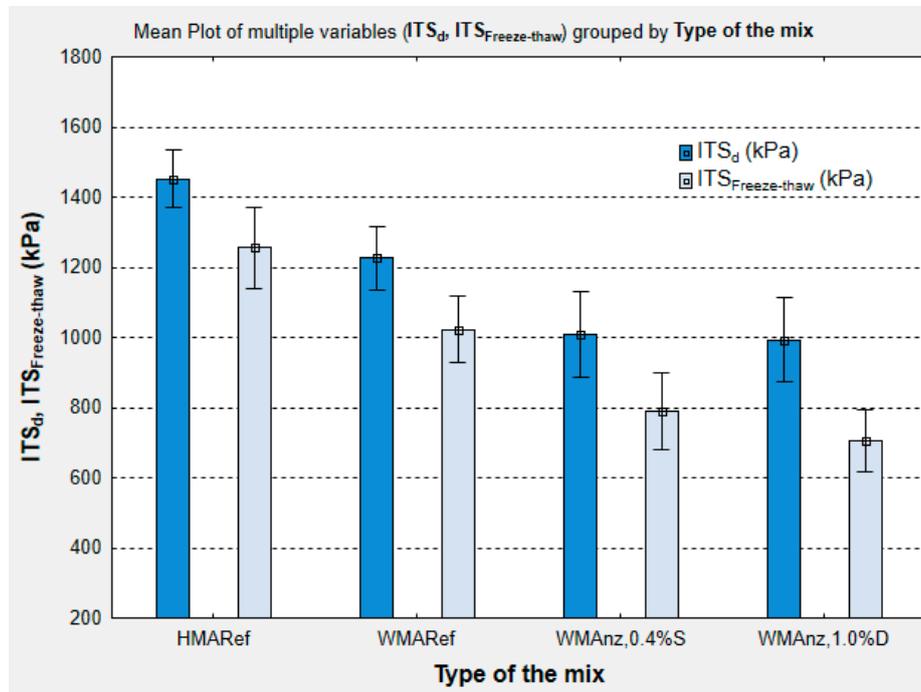


Descriptive Statistics	Type of Mix			
	HMA_{ref}	WMA_{ref}	$WMA_{nz,0.4\%S}$	$WMA_{nz,1.0\%D}$
Mean, \bar{X}	4.41	5.61	6.35	6.68
Standard deviation, s	0.27	0.30	0.46	0.60
Coefficient of variance, v	6.1	5.3	7.2	9.0

Figure 10. Results of air void content (V_a) determination in Marshall samples produced from the investigated AC 16 mixtures.

The determination of air void contents V_a in the Marshall compactor (75 impacts per side, 2×75 in total) samples confirmed the findings that were obtained in the compactability testing using the gyratory compactor, which indicated substantial impact of the natural zeolite (air-dry and water-soaked) addition to the foamed WMA mixes on their compaction. The zeolite-containing $WMA_{nz,0.4\%S}$ and $WMA_{nz,1.0\%D}$ mixtures obtained visibly higher air void contents than it was in the case of both reference mixes (HMA_{ref} and WMA_{ref}). The introduction of zeolites to the foamed WMA mixtures resulted in increased air void contents of the tested samples with only small difference in V_a over the two mixtures, with $V_a = 6.35\%$ and $V_a = 6.68\%$ in the $WMA_{nz,0.4\%S}$ and $WMA_{nz,1.0\%D}$ mixtures, respectively.

Figure 11 presents the results of indirect tensile strength testing of dry samples and samples subjected to conditioning with a single freeze-thaw cycle, produced from the tested asphalt mixes (HMA_{ref} , WMA_{ref} , $WMA_{nz,0.4\%S}$ and $WMA_{nz,1.0\%D}$), with the aim of designating the water and the frost sensitivity indices ($ITSR$).



Descriptive Statistics	Type of Mix							
	HMA_{ref}	WMA_{ref}	$WMA_{nz,0.4\%S}$	$WMA_{nz,1.0\%D}$	HMA_{ref}	WMA_{ref}	$WMA_{nz,0.4\%S}$	$WMA_{nz,1.0\%D}$
	ITSdry (kPa)				ITSfreeze-Thaw (kPa)			
Mean, X	1452.68	1225.65	1008.16	993.94	1255.17	1022.22	790.91	762.39
Standard deviation, s	82.10	92.27	121.20	121.35	113.92	94.70	109.02	97.10
Coefficient of variance of variance, v	5.7	7.7	121.35	12.2	9.1	9.3	13.8	12.7

Figure 11. Results of indirect tensile strength (ITS_{dry} and $ITS_{freeze-thaw}$) determination in Marshall samples produced from the investigated AC 16; error bars represent ± 1 standard deviation from the mean.

The results of tested mechanical parameters show that the addition of natural zeolite to the tested asphalt mixtures also had a substantial impact on the indirect tensile strength of the Marshall samples. Both of the tested mixes with zeolites achieved comparable indirect tensile strengths. In the case of the dry specimens, the difference between average ITS_{dry} values that are produced by the two zeolite-containing mixtures was only 14 kPa, whereas the results obtained in the samples subjected to a single freeze-thaw cycle, the difference was twice as high and amounted to 28.5 kPa. The strength results of the AC 16 mixes with zeolites were substantially lower than the results of the reference mixes, i.e., the ITS_{dry} values of the zeolite mixtures were on average lower by ca. 220 kPa than WMA_{ref} and by ca. 450 kPa than HMA_{ref} . In terms of the $ITS_{freeze-thaw}$ parameter, the mixes with zeolites achieved values that were lower by ca. 250 kPa and by approx. 500 kPa in comparison to the reference mixes produced, respectively, in the WMA and HMA technology.

The descriptive statistics (Figures 10 and 11), show that the WMAs containing natural zeolites exhibited the highest coefficients of variation in the tested volumetric and mechanical parameters when compared to the reference mixes, i.e., without zeolites.

The results of indirect tensile strength testing were used to calculate the water and frost susceptibility indices (*ITSR*), which Figure 12 presents.

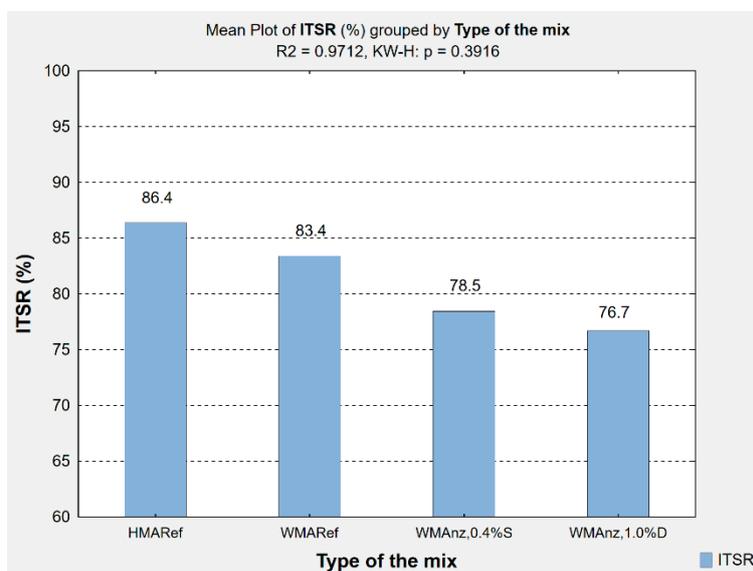


Figure 12. Results of water and frost susceptibility indices (*ITSR*) determination in the Marshall samples produced from the investigated AC 16.

The analysis of the water and frost susceptibility index after a single freeze-thaw cycle (*ITSR*) demonstrated a substantial impact of using natural zeolite, both dry and water-soaked, in the WMA mixes with foamed bitumen. In comparison to WMA_{ref} , the WMA mix with 0.4% of water-soaked zeolite was characterised by *ITSR* that was reduced by 4.95 percent points (78.54%), whereas the mix asphalt with 1% of dry zeolite achieved an *ITSR* of 76.7%. The decreased values of the *ITSR* parameter in the samples that were produced from the asphalt mixtures with zeolites can be partially attributed to the increased air void content and greater bitumen absorptivity of zeolites than in the case of limestone powder (the mineral filler used), as confirmed by other researchers' studies [27].

In reference to the requirements that were applicable to HMA mix asphalts, all of them met the requirements for the base course ($ITSR > 70\%$) in selected CEN member states [4], whereas the reference mix asphalts (HMA and WMA) have also met the requirements for the binding layer.

4.4.2. Statistical Analysis of the Test Results

A statistical analysis of the test results supplemented the estimation of the impact of using zeolites in the composition of warm mix asphalt with foamed bitumen on their physical and mechanical properties. The analyses included a deduction about the significance of differences between the average values of the measured variables (V_a , ITS_S , $ITS_{freeze-thaw}$) in terms of mixture composition and production method (HMA_{ref} , WMA_{ref} , $WMA_{nz,0.4\%S}$ and $WMA_{nz,1.0\%D}$) while using the analysis of variance (one-way ANOVA). It was possible to use the F (Fisher-Snedecor) parametric test that enables simultaneously comparing several mean values due to the conformity of the variables' distribution with the standard distribution and meeting the assumption of homogeneity of variances in the evaluated groups. The estimation of the significance in multiple comparisons of the differences between the tested groups was executed in a Tukey *post-hoc* test due to the fact that for all tested variables the main effects yielded statistical significance in the general F test. This allowed for identifying the specific mean values differing from one another.

Table 14 summarises the results of the one-way ANOVA testing for the impact of the type of mixture on the physical and mechanical test results. Table 15 presents the results of the Tukey multiple comparisons test.

Table 14. The results of one-way ANOVA investigating significance of the type of mixture (HMA_{ref} , WMA_{ref} , $WMA_{nz,0.4\%S}$ and $WMA_{nz,1.0\%D}$) in relation to the dependent variables: V_a , ITS_{dry} , $ITS_{freeze-thaw}$.

Dependent Variable	Effect	df	SS	MS	F	p-Value
V_a	Intercept	1	1328.256	1328.256	7246.132	<0.001
	Type of mixture	3	30.395	10.132	55.272	<0.001
	Error	36	6.599	0.183	–	–
ITS_{dry}	Intercept	1	43,812,546	43,812,546	3923.329	<0.001
	Type of mixture	3	1,121,516	373,839	33.477	<0.001
	Error	28	312,681	11,167	–	–
$ITS_{freeze-thaw}$	Intercept	1	28,493,702	28,493,702	2730.283	<0.001
	Type of mixture	3	1,463,382	487,794	46.741	<0.001
	Error	28	292,213	10,436	–	–

df—degrees of freedom, SS—Sum of Squares, MS—Mean squares.

Table 15. Results of post-hoc Tukey multiple comparison test.

Tukey HSD Test, Variable V_a (%)					
Approximate Probabilities for Post Hoc Tests					
Error: Between MS = 0.18331; df = 36					
Type of Mix		{1} 4,41	{2} 5,61	{3} 6,35	{4} 6,68
HMA_{ref}	{1}	-	0.000159	0.000159	0.000159
WMA_{ref}	{2}	0.000159	-	0.002522	0.000174
$WMA_{nz,0.4\%S}$	{3}	0.000159	0.002522	-	0.326804
$WMA_{nz,1.0\%D}$	{4}	0.000159	0.000174	0.326804	-
Tukey HSD Test; Variable ITS_{dry} (kPa)					
Approximate Probabilities for Post Hoc Tests					
Error: Between MS = 11167; df = 28					
Type of Mix		{1} 1452.7	{2} 1225.6	{3} 1008.2	{4} 993.94
HMA_{ref}	{1}	-	0.001146	0.000164	0.000164
WMA_{ref}	{2}	0.001146	-	0.001767	0.000936
$WMA_{nz,0.4\%S}$	{3}	0.000164	0.001767	-	0.993100
$WMA_{nz,1.0\%D}$	{4}	0.000164	0.000936	0.993100	-
Tukey HSD Test; Variable $ITS_{freeze-thaw}$ (kPa)					
Approximate Probabilities for Post Hoc Tests					
Error: Between MS = 10436; df = 28					
Type of Mix		{1} 1255.2	{2} 1022.2	{3} 790.90	{4} 762.39
HMA_{ref}	{1}	-	0.000640	0.000164	0.000164
WMA_{ref}	{2}	0.000640	-	0.000684	0.000168
$WMA_{nz,0.4\%S}$	{3}	0.000164	0.000684	-	0.364158
$WMA_{nz,1.0\%D}$	{4}	0.000164	0.000168	0.364158	-

The analysis of the ANOVA table and the obtained p -values for the F statistic (Table 14), with the assumed a significance level of $\alpha = 0.05$, it is possible to state that the type of the asphalt mix was statistically significant in the scope of all the tested parameters. It was possible to use the multiple comparisons test to determine which mix asphalts significantly differed from one another due to the fact that all considered parameters achieved a p -value < 0.05.

The multiple comparisons tests demonstrated (Table 15) that the performance of the WMA mixtures containing zeolites ($WMA_{nz,0.4\%S}$ and $WMA_{nz,1.0\%D}$) can be considered to be similar to each other, i.e., the differences between the measured average values of V_a , ITS_d and $ITS_{freeze-thaw}$ of these mixtures were not proven to be statistically significant. Meanwhile, the HMA_{ref} and WMA_{ref} mixtures significantly differed from each other and the WMA zeolite mixes in the terms of both the volumetric and mechanical performance.

5. Conclusions

The presented research was conducted to evaluate the impact of natural zeolites on the properties of warm mix AC 16 asphalt concrete mixtures with foamed bitumen.

The first stage of the investigations included the determination of the foaming performance of the bitumen with an adhesion promoter added in 0.0–0.9% concentration. It was found that the presence of the surfactant influenced the bitumen foam half-life to a higher degree than the maximum expansion ratio. The optimum foaming content was determined at 3.0%.

The main body of conducted research concerned the evaluation of two modes of zeolite dosing to the foamed WMA mixtures: air-dry zeolites (with ca. 7.4% moisture content) added at 1.0% by wt. of the mixture and water-soaked zeolites (with 20% total moisture content) added at 0.4% by wt. of the mix. The results of these investigations allowed for the formulation of the following conclusions:

- the use of natural zeolites in the AC 16 asphalt concrete mix that was produced in the WMA technology with foamed bitumen caused a change in its volumetric and mechanical parameters when compared to the reference asphalt mixes (HMA and WMA) without zeolites;
- the addition of natural zeolites has substantially affected the compactability of WMA mixtures measured in gyratory compactor: the tests demonstrated increased air void contents by as much 1.9 to 3.9% in comparison to the reference WMA mixture;
- in the evaluation of the Marshall compacted samples, natural zeolite dosage into the asphalt concrete mix caused an increase in the air void content by ca. 2% in the case the $WMA_{nz,0.4\%S}$ mixture containing water-soaked zeolite in the quantity of 0.4% and by ca. 3% for the $WMA_{nz,1.0\%D}$ mixtures containing 1.0% of dry zeolite in relation to reference warm mix asphalt;
- the amount and mode of dosing of the natural zeolites ($WMA_{nz,0.4\%S}$, $WMA_{nz,1.0\%D}$) had no significant impact on the tested properties (V_a , ITS_{dry} , $ITS_{freeze-thaw}$, $ITSR$) of Marshall compacted samples of the AC 16 foamed warm mix asphalt concrete; the difference in the ITS_{dry} between the $WMA_{nz,0.4\%S}$ and $WMA_{nz,1.0\%D}$ asphalt mixtures amounted to 14 kPa, and for $ITS_{freeze-thaw}$ it amounted to 28.5 kPa, which was also a minor difference;
- the indirect tensile strengths of the samples that were produced from asphalt mixtures containing natural zeolites in comparison to the reference WMA_{ref} mix were reduced by approx. 220 kPa in dry state (ITS_{dry}) and by approx. 250 kPa after a freeze-thaw cycle ($ITS_{freeze-thaw}$), as a result the warm mixtures containing zeolites exhibited increased susceptibility to water and frost ($ITSR$);
- based on the test results, it was inferred that the decreased mechanical parameters (ITS_d , $ITS_{freeze-thaw}$, $ITSR$) of the analysed WMA mixtures with foamed bitumen and zeolites were partially caused by the increased air void contents; and,
- all of the WMA mix asphalts with foamed bitumen, including those containing zeolites achieved low susceptibility to water and frost ($ITSR > 70\%$) fulfilling the requirements for the base courses in the selected CEN member states [4], whereas the reference asphalt mixes (HMA_{ref} and WMA_{ref}) have also met the requirements for the binding layers ($ITSR > 80\%$).

The study has shown that investigated WMA's with foamed bitumen produced at ca. 120 °C did not benefit from the addition of zeolites. The warm foamed mixtures with additional doses of zeolites exhibited decreased compactability, which resulted in increased air void contents, decreased ITS strengths and moisture resistance. Based on the findings of other researchers, several explanations have been proposed for these effects. The decreased compactability could be a result of the significantly increased amount of total foaming water introduced with the zeolites, which has been previously reported to worsen the workability of WMA's with foamed bitumen. Inferior mix performance could also stem from the increased bitumen absorptivity of the zeolite-bearing filler fraction, leaving less "free bitumen" in the mixture and, thus, rendering the designed mix composition suboptimal. It was also indicated that the simultaneous use of mechanical water foaming and introduction of zeolites could require increased mixture processing temperatures for improved performance.

Based on these premises, further works in this field are aimed at investigating the properties of the foamed WMA mixtures with different dosages of zeolites being produced at higher temperatures, as well as at broadening the scope of the tests to assess the rutting, low temperature, and stripping performance of this type of mixtures.

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References

- Jenkins, K.J. Mix Design Considerations for Cold and Half-Warm Bituminous Mixes with Emphasis on Foamed Bitumen. Ph.D. Thesis, University of Stellenbosch, Stellenbosch, South Africa, 2000.
- Jenkins, K.J.; de Groot, J.L.A.; Van de Ven, M.F.C.; Molenaar, A.A.A. Half-warm foamed bitumen treatment, a new process. In Proceedings of the 7th Conference on Asphalt Pavements for Southern Africa, Livingstone, Zimbabwe, 30 August–2 September 1999.
- Jenkins, K.J.; Molenaar, A.A.; de Groot, J.L.A.; Van de Ven, M.F.C. Foamed Asphalt Produced Using Warmed Aggregates. *J. Assoc. Asph. Paving Technol.* **2002**, *71*, 444–478.
- Chomicz-Kowalska, A.; Gardziejczyk, W.; Iwański, M.M. Moisture resistance and compactibility of asphalt concrete produced in half-warm mix asphalt technology with foamed bitumen. *Constr. Build. Mater.* **2016**, *108–118*. [[CrossRef](#)]
- Chomicz-Kowalska, A.; Gardziejczyk, W.; Iwański, M.M. Analysis of IT-CY stiffness modulus of foamed bitumen asphalt concrete compacted at 95 °C. *Procedia Eng.* **2017**, *172*, 550–559. [[CrossRef](#)]
- Woszek, A.; Panek, R.; Madej, J.; Zofka, A.; Franus, W. Mesoporous silica material MCM-41: Novel additive for warm mix asphalts. *Constr. Build. Mater.* **2018**, *183*, 270–274. [[CrossRef](#)]
- Iwański, M.M.; Chomicz-Kowalska, A.; Maciejewski, K. Impact of Additives on the Foamability of a Road Paving Bitumen. In *IOP Conference Series: Materials Science and Engineering 603*; IOP Publishing: Bristol, UK, 2019. [[CrossRef](#)]
- Prowell, B.; Hurley, G.; Frank, B. *Warm-Mix Asphalt: Best Practices*, 3rd ed.; National Asphalt Pavement Association: Greenbelt, MD, USA, 2012.
- Iwański, M.; Chomicz-Kowalska, A.; Maciejewski, K. Application of synthetic wax for improvement of foamed bitumen parameters. *Constr. Build. Mater.* **2015**, *83*, 62–69. [[CrossRef](#)]
- Iwański, M.M.; Chomicz-Kowalska, A.; Maciejewski, K. Effect of Surface Active Agent (SAA) on 50/70 Bitumen Foaming Characteristics. *Materials* **2019**, *12*, 3514. [[CrossRef](#)] [[PubMed](#)]
- Larsen, O.R.; Moen, O.; Robertus, C.; Koenders, B.G. WAM foam asphalt production at lower operating temperatures as an environmental friendly alternative to HMA. In Proceedings of the 3rd Eurasphalt & Eurobitume Congress, Vienna, Austria, 12–14 May 2004; p. 137.
- Auerbach, S.M.; Carrada, K.A.; Dutta, P.K. *Handbook of Zeolite Science and Technology*; Marcel Dekker, Inc.: New York, NY, USA, 2003.

13. Ciczyszwił, G.W.; Andronikaszwili, T.G. *Zeolity Naturalne [Natural Zeolites]*; Wydawnictwo Naukowo-Techniczne: Warszawa, Poland, 1990.
14. Kasperkowiak, M. *Materiały Mikro-i Mezoporowate Jako Napelnicze Aktywne. [Micro- and Mesoporous Materials as Active Fillers]*. Ph.D. Thesis, Poznan University of Technology, Poznań, Poland, 2014.
15. Lippmaa, E.; Mägi, M.; Samoson, A.; Tarmak, M.; Engelhardt, G. Investigation of the Structure of Zeolites by Solid-State High-Resolution Silicon-29 NMR Spectroscopy. *J. Am. Chem. Soc.* **1981**, *103*, 4992–4996. [[CrossRef](#)]
16. Sassani, A. *A Multi-Scale Approach to Characterization of Volcanic Natural Pozzolans*. Master's Thesis, Middle East Technical University, Ankara, Turkey, 2014.
17. Sassani, A.; Turanli, L.; Emwas, A.H.; Meral, C. Mechanical performance, durability and aluminosilicate chain structure of high volume zeolitic natural pozzolan-portland cement based systems. In *Proceedings of the ZEOLITE 2014—9th International Conference on the Occurrence, Properties, and Utilization of Natural Zeolites*, Belgrade, Serbia, 8–13 June 2014; Institute for Technology of Nuclear and Other Mineral Raw Materials: Belgrade, Serbia, 2014.
18. Feng, N.; Peng, G. Applications of natural zeolite to construction and building materials in China. *Constr. Build. Mater.* **2005**, *579–584*. [[CrossRef](#)]
19. Uzal, B.; Turanli, L. Blended cements containing high volume of natural zeolites: Properties, hydration and paste microstructure. *Cem. Concr. Compos.* **2012**, *34*, 101–109. [[CrossRef](#)]
20. Wdowin, M.; Wiatros-Motyka, M.; Panek, R.; Stevens Lee, A.; Franus, W.; Snape, C.E. Experimental study of mercury removal from exhaust gases. *Fuel* **2014**, *128*, 451–457. [[CrossRef](#)]
21. Wozzuk, A.; Franus, W. Properties of the Warm Mix Asphalt involving clinoptilolite and Na-P1 zeolite additive. *Constr. Build. Mater.* **2016**, *114*, 556–563. [[CrossRef](#)]
22. Vogt, E.T.C.; Whiting, G.T.; Chowdhury, D.T.; Weckhuysen, B.M. Chapter Two—Zeolites and Zeotypes for Oil and Gas Conversion. In *Advances in Catalysis*; Elsevier: Amsterdam, The Netherlands, 2015; Volume 58, pp. 143–314. [[CrossRef](#)]
23. Yusupov, T.S.; Shumskaya, L.G.; Kirillova, Y.A. State and perspectives of natural zeolite beneficiation. *J. Min. Sci.* **2000**, *36*, 299–304. [[CrossRef](#)]
24. Sarbak, Z. *Nieorganiczne Materiały Nanoporowate [Inorganic Nanoporous Materials]*; Wydawnictwo UAM: Poznań, Poland, 2009.
25. Barthel, W.; Marchand, J.-P.; Devivere, M. Warm asphalt mixes by adding a synthetic Zeolite. In *Proceedings of the 3rd Eurasphalt & Eurobitume Congress*, Vienna, Austria, 12–14 May 2004.
26. Lai, B.; Barros, C.; Yin, H. Investigation of rheological behaviour of asphalt binder modified by the Advera additive. In *Proceedings of the Poro-Mechanics IV: Fourth Biot Conference on Poromechanics*, New York, NY, USA, 8–10 June 2009.
27. Wozzuk, A. *Wpływ dodatku zeolitów na obniżenie temperatury produkcji i zagęszczania mieszanek mineralno-asfaltowych. [Influence of Zeolite Addition on the Decrease in Production and Compaction Temperatures of Bituminous Mixtures]*. Ph.D. Thesis, Lublin University of Technology, Lublin, Poland, 2016.
28. Technical recommendation IBDiM No. RT/2009-03-0012/1. In *Adhesion Promoters Wetfix BE and Wetfix AP17 for Use in Traffic Engineering*; Road and Bridge Research Institute: Warszawa, Poland, 2014.
29. WETFIX BE. *Thermally Stable Liquid Adhesion Promoter for Asphalt Binders*; Minova Ekochem, S.A.: Siemianowice Śląskie, Poland, 2010.
30. *EN 1426:2015-08 Bitumen and Bituminous Binders—Determination of Needle Penetration*; Polish Committee for Standardization: Warsaw, Poland, 2015.
31. *EN 1427:2015-08 Bitumen and Bituminous Binders—Determination of Softening Point—Ring and Ball Method*; Polish Committee for Standardization: Warsaw, Poland, 2015.
32. *EN 12593:2015-08 Bitumen and Bituminous Binders—Determination of the Fraass Breaking Point*; Polish Committee for Standardization: Warsaw, Poland, 2015.
33. *EN 12591:2009 Bitumen and Bituminous Binders—Specifications for Paving Grade*; Polish Committee for Standardization: Warsaw, Poland, 2009.
34. *EN 14023:2010 Bitumen and Bituminous Binders—Specification Framework for Polymer Modified Bitumens*; Polish Committee for Standardization: Warsaw, Poland, 2010.
35. Muthen, K.M. *Foamed Asphalt Mixes. Mix Design Procedure. Contract Report CR 98/077*; SABITA Ltd. & CSIR Transportek (Council for Scientific and Industrial Research Transportek): Pretoria, South Africa, 1999.

36. *Technical Guideline TG2, Bitumen Stabilised Materials, A Guideline for the Design and Construction of Bitumen Emulsion and Foamed Bitumen Stabilised Materials*, 2nd ed.; Asphalt Academy: Pretoria, South Africa, 2009.
37. Asphalt Academy. *The Design and Use of Foamed Bitumen Treated Materials. Interim Technical Guideline (TG2)*; Asphalt Academy: Pretoria, South Africa, 2002.
38. *Wirtgen Cold Recycling Technology. Manual*, 1st ed.; Wirtgen GmbH: Windhagen, Germany, 2012.
39. Wirtgen Group. *Podręcznik Recyklingu na Zimno [Cold Recycling Technology Manual]*, 2nd ed.; Wirtgen GmbH: Windhagen, Germany, 2004.
40. Chomicz-Kowalska, A. Laboratory testing of low temperature asphalt concrete produced in foamed bitumen technology with fiber reinforcement. *Bull. Pol. Acad. Sci. Tech. Sci.* **2017**, *65*, 779–790. [[CrossRef](#)]
41. Chomicz-Kowalska, A.; Mrugała, J.; Maciejewski, K. Evaluation of foaming performance of bitumens modified with the addition of surface active agent. In *IOP Conference Series: Materials Science and Engineering*; IOP Publishing: Bristol, UK, 2017; Volume 245, pp. 1–10. [[CrossRef](#)]
42. *EN 12594:2014-12 Bitumen and Bituminous Binders—Preparation of Test Samples*.
43. *EN 13043:2013 Aggregates for Bituminous Mixtures and Surface Treatments for Roads, Airfields and Other Trafficked Areas*.
44. WT-2 2014—Part II. Asphalt Mixes. Technical Requirements. Appendix to Ordinance No. 47 of the General Director of National Roads and Highways. Available online: www.gddkia.gov.pl (accessed on 18 September 2019).
45. Iwański, M.; Chomicz-Kowalska, A. Application of the foamed bitumen and bitumen emulsion to the road base mixes in the deep cold recycling technology. *Balt. J. Road Bridge Eng.* **2016**, *11*, 291–301. [[CrossRef](#)]
46. Iwański, M.M. Synergia Wapna Hydratyzowanego i Asfaltu Spienionego w Zapewnieniu Trwałości Eksploatacyjnej Betonu Asfaltowego w Technologii na Półciepło [Synergic Effects of Utilization of Hydrated Lime and Foamed Bitumen in Providing Service Durability of Half-Warm Mix Asphalt Concrete]. Ph.D. Thesis, Faculty of Civil Engineering and Architecture, Kielce University of Technology, Kielce, Poland, 2019.
47. *EN 12697-5:2010 Bituminous Mixtures. Test Methods. Determination of the Maximum Density*; Polish Committee for Standardization: Warsaw, Poland, 2010.
48. *EN 12697-6:2012 Bituminous Mixtures. Test Methods for Hot Mix Asphalt. Determination of Bulk Density of Bituminous Specimens*; Polish Committee for Standardization: Warsaw, Poland, 2012.
49. *EN 12697-8:2005 Bituminous Mixtures. Test Methods. Determination of Void Characteristics of Bituminous Specimens*; Polish Committee for Standardization: Warsaw, Poland, 2005.
50. *EN 12697-12:2008 Bituminous Mixtures. Test Methods. Determination of the Water Sensitivity of Bituminous Specimens*; Polish Committee for Standardization: Warsaw, Poland, 2008.
51. *EN 12697-31 Bituminous Mixtures. Test Methods. Specimen Preparation by Gyrotory Compactor*; Polish Committee for Standardization: Warsaw, Poland, 2008.
52. WT-1 2014. Kruszywa do Mieszanek Mineralno-Asfaltowych i Powierzchniowych Utrważeń na Drogach Krajowych. Wymagania Techniczne [Aggregates for Asphalt Mixes and Surface Dressings on National Highways. Technical Requirements]. 2014. Available online: www.gddkia.gov.pl (accessed on 18 September 2019).
53. *EN 933-10 Tests for Geometrical Properties of Aggregates. Assessment of Fines. Grading of Filler Aggregates (Air Jet Sieving)*; Polish Committee for Standardization: Warsaw, Poland, 2009.
54. *EN 933-1 Tests for Geometrical Properties of Aggregates. Determination of Particle Size Distribution. Sieving Method*; Polish Committee for Standardization: Warsaw, Poland, 2012.
55. Iwański, M.; Chomicz-Kowalska, A.; Stępień, J.; Maciejewski, K.; Ramiączek, P.; Iwański, M.M. *Zalecenia Dotyczące Projektowania, Wytwarzania i Wbudowywania Mieszanek Mineralno-Asfaltowych z Asfaltem Spienionym o Obniżonych Temperaturach Technologicznych [Technical Recommendations for Design, Production and Paving of Asphalt Mixes with Foamed Bitumen Characterized by Lowered Processing Temperatures]*. RID-I/6 Report Recommendations, NCBiR, GDDKiA; Kielce University of Technology: Kielce, Poland, 2018.
56. Radziszewski, P.; Piłat, J.; Król, K.; Kowalski, K.; Sarnowski, M.Ł. *Weryfikacja Wymagań i Metody Oceny Właściwości Lepkosprężystych Krajowych Asfaltów i Asfaltów modyfikowanych. [Verification of Requirements and Methods for assessment of Viscoelastic Properties of Domestic Bitumens and Polymer Modified Bitumens]*; Politechnika Warszawska: Warsaw, Poland, 2011.
57. Chomicz-Kowalska, A. Statistical methods for evaluating associations between selected foamed bitumen parameters. In *Proceedings of the 6th International Conference on Bituminous Mixtures and Pavements—ICONFBMP 2015, Thessaloniki, Greece, 10–12 June 2015*; Chapter I: Bituminous binders, Unbound materials. pp. 3–12.

58. Newcomb, D.E.; Arambula, E.; Yin, F.; Zhang, J.; Bhasin, A.; Li, W.; Zelalem, A. *Properties of Foamed Asphalt for Warm Mix Asphalt Applications*. NCHRP Report 807. TRB; AASHTO: Washington, DC, USA, 2015.



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