ZEOLITE AS ADDITIVE IN WARM MIX ASPHALT

Milan Marinković [1]
Tiana Milović [2]
Bojan Matić [3]

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Summary: *The use of warm mix asphalt (WMA) instead of hot mix asphalt (HMA) is more environmentally friendly. Developed WMA technologies allow to reduce the mixing and compaction temperatures by 20-40°C. One of them is asphalt foaming technology which provides a foaming effect in mixing phase by use of water-containing additives such as zeolites. Zeolite improves the performances of bitumen and asphalt mixtures. Adding zeolite, especially synthetic, reduces permanent deformation in the asphalt.*

Keywords: *Zeolite, warm mix asphalt, bitumen, performances*

1. INTRODUCTION

In recent years, there has been increased awareness of environmental problems caused by the asphalt paving industry. Convencional HMA (Hot Mix Asphalt) production and pavements emit large amounts of greenhouse gases such as CO_2, CH_4 and N_2O, [1] as well as aerosols [2]. In order to decrease mixing and compation temperatures and reduce the emission of harmful compounds, new technologies are used, such as WMAs (Warm Mix Asphalts) which allow temperature reduction of 20-40°C compared to HMA technology. Production of WMA in world in mil. tons per year (data from 2007 to 2013) is shown in Figure 1, while Figure 2 shows that the highest use of WMA is in USA, and in Europe is about 10 times lower [3]. The production temperature of HMA mixes is 150-190°C, production temperature of WMA mixes is 100-140°C, for HWMA (Half-Warm Mix Asphalt) is 60-100°C and for cold is 0-40°C [4]. Classification of mix asphalts by temperature range is shown in Figure3 [3]. Generaly, there are three categories of warm mix technology: foaming process, addition of organic additives and addition of chemical additives [4]. Further, asphalt foaming technology is devided into water-based and water-containig (storing) group e.g. natural or synthetic zeolites [2, 4]. Zeolites are a group of microporous aluminosilicate minerals with crystalline stricture containing water particles so-called "zeolitic water" in their composition. At 400°C comes to the continuous release of "zeolitic water", without damaging the crystalline structure [2].

[1] Milan Marinković, MSc CE, PhD student, University of Novi Sad, Faculty of Technical Sciences, Trg Dositeja Obradovića 6, Novi Sad, Serbia, tel: +381655773817, e – mail: milan.marinkovic@uns.ac.rs
[2] Tiana Milović, MSc CE, PhD student, University of Novi Sad, Faculty of Technical Sciences, Trg Dositeja Obradovića 6, Novi Sad, Serbia, tel: +381604671260, e – mail: tiana.milovic@uns.ac.rs
[3] Bojan Matić, PhD, Assistant Professor, University of Novi Sad, Faculty of Technical Sciences, Trg Dositeja Obradovića 6, Novi Sad, Serbia, tel: +381641849879, e – mail: bojan.matich@gmail.com

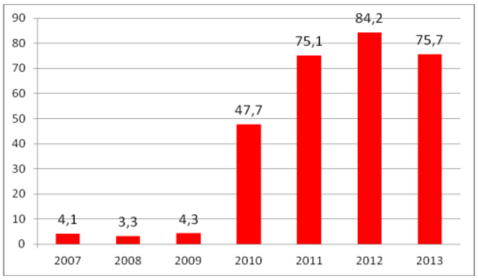

Figure 1- Production of WMA in world in mil. tons/year [3]

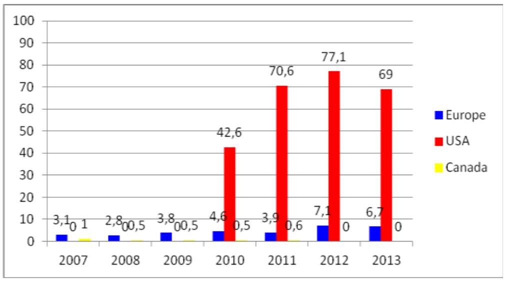

Figure 2- Production of WMA in mil. tons/year [3]

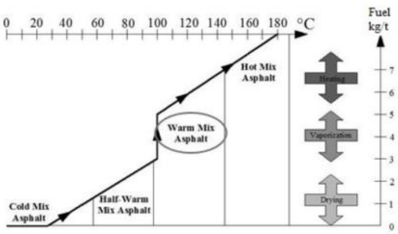

Figure 3- Classification by temperature range [3]

Zeolites used as material can be natural or synthetic origin. Group of natural zeolites includes about 100 different minerals, but only those which creating deposites (e.g. clinoptilolite, phillipsite, chabazite and modernite) are economically interesting [2]. In Serbia, the largest zeolite deposits are Beocin, Igros, Jablanica 1, Toponica and Zlatokop [5]. Synthetic zeolites are artificial made from the chemical reagents, mineral materials or some waste by-products of industry such as fly ash [2], which is expecially interesting because during coal combustion in thermal power plants about 5 million tons of fly ash is generated per year in Serbia [6].
The use of zeolite as additive in WMA is a new current topic, and up to now there are several published papers which deal with it, but in near future an increase in application of WMA is expected as well as more scientific papers on this topic.

2. ZEOLITE – DEFINITION AND STRUCTURE

The word "zeolites" comes from Greek words "ζειυ" and "λιθοσ" meaning "boiling stones", because when they release water vapour at elevated temperature it seems to boil [7].
Zeolites are hydrated aluminosilicate minerals of alkali and alkaline earth metal cations, which are microporous and have crystalline structure [8]. Tetrahedrons of silica $[SiO_4]^{4-}$ and alumina $[AlO_4]^{5-}$ are forming an open, three-dimensional framework in which "cages" and intraframe cavities are located extra framework cations and "zeolitic water" [7, 8], Figure 4 [9]. Honeycomb-like structure of zeolite with an open cavities provides large internal and external surface areas which represent the base of its high pozzolanic reactivity as well as its metastability due to negativ charge of framework [7, 10, 11, 12].

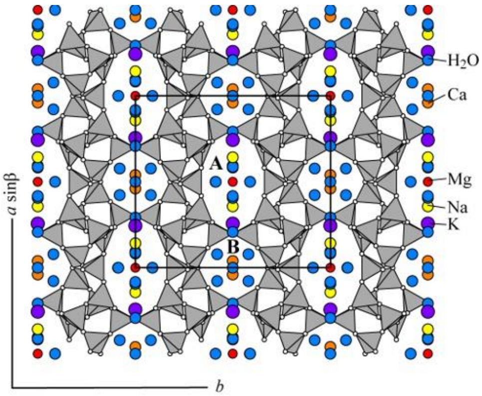

Figure 4- Model of clinoptilolite structure [9]

A special property of minerals from this group is ability to exchange extraframework cations and to adsorb and lose water up to 30% of their dry weight without any change of crystalline structure [12].
Zeolites are also known as pozzolanic materials which pozzolanic reaction stars in the presence of $Ca(OH)_2$. In a high pH solution, aluminosilicate network starts decomposing under attack of hydroxil ions (OH^-) making depolymerized "species [11].
Those "species" enter the solution, react with Ca^{2+} ions and form hydrated calcium silicate and calcium aluminate compounds, which improve the microstructure of hardened concrete due to pore refinement [11, 12].

3. EFFECT OF ZEOLITE ON THE PERFORMANCE OF BITUMEN

Asphalt concrete is a material which consists of mineral aggregate and bitumen. Bitumen is used as a binding agent that envelops aggregate. Bitumen is divided on the basis of the penetration depth and softening point into: BIT 160/220, BIT 100/150, BIT 70/100, BIT 50/70, BIT 40/60, BIT 35/50, BIT 30/45 and BIT 20/30 [13]. Penetration value determines the hardness of bitumen by measuring the depth (in tenths of a mm) to which a standard and loaded needle will vertically penetrate in 5 seconds, a sample of bitumen maintained at a temperature of 25°C (77°F). Table 1 shows the change of link performance of bitumen, depending on the amount and type of zeolite [14]. With increasing the content of zeolite, penetration value decreases [14, 15, 16, 17].

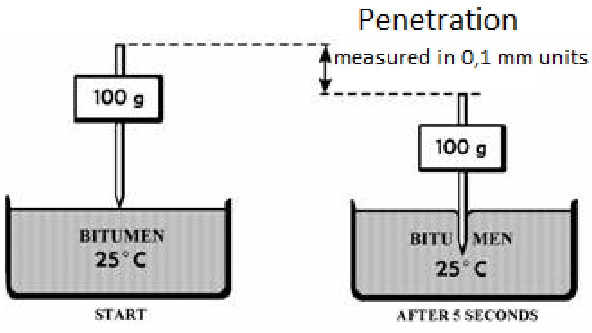

Figure 2- Penetration test of bitumen [18]

Table 1- Conventional properties of bitumen prepared with warm mix asphalt additives [14]

WMA types	Content (%)	Pen	SP	Viscosity		Rolling thin film test (RTF0)			
		0,1 mm	°C	135°C	160°C	Loss of mass (%)	Retained Pen. (%)	SP diff. (°C)	Pen. Ind.
Without zeolite	0	55	49,1	413	138	-0,04	26	5,3	-1,2
Natural zeolite	3	54	53,6	363	163	-0,16	22	4,4	-0,16
	4	53	54,1	350	126	-0,17	18	4,3	-0,1
	5	51	55,0	325	113	-0,17	17	3,7	0,02
	6	45	58,2	400	188	-0,17	15	3,2	0,4
	7	42	59,2	488	188	-0,17	13	3,0	0,44
Synthetic zeolite	3	55	53,1	350	138	-0,16	23	4,9	-0,26
	4	53	53,6	325	125	-0,17	21	4,7	-0,22
	5	52	56,0	313	113	-0,18	21	4,1	0,27
	6	45	59,9	438	150	-0,18	14	3,3	0,74
	7	43	61,2	513	175	-0,18	13	3,2	0,87

The softening point is determined as the temperature at which a sample of bitumen, subjected to a progressive increase of temperature and the weight of a steel sphere, reaches a consistence that leads to its flow through a ring of steel, until obtain a specific deformation. By increasing content of zeolite (natural and synthetic) softening point is also increased [14, 15, 16, 17].

Figure 3- Test of softening point of bitumen [19]

The Rolling Thin-Film Oven (RTFO) procedure provides simulated short term aged asphalt binder for physical property testing. Asphalt binder is exposed to elevated temperatures to simulate manufacturing and placement aging. The RTFO also provides a quantitative measure of the volatiles lost during the aging process. A mass loss is four time lower with increasing the content of zeolite than in the sample without zeolite. By increasing content of zeolite (natural and synthetic) softening point difference and retained penetration are lower .

4. EFFECT OF ZEOLITE ON THE PERFORMANCE OF ASPHALT MIXTURES

WMAs allow temperature reduction of 20-40°C compared to HMA technology [4]. Such reductions have the benefits of cutting fuel consumption and decreasing the production of greenhouse gases. In addition, engineering benefits include better compaction on the road, the ability to haul paving mix for longer distances, and extending the paving season by being able to pave at lower temperatures. The picture below (Fig. 3) shows the difference between HMA and WMA in asphalt mixing plant.

Figure 3- Difference between HMA and WMA (asphalt mixing plant) [20]

Serbian and EN norms define minimum and maximum temperature of asphalt mixtures. Mixture with temperatures which is lower than minimum would be impossible to compact because of viscosity. Table below (Tab. 2) shows how content of zeolite affects on mixing and compaction temperatures.

Table 2- Mixing and compaction temperatures of WMA additives [14]

WMA types	Content (%)	Mixing temperatures °C	Compaction temeperatures °C
Without zeolite	0	156-163	143-149
Natural zeolite	3	158-168	141-149
	4	153-160	139-142
	5	150-157	137-142
	6	165-174	145-154
	7	164-172	149-156
Synthetic zeolite	3	155-162	139-146
	4	152-159	136-143
	5	149-152	135-142
	6	158-165	145-151
	7	163-169	149-155

For mixing and compaction temperatures optimal content of zeolite is 5% relative to ashalt binder [14, 15, 16, 21]. With this percentage content minimal temperature range is obtained. That is very important because energy which is used for heating of asphalt mixtures can be saved. Figure 4 shows dependence permanent deformation of WMA or HMA type.

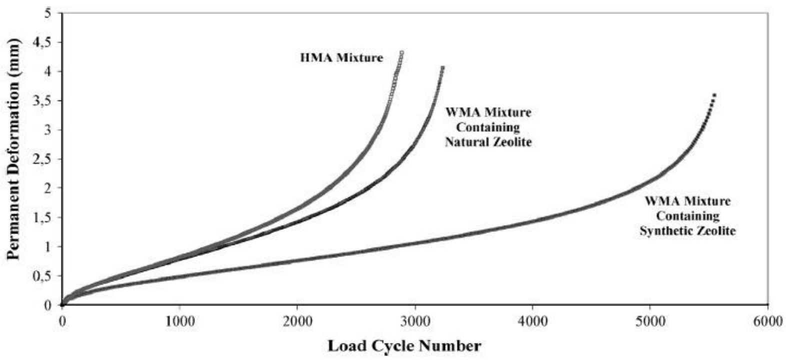

Figure 4- Dependece permanent deformation of MA type [22]

3000 load cycle WMA mixture with syntetic zeolite has more than four time lower permanent deformation compared to WMA mixture with natural zeolit or HMA mixture [22]. This data could be of great importance for Serbia because one way to produce synthetic zeolite is by using fly ash. Serbia has a lot of fly ash dumps obtained from thermal power plants.

5. CONCLUSION

Zeolites used as material can be natural or synthetic origin. Synthetic zeolites are made from the chemical reagents, mineral materials or some waste by-products of industry such as fly ash, which is expecially interesting because during coal combustion in thermal power plants about 5 million tons of fly ash is generated per year in Serbia. Zeolite can improve bitumen performance such as penetration and softening point. WMA technologies allow to reduce the mixing and compaction temperatures by 20-40°C. Adding zeolite in asphalt mixtures saves energy because of lower temperatures for mixing and compacting. Zeolite, especially synthetic, improves resistance to permanent deformation of asphalt layers.

ACKNOWLEDGEMENTS

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ЗЕОЛИТ КАО АДИТИВ У ТОПЛИМ АСФАЛТНИМ МЕШАВИНАМА

Резиме: *Употреба топлих асфалтних мешавина (WMA) уместо врућих (HMA) има своје еколошке предности. WMA технологије које су до сада развијене омогућавају снижавање температуре мешања и компактирања за 20-40°C. Једна од тих технологија је и пенушање асфалта која обезбеђује стварање ефекта пенушања у оквиру фазе мешања употребом адитива који садржи воду као што су зеолити. Зеолит побољшава перформансе битумена и асфалтне мешавине. Додавањем зеолита, нарочито синтетичког, смањују се заостале деформације у асфалту.*

Кључне речи: *Зеолит, топла асфалтна мешавина, битумен, перформансе*