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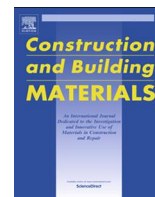
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Etchable iron content (FETCH) proposed as the missing parameter for the better prediction of asphalt mastic stiffening

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HIGHLIGHTS

- A novel parameter characterizing asphalt fillers, etchable iron, FETCH was introduced.
- FETCH was previously ignored component of fine material used in asphalt concrete production.
- Mastic stiffening was studied with the delta Ring and Ball Softening Point ($\Delta R\&B$) method.
- With FETCH the stiffening of asphalt mastic with ($\Delta R\&B$) could be enhanced.
- The developed models distinguished between fillers of very similar properties.

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ABSTRACT

The voids in the mineral filler are widely used to estimate the stiffening of asphalt mastic and mixture. Until now, there have not been major enhancements for the filler theory within the field. In this study, the discovery of the effect of etchable iron (FETCH) on the stiffening was made. The use of FETCH allowed us to predict the mastic stiffening with an error less than the allowable testing standard deviation. At first, range of fillers and aggregate fines were tested with bitumen in order to estimate mastic stiffening, as expressed by the increase in the Ring and Ball Softening Point. The results were then interpreted according to the most widespread filler models, but very small predictive power was found for the mastic compositions used typically in Finnish asphalt mixtures. The standard physical characterization techniques for the fillers employed by the asphalt industry were then extended for more advanced physical and chemical analysis techniques. This enabled us to discover the effect of etchable iron on the mastic stiffening, the mastic being composed of limestone, fly ash and variable aggregate fines. By including the concept of FETCH, the stiffening of asphalt can be predicted with greater accuracy.

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1. Introduction

While aiming at a lower dependence from crude oil products, the pressure to limit bitumen consumption has led to increased research effort within the field of the recycling of asphalt pavements [1,2] and setting performance criteria for mixtures containing Reclaimed Asphalt Pavement material (RAP) [3]. However, some of the asphalt recycling techniques, for example the hot in-place recycling, do not readily provide access to the milled RAP material necessary to prepare samples required for the performance evaluation. The ability to predict the performance of the hot in-place recycled pavement and to identify the inferior in-situ mix quality from only a limited number of samples collected is greatly desired.

Today, due to its fast construction time and affordability [4], hot-in-place recycling is the major highway maintenance technique in Finland for roads having rutting caused by studded tire wear. In this method asphalt pavement is first heated, scarified and blended with new fresh mixture ca. 18–20 kg/m² and then compacted. In effect, the constructed wearing courses in the high volume roads essentially consist of 70–80% of recycled material. Typically, based on government agency guidelines in Finland, the admixture mix design involves collecting a few representative cores from the road and optimizing aggregate gradation, bitumen content and bitumen rheological parameters of the fresh mixture to compensate for bitumen aging and aggregate wear.

However, the necessary pavement heating effort and energy consumption of the rehabilitation process are dependent on the stiffness of the aged in-situ asphalt and thereof the softening point of the aged mastics. The ability to deduct this information from the forensic filler characteristics would provide more accurate process

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control. It is also envisioned, that the ability to predict the stiffening of the final product induced by any recycled asphalt pavements would provide an additional valuable parameter for selecting the best matching materials for the fresh admixtures in the general asphalt recycling applications.

The overall goal of the study was to investigate the effect of chemical composition and physical properties of fillers on the stiffening of asphalt mastics. More specifically, how iron and calcium contents are influencing the softening point of mastics. The change of the latter was measured using Increase in the Ring and Ball Softening test, also known as delta Ring and Ball Softening Point test ($\Delta R\&B$) [5]. This study has been commissioned by the Finnish Transport Agency as a part of the forensic study of the failed Ring Road II pavement in the metropolitan area of Helsinki [6,7]. We previously reported the discovery of the raw material substitution between the stages of mix design and construction of the surface wearing course as the culprit. The second phase of our investigation, reported here, concentrated on two issues. First, we wanted to know whether the state-of-the-art knowledge at the time would have produced enough information to infer the possible problems related to the filler substitution [8,9]. The second aim was to review the existing models of mastic stiffening with the possibility of adopting them into the Finnish Asphalt Specifications and, if not adequate enough, to develop the new mastic stiffening model for the use of pavement engineers in Finland and elsewhere.

This article, thus, provides a review of the best existing prediction models for mastic stiffening proposed for the fresh raw materials. But most of all, it introduces a novel parameter, etchable iron content, as an excellent candidate to enhance stiffness predictions for the recycled asphalt and other asphalt mixtures.

2. Background

The pavement performance strongly depends on the compactability of asphalt concrete. Scientists [10–15], through decades, have tried to identify the reasons behind the increase in asphalt stiffening, failing to provide decisive answers. Quite early on it was agreed on, that stiffening of the asphalt mixture is due to the stiffening of mastic. This, on the other hand, was found to be dependent on filler characteristics. Hesami et al. [16] provide a comprehensive overview of methods and models available in literature for the particle suspensions. Perhaps, because of the limited possibilities for chemical analysis in pavement laboratories today and in the past and based on the assumptions that fillers are chemically inert, the conclusions drawn in many research projects until recently have suggested that the chemical composition of fillers is rather insignificant and a stronger attention should be paid to the physical properties of fillers.

Rigden [11] argued that just the amount of material passing 0.075 mm sieve (Sieve No. 200), used previously as a parameter, is insufficient in describing filler properties. He investigated primary (intrinsic) characteristics including particle density, shape, surface texture, size distribution and surface area; as well as secondary (derived) characteristics including filler's bulk density, fractional voids, the pore diameter distribution and permeability of packed fillers to fluids.

As a result of his study, Rigden proposed linking voids in the mineral filler (H_f), measured in dry powder or as a benzene number, to the stiffening of both mastic and mixture. Warden (cited in [12]) proposed the kerosene method of H_f determination, which could mitigate the problem of compacting fragile fillers, such as fly ashes, whereas van der Baan (cited in [12]) provided the water based paste method of establishing H_f as well. Heukelom compared the methods and found a good correlation between them.

The standard known since 1975 as the bulk density of filler in toluene (using benzene or toluene), so called benzene number proposed by Rigden [11], was still in use in 1990's across Europe [17]. The bulk density in benzene was also correlated to the surface area of fines and percent of particles smaller than 0.010 mm [11], which in both cases decrease with the increasing benzene number.

Because of the health risks associated with the use of benzene and toluene, the benzene number has been changed into the apparent density in kerosene test, available currently as a European standard (EN 1097-3). Those values can be also recalculated into voids in mineral filler, which is demonstrated below (see Section 4.2.3).

However, none of the methods is ideal for complex fillers composed of both organic and inorganic matter. Some information is lost when we consider only one parameter in the material description. For example, fly ash filler breaks during compaction; partially floats in water based solutions, even after the addition of dispersant, or partially dissolves in kerosene, due to the mutual solubility parameters [18] of kerosene with the unburnt carbon.

Heukelom [12] compared the above mentioned three approaches by Rigden, Warden and van der Baan and, to correlate stiffening and compactability, utilized the concept of apparent percentage of filler in the mastic (V_{APR}) which can be defined as

$$V_{APR} = \frac{100}{H_f} * V_F, \quad (1)$$

where H_f is voids in mineral aggregate [%] and V_F is volume of filler, or as

$$V_{APR} = V_F + V_{BFIX}, \quad (2)$$

where V_{BFIX} is volume of the fixed bitumen in the solid phase (Fig. 1). However, he [12] arrived at the conclusion that this value allows for only the first order approximation of the stiffening, and suggested rather to use a value corresponding to the free bitumen content in the mastic.

Rigden proposed in his work that fluidity of the asphalt mixes is dependent on the volume of the free bitumen (Fig. 1), which we designate here as a percent free bitumen by volume ($\%V_{BF}$), and his research focused on determining optimum binder content as a function of fractional voids in mineral filler. Heukelom investigated the effect of $\%V_{BF}$ on the effort of spreading and compaction of mixes. This was followed by the work of Anderson [14], who studied the use of dust in asphalt mixtures developing guidelines for the optimum dust to asphalt ratio (asphalt referring here to bitumen) also known as dust proportion. In his study, the stiffening ratio increased with the decreasing free bitumen ($\%V_{BF}$) (and this type of plot will be further called the Anderson Representation). Additionally, the stiffness increase was observed in the resilient modulus of asphalt concrete and in the amount of cycles to fatigue failure as a function of $\%V_{BF}$. It was concluded, however, that with decreasing $\%V_{BF}$ the effort necessary to compact a mixture to fixed air voids was increasing and this may cause construction problems. Faheem et al. [19] recently investigated the effect of mastic stiffening on the compactability of the asphalt mixes and found that the increase in the relative viscosity of mastic versus bitumen increases compaction effort for coarse asphalt mixtures, whereas it did not affect significantly the fine mixes. The adverse effect of air voids of total mixture on the aging of bitumen has been known previously [20], thus air void content should be limited and overly stiff mastic avoided. A hypothesis is sustained that there exists an ideal range of $\%V_{BF}$ which provides the best pavement durability and that $\%V_{BF}$ is the value to look at for the best mix design. An optimum range of 20–50 $\%V_{BF}$ was suggested [14]. Currently, the stiffening in the SUPERPAVE mix design (AASHTO M 323) is controlled by the dust proportion by mass (0.6–1.2) of material

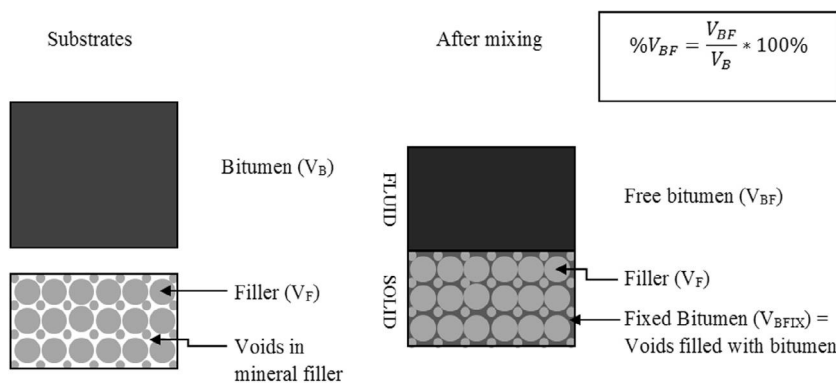


Fig. 1. The conceptual representation of bitumen and filler within the mastic.

passing 0.075 mm, which falls above the suggested $\%V_{BF}$ value. Despite being an extensive study, Anderson's work included only three filler material types such as quartz, limestones and granites. In case of investigating more modern man-made materials, a possibility of error exists when applying the rules developed based on only natural materials.

On the other hand, Tunnickliff [10] proposed that for the identical shape and gradation of fines, chemical interaction dominates and influences the stiffening. Additionally, he proposed that there exists an increased gradient of stiffening close to the surface of the filler particles. Clopotel et al. [13] provide a detailed review of models describing filler-bitumen interaction. Authors [13] concluded based on their findings, that there is a chemical component affecting the stiffening, and that physico-chemical interactions between fines and bitumen immobilize bitumen particles, leading to the collapse of the free volume, which in turn is expected to change mastic viscosity.

In more recent studies [21] it was observed that the calcium oxide content (CaO), as measured with X-ray fluorescence, as well as methylene blue test results are the most representative factors for the chemical properties of mastic.

Furthermore, an oil industry faces a daily problem with asphaltene precipitation in steel pipelines, which leads to clogging. Marczewski et al. [22], investigated asphaltene adsorption processes on different minerals, finding that at high asphaltene concentrations adsorption increases over the iron (III) oxides, when over silica oxides it levels off, suggesting or supporting a theory that a stronger interaction occurs between fines and asphaltenes in iron rich materials. Recent studies on the interaction of asphaltenes with the use of Fe_3O_4 nanoparticles for selective adsorption and catalytic oxidation [23], suggest that iron compounds may influence bitumen more than we previously believed.

Plancher et al. [24] investigated the precipitation of bitumen compounds from toluene solutions on the surface of a range of fillers and found that the type of molecules adsorbed on the surface depended on the type of aggregate used. In more recent studies, Horgnies et al. [25] demonstrated with a bitumen pull off test the effect of bitumen affinity toward different minerals in the aggregate. They studied whether the bond failure leading to moisture damage was due to interfacial (adhesive) or cohesive failure within the composite. The study found that mica rich aggregates (of high iron content) caused more of a cohesive failure.

Based on the literature cited, it is postulated that if any particular mineral had ability to increase the thickness of the adsorbed bitumen layer, it would be an iron based compound.

Even though many studies investigated the stiffening by means of the Increase in Ring and Ball Stiffening Point, Brookfield viscosity or Dynamic Shear Rheology, there is lack of the implementation

efforts of these practices among practitioners. All complex sample preparation techniques add time to perform the mix design and thus a set of simple parameters is preferred by the industry in order to predict the stiffening rather than to test it.

A major success in implementing technology for practitioners can be assigned to the popularization of H_f . In 1997s in Belgium, a system called PRADO was proposed – H_f based mix design, which incorporated stiffness (expressed by $\Delta R\&B$) predicting model, developed on the basis of various available fillers [5]. The appealing factor of the method lies in its simplicity. The equation proposed for prediction of volumetric ratio of filler to bitumen (f/b) in the mix (K_v) is given as

$$K_v = \frac{f}{b} = \frac{(100 - H_f) * (\Delta R\&B)}{1021.2 + (\Delta R\&B) * H_f} \quad (3)$$

One must determine only Rigden Voids in Mineral Filler (H_f), a relatively fast and simple test, and identify the mastic composition to calculate $\Delta R\&B$. On the other hand, the model allows one to engineer the mixture's desired K_v on the basis of experimentally obtained $\Delta R\&B$ and H_f . However, the equation provided is limited to a narrow range of filler concentrations in the bitumen. Additionally, filler is expected to pass 0.075 mm sieve, even though currently the European $\Delta R\&B$ standard (EN 13179-1) requires material passing 0.125 mm sieve and majority of state specifications define filler as material passing 0.125 mm [8,9], making it incompatible without annotation. Nevertheless, if the $\Delta R\&B$, executed according to the old standards, is between 12 and 16 °C, the filler is considered accepted for use in a mixture. Few European countries, e.g. United Kingdom, France, set similar requirements or have divided fillers into ranges based on the results of $\Delta R\&B$ tests [9,26]. Republic of South-Africa [27] and Poland [26] adapted $\Delta R\&B$ test as an evaluator of the acceptable filler to bitumen ($K_m = f/b$) ratio in the mix design, by defining maximum allowed temperature increase value. An adaptation to local situation, by change of desired value of $\Delta R\&B$, may be necessary due to differences in available mineral materials, different penetration grades of bitumen available (i.e. the prevailing use of 50/70 penetration grade bitumen in Poland [26]) or different dominant type of asphalt type surfacing (dense graded or SMA) within a country.

The Finnish mix design guidelines, on the other hand, allow four methods of determining the Job Mix Formula (JMF), of which only one takes H_f into consideration. Even if the evaluation of compactibility, as such, is required in the mix design report, the criteria or limiting values are not provided, which makes the stiffening of the mastic an ignored issue. However, the specification [8] gives criteria for the allowable properties for fillers including H_f , density,

calcium carbonate content and specific surface area. Fillers meeting the requirements are then proportioned to the gradation curves provided in the catalog of empirically defined mix recipes. This indirectly limits the stiffening of the mastic. However, very little direct studies [17] have been done with local materials up to date to confirm the correctness of this adapted approach. The research presented below is targeted at establishing the values of $\Delta R\&B$ for local materials and the possibility to predict them. However, criteria development is outside the scope of this paper.

3. Experimental plan

The objective of the study was to investigate mastic stiffening based on known filler concentrations and type of filler. The tasks performed were: basic and enhanced raw material characterization, the preparation of mastic blends and modeling. The modeling work included the investigation of physical stiffening phenomenon through various known and new predictor variables for fillers. Mathematical fitting including calibration and validation was conducted using linear and exponential functions which physically fitted the observed phenomenon. The term ‘calibration’ refers to the mathematical process through which the total error or difference between observed and predicted values is minimized. In our study customized i.e., the material specific development of regression coefficients for Finland is considered. Model validation, employing the same local materials from Finland but with variable quantities, intends to confirm that the calibrated model can produce robust and accurate predictions for cases other than those used for model calibration. For scaling up a successful validation process would require that the bias and precision statistics of the model obtained for the validation data set of different fillers be similar to those obtained during calibration.

The experimental plan consists of investigating typical fillers used in asphalt and then preparing mastic blends using one paving grade reference binder typically used in Finland for high volume roads. This was done to provide sufficient reference for the fines and mastic replicated based on the Ring Road II mixture forensic analysis [6,7], discussed further.

Two sources of stone fillers originating from fine and coarse aggregate fractions (TE, KK), two added fillers (KF, FA) and one with modification (FAW) were investigated and used for preparing mastic (Table 1). Three filler contents (volume percentages) were used, producing a total of 21 combinations of mastic blends for model calibration. Two fillers (TE and KK) with one filler concentration were used for model validation. All materials and blend combinations for model calibration and validation are listed in Table 1. The raw materials are further described in more detail in Sections 4.1 and 4.2, whereas the mastic composites in Section 5.1. For clarity, Table 2 lists material parameters studied and shows the test methods used for material characterization.

Table 1
Studied materials and blend combinations.

Materials/blends	Material ID	Material type	Properties studied	Prepared mastic			
				Calibration		Validation	
				Filler/bitumen (volume%)			
Bitumen 70/100	B		x	37/63	41/59	45/55	42/58
Stone filler	TE	Granodiorite	x	x	x	x	x
	KK	Granite	x	x	x	x	x
Added filler	KF	Limestone	x	x	x	x	
	FA	Fly ash	x	x	x	x	
	FAW	Fly ash	x	x	x	x	
Mix Design replica	REP ^a	KF + KK ^b	x	x	x	x	
As-constructed replica	EXP ^a	KF + KK + FA ^b	x	x	x	x	

^a A detailed composition of replicas is presented in Table 4.

Table 2
Filler and mastic parameters and test methods.

Material	Parameter ID	Description	Test method
Fillers	ρ	Bulk density	EN 1097-7
	ρ_{apk}	Apparent density in kerosene	EN 1097-3
	H_f	Rigden voids (voids in mineral filler)	EN 1097-4
	H_{fk}	Voids in mineral filler derived from apparent density in kerosene	–
	SA	Surface area	PANK 2401
	$Fe_2O_{3sol}\%$	Etchable iron (III) oxide content	Modified EN 196-2:2005, section in this article 4.2.4.
	$CaO_{sol}\%$	Etchable calcium oxide content	Modified EN 196-2:2005, section in this article 4.2.4
Mastic	Impure silica	Impure Silica content	EN 196-2:2005
	LOI	Loss of ignition	EN 196-2:2005
	$\Delta R\&B$	Increase in Ring and Ball Softening Point, a.k.a. delta ring and ball	EN 13179-1

4. Tested materials and their characterization

4.1. Bitumen

We used the reference bitumen of penetration grade 70/100 of Russian crude oil origin typically used for the construction of major highways in Finland, characterized in Table 3.

4.2. Fillers and their properties

Stone fillers (aggregate fines) were represented by granite and granodiorite, designated as KK and TE respectively, collected from local quarries. The added fillers were the commercial limestone filler (KF) and fly ash. The fly ash used was divided into two samples. The one designated as FA, was used as is, whereas the sample designated as FAW was water treated in order to simulate water damage to the filler and to concentrate on the effect of the organic component [28].

To obtain the FAW sample, a portion of FA was immersed in the reverse osmosis water and drained over a cellulose filter, removing water soluble salts. The filter residue was dried in the oven at 105 °C until constant weight. The material was removed from the filter and gently pulverized with a spatula. Afterward the residue was sieved to pass 0.125 mm sieve.

The filtrate was evaporated and the residue collected. The residue after evaporation was white or light gray in color and the

Table 3
Characteristic values of bitumen used.

Measurement	Unit	Result	Test method
Penetration	0.1 mm	65	EN 1426
Softening point	°C	48	EN 1427
Fraass breaking point	°C	−18.9	EN 12593
Kinematic viscosity	mm ² /s	240.5	EN 12595

shape of crystals looked like needles, suggesting a relatively high surface area and mainly inorganic character of the residue. The occurrence of this particular structure in the fly ash was not confirmed in-situ. However, the analysis with Fourier Transform Infra Red [29] suggests that this residue mainly contains anions such as CO₃²⁻, HCO₃⁻, NO₃⁻, SO₄²⁻, lattice water and silicates. The amount of this residue was minuscule (0.21 g from 100 g), yet in the end this process altered the properties of the FA and created a new material FAW, which turn out to behave differently as a mastic component than the original material.

Limestone of 91.4% solubility in hydrochloric acid [6] is denoted as KF.

To simulate the stiffening effect of fines passing 0.125 mm sieve on the asphalt concrete, we prepared two filler blends designated as REP and EXP utilizing raw materials KK, KF and FA, which are defined in Table 4. During the Ring Road II failure analysis, we found that Mix Design JMF (OREP) was replaced by Field JMF (OEXP) with filler substitution. The REP and EXP were intended to be reconstructions of the JMF fines [6].

4.2.1. Surface area

The BET-surface area was established in the dynamic flow equipment (HORIBA SA9601-MP) in a three-point measurement. Samples were conditioned at 200 °C for a period of one hour prior to measurement at the sample preparation station. The local standard (PANK 2401) requires the analysis of the fines passing 0.063 mm, and this was executed as the baseline measurement for the raw materials (KF, KK, TE and FA). The same measurement was executed also on the fraction passing 0.125 mm for all materials used further and only the later values were used as SA parameter during further model development. Results are collected in Table 5.

4.2.2. Dry voids in mineral filler (H_f)

Rigid voids or voids in mineral filler (H_f) were determined according to EN 1097-4 (Tests for mechanical and physical properties of aggregates. Part 4: Determination of the voids of dry compacted filler). Results are presented in Table 6.

4.2.3. Apparent Density of fines in kerosene and kerosene derived voids in mineral filler (H_{fk})

The apparent density of fines was determined according to EN 1097-3 (Annex A) and the results are presented in Table 6.

Kerosene derived voids in mineral filler (H_{fk}) were defined in this work as:

$$H_{fk} = \frac{\rho_{apk}}{\rho_s} * 100 [\%], \quad (4)$$

where ρ_s – bulk density of fines; ρ_{apk} – an apparent density of fines in kerosene.

4.2.4. Etchable iron, etchable calcium and filler solubility

Iron and calcium analysis was conducted on the basis of standard SFS-EN 196-2:2005 (Chemical analysis of cement) with slight modifications.

In Step 1, solutions were prepared according to the modified instruction provided in Section 13.5 of the standard EN

196-2:2005 (“Decomposition in hydrochloric acid and ammonium chloride”), which is given further.

Two representative samples, of each studied filler, were prepared for analysis.

The sample of 1.00 ± 0.05 g (m_1) were weighted, to ± 0.0005 g, and placed in a 100 ml beaker. About 1 g of ammonium chloride was added and mixed thoroughly with a glass stirring rod. The beaker was covered with a watch glass and 10 ml of concentrated hydrochloric acid was let down the side of the beaker. After the period of 5 days, when effervescence was terminated, 10 drops of concentrated nitric acid were added and all was stirred with a glass stirring rod, crushing any lumps.

Beakers were placed on a boiling water bath and left for 30 min. Contents of the beaker were diluted with a small quantity of hot water and all filtered through a coarse filter paper (previously weighted, m_2) into 500 ml volumetric flask. The precipitate was not transferred with the rubber spatula, but by rinsing the walls with a small amount of hot water shower. The beaker and precipitate were rinsed with hot hydrochloric acid (1:99 v/v H₂O) and then washed with small amounts of hot water until free from chloride ions (tested by the silver nitrate test). All the washings were collected into 500 ml volumetric flask (Solution A).

Solution A was cooled down and made up to 500 ml.

Filters were dried in the oven at 105 °C and weighted (m_3). The difference was recorded and Impure Silica percent was calculated from equation:

$$\text{Impure Silica} = 100 * \frac{m_3 - m_2}{m_1} [\%wt.] \quad (5)$$

Etchable iron (III) oxide content (Fe₂O_{3sol}%) was developed by analysis of such Solution A. Two samples were prepared for every analysis from each of the liquids – amounting to 4 tests per filler.

100 ml of the solution prepared in accordance with Step 1 was pipetted from the 500 ml volumetric flask into a 100 ml beaker and 0.5 g amino-acetic acid was added along 0.3–0.4 g of the sulfosalicylic acid indicator. Using a pH meter, the pH of this solution was adjusted to (1.5 ± 0.1) with the ammonium hydroxide solution (1 + 5 v/v H₂O).

All was heated to (47.5 ± 2.5) °C and temperature controlled throughout the whole measurement while stirring with the magnetic stirrer. Measurements of the solutions were done at 520 nm while stirring them and titrating with 0.03 mol/l EDTA solution. In the vicinity of the indicator color change, a curve of the readings from the measuring apparatus as a function of the volume of EDTA solution added was constructed. The volume at the end point (V_1) was determined from the intersection of the line of the greatest slope in the region of the color change and the line of almost constant absorbance after the color change.

During the titration, the temperature of the solution did not exceed 50 °C or dropped below 45 °C. Etchable iron (III) content is then calculated from the Eq. (3) of the iron (III) oxide content provided in Section 13.10.2 of the standard EN 196-2:2005, using m_1 and V_1 as the input values and is expressed in percent.

Etchable iron (III) oxide content in mastic (FETCH) is calculated from Eq. (5).

$$\text{FETCH} = \frac{30 * \text{Fe}_2\text{O}_{3\text{sol}}\% * m_F}{100\% * m_B} = \frac{30 * \text{Fe}_2\text{O}_{3\text{sol}}\%}{100\%} * K_m [\text{arb.u.}], \quad (6)$$

where m_F is a mass of filler and m_B is a mass of bitumen.

Etchable calcium oxide content (CaO_{sol}%) measurement was executed on the Solution A as well. Two samples were prepared for every analysis from each of the solutions obtained in Step 1 – amounting to 4 tests per filler.

25 ml of the solution A prepared in accordance with Step 1, from the 500 ml volumetric flask, was pipetted into a 100 ml beaker and then 25 ml of the triethanolamine solution (1:4 v/v H₂O)

Table 4
Blending ratios for reconstructed samples.

Type	Mix design stage						As-constructed <i>in situ</i>					
	Actual			Reconstructed			Actual			Reconstructed		
Abbrev.	OREP			REP			OEXP			EXP		
Blend density < 0.125 mm [kg/m ³]	2750 ^a			2710			2650			2610		
Raw material	KK	KF	FA	KK	KF	FA	KK	KF	FA	KK	KF	FA
Blend component	x	x	–	x	x	–	x	x	x	x	x	x
Blending ratio < 0.125 mm [%]	28.2	71.8	–	28.3	71.7	–	? ^b	? ^b	? ^b	28.0 ^c	52.0 ^c	20.0 ^c

^a Calculated value.
^b No data is available in reports.
^c Established to match best to OEXP, on the basis of [6].

Table 5
Results of the surface area measurements for all fillers investigated.

Fraction (mm)	Surface area [m ² /g]						
	KF	KK	TE	REP	EXP	FA	FAW
0.063	0.80	2.55	2.26	NA	NA	2.31	NA
0.125	0.61	2.18	1.55	1.01	1.37	3.86	2.36

at 620 nm, while stirring, during titration with the approximately 0.03 mol/l EGTA solution.

In the vicinity of the indicator color change, a curve of the readings from the measuring apparatus as a function of the volume of EGTA solution added was constructed. The volume at the end point V₂ was determined from the intersection of the line of greatest slope in the region of the color change and the line of almost constant absorbance after the color change.

The CaO_{sol}% was calculated from the equation of the calcium oxide content provided in Section 13.12.2 of the standard EN 196-2:2005, using m₁ and V₂ as the input values.

was added. Using the pH meter, the pH of this solution was adjusted to (12.5 ± 0.5) with sodium hydroxide solution (2 mol/l) and about 0.1 g of murexide was added. The mixture was analyzed

Table 6
Summary of filler properties (material passing 0.125 mm sieve).

Property	Unit	KF	FA	FAW	KK	TE	REP	EXP
H _f	[%]	28.12	37.73	34.26	33.49	33.82	27.17	31.81
ρ _{apk}	[g/cm ³]	0.67	0.63	0.63	0.83	0.85	0.76	0.71
ρ _s	[g/cm ³]	2.71	2.25	2.24	2.67	2.72	2.71	2.61
H _{fk} = 100 ^a ρ _{apk} /ρ _s	[%]	24.72	27.82	28.13	31.24	31.24	28.15	27.36
%Passing 0.063 mm/0.125 mm	[%]	77.47	85.94	84.6	57.54	58.95	73.21	74.83
Fe ₂ O _{3sol} %	[%]	0.32	4.54	4.68	3.69	4.05	1.20	2.15
CaO _{sol} %	[%]	45.72	3.45	3.40	0.79	0.90	32.43	25.10
Impure Silica	[%]	3.93	80.11	80.18	83.90	82.91	36.62	55.51
LOI ^b	[%]	39.32	5.20	4.73	1.43	1.63	28.36	21.77

^a In toluene.
^b According to EN 196-2:2005.

Table 7
Summary of the predictor variables by type of filler and by concentration of filler in mastic.

Type of filler (ID)	V _f [%vol.]	K _v = f/b [m ³ /m ³]	K _m = f/b [g/g]	V _{APR} [% vol.]	%V _{BF} [% vol.]	CaOetch [g]	FETCH [g]	ΔR&B [°C]
KF37	37.46	0.596	1.58	64.42	47.98	21.71	0.15	9.8
KF41	41.24	0.702	1.86	70.95	42.71	25.46	0.18	13.9
KF45	45.00	0.818	2.16	77.40	37.50	29.67	0.20	17.7
FA37	37.47	0.599	1.32	60.71	39.56	1.36	1.79	15.3
FA41	41.10	0.697	1.53	66.58	33.71	1.57	2.09	21.6
FA45	45.01	0.818	1.80	72.91	27.40	1.84	2.45	28.8
FAW37	37.54	0.601	1.31	64.56	43.12	1.34	1.74	15.8
FAW41	41.10	0.697	1.52	70.69	37.73	1.55	2.14	23.3
FAW45	44.98	0.818	1.79	77.37	31.85	1.82	2.51	33.2
KK37	37.50	0.600	1.56	62.62	44.03	0.37	1.73	11.6
KK41	41.10	0.698	1.82	68.64	38.65	0.43	2.01	18.9
KK42 ^a	42.04	0.725	1.89	70.22	53.34	–	2.09	20.1
KK45	44.99	0.818	2.13	75.13	32.86	0.51	2.36	26.7
TE37	37.61	0.600	1.59	62.44	43.01	0.43	1.93	14.6
TE41	41.13	0.699	1.85	68.27	37.69	0.50	2.25	22.0
TE42 ^a	41.92	0.721	1.92	69.58	54.90	–	2.32	21.9
TE45	44.98	0.818	2.17	74.68	31.84	0.58	2.63	30.3
REP37	37.55	0.601	1.59	64.97	40.39	15.47	0.57	10.5
REP41	41.16	0.699	1.85	71.20	34.67	17.99	0.67	14.8
REP45	45.00	0.819	2.17	77.92	28.51	21.05	0.78	19.8
EXP37	37.48	0.600	1.53	62.97	44.88	11.50	0.98	12.1
EXP41	41.21	0.701	1.79	69.25	39.39	13.44	1.15	15.9
EXP45	45.00	0.818	2.08	75.57	33.85	15.68	1.34	21.1

^a Validation experiments, not used in model calibration.

Etchable calcium oxide content in mastic (CaOetch) is calculated from equation

$$\text{CaOetch} = \frac{30 * \text{CaO}_{\text{sol}}\% * m_F}{100\% * m_B} \text{ [g].} \quad (7)$$

The results of Impure Silica content, $\text{Fe}_2\text{O}_{3\text{sol}}\%$ and $\text{CaO}_{\text{sol}}\%$ are collected in Table 6, where all filler properties are gathered. The FETCH and CaOetch values are provided in Table 7 with the summary of other mastic properties.

5. Model development: Increase in Ring and Ball Softening Point ($\Delta\text{R\&B}$)

5.1. Prepared mastic compositions

The experimental plan for the mastic studies was provided in Table 1. A total of 21 mastic blends were prepared. Preparation of the samples and execution of the experiments was done according to the standard SFS-EN 13179-1. However, instead of the round bottom evaporation bottle with the fitted heater, we used flat bottom beakers immersed in the temperature controlled oil bath.

We used 30 g of bitumen 70/100 and respective amount of filler according to the calculations, as this reduced the operator error.

For all fillers considered, a set of three mastic blends were prepared where filler volume was desired to be either at 37.5%, 41.1% or 45%. The value of 37.5% is required in the SFS-EN 13179-1, while 41.1 is an average volumetric filler to bitumen ratio in Finnish mix design. The value of 45% was the highest ratio found during the analysis of RR11 [7].

Each mastic was named after the filler used; therefore e.g. FA37 is for fly ash at 37.5% volume fraction. The actual V_F values are provided in Table 7.

For the purpose of model validation, two mastics blends were prepared, randomly choosing 42 vol.% filler concentration, using TE and KK material.

5.2. Analysis of existing mastic models

The $\Delta\text{R\&B}$ or other rheological representations of mastic stiffening have been suggested depending on many parameters and many graphical interpretations. We have analyzed our results using some of the most widespread representations such as that proposed by Heukelom and Warden [12] (as a function of the apparent volume of filler [V_{APR}] in mastic), by Anderson [14] (as a function of $\%V_{\text{BF}}$) and by the Belgian Specifications, called PRADO [5] (a function of H_f and volumetric composition of mastic [K_v]).

First, we have utilized the concept of voids in mineral filler (Fig. 2) established by the Rigden voids (H_f) as well as the parameters calculated from the apparent density of fines in kerosene (H_{fk}). From the first representation (Fig. 2), we can see that there is an exponential growth trend with the increasing apparent volume of filler in the mastic. However, the difference at equal V_{APR} for two different fillers (such as FAW and KF) increases with increasing $\%V_{\text{APR}}$ (from 6 to 15 °C). Even though the relative error remains the same, the absolute error increases with increasing V_{APR} . The use of kerosene derived voids in mineral aggregate $\%V_{\text{APK}}$ gives less scatter and a slightly better fit. However, as mentioned by Heukelom [12], this concept allows only the first order approximation of the stiffening.

Secondly, we plotted the results as a function of free bitumen $\%V_{\text{BF}}$ derived from H_f ($\%V_{\text{BF}}$) and $\%V_{\text{BF}}$ derived from H_{fk} ($\%V_{\text{BFK}}$), calling it Anderson's representation (AR). Fig. 3 shows that there is less scatter for H_{fk} based parameter. However, the absolute error increases with decreasing $\%V_{\text{BF}}$.

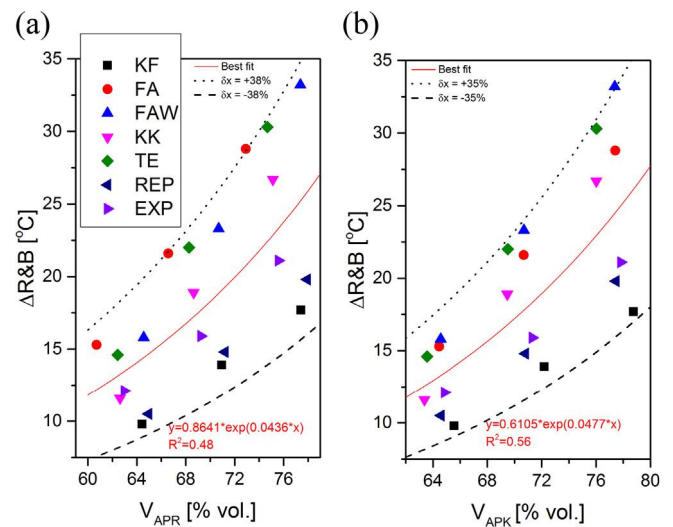


Fig. 2. Increase in Ring and Ball Softening Point expressed as a function of filler's apparent volumetric content in mastic, determined on the basis of the Rigden voids in mineral filler (a) and the apparent density derived voids in mineral filler (b). Dashed lines represent minimal and maximal relative error (δ_x) lines of $\pm 38\%$ and $\pm 35\%$, for (a) and (b) respectively.

Kerosene derived voids in mineral aggregate were hypothesized to compensate for some of the problems observed in the dry compacted samples. For materials containing fly ash, which partially contains organic material of high surface area [30], as mentioned before the dry compaction becomes problematic. Kerosene was hypothesized to dissolve the organic component at least partially. In our experiment, the color of the supernatant changed from transparent white to transparent gray (homogenous solution) confirming the hypothesis. As a result, the kerosene method would allow for evaluating the inorganic component, while reducing the discrepancy usually observed between natural aggregates and waste materials. As can be seen in Table 6, the voids in mineral aggregate are much more uniform when tested with H_{fk} , which then provides better fit of modeling leading us to believe that the hypothesis was correct.

Comparing $\Delta\text{R\&B}$ results obtained (Table 7) according to the contemporary standard (EN 13179-1) with predictions from the Belgian Specifications (Eq. (3)) [5], we observed quite substantial discrepancies. This is understandable as the model is presented as applicable [5] for a particular domain of $\Delta\text{R\&B}$ (up to 20 °C), K_v (0.3–0.8 v/v) and H_f (30–50%). In our case, the mastics with 45% volume fraction fell outside of the prediction capability of PRADO model.

At the beginning of our work, we hypothesized that bitumen adsorbs on the surface of iron oxides in a different manner than on other minerals. We believe that just like clogging of the oil pipes by asphaltenes during crude oil transport, asphaltenes or other heavy components of bitumen have tendencies to assemble in layers on the iron oxide sites, leading to increased stiffening, due to free volume collapse [13]. We combined the best (see Section 4.2.4) previously developed parameter, namely $\%V_{\text{BF}}$ with the proposed etchable iron content parameter (FETCH). The results based on $\%V_{\text{BF}}$ are presented in Fig. 4 and those based on $\%V_{\text{BFK}}$ in Fig. 5.

As can be observed, when a linear fit was used to correlate the natural logarithm of stiffening and volume of the filler for each type of filler separately, we obtained a set of almost parallel lines.

We observed that there is slight difference in the patterns of natural aggregates (NAT) and by products, called thereafter “man-made” (MM). At this point, we postulated that this is due

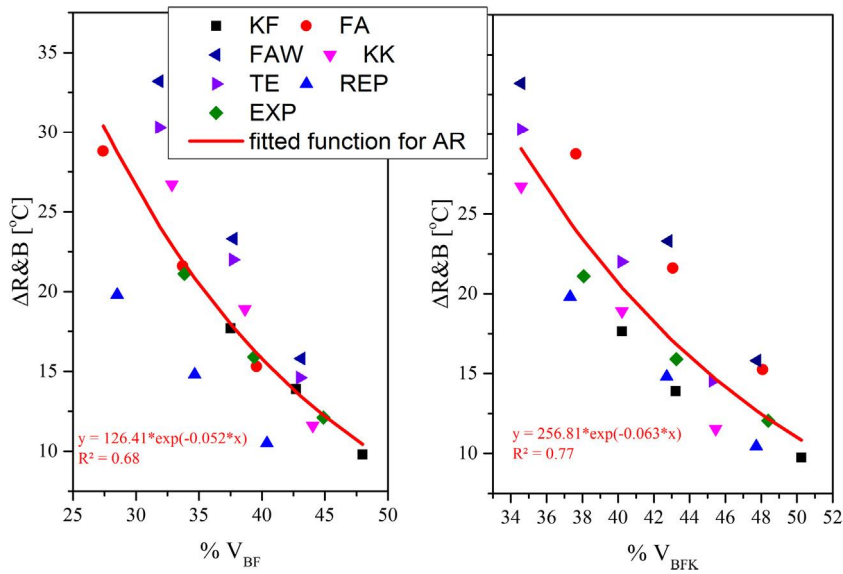


Fig. 3. Representation of delta Ring and Ball Softening Point dependence from Percent Free Bitumen (a) derived from Rigiden Voids (%V_{BF}) and (b) from apparent density in kerosene (%V_{BFK}).

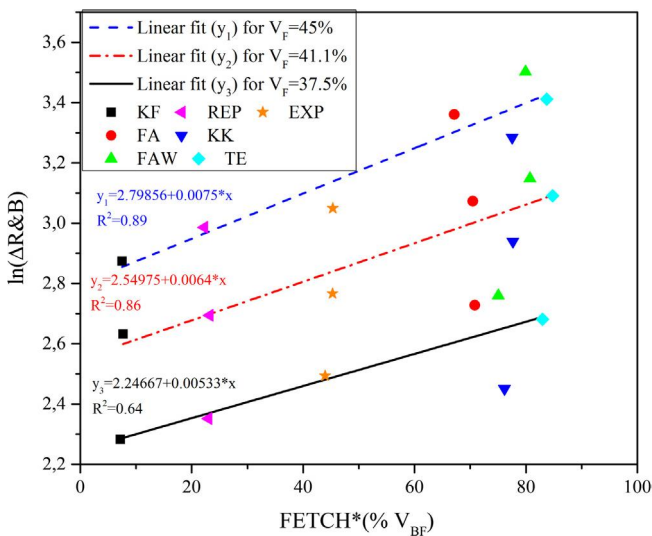


Fig. 4. Representation of delta Ring and Ball Softening Point dependence from Percent Free Bitumen (%V_{BF}) and FETCh parameter, when results are grouped by type of filler and by concentration of filler in mastic by volume.

to the surface area, shape or content of organic material which may indeed disturb the real value of %V_{BF}. In Fig. 6 we decided to divide the fillers into NAT (KK, TE, REP, KF) and MM (FA, FAW, EXP). This may lead to the over interpretation of results for the limited set of fillers and future work proving this hypothesis is required. Nevertheless we believe that demonstrating the difference between two types of materials, rather than blindly treating them as one, is important and the more drastic effect of such division is further presented.

The slopes and the intercepts of the almost parallel lines presented in Figs. 4 and 6 follow the relationship presented in Fig. 7. With such model, for a given volume of the filler, one is able to estimate the ΔR&B with quite high accuracy.

5.3. New understanding of mastic (the surface area factor)

We have incorporated one more parameter, namely surface area of fraction passing 0.125 mm sieve. The results are presented

in Fig. 8. It became even more evident that pure fly ashes constitute a different group of fillers, whereas to our surprise the filler being a mixture of MM and NAT aggregates (EXP) stayed in line with natural aggregates. The fitting of functions in Fig. 8 was conducted on the basis of five fillers, TE, KK, KF, REP and EXP. We trust that stiffening of the mastic containing fly ashes is predictable; however it will require additional parameter investigation. Most likely the content of organic matter in the fly ashes shifts the results into low FETCh*(%V_{BF})/SA values. The organic (at least up to some level) FA matter, also known as unburnt carbon, which in this case could be identified as coal tar pitch, is a mixture of hydrocarbons of the similar Hansen Solubility Parameters to those of bitumens [18,31] and could be identified as bitumen by means of solubility, for instance, in the toluene test.

In more classical understanding of the mastic, fly ash is a filler and bitumen is an organic liquid in which filler is suspended [12] (Fig. 9b). However, because the fly ash can be divided into organic and non-organic parts (Fig. 9a), we propose a mastic concept in which only non-organic part of fly ash is considered as filler, while organic part of fly ash becomes an extension of binder (Fig. 9c).

If we consider that our fly ash consists of about 4% (assumed value – deduced from the difference in LOI of FA and FAW presented in Table 6, allowing presence of some mineral salts insoluble in water yet able to decompose under 1000 °C [32]) “bitumen-like” substance, which could be identified as binder, we need to redefine the concept of mastic in the cases in which fly ash (FA) filler is used. The novel concept of understanding this system is provided in the form of schematic picture in Fig. 9 and the changes which this paradigm inflicts on the parameters are explained both in Fig. 9 and in the text below.

When our novel mastic concept (Fig. 9c) is applied; the inorganic part of FA increases slightly its Fe₂O_{3sol}%, but due to the increase of the binder amount, FETCh in e.g. mastic FA37 decreases by approximately 0.1%. In this case, we assume 4% unburnt carbon of mutual solubility [18], as Loss on Ignition (LOI) is in majority of the cases slightly bigger than the unburnt carbon content in fly ashes [32]. SA of fly ashes with LOI equal to 0.32%, fraction passing 0.0525 mm sieve (No. 300), was reported on 1.4 m²/g [33]. According to SA changes, observed in our study, with increased particle size, the value should decrease and is estimated for our materials to be 1.2 m²/g. When less dense material

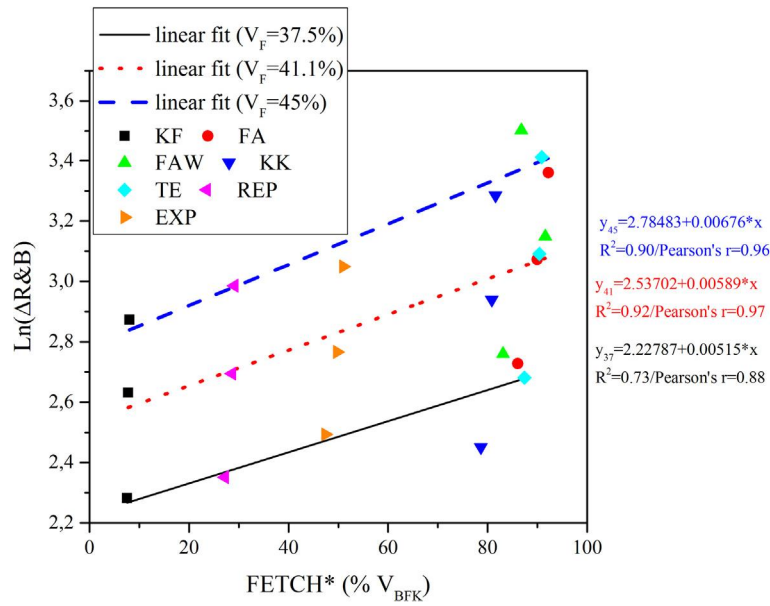


Fig. 5. Representation of delta Ring and Ball Softening Point dependence from Percent Free Bitumen ($\%V_{BFK}$) and FETCH parameter, when results are grouped by type of filler and by concentration of filler in mastic by volume.

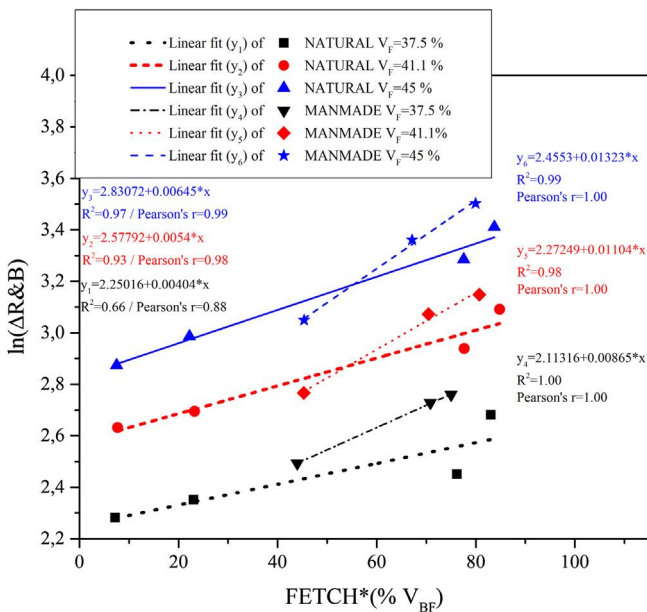


Fig. 6. Representation of delta Ring and Ball Softening Point dependence from Percent Free Bitumen ($\%V_{BF}$) and FETCH parameter, when fillers are grouped into natural and man-made types, within given volumetric concentration of filler.

(unburnt carbon) would be disregarded as mineral filler (see Fig. 9C), the voids in mineral aggregate would decrease and it is estimated hereby that the H_f would remain on the level similar to other inorganic aggregates (around 33%), which in effect would increase $\%V_{BF}$ value. Overall, those changes will lead to increase in the total value of $FETCH^* (\%V_{BF})/SA$ parameter, placing the FA and FAW fillers on the right side of the graph (Fig. 8.), within the values extrapolated on the basis of natural fillers. The estimate above was equal to ca. $66\%/m^2$, whereas $FETCH^* (\%V_{BF})/SA$ parameter calculated from function determined for 37.5% mastic on the basis of results for natural fillers, was found equal to ca. $61\%/m^2$. This leads us to trust that the mastic concept proposed above is justified.

However, the part of organic matter in the fly ash, which could be considered as bitumen, was not studied in this work in detail, thus further work is necessary to confirm this theory.

Additionally, the predictive strength of the models could be improved by utilizing data with more accurate V_F parameter. Currently, for line assignment of 37.5% the value ranged between 37.46% and 37.61%, for 41.1% between 41.1% and 41.24% and for 45% between 44.98% and 45.01%, and it is evident that the 45% line had least scatter and best fits in almost all FETCH representations (see Table 7, column V_f as well as Figs. 4–6).

5.4. New model for mastic stiffening

Figs. 4–7 gather majority of the results of the modeling work. Fig. 8 is developed on the basis of our new concept for asphalt mastic with MM materials, presented in Fig. 9. Based on normal modeling or the novel concept, the calculation algorithms to determine the $\Delta R \& B$ is presented in Fig. 10. The slope and intercept dependence in all proposed models, necessary for calculations, are provided in Table 8.

5.4.1. Model validation

Models were validated by predicting the mastic stiffening for KK and TE fillers at the volumetric filler concentration of 42% and comparing it with validation experiment results, as discussed in Section 5.1. The true values (y) were measured from prepared mastic blends (composition in Table 1), and the results of the validation experiments are provided in Table 7, whereas predictions (Y_i) are collected in Table 9.

To evaluate the soundness of the model we utilized the criterion given in the $\Delta R \& B$ standard. It states that if two results differ by $3^\circ C$, they should be rejected and repeated. Therefore, if the difference between predicted and obtained value differed by $\geq 3^\circ C$, the model is thought to be insufficient in this work.

It becomes evident that the simplest representations are incapable of distinguishing between the two aggregates of very similar voids in mineral aggregate (H_f or H_{fk}) and densities. The prediction using models 1, 2 and 3 give almost identical results for KK and TE, and the difference between the real value and the prediction is $\geq 3^\circ C$ for TE.

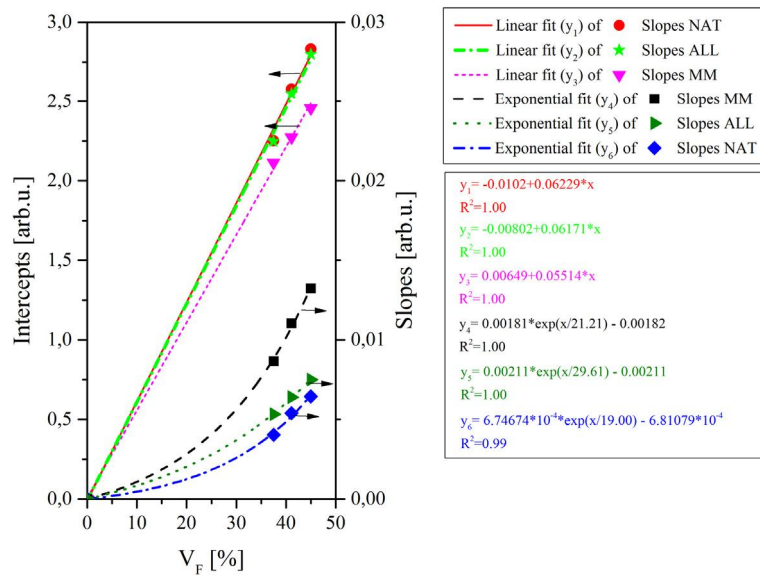


Fig. 7. Dependence of slope and intercepts of linear models developed in FETCH representation from filler concentration in mastic.

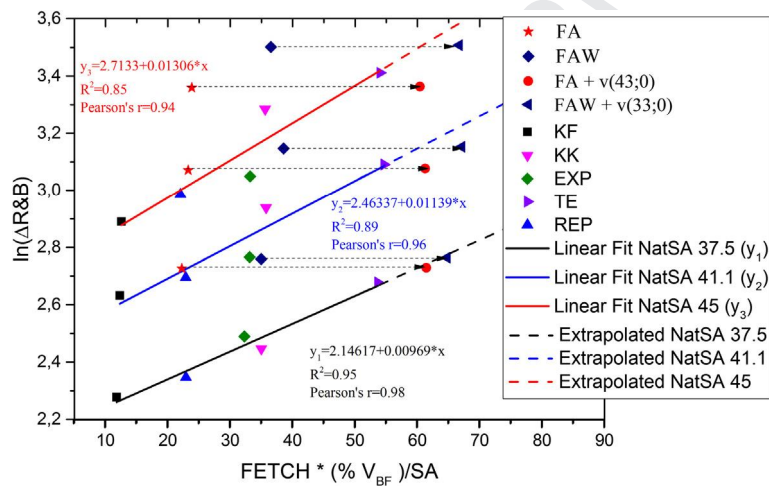


Fig. 8. Representation of delta Ring and Ball Softening Point dependence from percent free bitumen ($\%V_{BF}$), SA and FETCH parameter for all fillers. Linear fits for the corresponding V_F conducted for natural fillers only (excluding FA and FAW points). The dashed lines represent extrapolation of each function. FA and FAW are plotted as is (red star and navy diamond points) as well as translated by a vector determined by calculating $FETCH * (\%V_{BF}) / SA$ parameter from obtained $\ln(\Delta R\&B)$ values by fitting them into the y_1 function (red dot and navy triangle). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

714 The models 4 and 5 are still incapable of distinguishing
715 between the two fillers by failing to predict that KK causes less
716 stiffening than TE. However, the difference between the
717 measured and predicted value is clearly ≤ 3 °C. Although for those
718 two fillers this model seems somewhat adequate, we must
719 realize the influence of the scattered results (see Fig. 3) on the
720 universal prediction capability of the model. If we took, for example,
721 REP as evaluator of model 4, the error would increase up to
722 8 °C, as REP results are the furthest away from the fitted function.
723 Results of mastics composed of TE and KK are relatively close to
724 the fitted model.

725 All models utilizing FETCH parameter, regardless of the origin of
726 the voids in mineral filler, are capable of differentiating between
727 the fillers in the correct manner ($\Delta R\&B_{TE} > \Delta R\&B_{KK}$). Having the
728 small error and scatter of results, it is most likely that the predic-
729 tion of stiffening by using FETCH parameter is the most reliable
730 and universal for all tested fillers. The prediction error is most
731 likely to remain within the set limit of ≤ 3 °C.

6. Discussion

732
733 The water treatment of FA, which resulted in FAW created an
734 interesting material, which seemingly had lower surface area,
735 lower H_f and similar density to FA. Applying the concepts available
736 prior to date, one could predict a lower stiffening of the mastic
737 when in contact with this material, whereas in reality this was
738 the most stiffening inflicting material. This could be predicted only
739 by considering the FETCH parameter (Fig. 11).

740 The FETCH parameter was developed as a function of iron con-
741 taining compounds located on the surface of the filler capable of
742 interacting with a liquid (both acid and bitumen). This can be
743 explained by the fact that the chemical methodology used to deter-
744 mine FETCH is not dissolving the substrates in full (and thus we
745 call the method “modified” as in unmodified version a different
746 methodology is called upon to dissolve substrates in the occur-
747 rence of high Impure Silica content). The Impure Silica content of
748 fillers is presented in Table 6. In our work, only the dissolved part

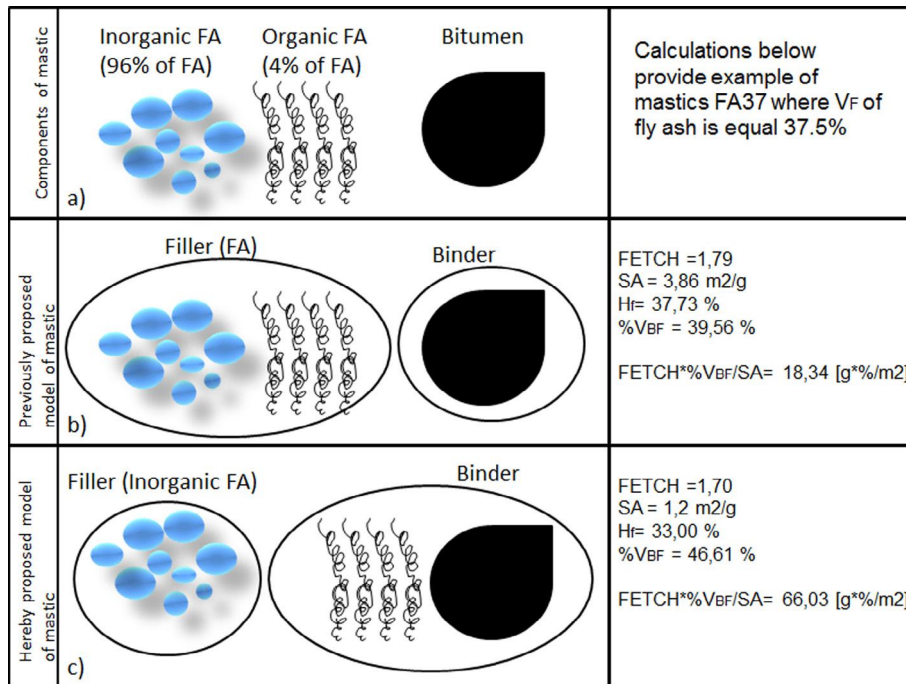


Fig. 9. Schematic representation of a novel mastic composition concept demonstrated on the example of FA37; (a) definition of mastic components, (b) current understanding of mastic [9], (c) proposed understanding of mastic incorporating fly ashes.

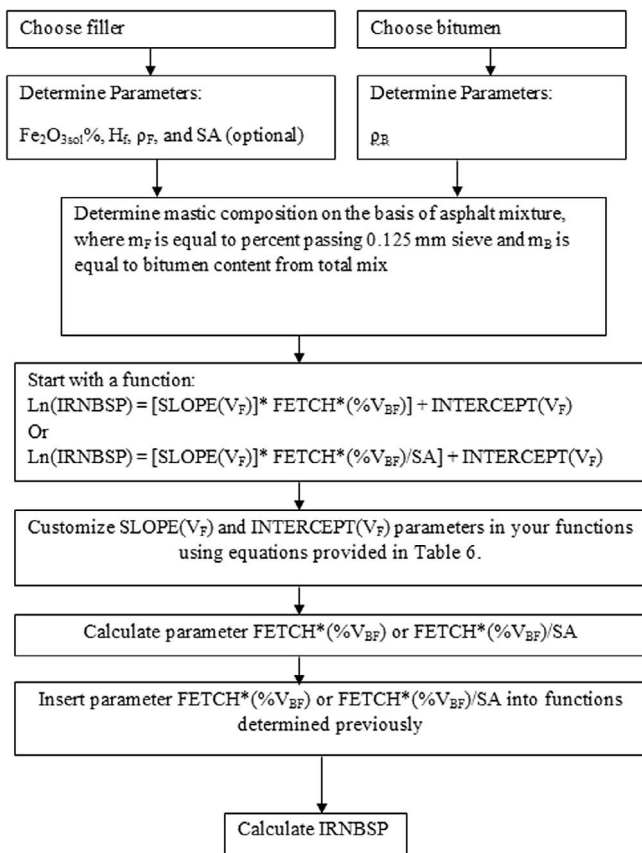


Fig. 10. Schematic algorithm for prediction of custom mastic stiffening expressed by $\Delta R\&B$.

ultimate analysis (SFS-EN 196-2 Section 13.2) than in the values reported here. Similar problems are met with other techniques such as for example X-ray Diffraction (popular method of determining mineral content in mineral fillers), which can only identify minerals in the form of the crystal [34] (the fused silica such as observed in the fly ash to some extent cannot be analyzed with the method). This is why we use etching as the describing word for the parameter as the analysis is not ultimate, but of only the soluble material accessible to etching by acid. The atoms trapped inside the insoluble (impure) silica remain invisible to the result of the test. Incidentally, those metals should not be in contact with bitumen coating. However, because the size of acid molecule and bitumen molecules are different, we are aware that most likely less of the minerals is accessible for contact with bitumen. The test is not as sophisticated as grain surface mapping, but provides close approximation in bulk of the surface composition of material. As mentioned, the ultimate iron content is expected to be higher in the studied materials. However, from the considered point of view that ultimate value is unimportant. According to our hypothesis, the iron compounds must be in physical contact and proximity with bitumen to be able to interact with its molecules and inflict the assembly on its surface. Comparing this value to X-ray fluorescence or X-ray Diffraction values of Fe₂O₃ could be misleading as those methods present much higher standard deviation in repeatability and possess own limitations [34].

Furthermore, it was found that the error margin for mineral analysis was extraordinarily low in this study. The SFS-EN 196-2:2005 standard suggested 0.08% repeatability for Iron (III) oxide analysis, and we obtained 0.028% (for all population of samples), 0.019% (natural fines) and 0.035% (man-made fines). Additionally, the change in this value between raw aggregates and materials extracted from the mastic (as is commonly practiced with materials collected from the actual roads) was in the range of 0.1%, which is very close to the repeatability limit. As a point of reference, the Voids in Mineral aggregate, from the data collected in our laboratory, may change by up to 10%, due to the residual bitumen in extracted samples.

Table 8
Customized regression coefficients developed on the basis of obtained data.

Type of fit	Slope dependence	R ²	Intercept dependence	R ²
(FETCH * %V _{BF}) all fillers	0.00211 * exp(V _f /29.61) – 0.00211	1.00	–0.00802 + 0.06171 * V _f	1.00
(FETCH * %V _{BF}) natural fillers	6.74674 * 10 ^{–4} * exp(V _f /19.00) – 6.81079 * 10 ^{–4}	0.99	–0.0102 + 0.06229 * V _f	1.00
(FETCH * %V _{BF}) man-made fillers	0.00181 * exp(V _f /21.21) – 0.00182	1.00	0.0065 + 0.05514 * V _f	1.00
(FETCH * %V _{BF/SA}) natural fillers	0.00604 * exp(V _f /39.02) – 0.00605	1.00	Y = –0.01083 + 0.0596 * V _f	1.00
(FETCH * %V _{BFK}) all fillers	0.00431 * exp(V _f /47.73) – 0.00431	1.00	Y = –0.0087 + 0.0614 * V _f	1.00
(FETCH * %V _{BFK/SA}) natural fillers	0.00711 * exp(V _f /44.87) – 0.00711	1.00	–0.0093 + 0.0593 * V _f	1.00

Table 9
Model evaluation by comparison to experimentally obtained IRNBSP (°C) results.

Model no.	Model name	TE_42%	Y _{l–y}	KK_42%	Y _{l–y}
1	Prado	17.7	4.2	17.6	2.5
2	Heukelom/H _f	18.0	3.9	18.5	1.6
3	Heukelom/H _{fK}	17.9	4.0	18.1	2.0
4	Anderson/H _f	19.0	2.9	19.2	0.9
5	Anderson/H _{fK}	22.0	0.1	22.2	2.1
6	FETCH * %V _{af} all fillers	23.2	1.3	22.2	2.1
7	FETCH * %V _{af} natural fillers	21.6	0.3	20.8	0.7
8	FETCH * %V _{af/SA} natural fillers	22.8	0.9	18.3	1.8
9	FETCH * %V _{afK} all fillers	22.6	0.7	21.4	1.3
10	FETCH * %V _{afK/SA} natural fillers	22.7	0.8	18.0	2.1

We are aware, that the method of determining the FETCH is not very simple and requires some chemical skills of the operator. There is a possibility to further improve the method, e.g. by the reduction of digestion time. However, the methodology is still simpler, cheaper and more feasible than collecting cores or RC material from the road, especially from busy highways, and running performance tests. Ability to predict mixture stiffness and workability from a small amount of material would be of most importance for the hot in-place recycling application.

Nevertheless, both Fe₂O_{3sol} and H_f for blended fillers (REP, EXP), can be easily calculated from the raw material data and estimated mass ratio of raw materials in the blend. The error between using raw material data and measuring of Fe₂O_{3sol} from extracted material (OEXP: average Fe₂O_{3sol}% = 2.31%) in the study presented here would be between 0.05% and 0.07%, whereas for H_f – between 0.27% and 2.46%. Both of those values stay within the limit of

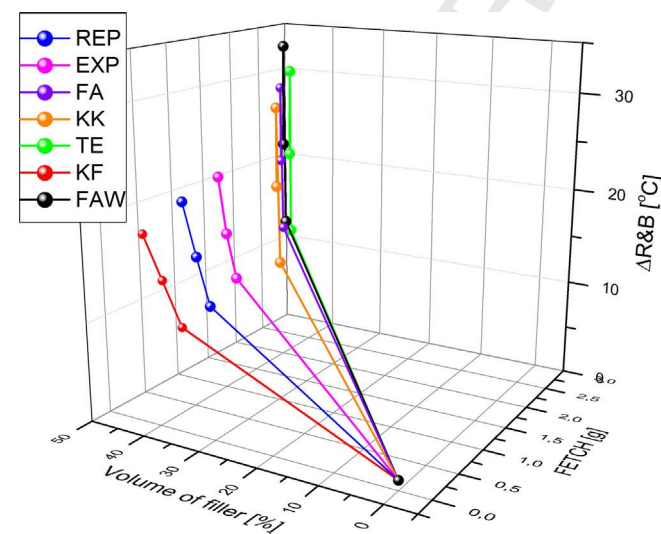


Fig. 11. A polygonal mesh representing the influence of the FETCH on the Increase in Ring and Ball Softening Point.

repeatability in corresponding standards. It would be advised to store those parameters in the road construction databases with the recycling of asphalt pavement in mind.

The calcium oxide content, proposed previously as a chemical parameter in stiffening [21,35], was found somewhat indicative of mastic stiffening inflicted by the filler, but it differentiated between only very different materials such as limestone and granite. When comparing granites and fly ashes, the CaO or CaOetch (calculated similarly to FETCH) as indicators lost its sensitivity.

It is proposed that the FETCH will be a better parameter, not only predicting stiffening between the fresh filler and bitumen which was presented here, but also predicting the stiffness of aged mastic in the field (necessary information in the hot in-place recycling during planning of the heating operations) or stiffening of mix inflicted by adding RAP into the fresh mixture (by the analysis of fines extracted from the RAP and fresh filler).

We are aware that this study was limited to one paving grade bitumen produced by the local refinery and that different penetration grades need to be studied. Due to the problem with studded tires wear, the focus on performance in Finland lays in aggregate quality. As a result, the recycling of the high class aggregates is promoted, rather than the bitumen modification. Because of that, usually one type of bitumen, of one origin and one supplier is used across the whole country. It is envisioned that the FETCH parameter will work for other filler materials around the world, but verification and then re-calibration of the models if needed is advised for the better adaptation of the local materials on the market.

The fly ash used during this research originated from one source and one batch. The term fly ash is used as a description of material with a variable composition, when the latter is a function of the fuel source used to obtain the product, e.g. coal fly ash [34] or biomass fly ash [30]. The fly ashes always contain silica, alumina and iron oxides, yet differ in the relative ratios of thereof. In geological terms, two rocks of a different composition are understood as different minerals. Similar classification exists in fly ashes e.g. class F and class C fly ash, and is applied around the world. Even tough, in Finland, the use of rock type for the road construction is specified closely because of the mineral content variation, similar classification does not exist for fly ash and perhaps further studies should look into this issue.

Currently worldwide, as a construction product, fly ashes are regulated and it is understood that their composition depends on factors such as feed composition [34], type of furnace [36], plant design [37]. The above presented work served the purpose of providing a tool for a more detailed characterization of fly ashes for the purpose of road construction. The project originated from a forensic study of a road constructed in 2002 and focused on the analysis of the materials available on the small local market, where fly ash classification does not exist. Authors suggest that a larger number of fly ash types should be tested in order to understand the phenomenon globally.

Additionally, the effect of surface area on the properties of the mastic and therefore the performance of asphalt concrete should be further studied. As demonstrated here, man-made materials such as fly ashes are not always following rules observed for the

natural materials. In the natural fines, the surface area gets smaller with increasing the size of particles, whereas for the fly ashes the situation is converse (Table 5). This is due to the fact that unburnt carbon, characterized by large surface area [33], has a tendency to accumulate in higher fractions [38,39]. Therefore, considering the fines as the material passing 0.063 mm or 0.075 mm sieve may be misleading, when the filler passing 2 mm sieve [9] is used.

Content of the organic material in the material considered as inorganic is suggested to be factor in the prediction of stiffening. This should be studied further.

In respect of Ring Road II analysis, it became obvious that changing the filler from low FETCH and low volume (REP, $V_F = 39\%$), into higher FETCH and high volume (EXP, $V_F = 45\%$), caused the $\Delta R\&B$ to increase by 10 °C, even though both fillers and filler blends met the given requirements [8]. This being equal to change in two penetration grades of bitumen, is believed to have affected to the compaction problems and suggests that a revisit of the Specifications should be conducted with above findings in consideration. Such behavior was already predictable by utilization of the oldest representations, e.g. Heukelom [12] and thus it is expected that the problems occurred mainly due to negligence of the effect of filler on the properties of asphalt concrete. Although there is increasing need for better use of waste products as construction materials, more emphasis should be given in the chemical and physical compatibility and long term performance.

One of the limitation of this study remains in the narrow range of V_F investigated. However, this range was found the most applicable for both asphalt concrete mixes and stone asphalt mastic mixes empirically developed for local market and available in form of gradation envelopes. This makes the models already usable in the forward prediction of stiffening in Finland.

Furthered enhancement would be to incorporate different viscosity evaluating techniques (e.g. Brookfield viscometer, Dynamic Shear Rheometer) to replace conventional softening point testing. In addition, the notion of tender mixtures implies that there are very fine fillers that can become the so called binder extenders in a similar manner as the organic component of fly ash. This is an issue that should be further studied for the refinement of these filler models. Tender mixtures are asphalt mixtures, which are unstable during rolling, i.e., they displace laterally and shove rather than compact under roller loads [40].

7. Conclusions

In this research a novel parameter, etchable iron, namely FETCH, describing previously ignored component of fine material used in asphalt concrete production was developed and presented. Mastic stiffening prediction, expressed by the Increase in Ring and Ball Softening Point, was found to be the most accurate when two concepts, the percent free bitumen and FETCH parameter, were combined. The review of mastic stiffening models as graphical representation was also provided.

By incorporating the FETCH we were able to characterize all fillers commonly used in Finland with one Russian based source of 70/100 grade bitumen, as if it was one type of material. The models developed with the FETCH parameter were found to distinguish between fillers which shared very similar densities and voids in mineral aggregate. This methodology is readily applicable for the practitioners to characterize their local materials. The FETCH parameter is promising candidate in predicting the stiffness of asphalt in the field. Particularly it is envisioned to be useful during hot in-place recycling while planning the necessary road surface heating effort which depends on asphalt aging and stiffness. What is more, the ability to predict the stiffness of the mix should be beneficial in prediction of compaction effort necessary to obtain desired air voids.

This work verified that the previously reported failures observed on Ring Road II in Finland were partially caused by failures to recognize the mastic stiffening issue. A better dissemination and implementation of existing and new research is therefore needed.

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