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Emission reduction agents : a solution to inhibit the emission of harmful volatile organic compounds from crumb rubber modified bitumen

## Emission reduction agents: a solution to inhibit the emission of harmful volatile organic compounds from crumb rubber modified bitumen

**Abstract:** Volatile organic compounds (VOCs) in bitumen fumes pose health risks to workers. Adding end-of-life tire crumb rubber (CR) to bitumen increases VOC emissions. To promote cleaner asphalt production, recycled materials like cementitious materials, activated carbon, zeolite, and geopolymers were incorporated into crumb rubber modified bitumen and explored as emission reduction agents (ERAs). Proton-transfer-reaction time-of-flight mass spectrometry was used to compare VOC emissions across blends. ERAs reduced emissions by at least 33%, with Portland cement, activated carbon, and geopolymer-based fly ash achieving up to 58%, 49%, and 48% reduction, respectively. Multivariable regression analyses showed that the BET surface area, BJH adsorption cumulative surface area, BJH desorption cumulative surface area, and average pore diameter of the ERAs were the predominant factors contributing to the reduction of VOC emissions.

### 1. Introduction

The use of crumb rubber (CR) derived from shredded end-of-life tires (ELT) in asphalt pavements is an evolving technology. Asphalt mixtures using CR have demonstrated improved performance compared to conventional asphalt pavements, reducing distresses and delaying maintenance procedures [1-4]. Two primary methods, the wet and dry processes, are used to incorporate CR into hot mix asphalt (HMA). These methods differ in terms of rubber particle size, CR concentration, rubber behaviour and function, and the resources required for CR integration into the asphalt mix. Crumb rubber modified bitumen (CRMB) is produced through the wet process, which involves blending CR with bituminous binders at concentrations ranging from 5 to 25% by weight of the base binder at temperatures above 175 °C [5-7]. However, CRMB requires high temperatures (above

150 °C) during the mixing, transportation, and paving processes to reduce viscosity and enable its application on construction sites. These high temperatures result in the release of greenhouse gas emissions, odour and toxic gases into the surrounding environment, posing potential health risks to workers exposed to harmful fumes [8-11]. The components present in these emissions are various classes of volatile organic compounds (VOCs), including polycyclic aromatic hydrocarbons (PAHs), oxides (e.g., $NO_x$, $CO_x$ and $SO_2$) and particulates (e.g., PM2.5 and PM10) [12-14]. VOCs are defined as atmospheric pollutants that can have an acute and chronic effect on human health through skin contamination and inhalation, posing a risk to pavement construction workers and also affecting the growth and development of animals and plants [12, 15, 16]. An investigation on the potential link between asphalt VOCs and human lung cancer was performed by Boffetta et al. [17]. Their findings suggest a link with the increase in lung cancer among workers from mixing and paving sites. Therefore, the control of VOC emission from bituminous materials has been investigated in more detail and addressed in protocols and policies by private and public agencies. In Europe, the Chemical Agents Directive (98/24/EC) [18] and the Directive on Carcinogens and Mutagens at Work (2004/37/EC) [19] ensure that workers are protected from chemical risks during work. In the United States, the Occupational Safety and Health Administration (OSHA), the Agency for Toxic Substances and Disease Registry (ATSDR), and the National Institute for Occupational Safety and Health (NIOSH) are taking actions to minimize possible acute or chronic health effects from exposure to asphalt fumes. NIOSH recommends a maximum VOC emission of 5 mg/m$^3$ during any 15-min period [20].

The origin of the crude oil, the manufacturing process and the production temperature affect the properties of bitumen and also determine the VOC emission profile of bitumen fumes. Moreover, the recurrent addition of additives and particles like CR from ELT to

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bitumen also contributes to the total VOC emission [9, 21], making it a downside of recycling old rubber. As reported by Borinelli et al. [21], incorporating CR into bitumen led to changes in the composition of alkanes, aromatic compounds, and sulphur-containing VOCs. They also emphasized the crucial role of temperature in VOC emissions, resulting in a significant rise in compound release, particularly within the 160-180°C range, which coincides not only with the typical production temperature of CRMB but also with the transportation and construction temperatures of the asphalt mixture. Yang et al. [9] reported similar findings, noting that CR modification significantly amplified emissions, particularly in the case of pollutants VOCs like xylene and toluene, where levels can be several times higher than asphalt without CR. In addition to highlighting the rise in VOC emissions resulting from the addition of CR to an unmodified bitumen, the research from Liu et al. [22] also underscored the substantial impact of CR on the significant increase in emissions of benzene, toluene, m-xylene, and p-xylene, which surged by more than tenfold.

In recent years, many researchers have performed studies to characterize the VOCs from bituminous binders and investigated ways to reduce these emissions. Emission reduction agents (ERA) have been added to the binder to effectively reduce emissions with limited changes to the production process and performance of the asphalt mixture. Classified as chemical or physical, adsorption is an emission reduction mechanism for bitumen [23]. Chemical adsorption is the process where the active functional groups of the ERA share electrons with the VOC molecules, making the latter get adsorbed on the surface of the ERA [24]. In physical adsorption, the micropore structure and specific surface area of the ERA are the key determinants. Physical adsorption can be separated into three steps. The first is external diffusion, in which the VOCs released from bitumen adhere to the ERA surface due to the high free energy associated with the large surface area of the ERA. In

the second step, called internal diffusion, the VOC molecules diffuse into the inner

aperture of the ERA. In the final stage, the VOC molecules are blocked in the pores due

to the labyrinth effect and intermolecular van der Waals force [25].

According to Wang et al. [23], the majority of ERA can be divided into three categories

based on their physical properties: organic polymer materials (OPM), inorganic materials

(IM), and composite materials (CM). Despite helping to reduce the emission of PAHs

from bituminous binders, OPM (e.g., resins, alcohols, aldehydes, olefins) are falling into

disuse as most of them are toxic and need a longer reaction time (about 2.5 h) than the

other two ERA categories. IMs (metal oxides, inorganic salts, and inorganic porous

materials) and CMs (developed from organic polymers and inorganic porous materials)

are usually mixed with asphalt binder using a high-shear mixing equipment at a shear rate

between 3000 and 5000 r.p.m. for 20 to 60 min at temperatures between 140 and 165 °C

[26-29]. IMs have shown a greater potential to reduce VOCs when compared to CMs:

more than 50% reduction in emissions for the former when using inorganic porous

materials and inorganic salts versus 30% reduction for the latter [23]. In addition to the

three categories mentioned above, organic materials (OM), such as activated carbon (AC)

and bentonite, have been used to reduce fumes due to their highly porous and amorphous

structures. OMs are mixed with bitumen using the same process as IMs and CMs. Li et

al. [30] used organo-montmorillonite nanoclays to modify a base bitumen and concluded

that nanoclay effectively inhibited VOC emission by capturing the light components of

bitumen in the interlayer space of nanoclay. Tang et al. [31] used metakaolin, silica fume

and blast-furnace slag as precursor materials to synthesize a geopolymer and mix it with

a base binder. Their results showed that the original and anhydrous geopolymer reduced

VOC emission during asphalt production. The use of activated carbon was evaluated by

Long et al. [24] and Xiao et al. [28]. Both studies concluded that its porous structure and

high specific surface area can significantly reduce VOC emissions when incorporated into the bituminous matrix at an optimum quantity between 4 and 5% by weight of bitumen.

Due to increased VOC emission rates in CRMB, which includes potentially toxic compounds, it is of paramount importance to reduce their impact on the human body and the surrounding environment. One approach is to add emission reduction agents (ERA) to bitumen, which can effectively reduce emissions with limited changes to the production process. However, the majority of ERA are falling into disuse as most of them are toxic or have not shown significant levels of emission reduction. Although separate efforts have been reported in the literature, there is still a need for a comprehensive evaluation of ERA of different nature aimed at identifying the best relative performers. Thus, the objectives of this study are as follows:

- to quantify the potential reduction in VOC emission of a selection of ERAs added to CRMB, including organic and inorganic materials.

- to investigate the relationship between the physical characteristics of ERAs and the VOC emission of the samples.

**2. Materials and methods**

VOC measurements using a proton-transfer reaction time-of-flight mass spectrometer (PTR-TOF-MS) were conducted on neat bitumen, polymer modified bitumen, and CRMB with different ERAs. The results allowed us to obtain the VOC profile and the total VOC emission for each sample and use them as input to investigate the emission reduction inhibition effect of the employed ERAs. A two-step normalization was adopted to assist in the process of selecting the most promising ERA in terms of VOC reduction.

128 A particle size analyser and a surface area and porosity analyser were used to measure

129 the physical parameters of the ERAs (average particle size, BET surface area, BJH

130 adsorption and desorption cumulative surface areas, total pore volume, and the average

131 pore diameter). Statistical analysis was performed using the physical parameters of the

132 ERA were used as input to predict the VOC emission of the CRMB samples modified

133 with ERA. An overview of the research steps taken in this study is presented in Figure 1.
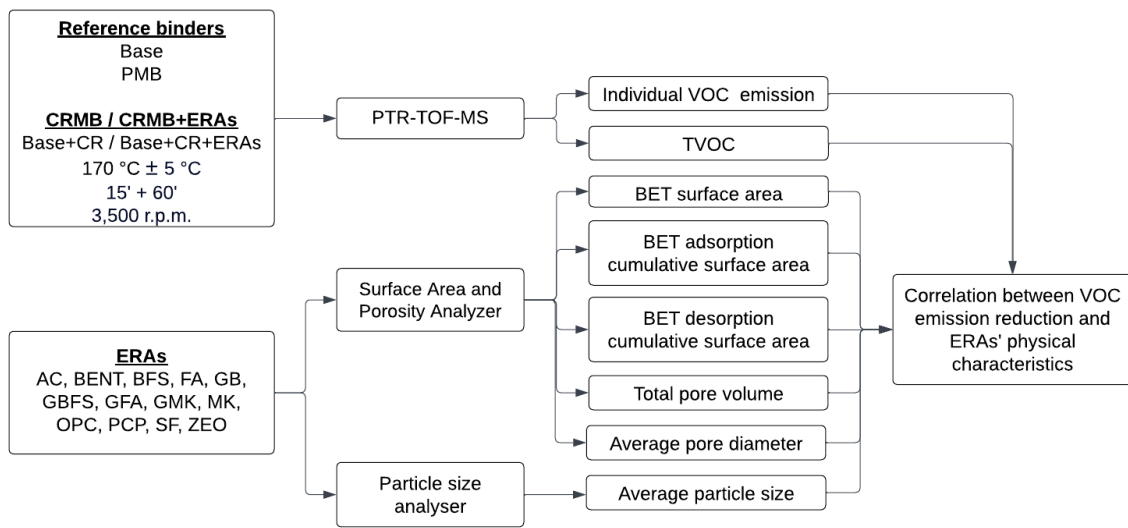


135 Figure 1. Flowchart of the research methodology

136 ## *2.1. Materials*

137 *2.1.1. Reference binders*

138 The base binder used for this study was a standard 50/70 unmodified bitumen (base).

139 Additionally, a 10/40-65 polymer-modified binder (PMB) was used, both commercially

140 available in Belgium. PMB was used for comparison purposes and its selection predicated

141 on its penetration grade, closely matching that of the CRMB. The basic physical

142 properties of the reference binders are given in Table 1. The penetration and softening

143 points were measured in the laboratory following the EN 1426 and EN 1427 standards.

144 The penetration index (PI) was calculated based on the softening point and penetration

145 values. The effect of polymer modification can be observed by a higher PI and softening

146 point.

147 Table 1. Basic physical properties of the reference binders

| Property | Results | | Unit | Test Standard |
|---|---|---|---|---|
| | Base | PMB | | |
| Penetration (at 25 °C) | 53.0 | 21.0 | 0.1 mm | EN 1426 |
| Softening point | 51.8 | 69.0 | °C | EN 1427 |
| Penetration index | − 0.6 | 0.7 | - | - |

148 *2.1.2. VOC emission reduction agents (ERA)*

149 Table 2 summarizes the ERA selected to promote the reduction of VOC. Activated carbon

150 (AC) was chosen for its high specific area and broad pore size distribution [24, 28].

151 Ground granulated blast furnace slag (BFS), class F fly ash (FA), silica fume (SF) and

152 metakaolin (MK) were used in their pure state (without being activated or hydrated), and

153 also employed as precursors in the preparation of geopolymers. Portland cement was

154 incorporated before and after hydration. Lastly, the experimental design included

155 bentonite and zeolite.

156 The geopolymers were prepared by mixing a precursor with an alkali source. The

157 activation of the precursors was carried out with an alkaline solution prepared with

158 sodium hydroxide (98% pure, pellets) and sodium silicate solution (25.9 wt.% sodium

159 oxide, 7.9 wt.% silicon oxide, and 66.2% water). The pastes were produced using the

160 following procedure: (i) the alkalis and water were mixed until fully dissolved and

161 allowed to cool down at room temperature; (ii) this solution was added to the powder

162 precursors and mixed for 2 minutes using a mechanical hand mixer; (iii) the fresh paste

163 was sealed and placed in an oven at 60 °C for 3 days. The Portland cement paste (PCP)

164 was produced using distilled water only and left in the oven for the same time and

165 temperature as the geopolymers.

166 Table 2. Description of the VOC reducers. OM = organic material, IM = inorganic
167 material

| Name | Description | Supplier | Class |
|------|-------------|----------|-------|
| AC | Steam-activated carbon/charcoal | Alfa Aesar | OM |
| BENT | Bentonite | Thermo Fisher Scientific | OM |
| BFS | Ground granulated blast furnace slag | Ecocem | IM |
| FA | Fly ash (class F) | Value Ash Technologies | IM |
| GB | Metakaolin, blast-furnace slag- and silica fume-based geopolymer | - | IM |
| GBFS | Ground granulated blast-furnace slag-based geopolymer | Ecocem | IM |
| GFA | Fly ash (class F) based geopolymer | Value Ash Technologies | IM |
| GMK | Metakaolin based geopolymer | Caltra | IM |
| MK | Metakaolin | Caltra | IM |
| OPC | Ordinary Portland cement | Sibelco | IM |
| PCP | Portland cement paste | Sibelco | IM |
| SF | Silica fume | Aerosil | IM |
| ZEO | Zeolite (type ZSM-5) | Thermo Fisher Scientific | IM |

168 The formulation of the geopolymer and PCP pastes is shown in Table 3. Before being

169 used as additives for VOC reduction, the hardened geopolymers and PCP were manually

170 crushed. The fraction passing the 0.125 mm sieve was selected and dried in the oven for

171 1 h before being added to the bituminous blends. The results of the element analysis for

172 the different ERA using a Niton XL3t-Goldd X-ray fluorescence analyzer (Thermo

173 Scientific) are presented in Table 4. X-ray fluorescence cannot measure elements lighter

174 than magnesium; for that reason, carbon is not presented in the element analysis. Silica

175 and calcium are the most abundant elements in most ERAs.

176 Table 3. Formulation of the pastes produced (% in mass)

| | BFS | FA | MK | OPC | SF | NaOH | $Na_2SiO_3$ | Water |
|------|------|------|------|------|------|------|------|------|
| GB | 31.53 | - | 7.19 | - | 7.19 | 1.32 | 9.01 | 43.76 |
| GMK | - | - | 39.08 | - | - | 7.17 | 29.26 | 24.49 |
| GBFS | 66.90 | - | - | - | - | 2.05 | 14.02 | 17.02 |
| GFA | - | 66.90 | - | - | - | 2.05 | 14.02 | 17.02 |
| PCP | - | - | - | 71.43 | - | - | - | 28.57 |

177 Table 4. X-ray fluorescence analysis of the ERAs (ppm)

| Element | AC | BFS | FA | MK | OPC | GB | GBFS | GFA | GMK | PCP | BENT | ZEO |
|---------|------|------|------|------|------|------|------|------|------|------|------|------|
| Fe | 2,510 | 3,178 | 66,679 | 4,055 | 32,038 | 1,813 | 2,612 | 54,608 | 3,035 | 24,262 | 33,704 | 292 |
| Ti | 225 | 2,437 | 7,836 | 11,069 | 2,715 | 3,148 | 2,644 | 7,555 | 6,782 | 1,851 | 3,603 | 193 |
| Ca | 41,457 | 308,970 | 23,746 | 2,836 | 486,842 | 170,584 | 249,577 | 19,006 | 4,326 | 380,537 | 12,095 | 1,169 |
| K | 9,926 | 4,854 | 28,182 | 1,697 | 8,167 | 3,493 | 4,932 | 22,785 | 1,318 | 5,684 | 4,993 | 283 |

| Element | AC | BFS | FA | MK | OPC | GB | GBFS | GFA | GMK | PCP | BENT | ZEO |
|---------|-----|-----|-----|-----|-----|-----|------|-----|-----|-----|------|-----|
| S | 48,946 | 10,040 | 5,086 | 795 | 21,575 | 4,694 | 10,152 | 2,348 | 747 | 12,421 | 7,148 | 1,465 |
| Al | 992 | 29,526 | 98,438 | 165,482 | 19,035 | 33,480 | 20,710 | 71,529 | 91,071 | 9,476 | 40,644 | 1,053 |
| P | 1,849 | <LOD | 1,473 | 5,360 | <LOD | <LOD | <LOD | 765 | 2,708 | <LOD | 718 | 730 |
| Si | 18,115 | 111,973 | 230,661 | 218,210 | 68,090 | 153,049 | 109,222 | 205,148 | 220,301 | 50,625 | 206,352 | 520,499 |
| Cl | 1,517 | 543 | <LOD | <LOD | 1,365 | 312 | 477 | 71 | 160 | 1,027 | 1,805 | 636 |
| Mg | <LOD | 16,552 | 5,408 | <LOD | <LOD | <LOD | 12,302 | <LOD | <LOD | <LOD | 6,296 | <LOD |

178 <LOD = less than the limit of detection

### 2.1.3. Crumb rubber

Crumb rubber was employed to modify the base bitumen. It was produced by Rubber Recycling (Pelt, Belgium) from passenger car tires milled into small particles at ambient temperature (ambient grinding). Ambient grinding creates a combination of irregularly shaped particles with a relatively large surface area and flat particles with a lower surface area (as shown by the scanning electron microscope analysis in Figure 2), which was reported to increase the interaction between bitumen and CR [32]. Table 5 shows the particle size distribution of the CR used for this study in which the fraction between 0.500 and 0.250 mm represents the majority of the used rubber particles. The composition of CR was determined from thermogravimetric analysis with the help of a Q50000IR Thermogravimetric Analyser (TA Instruments). Two atmospheres were used to decompose the samples. From 50 to 750 °C (with an increase rate of 20 °C/min), nitrogen was used to avoid the oxidation of carbon black. From 750 °C to 850 °C, oxygen was added to burn off the carbon black portion of CR. Table 6 presents the chemical composition of CR determined from the derivative thermogravimetry (DTG) curve. The decomposition peaks were based on the limits proposed by Ghavibazoo et al. [33] and Jamal et al. [34]: oils up to 300 °C, natural and synthetic rubber between 300 and 750 °C, carbon black above 750 °C, and the remaining part (> 750 °C) was considered inert filler.
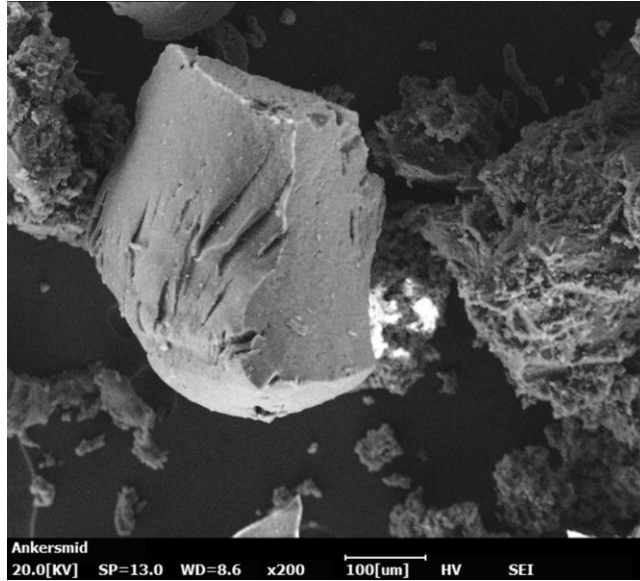
Figure 2. Scanning electron microscopy image of crumb rubber particles using a Coxem EM-30

Table 5. Crumb rubber average particle gradation (EN 933-1, EN 933-2)

| Sieve size (mm) | 1.000 | 0.500 | 0.250 | 0.125 | 0.063 |
|---|---|---|---|---|---|
| Passing (%) | 100.00 | 100.00 | 31.87 | 6.59 | 0.66 |

Table 6. Chemical composition of CR particles from thermogravimetric analysis (TGA) in percentage by weight

| Volatile compounds + oils | Natural and Synthetic rubber | Carbon Black | Inert filler |
|---|---|---|---|
| 9.14% | 53.73% | 28.51% | 8.62% |

*2.1.4. Crumb rubber modified bitumen*

The crumb rubber modified bitumen (CRMB) was prepared by blending the base bitumen (500 g) with CR particles at a ratio of 15% by mass of bitumen at a controlled temperature of 170 °C ± 5 °C. A high-shear mixer with a speed of 3500 r.p.m. was used for 75 min (15 min to reach temperature equilibrium and 60 min at 170 °C ± 5 °C) to prepare the samples. To properly digest CR into the bituminous matrix, the temperature was kept constant throughout the process using a heating plate and a thermocouple. A fume hood and an activated carbon filter were installed between the high-shear mixer and the heating mantle to prevent fumes and rubber odour from being released into the air. For the blends containing ERAs, the ERA was incorporated into the base binder and manually stirred

prior to the addition of CR, with a mass ratio of 5.75% by mass of bitumen based on previous studies [24, 28, 35]. The samples were labelled as shown in Table 7.

Table 7. Summary of the bituminous blends and their composition in percentage by weight of bitumen

| Samples | Binder | CR | ERA |
|---------|--------|-------|------|
| Base | Base | - | - |
| PMB | PMB | - | - |
| CRMB | Base | 15.00 | - |
| CRMB+ERA | Base | 15.00 | 5.75 |

*ERA: AC, BFS, FA, MK, OPC, GB, GBFS, GFA, GMK, PCP, BENT or ZEO

## 2.2. Sampling and analysis methods

### 2.2.1. VOC sampling method

VOC measurements were performed by means of a proton-transfer-reaction time-of-flight mass-spectrometer (PTR-TOF-MS) 8000 (Ionicon Analytik GmbH, Innsbruck, Austria). This technique has proven to be suitable for this kind of experiment as it can measure low concentrations of VOCs thanks to its extreme sensitivity of 100 counts per second/parts per billion by volume (cps/ppbv) and low limit of detection (<50 ppbv), and enables measuring the whole spectrum of VOCs in real time. The basic principle of the experimental setup was already discussed in a previous paper [21]. The samples went through a linear increase in temperature, from room temperature to 180 °C. This approach ensures that the results represent the cumulative VOC emissions over the entire temperature range from room temperature to 180°C, rather than being limited to just the point at 180°C. In order to indirectly control the temperature, temperature profiles were measured and 320 s was found to be the time for all samples to reach 180 °C. As reported in a previous study [21], the addition of CR contributes to the potentially harmful emission of, among others, benzothiazole, which belongs to the sulphur-containing compound class. However, due to a change in the measurement procedure, this compound

235   was not evaluated further in this study.

236   To perform the VOC measurements using the PTR-TOF-MS, 5 g (±0.01 g) of each blend

237   were poured into tin containers with an inner diameter of 17 mm. The samples were

238   prepared 24 h before the VOC measurements. The PTR-TOF-MS used $H_3O^+$ as the

239   primary ion, and the drift tube was operated at a field density ratio of ≈140 Townsend

240   (600 V, 80 °C and 2.3 mbar). The coefficients of reaction between each VOC and $H_3O^+$

241   were calculated by direct calibration for acetone, benzene, toluene and hexenol using

242   standard gas. When it comes to other VOCs, approximations were defined using the

243   values previously described by Cappellin et al. [36], or else, $2 \times 10^{-9}$ $cm^3\,s^{-1}$ was

244   assumed. A background measurement was executed in the empty glass chamber (120 mL)

245   on top of a hot plate equipped with a thermostat (Cimarec + HP88857105, ThermoFisher

246   Scientific, Waltham, MA, USA) before the measurements on the bituminous samples. A

247   1/16 inch (outside diameter) polyether ether ketone (PEEK) tube was placed 5 cm above

248   the tin containers to sample the fumes at 100 standard cubic centimeter per minute (sccm)

249   (0.682 µmol $s^{-1}$). Once the samples reached 180 °C, the accumulated emission per

250   compound was calculated for each sample. At least four samples of each blend were

251   tested and the average result and standard deviation were reported. A total of 35 VOCs

252   were selected to be measured by PTR-TOF-MS as previously reported by Borinelli et al.

253   [21]. Each VOC was then classified in terms of their hazardous potential according to the

254   PubChem National Center for Biotechnology Information [37].

255   *2.2.2 Physical characterization of the ERAs*

256   When studying the adsorption performance of ERAs it is important to characterize the

257   size of the material, the type of pore structure, the specific surface area and the pore

258   diameter distribution [24]. This characterization can be performed by means of particle

size distribution and gas adsorption techniques, in which the nitrogen adsorption test is

260 the most common and reliable method for the latter [31].

261 A Mastersizer Hydro 2000G Particle Size Analyser (Malvern, UK) was used to measure

262 the differential and cumulative volumes for each sample of ERAs in water dispersion.

263 This device is designed to carry out sub-micron analysis in the range of 0.02 to 2000 μm.

264 In order to disperse the agglomerates, the powders were subjected to ultrasonic agitation.

265 Figure 3 shows the differential volume and the cumulative volume for each sample. In all

266 cases, the maximum particle size was not larger than 1000 μm. The average particle size

267 for all ERAs ranged from 2.76 to 43.36 μm (Table 8).

268 Table 8. Average laser particle size of ERAs

| Average particle size (μm) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| AC | BFS | FA | MK | OPC | GB | GBFS | GFA | GMK | PCP | BENT | ZEO |
| 24.9 | 10.8 | 4.3 | 2.8 | 21.1 | 26.4 | 33.6 | 6.7 | 43.4 | 28.7 | 7.7 | 6.5 |

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(a)

(b)

(c)

(d)

**(e)**



**(f)**



**(g)**
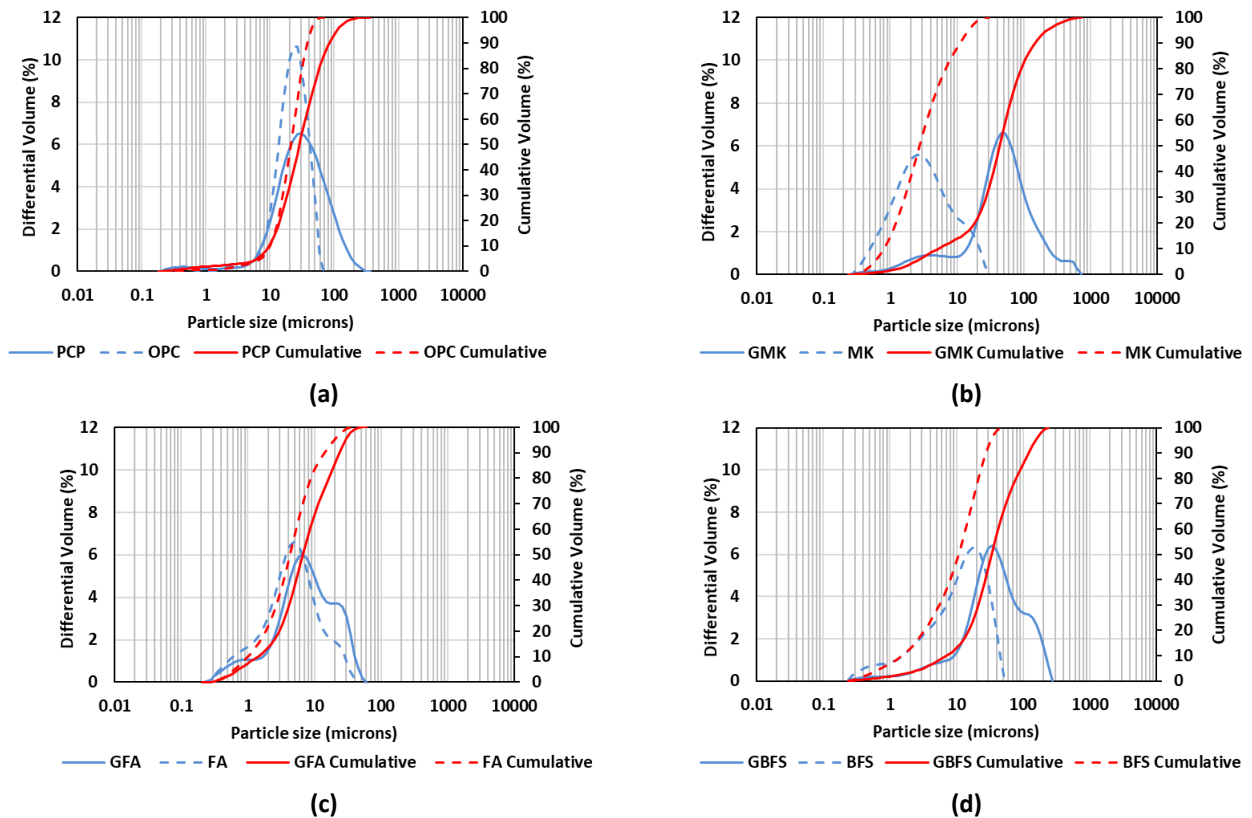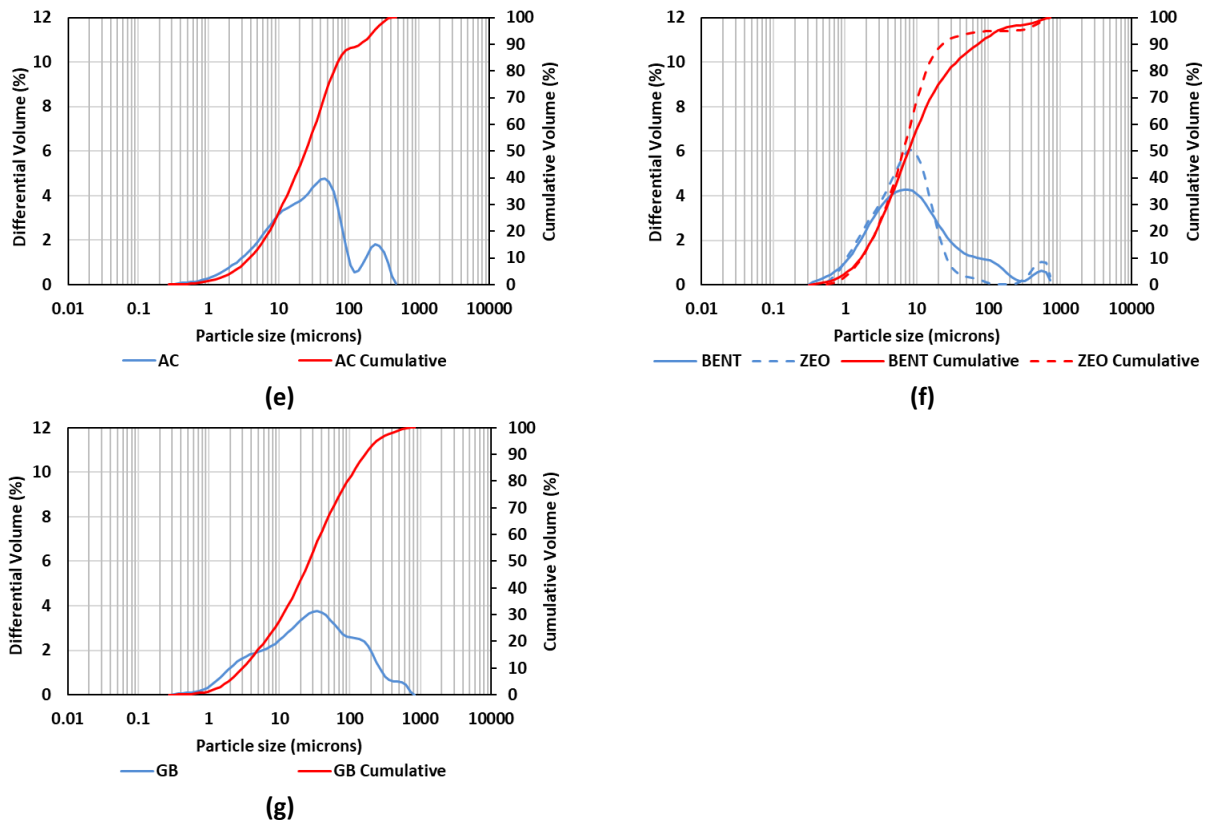
Figure 3. Differential (in blue) and cumulative (in red) volumes of the VOC reducers determined with a Mastersizer Hydro 2000G Particle Size Analyser: (a) PCP and OPC (b) GMK and MK (c) GFA and FA (d) GBFS and BFS (e) AC, (f) BENT and ZEO, and (g) GB.

Low-temperature nitrogen adsorption-desorption was carried out on the ERA particles using a Surface Area and Porosity Analyzer (3P Meso series —manufactured by 3P Instruments— Germany) at a temperature of -196 °C. This equipment is capable of measuring a pore size range from 0.35 nm up to 500 nm. Prior to testing, the samples were heated up to 110 °C for 24 h to eliminate any free water inside the pore structure.

The relationship between the maximum adsorbed quantity of nitrogen and the balance pressure at a certain temperature is represented by the nitrogen adsorption isotherm. A typical nitrogen adsorption-desorption isotherm is shown in Figure 4. Phase 1 (monolayer adsorption phase) is characterized by the micropores (< 2 nm) being filled with $N_2$. This phase starts at zero pressure and goes up to a relative pressure of 0.1 ($p/p_0$). After this

14

point, Phase 2 starts and a relatively slow adsorption process begins, meaning that the mesopores (2 to 50 nm) are occupied by $N_2$. This phase is called multilayer adsorption and can be described by the relatively slow increase in the slope of the isothermal curve ($p/p_0$ between 0.1 and 0.7 in this example). The last phase (Phase 3) is defined by a rapid increase in the slope due to the onset of the capillary condensation phenomena. In other words, the macropores (> 50 nm) are filled with condensed $N_2$. The desorption process happens in reverse order relative to the adsorption process. The $N_2$ desorbs from the macropores, then evaporates from mesopores and micropores.

Although various techniques for measuring surface areas based on the physical adsorption of gases were developed, the Brunauer, Emmett, and Teller (BET) method remains the most widely used technique for calculating the surface area of porous materials including carbon black, finely split silica, and hydrated cement paste and components. This technique is based on the experimental relationship between the pressure of gas that is in equilibrium with a solid surface and the volume of gas adsorbed at a particular pressure on the surface. The multi-molecular layer adsorption model, Equation (1), is the foundation for BET analysis. This equation is dependent on the nitrogen pressure (P), the saturated vapor pressure of nitrogen under liquid nitrogen temperature ($P_0$), actual adsorption quantity (V), monolayer saturation adsorption of nitrogen ($V_m$) and a constant related to the adsorption of the sample (C). A sample is subjected to different nitrogen pressures and the adsorption-desorption isotherm is drawn. The adsorption and desorption cumulative surface area were calculated according to the Barret-Joyner-Halenda (BJH) model which is based on the BET model. The BET surface area is defined as the total surface area per mass of material. The bigger the specific surface area, the bigger the total surface area of the material. The pore structure parameters (total pore volume and average pore diameter) were calculated according to the model proposed by Halsey [38].

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m \cdot C} + \frac{C-1}{V_m \cdot C} \times \left(\frac{P}{P_0}\right) \tag{1}$$
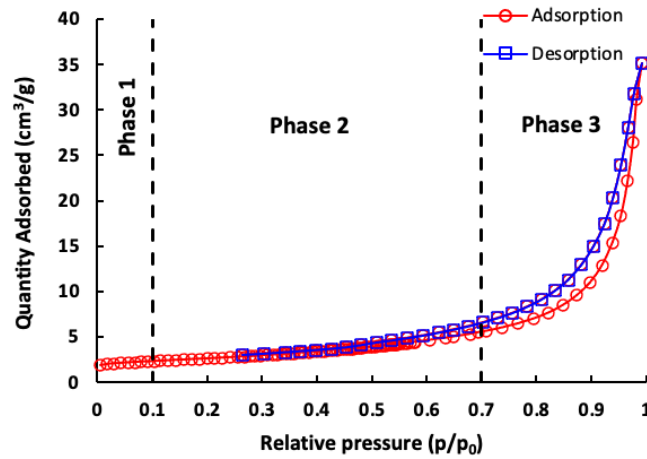


Figure 4. Typical nitrogen adsorption-desorption isotherm

**3. Results and discussion**

*3.1. Characterization of the VOC emission profile*

The VOC emission measurements using a PTR-TOF-MS was of fundamental importance for this study as it enabled us to obtain the VOC profile and the total VOC emission for each sample and use them as input to investigate the emission reduction inhibition effect of the employed ERAs. The TVOC emission rate after adding ERAs is represented by the sum of the 35 VOCs. Figure 5 shows the accumulated emission per VOC compound for base, PMB (for comparison purposes only) and CRMB. The individual compounds that represented less than 0.6% of the total VOC (TVOC) emission rate were grouped together and classified as Others, which amounted to less than 3.5% of the TVOC emission rate for all blends. Determining the emission of the base binder is of utmost importance because the composition and source of the binder directly impact the characteristics of the fumes produced and, consequently, the emission profile. The base bitumen showed the lowest emission rate for TVOC (59.99 $\mu$mol/m$^2$), followed at a long distance by

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CMRB with 108.19 µmol/m$^2$ and PMB with 114.88 µmol/m$^2$. The profile drawn for the base binder contained mostly toluene (23.55 µmol/m$^2$), followed by butanone (6.36 µmol/m$^2$), acetic acid (5.80 µmol/m$^2$), butylbenzene (4.55 µmol/m$^2$), acetone (4.17 µmol/m$^2$), isopropyltoluene (4.12 µmol/m$^2$), ethyltoluene + trimethylbenzene (3.46 µmol/m$^2$), pentadiene (2.43 µmol/m$^2$) and ethylbenzene + xylene (1.07 µmol/m$^2$). The same trend is observed for PMB, but with higher values, especially for toluene (59.00 µmol/m$^2$). CRMB showed similar levels of emission to the base binder but with a clear increase for toluene (30.05 µmol/m$^2$), ethylbenzene + xylene (16.44 µmol/m$^2$), cyclohexanone + ethylbutenal + hexadienol (16.26 µmol/m$^2$), acetone (7.65 µmol/m$^2$), and hexanal + hexenol + methyl isobutyl ketone (2.93 µmol/m$^2$). Some of these VOCs are classified as health hazard or acute toxic according to the GHS [37] and are highlighted in red dashed boxes. For all samples, toluene represents a significant share of the TVOC: 39.26% for base, 51.36% for PMB, and 27.77% for CRMB.
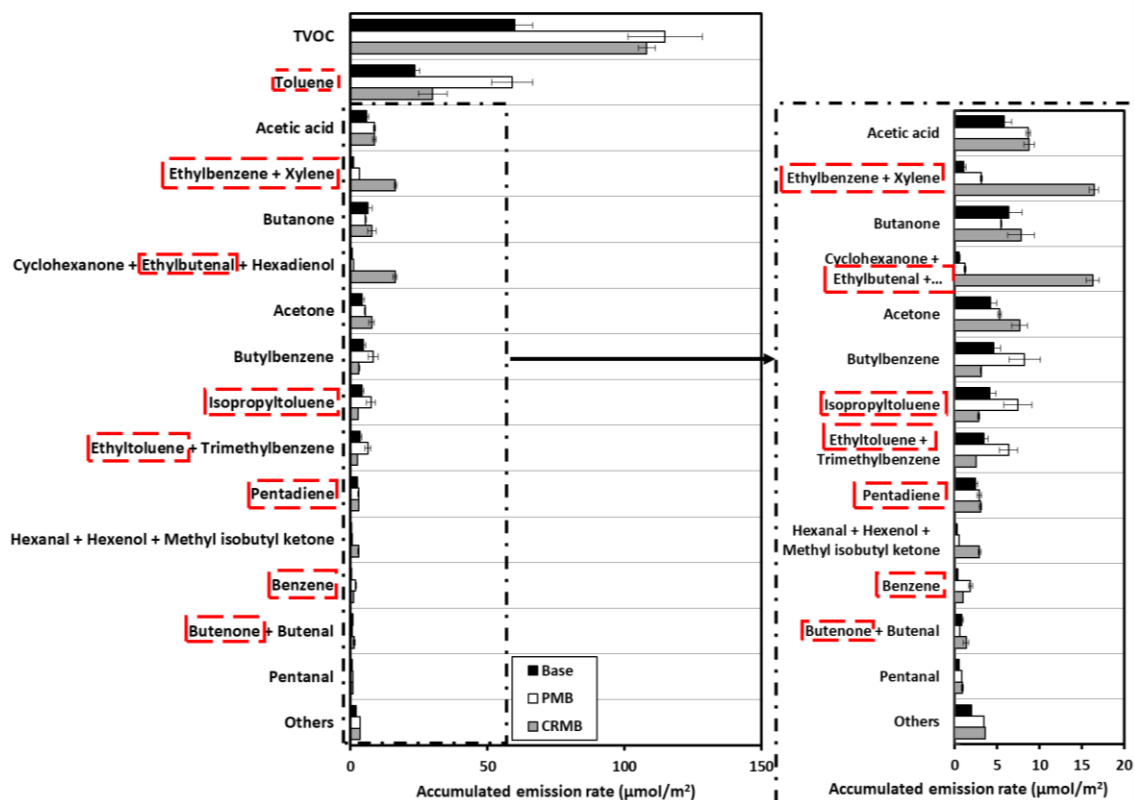
Figure 5. Accumulated emission rate for different VOCs for Base, PMB and CRMB. VOCs considered as health hazardous or acute toxic according to GHS are highlighted in dashed red boxes.

The individual contribution of CR was determined by subtracting the emission rate values for CRMB from the values for the base binder, as shown in Figure 6. The TVOC emission rate had an increase of 48.21 µmol/m$^2$, mainly due to cyclohexanone + ethylbutenal + hexadienol (15.77 µmol/m$^2$), ethylbenzene + xylene (15.37 µmol/m$^2$) and toluene (6.49 µmol/m$^2$). Ethylbenzene, xylene, and ethylbutenal are considered as health hazard or acute toxic according to GHS. Toluene and hexanal+hexenol+ethyl isobutyl ketone, also considered health hazardous, caused an increase of 6.49 µmol/m$^2$ and 2.62 µmol/m$^2$ in emission rate, respectively, when adding CR to the binder. The other VOC components either showed less than 4 µmol/m$^2$ of accumulated emission rate or are not considered as health hazardous or acute toxic according to GHS. When compared to the base binder, CRMB showed lower values of emission for butylbenzene (3.11 µmol/m$^2$), isopropyltoluene (2.81 µmol/m$^2$) and ethyltoluene + trimethylbenzene (2.54 µmol/m$^2$). This can be due to the fact that the polymeric compound from the CR chemically reacts with bitumen molecules creating more stable and less volatile compounds, leading to a decline in emission for specific VOCs.
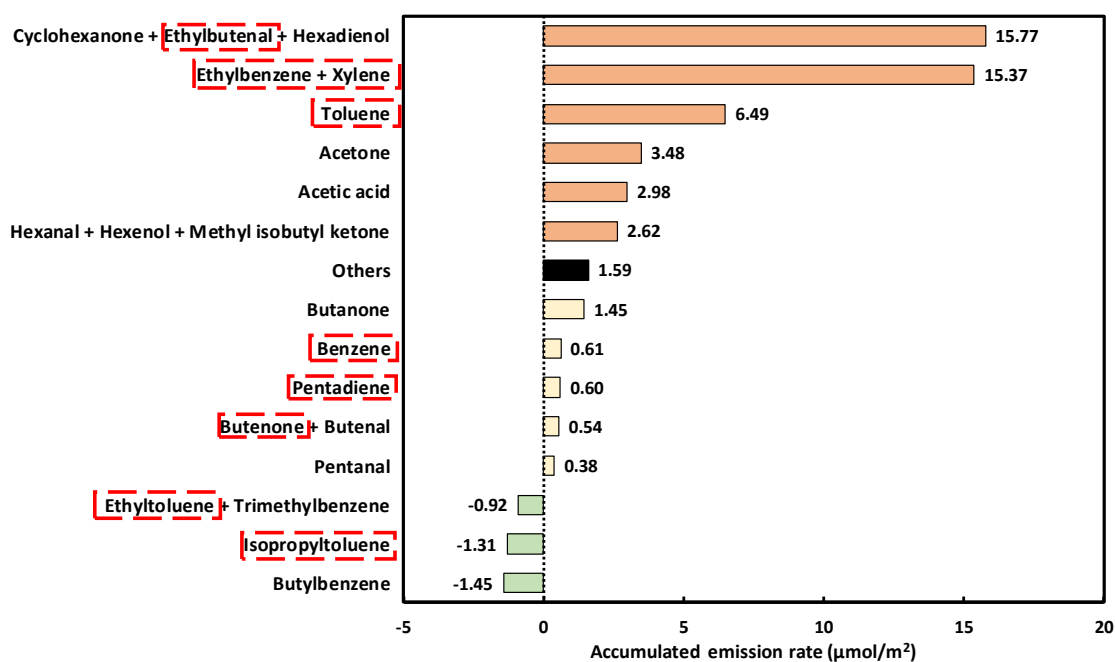
Figure 6. CR contribution to the accumulated emission rate for each VOC (highlighted in dashed red boxes are the ones considered as health hazardous or acute toxic according to GHS).

### 3.2. VOC emission reduction

To explore the inhibition effect of the selected ERA on the VOC emission from CRMB, the VOC emissions of the blends modified with ERA were also evaluated and cross-compared to the emission from CRMB (Figure 7). The TVOC emission rate after adding ERAs is represented by the sum of the 35 VOCs. All ERAs showed a significant decrease in TVOC emission rate when compared to CRMB, with reductions from 33% (CRMB+BENT) up to 48% (CRMB+GFA), 49% (CRMB+AC) and even up to 58% (CRMB+PCP), even when the standard deviation for each sample is considered. These values of reduction align with the studies summarized by Wang et al. [23], where reduction rates of 9.2-23.2% and 41.6-60.6% were reported for inorganic salts and inorganic porous materials, respectively. Of note, the CRMB samples containing PCP (45.31 µmol/m$^2$), AC (55.39 µmol/m$^2$), GFA (56.55 µmol/m$^2$), MK (58.10 µmol/m$^2$), OPC (58.89 µmol/m$^2$) and FA (59.93 µmol/m$^2$) yielded values even lower than those for

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374  the base binder (59.99 µmol/m$^2$). However, caution must be taken when interpreting this

375  data as the standard deviation for some samples had a larger range than others. AC and

376  BENT, both organic materials, had an average TVOC emission rate of 55.39 µmol/m$^2$

377  and 72.06 µmol/m$^2$, respectively. Note that when taking the standard deviation into

378  consideration, their values within the same range of those for the inorganic materials,

379  which makes it difficult to distinguish which blend had the best performance in reducing

380  TVOC emission.
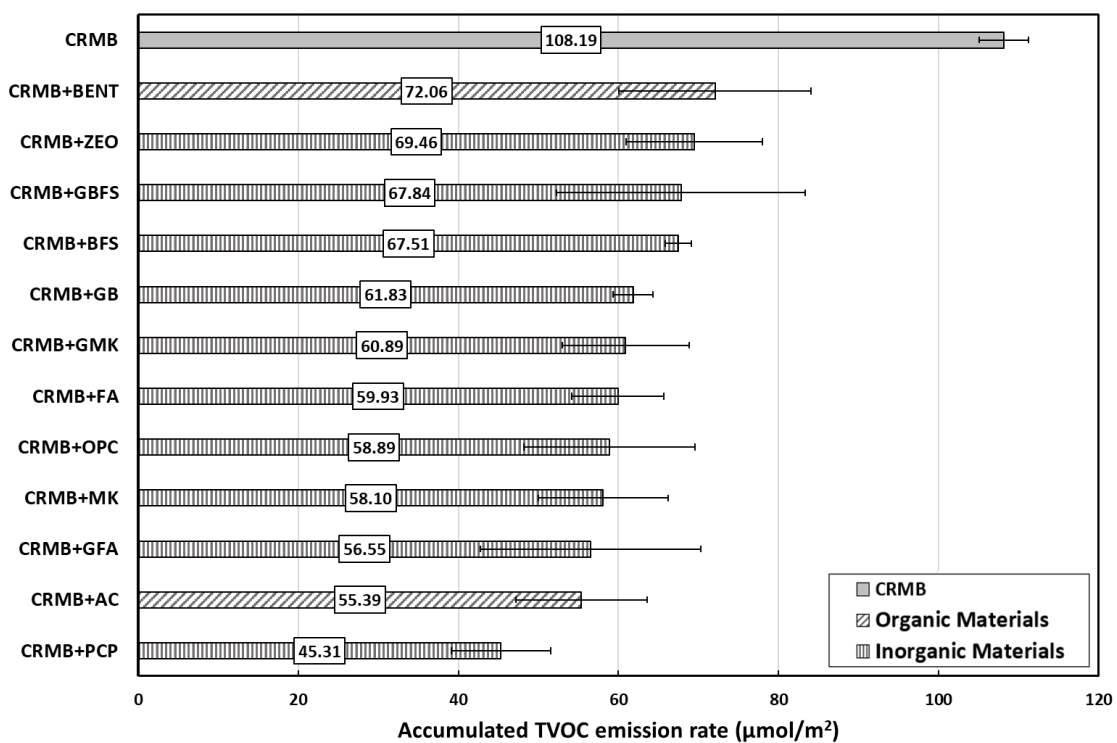


381

382  Figure 7. Total VOC emission rate for different binder blends

383  To help with the process of selecting the most promising ERA in terms of VOC reduction,

384  a Min-Max Normalization technique was adopted to simplify the analysis of results (as a

385  total of 35 VOCs were being analysed) and transform them into a common domain. This

386  technique is indicated when the maximum and minimum values are known; however,

387  attention should be given to outliers as this method is highly sensitive to them [39]. This

388  technique allows to shift values into scores from 0 to 1, while retaining the original

distribution of values and transforming them into a common range. For the purpose of this work, the score 1 was given to the emission of the individual VOC compound from CRMB and the score 0 was given for no emission. This means that samples with a lower VOC emission than CRMB have a greater potential to reduce VOCs. To take into account the magnitude of each VOC emission, an impact factor (IF) based on the percentage of each individual VOC within the TVOC of CRMB was applied to the Min-Max Normalization score. The total score was calculated as the sum of the individual results for each VOC after the two-step normalization and it is shown in Table 9. The results validated the normalization process as they show the same trends as observed in Figure 7. CRMB+PCP and CRMB+AC were the samples with the lowest scores; thus, these samples have the greatest potential to reduce TVOC emission from CRMB, while the samples with the addition of BENT, GBFS, ZEO and BFS were the ERA with the lowest potential to reduce TVOC emission.

Table 9. Score considering TVOCs multiplied by the individual impact factor based on the emission of each VOC

| CRMB +PCP | CRMB +AC | CRMB +GFA | CRMB +MK | CRMB +OPC | CRMB +FA | CRMB+ GMK | CRMB +GB | CRMB +BFS | CRMB+ GBFS | CRMB +ZEO | CRMB+ BENT |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.42 | 0.51 | 0.52 | 0.54 | 0.54 | 0.55 | 0.56 | 0.57 | 0.62 | 0.63 | 0.64 | 0.67 |

Note: VOCs considered for this score system and their respective impact factors: Toluene (0.278), Ethylbenzene + xylene (0.152), Cyclohexanone + ethylbutenal + hexadienol (0.150), Acetic acid (0.081), Butanone (0.072), Acetone (0.071), Butylbenzene (0.029), Pentadiene (0.028), Hexanal + hexenol + methyl isobutyl ketone (0.027), Isopropyltoluene (0.026), Ethyltoluene + trimethylbenzene (0.023), Butenone + butenal (0.012), Benzene (0.009), Pentanal (0.008), Methyl furan (0.006), Styrene (0.005), Methylheptyne (0.004), Heptanal (0.004), Methylheptane (0.004), Benzaldehyde (0.003), Methyl benzaldehyde (0.003), Diethylthiophene (0.002); Others had a null impact factor.

Not all VOCs from bitumen are harmful to humans. Therefore, an analysis was performed with a focus on the toxic substances classified as health hazards, acute toxic or environmental hazards according to the Globally Harmonized System of Classification

and Labelling of Chemicals (GHS). For the IF, the sum of the emissions registered for these compounds for CRMB (78.83 $\mu m/m^2$) was considered as 1 and no emission was considered as null. Table 10 shows the score for each sample, based on the two-step normalization for the selected VOCs. The total score is the sum of all scores for each sample. Once again, CRMB+PCP and CRMB+AC yielded the lowest score, which can be interpreted as being the best reducers of VOCs considered as a health hazardous, acute toxic or environmental hazardous. CRMB+MK, CRMB+GFA, CRMB+FA and CRMB+OPC were the samples located in the intermediate zone with a distinct change in position for CRMB+GBFS, which was the worst performer to reduce these VOCs, together with CRMB+GB and CRMB+BENT.

Table 10. Score considering only the VOCs classified as health hazards, acute toxic or environmental hazards according to GHS

| CRMB +PCP | CRMB +AC | CRMB +MK | CRMB +GFA | CRMB +FA | CRMB +OPC | CRMB +BFS | CRMB+ GMK | CRMB +ZEO | CRMB+ BENT | CRMB +GB | CRMB+ GBFS |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.38 | 0.43 | 0.44 | 0.44 | 0.44 | 0.45 | 0.49 | 0.51 | 0.52 | 0.54 | 0.54 | 0.60 |

Note: VOCs considered for this score system and their respective impact factors: Toluene (0.381), Ethylbenzene + xylene (0.209), Cyclohexanone + ethylbutenal + hexadienol (0.206), Butylbenzene (0.039), Pentadiene (0.038), Isopropyltoluene (0.036), Ethyltoluene + Trimethylbenzene (0.032), Butenone + butenal (0.017), Benzene (0.012), Methyl furan (0.009), Styrene (0.007), Methylheptyne (0.005), Methylheptane (0.005); Others had a null impact factor.

As mentioned above, cyclohexanone + ethylbutenal + hexadienol, ethylbenzene + xylene, toluene, and hexanal + hexenol + methyl isobutyl ketone were found when CR was added to the base bitumen and are considered as a health hazard or acute toxic by the GHS. In order to evaluate the effectiveness of the ERA in reducing these VOC compounds, the score system based on the two-step normalization was also applied. For the IF, the sum of the emissions registered for these compounds for CRMB (65.68 $\mu m/m^2$) was considered as 1 and no emission was considered as null. It is clear from Table 11 that

GBFS was the worst performer, followed by BENT, GB and GMK. In contrast, PCP, GFA, FA, MK and OPC proved to be more effective in reducing VOC emissions associated with the incorporation of CR. CRMB+AC showed a inferior performance to reduce these VOCs due to its worse scores for toluene, ethylbenzene+xylene, and cyclohexanone+ethylbutenal+hexadienol, which have higher impact factors (0.457, 0.250 and 0.248, respectively).

Table 11. Score considering only the most significant VOCs from the CR (Cyclohexanone + Ethylbutenal + Hexadienol, Ethylbenzene + Xylene, Toluene, and Hexanal + Hexenol + Methyl isobutyl ketone)

| CRMB +PCP | CRMB +GFA | CRMB +FA | CRMB +MK | CRMB +OPC | CRMB +ZEO | CRMB +AC | CRMB +BFS | CRMB+ GMK | CRMB +GB | CRMB+ BENT | CRMB+ GBFS |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.32 | 0.33 | 0.34 | 0.34 | 0.36 | 0.40 | 0.41 | 0.41 | 0.46 | 0.48 | 0.50 | 0.51 |

Note: VOCs considered for this score system and their respective impact factors: Toluene (0.457), Ethylbenzene + Xylene (0.250), Cyclohexanone + Ethylbutenal + Hexadienol (0.248), and Hexanal + Hexenol + Methyl isobutyl ketone (0.045).

### 3.3. Correlation between the physical parameters of ERAs and VOC emission reduction

The emission reduction performance of organic and inorganic materials can be related to the micropore structure and specific surface area of these materials. According to Chi et al. [40], as long as the pore diameter of inorganic porous materials is bigger than the molecular sizer of VOCs, the adsorption may take place under certain conditions. For that reason, this section is dedicated to the correlation study between the physical parameters of the ERA and its efficiency in reducing VOC emission.

Figure 8 illustrates that the average particle size did not explain the reduction in VOC emission. The component that exhibited the lowest TVOC emission rate was PCP ($45.31 \ \mu m/m^2$) with an average particle size of $28.71 \ \mu m$. Smaller particles, such as MK ($2.76 \ \mu m$) and FA ($4.33 \ \mu m$), showed higher emissions ($58.10 \ \mu m/m^2$ and $59.93 \ \mu m/m^2$,

respectively).
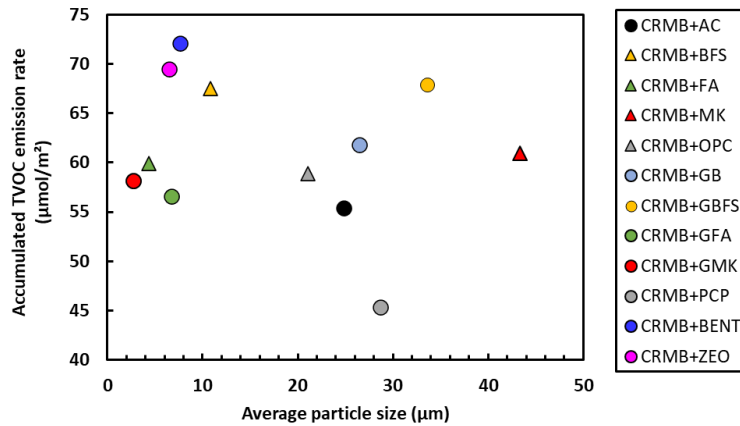


Figure 8. Analysis between accumulated TVOC emission rate and the average particle size of ERA

The values for the pore structure parameters according to the BJH model are shown in Figure 9. Activated carbon (AC) and zeolite (ZEO) yielded the largest surface area values: 1325.72 and 303.79 m²/g, respectively. They are one of the most and one of the least efficient ERAs in reducing TVOC emission from bituminous sources. The other ERAs showed specific areas between 1.32 and 41.35 m²/g. When it comes to the total pore volume (taken as the volume of nitrogen adsorbed at a given pressure), again AC and ZEO are the ones with the highest values but their efficiency in reducing VOCs differs. On the other hand, AC and ZEO are the ERAs with the lowest values for average pore diameter, 2.22 and 2.56 nm, respectively, while PCP, GFA and OPC showed the highest values for this parameter, 24.19, 19.21 and 18.87 nm, respectively. The abundant volume of pores and active surface area may not be sufficient to adsorb VOCs at their full potential, and the average pore diameter may be a parameter to evaluate in this sense. According to Biniak et al. [41], the pore diameter, the size of the ERA, and the adsorbed molecules are related as follows: when the size of the molecule (VOCs in this case) is larger than the pore diameter, the molecules cannot reach the interior of the ERA and the adsorption will not take place.
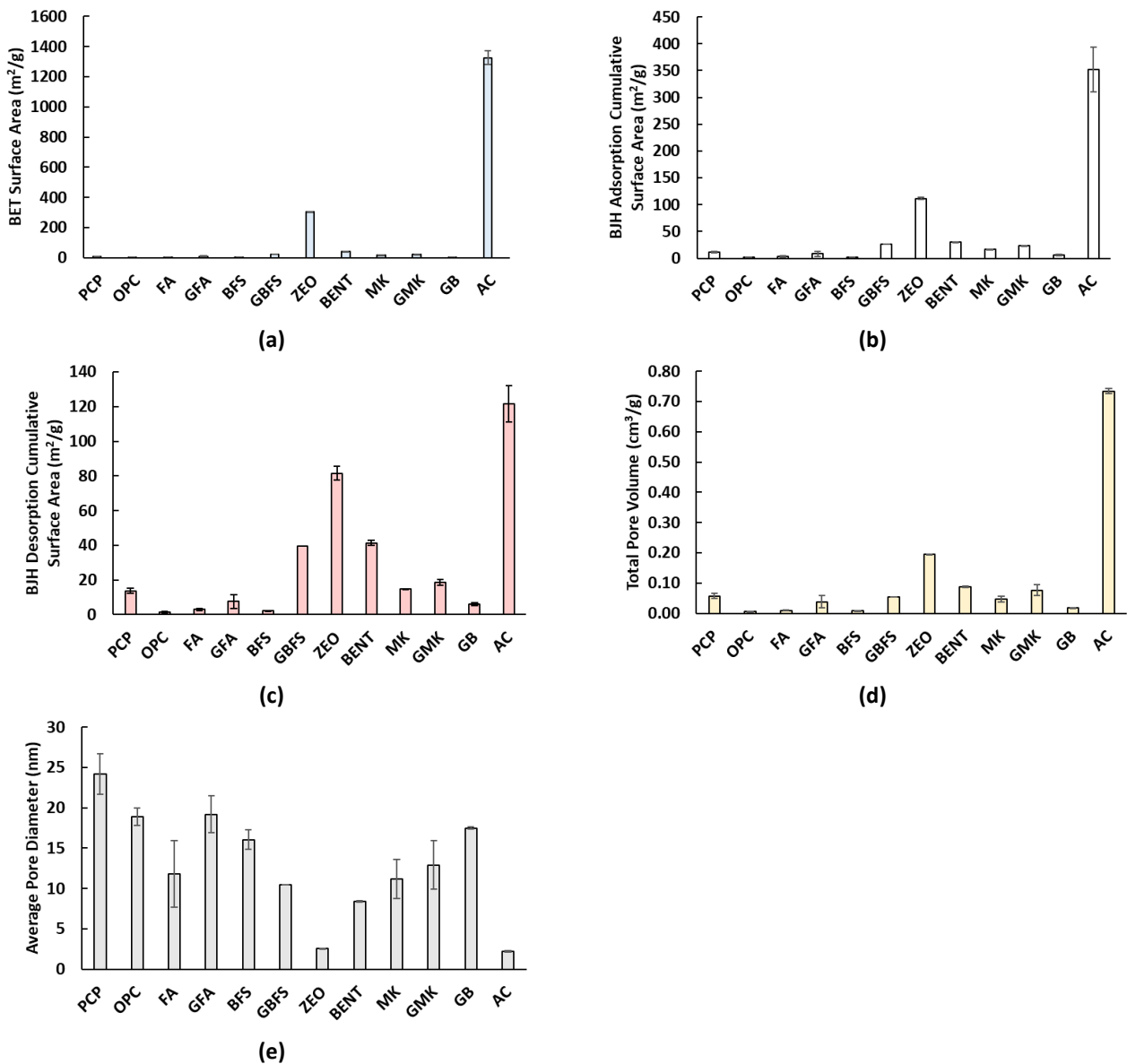
Figure 9. Pore structure parameters: (a) BET surface area, (b) BJH adsorption cumulative surface area, (c) BJH desorption cumulative surface area, (d) total pore volume, and (e) average pore diameter

To evaluate if VOC emission can be predicted from the physical characteristics of the ERA, linear regression analyses were performed. In the case of the TVOC emission (Table 12), the coefficient of determination ($R^2$) did not exceed 0.27 and none of the p-values were significant. These values can be explained by the different contributions that each VOC has to the TVOC matrix. A further analysis was conducted to investigate the correlation between the physical parameters and the individual VOC emission, however,

only weak correlations were found. To exemplify, the results of the linear regression for the four main VOCs contributed by CR are also shown in Table 12. Toluene was the only VOC with a significance below 0.05. However, the correlation coefficient for all physical characteristics was below 0.5, which represents a weak correlation. The same trend was also observed for the other VOCs measured. The linear regression approach proved unable to correlate the physical characteristics of the ERAs with the TVOC and VOC emission.

Although the physical characteristics of the ERAs showed a weak correlation with the VOC emission, the correlation may improve by combining physical and chemical characteristics. For that reason, a multivariable regression analysis considering up to six variables was performed to estimate the TVOC emission rate. The correlation with the most significance (0.0169) and highest coefficient of determination (0.7862) was the combination of BET surface area, BJH adsorption cumulative surface area, BJH desorption cumulative surface area, and average pore diameter. Table 13 shows the results for this multivariable regression, including the correlation coefficients for each variable (all significant at the 0.1 level). The average pore diameter was found to be the physical characteristic with the highest impact on the TVOC emission; the negative correlation coefficient indicates that the larger the pore diameter, the lower the TVOC emission. The same correlation trend was found for the BJH adsorption cumulative surface area. The BET surface area and the BJH desorption cumulative surface area had a positive correlation with the TVOC emission but with a lower impact than the other physical characteristics. These findings seem to agree with the physical adsorption process outlined in the introduction section. During external diffusion, VOCs emanating from the bitumen adhere to the ERA surface, making the active surface area a pivotal parameter. In the subsequent stages of internal diffusion and the final phase, VOC molecules

permeate the inner ERA apertures and are entrapped within the pores due to the labyrinth effect and intermolecular van der Waals forces. Here, the average pore diameter and the cumulative surface areas emerge as critical determinants for this phenomenon to happen.

Table 12. Correlation between VOC emissions and the physical characteristics of the ERAs

| | Parameters | Median particle size | BET surface area | BJH adsorption cumulative surface area | BJH desorption cumulative surface area | Total pore volume | Average pore diameter |
|---|---|---|---|---|---|---|---|
| Accumulated TVOC emission | $R^2$ | 0.054 | 0.024 | 0.012 | 0.018 | 0.023 | 0.273 |
| | p-value | 0.466 | 0.632 | 0.738 | 0.679 | 0.635 | 0.081 |
| Cyclohexanone + Ethylbutenal + Hexadienol | $R^2$ | 0.196 | 0.080 | 0.060 | 0.004 | 0.057 | 0.025 |
| | p-value | 0.150 | 0.374 | 0.441 | 0.853 | 0.454 | 0.623 |
| Ethylbenzene + Xylene | $R^2$ | 0.130 | 0.273 | 0.218 | 0.039 | 0.239 | 0.001 |
| | p-value | 0.249 | 0.082 | 0.126 | 0.540 | 0.107 | 0.912 |
| Toluene | $R^2$ | 0.056 | 0.483 | 0.461 | 0.316 | 0.453 | 0.137 |
| | p-value | 0.461 | 0.012 | 0.015 | 0.057 | 0.017 | 0.237 |
| Hexanal + Hexenol + Methyl isobutyl ketone | $R^2$ | 0.039 | 0.060 | 0.069 | 0.128 | 0.082 | 0.181 |
| | p-value | 0.539 | 0.444 | 0.411 | 0.253 | 0.368 | 0.168 |

Table 13. Parameters of the multivariable regression with the most significance between the accumulated TVOC emission and the physical characteristics of the ERAs

| Parameters | Coefficients | p-value |
|---|---|---|
| Intercept | 81.753 | 0.000 |
| BET surface area | 0.218 | 0.098 |
| BJH adsorption cumulative surface area | -1.081 | 0.080 |
| BJH desorption cumulative surface area | 0.557 | 0.096 |
| Average pore diameter | -1.198 | 0.012 |

## 4. Findings and Conclusions

Proton-transfer-reaction time-of-flight mass-spectrometer (PTR-TOF-MS) successfully quantified the volatile organic compounds (VOCs) emission from crumb rubber modified bitumen (CRMB) and enabled the evaluation of the potential of emission reduction agents (ERAs) to reduce VOC emission. Twelve ERAs were selected and the VOC emission for each compound was measured. Besides, the physical characteristics of the ERAs were determined by means of particle size distribution and nitrogen adsorption in order to

evaluate their potential relationship with the inhibition effect on the emission of VOCs from CRMB. The base binder showed the lowest accumulated VOC emission rate (59.99 µmol/m$^2$), followed by CRMB with 108.19 µmol/m$^2$ and PMB with 114.88 µmol/m$^2$. Toluene was the most abundant VOC for these three binders. The addition of CR increased the total VOC emission rate by 48.21 µmol/m$^2$, mostly due to ethylbenzene + xylene, cyclohexanone + ethylbutenal + hexadienol, and toluene. After a thorough analysis of the emission profiles, the following conclusions were drawn:

- All ERAs evaluated in this study effectively reduced the total VOC (TVOC) emission by more than 33%. The best performers were Portland cement paste (PCP), activated carbon (AC) and geopolymer-based fly ash (GFA) with reductions of 58%, 49%, and 48%, respectively. The ERAs with the lowest potential to reduce TVOC were bentonite and zeolite.

- When the VOC emission profiles were normalized in terms of TVOC, the results showed that PCP, AC and GFA were the samples with the greatest potential to reduce TVOC emission from CRMB. The normalized profile considering the VOCs classified as health hazard, acute toxic or environmental hazard according to GHS confirmed that PCP and AC could better tackle these compounds and were considered as the best reducers. Lastly, PCP and GFA showed the best performance in terms of reducing the VOCs released from the CR.

- Multivariable regression analyses showed that BET surface area, BJH adsorption cumulative surface area, BJH desorption cumulative surface area, and average pore diameter of the ERAs explained the differences in TVOC emission.

**5. Recommendations for future research**

- Further study is necessary to provide more clarification on the effect of the chemical composition of ERA on the reduction of VOC emissions. Furthermore, it is valuable to explore the potential benefits of utilizing ERAs for mitigating VOC emissions in a range of bitumen types, extending beyond CRMB.

- In order to promote the use of ERA as a viable alternative to reduce VOC emission for the pavement industry, the environmental impact of the ERAs must be assessed and new alternatives can be investigated, such as reclaimed material from demolition.

- Further investigation on the influence of ERA on the performance of bitumen and asphalt mixtures is necessary, which is included in follow-up papers.

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