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Review

State of the Art Review of Ageing of Bituminous Binders and Asphalt Mixtures: Ageing Simulation Techniques, Ageing Inhibitors and the Relationship between Simulated Ageing and Field Ageing

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Abstract: Asphalt mixtures age during service in the field, primarily as the result of chemical changes in the bituminous binder phase. The ageing phenomenon changes the properties of the asphalt mixture, including the stiffness modulus, the resistance to deformation and the resistance to cracking, and it leads to surface weathering or erosion that often leads to pavement resurfacing. Consequently, many researchers have attempted to understand and to simulate the ageing of bituminous binders and asphalt mixtures in the laboratory. This review of bituminous binder and asphalt mixture ageing considers ageing simulation techniques, the effect of ageing on both bituminous binders and asphalt mixtures, the potential benefits of ageing inhibitors, and efforts to relate simulated laboratory ageing to observed field ageing. It is concluded that ageing has a significant effect on the properties of bituminous binders and asphalt mixtures, and that improved simulated ageing is important for comparing the effect of ageing on different materials and mixtures, as well as for quantifying the potential benefits of ageing inhibitors, which have generally been promising. It is also concluded that current ageing protocols are based on heat only, omitting the important contribution of solar radiation to the weathering and ageing of asphalt surfaces in the field. In the future, different simulated ageing protocols should be developed for binder and mixture samples. Similarly, a different ageing protocol is appropriate for understanding base-layer fatigue, compared to research on surface-layer weathering. Finally, it is concluded that a universal ageing protocol is unlikely to be found and that mixture- and climate-specific protocols need to be developed. However, given the importance of simulated ageing to asphalt researchers, the development of reliable, robust and calibrated laboratory ageing protocols is essential for the future.

Keywords: field; laboratory; ageing; asphalt; mixtures; binders

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1. Introduction

Bitumen is one of the most widely used materials in highway and airport pavement construction, as it acts as a binder for mineral aggregates to form asphalt mixtures. As a viscoelastic material, bitumen plays a vital role in providing the mixture with the desired viscoelastic behaviour, provides durability and resistance to traffic and thermal cracking, and also preserves the mastic bridges between aggregate particles to avoid disintegration. Due to being an organic material, bitumen's viscoelastic properties deteriorate with time, due to environmental factors such as ultraviolet (UV) irradiation and thermal oxidation [1], which is a phenomenon known in this context as bitumen ageing. As an irreversible process, the ageing of asphalt mixtures is one of the main causes of pavement surface distresses, including cracking [2] and fretting/ravelling [3] or erosion. The ageing of asphalt mixtures is often associated with changes in the bitumen's rheological and physiochemical properties that affect the asphalt mixture performance greatly [4].

It follows that bitumen ageing is a critical factor in determining pavement surface durability. Consequently, the ability to accelerate ageing in the laboratory, and study its effects on asphalt mixtures over time, is very important to ensure the good performance of pavement surfaces over their expected service life. Most previous studies have confirmed that ageing is mainly caused by oxidation in the existence of UV irradiation. Oxidative surface ageing occurs due to the irreversible chemical reaction between hydrocarbons of bitumen and atmospheric free oxygen while UV and surface temperatures act as a catalyst for this chemical reaction [5,6].

The ageing of bitumen occurs in the construction phase and during the service life due to environmental exposure. The first stage of ageing occurs at a fast rate during the production of asphalt mixtures due to a rapid loss of mixing temperature, causing a physical hardening of the mixture, which is known as short-term ageing. In addition, during this stage, a thin film of a binder is exposed to air at elevated temperatures, which causes significant changes in the rheological properties of the bitumen [4]. During the service life of an asphalt surface, the second stage of ageing occurs when the pavement surface is exposed to environmental factors at a lower temperature but for a longer duration, causing hardening at different rates depending on different factors. This stage is referred to as long-term ageing. Several factors affect bitumen's short-term ageing, including external factors related to the asphalt mixture production process, including the plant type, mixing conditions and post-production hot-storage time. On the other hand, long-term ageing is always affected by the prevailing in-field conditions, including temperature, UV irradiation and other environmental factors combined with time [7]. In addition, some asphalt mixtures and bituminous binder properties can also determine the extent and severity of the ageing process [8].

From the previous discussion, understanding the ageing of bitumen and bituminous mixtures is crucial to pavement researchers. This paper has the main objective of presenting a state-of-the-art-review of bituminous binder and asphalt mixture ageing studies to reflect the present state of scientific knowledge in terms of ageing simulation techniques and the best indicators to evaluate ageing for both binders and mixtures. In addition, the additives that can improve ageing resistance, including antioxidants, UV absorbers and bitumen modifiers, are presented and discussed, including how they may positively affect the different ageing indicators. Finally, the effect of different rejuvenators on the different ageing indicators is discussed. Figure 1 presents a schematic of the skeleton of the paper, which is divided into four main parts. First, the current ageing simulation techniques are discussed, including thermal oxidation studies, photo-oxidation studies and any studies that adopt compressed gases and other novel techniques to simulate ageing. Second, the ageing effects on different bitumen properties are presented, including rheological and chemical properties and how these changes affect the mixture properties. Third, anti-ageing techniques are presented, including bitumen additives, antioxidants, UV absorbers and different rejuvenators. Finally, the studies that have correlated field ageing to the current lab ageing simulation techniques are reviewed.

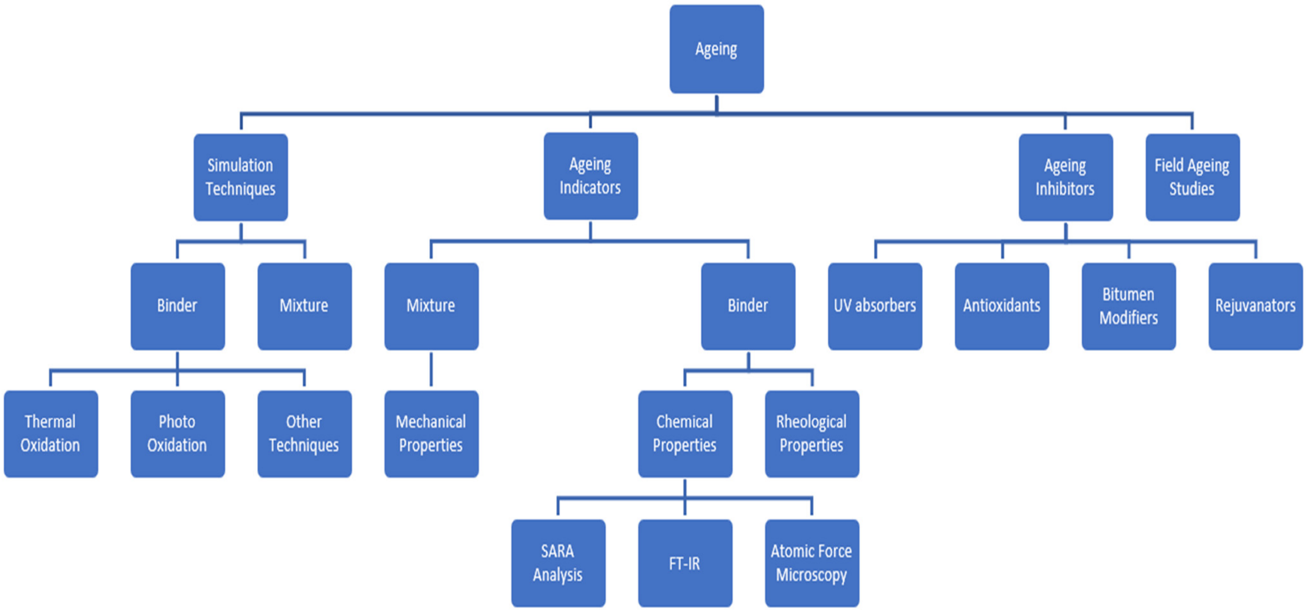

Figure 1. Schematic structure of this review.

2. Simulated Ageing Techniques

As discussed above, ageing is mainly caused by a combination of factors, including oxidation due to free oxygen in the existence of solar radiation, that works as a catalyst to the chemical reactions between the hydrocarbon molecules and free oxygen. In this section, ageing simulation techniques are classified into two main sections. First, thermal oxidation simulation techniques that depend mainly on adopting extended heat and pressure to simulate the hardening due to oxidation reaction in the existence of heat and oxidizing gases. Second, photo oxidation techniques that simulate ageing by exposing binders and mixtures to UV irradiation in the range of wavelengths intended to simulate sunlight. Each main section will be classified into two categories, including studies on the ageing of bituminous binder and studies on the ageing of asphalt mixtures.

2.1. Thermal Oxidation Techniques

Thermal oxidation techniques primarily rely on elevated temperatures in the atmosphere to accelerate the ageing of binders and mixtures. First, binder studies are considered, and then mixture studies are reviewed.

2.1.1. Thermal Oxidation Ageing of Bituminous Binders

Applying extended heating with air flow to a thin film of bitumen to simulate thermal oxidation is the basis of most thermal ageing binder studies. The rolling thin film oven test (RTFOT) or protocol, according to ASTM D2872 [9], is the major standard protocol used to simulate the short-term ageing of bituminous binders. Lewis and Welborn [10] first used the thin film oven test (TFOT) by applying an air flow at a temperature of 163 °C to a bitumen film 3.2 mm thick for 5 h. The non-uniform ageing through the thickness of the bitumen film, in addition to unrealistic bitumen film thickness, compared to with 8–12 µm that typically occurs in the field, was the limitation of the procedure, as noted by Airey [11].

Elder et al. [12] then applied the same procedure but with 100 µm thick bitumen film and increased the time of exposure to 24 h. However, the most important development was the introducing of a moving film introduced in the RTFOT, which was developed by the California Division of Highways [13]. In the TRFOT, glass bottles each containing 35 g of binder are aged by applying air and heat to a moving or rolling film of 1.25 mm, providing a uniform ageing of the binder, and this procedure was found to corelate well with hardening observed during hot mixed asphalt production processes [14]. Consequently, the RTFOT is the current standard for the simulated short-term ageing of bituminous binders in the laboratory, even though it does not include solar radiation simulation.

Long-term ageing simulation techniques are intended to simulate the binder ageing that occurs during the service life of an asphalt mixture. The pressure oxidation bomb [12], IOWA durability test [15] and accelerated ageing test device [16] have been used to simulate long-term ageing. However, the pressure air vessel (PAV) has proven to be the most reliable technique for simulating long-term ageing [17]. RTFOT aged samples are placed in the PAV and subjected to one of three temperatures, including 90 °C, 100 °C or 110 °C, for cold, moderate and hot climates, respectively, for 20 h at a 2.07 MPa pressure. The reason for choosing 20 h is that this time would enable the completion of one test in any one-day cycle. The increased pressure increases the diffusion of oxygen, which promotes the ageing process, as concluded by Bahia and Anderson [18]. However, the oxygen diffusion is more related to the temperature of the test and the voids in the asphalt mixture, and with the continuous hardening of the pavement, the rate of oxygen diffusion may slow down.

The efficiency of using PAV as a long-term ageing simulation technique is questionable, as the rheological properties of 325 min of RTFOT aged bitumen showed more severe effects in terms of changes in rheological properties compared to PAV ageing for up to 30 h, as concluded by Jiang et al. [19]. This supports the previous assumption that ageing occurs due to elevated temperatures only and the rate of oxygen diffusion is not affected by pressure, which may raise a question of whether the PAV is efficient in simulating long-term ageing or whether it can be substituted by another method, especially given that the PAV is relatively costly.

It is concluded that the RTFO can be reliable in simulating short-term ageing, while using PAV for the simulation of long-term ageing procedures needs more research. First, the same severity of ageing is achieved using a simpler technique such as RTFOT. Second, PAV can not simulate environmental conditions including UV irradiation. In addition, using the same conditions in the lab for all climatic regions is still questioned by researchers, particularly the temperature of the test and test duration, which were chosen based on the practicality of the test and not directly related to the actual field conditions as previously explained. Moreover, the PAV has been found to be less efficient in simulating the cross-linked chemical reactions in polymer-modified binders, with photo oxidation found to be more related to the polymer degradation which may cause some cross-linked chemical reactions that may accelerate the ageing process of bitumen.

2.1.2. Thermal Oxidation Ageing of Asphalt Mixtures

There is only limited research directed to the simulation of the ageing of asphalt mixtures compared to binder studies. Limited analyses of mixture ageing have generally been based on the comparisons of viscosity and the penetration of extracted binders from laboratory-aged mixture samples, and then related to the same properties of binders extracted from field-aged core samples [20–22]. The most significant finding of mixture ageing studies is that nonuniform field ageing of mixtures with a depth, which has been noticed as the surface of asphalt pavement, ages faster than the bottom [23,24]. In terms of asphalt mixtures' ageing simulation protocols, the current practices recommended by the American Association of State Highway and Transportation Officials (AASHTO) is to age mixture samples in three stages. First, mixture conditioning for 2 h to represent a volumetric mixture design. Then, short-term conditioning at 135 °C for 4 h to represent asphalt production, transportation and paving. Finally, long-term conditioning for 5 days at 85 °C to represent long-term field ageing. As stated in R30 AASHTO, the long-term ageing is intended to reflect up to ten years of field ageing based on limited field data [25]. The R30 protocol is the only standardized protocol to simulate the ageing of asphalt mixtures, and its validity is questioned by researchers for many reasons [26]. First, a single time–temperature combination may not be reasonable for all climatic regions. Second, the elevated temperatures of some regions promote higher oxidation compared to lower-temperature regions, and the protocol does not account for rainfall rates or UV light intensity in different regions [26].

In terms of the other methods to simulate the field ageing of mixtures, the Viennese Ageing Procedure (VAPro) is developed by Maschauer et al. [27] to simulate long-term ageing in which the asphalt mixture sample is exposed to a continuous flow of highly oxidant gases (ozone and nitric oxides) at a temperature of 60 °C for 3 days, and then the binder is extracted and compared to unaged binder from the same source. This technique has been found to be representative of the same pavement conditions in summer in moderate climates [28]. However, the principles and limitations are the same as for the PAV.

Regardless of the temperature–duration–atmosphere combination, one issue with the current R30 approach is determining which parameter to use to determine a duration of ageing equivalent to 10–15 years in the field [29]. In theory, if the accelerated ageing conditions are realistic, then all potential properties should reach values that are equivalent to field-aged samples at the same time. However, in practice, that is unlikely to be the case. The second, and arguably the greater issue, is the fundamental difference between ageing an asphalt sample in an oven at 85 °C and the conditions in the field.

Oven-aged samples are generally cylinders compacted by a Marshall hammer or in a gyratory compactor or cored from the freshly constructed asphalt layer. The oven is maintained at a constant elevated temperature, which creates a dark and dry environment. The samples are heated from all directions, which creates a uniform thermal distribution throughout the sample, meaning that ageing is almost uniform throughout the sample depth. This is not representative of the field ageing of asphalt surfaces.

In the field, an asphalt surface is exposed to cycles of temperature that are induced from the top, not from all directions. This means that the surface of the asphalt is aged much faster than the middle and bottom of the layer. Furthermore, the surface of the asphalt layer is exposed to UV irradiation, humidity and rain. Again, all these factors are applied to the top of the layer, resulting in a profile of ageing that was hypothesized by White and Abouelsaad [29] and schematically illustrated in Figure 2.

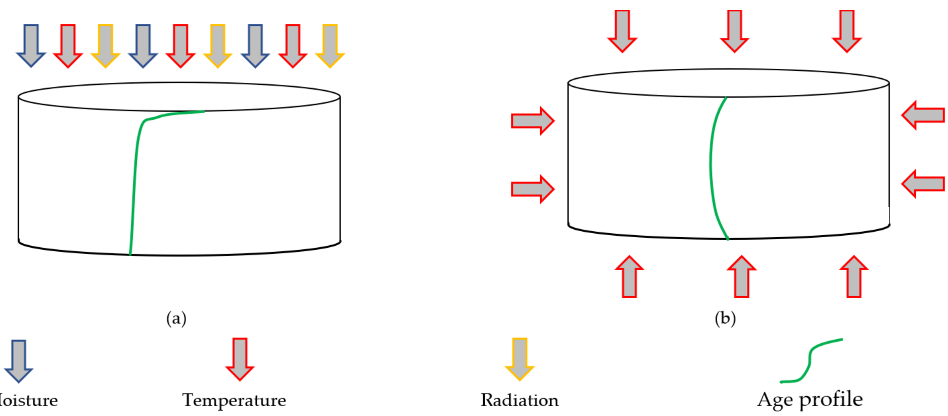

Figure 2. Schematic illustration of asphalt aged in the (**a**) field and (**b**) laboratory oven.

From the previous discussion, it is clear that the current protocols are not representative of the actual field conditions, and further investigations should be directed towards including other factors that promote asphalt ageing, including UV irradiation and humidity, which both increase the diffusion of oxygen and accelerate the chemical reactions which in turn accelerate bitumen degradation. Thus, a more realistic accelerated laboratory ageing protocol for asphalt must include surface exposure to UV irradiation, humidity and rain in order to develop a profile of ageing with depth through the surface that more realistically represents that of field-aged samples.

2.2. Photo Oxidation Techniques

Photo oxidation studies use a combination of simulated solar (UV) radiation, usually at elevated temperature, in the atmosphere to accelerate the ageing of binders and mixtures. First, the concept of photo oxidation is explained; then, binder studies are considered, and, finally, mixture studies are reviewed.

2.2.1. Concept of Photo Oxidation

Ageing occurs due to the reaction of environmental factors including oxygen, UV irradiation, moisture and heat. However, many studies have demonstrated that UV photo oxidation ageing effects are different from the ageing effects produced by standard thermal oxidation methods. Consequently, in recent times, UV simulation techniques have attracted the attention of researchers interested in accelerated bituminous binders and asphalt mixture ageing. To better understand how solar radiation can be adopted to simulate the hardening effects, it is crucial to first understand the full solar radiation spectrum and the spectral classification of solar radiation, with respect to each type of wavelength range.

Solar radiation is classified with respect to wavelength into seven spectral categories: gamma-rays, X-rays, UV, visible, infrared, microwave, and radio waves [30]. The ranges of wavelengths of each spectral category are summarized in Table 1. Ultraviolet rays are categorized into UVA, UVB, UVC and extreme-UV, as shown in Table 2. Extreme UV and UVC are completely absorbed by the earth's atmosphere, while UVB are mostly absorbed by the ozone layer, which also partially stops UVB, allowing only UVA to penetrate. The actual portion of penetrating UVB depends on factors including latitude and longitude, the season, weather, altitude, shading and level of atmospheric pollution [31].

Table 1. Solar irradiance spectral categories.

Category	Range (nm)
Gamma-Rays	10^{-5} to 10^{-3}
X-rays Ultraviolet	10^{-3} to 10
Ultraviolet	10 to 400
Visible	380 to 760
Infrared	760 to 10^{6}
Microwave	10^{6} to 1.5×10^{7}
Radio	10^{7} to 10^{10}

Table 2. Ultraviolet radiation spectral categories.

Category	Abbreviation	Range (nm)
Extreme Ultraviolet	EUV	10–121
Ultraviolet C	UVC	100–280
Ultraviolet B	UVB	280–315
Ultraviolet A	UVA	315–400

Solar radiation reaches the earth either as a direct normal solar irradiance (DNI) or after being scattered by molecules and particles in the atmosphere known as diffuse horizontal irradiance (DIF). Global horizontal irradiance (GHI) is the total amount of solar radiation including direct and diffuse received by a horizontal surface. The solar irradiance is measured and expressed in units of power per unit area, typically W/m^2.

2.2.2. Photo Oxidation Ageing of Bituminous Binders

The photo oxidation of binder films by extended exposure to UV from simulated sunlight has gained the attention of researchers in recent years. Although the qualitative effect of photo oxidation has been studied extensively in the past [32–34], recent studies have concentrated on quantitatively determining the effects of UV radiation on the degradation of bitumen. Most of the binder ageing studies have discussed the effect of the film thickness, the film preparation technique, the effect of UV wavelengths and the effect of combining thermal oxidation and photo oxidation on the rheological and chemical properties of bitumen [7]. This section presents a summary of the most recent studies that adopted UV irradiation to simulate field ageing in the laboratory, in addition to the most important factors considered by researchers.

Wu et al. [35] simulated short-term ageing using traditional RTFO and then used the UV radiation oven test (UROT). The UROT is a temperature-controlled vessel fitted with UV lamps with different UV radiation intensities to simulate long-term photo oxidation degradation effect on bitumen. A natural ventilated oven test (NVOT) has also been used to expose samples to the same environment, except for the UV effect to investigate the contribution of UV radiation to bitumen degradation. Fourier transform infra-red (FT-IR) analysis and dynamic shear rheometer (DSR) tests were adopted to measure the change in binder properties for the aged samples. The study concluded that UV radiation resulted in higher carbonyl formation and higher viscosity, indicating a higher degree of bitumen degradation due to the photo oxidation effect.

In another study on the effects of UV radiation on polymer degradation, Hossain and Wasiuddin [36] found that UV radiation caused a full degradation of SBS polymer-modified bitumen in terms of peak elongation forces. Yu et al. [37] supported this finding that UV radiation significantly reduced the network structure formed by the cross-linking effect of the SBS-modified binders, and that the degradation of the SBS network resulted in a significant change in the rheological properties of the binder after UV ageing.

Furthermore, Liu et al. [38] investigated the effect of UV ageing on polyphosphoric-acid-modified bitumen and concluded that the dynamic shear modulus over phase angle, softening point and dynamic stability all increased with extended UV ageing, while penetration and ductility reduced. In this study, the short-term ageing of binder samples was simulated using the TFOT at 163 °C for 5 h, and the residue was immediately placed in an oven with a controlled temperature of 60 °C, fitted with a UV lamp emitting UV irradiation at an intensity of 1000 W/m^2 for three ageing times: 2 days, 4 days and 6 days. It was concluded that changes in bitumen properties increased with increasing ageing time.

In another research, Mouillet et al. [39] found that photo oxidation generated by UV radiation dominated the change in the chemical properties of bitumen, in terms of the absorption of carbonyl groups (C=O), compared to thermal oxidation. Similarly, Kamal et al. [1] exposed bitumen samples to natural sunlight to understand the effect of UV ageing on the complex shear modulus of bitumen and concluded that complex modulus increased gradually with increasing UV exposure time. In the final report of the accelerated ageing of asphalt by UV-Oxidation by Manhattan College [40], thin-film bitumen binder samples were oxidized by fluorescent UVA and UVB lamps, and the level of ageing was evaluated by measuring the rotational viscosity. It was concluded that the viscosity increased with the increase in UV exposure time.

One of the most important factors that affect the ageing of bitumen by UV irradiation is the bitumen film thickness and the ability of UV irradiation to penetrate greater thicknesses of bitumen [41]. These studies are divided into two main sections. First, the effect of film thickness on the ageing of bitumen and the theories that explain energy transfer through bitumen film are discussed. Second, the different techniques of film application prior to simulated ageing are discussed.

Hu et al. [41] investigated the distinct effect of UV irradiation and ozone gases on the ageing depth with increasing ageing time. It was concluded that increasing ageing time increased the ageing depth in the case of using UV irradiation compared to using ozone only. The reason for the ageing depth increase was the permeation of the aged bitumen through the fresh bitumen, which resulted in changes in the rheological and chemical properties. Permeation is most likely to be related to the thermal stability of the binder, which highlights the importance of using thermally stable bitumen to ensure its performance. Li et al. [42] confirmed these finding and concluded that the ageing depth increased with increasing ageing time due to the increase in the UV light penetration depth due to the diffusion action of ageing products from the surface bitumen to the deeper layers. In another study, Wu el al. [43] concluded that a better correlation with natural exposure was noticed with a film thickness of less than 100 µm. Previous studies included a wide range of film thicknesses including 10 µm [44,45], 0.5 mm [46], 0.6 mm [47], 1.92 mm [48], 2 mm [49] and 3.2 mm [50].

On the other hand, developing a reliable technique for film application has become challenging to UV bitumen ageing studies. Recently, Sun et al. [51] developed a new technique of film application based on low-temperature slicing and ion thinning to a thickness of as small as 3 µm which can be considered a basis for future research. In practice, the film thickness in typical asphalt mixtures is 8 µm to 12 µm, and this is an appropriate target for the simulated ageing of binder samples in the laboratory. The ability to compare the findings of different researchers and between binder and mixture ageing research will be improved if a standard binder film ageing protocol is adopted by all researchers, similar to the AASHTO R30 protocol for asphalt mixtures.

As previously explained, the solar radiation spectrum has a wide range of wavelengths. Most researchers have ignored the effect of different radiation spectra of UV irradiation. The wavelength of UV irradiation is in the range 10 nm to 400 nm and cannot be seen by the human eye. Hu et al. [52] investigated the effect of UV irradiation in different wavebands on bitumen ageing and concluded that the UV irradiation in the range of 300 nm to 350 nm caused the most severe ageing, with the lowest effect noticed in the range of 350 nm to 400 nm. This confirms the distinct effect of different wavelengths on the ageing behaviour of bitumen.

Furthermore, Mirwald et al. [53] investigated the effect of wavelength in the range of visible light between 365 nm and 770 nm using FT-IR analysis. It was concluded that the visible light in the range of 365 nm to 460 nm, as well as in the range of 525 nm to 550 nm, caused higher oxidation rates than other wavelengths. It was recommended that these wavelengths be taken into consideration in the laboratory simulation of field ageing. In another study to understand the effect of UV radiation wavelength effects on bitumen ageing, Li et al. [54] also found that the dominant wavelength of UV radiation that affected the ageing behaviour was 360 nm. It is clear that UV radiation with different wavelengths have different effects on binder ageing. The comparison of results from different researchers can only be increased if a standard wavelength is focused on through a standard UV ageing protocol. Because 360 nm to 370 nm has been found by multiple researchers [53,54] to be the dominant wavelength for binder film ageing, this wavelength is recommended for all future research.

2.2.3. Photo Oxidation Ageing of Asphalt Mixtures

Less effort has been directed to the photo oxidative ageing of asphalt mixtures compared to bitumen ageing studies. Yu et al. [55] used an accelerated weathering machine (AWM) which can control temperature, oxygen and UV radiation ageing to simulate the combined effect of photo oxidation and thermal oxidation. After ageing, the aged binder was extracted and recovered bitumen tested by atomic force microscopy (AFM) and DSR to measure the shear modulus and phase angle of the aged binder. The results were compared to equivalent results for binder samples aged with the traditional RTFOT short-term ageing method and PAV long-term ageing. It was concluded that 2400 h of AWM weathering had the same effect as combined RTFOT and PAV, in terms of morphology, adhesion and modulus of elasticity measured by AFM, while 3000 h of weathering resulted in much more severe ageing. Similarly, Liu et al. [38] investigated the effect of UV irradiation on asphalt mixtures containing a polyphosphoric-acid-modified binder aged using the R30 protocol for loose asphalt mixtures to represent short-term mixture production ageing. Then, the aged loose mixtures were placed in the oven with a UV lamp for 2 days, 4 days and 6 days, with the same UV lamp irradiation intensity. It was concluded that ageing effects increased with increasing exposure time. However, no attempt was made to quantify the degree of ageing achieved.

In another study, Li et al. [56] investigated the effect of UV ageing on the adhesion performance of warm mix asphalt (WMA) and concluded that UV ageing leads to a decrease in the adhesion work and the compatibility of the warm asphalt and limestone aggregates based on surface energy theory calculations. Similarly, Gómez et al. [57] studied the effect of UV irradiation on the rutting and fatigue resistance of asphalt mixtures and concluded that the rutting resistance increases with increasing exposure time due to the increase in bitumen modulus, while noticing a fatigue resistance reduction with the increase in exposure time. Furthermore, Abouelsaad and White [58] compared the effect of heat only and the combined effect of heat and UV irradiation by conditioning asphalt mixtures in both an oven and a UV chamber at the same temperature. It was concluded that different ageing indices of samples conditioned in the UV chamber were consistently higher than for the samples aged in the oven, which confirmed the significant contribution of UV irradiation to the ageing of asphalt mixtures.

At Delft university, Hagos [59] combined oxidative ageing using heat alone with UV radiation in a weathering chamber to simulate UV radiation exposure. The study trialled different combinations of simulated heat, rain, humidity and UV radiation for 185 h. The overall conclusion was that neither the new nor the modified laboratory ageing techniques could adequately replicate the adverse effects on asphalt mixtures exhibited by just one year of in-field service. This requires further study with a longer exposure time and alternate simulated ageing factors.

In terms of fracture energy, Xiao et al. [60] compared the effect of ageing using the traditional R30 protocol, accelerated UV ageing, by developing an oven fitted with UV lamps. The results showed that the fracture energy of the unaged samples was higher, compared to both R30 and UV aged samples, and both ageing protocols showed similar fracture energy values, indicating that the fracture energy with ageing was less sensitive to UV irradiation than some other mixture properties [60].

In terms of binder ageing, the RTFOT and PAV protocols are well established and dominate research and practice. However, these short-term and long-term ageing processes do not take into account the UV irradiation associated with photo oxidation, rather relying on thermal oxidation and increased atmospheric pressure to accelerate the ageing process. This is useful for achieving rapid results in a relative manner. However, for asphalt mixture ageing, where researchers have made efforts of replicating the binder–aggregate interactions and the profile of surface ageing with depth, the ageing protocols must also represent in-field ageing. The current R30 protocol omits UV radiation, and this should be addressed in the future. Various researchers have used different approaches to the photo oxidation ageing of asphalt mixture samples, and a standard protocol is required in the future, which should be adjustable for application to different climatic conditions.

3. Ageing Effects on Binder and Mixture Properties

As discussed above, there is universal agreement that ageing changes the properties of the bituminous binder in asphalt mixtures. These changes can be measured in terms of binder properties or mixture properties. Binder properties are usually considered to be either the chemical properties or the rheological properties. Mixture properties are usually the physical or mechanical properties, measured by methods commonly used for routine asphalt mixture designs and analyses.

3.1. Ageing Effects on Binder Properties

Bitumen is an organic material which is either a naturally occurring material or a manufactured material produced as a by-product from the distillation of crude oil during a petroleum refining process. A wide variation is noticed in the chemical and rheological properties of bitumen based on the source of the bitumen and the refining processes used. It follows that the ageing behaviour also changes with different bitumen sources. In this section, the effects of binder ageing processes on the chemical and rheological properties of bitumen are summarized and discussed. It should also be noted that adding asphalt additives may change the ageing of the binder. For example, Jamshidi et al. [61,62] showed that the incorporation of different synthetic waxes changes the aging index of a binder depending on binder's performance grade, test temperature and the rheological parameter adopted for evaluation of ageing. In another study, Osei et al. [63] showed that adding 5% and 10% of natural rubber latex changed the density of the binder by 0.112% and 0.152%, respectively.

The binder additives not only change the ageing, but they also change other rheological characteristics, which can be used in the analysis of ageing as an ageing indicator. For instance, Jamshidi et al. [64] showed the effect of epoxy materials on the activation energy of a binder and its effect on the functional and filling performance of asphalt mixtures.

3.1.1. Ageing Effects on Chemical Properties of Bitumen

Because bitumen has a complicated nature that cannot be specified by chemical composition alone, it must be considered as a conglomerate material that relies on all its constituents to be characterized. However, understanding bitumen chemistry and the changes that take place due to exposure to different in-service conditions is of great importance to pavement researchers. Bitumen's composition and possible interactions determine its performance and durability as a pavement surface or material [65]. Hence, bitumen's composition and the association effect on asphalt mixture performance has attracted the interest of many researchers all over the world [66].

Although the chemistry of bitumen has always been described as mysterious and complicated in the literature, it is extremely important to collect as much information as possible to understand how different neat bitumen sources react with different modifiers, and how they react with the surrounding environmental conditions, to predict the performance of asphalt mixtures and the effectiveness of mixture rejuvenators. The problem of understanding bitumen chemistry lies in the complexity of the composition of the heavier distillates of crude oil compared to the lighter fractions. Hence, most of the trials to understand bitumen composition are based on the analysis of lighter fractions from the same sources [67]. Most bitumen molecules are hydrocarbons with small amounts of sulphur, nitrogen, oxygen, and traces of metals such as vanadium and nickel. The complexity of bitumen composition comes from the infinite number of different small molecular structures formed due to a combination of different polyaromatic structures which are considered the core structure of bitumen. These molecules exist only in small quantities, which make them difficult to isolate and characterize. However, the composition of these small molecules differs greatly with different sources of crude oil, which significantly affects bitumen properties.

The most typical and shared chemical property from a molecular point of view is its heterogeneity, and, thus, the most important finding from molecular analyses is that we can describe bitumen at a molecular level as a material that consists mainly of a number of compounds as previously illustrated, including hydrocarbons as the core structure. From another perspective and at the same molecular level, bitumen molecules are a combination of alkenes, cycloalkenes, aromatics and hetero molecules containing sulphur, oxygen, nitrogen and metals. Table 3 summarizes the elemental analyses of bitumen from different sources according to different studies [68]. It is worth mentioning that the higher the carbon-to-hydrogen ratio, the higher the bitumen yield from the crude oil, and this elemental analysis varies from a source of crude oil to another.

Table 3. Typical Elemental composition of bitumen [68].

Component	Portion (% by Mass)
Carbon	75% to 85%
Hydrogen	8% to 12%
Oxygen	0.1% to 3%
Nitrogen	0.1% to 0.5%
Sulphur	3% to 7%

At this molecular level, it is clear that it is difficult to understand the chemical interactions that take place with modifying bitumen and during ageing due to reactions with different environmental conditions. Pavement researchers have made much effort to adopt different chemical tests to quantifying the chemical composition and changes therein associated with the ageing of bitumen. The FT-IR and Saturates-Aromatics-Resins-Asphaltenes (SARA) analysis, in addition to the AFM analysis, has been widely used in previous research to quantify the changes in chemical composition due to binder ageing. In addition, a recent study evaluated the molecular structure of virgin, aged and recycled asphalt binder through small-angle X-ray scattering (SAXS) [69]. The SAXS data profiles obtained from virgin, aged and recycled asphalt binder samples showed a remarkable degree of similarity, indicating the microstructural features are not significantly changed by ageing. Furthermore, the scattering characteristics yielded from the analysis of the SAXS data showed the presence of secondary structure scatterers in the bituminous binder samples. The presence of secondary structure scatterers suggests that the binder structures consist of microstructural entities, such as micelles or aggregates, which form the basis for the scattering patterns observed.

FT-IR Analysis and Ageing Effects on Bitumen

The FT-IR technique is adapted to obtain the infrared spectrum of the absorption or emission of a gas, liquid or solid [70]. FT-IR spectroscopy is an analytical approach which has been widely used to study the changes in chemical behaviour and the oxidation rate of an aged bitumen [71]. Figure 3 shows a visual representation of valley-to-valley area integration and absorptions band characteristics of bitumen from FT-IR analysis. Changes in bitumen due to oxidation are characterized in terms of structural and functional indices, calculated from the band areas measured from valley to valley. Oxidation rate, which in turns means the extent of ageing, is characterized through two evident peaks at 1700 cm^{-1}, which represents carbonyl peaks (C=O), and 1030 cm^{-1}, which represents the sulfoxide functional groups (S=O) [72].

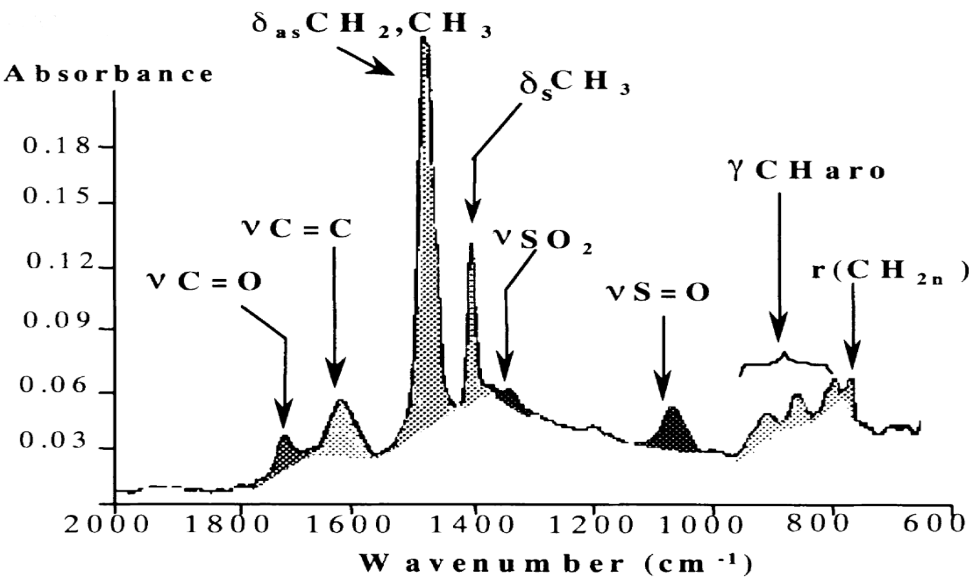

Figure 3. Visual representation of valley-to-valley area integration and absorptions band characteristics of bitumen [71].

The FT-IR approach has been used in several studies to either explain the ageing behaviour of bitumen or to evaluate the efficacy of anti-ageing additives. The carbonyl index ($I_{C=O}$) (Equation (1)) and the sulfoxide index ($I_{S=O}$) (Equation (2)) have been used by many researchers to quantify the evident changes in the chemical composition of bitumen [73].

$$I_{C=O} = {}^{A_{1699}}/\sum A \tag{1}$$

$$I_{S=O} = {}^{A_{1032}}/\sum A \tag{2}$$

where:

$$\sum A = A_{2924} + A_{2852} + A_{2729} + A_{1699} + A_{1601} + A_{1462} + A_{1377} + A_{1032} + A_{866} + A_{814} + A_{723}$$

AX = absorbance at wavelength X cm^{-1}

Omairey et al. [74] first developed this carbonyl index as the ratio between carbonyl peak at 1700 cm^{-1} and a functional reference peak (CH_3 group) at 1377 cm^{-1}, and the sulfoxide index as the ratio between sulfoxide peak at 1030 cm^{-1} to the same reference peak. In addition, a normalized carbonyl index was developed according to Equation (3), as a quantitative representation of ageing behaviour. Banja et al. added aromatic band index (I_{ARO}) as an indicative index of the ageing process as calculated in Equation (4). In this adaptation, the carbonyl and sulphoxide indices were calculated with respect to the summation of CH_2 and CH_3 bands.

$$NCI = \frac{CI_{LTaged} - CI_{Unaged}}{CI_{Unaged}} \tag{3}$$

$$I_{ARO} = \frac{Area\ of\ the\ Aromatic\ band\ centered\ around\ 1600\ \mathrm{cm}^{-1}}{Area\ of\ CH_2\ centered\ around\ 1454\ \mathrm{cm}^{-1} + Area\ of\ CH_3\ centered\ around\ 1375\ \mathrm{cm}^{-1}} \tag{4}$$

Table 4 summarizes the results of studies that have used FT-IR in the evaluation of the ageing behaviour of bituminous binder samples. It can be concluded from all studies that carbonyl index, sulfoxide index and normalised carbonyl index can provide a reliable indication of binder ageing behaviour. In addition, all anti-ageing additives were found to play a positive role in improving the ageing behaviour of the base bitumen. Some studies suggested a preference for carbonyl index as an indicator of ageing behaviour, specifically because it keeps increasing with ageing duration, compared to sulphoxide index. FT-IR can also be used as a reliable approach to comparing the different ageing techniques for bitumen, including the thermal oxidation and photo oxidation of bitumen samples.

Table 4. Summary of FT-IR studies.

Study/Year	Ageing Technique	Findings
Çalışıcı et al. [72]/2018	TFOT for short-term ageing simulation.	Lower (C=O) and (S=O) using diethylene glycol-based polyboron compound (DEGPB) additive.
Omairey et al. [74]/2020	TFOT for short-term ageing simulation. PAV for long-term ageing simulation.	Higher carbonyl, sulphoxide and normalized carbonyl indices of long-term aged samples compared to short-term aged samples and base bitumen. Anti-ageing compounds can improve ageing susceptibility.
Nie et al. [75]/2021	RTFOT	Carbonyl, sulphoxide and normalized carbonyl indices increased with the ageing time, which follows ageing kinetics law. Normalized carbonyl index is the easiest index to obtain and the best ageing evaluation index among other indices. Modified bitumen showed better ageing resistance in terms of FT-IR results.

Table 4. *Cont.*

Study/Year	Ageing Technique	Findings
Zhang et al. [76]/2015	TFOT for short-term ageing. UV long-term ageing for 12 days using 500 w. UV lamp for 12 days.	Carbonyl index increased from 0.0161 to 0.5310 after UV ageing.
Olabemiwo et al. [77]/2020	Thermal oxidative ageing at 60 °C for long-term ageing simulation.	The sulphoxide peak at 1031 cm^{-1} was completely obliterated. Carbonyl index was lowered with the increase in silver nanoparticles as anti-ageing compound.
Kleizienė et al. [78]/2019	RTFOT for short-term ageing. PAV for long-term ageing.	Sulphoxide index increases after the first long-term ageing period and then stabilizes while carbonyl index increases with every ageing step and with extending ageing time.
Cheraghian and Wistuba [79]/2020	RTFOT for short-term ageing and UV for long-term ageing for 12 days.	Higher carbonyl and sulphoxide indices after long-term ageing and better performance of bitumen samples modified with clay and silica nanoparticles.
Cong et al. [80]/2019	Thermal oxidative ageing.	Anti-oxidants including waste cooking oil played a positive role in reducing carbonyl index with thermal oxidative ageing.
Benja et al. [81]/2019	RTFOT for short-term ageing. Xenon lamps for long-term ageing and photo degradation.	Aromatic band index in addition to carbonyl and sulphoxide indices are calculated.

SARA Analysis and Ageing Effects on Bitumen

As stated above, studying the chemical composition of bitumen is challenging to researchers due to its complex molecular structure that changes with changing crude oil source and refining process. Bitumen chemistry has previously been characterized based on different approaches, including elemental composition [82], analysis of bitumen functional groups [83] and polar characteristics. Among different chemical analysis approaches, the polarity-based distribution of molecules has proven to have a strong relationship with bituminous binder and asphalt mixture performance over time [66,84,85]. The chromatographic separation of bitumen into four fractions, namely, saturates, aromatics, resins and asphaltenes, usually referred as SARA analysis, has been used since the 1970s [86]. SARA analysis has been used by many pavement researchers using different methods and protocols. One of the most common practices to quantify SARA fractions is thin layer chromatography (TLC) for separation, then using a flame ionization detector (FLD) [87,88] to quantify each fraction. Taking a different approach, several studies have used the SARA analysis to study and quantify the ageing effect of bitumen. Lu et al. [89] investigated the ageing effect using the SARA analysis and concluded that prolonged oxidative ageing resulted in a significant decrease in aromatics and an increase in both resins and asphaltenes but almost no change in saturates' fraction. Mirwald et al. [90] used chromatography techniques and solid phase extraction to separate bitumen into the four fractions of long-term aged bitumen samples using the PAV protocol. A new ageing protocol was also developed, referred to as Viennese binder ageing (VBA) for 3 days, and the samples were short-term aged using the RTFOT. It was found that a significant reduction in aromatics and a significant increase in asphaltenes fractions occurred for both long-term ageing techniques. In addition, a slight increase in the resins fraction and a decrease in the saturates was recorded. Mirwald et al. [90] also obtained colloidal stability index (CI) obtained using Equation (5) as a quantitative index of ageing. A strong correlation was found between the changes in the SARA fractions and the FT-IR analysis, which promotes the importance of using SARA fractions in ageing studies analysis.

$$CI = \frac{Aromatics + Resins}{Saturates + Asphaltenes} \tag{5}$$

Similarly, Sreeram et al. [91] used the colloidal instability index (*Ic*) of binders using Equation (6), which is the inverse of the index used by Mirwald et al. [90] and is commonly known as the Gaestal Index [92]. Lower values of the index indicate less ageing, as it indicates the ratio between insoluble fractions to the solvent phase, which in turn indicates that lower values of Ic mean better dispersion of micelle fractions in the binder and better ageing behaviour.

$$Ic = \frac{Saturates + Asphaltenes}{Aromatics + Resins} \tag{6}$$

Falchetto et al. [93] also used RTFOT and PAV protocols for ageing and recorded the changes in SARA fractions and found an increase in the resin fraction and a loss in aromatics, along with a slight increase in asphaltenes and saturates for aged samples, compared to unaged bitumen. Furthermore, Handle et al. [94] tracked changes in SARA fractions after the PAV long-term ageing procedure and concluded that unsaturated compounds turned into highly saturated oxygenated compounds with ageing, particularly aromatics with low polarity that rapidly degrade in mass with ageing through oxygenation. Moreover, it was concluded that the embrittlement and corrosion of bitumen can be explained through the depredation of low to average polarity aromatics. The findings indicate the importance of understanding the ageing behaviour related to a loss of aromatics rather than the increase/decrease in the other fractions.

In similar research, Sreeram et al. [91] adapted a novel accelerated ageing protocol for loose mixtures that depend on ozone and other reactive oxygen species, referred to as reactive oxygen species (ROS) for oxidation, and found that extracted bitumen showed an increase in asphaltenes and a loss in aromatics for both 5-day PAV aged samples and 24 h ROS aged samples. Although both Sreeram et al. [91] and Mirwald et al. [90] suggested using colloidal index or Gaestal index, the deeper understanding provided by other studies into how oxidative ageing affects the four fractions may lead to a debate regarding whether or not the Gaestal index or colloidal instability index is a useful indicator of binder ageing. Based on these recent studies, the SARA analysis is concluded to be a promising technology for understanding the bituminous binders and extracted binders from aged asphalt mixtures.

FT-IR and SARA Analysis Results Relationships

As previously discussed, the ageing of bitumen results in an increase in functional groups, including carbonyls and sulphoxides. Furthermore, regarding the SARA analysis of bitumen fractions, an increase in asphaltenes and/or resins and a decrease in aromatics is noticed with ageing. Hence, understanding the relationships between the shifts in FT-IR spectrum and the changes in SARA fractions may provide an improved understanding of the chemical reactions associated with bitumen ageing. Mirwald et al. [90] separated the four fractions and examined the shift in the FT-IR spectrum of each fraction at all possible bitumen functional groups and the possibly associated fraction with each functional group. Table 5 summarizes the FT-IR spectrum shifts and the changes in SARA fractions. The fourth column shows the trends of increase or decrease with ageing. It is clear that ageing in the field, or in a laboratory, is associated with an increase in the three main bands of ketone (C=O at 1700 cm^{-1}), sulphoxides (S=O at 1030 cm^{-1}) and the main aromatic band (C=C at 1600 cm^{-1}), as well as a reduction in the other two bands of carbonyls, in terms of the resin fraction conversion to ketones. Therefore, it is concluded that in most bitumen ageing studies, the ageing effects are limited to shifts in the C=O, S=O and C=C bands only.

Table 5. Summary of the functional groups and SARA fractions relationships.

Functional Group	Assigned Vibration	Wavelengths	Associated Sara Fractions				Associated Sara Fractions Changes			
			Sa	As	Re	Ar	Sa	As	Re	Ar
Alkyls	CH_2/CH_3	2920	✔	×	×	×	×	×	×	×
Alkyls	CH_2/CH_3	2850	✔	×	×	×	×	×	×	×
Alkyls	CH_2/CH_3	1455	✔	×	×	×	×	×	×	×
Alkyls	CH_2/CH_3	1380	✔	×	×	×	×	×	×	×
Alkyls	CH_2/CH_3	720	✔	×	×	×	×	×	×	×
Aromatic	C=C	1600	✔	✔	×	✔	×	+	+	+
Aromatic	CHAro	860	✔	✔	×	✔	×	×	×	×
Aromatic	CHAro	810	✔	×	×	✔	×	×	×	×
Aromatic	CHAro	750	×	×	×	✔	×	×	×	×
Alkene	C-H	960	✔	×	×	×	×	×	×	×
Ketone	C=O	1700	×	×	✔	✔	×	+	+	+
2-Quinolone	C=O	1655	×	×	✔	✔	×	×	-	×
Carboxylic Acids	C=O	1730	×	×	✔	✔	×	×	-	×
Sulphoxides	S=O	1030	×	✔	✔	×	×	+	+	+
Sulfones	SO_2	1310	✔	✔	✔	✔	×	×	+	×
Sulfones	SO_2	1160	✔	✔	✔	✔	×	×	+	×
Sulfones	SO_2	1260	×	✔	✔	✔	×	×	+	×
Sulfate ester	SO_2	1080	×	✔	✔	✔	×	×	+	×
Sulfate ester	S-O-C	810	×	×	✔	✔	×	×	+	×

✔ Yes/Change Occurs. × No/No Change Occurs. + Increase in Fraction.

Atomic Force Microscopy and Ageing Effects on Bitumen

The AFM was first used by Binnig and Quate [95] to image the structure of graphite, with other materials investigated consequently. The AFM is a high-resolution scanning microscope which generates images of a sample to identify topographic features at an atomic-scale resolution [96]. The AFM has an advantage of imaging any surface type, including polymers, glass and other types of surfaces [96].

Zhang et al. [96] used the AFM to investigate the effect of UV ageing on organo-montmorillonite-modified bitumen and observed bee-like structures, which were correlated to asphaltenes, and found that the dimension and amount of the bee-like structures were reduced due to the increased solubility of waxy molecules during ageing. In another AFM study on adhesive surface characteristics, Lyne et al. [97] concluded that a correlation existed between elastic modulus, adhesion forces and morphology of bitumen. In similar research, Omar et al. [98] investigated the effect of nano-clay as a bitumen modifier and its effect on bitumen ageing behaviour using AFM. It was concluded that AFM has the ability to identify changes in bitumen fluidity, and different bee-like structures were recorded in different bitumen samples, even though they all had the same penetration value.

In a review of AFM bitumen studies, Yu et al. [99] concluded that even though bee-like structures with wavy patterns are more often seen in some bitumen samples, whereas other bitumen samples show a homogenous morphology without any apparent structural features, specifically bitumen samples with low wax contents. The AFM was also used by Rebelo et al. [100] to show that both unaged and aged bitumen samples are composed of asphaltenes (micelles) in a sea of hydrocarbons (maltenes), and an increase in the size of asphaltene micelles was demonstrated with long-term ageing. In addition, short-term ageing induced fractal-like microstructures. Xing et al. [101] reported conflicting results with previous studies, finding that the surface roughness in terms of bee-like structure size increases after 25 h PAV ageing but decreased after 55 h of PAV ageing. Zhang et al. [102] also noticed a significant reduction in bee-like structures which was correlated to the presence of asphaltenes. One bitumen sample even showed a reduction in bee-like structures after short-term ageing. It is worth mentioning that of the two bitumen sources tested by Zhang et al. [102], the bitumen that showed no bee-structure shape after short-term ageing had a high colloidal index. This indicates that there is likely a correlation between the surface topography of bitumen after ageing and the SARA analysis results. Loeber et al. [103] explained that the higher colloidal index means that the asphaltenes were peptized by the resins in an oil-based medium.

From these previous studies, it is clear that the AFM has the potential to identify ageing in bituminous binders. However, because of the diverse nature of bitumen from different sources, it is important to always test unaged binder samples as well as aged binder samples from the same source. This means that indices of ageing are more reliable than aged bitumen test results.

3.1.2. Ageing Effects on Bitumen Rheology

Studying the rheological properties of bituminous binders used for asphalt mixture production is crucial for overall pavement performance. Bitumen exhibits elastic-solid behaviour at a low temperature and/or short loading time but viscous behaviour at a higher temperature and/or longer loading time [104]. Rheology, as defined by Morrison [105], is the study of the flow of materials that have non-linear and unusual behaviour, such as bitumen. Bituminous binder rheology is a fundamental measure of deformation at in-service temperatures [106]. The rheological testing of bitumen commenced in 1927, with the pitch drop test developed at the University of Queensland (Australia) [107]. Since then, valuable efforts have been made to better understand bitumen rheology, flow and deformation characteristics of bituminous materials. The rheological properties of bitumen can be measured using different tests including softening point, viscosity, elastic recovery and response to shear strain in the DSR.

Ageing Effects on Softening Point

A softening point is the temperature at which a bitumen sample fails to bear the weight of a standard steel ball [108]. The softening point of bitumen can be used as an indication of the extent of ageing, with the softening point increasing with binder ageing. Iwanski et al. [109] investigated the effect of fatty amines on the softening point of bitumen and found that it acted as an ageing inhibitor, with the softening point decreasing compared to the samples without amines added. Similarly, Hofko et al. [110] concluded that the RTFOT ageing temperature has a positive correlation with softening point.

Ageing Effects on Bitumen Dynamic Moduli

Bitumen does not have an elastic, linear, homogenous and isotropic behaviour, meaning it is generally classified as a visco-elastic material [111] that has either elastic or viscous behaviour, depending on the time of loading and temperature [104]. Based on this theory, bitumen can be in one of three phases. First, at a low temperature and/or short loading time, bitumen behaves as an elastic solid. Second, at a high temperature and/or long loading time, bitumen behaves as a viscous non-Newtonian liquid. Third, at a sufficiently higher temperature, bitumen behaves as a Newtonian fluid.

This complex nature of bitumen also affects the overall performance of asphalt mixtures. Consequently, the effects of ageing on the behaviour of bitumen have become increasingly important. Many studies have investigated the effect of different ageing procedures on the various measures of dynamic moduli, including complex modulus (G^*), storage modulus (G'), the loss modulus (G'') in addition to phase angle (δ), and how this affects asphalt mixture performance.

Lu and Isacsson [104] studied the effect of RTFOT and TFOT on bitumen samples and concluded that ageing caused an increase in dynamic moduli and a decrease in phase angle but with minimal effect at low temperatures. Kleiziene et al. [78] also evaluated binder ageing effects using the DSR, including two novel procedures. First, strain sweeps were used to determine the linear visco-elastic behaviour. Then, frequency sweeps were used to determine the dynamic shear modulus (G*) at a linear strain. The resulting crossover temperature, which represents the point of colloidal stability and the balance between the storage modulus (G') and the loss modulus (G'') as an indication of the effect of ageing, was determined. It was concluded that the crossover temperature increased by 7.9 °C and 12.8 °C after 22 h and 44 h of PAV ageing, respectively. Wang et al. [112] used an alternative procedure to RTFOT by using a static oven and found that the changes in the rheological properties of bitumen aged for 2 h were equivalent to standard RTFOT conditioning. DSR frequency sweeps, in addition to the multiple stress creep and recovery (MSCR) test [113], were combined to find the equivalent time in a static oven that caused the same ageing effect as the RTFOT procedure.

Similarly, Laukkanen et al. [114] used the Time-Resolved Rheometery (TRR) concept to characterize the time-dependent rheological behaviour of materials by performing cyclic frequency sweeps (CFSs) over an extended period. The results showed that the change in rheological properties was relatively slow during physical ageing. Furthermore, Tarsi et al. [115] studied different short-term and long-term ageing procedures and concluded that the significant changes in the complex moduli of aged samples of low frequencies were reduced to only minor changes when tested at higher load frequencies. This, again, emphasizes complex and non-linear materials such as bitumen. However, all the studies recorded an increase in modulus values and reduced phase angles with bitumen ageing, which indicates that relative rheology or relative bitumen ageing is a sound indicator.

3.2. Ageing Effects on Asphalt Mixture Properties

Like bituminous binder, asphalt mixtures are temperature-sensitive materials, and this means that the mechanical or physical properties change significantly with temperature variations [116] and that each asphalt mixture behaves differently at different temperatures. Physical properties of interest are usually deformation resistance, fracture resistance and resilient modulus. Binder ageing, which is strongly related to temperature variations and different environmental factors, plays an important role in defining the mechanical properties of asphalt mixtures. While the rheological DSR testing of binders can characterize the linear visco-elastic behaviour of a binder, resilient modulus and indirect tensile testing can characterize the elastic response of the asphalt mixture [117].

Several studies have investigated the effect of binder ageing on the mechanical properties of asphalt mixtures. Baek et al. [22] found that ageing significantly changed many of the commonly measured asphalt mixture properties, including resilient modulus and surface texture. Idham et al. [118] also investigated the effect of 5 days ageing of mixtures at 85 °C on the resilient modulus. It was concluded that for both dense graded and porous asphalt (PA) mixtures, the resilient modulus increased compared to unaged mixtures. In addition, the significant effect of test temperature on modulus was observed, with an increase in modulus of up to 88% when the temperature was increased from 25 °C to 40 °C. Brilliak and Remišová [119] also investigated the changes in asphalt mixture stiffness due to short-term and long-term ageing and concluded that an increase in a mixture's stiffness was consistently noticed with ageing.

Most of the studies that have investigated the effect of ageing on the stiffness of asphalt mixtures aged the asphalt mixtures in a conventional oven, which may raise questions of whether other climatic and environmental factors including UV irradiation and humidity have an effect on the mixture properties or not. Most studies have also focused on resilient modulus as the physical property of interest. As recommended by White and Abouelsaad [120], further research is required to first develop more realistic ageing protocols for asphalt mixtures, and second, to consider deformation resistance, fracture resistance and fretting/ravelling resistance as key indicators of relative asphalt mixture ageing over time.

4. Idealised Ageing Protocols

It is clear from the above discussion that the current ageing protocols are not ideal, each with its own various advantages and disadvantages, as summarised in Table 6. Furthermore, there are a range of indicators of ageing that can be used to determine either the effects of ageing or to compare different ageing protocols or compare different mixture types, and these also have their own advantages and disadvantages (Table 7). As stated above, it is concluded that there is no universally appropriate ageing protocol and that accelerated ageing protocols used in laboratory research should be determined based on the aim of the research. A flow chart recommended for determining the appropriate ageing techniques for different circumstances is shown in Figure 4. This approach to ageing protocol selection can be used for comparing the effects of ageing inhibitors, additives and surface rejuvenators, as well as for calibrating laboratory ageing protocols to field ageing effects, via a laboratory-to-field relationship development. Both of these concepts are reviewed in the subsequent sections.

Table 6. Summary of advantages and disadvantages of ageing techniques.

	Ageing Technique	Examples	Advantages	Disadvantages
Asphalt Mixture Ageing				
1	Dry oven ageing	AASTHO R30	Fast and low cost. Equipment is readily available.	Does not induce a gradient of ageing. Does not satisfy the realistic exposure of field conditions as the samples are exposed to heat from all directions. Does not account for the variability in climate conditions. Does not account for UV light intensity variability.
2	Highly oxidant gas exposure	VAPro	Representative of effects of ageing in summer moderate climates.	Does not account for the variability in climate conditions. Limited studies are available.
3	UV ageing	Suntest	Combines the effect of heat and UV light. Showed a more realistic representation of the ageing gradient. Accelerates the effects of ageing.	Expensive and further studies are needed to evaluate the effects of the variability of different light simulation techniques between different commercial chambers.
Bituminous binder aging				
1	Dry oven ageing	RTFOT	Fast and effective method for simulation of short-term ageing. Equipment is readily available.	Does not account for solar radiation, which can be of a minimal effect in the case of short-term ageing.
2	Pressurized dry oven ageing	PAV	Equipment is readily available. There is a standard protocol available.	The efficiency of the ability of pressure to simulate air diffusion is still questionable. RTFOT ageing for shorter periods showed more severe effects of ageing than PAV. Does not account for UV irradiation and the cross-linked chemical reactions especially for the modified binders. Does not account for the different climates.

Table 6. *Cont.*

	Ageing Technique	Examples	Advantages	Disadvantages
3	UV ageing	Suntest	Combines the effect of heat and UV irradiation. Efficient in simulating the cross-linked chemical reactions associated with polymer degradation.	The application of ultra-thin bitumen films is challenging. There is no standard for film application techniques. Further studies are needed to evaluate the effects of the variability in wavelengths. UV chambers are prototypes or commercial products and vary greatly.

Table 7. Summary of advantages and disadvantages of ageing indicators.

	Ageing Indicator Test	Indicators of Ageing	Advantages	Disadvantages
Asphalt mixture tests				
1	Elastic modulus	Resilient modulus, dynamic modulus	A sound indicator of asphalt mixture mechanical property changes with ageing.	Tests the whole specimen, so not suited to UV aged specimens with a gradient of ageing. Specialised and expensive equipment required.
2	Surface Texture	Mean texture depth	Easy procedure to evaluate fretting and ravelling of asphalt mixtures with ageing.	Not applicable to non-surface ageing. Results are highly variable, even before ageing. Only limited research is available.
Bituminous binder tests				
1	Simple properties	Penetration, viscosity and softening point.	Simple procedures to compare different ageing techniques.	Does not give a deep understanding of the complex bitumen rheology changes.
2	DSR	Complex modulus, Phase angle, MSCR.	Relative rheology changes can be considered a sound indicator of ageing. Gives a better understanding of bitumen rheology changes with ageing.	Expensive and time consuming.
3	FT-IR	Carbonyl, sulfoxide and aromatic functional groups.	A reliable and good indicator with significant changes in age-related functional groups with ageing. Simple and rapid.	There is no standard procedure for quantitative tracking of ageing effects specially. Specialised equipment required.
4	SARA analysis	Saturates, asphaltenes, resins and aromatics fractions change. Gaestel and instability Indices.	Significant changes have been recorded in fractions and indices with ageing. Gives a good understanding of chemical changes.	Expensive and time consuming. The behaviour of polymer-modified binder is opposite to that of unmodified bitumen. Does not address the cross-linked chemical reactions due to polymer degradation.
5	Atomic Force Microscopy	Bee-like structures. Morphology changes with ageing. Changes in surface topography of bitumen.	Promising technique to track the changes in bitumen morphology with a good correlation with the adhesive properties of bitumen.	Expensive equipment is needed. Only limited studies available.

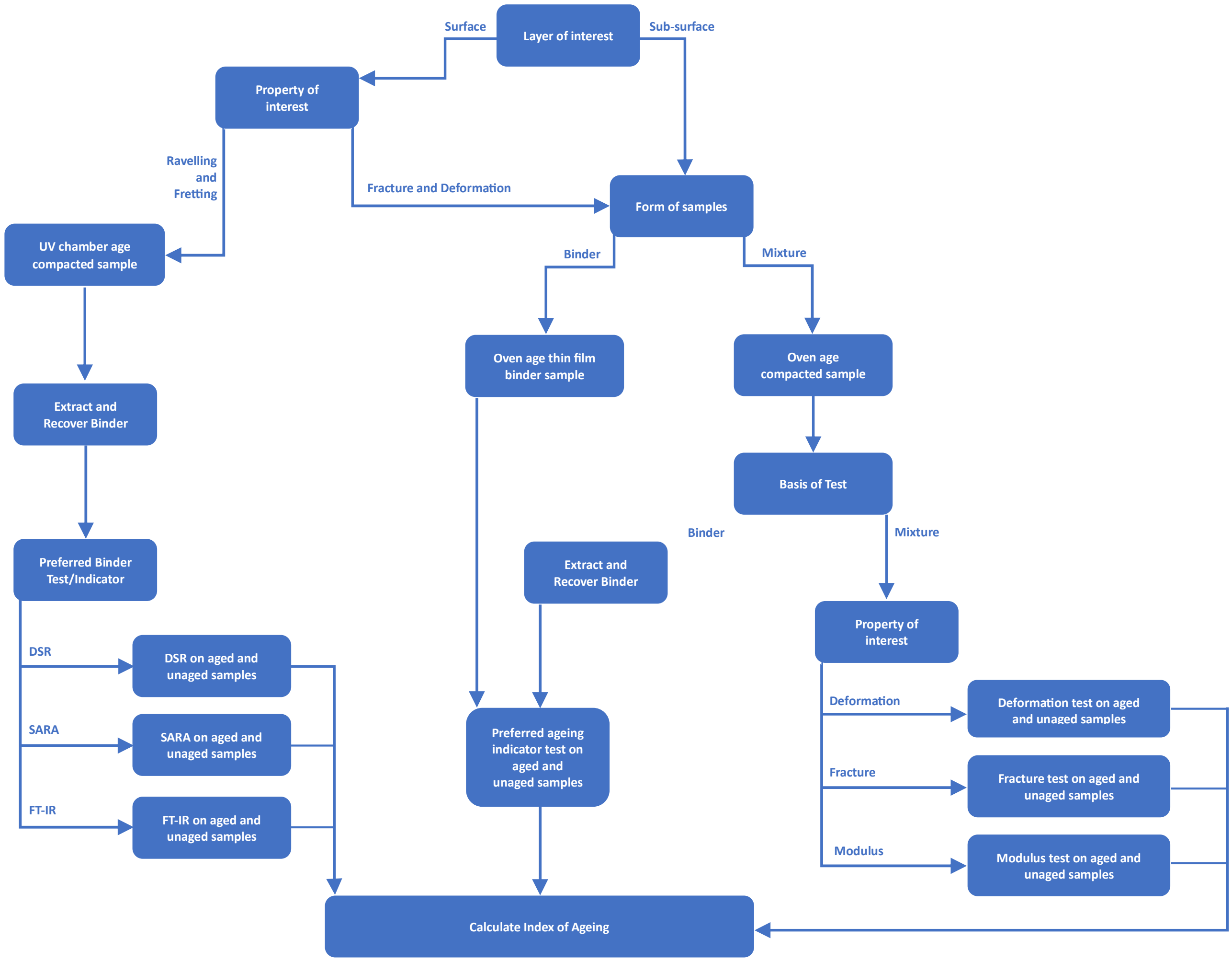

Figure 4. Recommended laboratory ageing protocol determination.

5. Ageing Inhibitors, Additives and Rejuvenators

One of the main objectives of flexible pavement management is to extend the life of asphalt surface, and this is why inhibiting ageing effects is of a great interest to pavement researchers [121]. Furthermore, rejuvenating additives balance the effect of excessively hard binders associated with high-percentage recycled asphalt use [122]. Ageing inhibitors may include antioxidants, UV absorbers and any additives that can slow down the bitumen oxidation rate.

5.1. Antioxidants and Ageing Reduction

As described above, the ageing of a bituminous binder is the reaction between the bitumen and oxygen in the presence of UV irradiation, which in turns leads to the formation of sulphoxides and carbonyls, which are sometimes referred to as free radicals [123]. Antioxidants work as free radical scavengers that can reduce the susceptibility of bitumen to ageing effects.

Antioxidants can be obtained from natural sources or manufactured synthetics. Natural materials and by-products such as rice husks [124], by-products from red wine industry [125], vitamin E [126], or a combination of natural materials including phospholipids [127] have all been shown to reduce the ageing susceptibility of bitumen. On the other hand, many studies have adopted manufactured synthetics as antioxidants. Xu et al. [128] investigated the effect of antioxidants including pentaerythritol tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate) (1010), tris (2,4-di-tert-butylphenyl) phosphite

(168) and lactate layered double hydroxides (LDH), the composite of octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate (1076), tris (2,4-di-tert-butylphenyl) phosphite (168) and CA-LDHs. Better mixture performance, in terms of ageing resistance, was reported as LDHs were found to shield the UV light and prevent oxygen penetration, while antioxidants can capture the free radicals, which results in a lower rate of oxidative ageing. Furfural, which is an agricultural byproduct of sugar dehydration has been used as a synthetic antioxidant by many researchers [129] and has also been demonstrated to also inhibit the ageing of bitumen. These promising results require field verifications so that they can be routinely specified and incorporated into asphalt mixture production in the future for better asphalt surface durability.

5.2. Anti-UV Ageing Additives

Many additives have been used as anti-UV ageing additives to inhibit the penetration of UV irradiation into asphalt surface mixtures and reduce the photo oxidative ageing effects in terms of the changes in the rheological and chemical properties of bituminous binders [130,131]. The LDHs are used as bitumen modifiers; however, the anti-UV effect was evaluated by Jia et al. [132]. It was concluded that LDHs can inhibit the photo oxidation effect of aromatics and asphaltenes, thereby resulting slower binder ageing. Liu et al. [133] concluded that LDHs were able to absorb and reflect the UV irradiation, which may improve the UV ageing resistance of binders. Furthermore, Zhang et al. [134] concluded that the organic grafted LDHs showed better performance for inhibiting the deterioration and gelefication of bitumen after UV ageing, compared to normal LDHs. Similarly, Xu et al. [135] reached the same conclusion that organic LDHs showed better ageing resistance by slowing down the photo oxidation effects in terms of the stacking of asphaltene clusters during UV exposure. Furthermore, Pang et al. [136] also concluded that LDHs play a significant role in inhibiting the UV irradiation effects, while Wang et al. [137] used LDHs with magnesium, zinc and aluminium and concluded that the resistance to UV ageing increased with an increase in zinc content.

Most of these studies show that LDHs provided promising performance in terms of ageing resistance. However, the strong hydrophilicity of inorganic layers can lead to poor compatibility between LDH and bitumen [138]. Hence, first converting the hydrophilic behaviour of LDHs into a hydrophobic behaviour is essential [139]. This can be achieved by the intercalation of organic anions into the LDH, which makes the LDH particles more compatible with the organic bitumen [140]. More studies are recommended in the future to better understand how the LDHs inhibit the UV ageing behaviour in addition to improving the compatibility with bitumen.

On the other hand, UV absorbers are currently widely used to reduce the effect of photo oxidation by UV irradiation. Feng et al. [141] used octabenzone and bumetrizole as UV absorbers and found significantly improved photostability of bitumen, depending on the origin of the bitumen. This is because UV absorbers can protect some bitumen types from photo oxidation, while they may accelerate the photo oxidation of other types. This was further studied by Feng et al. [142] who evaluated the effect of octabenzone and bumetrizole as UV absorbers and concluded that the UV ageing was reduced by both products for radial SBS modified binder. However, only the bumetrizole compound was beneficial for alternate SBS polymer types. Similarly, Gao et al. [143] evaluated the efficiency of using black powder UV absorbers and found that the UV absorbers can restrain the gelatinization of bitumen, which resulted in the physical sorption of activated carbon to lighter components. Furthermore, composites of clay and fumed nano silica particles were used by Cheraghian and Witsuba [79,144], and it was concluded that fumed silica had a high UV reflectivity that can provide a UV shield coating in asphalt mixtures. Butylated hydroxytoluene (BHT) and titanium dioxide (TiO_2) were also used by Zhang et al. [145] and were found to have a good UV anti-ageing performance at 0.3% and 0.1% contents of BHT and TiO_2, respectively.

Many researchers have reported potential benefits associated with a range of anti-ageing chemicals. Although some of these are readily added to bituminous binder production, some have practical challenges that need to be overcome before their benefits can be routinely employed. Furthermore, all these products require field verification prior to their routine use.

5.3. Ageing and Rejuvenation

Rejuvenation uses chemical agents intended to recover the flexibility of asphalt mixtures which is lost due to bitumen degradation or hardening as a result of bitumen ageing. Hence, rejuvenators should be able to reduce aged-bitumen viscosity and stiffness and improve ductility [146]. Various studies have demonstrated that rejuvenators have the potential to improve the rheological properties [147,148], penetration [149] and softening point [150]. Rejuvenators can generally be classified into vegetable oils, waste oils and organic oils. The recent studies that adopted different types of rejuvenators are summarised in Table 8. The various products are categorised as either vegetable, waste petroleum or other organic oils. The softness of the oils reduces the hardness of the aged binder when the two are combined. Whether this is true rejuvenation or simply a dilution of the aged binder in a softer oil is not clear.

Table 8. Summary of main categories of rejuvenators.

Rejuvenator Category	Rejuvenator	References/Year
Vegetable Oils	Corn oil	Zhao et al. [151]/2018. Suo et al. [152]/2021. Ji et al. [153]/2017.
	Soybean oil	Król et al. [154]/2016. Somé et al. [155]/2016. Elkashef et al. [156]/2018. Zhang et al. [157]/2018. White, G. [158]/2021.
	Sunflower oil	Cavalli et al. [159]/2018. Shirzad et al. [160]/2016. Tarar et al. [161]/2020. Zheng [162]/2019.
	Cotton seed oil	Zaumanis [163]/2014.
	Castor oil	Zeng et al. [147]/2018. Nayak et al. [164]/2016.
Waste Oils	Waste cooking oils	Noor et al. [165]/2019. Zargar et al. [166]/2012. Zaumanis et al. [167]/2014. Zaumanis et al. [168]/2013. Elshorbagy et al. [169]/2019. Zahoor et al. [170]/2021. Yan et al. [171]/2022.
	Waste engine oils	Tadele et al. [172]/2021. Arshad et al. [173]/2015. Gökalp et al. [174]/2021. Farooq et al. [175]/2018. Fernandes et al. [176]/2018. Romera et al. [177]/2016.
Organic Oils	Rubber powder tires	Rzek et al. [178]/2020.
	Naphthenic oil	Zaumanis et al. [168]/2013.
	Aromatic extract	Mogawer et al. [179]/2015. Garcia et al. [180]/2010.

6. Field and Lab Ageing Relationships

The ultimate goal of all simulated ageing of bituminous binders and asphalt mixtures is the replication of field ageing over the typical service life of a flexible pavement surface [120]. It is clear that the ageing of asphalt mixtures is more realistic compared to bituminous binder ageing because it takes into consideration the bitumen–aggregate interaction system, as well as the ageing profile with depth below the surface.

One of the clearest research gaps in simulated asphalt mixture ageing protocols is the lack of studies that correlate ageing in the field to that in the lab. For example, the R30 [25] long-term ageing protocol claimed that conditioning compacted samples at 85 °C for 5 days is equivalent to 5 to 10 years of field ageing, which is criticized by many researchers for three reasons. First, it is not clear at which climatic condition this protocol is valid. Second, the protocol omits other environmental factors that are scientifically proven to have a significant effect on the ageing of bitumen, including UV irradiation and humidity. Third, the reliance on thermal oxidation only does not result in a profile of ageing with depth, as occurs for surface layers in the field. It is important that improved simulated ageing protocols be developed in the future. These improved protocols should address the limitations and should be calibrated to a robust dataset of otherwise comparable field-aged sample test results.

6.1. Limitations of Current Laboratory Protocols

As previously discussed, bitumen ageing is a complex phenomenon that causes the hardening of asphalt mixtures and results in many distresses in asphalt pavements including fatigue cracks and ravelling. To better understand the ageing phenomenon in terms of multi-physics, Omairey and Zhang [181] suggested a model to simulate the ageing phenomenon as shown in Figure 5. This model provides for the oxidation of asphalt mixtures due to reactions with ambient environmental conditions for extended periods and can be affected by the following factors:

- Heat transfer that defines the pavement temperature profile.
- Oxygen diffusion from the air-to-air voids of asphalt pavement.
- Diffusion of oxygen from the air voids to the coating film of the asphalt binder.
- Oxygen products' growth in the asphalt binder.

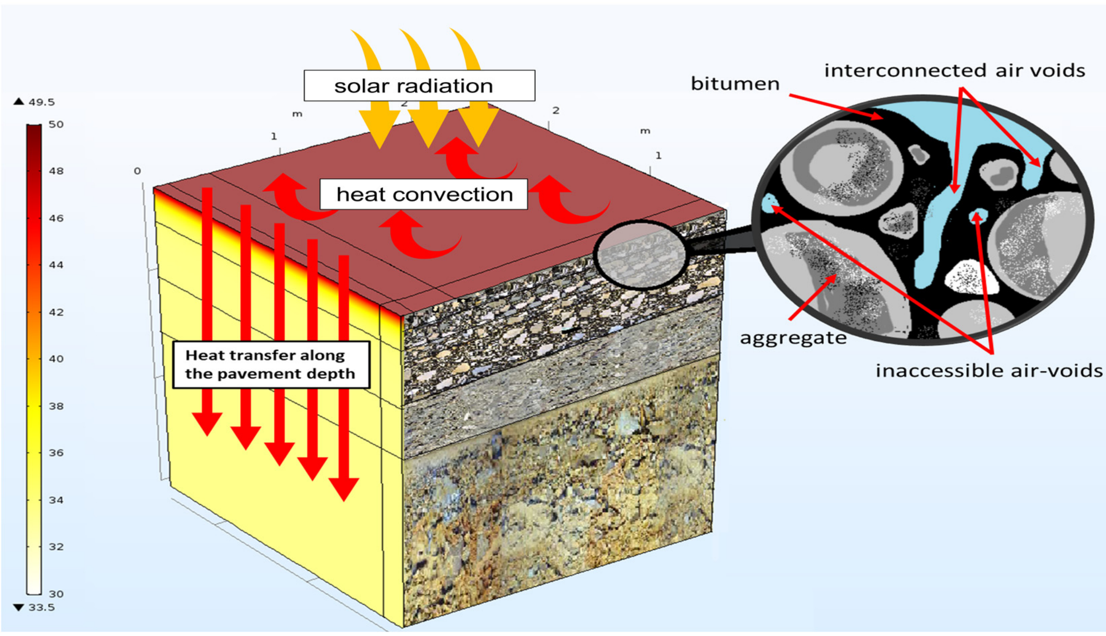

Figure 5. Ageing simulation model [181].

The complexity of developing a model that can predict field ageing lies in the circular dependence of the four factors and the complexity of the mathematical model development due to the nonlinearity caused by this circular interdependency [181]. This model indicates the ageing profile with a depth below the pavement surface, in addition to an ageing gradient in the bitumen film thickness surrounding the interconnected air voids channel. This can not be replicated by bituminous binder ageing in the laboratory.

Based on the suggested model, the ageing behaviour depends on many factors, including the mixture properties that affect the air voids interconnectivity which in turn affect the energy diffusion. In addition, the complexity of the model highlights the importance of finding a suitable approach to predicting the field duration based on any developed ageing simulation technique. On the other hand, as previously discussed, the standard protocol for asphalt mixture ageing in the USA is R30 [25], in which the compacted asphalt mixture samples are conditioned at 85 °C for 5 days. One limitation of this protocol is that conditioning of compacted samples leads to radial and vertical ageing gradients, which may affect the results of performance testing, because the properties throughout the specimen can vary [7]. Secondly, the rate of oxidation is directly proportional to the ageing temperature, which means that a higher temperature leads to more rapid ageing, and this may affect the physical properties of the asphalt mixture. Hence, some recent studies have proposed conditioning loose mixtures at 135 °C as an alternative [182]. Although the higher ageing temperature increases the rate of oxidation, the chemical and polar fractions may also be disrupted in the process, which means the changes in the bitumen may be different from the changes that occur in the field, at lower temperatures, and over longer durations. It has been established that 100 °C is the critical temperature that does not change the chemical behaviour of bitumen [183,184], so simulated ageing at temperatures above 100 °C should be avoided. Further research is required to confirm if there is a relationship between the undesirable chemical changes associated with higher ageing temperature and the physical properties of asphalt mixtures.

One other limitation of the current asphalt mixture ageing protocol is the potential for distortion or changes in air voids content and the geometry of the sample at elevated temperatures. Reed [185] suggested wrapping specimens in metal wire mesh secured with three clamps to prevent geometry sample distortion, but it was found that this may reduce the distortions, and it was unable to be eliminated. Hence, some recent studies have proposed conditioning loose mixtures at 135 °C as an alternative [182]. The limitation of this procedure is that compacting an aged loose mixture requires more compacting effort, but this may cause the degradation of the aggregate structure and subsequently affect the mixture properties.

6.2. Ageing Laboratory Protocols and Field Ageing Relationships

As discussed above, the degree of simulated ageing achieved in the laboratory must be calibrated to field ageing. Only with reliable calibration can field ageing effects be predicted by simulated ageing. This requires the laboratory ageing protocol and for the indicator of ageing to first be selected, and then the simulated ageing duration can be calibrated to an equivalent field ageing period by comparing results for the preferred ageing indictor for field-aged and laboratory-aged specimens. The result was conceptualized by White [186] as adapted in Figure 6. This indicates that laboratory ageing protocol 1, which produces an ageing index of 4.5, is equivalent to approximately 9 years of field ageing, while laboratory ageing protocol 2 produces an ageing index of 5.1, and this is equivalent to approximately 15 years of field ageing. However, the calibration is likely to be affected by mixture type and the climatic conditions in the area of interest, so a mixture and location-specific calibration is likely to be required. Given the number of field-aged samples required from surfaces of different ages, this is a significant undertaking, but it is essential to developing a reliable simulated ageing procedure.

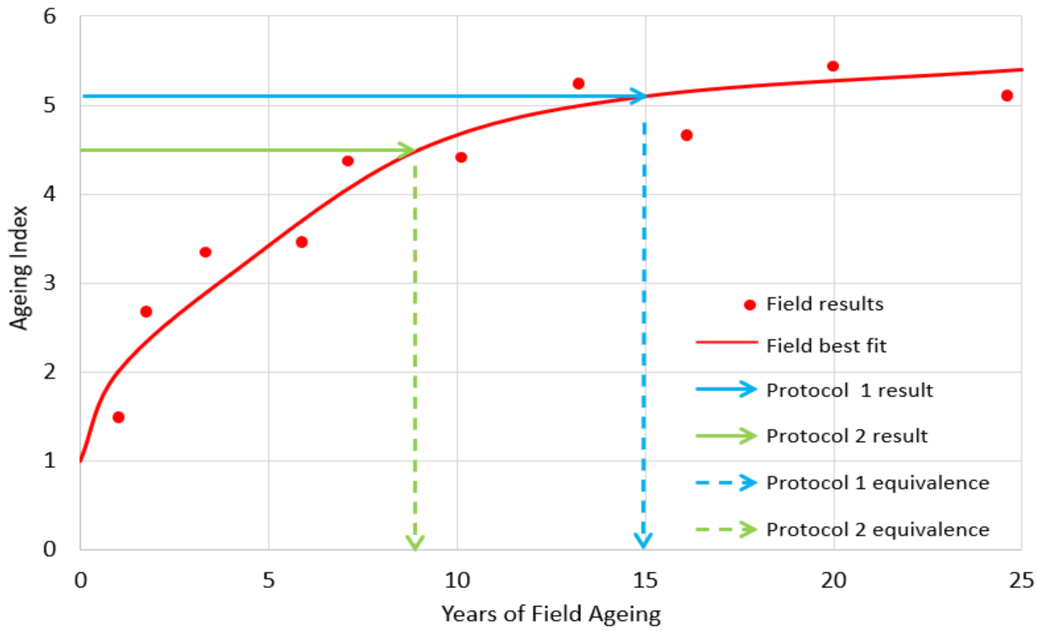

Figure 6. Conceptualization of calibration of simulated ageing protocol to field ageing.

In the meantime, existing data sets and research must be relied upon. The single greatest effort at calibrating laboratory to field ageing of asphalt mixtures was performed as part of the R30 [25] protocol development. This relied on dense graded asphalt cores extracted from road pavements in McLean, Virginia, USA. In contrast to the testing of cores extracted from the field, other research from the USA recommended against the ageing of compacted asphalt mixture samples, recommending ageing loose mixture at 95 °C [7,187,188]. This highlights the fact that different simulated ageing protocols are more or less suited to different research goals. For research into base asphalt course fatigue life, the ageing of loose asphalt mixture samples in a dry oven may be appropriate because there is no exposure to UV radiation and the whole layer is subject to approximately the same temperature in the field. In contrast, research focused on the weathering, fretting and ravelling of an asphalt surface layer will have a profile of ageing and the surface will be exposed to significant UV radiation, making photo oxidation-based ageing of compacted asphalt mixture specimens important. This difference indicates that different ageing protocols should be developed for base course asphalt and surface layer asphalt ageing research, both of which rely on different calibrations for field ageing.

For loose mixture ageing, Rad et al. [188] conditioned loose asphalt mixtures at 70 °C, 85 °C, 95 °C and, 135 °C for different durations followed by the extraction of the binder for testing. The results of DSR and FT-IR were compared to field data to determine the required durations to simulate the field conditions in terms of complex modulus results at a reference temperature and a reference frequency (G* at 64 °C and 10 Hz). It is worth mentioning that the loose mixtures were first conditioned for 4 h at 135 °C to simulate short-term ageing.

Returning to field-aged cores, the McLean samples were assessed in three stages. The second phase compared the obtained results from thermal oxidation ageing in a laboratory oven with those from the field-aged cores. It was found that 21 days at 95 °C in the oven was equivalent to 8 years of field ageing. Furthermore, 52 h at 135 °C was also found to be equivalent to 8 years of field ageing. These comparisons were both based on the G* value measure for extracted bitumen from the top 6 mm of core samples recovered from the 8-year-old pavement surface. Thus, the ageing temperature was concluded to play a crucial role in the accelerated ageing of asphalt mixtures because increasing the temperature from 95 °C to 135 °C caused a reduction in the required simulated ageing period from 504 h to 52 h. However, in terms of chemical changes presented as carbonyl and sulphoxides peaks, the 70 °C, 85 °C and 95 °C all showed similar correlation between bitumen rheology (DSR response) and the summation of carbonyls and sulphoxides (from FT-IR). However, at 135 °C, a clear shift in the relationship was noticed, which means that a temperature exceeding 95 °C may affect the kinetics of the oxidation reaction.

It is also important to understand that the field data were more consistent with the laboratory relationships at lower temperatures. This also indicates some changes in the ageing processes at simulated temperatures above 95 °C. Although the 135 °C conditioning temperature showed a significant reduction in the required simulated ageing time, it also resulted in unrealistic chemical changes in terms of FT-IR results. This suggests that simulated ageing should be limited to a maximum temperature of 95 °C in order to better replicate field ageing. One more important finding is that by changing the source of the bitumen, the required simulated ageing durations changed significantly, which needs further research on the effect of binder type and bitumen source on the ageing behaviour of asphalt mixtures.

The report relating to more realistic ageing protocols [7] compared the ageing of compacted asphalt mixture samples and loose asphalt mixtures at different temperatures and durations. First, oven conditioning of loose mixtures was recommended over compacted-mixtures conditioning despite the effort required for compaction after ageing. In terms of oven conditioning duration, which was equivalent to 8 years of field ageing, recovered field cores were cut into three disks, and the bitumen was extracted from each disk and tested for FT-IR and DSR. This use of field cores from the surface layer, and slicing the cores into top, middle and bottom cores, appears to accept an ageing profile and the effect of UV radiation on the upper surface. This contradicts the ageing of loose mixtures in the oven, which omits UV radiation and avoids an ageing profile with depth. Table 9 summarises the results from 8-year-old field cores.

Table 9. Chemical and rheological of 8-year field cores.

Sample Type		Carbonyls + Sulphoxides Peaks	Log G*
8 years old field cores	Top	0.111	5.33
	Middle	0.106	4.90
	Bottom	0.105	4.81

Table 10 summarises the interpolated oven ageing durations to simulate 8-year-old field ageing based on the FT-IR test results. It can be noticed that as the ageing temperature increased, the required ageing duration reduced significantly. For example, at 95 °C 21 days is required to simulate the ageing of the top disk, while at 70 °C, 117 days of simulated ageing was required. That is, the additional 15 °C reduced the equivalent ageing duration required by approximately 90%.

Table 10. Required ageing durations to simulate 8-Year field conditions.

Field Core Disk	Carbonyls + Sulphoxides Peaks	Required Ageing Durations (Days)		
		95 °C	85 °C	70 °C
Top	0.111	21	41	117
Middle	0.106	15	35	101
Bottom	0.105	13	33	97

In another study, Jing et al. [189] compared the effect of laboratory ageing using RTFOT for the simulation of short-term ageing and PAV for long-term ageing to field data from recovered cores at different depths from the pavement surfaces. In this study, the recovered cores of PA were cut into three slices, each 13 mm thick. The climatic condition of the site is described as cool summers and moderate winters with a temperature that varies from 2 °C to 7 °C in winter, and 15 °C to 20 °C in summer. The field cores were recovered one month after laying and then annually for four years. Afterwards, the bitumen from each slice or each core was extracted and tested for DSR response (rheology) and FT-IR (chemistry).

The FT-IR results from the cores, in addition to fresh and laboratory-aged bitumen, are summarised in Table 11. The first finding of this study is that the top slices were more aged in terms of complex modulus and FT-IR results, compared to middle and bottom disks. This again verified the ageing profile with depth. The extracted bitumen was more severely aged for the top disks, which is explained in terms of the exposure to environmental factors including UV and temperature. Moreover, in terms of carbonyls, the long-term ageing procedure in the laboratory was not sufficient to simulate even three years of field ageing, while in terms of sulphoxides, the long-term ageing procedure was more than sufficient to simulate 3 years of field ageing. This contradiction highlights different equivalent ageing conclusions that can result when different indicators of ageing are focused on. In terms of the summation of carbonyls and sulphoxides, the long-term ageing protocol was sufficient to simulate the three years field ageing. This may be explained in terms of previous studies that also found the formation of sulphoxides at the early stages of pavement life, while carbonyls formation took longer.

Table 11. Carbonyls and sulphoxides peaks at different ageing conditions.

Sample		Age	Carbonyls	Sulphoxides
Field	Top	0 years	0.0025	0.0180
	Middle		0.0024	0.0160
	Bottom		0.0022	0.0160
Field	Top	1 year	0.0075	0.0180
	Middle		0.0050	0.0170
	Bottom		0.0048	0.0168
Field	Top	2 years	0.0100	0.0185
	Middle		0.0090	0.0170
	Bottom		0.0050	0.0168
Field	Top	3 years	0.0120	0.0210
	Middle		0.0090	0.0200
	Bottom		0.0060	0.0190
Laboratory	Fresh	Unaged	N/A	0.0230
	RTFOT	Short-term aged	N/A	0.0110
	PAV	Long-term aged	0.0090	0.0140

On the other hand, in terms of DSR, the short-term and long-term ageing protocols were found to be far less severe than the field ageing, which raises an important question of the claim that long-term ageing protocols are equivalent to 5–10 years of field ageing. The current protocols must be re-examined, and different procedures required, including the use UV irradiation in simulated surface ageing, should be developed in the future.

As a continuation to the previous study, Jing et al. [190] investigated the difference in the ageing behaviour between PA and stone mastic asphalt (SMA) mixtures, in which the same techniques of short-term ageing and long-term ageing were followed. However, this time the field cores were recovered from an existing pavement from 2014 and every year since 2013 and up to the end of the study in 2017. The field cores were again cut into three disks, each 13 mm thick. The main finding of this study was that the ageing in the field has a more severe effect on porous asphalt mixtures compared to SMA mixtures, in terms of both FT-IR results and DSR. This highlights the importance of mixture specific simulated mixture ageing protocols. In addition, the most severe effect of ageing was noticed at the surface of the SMA, and a clearer ageing gradient exists in the SMA compared to the PA. This may be explained by the lower interconnectivity of air void networks in SMA, which prevents the oxygen from penetrating deeper layers and slows down oxidation. Regarding the laboratory ageing protocols, it was found that PAV was far less severe than four years of field ageing. Moreover, the PAV ageing protocol was not sensitive to the type of mixture and, therefore, cannot simulate the ageing profile with depth, or account for the difference in ageing of the different mixture types.

Cui [191] also investigated asphalt mixture ageing in different climatic regions in the USA to provide general conclusions about the ageing patterns of different asphalt mixtures. First, ageing rates were found to vary with pavement depth, which is supported by the previously discussed studies. In addition, the study highlighted the significant impact of temperature on the severity, and ageing as the hot climatic regions like Texas showed more severe ageing compared to cooler states such as Minnesota. The study highlighted the problem of limited field data due to the limited number of field cores, reflecting the high expense and time required for curing. It was recommended that a database be developed for future research. On the other hand, collected field cores showed the formation of carbonyls with field ageing, which agreed with the increase in carbonyls with increasing simulated laboratory ageing durations [191]. Some other researchers [192] also confirmed the severe ageing of the top surface compared to the bottom surface in terms of penetration and ductility.

Abouelsaad and White [193] attempted to combine the results of different field-aged core testing [90,189,194] and to calibrate a laboratory ageing protocol that includes by thermal and photo oxidative ageing. The laboratory ageing protocol included 90 days of ageing at 70 °C, with and without 300–400 nm wavelength, UV irradiation at an intensity of 50 w/m^2 [24]. A relationship was developed between the ageing index from FT-IR carbonyl and sulphoxide groups, and the actual age of surfaces from which cores were recovered, and the binder was extracted and tested (Figure 7). It was concluded that the 98 days of laboratory ageing without UV irradiation was equivalent to 18.1 to 19.7 years of field ageing, and when UV irradiation was included, the equivalent field age increased to 20.9 to 23.5 years. However, the field ageing relationship was limited to the results of only three previous studies, was limited to DGA samples and was limited only to FT-IR based age index values. Further work is required to develop a larger database of field-aged asphalt surface ageing indicators against which to compare laboratory ageing protocols.

It should be noted that complex models were developed based on different variables to predict the trend of ageing. As an example, Guan et al. [195] proposed a model based on Glower–Rowe (G-R) parameter as a function of stiffness modulus, creep rate, continuous grading temperature, critical temperature difference, relaxation time, dissipation energy ratio, low-temperature indicator ratio, and low-temperature comprehensive compliance parameter. The outputs of the model showed that ageing had a significant impact on the low-temperature properties of the asphalt binder. In addition, it was found that the G-R parameter, continuous grading temperature and relaxation time increased with the growth of aging severity, whereas creep rate, critical temperature difference, and dissipation energy ratio were contrary to this trend. Moreover, stiffness modulus, low-temperature ratio indicator and low-temperature comprehensive compliance parameter had no significant correlation with the degree of aging.

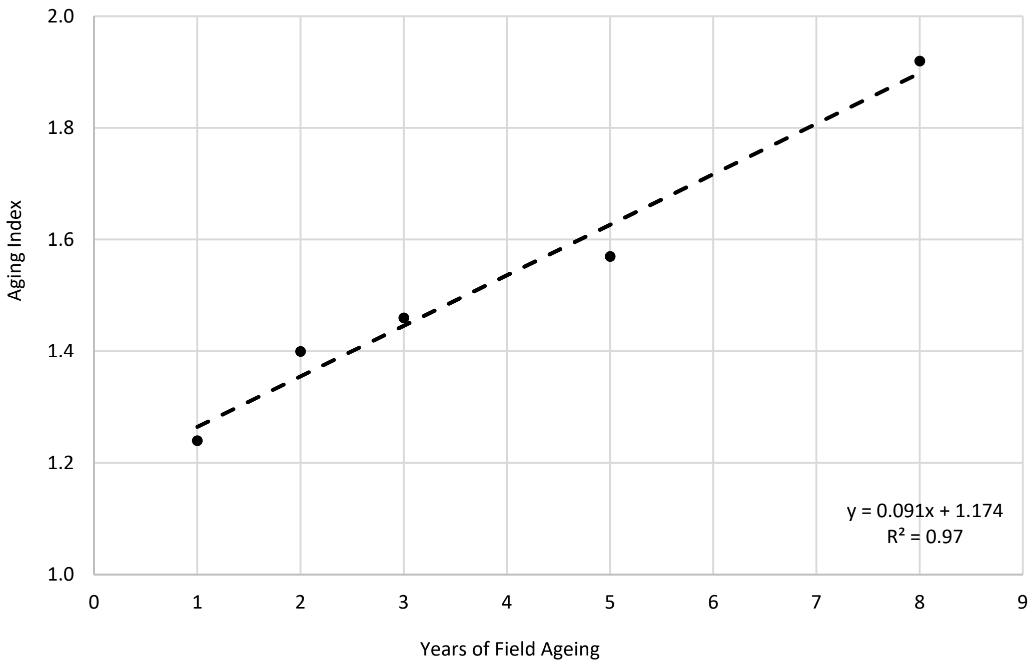

Figure 7. Relationship between field aged FT-IR age index and asphalt surface age.

7. Conclusions and Recommendations

This critical review of accelerated or simulated ageing of asphalt mixtures and bituminous binders has considered ageing simulation techniques, ageing effects on binder and mixture properties, ageing inhibitors and correlating simulated laboratory ageing to real field ageing. The findings and recommendations for future research are based on the gaps identified in the existing knowledge.

There is a significant gap in simulated ageing protocols that use heat only or a combination of heat and pressure, known as thermal oxidation techniques. These are applied to both binders and mixtures and do not take into consideration the UV irradiation, which contributes significantly to the chemical and rheological changes associated with field ageing. Furthermore, asphalt mixture ageing is preferred to binder ageing because it takes into consideration the interrelations between the bituminous binder and mineral aggregate systems, which significantly influences the ageing of the asphalt mixtures. Based on this review of the current knowledge, it was concluded that:

- Current ageing protocols are generally less severe than field conditions, with less than 5 years of equivalent ageing achieved by the protocols that are intended to represent 5–10 years of field ageing.
- The laboratory ageing of compacted asphalt mixture samples at more than 90 °C caused sample integrity issues, including changes in air voids and distortions, and this should be avoided in any laboratory ageing protocols developed in the future.
- The ageing of compacted asphalt mixture samples with a combination of moderately elevated heat and UV irradiation is recommended where replication of the ageing profile with depth observed in the field is intended to be replicated in the laboratory.
- The field ageing of asphalt mixtures and their bituminous binders is mixture, binder and environment and pavement-layer-specific; therefore, a universal laboratory ageing protocol is unlikely to be determined.

It was also concluded that there are many indicators of ageing that can be used for comparing mixtures and calibrating simulated ageing to field ageing durations. The asphalt mixture modulus can be measured on compacted asphalt samples or field cores, but the ageing gradient with depth makes testing complicated. Therefore, a binder extracted from the top, middle and bottom disks of a surface layer of asphalt is recommended.

The extracted binder can be tested for rheology (DSR), chemical composition (SARA), chemical oxides (FT-IR) and structure (AFM). Different extracted binder properties can indicate different degrees of ageing, even for the same material aged in the same manner. The rheological properties, including softening point and the dynamic modulus (from DSR response), are the preferred properties for comparing different ageing techniques and effects. The binder life span in terms of ageing depends on many factors which interact with each other, including temperature, moisture, wind speed/direction, traffic loading, binder type, aggregate type, air void percentage and binder content. Therefore, there is no universal procedure to estimate binder age. To estimate the age of an asphalt surface, engineering judgment is required based on local service conditions and materials. Furthermore, because each mixture and bituminous binder has different initial properties, indices of ageing, calculated as the ratio between the terminal and initial properties, are critically important to quantifying both simulated ageing and ageing in the field.

Many efforts have been made by various researchers to understand the potential of various antioxidants, modifiers and UV absorbers to slow down the rate of ageing or to reverse its effects. Many approaches have demonstrated promising results in terms of slowing down the rate of thermal oxidation and increasing the photostability of bitumen. Better simulated ageing protocols for bituminous binders and asphalt mixtures will increase the effectiveness of these research efforts, and developing standard simulated ageing protocols will improve the ability to compare results from different researchers in the future.

Finally, the efforts made to date to calibrate simulated ageing in the laboratory to field ageing conditions have been limited and show conflicting results depending on the asphalt material aged, the field ageing climatic conditions and the indicator of ageing used. It was concluded that mixture and climate-specific field core recovery and extracted binder testing are required to calibrate simulated ageing techniques to the field, and the preferred ageing protocol may differ for research focused on surface weathering, compared to research on base course properties.

Simulating field ageing in the laboratory is a significant challenge for asphalt and binder researchers. A universal ageing protocol is unlikely to be determined, and any mixture-climate-specific protocol will require a large number of cores to be recovered from the field from surfaces of different ages but with a comparable mixture composition and constituent ingredients. However, given the importance of simulated ageing to quantifying the benefits of ageing inhibitors, as well as comparing the ageing of different materials and mixture types, the development of a reliable, robust and calibrated laboratory ageing protocol is essential for the future.

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