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Fire Behaviour and Heat Release Properties of Asphalt Mixtures

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Abstract: A comprehensive analysis of the fire properties of asphaltic materials has undoubtedly become a primary need to provide proper instruments for the fire safety engineering in highway tunnels. Here, a propaedeutic research is proposed to define and develop fire-safe road construction materials. Limiting Oxygen Index test was performed to investigate the influence of magnesium hydroxide (MH) and aluminium hydroxide (ATH) in asphalt mastics ignitability. The most remarkable improvement was achieved with the 100% by weight of ATH. Limestone filler mainly composed of calcium carbonate was also investigated and resulted poorly influent in enhancing asphalt binder fire reaction. Cone calorimeter tests were then performed to evaluate fire properties of wearing course asphalt mixtures. As the bitumen content increases, the heat release significantly rises and the same occurs for incomplete combustion products, such as smoke and carbon monoxide. At constant bitumen content, the use of aluminium hydroxide instead of traditional limestone filler leads to a significant reduction in the Peak of Heat Release, the Total Smoke Release and the CO Yield.

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Key words: *Aluminium hydroxide; Asphalt; Cone calorimeter; Flame retardant; Limiting oxygen index; Magnesium hydroxide.*

Introduction

Vehicle fires in highway tunnels have become a problem of primary concern since the two last decades, after severe accidents happened in the most important tunnels [1, 2]. When a vehicle fire occurs, pavements are subjected to a consistent radiation due to the fire itself and the hot smoke layer accumulated at the ceiling, thus resulting in extremely high temperatures. Nevertheless, till now only few studies have been carried in order to deepen the understanding of their fire behaviour [3-6]. The common conclusion was that, due to the organic nature of the asphalt binders, asphalt mixture flexible pavements can ignite when subjected to heat fluxes which are far smaller than the ones reached during vehicle fires in tunnels [7].

In order to improve asphalt pavements fire behaviour, recent studies focused on the modification of the asphalt binders through several flame retardant (FR) additives. First attempts to enhance asphalt fire reaction involved the use of conventional additives traditionally applied in polymer technology [8-10]. Wu et al. (2006) highlighted the effectiveness of halogen-based materials, such as decabromodiphenyl-ether. Promising results in terms of Limiting Oxygen Index (LOI) were obtained with only 8% of these mixed flame-retardants [8]. However, important drawbacks in terms of smoke production and corrosive gases, due to the specific gas-phase action of halogen-based additives, addressed the research to the use of alternative metallic hydroxide fillers [11, 12]. Thus, the most frequent approach to enhance asphalt mixture fire reaction consists in creating flame-retardant asphalt mastics by adding aluminium hydroxide (ATH) or magnesium hydroxide (MH) to asphalt binders. Thanks to their endothermic decomposition, these FR-fillers led to encouraging results in terms of LOI and thermal stability [13, 14]. The testing methods used in all the above-cited experiences to assess asphalt binder and mastics fire reaction were commonly based on LOI and Thermal Gravimetric Analysis (TGA), in some cases integrated by Differential Scanning Calorimetry (DSC). However, all these studies were performed by testing only asphalt binders or mastics while FR-asphalt mixtures have never been properly considered. Indeed, the specific geometry of LOI samples does not allow to properly test asphalt mixture fire reaction because coarse aggregates generally exceed the cross section of the specimen. Moreover, melting and dripping negatively affect the test performance. As a logical consequence, a testing method specifically aimed at the assessment of asphalt mixture becomes a primary need. The present investigation focuses on this context and aims at evaluating the fire reaction of asphalt mixtures and the consequent main engineering implications.

The experimental program starts from the assessment of the fire response in asphalt mastics evaluated by LOI tests, thus searching basic information on the fire properties of bituminous materials. A subsequent more extensive experimental phase focuses on combustion processes in asphalt mixtures through the Cone Calorimeter test.

Experimental Program

Materials

All the asphalt mastics and mixtures were produced starting from the same base asphalt binder, referred to as B in the following text and kindly provided by ENI S.p.A. The base asphalt B is a 50/70 Penetration Grade unmodified bitumen characterized by softening

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Table 1. Asphalt Mixture Aggregate Grading.

Sieve Size - [mm]	16	12.5	8	4	2	0.5	0.25	0.063
Total Cumulative Passing - [%]	100	95	79	45	35	19	13	9

Table 2. Identification and Basic Properties of Asphalt Mixtures.

Asphalt Mixture	Asphalt Binder Content (%wt)	Additional Mineral Filler	Bulk Specific Gravity - G_{mb}	Theoretical Maximum Specific Gravity - G_{mm}	Air Voids
	[%]	[-]	[g/cm^3]	[g/cm^3]	[%]
W-550C	5.50	Limestone	2.299	2.408	4.5
W-575C	5.75	Limestone	2.306	2.388	3.4
W-600C	6.00	Limestone	2.363	2.363	2.0
W-550A	5.50	$Al(OH)_3$	2.310	2.366	2.3

point of 52°C (ASTM D36-95) and penetration equal to 44 dmm (ASTM D5 - 06e1).

Asphalt mastics were prepared with a high shear mixer Silverson L4R, by heating asphalt binder until 170 ± 5°C and then gradually adding (5 g/min) the desired percentage of filler. The mixing process lasted 30 minutes.

Three different kinds of fillers were used: ATH, MH and limestone, subsequently referred to as A, M and C respectively. ATH was kindly provided by J.M. Huber Co. while MH by Sigma Aldrich Co. LLC. The fillers differ not only for the chemical composition but also for the median particle size: C was characterized by a median particle size (d_{50}) equal to 3.2 µm while A and M showed d_{50} equal to 9.8 µm and 0.9 µm respectively.

Different binary blends were obtained by mixing B with A or M separately. The filler content was variable and ranged from 20% to 100% referred to the weight of the base asphalt binder; these binary blends are marked as follows: A20-A40-A60-A80-A100 and M20-M40-M60-M80-M100, where A or M identifies the used filler, while the numbers indicates the percentages of filler. Then, ternary blends were obtained by adding one of the two FR-fillers (A or M) coupled with C to the base asphalt binder. In this case, the overall filler content (intended here as the sum of FR-filler and limestone) was always equal to 100% by weight of the base bitumen. These ternary blends are consequently defined as CAx or CMx where x is the weight fraction relative to the FR-filler (e.g. in CA20 total filler is composed by 80% of limestone and 20% of ATH).

Different series of asphalt mixtures were then prepared using the same aggregate gradation and asphalt, but different additional fillers. The aggregate grading curve was defined according to SHRP-Superpave requirements for a dense wearing course (AASHTO M323-04: Standard Specification for Superpave Volumetric Mix Design). The nominal maximum aggregate size is 12.5 mm and the specific aggregate gradation is reported in Table 1.

Within the range 4-16 mm crushed porphyry aggregate was exclusively used while limestone aggregate was employed for the 0-4 mm range. The overall filler content is 9.0% by weight referred to the total weight of mineral aggregates. More precisely, 5.5% wt is additional FR-filler or limestone while the remaining 3.5% is provided by the 0-4 mm limestone fraction.

Four different asphalt mixtures were prepared and are referred to as W-550C, W-575C, W-600C and W-550A.

More specifically, asphalt mixtures W-550C, W-575C and W-600C are characterized by the addition of 5.5% of C. The difference among these three series of specimens is the bitumen content, respectively equal to 5.50% in W-550C, 5.75% in W-575C and 6.00% in W-600C. The fourth series of specimens, named W-550A, contains ATH. In this case only one bitumen content was considered, equal to 5.50%.

The asphalt mixture production process was the same for all the mixtures. Asphalt binder, aggregates and filler were heated until a constant temperature equal to 140°C was reached. Coarse aggregates (4-16 mm) were first mixed with the defined amount of asphalt binder and then, after having the aggregate surface completely and uniformly coated, the 0-4 mm limestone fraction was added. Finally, the additional filler was introduced and the mixing operations were carried out. Cylindrical samples characterized by 100 mm diameter were obtained by using a Superpave gyratory shear compaction technique, with a vertical pressure of 600 kPa and setting the compaction level to 125 rotations which is the N_{des} recommended value for traffic higher than 30 MESALs.

For each asphalt mixture three different samples were produced and subsequently cut into two smaller samples dimensionally compatible with the specimen holder of the cone calorimeter, thus obtaining six cylindrical samples for each asphalt mixture characterized by having diameter equal to 100 mm and height equal to 48 ± 2 mm. Finally, two other 150 mm diameter cylindrical specimens were produced for the W-550C asphalt mixture in order to obtain 98±2 x 98±2 mm square specimens with the height of 35 ± 2 mm, as requested by the standard specification for the Cone Calorimeter test (ISO 5660-1). Theoretical maximum specific gravity (G_{mm}) was determined for each asphalt mixture according to ASTM D6857-09. Asphalt mixtures composition and basic properties are synthetically reported in Table 2. All physical properties are reported in terms of average values for the six samples of each asphalt mixture series.

Testing Methods

The experimental program is composed of two main phases. The first phase focuses on the evaluation of asphalt mastics ignitability, the second phase deals with the assessment of asphalt mixture fire properties.

Asphalt mastics ignitability was measured through LOI test. This test allows to measure the minimum oxygen concentration, in an oxygen/nitrogen mixture, required to support the flaming combustion of the specimen. A specific sample preparation, deeply discussed in [15], was followed to avoid melting. Testing procedure was the same as required by ASTM D2863-10: the specimen was placed inside a glass chimney saturated with an oxygen/nitrogen mixture with a set oxygen volume concentration called Oxygen Index (OI). A gas flame was then drawn up to the top surface of the upper end of the sample until ignition occurred. Limiting Oxygen Index was then defined as the minimum OI that met the criteria specified in the ASTM D2863-10 for self-supporting moulding materials: 1) OI correspondent to a period of burning after ignition equal to 180 s, or 2) OI correspondent to an extent of burning below the top of the specimen equal to 50 mm. When 180 s or 50 mm were reached, test was forcedly stopped by turning off oxygen flow. FR-fillers effectiveness could be then outlined comparing LOI values of the unmodified asphalt binder and the ones of FR-asphalt mastics.

Because of the specific sample geometry and test procedure, LOI test cannot be performed to assess asphalt mixture ignitability. So, another testing method must be defined to deepen asphalt mixture fire behaviour. Colwell [5] indicated the Cone Calorimeter test as the most appropriate bench-scale test to study asphalt mixture fire properties. According to the most advanced testing methodology, the standard described by ISO 5660-1:2002 (Reaction to fire tests - Heat release, smoke production and mass loss rate. Cone calorimeter method) was used.

Cone Calorimeter has been widely used to analyse fire properties of several materials and it is extensively described by Babrauskas [16,17] and Schartel [18,19]. This test consists in subjecting samples exposed in horizontal orientation to a specified external heat flux within the range 0-100 kW/m^2. ISO 5660 requires squared samples with sides measuring 100 mm while the maximum allowed thickness is equal to 50 mm. The external irradiance is provided by a cone-shaped radiant electric heater; the specified heat flux is kept at the defined level through three thermocouples symmetrically positioned and in contact with the heater element. Schartel [19] highlights the key-role of the specimen thickness in influencing all the important fire properties which can be defined through this test. Moreover, the thickness to be tested should be defined by the end-use conditions, preferring thicker samples to study material properties. So, keeping in mind that the main objective of the present research is the assessment of asphalt pavements fire properties, the maximum allowed thickness equal to 50 mm was chosen. This choice is also supported by previous literature (Babrauskas [16] and Drysdale [20]).

Before testing, samples were conditioned at 23 ± 2°C, and relative humidity equal to 50 ± 5% in accordance with ISO 554. Then, conditioned samples were wrapped in a single layer of aluminium foil to cover the bottom and sides of the specimen, thus avoiding mass-transfer along all boundaries except for the burning face of the specimen. Finally, the wrapped specimen was adjusted in a specimen holder and covered by a stainless steel retainer frame. The distance between the bottom surface of the electric heater and the top of the specimen was set to 25 ± 1 mm.

A fundamental parameter to be set is the external heat flux applied to the samples. In previous experiences [4, 5], it was observed that asphalt mixture samples did not ignite if exposed to radiant fluxes smaller than 30 kW/m^2. It is also worth noting that cone calorimeter setup aims at reproducing a forced-flaming combustion scenario which is typical of developing fires or of well-developed fires in a post-flashover scenario (heat fluxes higher than 50 kW/m^2). Moreover, the external irradiance should be defined considering what happens during a vehicle fire in tunnel where gas temperature over 1000°C can be reached. These values can be extensively found in full-scale tests or CFD-modelling literature [7, 21, 22]. Thus, if ignition in post-flashover fires is the condition to be simulated, external heat fluxes over 75 kW/m^2 should be considered, and preferably closer to 100 kW/m^2 which is the maximum attainable flux by the standard Cone Calorimeter. Moreover, higher heat fluxes allow to achieve better reproducibility, more clearly defined ignition, and more significant differences between materials in the heat release rates measurements [19]. Nevertheless, when cone calorimeter had been applied to polymeric materials to optimize fire retardancy in terms of ignition and flammability, such higher heat fluxes were found to be potentially misleading [18]. Based on all these preliminary findings, an external heat flux of 70 kW/m^2 was applied.

Once all the samples had been burnt, they were weighted to highlight the mass loss during combustion. Subsequently, the top surface of each specimen was mechanically brushed to analyse how deep the flames spread into the samples.

Finally, the brushed specimens were subjected to diametrical compression following the same test procedure as for the Indirect Tensile Strength Test (IDT). The significant irregularity of the brushed samples did not allow to identify univocally the thickness, so the peak load was used here as indirect indicator of degradation evolution in the residual asphalt.

Results and Discussion

Asphalt Mastics

The LOI results obtained for binary blends are shown in Fig. 1, where the LOI is plotted versus the FR-filler content. The A-series is referred to asphalt mastics containing increasing content of ATH. The same binary composition characterizes M-series, where the FR-filler is MH. The markers representing asphalt mastics with 0% FR-filler correspond to the base asphalt binder B and indeed overlap (Fig. 1).

The first general observation is that all asphalt mastics show an improvement in terms of ignitability compared to base asphalt binder, being the LOI increase almost proportional to the FR-filler content. This outcome should be ascribed to both the endothermic decomposition of the filler and to the fact that the total amount of burning matter within the specimen reduces according to the increasing filler content (the quantity of fuel available for sustained burning reduces as the filler content grows). Moreover, the effectiveness of the two fillers becomes remarkable only with high percentages of loading (> 40%), which is in agreement with well-established results for polymeric materials containing the same FR [23].

The second important point is that the FR effect observed in mastics A is dramatically more incisive than that relative to mastics M. These results can be explained keeping in mind how FR-fillers work. As it is well-known, ATH and MH decompose with an

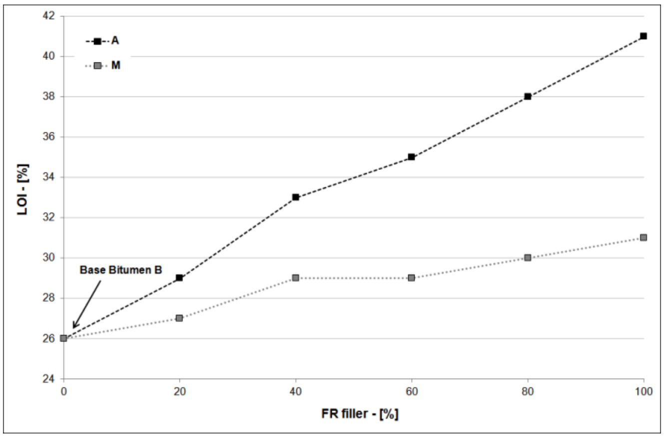

Fig. 1. LOI Values of Asphalt Mastics – Binary Blends.

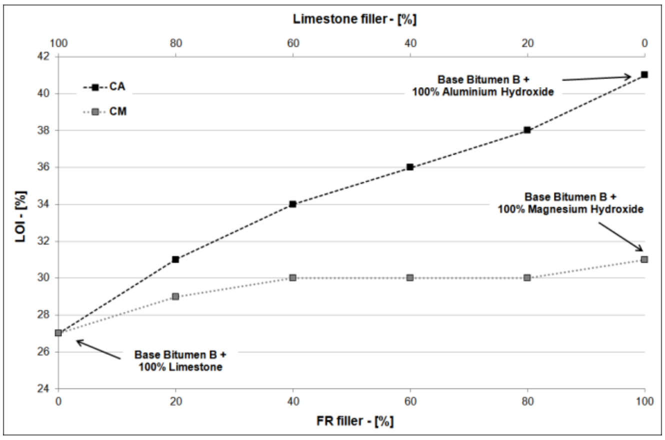

Fig. 2. LOI Values of Asphalt Mastics – Ternary Blends.

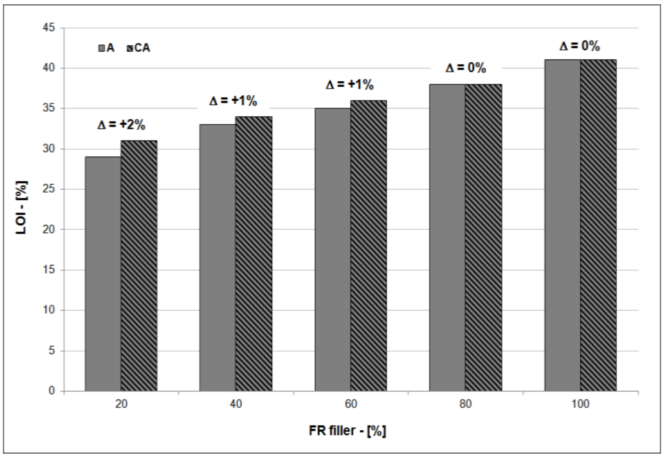

Fig. 3. Effect of Limestone Filler in Increasing LOI of Ternary Blends.

endothermic reaction forming aluminium or magnesium oxide and water [13, 15]. This endothermic reaction leads to a considerable heat absorption which cools the asphalt matrix, thus slowing down its pyrolysis. In addition, the released water vapour plays another considerable part in diluting flammable volatiles, thus significantly reducing fuel availability. Finally, the aluminium or magnesium oxide promote the creation of a charring layer that reduces the radiation and heat spread into the asphalt mastic. This barrier should also limit the flammable volatiles leaving the asphalt matrix, thus further reducing the fuel concentration. These mechanisms are present for both ATH and MH, but the two fillers have quite different onset decomposition temperatures: ATH starts decomposing around 200°C, which is similar or slightly lower than that of the base asphalt binder [15], while MH does not decompose before 300°C [15]. In other words, ATH exerts its FR effect from the very first stage of asphalt decomposition, while MH degrades too late, when the asphalt decomposition is already in progress.

The addition of limestone to the asphalt mastics introduces further elements of discussion. CA-series and CM-series are ternary blends characterized by total filler ratio equal to 1/1 by weight, where the overall filler consists in a blend of limestone and FR-filler. The results collected on ternary blends are displayed in Fig. 2.

By comparing the first data on the left hand side of Figs. 1 and 2, it can be noticed that limestone has a very limited influence on asphalt binder flammability (the LOI increases from 26% to 27%). Again, this data can be easily related to the nature of the filler, which is mainly composed of calcium carbonate whose onset decomposition temperature is approximately equal to 700°C [15]. Thus, all the above-mentioned mechanisms of flame retardancy are expected to happen when asphalt is almost completely degraded, so that limestone simply works as an inert material, which reduces the total amount of fuel available for combustion.

The same scarce contribution of limestone filler is observed in all the CA and CM sample series. A more clear comparison between A-series and CA-series can be observed in Fig. 3 where the effect of limestone in increasing LOI is displayed.

For the sake of brevity, binary and ternary blends containing MH are not reported since they show almost the same trend. As it can be observed, the difference in LOI is 2% when 20% of FR-filler is considered, then it goes to 1% and finally the effect of limestone completely vanishes at high FR-filler contents (≥ 80%). This is probably due to the fact that the physical effect is strictly related to the inert material's volume fraction, so when this fraction decreases below a critical threshold, it becomes inappreciable.

Apart from the effect of limestone filler, remarkable differences between ternary blends of different composition can be outlined again. The most important one regards the general trends of CA-series and CM-series. Indeed, CM-series shows a slight rise in LOI from CM0 to CM40, then the results seem to flatten out producing a plateau (between 40% and 80%) which ends with a small final increase. On the contrary, CA-series is characterized by a gradual but uniform growth which leads to the highest LOI value equal to 41% (of course, the right hand side of the diagram in Fig. 2 coincide with the respective binary blends on the right hand side of Fig. 1). A total overview of experimental data deduced from LOI test highlights that the best flame retardant performance is univocally ascribable to the asphalt mastic CA100, containing ATH. Therefore, this is the asphalt binder/FR-filler ratio (1:1) selected for asphalt mixtures used in the subsequent phase of the experimental program.

A Brief Introduction to the Cone Calorimeter Test

Cone Calorimeter test covers the ignition phase, followed by flaming combustion. During the test, a number of important fire properties can be defined, thus allowing a comparison between different materials in terms of fire performance. The most important parameters are the Heat Release Rate (HRR), the Total Heat Release (THR), the mass loss, the time to ignition (TTI), the Total Smoke Release (TSR), and the CO and CO_2 emissions. Among these, HRR is broadly considered the most significant factor in the assessment of materials' fire hazard [17]. HRR is evaluated through the oxygen consumption method, introduced by Thornton [24] and Huggett [25], by measuring the flow rate of the exhaust gases through the duct system and the oxygen depletion in this flow. The whole HRR curve represents the evolution of the Heat Release Rate with respect to time and provides the best representation of the fire behaviour controlled by specific properties of the tested materials. However, for practical reasons, it is often condensed by few characteristic values, such as its maximum (Peak of Heat Release Rate, PHRR) and the average evaluated referring to the first 180 seconds after ignition (HRR-180). The latter is considered more reliable than the former to predict the peak real-scale HRR in actual fire scenarios [17]. Another important parameter defined through the Cone Calorimeter test is the THR which is formally the integral of the HRR curve with respect to time, thus determining the heat output up to an assigned point. THR is strictly related to the mass loss which is measured through a weighing device during all the duration of the test. Of course, mass loss is mainly governed by the pyrolysis, which is in turn controlled by the net heat flux applied to the surface, the decomposition temperatures, heat transfer and kinetics. Here the total mass loss is reported, calculated as the difference between the weights of the specimen at the beginning and at the end of the test. From Cone Calorimeter test, the main parameter which gives information about ignition is the TTI which can be defined as the time necessary for the mass loss rate to reach its critical value or, in other words, it is the time necessary for the top surface to reach its ignition temperature. Finally, the products of combustion, such as smoke, CO and CO_2 production can highlight further more important information about the fire risks in confined environments like highway tunnels, even if correlations between data obtained from this bench-scale test and large-scale tests are complex and not yet fully understood [19]. The smoke production is evaluated on the basis of the theory of the attenuation of a beam of light by suspended aerosol particulates, thus it is expressed in m^2. The amount of smoke is measured during all the duration of the test and the Total Smoke Production (TSP) is referred to the entire testing period. The TSR is then calculated as the ratio of the TSP to the exposed surface area; this is the reason why TSR is expressed in terms of $m^2 \cdot m^{-2}$. Finally, CO and CO_2 yields are measured through gas analyser and are evaluated per unit of mass loss ($kg \cdot kg^{-1}$).

A preliminary phase was planned in order to verify the effective applicability of the Cone Calorimeter test to asphaltic materials. First, the influence of the specimen shape was analysed by considering two possible geometries: circular shape (100 mm diameter) or square shape (98 mm side), see Fig. 4. The latter is specifically required by the ISO 5660-1 but the former is doubtless the most common for road engineering, both for laboratory samples and for in-situ core drilling. However, the circular shape specimens have side protected only by the aluminium foil and not by the retainer frame, so possible influence of lateral flame spreading deserves careful analysis.

Fig. 4. Square and Circular Samples for the Cone Calorimeter Test.

Table 3. Fire Response Parameters for Two Different Sample Geometries.

Sample Geometry	TTI [s]	PHRR [$kW \cdot m^{-2}$]	HRR-180 [$kW \cdot m^{-2}$]	THR-600 [$MJ \cdot m^{-2}$]
Circular	90±14	82±11	57±8	23±3
Square	103±4	91±5	64±4	26±2

A standard asphalt mixture with 5.5% bitumen content and no flame retardant additive (W-550C) was used in this preliminary study.

The comparison between the two geometries was assessed on the basis of the main results reported in Table 3.

Circular specimens generally showed a greater standard deviation than the square ones. Moreover, square specimens lead to slightly higher values for each considered parameter. However, the fire response parameters defined using square samples remain always inside the variability range identified by circular specimens, as can be observed in the reported results. Moreover, the main geometrical parameter that influences the cone calorimeter test is the total exposed sample surface [26] and in this case, the two exposed areas are negligibly different (88.4 cm^2 vs. 75.3 cm^2). Of course, the main weak point of the circular geometry remains the poor protection of the specimen side, provided only by the aluminium foil. Furthermore, samples obtained by cutting into two parts a single lab compacted asphalt mixture could be characterized by different bitumen contents, thus negatively affecting the reliability of the assessed fire performance. However, the obtained results didn't show significant differences depending on the position of the sample in the original specimen, thus this aspect can be assumed negligible for this particular case.

Finally, both the visual observation of the combustion process and the results reported in Table 3 allow to consider the circular shape, basic for road pavements, satisfactory enough for the main purpose of the present research, which is the definition of a proper testing method to be applied for the assessment of asphalt mixture fire properties.

Once the sample geometry was chosen, different asphalt mixtures were tested to outline possible relation between their composition and fire properties.

Asphalt Mixtures Fire Properties

Asphalt mixtures were analysed though the Cone Calorimeter test, according to ISO 5660-1:2002 and following the testing method previously explained.

The obtained results are synthetically reported in Table 4 as averages from 6 independent replications for each kind of mixtures.

Table 4. Fire Response Parameters.

Asphalt Mixture	TTI	PHRR	HRR-180	THR-600	CO Yield	CO_2 Yield	TSR
	[s]	$[kW \cdot m^{-2}]$	$[kW \cdot m^{-2}]$	$[MJ \cdot m^{-2}]$	$[kg \cdot kg^{-1}]$	$[kg \cdot kg^{-1}]$	$[m^2 \cdot m^{-2}]$
W-550C	90±14	82±11	57±8	23±3	0.046±0.009	2.108±0.416	326±66
W-575C	70±10	103±11	77±6	30±1	0.033±0.005	2.130±0.155	371±57
W-600C	72±9	124±10	87±8	34±3	0.035±0.006	2.318±0.228	693±55
W-550A	71±6	74±7	61±5	27±3	0.038±0.005	1.548±0.033	133±58

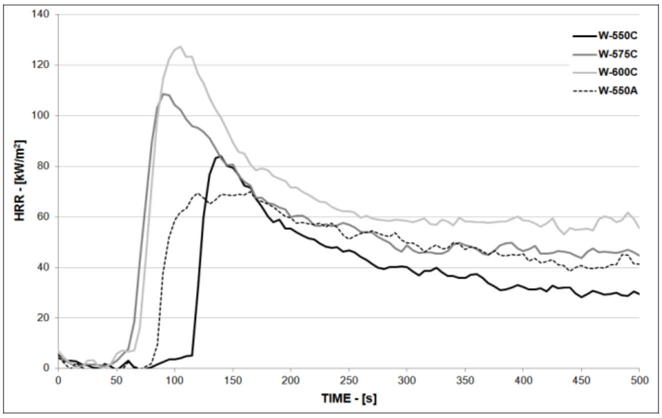

Fig. 5. HRR Curves of Asphalt Mixtures (one Specimen for Each Series).

Fig. 6. Samples of W-550A (Right) and W-550C (Left) Asphalt Mixtures After Cone Calorimeter Test. Top Surface.

The first important result is that all the samples ignite when exposed to the external irradiance of 70 kW/m^2. Of course, a pilot ignition occurs thanks to a spark igniter, since no auto-ignition can be defined through this test. This means that the mass loss rate, due to the pyrolysis of the binder exposed to the radiant heating, produced sufficient flammable volatiles whose effective heat of combustion made the gas mixture capable of being ignited by a spark.

Comparing asphalt mixtures with only limestone filler and no FR-additive (W-550C, W-575C, W-600C), it can be observed that TTI significantly decreases as the asphalt binder content increases. This fact can be explained by the thicker film of asphalt binder covering the aggregates and exposed to the radiant heating. This major exposition leads to achieve the critical concentration of flammable volatiles faster, thus reducing the TTI. Moreover, the greater content of asphalt binder leads to a smaller thermal inertia, which provides a further acceleration in reaching the ignition temperature on the exposed surface of the sample. So, the higher the bitumen content, the shorter the TTI.

Another interesting data is the one found at constant asphalt binder content, but varying the additional filler: among W-550C and W-550A, the latter has the lower TTI. This is somehow surprising and appears in contrast with LOI. However, it is worth noting that the heat applied to the samples is not comparable and the TTI is strictly dependent on the applied heat flux [20]. Therefore, a correlation between LOI and ignitability measurements through Cone Calorimeter should be assessed with extreme carefulness.

In Fig. 5, the whole HRR curves are displayed for four specimens. It can be observed that, qualitatively, the three asphalt mixtures without the FR-additive gave similar curves. There is a rapid increase immediately after ignition, a peak and finally HRR remains almost constant until the end of the test. This specific trend is typical of residue-forming or charring materials [19] where the HRR reaches its peak immediately after ignition and then decreases due to the formation of an efficient charring layer which acts as a barrier.

Another essential parameter to describe the geometrical shape is the PHRR. Among the three asphalt without additives, the PHRR increases with increasing content of asphalt binder. So, PHRR respects the trend above outlined for the TTI. Then there is the asphalt containing the ATH (W-550A) where the FR filler plays an important contribution. Comparing W-550C and W-550A in Fig. 5, the latter has a less steep slope in the rising branch, the peak is smoothed and the curve is almost plateau-like after the peak. These changes in the geometrical form of the HRR curves are also reflected in the numerical value of the PHRR (Table 4). Asphalt mixture W-550A has lower PHRR than W-550C and ATH proved to be effective in reducing the maximum heat release. Of course, this is an important evidence for engineering purposes that also agrees with LOI results.

HRR-180, which is often preferred by fire technologists, confirms these assumptions, so the higher the bitumen content and the higher the HRR-180 (Table 4). Anyway, referring to this second heat rate parameter, ATH seems not to be so effective. In fact, the HRR-180 of W-550A is 61 kW/m^2, thus lower than that of W-575C and W-600C but higher than that of the traditional asphalt mixture with the same bitumen content (W-550C). This occurs because the HRR-180 is calculated as numerical average during the first 180 s after ignition and for all the four asphalt series the peak in HRR occurs before the end of this period. Evidently, within this duration, the particular shape of the HRR curve of W-550A influences the HRR-180 because of its plateau and its less significant decrease after the peak (Fig. 5).

The overall differences emerged in fire behaviour of W-550A can be related to the significantly different charring residues which can be observed after the test (Fig. 6).

Asphalt mixture with limestone as mineral filler shows a dense and homogeneous residue layer, while W-550A samples have a thin

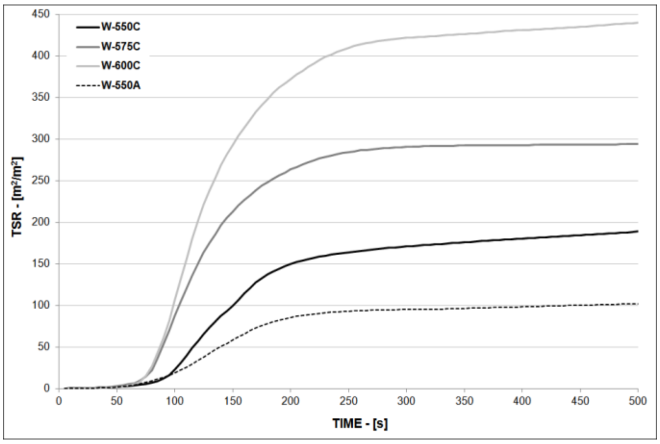

Fig. 7. TSR Curves of Asphalt Mixtures (One Specimen for Each Series)

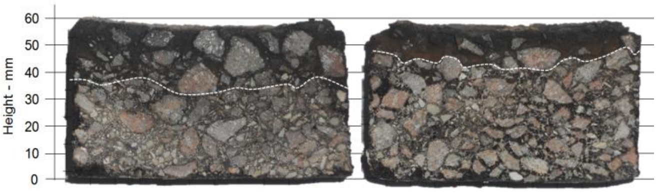

Fig. 8. Samples of W-550A (right) and W-550C (left) Asphalt Mixtures after Cone Calorimeter Test. Cross Section.

Table 5. Mass Losses and Peak Load after Cone Calorimeter Test.

Asphalt Mixture	Mass Loss Post-combustion	Mass Loss Post-brushing	Peak Load
	[%]	[%]	[kN]
W-550C	1.23	2.2	4.3
W-575C	1.76	2.4	4.5
W-600C	1.54	2.7	3.8
W-550A	1.88	6.1	5.8

residue layer with lots of small craters near the edge. The colour of the surface is also completely different: white with some black zones near the edge with limestone and made of brown-black alternating zones with ATH. Therefore, it can be intuitively assumed that limestone filler does not limit the fire reaction of the bitumen but, once the combustion is started, it fosters the formation of a solid and uniform char barrier. Thanks to its chemical composition, this char barrier is more stable versus thermal decomposition and thus more effective in slowing down the heat release rate. This could explain the differences in HRR post-peak trends, also reflected in the HRR-180.

With regard to THR, the tested samples showed different durations of the test, so the comparison is referred to a period of 600 s (THR-600) which was reached by all the specimens. Once again, the higher the bitumen content, the higher the THR-600 (Table 4). Coherently with HRR-180 values, asphalt mixture W-550C shows lower THR-600 than asphalt mixture W-550A. Once again, the obtained results must be analysed keeping in mind the different residue formed during combustion. For this specific Cone Calorimeter set-up, asphalt mixture with limestone proved to be able to produce a more effective protecting residue while the main benefit produced by the use of ATH is the reduction in PHRR.

To conclude the analysis of the thermal parameters, the attention goes to the combustion products, represented by the TSR, CO and CO_2 yields reported in Table 4. Comparing asphalt mixtures with limestone as additional filler, significant differences are noticed only for the TSR values (Fig. 7), while the CO and CO_2 yields are quite similar. Once again, increasing the amount of asphalt binder leads to considerably higher smoke productions.

Comparing asphalt mixtures W-550C and W-550A, we have the most interesting results. Indeed, ATH allows to reduce the CO formation by 18% and the CO_2 yield by 26%. Moreover, the TSR is dramatically decreased by 59%, as it can be better observed by analysing the overall trends displayed in Fig. 7.

Keeping in mind that CO and smoke production are mainly due to an incomplete combustion process, another important consideration regarding the residue can be drawn. Comparing W550-A and W-550C, the latter showed a more effective residue in terms of HRR-180 and THR-600 reduction. At the same time, this leads to greater obstacle for the oxygen and flammable volatiles, thus favouring an incomplete oxidation reaction. So, production of smoke and CO is favoured. Being these two aspects extremely relevant during vehicle fires in tunnels, ATH proved to be an essential component for an effective flame retardant asphalt mixture.

Additional Features

After the Cone Calorimeter test, all samples were cooled down to ambient temperature and cut to analyse their cross-section. This allowed to observe how deep the flames propagate down the specimen, or more precisely, the zone affected by the pyrolysis process with and without flaming. From a simple visual analysis, all samples with limestone showed almost the same depth, equal to 20 ± 5 mm while the W-550A series exhibits an apparent slightly smaller extension equal to 12 ± 5 mm (Fig. 8). Moreover, it is worth noting that the bottom of all the samples seems not to be interested by the combustion process. This fact can be relevant in case of fires in highway tunnel where the rehabilitation of the involved pavement may interest only the most superficial courses.

This difference in flame spreading into the samples indicates a bigger resistance of W-550A with respect to W-550C. However, this point can be somehow misleading as demonstrated when the surfaces exposed to the radiant heat flux and flames were subjected to mechanical brushing (Table 5).

The most remarkable difference resides in the comparison between W-550A and the other three mixtures after brushing: the mass loss is significantly higher in the case of ATH. This is not surprising if we consider that ATH decomposes at temperatures much lower than limestone [15]. Therefore, ATH limits the fire spread thanks to its decomposition, which happens also below the layer directly interested by flame propagation or pyrolysis. This process generates an interlayer region where the samples containing ATH appear macroscopically intact, but are actually degraded.

Further description of this effect of fire exposure on asphalt mixtures can be derived from the analyses of the data obtained in a last test, where the brushed samples were subjected to a diametrical compression following the testing procedure ASTM D6931 – 12 (Table 5). The reported parameter is the Peak Load, since Indirect

Tensile Strength could not be properly evaluated because of the extreme irregularity of the brushed samples.

In our purpose, the residual mechanical strength should be viewed mainly as an indirect indicator of combustion penetration. Hence, even if W-550A preserves a major integrity of the cross section (Fig. 8), when compared with the samples of the C-series it only shows a slightly higher mechanical performance after combustion.

Conclusions

Limiting Oxygen Index test and Cone Calorimeter test were performed to analyse fire properties of asphalt mastics and mixtures characterized by different content of ATH and MH as fire retardants. Thanks to their endothermic decompositions, both fillers showed to contribute in enhancing asphalt binders fire behaviour by limiting its ignitability, being ATH the one that leads to the most satisfactory results. Limestone filler was then added to asphalt mastics characterized by 1/1 asphalt binder/total filler composition as a complementary component, thereby identifying a ternary blend. The influence of limestone filler on asphalt ignitability was found to be not determinant, as testified by the scarce increase recorded in LOI.

Cone Calorimeter tests were subsequently performed, providing several important indicators of asphalt mixtures' fire behaviour. The first effort was done in order to define the most proper testing conditions. It was found that the sample geometry has no particular impact on the fire response parameters, so that circular samples of 100 mm diameter, traditionally used for road engineering, can be effectively used. With regard to the asphalt mixture composition, two main elements were found to be important in controlling the fire behaviour. The first one was the asphalt binder content: the higher the binder content, the lower is the time to ignition and the higher is the heat release rate. A more articulated scenario emerged from the analysis of the effect of the FR-filler addition. Asphalt mixtures containing ATH showed fire reaction parameters characterized by a very specific behaviour. The time to ignition was lower than that of the asphalt mixtures without FR-additive, thus indicating a higher predisposition to ignite. However, the presence of the FR-filler effectively reduces both the peak of heat release rate and the smoke and CO production.

In summary, LOI test allowed to identify the most effective FR-filler in improving asphalt mastics ignitability while the Cone Calorimeter test provided a comprehensive description of the combustion process characterizing asphalt mixtures in a small-scale context. Results obtained by the two tests are difficult to compare because they are referred to completely different fire-scenario. Nevertheless, experimental data provide some significant preliminary indications for the formulation of Flame-Retardant asphalt mixtures specifically developed to minimize the fire-risks in highway tunnels.

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