Comparing Field and Laboratory Aging of Bitumens on a Kinetic Basis

A. F. Verhasselt and F. S. Choquet

Studying accelerated bitumen aging in the laboratory on a kinetic basis leads to evaluating the activation energy of oxidation reactions from developments in certain characteristics such as asphaltene content, penetration, and ring-and-ball softening point. In Belgium, temperatures 5 mm deep in bituminous road pavements have been measured and recorded for several years, thus making it possible to draw a frequency distribution curve of those temperatures. From this distribution and the activation energy evaluated in the laboratory, it has been established that the annual value of kinetic mean temperature lies around 19.5°C for field aging. Using measurements of bitumen characteristics published in the literature, and referring to the original condition as well as the conditions at the time of opening to traffic and at various stages of aging, the reaction constants can be estimated for the road pavements under consideration. This approach enables the estimated constants to be related to the specific climatic environments of the various countries or regions concerned.

From the point of view of chemical constitution and composition, the aging of bitumens results mainly from oxidation reactions affecting certain functionalities in the more or less complex fabrics of molecules that constitute their structure.

During its life, any bitumen or other bituminous binder is subject to two types of aging:

- 1. A rapid aging in manufacture and laying (coating, mixing, compaction, cooling). The effects of this aging in construction are well simulated by standard aging tests such as a thin film oven test (TFOT) and a rolling thin film oven test (RTFOT) (ASTM D2872-88) or by the DIN 52016 test.
- 2. A slow aging in the climatic environment in service (field aging), which is composed of all the changes occurring in the bitumen during its life on site.

The laws governing the aging process still remain to be discovered. Most of the usual aging tests do not make it possible to predict field aging because they are conducted at too high a temperature and on too small a quantity of bitumen, which reduces the possibilities for technological and physicochemical measurements on the aged sample. To accurately monitor the progress of aging with exposure time, the relevant measurements must be made on a single sample of sufficient mass (e.g., 500 to 600 g).

A laboratory aging device has been designed and tried at the Belgian Road Research Centre (BRRC). With this device, it has been possible to develop an overall kinetic approach to aging that agrees relatively well with findings and observations with respect to actual field aging.

BITUMEN AGING IN SERVICE

The progress of in-service aging depends on a number of factors, including

- 1. Susceptibility of the binder to aging (i.e., the ease or difficulty with which it can be oxidized). An oxidized bitumen will obviously be less susceptible to aging. It is being tried to assess this property from accelerated tests conducted mainly at temperatures above 100°C, the extrapolation of which to ambient temperatures is unreliable.
- 2. Porosity of the bituminous pavement, as characterized by the percentage of voids. A dense pavement ages almost exclusively at the surface.
- 3. Temperature: oxidation reactions are stimulated by an increase in exposure temperature.
- 4. Sun radiation: the ultraviolet component of it affects only a very thin layer of the binder at the surface of the pavement, whereas the infrared (IR) part increases the mean temperature in the pavement as they are absorbed.
- 5. The nature of the aggregates—a difficult factor to demonstrate.
- 6. Other factors such as moisture, precipitation, aggregate porosity (preferential adsorption of certain bitumen components), and deicing salts.

When considering these factors, it will be obvious that accurate simulation of field aging in the laboratory is a utopian objective. The situation can, however, be simplified by starting from the rather realistic assumption that, all other factors remaining equal, the aging process observed in the field will depend mainly on the binder's susceptibility to oxidation. Accelerated aging tests in the laboratory should, therefore, aim at evaluating the reaction constants in the asphalt concrete at service temperature, using a kinetic approach to binder aging (1).

KINETIC DEVELOPMENT

Some Concepts in Chemical Reaction Kinetics

Taking classical kinetic theory and the concept of extent of reaction, α , as a basis, and using the one-dimensional diffusion

model (2) for solid-state reactions (exponent = 2 in following equation), it is possible to clarify the process of bitumen aging in time. The mathematics involved are explained in Verhasselt (1), Brown and Galwey (2), Verhasselt and Choquet (3), and Choquet and Verhasselt (4).

By randomly selecting a reaction indicator S, the general equation representing the development of aging can be written as follows:

$$a^2 = \left[\frac{S_t - S_o}{S_f - S_o} \right]^2 = \left(\frac{DS_t}{DS_\infty} \right)^2 = kt \tag{1}$$

where

 α = extent of reaction,

 S_o = value of the indicator being considered at time t = 0,

 S_t = value of the indicator being considered at time t,

 S_f = value of the indicator being considered at time $t = t_{t_0}$, and

k = reaction or rate constant (at the test temperature).

As term DS_{∞} is hardly accessible by experiment and represents a constant for the bitumen being considered, this equation can be transformed into two others that are markedly more practical:

$$(S_t - S_o)^2 = DS_t^2$$

$$= Kt$$
(2)

By transformation this equation becomes

$$S_t = S_o + K^{1/2} \cdot t^{1/2} \tag{3}$$

Using these two equations, it is possible to determine the overall reaction constant, K, from experimental data as far as the tests have been conducted at an exposure temperature no higher than 100°C on an original bitumen (i.e., still virtually unaffected by oxidation) (1).

The following indicators have proved to be suitable for the kinetic study:

- 1. Asphaltenes' content (insoluble in hot n-heptane), A7;
- 2. Ring-and-ball (R&B) softening temperature; and
- 3. The reciprocal of penetration, 1/penetration.

The logarithms of viscosity at 60°C and 135°C could also be suitable as indicators in the suggested kinetic approach.

Generalization of This Theoretical Approach

When a bitumen in the laboratory has already been subject to some aging before the beginning of the test, this aging corresponds with a time of reaction, t_o , at the test temperature. Likewise, in a pavement that starts its service life, the bitumen has already undergone an aging process, for example, in construction. Equation 3 can, consequently, be rewritten as follows:

$$(S_t - S_o)^2 = DS_t^2 = Kt_a = K(t_o + t) = Kt_o + Kt$$
 (4)

where t_a is the actual reaction time defined as the sum of the exposure time chosen for the test or the field time of service in the road and the fictitious time, t_a .

Where S_o is known, Equation 4 can be applied directly to the experimental results and the value of t_o can be estimated from the ordinate at the origin (= Kt_o). If, in addition, the initial value of S (i.e., S_i) is known, a second (generally less reliable) estimation of t_o will be possible:

$$(S_i - S_o)^{2^i} = Kt_o \tag{5}$$

By transformation, Equation 4 becomes

$$S_t = S_o + K^{1/2} (t_o + t)^{1/2}$$
 (6)

in which the estimated value of t_o is entered for the regression calculation.

It is also possible, by successive approximation, to find the value of t_o that leads to the best degree of correlation for Equation 6 applied to the experimental results.

In practice, however, the values of S_o and t_o are generally unknown. In such cases, processing data by means of Equation 6 often results in unrealistic estimates of S_o and/or t_o , and hence of K, because of experimental errors. This difficulty can be met to some degree by estimating S_o from information and specifications contained in standard tender specifications.

KINETIC MEAN TEMPERATURE ON SITE

One of the important factors in the kinetic approach to aging is temperature (1). Accelerated laboratory tests make it possible to determine the overall reaction constant, K, for various indicators at several exposure temperatures and, hence, to evaluate the activation energy of the aging reactions (1,3). To transfer this approach to in-service road conditions, use must be made of the concept of kinetic mean temperature.

On site, a road pavement does not remain at constant temperature throughout the year. It is subject to variations in temperature according to the surrounding climatic conditions, the most important of which are air temperature and sun radiation. (C. De Backer, unpublished data, BRRC) and De Backer (5). As is the case for all other exposed layers on earth, temperature and its variations depend on the depth of measurement and the nature of the material (C. De Backer, unpublished data, BRRC). In Belgium, the temperature of an asphalt pavement ranges from -10 to $+50^{\circ}$ C and from -5 to $+40^{\circ}$ C at the surface (-0.5 cm) and at a depth of 4-5 cm, respectively (5).

Equal times of exposure to various temperatures will obviously contribute in different ways to the aging of the binder. For example, 24 hr at 0°C will have a markedly smaller aging effect than 24 hr at 40°C (smaller by a factor of about 16, as the rate of aging almost doubles with a 10°C increase in temperature). In fact, the exact value of this factor depends on the activation energy of the aging reactions, because it is this energy that determines the value of the (overall) reaction

constant and hence the reaction rate at the temperature under consideration.

Because of the variations in field temperature, the total inservice aging of a binder will be the sum of a series of partial aging processes, the contributions of which depend on the time of exposure to a given temperature. To be fully correct, the assessment of field aging must therefore by made by integrating these contributions on the basis of the histogram of the distribution of temperatures over the period being examined.

Another approach that is more practical and more centered on predicting binder aging in service consists of estimating the kinetic mean temperature of the pavement annually under the local climatic conditions of the region or country where the road is situated. This requires the availability of statistical data on temperatures at various depths in, but mainly at the surface of, asphalt pavements.

Some ground in this field has already been covered in Belgium (5,6):

- 1. Data on temperature at different depths in various asphalt pavements are available in addition to a set of meteorological data relating to air temperature, minimum and maximum temperature, amplitude of daily variation, sun radiation, and so on. They are the result of several years of measurements of BRRC and systematic measurements by the Royal Belgian Meteorological Institute (7);
- 2. From these measured data, a mean curve of temperature distribution (per 5°C interval) at different depths in asphalt concrete has been established, especially for temperatures at the surface (-0.5 cm), which are the most relevant to road binder aging (Figure 1, Curve 1);
- 3. Using the data on mean air temperature, the amplitude of variation in air temperature, and total sun radiation on a horizontal surface, it has been possible to reproduce with a good approximation the mean curve of temperature distribution at the surface of asphalt concrete (5). This predictive method can be transferred to other countries and other climates (6).

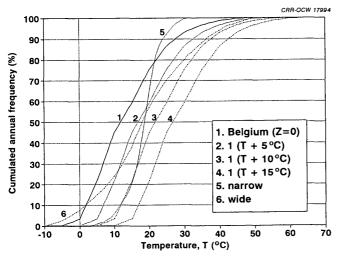


FIGURE 1 Examples of annual distribution curves of temperature (1. relates to the surface of asphalt pavements in the Brussels region).

To estimate the annual value of kinetic mean temperature at the surface of asphalt pavements in Belgium (more precisely in the region of Brussels), the following procedure was used:

- 1. Starting from the mean distribution curve already described (Figure 1, Curve 1), the fraction of time per year, f_i , during which the binder is exposed to temperatures between T_{i-1} and T_i is determined. The temperature interval used being 1°C, a linear interpolation is made for each 5°C interval on the curve between the frequency values corresponding to the limits of the 5°C temperature interval being considered (Figure 1):
 - 2. The following sum is calculated:

$$SCR = \sum f_i \exp[-E/R(T_i - 0.5)]$$

where

E is the activation energy of the reaction,

R is the perfect gas constant, and

 $(T_i - 0.5)$ the absolute temperature corresponding to the middle of the temperature interval under consideration (in ${}^{\circ}$ K).

Given the activation energies found in the accelerated aging tests at temperatures below 100° C, E/R is taken to be 9,000 (1,3);

3. The value of temperature T_k , which leads to the same SCR value, represents the annual kinetic mean temperature of the country or region concerned:

$$T_k(^{\circ}K) = -E/R\ln(SCR)$$

or, in °C:

$$T_k(^{\circ}C) = T_k(^{\circ}K) - 273.2$$

By way of example, the arithmetic mean temperature and the annual value of kinetic mean temperature for the temperature distributions represented in Figure 1, assuming an E/R of 9,000, are respectively:

```
13.2 and 19.55°C (Curve 1),

18.2 and 24.35°C (Curve 2),

23.2 and 29.1°C (Curve 3),

28.2 and 33.95°C (Curve 4),

18.2 and 19.4°C (Curve 5, narrow distribution), and

18.2 and 26.25°C (Curve 6, wide distribution).
```

The kinetic mean temperature 0.5 cm deep in bituminous pavements in Belgium is thus 19.5°C.

The divergence between arithmetic mean temperature and kinetic mean temperature increases with the width of the distribution curve (curves 5, 3 and 6) and remains more or less constant when the curve has been subjected to a simple translation (curves 1 to 4).

The mean temperature at the surface (13.2°C) is higher than the annual mean air temperature in Belgium, which is about 10°C. This difference is due mainly to the absorption of sun radiation by the pavement.

LABORATORY TESTS: EXPERIMENTAL APPROACH

Accelerated Aging Test Device

The description and performance potential of this device are given in Verhasselt and Verhasselt and Choquet (1,3). It will be noted that a thermocouple fixed inside the cylinder measures and controls the test temperature with an accuracy of ± 0.5 °C.

The load of binder per aging test is 500 g and samples of 20 to 25 g are taken at each exposure time to measure technological characteristics and determine generic composition. It is thus possible to monitor binder characteristics with age and to develop a kinetic approach to the phenomenon, as set out earlier in this paper and others (1,3).

Bitumens Investigated and Interpretation

Three straight-run bitumens of penetration grade 80/100 were aged in the laboratory at temperatures ranging from 70 to 100°C (1). Their initial physicochemical characteristics are given in Table 1. From the developments in the values of

these characteristics recorded during aging, highly significant relations have been established, more particularly among

R&B and A7, 1/penetration and A7, 1/penetration and R&B, and IR absorbance at 1700 cm⁻¹ and A7 or R&B.

Examples are presented and discussed by Verhasselt and Choquet (3).

Reviewed in Table 2 for the three indicators considered are the S_o values adopted and the K_T constants calculated as follows from the results obtained under normal test conditions (1 rpm under a flow of oxygen) (1):

- 1. Equations 2 and 3 are applied while determining the exponent that agrees best with the experimental results. Generally, exponent 2 is most suitable;
- 2. Using Equation 3, S_o is evaluated for the different test temperatures. The mean value of S_o is then calculated and this will be used in the subsequent calculations if it is compatible with the S_o of the bitumen before aging. If such is not the case, the S_o of the unaged bitumen is adopted;

TABLE 1 Main characteristics of the investigated bitumens

| | | Bitumen | | |
|---|---------|---------|-------|-------|
| Technological and physicochemical characteristics | | 472 | 481 | 577 |
| Pen 25°C, 100 g, 5sec | (mm/10) | 92 | 89 | 87 |
| R&B Temperature | (°C) | 47.0 | 46.0 | 46.5 |
| Viscosity at 135°C | (Pa.s) | 0.308 | 0.336 | - |
| Density | (g/cm³) | 1.012 | 1.019 | 1.020 |
| Neutralization Value (%) | | | | |
| (Method I.P. 213/82-BS) | | 0.3 | 3.3 | - |
| | | Bitumen | | |
| Generic composition (% by mass) | | 472 | 481 | 577 |
| Asphaltenes content (A7) | | 10.7 | 9.4 | 9.2 |
| Saturates | 20.8 | 20.2 | 14.4 | |
| Cyclics (nonpolar aromatics) | | 43.7 | 44.5 | 43.3 |
| Resins (polar aromatics) | R1 | - | 15.4 | 21.8 |
| • | R2 | - | 10.3 | 11.4 |
| | R1 + R2 | 24.9 | 25.7 | 33.2 |

^{-:} missing data

TABLE 2 Initial value S_o and mean overall reaction constant K_T according to equations 2 and 3

| | A7 (%².h ⁻¹) | | | R&B (°C².h-¹) | | | 1/pen [10 ⁻⁶ (10/mm) ² .h ⁻¹] | | |
|------------------|-----------------------------|--------|--------|------------------|-------|-------|--|-------|-------|
| T°C 4 | 472 | 481 | 577 | 472 | 481 | 577 | 472 | 481 | 577 |
| 70 | 0.0556 | 0.0408 | 0.0524 | 0.380 | 0.327 | 0.291 | 0.823 | 0.894 | 0.681 |
| 80 | 0.105 | 0.1095 | - | 0.847 | 0.673 | - | 1.73 | 1.78 | |
| 82.5 | - | - | 0.112 | - | - | 0.634 | - | - | 1.82 |
| 90 | 0.196 | - | - | 1.59 | - | - | 4.34 | - | - |
| 95 | - | - | 0.346 | - | _ | 1.425 | - | - | 5.17 |
| 100 | 0.357 | 0.473 | - | 2.35 | 3.22 | - | 6.38 | 10.1 | - |
| S _o : | 10.4 | 9.4 | 9.1 | 46.8 | 46 | 46.8 | 92 | 89 | 90 |

^{- :} not investigated

- 3. The overall reaction constant, K, is calculated using Equation 2 on the one hand and Equation 3 on the other. The mean of the two constants thus calculated is taken as the K_T constant for the exposure temperature and indicator being considered;
- 4. The K_T constants obtained are used as real reaction constants k_T and entered in an Arrhenius equation in order to evaluate the activation energy of the reaction.

To pass from the laboratory to the field, where there is no rotation of the bitumen nor flow of oxygen, the effects of the experimental parameters have been determined when changing over from oxygen to air and when extrapolating the rotation rate to the zero value (1):

- 1. On average, the "gas" correction factor, G (i.e., the ratio between the reaction constants, K_{air}/K_{O2}) is 0.570 (with individual values ranging from 0.484, to 0.617);
- 2. Accelerating the rotation of the container from 1 to 5 or to 10 rpm causes the reaction constant to increase by an average factor of 1.57 (1.44 to 1.72 individually) or 2.18 (1.63 to 2.66 individually), respectively.

From this it can be concluded that the total correction factor for tests conducted under the "standard" conditions (1 rpm and oxygen flow) is 0.502.

LABORATORY/FIELD COMPARISON

Extrapolation to Field Conditions

In Table 3, among other things, the values of the overall reaction constants extrapolated to the field conditions pre-

vailing in the region of Brussels are given: surface of the pavement, static binder, and annual value of kinetic mean temperature 19.5°C. For the three bitumens considered, the differences in overall reaction constants may reach almost 40 percent.

Measurements of air temperature and pavement surface temperature (i.e., at a depth of 0.5 cm) carried out in the region of Brussels over a long period of time have yielded mean values of 10°C and 13.2°C, respectively. From these statistics, a kinetic mean temperature of 19.5°C can be calculated, as previously explained. A 10°C translation of Curve 1 in Figure 1 results in Curve 3, which would correspond more or less with a mean air temperature of about 20°C and a kinetic mean temperature of 29.1°C.

It is shown in Table 3 how the values of the overall reaction constants for the three selected indicators are affected by an increase in kinetic mean temperature from 19.5°C to 29.1°C. The K_T values are almost tripled. The value of 29.1°C for kinetic mean temperature would roughly correspond to the situation in states and provinces such as Ontario, Pennsylvania, and Texas.

In Table 4, mean air temperatures are associated with kinetic mean temperatures. The latter are presumed values as they have been calculated from data on mean air temperature in the state or region being considered and the existing relation between this temperature and the period of sunshine (generally these two parameters increase concurrently, thus causing the temperature in the road to rise).

In Figure 2 are simulated the developments in R&B temperature that would be observed on site with two Belgian bitumens (472 and 577) if they were exposed to exactly the same conditions of aging (also in construction). The difference in development is clearly visible. For example, an R&B temperature of 65°C would be reached in 10 or 26 years for

| TABLE 3 Overall reaction constant on site at two kinetic mean temperatures | ; |
|--|----|
| for three Belgian penetration 80/100 bitumens (laboratory-to-field extrapolation | n) |

| | K on site | | |
|--|-------------------------------|--------------------------------------|--|
| | $T_k = 19.5$ °C (Brussels) | $T_k = 29.1^{\circ}C^*$ | |
| A7 (%2.h-1) | 1.7 to 2.7 x 10 ⁻⁴ | 4.9 to 7.1 x 10 ⁻⁴ | |
| $R\&B (^{\circ}C^{2}.h^{-1})$ | 1.2 to 2.1 x 10 ⁻³ | $3.3 \text{ to } 5.4 \times 10^{-3}$ | |
| 1/pen [(10/mm) ² .h ⁻¹] | 3.2 to 4.7 x 10 ⁻⁹ | 9 to 12 x 10 ⁻⁹ | |

^{*} This would roughly correspond with the situation in Ontario, Pennsylvania and Texas.

TABLE 4 Annual values of mean air temperature and kinetic mean temperature

| State or region | Annual mean air temperature (°C) | Annual kinetic mean temperature (°C) | | |
|-----------------|----------------------------------|--------------------------------------|--|--|
| Brussels | 10 | 19.5 | | |
| Alberta | 0 | (≤ 10) | | |
| Saskatchewan | 3 | (≤ 13) | | |
| Iowa | 10.1 - 10.4 | (≈ 20) | | |
| Delaware | 13 | (≥ 22) | | |
| Ontario | 18 | (> 27) | | |
| Pennsylvania | 18 | (> 27) | | |
| Texas | (13) 17 - 23 | (> 29) | | |
| Arizona | 20.5 - 21.4 | (> 30) | | |

^{* () =} presumed value (see text).

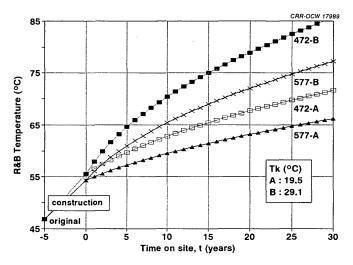


FIGURE 2 Comparison of simulated field aging of bitumens 472 and 577 for a kinetic mean temperature of 19.5°C (Brussels) and 29.1°C (probably applying to Ontario, Pennsylvania, and Texas).

Bitumen 577 and in 5 or 14 years for Bitumen 472, according to whether the kinetic mean temperature is 19.5°C or 29.1°C. This means that with the latter temperature the rate of aging is 2.6 to 2.8 times higher.

By assuming a linear relationship between the annual values of kinetic mean temperature and mean air temperature, it is possible to evaluate annual kinetic mean temperature in different states and regions. The results are discussed further in this paper. The > or < signs in Table 4 indicate the trend to be expected on account of the greater or smaller amount of sun radiation in those regions. The case of 29.1°C (B), considered in Figure 3, could represent the situation in states or provinces such as Ontario, Pennsylvania, and Texas.

The long-term in-service behavior of different bitumens thus seems to be predictable, at least in a relative way, from kinetic data yielded by accelerated tests in the laboratory. The important parameters are the overall reaction constant

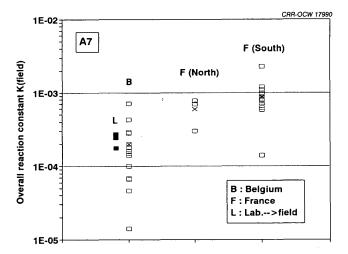


FIGURE 3 Laboratory/field comparison for the overall reaction constant relating to development of asphaltenes content $(x = \text{mean } K_T \text{ value})$.

at various temperatures (between 70 and approximately 95°C) and the activation energy of the reactions.

Comparison of Different Results Reported in the Literature

Two different ways to proceed may be adopted:

- 1. Confront the overall reaction constants estimated for the binder on site with the laboratory test results;
- 2. With due consideration of age in service, compare the variations in characteristics with those that can be estimated from the laboratory test results.

Ideally, the following data should be known on an in-service aged binder:

- S_t : the value at time t of characteristic S of the binder recovered from the top slice (approximately 0.5 cm) of the pavement. The more there are different t values, the better;
- S_i : the value of S at the beginning of in-service aging. This value is know if samples were taken during or the day after laying. If not, the value of S in the bulk of core samples (excluding the top slice) is a very good approximation of S_i in the case of a well-compacted dense mix (less than about 3 percent of voids); and
- S_o : the S value of the original bitumen. If it is unknown, an estimation of R&B temperature and penetration can be made from the tender specifications for the binder.

Comparison of Different Overall Reaction Constants K_T

From data found in the literature it is possible to evaluate the overall field reaction constant as previously described for the different indicators, and to compare it with laboratory test results. Examples of this are given in Figures 3, 4, and 5 for A7 content, R&B temperature, and 1/penetration, respec-

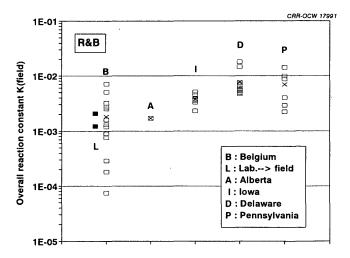


FIGURE 4 Laboratory-field comparison for the overall reaction constant relating to development of R&B softening temperatures $(x = \text{mean } K_T \text{ value})$.

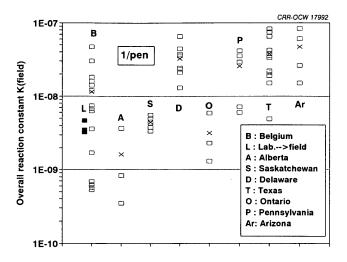


FIGURE 5 Laboratory-field comparison for the overall reaction constant relating to development of penetration $(x = \text{mean } K_T \text{ value})$.

tively. The processing of results, based on data, is presented for the different states, provinces, and regions as follows (8–11):

| State, Province, or Region | A7 (%). | R&B (°C) | Penetration (1/10 mm) |
|---------------------------------|--------------|--------------------------------|-----------------------|
| Alberta (8) Arizona (8) | | A.52 | A.52 B.13 |
| Belgium (10,11) Delaware (8) | (10,11) — | (10,11) A.36, 38 | (10,11) A36,38 |
| France N (9) France S (8) | (9) A.14 | _ | |
| Iowa (8) | — · | A.34 | |
| Ontario (8) Pennsylvania (8) | _ | \overline{A} .4 a ,4 b , | A.48 A.4a, 4b, 8 |
| Saskatchewan (8) | _ | 8 | A.26 |
| Texas (8) | | | B.27 |

From these data it has been possible to calculate the overall reaction constant, K_T . Figure 3 represents the development of this constant for Belgium and the north and south of France, using A7 content as an indicator. The values of the overall reaction constant, K_T , for Belgium and various American and

Canadian States, respectively, based on R&B and the reciprocal of penetration, are given in Figures 4 and 5.

It can be seen in these three figures that the K_T values are different from one state, province, or region to another and that the shift to higher K_T values follows the trend of mean air temperature and sunshine in the different states, provinces, or regions, as mentioned in Table 4.

The calculated overall reaction constants, K_T is reviewed in Table 5 as follows:

- 1. K_T field: these are constants calculated from indicator values found in the literature for the bitumens used.
- 2. K_T extrapolated: from the K_T values calculated for three laboratory-aged Belgian 80/100 grade bitumens extrapolated K_T values have been calculated for the climatic conditions in the states, provinces, or regions considered, using the relevant presumed kinetic mean temperatures mentioned in Table 4.

Figure 6 represents mean overall reaction constants against the mean air temperatures in the states, provinces, or regions concerned, with 1/pen as an indicator.

Comments

The overall reaction constants K_T given in Table 5 and plotted on Figure 6 may be noted as follows:

- 1. Except for the state of Ontario, the values of the constants calculated for field aging and by extrapolation are more or less in agreement for the three indicators when these are available:
- 2. The value of K_T increases with mean air temperature and with kinetic temperature;
- 3. The K_T values for Ontario and Delaware apart, there is a good correlation between the logarithm of K_T (mean and field) and mean air temperature. The examples of Ontario (18°C) and Delaware (13°C) show that it is indeed the temperature of the pavement that should be considered. The results for Ontario actually concern the northern part (7);
- 4. Great differences can nevertheless be observed in the K_T values of a given state, province, or region. They suggest that the bitumen can play a major role by its properties and

TABLE 5 Overall field reaction constants (different results from the literature)

| | | A7 (10 ⁻⁴ .% ² .h ⁻¹) | | R&B (10 ⁻³ .°C ² .h ⁻¹) | | 1/pen [10 ⁻⁹ .(10/mm) ² .h ⁻¹] | |
|-----------------|---------------|--|----------|--|----------|---|----------|
| State or region | T air (°C) | extrapol. | field | extrapol. | field | extrapol. | field |
| Alberta | 0 | | - | ≤0.4-0.7 | 1.7 | ≤1.1-1.7 | 0.35-3.7 |
| Saskatchewan | 3 . | - | • | - | - | ≤1.5-2.3 | 3.4-5.6 |
| Belgium | 10 | 1.7-2.7 | 0.14-7.1 | 1.2-2.1 | 0.07-7.1 | 3.2-4.7 | 0.53-30 |
| Iowa | 10.3 | - | - | 1.3-2.2 | 2.3-5.1 | - | - |
| France (North) | (12) | 2.2-3.2 | 3-8 | _ | - | | - |
| Delaware | 13 | | _ | ≥1.6-2.7 | 4.7-18 | ≥4.3-6.1 | 13-65 |
| France (South) | (15) | 3.4-5.4 | 1.4-23 | - | - | - | - |
| Ontario | 18 | - | _ | - | - | >7.5-10 | 1.3-5.9 |
| Pennsylvania | 18 | - | _ | >2.7-4.4 | 2.2-14 | >7.5-10 | 6-41 |
| Texas | 17-23 | | - | - | - | >9.2-12 | 4.9-83 |
| Arizona | 21 | - | - | - | - | >10-14 | 15-84 |

^{- :} no results available

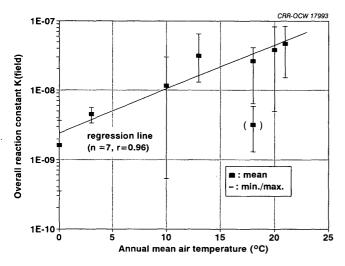


FIGURE 6 Mean overall reaction constant relating to the development of penetration versus annual mean air temperature of the considered region.

characteristics and that it may behave differently, perhaps also as a result of widely varying susceptibility of aging.

Comparison of Simulated Indicator Development with Field Results

The second way to proceed is to monitor the development of indicators in service and to compare this with the field development calculated from laboratory-aged bitumens. In Figure 7 the increase of R&B temperature is plotted against the age of the asphalt pavement. The field development calculated for Bitumens 472 and 577 in the region of Brussels is represented by two dotted lines.

In both cases, a good agreement is found between aging observed on site and aging estimated from the accelerated laboratory tests on three 80/100-grade bitumens. As for the

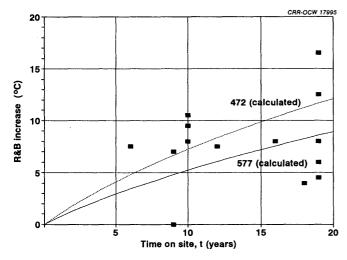


FIGURE 7 Increase in R&B temperature with the years of service of the pavement (Belgium). Comparison with calculated development for Bitumens 472 and 577.

overall reaction constants (Figure 3), their values increase in ascending order in Belgium, the north of France and south of France. Such is also the case of mean air temperature and, consequently, kinetic mean temperature.

CONCLUSIONS

- 1. Any binder for bituminous road pavements is subject to two types of aging during its life: rapid aging in construction and slow aging in service. The standard tests (RTFOT and DIN 52016) simulate in-construction aging adequately.
- 2. On the other hand, laboratory tests must be conducted at a temperature below 100°C to simulate the in-service aging of a bituminous binder; at higher temperatures the reaction mechanism is different from that which occurs on site.
- 3. The equipment developed at BRRC and the range of temperatures adopted (70 to maximum 95°C) seem appropriate for accelerated simulations of the field aging of bituminous binders.
- 4. The kinetic approach developed from the extent of reaction concept and involving technological characteristics of the bitumen as reaction indicators has proved feasible both in interpreting laboratory tests and in assessing field behavior. Below 100°C the kinetic model of diffusion most accurately fits the set of results obtained.
- 5. The characteristics used as indicators in the kinetic study are asphaltenes content, R&B-softening temperature and the reciprocal of penetration.
- 6. To pass on from laboratory data to field behavior, it is necessary to consider an annual value of kinetic mean temperature. This temperature can be evaluated:
- On the one hand, from the activation energy of the reactions investigated;
- On the other, from statical data on the distribution of temperatures at the surface of road structures. This distribution can be estimated from climatic data (air temperature, amplitude of daily variation, sun radiation, etc.) in the region concerned.
- 7. When overall reaction constants calculated from the results obtained on sites in regions with different climates are compared with those extrapolated from the results of accelerated laboratory aging tests and from the relevant presumed kinetic mean temperatures (which depend on mean air temperature and on sun radiation), the proposed kinetic approach is found to be valid for assessing the aging of bituminous binders in service.
- 8. The kinetic approach enables estimated constants for inservice aging to be related to the specific climate environment of the various countries or regions concerned.

REFERENCES

 A. F. Verhasselt. A Kinetic Approach of the Aging of Bitumens. Asphaltenes and Asphalts, Vol. II, T. F. Yen and G. V. Chilingarian, eds. Development in Petroleum Science Series, to be published by Elsevier Science Publishers, The Netherlands, 1993/94.

- M. E. Brown and A. Galwey. Arrhenius Parameters for Solid-State Reactions from Isothermal Rate-Time Curves. *Analytical Chemistry*, No. 61, pp. 1136–1139, 1989.
- A. F. Verhasselt and F. S. Choquet. A New Approach to Studying the Kinetics of Bitumen Aging. In *Proc.*, *International Symposium on Chemistry of Bitumens*, Vol. II, Rome, 1991, pp. 686–705.
- F. S. Choquet and A. F. Verhasselt. Natural and Accelerated Aging of Bitumens—Effects on the Asphaltenes. In Symposium, Asphaltene Particles in Fossil Fuel Exploration, Recovery, Refining, and Production Processes. Las Vegas, July 13-17, 1992.
- C. De Backer. Les températures dans les structures routières. La Technique Routière, XXV/2, Brussels, 1980, pp. 1-29.
- V. Veverka and C. De Backer. Aspects techniques du renforcement des chaussées. Ve Conférence routière africaine de l'IRF, Formation technique et recherche, Libreville, Gabon, 1983, pp. 151-160.

- 7. Institut Royal Météorologique de Belgique. Bulletin mensuel, Observations climatologiques, Bruxelles.
- 8. Summary Report on Asphalt Properties and Relationship to Pavement Performance (SHRP Task 1.4), Strategic Highway Research Program, ARE Inc., Scotts Valley, Calif., May 1990.
- F. Farcas and C. Such. Influence de la structure chimique des bitumes sur leur comportement rhéologique. Description des méthodes analytiques utilisées. *Journée d'étudies AFREM—Les Bitumes*, pp. 29-55, Saint-Rémy-lès-Chevreuse, 1991.
- F. Choquet. The Development of Bituminous Binders in Pavements in Service. In 4th Eurobitume Symposium, Vol. I, Summaries and Papers, Madrid, Spain, 1989, pp. 30-34.
- F. S. Choquet. The Search for an Aging Test Based on Changes in the Generic Composition of Bitumens. In *Proc.*, *International Symposium on Chemistry of Bitumens*, Vol. II, Rome, 1991, pp. 787-812.