

## Effect of Aggregates on Isothermal (Steric) Hardening of Asphalts

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**ABSTRACT.** Extreme embrittlement in pavements during early years of service has been described, but is a poorly documented phenomenon. This study was undertaken to determine whether extreme embrittlement results from specific combinations of asphalts and aggregates. The time-dependent hardening rates (steric hardening, reversible hardening) of 18 different briquette combinations were measured over a period of eight months. A wide variety of asphalt and aggregate types were used. Extreme embrittlement was not observed in any samples. Hardening was observed to depend on the degree of oxidation of the asphalts and the chemical composition of the asphalts. For the combinations studied, extreme hardening was not induced (i.e., not "catalysed") by aggregates. The results suggest that extreme, early embrittlement in pavement likely results from causes other than from specific asphalt-aggregate combinations.

**RÉSUMÉ.** La susceptibilité à la fissuration extrême des chaussées au cours des premières années de service a été décrite mais reste un phénomène peu documenté. Cette étude a été entreprise afin de déterminer si la susceptibilité à la fissuration extrême résulte de combinaisons spécifiques bitumes/agrégats. Les variations de durcissements dépendants du temps (durcissement stérique et durcissement réversible) de 18 combinaisons spécifiques bitumes/agrégats ont été mesurées sur une période de huit mois. Une large variété de types de bitumes et d'agréats ont été utilisés. La fissuration extrême n'a été observée dans aucun des échantillons étudiés. Il a été observé que le durcissement dépendait du degré d'oxydation du bitume et de la composition chimique du bitume. Pour les combinaisons étudiées, le durcissement extrême n'a pas été induit (i.e. non "catalysé") par les agrégats. Ces résultats suggèrent que la susceptibilité à la fissuration extrême de la chaussée résulte de paramètres autres que des combinaisons spécifiques bitumes/agrégats.

**KEY WORDS:** asphalt, steric hardening, reversible hardening, embrittlement, cracking.

**MOTS-CLÉS:** bitume, durcissement stérique, durcissement réversible, fissuration.

## 1. Introduction

Extreme embrittlement of asphalt concrete pavement, which typically results in severe cracking, has been reported by state highway departments for many years. Historically, these have been poorly documented events and many questions remain as to the cause(s) of these unusual events. One possibility is that extreme embrittlement results from some specific asphalt composition, or from some specific combinations of asphalt and aggregate. We undertook this study, using widely varied asphalts, aggregates and levels of oxidation to determine whether extreme embrittlement is likely to be a simple materials problem.

The objective of this study was to measure the steric hardening (isothermal, reversible hardening) of asphalt/aggregate mixes over time to determine whether or not extreme hardness or embrittlement can be induced by an aggregate. Previous laboratory studies have shown that unoxidized neat asphalts, oxidized neat asphalts, and selected asphalt/aggregate mixes harden over time by factors of 10 to 300% depending on the composition of the asphalts, but the influence of aggregate on the hardening process was not clear. In this work, hardening of asphalt mixes was measured and compared with hardening of the same asphalts alone to determine whether or not aggregate compositions influence the rate and magnitude of steric hardening and are therefore, in the field, likely to contribute to extreme embrittlement and cracking of pavements.

Hardening of eighteen (18) different asphalt/aggregate mastic combinations was studied over a period of eight months. Ten (10) identical Marshall-like briquette specimens were prepared from each mix. Each mix was formulated to contain 85 wt % aggregate (-200 mesh particle size) and 15 wt % asphalt. The experimental matrix was designed to maximize the probability of finding examples of aggregate-induced embrittlement by testing mixes having high-surface-area (potentially highly reactive) aggregates and highly oxidized asphalts having substantially different chemical compositions. For these experiments, ultimate compression strength (measured in an axial geometry and recorded at the point of failure of each briquette) was used as the measure of hardness.

## 2. Experimental

### 2.1. Materials

Asphalts and aggregates were obtained from the Materials Reference Library (MRL) now located in Sparks, Nevada. The asphalts used in this study were used in the previous Strategic Highway Research Program (SHRP) and were coded AAD-1, AAM-1, and AAG-1. Asphalt AAD-1 is characterized as being an asphalt containing large amounts of carboxylic acids, AAM-1 is characterized as an asphalt high in waxes, and AAG-1 as an asphalt previously treated with lime such that it contains

large amounts of calcium salts of carboxylic acids. Both unoxidized and highly oxidized asphalts were used to prepare mastics for the steric hardening experiments. The aggregates were also from the SHRP program and were coded RB, RC, and RD. RB is a granite and RC and RD are predominantly calcium and magnesium carbonates (limestones). The mastics prepared for this study thus contained both asphalts and aggregates having large differences in chemical compositions.

Highly oxidized asphalt samples were prepared in a pressure aging vessel (PAV) using oxidation conditions surpassing those of the SHRP specification oxidation conditions. The asphalts were oxidized for 120 hours at 90°C in an atmosphere of air at 2.1 Pa.

## 2.2. Preparation of Mastic Briquettes

Mastic mixes were prepared by mixing 200 mesh aggregates with oxidized or unoxidized asphalts for 1 hour at 160°C in a mechanical stirrer to produce mixes having 15 wt % asphalt and 85 wt % aggregate. Mixing was enhanced by preheating the aggregates and asphalts for 1 hour at 135°C.

Ten identical mastic briquettes (50 g each) were prepared simultaneously by filling a specially designed twelve-cavity steel mold. Briquettes were 38 mm (1.5 in) diameter cylinders, nominally 18 mm (0.71 in) tall. The mold was heated to 150°C. Specimens were maintained at 150°C and a pressure of 28 Pa (4 ksi) for 1 hour, then cooled to room temperature (maintaining pressure) over a 1-hour period. To test sample uniformity, 3 series of 10 specimens each were tested. The initial batch of specimens had a coefficient of variation of 21% in static strength. This was improved to 3% variation in strength with additional fabrication practice.

## 2.3. Steric Hardening Tests

Steric hardening tests were conducted on 10 specimens of each asphalt-aggregate mixture. All samples were allowed to stand at room temperature for 3 days to permit initial steric hardening. The 10 samples were divided into 2 sets of 5 samples, and tested at 3 days, 1, 2, 4 and 8 months. The 1, 2, 4 and 8 month samples were stored at 40°C until time to be tested. All compression tests were conducted at 25°C. Specimens were compression loaded parallel to the cylinder axis using an Instron 1125 electromechanical testing machine in order to measure ultimate compression strength.

## 3. Results and Discussion

The ultimate compression strengths (recorded at the point of failure) of eighteen different mastics were studied over time in order to identify combinations of

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aggregates and asphalts that were susceptible to extreme embrittlement. The purpose was to determine if any aggregates alone or any combinations of aggregates and asphalts having different compositions caused embrittlement and could therefore be used to predict when extreme embrittlement or cracking would occur in a pavement. The compression strength tests also allowed aggregate-induced hardening, if measurable amounts occurred, to be measured. The magnitudes of steric hardening measured in the mastic specimens reported here were compared with the magnitudes of steric hardening previously measured in neat asphalts, thus allowing the amounts of aggregate-induced hardening of the mastics to be determined.

### *3.1. Effect of Oxidation on Ultimate Compression Strength of Mastics*

Figures 1-3 show representative examples of how mastics prepared from unoxidized asphalts and oxidized asphalts harden over time. In these figures the compression strength at the point of failure of the briquette is plotted versus time. The figures show that, as usually observed, mastics prepared from soft, unoxidized asphalts have less compression strength than mastics prepared from harder, highly oxidized asphalts. In this study, mastic briquettes prepared from highly oxidized asphalts showed compression strengths from 33 to 108% greater than mastics prepared from unoxidized asphalts. These increases in hardness of mastics due to severe oxidation are similar in magnitude to the increases in viscosity, due to RTFO/PAV oxidation, of the same asphalts alone, AAD-1, AAM-1, and AAG-1 as measured in previous work [MCK 97].

The previous work showed that oxidized asphalts, containing large amounts of polar compounds, have higher inherent viscosities than corresponding unoxidized asphalts. In addition, the rates of steric hardening of oxidized asphalts were seen to be only slightly slower than the rates of steric hardening of unoxidized asphalts.

### *3.2. Effect of Time on the Magnitude of Steric Hardening*

Figures 1-3 also show that, on a percent basis, neither the mastics prepared from unoxidized asphalts nor the mastics prepared from highly oxidized asphalts hardened significantly over the eight-month test period. None of the samples showed increased hardening of more than 50% in eight months. In separate experiments to measure standard deviation, the experimental standard deviations for compression strength measurements on mastics prepared from highly oxidized asphalts were measured to be almost 25%, such that any increases in strength of less than 25% caused by steric hardening were still within experimental variation. In the earlier work cited above [MCK 97] neat unoxidized asphalts alone and neat oxidized asphalts alone showed steric hardening (viscosity) increases of 10-140% over a 3-month period at 25°C. Thus, Figures 1-3 show that only a small amount of steric

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hardening was observed in mastics and, compared with the hardening of neat asphalts alone, the mastics showed no evidence for steric hardening induced by aggregates.

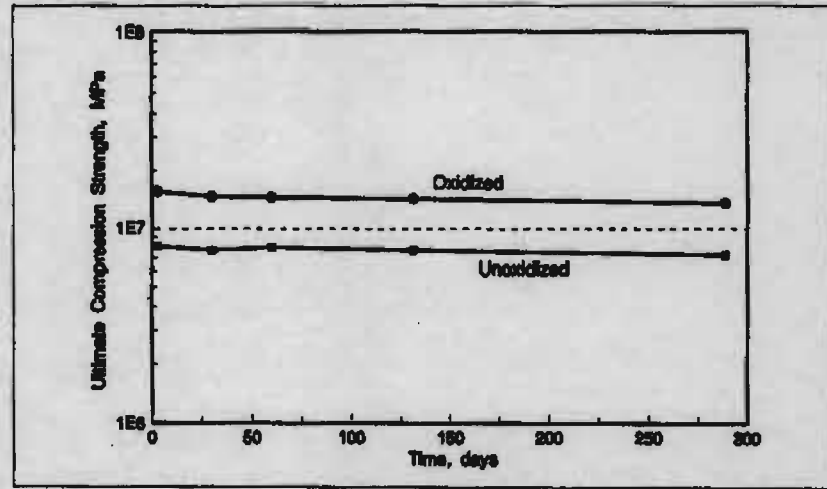


Figure 1. Ultimate compression strength at failure of unoxidized and oxidized mastics RC limestone/asphalt AAD-1 as a function of time

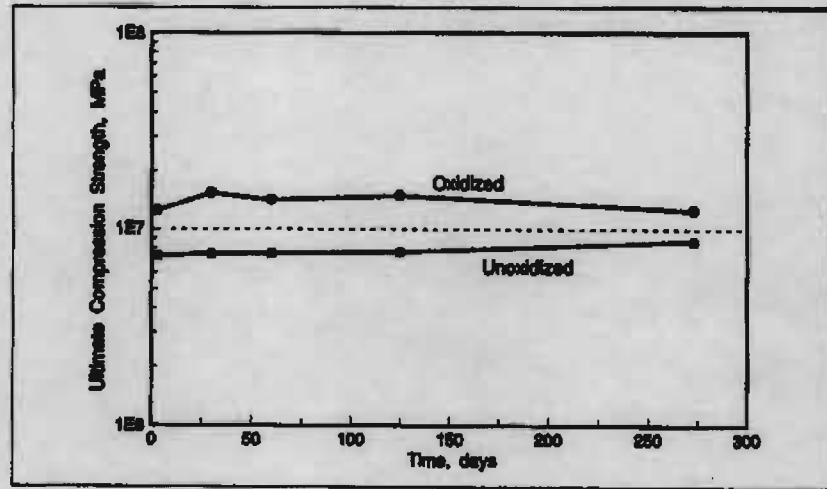


Figure 2. Ultimate compression strength at failure of unoxidized and oxidized mastics RD limestone/asphalt AAG-1 as a function of time

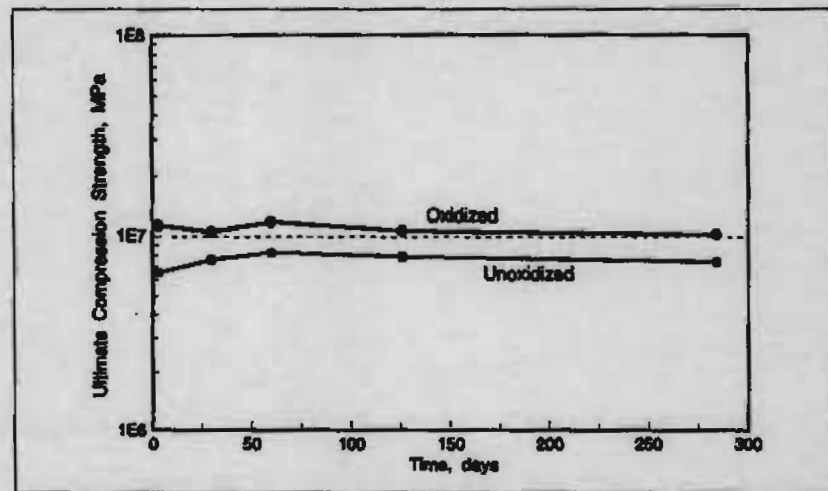


Figure 3. Ultimate compression strength at failure of unoxidized and oxidized mastics RD limestone/asphalt AAM-1 as a function of time

In this study modulus data were also obtained as a measure of briquette hardening but, to save space, the data are not presented. Comparison of modulus data with compression strength data showed parallel results, thus the conclusions concerning the effect of aggregate on steric hardening were derived from both sets of data. The modulus results obtained in this work are also similar to the results of Bell and Sosnovske [BEL 94] that measured changes in modulus of several asphalt/aggregate mixes over a period of 15 months. In that study, depending on the compositions of the mixes, hardening (increases in modulus) was observed to increase by about 0 to 300% over a 15-month period. Dramatic increases in hardening or embrittlement were not observed and no evidence was obtained that aggregates induced hardening in the three asphalts studied. Previous workers suggested [ENS 93] that aggregates induce steric hardening by inducing dipolar multilayer buildup at the molecular level in the asphalts, but the current experiments using high-surface-area aggregates and Bell's work on larger particle size mixes show no evidence that aggregates promote or induce measurable amounts of steric hardening over time at 40°C.

### 3.3. Effect of Aggregate Composition on Steric Hardening

Figures 4 and 5 show the effect of aggregate composition on steric hardening. In these figures compression strength at failure is plotted versus time for mastics that have been prepared from three different aggregates and the same asphalt in order to emphasize the effect of aggregate on hardening. The general conclusions derived from the figures are that (1) only small amounts of steric hardening were measured and (2) hardening was not measurably influenced or induced by the chemical nature

of the aggregate. Hardening, for the mastics studied, was found to be independent of the chemical composition of the aggregate.

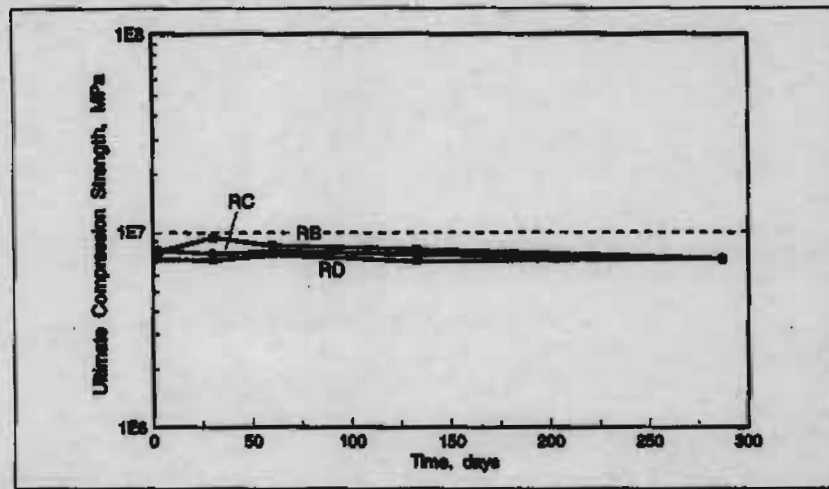


Figure 4. Ultimate compression strength at failure of mastic briquettes prepared from aggregates RB granite, RC limestone, and unoxidized asphalt AAD-1 as a function of time

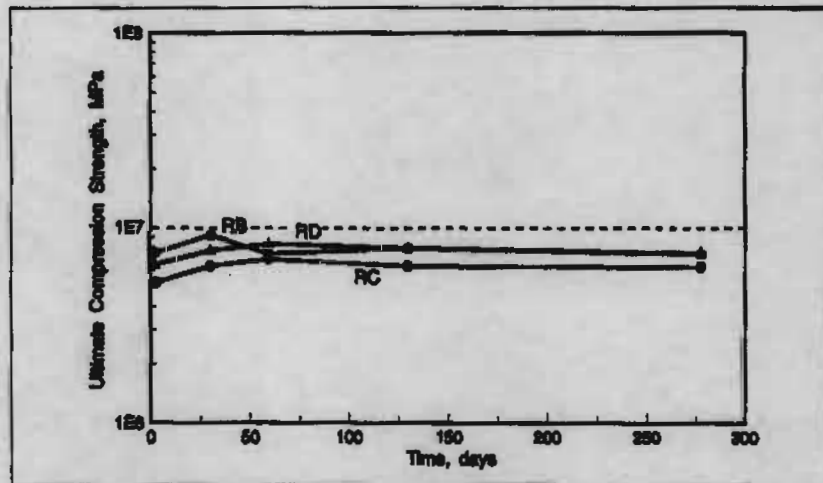


Figure 5. Ultimate compression strength at failure of mastic briquettes prepared from aggregates RB granite, RC limestone, RD limestone, and unoxidized asphalt AAM-1 as a function of time

3.4. Effect of Asphalt Composition on Steric Hardening

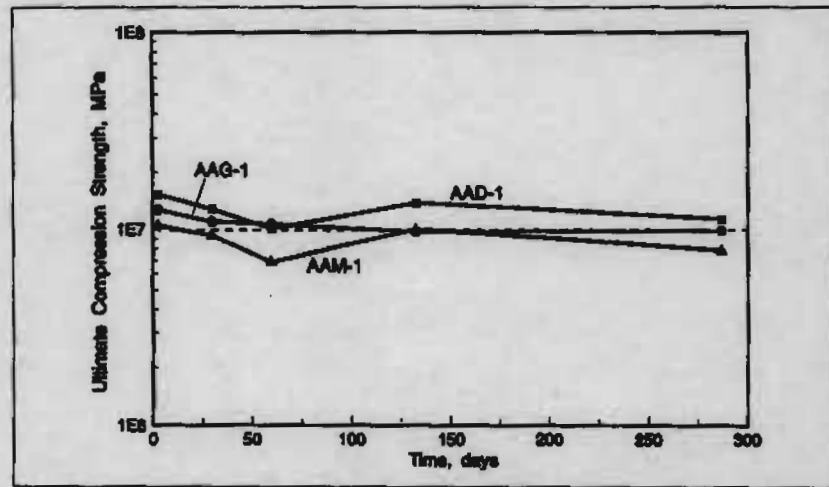


Figure 6. Ultimate compression strength at failure of mastic briquettes prepared from aggregate RB granite and oxidized asphalts AAD-1, AAG-1, and AAM-1 as a function of time

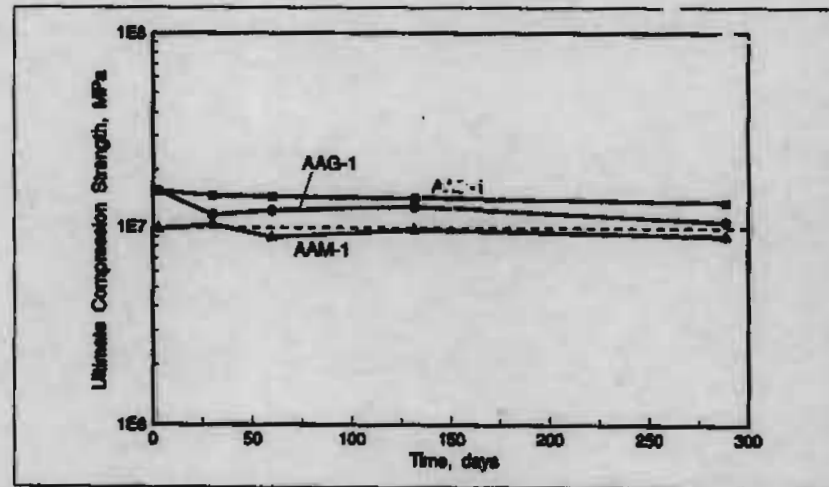


Figure 7. Ultimate compression strength at failure of mastic briquettes prepared from aggregate RC limestone and oxidized asphalts AAD-1, AAG-1, and AAM-1 as a function of time

Figures 6 and 7 show the effect of asphalt composition on steric hardening. In these figures compression strength at failure is again plotted versus time. However, data for mastics prepared from three different asphalts and a single aggregate are plotted in order to emphasize the effect of asphalt composition on steric hardening. The general conclusion derived from these examples is that (1) only small amounts of steric hardening were measured and (2) the degree of hardening was determined by the chemical composition of the asphalt. The chemical composition of the aggregate did not induce significant steric hardening in the mastic mixture. Earlier steric hardening work [MCK 95] showed that the degree of steric hardening exhibited by neat asphalts, both oxidized and unoxidized, was determined by the chemical compositions of the asphalts.

#### 4. Conclusions

The time-dependent hardening of mastic briquettes was measured over a period of eight months to (1) determine the effect of aggregate on the rate and degree of hardening and to (2) identify combinations of chemically different aggregates and asphalts that were susceptible to extreme embrittlement.

The degree of oxidation of the asphalt was observed to have a large effect on the initial hardness of the mastic briquettes at time zero but did not significantly determine the degree to which the mastics hardened. These results were similar to the steric hardening results from the previous study using the same neat asphalts. Both neat and highly oxidized asphalts undergo steric hardening.

The mastic samples in this study sterically hardened over time, but the degree of hardening was not over 50% for any of the 18 samples over an 8-month period. This is the same general degree of hardening observed earlier in the same neat asphalts. The addition of aggregates to form the mastic did not induce or "catalyze" steric hardening of the mix.

Aggregate composition had no measurable effect on steric hardening. Mastics prepared from asphalts of the same chemical composition but different aggregate composition showed the same rate and degree of steric hardening.

Asphalt composition was the most significant factor in determining the steric hardening characteristics of a mastic. Mastic samples prepared from relatively soft asphalts sterically harden more than more viscous asphalts, due probably to the greater molecular mobility of the softer asphalts.

No mastics were observed to undergo severe embrittlement in the eight month test period. The array of 18 mastics having different combinations of aggregates and asphalts was designed to maximize the probability of finding chemical combinations that would cause extreme embrittlement. None were found in this study.

Finally, we conclude that instances of rapid, extreme embrittlement and severe cracking occasionally reported by state highway departments are probably caused by factors other than asphalt or aggregate composition. Some possibilities include overheating of asphalt in the hot mix plant, poor compaction leading to rapid aging, excessive loads on the road structure, or deleterious effects of moisture. The results shown here suggest strongly that extreme embrittlement of pavement is not likely to be a simple materials problem.

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