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Characteristics of Aggregates and Fillers
for Bituminous Construction



THERMODYNAMIC ASPECTS OF THE STRIPPING PROBLEM

Foreword

The report which follows presents a review of the literature on the question of stripping of binder from aggregates in bituminous mixtures. The information concerns mostly the thermodynamic approach to the stripping problem. Assuming the presence of a three-phase interface - aggregate, bitumen, and water - the processes that may occur are described. The report also mentions some of the limitations of this approach, mainly the role of adhesion dynamics arising from the application of external forces, i.e., traffic. Also included are recommendations for lines of further research.

It is believed that this report will be stimulating to engineers, chemists, and physicists who are interested in the more fundamental aspects of the water resistance of bituminous mixtures. The Committee solicits the comments of these persons and any others who may be concerned.

This report has been prepared by Subcommittee (5) of MC-A6 under the Chairmanship of Dr. Wm. L. Dolch. Other members were Drs. F. C. Gzemski and D. W. McGlashan. The entire Committee has reviewed and approved the report.

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Report of Subcommittee on Adsorption and Absorption, MC-A6(5)

The assignment of this subcommittee is to review the literature with respect to adsorption and absorption of bitumens by aggregate and to indicate fruitful courses for research.

This is a partial report restricted to the question of the stripping of binder from aggregates in bituminous mixtures. The literature to 1954 has been listed in a Highway Research Board bibliography (1). The subject has been recently discussed by Michaels (2) and reviewed by Mathews (3). Pfeiffer's book (4) is a source of pertinent data. The chapter by Mack (5) is also a recent discussion.

There are many aspects of the stripping problem. Perhaps most important are the nature and roughness of the aggregate surface, its dryness, any films that may be present, the type of bitumen and its viscosity, the presence of additives and fillers, and conditions of traffic and temperature.

The large number of variables makes the subject difficult to analyze. There has also been an unfortunate disinclination to break up the problem into its basic parts. Much work has resulted in few generalities and little insight.

The question of the harm done by stripping is also unresolved. It is assumed in this report that stripping is harmful and to be avoided.

What follows is mostly the thermodynamic approach to the stripping problem. If the removal of binder by water action is to proceed spontaneously, without the application of external forces to the system, then certain thermodynamic conditions must be fulfilled.

This approach and some of its limitations are emphasized here because this basic approach has not so far resulted in as much insight and progress as was hoped. An important question, therefore, is whether the failure has been because of a poor model and naive analysis or because the thermodynamic approach excludes important aspects of the process.

The usual models for stripping have been given by Thelen (6). They are reproduced here with some alternates and conventional thermodynamic notation.

Axiomatic to the usual concept of stripping is the presence of a three-phase interface, i.e. aggregate, bitumen, and water. How this interface may come about is a subject for research in itself. The interface can come about because of pinholes, the penetration of water drops (6), breaking of blisters, and other mechanical ruptures. The details of these processes are important. Stripping usually is more severe, at least in laboratory tests, with angular aggregates, presumably because the sharp edges are places of early rupture of the binder film with consequent production of the needed three-phase region. Practically no basic work has been done on these questions. Once they are understood and measures are taken to prevent the occurrence of three-phase interfaces much of the stripping problem may be solved. On the other hand, a pore in the surface of the aggregate that contains water will be, ipso facto, such a three-phase region. It seems that the only thing to do about such cases is to keep the aggregate dry.

This report is, however, concerned chiefly with the processes that occur once the three-phase interface is formed. If then the binder is removed spontaneously from the aggregate by the stripping action, without the application of external forces, the free energy of the system must decrease. Expressions for the free energy change can be written for simple models.

Figure 1 shows an interface between a plane aggregate surface, binder, and water. The abbreviations A, B, and W refer to aggregate, bitumen, and water respectively.

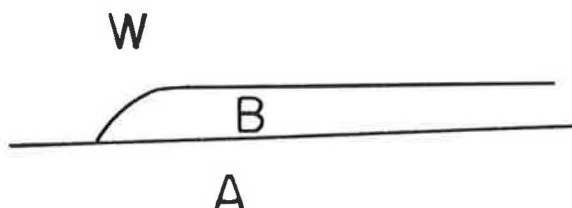


Fig. 1.

It is not intended in these illustrations that the contact angle of the bitumen on the aggregate be an equilibrium one.

The binder can be spontaneously removed from the aggregate surface in one of two ways. These are illustrated in Figures 2 and 3.

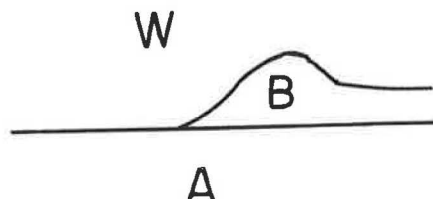


Fig. 2.

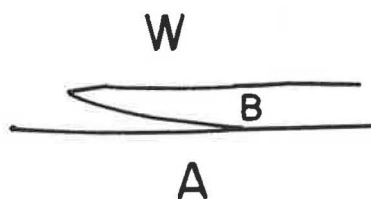


Fig. 3.

For short, the condition illustrated in Figure 2 is called the "roll-back" case and in Figure 3 the "lift-off" case. Apparently, according to experience, the roll-back case is the one usually encountered.

Whenever unit area of a surface or interface is created the system absorbs energy equal to the free surface energy or surface tension of the interface in question. When an interface is destroyed the corresponding energy is released by the system.

For unit change in the aggregate-water interfaces depicted above the free energy changes are as follows. For the roll-back

$$\Delta F_1 = \gamma_{AW} - \gamma_{AB} - C_1 \gamma_{BW} \quad (1)$$

where the γ 's are the appropriate interfacial tensions. This equation implies that, in addition to the creation of an aggregate-water interface

and the destruction of an aggregate-bitumen interface, a bitumen-water interface is destroyed. The coefficient C_1 is the area of bitumen-water interface destroyed per unit change of the area of the other two interfaces and is smaller than 1. For the lift-off case the free energy change is

$$\Delta F_2 = \gamma_{AW} - \gamma_{AB} + \gamma_{BW} \quad (2)$$

In this process a bitumen-water interface is created rather than destroyed.

If the free energy changes given in equations (1) and (2) are negative, the process can occur spontaneously. Whether it will occur or not involves rate questions. If ΔF is positive the process cannot occur spontaneously. Therefore, it seems axiomatic that, if possible, conditions should be arranged so that ΔF is positive. The free energy change given here is the negative of what is sometimes called the "stripping potential". A positive stripping potential therefore is the case for possible spontaneous stripping.

Equations (1) and (2) show that, other things being equal, the roll-back case of stripping is more likely than the lift-off case.

So a chief problem in the thermodynamic approach to the stripping question is the accurate knowledge of the interfacial tensions involved in the foregoing equations. This has, of course, been realized for a long time and has been the subject of several studies. The fact that these studies have not given the hoped-for insight into the problem (3) is partly due to the experimental difficulties involved.

One major experimental difficulty is the slowness of liquids of such high viscosity as bituminous materials to assume equilibrium positions and the resultant uncertainty about the applicability of the measured parameters. In an attempt to circumvent this difficulty some workers (7) have used hydrocarbon liquids of lower viscosities and assumed their other properties to be equivalent to those of the bitumens for which they were substituted. The accuracy of this assumption is debatable.

Of all the interfacial tensions of interest, the only one on which there is reasonable agreement is the surface tension of the bitumen itself, which is the least important to the stripping question. It does not appear in equations (1) and (2), but will be shown to have application to the considerations of incompletely-covered aggregates. This tension is of interest in the problem of the wetting of aggregates by bitumen and its consequent spreading.

In the determination of the surface tension of bitumen it has usually been necessary to measure at higher temperatures at which the sample is sufficiently fluid and extrapolate to the lower temperatures of more interest. The results of these measurements, as summarized by Mathews (3), have been values of about 25-35 dynes/cm for asphalts. Thelon (6) gives 26, Pfeiffer (4) 33.

These measurements have been made on various types of asphalts. Pfeiffer (4) summarizes work showing that the total, as contrasted with the free surface energy, is about 50 dynes/cm for a variety of asphalts. The implication of this result is that the same general sort of hydrocarbon structure is presented at the surface by molecular orientation in asphalts that have considerable compo-

sitional variability. This is the same conclusion that has been reached for lower hydrocarbons (5).

For the bitumen-water interfacial tension there is less agreement. Various workers (4, 6) have obtained values ranging from 20 to 40 dynes/cm. In Bikerman's book (8) he has given "about 50" dynes/cm for the interfacial tension of water with various hydrocarbons.

The interfacial tensions between aggregate and bitumen or water have been measured with even less agreement. Various ingenious techniques have been devised for relative or absolute interfacial tensions. These techniques are open to criticism.

Thelen (6) has given a value of zero for γ_{AW} and 17 dynes/cm for γ_{AB} . He gave no details of how these were measured. The bitumen in question was an "asphalt", but the aggregate was unspecified. He stated that the zero interfacial tension between the aggregate and water is valid, because a "stone" surface is approximately a free water surface, due no doubt to adsorption. If the stone is actually wet or even has been exposed to water vapor in the air, there will be some such film. This will be true under all circumstances except when the aggregate is fresh from a dryer. And this film will reduce the aggregate-water interfacial tension that is appropriate to the issue of stripping. But it is difficult to agree with the value of zero.

However, if the aforementioned value of zero for γ_{AW} is valid, ΔF of equations (1) or (2) will always be negative. This would mean one would have in all cases the potential for stripping, and the practical outcome would depend only on rate-determining factors such as viscosity of the bitumen.

Arguments such as this are advanced for drying the aggregate prior to making a bituminous mixture. No doubt drying helps a great deal and is one of the factors responsible for the comparative freedom from stripping of hot mixes.

The difficulty, however, goes deeper than experimental problems. The thermodynamic approach to stripping implies that one needs to know the interfacial tensions, particularly γ_{AW} , that apply to the surfaces as they are actually produced in the stripping process. This may be a very different matter from those that might be determined by the use of some of the conventional techniques, because the departure of the bitumen may leave the surface in a state that is preconditioned by its former cover, owing perhaps to some adsorption process (5). The invading water would then be covering a film-covered solid, and the interfacial free energy of the interface produced would be different from that of a "pure" or clean aggregate-water interface; it would probably be much lower.

While the measurement of the interfacial tensions themselves is difficult, it is easier and relatively unambiguous to determine the difference between the aggregate-water and the aggregate-bitumen interfacial tensions. The classical equation of Young is

$$\gamma_{AW} - \gamma_{AB} = \gamma_{BW} \cos \theta \quad (3)$$

where θ is the equilibrium contact angle at the three-phase interface of Figure 1.

A measurement of θ and of γ_{BW} , therefore, permits a determination of $\gamma_{AW} - \gamma_{AB}$. If this difference is known, and also the value of γ_{BW} , the values of ΔF in equations (1) and (2) can be calculated after making some assumption about the geometric coefficients. One difficulty has been the determination of the contact angle, which is notoriously hard to measure accurately. The system in question here is complicated by the great slowness in assuming an equilibrium position, because of the high viscosity of bitumens at room temperatures.

Further, the validity of equation (3) has been challenged (9) on seemingly sound mechanical grounds. Recent discussions of contact angle are (10) and the book listed in (7).

Another question is the hysteresis exhibited by the contact angle, depending on whether the three-phase interface is moving in one direction or another. This difference gives rise to the existence of the so-called advancing and receding contact angles. In the stripping process the angle in question is the receding one, when measured in the bitumen; the angle should be measured when water is being caused to advance onto a previously bitumen-covered surface, in the same manner as in the stripping process itself.

It seems that a sufficiently careful study of the bitumen-aggregate-water contact angles has not yet been made. Such a study would probably involve, among other things, the use of very flat surfaces, more than one method of determining the angle, and the lapse of sufficient time so equilibrium could be attained after migration of any surface active components to surfaces was complete. Of the various methods available, the tilting plate (11) and sessile drop (12) seem to be well-adapted to the problem.

Implicit in Figures 1-3 is a perfectly smooth homogeneous solid surface. Such surfaces are, of course, not really found. Any solid has a surface that is rough on an atomic scale. But almost all have a very complicated surface that has both chemical and physical inhomogeneities of a comparatively large order. The subject has been discussed by many workers. See Bikerman's book (8) for a summary.

Surface roughness may be comparatively important to the stripping problem and has been emphasized recently in connection with adhesive action (13, 14). Most aggregates used in bituminous mixtures have a comparatively rough texture and a surface that is chemically and mineralogically heterogeneous. The roughness is composed of irregularities and of pores or capillaries, although the dividing line between the classes is not clear.

It would be best if the binder penetrated all the surface roughness and well into the pore structure. Whether this will happen depends on the spreading properties of the bitumen in a thermodynamic sense but also upon its viscosity and the degree of surface roughness.

The presence of surface roughness also affects the thermodynamic considerations of stripping mentioned earlier. Huntsberger (13) has shown that partial wetting with failure to penetrate into surface crevices may be either a metastable or an equilibrium state. He also mentioned that the surface roughness of most importance is of a comparatively small dimension that corresponds roughly to the size of polymer crystallites, micelles, etc., and so may be important in the question of the "fit" of binders onto aggregate surfaces.

If the surface roughness is taken into consideration, the previously given figures would become changed. For a "roll-back" case corresponding to Figure 2 the situation would be as in Figure 4.

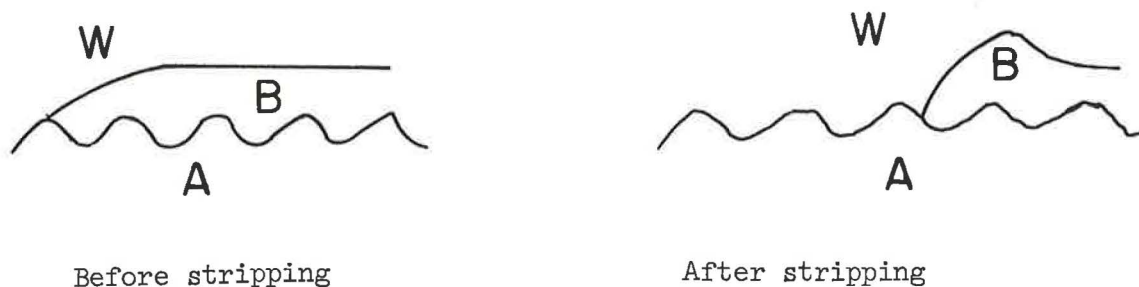


Fig. 4.

The free energy of stripping for this case would be, again for the production of unit area of aggregate water interface,

$$\Delta F_3 = \gamma_{AW} - \gamma_{AB} - C_2 \gamma_{BW} \quad (4)$$

where $C_2 < C_1$.

An incompletely covered rough surface is illustrated, for the "roll-back" action, in Figure 5.

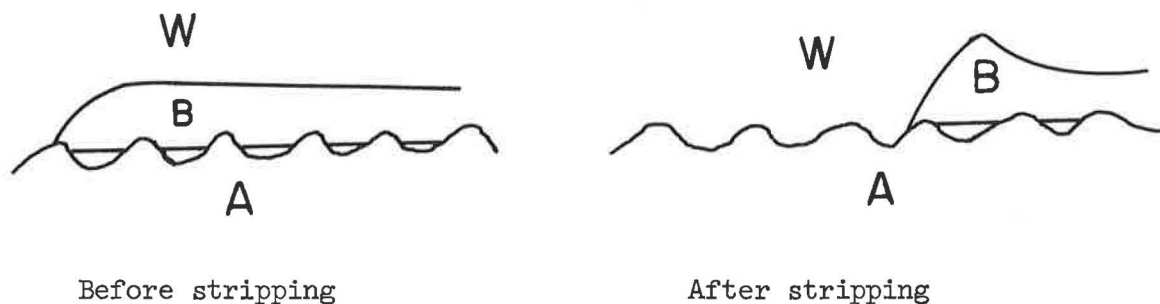


Fig. 5.

The free energy of stripping for this case would be, on the same basis as before,

$$\Delta F_4 = \gamma_{AW} - C_3 \gamma_A - C_4 \gamma_B - C_5 \gamma_{AB} - C_2 \gamma_{BW} \quad (5)$$

where $C_3 + C_5 = 1$ and $C_4 < C_3$.

Equation (4) would result in a more positive, or less likely, ΔF than that of equation (1) because of the roughness. But if the surface is incompletely covered, as in Figure 5, the result would be a more negative ΔF than equations (1) or (4), assuming all the invading water entered the crevices in the aggregate surface, which is likely.

In a general sense, it is difficult to separate porosity near the surface from surface roughness. Any surface porosity that is penetrated by bitumen or water in the course of the processes under consideration here will act in the same way as surface roughness, and the two can be considered together.

Equations analogous to (4) and (5) could be written for the "lift-off" case, but what has already been given will illustrate the point.

Equation (5) is the general representation of the thermodynamic approach, the spontaneous stripping of binder from a rough or porous incompletely covered aggregate surface. Evaluation of equation (5) would involve not only the already considered difficulties in determining the interfacial tensions, but would also require knowledge of the geometric factors and degree of coverage that are represented by the various coefficients.

There has been considerable work done and some practical success with surface active additives to prevent stripping (3, 5, 7, 15, 16, 17). Their chief function seems to be to change the interfacial tensions by adsorption at the interfaces so as to make ΔF more positive and, therefore, stripping less likely. If γ_{AB} in the various equations for ΔF is decreased, the result is an increase in ΔF . A surface active substance that is positively adsorbed at the aggregate-bitumen interface will lower γ_{AB} in the same way that a soap lowers the surface tension of water. Such surface active materials have been used both by direct application to the aggregate and by dissolution in the binder. In the latter case there may be important questions of the speed with which the dissolved material migrates to the aggregate-binder interface and of the concentration needed in order to have sufficient adsorption at the interface to do the job. On the face of it, the application of such substances directly to the aggregate would seem more efficient, although this involves difficulties. A practical question that has limited the usefulness of most additives has been that of heat stability when used with a hot mix.

The foregoing has been a brief review of the thermodynamic approach to the stripping problem. This report will conclude with a mention of the aspect that seems most seriously to challenge the adequacy of the purely thermodynamic approach.

Field experience has shown traffic to be an important variable in stripping, there being many examples where difficulty occurred only in those places where the pavement was subject to traffic.

The exact role played by traffic is less clear. Mathews (3) mentioned that the important action may be a mechanical breaking away of films of binder already loosened from the aggregate surface by spontaneous stripping action. From this point of view the main action of traffic is to prevent the self-healing of a pavement that would otherwise occur when it dries out.

Mack (5), on the other hand, described the pumping action by which tires cause movement of water in a wet pavement. He stated that these forces are far greater than thermodynamic ones and gave primary importance to the resulting loosening and perhaps emulsification of the binder. He called this action the "main factor" in displacement of the binder.

It is logical to assume that in either case surface roughness may be important. A situation in which a large proportion of the surface roughness was not penetrated by the binder would be conducive to poor resistance to imposed loads and to an increased effect of traffic on any other processes, such as the pumping action.

The actions of traffic cannot yet be assessed. All that can be concluded is that water is needed, since a perfectly dry bituminous mixture is not subject to the same difficulties as a wet one. The extent to which the problem should be approached by thermodynamics and, alternately, by adhesion mechanics cannot be decided with present knowledge. Indeed, the acquisition of the basis for this decision may be an important matter for research.

Based on the foregoing analysis, the most important lines of research seem to be the following:

1. Measurement of interfacial energies, contact angles, and adhesion tensions of typical binder materials against very carefully prepared surfaces of glass, minerals, and so forth. The binder material may be approximated by more fluid but chemically similar systems. This should perhaps settle the question of the chemical influence of the aggregate. The matter of "acid" vs "basic" rocks is still debated, but there seems little doubt that it is a poor generalization.
2. Careful measurement of the dynamic variables. The effects of binder viscosity are important. Measurements with the sliding plate viscosimeter may be useful. The use of surfaces artificially roughened and binders of varying viscosity should be interesting.
3. The influence of surfactant additives deserves more study. There have been few systematic studies of the effects of concentration of additives and hardly any that were designed to show the influence of particular molecular characteristics of the additive on interfacial tensions and similar thermodynamic variables as well as on the results of ordinary stripping tests. Questions of the rate of adsorption of these additives should be considered.
4. The effects of surface roughness on the general stripping problem should be studied. These effects may be important. The amount of roughness, depth of surface depressions, and size of surface depressions should be considered. It is possible to make artificially roughened surfaces, say of glass, with known or measurable properties. The mechanical effects, perhaps in some sort of peel or shear test, should be considered.
5. Further attention should be given to simpler and better test methods to predict the likelihood of stripping with given materials and with proposed additives.

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