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# A Study of Cement Modified Bitumen Emulsion Mixtures

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## Abstract

Earlier studies have demonstrated the beneficial effects of adding Ordinary Portland Cement (OPC) to bitumen emulsion mixtures. These effects were confirmed for some dense graded mixtures based on recipes currently used for hot mix in the UK and being considered for use in cold mix. Laboratory tests included stiffness modulus, resistance to permanent deformation and resistance to fatigue cracking. In order to obtain a clearer understanding of the mechanisms causing the improvements in properties, some basic studies were carried out. These included measurement of the rate at which coalescence of bitumen droplets developed and adhered to the aggregate particles, since this is the initial mechanism by which mechanical properties of the mixture are developed. The study was then extended to obtain an understanding of the properties of emulsion blended with OPC, hydrated lime or limestone filler. This was done since it was thought that a contribution to 'binding' of the aggregate in mixtures came from the hydration of cement as well as from the coalesced bitumen. Dynamic Shear Rheometer tests were used on various blends demonstrating the stiffening effects of both OPC and hydrated lime and that filler had little influence. The emulsifying process was also shown to have no effect on the characteristics of the base bitumen. Electron microscopy was used to study the crystalline structures of fully cured mixtures with and without OPC addition. Expert interpretation considered that some of the characteristics of cement hydration effects were present in those mixtures incorporating OPC. The study concluded that the improvements to key properties of cold mix by the addition of OPC can be explained by a range of mechanisms, including improved rate of emulsion coalescence after compaction, cement hydration and enhancement of binder viscosity.

## Introduction

The use of bitumen emulsion in the United Kingdom is largely restricted to various types of surface treatment (such as slurry surfacing and surface dressing) and bond / tack coat. Recently, efforts have been made to use emulsions in mixtures used for trench reinstatements and patching. Its use as a binder in cold mix for structural layers has attracted relatively little attention, largely because of the problems associated with the time taken for full strength to be achieved after paving in the UK climate and the susceptibility to early life damage by rainfall.

The research reported in this paper formed part of a three year study to investigate the fundamentals of emulsion breaking and mixture curing. This was done in order to provide an improved insight into how the mechanical properties of cold mix might be improved.

The central theme of the work reported here concerns the use of Ordinary Portland Cement (OPC) as an additive in cold mix. Earlier studies (1, 2, 3) clearly demonstrated various benefits from OPC addition and this investigation has extended

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that work both in terms of quantifying performance-based mechanical properties and in understanding the basic mechanisms involved.

The work began by measuring the mechanical properties of OPC modified cold mix and went on to look at how coalescence of bitumen droplets was enhanced. The work concluded with a study of bitumen emulsion residues to examine the influence of OPC in the binder matrix.

## Mechanical Properties

***Stiffness Modulus***

A 20mm maximum sized granite aggregate with a grading curve in the middle of the 20 mm UK Dense Bitumen Macadam (DBM) specification was used (4). Details of the mixture recipe are given in Table 1, including the OPC, pre-wet water and emulsion addition levels. The same cationic slow setting emulsion was used throughout the studies described in this paper and was based on bitumen from Venezuelan crude. The emulsion formulation and basic characteristics are given in Table 2. It was necessary to adjust the pre-wet water addition level to accommodate the extra water absorption of the OPC in order to achieve a workable mixture.

**Table 1 : Mixture compositions used to study effect of OPC**

| Mix component | Percentage on aggregate mix | | | | |
|---|---|---|---|---|---|
| Granite aggregate 20 mm | 26 | | | | |
| 14 mm | 15 | | | | |
| 10 mm | 9 | | | | |
| 6 mm | 15 | | | | |
| Dust | 35 | | | | |
| Ordinary Portland Cement | 0 | 1 | 2 | 3 | 4 |
| Pre-wet water | 2.5 | 2.5 | 3.0 | 3.5 | 4.0 |
| Bitumen emulsion | 8.06 | | | | |

In addition to the emulsion mixtures, conventional hot mixtures, with exactly the same aggregate type and grading, were prepared for comparison with 0 and 1% OPC added. A bitumen content equivalent to the residual binder content of the emulsion mixtures was used, which was 4.7 % .

**Table 2 : Emulsion formulation and properties**

| Property | Value |
|---|---|
| Binder grade (pen) | 100 |
| Binder level (%) | 62 |
| Emulsifier level (%) | 1.2 |
| Water phase pH (HCl) | 2.3 |
| Median particle size (μm) | 2.65 |
| Break index, Indice de Rupture (g) | 149 |
| Viscosity (mPa.s) | 87 |

The material components were mixed using a Hobart mixer and moulded specimens fabricated using Marshall hammer compaction with 50 blows to each end of the specimen. Both the emulsion and hot mixtures were prepared in sufficient quantity to allow three 1200 g specimens to be produced from each mixture. The emulsion mixtures were manufactured and compacted at ambient temperature, whereas the hot mix specimens were produced at a temperature of 135 to 140 °C. Specimens were extracted from their moulds after about 16 hours and then stored in an environmentally controlled room at a temperature of 20°C and a relative humidity of 50% during the testing period.

Stiffness was determined using the Indirect Tensile Stiffness Modulus (ITSM) test in the Nottingham Asphalt Tester (NAT). The test details are described elsewhere (5). ITSM tests on the emulsion specimens were first carried out after 5 days and then, periodically, as the specimens cured, on two out of the three cores produced. Specimens were tested at 20°C, with a target load rise time of 120 ms. The results of these tests are shown in Fig 1. The third cores were used for water-loss measurements, which were simply taken as the loss in mass. The results of these tests are shown in Fig 2. When the ambient curing tests had been completed, the weight loss cores were fully dried in an oven at 60°C, to constant weight. This served two purposes. Firstly, it allowed the weight of the aggregate, OPC and bitumen mixture, in the absence of water, to be measured. This figure allowed back-calculation of the water loss over the curing period. Secondly, these cores were used for ITSM tests to obtain stiffness figures for "fully cured" cores (plotted as the values after 365 days) in Fig 1. The hot mix specimens were subjected to the ITSM test after 5 days and, again, after approximately two months to see if any changes had occurred.

Unfortunately, no void content measurements were made on specimens used in these tests but the dimensions recorded as part of the stiffness testing showed an increased thickness of the briquettes with increasing OPC level. This suggested that the voids increased slightly with increasing OPC level. Later in this research the same mixtures were prepared and compacted in the manner used here and void contents of 10 to 15% were obtained for cold mix, whereas equivalent hot mix normally has voids of around 5 to 8%.

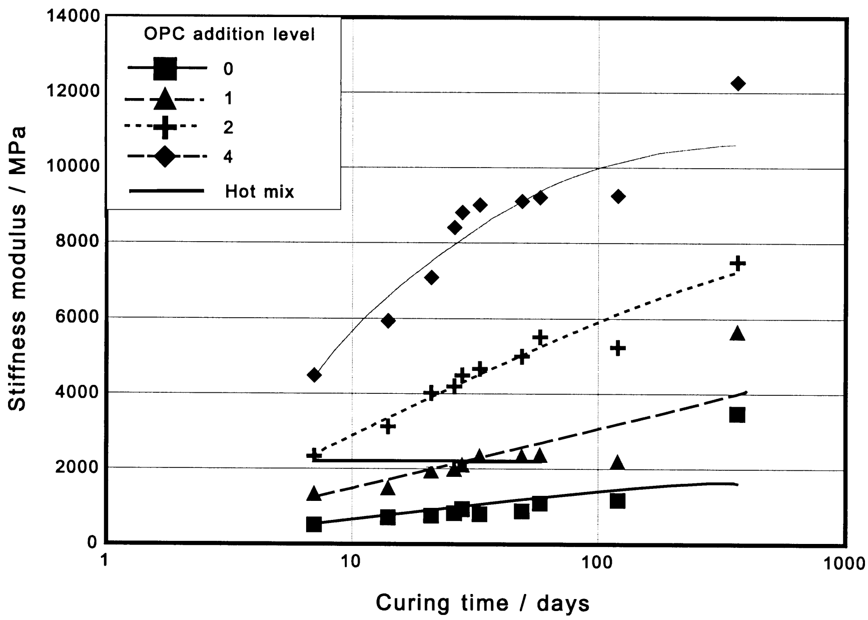


**Figure 1. Effect of OPC on Stiffness Modulus**

From the stiffness modulus test results in Fig 1, the following points are worthy of note.

- Stiffness moduli of the emulsion mixtures increased steadily over several weeks, in contrast with the hot mix which showed no discernable change.
- The rate of stiffness increase of the emulsion mixtures increased with OPC addition level, whereas the hot mix was unaffected by cement.
- The final stiffness of the emulsion mixtures increased with OPC addition level.
- The stiffness recorded for oven-cured specimens seemed disproportionately high compared with those after ambient cure. This raises the question as to whether oven curing at 60°C affects the binder viscosity through chemical changes such as oxidation or loss of components which are volatile at this temperature.

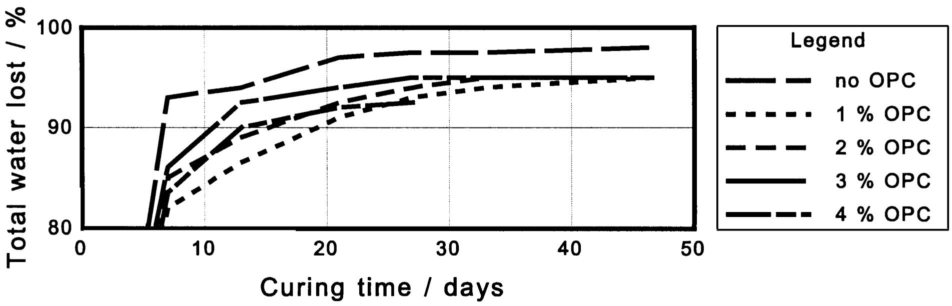


**Figure 2. Water loss from cores with various levels of OPC**

From the water loss results in Fig 2, the following points are worthy of note :

- The majority of the water loss occurred in the first week after specimen manufacture
- Generally, it can be said that the addition of OPC slowed down the rate of water loss but the results did not truly follow a trend
- The remainder of the water continued to evaporate over several weeks and it seems likely that it may never disappear completely.

These data are in good agreement with the findings of Puzinauskis and Jester (6) who also found that the majority of water loss occurred in the first few days after compaction regardless of the emulsion type or water content. The mechanisms which caused the increased stiffness in cold mix were studied subsequently and are discussed in later sections of this paper.

Previous studies (1, 2, 3) have indicated that hydrated lime can have a similar effect to cement on the breaking of bitumen emulsions and curing of mixtures. In these studies Zeta potential measurements were used to assess the electrical change in various emulsions with different bitumens and additives (7), since this is one of the parameters influencing breaking characteristics. The results indicated that lime and $CaCl_2$ render the emulsion more cationic or less anionic under certain conditions. This can have an effect on the interaction between emulsion droplets and negatively charged aggregate surfaces. Hence it seemed possible that $Ca^{2+}$ may be partly responsible for the curing mechanism and that a mixture containing a small amount of $CaCl_2$ may also exhibit accelerated curing. This compound would provide the mixture with a source of $Ca^{2+}$ ions but should not offer any secondary binding effect. Thus, a series of tests was carried out in order to compare the performance of lime and $CaCl_2$ with OPC.

Moulded specimens were manufactured in exactly the same way as those used in the measurements described above. OPC and hydrated lime were used at a level of 1

% by mass of aggregate, whereas the $CaCl_2$ was added to the emulsion at a level of 1 %. The samples were stored at 20 °C and 50 % relative humidity and periodically tested for stiffness modulus in the ITSM test. The results are shown in Fig 3.

It can be seen that hydrated lime and $CaCl_2$ do not have the same beneficial effect as OPC on stiffness. As lime has been seen to cause bitumen emulsion to break in other tests, these results suggest that OPC enhances the stiffness of a mixture by stiffening the binder but lime does not. Rheological tests described in Section 4.4 measured this effect directly.

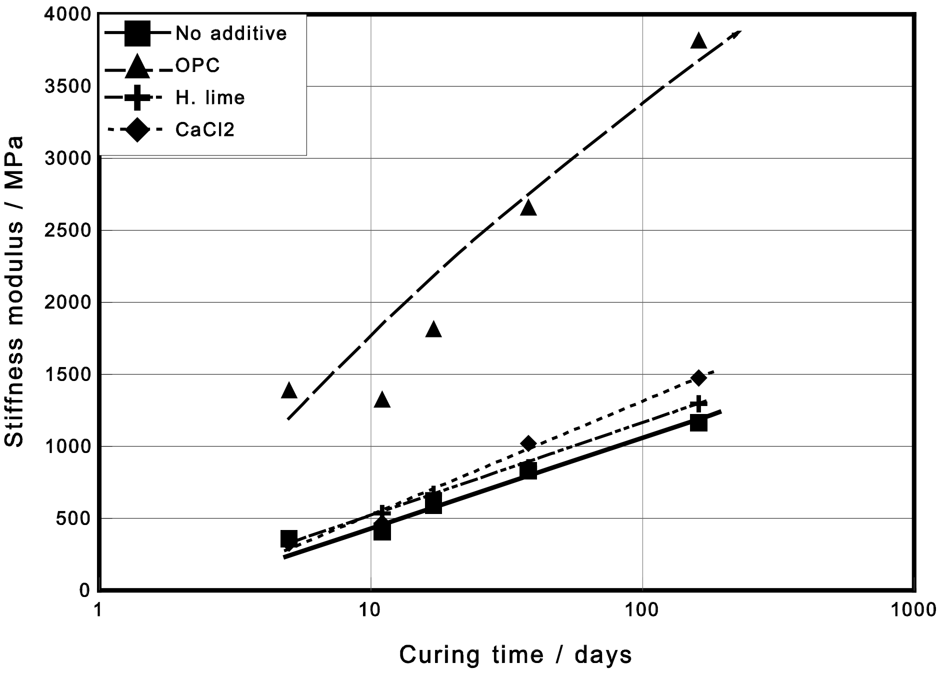


**Figure 3. Stiffness moduli of cold mix specimens with OPC, lime and $CaCI_2$**

***Resistance to Permanent Deformation***

Having established that OPC had the expected effect on stiffness modulus, the investigation proceeded to study the effect on resistance to permanent deformation. Dense bitumen macadam specimens of the same design as those used in the stiffness modulus tests were subjected to the Repeated Load Axial (RLA) test in the NAT. This is a repeated load uniaxial compression test, details of which are described elsewhere (5). However, these specimens were manufactured using a different method of compaction. A laboratory roller compactor was used with the aim of producing specimens more representative of field conditions in terms of aggregate packing characteristics. Slabs 400 x 280 x 120 mm were compacted to refusal (approximately 10 passes) and were cured at 20 °C and 50 % relative humidity for four months to allow adequate curing before 100mm diameter cores were cut and trimmed. The average void contents for each set of three cores are given in Table 3. The values were higher than those obtained by Marshall 50 blow compaction.

The cores were allowed to dry for one to two weeks and then three of the six cores were subjected to the RLA test. The test temperature was 30 °C, in keeping with normal UK practice (5). A static conditioning stress of 10 kPa for 10 minutes was used prior to testing at 100 kPa, cycled at a frequency of 0.5 Hz for 3600 cycles.

In order to allow a comparison between similar hot and cold mixtures, hot mix slabs with the same mixture design were manufactured. The aggregate mixture, binder contents and OPC addition levels were identical to those for the cold mix slabs. The cores were stored at 20 °C and then three cold mix specimens were tested under the same conditions.

Fig 4 shows the averaged results obtained from the sets of three RLA tests on cores with different levels of OPC. Logarithmic scales are used to facilitate plotting all the lines on one graph as there was a wide range of permanent axial strains.

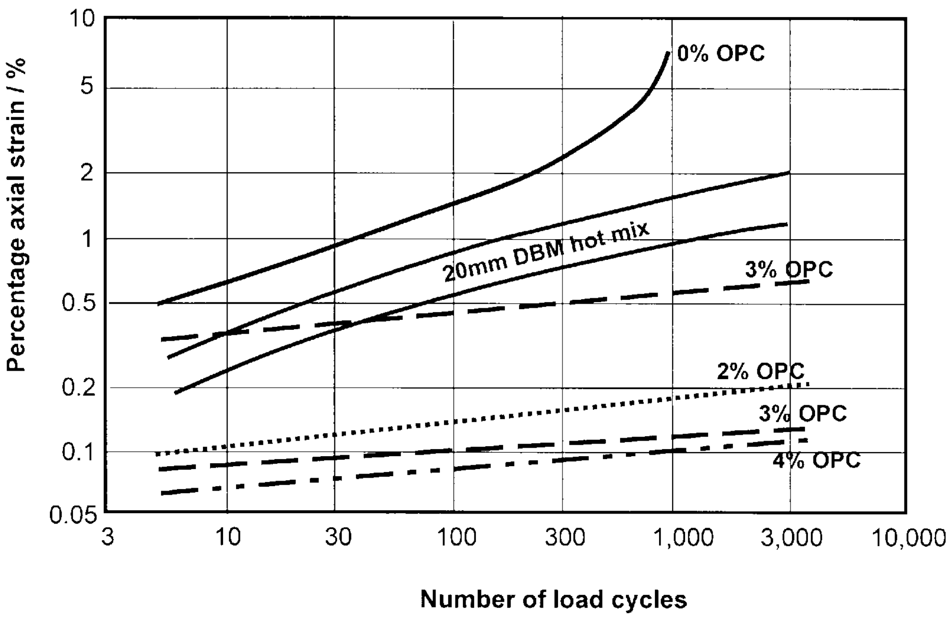


**Figure 4. Development of permanent axial strain at 30°C for various OPC contents compared with hot mix results**

**Table 3 : Void contents of cold mix cores used in RLA tests**

| OPC addition level (%) | Void content (%) |
|---|---|
| 0 | 16.4 |
| 1 | 20.3 |
| 2 | 18.2 |
| 3 | 16.6 |
| 4 | 14.7 |

The results of the RLA tests on the equivalent hot mix cores are also shown in Fig 4. The void contents of the specimens ranged from 4.2 to 5%, which are much lower than those for the cold mix specimens (Table 3).

There was a slight decrease in deformation resistance for the hot mix as OPC content increased. The results, shown in Fig 4, reveal the following points :

- Without OPC, cold mix specimens failed after less than 1,000 cycles, indicating that unmodified cold mix of the type used in this test has rather poor resistance to permanent deformation. It must, however, be noted that better performance would result from tests involving a confining stress to mobilise the deformation resistance of the aggregate skeleton.
- The resistance to permanent deformation of cold mix was increased by the addition of OPC whereas the opposite effect was seen in hot mix.
- The cold mix specimens with OPC offered better resistance to permanent

deformation than the hot mix, with or without OPC, under these unconfined test conditions, despite having higher void contents.

These results suggest that OPC acts as a secondary binder in cold mix. Hydration is necessary to activate the cement and this can only occur in the cold mix material in which water is available. In the absence of water, OPC merely acts as an inert filler.

In a road situation, the material is supported laterally so the RLA configuration presents a relatively severe test which, perhaps, over-emphasises the role of the binder. The confined version of the RLA test (8) was not available at the time this research was conducted.

***Fatigue Strength***

The resistance to fatigue cracking of mixtures with a range of OPC addition levels was determined using the Indirect Tensile Fatigue Test (ITFT) in the NAT, details of which are described elsewhere (5). This test procedure can give useful data on the relative fatigue performance of mixtures, so the effect of OPC could be quantified. Specimens were manufactured using mixture designs similar to those used in the stiffness and permanent deformation tests. OPC levels of 0, 1 and 3 % were used, and 50 blow Marshall compaction was adopted. Twelve moulded specimens of each mixture were prepared and cured for two weeks at ambient temperature and then in an oven at 60 °C for three days. Specimens were then stored at 20 °C and 50 % relative humidity over the several week long ITFT testing period. The results are shown in Fig 5 and the specimen void contents are presented in Table 4.

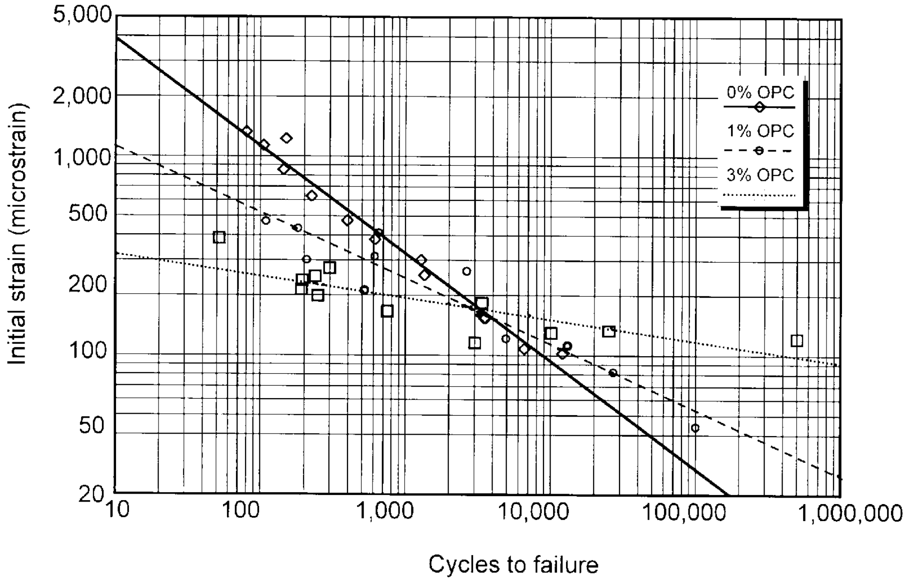


**Figure 5. Cycles to failure v initial strain for mixtures with range of OPC addition levels**

**Table 4 : Void contents of specimens with OPC used for ITF tests**

| OPC level (%) | Voids (%) |
|---|---|
| 0 | 9.9 |
| 1 | 10.6 |
| 3 | 13.4 |

The spread of data for the 0 and 1 % OPC mixtures was quite narrow ($R^2$ of 0.90 to 0.98) but, for the 3 % mixtures, there was quite a wide distribution ($R^2$ of 0.61). This was thought to be due to the brittleness of the mixture with high cement content, which had the effect of causing the specimens to split very quickly once crack initiation had occurred. Minor differences in specimens may have led to very different numbers of cycles to crack initiation. The reduction in slope of the line with increased OPC content changed the characteristics from those of a typical asphalt mixture to those of a cement treated material. The data in Fig 5 show that above 200 microstrain, the addition of OPC caused a reduction in fatigue life, whereas below 200 microstrain the reverse was true. Strain levels likely to be experienced in a pavement structure are below 200 microstrain, the actual value depending on variables such as mixture and subgrade stiffness, load and layer thickness. It can, therefore, be argued that the data below 200 microstrain are of most interest for practical purposes. Therefore the addition of OPC clearly extends the fatigue life. This effect is magnified in design since the parallel increase in stiffness reduces in situ strain.

***Influence of Water***

The effect of OPC on the resistance to water damage of mixtures has been reported by a number of authors including Ishai and Nesichi (9) and Lottman (10). Its effect on durability of mixtures used in these studies was appraised by measuring the stiffness of mixtures before and after soaking. In addition to OPC, hydrated lime and $CaCl_2$ were also assessed. Hydrated lime has been used extensively in hot mix to improve adhesion and has also been found to offer similar benefits in emulsion mixtures (1, 2). The $CaCl_2$ was incorporated in the emulsion at a level of 1% while the OPC and lime were added to the dry aggregate mixture at a level of 1%. Mixtures with the same design as those used in the tests described above were assessed by measuring the stiffness modulus in the ITSM test (5) before and after soaking. The mixtures were compacted using the 50 blow Marshall procedure. Specimens were subjected to the following soaking and testing protocol :

- Cured for 11 days at 20 °C
- 5 days under water at room temperature
- ITSM test 1
- Soaked under 28" Hg vacuum for 20 mins
- 12 days under water at room temperature
- ITSM test 2

The results shown in Fig 6 reveal a number of interesting facts :

- The mixture with OPC had a higher stiffness than the other mixtures after the first soaking period.
- Only the mixtures with OPC and hydrated lime survived the second soak.
- The mixtures with OPC and with hydrated lime exhibited a small increase in

stiffness during the second soak but this was much less than has been observed if samples are stored in a dry state.

These results indicate that OPC and hydrated lime are effective adhesion agents for emulsion mixtures. Without these additives, the mixtures studied in these tests had poor resistance to water damage. As the addition of $CaCl_2$ to the emulsion did not offer any improvement, it may be concluded that this material is ineffective and indicates that the addition of $Ca^{2+}$ ions alone is not the mechanism by which OPC and hydrated lime work.

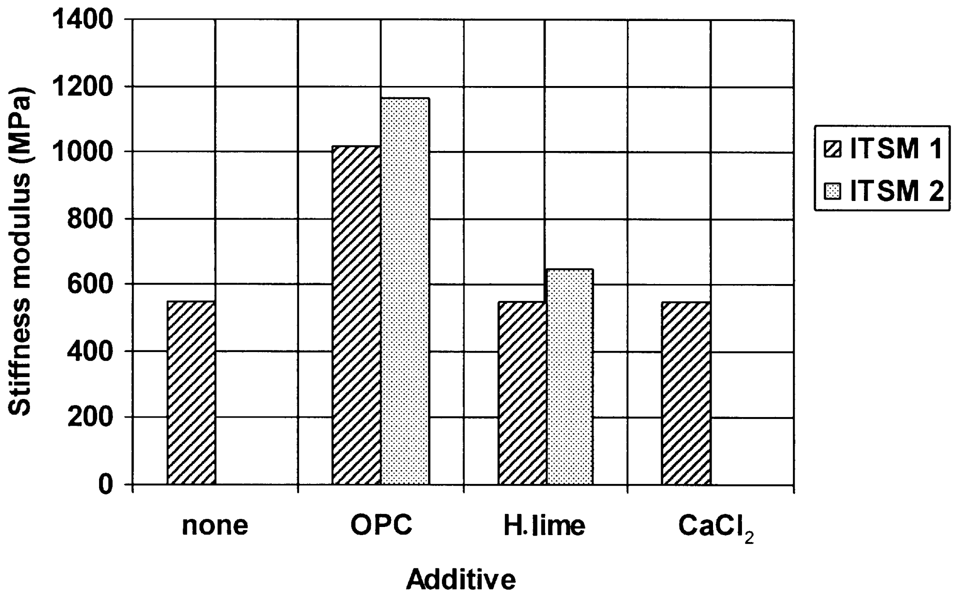


**Figure 6. Effect of OPC, Hydrated Lime and $CaCl_2$ on Stiffness Modulus**

In order to directly measure the adhesion effect of OPC, a simple boiling adhesion test was carried out according to a standard ISSA test (11) normally used to test wet stripping resistance of cured slurry seals. Uncompacted samples of mixtures with and without cement were fully cured in an oven at 60 °C for 3 days. 10 g samples were boiled in water in a beaker for 3 minutes and allowed to cool. When ebullition had ceased, cold water was run into the beaker until the overflow became clear. The mixtures were removed from the beakers and placed on a filter paper. A visual appraisal of the percentage coverage of the mixtures was then made. The mixture with no OPC had only 50 % coverage whilst the mixture with 1% OPC still had 95 to 100 % binder on its surface. This illustrates the improved adhesion of the binder in the presence of OPC.

## Coalescence Tests

### *Introduction*

Immediately after compaction, it is clear from studies of mechanical properties, that cold mix has a limited amount of strength arising from interlock and friction of the aggregate structure, cohesion arising from the capillary action of water in the mixture and, possibly, a small amount of cohesion from the partially coalesced bitumen. The latter is dependent in magnitude on the amount of coalescence of bitumen which has occurred during compaction and its adhesion to the aggregate. Coalescence is the term used to describe the transition from emulsified bitumen droplets to continuous bitumen. This is the process by which an effective bituminous binder is obtained from bitumen emulsion. Binder cohesion is necessary to give the mixture its stiffness, tensile strength and durability.

***Test Method***

Testing of the mechanical properties of bitumen emulsion does not directly measure coalescence. In order to gain an insight into the curing process, a test method was developed to measure the quantity of emulsified bitumen which coalesces during compaction and in the early life of a compacted mixture to give a continuous bituminous phase which is resistant to re-dispersion by water rinsing. These experiments, detailed elsewhere (7), investigated a range of relevant parameters and included the effects of cement addition.

The test involved mixing an aggregate sample with emulsion, followed by compaction, rinsing off the free emulsion and, finally, measurement of the retained bitumen content by solvent extraction. This was taken as the percentage coalescence of the emulsion during compaction.

***Results***

Mixtures were prepared with different levels of OPC added to the aggregate, prior to pre-wet water and standard bitumen emulsion, and compacted using a static pressure of 16 MPa applied in three periods of 30 seconds.

Fig 7 shows that the addition of OPC increased the amount of coalescence. The results showed some scatter which was probably caused by loss of OPC during the rinsing or extraction processes.

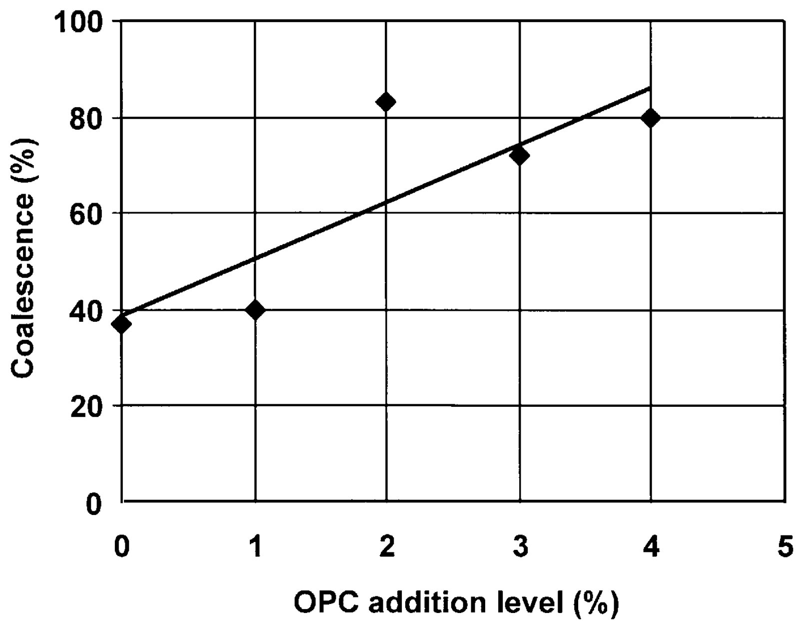


**Figure 7. Effect of OPC on Coalescence**

## Properties of Bitumen Emulsion Residues

***Introduction***

In the foregoing sections of this paper, the results of various tests have illustrated the ways in which the mechanical properties of bitumen emulsion mixtures develop over time and how the addition of OPC affects the process, particularly with regard to coalescence of bitumen droplets. The main variable in these tests was the binder, as the same aggregate was used throughout. The tests described in this section were aimed at studying the behaviour and properties of the binder in combination with OPC, in the absence of aggregate with a view to understanding the fundamental processes which influence the mechanical properties of cold mix. Mixtures of emulsion and cement were studied in order to determine the emulsion breaking process and also the properties of the composite binder.

***Breaking behaviour of emulsion and OPC mixtures***

Mixtures of bitumen emulsion and cement were produced. 200g samples of the emulsion were used, to which a certain amount of water had been added based on that which would be required in a real mixture with aggregate. Cement was added at levels of 1 to 10 %, by weight of a hypothetical aggregate mixture, and stirred for about 30 seconds. In most of the mixtures made throughout the course of these studies, emulsion was normally added at a level of 8.1% of the aggregate mass and so, in relation to the emulsion, these addition levels corresponded to a range of ratios from 1:8.1 to 10:8.1 (cement : emulsion). The mixtures were sealed with plastic film and inspected periodically. An assessment of the percentage break of the emulsion was made by means of a comparative estimate. This method was very subjective but it was felt that the decisions recorded were fairly accurate, at least within this set of tests. After 48 hours, all of the mixtures had set completely and were found to consist of a solid mass of bitumen - cement mastic with slightly yellow coloured clear water on top. The setting times of mixtures with various OPC addition levels are given in Table 5.

**Table 5 : Breaking behaviour of bitumen emulsion with cement**

| Cement * | Percentage coalescence of mix | | | | |
|---|---|---|---|---|---|
| | 1 hr | 4 hr | 6.5 hr | 24 hrs | 48 hrs |
| 1 | 0 | 0 | 5 | 10 | 100 |
| 2 | 0 | 0 | 10 | 100 | - |
| 3 | 0 | 10 | 50 | 100 | - |
| 4 | 0 | 10 | 100 | - | - |
| 5 | 0 | 50 | 100 | - | - |
| 6 | 10 | 100 | - | - | - |
| 7 | 15 | 100 | - | - | - |
| 8 | 15 | 100 | - | - | - |
| 9 | 15 | 100 | - | - | - |
| 10 | 15 | 100 | - | - | - |

* - expressed as percentage weight on a hypothetical aggregate mix

These results show that the addition of as little as 1 % OPC to an aggregate mixture (corresponding to 12 % OPC in the emulsion), caused the emulsion to fully break within 48 hours. Increasing the level of OPC resulted in decreasing break times. The speed with which the emulsion broke contrasted with the findings from the stiffness modulus tests on full mixtures containing cement. In these tests, stiffness was found to build steadily over a number of weeks. According to the tests described here, the binder should be fully cured after only 48 hours, resulting in the ultimate stiffness being reached. It is, therefore, apparent that the presence of the aggregate has an important effect on the process.

***Penetration and pH tests***

The mixtures obtained from the breaking tests described above were used for the tests which follow. Water was poured off the solidified binder residues, weighed and a measurement of pH taken. After a further 48-hour drying period at ambient temperature, the mixtures were all brought to a temperature of 25°C in a water bath. The penetrations of the cured mastics were then measured, using a standard penetrometer (12) with a total needle weight of 100 g, and load times of 5 and 60 s. The 60 s load time was used as the 5 s period gave very low values due to the very hard nature of some of the mastics.

From the results of the pH measurements on the water evolved from emulsion breaking, the addition of only 1 % OPC increased the pH from about 6 to over 13. Increasing the level of OPC only caused a slight further increase in pH. OPC is a very alkaline substance and, therefore, the results were not surprising. The mechanism of emulsion break through the addition of OPC may, therefore, be partly due to the pH shift. However, the fact that 1 % OPC has almost the same effect on pH as 10 % OPC indicates that the increase in breaking rate of mixtures with higher levels of OPC was not due to a pH effect. It should be noted that the pH of run-off water from a full mixture was found to be 11.7. This is slightly lower than the pH's reported here but still very alkaline.

**Table 6 : Penetration of cured mastics**

| Cement * | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Pen / 5 s (dmm) | 112 | 82 | 27 | 10 | 13 | 10 | 4 | 3 | 5 | 5 |
| Pen / 60 s (dmm) | 189 | 157 | 100 | 48 | 36 | 30 | 20 | 18 | 18 | 15 |

* - expressed as percentage weight on a hypothetical aggregate mix

The results shown in Table 6 revealed that the presence of OPC had a significant effect on penetration. The bitumen in the emulsion used for these tests was nominally 100 pen. The addition of 2 % or more of OPC resulted in a reduction in penetration of the residual binder. Stiffening of the binder in this way would have a major effect on the mixture stiffness. It is unclear why the mastic with 1 % OPC was softer than the virgin bitumen but it was probably caused by the entrainment of a small amount of water in the mixture.

***Rheological Properties***

Mixtures of bitumen emulsion with OPC and with hydrated lime and of 100 pen Venezuelan bitumen with limestone filler were prepared and used for rheological measurements using a Bohlin Dynamic Shear Rheometer.

Mixtures similar to those used for the penetration measurements were prepared, by adding OPC or hydrated lime, at a range of addition levels, to samples of the standard emulsion and rolling in bottles for several days until full emulsion break had occurred. In addition, mixtures of hot binder with OPC, hydrated lime and limestone filler were produced to provide a comparison between the inert filler and the chemically active materials. The initial particle sizes of all three additives were similar (ie, < 75 µm). Samples of 100 pen bitumen recovered from an emulsion mixture were also tested. All of the samples produced were then used for rheological measurements in the DSR at 20°C.

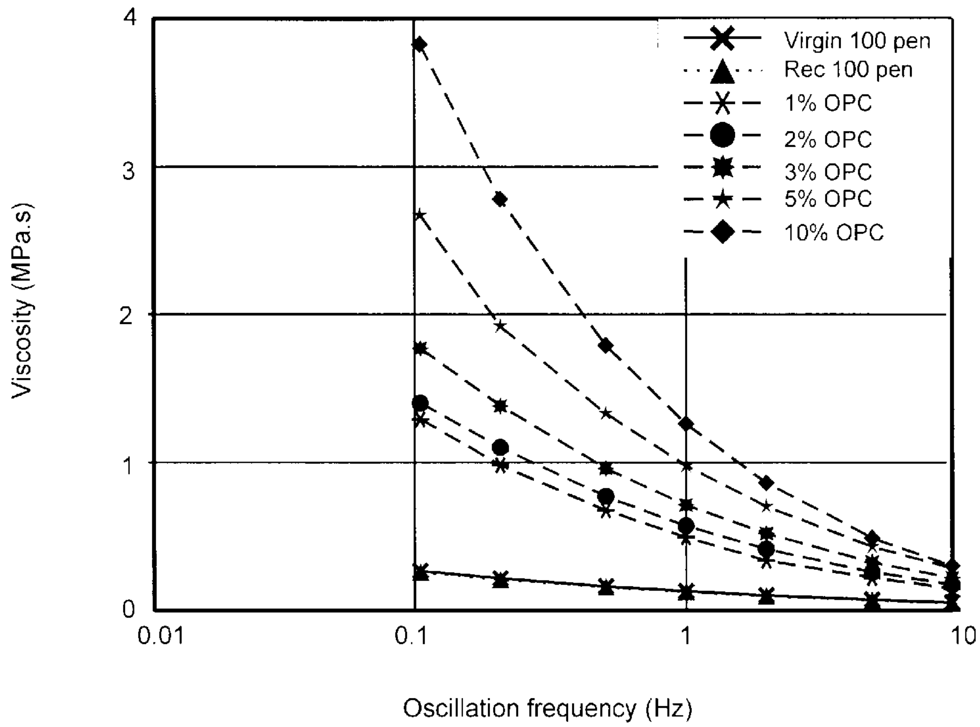


**Figure 8. Viscosity of bitumen and emulsion residues with different levels of OPC**

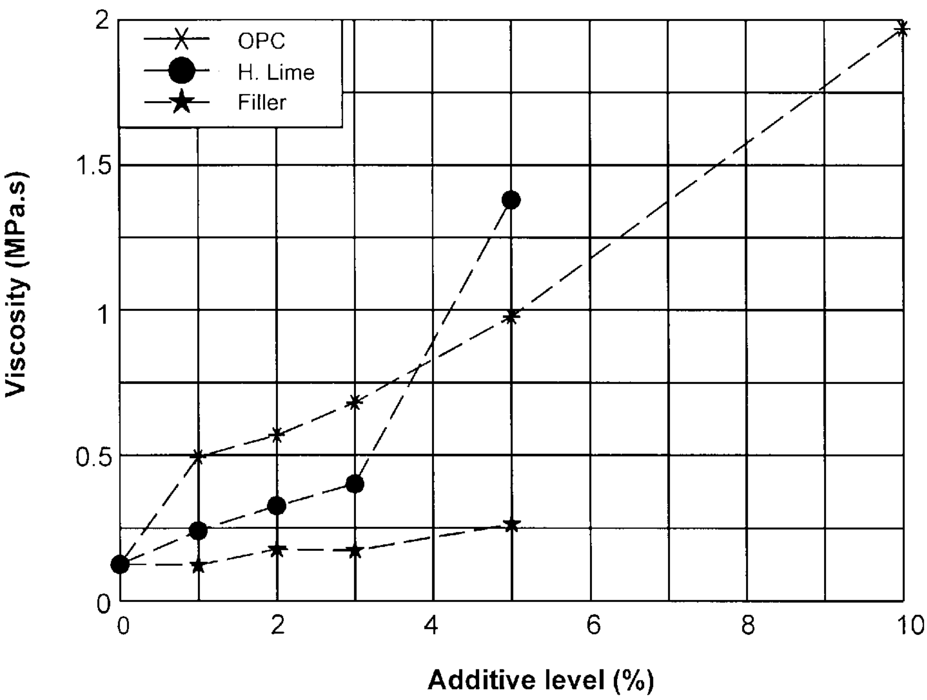


**Figure 9. Viscosity of emulsion residues v additive level for 1Hz oscillation frequency**

The results revealed a number of interesting features regarding the rheological effects of OPC, hydrated lime and limestone filler on bitumen and bitumen emulsion residues. The stiffening effect of increased quantities of OPC is very apparent from Fig 8. It also shows that the viscosity characteristics of virgin 100 pen bitumen and the same binder recovered from an emulsion without modification were identical.

In Fig 9, it can be seen that hydrated lime also increased the viscosity of the recovered binders with OPC having the larger effect up to the 3 % addition level. Above 3 %, lime had the greater effect. This may be caused by hydrated lime having a lower bulk density and, hence, occupying a larger volume than OPC. It may be that a point is reached at which the lime contributes such a large volume to the binder that it becomes the predominant component in the binder / lime mixture in terms of volume, thereby having a dramatic effect on viscosity. This situation could be envisaged as a paste in which the lime solids were merely partially coated with bitumen rather than being fully dispersed.

Fig 9 also shows that limestone filler had a very limited effect on viscosity compared with OPC and lime, so it would appear that these chemically active additives contribute something which filler alone cannot.

The other DSR data showed that the effects in Figs 8 and 9 on viscosity were the same as those on storage modulus and on loss modulus.

***Heat of hydration effects***

It is well known that the hydration reaction of OPC can cause a noticeable temperature rise in concrete mixtures (13). The effect of heat of cement hydration on bitumen emulsion mixtures may also be significant. A rise in temperature would increase the rate of reaction between aggregate and emulsion and, if large, could increase the rate of water evaporation from a mixture. Both of these effects could increase the breaking rate of the emulsion and the curing rate of the mixture. Due to the acidity of some emulsions, such as the one used as the standard in these studies, the cement hydration reaction may be even more rapid and exothermic.

A test was carried out to measure the temperature rise which occurs during the reaction between cement and the acidic bitumen emulsion in the absence of aggregate. A mixture of the emulsion and 10 % OPC was produced and placed in an insulated beaker. The change in temperature was monitored over a period of time by means of a sensitive mercury thermometer. The pH was also monitored, in an attempt to follow the progress of the reaction. The results showed only a small temperature rise (22.2 to 25°C) in 30 minutes. The pH was seen to jump from 3.47 before the addition of OPC to 12.25 immediately after and then rose very slightly to 12.62 and stabilized at this level. These results suggests that the reaction was complete after 30 minutes and that it did not result in a temperature rise large enough to affect the curing rate of an emulsion mixture.

### *Cement and water mixtures*

Emulsion mixtures consist of aggregate, water and bitumen emulsion, and sometimes, as in this research, additives such as cement. As the emulsion, added at a level of about 8%, contains around 38% water, and pre-wet water is added at a level of 2 to 3 %, the total amount of water in a mixture is about 5 to 6% by mass of aggregate. When cement is added to the mixture, at a level of 1 or 2% by mass of the aggregate, the ratio of cement to water is very high at 1 : 6 to 2 : 6. According to the literature (13), cement is able to absorb only 20 to 25% of its own mass in water. There is, therefore, a large excess of water in an emulsion mixture, with respect to the cement. It is true to say that the aggregate will absorb some of the available water but there will still be an excess. This was confirmed by observing water cement mixtures with cement : water ratios between 1:6 and 6:1.

The samples were inspected after intervals of 2 hours, 24 hours and 1 week. After 1 week, the cement and water phases had separated in all cases, resulting in either fully set cement or a cementitious precipitate.

The OPC was able to fully absorb a maximum of 33 % its own mass in water. At a ratio of 1:1 OPC to water, the cement was still able to set and excess water separated out. Above this ratio, the cement was unable to set properly and merely formed a soft precipitate. In a real mixture, the ratio of cement to water is 1:6 if 1 % OPC is employed. According to these tests, in this situation, the cement would be unable to set initially and would only do so after a substantial amount of the excess water had evaporated. This is probably the cause for the steady increase in stiffness of mixtures containing OPC, albeit more rapid than mixtures without. In advanced stages of curing, when the water content was low, OPC would have been able to set properly and act as a competent binder.

### *Electron microscopy studies of binder residues and OPC*

It has been well established, through the results from tests described above, that OPC has a beneficial effect on an emulsion mixture in a number of ways. The coalescence tests showed that it increases the breaking rate of the bitumen emulsion, which will increase the curing rate of the mixture. Mechanical property measurements showed that OPC increases the curing rate and final stiffness of a mixture, and that cold mix with 1% or more of cement can reach a higher stiffness modulus than an equivalent hot mix. It has been shown that this is not due to a filler effect, as hot mix with 1% OPC is little different from that without. Rheological measurements showed that OPC increases the viscosity of the cured mastic. The evidence seems to suggest that the incorporation of cement causes a composite binder to be formed with the curing or cured bituminous binder. This composite has very much improved properties compared with bitumen alone.

In an attempt to improve understanding of the mechanisms involved, electron microscope observations were made to examine the cement/bitumen mastic. As cement particles are in the region of 5 to 75 μm in size and recrystallized cementitious crystals are in the order of a few microns, and emulsified bitumen droplets average 5 to 10 μm, it was considered that there should be a good chance of observing any features which may evolve following the cure of a cementitious cold mix.

A selection of specimens was prepared from emulsion mixtures, with and without OPC, and observed through an electron microscope after a prolonged period of curing to ensure full cement cure was achieved.

Mixtures were prepared using the standard emulsion and granite aggregate with a mid 20 mm DBM grading. OPC was added to the dry aggregate mixture at levels of 0 and 2 %. The specimens thus produced were stored at 20°C and 50% relative humidity for several months to allow sufficient time for any composite structures to form. Mixtures of granite aggregate and the cement were also prepared to enable the appearance of normal concrete-type mixtures to be observed.

In addition to the full mixtures, blends of emulsion and cement were prepared in the absence of water, as it was suspected that it may be difficult to see any features in the mixtures which contained aggregate. The proportions of emulsion and cement were such that the ratio of ingredients was the same as that which would be used in a full mixture.

After curing, the mixture specimens and emulsion / cement mastics were crudely broken into small pieces by hand. The intention was to produce surfaces showing exposed binder which had not been subjected to any treatment that might alter its appearance.

The samples were mounted and coated in gold according to the normal procedure used to produce samples for electron microscopy. Samples were photographed at a range of magnifications from x 20 to x 3000. At medium magnification, features of interest were picked out and further magnified if this proved beneficial. Thus, a series of micrographs of the mixtures without OPC and with 2 % OPC, the granite and OPC alone and the bitumen and cement mastics were obtained at a number of magnifications.

In addition to producing magnified images, a selection of which are shown in Figs 10 to 16, the electron microscope is able to analyse the elemental composition of selected areas of a specimen. Elemental analysis was carried out during microscopy on the full mixtures to determine which features were aggregate and which were cementitious. This was not done on the emulsion / cement residues as all crystalline structures could only be cementitious and the crystal morphologies alone were sufficient to allow identification.

Elemental analysis showed up a clear difference between aggregate and cement in full mixtures with and without cement. The difference was in the calcium content, with cement showing much higher levels than other components. Consequently, the particles shown in Figs 11 and 13 were identified as cementitious due to their high calcium content.

It is clear from Figs 10 and 11 that the mixture with 2% cement is much rougher in texture, having a pock marked surface compared with the smooth surface of the mixture with no cement. At higher magnifications (Figs 12 and 13), the mixture containing cement has many crystalline features, which are not evident in the other specimen, and some definite bubble type artifacts can also be seen. The elemental analysis results confirmed that these are cementitious regions.

A lot more features can be seen in the photographs of the cement/emulsion. (Figs 14 to 16). The smooth areas are certainly bitumen and the different phases of recrystallized cement can also be seen. These photographs were interpreted by a concrete specialist (Dr I G Richardson from the University of Leeds, UK) who confirmed that the characteristics of ettringite, calcium hydroxide and calcium silicate structures were present. All of these species are to be found in normal hardened concrete. In addition to the crystal groundmass, as it is termed, concrete also normally contains pores which arise mostly from gas bubbles or evaporation of water droplets. Some pores were evident in the mixtures observed here. Most of the evidence of these observations, therefore, seems to suggest that the cement cured in much the same manner as it would in a normal concrete mixture. Thus, it would be expected that the material acts as a binder to some extent. Some of the images also suggest that the cementitious phase is dispersed within the bituminous binder. This could have the additional effect of stiffening the organic binder.

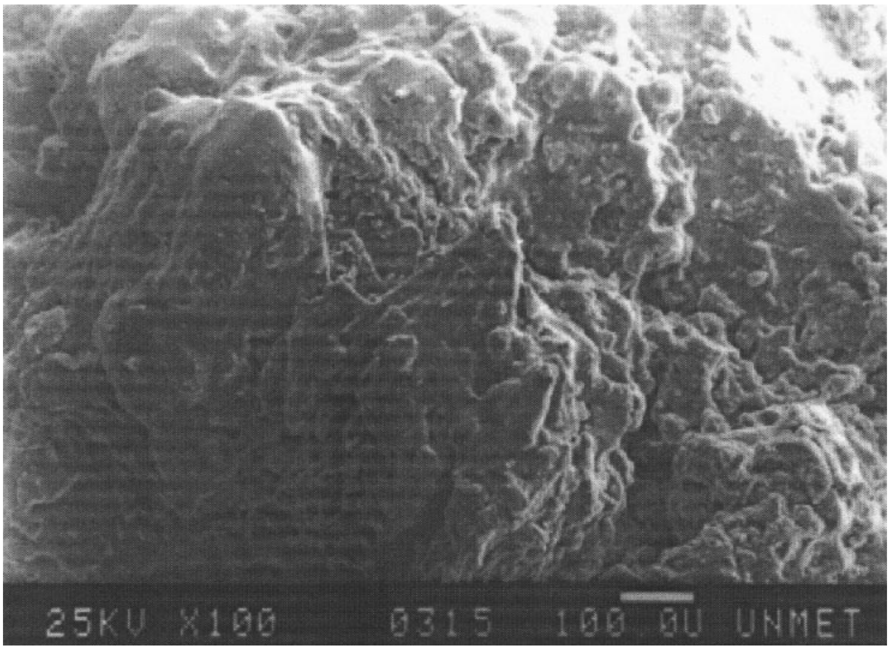


**Figure 10. Mixture with no OPC**

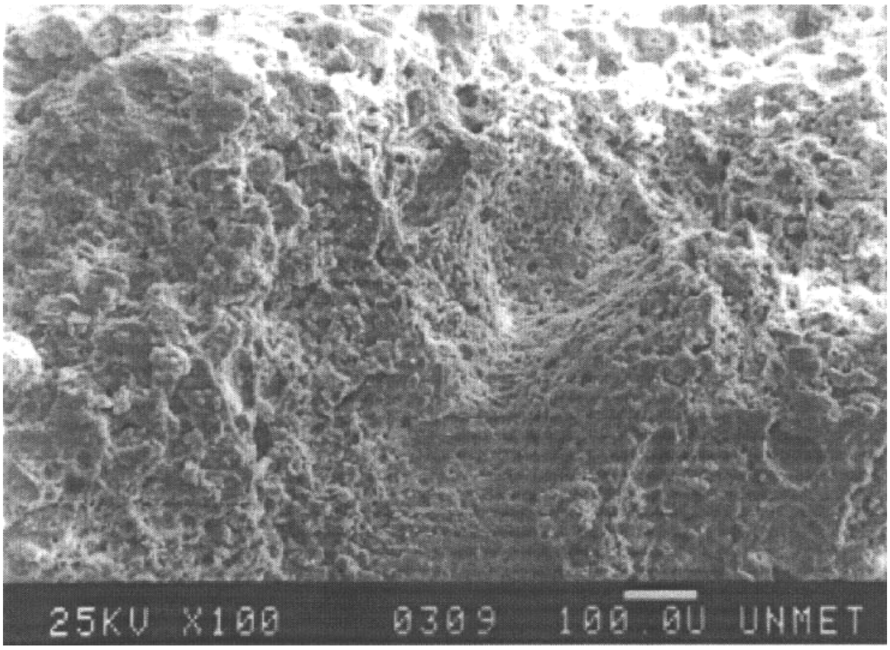


**Figure 11. Mixture with 2% OPC**

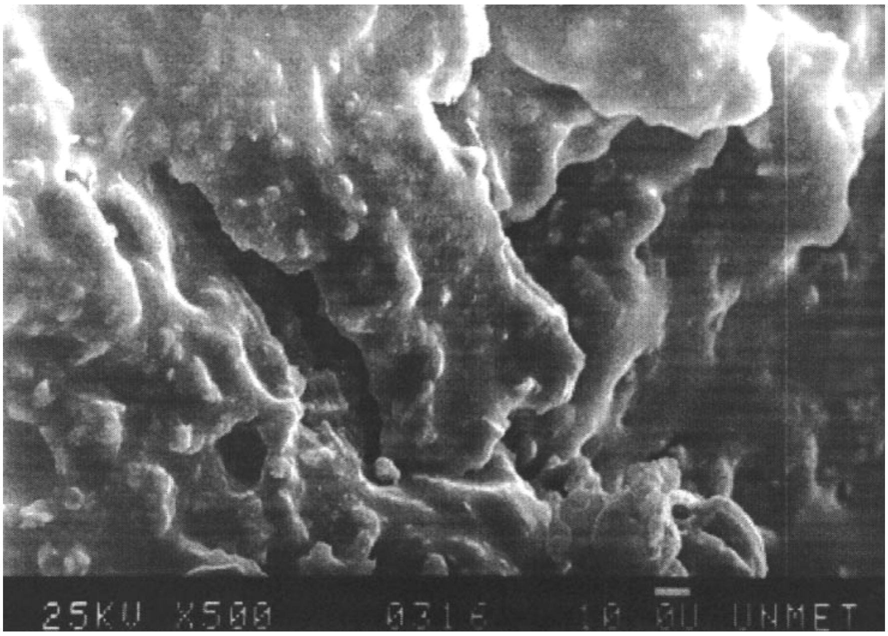


**Figure 12. Mixture with no OPC**

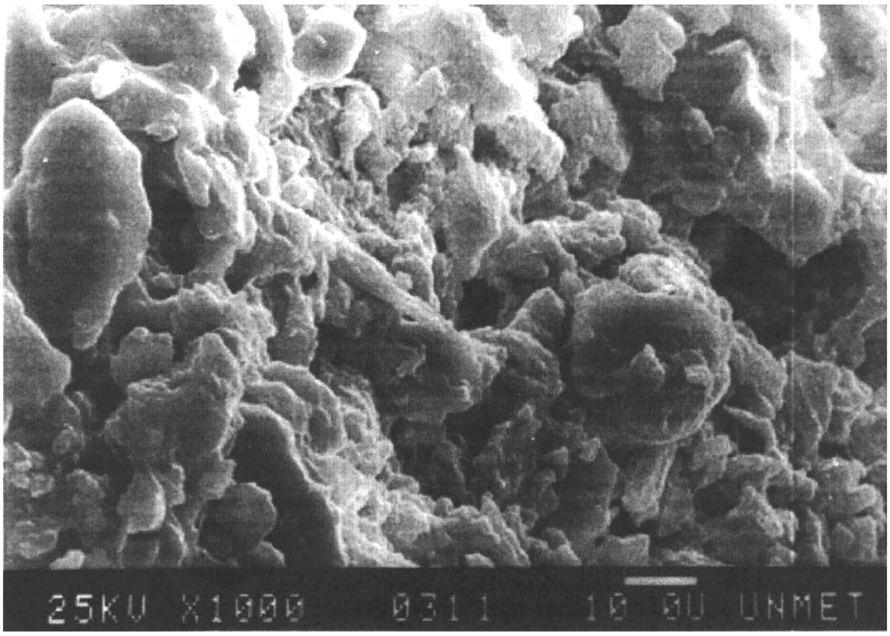


**Figure 13. Mixture with 2% OPC**

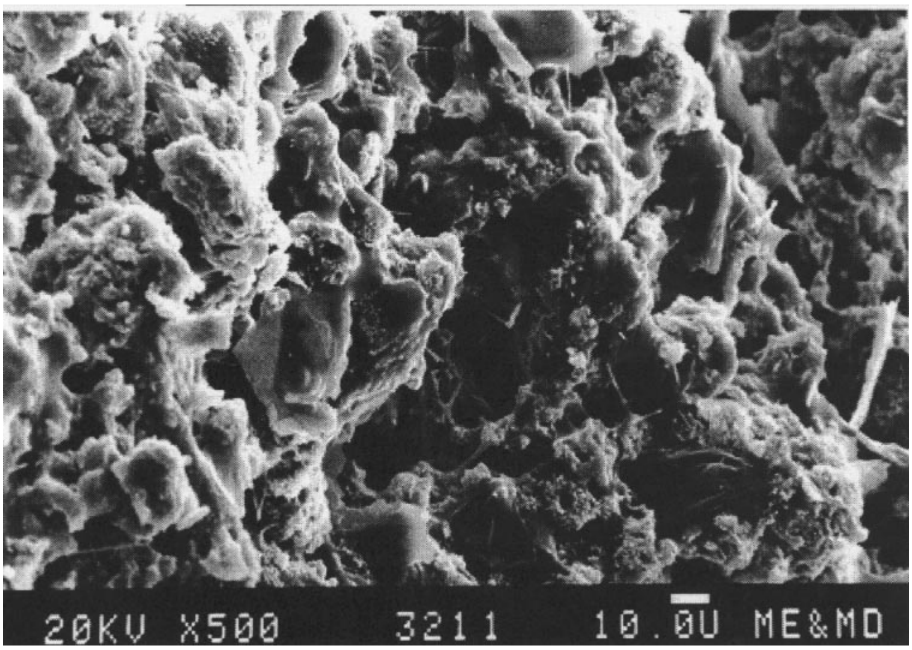


**Figure 14. Ettringite crystals in mastic**

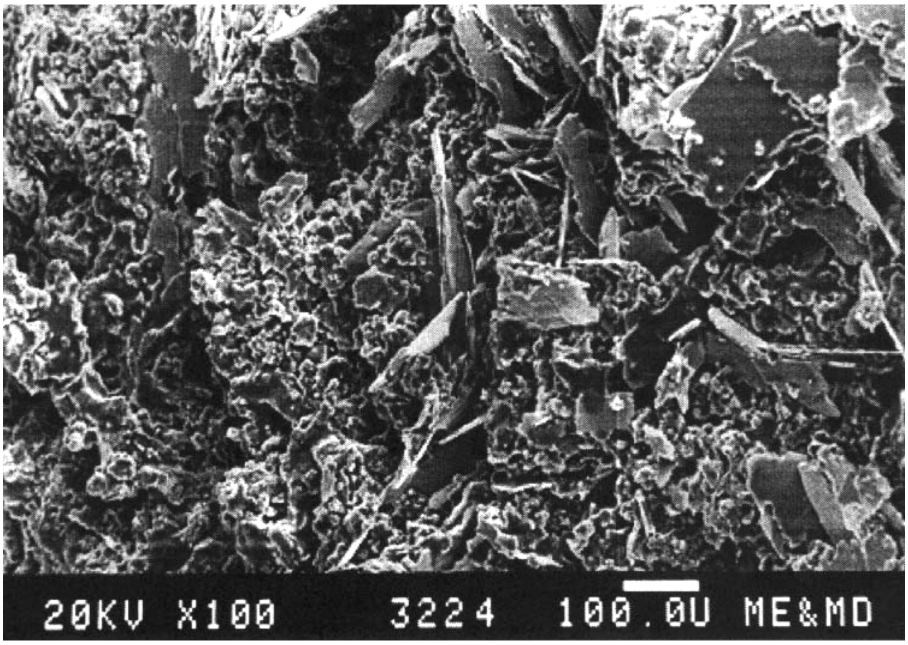


**Figure 15. CH crystals in mastic**

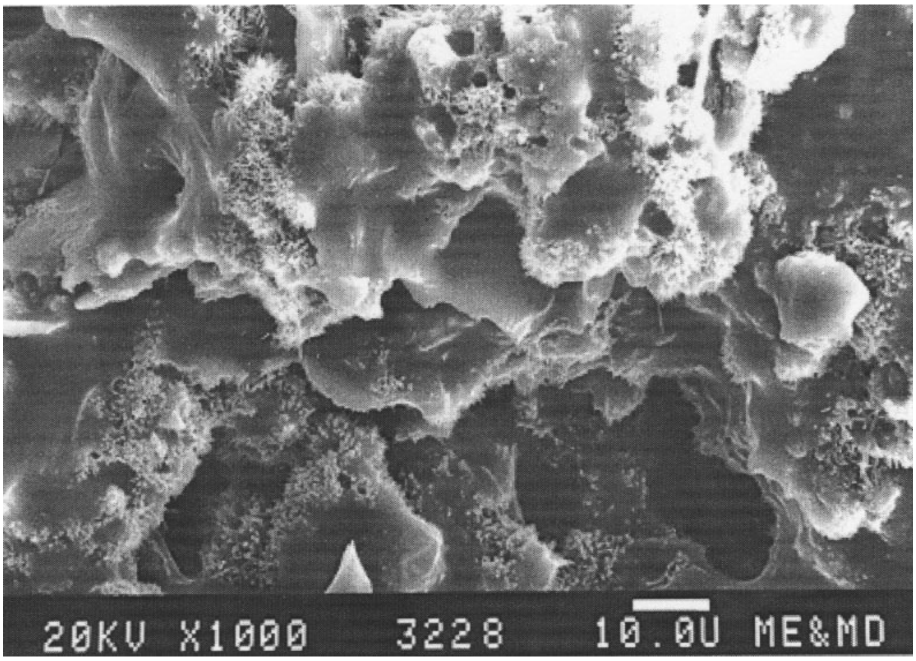


**Figure 16. C-S-H crystals in mastic**

## Discussion and Conclusions

The experimental results reported in this paper have focussed on developing an improved understanding of the role of Ordinary Portland Cement in enhancing the mechanical properties of bitumen emulsion mixtures for structural layers in roads.

The results of tests to measure mechanical properties confirmed earlier research findings that the three key mechanical properties, stiffness modulus, permanent deformation resistance and fatigue strength are all improved by OPC addition. The work further demonstrated that the ultimate stiffness achieved after curing and the rate of stiffness gain increased with increasing OPC content up to the 4% level applied here.

Stiffness modulus and permanent deformation resistance levels in OPC modified cold mix were shown to be comparable with equivalent hot mix, even though the compaction levels were lower. These properties, however, take some time to develop but OPC addition certainly improves the critical early life properties too.

Water in emulsion mixtures is a vital ingredient of the process but becomes a problem in terms of inhibiting compaction and delaying strength gain. Tests showed that most of the water loss was achieved in the first seven days but some remained in the longer term. This is considered to explain the increase in stiffness over several weeks or months, particularly in the presence of cement.

A major theme of this work has been to demonstrate that OPC has a role as a binder in the mixtures through the normal hydration process which takes place in concrete. The presence of too much water inhibits this process initially but it gradually develops with time as the appropriate water : cement ratio develops due to evaporation.

The idea that calcium is the active ingredient was disproved through tests on mixtures with calcium chloride and with hydrated lime, neither of which enhanced the stiffness modulus.

The data on fatigue strength was less certain than the other mechanical properties and further work on this matter is required. However, at the tensile strain levels normally occurring in pavements, an extension of life is likely for OPC modified cold mix, particularly noting that increased stiffness will cause a reduction in the strain magnitude.

One of the other benefits of OPC addition was to increase resistance to water damage as effectively as hydrated lime. The basic studies to understand how OPC causes enhancement of mechanical properties showed that one of the effects is to increase the rate of coalescence of bitumen droplets which speeds up the overall strength gain process. This was not simply a matter of absorbing water, since rapid hardening cements, which are more effective at this, did not have the same effect.

In the absence of the aggregate, bitumen emulsion/cement residues break within 48 hours. Clearly the process takes longer in the presence of the aggregate. The increase in pH caused by the OPC helps with breaking but only a 1% addition is required for this.

OPC addition was shown to increase the penetration value of residues and to increase viscosity significantly. It was noted that OPC, which is a chemically active filler in cold mix, achieved this but that limestone filler did not.

The Scanning Electron Microscope studies provided evidence that hydration of the cement occurs and that some of the cement becomes a part of the binder. Hence, the stiffening effect is through two mechanisms.

The background insight provided by this research provides a good basis for the design of improved cold mix for structural use in pavements in climates where this material has not previously been used.

The main conclusions from the study, based on the particular materials which were used, are:-

1. Addition of Ordinary Portland Cement to bitumen emulsion mixtures provides a general enhancement of mechanical properties to levels that are comparable with

those of hot mix.
2. The mechanisms which cause this effect include hydration of the cement, increasing the rate of coalescence and increasing the binder viscosity.


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## References


1. R.L. Terrel and C.K. Wang, "Early Curing behaviour of Cement Modified Asphalt Emulsion Mixtures", Proc. of the AAPT, Vol 40, pp 108-125, 1971.
2. R.J Schmidt, L.E. Santucci and L.D. Coyne, "Performance Characteristics of Cement Modified Asphalt Emulsion Mixes", Proc. of the AAPT, Vol. 42, pp 300-319, 1973.
3. R.W. Head, "An Informal Report of Cold Mix Research using Emulsified Asphalt as Binder", Proc. of the AAPT, Vol 43, pp 110-131, 1974.
4. British Standards Institution, BS 4987 : Part 1 "Coated macadam for roads and other paved areas", HMSO, 1988.
5. S.F. Brown, "Practical Test Procedures for the Mechanical Properties of Bituminous Materials", Proc. Inst. Civ. Engrs. Transp., pp 289-297, Nov. 1995.
6. V.P. Puzinauskis and R.N. Jester, "Design of Emulsified paving Mixtures", NCHRP Report No. 259, Transp. Res. Board, Washington, DC,1983.
7. D. Needham, "Developments in Bitumen Emulsion Mixtures for Roads", PhD thesis, University of Nottingham, 1996.
8. S.F. Brown and T.V. Scholz, "Permanent deformation characteristics of porous asphalt determined in the confined repeated load axial test", Highways and Transportation, Vol. 45, No. 12 , pp 7-10, 1998.
9. I. Ishai, S. Nesichi, "Laboratory Evaluation of Moisture Damage to Bituminous Paving Mixtures by Long-Term Hot Immersion", TRR 1171, Transportation Research Board, Washington D.C., 1988.
10. R.P. Lottman, "Laboratory Test Method for Predicting Moisture-Induced Damage to Asphalt Concrete", TRR 843, Transportation Research Board, Washington D.C., 1982.
11. International Slurry Seal Association, Technical Bulletin No. 114, "Wet Stripping Test for Cured Slurry Seal Mix", ISSA, 1990.
12. British Standards Institution, BS 2000, "petroleum and its products, part 49, Penetrtion of bituminous materials", London, 1993.
13. S.H. Kosmatka, W.C Panarese, "Design and Control of Concrete Mixtures", 13th edition, Portland Cement Association, 1988, Skokie, Illinois.