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The benefits of using Ordinary Portland Cement in solvent free dense graded bituminous emulsion mixtures

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ABSTRACT

It has been known for a number of years that the addition of Ordinary Portland Cement (OPC) to bituminous emulsion mixtures can yield certain benefits. Mixtures with slow setting emulsions can be slow to cure. Laboratory and field studies have demonstrated that OPC increases the rate of strength build up, the final strength and the resistance to damage from water in these mixtures. However, little is known about the mechanisms behind these effects and the influence of OPC on resistance to permanent deformation and fatigue cracking of the mixtures.

Indirect Tensile Stiffness Modulus tests have shown that with the addition of 1% OPC, the rate of increase of stiffness over several weeks, and the final stiffness, are substantially improved compared to cement-free mixtures, reaching levels comparable with or higher than equivalent hot mix materials. Repeated load axial tests have revealed that cement increases a mixture's resistance to permanent deformation. The mechanisms behind these effects have been studied using mixtures of cement and emulsion alone and by a new technique which measures the coalescence of bitumen emulsion which occurs during compaction. Mixtures of emulsion and cement alone have revealed that the addition of OPC to the emulsion causes it to break, forming a bitumen - cement mastic which can be of significantly higher viscosity than the base bitumen. Coalescence tests have shown that OPC significantly increases the degree of emulsion break under compaction.

Measurements on the electrochemical properties of mixtures of bitumen emulsion and aggregate showed that the presence of OPC generates a small attractive charge between emulsion and aggregate.

Electron microscopy observations have started to show differences in the state of the binder in mixtures with and without cement.

The results confirm the beneficial effect of OPC in solvent-free, dense-graded emulsion mixtures and a mechanism for the effects is proposed. Cement acts to increase the rate of 'breaking' and coalescence of the emulsion, increases the electrostatic interaction between bitumen emulsion droplets and s~iceous aggregate surfaces and forms a composite mastic with enhanced properties relative to an unmodified binder.

1.0 INTRODUCTION

Bitumen emulsion has been used in place of hot bitumen in bituminous mixtures since the 1920's. A bitumen emulsion is a dispersion of bitumen in water in which the bitumen droplets are 1 to 20 μm in diameter. The system is stabilized by surfactant molecules, or emulsifiers, at the bitumen-water interface. Emulsions with different setting characteristics can be produced by use of special emulsifiers. Rapid setting emulsions are used for surface dressing applications where very fast curing is required. Through the use of slow-setting emulsifiers, emulsions can be manufactured which can be combined with dense graded aggregate mixtures in much the same way as hot bitumen in "hot mix". A very stable emulsion is necessary to enable the binder to fully coat these aggregate mixtures which have very high surface areas. As emulsion mixtures are produced without heating at any stage, these mixtures have been given the generic name of "cold mix". For a hot mix to cure, the hot, fluid bitumen need only cool to revert to its original viscous state. As a cold mix cures the emulsified bitumen droplets must coalesce to revert to a continuous hinder phase. This is known as "breaking" of the emulsion. In mixtures utilizing slow-setting emulsifiers, this process can he very' slow and during the curing period the mixtures arc susceptible to water damage.

The fact that the use of emulsified asphalt mixtures (cold mix) offers certain benefits over hot mix has been accepted for many years. Cold mix has logistical advantages over hot mix, in that it can be stockpiled or transported over long distances without special precautions. Additionally, investment in cold mix plant is far lower than in the more complicated hot mix plant which is particularly advantageous in developing countries. There are also environmental benefits. As aggregate sdo not have to be dried for use in emulsion mixtures, dust emissions are eliminated. Gaseous emissions typical of hot mix road construction, which are potentially harmful to health (Gorkum et. al., 1993) and the environment, are reduced enormously, as bitumen is only heated during the emulsification process. Energy savings can also be realized through the use of cold mixtures. A number of reports have shown that cold mix uses about half the energy of hot mix on a tonne for tonne basis (OECD, 1984, USEPA 1.978). An emerging problem in certain countries is being solved by the use of emulsion mixtures. Old roads containing tar release harmful polycyclic aromatic compounds into the environment (Hiersche and Chant, 1994). Mixtures of slow setting emulsions and cement allow these old pavements to be safely recycled without any potentially hazardous heating process. Emulsion mixtures also offer potential improvements in performance. Firstly, hardening of the binder through oxidation and other processes, which can occur during the heating process (James and Stewart, 1991), is avoided. Additionally, polymers in latex form can be easily incorporated which is not possible with hot mix.

For these reasons, suitable cold mix materials are in great demand but at present products are not available for use in all situations. Roads carrying low traffic volumes or roads in warm dry climates can be constructed using current emulsion mixture technology. However, high performance asphalt pavements in temperate regions still rely principally on hot mix. It has been Itnown for a number of years that the incorporation of small amounts of ordinary Portland cement (OPC) significantly eiiltances the performance of emulsion mixtures (Schmidt and Santucci, 1973, Terrel and Wang, 1971).

The main objectives of the studies described in this paper were to gain an understanding of the fundamental behaviour of the emulsion in a mixture, and particularly to quantify the beneficial effects of OPC and identify the mechanisms involved, thereby to ultimately improve performance. The mechanical properties and durability of moulded specimens were determined to verify the claims in the literature. The properties of the cement modified binder were assessed. A new method was developed to measure the amount of bitunien coalescence which occurs during compaction of mixtures and what factors affect this. The electrochemical properties of the slow setting emulsion and aggregate were studied. Electron microscopy was carried out on samples of bitumen cement mastics to observe the structure of the modified binder.

2.0 EXPERIMENTAL WORK

2.1 Bitumen emulsion manufacture

A single slow-setting emulsion was used throughout the studies described in this paper. The formulation is given in Table I. The emulsion was prepared on a Hurrell laboratory colloid mill with bitumen and water-phase temperatures of 135^{0}C and 30C respectively.

Table I Emulsion formulation

Venezuelan 100 pen bitumen (supplied by Nynas UK AB)	62 %
Slow setting emulsifier (supplied by Akzo Nobel Chemicals Ltd.)	1.2%
33% Hydrochloric acid	to waterphase p11 2.5
Water	to 100 %

2.2 Mechanical properties tests on moulded specimens

A granite aggregate from CAMAS Aggregate's quarry at Croft in Leicestershire in the UK was used. The aggregate grading was in the middle of the 2Omm dense bituminous macadam specification (BS 4987, 1988) as shown in Figure 1. Fractions with nominal sizes of 20, 14, 10, 6 and <3mm were obtained and fully dried in an oven at 120^{0}C. The gradings were analysed by sieving and the fractions were recombined to give the desired grading for the manufacture of mixtures.

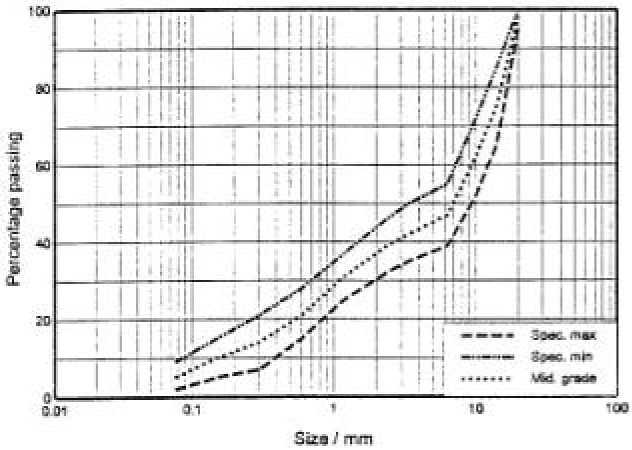

Figure 1: Aggregate grading curve

Emulsion mixtures were prepared on 3600g batches of the dry aggregate mixture by first adding OPC, if required. Pre-wet water was added next, followed by the emulsion. The materials were thoroughly mixed at each stage of addition by means of a Hobart mechanical mixer. The final mixing time was normally 45 seconds; the aim was to obtain maximum coating without over-breaking the emulsion.

Specimens were prepared by compacting mixtures in three 1200g portions in Marshall moulds. Compaction was carried out by means of a Marshall harnmer, using 50 blows to each face of the specimen. The specimens were left in their moulds ovemight, extruded, and then stored at 20^0C and *50%* relative humidity throughout the test period.

The mechanical properties of the moulded specimens were tested using a Nottingham Asphalt Tester (NAT) in the Indirect Tensile Stiffness Modulus (ITSM) and Repeated Load Axial (RLA) test modes (Brown and Cooper, 1993). The ITSM test enables the stiffness modulus of cores or moulded specimens to be determined. The structural layers of a road must have a high stiffness modulus in order in order to distribute the wheel load over a large area, thus protecting the underlying layers of the pavement. The ITSM test software was modified slightly to ensure that the loading system always delivered small and therefore non-destructive load pulses. This allowed the stiffness moduli of all specimens to be measured periodically during their curing period. The RLA test measures a compacted mixture's resistance to permanent deformation or rutting. The results obtained from the test show percentage permanent axial strain, or deformation, versus number of load cycles. A test temperature of 20^0C and a rise time of 120 ms were used in the ITSM test. A test temperature of 30^0C, a load cycle time of 1s and an axial stress of 100 kPa were used in the RLA test.

The results obtained from the stiffness modulus and permanent deformation tests were as shown in Figures 2 and 3 respectively.

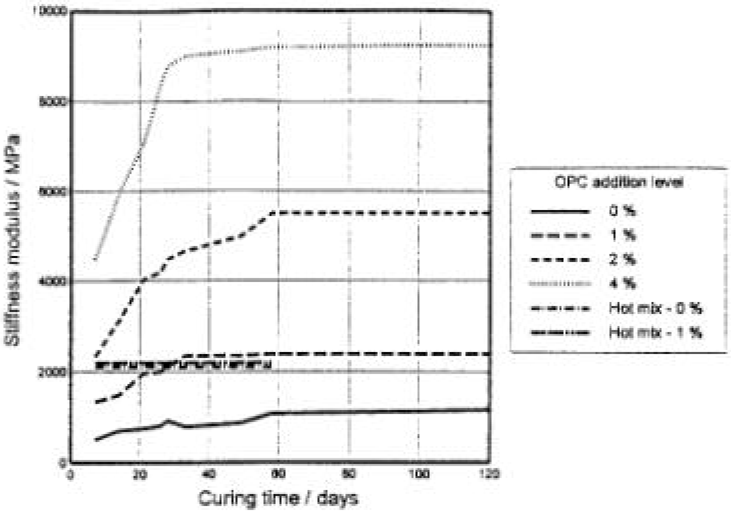

Figure 2 Effect of OPC on stiffness modulus v curing time

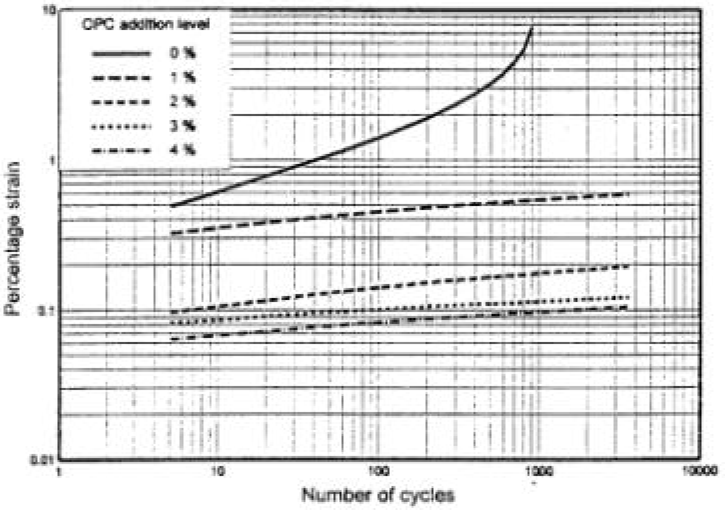

Figure 3 : Effect of OPC on resistance to permanent deformation

2.3 Durability tests

During the curing period of an emulsion mixture the semi-cured binder is susceptible to damage from water, due to the bitumen still being in a semi-emulsified state. Durability is therefore a potential problem for normal cold mix. The use of cement has been shown to improve resistance to water damage (Terrel & Wang, 1971) and this parameter was quantified again in these studies. Moulded specimens were prepared as described above with 0 and 1% OPC and cured at 20^0C for only 10 days. The specimens were therefore only partially cured. The samples were then soaked under vacuum and stored under water for 20 days. After drying for a further two days at ambient temperature, the retained stiffness moduli were determined using the NAT. It was found that as a result of soaking, the cores without cement had cracked badly and had no measurable stiflhess modulus. However, with 1% cement, the stiffness moduli of the specimens was found to be about 1200 MPa which is more than half of the value obtained for unsoaked samples.

2.4 Cement and emulsion mixtures

Mixtures of cement and emulsion alone, in the absence of aggregate, were prepared, in order to assess the behaviour of this mixture and also the properties of the cured composite binder. Mixtures were inspected periodically to assess the degree of emulsion break which had occurred. It was found that with an equivalent of 1% cement on an aggregate mixture (corresponding to 12.5% on the emulsion), complete break of the emulsion occurred within 48 hours. With higher levels of cement, the break was much faster After all the mixtures had broken completely, the break water was poured off and the penetration of the cured mastics measured at 25^0C with a needle weight of bOg applied for 5s. Figure 4 shows the results of the penetration tests on the cured bitumen-cement mastics. Note that cement addition levels are expressed as those which would be added to a hypothetical aggregate mixture with 8.1% emulsion being added. For comparison, bitumen was recovered from an emulsion by electrolysis. This method was chosen to avoid hardening of the binder that would have occurred had a heating process been used to remove water. The penetration was measured and found to be about 110. The slight softening was attributed to the entrainment of a small amount of water.

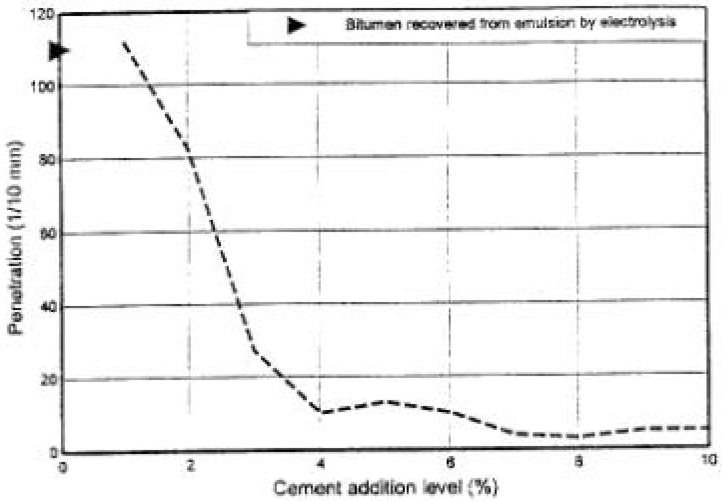

Figure 4 : Penetration of cured mastics

2.5 Emulsion coalescence tests

A new test was developed in order to measure the amount of coalescence of bitumen droplets occurring in an emulsion during compaction, and to study the factors affecting it. As the emulsified bitumen must coalesce to form a durable and viscous binder, it is preferable that as much coalescence as possible occurs during the compaction process. Mixtures were produced by adding different levels of OPC, pre-wet water and emulsion to a 200g portion of washed and dried 300 tim to 1.1 8mm aggregate and mixing by hand. The mixtures were compacted in Marshall moulds using a static load press at a range of compaction pressures and then extruded immediately. The cores were broken up with a spatula and all of the unbroken emulsion was removed by washing with dilute emulsifier solution. The coated aggregate samples were dried in an oven at 60^{0}C and allowed to cool. The binder contents were analysed by xylene extraction of the bitumen. Thus, the amount of bitumen which coalesced during compaction could be calculated as a percentage of that added to the mix in the form of emulsion.

Figure 5 shows the effect of compaction pressure on the percentage coalescence of bitumen from an emulsion. Figure 6 shows the effect of OPC addition level.

2.6 Electron microscopy

An electron microscope was used to observe the nature of the bitumen-cement mastic obtained from emulsion and cement mixtures. Mixtures were cured for several weeks to allow full recrystallization of the cement to occur. Pieces were then broken off the cured mastic samples to expose fresh surfaces, mounted and sputtered with gold to provide a conducting surface. Photographs were taken through an electron microscope at a number of magnifications to record features of interest. The photographs were too numerous and difficult to reproduce to he included in this paper. However, they clearly showed all of the crystalline species which are normally found in cementitious mixtures. Additionally, crystallization appeared to have occurred around what were originally bitumen droplets which might be expected due to reaction of the cement with the aqueous disperse phase of the emulsion.

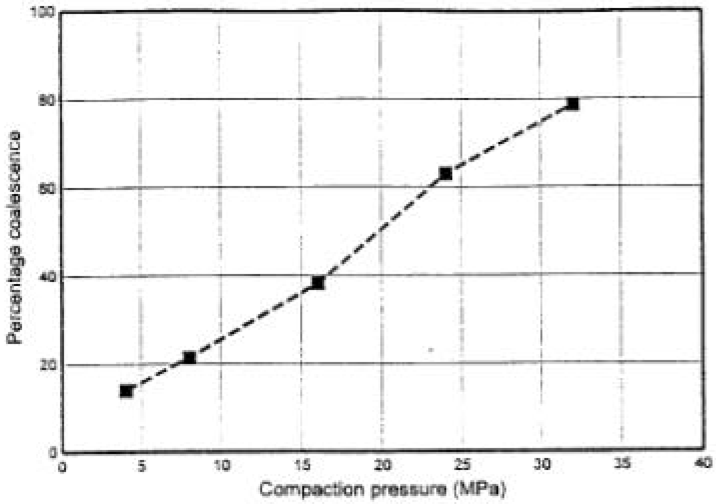

Figure 5 Effect of compaction pressure on coalescence

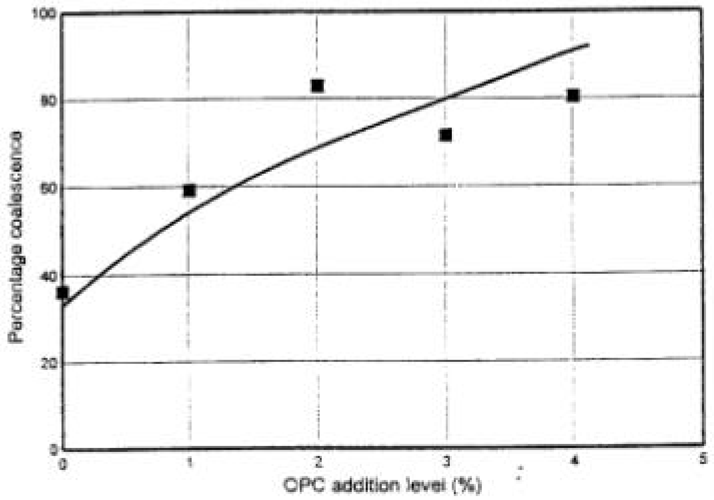

Figure 6: Effect of OPC on coalescence

2.7 Measurement of electrochemical properties

The interaction between emulsion and aggregate in a mixture is dependent on the electrochemical propetties of the components. N lost aggregates, including granite, are negatively charged under normal conditions (Sherwood, 1967). Combinations of these aggregates and cationic emulsions are therefore electrically attractive and thus emulsion break is caused by adsorption ofbitumen droplets onto the aggregate surface which leads to coalescence. This is applied in bitumen emulsion applications such as surface dressing, in which a quick break of the emulsion onto the aggregate is essential. The situation is different in the case of emulsion mixtures, as the bitumen emulsion must not break too quickly, in order to allow it to mix full)' with the dense graded aggregate mixture and remain workable for some length of time. The charge differential between aggregate and emulsion in a mixture is of great importance, as it dictates the mixing and curing behaviour of the material.

In order to study the electrochemical situation in the mixtures described in this paper, zeta potential measurements were made on the emulsion and aggregate under various conditions. Zeta potential is a measurable property of particles dispersed in aqueous solution, which is proportional to the charge on their surfaces. It is dependent on the pH and ionic conditions of the solution. For this reason, measurements were made on dispersions of emulsion and aggregate in run-off water obtained from compaction of mixtures with and without OPC as described above. The pH's of the samples were determined and found to be 7.4 for the mixture without OPC and 11.7 for the mixture with 1% OPC. Additionally, zeta potential measurements were made on emulsion and aggregate dispersed in two batches of distilled water which had been adjusted to pH's equal to those of the run-off water samples. Very dilute dispersions were made by adding small amounts of bitumen emulsion and *<63* tim aggregate to pH adjusted distilled water and run-off water, and used for zeta potential measurements on a Brookhaven Zeta plus zeta potential analyzer. The results of these measurements are given in Table 2.

Table 2 Results of zeta potential measurements

Dispersing solution	Zeta potential (mV)	
	Aggregate	Bitumen emulsion
Distilled water (pH 7.4)	-30.5	-12
Distilled water (pH 11.7)	-12.5	-19.5
Run-off water (ex mixture with no OPC pH 7.4)	0	-2.5
Run-off water (ex mixture with 1% OPC - pH 11.7)	+4	-2

3.0 DISCUSSION

The work described in this paper confirms established know ledge on emulsified asphalt mixtures and also reveals new information about what happens in mixtures during and after compaction. More specifically, it shows some of the ways in which Ordinary Portland Cement improves performance.

Mechanical properties tests on laboratory prepared samples showed that emulsion mixtures normally have quite low stiffness even after long curing periods (Figure 2). However, it may be that in practical situations, trafficking itself may accelerate the curing process by providing some additional compaction (Dybalski, 1984). The addition of OPC greatly improved performance iD terms of stiffness modulus and resistance to permanent deformation (Figure 3). It was also shown that OPC increases the resistance to water damage of a compacted mixture. This would greatly improve the performance in situ.

Mixtures of emulsion and cement clearly showed that OPC is capable of breaking a bitumen emulsion and that the higher the addition level the faster the break becomes. The penetration of the resulting bitumen - cement composite arising from the break is lower than that of the original binder if more than 1% OPC is used (Figure 4). OPC is, therefore, performing a dual role in increasing the curing rate and also stiffening the cured binder.

The newly developed coalescence test yielded interesting results regarding the rate of break of emulsion in mixtures under compaction. Emulsion coalescence was shown to be pressure sensitive (Figure 5) and also to be affected by OPC (Figure

6). This suggests that the greater the compaction pressure, the more emulsion droplets are forced into contact and to join together. Intensive compaction of emulsified asphalt mixtures in the field should, therefore, lead to increased break of the emulsion in the mixture, as would the addition of OPC.

Electron microscope images revealed two features which could assist performance in mixtures containing cement. Firstly, OPC appeared to recrystallize in its normal fashion and would, therefore, act as a secondary binder. Secondly, crystallization seems to take place between droplets which would withdraw water from the interface, thus bringing droplets into contact leading to coalescence.

The zeta potential measurements revealed a number of interesting facts regarding the electrochemical nature of emulsified asphalt mixtures. Under normal conditions (in distilled water), both the granite aggregate and bitumen emulsion had negative charges. The aggregate became less negative with increasing pH whereas the emulsion became more negative. When the emulsion and aggregate were placed in run-off water, to mimic conditions in a mixture, the charges shifted quite significantly. Although all of the charges measured were very close to neutral, it can be seen that in the presence of OPC, the aggregate takes on a small positive charge, and the emulsion remains slightly negative. It is postulated that this is due to the adsorption of calcium cations onto the aggregate surface. In a real mixture, where the calcium ion concentration could be much higher, the positive charge on the aggregate may be larger still and therefore more attractive to the anionic emulsion. It is suggested that this ma)' be one cause of the accelerated curing process seen in mixtures containing OPC.

4.0 CONCLUSION

The addition of Ordinary Portland Cement to bitumen emulsion mixtures improves the rate of increase and also the ultimate magnitude of stiffness modulus. Resistance to permanent deformation and durability are likewise enhanced. It is postulated that this is be due to increased rate of emulsion break, stiffening of cured bitumen, improvement in bitumen adhesion and development of a 'fibre" matrix of cement crystals. The acceleration of break could be due to the generation of an attractive charge between the emulsion and aggregate in a mixture, and absorption of water which destabilizes the emulsion.

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