

## **DETERMINATION OF ADHESION IN BITUMEN-MINERAL SYSTEMS BY HEAT-OF-IMMERSION CALORIMETRY**

### **I. The effect of crude oil source on adhesive performance**

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Chemical factors influencing bitumen-mineral adhesion have been examined by heat-of-immersion calorimetry. Two chosen minerals (quartz and calcite) and bitumen derived from Venezuelan and Middle East crude oils were characterised and the energy released by the bitumen-mineral interaction measured. Heat-of-immersion data are correlated with the concentration of heteroatomic species present in the bitumen and the structure of the mineral surfaces. Bitumen-quartz bonding is promoted by the presence of basic species in the bitumen and bitumen-calcite adhesion is favoured by the presence of acidic groups. A mechanism is proposed to account for the observed bond energies.

### **Introduction**

Premature deterioration of bituminous road surfaces has been recognised as a problem in many parts of the world. In some cases, disintegration has occurred only weeks or months after laying, despite an expected life for the road of ten to fifteen years. The durability of bituminous roads can be influenced by a number of factors, including compaction, mix design, bitumen viscosity, thickness, aggregate quality and degree of adhesion between the bituminous binder and the aggregate [1-3]. Loss of adhesion, resulting in retraction of the binder film from the aggregate surface, is promoted by the presence of water on the road surface [4] and is a particular problem in areas with a high annual rainfall. It is also recognised that some bitumens and aggregates produce road surfaces which lack durability owing to poor adhesion, even in the absence of water. This report describes an examination of the chemical factors influencing bitumen-aggregate adhesion, using heat-of-immersion calorimetry to quantify the strength of the initial adhesive bond.

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Bitumen used in road construction is currently characterised by its resistance to penetration by a weighted needle in a procedure known as the Penetration Test (BS2000 Part 49, 1983). High penetration values denote a soft bitumen and low values a relatively hard bitumen. Bitumens used in road construction generally have penetration ('pen') values ranging from 50 to 300. Although the Penetration Test provides the highway engineer with a rough indication of the hardness of the bitumen, there are other important factors that affect its in-service performance. In particular, the Penetration Test gives no information about the adhesive potential of the binder and certain mechanical tests have been devised to predict the degree of adhesion in a particular mix [5, 6]. Amongst these, the boiling test has gained popularity for its speed and simplicity. The test involves boiling bitumen-coated aggregate in water and visually assessing the amount of binder remaining on the surface after a given time. This method lacks reproducibility and relies on a visual estimation of the stripped area. Gourley and coworkers [3] have shown that a thin film of bitumen is often present on apparently clean aggregate surfaces after stripping in boiling water, raising further doubt as to the test's suitability.

Plancher *et al.* [7] studied the chemical types strongly adsorbed at the bitumen-mineral interface and their displacement by water. They identified five oxygen-containing groups and a nitrogen-containing compound which they tentatively classified as pyridine-like, on the basis of infrared spectra and pyridine-mineral adsorption data. Sulphoxide compounds were also found to be concentrated at the interface, but Plancher and co-workers found them to be less strongly adsorbed.

The adhesive performance of several bitumen/mineral systems has been investigated by measuring their heats of immersion. The immersion of a clean solid surface generally results in the liberation of heat, and this heat of immersion ( $q_{imm}$ ) may be written:

$$q_{imm} = E_S - E_{SL} \quad (1)$$

where

$E_S$  = total surface energy of the solid/air interface

$E_{SL}$  = total surface energy of the solid/liquid interface

Energy of adhesion ( $E_{A(SL)}$ ) is analogous to work of adhesion (the energy required to separate unit area of solid/liquid interface) and may be defined thus:

$$E_{A(SL)} = E_S + E_L - E_{SL} \quad (2)$$

where

$E_L$  = total surface energy of the liquid/air interface.

Substituting (1) in (2), we can relate the heat of immersion to the energy of adhesion as follows:

$$E_{A(SL)} = q_{imm} + E_L \quad (3)$$

The heat of immersion of bitumen-aggregate systems was first studied by Ensley and Scholz [8] using a purpose-built Tian-Calvet heatflow calorimeter. They studied various combinations of bitumen and ground aggregate at 150°, including a study of the effects of surfactant addition. They were surprised at the large amount of energy released by the wetting process and by the duration of the reaction; in some cases, they reported, the reaction lasted for days. Most wetting reactions are complete after 30 mins and Ensley [9] sought to explain his observations by proposing a multi-layer adsorption mechanism for the bitumen-aggregate interaction. Subsequent work has confirmed that a reasonably thick interphase region does, indeed, exist [10].

Ensley and Scholz did not attempt to correlate their heat of immersion data with the fundamental properties of the materials. The aim of the present work is to seek such a correlation to enable the prediction of the initial adhesive performance for a given bitumen-aggregate system to be made. In this first study, the effect of crude oil source on adhesion will be examined, using bitumens derived from Venezuelan and Middle Eastern crude oils. These two sources provide most of the petroleum bitumen used for road construction in the United Kingdom.

## Experimental

### *Materials characterisation*

Two naturally occurring minerals, quartz and calcite, were selected for use in the study since quartz-rich rocks often adhere poorly to bitumen and calcite has a reputation as a good adherend. These samples were characterised by X-ray fluorescence (XRF), X-ray diffraction (XRD), optical microscopy, scanning electron microscopy (SEM) and gas adsorption surface area determination. Specimen grade quartz and calcite samples were crushed, sieved to collect particles in the range 63–125  $\mu\text{m}$ , washed on the sieve with distilled water to remove dust, and dried for 24 hours at 150°.

Before crushing, a small piece of each mineral was set aside and used to prepare a thin section for analysis by optical microscopy. After drying, the minerals were stored under high vacuum until required. A multipoint BET surface area determination of the mineral samples was made, using a Quantasorb sorption analyser with krypton as the adsorbate. A helium/krypton flow technique was used, as described by Lowell [11]. XRD analysis was carried out on a Philips PW1050 spectrometer with 40kV  $\text{CuK}\alpha$  radiation and a nickel filter at a scanning rate of  $1 \text{ deg min}^{-1}$ . XRF data were obtained on an ARL 8420 spectrometer using the fusion technique of Norrish & Hutton [12]; the quartz sample being fused with lithium metaborate flux and the calcite sample prepared with lithium tetraborate.

Six bitumen samples were selected for study; three each from Venezuelan and Middle East crude oils of 50, 100 and 200 penetration grade. The required 'pen' value for each bitumen was achieved at the refinery as follows. The crude oils were distilled to produce a residue of 57 pen, which was then mixed with a lighter petroleum distillate to achieve penetration grades of 100 and 200 pen. To reach a penetration value of 50, the 57 pen residue was mixed with oxidised 25 pen bitumen to lower the penetration value to below 50, and the resulting bitumen mixed with flux oil to raise the penetration value to 50.

The bitumen samples were characterised by high pressure gel permeation chromatography (HP-GPC), UV spectroscopy, their trace metal content was analysed by inductively coupled plasma spectrometry (ICP) and the relative abundance of their constituent atoms determined by microanalysis. UV spectra were recorded from 220 nm to 500 nm on a Philips PU8720 UV/visible scanning spectrophotometer. Samples were dissolved in dichloromethane and contained in 1 cm cuvettes. The apparent molecular weight distribution of the bitumen samples was determined qualitatively by HP-GPC using four  $5 \mu\text{m}$  Phenogel columns ( $1 \times 10^5 \text{ \AA}$ ;  $3 \times 500 \text{ \AA}$ ) in series and dichloromethane at  $1 \text{ cm}^3 \text{ min}^{-1}$  as the mobile phase. The sample (1% w/w bitumen/dichloromethane) was loaded into a  $20 \mu\text{l}$  loop attached to a Rheodyne valve prior to injection and detected after elution using a variable wavelength UV detector set at 235 nm. Bitumen samples for trace metal analysis (approximately 0.7 g) were digested in a mixture of concentrated Aristar grade nitric and sulphuric acids and the resulting solutions were made up to  $50.0 \text{ cm}^3$ . The solutions were analysed for nickel and vanadium on a Perkin-Elmer Plasma 40 ICP spectrometer. Microanalysis was performed using a CEC 240XA elemental analyser for carbon, hydrogen and nitrogen determinations, and a Carlo Erba 1106 elemental analyser for sul-

phur analysis. The concentration of oxygen present in the sample was calculated by difference.

### *Heat-of-immersion analysis*

A Setaram C80D heatflow calorimeter in isothermal mode at 100° was used for the heat of immersion study. The operating temperature was sufficiently high to allow the bitumen to flow freely, but low enough to prevent appreciable volatile loss. The calorimeter was fitted with sample vessels designed to isolate the two phases whilst thermal equilibrium was established. The sample and reference cells contained bitumen (1.5 g) and the mineral sample (63–125  $\mu\text{m}$ ; 500 mg); the contents of the reference cell were premixed. After the baseline had remained stable for 60 min the reaction was started by inverting the calorimeter on a specially designed stand. Heatflow data were recorded for approximately 2 hours and the heatflow curve integrated. A typical heatflow curve is shown in Fig. 1. The initial endotherm is possibly due to an increase in  $E_L$ , the total energy of the bitumen/air interface, as the calorimeter is inverted and the bitumen flows onto the mineral, increasing in surface area in the process. When the calorimeter was inverted with a completely empty sample container, a slight exothermic perturbation of the baseline was seen but the initial endotherm was absent, lending support to this theory. The difference between the ini-

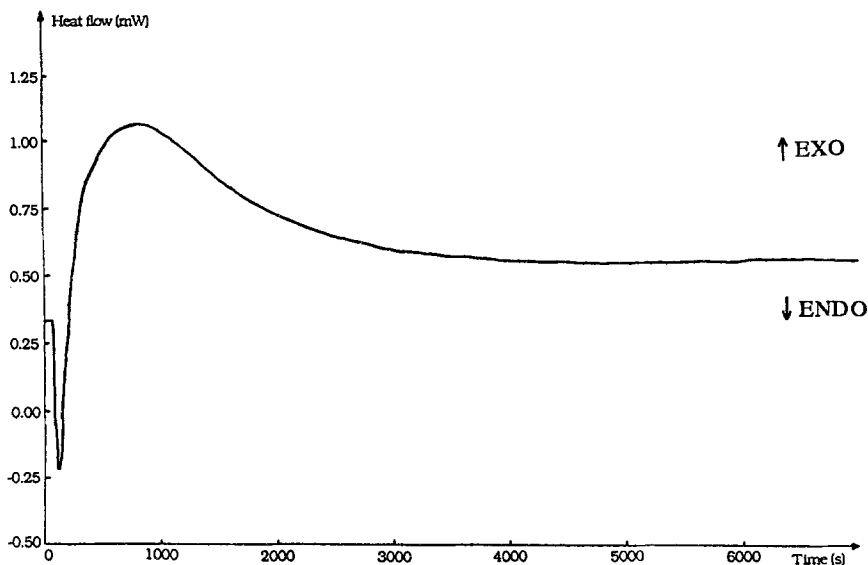


Fig. 1 Typical heatflow curve produced by the immersion of a mineral sample in bitumen

tial and final baseline was a consistent feature of the tests and is thought to be due to the change in position of the contents of the sample cell on inversion. Blank determinations were run for each bitumen sample with the sample cell containing bitumen only. The heat-of-immersion values were calculated by dividing the corrected mineral immersion results by the BET surface area of the mineral sample.

## Results

### *Mineral characterisation*

Major element oxide concentrations for quartz and calcite, calculated from the XRF results, are given in Table 1. These data enable the purity of the minerals to be quantified, and the quartz and calcite samples were 99.9% and 97.3% pure respectively. The high loss on ignition value for calcite was due to the evolution of CO<sub>2</sub> during sample preparation.

Table 1 Mineral elemental composition determined by XRF

Oxide	Concentration, wt %	
	Quartz	Calcite
SiO <sub>2</sub>	100.44	0.00
TiO <sub>2</sub>	0.03	0.01
MnO	0.01	0.05
MgO	0.00	1.51
CaO	0.04	54.87
P <sub>2</sub> O <sub>5</sub>	0.01	0.01
Loss on Ignition	0.01	43.54
Total	100.54	99.99

Results from the XRD analysis of the two mineral samples are shown in Table 2. Experimental results are in good agreement with literature values for the inter-planar spacings,  $d$ , but there is some discrepancy between our data and literature values for relative intensity,  $I$ . This is probably due to the mineral samples adopting a preferred orientation in the diffractometer.

Optical microscopy revealed that both minerals are basically monomineralic; no identifiable impurities were seen. SEM photographs of the minerals (Figs 2 and 3) show clean surfaces with an extremely low con-

**Table 2** X-ray diffraction data for the mineral samples. Literature data are taken from JCPDS (XRD) No 33-1161 (Quartz) and 24-27 (Calcite)

Quartz				Calcite			
Observed values		Literature values		Observed values		Literature values	
<i>d</i> , Å	<i>I</i> , %	<i>d</i> , Å	<i>I</i> , %	<i>d</i> , Å	<i>I</i> , %	<i>d</i> , Å	<i>I</i> , %
4.246	62	4.257	22	3.832	<1	3.852	29
3.339	100	3.342	100	3.020	100	3.030	100
2.455	14	2.457	8	2.835	<1	2.835	2
2.277	7	2.282	8	2.486	1	2.495	7
2.235	13	2.237	4	2.278	2	2.284	18
2.127	46	2.127	6	2.089	2	2.094	27
1.9774	2	1.9792	4	1.9072	2	1.9071	17
1.8158	59	1.8179	14	1.8707	2	1.8726	34
1.6706	2	1.6719	4	1.5060	<1	1.5061	2
1.5405	7	1.5418	9	1.4188	<1	1.4168	3
1.4515	6	1.4536	1				
1.4190	8	1.4189	<1				
1.3819	4	1.3820	6				
1.3748	2	1.3752	7				
1.3712	7	1.3718	8				
1.2875	1	1.2880	2				
1.2557	11	1.2558	2				
1.2283	2	1.2285	1				
1.1996	4	1.1999	2				
1.1800	1	1.1804	3				
1.1528	<1	1.1532	1				
1.0815	2	1.0813	2				
1.0647	7	1.0635	<1				

centration of surface dust (less than 1% coverage). Some of the calcite grains appear to be slightly porous and their surface is rougher than the quartz sample. A number of the quartz particles show conchoidal fracture and sharp edges, features which are typical of the mineral. The flat surfaces seen on some of the quartz grains, and most of the calcite grains, correspond to crystallographic planes and explain the preferred orientation adopted by the mineral samples during XRD analysis.

The krypton surface areas of the quartz and calcite samples were  $0.105 \text{ m}^2 \text{ g}^{-1}$  and  $0.207 \text{ m}^2 \text{ g}^{-1}$  respectively. This result is in the order predicted by the SEM observations regarding surface roughness.

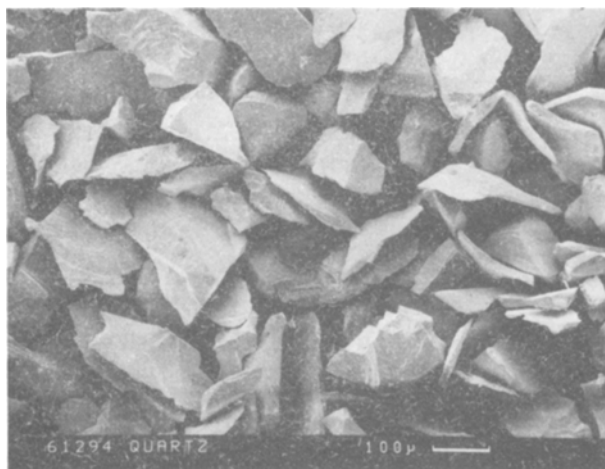


Fig. 2 Scanning electron micrograph of the quartz sample

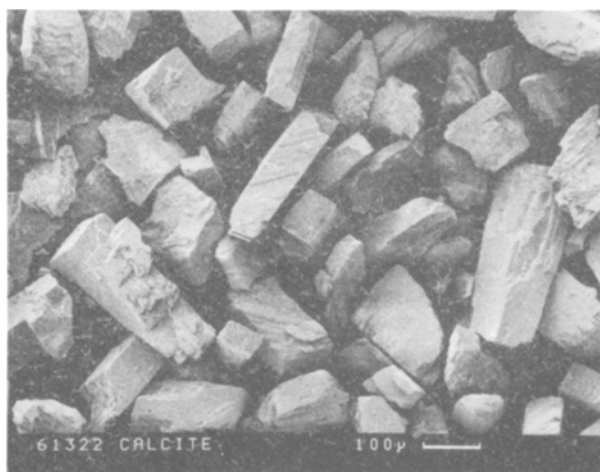


Fig. 3 Scanning electron micrograph of the calcite sample

### *Bitumen characterisation*

The following convention has been adopted to identify the bitumen samples: each sample has a number, which corresponds to its penetration grade, and a letter which identifies the crude source (V for Venezuela and M for the Middle East). HP-GPC profiles of the bitumen samples are shown



in Fig. 4. The Middle East bitumens produced symmetrical curves with the retention time increasing slightly with increasing penetration grade. The Venezuelan bitumens gave leading peaks and slightly longer retention times than their Middle East equivalents. The same increase in retention time with penetration grade was seen.

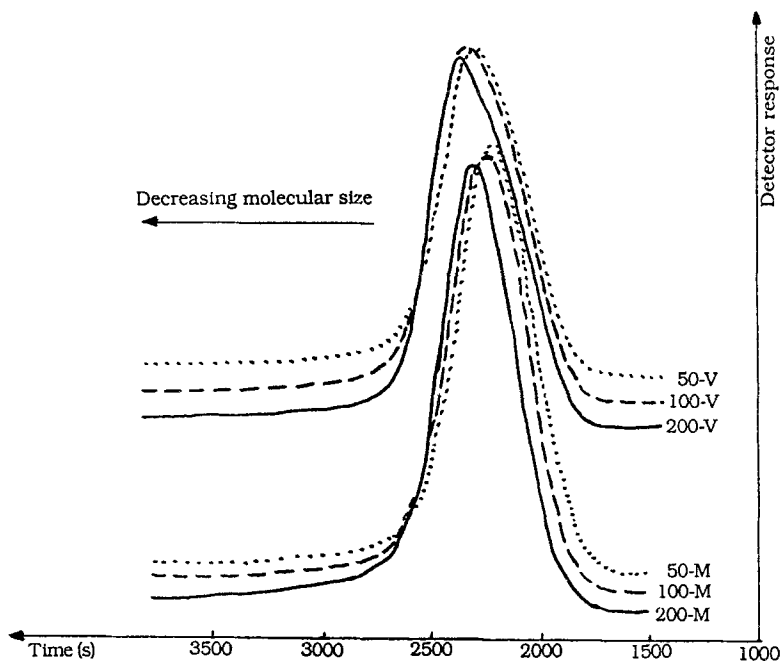


Fig. 4 Molecular size profiles of the bitumen samples determined by gel permeation chromatograph

Within each crude source group, UV spectra were identical. The typical spectra of the two groups are broadly similar, with  $\lambda_{max}$  at approximately 235 nm and a peak tail decreasing asymptotically with increasing wavelength. The Venezuelan samples have a small hump on the peak tail at approximately 410 nm; this feature is missing from the UV spectra of the Middle East samples. Typical UV spectra of the two bitumen groups are shown in Fig. 5.

The trace metal concentrations of the bitumen samples, as determined by ICP analysis, are given in Table 3. The Venezuelan bitumens are consistently richer in trace metals than the Middle East samples.

The elemental composition of the bitumen samples is given in Table 4. The C:H ratio is included in the table since the degree of saturation has an important effect on bitumen properties [1]. The Venezuelan bitumens con-

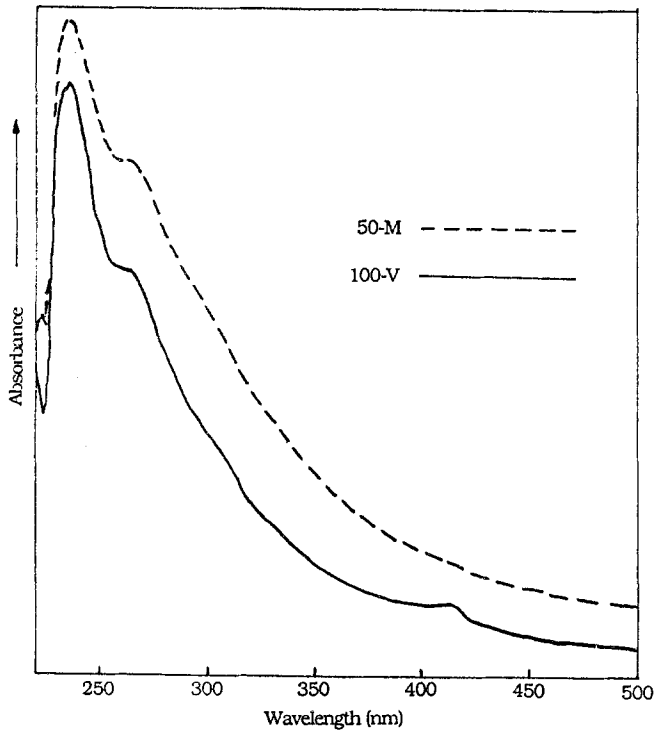


Fig. 5 Typical ultraviolet spectra of the two bitumen sample groups

tain significantly more nitrogen and slightly less sulphur than those derived from Middle East crude oil. The Middle East bitumens have higher C:H ratios and are therefore less saturated. The concentration of oxygen in the bitumen samples decreases with increasing penetration grade.

Table 3 Bitumen trace metal concentration determined by ICP

Sample	Concentration, ppm	
	Ni	V
50-V	123	515
100-V	114	513
200-V	108	515
50-M	67	174
100-M	49	199
200-M	57	159

**Table 4** Bitumen elemental composition determined by microanalysis

Sample	Concentration, wt %					C:H atomic ratio
	C	H	N	S	O	
50-V	84.30	10.22	0.80	3.88	0.80	0.69
100-V	84.25	10.20	0.79	4.03	0.73	0.69
200-V	84.45	10.22	0.70	3.96	0.67	0.69
50-M	83.51	9.78	0.45	5.45	0.81	0.71
100-M	83.76	9.95	0.45	5.03	0.81	0.70
200-M	83.80	9.98	0.44	5.17	0.61	0.70

*Heat of immersion data*

Bitumen-mineral heat of immersion data are given in Table 5. Each result is the mean of at least 2 determinations. The Venezuelan bitumens interact more strongly with both mineral types than their Middle East equivalents, and the 50 pen bitumens adhere better to calcite than quartz. Both sets of bitumen samples show a weaker interaction with calcite as the penetration grade increases and the strongest interaction with quartz is shown by the 100 pen samples. In every case, the reaction was complete within 2 hours and most of the energy was released within 1 hour.

**Table 5** Bitumen-mineral heat-of-immersion data

Bitumen sample	Heat-of-immersion, Jm <sup>-2</sup>	
	Quartz	Calcite
50-V	3.18	4.43
100-V	9.73	4.41
200-V	6.26	0.88
50-M	2.05	3.58
100-M	5.80	3.09
200-M	3.27	1.46

**Discussion**

The purpose of this study was to identify the chemical factors, related to crude oil source, that affect bitumen-aggregate adhesion. It is generally accepted that the adhesive properties of bitumen are governed by the type and concentration of heteroatomic species either present in the original crude oil or introduced at the refinery by oxidation or blending. Oxygen and

nitrogen-containing species have been identified as the principal adhesion-promoting groups in bitumen [7].

The microanalysis data show very little difference between the oxygen concentrations of the two bitumen groups. Since the oxygen concentration data are derived by difference they are, in this case, less reliable than the other elemental concentration results. The expected trend of decreasing oxygen concentration with increasing penetration grade is seen, however, and this agrees with the known processing history of the bitumen samples. The concentration of nitrogen compounds in the bitumen is obviously related to crude source. It is proposed that one reason for the greater concentration of nitrogen species in the Venezuelan bitumen is the higher number of porphyrin groups that they contain. Evidence for the presence of porphyrins in these bitumens is provided by the high concentrations of nickel and vanadium, which are known to form co-ordination compounds with porphyrin rings in crude oil [13], and the appearance of a small peak at 410 nm in the UV spectra of the Venezuelan bitumens. This peak is probably due to the Soret absorption band [14], an intense peak present in the UV spectra of all porphyrins.

The higher C:H ratios of the Middle East bitumens imply a higher degree of aromaticity. Aromatic systems are able to lower the surface energy of electron-deficient substrates by donating  $\pi$ -electron density; the surface of quartz under normal conditions is known to comprise mainly silicon-bonded hydroxyl groups, presenting an electron-poor surface to an incoming nucleophile [15]. The strength of this interaction would depend on the distance from the interface of the  $\pi$ -electron cloud, and, since aromatic systems in bitumen tend to consist of large, planar sheets, such a mechanism would be prone to steric interference. Since the quartz sample liberates less energy after immersion in the Middle East bitumens than with the Venezuelan samples, the adsorption of aromatic species at the interface is thought unlikely to be a major factor in bond formation.

The HP-GPC traces show slightly longer retention times for the Venezuelan bitumens, indicating either a lower average molecular size or a lesser degree of inter-molecular aggregation into micelle-type structures. Although bitumen molecules are known to form micelles even in dilute solution [16], it is considered that the difference in retention times is more likely to be due to differences in molecular size. This is because the expected increase in the proportion of the high molecular weight fraction of the Venezuelan bitumens, due to the higher concentration of micelle-promoting heteroatomic species is not seen. The lower average molecular size of the Venezuelan bitumens may help to explain their better adhesive performance,

since smaller molecules are able to migrate to, and interact with, the interface more easily than larger species.

The heat of immersion data enable a bonding mechanism to be proposed for the two mineral substrates. Bitumen-quartz bond formation is expected to be favoured by the presence of nucleophilic species in the bitumen and electronegative groups, such as O and N, which are known to be concentrated at the interface, might be expected to interact with the surface hydroxyl groups. In order to compare the experimental results with literature bond energy data, the density of the Si-O-H groups on the surface of quartz has been calculated, based on a distance between SiO<sub>4</sub> tetrahedra of 2.45 Å and assuming that each tetrahedron at the interface is oriented with a Si-O-H group uppermost. In this case, the density of the hydroxyl groups at the quartz surface would be  $1.67 \times 10^{19} \text{ m}^{-2}$  and, assuming that every group is involved in bonding, the experimental heat-of-immersion data for quartz would yield values of between 70 and 360 kJ mol<sup>-1</sup>. These values are consistent with the formation of strong chemical bonds and the mechanism is suggested to involve transfer of the proton from the hydroxyl groups to the basic species in the bitumen. This mechanism is favoured by the ability of the quartz lattice to delocalise the resulting negative charge. It is possible that a multi-layer adsorption mechanism, similar to that proposed by Ensley [9], contributes to the overall enthalpy, but this would not, by itself, account for the magnitude of the heat evolved since the energy released by intermolecular dipole-dipole interactions would be significantly lower than the energy liberated by the formation of chemical bonds at the interface.

The functional groups in bitumen most likely to react in this way are the nitrogen bases, and the proposed mechanism is supported by the higher concentration of nitrogen species in the Venezuelan bitumens, determined by microanalysis. Direct evidence exists for the presence of porphyrin species in these strongly bonded bitumens, but the porphyrin ring is known to be an extremely weak base, due to delocalisation of electron density around the ring. Its basic strength might be expected to be further reduced by solvation in a non-polar medium such as the predominantly aliphatic lighter bitumen fractions, which would destabilise the ammonium cation formed on protonation. It is more likely, therefore, that other, more basic nitrogen species are responsible for bond formation. These might be pyridine-type compounds, as suggested by Plancher *et al.* [7], or pyrrole fragments of porphyrin rings. It is likely that oxygen-containing species are also involved in bonding through dipole interactions with the polar mineral surface. These bonds would be expected to be considerably weaker than those formed by the

nitrogen bases and would not, by themselves, explain the magnitude of energy released.

The surface chemistry of calcite is less well established than that of quartz. In order to compare the surface concentration of active species with quartz, however, we can take the C-O bond length in  $\text{CO}_3^{2-}$  to be 1.29 Å and the ionic radius of  $\text{Ca}^{2+}$  is 0.99 Å [17]. As a rough approximation, the distance between these species at the interface will be in the order of 2.28 Å, but may vary depending on the orientation of the trigonal planar  $\text{CO}_3^{2-}$  anion. The surface density of active species in calcite is, therefore, similar to the hydroxyl group density at the quartz surface.

A similar mechanism to that set out for quartz can be constructed for nucleophilic attack by basic species at  $\text{Ca}^{2+}$  lattice sites, but the interaction would probably be weaker due to the formation of co-ordinate bonds rather than the proton transfer mechanism proposed for quartz. The bitumens which interact most strongly with calcite are the 50 pen air blown samples. Air blowing is known to increase the concentration of acid species in bitumen and the main mechanism of bitumen-calcite bond formation is, therefore, thought to involve electrophilic attack at the carbonate ion.

The heat-of-immersion data show consistent trends; the bitumen-quartz interaction is in the order 100>200>50 pen for both bitumen groups and the corresponding trend for calcite is 50>100>200 pen. These trends are not a function of penetration grade but rather the result of the processing methods used to produce these bitumens. It has already been suggested that the 50 pen bitumens contain a higher proportion of acidic species due to oxidation at the refinery and these bitumens interact most strongly with calcite. The 200 pen bitumens have been diluted with an unspecified distillate extract to a greater extent than the other bitumens to reduce their viscosity by the required amount. The distillate extract, although of unknown composition, is most unlikely to contain appreciable concentrations of heteroatomic species and is probably largely paraffinic in nature. Indeed, the microanalysis results show that the 200 pen samples are relatively poor in nitrogen and oxygen species, and this accounts for their weaker interaction with the mineral substrates. The 50 pen bitumens are thought to interact weakly with quartz for the same reason that they bond strongly to calcite. During oxidation, it is likely that the acidic species formed interact with the nitrogen bases, preventing them from taking part in bond formation. Since these basic groups are responsible for bitumen-quartz bonding, adhesive performance is reduced.

The superior adherend properties of calcite, predicted by the experience of adhesive failures gained by the road industry over a number of years, is observed for the 50 pen bitumens only. The problems experienced with in-service disbonding of bitumen from quartz-rich substrates is possibly due to attack by water at the interface, where the Si-O-H groups would provide an ideal hydrophilic substrate. The strength of the initial bitumen-quartz bond, made in the absence of water, appears to be superior to the bitumen-calcite interaction in the case of the 100 and 200 pen bitumens.

## Conclusions

It is clear that significant chemical differences exist between bitumens used in road construction in the United Kingdom. These differences are due to crude oil source and the processing route followed at the refinery. Bonding of bitumen to quartz is promoted by the presence of basic nitrogen species and adhesion to calcite by acidic groups.

The strength of the interaction between bitumen and the mineral substrates is consistent with the formation of strong chemical bonds. The initial bond strength, as measured by heat-of-immersion calorimetry, may not predict the in-service performance of the bitumen-mineral systems due to the subsequent action of water at the interface.

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**Zusammenfassung** — Mittels Eintauchkalorimetrie wurden chemische Faktoren bestimmt, die die Adhäsion zwischen Bitumen und Mineralstoffen beeinflussen. Es werden zwei Mineralstoffe (Quarz und Kalzit) sowie Bitumen aus Rohölen aus Venezuela und dem Mittleren Osten beschrieben und die durch Wechselwirkung zwischen Bitumen und Mineralstoff freigesetzte Energie gemessen. Immersionswärmedaten wurden mit der Konzentration von Heteroatomen im Bitumen sowie mit der Oberflächenstruktur des Mineralstoffes korreliert. Die Bitumen-Quarz-Bindung wird durch Gegenwart von basischen Komponenten im Bitumen gefördert, die Bitumen-Kalzit-Adhäsion wird durch die Gegenwart saurerer Gruppen gefördert. Es wird ein Mechanismus vorgeschlagen, um die beobachteten Energien erklären zu können.