Selective sorption in filler-bitumen systems

J. CRAUS, I. ISHAI
Transportation Research Institute, Technion-Israel Institute of Technology, Haifa, Israel

N. POR
Oil Refineries Ltd., Haifa, Israel

Factors affecting selective sorption in the bitumen—filler interface and the difference in the capacity of various fillers for selective sorption of the chemical groups combining the bitumen are investigated and described. The effect, in this respect, of the type of diluent, the environmental conditions and the experimental methods are also studied.

Quantitative evaluation of selective sorption was made using a chromatographic method, by percolation of diluted bitumen through columns of different types of filler. Among the fillers investigated, hydrated lime and limestone were the most effective, basalt was intermediate, while sandstone and mainly glass beads showed almost no capacity for selective sorption. In addition, the changes in the composition of the chemical groups, while percolating bitumen through a hydrated lime layer, were investigated and reported in this paper.

The evaluation of selective sorption capacity of the filler is of great importance in bituminous mixture technology. Since the filler constitutes the ingredient with the highest specific surface in the granular mass of the bituminous mixture, its surface activity properties influence the mechanical properties of the bitumen—filler system and the behaviour of the mixture. Therefore, the capacity of selective sorption can serve as an indication to the future effect of the filler on the aggregate—bitumen—filler adhesion and the stability and deformability of the bituminous mixture. In this respect, the behaviour of sand asphalt mixtures with different types of filler was studied. Actual results were in agreement with the behaviour of the different fillers under selective sorption.

1. Introduction

The filler constitutes a major component in the high quality bituminous concrete mixture used for highway and airport pavements. The role of the filler in the mixture is very complex. On one hand, the filler serves as inert material for filling the voids between coarser aggregate particles in the mixture. On the other hand, because of its fineness and surface characteristics, the filler serves also as an active material. The activity of the filler is expressed in the physico-chemical and rheological properties of the interface between the filler and the bitumen. These properties have great influence on improving the properties of the binder and on improving the bonds between the filler—bitumen

system and the aggregate. The result is a better and more durable bituminous concrete.

One of the most important filler—bitumen interface properties is the selective sorption (adsorption and absorption) of chemical groups in the bitumen on various fillers. The accumulated result of the selective adsorption and absorption is that the filler particles are coated with a bituminous film that has high concentration of constituents with higher molecular weight and higher potential of surface activity. This film is of higher viscosity and adhesion properties.

The objective of the research described in the paper is to make evident the phenomenon of this selective sorption in the laboratory, and to investi-

gate the difference in the capacity of various types of filler for selective sorption of the chemical groups combining the bitumen. The effect, in this respect, of type of diluent, environmental conditions and the experimental methods were also studied, and are described in the paper. A verification test series was also made on sand—asphalt mixtures.

2. Factors affecting selective sorption in the bitumen—filler interface

Selective sorption in the bitumen—filler interface is a complex phenomenon since it involves both selective adsorption and selective absorption [1, 2]. Usually, it is very difficult to separate these two processes because they are influenced by combined and interacted factors such as: the complex group composition of the bitumen, physicochemical properties of the filler surfaces, and internal structure of the filler particles.

Selective adsorption in the filler—bitumen interface is primarily affected by the colloidal system composing the bitumen. In this system the asphaltenes represent the dispersed phase and malthenes the dispersing phase — but this is in the broadest sense only. The dispersed phase includes, in addition to the asphaltenes, also the most aormatic porrtion of the dispersing phase which is adsorbed on the asphaltene particles, thus forming a system defined as micelles. In general, the highest molecular weight resinous material is adsorbed first on the surface of the asphaltene particles, which form a sort of a nuclei to a system in which the resinous aromatic materials of progressively lower molecular weights are less and less rigidly adsorbed. Depending on the experimental conditions, a shifting of the less aromatic portions from the dispersed phase, and vice versa, may be observed. Moreover, in the micelles themselves, no definite boundaries exist between the asphaltene particles and the adsorbed or semi-adsorbed resinous aromatic material; the same is true regarding the micelles and the dispersing phase, the latter consisting not only of oily material of a paraffinic structure, but also some aromatic matter or even asphaltics. The system as a whole exists, therefore, in a sort of equilibrium in which one phase merges into the other, depending on environmental conditions such as: temperature; aeration (blowing) conditions to which the bitumen was exposed; and type of diluent involved.

The active colloidal system of the bitumen, as

described above, constitutes the potential of selective adsorption. However, this potential can be expressed only when the bitumen is interacted with active surfaces, such as the surfaces of certain types of filler. The contribution of the filler to selective adsorption in the bitumen—filler interfaces is both chemical and physical [3]. The chemical properties of the filler surfaces create the possibility and the specific intensity of adsorption, while the physical properties of the surfaces (such as, surface texture, shape, and specific surface), determine the magnitude of the adsorption.

Depending on the chemical properties of the filler surfaces, several types of adsorption, with different intensitites, can be observed in the interface. The range of intensities varies between the weak mobile adsorption created by Van der Waals forces (i.e. adsorption of the bitumen by siliceous fillers) and the strong active adsorption created by the affinity between some components of the bitumen (constituents with high polarity and aromatic nature and organic acidity), and certain types of basic fillers (i.e. adsorption of the bitumen by hydrated lime filler) [2].

In case of active adsorption in filler—bitumen interfaces, there is a selective tendency of the active filler surfaces to adsorb first a very thin film of the bitumen components with the higher molecular weight. This film creates a potential of further adsorption of other group components of the bitumen with gradually lower molecular weights. This process is continued to a distance where the interface does not influence the adsorption any more. At this distance from the interface, a dynamic equilibrium is reached. Therefore, the intensity of adsorption is decreased with increasing the distance from the interface. The specified distance at which the interface ceases to influence the adsoprtion depends on the degree of activity of the filler, the bitumen/filler ratio and the environmental conditions. Simultaneously, the adsorbed components of the bitumen are being structured in such a way that at the interface zone the coating bitumen is in a gel state, and with increasing distance from the interface it is gradually becoming sol—gel to the sol state. This phenomenon is important since in bituminous mixtures technology is desirable to use certain types of active filler which have greater intensity of selective adsorption. In this case, the result is thicker films of strongly adsorbed bitumen and less free bitumen.

It should be noted that the specific intensity of

the process described above is related to a unit surface area. Therefore, the total magnitude of the adsorption is a function of the phyical properties of the filler surface, such as specific surface and surface texture [5].

In the case of fillers which contain relatively high proportion of particles finer than $5 \mu m$, (e.g. hydrated lime, see Table II), the total potential of selective sorption can be also dependent on the absortive properties of the filler particles. Here, the magnitude of absorption is a function of the fine surface pore characteristics or the exposed internal pore structure. In this case, due to the capillary effect of the fine pores, the filler particles absorb first the low viscosity components of the bitumen with the lower molecular weight (ultra filtration of the oils). Therefore, again the particles are coated by a membrane of bitumen which contains therein relatively more components with higher molecular weights. Now, depending on the degree of activity of the filler surface, the process of selective adsorption, as described previously, takes place and intensifies the total potential of selective sorption.

3. Practical evaluation of selective sorption
3.1. Basic concept
The total process of selective sorption, as described above, is a phenomenon on a micro scale. However, a simulation of this process in a macro scale can be obtained by a certain testing technique. In this work, the chromatographic method of selective sorption from the liquid phase was used [1, 3].

The general principle of this method is that the vertical location of a component of a liquid mixture that percolates through a column of an active adsorbent depends on the potential and intensity of selective sorption of this component relative to the physico-chemical properties of the adsorbent. The specific layer of each component is manifested by a specific colour in the column.

The application of this principle to selective sorption in bitumen-filler systems is made by percolation of a diluted bitumen through columns of different types of filler. Under selective sorption the different colours represent a layer of bitumen with group components which are different from the original group components of the bitumen. In an active filler column the upper layer is very dark, due to the higher proportion of asphaltenes which are adsorbed first. The layers become brighter and brighter at the lower parts of the column, rep-

resenting the higher proportion of oils (see Fig. 1). Quantitative evaluation of the selective sorption can be made by analytical determination of the group components of the bitumen in each specific coloured layer of the percolated column.

3.2. Description of materials and testing method
3.2.1. Materials
One type of bitumen and six types of filler were involved in the investigation. A 60/70 original asphaltic bitumen was used. Its physical properties and group composition are presented in Table I. Properties of the fillers are summarized in Table II.

For the investigation of the changes in the composition of the chemical groups, only one type of filler was used. The filler chosen was hydrated lime, this being the most active adsorbent.

3.2.2. Preparation of the bitumen samples
In order to ensure a satisfactory percolation of the original viscous asphaltic bitumen, its viscosity had to be reduced to below 10 cSt at $50°$ C. This was done by blending the fresh bitumen with suitable diluents: gas—oil and normal heptane. 20% bitumen and 80% gas—oil yield a blend of a viscosity of 7.6 cSt at $50°$ C and 40% bitumen and 60% normal heptane yield 9.5 cSt at the same temperature.

3.2.3. Preparation of filler columns
Transparent plastic cylinders of 500 cm³ volume

TABLE I Physical properties and group composition of the 60/70 asphaltic bitumen used

| Property	Units	Test value
Softening point R and B	$°$ C	54
Penetration at $25°$ C	1/10 mm	61.5
Penetration index		+0.3
Ductility at $25°$ C	cm	> 100
Fraas breaking point	$°$ C	− 14
Loss on heating	%	0.05
Specific gravity at $25°$ C		1.02
Kinematic viscosity:		
at $50°$ C	cSt	350 000
at $60°$ C	cSt	100 000
at $71°$ C	cSt	30 000
Amount of malthenes	% of bitumen	72.7
Resins	% of bitumen	17.5
Saturates	% of bitumen	31.3
Cyclics	% of bitumen	23.9
Amount of asphaltenes	% of bitumen	27.3
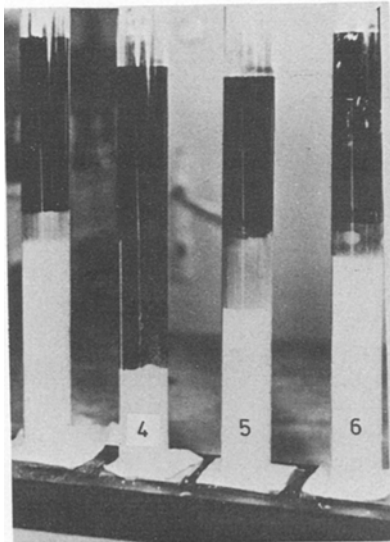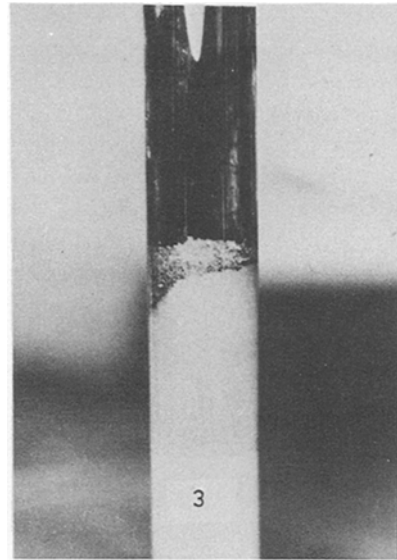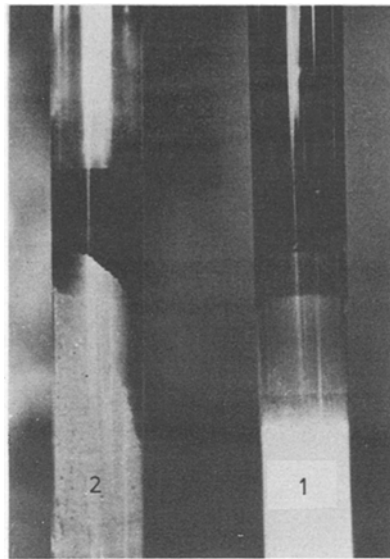
Figure 1 Typical example of selective sorption by percolation of diluted bitumen through columns of different types of filler. (1) Hydrated lime column at optimum density. (2) Channelling effect in hydrated lime column at lower density. (3) Limestone filler column with slight channelling. (4) Sandstone filler column. (5, 6) Basalt filler columns at the beginning of percolation process.

were used. Near the bottom of the cylinders a hole was bored in order to allow air to escape during the flow of the bitumen solution. The cylinders were filled with the oven dried filler up to the 400 cm³ mark. In order to ensure homogeneity, a vibratory compaction was used, but care was taken not to compress the filler excessively, since a too dense filler will prevent the free flow of the bitumen solution through the cylinder. The density of

TABLE II Properties of the fillers tested

Material	Apparent specific gravity	Specific surface ($m^2 \, kg^{-1}$)*	Voids of dry compacted filler (% voids)†	Particle size distribution: % material finer than given length (mm)							
				0.074	0.06	0.05	0.04	0.03	0.02	0.01	0.005
Glass beads	2.30	86	32.5	100	70	48	27	12	7	5	2.4
Sandstone	2.64	334	35.7	100	90	83	73	60	47	34	22
Basalt	2.88	247	37.7	100	87	78	66	55	43	30	20
Limestone	2.88	263	42.4	100	94	89	83	76	65	45	24
Hydrated lime	2.30	869	54.8	100	99.5	99	98.5	98	97.5	87	35

*Blaine's Method (ASTM C 204).
†Rigden's Method (British Standard B.S. 812).

the filler column should be such as to allow the bitumen solution to percolate smoothly through the cylinder in the given interval of time (between 8 to 24 h), but without leaving patches of unadsorbed bitumen and without channelling. The colour gradient should be progressive and continuous, from dark at the top to very light at the bottom. In each case, the density of the filler at which the percolation was performed, was established and recorded. This was done by weighing the cylinder while it was empty, and again when filled with the filler. The weight per unit volume of the filler was so calculated. Alternatively, the porosity of the filler was also established, since all the necessary data were available.

3.2.4. The percolation process and withdrawl of samples from the various layers

$100 \, cm^3$ of bitumen solution (see above) was introduced carefully into the cylinder. The bitumen solution was allowed to pass through the cylinder; this stage may take from 8 to 24 h. The sampling of the layers and the consequent analysis were carried out not later than 48 h after the start of the percolation, in order to prevent analysing aged bitumen samples. Three layers were separated in the following way, but first, the uppermost top, consisting of unadsorbed bitumen solution that did not percolate, was discarded. The bottom part, which was not reached properly by the bitumen solution, was also disregarded. Now, the rest was divided into three parts, each being separated from the other by cutting the cylinder together with the filler and the adsorbed bitumen. From each of the layers samples were drawn for analysis.

3.2.5. Analysis of the bitumen in the various layers

Every sample drawn from each of the layers was analysed in duplicate. The four groups, malthenes, asphaltenes, carbenes and carboids, are established by consecutive extraction with normal heptane carbon tetrachloride and carbon disulphide (ASTM D 2042 [6]). Percolated hydrated lime samples were also analysed for the change in saturates and cyclics in the malthenes system by consecutive extractions with normal butanol and acetone [1].

4. Selective sorption test results and discussion

The major objective of the testing phase is to study the effect of the filler type on the potential and intensity of selective sorption in bitumen—filler systems. Table III describes quantitatively the effect of type of filler on adsorption rate of the asphaltenes using gas—oil and normal heptane as diluents for the bitumen, respectively. The adsorption rate of the asphaltenes in the different layers of the column is expressed in two ways. Firstly, by the weight proportions of the asphaltenes in the different layers, taking the total weight of the asphaltenes in the column at 100% (for all types of filler). Secondly, by expressing the weight of asphaltenes in each layer as percent of the weight of the bitumen in the layer (for two types of filler respresenting the lower and upper limits of the adsorption range). In this second way, a comparison can be made with the original bitumen (see Table I).

It can be seen from Table III that there is a marked difference in the selective sorption capacity of the various fillers, due to the chemical and physical properties of the particles' surfaces. Glass beads, due to their non-active siliceous surfaces and their very smooth texture and regular shape, represent almost no selective sorption. This is expressed by the uniform colour distribution in the coloumn, by the identical amount of adsorbed asphaltenes in all three layers, and by the closeness of this amount to the amount of asphaltenes in the original bitumen. On the other hand, hydrated lime has a high selective sorption capacity. This is due to the strong, active adsorption of its surfaces, to the rough surface texture, and to the relatively high specific surface of the particles. This sorption capacity is expressed by the distinct colour difference in the column (see Fig. 1), by the high concentration of asphaltenes in the upper layer in such a magnitude that vary considerably from the amount of asphaltenes in the original bitumen. Other types of filler, such as sandstone and basalt, represent intermediate capacity of selective sorption.

It should be emphasized that the results as described in Table III and discussed above, represent optimum density conditions of the filler mass in the columns. These optimum conditions were achieved after several test trials of filler columns at different densities. Table IV represents the effect of the density of two types of filler on the adsorption rate of the chemical groups of the bitumen. It can be seen that when the filler mass is compacted to lower densities than the optimum,

Type of filler	Optimum density of filler column ($g\,cm^{-3}$)	Gas–oil diluent	Normal heptane		Gas–oil diluent	
		Distribution of asphaltenes in the various layers (wt % of total asphaltenes) using gas–oil as diluent	Amount of asphaltenes (wt % of bitumen in layer)	Amount of malthenes (wt % of bitumen in layer)	Amount of asphaltenes (wt % of bitumen in layer)	Amount of malthenes (wt % of bitumen in layer)
Glass beads	1.34					
Top layer		32.5	26.0	74.0	26.0	74.0
Middle layer		31.6	20.5	79.5	25.0	75.0
Bottom layer		35.9	16.5	83.5	29.0	71.0
Sandstone	1.29					
Top layer		39.3				
Middle layer		31.6				
Bottom layer		29.1				
Basalt	1.45					
Top layer		40.6				
Middle layer		38.8				
Bottom layer		20.6				
Limestone	1.51					
Top layer		67.2				
Middle layer		23.1				
Bottom layer		9.7				
Hydrated lime	0.70					
Top layer		71.0	72.8	27.2	70.0	30.0
Middle layer		29.0	44.8	55.2	29.0	71.0
Bottom layer		traces	4.0	96.0	traces	100

there is much higher concentration of asphaltenes in the lower layer compared to the optimum density conditions. This is due to channelling of the diluent bitumen which occurs when the filler mass possesses too high porosity. It was also noticed that the good reproductibility of the results that were obtained under optimum density conditions was distorted to be poor under lower density conditions.

The change in the chemical components of the malthenes, when the bitumen was percolated through a layer of an active filler bed, such as hydrated lime, was further studied. The results obtained — characteristic of one of the set of experiments — are given in Table V. Since the total amount of the malthenes in the top layer decreased substantially after percolation (from 72.7% of the bitumen down to 27.2%), the components of the malthenes also decreased. However, when studying the change of these components with respect to the amount of the malthenes, different trends can be observed. In this respect, there is an increase in the relative proportion of the saturates, while the proportion

Type of filler	Limestone						Hydrated lime					
Density of filler column	$1.51\,g\,cm^{-3}$ (optimum)			Lower			$0.70\,g\,cm^{-3}$ (optimum)			Lower		
Layer	Top	Middle	Bottom	Top	Middle	Bottom	Top	Middle	Bottom	Top	Middle	Bottom
Amount of asphaltenes (% weight of the bitumen in the layer)	69.0	60.6	10.6	72.8	62.5	34.7	72.8	44.8	4.0	75.5	69.8	44.7
Amount of malthenes (% weight of the bitumen in the layer)	31.0	39.4	89.4	27.2	37.5	65.3	27.2	55.2	96.0	24.5	30.2	55.3

TABLE V The change in the chemical components of the malthene system after percolation through hydrated lime column

Component		Total amount of malthenes	Components of the malthenes		
			Resins	Saturates	Cyclics
Proportion by weight in	% of total bitumen	72.7	17.5	31.3	23.9
the original bitumen	% of malthenes	100	24.1	43.0	32.9
Proportion by weight in	% of total bitumen	27.2	2.9	15.4	8.9
the top layer of hydrated	% of malthenes	100	10.6	56.7	32.7
lime column after					
percolation					

of cyclics remains the same. Table V also indicates a decrease in the proportion of the resins. This tendency can be explained by the fact that a redistribution of the resins between the dispersed and the dispersing phase took place during the selective sorption process. The rate of change of these components, comprising the malthene system, is affected by the chemical composition of the bitumen, the nature of the colloidal system, the shape and size of the filler particles and their physical characteristics.

In this paper only the tendency of these changes was studied, since accurate quantitative data can be obtained only by an extensive study of a very large number of samples that may allow drawing quantitative conclusions as to the effect of each of the many parameters involved.

5. Behaviour of sand—asphalt mixtures

In order to stress the engineering application of the selective sorption effect of different types of filler, a test series was performed on sand asphalt mixtures. Three types of filler were tested: glass beads, limestone, and hydrated lime. These types represent the total range of selective sorption properties of the fillers. Samples were prepared according to the Marshall procedure (ASTM D 1559). The following factors were involved in the testing programme:

Aggregate (1 level): A well-graded quartzite sand (80% SiO_2). The graduation of the sand was held constant during the entire testing programme. Properties of the sand are described in Fig. 2.

Bitumen (1 level): A 60/70 asphalt cement. Properties are described in Table I.

Fillers (3 levels): Limestone dust, hydrated lime and glass beads. Properties of the fillers are described in Table II.

Filler proportions: The following filler proportions (by weight of the entire aggregate in the mixture) were used: for the hydrated lime, 0, 5,

10, 15, and 20%; for the limestone, 5, 10, 15, 20, and 25%; and for the glass beads, 15, 20, and 25%.

Filler proportion combination samples were prepared for each filler type in various bitumen contents for obtaining optimum conditions. Generally, five contents were used at intervals of 1%. Two samples were tested with each content. The values of the bitumen content vary according to filler type and filler proportion. Samples were tested for weight—volume analysis, Resilient Modulus [8], Marshall stability and flow. For each combination, the optimum bitumen content was determined, based on Resilient Modulus and Marshall stability criteria. Test results are summarized in Table VI and Fig. 3. The following trends can reflect the relationship between the selective sorption properties of the various fillers tested and the sand—asphalt mixture behaviour.

There is a marked difference in the strength properties (at optimum bitumen content) of sand—asphalt mixtures with different types of filler. In Fig. 3, it can be seen that the hydrated lime mixtures possess the highest optimum Resilient Modulus (M_r) and Marshall stability, and the
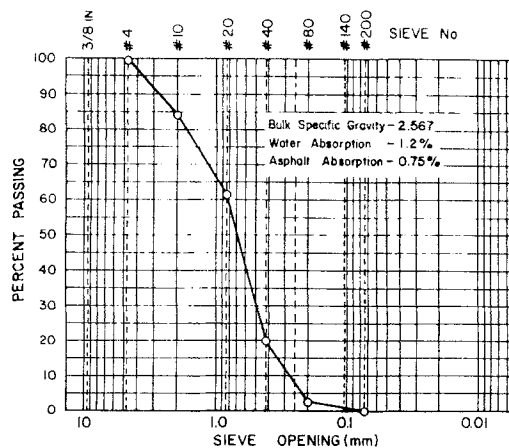

Figure 2 Properties of the siliceous sand used for the sand—asphalt mixtures.
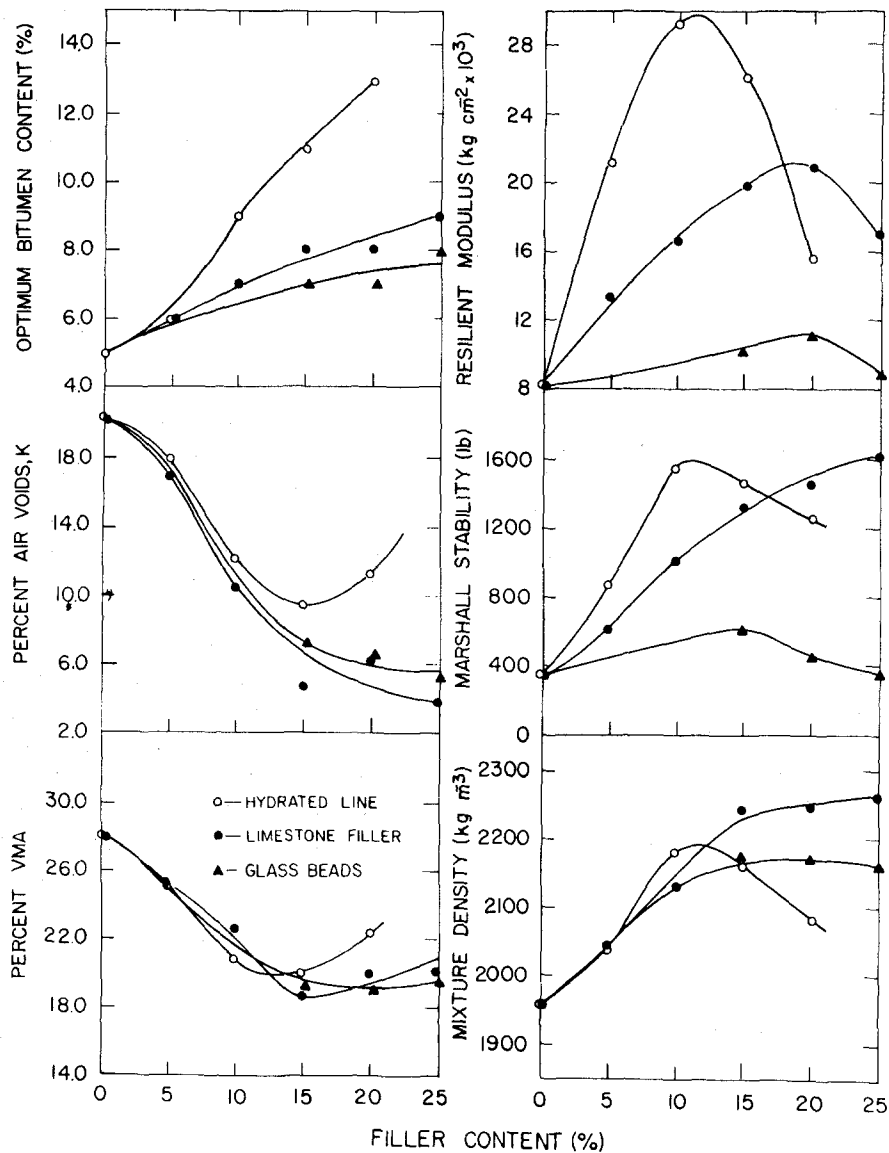
Figure 3 Basic properties of the sand–asphalt mixtures at their optimum bitumen contents, as a function of filler type and filler content.

glass beads the lowest. The limestone filler mixtures are of intermediate strength. It should be noted that the marked difference in optimum M_r between the limestone and glass bead mixtures is with the same filler content. These differences in strength are due to the combined effect of higher potential for selective sorption and higher geometric irregularity of the particles. As a result, the hydrated lime displays more efficient interlocking between particles, stronger bonds at the bitumen–filler interface, and lower amount of free bitumen in the mixture. These facts are valid despite the

higher air voids of the hydrated lime at total optimum conditions.

The optimum bitumen content also varies according to the type of filler. From Fig. 3, it can be seen that at a given filler content, and also at total optimum strength condition, mixtures with hydrated lime possess the highest optimum bitumen content, and those with glass beads the lowest. Limestone mixtures are intermediate. These trends were quite expected, and can be explained by the differences in the relative amount of free and fixed bitumen as affected by the selective sorption.

TABLE VI Properties of sand–asphalt mixtures at optimum bitumen content for three filler types and various filler content

Filler type	Filler content (%)	Optimum bitumen content (%)	Mixture density (kg m^{-3}) K	Per cent air voids	Per cent VMA	Per cent bitumen saturation S_b	Aggregate concentration C_v	Resilient modulus M_r (kg cm^{-2})	Marshall stability (1b)	Marshall flow (1/100")
Hydrated lime	0	5	1959	20.35	28.05	27.44	0.769	8 226	360	3.5
	5	6	2040	17.97	25.12	28.47	0.794	21 217	866	6
	10	9	2182	12.14	20.88	41.85	0.826	28 910	1551	10.5
	15	11	2160	9.43	20.08	13.02	0.829	26 215	1461	17
	20	13	2083	11.26	22.42	49.81	0.807	15 580	1261	18
Limestone	5	6	2041	16.91	25.34	32.94	0.790	13 269	617	7
	10	7	2133	10.44	22.52	53.74	0.806	16 612	1011	10.5
	15	8	2244	4.75	18.66	74.52	0.839	19 816	1318	10.5
	20	8	2246	6.12	19.88	69.26	0.827	20 914	1466	12
	25	9	2262	3.77	20.06	81.27	0.825	18 984	1621	14
Glass beads	15	7	2170	7.00	19.63	64.50	0.864	10 387	635	5.5
	20	7	2174	6.30	19.00	67.00	0.864	11 034	452	5
	25	8	2163	5.10	19.70	74.00	0.846	9 203	370	6

This phenomenon was discussed earlier in this paper.

This series of tests also confirms the rating of the different types of filler, as stated before, which stresses the extreme boundaries of the range as represented by the hydrated lime and the glass beads, and the intermediate behaviour by the limestone. The results also stress the physico-chemical effect of the filler on the behaviour of actual bituminous mixtures.

6. Summary and conclusions

The factors affecting selective sorption in the bitumen–filler interface and the difference in the capacity of various fillers for selective sorption of the chemical groups combining the bitumen were investigated and described in this paper. Test results were correlated with the behaviour of sand–asphalt mixtures. The following conclusions were arrived at:

(1) Among the fillers investigated, hydrated lime and limestone were the most effective, basalt was intermediate, while sandstone and mainly glass beads showed almost no capacity for selective sorption.

(2) Reproducibility of results was satisfactory only at suitable optimum densities of the filler column, although it could be observed that lower densities, i.e. less dense filler masses, result generally in an inferior capacity for separating the chemical groups composing the bitumen, due to channelling effects.

(3) Experimental conditions, such as perco-lation rate, affect the results appreciably and influence the reproducibilities considerably; they have, therefore, to be kept constant in order to allow a correct interpretation of the parameters representing the subject of this investigation.

(4) During percolation of bitumen through active filler column, such as hydrated lime, an increase was observed in the proportion of the saturates in the malthenes system, decrease in the resins, while the proportion of cyclics remained the same.

(5) The rating of the different types of filler based on their capacity of selective sorption is very well correlated with the physical and mechanical behaviour of actual sand–asphalt paving mixtures.

(6) The evaluation of selective sorption capacity of the filler is of great importance in bituminous mixture technology. Since the filler constitutes the ingredient with the highest specific mixture surface in the granular mass of the bituminous mixture, its surface activity properties influence the mechanical properties of the bitumen–filler system and the behaviour of the mixture. Therefore, the capacity of selective sorption can serve as an indication to the future effect of the filler on the aggregate–bitumen–filler adhesion and the stability and deformability of the bituminous mixture.

References

1. R. N. TRAXLER, "Asphalt, Its Composition, Properties and Uses" (Reinhold Publishing Corp., New York, 1961).

2. E. J. BARTH, "Asphalt Science and Technology" (Gordon & Breach Science Publishers, New York, 1962).
3. J. CRAUS, D.Sc. Thesis, Polytechnique of Bucharest (1969).
4. I. ISHAI and J. CRAUS, *Asphalt Paving Technol.* 46 (1977) 228.
5. J. CRAUS and I. ISHAI, ASTM *J. Testing & Evaluation* 5 (1977) 284.
6. Annual Book of ASTM Standards, Part 15 American Society for Testing and Materials, Metals Park, Ohio, 1977).
7. I. P. Standards for Petroleum and its Products (The Institute of Petroleum, Applied Science Publishers, London, 1976).
8. R. J. SCHMIDT, Highway Research Record No. 404 (Highway Research Board, Washington D.C., 1972) 22.