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HEALTH SAFETY AND THE ENVIRONMENT-AQUEOUS LEACHING OF PAC'S FROM BITUMEN

Bowen C., de Groot P.
(Shell Global Solutions International BV, The Netherlands)
Brandt C. A.
(Consultant, The Netherlands).
Paper will be presented by C. Bowen

ABSTRACT

The main applications of bitumen are in e.g. asphalt roads, roofs and hydraulic applications, where there is contact with water and therefore the potential for leaching of compounds into the environment. Polycyclic Aromatic Hydrocarbons (PAHs) are present at low levels in bitumen. Leach tests have therefore been performed to study the leaching behaviour of PAHs from nine petroleum bitumens, representative of commercially available products, and one asphalt made from one of the bitumens. The equilibrium PAH concentrations in the leach water from bitumens were found to stay well below the surface water limits that exist in several EEC-countries and also to be more than an order of magnitude lower than the current EEC limits for potable water. Leach water was also analysed for substances other than PAHs, such as metals; all were below the detection limit

Keywords: Leaching, Polycyclic aromatic hydrocarbons, bitumen, asphalt

1. INTRODUCTION

The main applications of bitumen are in the coating of the surfaces e.g. of roads, roofs, linings of water basins and pipes. All these applications have a potential for contact with water and this may lead to the leaching of components from the bitumen into the environment. In recent years there has been increased focus on environmental issues. This has cumulated in several countries setting limits for the release of potentially harmful substances into the environment and specifically, into surface and/or drinking water. Bitumen has a long history of use as a waterproofing agent and is traditionally regarded as a safe product. It does however contain low levels of potentially hazardous materials *viz*. Polycyclic Aromatic Hydrocarbons (PAHs) for which limits exist. This prompted us to study the leaching behaviour of this class of compounds from bitumen.

Few results of aqueous leaching of PAHs from bitumen (or asphalt) exist. In 1982 Miller[1] determined the sum of the 6 World Health Organisation (WHO) PAHs (fluoranthene, benzo(b)- and benzo(k)-fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene) The sum was less than 10 ng/l while the highest concentration for any one individual PAH was less than 5ng/l. The detection limit was 0.2-0.75 ng/l. The American Asphalt Institute[2] has reported leach tests of hot mix asphalt for metals, volatile and semi-volatile hydrocarbons and PAHs. Except for naphthalene (250 ng/l) all PAHs were below the detection limit which ranged from 194 ng/l for the 2-ring PAHs to 20 ng/l for the 3 to 6-ring PAHs. In a more recent study Brantley & Townsend examined leaching from reclaimed asphalt pavement[3]. Detection limits in this study for the 16 EPA PAHs were in the range 0.25 - 5 µg/l range. The results for all samples analysed were below these detection limits.

Many existing tests for leaching, applicable to bitumen/asphalt or solid waste, have a weak point in the working up procedure of the aqueous leachate and consequently unsatisfactory data for the higher PAH. A working-up system was therefore been developed including an enrichment procedure for PAH in aqueous leachate prior to analysis[4].

Nine bitumen samples were selected, covering a representative range of commercially available products. In addition to the bitumens one asphalt, made from one of the bitumens was tested. In this paper we will present data on the leaching of PAHs from those bitumens, showing that after a number of days equilibrium is reached and give a relation describing the leach concentrations as function of time. In addition it will be shown that pollutants other than PAHs virtually do not leach from petroleum bitumens.

2. METHODS AND MATERIALS

In principle two types of leaching methods can be distinguished:

1. Dynamic extraction methods. These are generally methods of wide applicability for solid wastes. Most methods prescribe a sampling technique, a size reduction step, the extraction medium, the solid/liquid ratio, extraction time and sometimes the apparatus.
2. Static Migration Tests, which generally measure the diffusion out of an intact surface into a known volume of water of specified quality, which is refreshed a number of times.

Because the primary use of bitumen is in intact structures, we chose to use a static leach test. For comparison we subjected an asphalt made from one of the bitumens to both the static and a dynamic test. Furthermore for a number of bitumens the water from one leach experiment was analysed for metals, volatile hydrocarbons, phenols and halogenated compounds

The static leach test chosen follows an existing Dutch test for building materials, NEN 7345 as far as possible[5]. This test comprises leaching with a fixed liquid / solid ratio of 4:1, using water acidified to pH 4, with refreshing of the leach water after 0.25, 1, 2.25, 4, 9, 16, 36 and 64 days. A cylindrical block of asphalt (100mm diameter, 64 mm high) was placed on glass rods in a covered glass dish. Because of the liquid-like nature of bitumen the test had to be slightly modified: instead of a block of bitumen, a layer of bitumen contained in a petri-dish has been used. Hence leaching takes place only from the bitumen surface that is in contact with water. The amount of water used was comparable for the asphalt and the bitumens.

The dynamic leach test has been performed following a European CEN test[6] using the "Zero Head Space Extractor" from Millipore, Bedford USA. The CEN test conditions are: size reduction of the sample to ≤ 4mm, leaching with water acidified to pH 4, with a liquid solids ratio of 10:1, agitating for 30 h at 30 rpm.

In order to attain a low limit of detection, double-distilled deinonised water purified over a XAD-2 column was used and great care was given to thorough cleaning of the glassware, preventing contamination with PAH from the environment and containers etc. In order to attain a low limit of detection 200 ml water was enriched by adsorption on an extra HPLC-pre-column (C_{18}) followed by back-flushing to the analytical column (all inline). PAC analysis was performed by HPLC with UV-fluorescence detection[7].

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3. BITUMENS TESTED

Nine bitumens have been tested, covering a representative range of commercially available products. A description of the samples is given in Table 1.

Table 1: Description of samples

Code	Description
A	Conventional Middle East penetration bitumen
B	Conventional Heavy Venezuelan penetration bitumen
C	Conventional Heavy Venezuelan penetration bitumen
D	Straight run vacuum residue of Middle East origin
E	Deeply vacuum flashed conversion residue from a thermal cracker ex D
F	Conventionally blown roofing bitumen ex D
G	Conventionally blown roofing bitumen of Middle East origin
H	Blown roofing bitumen of Middle East origin
I	Multigrade bitumen

In addition to the bitumens one asphalt, made from bitumen A was tested. For the static test a “Marshall” block made from a dense asphalt mix with aggregate < 4mm was used (weight 1192 g of which bitumen 7.9%m). For the dynamic leach test the same mix was used uncompacted.

4. RESULTS

PAHS - STATIC TEST

PAH concentrations were determined after each leaching period. Generally only the PAHs with 4 rings or less, which have the highest water solubility, were found in concentrations above 0.1 ng/l. Naphthalene was found in concentrations in the order of 10 to 100 ng/l, phenanthrene was the next highest and dominated the other 2+ring PAHs. Graphic representations of the naphthalene and Σ2+ringPAHs concentration against leach period are given in Figures 1 and 2 respectively.

Figure 1: Aqueous leaching of naphthalene from bitumen in static leach test

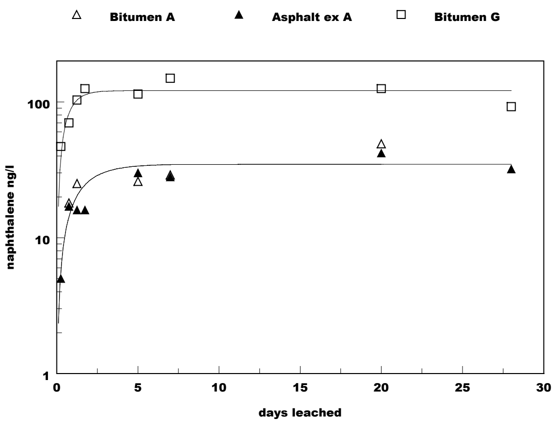
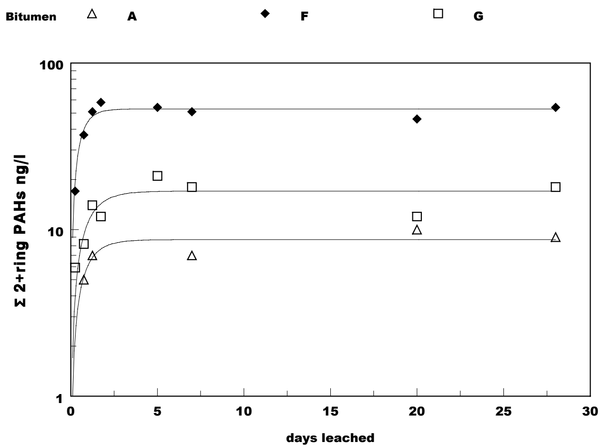


Figure 2: Aqueous leaching of Σ2+PAHs, in static leach test



The general pattern is that the concentration in the leach water increases and reaches a steady state concentration between 4 and 9 days. The average plateau concentrations (9+ days) are given in Table 2.

Table 2: Average plateau concentrations reached in the static leach test, ng/l

Bitumen code	A	B	C	D	E	F	G	H	I	DL*
1 Naphthalene	35	371	51	175	30	n.v.	120	0.9	168	0.3
2 Acenaphthene	1.3	17	5	2.4	0.6	2.7	0	0.3	11	0.04
3 Fluorene	2.1	42	7	3.6	0.8	19.4	11	3.8	44	0.02
4 Phenanthrene	4.1	180	47	2.9	3.3	15.9	5	1.0	82	0.06
5 Anthracene	0.1	12	5	0.5	0.5	6.1	0.3	0.1	28	0.07
6 Fluoranthene	0.4	1.7	0.8	0.16	0.1	1.7	0.1	0.1	1	0.05
7 Pyrene	0.4	3.9	1.4	0.47	0.5	4.3	0.3	0.1	4	0.04
8 Benz(a)anthracene	0.1	1.4	0.45	0.04	0.1	0.5	0.1	b.d.l.	b.d.l.	0.05
9 Chrysene	0.3	5.3	0.83	0.13	b.d.l.	0.5	0.1	b.d.l.	b.d.l.	0.06
10 Benzo(b)fluoranthene	b.d.l.	0.4	0.14	0.01	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.01
11 Benzo(k)fluoranthene	b.d.l.	0.2	0.14	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.02
12 Benzo(a)pyrene	b.d.l.	0.1	0.3	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.02
13 Dibenz(a,h)anthracene	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.04
14 Benzo(g,h,i)perylene	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.02
15 Indeno(1,2,3-c,d)pyrene	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.1
16 Coronene	0.03	0.05	0.09	0.04	0.01	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.03
Σ2+ringPAHs	8.8	263	68	10	5.9	51	17	5.4	172	
sum 6 WHO PAHs	0.43	2.33	1.38	0.17	0.08	1.7	0.07	0.07	1.47	

Notes: Calculated from the concentrations in the samples taken after 9,16,36 & 64 days; DL = Detection Limit for 200 ml; b.d.l. = below detection limit; n.v. - not valid.

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Table 3: PAH analyses in selected bitumen, (mg/kg)

	bitumen			Bsb limit
	A	E	G	
Napthalene	2.7	3.0	2.5	5
Acenaphthene	0.2	0.7	b.d.l.	
Fluorene	0.3	0.4	0.4	
Phenanthrene	1.8	2.0	1.1	20
Anthracene	0.2	0.2	0.1	10
Fluoranthene	0.9	0.8	0.3	35
Pyrene	0.9	1.0	0.3	
Benz(a)anthracene	0.7	0.2	b.d.l.	50
Chrysene	2.4	1.0	0.5	10
Benzo(b)fluoranthene	1.0	0.7	0.4	
Benzo(k)fluoranthene	0.4	0.3	b.d.l.	10
Benzo(a)pyrene	0.7	0.5	b.d.l.	50
Dibenzo(a,h)anthracene	0.5	0.3	b.d.l.	
Benzo(g,h,I)perylene	2.0	2.0	0.8	50
Indeno(1,2,3-c,d)pyrene	0.5	0.2	b.d.l.	50

Note:
Bsb = Dutch Bouwstoffenbesluit[8]; there is an additional limit, Σ 10 PAH 75 max.

The amounts leached in the whole static test range, as a % of that present in the bitumen (see Table 3) ranged from a maximum of 1.3% for naphthalene, less than 0.1 % for phenanthrene to <0.01% for the higher molecular weight PAHs. Assuming equilibrium for the longer leach periods the equilibrium concentration will depend on the concentration of the PAH in bitumen (C_{bit}) and the distribution coefficient between bitumen and water ($K_{BitWater}$).

$$K_{BitWater} = C_{bit}/C_w \qquad (1)$$

And the whole curve can be empirically described by

$$C_w = C_{bit}/K_{BitWater} \times (1 - \exp -kt) \quad (2)$$

where t = leach time and k = a constant that determines how fast equilibrium is reached. It is not possible to calculate a reliable k-value for comparing between bitumen, because the data in the first days are too imprecise.

5. BITUMEN VS. ASPHALT, STATIC AND DYNAMIC

In Table 4 the average plateau concentrations reached in the static tests on bitumen A and the asphalt made from it and the concentrations measured in the dynamic leach test are given.

Table 4 : Leaching of bitumen and Asphalt (static and dynamic) compared

	Bitumen A, concentrations in leachate, ng/l			
	static		dynamic asphalt	
	bitumen	asphalt	bitumen + aggregate	bitumen contribution
Naphthalene	35	33	52	52
Acenaphthene	1.3	0.8	1.0	0.4
Fluorene	2.1	b.d.l.	1.9	1.4
Phenanthrene	4.1	1.2	2.5	1.4
Anthracene	0.09	0.1	0.3	0.3
Fluoranthene	0.4	0.08	b.d.l.	b.d.l.
Pyrene	0.4	0.1	0.03	0.03
Benz(a)anthracene	0.06	b.d.l.	0.2	0.2
Chrysene	0.3	0.09	0.2	0.2
Benzo(b)fluoranthene	b.d.l.	b.d.l.	0.2	0.2
Benzo(b)fluoranthene	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Benzo(a)pyrene	b.d.l.	b.d.l.	0.2	0.2
Dibenzo(a,h)anthracene	b.d.l.	b.d.l.	0.1	0.1
Benzo(g,h,I)perylene	b.d.l.	b.d.l.	0.2	0.2
Indeno(1,2,3-c,d)pyrene	b.d.l.	b.d.l.	b.d.l.	b.d.l.

Note: b.d.l. = below detection limit

No significant difference exists between the outcome of the static test with bitumen or asphalt, also the build up of the concentration with time is very similar as is shown in figure 1 (open and closed triangles). In the dynamic test some of the 3-ring aromatics in the leach water seem partly to originate from the (new) aggregate. A comparison of the static leach tests with the dynamic test shows that for most of the PAHs the concentrations are similar, except for the 5-ring PAHs, where in the dynamic test concentrations in the order of 0.1 ng/l are found, whereas in the static test these are at least a factor of 10 lower. Because these results are based on one leach test more tests have to be performed to establish whether this difference is statistically significant.

6. COMPOUNDS OTHER THAN PAHS

In the Netherlands asphalt roads and (bituminous) roofing materials are considered to be construction materials as covered by the "Bouwstoffenbesluit"[8]. Limits exist for the leaching of various organic and inorganic materials (although not including PAHs) from these materials. The water from one leach experiment was therefore also analysed for metals, volatile hydrocarbons, phenols and halogenated compounds[9]. The data have been summarised in Table 5.

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Table 5: Compounds other than PAHs

Compounds	result	detection limit µg/l
Phenol and cresoles	all b.d.l.	<1
Chlorophenoles	all b.d.l.	<1.5
Chlorinated hydrocarbons and chlorobenzenes	all b.d.l.	<0.2
PCBs	all b.d.l.	<0.05
Chloro-pesticides	all b.d.l.	<0.05
Volatile aromatics = ≤C2-benzene	most b.d.l. toluene[1] between 0.2 and 0.4	<0.2
Metals		
Arsenic	all b.d.l.	<2.5
Cadmium	all b.d.l.	<1
Chromium[2]	range 4-20	
Copper	all b.d.l.	<10
Mercury	all b.d.l.	<0.1
Lead	all b.d.l.	<10
Nickel	all b.d.l.	<10
Zinc	all b.d.l	<20

Notes: b.d.l. = below detection limit

1. High toluene backgrounds were experienced.
2. In all samples, including the blank, chromium has been found that stems from the cleaning of the glassware.

Of the metals only chromium was found in the leach water. The chromium was also present in the blanks and originated from the bichromate/sulphuric acid used for cleaning the glassware. Apart from toluene, which probably originates from the atmosphere in the analytical laboratory, all other compounds analysed for were below the detection limit. This was not unexpected, because apart from traces of metals, none of these compounds is normally present in bitumen.

7. DISCUSSION

Leach tests, both static and dynamic have been performed on bitumen and one asphalt derived from one of the bitumens. The general pattern observed in the static leach test shows a diffusion controlled process in the first few days, after which equilibrium is reached. The equilibrium concentration depends on the PAH concentration in the bitumen and the distribution constant.

The PAH concentrations in the leach water stay well below the surface water limits that exist in several EEC countries and are also more than an order of magnitude lower than the current EEC limits for potable water[10]. For example, the Dutch limits[11] for PAHs in groundwater range from 7000 ng/l for naphthalene, 2000 ng/l for phenanthrene to 200 ng/l for benzo(a)pyrene; the maximum equilibrium concentrations in the leachate were > 400 ng/l, > 200 ng/l and 0.3 ng/l for naphthalene, phenanthrene & benzo(a)pyrene respectively.

It is interesting to note that, although the intention of the "Bouwstoffenbesluit" is to protect the environment and to govern emissions (including leaching) into the same, the Bouwstoffenbesluit does not place limits on the leaching of PAHs from construction materials. There are however compositional limits for 10 PAHs in the construction material - in this case asphalt. All PAH values, and Σ 10 PAH, for the bitumens examined comply with the limit applicable for asphalt.

The range of bitumens we have tested is fairly representative for current commercial practice. All bitumens showed the same leaching behaviour against time. This indicates that our findings will be valid for other petroleum bitumens. The results from the dynamic test show that it is possible to eliminate the long static leach test. If one wants to determine the equilibrium concentration one can use a dynamic test. As an alternative one can calculate the aqueous concentrations from the PAH content of the bitumen. Because no difference was found between bitumen and asphalt one can use these calculated values also for asphalt.

8. CONCLUSIONS

In the static leach test a range of petroleum bitumens, representative for current commercial practice all show the same leaching behaviour against time. In the first days the PAH concentration in the leach water increases and reaches a steady state concentration between 4 and 9 days.

Bitumen and asphalt, the latter both in the static and a dynamic leach test give similar results. For obtaining the equilibrium aqueous concentration, instead of the static leach test a dynamic leach test can be used. Instead of performing a leach test the aqueous PAH concentration can be calculated from $K_{bitwater}$ and the PAH concentration in the bitumen.

The PAH concentrations in the leach water from bitumens (plateau values) stay well below the surface water limits that exist in several EEC countries. They are also more than an order of magnitude lower than the current EEC limits for potable water.

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