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ADSORPTION AND DESORPTION PHENOMENA OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH) ON COAL FLY-ASH

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OBJECTIVES OF THE R&D PROJECT

The analysis of polycyclic aromatic hydrocarbons (PAH) is of great importance in environmental research. It is known from the literature that extraction of PAH from environmental samples is incomplete, so that there is still uncertainty about the absolute amounts of PAH in these samples. It is, therefore, necessary to develop and evaluate techniques suitable for the isolation of adsorbed PAH for analytical purposes.

To assess the feasibility of a reduction of PAH emissions in case of temperature-assisted adsorption of PAH on fly-ash in the bag-filter house of coal-fired installations, it is necessary to gain an insight into the absorption behaviour of PAH on fly-ash. The answers available from literature are insufficient.

This project can be divided into:

- Extraction of PAH from fly-ash for analytical purposes
- Study of the adsorption behaviour of PAH on fly-ash.

SUMMARY

Extraction of PAH from fly-ash for analytical purposes

Upon finding that the CO_2 pump was a source of oil (mentioned MT-TNO report R 89/074) the oil was replaced by a water/glycerol mixture in anticipation of another pump. This new pump, one with a stainless steel membrane, was ordered immediately but due to the long delivery time experiments had to start with the old pump. Test runs gave extracts containing some water, indicating diffusion through the teflon pump-membrane.
Three fly-ashes have been extracted, the results indicate a high extraction capacity.

Study of the adsorption behaviour of PAH on fly-ash

The set-up described in the semi-annual progress report MT-TNO R 88/127 has been made easier to operate by incorporation of a flame-ionisation detector (Figure 1). The performance of the adsorption-apparatus is satisfactory.
Adsorption experiments using fluoranthene and Fluidized Bed Combustion (FBC) fly-ash show a distinctive temperature influence: a rise in temperature in the range between 91 and 111°C shows an increase of adsorbed amounts of fluoranthene and a considerable decrease in the temperature range between 111 and 121°C.

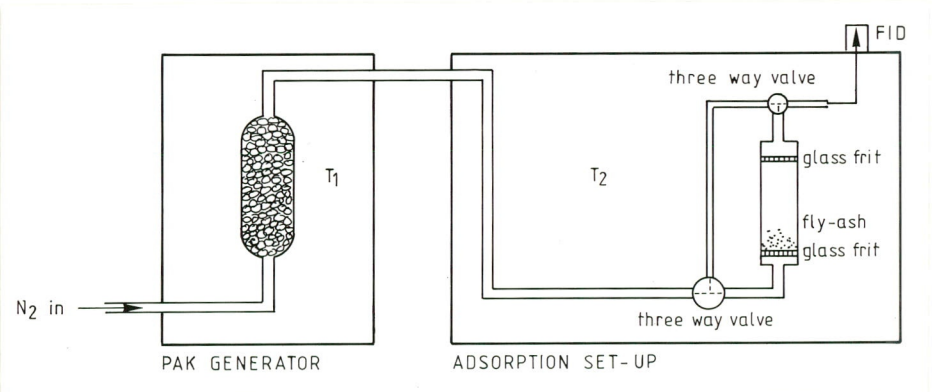


Figure 1 *Schematic representation of PAH adsorption apparatus.*

T_1 : Temperature gaseous PAH generator
T_2 : Temperature in adsorption set-up

INTRODUCTION

Extraction of PAH from fly-ash for analytical purposes

For analytical purposes it is necessary to develop methods for the extraction of PAH from fly-ash at the highest possible yield. Several extraction techniques will therefore be compared to establish which of them appear most suitable for fly-ashes.
The research programme is performed in co-operation with Bergbau Forschung GmbH (BBF, Essen, FRG).

Several methods for the extraction of PAH from fly-ash are:

a. ultrasonic extraction;
b. Soxhlet extraction;
c. liquid extraction;
d. vacuum sublimation;
e. supercritical CO_2 extraction.

Extraction methods a-c will be performed by BBF, and methods d and e by TNO.

Adsorption behaviour of PAH on fly-ash

Reduction of PAH emissions by coal-fired installations may be achieved by adsorption of PAH on fly-ash in the bag filter house of such installations. To study the gaseous adsorptive behaviour of PAH on fly-ash, PAH has to be generated in the gas phase. A so-called "shallow bed" apparatus will be used for the exposure of fly-ash to the stream of gaseous PAH. PAH concentration in the gas phase will be determined by using a Flame Ionisation Detector (F.I.D.).

RESULTS AND DISCUSSION

Supercritical CO_2 extraction of PAH from fly-ash for analytical purposes

Upon finding that the CO_2 pump was a source of soil of oil (mentioned in the semi-annual progress report MT-TNO R 89/074), probably caused by diffusion of the oil through the teflon pump membrane, a new CO_2 pump with a stainless steel membrane was ordered. In the meantime, the oil was replaced by a water/glycerol mixture. Extractions with CO_2 pressures of 150 bar were possible and consequently performed.

All samples were analysed with reversed phase HPLC. The column used was a "Supelco PAH" column. A methanol-water gradient was used to separate the components. The PAH were monitored by their fluorescence (g_{exc} = 254 nm, g_{det} > 380 nm). Use of a standard PAH solution (Figure 2) made it possible to identify and quantify the PAH in the samples obtained. The samples were qualitatively and quantitatively analysed for 22 PAH, i.e. phenanthrene, anthracene, fluoranthene, pyrene, 3,6-dimethylphenanthrene, triphenylene, benzo(b)fluorene, benzo[a]anthracene, chrysene, benzo[e]pyrene, benzo(j)fluoranthene, perylene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo(a,j)-anthracene, benzo(a,l)pyrene, benzo[ghi]perylene, ideno[1,2,3-cd]pyrene, 3-methylchol-anthrene and anthanthrene.

The following three fly-ashes have been extracted: DL/840215, Z/840208, and HD/180. See for the origins of the ashes semi-annual progress report MT-TNO R 88/287.
All extractions were carried out under the same conditions regarding CO_2 pressure (150 bar) and temperature (55°C), whereas the extraction duration varied. Each extract was removed and analysed at regular time intervals. The extraction was stopped when the amount of extracted PAH reached the detection limits (see Table 1 for extraction times used). In all cases 1.0 gram of fly-ash was extracted.
No PAH were found in runs without fly-ash.

With each subsequent extraction less PAH was found, more than half of the total amount extracted was found after three hours of extraction, furthermore no difference in extraction behaviour was found between PAH of different molecular weight. See for the results of the individual extractions of ash DL/840215, Table 4.

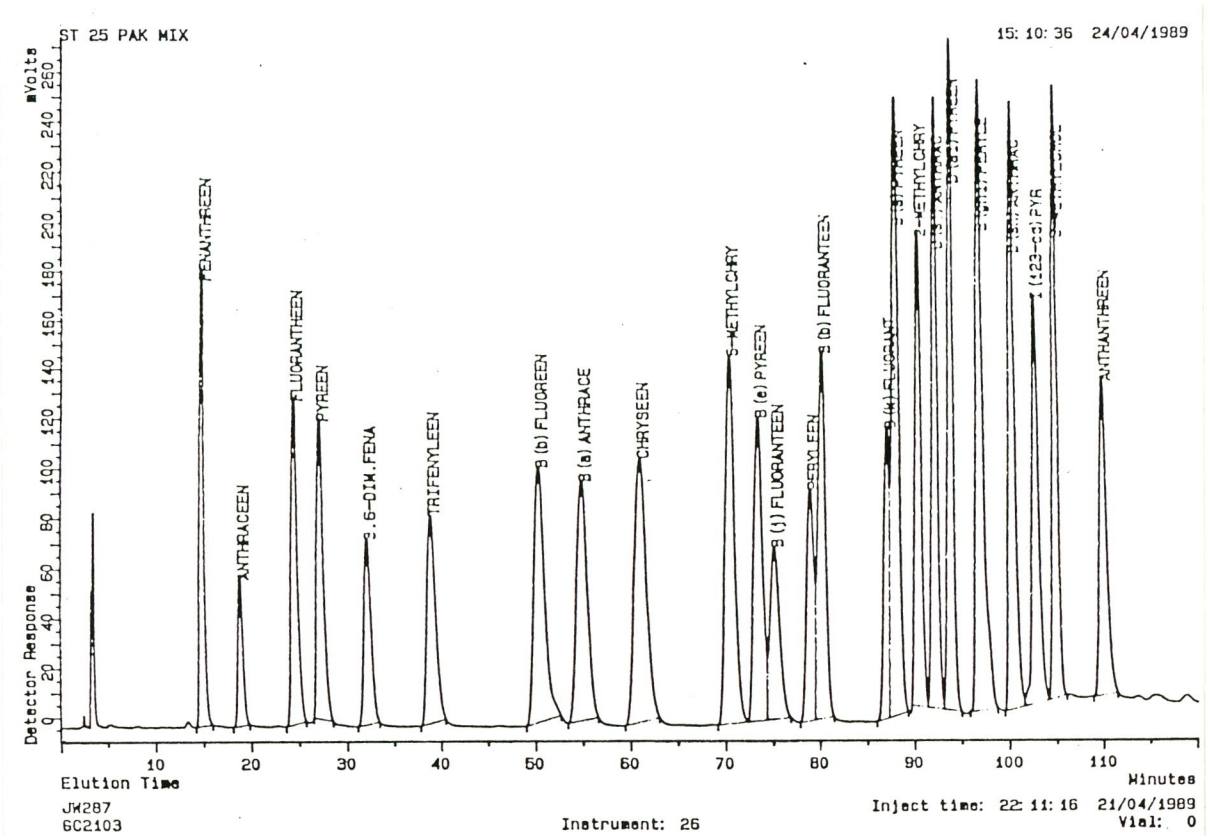


Figure 2 *Reversed phase HPLC chromatogram of the standard PAH solution.*

Table 1 *Extraction and sampling times.*

Fly-ash	Sample taken after extraction time (hours)	Total extraction time (hours)
DL/840215	3, 7 10.5, 14.5, 20, 22, 27, 34, 41, 47, 53, 62.5	62.5
Z/840208	6, 12, 16	16
HD/180	4, 8.5, 14	14

The total amounts extracted from the three fly-ashes are listed in Table 2. When compared with the results of the vacuum sublimation of the same ashes (Tables 5, 6, 7) one can see that the amounts of PAH extracted with supercritical CO_2 are much higher. Besides in the case of fly-ash Z/840208 some PAH were extracted which were not found with vacuum sublimation (see Table 6). The preliminary conclusion could therefore be that supercritical CO_2 extraction is a better extraction method than vacuum sublimation.

Table 2 *Total amount PAH extracted from fly-ash (ng/g ash).*

Fly-ash	DI/840215	Z/840208	HD/180
phenanthrene	6732	797	173
anthracene	561	24	–
fluoranthene	11516	324	36
pyrene	8297	215	–
3,6-dimethylphenanthrene	–	24	–
triphenylene	–	–	–
benzo(b)fluorene	–	152	–
benzo[a]anthracene	4953	15	–
chrysene	6095	–	–
benzo[e]pyrene	–	248	–
benzo(j)fluoranthene	–	–	–
perylene	8	–	–
benzo[b]fluoranthene	12117	18	–
benzo[k]fluoranthene	5017	2	–
benzo[a]pyrene	3945	–	–
dibenzo[a,j]anthracene	9	–	–
dibenzo[a,l]pyrene	2868	–	–
benzo[ghi]perylene	23217*	–	–
dibenzo[a,h]anthracene	8806*	–	–
indeno[1,2,3-cd]pyrene	12885*	–	–
3-methylcholanthrene	3044*	–	–
anthanthrene	1109*	–	–

* maximum amount extracted, uncertainty due to interference by unknown compounds.
– = not detectable.

The striking difference in amounts PAH extracted between the three ashes was also encountered in the vacuum sublimation experiments (Tables 5, 6, 7). This difference might be explained by either a different PAH content of the ashes or a different stabilisation of the PAH on the surface of the ashes. The latter could have influenced the ease of extraction, as indicated by the lower overall PAH content and absence of PAH with higher molecular masses on ashes Z/840208 and HD/180 or decomposition of PAH during storage as indicated by the decomposition of PAH on the ashes Z/840208 and HD/180 during the

vacuum sublimation experiments at higher temperatures while no such effects were observed with ash DL/840215.

Adsorption behaviour of PAH on fly ash

The experimental set-up described in the semi-annual progress report MT-TNO R 88/127 has been modified by using a flame ionisation detector (F.I.D.) as the detection method instead of using a fluoresence detector.
This set-up was placed inside a oven with an accurate temperature control.
The PAH gas stream was generated by leading a constant nitrogen stream over glass pearls which were spiked with PAH (fluoranthene) and kept at a constant temperature. By turning the valves the PAH gas stream could be directed either through the bypass or through the fly-ash. The concentration of the gas stream is monitored continually for it was led through an F.I.D. (Figure 1).

The experimental results are described in Table 3.
In all cases 0.2 gram of fly-ash A4 870116 04 441 P.M. and fluoranthene were used. The fluoranthene gas stream was generated at 64.5°C, the nitrogen flow was 1.5 l/h and the fluoranthene concentration was $6.9*10^{-6}$ g/l.

Table 3 *Total amount adsorbed and/or decomposed (μg).*

Adsorption time (hours)	Adsorption temperature (°C)			
	91	101	111	121
10	43.6	48.5	51.9	29.9
15	60.0	65.7	71.1	39.6
20	74.4	80.2	87.2	46.8
22	79.8	85.3	93.4	49.2
24	85.3			52.3
30				59.4

The data show that in the temperature range between 91 and 111°C adsorption (/reaction) proceeds faster with an increase of temperature. However between 111°C and 121°C the total amount adsorbed (/reacted) and the adsorption (/reaction) rate decrease considerably.

This change of adsorption behaviour occurs approximately when the temperature rises above the melting point temperature of fluoranthene. Further experiments with other PAH will show whether this is systematic.

Table 4 *Amount PAH (ng) extracted at individual runs (fly-ash DL/840215). "–" = not detectable*

	Duration of subsequent extractions (hours)											
	3	**4**	**3.5**	**4**	**5.5**	**2**	**5**	**7**	**7**	**6**	**6**	**9.5**
phenanthrene	3672	1010	248	418	353	147	211	489	46	55	128	–
anthracene	340	102	20	37	21	12	19	5	2	1	1	–
fluoranthene	6662	1991	536	693	577	295	422	206	70	23	20	21
pyrene	4145	1508	497	561	483	209	352	117	153	114	64	94
3,6-dimethylphenanthrene	–	–	–	–	–	–	–	–	–	–	–	–
triphenylene	–	–	–	–	–	–	–	–	–	–	–	–
benzo(b)fluorene	–	–	–	–	–	–	–	–	13	–	–	–
benzo[a]anthracene	2961	853	274	296	247	123	175	6	18	–	–	–
chrysene	3701	1038	300	337	294	135	199	63	28	–	–	–
benzo[e]pyrene	8586	–	–	–	–	–	–	–	–	–	–	–
benzo(j)fluoranthene	–	–	–	–	–	–	–	–	–	–	–	–
perylene	–	–	–	–	–	–	–	–	8	–	–	–
benzo[b]fluoranthene	6810	2134	760	765	660	334	492	108	55	10	9	13
benzo[k]fluoranthene	2813	910	314	316	270	135	199	34	20	3	3	4
benzo[a]pyrene	1925	839	301	296	247	122	188	–	18	4	3	4
dibenzo[a.j]anthracene	–	–	–	–	–	–	–	9	–	–	–	–
dibenzo[a.l]pyrene	1400	597	209	214	177	114	129	16	12	–	–	–
benzo[ghi]perylene*	9400	5405	2092	2141	1884	947	1348	–	–	–	–	–
dibenzo[a.h]anthracene*	4300	1849	669	683	600	295	410	–	–	–	–	–
indeno[1,2,3-cd]pyrene*	6218	2560	1007	1071	730	431	668	–	–	–	–	–
3-methylcholanthrene*	1258	683	275	286	259	112	152	19	10	–	–	–
anthanthrene*	311	285	110	138	141	47	77	–	–	–	–	–

* maximum amount extracted, uncertainty due to interference by unknown compounds.

Table 5 *Yields of PAH (ng/g ash) in vacuum sublimation samples from fly-ash DL/840215 (– = not detectable).*

	Temperature (°C)			
	20	**30**	**60**	**175**
phenanthrene	120.4	27.4	462.0	2500.0
anthracene	2.6	0.8	8.5	> 320.0
fluoranthene	42.1	14.1	161.7	> 4100.0
pyrene	–	–	–	1400.0
triphenylene	–	–	–	–
benzo[a]anthracene	14.6	–	62.4	1600.0
chrysene	35.3	–	154.0	1900.0
benzo[e]pyrene	–	–	184.8	2200.0
perylene	–	–	–	130.0
benzo[b]fluoranthene	34.4	9.1	146.3	> 2000.0
benzo[k]fluoranthene	13.8	4.2	59.3	> 830.0
benzo[a]pyrene	13.8	5.0	62.4	700.0
benzo[ghi]perylene	–	–	≤ 238.7	1100.0
indeno[1,2,3-cd]pyrene	45.6	11.6	200.2	1300.0
anthanthrene	3.5	–	14.6	47.0

Table 6 *Yields of PAH (ng/g ash) in vacuum sublimation samples from fly-ash Z/840208 (– = not detectable).*

	Temperature (°C)			
	20	**30**	**60**	**175**
phenanthrene	21.3	20.77	37.4	2.6
anthracene	2.13	2.01	2.04	0.1
fluoranthene	11.36	9.38	24.48	1.7
pyrene	–	–	14.28	0.6
triphenylene	–	–	–	–
benzo[a]anthracene	–	–	–	–
chrysene	–	–	–	–
benzo[e]pyrene	–	–	–	–
perylene	–	–	–	–
benzo[b]fluoranthene	–	–	–	–
benzo[k]fluoranthene	–	–	–	–
benzo[a]pyrene	–	–	–	–
benzo[ghi]perylene	–	–	–	–
indeno[1,2,3-cd]pyrene	–	–	–	–
anthanthrene	–	–	–	–

Table 7 *Yields of PAH (ng/g ash) in vacuum sublimation samples from fly-ash HD/180 (– = not detectable).*

	Temperature (°C)			
	20	**30**	**60**	**175**
phenanthrene	–	–	–	2.7
anthracene	0.76	–	–	0.1
fluoranthene	–	–	–	0.6
pyrene	–	–	–	–
triphenylene	–	–	–	–
benzo[a]anthracene	–	–	–	–
chrysene	–	–	–	–
benzo[e]pyrene	–	–	–	–
perylene	–	–	–	–
benzo[b]fluoranthene	–	–	–	–
benzo[k]fluoranthene	–	–	–	–
benzo[a]pyrene	–	–	–	–
benzo[ghi]perylene	–	–	–	–
indeno[1,2,3-cd]pyrene	–	–	–	–
anthanthrene	–	–	–	–

CONCLUSIONS

- The preliminary conclusion is that supercritical CO_2 extraction is a better extraction method than vacuum sublimation for the extraction of fly-ash.
- Fly-ash DL/840215 has a much higher extractable PAH content than the fly-ashes Z/840208 and HD/180 which is in accordance with the results from the vacuum sublimation.
- The set-up for gas phase PAH adsorption experiments is working properly. The results of the experiments show a distinctive temperature influence, indicating the existence of a "critical" temperature above which the adsorption decreases considerably.

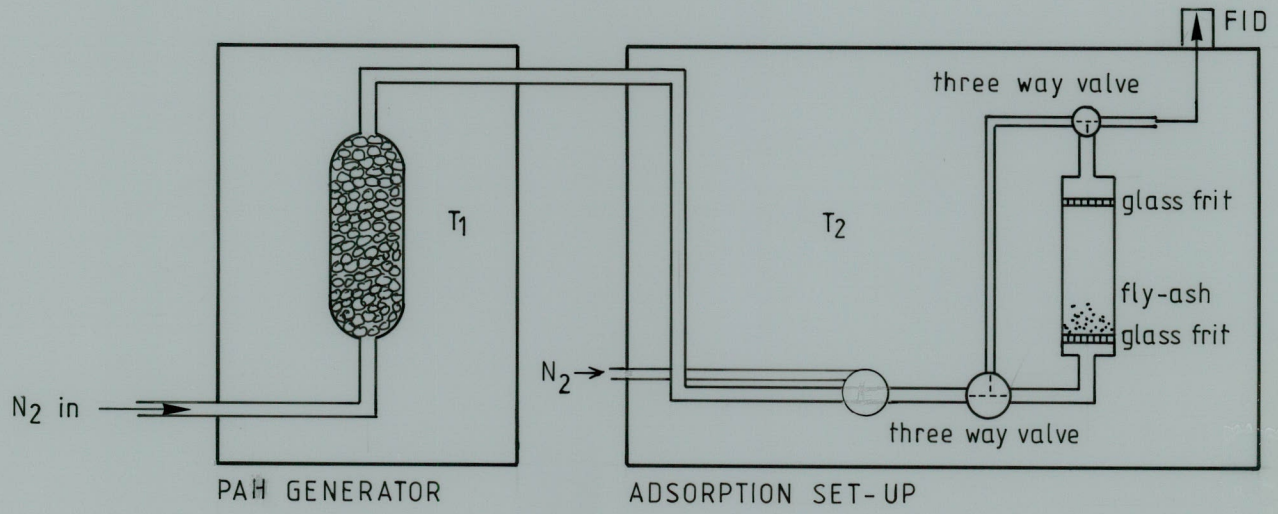
PROPOSED WORK FOR THE NEXT PERIOD (JULY - DECEMBER 1989)

A. *Supercritical CO_2 extraction of PAH from fly-ash for analytical purposes*

- The remaining four fly-ashes will be extracted using the same experimental conditions.
- Extractions will be done using different temperatures and CO_2 pressures to perfect extraction efficiency.
- The same fly-ash spiked with PAH used in the Sohxlet extractions by Bergbau Forschung GmbH will be extracted with supercritical CO_2.

B. *Adsorption behaviour of PAH on fly ash*

- Adsorption experiments will be done using other PAH.
- A model description of the adsorption process will be developed and computer simulations of the adsorption process will be carried out.



PAH GENERATOR
ADSORPTION SET-UP
N_2 in
N_2
three way valve
glass frit
fly-ash
glass frit
three way valve
FID
T1
T2