POSTER

EVAPORATION AND VAPOUR CHARACTERISATION OF LOW-PAH ANODE BINDERS

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INTRODUCTION

Organic vapour emissions from coal-tar pitch used as a binder in the anode paste are a concern for the aluminium smelters. The Søderberg anode technology is the greatest contributor, but it is also a problem for the baking plants for prebaked anodes. The government has imposed concentrations limits for the group of the organic emissions called polyaromatic hydrocarbons (PAH). Pitch producers have responded to this by offering PAH-reduced anode binders. These are coal-tar pitches distilled to a significantly higher softening point than ordinary binders. They are then refluxed with an oil or distillate fraction to a more normal softening point. The reflux oil contains no PAH or it contains PAH species which are found not to be carcinogenic. The quantification of the PAH and limit values can vary from one target compound and up to 16, dependent on each country's regulations and legislation. In this work we have analysed 16 PAH compounds, from phenanthrene to dibenzopyrenes (Table 1).

EXPERIMENTAL

The pitches used in this investigation (Table 2) were received from two commercial pitch distillers (A and B). They are samples from shipments to aluminium smelters and samples of more experimental types which the distillers are capable of producing at a larger scale. The pitch vaporisation experiments were performed at 150°C, 185°C and 220°C, which covers the normal temperature variation on a Søderberg anode top. The pitch (300 g) was heated in an oil bath rotary evaporator. During the vapour collection, the flask was flushed with argon. The vapour was sucked through a glass tube (id=7mm, l=430mm) filled with an adsorbent (XAD-2) to collect the lighter compounds. The tube had a glass frit at the lower end to prevent condensed vapours from run back into the melt. The carrier gas volume sucked through the absorbent was measured at the pump. The condensed phase in the glass tube was dissolved in toluene and the PAH in the adsorbent removed by Soxlet extraction for 15 hours with toluene. The sample was immediately analysed on a gas chromatograph.

RESULTS AND DISCUSSIONS

Total PAH. An anode paste plant can often handle a minor increase in pitch softening point, say 10-20°C, without major investments or replacements of existing mixing equipment. However, a simple continuous distillation of a pitch to 10°C higher softening point, from nominal 120°C Mettler (A1) to a nominal 130°C (A2) pitch, will not decrease the total PAH emissions from the anode top substantially, as shown in Figure 1. Two cut-back pitches from producer A (A3,A4) have markedly reduced their PAH emissions, as shown in Figure 1. The data also shows the importance of

Table 1. PAH compounds analysed.

No.	PAH compound	Abbrev.	Clin. test
1	Phenanthrene	PH	ue
2	Anthracene	A	ne
3	Fluoranthene	FA	ne
4	Pyrene	P	ne
5	Benzo(a)fluorene	BaF	ue
6	Benzo(b)fluorene	BbF	ue
7	Benzo(a)anthracene	BaA	se
8	Chrysene/Triphenylene	C/T	se
9	Benzo(b)fluoranthene	BFA	se
10	Benzo(k)fluoranthene	BFA	se
11	Benzo(e)pyrene	BeP	ue
12	Benzo(a)pyrene	BaP	se
13	Indeno(1,2,3-cd)pyrene	IP	se
14	Dibenzo(a,h)anthracene	DBA	se
15	Dibenzo(g,h,i)perylene	BPE	ue
16	Dibenzopyrenes;((a,e),(a,h),(a,i))	DBP	se

ne: No evidence of cancer in animals.
ue: Unsufficient evidence of cancer in animals.
se: Sufficient evidence of cancer in animals.

Table 2. Investigated pitches.

Pitch	Production process	Soft.pt., Mettler (°C)
A1	Vacuum dist. anode pitch, continuous still	119.2
A2	Vacuum dist. anode pitch, continuous still	131.1
B1	Vacuum dist. anode pitch, continuous still	122.4
A3	Vacuum distilled to high soft.pt., refluxed	122.4
A4	Vacuum distilled to high soft.pt., refluxed	132.0
B2	Vacuum distilled to high soft.pt., refluxed	130.7
B3	Vacuum distilled to high soft.pt., refluxed	131.8

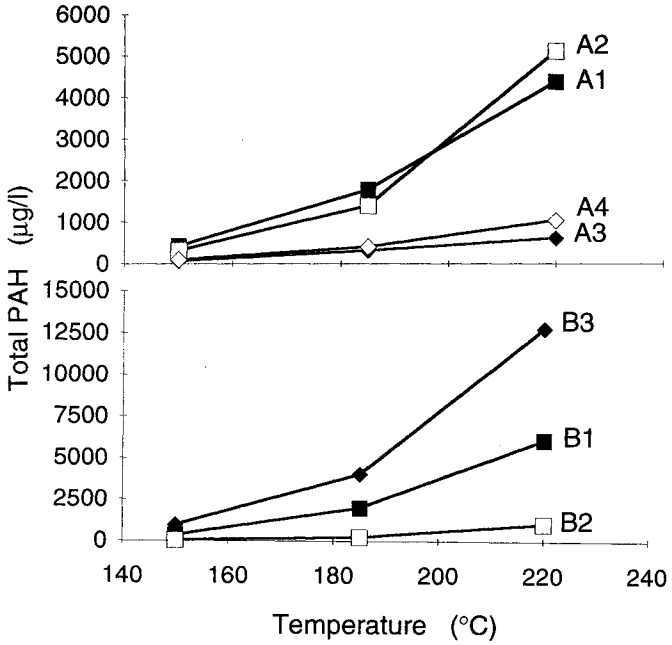

Figure 1. Total PAH emissions as function of temperature.

maintaining a low anode top temperature. For pitch A1 the PAH emissions are increased by a factor of 4.3 from 150-185°C and by a factor of >10 at 220°C. Pitch B1 is a normal vacuum distilled anode pitch while B2 is a cut-back pitch refluxed with a non-PAH oil. B3 is also a cut-back pitch but has been refluxed with an oil with a high content of light PAH species. Its total PAH emission is therefore much higher than for a standard anode pitch.

The PAH vapour distribution. PAH emissions from phenanthrene to benzo(a)pyrene were observed above most pitches. The PAH vapour distributions at 220°C are shown in Figure 2 for the A pitches. Vapour species from phenanthrene to chrysene are reduced above the cut-back pitches (A3,A4) compared to the standard pitches (A1,A2). However, the vapour emissions of the heavier compounds are, within the experimental uncertainty of the experiments, not reduced above the cut-back pitches.

Figure 3 shows the PAH distribution above the B pitches. The vapour PAH distribution above cut-back pitch B2 indicates that this pitch has been subjected to a severe vacuum distillation (very high softening point) prior to reflux. The use of a phenanthrene oil is evident from the PAH vapour profile from B3. Depending on local regulations and legislation, PAH emissions from B3 can be classified as being either low or excessive.

CONCLUSIONS

A modest softening point increase (10-20°C) in continuous vacuum distilled pitches does not give a significant reduction in the PAH vapour emissions.

The maintenance of a low anode top temperature is important in controlling PAH emissions.

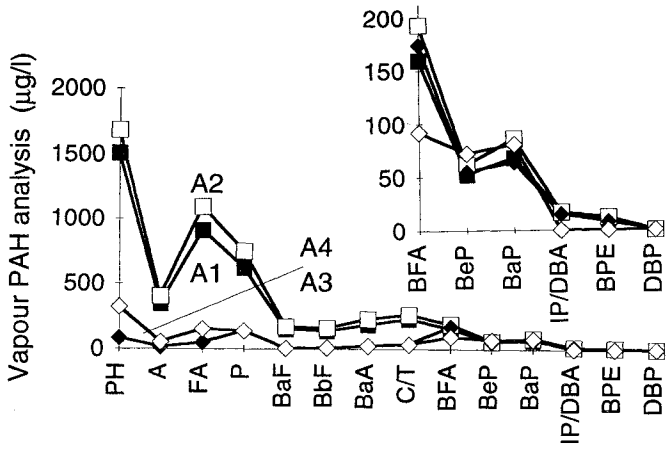

Figure 2. Vapour PAH distribution above A pitches at 220°C.

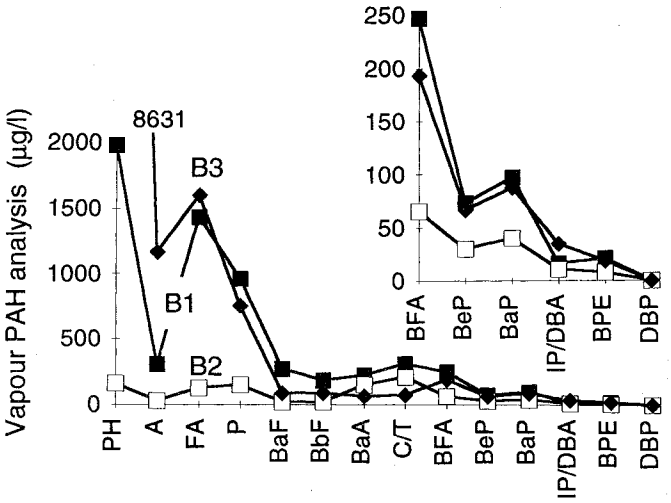

Figure 3. Vapour PAH distribution above B pitches at 220°C.

The use of cut-back pitches can significantly lower the emissions of light PAH species. Emissions of the heaviest PAH compounds are not significantly influenced.

Each individual country's PAH regulation and legislation may influence the make-up of reflux oils used in cut-back anode pitches. Similar PAH emission profiles may be classified as being low PAH and acceptable in one country or excessively high and unacceptable in another. Since this is a definition item, and anode binder pitches are an internationally traded commodity, it adds confusion to the end user of this important raw material.

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