Level of activated-coke technology for flue gas dust collection behind refuse destruction plants looking at the problem from the special aspects of dioxin separation

Walter Dannecker, University Hamburg

Hans Hemschemeier, HUGO PETERSEN, Wiesbaden

1. Summary

When searching for processes and methods for the most extensive removal of harmful and toxic substances from the air and sewage water the highly effective adsorptive characteristics of activated carbons had been discovered by the turn of the century. The large-scale use of activated coke filters for flue gas dust collection behind power stations did not begin until really late in the 80s with the primary objective of removing sulphur dioxide extensively from the flue gases. Today, in the Federal Republic of Germany, approx. 4 million Nm^3/h of flue gases from power stations are purified by means of activated-coke filters. In the process different kinds of plant engineering and activated-coke qualities are used.

After the experience had been gained in the power station sector regarding the separation of SO_2 and the catalytic reduction of NO_x, when introducing this technology for subsequent dust collection at refuse destruction plants, there was the additional task of investigating the separating ability of activated coke for the wide range of different specific harmful substances. Above all, these include the groups of organic harmful substances, such as PCDD, PCDF, PAH and PCBs, as well as the toxic, anorganic harmful substances such as heavy metals and their compounds, but above all mercury, however, and also the hydrogen halides which exist in high concentrations, HCl and HF. Investigations of this have been carried out at the refuse destruction plant in Hamburg-Stapelfeld with form-activated coke, as well as at the refuse destruction plant in Dusseldorf-Flingern, which belongs to the city's department of works, using lignite coke. In the following article, the level of activated-coke technology that has been reached is introduced and, using the proven purification performance of the activated coke in the investigations carried out by Prof. Dannecker, University Hamburg, particularly for dioxins, furans and mercury as well as the possible potential for the application of this technology both in refuse and waste disposal and also in all other processes involving particular emissions of harmful substances is made clear.

2. Adsorption Material

Nowadays, there are essentially two commercial types of activated coke on the market which are used. Here it concerns, on the one hand, the form-activated coke developed and sold by BERGBAU-FORSCHUNG (mining research) on a hard coal basis and, on the other hand, the open-hearth furnace coke on a lignite basis sold by RHEINBRAUN. Cokes or activated carbons are characterized by a large internal pore surface, which can bind a very wide spectrum of materials adsorptively. The pore surfaces of the activated cokes used nowadays on an industrial scale are between 300 and 800 m^2/g of activated coke. Between the price of openhearth furnace coke and the price of form-activated coke there is nowadays a proportional difference of approx. 1:10 to 1:20, depending on the quality. At the beginning of the development of activated-coke technology, this price difference led to two fundamentally different directions of development. When form-activated coke is used and has been saturated with impurities and harmful substances, it is purified or desorbed mechanically, in order to recover it in this way and be able to use it again. When the open-hearth furnace coke, which is good value, is used and has been loaded with harmful substances, the waste is normally disposed of by combustion in the subsequent combustion plant.

For many years now, the use of activated coke or carbon has been tested at numerous pilot and demonstration plants. In the end, the experience gained here, and in particular the negative experience, determines the present-day reactor conception of HUGO PETERSEN, which, up to now, has proven itself on an industrial scale up to now regarding the pollution of over 2,5 million Nm^3/h of flue gases behind power stations.

3. Description of Process

The activated-coke filter developed by HUGO PETERSEN is normally used for the final purification. Depending on the conception of the combustion plant, the activated-coke filter is arranged after a wet wash or after a dry flue gas purification plant. In the case of a flue-gas preliminary purification, which is normally wet, the flue gas, which has a temperature of 60°C, is firstly heated up in a heat exchanger to about 120°C as the operating temperature for the activated-coke filter. HUGO PETERSEN activated-coke filters are based on the so-called cross-flow principle, i.e. the flue gases are passed transversely towards the shifting movement of the coke, which is directed from top to bottom.

The cross-flow technology permits the coke bed to be subdivided vertically into three layers, from where the waste can be disposed of separately and according to the different loading concentrations or other defined command variables via individual extractors which can be controlled. Through this multilayered technology a minimal amount of coke is used up, selective adsorption of harmful substances (over the first 100 mm of the coke layer the various kinds of dust, Hg, dioxins and furans are already separated) is achieved and also selective waste disposal of coke loaded with harmful substances from the first layer and of coke loaded with SO_2 and HCl from the second layer. Since the individual layers of coke are not drawn off at the same time and a third quasi static "police layer" represents the last barrier for the purified gases, the extraction of coke dust is prevented when the first layer has to be drawn off more freqently due to dust which has been added, and when the second layer has to be drawn off less frequently due to the command variable SO_2. The amount of coke loaded with harmful substances from which the waste has to be disposed of in this way is only approx. 10 % of the total amount of waste used. By injecting ammonia into the flow of crude gas and by using the form-activated coke, which is a more effective

catalyst compared to the open-hearth furnace coke, nitrogen oxides can also be effectively removed from the flue gases in the course of the continued reduction of harmful substances.

4. Separating Efficiencies

The separating efficiency of activated coke for SO_2 and the catalytic effectiveness for the reduction of NO_x have been adequately proven at large scale industrial plants. To prove the separating efficiency of activated coke for organic and anorganic harmful substances, numerous tests have been carried out over the past few years. Here we are referring to measurements taken in the special field of Refuse and Waste Industry at the Technological University in Berlin at the large-scale test plant BEWAG, Oberhavel power station, and to the tests made by Prof. Vogg - the results were published in the magazine "Refuse and Waste" in 1986 - but we are also referring to the tests carried out by DUSSELDORF DEPARTMENT OF WORKS behind Flingern refuse incinerating plant and the tests carried out by RHEINBRAUN or BERGBAU-FORSCHUNG (today: DMT - Company for Research and Testing Ltd.).

The investigations carried out by Prof. Dannecker at Stapelfeld incinerating plant are of particular significance. The aim of these extensive tests was to investigate the separation of the entire spectrum of harmful substances in the flue gases behind incinerating plants. The reults were to be the basis for the planning of plant units. The test results can be summarized as follows.

The average results of all 16 samples for separating mercury show that filterable mercury with an efficiency of over 98 % was separated. The emissions of the sums taken from dust-bound heavy metals and those emitted gaseously from the various classes of harmful substances were clearly less than the values permitted in the TA Luft '86 (Technical Instruction for Air) or new ordinance BImSch (draft 05.04.90), and they were the sum of the mass concentration of substances

in	class III	341 g/Nm³,	permissible	5000 g/Nm³,
for the sum	class II	8,8 g/Nm³,	compared to	1000 g/Nm³ and
in	class I	4,4 g/Nm³,	permissible	200 g/Nm³

The sampling for the organic harmful substances was carried out by IGU, Hamburg, and the analytics by the organic institute of the University of Tübingen under Prof. Hagenmaier. The test results are just as convincing as they are impressive. Incidentally, there is very good agreement with the test results at the installation in Flingern, although there were essential differences in the entire way the process was carried out. Thus the main sink for harmful substances in Flingern was the quasi dry process with subsequent open-hearth furnace coke, and in Stapelfeld a wet process with subsequent form-activated coke, type BF-VA 5.

Even in the nanogram area PCDD and PCDF were separated with a separation efficiency of over 99 %, the tests having shown that the separating efficiency for PCDF is even greater than that for PCDD. An evaluation of various test runs over 65 working days for all of the isomers measured or analysed, and assessment of the toxicity in accordance with the assessment standards of the Federal Public Health Department produced an area for the sum of the dioxin values between the detection limit (i.e. 0.003 ng/m³) and 0,06 ng/m³. Here, it should be mentioned that the test reactor had a coke

filling of 0,25 m^3 with a residence time of flue gas of approx. 4,5 seconds, large reactors being operated with a thousand times the volume of activated coke and residence times of up to 60 seconds. It can therefore be established, we believe, that activated coke is able to separate the highly toxic organic harmful substances - here, in particular, dioxins and furans - almost completely. In addition, the tests in Hamburg-Stapelfeld have shown that even the separation of polycyclic aromatic hydrocarbons and also polychlorinated biphenyls is sometimes possible up to 99 %.

5. **Concept Regarding Safety Regulations**

At the beginning of the development of activated-coke technology, thermal excursions in the activated-coke bed were repeatedly the cause of serious breakdowns and damage to installations. In nearly all cases, the reason for these breakdowns was that the flow through the activated coke filters was insufficient or homogeneous. For this reason, the crux of our safety philosophy is the preventive avoidance of temperature excursions through the homogeneous and sufficient heat flow, which is guaranteed from the point of view of apparatus and installations. Up to now, we have operating experience with cross-flow filters designed by HUGO PETERSEN amounting to a total of more than 50.000 hours. Temperature excursions or hot spots, which are due to the process, have not occurred in any of the large-scale coke filter installations built by HUGO PETERSEN up to now. In order to detect hot spots at an early stage, a threefold-redundancy safety system is installed in the large-scale installations operated today: CO differential measurement, grid temperature measurement, gas probes for localizing possible hot spots.

CO differential measurement, in particular, has proven to be a very sensitive measuring procedure for detecting hot spots at an early stage. Since even very low CO differential values are registered, the operating crew has a reaction time of several hours for detecting and assessing breakdowns that have occurred and to introduce countermeasure. The countermeasures are taken in stages, and normally they do not lead to drawbacks when the entire installation is in operation.

6. **Concept for Waste Disposal**

The problem of waste disposal with respect to the coke which is loaded with SO_2 and HCl is regarded as solved through incineration in one's own refuse incineration plant. For the activated coke drawn out of the first layer in the reactors, which contains heavy metals and organic compounds such as dioxins and furans, a thermal treatment for the desorption of the heavy metals and for the catalytic destruction of the dioxins and furans is being planned. A suitable process has been developed in cooperation with Prof. Hagenmaier from Tübingen University and is in the initial phase of a pilot plant.

7. **Guaranteed Values**

The limiting values of the Federal Immission Protection Ordinance, dated April 1990, are never approached. This applies, in particular, to the limiting value for dioxin even with higher concentrations of crude gas, such as those that can quite easily occur in the case of old installations.