Implementation of Process-Integrated Waste Gas Cleaning Using Activated Lignite

Juergen Wirling

Rheinbraun Brennstoff GmbH, Stüttgenweg 2, 50935 Cologne, Germany

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ABSTRACT

Numerous investigations made during the last few years have substantially extended the knowledge of environmental pollutants and their impact on Nature and Man. This knowledge and the growing environmental awareness of the population have caused environmental requirements to be constantly tightened and legislation introduced to prescribe lower emission limits. It is in particular the emissions of toxic organic compounds such as polychlorinated dioxins and furans as well as heavy metals which have been gaining importance in the industrial countries worldwide due to the increasing amounts of residues being incinerated and the application of recycling processes. Since primary measures alone do not permit sufficient reduction in emissions, additional cleaning systems have to be installed. In this context, process solutions are being sought which allow the gases to be cleaned in a technically efficient and inexpensive way.

A cleaning measure covering all emission-relevant pollutants is adsorption using carbon-containing adsorbents such as activated lignite or activated carbon which are comparatively easy to integrate into dedusting, scrubbing and absorption processes. By contrast with adsorption in separate waste gas cleaning processes, which has been common practice to date, and thanks to extensive investigations and plant optimisations, entrained-phase adsorption can now be operated as a process-integrated low-cost and highly efficient technology. The latter can as a rule be confined to the simple injection of pulverised sorbents into the raw gas flow of existing dedusting units.

For some years, process-integrated adsorption by means of activated lignite has been state of the art and has been successfully implemented in the most varied applications. Different systems are taken as an example to illustrate that the adsorption of emission-relevant pollutants - dioxins, furans and heavy metals - using activated lignite in an entrained-dust cloud with downstream dedusting units, such as fabric filters, electrostatic precipitators and scrubbers, is a technically efficient and at the same time reasonably priced emission reduction technology.

With a production capacity of 200,000 t/a, RWE Power AG, Germany, is Europe's biggest producer of activated lignite for the adsorptive cleaning of furnace waste gases. RWE Power is the market leader for these applications in Europe. The reason for this is the low-priced production of this activated lignite as a mass product in large quantities which has at the same time good adsorption properties comparable with those of high-grade activated carbon. This activated lignite is produced in four grain sizes and can be supplied for any possible adsorption technique. Around the world approx. 500 systems are operating with activated lignite for waste gas cleaning.

INTRODUCTION

Thanks to its versatile properties, activated lignite has become established in different fields of application [1], with the environmental sector and its extended adsorptive waste gas cleaning processes gaining more and more importance.

Since in many cases primary measures to avoid and reduce the formation of pollutants do not allow the principal requirements of emission reduction to be fulfilled, highly efficient, extended cleaning systems are increasingly being used. They include, e.g., the adsorptive/catalytic processes for waste gas cleaning based on activated lignite. The adsorption equipment to be employed consists of different types of conventional moving-bed filters. The development activities in recent years, however, have been focussed on the use of activated lignite which as an entrained-dust cloud permits adsorption/chemisorption in the waste gas flow. This simple technique forms the basis for process-integrated solutions where, e.g., the dust separator, a spray drier or a scrubber, etc., can be used as reaction zone for adsorption as well. For these fields of application, activated lignite has proved to be the economically most interesting solution.

The special characteristics of the lignite mined in the Cologne/Bonn area (Germany) and the specific coking conditions result in a carbon concentrate with activated coal-like properties. Owing to its catalytic and adsorptive characteristics and its special grain-size structure, activated lignite offers a great variety of possibilities for pollutant retention in gas cleaning processes. The large specific surface and the predominantly basic ash composition permit the absorption of a multitude of pollutants, such as sulphur dioxide, hydrogen chloride, hydrogen fluoride, hydrogen sulphide, heavy metals as well as the highly toxic dioxins and furans. An impressive example demonstrating this capacity was, e.g., in the field of waste incineration where the activated lignite-based adsorption technique has been established as fixed-bed and moving-bed as well as entrained-phase techniques for years [2,3,8]. Here, its price, being much more favourable than that of activated carbon, allows the activated lignite to be employed as non-returnable adsorbent. Against this background, fields of application were and are being opened up in the environmental sector where due to the cost of conventional activated coals the adsorption techniques have not yet been implemented.

The cost of high-quality activated carbons and synthetic sorbents have so far only allowed the implementation of adsorption technology in processes where less important volumetric rates of flow are treated. From the point of view of costs, these applications normally include regeneration of the spent sorbent, which requires costly and complex equipment. In recent years, activated lignite has proved to be eminently suitable for the adsorption of large molecules or chemisorption. This attractively priced mass product opens up new possible process engineering applications of adsorption. In particular simple solutions without activated lignite regeneration, i.e. its use as a non-returnable sorbent, which allows integration into existing dedusting processes have been implemented [2, 4].

This contribution is aimed at showing the possibilities of pollutant reduction by means of integrated waste gas cleaning techniques based on activated lignite, taking the example of some applications. In addition to its effectiveness, special importance is attributed to the economic efficiency of the processes. For the techniques described, pollutant separation is based on adsorption or chemisorption of pollutants in the entrained phase or in the filter bed of an existing fabric filter.

ACTIVATED LIGNITE

Activated lignite is produced in so-called rotary hearth furnaces. This special production process has given the product its name, viz. HOK which is a German abbreviation standing for rotary hearth furnace coke (“Herdofenkoks”). The grain-size spectrum of the finished product comprises four different sizes starting from granules (HOK grains) all the way down to super-fine milled activated lignite (HOK super). The physical and chemical properties of activated lignite which are essential to its use in waste gas cleaning are listed in Table 1. It also includes the relevant data on thermal utilisation of the feed coke which is reasonable in many cases. The crucial criterion for the activated lignites favourable adsorption properties is its large active surface of approx. 300 m^2/g, which results from the sponge-like pore structure (Figure 1). Moreover, the cleaning efficiency is promoted by the easy accessibility of the inner coke surface for the pollutants which is due to its favourable pore structure with a large portion of macropores.

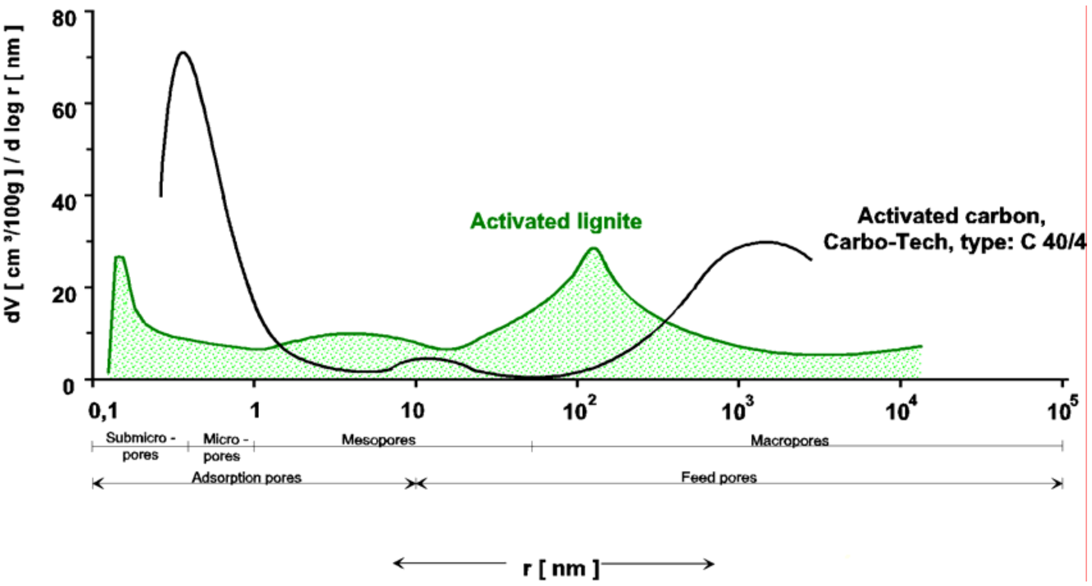
Table 1. Physical and chemical parameters of activated lignite

Physical parameters	HOK grains	HOK medium	HOK pulverised		HOK super
Grain size [mm]	1.25 – 5	0 - 1.5	< 0.4		< 0.2
Bulk density [t/m^3]	0.45	0.53	0.55		0.55
Specific surface area	300 m^2/g	300 m^2/g	300 m^2/g		300 m^2/g
Proximate analysis	Moisture content		0.5	% wt	
	Ash content		9	% wt	
	Calorific value		29.9	MJ/kg	
	Volatiles		3	% wt	
Ultimate analysis	Carbon (C-H-N-O)		88.5	% wt	
	Sulphur		0.5	% wt	
Ash analysis	CaO		41	% wt	
	MgO		14	% wt	

Figure 1. Microscopically magnified activated lignite

Activated lignite, having a specific BET surface area of around 300 m^2/g, differs from activated carbons whose surface area can amount to up to 2,000 m^2/g. The specific surface area is, however, not the only factor indicating the suitability of the products for this application. In each particular case, there are other characteristic values, such as e.g. the pore radii distribution and the pore volume that have a decisive effect. Figure 2 shows the pore radii distribution of activated lignite compared with that of activated carbon. When we consider that the dioxins and furans relevant to the specific application have - depending upon the chlorination level - a molecular diameter of approx. 0.4 nm to 1 nm and are 1 to 2 nm in length [6], it becomes obvious that the more pronounced submicropore structure of the activated carbons cannot be used at all, or is only to a limited extent suitable for the separation of these pollutants. For pollutant separation in the inner grain, it is furthermore the mass transport in the pores which exerts a crucial influence. While the macro- and mesopores can be described as having a 'highway character', the submicropore ranges can be compared with 'pedestrian areas' (concerning the adsorption kinetics). For dioxin and furan adsorption, activated lignite is the preferred material whose focus of pore radii distribution is in the macro- and micropore ranges. High-quality and thus expensive activated carbons are not required or less suitable for these applications.

Figure 2. Pore radii distribution



In addition to the pore radii distribution/volume, it is also the fine grain-ness of the pulverised coal used which exerts a substantial influence on the potential separation efficiency. With so-called reactivity enhanced pulverised sorbents (HOK super), viz. extra-finely milled products with larger outer surfaces, it is possible to considerably increase the separation efficiency at the same dosing rate, or the use of lower dosing rates ensures the same separation efficiency.[7]

SEPARATION MECHANISMS AND CLEANING EFFICIENCY

Table 2 shows typical clean gas concentrations for refuse incineration plants which are equipped with activated lignite-based adsorbers. Depending upon the adsorption technique, the raw gas condition and the operating mode of the adsorber, it is possible to vary the concentrations. The stringent emission requirements governing the operation of refuse incineration plants in Europe can in any case be fulfilled by means of the lignite-based adsorption techniques [8]. In some cases, it is even possible to attain values that remain considerably under the limit values. Using fixed-bed or moving-bed adsorbers, the pollutant contents in the cleaned gas often fall below the limiting concentrations that can currently be detected by the measuring equipment.

Table 2. Pollutant separating mechanism using activated lignite (AL) in waste gas cleaning

Component	Mechanism	Possible coke loading
SO_3	Chemisorption into H_2SO_4 and sulphate formation with ash	< 30 % wt as H_2SO_4
HCl	Adsorption and chloride formation with ash	approx. 5 % wt < 2 % wt
HF	like HCl	approx. 1 % wt
HBr	like HCl	approx. 1.5 % wt
H_2S	catalytic oxidation to sulphur	> 50 % wt
Heavy metals, e.g. Hg, Cd, As, Pb ...	Adsorption and chemisorption and filtration	e.g. Hg < 30 % wt
Dioxins/furans	Adsorption and filtration	up to 1000 ngTE/g
Organic compounds,	Adsorption	
Dust	Filter-medium filtration/cake filtration	

The pollutants are separated according to different mechanisms. **Sulphur dioxide (SO_2)**, e.g., oxidises at the activated lignite (AL) surface to form SO_3 which converts by water into sulphuric acid (H_2SO_4). Up to a H_2SO_4 level of some 25 grams per kilogram of AL, this acid is firmly retained in the ash components of AL, with sulphate being formed. In addition, SO_2 separated from the gas occurs as a free acid in the AL's pore system.

Hydrogen chloride, hydrogen bromide and hydrogen fluoride are likewise separated by being retained in the activated lignite ash.

Heavy metals are captured by the AL according to different mechanisms. Besides physisorption, chemisorption and absorption also have an effect. Elemental mercury, e.g., is converted into sulphates (Hg_2SO_4, $HgSO_4$) by means of the sulphuric acid occurring on the AL while mercury chloride ($HgCl_2$) is dissolved in the sulphuric acid without reacting with the acid [9].

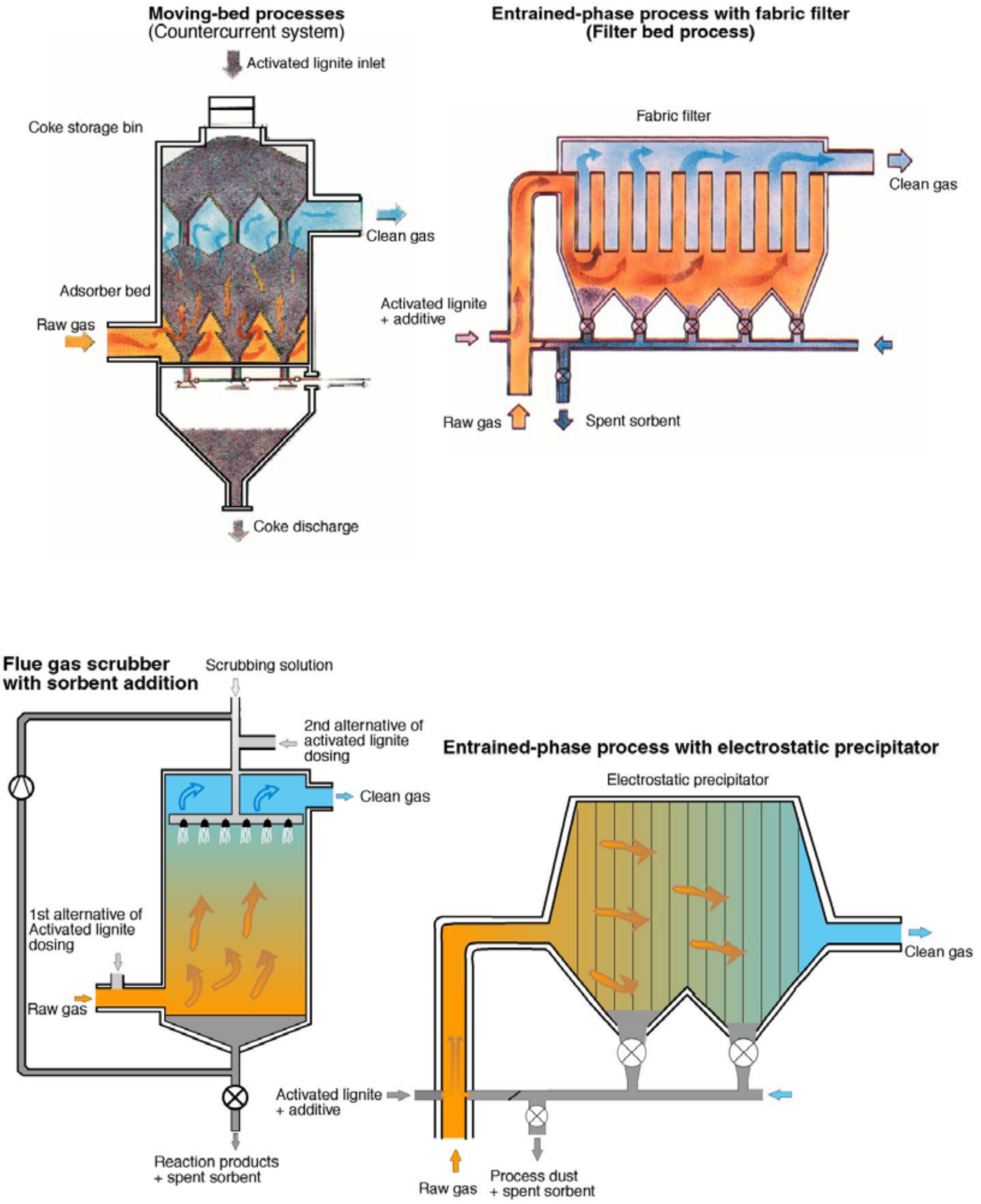
Thanks to their molecular diameters, large-molecular compounds, such as polychlorinated **dibenzodioxins/furans**, can advantageously be adsorbed by wide-pore sorbents. For this group of substances, AL is the preferred material. These substances are physisorptively retained at the coke surface, with equilibrium loads of 8 to 9 % wt being measured on the AL[10]. Owing to dioxin and furan concentrations which are very low compared to other adsorbable components, this high absorbing capacity of AL cannot be utilised fully. Investigations carried out in refuse incineration plants show that in some cases only about one millionth of the capacity is used. The separation of dioxins and furans is therefore independent of adsorption capacity; it is – on the contrary – determined by adsorption kinetics, viz. by the ratio of feed pores to adsorption pores, the grain size of sorbents and the flow rate.

In addition, aromatics, such as **toluene, xylene** or **benzene** which are classified as carcinogenic, can be separated (using physisorption) by activated lignite in the fixed-bed or moving-bed systems down to the range of their respective detection limits.

PROCESSES FOR ADSORPTIVE WASTE GAS CLEANING WITH ACTIVATED LIGNITE

For the implementation of adsorption, different processes are available [3]. These include the conventional adsorption in moving-bed filters as fixed-bed or moving-bed techniques, the technique of adsorption in a filter bed using fabric filters as well as the relatively new technique of adsorption in an entrained dust cloud (see Figure 3).

Figure 3. Adsorptive gas cleaning process

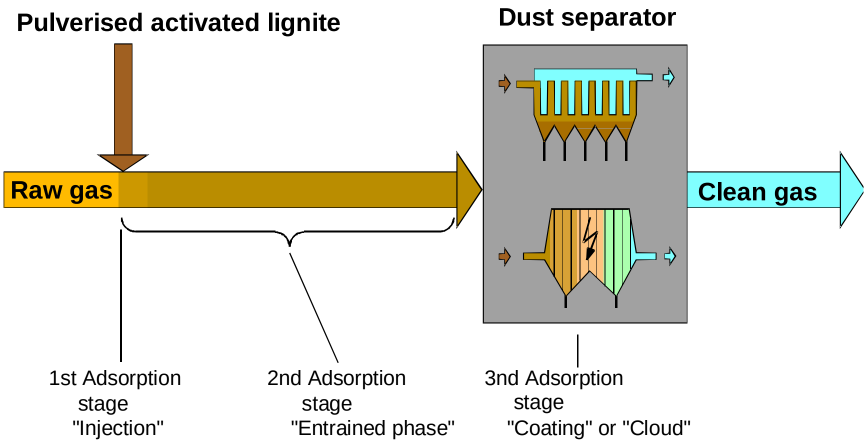


In the ***fixed-bed or moving-bed process***, the pollutant-loaded flue gases are passed through a bed consisting of granular activated lignite (AL), with the flow velocities ranging between 0.1 and 0.3 m/s. Thanks to the high separation capability of AL and the long residence time of the waste gases in the adsorber, this technique is characterised by the highest separation efficiencies. In process terms, however, it is comparatively expensive. In Europe, the moving-bed process using AL has been employed on an industrial scale since 1988 and permits the separation of a multitude of pollutants down to their detection limits.

In the ***filter-bed process***, AL is injected as the only substance or in a mixture with lime into the waste gas flow on the raw gas side upstream of a fabric filter. On the filter cloths, a coating of pulverised AL is formed where the separation of the gaseous pollutants takes place. Besides the purely adsorptive parameters, it is the fine grain-ness of the pulverised material used which is of major importance in this process. With so-called super-fine milled activated lignite (HOK super) having large outer and inner surfaces it is possible to considerably improve the separation efficiency. As with the moving-bed process, the filter-bed technique using activated lignite is state of the art in several hundred individual applications.

Compared with the pure filter-bed technique, ***process-integrated adsorption in an entrained dust cloud*** with downstream electrostatic precipitator or fabric filter constitutes a new application. Here, the important criterion for an optimum separation efficiency is the presence of a homogeneous and at the same time turbulent mixture existing at the injection point where the first stage of pollutant separation takes place.

Figure 4. Entrained dust cloud process



During the transport in the waste gas duct, further pollutant separation occurs, with the homogeneity of the sorbent in the gas phase and the residence time in the "entrained phase" influencing the adsorption of the pollutants contained in the waste gas flow. The "entrained dust cloud" occurring in the electrostatic precipitator with a high relative velocity between activated lignite and gas [14] or the activated lignite coatings formed on the filter cloths of fabric filters bring about the third stage of pollutant separation.

Activated lignite can be used in waste gas scrubbers as well. The latter are normally characterised by an inadequate separation efficiency regarding dioxins, furans and metallic mercury. The addition of activated lignite upstream of or to the scrubbers allows the efficiency of existing scrubbing systems to be markedly improved.

The adsorption in an entrained dust cloud can very easily be integrated into existing dust separation, scrubbing and absorption processes, with the activated lignite adsorbent being dosed as fine-grained powder into the gas flow upstream of the actual cleaning stage. In this way, the investment costs can substantially be lowered without any major losses in the separation efficiency compared to that of self-contained adsorption processes.

As in the case of entrained-phase adsorption in general, the following boundary conditions are of critical importance:

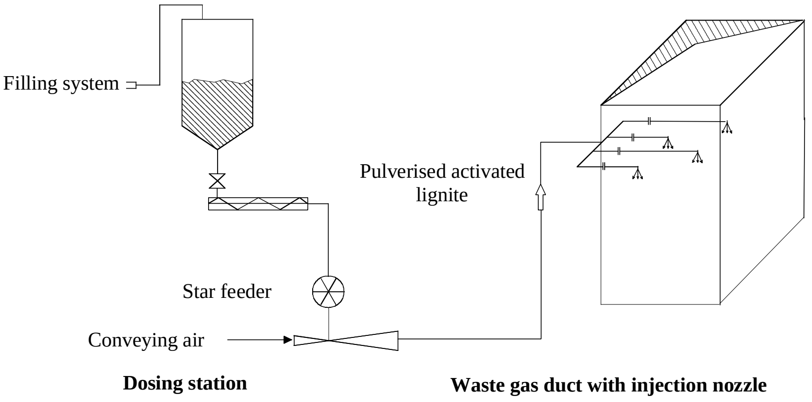
O ***Large inner and outer surfaces of the adsorbent.***
With an inner surface of some 300 m²/g and the typical pore radii distribution of activated lignite, this material having an average grain size of 63 µm (HOK pulverised) or super-fine milled activated lignite with an average grain size of approx. 28 µm (HOK super) presents optimum conditions for this purpose.

O ***Uniform distribution of activated lignite in the gas flow upstream of the dust separator.***
The uniform distribution of activated lignite in the process gas flow is attained by the number of injection points adapted to the flow area of the waste gas duct and the high exit velocity of the sorbent particles from the nozzles. The directional distribution of the nozzles towards the process gas flow has proved advantageous in this system. This configuration permits homogeneous and at the same time turbulent distribution of the activated lignite in the gas flow over the shortest distance.

O ***Sufficient dust separation in the existing dust separator***.
While for a fabric filter system, super-fine milled activated lignite is to be preferred due to its larger outer surface, the choice as to what grain size of the activated lignite is to be used in electrostatic precipitators or waste gas scrubbers has to be made depending upon the separation efficiency of the dust separator.

Figure 5 gives a diagrammatic view of the simple set-up of the devices required to dose activated lignite into the waste gas flow. In addition to a silo system or big bag station for activated lignite storage, the other necessary equipment units merely include a dosing system, a pneumatic conveyor with conveying air supply, a conveying pipe and the injection system into the waste gas duct. In plants where due to the induced draught fan upstream of the stack in the waste gas duct an adequate vacuum exists towards the atmosphere, it is even possible to dispense with feed pressure supply since pneumatic transport takes place by suction of atmospheric air [15].

Figure 5. Activated lignite dosing system



EXAMPLES OF PROCESS-INTEGRATED ADSORPTION USING ACTIVATED LIGNITE

The successful integration of entrained-phase adsorption into the existing plant is demonstrated by the following examples.

Integration of adsorption into the dedusting process

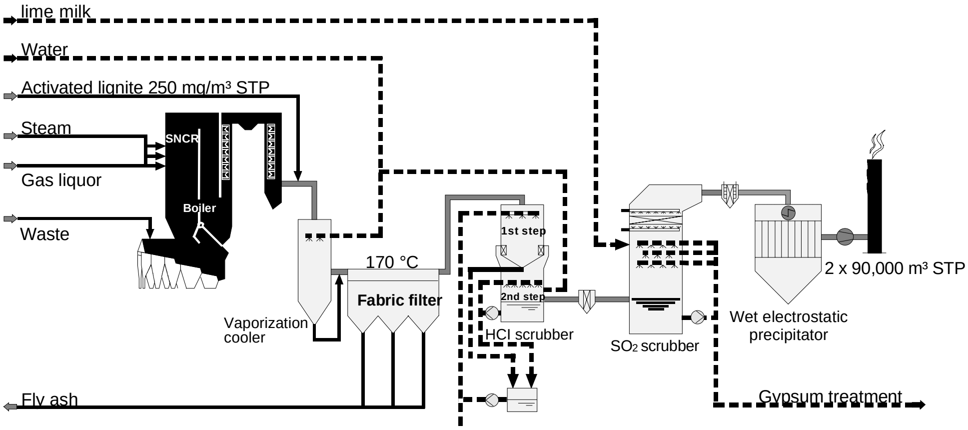
Adsorption according to the entrained-phase technique can easily be integrated into the dedusting process by dosing the fine-grained pulverised sorbent into the waste gas flow upstream of the dedusting system. A large number of investigations have been made in respect of fabric filter systems. Even if the filter dust content reaches extremely high values, very low coke doses are sufficient to obtain a considerable PCDD/F separation efficiency amounting to about 99.9 %.

Dedusting in a fabric filter

Figure 6 shows the integration of the adsorption process of dioxins, furans and heavy metals into the dedusting process of a household refuse incineration plant. Activated lignite is injected in its pulverised form upstream of a vaporisation cooler designed as a spray tower which follows the boiler. Residence time and turbulence ensure an intimate mixture of the substances, and even in the case of outlet temperatures of 170 °C spontaneous adsorption of dioxins and furans take place. The downstream fabric filter is used to separate the entrained dust and the loaded activated lignite. In order to improve the adsorption process, a slightly higher pressure loss is adjusted to ensure the formation of a filter cake which supports the adsorption.

The installation of the adsorption stage at the beginning of the described complex gas cleaning process ensures that the produced residues, viz. gypsum and hydrochloric acid, are largely free of toxic pollutants. This is an essential prerequisite for the possible economic utilisation of these reaction products. The illustrated overall process is a consistent further development of process-integrated adsorption without a separate process stage that can only be operated economically by using low-priced non-returnable sorbents. Particularly interesting is the fact that as early as in the dust separation stage dioxin and mercury values fall well below the emission limits (0.1 ngTE/m³ for dioxins and 50 µm³ for Hg) if activated lignite is used.

Figure 6. PCDD/F and heavy metal adsorption integrated into the dust separation stage[11]



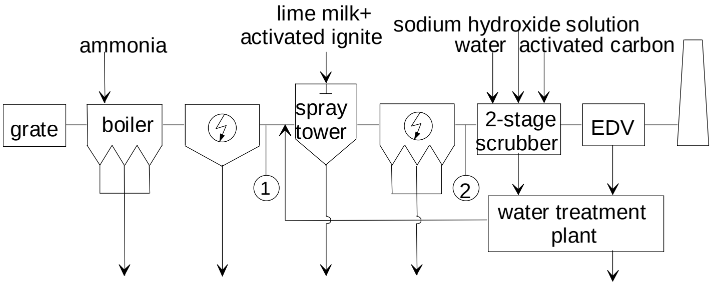
Waste gas values - fabric filter:

	Raw gas	Clean gas	Separation efficiency
PCDD/F	1 -2 ng/m³ STP	0.03 ng/m³ STP	98 %
Hg	50 - 160 µg/m³ STP	0.1 µg/m³ STP	99.9 %

Dedusting in an electrostatic precipitator

This technique can equally be used for dust separation by means of an electrostatic precipitator. Owing to the missing filtering layer of the filter cloth, the sorbent doses are higher, it is true, but this process can also yield interesting separation results (Figure 7).

Figure 7. Electrostatic precipitator – adsorption[13]



Adsorbent		Measured PCDD/F value [ng TE / m^3]		PCDD/F separation
activated carbon [mg/m^3]	activated lignite [mg/m^3]	measuring point 1	measuring point 2	[%]
50		0.44	0.12	73
50		1.17	0.06	95
50		1.48	0.20	99
50		2.42	0.54	78
	80		0.06	96 1)
	80		0.05	97 1)
	80		0.24	86 1)
	80		0.08	95 1)
	55		0.13	92 1)
	55		0.14	92 1)
	55		0.31	82 1)
	55		0.10	94 1)

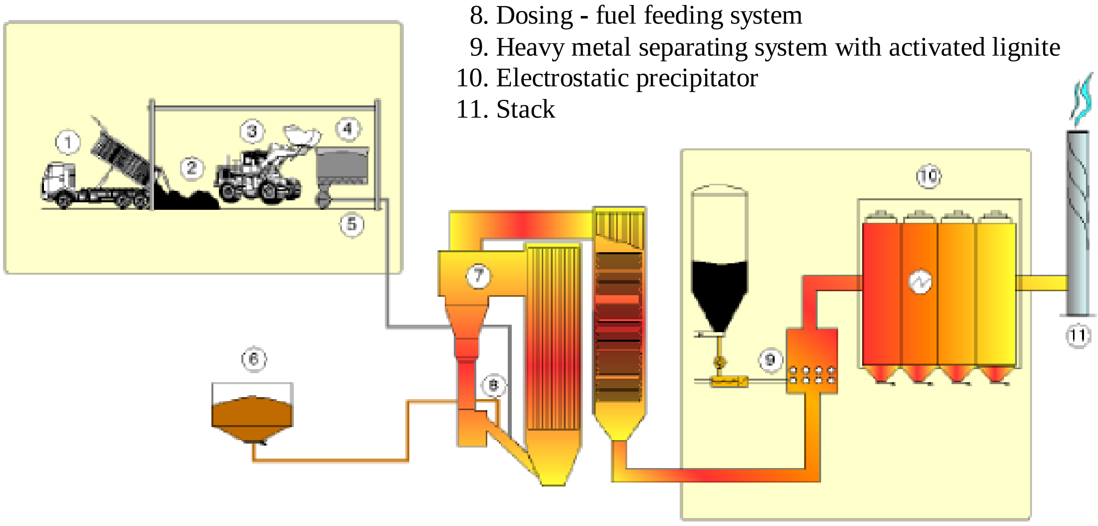
1) Separation calculated on the basis of the average value obtained at measuring point 1, no. 2 - 4

Another example of entrained-phase adsorption and the use of an electrostatic precipitator for dust separation is the waste gas cleaning technique employed in an industrial power plant for sewage sludge co-combustion (Figure 8). The separation of the particularly high-volatile mercury shows that the simple addition of activated lignite as an adsorbent to the waste gas flow with subsequent separation in an electrostatic precipitator permits a reduction to far below the limiting concentration. The 275 MW_{th} steam generator working according to the circulating fluidised-bed combustion principle is fired with raw lignite (93 t/hr) as the principal fuel; the raw lignite as well as the mechanically dewatered sewage sludge are fed via the ash recirculation systems of the cyclones.

The dust contained in the flue gases which occur during combustion and total approx. 350,000 $m^3_{(STP,\ dry/)}$/hr is separated by means of a four-compartment electrostatic precipitator. After dust separation, the clean gas is supplied at a temperature of approx. 160 °C through an induced draught fan to the stack and then discharged into the atmosphere. The process ash occurring - in the case of sewage sludge co-combustion, it averages 5 tonnes per hour - is continuously removed and landfilled.

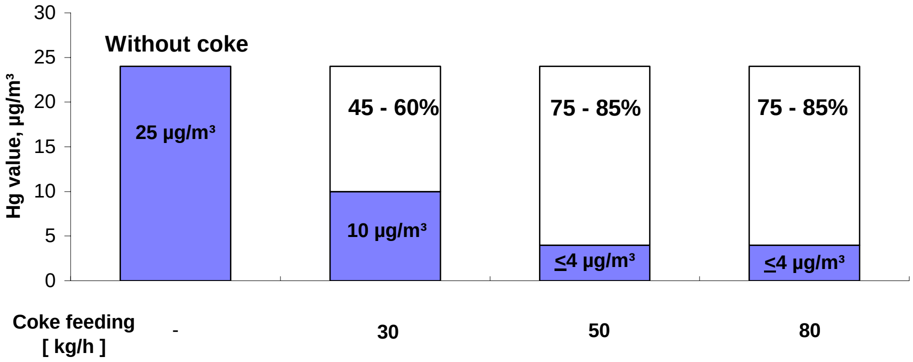
Figure 8. Sewage sludge co-combustion in an industrial power plant [12]

1. Sewage sludge transport (truck / container)
2. Sewage sludge storage
3. Wheel loader
4. Feeding hopper / discharging system with screw
5. Solids pump
6. Raw lignite bunker
7. Circulating fluidised-bed firing system
8. Dosing - fuel feeding system
9. Heavy metal separating system with activated lignite
10. Electrostatic precipitator
11. Stack



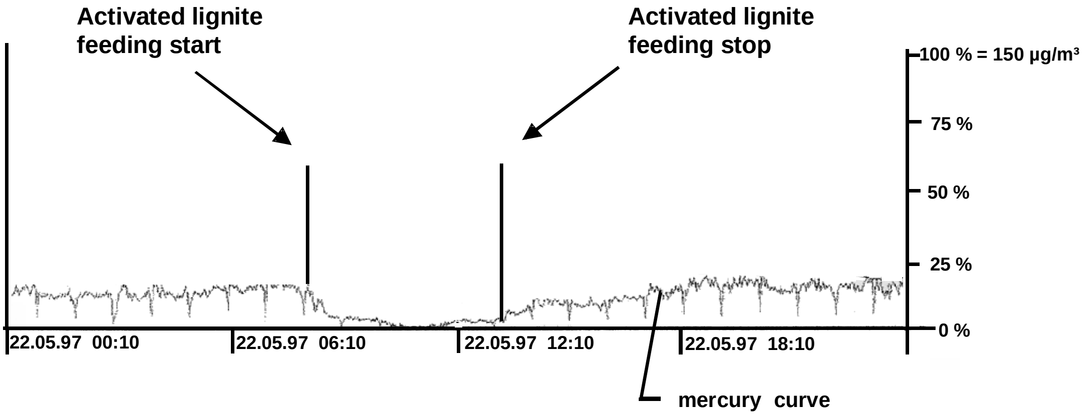
By means of several injection nozzles arranged around the circumference of the waste gas duct, the activated lignite adsorbent is added directly to the flue gas flow upstream of the electrostatic precipitator. The important factor here is rapid and homogeneous distribution of the pulverised activated lignite in the total waste gas flow. The loaded pulverised activated lignite is separated together with the process ash collected in the electrostatic precipitator.

Figure 9. Mercury separation by means of activated lignite during sewage sludge co-combustion



Related to the mercury emission of about 25 µg/m³ occurring on average without activated lignite (AL) addition during sewage sludge co-combustion, separation efficiencies of 75 to 85 % are obtained with an hourly AL dosing rate of 80 kg. An hourly AL dosing rate of 50 kg allows similar separation efficiencies to be reached which compared to the higher dosing rate, however, are recorded only after approx. two hours. Only at an hourly dosing rate of 30 kg can a marked drop of the separation efficiency be noticed. Then, the separation efficiencies reached range between 45 and 55 %.

Figure 10. Curve of Hg emission before and after activated lignite addition (dosing rate of 80 kg/h)

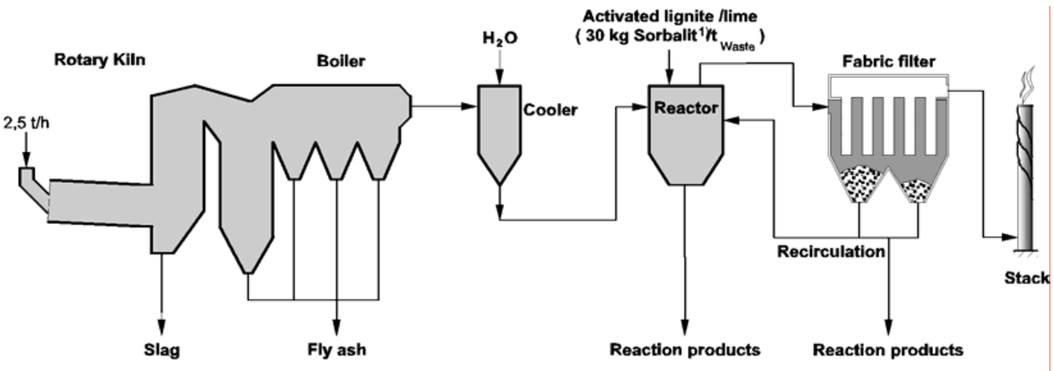


Due to the somewhat time-delayed effect occurring during the start-up and shutdown of AL feeding, the buffering behaviour of an electrostatic precipitator can also be observed during the respective periods. The advantage here is that short-time dosing failures and fluctuations in the raw gas concentration do not result in an immediate rise of emissions. The waste gas cleaning results recorded for sewage sludge co-combustion can also be obtained for other pollutants such as dioxins and furans.

Integration of adsorption into a dry/quasi-dry SO_2/HCl absorption process

Adsorptive separation of trace elements by adding activated lignite (AL) to dry and spray sorption processes is today being practised in many plants. Being used at the same time for dedusting of flue gases, this technique allows all current waste gas limits to be observed by one process stage involving the least possible plant engineering equipment. NO_x has to be considered separately. The AL is added together with lime or lime hydrate in the form of a ready-mixed product (e.g. Sorbalit by the Märker company); depending on the plant size the components can be mixed in the process as well. The presence of a homogeneous mixture in the waste gas duct is at any rate essential for optimum separation efficiency. Exemplary measurement results of such a plant configuration are shown in Figure 11. This process combination can naturally also be deployed if an electrostatic precipitator is used.

Figure 11. PCDD/F and heavy metal adsorption integrated into the adsorption stage of a Special waste incineration[14]



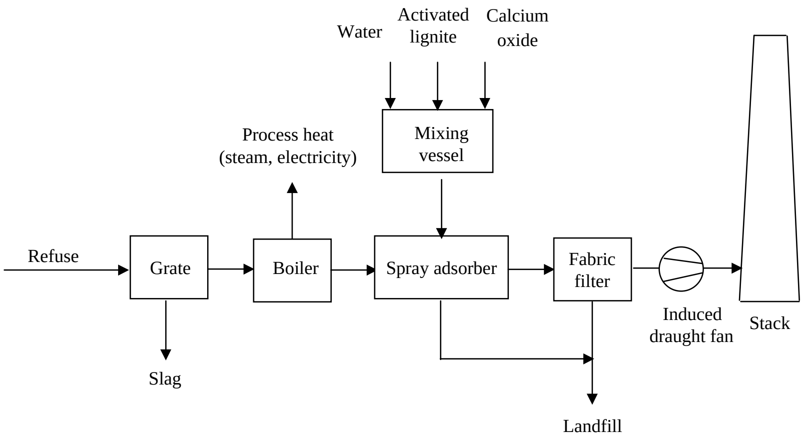
Measuring results:

No.	Activateded lignite portion of Sorbalit [%]	PCDD/F raw gas [ng TE/m³ STP]	PCDD/F clean gas [ng TE/m³ STP]	Remark
1	2	4.19	0.03	HOK pulverized
2	2	0.34	0.015	HOK pulverized
3	2	1.74	0.022	HOK pulverized
4	3	3.61	0.006	HOK pulverized
5	4	3.52	0.004	HOK pulverized
6	4	4.71	0.0002	HOK super

1) Sorbalit is a mixed sorbent by the German firm Märker Umwelttechnik

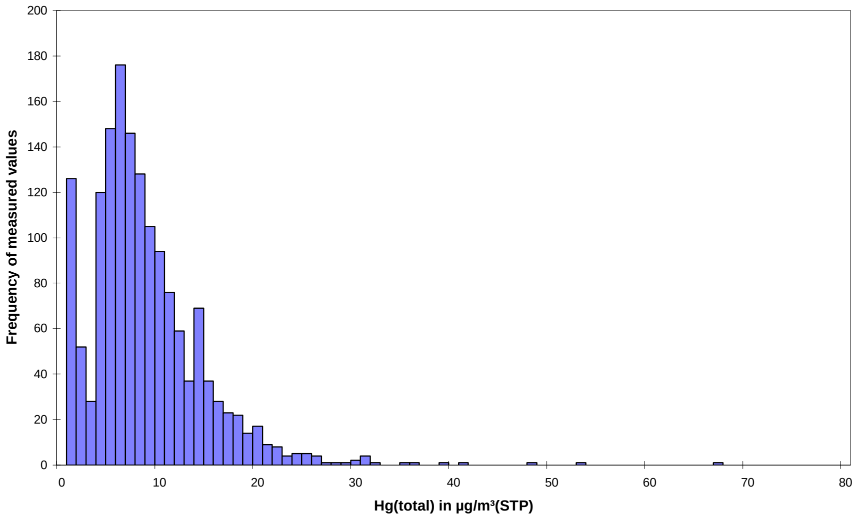
Another example of the integration of adsorption into the quasi-dry waste gas cleaning system is the waste gas line of a refuse-fired combined heat and power plant. For the separation of chlorinated organic pollutants and high-volatile heavy metals, in particular dioxins/furans and mercury, an entrained-phase process based on activated lignite was subsequently integrated into the existing quasi-dry waste gas cleaning system of this plant. The activated lignite is admixed with the lime milk which is sprayed for the separation of acid pollutant gases in the waste gas. Since it was possible to employ the existing spray unit for that purpose, no additional plant-related outlays were required for adsorbent distribution in the waste gas. The salts being formed by the acid pollutants and the lime milk, the activated lignite loaded with pollutants as well as the entrained dusts are all separated in the downstream fabric filter.

Figure 12. Integrated adsorption system for dust separation by means of activated lignite [15] (Refuse incineration plant)



The results obtained for mercury emission demonstrate that the addition of only 10 % wt of activated lignite to the lime milk (related to CaO), which corresponds to 1.8 kg of activated lignite per tonne of refuse, permits a reliable reduction in the mercury contents to below the maximum permissible concentration of 50 µg/m³. In the case of raw gas concentrations of 50 to 200 µg/m³ with peak values of more than 1,000 µg/m³, an average mercury concentration of 8 µg/m³ is reached in the clean gas (Figure 13).

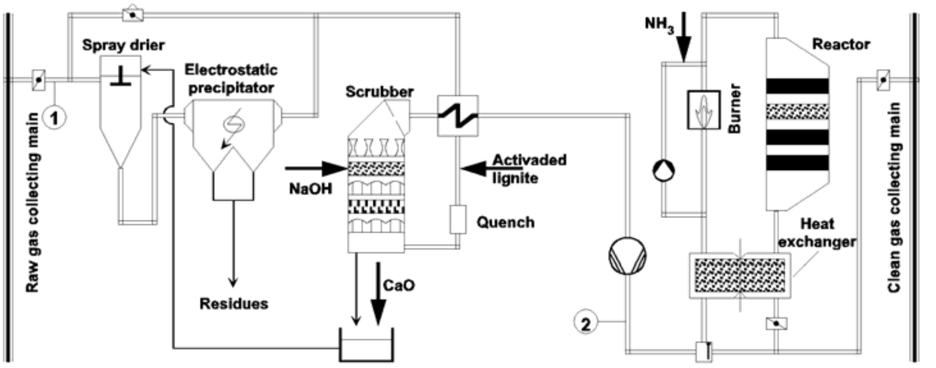
Figure 13. Mercury reduction in the case of quasi-dry waste gas cleaning [15]



Integration of adsorption into a scrubbing process

Scrubbers have insufficient separation characteristics in respect of dioxins/furans and metallic mercury. To enable partial adsorption to take place at the same time as the absorption processes, activated lignite can be added upstream of the scrubber, where activated lignite is injected upstream of the scrubber. In this way, the efficiency of existing scrubbing systems can be significantly improved. Figure 14 shows exemplary measuring results of a refuse incineration plant.

Figure 14. Use of activated lignite upstream of wet scrubber
(Refuse incineration plant, Stuttgart, Germany) [16]



Plant data

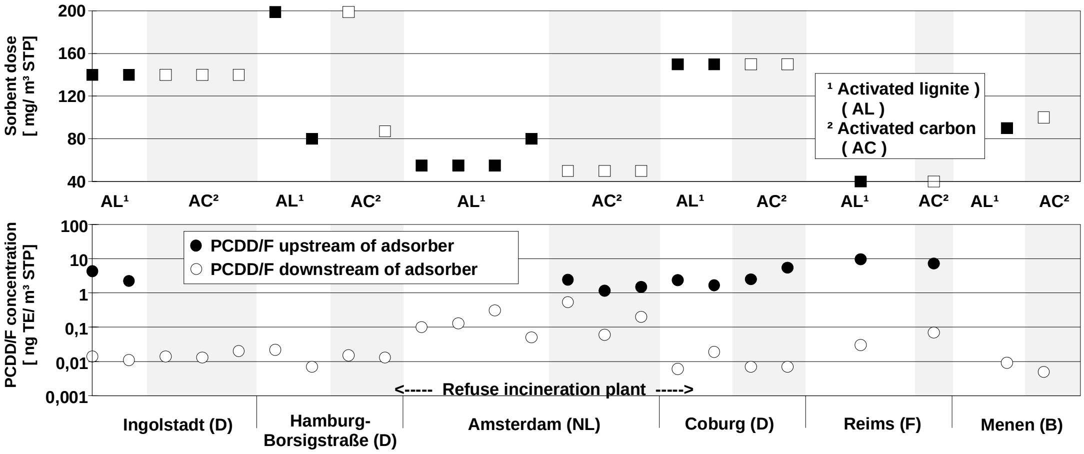
Waste throughput : 3 x 20 t/h
Volumetric rate of waste gas flow : 3 x 150,000 m³/h STP, wet
Lignite coke addition : 17 mg/m³ STP, wet

Pollutant separation		Dioxins / furans	Mercury
Measuring point 1	:	1 - 6 ng TE/m³	100-200 µg/m³
Separation efficiency without coke addition	:	Ø 31 %	
Separation efficiency with coke addition	:	Ø 93 %	
Measuring point 2 (with coke addition)	:		0.9-19 µg/m³

COMPARISON OF THE EFFICIENCY OF ACTIVATED CARBONS AND ACTIVATED LIGNITE IN INTEGRATED ADSORPTION PROCESSES

The above remarks have dealt with the technical difference of carbon sorbents suited for trace element adsorption, i.e. technically complex and hence expensive activated carbons and low-priced activated lignite. The possible options of an integration of the adsorption technique into the dedusting, dry/quasi-dry sorption and scrubbing process stages have been described. Figure 15 shows a summarised comparison of the separation efficiency in respect of dioxins and furans by activated carbon and activated lignite for widely different entrained-phase adsorption variants. The results impressively demonstrate the technical comparability of the two sorbents if the same quantities are added to the waste gas. Gas cleaning can be implemented with low-priced activated lignite at considerably reduced costs.

Figure 15. Dioxin/furan separation by sorbent injection
(Comparative measuring results for activated lignite and activated carbon)



Ingolstadt (D) : **Entrained-phase process as a sentinel filter downstream of electrostatic precipitator, scrubber, SCR-cat**
Hamburg-Borsigstraße (D) : **Entrained-phase process as raw gas process configuration downstream of boiler**
Amsterdam (NL) : **Entrained-phase process downstream of electrostatic precipitator, sorbent addition with milk of lime in the spray tower, separation in the electrostatic precipitator**
Coburg (D) : **Sorbent addition (Sorbalit) with milk of lime in the spray tower**
Reims (F) : **Dry sorption process with Bicar, separation by fabric filter**
Menen (B) : **Semi-wet process, separation by fabric filter**

SAFETY ENGINEERING

All carbon-containing sorbents are combustible, under certain conditions self-igniting, and basically explosible. Their tendency in this respect is characterised by safety parameters that are listed for activated lignite/activated carbon in Table 3. The sorbents used in the described applications can accordingly be regarded as inactive with regard to their self-ignition tendency and their explosion tendency can be described as restricted due to the extremely high minimum ignition energy required. Very simple measures are sufficient to ensure fire and explosion protection. Detailed information on this subject can be found in Reference 17. An important fact to be emphasised is that there are no process engineering-relevant differences between activated lignite and activated carbon. Both groups of products have to be treated identically in respect of safety engineering, which – according to expert opinions – applies to any type of plant.

Table 3. Combustion and explosion characteristics of activated carbons and activated lignite

	Granules	**Pulverised coals**		
	Activated lignite	**Activated lignite**		**Activated carbon**
Characteristic	**HOK grained**	**HOK pulverised**	**HOK super**	**Norit GL 50**
Moisture	0.5 % wt.	0.5 % wt.	0.5 % wt.	1.0 % wt.
Grain size	1.25 - 5 mm	0 - 0.4 mm	0 - 0.1 mm	0 - 0.2 mm
Median	2,000 µm	63 µm	28 µm	22 µm
Combustibility (20°C)	2	2	3	2
Self-ignition temperature	280 °C	250 °C	250 °C	250 °C
Smouldering temperature	> 450 °C	> 450 °C	> 450 °C	> 450 °C
Ignition temperature		560 °C	590 °C	700 °C
Lower explosion limit (20 °C)	**non-explosible**	60 g/m^3	60 g/m^3	125 g/m^3
21%vol. O_2 (200 °C)		30 g/m^3		30 g/m^3
Max. explosion overpressure		7.6 bar	8.6 bar	8.1 bar
K_{St} value		96 bar · m/s	92 bar · m/s	78 bar · m/s
Dust explosion class		St 1	St 1	St 1
Min. ignition energy (20 °C)		200 - 500 J	200 - 500 J	200 - 500 J

REFERENCES

1. Engelhard, J.; Lenz, U.: *Activated lignite coke in Water and Waste Gas Clean-up*; 11th International Conference on Coal Research, Calgary 1997

2. Esser-Schmittmann, W.; Lenz, U.; Erken, M.: *Activated lignite coke adsorption as a means of waste incineration stack gas cleaning*; International Workshop on Advanced and Clean Gasification and Incineration of Solid Wastes; Barcelona (Spain) 1996

3. Reich-Walber, M.; Esser-Schmittmann, W.; Lenz, U.: *Abgasfeinreinigung bei Abfallverbrennungsanlagen mittels Braunkohlenkoks*; Müll und Abfall 24, 1992

4. Wirling, J. et al.: *Adsorptive Practice in the Metallurgical Industry*; Brussels (Belgium) 1998

5. Informative brochure of Rheinbraun Brennstoff GmbH: *Activated lignite, Manufacture and fields of application*

6. Safe, S.; Phil, D.: *Polychlorinated Biphenyls (PCB), Dibenzo-p-dioxins (PCDD), Dibenzofurans (PCDF) and Related Compounds; Environmental and Mechanistic Considerations which Support the Development of Toxic Equivalency Factors (TEFs)*; Critical Reviews in Toxicology 21, 1990

7. Wirling, J et al.: *Process Optimisation of Quasi-Dry Waste Gas Cleaning with Integrated Dioxin and Furan Adsorption*; Dioxin symposium, Brussels (Belgium) 1997

8. Esser-Schmittmann, W.; Boelitz, J.: *Dioxinminderung durch Adsorption an Braunkohlenkoks – Umsetzung der 17. BImSchV*; Braunkohle 1993

9. Wirling, J. et al.: *Reduction in Mercury Emissions with Activated Lignite Coke* ; Nashville (USA) 2000

10. Modolo, G.: *Chemische und Physikochemische Untersuchungen an Sorptionsmaterialien zur Abgasreinigung*. Dissertation an der RWTH Aachen, 1993

11. Menke, d.: *Dioxin- und Schwermetallemissionsüberwachung im ersten Betriebsjahr der MVA Borsigstraße*. Stuttgart 1996

12. Wirling, J.; Schiffer, H.-P.; Merzbach, F.: *Adsorptive Waste Gas Cleaning During the Co-Combustion of Sewage Sludge in a Lignite-Fired Industrial Power Plant*; VGB-Power Tech 12/2000

13. Informative brochure of Rheinbraun Brennstoff GmbH: *Successful Use of Rotary Hearth Furnace Coke for Further Waste Gas Cleaning in the Amsterdam AVI Refuse Incineration Plant*, 1995

14. Regeler, H.: *Erfahrungen mit dem Flugstromverfahren zur Rauchgasreinigung bei Abfallverbrennungsanlagen*. VGB Kraftwerkstechnik 73, 1993.

15. Egeler, R.; Seitz, B.: *Emissionsminderung von Quecksilber und chlororganischen Schadstoffen mittels Braunkohlenkoks*. VDI-Seminar 09/1997.

16. Klein, K. E.: *Maßnahmen zur Minderung der Dioxin-/Furanemissionen in der Rauchgasreinigung der Abfallverbrennungsanlage Stuttgart (Germany) mit zum Teil unerwarteten Ergebnissen.* VGB Kraftwerkstechnik 4/1998

17. Esser-Schmittmann, W.; Boelitz, J.: *Safety Aspects when Using Activated Lignite Coke and Activated Carbon for Adsorptive Waste Gas Cleaning*, VDI seminar Additives in combustion and firing systems Düsseldorf (Germany) 1995

KEY WORDS

Activated Lignite Coke,
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Process-Integrated Adsorption
Waste Gas Cleaning,
Filter-Bed Process,
Refuse Incineration Plant