

Safety aspects in the use of carbonaceous sorbents during waste gas treatment

Activated carbon technology ranks among the most effective processes in the cleaning of heavy metals and organics from flue gas streams. Injection of activated carbon upstream of an existing particulate collector has been used with increasing frequency during recent years. Safe handling of this technology requires knowledge of the properties of the activated carbon used and its behavior under process conditions. This paper uses the example of Activated Lignite HOK® to give an account of its reactive behaviour and the resulting safety aspects. In addition to general statements on fire and explosion protection, specific measures for the application of carbonaceous sorbents in flue gas cleaning using baghouses or electrostatic precipitators are identified.

Introduction

Flue gas cleaning with carbonaceous sorbents such as Activated Lignite HOK® or activated carbon is widely applied today. It is commonly used in waste-to-energy plants to remove mercury, as well as dioxins and furans. In addition to its application in separate, dedicated equipment, entrained-phase adsorption is increasingly integrated into existing baghouses and electrostatic precipitators (ESPs) by adding the adsorbent as a fine-grained powder to the gas flow upstream of the actual dust collection stage. This allows investment costs to be reduced substantially without a major loss in separation efficiency.

All activated carbons are combustible and, under certain conditions, auto-ignitable and explosive. The fire and explosion risk is dependent on the combustion and explosion characteristics of the pulverized product, as well as on the process and plant conditions. The evaluation and

General information on safety engineering and specific measures for entrained-phase adsorption are given below. This is followed by a review of an operating coal-fired power plant in which Activated Lignite HOK® is used for mercury separation. This plant shows that effective protection can be implemented with relatively simple measures.

General entrained-phase adsorption process concept

In an entrained-phase process, activated carbon in pulverized form is injected into the raw gas flow upstream of an existing dust collection unit, shown as a baghouse or ESP in **figure 1**. In order to reach optimum separation efficiency, it is important that the sorbent is put into contact with, and distributed uniformly through, the flue gas at the injection point. The dust layer formed on the filter bags or the dust cloud in the ESP completes the final step of pollutant separation [1, 2].

By using the existing fly ash collection units, the sorbent is separated along with the dust produced in the process. For efficient pollutant separation, and for reasons of safety, the distribution of the sorbent in the flue gas flow is of great importance.

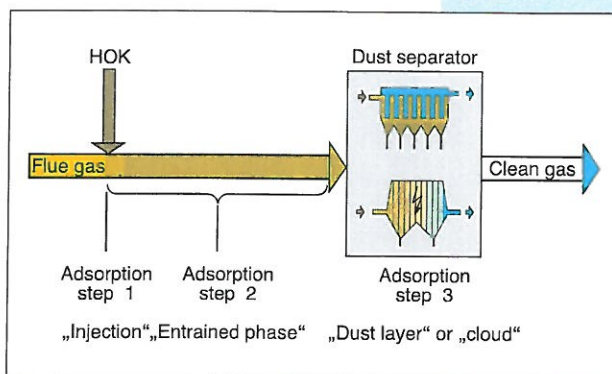


Figure 1.
Entrained-phase adsorption process

Production and characteristics of Activated Lignite HOK®

HOK® is manufactured from lignite mined in the Rhineland region of Germany, and differs from most activated carbons in both production and adsorptive properties. The lignite extracted in the surface mines of RWE Power AG near Cologne is activated by the rotary hearth furnace process that also gives the product its trade name HOK®. The abbreviation HOK refers to the German product name "Herd Ofen Koks". The resulting activated lignite has a pore structure that allows

definition of safety measures for fire and explosion protection covers all plant areas and process steps where activated carbon is present. From a safety engineering viewpoint, knowledge of the activated carbon's combustion and explosion behaviour in connection with the prevailing process and plant conditions is necessary.

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for high separation efficiency of many pollutants [1, 2].

Since Activated Lignite is produced by the hearth furnace process at a temperature of more than 900°C, the flammable, primary volatile constituents are completely expelled. During subsequent cooling and ageing, secondary volatiles are formed through the reaction with oxygen and the saturation of the active sites. These volatiles are mostly CO₂ and CO bound by adsorption, and not highly flammable hydrocarbon compounds. Therefore, Activated Lignite HOK can be used safely even at high temperatures. The reaction behaviour is described below in greater detail.

The main characteristics of Activated Lignite are summarized in table 1. The activated carbons employed in adsorption are combustible in principle. Their high surface area and porosity make these activated carbons able to adsorb pollutants, and to also react with oxygen, thereby releasing heat. As with any other combustible dust, pulverized activated carbons can be explosive under certain circumstances.

An explosion hazard only exists if the following conditions are fulfilled simultaneously:

- Activated carbon is dispersed in air, in a concentration range between lower and upper explosive concentration limits.
- The limiting oxygen concentration required for an explosion of the mixture is exceeded.
- An ignition source sufficient for ignition of the dust/air mixture is present.

If any one of these conditions can be ruled out there is no explosion hazard. Beside this and in comparison to typical pulverized coal, a very strong ignition source is required to ignite activated carbon. In addition to the elimination of efficient ignition sources, entrained-phase processes offer the possibility of diluting activated carbons with a pulverized inert material

	HOK pulverized	HOK super
Top grain size, mm	< 0.4	< 0.13
d50, µm	63	24
Bulk density, g/cm ³	0.55	0.44
Specific surface, m ² /g	300	300

Table 1. Physical characteristics of pulverized Activated Lignite HOK

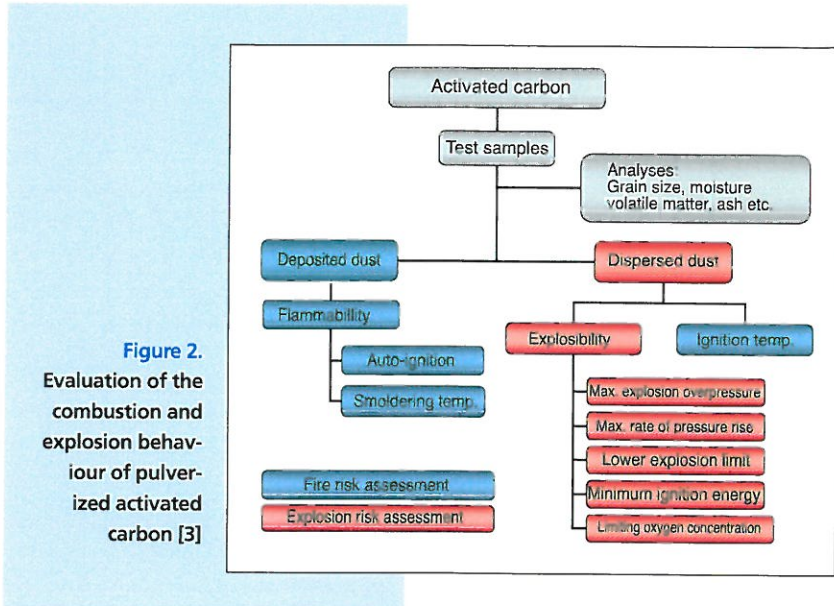


Figure 2. Evaluation of the combustion and explosion behaviour of pulverized activated carbon [3]

such as hydrated lime, pulverized limestone or process dust to obtain a mixture of activated carbon and inert dust that is no longer explosive.

In order to avoid fires in beds or deposits containing carbon, two aspects must be taken into account

- the fire risk from ignition sources,
- the potential for auto-ignition.

Possible ignition sources include static build-up from conveying solids, spark discharge in an ESP, hot equipment surfaces, and carryover of burning fuel from plant upset conditions.

The potential for auto-ignition is due to the well-known exothermic reaction of carbon with oxygen. The velocity of this reaction is mainly influenced by the gas composition, the bed volume and the temperature, and can be observed to a minor extent even at ambient temperatures. If the reaction heat is not dissipated, localized heating of the activated carbon bed can occur and result in auto-ignition of the bed.

To avoid auto-ignition, the following measures are recommended:

- Avoid major dust deposits in the process stream through, for example, continuous dust discharge from the ESP or baghouse hoppers.
- Preclude low-velocity air flows through the stored carbon or in spent solids. Low-velocity gas flows involve the danger that the reaction heat developed in the gas flow channel causes local overheating in the bed.

Combustion parameters

The extent of the combustion and explosion risk is a function of not only the existing process and plant technology, but also of the characteristics of the activated carbon used. The fire and explosion characteristics are described by standard parameters as defined in the German guideline VDI 2263 [3, 4]. A schematic overview of the test methods is given in figure 2.

	HOK pulverized	HOK super	Coal, pulverized
Moisture, wt%	0.5	0.5	11
Combustibility class (100°C)	B22	B23	B24
Self-ignition temperature, °C	250	250	110
Smoldering temperature, °C	>450	>450	240
Ignition temperature, °C	560	590	450
Lower explosion limit (at 20°C), g/m ³	60	60	40
Maximum overpressure, bar	7.6	8.6	9
KSt value, bar-m/s	96	92	150
Dust explosion class	St1	St1	St1
Minimum ignition energy, J	200-500	200-500	0.185-0.245

Table 2. Typical combustion parameters of Activated Lignite HOK®

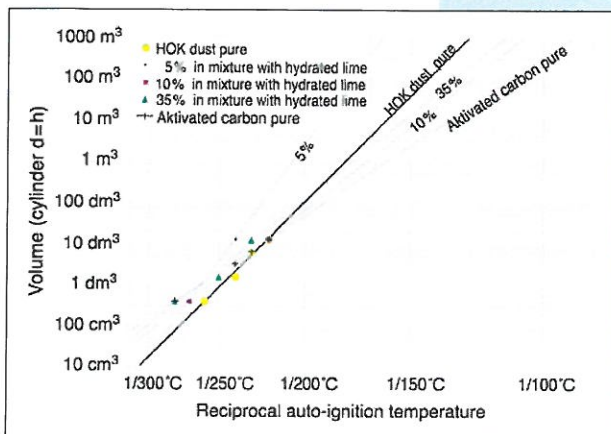


Figure 3.
Volume-dependent auto-ignition temperature

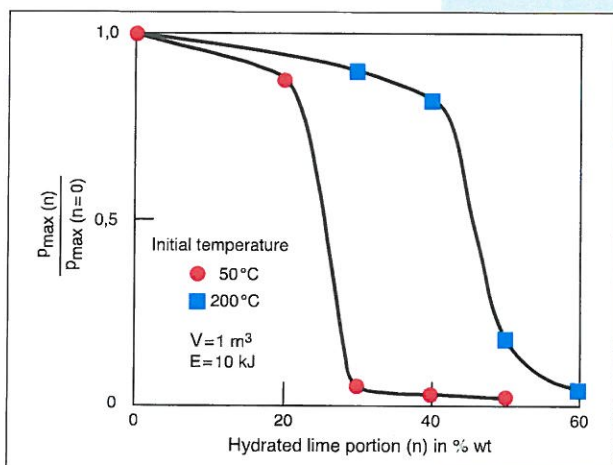


Figure 4.
Influence of the inert portion on explosibility [5]

Since the reaction behavior is material-specific, the major material parameters of the activated carbon must be stated. Reactivity is influenced by the volatile content, dust fineness and moisture of the activated carbon. In a comparison of sorbents, special attention must be paid to variable material parameters such as moisture and fineness.

Ignition behaviour of carbon deposits

Combustibility. The combustibility index is a measure of whether, and to what extent, a fire started by external ignition will spread in deposited dust. The sample is contacted at one end with a glowing platinum wire with a temperature of 1,000°C. The combustibility is characterized with class numbers ranging from 1 (no ignition) to 6 (rapid combustion and propagation). Classes 1, 2, and 3 exhibit no spreading of fire. In terms of fire protection, class 4 is critical because it is

characterized by a glowing fire spreading after ignition. Most activated carbons, including Activated Lignite HOK®, can be classified into combustion class 2 or 3, which do not exhibit spreading of fire [5, 6].

Auto-ignition. This refers to a process in which a bed of material ignites after spontaneous heating due to exothermic reaction with air. Auto-ignition depends not only on the type of material, but also on the surrounding temperature, since this influences the reaction rate, and the volume of the bed, because the reaction heat cannot be dissipated as quickly in larger beds. This is shown by the hot storage test, in which a defined dust volume is held in an oven for 48 hours at a controlled temperature, and the bed temperature is monitored to detect any increase due to exothermic reaction. This is repeated at successively lower temperatures, until no exothermic reaction is observed in the entire test period.

The auto-ignition temperatures of Activated Lignite HOK® and another

typical activated carbon are given in **figure 3**, as a function of the bed volume. This shows that the auto-ignition temperature decreases with increasing bed volume. The potential for auto-ignition exists even if a mixture contains a high proportion of inert material [5].

Given the auto-ignition behavior of Activated Lignite HOK®, the risk of ignition from self-heating during storage in closed silos is excluded. At the normal service temperatures of some 150°C in the entrained phase adsorption process, smaller beds of dust are not subject to auto-ignition. Due to their temperature level, large-volume deposits in the process should be avoided by continuous and monitored discharge from the hoppers.

What must be precluded for activated carbons in general, both in storage and in the adsorption process, are low-velocity air flows through beds that, as a result of an exothermic reaction with air, may give rise to local overheating and, under certain conditions, to subsequent auto-ignition.

Smoldering temperature. The smoldering temperature describes the ignition behavior of a dust layer on a hot surface. It refers to the lowest temperature of a hot surface on which a 5mm-thick dust layer ignites within 2 hours. In the case of Activated Lignite HOK® it is above the maximum test temperature of 450°C [5, 6]. Ignition of HOK deposits by hot surfaces in entrained-phase adsorbers and duct work can be excluded due to the much lower temperatures prevailing there, typically no more than 150-200°C.

Ignition behaviour of dispersed carbon

Ignition temperature. The minimum ignition temperature is the lowest temperature of a surface which will ignite dispersed dust blown against it. At $T_{at} = 560^\circ\text{C}$, the ignition temperature of Activated Lignite HOK® is well above the normal service temperature of 150-200°C, and significantly higher than the ignition temperature of pulverized fuel.

Minimum explosive concentration (MEC). This is the minimum concentration of dust in air that can be ignited

under standardized conditions, with a very strong ignition source. Tests carried out with Activated Lignite yielded a MEC of 60 g/m^3 at 50°C . At a temperature of 200°C , the MEC falls to 30 g/m^3 (HOK pulverized).

Dilution of carbon with inert material can suppress the potential for explosion. The minimum inert portion required to suppress explosiveness is not only dependent on the temperature but also on the type of

200°C [5]. The oxygen concentration below 10% normally prevailing in power plants is well below this limiting concentration.

Minimum ignition energy. A measure of the ignitability of fly ash/air mixtures by an electric spark. Tests with Activated Lignite HOK[®] at an initial temperature of 20°C yielded a minimum ignition energy of 200-500 J [5, 6].

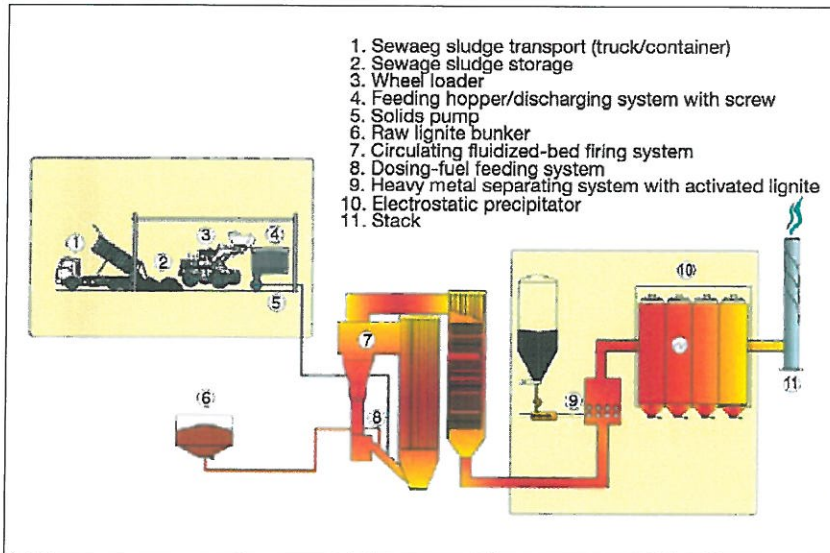


Figure 5. HOK addition for mercury separation in an industrial power plant [8]

activated carbon and the inert material. Tests performed with Activated Lignite HOK[®] and hydrated lime show that the explosion potential of a dust mixture with a hydrated lime portion of 60% is greatly reduced, even at a temperature of 200°C (figure 4). In typical entrained-phase adsorption systems for pulverized coal, the inert portion is often much higher than 80% due to the dust load from fuel ash, providing no separation into the individual components takes place. In applications with little process dust, it may be advantageous to blend carbon with non-combustible sorbents.

Limiting oxygen concentration. The oxygen concentration below which deflagration of a fly ash/air/inert gas mixture cannot occur. For Activated Lignite HOK[®] in nitrogen, the limiting oxygen concentration is 15% at ambient temperature. With rising temperature the limiting oxygen concentration declines and can be some 12% at

Safety considerations for the use of Activated Lignite in entrained-phase adsorption

The following example of entrained-phase adsorption based on Activated Lignite HOK[®], in a power plant equipped with an ESP for dust separation, illustrates key safety protection measures. Figure 5 shows the arrangement of the power plant with an entrained-phase adsorption system installed for mercury separation [8]. The 275 MW fluidized-bed boiler is fired with raw lignite as the primary fuel. In addition to the lignite, partly dewatered sewage sludge is co-fired. The flue gas flow is approximately $350,000 \text{ m}^3/\text{h}$ (stp). Fly ash is removed in a four-field ESP at about 160°C .

The Activated Lignite HOK is added directly to the flue gas flow upstream of the ESP. The adsorbent is separated together with the fly ash in the ESP. The separated mixed filter dust is discharged continuously, stored in a silo and then dumped.

The HOK used in flue gas cleaning is delivered by truck and conveyed pneumatically to a silo (figure 6). Via a feeding system it is then transported pneumatically to the flue gas duct. For the safety analysis, the overall plant can be subdivided into the following activated carbon-carrying areas.

HOK storage and feeding. The HOK is stored in an atmospheric pressure, carbon steel silo. The storage silo does not include structural explosion protection such as pressure-containment design, pressure relief areas, or inert storage. While such construction could be required for specific installations (e.g., locations in confined areas, or subject to local codes or insurance requirements), conventional construction is standard throughout the industry.

Ignition sources must be excluded. All components of the storage and conveying system are securely grounded to avoid static discharges. Temperature sensors are provided for monitoring at the silo top and outlet. All silo connections are designed to avoid any uncontrolled ingress of air into the silo that may cause low-velocity air flows in the bed. Special attention must be paid to sorbent transfer into the pneumatic conveyor pipe. Owing to the overpressure or vacuum existing at the transfer point, pressure decoupling must be provided to avoid low-velocity air flows into the silo. Fluidizing air used to assist solids discharge is positively controlled, again, to avoid continuous, low velocity air infiltration.

Electrical equipment in the vicinity of the storage and feeding system is dust-tight to protect the electrical components, but in the absence of site-specific requirements, dust-ignition proof, classified-area equipment is not generally required. Any equipment installed in the silo interior, normally limited to level or temperature sensors, would be of dust-ignition-proof or of intrinsically safe design.

The storage and feeding system was built in accordance with the "Recommendations for Activated Lignite HOK Handling" published by RWE Power AG [7]. The safety record of more than 100 silo and conveying plants using Activated Lignite HOK confirm the efficacy of RWE's recommendations.

Flue gas line and ESP. In the flue gas duct downstream of the HOK injection point, as well as in the ESP, several factors ensure safe operation:

- Mixture of the injected 80 kg/h HOK with fly ash of some 4 to 5 t/h gives a dust mixture with an HOK portion of well below 5% wt., so that this mixture is not explosive.
- The dose rate of about 200 mg/m³ (stp) pulverized HOK flue gas for mercury control, or 0.2 g/m³, is well below the minimum explosive concentration.
- The average oxygen concentration of 7% during normal operation is below the limiting oxygen concentration.

In view of fire protection, the flue gas duct and the ESP are designed to avoid the formation of large-volume deposits. The precipitator plates are rapped at regular intervals and the collected dust

In the ESP, possible auto-ignition hazards are avoided by:

- temperature monitoring of the flue gases and the ash hoppers,
- prevention of large-volume dust accumulations in the hoppers by means of continuous dust discharge and level monitoring.

Major fly ash accumulations frequently observed in the hoppers of existing plants have the potential for smoldering fires. Causes can be air leakage, failure of the discharge units, bridging in the ash hoppers, or malfunction of hopper heaters. The use of level and temperature sensors allows these conditions to be detected, so that countermeasures can be initiated. Since most plants are operated under negative pressure conditions, the discharge units should be designed so as to avoid any backflow and ingress of ambient air.

Conclusions

The combustion and explosion properties of the specific activated carbon must be known in order to assess the hazard posed in the process. This forms the basis for the selection of appropriate protective measures.

In the case of Activated Lignite HOK[®] the safety criteria are known, and protective measures required for the operation of entrained-phase adsorbers can be implemented reliably and easily. Entrained-phase adsorption using Activated Lignite HOK has been practiced for many years in a wide variety of plants. Process-integrated adsorption based on HOK has proved to be an efficient and safe process.

As far as the transferability of the described safety engineering to other activated carbons is concerned, it must be stressed that the safety measures to be provided are dependent on the type and quality of the adsorbent used and further protective measures might be necessary. Furthermore, each facility has its own unique characteristics that will require a review of specific safety practices.

References

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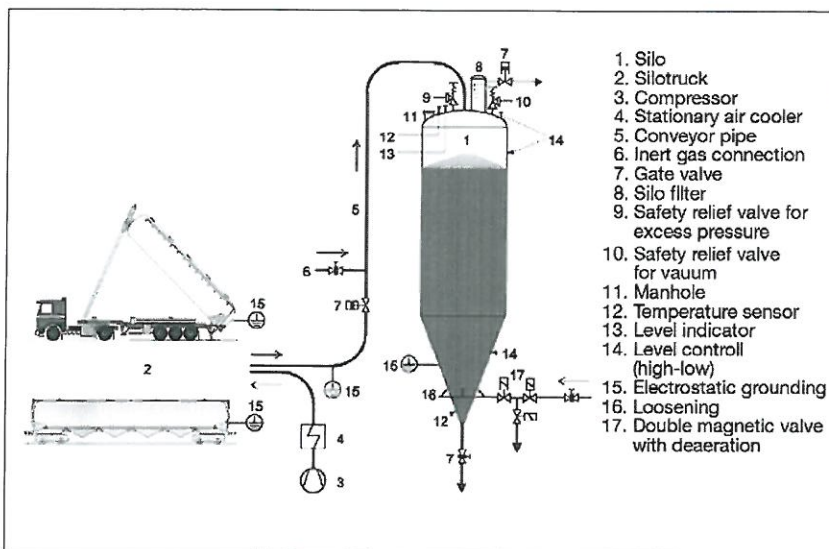


Figure 6. Pneumatic transloading of Activated Lignite HOK[®] [7]

continuously discharged. This ensures that no major dust quantities can accumulate long term in the flue gas duct or the precipitator. In connection with the service temperature of approximately 160°C, auto-ignition reactions can be excluded. Because of HOK's low combustion reactivity, the minor dust deposits normally occurring during operation in the flue gas duct and the ESP do not present an ignition hazard under the prevailing conditions.

Handling. Aside from the combustion characteristics discussed above, Activated Lignite HOK[®] is classified as a non-hazardous, non-toxic, environmentally benign material. In direct handling, personal protective clothing such as safety goggles, gloves and, if necessary, dust protection, is sufficient. More detailed information on handling and is given in the EU safety data sheet for Activated Lignite HOK [9].