

Reduction in Mercury Emissions with Activated Lignite HOK[®]

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Due to their toxicological relevance, mercury emissions are restricted by law in many countries. The highly volatile mercury element is known to be released during the thermal treatment of Hg-containing residues and leave the combustion chamber almost completely with the waste gas. This in particular applies to the poorly water-soluble metallic mercury; it passes the conventional waste gas cleaning system almost without any difficulties, thus giving rise to problems with the adherence to the required limit value.

One cleaning measure applicable for all emission-relevant pollutants involves adsorptive processes that are implemented as moving-bed adsorbers with granular sorbents or as entrained-phase techniques with pulverised sorbents. Adsorptive waste gas cleaning with the favourably-priced mass sorbent Activated Lignite HOK[®] in an entrained-phase process constitutes one of the simplest and, at the same time, most reasonably-priced cleaning techniques. The example of some representative applications is used to illustrate the efficiency of Activated Lignite HOK[®] for mercury reduction. The process concepts described are employed not only in new plants, but are also especially suitable for subsequent integration into existing plants.

Introduction

Numerous investigations in recent years have helped considerably enlarge the knowledge of environmental toxicants and their effects. This has also stepped up the population's sensitisation which has resulted in environmental protection regulations becoming severer and severer. This in particular applies to the emission limit values of organic compounds, such as dioxins and furans, as well as to those of heavy metals.

The separation of mercury entails particular problems in the case of combustion plants. Due to the high vapor pressure of mercury, almost no retention in the slag or the filter dusts is obtained; thus, it remains almost exclusively in the gas phase. The requirement for the reduction in mercury emissions into the environment calls for the use of highly efficient

emission mitigation techniques. These include the adsorption techniques with activated carbon/activated coke as sorbent.

In addition to its application in self-contained adsorption equipment items, the sorbent variant is increasingly integrated into dust separation, scrubbing and absorption processes. In this way, the investment costs can substantially be lowered, with the separation efficiency remaining sufficient. Today, trace constituent adsorption is--to an increasing extent--an individual, process-integrated technique that in many cases only consists of a simple technical device for sorbent feeding into the waste gas flow. This in turn opens up options of transferring this process to other fields of waste gas treatment, e.g. the treatment of waste gases from metallurgical processes or those from the co-combustion of residues in power plants.

In co-operation with plant operators, RWE Power AG is developing applications which permit the use of Activated Lignite HOK[®] as a favourably-priced mass sorbent in the existing waste gas line, with low technical outlays being involved. Thanks to its catalytic and adsorptive properties and its special grain structure, Activated Lignite HOK[®] offers a multitude of possibilities allowing the pollutants to be retained in gas cleaning processes. Its large specific surface and mainly basic ash composition make it possible to absorb a large number of pollutants, such as sulphur dioxide, hydrogen chloride, hydrogen fluoride, hydrogen sulphide, heavy metals as well as the highly toxic dioxins and furans [3].

This contribution is aimed at illustrating the possibilities of reducing the mercury contents by the use of integrated waste gas cleaning techniques on Activated Lignite HOK[®] basis, with some applications being taken as an example. Here, the focus is not only the effectiveness of the processes, but also their economic efficiency.

Characterisation of Activated Lignite HOK

Thanks to its porosity and the resulting large inner surface and pore structure, Activated Lignite HOK produced according to the so-called rotary-hearth furnace process [2] is as suitable as high-grade activated carbon for use as adsorbent. Unlike activated carbon, Activated Lignite HOK[®] is produced as mass product with an annual output of 200,000 tonnes at a much lower price than that of activated carbon.

Table 1 shows the physical and chemical properties of Activated Lignite HOK[®] that are of importance to its use for waste gas cleaning. With regard to thermal utilisation of coke,

which is reasonable in many cases, the relevant data for that purpose are listed as well. The decisive criterion permitting the favourable adsorption properties is the large active HOK[®] surface of some 300 m²/g which is provided by the sponge-like pore structure (Figure 1). Activated Lignite HOK[®] is available as granules for use in moving-bed filters and as different activated pulverised materials for adsorption in an entrained dust cloud.

Table 1: Physical and chemical parameters of Activated Lignite HOK[®]

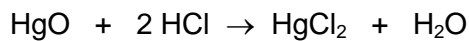
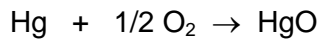
Physical parameters	HOK granular	HOK medium	HOK pulverized	HOK super
Grain size [mm]	1.25 - 5	0 - 1.5	< 0.4	< 0.2
Bulk density [t/m ³]	0.45	0.53	0.55	0.55
Specific surface	300 m ² /g	300 m ² /g	300 m ² /g	300 m ² /g
Proximate analysis	Moisture content		0.5	% wt
	Ash content		9	% wt
	Heating value		29.9	MJ/kg
	Volatiles		3	% wt
Ultimate analysis	Carbon (C-H-N-O)		87.9	% wt
	Sulphur		0.5	% wt
Ash analysis	CaO		35	% wt
	MgO		14	% wt



Fig. 1: Microscopically magnified Activated Lignite HOK[®]

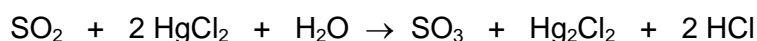
Separation of Mercury and Its Compounds

Due to the high temperatures already existing in the combustion chamber, mercury occurs in its elemental form [6]. As a result of its high vapor pressure, almost no mercury is retained in the ash; together with the waste gas it leaves the combustion chamber in its gaseous state. During the cooling-down of waste gas, mercury(II) chloride is formed via the oxidic form of HgO and the hydrogen chloride contained in the waste gas according to the following reaction equations:



Depending upon the reaction equilibrium obtained, mercury occurs in the waste gas in its elemental form as Hg or in its oxidised form as HgCl₂. In the case of high HCl contents, as are common to refuse incineration plants, the HgCl₂ portion prevails. In contrast to this, sewage sludge combustion is expected to produce a high content of elemental mercury due to the fuel's low chlorine content.

This phenomenon has a crucial influence on the choice of the waste gas cleaning technique to be employed. HgCl₂ easily dissolves in water and can be separated in waste gas scrubber stages from the gas phase, with high separation efficiencies being obtained. Separation primarily takes place in the acid scrubber stage. Attention has to be paid to the reduction of Hg_{ion} to Hg⁰ that may occur owing to reduction and disproportionation reactions. In this case, Hg⁰ again changes from the solution to the waste gas and is discharged together with the gas flow.



Unlike the oxidised mercury, the poor solubility of the elemental mercury causes this substance to be not at all or only to a small extent separated in the scrubber. Hg separation calls for an additional waste gas cleaning measure. For this purpose, adsorptive processes on Activated Lignite HOK[®] or activated carbon basis are primarily applied that permit simultaneous separation of elemental mercury and ionogenic mercury.

The decisive factor for optimum Hg retention is appropriate doping of the adsorbent with sulphuric acid. This is normally done with the residual SO₂ and H₂O contents occurring in the waste gas. In the presence of oxygen and water, the SO₂ contained in the waste gas is

catalytically converted on the coke surface into sulphuric acid. Due to the sulphuric acid thus adsorptively bound on the coke surface, the mercury contained in the gas is separated by means of chemisorption.

Elemental mercury (Hg^0) reacts with the sulphuric acid on the coke to form mercury(I) sulphate (Hg_2SO_4) or--in the case of sufficient sulphuric acid being available--to mercury(II) sulphate ($HgSO_4$).

Mercury(II) chloride ($HgCl_2$) is dissolved in the sulphuric acid.

Figure 2 shows a matrix investigation conducted in the laboratory with the object of studying the effect of different influencing boundary conditions on Hg separation by means of Activated Lignite HOK[®].

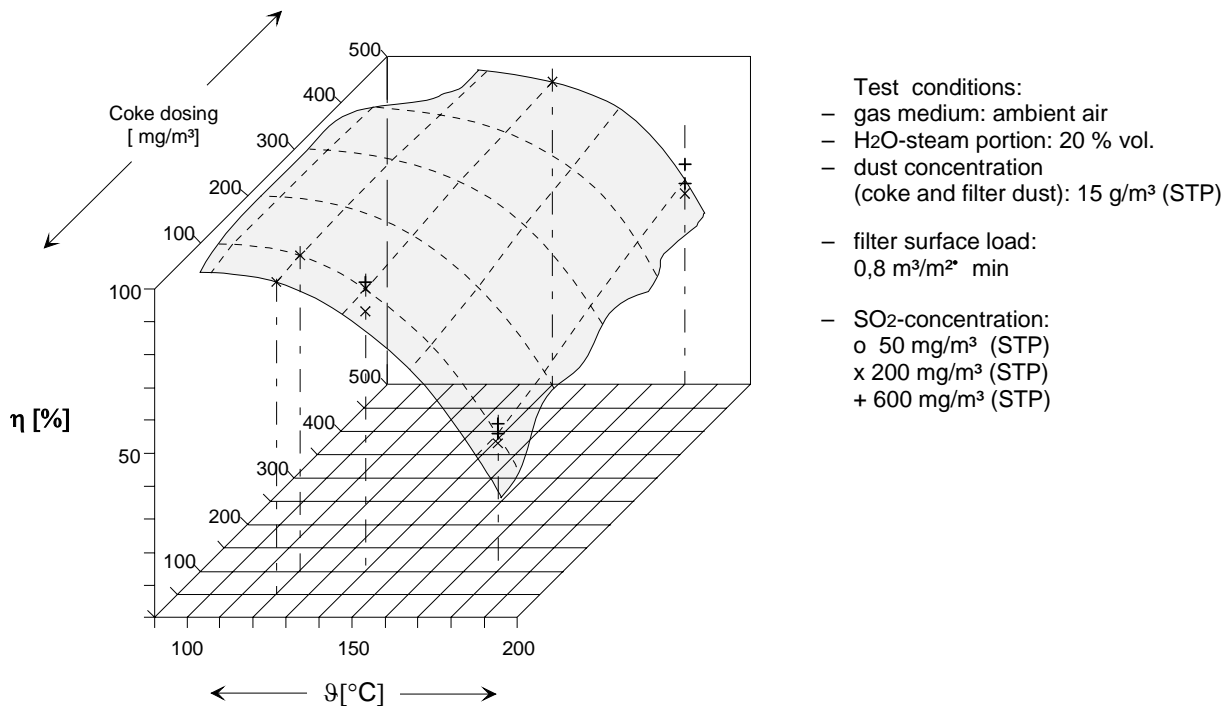


Fig. 2: Dependence of Hg separation on temperature, coke dosing rate and SO₂ concentration

Processes for Adsorptive Waste Gas Cleaning with Activated Lignite HOK

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 and 4).

In the *fixed-bed or moving-bed process*, the pollutant-loaded flue gases are conducted through a fill consisting of granular Activated Lignite HOK[®], with the flow velocities ranging between 0.1 and 0.3 m/s. Thanks to the high separation capability of coke 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 Activated Lignite HOK[®] 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*, pulverised Activated Lignite HOK[®] 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 filter coating of pulverised coke is formed where the separation of the gaseous pollutants takes place. Besides the purely adsorptive parameters, it is the fine graininess of the pulverised material used that is of major importance to this process. With so-called reactivity-enhanced pulverised coke having large outer and inner surfaces it is possible to considerably improve the separation efficiency. Like the moving-bed process, the filter-bed technique on Activated Lignite HOK[®] basis 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 already at the injection point where the first stage of pollutant separation takes place.

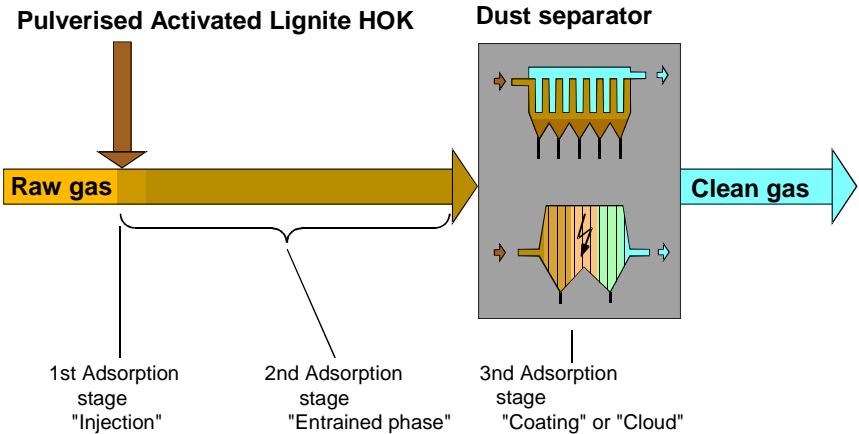


Fig. 3: Entrained dust cloud process

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 HOK[®] and gas or the pulverised coke coatings formed on the filter cloths of fabric filters bring about the third stage of pollutant separation [4,5].

Activated Lignite HOK[®] can be used in waste gas scrubbers as well. The latter are normally marked by an only inadequate separation efficiency regarding dioxins, furans and metallic mercury. The addition of pulverised Activated Lignite HOK[®] upstream of or to the scrubbers allows the efficiency of already existing scrubbing systems to be markedly improved.

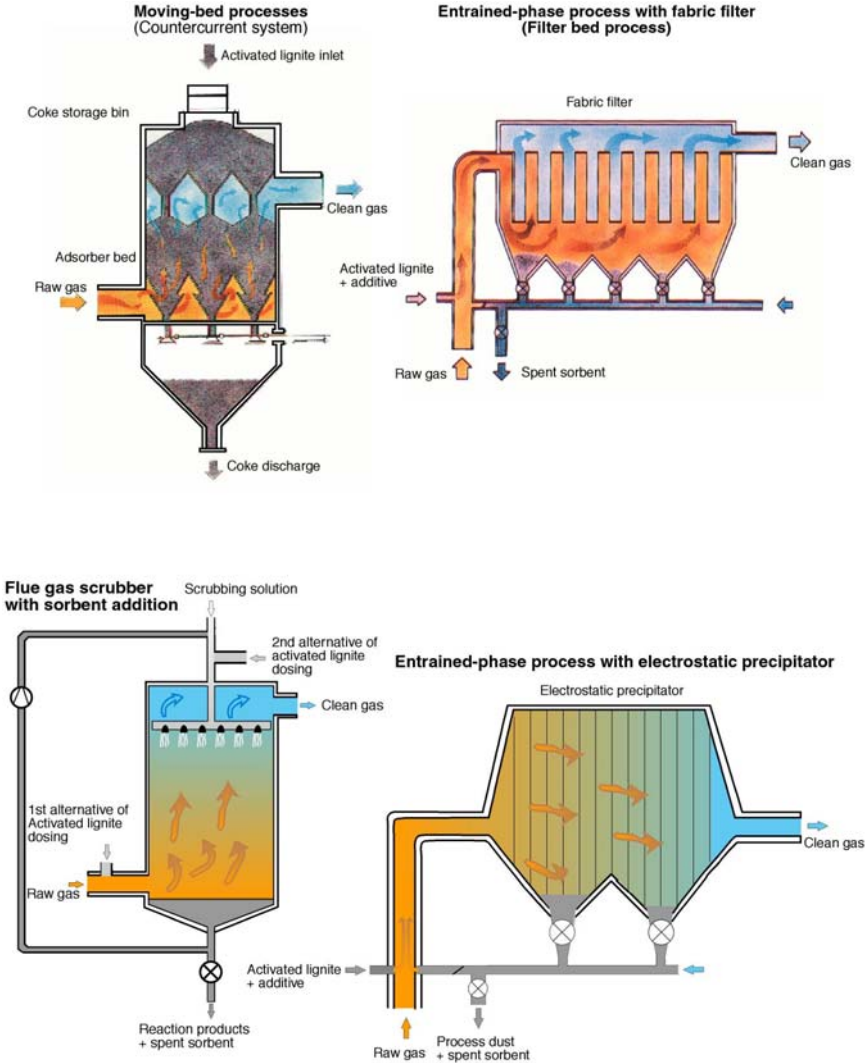


Fig. 4: Processes for adsorptive gas cleaning

The adsorption in an entrained dust cloud can very easily be integrated into existing dust separation, scrubbing and absorption processes, with the Activated Lignite HOK[®] 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.

Results of Hg Separation For Different Tasks

In the following, examples of some process concepts are taken to elucidate mercury separation on Activated Lignite HOK[®] basis.

Mercury Reduction in the Case of Sewage Sludge Combustion

The energetic utilisation by means of sewage sludge combustion is gaining more and more importance. Most of the mercury entering the boiler together with the sewage sludge is re-released and leaves the boiler in a gaseous state. *Waste gas cleaning in the case of sewage sludge co-combustion in an industrial power plant* and *waste gas cleaning in a sewage sludge mono-combustion plant* are taken as examples to demonstrate that the use of pulverised Activated Lignite HOK[®] in the so-called entrained dust cloud process and the separation in an electrostatic precipitator constitute very efficient, but simple and favourably-priced solutions for mercury reduction.

Waste gas cleaning in the case of sewage sludge co-combustion in an industrial power plant
[5]

With regard to co-combustion of sewage sludges, free combustion capacities in existing industrial power plants represent an ecologically and economically reasonable alternative to sewage sludge mono-combustion, provided that the stringent emission limit values are observed. Since primary measures do not permit any reduction in the volatile heavy metals released during the co-combustion of sewage sludge, the injection of Activated Lignite HOK into existing systems is again a recommendable solution.

Figure 5 shows the basic structure of a lignite-based industrial power plant for sewage sludge co-combustion. 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 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 m³_(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.

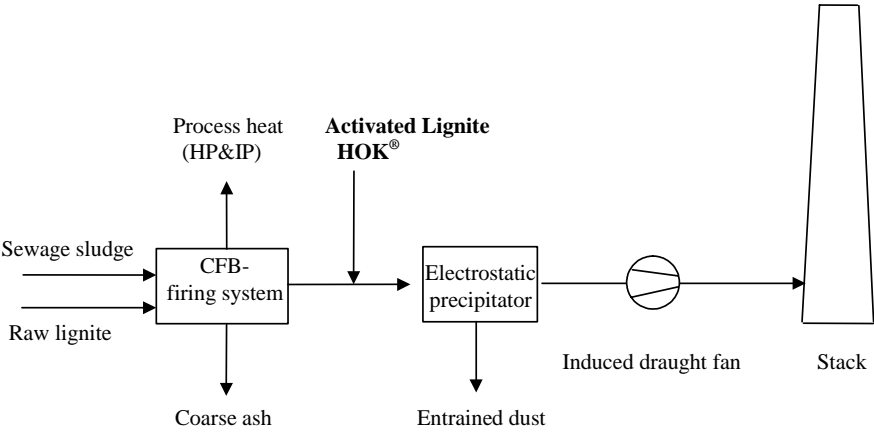


Fig. 5: Sewage sludge co-combustion in an industrial power plant

By means of several injection nozzles arranged around the circumference of the waste gas duct, the pulverised Activated Lignite HOK[®] 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 HOK[®] in the total waste gas flow. The loaded pulverised coke is separated together with the occurring process ash in the electrostatic precipitator. Figure 6 shows the results of the separation efficiencies obtained for mercury with different coke dosing rates.

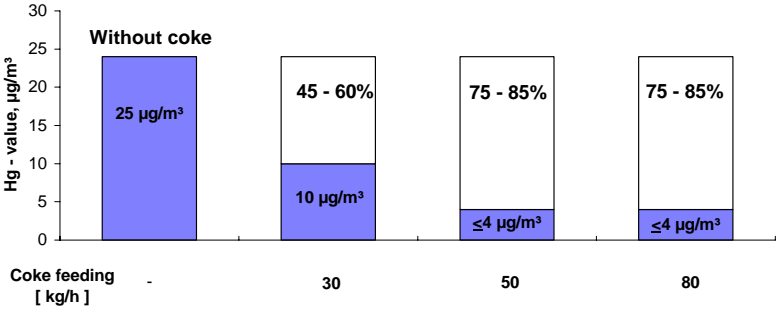


Fig. 6: Mercury separation by means of Activated Lignite HOK[®] during sewage sludge co-combustion

Related to the mercury emission of about $25 \mu\text{g}/\text{m}^3$ occurring on average without coke addition during sewage sludge co-combustion, separation efficiencies of 75 to 85 % are obtained with an hourly coke dosing rate of 80 kg. An hourly coke 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 7 shows an example of the characteristic time curve of the Hg emission obtained during HOK[®] dosing operation and an hourly dosing rate of 80 kg.

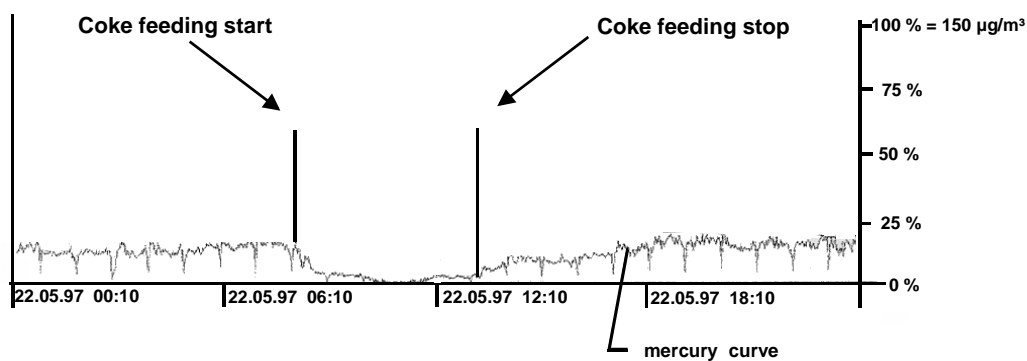


Fig. 7: Curve of Hg emission before and after Activated Lignite HOK[®] addition

Due to the somewhat time-delayed effect occurring during the start-up and shutdown of coke feeding, the buffering behaviour of an electrostatic precipitator can also be observed during considerable 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.

As already explained above, it is also the sulphur content of the waste gas that in addition to the carbon content has a decisive influence on mercury retention. The results regarding mercury reduction show that, in view of the present gas-specific conditions with SO_2 contents of 100 to $150 \text{ mg}/\text{m}^3$ and steam portions of around 30 % vol., efficient self-doping of coke with sulphuric acid is obtained.

Waste gas cleaning in the case of sewage sludge mono-combustion [1]

The separation of elemental mercury gives rise to special problems in sewage sludge mono-combustion plants. In most cases, ionogenic mercury is separated together with the

acid pollutant gas components in wet scrubbing systems while the insoluble metallic mercury passes the conventional waste gas cleaning stages almost without any hindrance. Figure 8 shows the waste gas line of sewage sludge combustion with Activated Lignite HOK[®] injection.

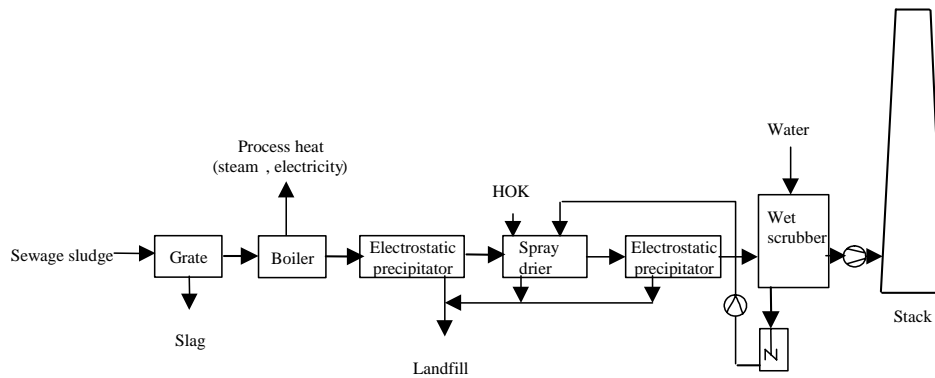


Fig. 8: Waste gas line of sewage sludge combustion in Stuttgart

The waste gas line consists of a pre-dedusting system in an electrostatic precipitator, a spray drier with downstream dust separation in another electrostatic precipitator and a two-stage wet scrubber. The liquid flows occurring during waste gas scrubbing evaporate in the spray drier. After wet scrubbing, the clean gas is conducted through an induced draught fan to the stack and then discharged into the atmosphere.

HOK[®] is dosed directly into the spray drier head in the area of the scrubber residues fed. Figure 9 shows the gaseous contents of Hg_{total}, Hg⁰ and Hg_{ion.} measured in the clean gas.

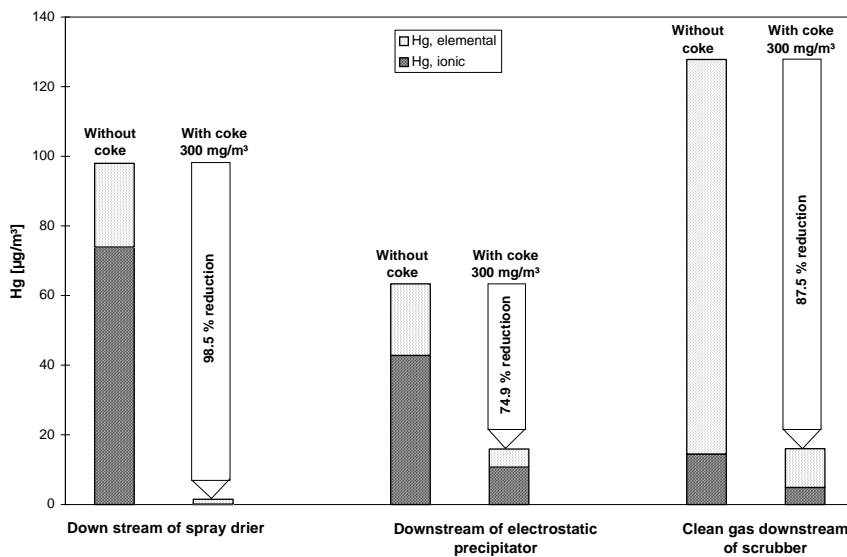


Fig. 9: Mercury separation by means of HOK[®] during sewage sludge combustion

It is already in the waste gas flow downstream of the spray drier and upstream of the electrostatic precipitator that the high adsorption effect of lignite on mercury reduction becomes noticeable. The Hg contents measured downstream of the spray drier are far below $5 \mu\text{g}/\text{m}^3$. In particular the elemental mercury is adsorbed by HOK[®] with a high separation efficiency. The Hg concentrations determined downstream of the electrostatic precipitator show a slightly increased level. The rise in the Hg contents suggests mercury desorption in the electrostatic precipitator which is due to Hg-loaded residues.

The values obtained for the clean gas downstream of the scrubber correspond to the Hg contents measured downstream of the electrostatic precipitator. The markedly higher Hg level compared to that of the mercury input without pulverised coke addition is due to the storage effect of the system. This results in an increase of the low inlet concentration existing in the measuring period.

The Hg concentration in the electrostatic precipitator dust rises from $< 6 \text{ mg}/\text{kg}$ to up to $100 \text{ mg}/\text{kg}$ which confirms the adsorptive efficiency of Activated Lignite HOK[®].

Mercury Separation during the Processing of Hg-Contaminated Scraps [8]

After their use, oil and natural gas production equipment as well as chlor-alkali plants are contaminated with mercury. These are problems that are currently in the limelight of ecological interest since the recycling process of these components gives rise to the corresponding emissions from steel melts.

In view of this situation, the Siempelkamp Giesserei company (Germany) has developed a process for the decontamination of these scraps.

Figure 10 shows the structure of the melting plant with downstream waste gas cleaning. The mercury adhering to the steel scrap up to the amount of one percentage by weight evaporates from the molten metal. In a cyclone, the coarse dust is separated while a fabric filter retains extra-fine dust and particle-adsorbed Hg. This involves a reduction in the Hg concentration to approx. $20 \text{ mg}/\text{m}^3$ downstream of the fabric filter.

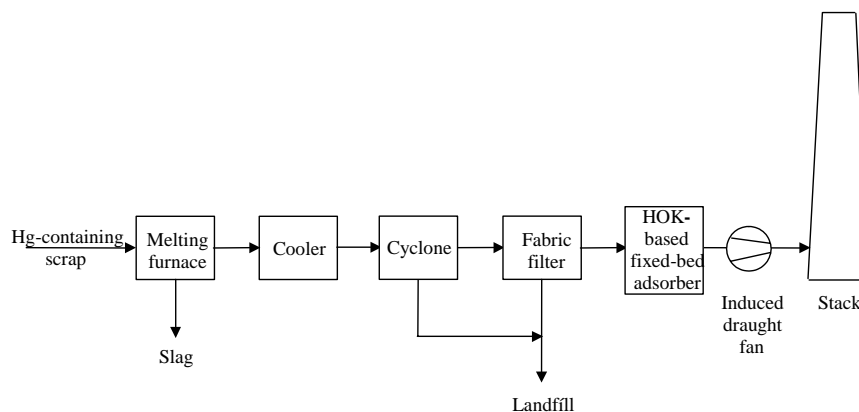


Fig. 10: Melting plant for reprocessing of Hg-contaminated scraps

In the second cleaning stage, viz. a fixed-bed adsorber with sulphuric acid-doped Activated Lignite HOK[®], residual cleaning takes place with the object of obtaining values that remain under the analytical detection limit. Figure 11 shows the Hg concentrations at various points in the process.

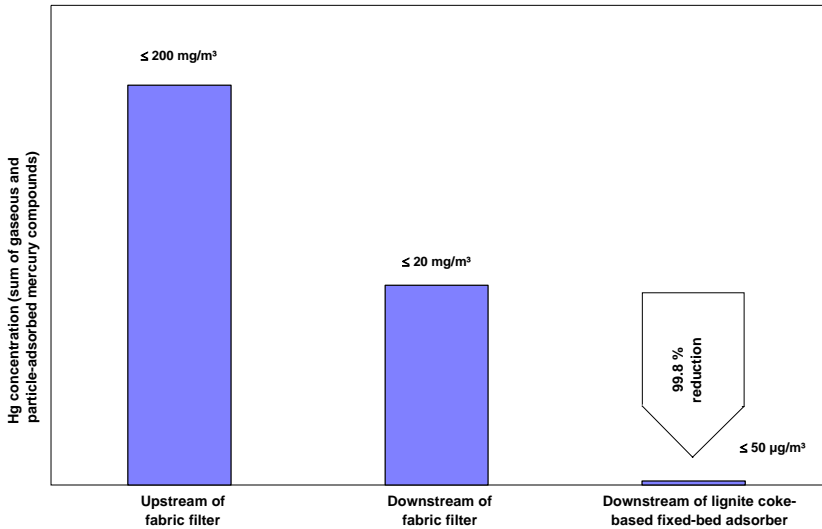


Fig. 11: Mercury separation with Activated Lignite HOK[®] from the waste gas of scrap melting using the fixed-bed process

Mercury Separation in Refuse Incineration Plants [7]

During refuse incineration it is not only the emissions of heavy metals that are of interest; attention has also to be paid to those of toxic trace constituents, such as dioxins and furans. Figure 12 shows a solution to this problem. It is based on Activated Lignite HOK[®] addition--a system that can be retrofitted with low outlays involved. This variant allowed an additional separating device for heavy metals and dioxins/furans to be integrated into an existing quasi-dry SO₂ and HCl adsorption system.

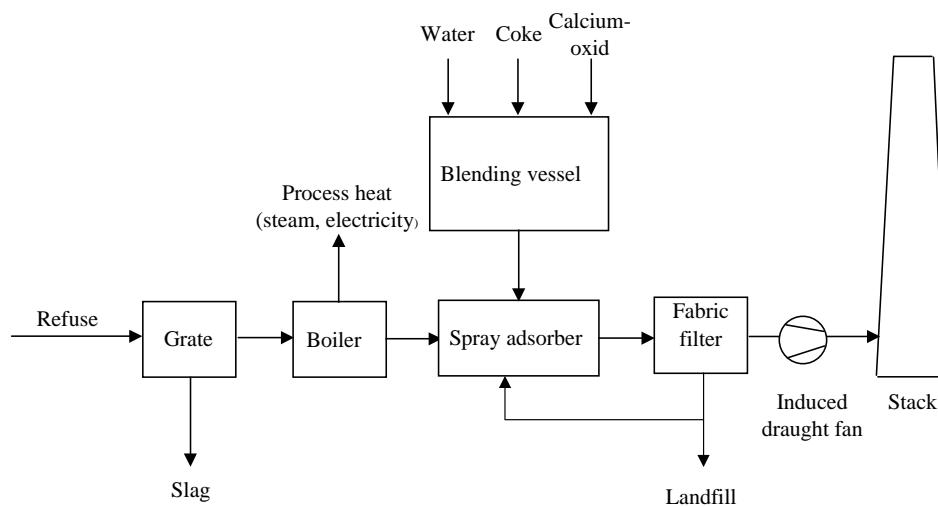


Fig. 12: Integrated adsorption system for dust separation by means of Activated Lignite HOK[®] in the Rosenheim refuse incineration plant (Germany)

The waste gas line of the plant consists of a heat recovery system, a spray adsorption tower and the downstream fabric filter for dust separation. Pulverised Activated Lignite HOK[®] is admixed to the lime milk and added to the waste gas by means of the atomising device installed. In the spray adsorber, the lime milk mixed with Activated Lignite HOK[®] is dispersed to ensure intensive contact with the pollutants in the waste gas. The salts forming from the acid pollutants and the lime milk, the pulverised Activated Lignite HOK[®] loaded with pollutants and the entrained dust are separated in the downstream fabric filter.

The results obtained for mercury emission demonstrate that the addition of only 10 % wt of pulverised HOK[®] to the lime milk (related to CaO), which corresponds to 1.8 kg of pulverised Activated Lignite HOK[®] 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).

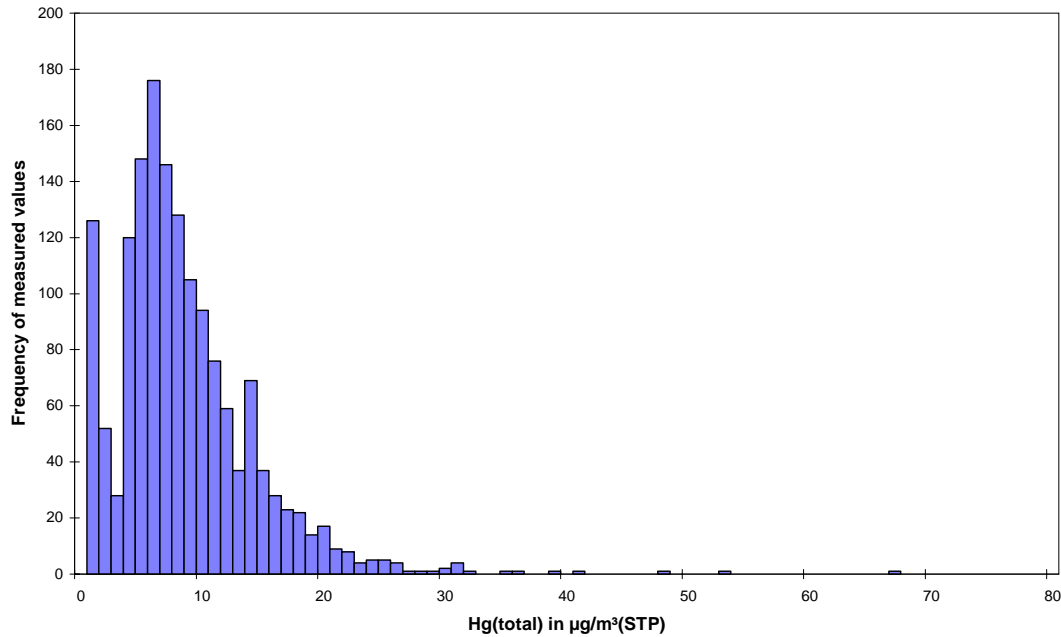


Fig. 13: Mercury reduction in the case of quasi-dry waste gas cleaning [7]

Summary

Mercury is a considerably toxic element. In order to protect the environment, measures to reduce the mercury emissions from industrial-scale plants are necessary. One cleaning option for all emission-relevant pollutants includes adsorptive processes with Activated Lignite HOK[®] that are implemented according to the moving-bed or entrained-phase process. Due to its specific surface and porosity, Activated Lignite HOK[®] belongs to the group of activated coke substances. Its considerably more favourable price than that of activated carbon or synthetic adsorbents allows the coke to be used as non-returnable adsorbent. The plants for Activated Lignite HOK[®]-based waste gas cleaning represent state-of-the-art facilities and are successfully working in several hundred individual plants all over the world. For the implementation of trace constituent separation, Activated Lignite HOK[®] permits the extension of existing dust separation and waste gas scrubbing systems by the adsorption of trace constituents using Activated Lignite HOK[®] injection. Compared with the adsorption in self-contained process-specific plant components, this process-integrated adsorption constitutes one of the simplest and at the same time most favourably-priced emission reduction measures.

Taking the example of some applications regarding mercury separation, this contribution shows that individual Activated Lignite HOK[®]-based process variants represent efficient solutions, without having a negative effect on the economic efficiency of the overall process. It explains the adsorption processes and their technical integration into the complete chain of

waste gas cleaning. The findings obtained in the field of Activated Lignite HOK[®]-based waste gas cleaning can be applied to other industrial sectors as well.

Literature

- /1/ J. Wirling, H. Schroth:
Quecksilberabscheidung aus Abgasen einer Klärschlammverbrennungsanlage an Braunkohlenkoks - Müll und Abfall, October 1996
- /2/ "Activated Lignite HOK, Manufacture and Fields of Application"
Informative brochure of Rheinbraun Brennstoff GmbH, Cologne
- /3/ Reich-Walber M. et al.:
Abgasfeinreinigung bei Abfallverbrennungsanlagen mittels Braunkohlenkoks
Müll und Abfall 9, 1992, pp. 640 - 648
- /4/ K. Kersting, J. Wirling, W. Esser-Schmittmann, U. Lenz:
Dioxin- und Furanabscheidung aus Abgasen einer Sinteranlage an Braunkohlenkoks
Stahl und Eisen 117 (1997), no. 11 - pp. 49 - 55 + 150
- /5/ J. Wirling, H.-J. Lang:
Abgasreinigung bei der Klärschlamm-Mitverbrennung in einem Industriekraftwerk
awt Abwassertechnik 1/99, pp. 77 - 82
- /6/ P. Neumann, K. Schmidt:
Quecksilber in Verbrennungsanlagen
BWK/TÜ/Umwelt-Special, March 1993
- /7/ R. Egeler, B. Seitz:
Emissionsminderung von Quecksilber und chlororganischen Schadstoffen mittels Braunkohlenkoks
VDI seminar "Primär- und sekundärseitige Dioxin-/Gesamtemissionsminderungs-
techniken" (Primary and secondary dioxin/total emission reduction techniques)
Munich, Sept. 18 and 19, 1997
- /8/ Neues Einsatzgebiet für Braunkohlenkoks
Abscheidung hoher Quecksilberemissionen im Abgas bei der Schrottschmelze
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