Adsorptive Waste Gas Cleaning in an Industrial-Scale Coal-Fired Power Plant

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ABSTRACT

The U.S. EPA's decision December 2000 to regulate mercury emissions from coal-fired boilers set a schedule of three years for promulgation of a draft rule, with a final rule by December 2004. This heightens the need for the timely identification and demonstration of cost-effective mercury control technologies for retrofit application to existing coal-fired boilers. Complex technologies that involve high investment or operating costs, or create solid waste management problems, are unlikely to find commercial application. Faced with increasing pressure to control costs, generators need demonstrated process engineering solutions that avoid or minimize these disadvantages. RWE Power AG, Germany, has demonstrated a simple and effective mercury control process in Europe that is well suited to help meet the U.S. mercury control requirements.

Extensive measurements performed during sewage sludge co-combustion in an industrial power plant of RWE Power AG have shown that process-integrated entrained-phase adsorption using activated lignite constitutes a technically reliable, ecologically reasonable and, at the same time, low-cost solution ensuring compliance with the limit values. Compared to adsorption in fabric filter systems, this adsorption in a dust cloud with downstream electrostatic precipitator is a novel application.

The steam generator working according to the principle of circulating fluidized-bed combustion (275 MWth) is fired with coal (raw lignite) as the main fuel. Both the dewatered sewage sludge and the coal are added via the ash recirculation pipes of the cyclones. In an entrained-phase reactor, the cooled flue gas is brought into contact with the adsorption agent, viz. activated lignite. Subsequently, the activated lignite is separated together with the produced filter ash via an electrostatic precipitator and the cleaned waste gas released into the atmosphere via the stack.

The results obtained from the separation of the highly-volatile mercury show that the addition of activated lignite and dust separation in an electrostatic precipitator can ensure efficient emission reduction.

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 sensitization 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 [10]. This in turn opens up options of transferring this process to other fields of waste gas treatment, for example, the treatment of waste gases from the co-combustion of residues in power plants or those from metallurgical processes [4, 7, 9].

In co-operation with plant operators, RWE Power AG, Germany, is developing applications which permit the use of activated lignite as a favorably-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 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 sulfur dioxide, hydrogen chloride, hydrogen fluoride, hydrogen sulfide, heavy metals as well as the highly toxic dioxins and furans [1, 2, 3].

Taking the example of the waste gas treatment in a coal-fired industrial power plant and during the co-combustion of sewage sludge, the following report demonstrates the good suitability of activated lignite for mercury separation in the favorably priced entrained-phase process. The results obtained by means of activated lignite added in dosed quantities to the waste gas flow upstream of an existing electrostatic precipitator show in an impressive way that integrated adsorption constitutes a simple and, at the same time, reasonably priced solution for emission reduction, which – what is more - can rapidly be implemented in existing plants with low outlays involved. Since December 1999 - after two years of testing and optimization - the integrated entrained-phase adsorption process with activated lignite has been successfully employed for mercury separation.

ACTIVATED LIGNITE AND SEPARATION OF MERCURY AND ITS COMPOUNDS

Activated lignite

Thanks to its porosity and the resulting large inner surface and pore structure, activated lignite produced according to the so-called rotary-hearth furnace process [5] is as suitable as high-grade activated carbon for use as adsorbent. Unlike activated carbon, activated lignite 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 that are of importance to its use for waste gas cleaning. With regard to thermal utilization of activated lignite, which is reasonable in many cases, the relevant data for that purpose are listed as well. The decisive criterion permitting the favorable adsorption properties is the large active activated lignite surface of some 300 m²/g which is provided by the sponge-like pore structure (Figure 1). From grains (HOK grain) all the way to super-milled activated lignite (HOK super), four qualities are available which permits the use of this sorbent in the most different applications of adsorption. Further information about the characteristics of activated lignite and its application potential in environmental protection is given in [2,3,4] and [10].

Table 1. Physical and chemical parameters of activated lignite

Physical parameters	HOK grains	HOK medium	HOK pulverized*)		HOK super
Grain size [mm]	1.25 – 5	0 - 1.5	< 0.4		< 0.2
Bulk density [t/m³]	0.45	0.53	0.55		0.55
Specific surface area	300 m²/g	300 m²/g	300 m²/g		300 m²/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	
	Sulfur		0.5	% wt	
Ash analysis	CaO		41	% wt	
	MgO		14	% wt	

*) Sorbent used in the application described

Figure 1. Microscopically magnified activated lignite

Separation of mercury and its compounds

Due to the high temperatures already existing in the combustion chamber, mercury occurs in its elemental form [11]. 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:

$$Hg + 1/2\ O_2 \rightarrow HgO$$

$$HgO + 2\ HCl \rightarrow HgCl_2 + H_2O$$

Depending upon the reaction equilibrium obtained, mercury occurs in the waste gas in its elemental form as Hg or in its oxidized form as $HgCl_2$. In the case of high HCl contents, as are common to refuse incineration plants, the $HgCl_2$ 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. $HgCl_2$ 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 Hg^o that may occur owing to reduction and disproportionation reactions. In this case, Hg^o again changes from the solution to the waste gas and is discharged together with the gas flow.

$$SO_2 + 2\ HgCl_2 + H_2O \rightarrow SO_3 + Hg_2Cl_2 + 2\ HCl$$

$$Hg_2Cl_2 \rightarrow HgCl_2 + Hg\uparrow$$

Unlike the oxidized 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 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 sulfuric acid. This is normally done with the residual SO_2 and H_2O contents occurring in the waste gas. In the presence of oxygen and water, the SO_2 contained in the waste gas is catalytically converted on the activated lignite surface into sulfuric acid. Due to the sulfuric acid thus adsorptively bound on the activated lignite surface, the mercury contained in the gas is separated by means of chemisorption.

Elemental mercury (Hg°) reacts with the sulfuric acid on the activated lignite to form mercury(I) sulfate (Hg_2SO_4) or - in the case of sufficient sulfuric acid being available - to mercury(II) sulfate ($HgSO_4$).

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

PROCESS FOR ADSORPTIVE WASTE GAS CLEANING

For adsorption there are primarily the moving-bed, entrained-phase and filter-bed systems to choose from. In addition to their use in self-contained adsorption apparatuses, sorbent-based techniques are increasingly integrated into existing dedusting, scrubbing and absorption processes where the activated lignite adsorbent is dosed as a fine-grained powder to the gas flow upstream of the actual cleaning stage [7,8,9]. In this way, it is above all the investment costs that can be markedly reduced without impairing the separation efficiency to a considerable extent.

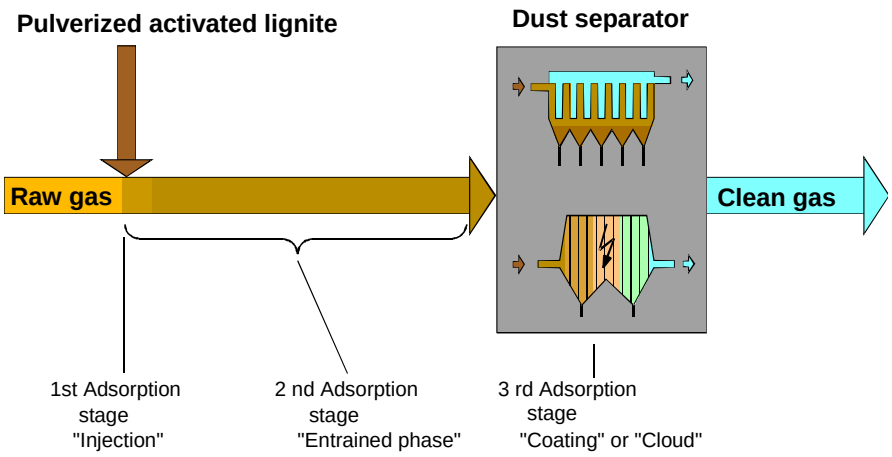
As far as the application of activated lignite adsorption as process-integrated adsorption stage in fabric filter systems is concerned, extensive investigations have already been conducted. Even in the case of high filter dust contents, small activated lignite additions allow considerable separation efficiencies to be attained, which, for example, amount to up to 99.9 % for dioxin and furan.

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 (Figure 3). 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 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 marked by an only inadequate separation efficiency regarding dioxins, furans and metallic mercury. The addition of

activated lignite upstream of or to the scrubbers allows the efficiency of already 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.

Figure 3. Entrained dust cloud process

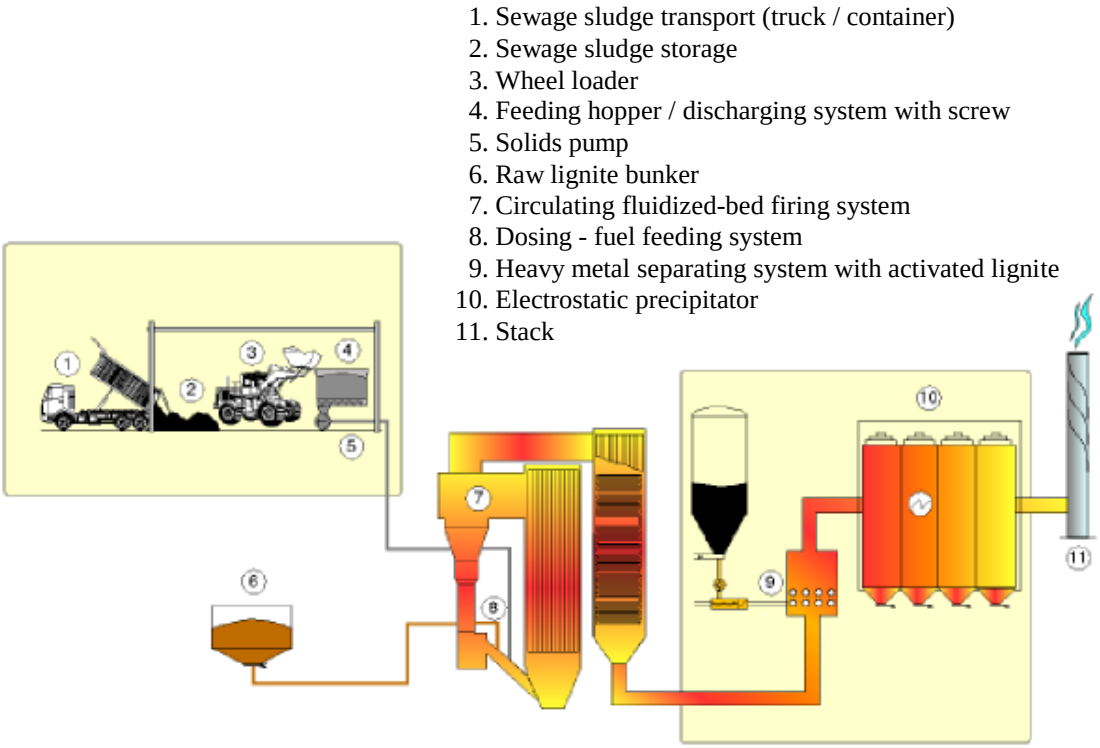


SYSTEM CONFIGURATION IN THE INDUSTRIAL COAL FIRED POWER PLANT

Figure 4 shows the system configuration, including the systems for sewage sludge co-combustion and final flue gas cleaning, which is implemented on the basis of a CAFBC steam generator in RWE's industrial power plant on the premises of the Ville-Berrenrath plant complex. The 275 MW_{th} steam generator operating according to the principle of circulating atmospheric fluidized-bed combustion is fed with raw lignite (93 t/h) as principal fuel. Raw lignite as well as mechanically dried sewage sludge are added through the recirculating cyclone ash system. As specified by the German Regulation to the Federal Immission Control Act governing, inter alia, co-combustion, up to 4 % of the furnace heat capacity of the overall plant is accounted for by the sewage sludge. [12]

The flue gases totaling approx. 350,000 m³(STP), dry/h and occurring during combustion are dedusted by means of a four-compartment electrostatic precipitator. After this process, the flue gas is conducted at a temperature of approx. 160 °C via an induced draught fan to the stack and discharged into the atmosphere. The fly ash occurring during dedusting- -averaging 5 tonnes per hour in the case of sewage sludge co-combustion- -is continuously removed from the electrostatic precipitator.

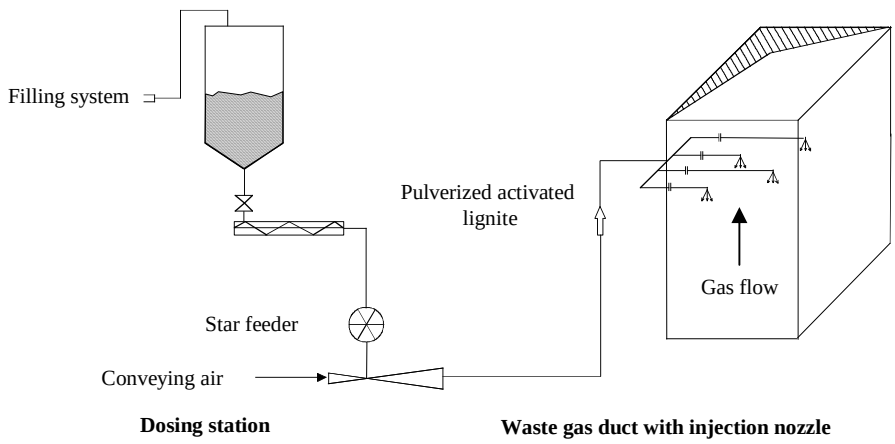
Figure 4. Sewage sludge co-combustion in an industrial power plant



The adsorbent is directly added to the flue gas flow upstream of the electrostatic precipitator which allows the gaseous pollutants to be reduced already in the dust-loaded raw gas. After having passed a reaction route of about 20 m, the loaded activated lignite (HOK pulverized) is separated together with the occurring fly ash in the four compartments of the electrostatic precipitator.

Figure 5 is a schematic representation of the activated lignite dosing system. The activated lignite (HOK pulverized) used for final flue gas cleaning is delivered by means of silo trucks and pneumatically conveyed to a receiving bin. Via a dosing system, the activated lignite (HOK pulverized) is then transported by means of compressed air to the injection point. To ensure uniform distribution of the activated lignite (HOK pulverized) over the cross section of the flue gas pipe, the activated lignite spread over the circumference of the duct is injected into the waste gas flow so that within the shortest distance distribution of the activated lignite (HOK pulverized) particles is attained in the waste gas flow of the duct cross section.

Figure 5. Activated lignite dosing system



OPERATING RESULTS WITH THE INTEGRATED ADSORPTION SYSTEM IN THE INDUSTRIAL POWER PLANT

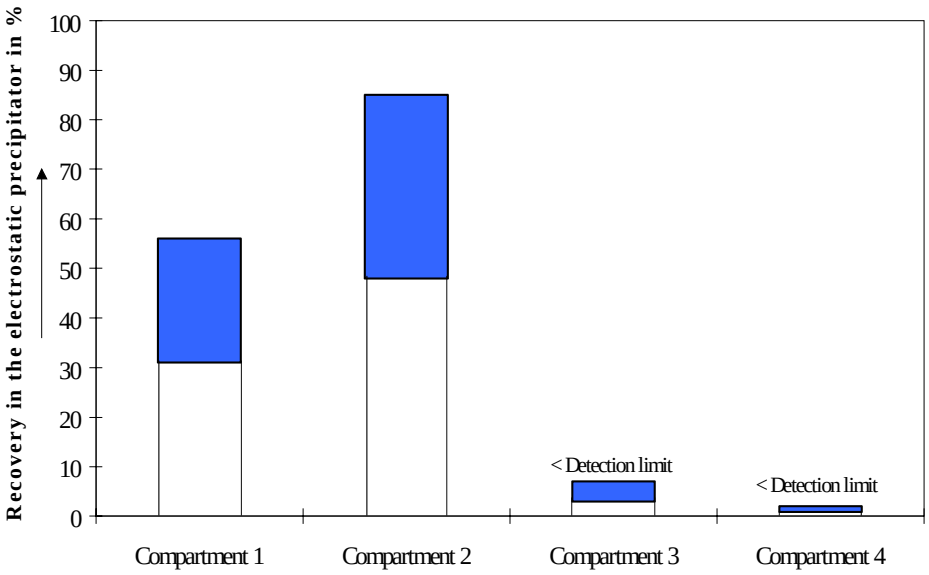
The final flue gas cleaning system installed in the RWE Power industrial power plant has already been working for more than four years. In this time, comprehensive measuring series for process assessment and optimization have been conducted by means of discontinuous and continuous measuring and analyzing techniques. Focal points of investigation were in particular the separation of mercury, an emission-relevant pollutant in the case of sewage sludge co-combustion, by means of activated lignite and the performance of the electrostatic precipitator in the case of activated lignite (HOK pulverized) addition.

Activated lignite separation in the electrostatic precipitator

A vital element of the adsorption process employed in the power plant is the suitability of the electrostatic precipitator for reliable separation of the activated lignite (HOK pulverized) fed. The question of whether or not the dust separator works smoothly is cleared up by the monitoring function of the on-line dust measurement system installed in the stack. The dust measurement data recorded during operation as well as the individual measurements taken according to VDI guideline 2066 (VDI is a German abbreviation standing for Association of German Engineers) do not reveal any change in the dust emissions, with activated lignite (HOK pulverized) being added as an adsorbent. With values of much lower than 10 mg/m³, the dust emissions remain at a very low level.
The almost complete separation of activated lignite (HOK pulverized) in the electrostatic precipitator is confirmed by the activated lignite (HOK pulverized) distribution detected in the ash discharging system. The relevant values measured are shown in Figure 6.

The drop in the carbon content of the fly ash that is much more pronounced in the third and fourth compartments than in the first two demonstrates that the existing electrostatic precipitator guarantees complete separation of the activated lignite (HOK pulverized).

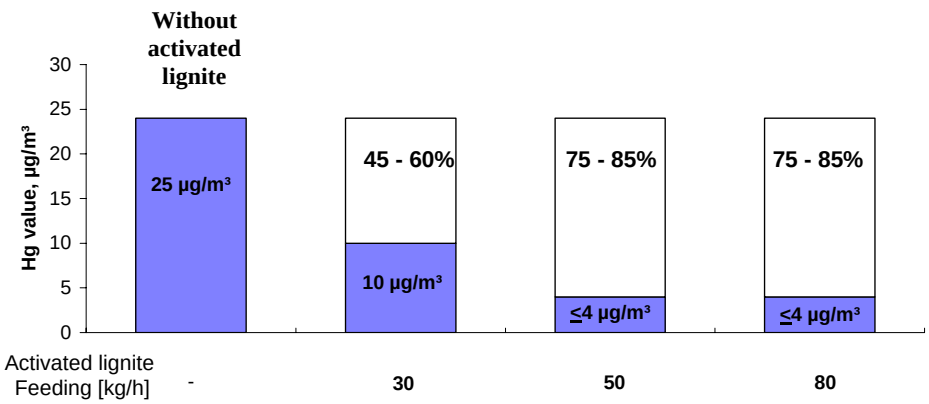
Figure 6: Activated lignite separation in the electrostatic precipitator



Mercury separation

Figure 7 shows the results of the mercury-related separation efficiencies obtained with different dosing rates.

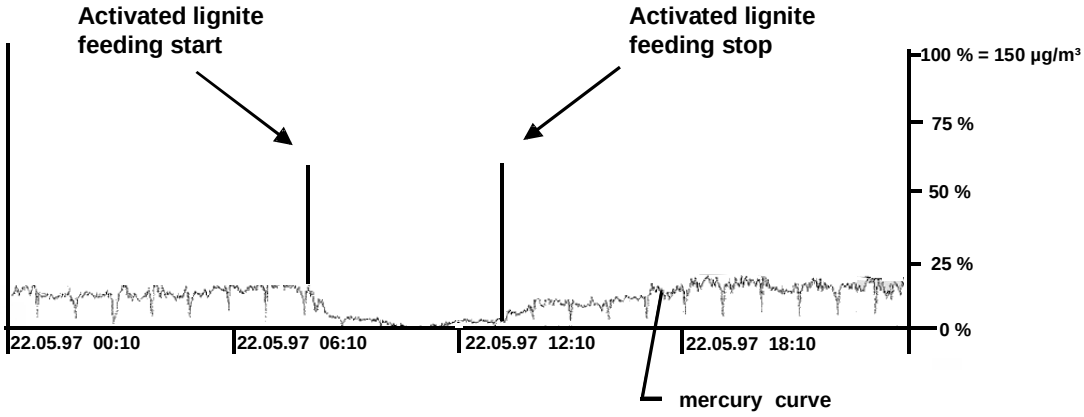
Figure 7: Mercury separation using activated lignite during sewage sludge co-combustion as a function of activated lignite dosing



Related to the mercury emission averaging approx. 25 µg/m³ without activated lignite addition during sewage sludge co-combustion, separation efficiencies of 75 to 85 % are achieved with an hourly activated lignite dosing rate of 80 kg. With the hourly activated lignite dosing rate of 50 kg, nearly the same separation efficiencies are attained; unlike the higher dosing rate, however, the efficiency is reached here only after approx. two hours (see Figure 9). Only at a dosing rate of 30 kg/h will the separation efficiency decline noticeably. Then, the separation efficiencies will just range between 45 and 55 %.

Figure 8 shows an example of the mercury emission curve recorded during activated lignite dosing operation and an hourly dosing rate of 80 kg.

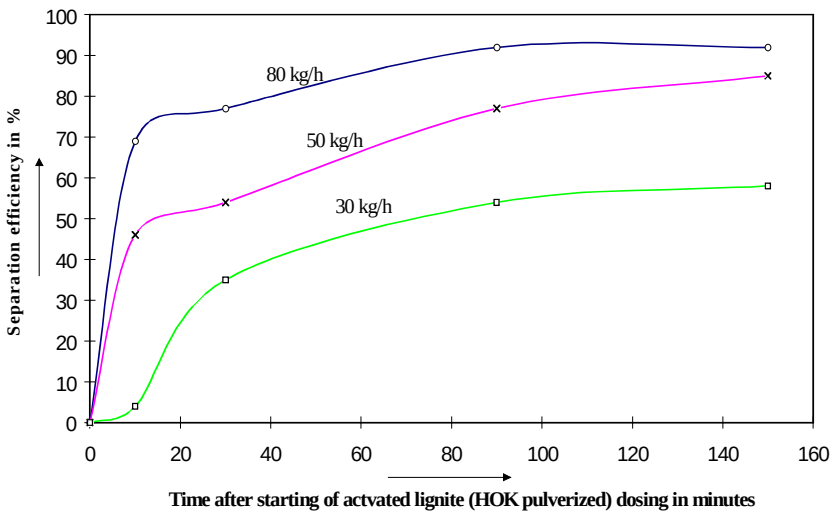
Figure 8. Course of Hg emission before and after activated lignite addition (dosing rate of 80 kg/h)



Immediately after the start of the activated lignite dosing system, the mercury emissions begin to decline. Following switching-off of the activated lignite dosing system, on the other hand, the mercury emissions only slowly rise to their original value again. This shows that the dosed activated lignite

(HOK pulverized) remains in the system for a certain period so that pollutant separation continues. The existing buffering effect has the advantage that short-time failures of the dosing system and fluctuations in the raw gas concentration do not entail any immediate rise in emissions. Figure 9 shows the chronological sequence of mercury separation as a function of the dosing rate.

Figure 9. Hg separation after start of dosing

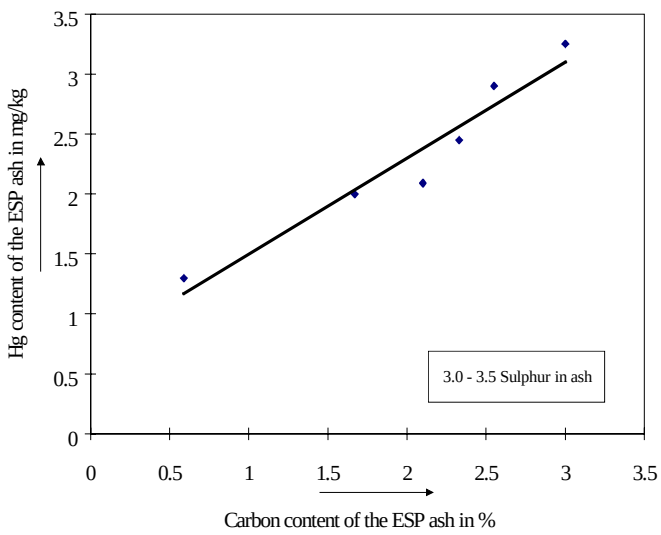


With the dosing rates of 80 kg/h and 50 kg/h, mercury is already reduced by more than 50 % directly upon the start of activated lignite dosing. After a dosing period of about two hours, the separation efficiencies amount to over 80 %. The slow rise in mercury reduction reveals that an "adsorbing activated lignite (HOK pulverized) cloud" is really developing in the electrostatic precipitator which makes the third adsorption stage feasible.

Mercury loading in the mixed ash discharged

Figure 10 shows the mercury loading of fly ash separated by the electrostatic precipitators as a function of the average carbon concentration in the precipitator dust due to activated lignite addition.

Figure 10. Hg retention as a function of the carbon content in the mixed ash



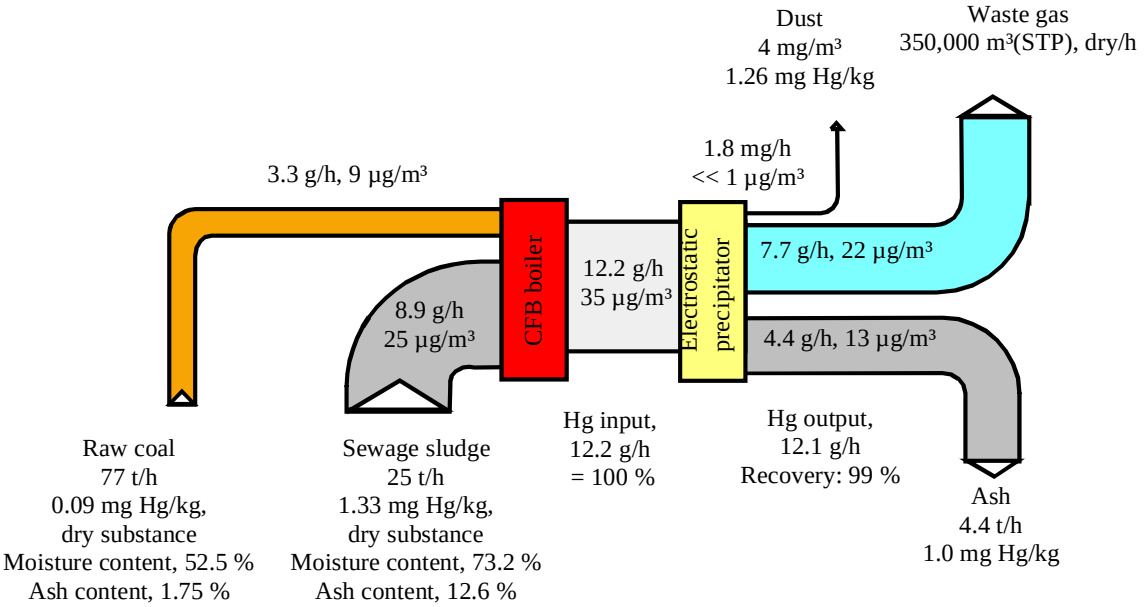
Sampling of the mixed ash resulting from fly ash and activated lignite separated in the electrostatic precipitator in the case of activated lignite dosing and the analysis of these samples for their mercury and carbon contents verify the adsorptive effect of activated lignite, thus making separation of the gaseous mercury compounds contained in the waste gas possible. The feasible mercury retention in the case of activated lignite (HOK pulverized) addition rises proportionally to the dosing rate.

In addition to the carbon content, that of sulfuric acid in the ash has a considerable influence on mercury retention as well. The results obtained from mercury adsorption demonstrate that the existing flue gas composition with SO_2 contents ranging between 100 and 150 mg/m³ and steam portions of around 30 % vol. allow the activated lignite to be efficiently loaded with sulfuric acid.

Mercury balance

Figures 11 and 12 show the mercury balances obtained from test operation <u>without</u> and <u>with</u> activated lignite (HOK pulverized) addition.

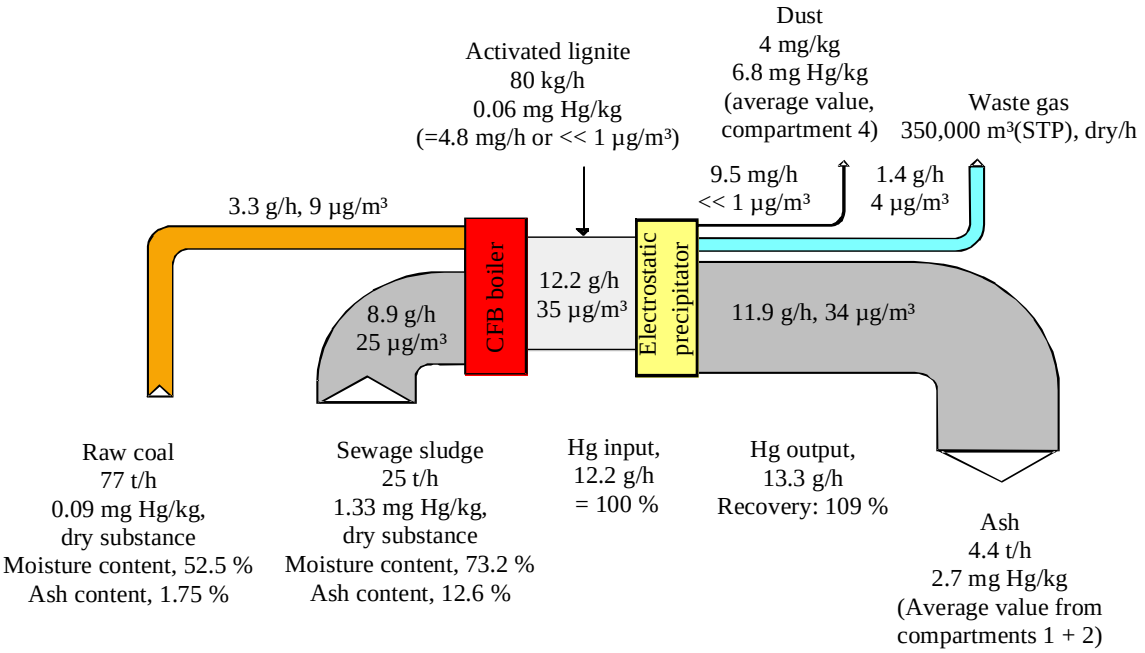
Figure 11: Hg balance in the case of sewage sludge co-combustion without AL addition



Without activated lignite addition, approx. 60 % of the mercury input is emitted with the flue gas. In the fly ash of the electrostatic precipitator, the remaining 40 % of the mercury input is retained and discharged via the ash route.

With activated lignite addition (Figure 12), the remaining mercury emissions in the flue gas are reduced by retention in the activated lignite down to their detection limit. The mercury amounts discharged via the ash route increase correspondingly.

Figure 12: Hg balance in the case of sewage sludge co-combustion with AL addition



Eluation behavior of ash

Several eluate-related investigations of the mixed ash demonstrate that the heavy metals separated in the case of activated lignite addition are fixedly bound to the activated lignite and do not cause any change in the eluate values.

Performance

The operating experience gained with the integrated adsorption system - with the electrostatic precipitator acting as dust separator - can be described as positive. It was already directly upon commissioning that continuous operation of the flue gas cleaning system during sewage sludge co-combustion was implemented. Since commissioning the activated lignite-based entrained-phase process has proved a reliable technique with low maintenance outlays involved. The activity of the electrostatic precipitator was not found to be impaired in any way by the addition of activated lignite.

CONCLUSION

Sewage sludge co-combustion in a coal-fired industrial power plant – the application dealt with by this report – calls for further waste gas cleaning for pollutant reduction, in particular that of mercury. Entrained-phase adsorption using activated lignite and separation of the loaded activated lignite in the electrostatic precipitator have proved to be a very efficient process that – as a consequence – can be used for other comparable applications as well.

REFERENCES

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

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

7. 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

8. Wirling, J., Schroth, H., *Quecksilberabscheidung aus Abgasen einer Klärschlammverbrennungsanlage an Braunkohlenkoks*, Müll und Abfall, October 1996

9. Kersting, K.,. Wirling, J., Esser-Schmittmann, W., Lenz, U., *Dioxin- und Furanabscheidung aus Abgasen einer Sinteranlage an Braunkohlenkoks*, Stahl und Eisen 117 (1997), No. 11, pp. 49 - 55 + 150

10. Wirling, J.: *Implementation of Process-Integrated Waste Gas Cleaning Using Activated Lignite*, AWMA, Kansas City, March 2001

11. Neumann, P., Schmidt, K.,: *Quecksilber in Verbrennungsanlagen* BWK/TÜ/Umwelt-Special, March 1993

12. Bierbaum, K., Lambertz, L., Thomas, G.,: *Klärschlamm-Mitverbrennung in einem braunkohlegefeuerten Industriekraftwerk*, Chemie Ingenieur Technik (69) 7/97, pp. 973-975