# ADSORPTION TECHNOLOGY BRINGS WASTE INCINERATORS INTO COMPLIANCE - STEAG'S /a/c/t™-PROCESS IN EUROPEAN FACILITIES -

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Keywords: Flue Gas Cleaning, Adsorption Technology, Carbon Fixed Bed Adsorber

ABSTRACT

Due to the stringent emission limits for waste incinerators in Europe, the use of activated carbon technology became necessary.
STEAG is a licensor for the design and construction of an activated carbon fixed bed adsorber , the so called /a/c/t™-process with licensees in Europe and the United States.
The following paper provides a short desription of this technology and experience in commisioning and operation of the system.
The effectiveness of the /a/c/t™-process is demonstrated.

Emission control is an issue affecting many different sectors of industry. Some of the most stringent regulations apply to waste incinerators and Waste-to-Energy facilities.

Activated carbon technology is used in Europe to comply with these regulations. This technology makes it possible to reduce dioxin, furan, heavy metal, sulfur and acid emissions far below the required limits. Activated carbon processes are installed in Europe downstream of the flue gas desulfurization at medical, hazardous and municipal waste incineration plants.

The development of this technology occurred when the legal emission limits in Germany, the Netherlands, and Austria were tightened significantly.

Table 1 shows a comparison of the current legal emission limits in Europe and the United States.

STEAG has nearly 20 years experience in carbon technology. Since 1978 STEAG operates pilot plants to investigate the efficiency of this technology and to optimize the process. This resulted in the the "know-how" needed to design a cost effective adsorption system with guaranteed safe operation. Although STEAG has licensee AE&E (Austrian Energy and Environment), K+L (Kessler and Luch, Germany), and Black & Veatch (Kansas City, USA), STEAG has been involved in the design and commissioning of all /a/c/t™ facilities.

The proprietary fixed bed design is shown in figure 1. It is a cross flow fixed adsorber system. The flue gas flows horizontally through it. The bed consists of three vertical layers of activated carbon. Each layer is subdivided by perforated plates and each layer has it own coke discharge equipment so it can be moved and extracted separately and independently from the others. The first layer - the inflow layer - removes particulates, gaseous heavy metals and dioxins and furans, the second layer removes sulfur oxides ($SO_2$/SO3) and the third layer halogenated hydrogen (acid gases). The adsorbent in each layer can be replaced according to its capacity, providing the most efficient use of the carbon. The adsorption unit is designed to hold a supply of fresh carbon in a hopper at the top of the bed, which continually replenishes the supply. Each layer can be replenished individually, based on the conditions at the gas inlet. The carbon supply hopper needs to be filled only periodically. The unit's unique, patented features ensure the safe and efficient use of activated carbon while operating at temperatures between 215 to 300 F.

Since 1990, when the first contract was signed, STEAG and their licences have installed /a/c/t™-systems at 8 different sites in Europe with a total flue gas volume of more than 2.2 million dscm. Black & Veatch signed a contract to construct the first carbon adsorber of its kind in the United States. This was a team effort between Black & Veatch and STEAG.

In table 2 a reference list of the /a/c/t™--systems installed downstream of Waste Incineration plants in Europe is shown.

Following is a brief description of the operating experience at three of the European sites.

## THE MUNICIPAL WASTE INCINERATOR AT AVR ROTTERDAM

This facility is the largest municipal waste incineration plant in Europe. It consists of 7 independent units, all equipped with roller grate incinerators, electrostatic precipitators, two-stage wet scrubbing systems, /a/c/t™-systems, and a low temperature SCR-DeNO$_X$. This facility has a total capacity of over 1,000,000 tons of waste per year (20 to/hr per unit).

Each unit has an a/c/t™-system consisting of two beds, which are installed parallel to the flue gas flow. The main dimensions of the adsorber are 52 ft (length), 16 ft (width), and 88 ft (height). The total filter surface is approximately 5340 sqft.

The guarantee measurements were carried out separately for each unit between April and October 1994. Table 3 presents actual measured emission values.

It can be seen, that all the emissions are clearly far below the legal emission limits and the specified levels. The carbon consumption is about 1.65 lbs/t of burned waste.

This state-of-the-art flue gas cleaning system shows impressive results, proving it is possible to operate even an old incinerator while protecting the people and the environment most effectively from air pollution.

## THE HAZARDOUS WASTE INCINERATOR AT AVR ROTTERDAM

At the same site there are three rotary kilns for incineration of industrial and chemical wastes with a total capacity of approx. 80,000 tons per year of hazardous waste.

The relevant main components of this hazardous waste incineration plant are as follows: rotary kilu, waste heat boiler, spray quencher, electrostatic precipitator, two stage wet scrubbing system, /a/c/t™-system.

Trial operation of this hazardous waste incineration plant ended in October 1992, the results are shown in table 4. Several series of emission measurements have shown that the actual levels are clearly far below the emission standards and the specified levels.

THE HYDROCHLORIC ACID PRODUCTION FACILITY AT SOLVAY, RHEINBERG

The /a/c/t™-system is not only able to clean flue gases but also any other gases containing air pollutants.

The HCl-production facility consists of a combustor, which burns liquid chlorinated hydrocarbons. In a two stage wet scrubber with acid recirculation a purchasable hydrochloric acid is formed. The gas cleaning system consists of two-stage neutralization and an /a/c/t™-system in order to remove dioxins, furans, and other organic substances.

The /a/c/t™-system is a single bed adsorber with a height of 63 ft, a width of 17 ft, and a length of 8 ft. The total filter surface is approximately 360 sqft.

Table 5 shows a comparison of the legal emissions limits, the guaranteed values and the results of the emissions measurements

The /a/c/t™-system removes the air pollutants with a very high efficiency and helped to increase the acceptance of this facility in the surrounding region.

CONCLUSION

With the /a/c/t™-system STEAG and their licensees can provide a state-of-the-art flue gas cleaning technology with the highest removal efficiency available. This system can clean all kinds of gases containing air pollutants or odorous substances and can be operated safely and with minimum maintenance.

TABLE 1: Legal Emission Limits for Waste Incinerators

| Substance | Unit [1] | Germany[6] | Netherlands[7] | Austria[8] | European Union [3][6] | USA [4] |
|---|---|---|---|---|---|---|
| Total dust | mg/dscm | 10 | 5 | 15 | 10 | 12 |
| HCl | mg/dscm | 10 | 10 | 10 | 10 | 32 |
| HF | mg/dscm | 1 | 1 | 0.7 | 1 | - |
| $SO_2$ | mg/dscm | 50 | 40 | 50 | 50 | 67 |
| $NO_x$ | mg/dscm | 100 [2] | 70 | 100 | - | 288 |
| Hg | mg/dscm | 0.05 | 0.05 | 0.05 | 0.05 | 0.06 |
| Cd, Tl | mg/dscm | 0.05 | | | 0.05 | 0.01 |
| Dioxins, Furans | mg/dscm | 0.1 [5] | 0.1 [5] | 0.1 [5] | 0.1 [5] | 0.16 |

[1] related to 11 % oxygen, dry at 273 K and 1 atm [2] general value-depending on local standards

[3] guideline [4] municipal waste incinerators only [5] corrected by toxic equivalent factors

[6] one day mean value [7] one hour mean value [8] half hour mean value

TABLE 2: Reference list of the /a/c/t™--systems installed downstream of Waste Incineration plants in Europe.

| Type | Location | Owner/Operator | Commissioning | Flue gas Volume/dscm |
|---|---|---|---|---|
| Medical waste | Heidelberg, Germany | University | Oct 1991 | 2 x 6,500 |
| Hazardous waste | Rotterdam, Netherlands | AVR Chemie | Oct 1992 | 1 x 77,000 |
| Industrial flue gas | Freiberg, Germany | NE-Metall GmbH | Jun 1993 | 1 x 1,500 |
| Municipal waste | Rotterdam, Netherlands | AVR | Nov 1993 | 6 x 155,000 |
| Municipal waste | Essen, Germany | RWE-Energie AG | May 1995 | 4 x 168,000 |
| Municipal waste | Wels, Austria | WAV | Jul 1995 | 1 x 55,000 |
| Municipal waste | Mannheim Germany | RHE | Jun 1995 | 1 x 295,000 |
| Municipal waste | Rotterdam, Netherlands | AVR | Aug 1995 | 1 x 155,000 |
| Industr. flue gas | Rheinberg, Germany | Solvay GmbH | Apr 1995 | 1 x 15,380 |
| Crematory | Gießen, Germany | Stadt Giessen | Dec 1993 | 1 x 1,500 |
| Liq. hazard. waste | Southeast, USA | Commercial Fac. | N/A | 1 x 28,000 |

TABLE 3: Results of the Emission Measurements at AVR Rotterdam (unit 1 to 6, unit 7 under construction)

| Substance | Unit | RV[1)] 1989 | Unit 1 | Unit 2 | Unit 3 | Unit 4 | Unit 5 | Unit 6 |
|---|---|---|---|---|---|---|---|---|
| Dust | mg/Nm³ | 5 | < 1.0 | < 1.0 | < 1.0 | < 1.0 | < 1.0 | < 1.0 |
| HCl | mg/Nm³ | 10 | 0.9 | < 0.7 | 1.0 | 1.8 | < 0.5 | < 0.6 |
| HF | mg/Nm³ | 1 | < 0.4 | < 0.2 | < 0.4 | < 0.4 | < 0.1 | < 0.1 |
| $SO_x$ (as $SO_2$) | mg/Nm³ | 40 | 12 | < 5 | 23 | 11 | < 5 | < 5 |
| $SO_x$ (as $NO_2$) | mg/Nm³ | 70 | 36 | 32 | 36 | 41 | 23 | 26 |
| Cd | mg/Nm³ | 0.05 | < 0.003 | < 0.001 | < 0.003 | < 0.003 | < 0.001 | < 0.001 |
| Hg | mg/Nm³ | 0.05 | 0.03 | 0.003 | 0.002 | 0.004 | 0.001 | 0.001 |
| As, Co, Cu, Cr, Mn, Ni, Pb, Sb, Se, Sn, Te, V | mg/Nm³ | 1 | 0.030 | < 0.050 | 0.03 | 0.04 | < 0.050 | < 0.050 |
| PCDD/F (TEQ) | ng/Nm³ | 0.1 | 0.01 | 0.030 | 0.01 | 0.015 | 0.013 | 0.009 |

[1)] RV means: Dutch legal emission limits

All values refer to standard condition (273 K, 1013 hPa dry) and 11 % $O_2$

TABLE 4: Emission Measurements at AVR Rotterdam Hazardous Waste Incineration Plant

| | Unit | RV 1989 | Results of the accept. measurements Dec. 1992 |
|---|---|---|---|
| Dust | mg/Nm³ | 5 | < 0.5 |
| HCl | mg/Nm³ | 10 | 0.19 |
| HF | mg/Nm³ | 1 | 0.05 |
| $SO_2$ | mg/Nm³ | 40 | 6 |
| Cd | mg/Nm³ | 0.05 | < 0.0001 |
| Hg | mg/Nm³ | 0.05 | 0.0022 |
| Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V, Sn, Se, Te | mg/Nm³ | 1 | < 0.025 |
| PCDD/PCDF in TEQ | ng/Nm³ | 0.1 | 0.03 |

RV means: Dutch legal emission limits

TABLE 5: Comparison of the legal emissions limits, the guaranteed values and the results of the emissions measurements

| Chemical Compounds | Unit | Emission Standards as per Clean Air Act 17. BImSchV | Guaranteed Emissions | Measured Emissions Mean values over the sampling time |
|---|---|---|---|---|
| Total Dust | mg/dscm | 10 | 5 | < 1 |
| HCl | mg/dscm | 10 | 10 | 4 |
| HF | mg/dscm | 1 | 0.1 | not detected |
| $SO_2$ | mg/dscm | 50 | 5 | not detected |
| Hg | mg/dscm | 0.05 | 0.03 | not detected |
| Dioxins, Furans | ng/dscm TE | 0.1 | 0.05 | not yet measured |

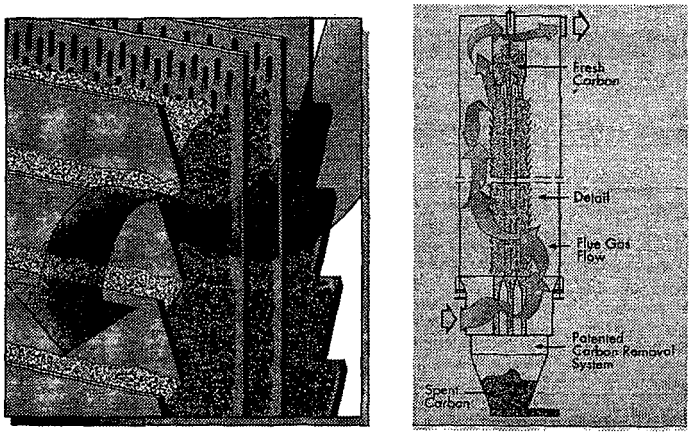


Figure 1: STEAG's /a/c/t™-process

# THE COMBINED SOX / NOX / AIR TOXICS REDUCTION PROCESS USING ACTIVATED COKE FOR FLUE GAS CLEANUP

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Keywords : Activated Coke(AC), DeSOx and DeNOx with chemically modified AC surface, Toxic reduction with AC

## INTRODUCTION

The dry desulfurization and denitrification process using activated coke(AC) as a dry type flue gas cleanup technology was originally researched and developed during the nineteen-sixties by Bergbau Forschung(BF) [*1], now called Deutsche Montan Technologies. Mitsui Mining company(MMC) concluded a licensing agreement with BF in 1982 to investigate, test and adapt the system to the facilities in Japan where the regulations are stricter towords SOx/NOx pollutants, as well as dust emissions from utility industries, oil refineries, and other industries. There are three commercial plants of this process installed to coal fired boiler, FCC units, and incinerator in Japan and two plants in Germany(the latter two plants were constructed by Uhde GmbH). Recently, the capability of AC process to adsorb and reduce toxic trace materials, such as Hg vapor and dioxines, is attractive for flue gas cleanup of waste incinerators or coal combustion boilers. General Electric Environmental Survices, Inc.(GEESI) signed a license agreement in 1992 with MMC. Under this agreement, GEESI will market, design, fabricate and install the AC process for flue gas cleaning applications in North America.

MMC also developed a technology to produce activated coke to be used in the DeSOx/DeNOx process, based on our own metallurgical coke manufacturing technology. The commecial plant with the capacity of 3,000tons per year to produce MMC's activated coke has been in operation. We have a plan to construct a larger plant of activated coke production in Japan preparing for the increase of demands for AC process in the near future.

In this paper,we would like to present some data of DeSOx, DeNOx and toxic removal with MMC's AC, which include basic data from laboratory tests, characteristic data of sampled AC from test plants, and performance data of commercial plants. Furthermore, we will put a focus on the relationship of the DeSOx and DeNOx activities of AC to the surface functionalities of chemically modified AC in both labo. tests and pilot tests.

## MMC's ACTEVATED COKE AND GE-MITSUI-BF PROCESS

Activated coke(AC) is a formed carbonaceous material designed for dry DeSOx/DeNOx and Toxic removal process of flue gas cleanup. For this purpose, we selected a suitable raw coal from bituminous coals and investigated an appropriate process for production [*2], which include a pretreatment of raw coal, blending of raw materials, briquetting, carbonization and activation, to give AC high DeSOx/DeNOx activities and high mechanical strength against abrasion and crush during circulation and handling in the flue gas cleanup process.

There are several differences in characteristics of MMC's AC compared to an activated carbon using criteria such as gas recovering or deoderizing processes. BET surface area of MMC's AC is 150-250m$^2$/g, which is less than one-third that of activated carbon. BET surface area of the carbon materials represents their micro-porous structure, which becomes larger during the manufacturing process where the chemical activation condition is severe. As the activation becomes more severe, the yield of the product decreases and the mechanical strength of the product falls. A decrease in yield results in increased product cost and a decrease in mechanical strength causes greater material loss during the flue gas cleanup process. As MMC's AC is processed with a temperate activation procedure, it is one-fourth to one-third the price and has a higher mechanical strength compared to activated carbon. MMC's AC also has advantages in its abilities to remove SOx and NOx as compared with activated carbon.

Figure 1 illustrates a schematic of the GE-Mitsui-BF DeSOx/DeNOx/Toxic removal process, which is designed for SOx/NOx containing flue gas treatment system consisting of twin AC beds and an AC regenerator. In this system, AC moves continuously from top to bottom through the AC beds. The regenerated AC with some part of fresh make-up AC enters in DeNOx zone( I ) at first, where NOx reduction occurs with the addition of $NH_3$. The discharged AC from I enters into DeSOx zone( II ), where the majority of the SOx and air toxics adsorption and the minor NOx reduction without $NH_3$ (we call now non-SCR DeNOx) occur. The SOx/air toxics-loaded AC discharged from II is sent to the regenerator by backet conveyers. In the case of NOx with low-SOx or SOx with low-NOx containing flu gas treatments, single AC bed system can be designed. Table 1 summarizes a designed system, efficiencies and applications of GE-Mitsui-BF process.

## DESULFURIZATION (DESOX) WITH ACTIVATED COKE

Figure 2 shows the $SO_2$ adsorption capacity of activated coke and a commercial activated carbon with fresh one and used one. With fresh one, the $SO_2$ adsorption capacity becomes higher as surface area of adsorbent increases. On the other hand, with used one, which has experienced four times of desulfurization–regeneration cycle of labo. test, $SO_2$ adsorption capacity of the used activated carbon drastically decreased to about one–third of the fresh one, while the used activated cokes, having lower surface area and still less micro–porous than activated carbon, are less influenced. There has been several observations [3, 4] of the similar phenomenon with activated carbons of those surface area ranging 300–900$m^2/g$, where a marked decrease in adsorbed $SO_2$ amount along with cycle has been explained due to the increase in the amount of acidic groups on the surface of activated carbons. It is supposed that there is an appropriate activation level where the $SO_2$ adsorption capacity is less influenced with the cycle of $SO_2$ adsorption–desorption. MMC's activated coke seems to be on a such level. It has been confirmed that MMC's activated coke keeps a stable deSOx performance during the process [5].
Table 2 shows the characteristics and the deSOx activities measured in labo. test with MMC's activated coke, fresh one and used ones, which were sampled from two test plants under operation. Used ones are characterized with an enlarged surface area, an increased O/C and N/C values, and an enhanced deSOx activity than fresh one. These changes in characteristics are derived from operation conditions, such as the molar ratio of adsorbed $NH_3$ –SOx species on AC and the types of reactions(oxidation–reduction) between $NH_3$ –SOx species and AC surface in regenerator. It is noticiable that the surface area and O/C value are higher in used I (the adsorbed $NH_3$/SOx molar ratio is approx. 0.2) and N/C value is higher in used II (the ratio is approx. 1.5). The increased deSOx activities( $\eta$ SOx %) of used AC to fresh one relate to both the surface area enlargement and the modified surface functionality. It is supposed that k(rate constant) especially correlates to N/C and $q_0$ (adsorption capacity) relatively correlates to surface area. $\eta$ SOx is the highest in used II , supporting that N/C is the most influencing factor to deSOx rate.
It has been reported that nitrogen–containing activated carbon [6] and activated carbon fiber [7] from PAN and brown coal char via sulfuric acid activation followed by ammonia treatment [8] show the remarkable high deSOx activities.

## DENITRIFICATION (DENOX) WITH ACTIVATED COKE

Figure 3 shows the profiles of two types DeNOx(SCR and non–SCR) reactions in labo. tests with the used II AC(Table 2), which exhibited a high non–SCR DeNOx activity. Non–SCR DeNOx proceeds without $NH_3$ in gas phase and an active N–species on AC surface seems to react with NOx, because non–SCR activity is deactivated along with reaction time. $NH_3$ treatment at 400–500 ℃ is effective to reactivate AC for the non–SCR reaction. There has been several observations of the effects of $NH_3$ treatment to the preoxidized activated carbon [9] and brown coal char [8] on the enhancement of their SCR DeNOx activities. Now, we would like to put attention upon the non–SCR DeNOx activity of AC and have interest in the effect of $NH_3$ treatment on the non–SCR DeNOx activity of AC, because the non–SCR DeNOx is useful as a no $NH_3$ leakage process for flue gas cleanup with AC. We can expect to remove approx. 10–20% of inlet NOx concentration with non–SCR DeNOx in the DeSOx zone, where no $NH_3$ is added in gas phase, under coexisting of high SOx concentration in the DeSOx/DeNOx proces(Figure 1).
The efficiency of non–SCR DeNOx becomes higher in proportion with lowering of inlet NOx concentration. Figure 4 shows approx. 60–70% high efficiencies of non–SCR DeNOx with 24ppm of inlet NOx concentration. Figure 4 also shows the increasing non–SCR DeNOx efficiency along with a cycle testing, where simultaneous deSOx/deNOx run, regeneration after the run and $NH_3$ treatment at 500 ℃ to the regenerated AC were cycled 10 times, showing the effect of $NH_3$ treatment. DeSOx efficiency is also increasing with this cycle test, supporting the effect of $NH_3$ treatment on the DeSOx activity of AC(former discussion). Figure 5 shows the increasing non–SCR DeNOx efficiency with increase of $NH_3$ treatment amount. Although we scarcely have informations to identify an active N–species on AC surface, it is probably thinkable that an active N–species being produced by $NH_3$ treatment contributes to the non–SCR DeNOx reaction.

## TOXIC REDUCTION WITH ACTIVATED COKE

The AC process can also remove trace toxic compounds such as mercury and dioxines that are present in waste incinerator flue gas. Several pilot and demonstration tests [10, 11] have been done to confirm the ability of the AC process to remove NOx and trace toxic compounds with AC from waste incinerator flue gas at low temperature, where the mercury removal efficiencies of approx. 80–90% at 150–180 ℃ and the dioxines removal efficiencies of approx. 90–98% at the same temperature range were observed.

## CONCLUSION

- The dry DeSOx/DeNOx/Toxic removal process with activated coke is applicable for various flue gas cleanup with high efficiencies(Table 1).
- Activated coke has an appropriate activation level where the $SO_2$ adsorption capacity is less influenced with the cycle of $SO_2$ adsorption–desorption. It has been confirmed that MMC's activated coke keeps a stable deSOx performance during flue gas cleanup process.
  It is supposing that N/C value of AC is influencing factor to the deSOx activity.
- Activated coke has non–SCR DeNOx activity, which proceeds without $NH_3$ in the gas phase. The non–SCR DeNOx is useful as a no $NH_3$ leakage process for flu gas cleanup.
  It is supposing that an active N–species being produced by $NH_3$ treatment at 400–500 ℃ contributes to non–SCR DeNOx reaction.
- Activated coke can also remove trace toxic compounds such as mercury and dioxines with high efficiencies from flue gases of waste incinerators and coal combustion boilers at low temperature.

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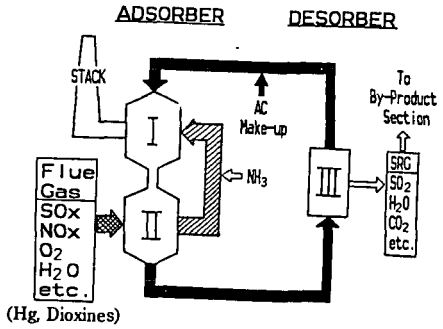



(Hg, Dioxines)

I: $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$

II: $SO_2 + 1/2O_2 + H_2O \rightarrow H_2SO_4/AC$

III: $H_2SO_4 + 1/2C \rightarrow SO_2 + H_2O + 1/2CO_2$

Figure 1 : The combined SOx/NOx/Air toxics reduction process using AC
( GE–Mitsui–BF Process / Schematic flow diagram with twin AC beds )

Table 1 : A designed system and efficiencies of GE−Mitsui−BF process applications

| Flue Gas | Designed system | Efficiencies | Applications |
|---|---|---|---|
| SOx and NOx | Twin AC beds | • $\eta$ SOx ≧ 98%<br>• $\eta$ NOx ≧ 80% | • Utility boilers<br>• RFCC Units<br>• Other industries |
| NOx with−low SOx | Single AC bed | • $\eta$ NOx ≧ 80%<br>• $\eta$ SOx ≧ 98% | • FBC boiler<br>• Waste incinerator (After pre−scrubber) |
| SOx with low−NOx | Single AC bed | • $\eta$ SOx ≧ 98%<br>• non−SCR DeNOx expected | • Combination with other DeNOx system |

All systems can remove trace toxic materials such as Hg vapour and dioxines with high efficiencies.

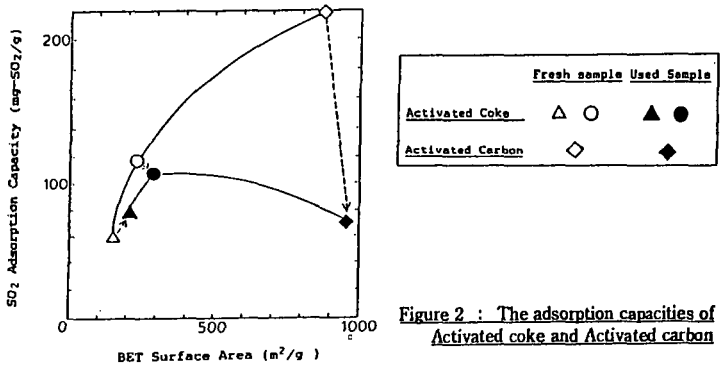


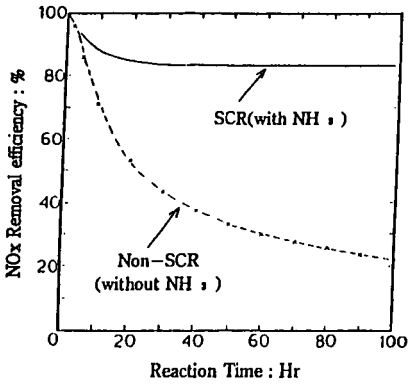

Figure 2 : The adsorption capacities of Activated coke and Activated carbon

- Used samples are those after the 4th cycle of deSOx (SO₂ 2000ppm, O₂ 5%, H₂O 10%) at 130 ℃ and regeneration under N₂ at 400 ℃ .
- SO₂ adsorption capacity was measured by contacting 10cc of AC sample with SO₂ containing gas flow(SO₂ 2%, O₂ 5%, H₂O 10%) at 100 ℃ for 3hours.

Table 2 : The characteristics and DeSOx activities of sampled AC from test plants

| AC sample | Surface area($m^2$/g) | | Elemental analysis | | DeSOx Activity [labo. test] | | |
|---|---|---|---|---|---|---|---|
| | S($CO_2$) | S($N_2$) | O/C | N/C | $\eta$ SOx(%) | k($10^4$) | $q_0$ ($10^2$) |
| Fresh | 150 | 150 | 0.019 | 0.012 | 64.7 | 3.87 | 0.87 |
| Used I | 300 | 500 | 0.073 | 0.034 | 91.3 | 4.62 | 2.15 |
| Used II | 230 | 270 | 0.046 | 0.040 | 98.3 | 5.82 | 1.78 |

- Used I and II were sampled at the operation time of approx. 4000hours from the outlet of regenerator of test plant I and II , respectively.
- Test plant I was a DeSOx/DeNOx plant with twin AC beds as illustrated in Figure 1. $NH_3$ was added after DeSOx zone( II ). The adsorbed $NH_3$/SOx molar ratio was approx. 0.2 [SOx rich] with AC of the inlet of regenerator.
- Test plant II was a DeNOx plant with single AC bed, which is almost equivalent to the DeNOx zone( I ) in Figure 1. The adsorbed $NH_3$/SOx molar ratio was approx. 1.5 [$NH_3$ rich] with AC of the inlet of regenerator.
- DeSOx activity was measured by contacting 4.3 liters of AC sample with 28.7 liters of $SO_2$ containing gas flow ($SO_2$ 2000ppm, $O_2$ 5%, $H_2O$ 10%) at 130 ℃.
  $\eta$ SOx is the DeSOx efficiency(average of integration during 25 hours reaction)
  k is the deSOx reaction rate constant.
  $q_0$ is the amount of adsorbed SO2 at equilibrium condition.




[Test Conditions]
SV 400h $^{-1}$, Temp.140 ℃
NO 200ppm
$NH_3$ 200ppm(SCR) or none(non−SCR)
$O_2$ 5%, $H_2O$ 7%, $N_2$ Balance
Used II AC(Table 2) was tested.

Figure 3 : The DeNOx profile of SCR and Non−SCR reactions on Activated coke

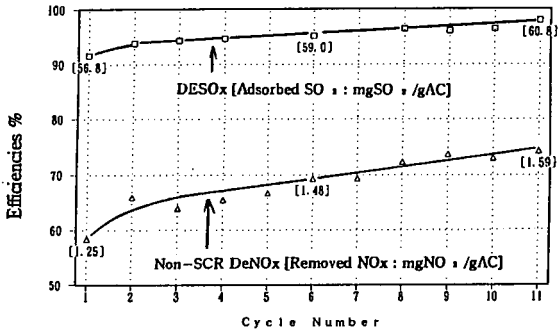



Figure 4 : The effect of $NH_3$ treatment on Non−SCR DeNOx and DeSOx activities of AC

- DeSOx/DeNOx Run Conditions : SV 400h $^{-1}$, Temp.140 ℃, Time 70Hr
  NO 24ppm, $SO_2$ 500ppm, $NH_3$ *) 250ppm, $O_2$ 5%, $H_2O$ 7%, $N_2$ Balance
  *)$NH_3$ will react with $SO_2$ almost selectively. SCR DeNOx can't proceed.
- Efficiencies denotes an average of integration during 70 hours reaction.
- $NH_3$ leakage was not detected during the DeSOx/DeNOx test run.
- $NH_3$ treatment (1.48ccNH ₃ /ccAC) was done at 500 ℃ to the regenerated AC
- Testing AC is a used AC sampled from another test plant differing from I , II (Table 2).

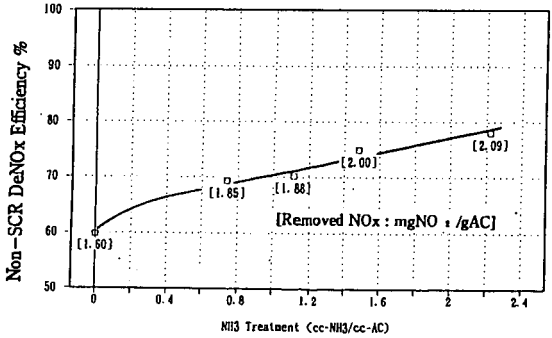



Figure 5 : Increasing Non−SCR DeNOx activity with increase of $NH_3$ treatment amount

- Test conditions is the same as Figure 4.
- Used II AC(Table 2) was tested.

# The Use Of Activated Char For Flue Gas Polishing In Municipal And Hazardous Waste Combustors

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Keywords: Activated Char Reactor (ACR), Flue Gas Polishing, Municipal and Hazardous Waste Combustors

## INTRODUCTION

During the late 1980's and the early 1990's legislation on emissions from waste combustors were tightened drastically [1, 2]. Also emission limits on „new" pollutants like dioxins and furans were introduced. Since the flue gas cleaning equipment commonly used before was not designed to meet these emission limits, new technologies had to be developed. Most of these new technologies rely on the use of activated carbon or char for the adsorption of the pollutants [3].

Due to the fact that the amount of activated char used is directly proportional to the mass flow rate of pollutants entering the adsorber, the bulk part of the pollutants has been removed in the preceeding gas cleaning stages. Thus the activated char adsorption reactor is employed as a flue gas polishing stage at the end of the APC-train.

In 1984 Steinmüller and its 100 % subsidiary, Hugo Petersen, began to develop flue gas filters for large volume flow rates based on the use of activated carbon. The original goal of development was the removal of residual $SO_2$ left after the FGD-scrubber, in order to eliminate the problem of ammonia sulfate formation in low-dust SCR-DeNO$_x$-systems. Shortly after that the catalytic capability of activated carbon to reduce $NO_x$ in the presence of $NH_3$ was recognized; as well as the suitability of this technology for the flue gas polishing of waste incinerators. In the latter case the removal capability of activated char for a wide range of different pollutants, mainly organics, like PCDD/F's, PCB's, PAH's, etc., highly toxic heavy metals such as Hg, Cd, Pb, etc. and acid gases was of primary interest.

## ADSORBER DESIGN

The Steinmüller / Hugo Petersen ACR-technology follows the crossflow principle. Where as the char migrates through the ACR-adsorber vertically from top to bottom, the flue gas flows through the activated char bed horizontally. Figure 1 shows the concept of the adsorber providing a vertical cross section of an activated char bed. Each bed consists of 3 individual layers separated by a perforated shroud. Each layer can be extracted independently, according to its pressure drop, saturation or other guiding parameters. As described in previous papers [4, 5, 6] especially designed cellular discharge cylinders at the bottom of each bed allow the extraction of a precisely defined amount of activated char from each layer individually. Besides a minimization of char consumption, this multilayer design allows for the adaptation of the discharge program to the well known selective adsorption characteristics of the various pollutants [6, 7]. Figure 2 shows how the multilayer design is matched to the characteristic concentrations of adsorbed pollutants within the char bed. The fresh char is conveyed to, and evenly distributed within, the bed by screw conveyors on the top of the bed. The flue gas inlet as well as the outlet of the bed perform important tasks for the correct operation of the filters. The gas outlet insures the retention of even small char particles within the bed. The compounds with a high molecular weight are adsorbed quickly within the first few inches of the activated char, thus pushing the lower molecular weight compounds towards the end of the bed. Due to this reason HCl leaves the bed first, indicating an approaching break-through.

The size of a bed is limited due to specific restrictions, such as the height of the bed, the lengths of the screw conveyors and the discharge cylinders. In order to allow the treatment of large volume flow rates one adsorber unit can be expanded to contain 2, 4, 6 or 8 beds. In this case each bed acts as an individual module within the ACR-unit. Figure 3 shows such an arrangement. ACR's built by Steinmüller / Hugo Petersen treating volume flow rates between 5.000 and 250.000 $m^3/h$ and containing up to 8 modules are in operation in power plants as well as in municipal and hazardous waste combustors.

## ACR PERFORMANCE

Extensive measurements of the performance of the ACR-technology were obtained at various full scale installations. Among those were municipal as well as hazardous waste combustors in Holland as well as in Germany.

Table I presents a summary of the emission data collected at these facilities. It has to be pointed out that the extremely low emission values reported were measured over a longer period of time, thus accounting for the fluctuations in the inlet pollutant concentration.

The removal efficiency for acid gases, heavy metals and high molecular weight organics was determined to range in the 99.9 % to + 99.99 % region. Especially for acid gases the buffering capacity of the ACR-plant is remarkable. The outlet value of below 1 $mg/m^3$ @ STP for $SO_2$, for example, remained unaffected even by extremely high peak inlet concentrations of up to 700 $mg/m^3$ @ STP.

Due to the very low outlet concentrations of the various pollutants, significant difficulties were encountered concerning sampling and analysis. Very much care has to be taken regarding the stack sampling and analytical procedures in the lab in order to ensure a reasonable accuracy and precision of the results.

## ACR-RETROFITS TO EXISTING MWC'S AND HWC'S

During the early 1980's a significant number of MWC's and few HWC's were built using an APC-train comprised of an ESP, a spray dryer and a baghouse. Representing the state-of-the-art technology 10 to 15 years ago, these APC-trains are unable to meet the stringent emission limits introduced in the early 1990's. Therefore those plants had to be retrofitted. A spray dryer / baghouse combination is capable of removing 90 to 95 % of the pollutants. However, it usually fails to meet the required emission limits by a factor of 1.5 to 2 for the acid gases, and by a factor of 2 to 4 for the heavy metals and the organics. Even though these factors seem high, they represent only a rather small mass flow rate of pollutants. Combined with the fact that the flue gas temperature at the outlet of the spray dryer / baghouse system is commonly adjusted to around 140°C, this makes an excellent basis for a retrofit using the ACR-technology. Figure 4 shows a process flow scheme of such a retrofit at a MWC. The temperature of 140°C is ideally suited for the ACR by being low enough for enhanced adsorption and high enough to avoid any condensation of moisture and/or acids. In most cases a Low Temperature SCR (LTSCR) $DeNO_x$ plant is added at the end of the train. Due to the virtual absence of any pollutants after the ACR, the SCR operational temperature can be reduced to as low as 150 -170°C. This makes the use of SCR a very economical alternative to SNCR, avoiding $NH_3$-contamination of the fly ash and the spray dryer/baghouse residue. $NH_3$-contents typically found after SNCR increase the disposal cost of these residues significantly.

Most HWC's built in Europe were equipped with wet scrubbers, even before 1990. The most common APC-train used on HWC's was an ESP followed by a one or two stage HCl-scrubber operated at a pH below 2 and a $SO_2$-scrubber operated of a pH of around 5 to 6. These systems are better suited to handle the significantly higher pollutant concentrations of HWC's at the inlet of the APC-train. Besides the possibility of retrofitting these facilities with an ACR / LTSCR combination as described above, another option is to add an ACR / ACCR combination as presented in Figure 5. This 125 tpd HWC was retrofitted with an ACR and the ACCR-DeNOx system [8]. Both the ACR and ACCR are combined in one reactor with the $NH_3$-injection system upstream of the ACR. In the ACR lignite based hearth oven char (HOC) is used, whereas the ACCR utilizes the catalytic capabilities of hard coal based form activated carbon (FAC). The plant has been in operation since 1991 and $NO_x$ emission values of less than 100 $mg/m^3$ @ STP, 11 % $O_2$ have been obtained continuously. The advantage of ACCR is its low operating temperature of between 120°C and 140°C. Its disadvantage is that high $NO_x$-removal efficiencies (> 85 %) cannot be realized due to the catalytic limitations of the activated carbon [8].

## ACR FOR NEW MWC'S and HWC'S

In new installations, the ACR forms an integrated part of the APC-train. As presented in Figure 6 such a modern five-stage gas cleaning system is designed to achieve the lowest possible emission limits. Thus a baghouse is employed to insure the best possible removal of particulate matter.

It is followed by a multi-stage wet scrubbing system designed to recover hydrochloric acid from the removed HCl and wall board quality gypsum from neutralized $SO_2$ [9]. The heat losses through evaporation in the scrubbers are minimized by employing a cross-flow heat exchanger. It cools the flue gas before entering the first scrubber and then reheats the flue gas after leaving the second scrubber. Thus the flue gas is prepared for the final polishing by the ACR before it enters the stack via a LTSCR-$DeNO_x$ plant. To adjust for the appropriate LTSCR-temperature the compression heat liberated in the fan is utilized. The remaining heating is done by a low pressure steam heater. The specific advantages of LTSCR as described elsewhere [10] are ideally enhanced in combination with an ACR.

## CONCLUSION

Today, little over 5 years after the introduction of new and stringent emission regulations for MWC's and HWC's, ACR ist a well proven, accepted technology. Table II provides a list of installations of new and retrofitted MWC's and HWC's in Holland, Germany and Austria employing ACR. In these countries the market share of the ACR-technology with respect to other technologies ist about 35 % in the retrofit market and about 65 % in the market for new facilities. The ACR-technology developed by Steinmüller / Hugo Petersen was not only the first of its kind but still leads the way. As can be seen in Table III, Steinmüller / Hugo Petersen holds about 50 % of the ACR-market for power plants and municipal and hazardous waste combustors. The ACR-technology integrated in a modern state-of-the-art multi-stage APC-train represents the leading edge of pollution control for HWC's and MWC's. The fast increasing interest in this technology, especially in environmentally aware countries like Japan, South Korea, Taiwan and the US-leads to the expectation that ACR will soon be considered the best available control technology not only in Europe but all over the world as well.

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***Table I*** Emission Data Obtained at Various Full-Scale MWC's and HWC's

| | | Data- | Points | | | |
|---|---|---|---|---|---|---|
| ***Group*** | ***Compound*** | ***1*** | ***2*** | ***3*** | ***4*** | ***Unit*** |
| Acid Gases | $SO_2$ | 0.11 | 0.20 | 0.47 | 0.14 | mg/m³ |
| | $SO_3$ | 0.04 | 0.07 | 0.03 | 0.06 | mg/m³ |
| | HCl | 0.84 | 0.45 | 0.63 | 0.79 | mg/m³ |
| | HF | 0.03 | 0.02 | 0.03 | 0.02 | mg/m³ |
| | HBr | 0.07 | 0.15 | 0.13 | 0.07 | mg/m³ |
| | HJ | 0.10 | 0.19 | 0.22 | 0.10 | mg/m³ |
| | | | | | | |
| Heavy Metals | Sb | < 3 | < 6 | < 4 | < 4 | µg/m³ |
| | As | < 5 | < 7 | < 8 | < 7 | µg/m³ |
| | Cd | < 0.5 | < 0.9 | < 0.8 | < 0.7 | µg/m³ |
| | Co | < 3 | < 4 | < 4 | < 4 | µg/m³ |
| | Cr | < 3 | < 4 | < 4 | < 4 | µg/m³ |
| | Cu | < 4 | < 5 | < 5 | < 15 | µg/m³ |
| | Pb | < 5 | < 8 | < 8 | < 7 | µg/m³ |
| | Mu | < 3 | < 8 | < 5 | < 4 | µg/m³ |
| | Hg | < 0.9 | < 1.1 | < 0.7 | < 0.9 | µg/m³ |
| | Ni | < 3 | < 4 | < 4 | < 4 | µg/m³ |
| | Te | < 0.3 | < 0.4 | < 0.4 | < 0.4 | µg/m³ |
| | Sn | < 3 | < 8 | < 4 | < 8 | µg/m³ |
| | V | < 3 | < 4 | < 4 | < 4 | µg/m³ |
| | | | | | | |
| Other Elements | Al | 257 | 97 | 278 | 93 | µg/m³ |
| | Ba | 6 | 11 | 15 | 10 | µg/m³ |
| | Be | < 0,5 | < 0.7 | < 0.8 | < 0.7 | µg/m³ |
| | B | 52 | 27 | 46 | 48 | µg/m³ |
| | Fe | 22 | 41 | 120 | 52 | µg/m³ |
| | Mg | 16 | 29 | 36 | 29 | µg/m³ |
| | K | 52 | 104 | 99 | 60 | µg/m³ |
| | Se | < 5 | < 7 | < 7 | < 8 | µg/m³ |
| | Si | 78 | 45 | 34 | 80 | µg/m³ |
| | Ag | < 3 | < 4 | < 4 | < 4 | µg/m³ |
| | Na | 279 | 665 | 405 | 321 | µg/m³ |
| | Te | < 9 | < 15 | < 14 | < 13 | µg/m³ |
| | Zn | 10 | 23 | 19 | 26 | µg/m³ |
| | | | | | | |
| Organics | PCDD | | | 0.0238 | 0.0261 | ng/m3 |
| | PCDF | | | 0.0222 | 0.0223 | ng/m3 |
| | TEQ (NATO CCMS incl ½ the detection limits) | | | 0.0009 | 0.0014 | ng/m3 |
| | PBrDD | | | < 0.760 | < 0.815 | ng/m3 |
| | PBrDF | | | < 0.760 | < 0.815 | ng/m3 |
| | PAH (E/PA/ 610) | | | 6.282 | 4.146 | ng/m3 |
| | $PCB_4$ (Di-Hexa) | | | 3.2 | 1.8 | ng/m3 |
| | $PCP_h$ | | | 12.3 | 9.2 | ng/m3 |
| | PCB (Ballschmiter) | | | 10.4 | 10.4 | ng/m3 |
| | Benzene | | | < 95 | < 90 | µg/m³ |
| | Toluene | | | < 95 | < 90 | µg/m³ |
| | Ethylbenezne | | | < 95 | < 90 | µg/m³ |
| | p- and m-Xylene | | | < 95 | < 90 | µg/m³ |
| | O-Xylene | | | < 95 | < 90 | µg/m³ |
| | Dichloromethane | | | < 160 | < 150 | µg/m³ |
| | 1-1, Dichloroethane | | | < 265 | < 250 | µg/m³ |
| | Trichloromethane | | | 2 | 2 | µg/m³ |
| | 1-1-1, Trichchloromethane | | | < 1.1 | < 1 | µg/m³ |
| | Tetrachloromethane | | | < 1.1 | < 1 | µg/m³ |
| | Trichloroethene | | | < 1.1 | < 1 | µg/m³ |
| | Tetrachloroethene | | | < 1.1 | < 1 | µg/m³ |
| | 1-1-1-2, Tetrachloroethane | | | < 1.1 | < 1 | µg/m³ |
| | 1-1-2-2, Tetrachloroethane | | | < 11 | < 1 | µg/m³ |
| | trans-1-2, Dichloroethene | | | < 160 | < 150 | µg/m³ |
| | cis-1-1, Dichloroethene | | | < 160 | < 250 | µg/m³ |
| | Dichlorobromomenthane | | | < 1.1 | < 1 | µg/m³ |
| | Dibromochloromethane | | | < 1.1 | < 1 | µg/m³ |

< means that the actual value is below the given number, which represents the dection limit

***Table II*** List of Installations equipped with activated char adsorbers in Austria, Germany and the Netherlands

| *Name of Plant* | *Country* | *Operator / Consultants* | *Employed APC-train* | *Volume Flow Rate* | *Type of waste* | *ACR supplier / Lizensor* | *Start-up* |
|---|---|---|---|---|---|---|---|
| AVR RO-0 - RO 6 | NL | AVR / Tebodin | ESP-HCl-$SO_2$-ACR-LTSCR | 7 x 155.000 | MW | AE / | 1993 |
| AVR RO-0 | NL | | ESP-HCl-$SO_2$-ACR-LTSCR | 1 x 155.000 | MW | STEAG | 1995 |
| AVR DTO-9 | NL | AVR / Tebodin | Q-ESP-HCl-$SO_2$-ACR | 1 x 77.000 | HW | AE / STEAG | 1992 |
| AVR DTO-8 | NL | AVR / AVR | ESP-HCl-ACR | 1 x 77.000 | HW | LCS / HP | 1994 |
| RZR Herten IM 1 | D | STEAG / STEAG | ESP-HCl-$SO_2$-ACR-ACCR | 1 x 70.000 | HW | LCS / HP | 1991 |
| RZR Herten IM 2 | D | STEAG / STEAG | ESP-HCl-$SO_2$-ACR-LTSCR | 1 x 70.000 | HW | LCS / HP | 1995 |
| RZR Herten SM 1/2 | D | STEAG / STEAG | SD-ESP-HCl-$SO_2$-ACR-LTSCR | 2 x 120.000 | MW | LUT / WKV | 1994 |
| RZR Herten SM 3/4 | D | STEAG / STEAG | FF-HCl-$SO_2$-ACR-LTSCR | 2 x 157.000 | MW | LCS / HP | 1999 |
| MVA Düsseldorf-Flingern | D | SWD / SWD | ESP-SD-ESP-ACR-LTSCR | 4 x 160.000 | MW | LUT / WKV | 1993 |
| | D | SWD / SWD | ESP-SD-ESP-ACR-LTSCR | 1 x 180.000 | MW | LUT / WKV | 1997 |
| MHKW Hameln | D | EWAG / VGU | SNCR-DIP-FF-ACR-LTSCR | 3 x 60.000 | MW | LUT / WKV | 1993 |
| EBS Wien | A | EBS / Fichtner | ESP-HCl-$SO_2$-ACR | 2 x 68.500 | HW | INT / WKV | 1992 |
| | | EBS / Fichtner | ESP-HCl-$SO_2$-ACR | 2 x 126.500 | SS | INT / WKV | 1992 |
| | | EBS / Fichtner | ESP-HCl-$SO_2$-ACR | 1 x 74.000 | HW | INT / WKV | 1992 |
| | | EBS / Fichtner | ESP-HCl-$SO_2$-ACR | 1 x 15.000 | CW | INT / WKV | 1990 |
| Hoechst-Frankfurt | D | Hoechst / Hoechst | ESP-HCl-$SO_2$-ACR | 1 x 75.000 | HW | LUT / WKV | 1994 |
| AVG Hamburg | D | AVG / VKR | ESP-HCl-$SO_2$-ACR-LTSCR | 2 x 78.000 | HW | LUT / WKV | 1996 |
| MVA II Stellinger-Moor | D | Hamburg / GRP | ESP-HCl-$SO_2$-ACR-LTSCR | 2 x 131.000 | MW | LUT / WWK | 1995 |
| AWG Wuppertal | D | AWG / AWG | ESP-HCl-$SO_2$-ACR-LTSCR | 3 x 135.000 | MW | LTU / WKV | 1995 |
| MHKW Essen-Karnap | D | RWE / RWE | ESP-HCl-ACR-LTSCR | 4 x 168.000 | MW | AE / STEAG | 1995 |
| MVA Wels | A | WAV / GRP | ESP-HCl-$SO_2$-ACR-LTSCR | 1 x 62.000 | MW | AE / STEAG | 1995 |
| KVA Uni Heidelberg | D | Hospital / ECH | ESP-HCl-$SO_2$-ACR-LTSCR | 2 x 65.000 | CW | AE / STEAG | 1991 |
| AVI ROTEB | NL | ROTEB / Tebodin | HCl-$SO_2$-ACR-LTSCR | 4 x 75.000 | MW | LCS / HP | 1993 |
| MVA Kassel | D | Stadtreiniger / GRP | ESP-SD-FF-ACR-LTSCR | 2 x 70.000 | MW | LCS / HP | 1996 |
| MVA Stapelfeld 1+2 | D | MVA Stapelfeld | ESP-HCl-$SO_2$-ACR-LTSCR | 2 x 120.000 | MW | LCS / HP | 1996 |
| MVA Stapelfeld 3+4 | D | GmbH / MVS | FF-HCl-$SO_2$-ACR-LTSCR | 2 157.000 | MW | LCS / HP | |
| MWA Weissenhorn | D | County / AEW | DIP-FF-$SO_2$-ACR-LTSCR | 2 x 51.000 | MW | LCS / HP | 1996 |
| AEZ Kreis Wesel | D | STEAG / STEAG | ESP-SD-ESP-HCl-$SO_2$-SCR-Oc-ACR | 2 x 120.000 | MW | LCS / HP | 1997 |
| RVA Böhlen | D | BAS / STEAG | ESP-SD-FF-HCl-$SO_2$-ACR-LTSCR | 1 x 40.000 | HW | LCS / HP | 1997 |
| MVA Köln | D | AVG / ITG | SD-FF-HCl-$SO_2$-ACR-Oc-SCR | 4 x 95.000 | MW | LCS / HP | 1998 |
| RMHKW Böblingen | D | ABB / GRP | FF-HCl-$SO_2$-ACR-LTSCR | 2 x 62.000 | MW | LCS / HP | 1999 |
| TAD Dortmund | | ABB / GRP | ESP-Q-HCl-$SO_2$-ACR-LTSCR | 2 x 63.000 | MW | LCS / HP | 2003 |

| | | | |
|---|---|---|---|
| ESP | = electrostatic precipitator | FF | = fabric filter |
| SD | = spray dryer | HCl | = HCl-scrubber |
| $SO_2$ | = $SO_2$-scrubber | DIP | = direct injection process |
| ACR | = activated char reactor | ACCR | = activated carbon catalytic reduction |
| SNCR | = selective non catalytic reduction | SCR | = selective catalytic reduction |
| LTSCR | = low temperature selective catalytic reduction | SCR-Oc | = SCR + oxidation catalyst |
| MW | = municipal waste | HW | = hazardous waste |
| SS | = sewage sludge | CW | = clinical waste |
| AE / STEAG | = Austrian Energy & Environment / STEAG AG | LUT / WKV | = Lentjes Umwelttechnik / Grochowski |
| INT / WKV | = Integral Engineering / Grochowski | LCS / HP | = L. & C. Steinmüller GmbH / Hugo Petersen |

***Table III*** Market Share of Steinmüller / HP of ACR for Power Plants and Waste Combustors in January 1996

Total Number of Plants (larger than 5.000 $m^3/h$) : 84
delivered by

| | |
|---|---|
| LCS/HP | 50.0 % |
| LUT/INT | 22.6 % |
| AE/STEAG | 21.0 % |
| Uhde* | 3.6% |

Total Volume Flow Rate treated : 11.045.000 $m^3/h$ net @ STP in ACR's by

| | |
|---|---|
| LCS/HP | 47.2 % |
| LUT/INT | 22.6 % |
| AE/STEAG | 21.0 % |
| Uhde* | 9.2 % |

| | |
|---|---|
| LCS/HP | = Steinmüller / Hugo Petersen |
| LUT/INT | = Lentjes Umwelttechnik / Integral Engineering |
| AE/STEAG | = Austrian Energy & Environment / STEAG |
| Uhde | = Uhde Engineering GmbH |

- Uhde gave up the ACR product line in 1990 after delivering only 3 ACR units for power plants

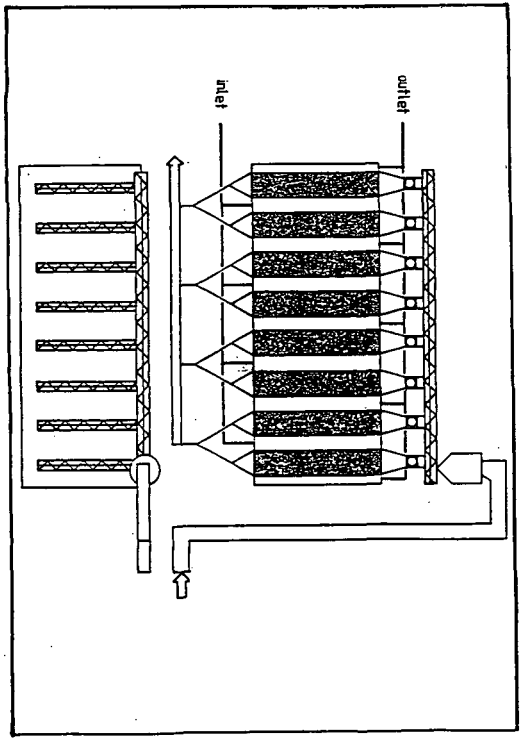


Figure 3 Moduler Arrangement Within the ACR Adsorber

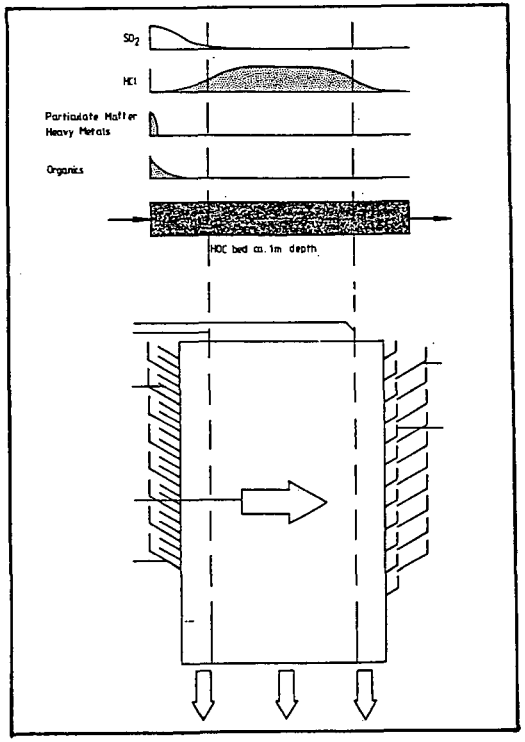


Figure 2 Adsorption Characteristics Adapted by the Adsorber Design

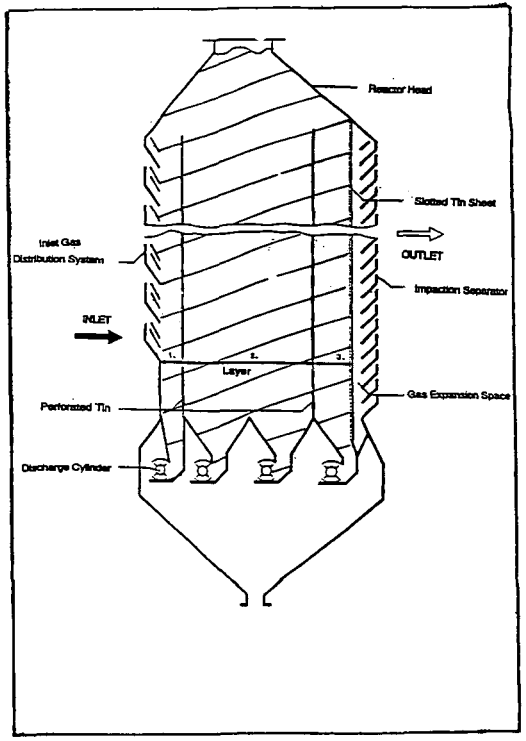


Figure 1 ACR Adsorber Concept

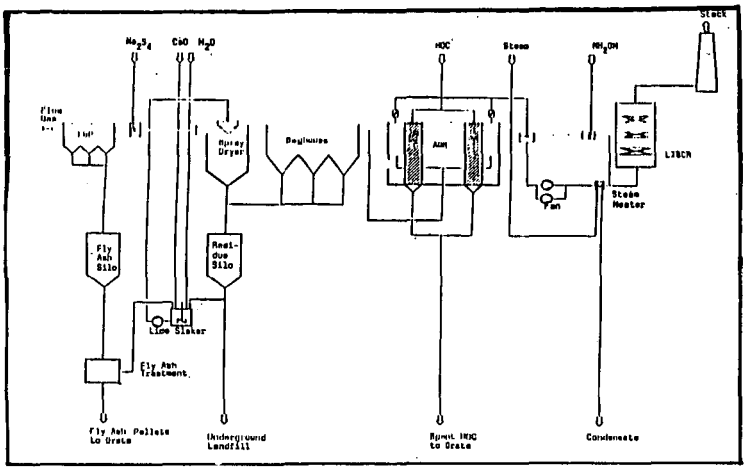


Figure 4 17. BImSchV Retrofit of an Existing MWC

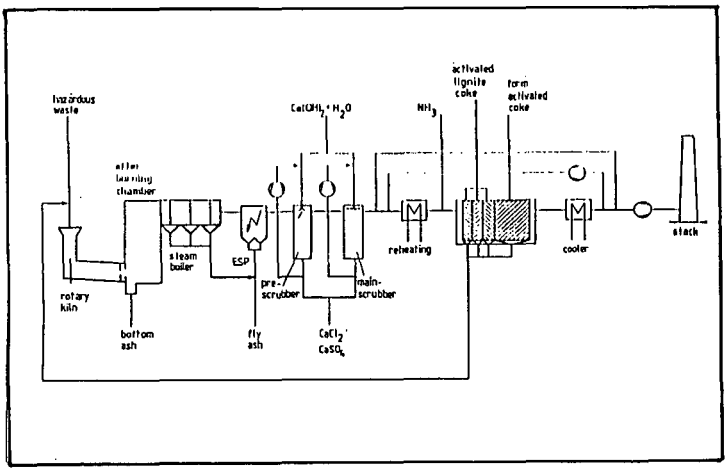


Figure 5 17. BImSchV Retrofit of an Existing HWC

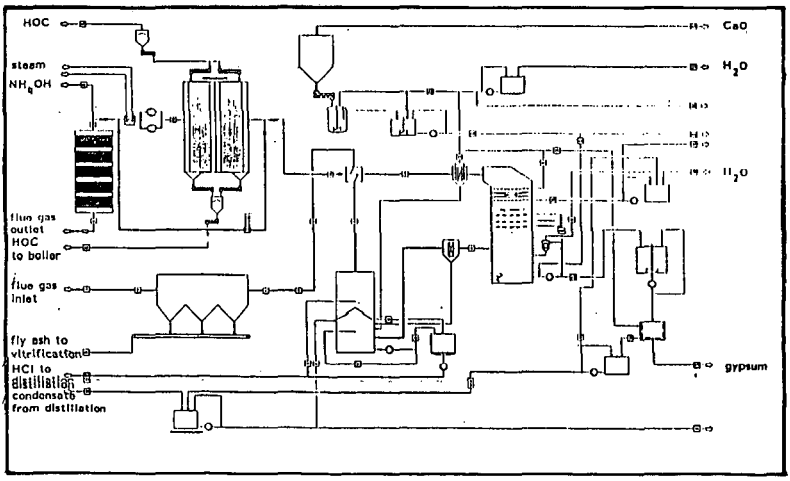


Figure 6 Modern 5-stage APC-Train for MWC's and HWC's

# THE APPLICATION OF ACTIVATED CARBON ENHANCED LIME FOR CONTROLLING ACID GASES, MERCURY, AND DIOXINS FROM MWCs

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Key Words: Activated Carbon, Dioxins, Mercury

## INTRODUCTION

Environmental control agencies have sought to reduce Municipal Waste Combustor (MWC) emission rates by the implementation of new regulations. Examples of these regulations are Germany's 17th Federal Regulation on Emission Protection; the Clean Air Act Amendments of 1990; EPA's New Source Performance Standards (NSPS) and Emission Guidelines; and recent regulatory actions in Minnesota, New Jersey, and Florida to adopt Hg standards for MWCs.

Sorbalit® is an activated carbon enhanced lime process that reduces MWC emissions and has been successfully demonstrated in Europe and the U.S. The process consists of two components: 1) a specially developed agent characterized by a high adsorption material capable of adsorbing toxic elements and acid gases, and 2) highly efficient air pollution control systems used by MWCs and various other types of combustion sources, which provide through agitation, a vortexing of the adsorbing agent mixture in a collection device, usually a fabric filter or ESP.

This paper presents the theoretical design of the Sorbalit technology. Actual field test results illustrate applications that reduce the concerns related to mercury and dioxin emissions based on practical experience. The adsorbing agent is described in detail and results obtained in various types of air pollution control systems which are applicable to the U.S. are presented.

## THE SORBALIT SYSTEM

Sorbalit is a patented system for controlling emissions of acid gases, mercury, and organics in a single application. The sorbent component of the technology is produced by mixing lime, either calcium hydroxide or calcium oxide, with surface-activated substances such as activated carbon or lignite coke and sulfur-based components in a proprietary process. Sorbalit can be produced with carbon contents ranging from 4% to 65% depending on the operational requirements of each project.

The Sorbalit process produces a homogeneous formulation containing calcium, carbon, and sulfur compounds that will not dissociate (demix) when used, either in a slurry or dry form. It is particularly important to avoid flotation or separation of the carbon and sulfur substances that have been added to the lime. To maintain product quality and effective levels of air pollution control, the components must stay as a uniform mix from the manufacturing process through transportation and use in the air pollution control system.

### Theory of Lime Adsorption

Lime is the largest component of Sorbalit and has the primary role of adsorption of the acid gases present in the flue gas such as $SO_2$, HCl, and HF. Calcium oxide (CaO) is called "pebble lime" or "quicklime". Hydrated lime [$Ca(OH)_2$] is made from CaO by adding 32% by weight of water in a hydrator. CaO is not very reactive with acid gases for scrubbing at the temperatures and conditions that exist in MWC facilities and has to be converted into the hydrate form to be reactive in scrubbing systems. CaO converts to $Ca(OH)_2$ in the slaking process in which four parts of water are added to one part CaO to form $Ca(OH)_2$ in a slurry that has about 25% solids. This conversion requires two phases that takes place in a slaker. The first phase converts the CaO into $Ca(OH)_2$. The second phase is to convert the hydrate by mixing 3.96 lbs of free water with one part hydrate that results in a 25% solids slurry.

### Theory of Carbon Adsorption

The adsorption of mercury and organics such as dioxin into activated carbon and coke is controlled by the properties of both the carbon and the adsorbate, and by the conditions under which they are contacted. This phenomenon is generally believed to result from the diffusion of vapor molecules into the surface of the carbon. These molecules are retained at the surface in the liquid state because of intermolecular or Van der Waals forces.

As the temperature falls, or as the partial pressure of the vapor above the carbon rises, the average time that a molecule resides on the surface increases. So does the fraction of the available surface covered by the adsorbate. However, the carbon surface is not uniform and consists of sites whose

activities vary. More active sites will become occupied first and, as the activity of the remaining available sites decreases, the adsorption energy will change.

The physical structure of activated carbon and coke is not known in detail, but it is believed to contain randomly distributed pores in the carbon, between which lies a complex network of irregular interconnected passages. Pores range in diameter down to a few angstroms, and provide a internal surface area from 300 to 1,000 $m^2$/gram of carbon. The volume of pores at each diameter is an important variable that directly affects carbon performance. Diagrams illustrating the structure of carbon particles and the adsorption of dioxin and mercury are presented in Figures 1 and 2.

Since adsorption takes place at the carbon-gas interface, the surface area of the carbon is one of the most important factors to consider. The second factor is the pore radius distribution. Laboratory bench scale tests have shown that both increasing the surface area and the addition of sulfur compounds result in higher adsorption rates of elemental mercury ($Hg^o$). Most of the laboratory work on carbon adsorption has been done on $Hg^o$, not with the Hg compounds we normally see in MWC emissions and without humidification.

Field tests at MWCs injected with carbon products with a wide range of surface areas have shown that there is not a significant improvement in Hg (total) capture based on the increased carbon surface area. It is important that laboratory programs be developed that simulate field conditions to consider the effects of the surface area of various products. Since high surface area products are more expensive, their performance advantages and cost trade-offs have to be demonstrated.

However, the surface area must be available in the proper range of pore sizes. If too much of the area is available in pores smaller than 5 Å, many molecules will be unable to penetrate the pores and that area of the carbon will essentially be unavailable for adsorption. For most pollution-control applications, the surface areas of pores whose diameters range between 5 and 50 Å yield good efficiency rates because the relative pressure of the vapor is usually too low for the larger pores to become filled. At high relative pressures, however, the total pore volume becomes important because the macropores also become active.

The adsorption of benzene, for example, has been shown to be affected by pore size distribution. At high benzene concentrations, carbons in which large pores predominate have higher capacities than those in which medium or small pores predominate. But at low concentrations, the large-pore carbon has a lower capacity.

The size of the $Hg^o$ molecule is approximately 4.5 Å and the dioxin molecule is 10 Å x 3 Å. Both molecules are adsorbed in different parts of the carbon particle. In theory, dioxins are collected in the macropores while the mercury is collected in the micropores. Dioxin, being larger, blocks the passages, preventing mercury from entering the micropores. To increase the mercury capture rate, the amount of carbon used must be significantly increased, the surface area of the carbon must be increased, or sulfur added.

The carbon/mercury balance has been established through laboratory experiments where they found that under ideal conditions, three grams of carbon will adsorb one gram of mercury. However, in operating facilities, considerably more carbon is required to reduce Hg emissions from 600 $\mu g/Nm^3$ to 70 $\mu g/Nm^3$; approximately 300 grams of carbon per gram of Hg are used in MWC applications with a baghouse operating at 135°C.

The actual adsorption capacity of carbon is affected by:

- Gas temperature
- Flue gas moisture
- Inlet concentrations of Hg
- Species of Hg
- Acid content of the flue gas
- Concentration of organics such as dioxin
- Type of carbon used and surface area
- Contact time

The effects of each of these variables has not been quantified. However, field test programs have demonstrated the relative effect that flue gas temperature has on Hg adsorption as follows:

Carbon/Coke Adsorption

| Flue Gas °C | gC/ gHg |
|---|---|
| 135 - 145 | 300 - 400 |
| 145 - 165 | 400 - 500 |
| 165 - 185 | 500 - 600 |
| 185 - 200 | 600 - 800 |

**Theory of Sulfur Adsorption**

The addition of sulfur compounds to the process plays a major role in the adsorption of mercury but not in the adsorption of dioxin. Sulfur's role in the adsorption is two fold, first the sulfur compounds maintain the active state of the carbon. Activity is defined as the amount of open pores in the carbon. Sulfur's role is to keep these pores open and to allow the mercury to get into the sub-structure pores. The exact process in which the sulfur keeps the pores open has not been defined. One theory is that the sulfur reacts with water which is adsorbed or is on the surface of the carbon particles to form an acid that penetrates the pores. No measurable acids have been observed when applying Sorbalit, most likely because any excess acids would react with the lime.

The second role for sulfur is converting Hg° to a sulfate. Hg° is more difficult to capture than $Hg_2Cl_2$, which is the predominant species in MWC emissions or $Hg_2SO_4$. Hg° accounts for only 5% to 10% of the total mercury emissions from an MWC. Flue gas constituents such as $SO_2$ can reduce the dissolved $HgCl_2$ to Hg° that is driven into the gas stream due to its poor solubility.

$$SO_2 + 2\ HgCl_2 + H_2O \Rightarrow SO_3 + Hg_2Cl_2 + 2\ HCl$$
$$Hg_2Cl_2 \Rightarrow HgCl_2 + Hg\uparrow$$

The adsorption capacity of carbon is affected by formation of sulfuric acid on the carbon owing to adsorption of the flue gas constituents $SO_2$ and $H_2O$:

$$SO_{2,\,gas} \Rightarrow SO_{2,\,ads}$$
$$SO_{2,\,ads} + 1/2\ O_{2,ads} \Rightarrow SO_{3,\,ads}$$
$$SO_{3,\,ads} + H_2O \Rightarrow H_2\ SO_{4,\,ads}$$

Hg° then reacts with the sulfuric acid to form mercurous sulfate ($Hg_2SO_4$) or in the presence of excess acid mercuric sulfate ($HgSO_4$):

$$2\ Hg + 2\ H_2SO_{4,\,ads} \Rightarrow Hg_2SO_{4,\,ads} + 2\ H_2O + SO_2 \qquad \text{or}$$
$$Hg_2SO_{4,\,ads} + 2\ H_2SO_{4,\,ads} \Rightarrow 2\ HgSO_{4,\,ads} + 2\ H_2O + SO_2$$

Since the lime component of Sorbalit removes the $SO_2$ from the flue gas, some adsorption capacity of the carbon for Hg° is diminished. The sulfur component in Sorbalit added during manufacturing, replaces the missing $SO_2$ and enhances the adsorption of Hg°. Mercuric chloride does not react with the sulfuric acid, but is dissolved in sulfuric acid.

Recent tests have demonstrated the significance that sulfur plays in capturing Hg. The test program conducted at the Marion County, OR MWC showed Sorbalit captured more Hg (total and vapor phase) than dry carbon injection. To determine the equivalent performance of carbon and Sorbalit, both were injected at the same carbon feed rate of 5 lbs/hr. Sorbalit captured 87.7% of the total Hg while carbon injection captured 84.2%. More importantly, Sorbalit captured 83.2% of the vapor phase Hg while carbon collected 77.6%.

Hg emissions from coal fired plants are significantly different in two ways from those of MWCs. First, the uncontrolled Hg emissions from U.S. eastern coal ranges from 8 to 30 $\mu$g/dscm while a typical mass burn MWC would emit 600 $\mu$g/dscm. Secondly, since there is a relatively low chlorine content in coal, the percentage of vapor phase Hg is much higher than in a MWC. As a result, the capture of Hg emissions is more difficult via dry injection. In a test program on a coal fired plant, Sorbalit captured between 44% to 55% of the vapor phase Hg while carbon injection only captured 10% to 15%. These tests were conducted under difficult Hg capture conditions: high temperatures and low moisture.

## AREAS OF APPLICATION

In its simplest form, the air pollution control system consists of a duct or pipe, through which Sorbalit is injected into the flue gas, and a fabric filter or ESP located down stream. This simple solution has an economic advantage because it is easily integrated into existing plants without having to expend significant capital for new equipment.

This Section deals with the applications for the air pollution control systems employed in various waste treatment plants. Systems which are typically used in MWCs include dry injection, water conditioning followed by dry injection, and spray dryer technologies. Since spray dryer application will become standard practice in the U.S. we will only present data on this technology. Data on other technologies has been previously published.

**MWC Marion County, OR**

In July of 1992 Sorbalit was tested at an MWC in Marion County, Oregon. Tests were conducted on Unit #1 which is rated at 10.4 Mt/h (275 T/D) of MSW. The air pollution control system consists of a spray dryer and a fabric filter. During the test program, up to .75 Mt/h (20 T/D) of medical waste was also combusted in the units.

Sorbalit was injected dry after the spray dryers in the dry venturi feed duct and before the pulse jet fabric filter at a flue gas temperature of 148°C (300°F). Seven efficiency tests were performed over the four day test program. The inlet concentration averaged 935 $\mu g/dscm^3$ @ 12% $CO_2$ and ranged from 508 to 2,695 $\mu g/dscm^3$ @ 12% $CO_2$. The outlet emissions averaged 131 $\mu g/dscm^3$ @ 12% $CO_2$ and ranged from 10 to 465 $\mu g/dscm^3$ @ 12% $CO_2$. The average Hg removal efficiency for the test program was 87.7%.

**Hazardous Waste Incineration Plant Schöneiche/Berlin**

The incineration plant at Schöneiche near Berlin, in the former GDR, has a hazardous waste capacity of 2.3 Mt/h (60 T/D). Flue gases down stream of the boiler are cooled to a temperature of 140°C (284°F) by water sprays. The gas volume rate during the test was 31,000 $Nm^3/h$ (19,657 scfm). The plant decided to use the carbon enhanced lime technology because it was the only way in which the approved limits for mercury could be achieved without the addition of new control equipment. Before the use of Sorbalit, hydrated lime was employed as the adsorbing agent.

Mercury test measurements made in January 1990, on the untreated flue gases before and after the injection of Sorbalit are shown Table 1. The measurements showed that reductions in Hg emissions were in excess of 88%. These figures represent values well below the maximum emission limit for mercury as stipulated in the German's 17th Federal Pollution Control Directive (17.BimSchV). Since the initial test, over 80 measurements for mercury have been made, confirming the initial test results.

The Table 1 shows the respective levels of the dioxin and furan concentrations in the untreated and in the cleaned flue gases. The dioxin concentration in the Sorbalit treated flue gas was undetectable in some cases.

Concentrations of polychlorinated biphenyls (PCBs) in the untreated and in the cleaned flue gas were also measured. The values are shown in Table 1. The level of PCB content in the untreated flue gas was 130 $ng/Nm^3$. Various types of PCBs were no longer detectable in the cleaned flue gas. The high rate of removal of the PCBs also leads us to the assumption that additional heavy superchlorinated compounds such as hexachlorobenzene and hexachlorocyclohexane are removed from the flue gases. Separation rates for the polyaromatic hydrocarbons cannot be established until the relevant measurements are available, however, high levels of removal are expected.

It should be emphasized again that these levels for the treated cleaned flue gases were attained without any modifications to the plant or the air pollution control system. The viability of the concept of improving a flue gas cleaning system via the use of modified hydrated lime with carbon is thus confirmed. The air pollution control system at the Schöneiche hazardous waste incineration plant has been using Sorbalit since December 1989. About 50 dioxin measurements have been taken since; never have the limits been exceeded.

**Hazardous Waste Incineration Plant Schweinfurt**

At the hazardous waste plant at Schweinfurt 2.5 Mt/h (66 T/D) of hazardous waste are converted to energy. The flue gas volume rate is 28,000 $Nm^3/h$ (17,755 scfm). The original plant consists of a pebble lime slurry preparation plant (slaker) with a spray dryer and a pulse jet fabric filter. In the retrofit, instead of the traditional lime slurry, a Sorbalit with 3% carbon suspension was employed, with no further modifications to the plant being employed. Test results showing the range of emission reductions for dioxin and mercury are presented in Table 1. Based on these results, the test program was immediately followed by continuous operation.

## CONCLUSIONS

When an activated carbon enhanced lime product such as Sorbalit is employed, the following emission values have been reliably attained:

- $< 50$ $\mu g$ $Hg/Nm^3$ for mercury at 11% $O_2$ (70 $\mu g/Nm^3$ at 7% $O_2$)
- $< 0.1$ ng $TEQ/Nm^3$ for dioxin and furans at 11% $O_2$
- Reduction to the detectable limit for PCBs
- EPA's NSPS and Emission Guidelines for $SO_2$ and HCl

Furthermore, the use of this technology in waste combustion processes obtains a number of advantages in process engineering and modification to the facilities involved. Sorbalit can be stored and added using standard lime and hydrated lime handling equipment. In retrofit applications where lime or hydrated lime is used, no new equipment may be required. Material handling equipment in most facilities, from the supply silo through conveying and dosing equipment to the mixing lines, filters, and flow controllers, all remain in use.

The gas cleaning process, that is, the injection of Sorbalit into the flue gas flow, followed by vortexing of the flow and subsequent separation on the fabric filter or ESP, can be installed as a

"Sorbalit System" downstream of any combustion plant. Many areas of application are envisioned for Sorbalit in the field of flue gas cleaning, some of which have already been put into practice. Activated carbon enhanced lime technology used for separating volatile inorganic and organic substances can be integrated into the flue gas cleaning systems of the following processes:

- Solid & hazardous waste incineration plants
- Sewage/sludge incineration plants
- Coal fired power plants
- Aluminum smelting plants
- Wood drying plants
- Steel mills
- Glass/ceramic furnaces
- Wood fired boilers

Sorbalit is effective in removing mercury over a wide range of operating conditions and applications. The test data indicates that two of the key parameters in deciding the overall removal efficiency of mercury are the inlet concentration and the temperature of the flue gas.

The data in this paper have demonstrated that Sorbalit has the flexibility to be integrated into many existing U.S. applications and systems. Additional information on new systems and wet scrubbers will be published in the near future.

**Table 1**

| Pollutant | | Schöneiche Test | | | Schweinfurt Test | | |
|---|---|---|---|---|---|---|---|
| | | Inlet | Outlet | % Removal | Inlet | Outlet | % Removal |
| Total PCBs | ng/Nm³ | 130 | >1 (nd) | N/A | - | - | - |
| Dioxins ITEQ | ng/Nm³ | 1.74 | 0.02 | 98.8 | 11.59 | 0.085 | 99.2 |
| Dioxins ITEQ | ng/Nm³ | 0.34 | nd | N/A | 6.79 | 0.06 | 91.1 |
| Hg | μg/Nm³ | 250.9 | 29 | 88.4 | 765 | 47 | 93.8 |
| Hg | μg/Nm³ | 180 | 2.5 | 98.6 | 40 | 8 | 80.0 |

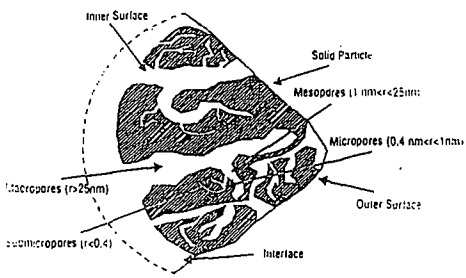


Figure 1: Distribution of pores in a grain of activated carbon

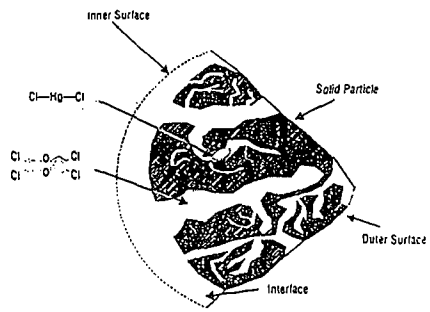


Figure 2: Structure of pores in a lignite coke particle

# LOW TEMPERATURE $SO_2$ CAPTURE BY CALCIUM BASED SORBENTS: CHARACTERIZATION OF THE ACTIVE CALCIUM.

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Keywords: $SO_2$ retention, $CO_2$ chemisorption, calcium sorbents, calcium supported on carbon.

## INTRODUCTION

Well dispersed CaO particles play an important role in some heterogeneous solid-gas reactions. Examples are the carbon-gas reactions catalyzed by calcium and the $SO_2$ retention by calcium-based sorbents. In these solid-gas reactions the characteristics of the CaO particles (i.e., dispersion, available surface area, etc.) have to be known to understand their behavior and their catalytic activity. Unfortunately, the characterization of well dispersed CaO particles by XRD does not give valuable information[1-3].

Selective $CO_2$ chemisorption has been deeply analyzed to characterize both CaO and CaO-carbon samples; thermodynamic arguments and details of the method have been discussed elsewhere[3-5]. The results show that $CO_2$ chemisorbs on CaO in an irreversible manner, and is restricted to the surface of the CaO particles, provided that the chemisorption temperature is lower than 573K. Therefore, this technique allows to assess the available surface area of the particles (active calcium) and consequently CaO dispersion. These two parameters were used to interpret the catalytic activity of calcium in different carbon-gas reactions. The usefulness of the method has been shown, gasification rate shows a close relationship with the area of the CaO particles[3,6,7]. Based on the above results, and considering that the $SO_2$-CaO interaction might depends on the surface of CaO, the $CO_2$ chemisorption has been used to characterize the $SO_2$ retention by CaO prepared from thermal decomposition of several limestones[8-10]. The observation that $SO_2$ retention at 573K depends strongly on the dispersion and surface area of the CaO particles leads us to propose the use of carbon supports to improve the dispersion of the CaO particles[11,12]. In this context, this paper extends and analyzes the usefulness of the $CO_2$ chemisorption method to characterize the active calcium in a wide variety of CaO-carbon samples. Several parameters, preparation conditions, nature of the calcium compounds, porosity of the carbons, etc. have been used to vary the available surface of the CaO particles.

## EXPERIMENTAL

CaO samples. CaO samples were prepared by thermal decomposition of commercially available $CaCO_3$ and several limestones of very different origins. Decomposition was carried out in a thermobalance (Stanton-Redcroft) as described elsewhere[10].

CaO-carbon samples. A large number of samples of calcium containing carbon have been selected for this study. The samples have been prepared varying calcium precursors, calcium content, carbon support properties (porosity, surface area, surface chemistry, etc.), and preparation methods (impregnation, ion-exchange).

$CO_2$ chemisorption. As described elsewhere[3,4] the sample (CaO or CaO-carbon) is heated in $N_2$, at 20K/min, up to 1173K, subsequently it is cooled to 573K and then $N_2$ is switched to $CO_2$. From the $CO_2$ uptake, and assuming that one $CO_2$ molecule chemisorbs on one CaO site (1:1 stoichiometry), the number of calcium atoms, the available surface area and dispersion can be estimated[3,4].

$SO_2$ retention experiments. Isothermal $SO_2$ retention measurements of calcium-based samples were mainly performed by TG at 573K (other temperatures have also been tested). Details of the procedure used are described elsewhere[10,12]. Prior the retention run, the sample was heated, at 20K/min, up to 1173K, in a $N_2$ flow (60 mL/min), for 10 min. Subsequently, the sample was cooled to 573K and $N_2$ flow was changed to a gas mixture containing 0.3 vol% $SO_2$ in He. The amount of $SO_2$ retained by the sample, after 1.5-2 h of reaction, was determined by the increase in weight.

**RESULTS AND DISCUSSION**

The retention of $SO_2$ by CaO has been analyzed in our laboratory in a wide range of reaction temperatures (298-1173K)[8-10]. At temperatures lower than 673K the interaction of $SO_2$ with CaO forms $CaSO_3$[8-10,13,14], being this compound an intermediate of the formation of $CaSO_4$ at higher temperatures[8-10,14,15]. Depending on the reaction temperature considered (T< 673K) two processes are distinguished during the formation of $CaSO_3$. For higher temperatures than 573K the formation of $CaSO_3$ occurs through a bulk process, however at temperatures below 573K, the $SO_2$ retained produces surface $CaSO_3$[10], both in presence and in the absence of $O_2$, through the reaction[9]:

$$CaO_{(surface)} + SO_2 \text{ ---> } CaSO_{3\ (surface)}$$

Figure 1 presents the isothermal retention of $SO_2$ at 573K, expressed as mol of $SO_2$ retained per gram of sample, versus time. After a period slightly over 1h, the uptake of $SO_2$ is practically constant. The $SO_2$-CaO surface reaction is confirmed on a large number of CaO by the observation that the ratio between mol of $SO_2$ (obtained from runs like that of Figure 1) per mol of CaO on the surface (determined from $CO_2$ chemisorption) is very close to one (see Figure 2). The extend of this surface reaction can not be explained by referring to any "classical" textural parameter of the limestones ($N_2$ (BET) surface area, pore volume, etc.) or those of CaO[10]. On the contrary, an interesting correlation between the $SO_2$ retention degree and the surface CaO is obtained, as shown in Figure 2. From this correlation, that shows the importance of the CaO surface area, it follows that the higher the dispersion of CaO, the higher the retention of $SO_2$. By selecting systems with high CaO dispersion[12], the efficiency to retain $SO_2$ can be increased. Activated carbons can act as dispersing agent as it is shown next.

A large number of CaO containing activated carbons prepared with different type of activated carbons, calcium compounds, calcium loadings and method of preparation have been selected for this study. Figure 3 compiles the $SO_2$ retention by these CaO-carbon samples which have been determined at 573K from runs similar to

that of Figure 1. It is interesting to note that samples containing less than 15% in weight of calcium exhibit retentions similar to those of bulk CaO (Figures 2 and 3).

The $SO_2$ retention (Figure 3) shows a marked dependence on the calcium content. Increasing the calcium content, the available CaO surface will increase, if there is not an important loss of dispersion. Figure 4 presents the $CO_2$ chemisorption data plotted versus calcium content of the supported samples. The results show that activated carbons act as good dispersing agents, they allow to increase the available CaO surface in respect to unsupported CaO.

Despite some data dispersion, both Figures 3 and 4 indicate that correlations between the calcium content and the CaO surface or the $SO_2$ retention exist. Figure 5, that presents the $SO_2$ retention per gram of sample versus the CaO surface, confirms the existence of a correlation among $SO_2$ retention and CaO surface as observed for unsupported CaO (Figure 2). Nevertheless, two aspects of Figure 5 need to be pointed out: 1) the ratio mol $SO_2$/mol $CaO_s$ is usually higher than unity, contrary to that found on Figure 2 for unsupported CaO. It means that the $SO_2$ retention by CaO-carbon is not restricted to the CaO surface and that some bulk $CaSO_3$ occurs. 2) this behaviour is more pronounced in highly dispersed CaO (high CaOs values).

To prove the formation of bulk $CaSO_3$, $SO_2$ retentions have been conducted at different temperatures. Figure 6 presents the results obtained on two CaO samples (unsupported and supported one). An important shift to lower temperatures (about 200K) is observed in the transition from surface to bulk $CaSO_3$ formation, in the case of carbon supported CaO. For practical applications of these supported CaO samples to remove $SO_2$, the observation that in the temperature range of 573-673K the CaO conversion is almost 100% is very interesting. It has to be noted that the application of these results is based on the fact that CaO can be regenerated, and hence reused for $SO_2$ removal, by thermal decomposition (873-973K) of $CaSO_3$[9,10,16,17].

The most serious challenge at this moment is to be able to increase the amount of CaO supported on a given activated carbon. In fact, the maximun $SO_2$ retention reached with these supported CaO, expressed per gram of sample, is comparable to those obtained with some bulk CaO, as can be seen comparing Figures 2 and 5.

**CONCLUSIONS**

$SO_2$ retention by CaO and CaO-carbon depends very much on the CaO surface area which can be determined by $CO_2$ chemisorption. For unsupported CaO the retention is a surface process whereas for carbon supported CaO both surface and bulk reaction take place. Activated carbons act as good dispersing agent enhancing the $SO_2$ retention. The usefulness of the $SO_2$ removal at low temperatures by CaO supported on carbon appears to be limited by the amount of CaO that can be loaded on the carbon. This point needs further studies.

*Acknowledgements:* The authors thank the EC (CSEC project, 7220-ED/053) and OCICARBON (project C23-435) for financial support and CAM for the grant Thesis of M.C. Macías.

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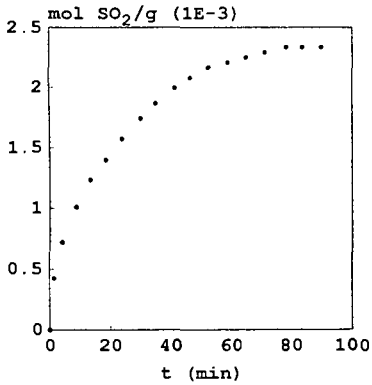


Figure 1. Sulfur dioxide retention by CaO at 573K versus time.

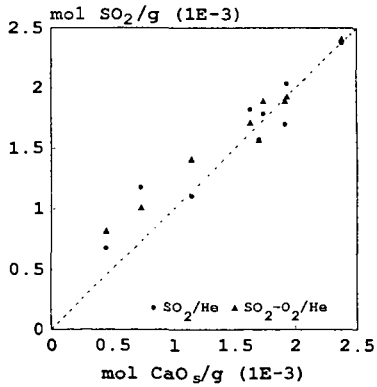


Figure 2. $SO_2$ retention versus surface CaO (unsupported CaO).

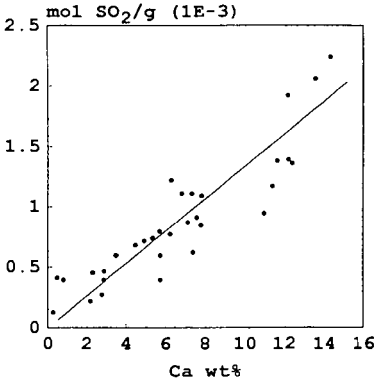


Figure 3. $SO_2$ retention versus Ca wt% (CaO/activated carbon samples).

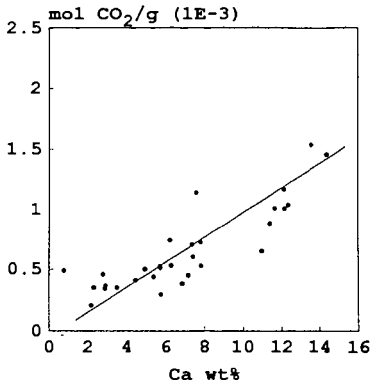


Figure 4. Chemisorbed $CO_2$ versus Ca wt% (CaO/activated carbon samples).

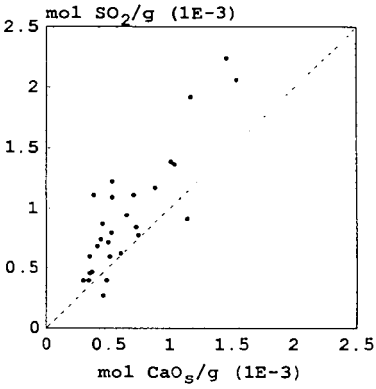


Figure 5. $SO_2$ retention versus surface CaO (CaO/activated carbon samples).

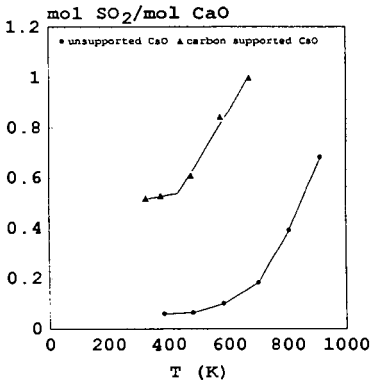


Figure 6. $SO_2$ molar conversion versus temperature.

# PRODUCTION OF ACTIVATED CHAR FROM ILLINOIS COAL FOR FLUE GAS CLEANUP

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Keywords: coal, activated char, flue gas cleanup.

## INTRODUCTION

One of the unique properties of activated carbon is that it can remove nearly every impurity found in flue gas including $SO_2$, $NO_x$, particulates, mercury, dioxins, furans, heavy metals, volatile organic compounds, and other trace elements [1-6]. No other existing sorbent has that capability. An activated carbon-based process, typically placed after the precipitator and just before the stack, can be used alone or in conjunction with other control methods to remove $SO_2$ and $NO_x$ from flue gas [7-10]. This technology has been used in Europe and Japan for cleanup of flue gas from both coal combustion and waste incineration. Currently, no U.S. utility employs a carbon-based process to clean flue gas. An ongoing research program [10-19] at the Illinois State Geological Survey (ISGS) has as one of its principal objectives the development of activated char from Illinois coal suitable for cleaning flue gas. This paper summarizes some of our recent efforts to produce activated char for several flue gas cleanup applications, including coal-fired utilities, diesel engine exhaust and waste incinerators.

## RESULTS AND DISCUSSION

### $SO_2$ Removal

The initial aim of this study was to identify process conditions for production of activated char with optimal $SO_2$ removal characteristics [10-16]. Chars with varying pore structure and surface chemistry were prepared from an Illinois hvC bituminous coal (IBC-102) under a wide range of pyrolysis and activation conditions, and tested for their ability to remove $SO_2$ from simulated flue gas (2500 ppm $SO_2$, 5% $O_2$, 10% $H_2O$, balance He). Table 1 summarizes the results. A novel char preparation method, involving nitric acid treatment followed by thermal desorption of carbon-oxygen (C-O) complexes, was developed to produce activated chars with $SO_2$ adsorption capacities comparable to those of commercial activated carbons. An attempt was made to relate the observed $SO_2$ adsorption behavior to the physical and chemical properties of the char. There was no correlation between $SO_2$ capacity and $N_2$ BET surface area. A TPD method was used to determine the nature and extent of C-O complexes formed on the char surface. TPD data revealed that $SO_2$ adsorption was inversely proportional to the amount of stable C-O complex. The formation of stable C-O complex may have served only to occupy carbon sites that were otherwise reactive to $SO_2$ adsorption. TPD data also revealed that $SO_2$ adsorption was directly proportional to the number of free adsorption sites on the carbon surface [12-15]. Based on these results, a detailed mechanism for $SO_2$ removal by carbon has been proposed [19].

### $NO_x$ Removal

Carbon can also be used to remove $NO_x$ from flue gas at temperatures between 80 and 150° C. Carbon may act as both a sorbent [20-22] and a catalyst [23-25]; the extent of each depending on the physical/chemical properties of the carbon and flue gas conditions. Sorbent Technologies Corporation (STC) is presently developing a carbon-based process for low-temperature (20-100°C) removal of $NO_x$ from exhaust streams from jet engine test cells and other combustion sources such as diesel engines that would not require the use of ammonia [22]. The carbon filter being developed is a relatively simple $NO_x$ control device that is placed directly into the exhaust duct path. There it substantially removes the $NO_x$ as well as other contaminants such as $SO_2$, HCl and organics.

The ISGS and STC are working together to develop a carbon for this process. Several carbons prepared at the ISGS were tested by STC. The experimental conditions used were: 10 g of carbon, 1 in. ID fixed bed reactor, 500 ppm NO in air, and a flow rate of 4 L/min. Figure 1 shows that a steam activated Illinois coal char treated with $HNO_3$ and thermally desorbed at 925°C for 1 h in flowing $N_2$ (IBC-102, $HNO_3$-925°C) removed 100% of the $NO_x$ during a one hour test. Recall that this char also adsorbed the greatest amount of $SO_2$ (Table 1). The $NO_x$ removal efficiency of a similarly treated Calgon F400 carbon (Calgon, $HNO_3$, 925°C) decreased from 100% to 70% after 1 h. The $HNO_3$-treated Calgon carbon that was not heat treated at 925°C (Calgon, $HNO_3$) removed only 10% of the $NO_x$ after 60 minutes illustrating the importance of the thermal desorption step in our char preparation method. Thermal desorption of C-O complexes opens closed porosity and widens pores, but more importantly, creates nascent sites on the carbon surface that react vigourously with $NO_x$. Figure 2 shows that the $NO_x$ removal performance of the IBC-102, $HNO_3$-925°C char decreases as flue gas temperature increases from 22°C to 150°C. The $NO_x$ removal efficiencies of IBC-102, $HNO_3$-treated chars thermally desorbed at 525°C, 725°C and 1075°C were all less than that of the IBC-102, $HNO_3$-925°C char. It was interesting that the $NO_x$ removal efficiencies of the KOH activated chars listed in Table 1 were comparable to those of the IBC-102, $HNO_3$-925°C char. These chars contained some leftover potassium, about 0.5% by weight. Potassium has been found to be an excellent catalyst for NO reduction [26-29].

Figure 3 compares the $NO_x$ removal behavior of the IBC-102, $HNO_3$-925°C char and the Centaur carbon, a catalytic carbon manufactured by the Calgon Carbon Corporation. The $HNO_3$-925°C char

achieves nearly 100% $NO_x$ removal for the first 8 h compared to only 4 h for the Centaur carbon. For the $HNO_3$-925°C char, the concentration of NO in the effluent increases from about 3% to 80% between 8 and 15 h, while the Centaur carbon continues to remove 50% of the NO after 20 h. It is interesting to note that $NO_2$ is generated by both carbons, and that its onset occurs at 15 h (50% of maximum breakthrough). The formation of $NO_2$ during the low temperature reaction of activated carbon fibers with NO was recently observed [30,31]. It seems that once the carbon surface becomes saturated with C-O, C-N and C-NO functional groups, $NO_2$ formation is initiated. Eventually, a char would require regeneration as these functional groups accumulate on the carbon surface and block the sites responsible for NO reduction. Preliminary tests suggest that the $NO_x$ removal activity of the spent $HNO_3$-925°C char can be partially restored by thermal regeneration. Further work is needed to determine the mechanism by which this high activity carbon removes $NO_x$ from flue gas.

**Combined $SO_2/NO_x$ Removal**

The Research Triangle Institute (RTI) in conjunction with the University of Waterloo developed a low temperature process capable of removing more than 95% of the $SO_2$ and 75% of the $NO_x$ from coal combustion flue gas [32,33]. The flue gas is cooled to 100°C and the $SO_2$ is catalytically oxidized to $SO_3$ by one type of carbon and converted to medium strength $H_2SO_4$ in a series of periodically flushed trickle-bed reactors. The $SO_2$ free gas is reheated to 150°C and $NH_3$ is injected over a different carbon to reduce $NO_x$ to $N_2$ and $H_2O$.

In this study, RTI performed $SO_2$ removal tests on five ISGS chars under conditions simulating those used in the RTI-Waterloo process: 100°C, 2500 ppm $SO_2$, 5% $O_2$, 10% $H_2O$, balance helium, space velocity of 1400 $h^{-1}$. Each adsorption cycle was followed by a 0.2 L wash with 4.32 N $H_2SO_4$. The results of nine adsorption/desorption cycles performed with the $HNO_3$-925°C char are summarized in Table 5. After the first cycle, the 20% breakthrough time (BT), i.e., when 20% of inlet concentration of $SO_2$ is measured in the effluent, was extended from 3 to 80 minutes, however, BT decreased steadily thereafter. Also, the lowest emission (LE), i.e., the minimum $SO_2$ concentration detected in the effluent, increased with each subsequent cycle. It should be mentioned that the $NO_x$ removal tests for the $HNO_3$-925°C char were performed prior to these $SO_2$ removal tests. The poor performance of this char may be attributed to adsorbed NO, $NH_3$ and $O_2$ poisoning $SO_2$ adsorption sites. Commercial processes typically remove $SO_2$ before $NO_x$ to avoid production of ammonium sulfate, which can also reduce catalytic activity [3,8]. All subsequent $SO_2$ removal tests were performed on carbons that were not previously exposed to NO or $NH_3$. The KOH activated char was also tested (Table 5). A relatively low concentration of $SO_2$ in the effluent was achieved and the 20% BT was 45 minutes, but after the first cycle, performance decreased dramatically.

Table 6 shows that the $SO_2$ removal performance of the Centaur carbon was superior to all other carbons tested. Its 5% BT, however, also decreased after the first cycle. The IBC-102, $HNO_3$-725°C char performed best among the ISGS chars tested. Its initial LE was 10 ppm $SO_2$ (equivalent to 99% removal efficiency), but this increased to 1200 ppm $SO_2$ after just the first acid wash. An RTI carbon (not listed in Table 6) showed similar deactivation after the first cycle. The integral feature of the RTI-Waterloo process is its regeneration step involving a water wash with dilute $H_2SO_4$. One important advantage of doing this instead of thermal regeneration is that it does not consume carbon. Thus, a carbon catalyst in this process could last for many years without having to be replaced. The $SO_2$ removal performance of all the carbons tested by RTI in this study decreased markedly after the first cycle. Whether a low cost carbon having a high concentration of free sites resistant to poisoning by the dilute acid wash can be developed for this process remains to be determined.

The $NO_x$ removal capabilities of these chars in the presence of ammonia were also tested. The following reaction conditions were used: 40 $cm^3$ carbon, 130-160°C, 500 ppm NO, 690 ppm $NH_3$, 5% $O_2$, 10% $H_2O$ and 1400 $h^{-1}$ space velocity. Table 4 shows that the $NO_x$ removal activity of the $HNO_3$-925°C char, alhough highest among the ISGS chars tested, was still significantly lower than that of the carbon catalyst developed and tested by RTI (commercial activated carbon impregnated with a metal catalyst). The RTI carbon, although it achieved better than 99% conversion of NO to $N_2$, remains quite costly to produce. Table 4 also shows that the five ISGS samples responded differently to variations in reaction temperature. The NO removal activity of the $HNO_3$-925°C char went through a maximum at 150°C. $NO_x$ conversion with the air-925°C char decreased with increasing temperature, while the steam activated char maintained essentially the same level of activity between 130 and 160°C. The $NO_x$ reduction activity of the $HNO_3$-725°C char increased from 3% to 22% between 130 and 160°C, whereas that of the KOH activated char decreased from 22% to 7%. The Centaur carbon performed rather poorly at the two temperatures studied. Note that the ISGS chars tested were not representative of chars optimized for this application. Typically, commercial selective catalytic reduction (SCR) processes use higher surface area (1000-1500 $m^2/g$) activated carbons made from bituminous coal. Carbo Tech (Essen, Germany) presently manufactures ton quantities of this carbon for carbon-based SCR processes operating in Europe. Singoredjo et al. [34] recently noticed that $NO_x$ removal with carbon in the presence of ammonia was influenced by a number of factors including the number and type of C-O complexes on the carbon surface, nitrogen content of the char, and accessibility of the pores. The oxygen contents of most of our chars were minimized due to the steam activation or thermal desorption treatments used in their preparation.

**Incinerator Flue Gas**

Incinerator flue gas typically contains much lower concentrations of $SO_2$ (20-100 ppm) compared to

those found in coal combustion flue gas (500-3000 ppm), but also contains much higher levels of other pollutants such as mercury, dioxins, furans, heavy metals, and hydrochloric acid. STEAG Aktiengesellschaft (Essen, Germany) has pioneered the cleanup of incinerator flue gas using their patented /a/c/t™ process and a low cost (< $300/ton), low surface area (< 300 $m^2/g$) activated carbon made from German brown coal [1,2]. A U.S. source of this carbon is currently needed for their processes soon to be installed on waste incinerators in the U.S. A market potential of 80,000 tons/year of activated char (160,000 tons of coal) has been estimated, assuming 10% of U.S. incinerators adopt their technology to meet needs emanating from anticipated regulation of emissions from existing incinerators. This potential market for Illinois coal was of interest to us, so we agreed to produce this type of carbon for STEAG.

The laboratory conditions needed to produce a suitable sorbent from a Colchester (Illinois No. 2) hvC bituminous coal were first identified. Char production runs were performed at the ISGS using a 2 in. ID horizontal tube furnace, 4 in. ID, 4 ft. heated zone, continuous feed rotary tube kiln, and a continuous feed charring oven. With the assistance of Allis Mineral Systems (Milwaukee, WI), the production steps were carried through two levels of scale up, culminating in the production of 610 pounds of activated char in an 18 in. ID, 10 ft. heated zone, externally fired rotary tube kiln. A 1500 pound sample of size-graded bituminous coal having a free swelling index of 4.5 was used as feedstock for the production run. A three-step process, which included preoxidation, pyrolysis and activation, was necessary to process this coal. Details of the conditions used in the production runs are described elsewhere [10,16,17]. Table 7 compares the properties of the ISGS char and the char presently used by STEAG (hereafter referred to as Herdofenkoks). It shows that ISGS char had a $N_2$ BET surface area of only 110 $m^2/g$, but an $SO_2$ capacity after 4 h greater than that of the Herdofenkoks. The iodine number of the Herdofenkoks was about three times greater than that of ISGS char. (This number relates to the surface area contained in pores greater than 10 Å.) The mechanical strength of ISGS char, although not as good as Herdofenkoks, was still considered satisfactory for this application. Note that the carbon tetrachloride activity of ISGS char is 51 mg/100 g char, about three times that of the Herdofenkoks. The carbon tetrachloride activity is used as an indicator of carbon performance in vapor phase applications, e.g., VOC removal. Normally, one would not expect a carbon tetrachloride activity to be this high given the $N_2$ BET surface area of the char (110 $m^2/g$). The observed value of 51 is more typical of carbons having surface areas of 800-1200 $m^2/g$. Evidently, the ISGS char (bituminous coal char activated in $CO_2$ for 2 h) developed a more extensive microporosity than the Herdofenkoks (brown coal pyrolyzed at 950°C for 0.75 h).

Commercial activated carbons available in the U.S. are believed to be too reactive due to their relatively high surface area (> 600 $m^2/g$) and propensity to adsorb and react with $NO_x$. The reaction of carbon with adsorbed $NO_x$ is exothermic and can ignite the carbon bed under certain conditions, e.g., in the absence of gas flow. The STEAG /a/c/t™ process requires the use of a low activity char having a surface area less than 300 $m^2/g$. A 550 pound sample of low surface area activated char produced in this study was shipped to Essen, Germany where it was installed in a pilot plant unit and subjected to a $NO_x$ self heating test. This involved adsorbing $NO_x$ on the carbon until saturated, shutting off the flow of gas to the adsorber, and measuring the temperature rise of the char bed. The ISGS char passed the test and is the only U.S. material known to have done so. (Figure 1 also shows that the $NO_x$ removal efficiency of this char was less than that of the Herdofenkoks.)

The test unit containing ISGS char was then installed on a slipstream of flue gas from a commercial waste incinerator in Germany. Flue gas velocity through the 800 mm char bed was 0.15 m/s. The ISGS activated char removed more than 99.7% of the dioxins and furans from the incinerator flue gas (Table 8). Also, the mercury, which was present in the inlet gas, was not detected in the exit gas. The removal efficiencies achieved by ISGS char were at least as good as, if not better than, those achieved with Herdofenkoks. The two-week test, however, was not of ample duration to observe complete breakthrough of any of the pollutants listed in Table 8, so there was no information on total adsorption capacity. Typically other pollutants do not breakthrough the bed before $SO_2$, so the $SO_2$ capacity is considered a good measure of the total adsorption capacity of the char. An economic analysis indicates that it would cost between $325 and $400 to produce one ton of ISGS char with a plant designed and constructed to produce 80,000 tons per year, assuming a 20% rate of return on initial investment.

Another potential market for low cost char is the cleanup of coal combustion flue gas. The Mitsui Mining Company Limited (Tokyo, Japan) has developed a combined $SO_2/NO_x$ removal process featuring a two stage adsorber in which flue gas is contacted with activated coke at temperatures between 100 and 200°C [3]. Sulfur oxides are adsorbed onto the activated coke in the first stage resulting in the formation of sulfuric acid. The flue gas moves into the second stage where $NO_x$ reacts with $NH_3$ to form $N_2$ and $H_2O$. The coke from the first stage is thermally regenerated at temperatures between 300 and 500°C. Mitsui has licensed their technology to General Electric and both are working together to develop new markets in the U.S. for their process. (They have also developed a process to clean incinerator flue gas [4].) A carbon having a selling price less than $600/ton is needed.

Our low cost char was tested by Mitsui Mining under the following conditions: 140°C, 1000 ppm $SO_2$, 200 ppm $NO_x$. Table 9 compares the properties of ISGS char and Mitsui Mining activated coke. The $N_2$ BET surface area and $SO_2$ adsorption capacity of ISGS char is less than that of Mitsui coke. Also, the $NO_x$ removal efficiency of Mitsui coke is significantly greater than that of ISGS char. The surface of the Mitsui coke is said to contain functional groups (C-O, C-N and C-OH) that react more effectively with $SO_2$ and $NO_x$. Note that the ISGS char tested by Mitsui Mining was not optimized for this process. These tests were performed only to evaluate the potential of our low cost char in other applications.

## SUMMARY

Activated chars were produced from Illinois coal and tested in various flue gas cleanup applications. A low cost, low surface area char was developed for cleanup of incinerator flue gas. Five hundred pounds of the char was tested on a slipstream of flue gas from a commercial incinerator. The char was effective in removing more than 97% of the dioxins and furans present in the flue gas; mercury levels in the effluent were below detectable limits. Higher activity chars that showed excellent potential for both $SO_2$ and $NO_x$ removal were also produced. The performance of one char compared favorably with that of a commercial carbon catalyst.



## ACKNOWLEDGEMENTS

This work was supported by the Illinois Clean Coal Institute through the Illinois Coal Development Board and the United States Department of Energy. Collaboration with Carl Kruse of the ISGS, Santosh Gangwal and Ben Jang of RTI, Sidney Nelson, Sr. and Sidney Nelson, Jr. of STC, Hermann Brueggendick and Herbert Schumann of STEAG, and Tak Inagaki and Tak Fujimoto of Mitsui Mining are appreciated. The authors gratefully acknowledge the technical assistance of Gwen Donnals.


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Table 1. Correlation of $SO_2$ adsorption capacity with surface area and chemisorbed oxygen.

| Sample | $SO_2$ Capacity[1] (mg $SO_2$/g char) | $N_2$ BET ($m^2/g$) | $CO_2$ BET ($m^2/g$) | $SO_2/N_2$ ($mg/m^2$) | $SO_2/CO_2$ ($mg/m^2$) | $O_2$ (wt%) | $SO_2/O_2$ |
|---|---|---|---|---|---|---|---|
| Calgon F400 | 206 | 1000 | 1000 | 0.21 | 0.21 | 0.5 | 41.2 |
| Calgon Centaur | 327 | 360 | ...[2] | 0.91 | ...[2] | ...[2] | ...[2] |
| IBC-102, $N_2$, 500°C, 0.5 h | 19 | 1.2 | 270 | 15.8 | 0.07 | 8.8 | 0.22 |
| IBC-102, $N_2$, 700°C, 0.5 h | 33 | 10 | 315 | 3.3 | 0.10 | 1.5 | 2.20 |
| IBC-102, $N_2$, 900°C, 0.5 h | 7 | 1.2 | 98 | 5.8 | 0.07 | 0.5 | 1.40 |
| IBC-102 + KOH, $N_2$, 600°C, 0.5 h | 157 | 500 | 725 | 0.31 | 0.22 | 7.4 | 2.12 |
| IBC-102 + KOH, $N_2$, 800°C, 0.5 h | 176 | 800 | 1155 | 0.22 | 0.15 | 5.6 | 3.14 |
| IBC-102, 500°C; 10% $O_2$, 390°C | 13 | 220 | 422 | 0.06 | 0.03 | 8.6 | 0.15 |
| IBC-102, 700°C; 10% $O_2$, 440°C | 37 | 320 | 490 | 0.11 | 0.08 | 8.9 | 0.42 |
| IBC-102, 900°C; 10% $O_2$, 500°C | 42 | 230 | 395 | 0.18 | 0.11 | 5.2 | 0.81 |
| IBC-102, 900°C; $H_2O$, 860°C | 176 | 220 | 613 | 0.80 | 0.29 | 1.1 | 16.0 |
| IBC-102, 900°C; $H_2O$, 860°C; 45% $HNO_3$, 2.5 h, 25°C | ...[2] | 400 | 585 | 0.06 | 0.04 | 16.4 | ...[2] |
| IBC-102, 900°C; $H_2O$, 860°C; 45% $HNO_3$, desorbed at 525°C | 91 | 460 | 693 | 0.20 | 0.13 | 5.9 | 1.54 |
| IBC-102, 900°C; $H_2O$, 860°C; 45% $HNO_3$, desorbed at 725°C | 241 | 500 | 727 | 0.48 | 0.33 | 1.6 | 15.0 |
| IBC-102, 900°C; $H_2O$, 860°C; 45% $HNO_3$, desorbed at 925°C | 287 | 550 | 726 | 0.05 | 0.39 | 0.5 | 57.4 |

[1] $SO_2$ capacity determined after 6 h.
[2] not determined.

Table 2. $SO_2$ removal tests.

| Cycle | Low Emission (ppm $SO_2$) | 20% BT (min) |
|---|---|---|
| $HNO_3$-925°C | | |
| 1 | 80 | 3 |
| 2 | 100 | 80 |
| 3 | 80 | 60 |
| 4 | 150 | 25 |
| 5 | 160 | 35 |
| 6 | 240 | 30 |
| 7 | 300 | 20 |
| 8 | 350 | 15 |
| 9 | 400 | 10 |
| KOH activated | | |
| 1 | 25 | 45 |
| 2 | 1800 | ---- |

Table 3. $SO_2$ removal tests.

| Cycle | Low Emission (ppm $SO_2$) | 5% BT (min) |
|---|---|---|
| $HNO_3$-725°C | | |
| 1 | 10 | 60 |
| 2 | 1200 | ---- |
| Centaur | | |
| 1 | 0 | 725 |
| 2 | 10 | 40 |

Table 4. $NO_x$ reduction with ammonia.

| Sample | 130°C | 140°C | 150°C | 160°C |
|---|---|---|---|---|
| $HNO_3$-925°C | 20 | 29 | 33 | 30 |
| air-925°C | 14 | 8 | 3 | 0 |
| $H_2O$ activated | 16 | 14 | 14 | 14 |
| $HNO_3$-725°C | 3 | 6 | ---- | 22 |
| KOH activated | 22 | 8 | 7 | ---- |
| Centaur carbon | 0 | ---- | ---- | 4 |
| RTI carbon | 99 | 99 | 99 | 99 |

Table 7. Comparison of Mitsui coke and ISGS char.

| Property | Mitsui coke | ISGS char |
|---|---|---|
| $N_2$ BET surface area ($m^2/g$) | 200 | 105 |
| $CO_2$ BET surface area ($m^2/g$) | --- | 142 |
| $SO_2$ capacity (mg $SO_2/g$) | 100 | 27.1 |
| DeNOx efficiency (%) | 55 | 18.8 |
| Bulk density (g/ml) | 0.60 | 0.39 |
| Micro strength (%) | 70 | 48 |
| Ignition point (°C) | 420 | 468 |

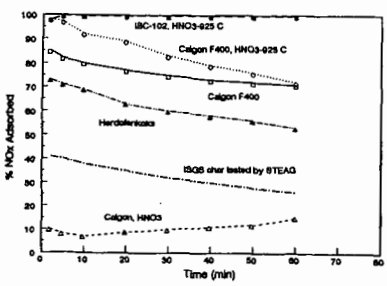


Figure 1. NOx removal efficiency at 22 C.

Table 5. Comparison of Herdofenkoks and ISGS char.

| Property | Herdofenkoks | ISGS char |
|---|---|---|
| $N_2$ BET Surface Area ($m^2/g$) | 275 | 110 |
| Iodine Number | 349 | 137 |
| $SO_2$ Capacity (wt%, 120°C, 4 h) | 2.8 | 4.2 |
| $SO_2$ Capacity (wt%, 120°C, 15 h) | 7.6 | 5.8 |
| Bulk Density ($lb/ft^3$) | 29.8 | 23.8 |
| Carbon (wt%) | 83.1 | 87.0 |
| Volatile Matter (wt%) | 7.7 | 4.7 |
| Ash (wt%) | 8.7 | 8.3 |
| Mechanical Strength | 98.8 | 78.3 |
| Ignition Point (°C) | 405 | 395 |
| Carbon Tetrachloride Activity (mg/100 mg char) | 17 | 51 |

Table 6. Pilot plant tests with ISGS char.

| Pollutant | Inlet | Outlet | Efficiency (%) |
|---|---|---|---|
| Dioxins, Furans | | | |
| Test 1 ($ng/m^3$) | 333.3 | 0.062 | 99.98 |
| Test 2 ($ng/m^3$) | 337.9 | 0.052 | 99.98 |
| Test 3 ($ng/m^3$) | 282.3 | 0.789 | 99.72 |
| Cadmium, Titanium | | | |
| Test 1 ($mg/m^3$) | 0.0140 | 0.0012 | 91 |
| Test 2 ($mg/m^3$) | 0.0062 | 0.0012 | 81 |
| Test 3 ($mg/m^3$) | 0.0052 | 0.0004 | 92 |
| Mercury | | | |
| Test 1 ($mg/m^3$) | 0.0177 | ----[1] | ----[1] |
| Test 2 ($mg/m^3$) | 0.0384 | ----[1] | ----[1] |
| Test 3 ($mg/m^3$) | 0.0223 | ----[1] | ----[1] |
| Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V, Sn | | | |
| Test 1 ($mg/m^3$) | 0.2698 | 0.0744 | 72 |
| Test 2 ($mg/m^3$) | 0.0805 | 0.0347 | 57 |
| Test 3 ($mg/m^3$) | 0.0634 | 0.0185 | 71 |

[1] below detection limits.

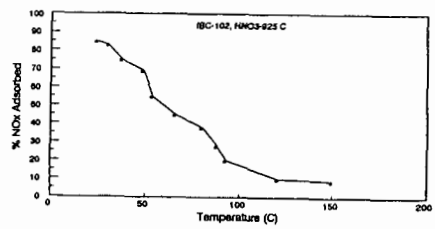


Figure 2. Effect of temperature on NOx removal efficiency.

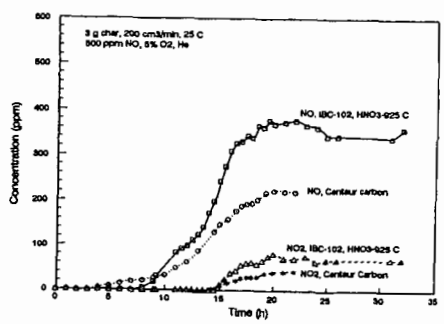


Figure 3. NOx removal with Centaur carbon and IBC-102, HNO3-925 C char.

# HIGH EFFICIENCY, STRUCTURED-PACKING CATALYSTS WITH ACTIVATED CARBON FOR $SO_2$ OXIDATION FROM FLUE GAS

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Keywords: Environmental catalysis, structured packing catalyst, $SO_2$ removal from flue gas

**ABSTRACT**
Monolithic or Sulzer CY gauze structured packings were loaded with hydrophobized activated carbon. Studies of their activity for $SO_2$ conversion to sulfuric acid were carried out with respect to principal scale-up variables of the process: temperature, pressure drop, periodic vs. continuous operation, gas and liquid flow rates. High conversions, high catalyst efficiency, and low pressure drops, long catalyst lifetime, easy of handling catalyst packings are some of the outstanding features of the system.

**INTRODUCTION**
Environmental regulations impose a removal of at least 85 - 90% of sulfur from fuel. Huge volumes of flue gases (e.g., that of a 700 MW oil-fired power station is equivalent to ca. 2 million cubic meters per hour) containing up to 0.3% $SO_2$, impose severe requirements on industrial flue gas clean-up plants: low pressure drops at high gas flow rates (>10,000 $h^{-1}$), sulfuric acid solutions of at least 15 wt% concentration, small volume, easy-to-handle catalysts, long catalyst lifetimes, no waste products generated by the exhausted catalyst, almost constant temperature profiles.

One of the most attractive method is to use activated carbon catalyst to oxidize $SO_2$. Over the last three decades, numerous studies have described the oxidation of $SO_2$ on activated carbon catalysts either in gas-solid system when $H_2SO_4$ is thermally desorbed, or in gas-liquid-solid systems (trickle-bed or slurry) when $H_2SO_4$ is washed with water [1-10]. As the gas-solid system involves catalyst reheating to accomplish desorption in which the adsorbed sulfuric acid reacts with carbon to form $CO_2$, $H_2O$ and $SO_2$, the three phase system seems to be more attractive. Use of large-scale trickle-bed reactors is still hindered by some specific drawbacks: very low effectiveness factor (0.021 for 2.59 mm particle diameter, and 0.45 for 99 μm) , high pressure drops over the catalyst bed, maldistribution of various kinds (including a non-uniform access of reactants to the catalytic surface), rapid $SO_2$ breakthrough due to sulfuric acid entrapped in pores, and very low concentrations of the sulfuric acid in the effluent. Recognizing that reaction in dumped catalysts is controlled by mass transfer to and from the catalyst, we have studied a three-phase reactor in which the catalyst is deposited as a thin layer (micrometers) on screens of appropriate hydrophobicity. Either monolithic or static mixers configurations, known for their low pressure drops, are used. Their hydrophobic-hydrophilic characteristics determine the distribution of dry and wet zones that spontaneously change with time ensuring both higher access for gaseous reactants to the catalyst and more efficient removal of product from it. The frequency of shifting depends on the gas and liquid flow rates and the catalyst geometry which determines the flow pattern. Because of this dynamic alternation, almost the entire catalytic surface is involved in the oxidation process.

$SO_2$ oxidation on activated carbon involves a reaction among three species: $SO_2$, $O_2$, and $H_2O$ adsorbed on the carbon surface. A reaction of three adsorbed species simultaneously is, statistically speaking, possible but quite unlikely. Nevertheless, activated carbon has an affinity for molecular $SO_2$, 2.7 times larger than for oxygen [13]. As the solubility of $SO_2$ in water is more than 10 times larger than for oxygen, $O_2$ is the thus limiting reactant despite a 100 fold larger partial pressure than that of sulfur dioxide. It is thus intuitive that carbon surfaces are readily populated with $SO_2$, so that the rate of uptake of oxygen on the active sites is almost certain to be rate-limiting. Infrared analysis demonstrated that in the presence of water vapor and oxygen, sulfuric acid is formed on

carbon. In addition to sulfuric acid, a small quantity of chemisorbed $SO_2$ was found, as well as some residual water [11]. Once $H_2SO_4$ is formed, it becomes a competitor for active sites, along with $SO_2$, $O_2$, and $H_2O$. Meanwhile, sulfuric acid decreases $SO_2$ and $O_2$ solubilities but not in the intrinsic rate of surface reaction itself, within reasonable limits (up to 30 wt% $H_2SO_4$).

Sulfuric acid formation is ensured by the water vapor present in flue gas, liquid water only playing the role of product carrier from the catalyst pores. Therefore water flow rate affects the liquid film resistance to the reactants transferring from gas onto the active catalyst sites. The preparation method of our catalysts ensures a hydrophobic catalytic surface still keeping a polar character inside the pores. As was shown [16], pyrone and pyrone-like structures are responsible for the catalytic activity. The presence of hydroxyl groups on the activated carbon provides an additional opportunity for controlling the hydrophobicity inside the pores in order to obtain a controlled wet-proofing.

## EXPERIMENTAL

*Catalyst*

Two basic types of structured packings were used: monoliths and static mixers (Sulzer CY) gauze. Monoliths were built up by rolling together a corrugated gauze, on which activated carbon was loaded using a hydrophobic binder, with a flat screen which was either hydrophilic or hydrophobic. Monolithic catalysts were supplied by Atomic Energy of Canada Limited (AECL). Static mixers were supplied by Sulzer Chemtech, Winterthur, Switzerland, and loaded with activated carbon by AECL. Properties of activated carbon and catalyst beds are given in Table 1. Centaur™ activated carbon (Calgon Carbon Corp.) with an average particle diameter of 0.3 μm has been used for loading the screens in all runs. BET surface areas of the bound carbon were determined at -195.5°C by nitrogen adsorption using a Quantachrome Autosorb Automated Gas Sorption System, Micropore Version 2.44. Typical values were 139.9 $m^2/g$ for overall surface area, 95.7 $m^2/g$ for mesopore area, and 44.2 $m^2/g$ for micropore area.

Table 1. Properties of activated carbon and catalyst beds.

| Catalyst | Type | Carbon type/weight (g) | Height cm | Cross-section area $cm^2$ | Volume $cm^3$ |
|---|---|---|---|---|---|
| QA 95-8 | Monolith-hydrophilic sep. screen, 120 mesh | Centaur/ 10.23 | 3x10 | 19.63 | 589.1 |
| QA 95-9-0 | Monolith-hydrophilic sep. screen, 20 mesh | Centaur/ 23.43 | 3x10 | 19.63 | 589.1 |
| QA 95- 9-1 | Monolith-hydrophilic sep. screen, 20 mesh | Centaur/ 22.52 | 3x10 | 19.63 | 589.1 |
| QA 95-11-0 | Monolith-hydrophilic sep. screen, 28 mesh | Centaur/ 28.44 | 1x10 | 19.63 | 196.3 |
| QA 95-11-1 | Monolith-hydrophobic sep. screen, 28 mesh | Centaur/ 28.44 | 1x10 | 19.63 | 196.3 |
| QA 95-12 | Static mixers CY | Centaur/ 23.28 | 2x15 | 15.90 | 476.8 |

*Apparatus*

The $SO_2$ oxidation was carried out in a glass reactor of 600 mm length and 50 mm id. Gaseous reactants and water were fed concurrently in the top of reactor. Water was supplied by a micropump Gear Pump - Model 130/150, (Micropump Corporation, Vancouver, WA), after preheating (as needed) and saturation with oxygen in a saturation column filled with static mixers Sulzer Mellapak 125.Y of polypropylene. An adjustable height spray nozzle was used to distribute washing liquids evenly over the cross section of the reactor. Periodic liquid interruptions were achieved by means of a solenoid valve in the feed line to the reactor vessel. The valve was controlled by a microcomputer through a D/A interface. Feed gas with a volumetric composition of 10% $CO_2$, 5% $O_2$, and 0.3 % $SO_2$ was preheated (as needed) and saturated with water at 45°C correspondent to 10% $H_2O$ in the gas mixture, the balance being $N_2$. Flow rates of the individual gaseous streams were controlled by mass flowmeters Unit (Unit Instruments, Inc., Orange, CA). The reactor was heated using three heating tapes, and temperatures were measured by 0.2 mm o.d. type K thermocouples and recorded by the data acquisition system. Pressure drop in the catalytic bed was measured with a water-filled manometer connected to taps located above and below the bed. The reactor effluent

was cooled and liquid and gas phases were separated. $SO_2$ concentration in the gaseous effluent was continuously monitored by a UV spectrometer (Western Research, model 721 AT) and recorded by the data acquisition system. The liquid phase was analysed for $H_2SO_4$ by titration with 0.1 N solution of NaOH. Sulfur dioxide dissolved in liquid effluent was determined by means of a conventional iodine titration. Typical operation conditions are summarized in Table 2.

Table 2. Operating conditions for the reaction studies.

| | |
|---|---|
| Temperature, $^oC$ | 23 to 80 |
| Pressure, MPa | 1.013 E - 01 |
| Liquid phase | Deionized water (DI), DI + Tween 20 (4 E - 07 mol/l), DI + acetone (20 wt %) |
| Gas flow rate, $m^3/s$, at 25$^oC$ | (5.5 to 33) E - 05 |
| Liquid flow rate, $m^3/s$ | (5.3 to 55) E - 09 |

## RESULTS AND DISCUSSIONS

The exploratory investigations were carried out on three main catalytic configurations: monoliths with hydrophilic separation screens (QA 95-9 and QA 95-11-0), monoliths with hydrophobized catalyst and separation screen (QA 95-11-1), and hydrophobized static mixers CY (QA 95-12).

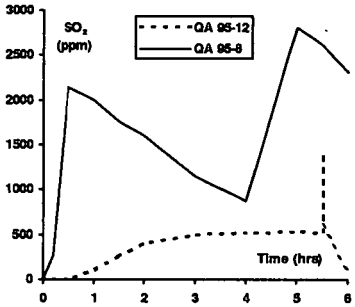


Figure 1. Concentration Profiles of Free $SO_2$ in the Reactor Effluent for Different catalysts

Monoliths with hydrophilic-hydrophobic screens (QA 95-9 and QA 95-11-1) give rise to high liquid static hold-up over the catalyst bed (equivalent to 20 wt% of catalytic stack weight). With these stagnant columns of liquid in each channel, there was poor reproducibility of data preventing a clear conclusion. Obviously, a higher contact time between liquid and catalytic surface improves sulfuric acid removal but, on the other hand, reduces the mass transfer rates of gaseous species onto the catalytic surface. Both periodic operation (flushing periods of 30 to 45 seconds followed by "dry" periods of 255 to 270 seconds) and continuous flushing, gave non-reproducible results. Periods of high conversions alternate with lower removal of $SO_2$ in a random way due, probably, to a very complex hydrodynamic regime in the channels which creates a "storage effect" of $SO_2$. A typical concentration profile for the "free" $SO_2$ released in the effluent is shown in Figure 1 (QA 95-8). In spite of high conversions periods - especially in forced periodic operation - the system didn't permit further studies of the influence of other process variables, because of high oscillations in $SO_2$ conversions during the same run.

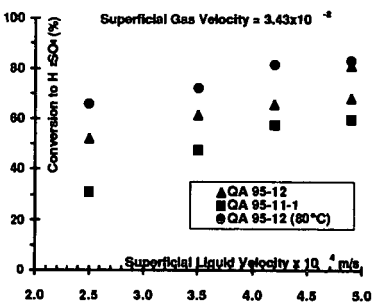


Figure 2. Conversion to $H_2SO_4$ vs. Superficial Liquid Velocity

Initially with low temperature runs, negligible $H_2SO_4$ is formed in the micropores because of low reaction rate; the diffusing species ($SO_2$, $O_2$, and $H_2O$) fill the micropore volume taking up the available vacant sites. However, beyond this initial period, reaction occurs on a time-scale longer than the adsorption time-scale, the product $H_2SO_4$ forms and displaces other molecules ($SO_2$, $O_2$, $H_2O$) until a new steady-state between sorption and reaction prevails.

The influence of liquid flow rate on the $SO_2$ conversion is shown in Figure 2. An increase in conversion is expected due to the improvement of sulfuric acid removal. Obviously, better contact between catalyst surface and washing liquid will facilitate efficient cleaning of the catalyst. Runs with a mixture of deionized water and 20 wt% acetone or with a wetting agent (Tween 20, $10^{-6}$ M) which facilitate penetration in the meso- and micro-pores and faster removal of sulfuric acid, led to an increase of conversion with 10 to 18%. This is contrary to the contention [8]

that the higher the liquid flow rate the lower is the fraction of $SO_2$ oxidized to sulfuric acid. In the range of interest, due to the hydrophobicity of the catalyst surface, reactants are mainly supplied directly from the gaseous phase.

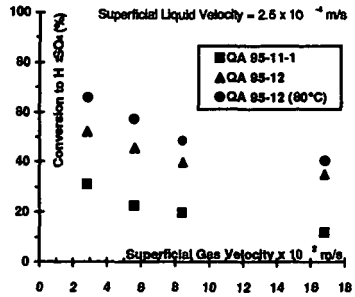

Figure 3. Conversion to $H_2SO_4$ vs. Superficial Gas Velocity

Meanwhile, at temperatures higher than 80°C, sulfuric acid present in catalyst pores has such high concentrations as to allow the use of sulfuric acid solutions (7 to 15%) as washing liquids. In this way it is possible to use optimum flow rates of liquid, without an undesirable dilution of the solution. On the other hand, preliminary tests done with an organic substrate (dodecylbenzene) gave very promising results in a reactive removal of sulfuric acid with production of surfactants, which might be a novel route for $SO_2$ removal.

Increasing the gas flow rate cause a decrease in conversion (Figure 3). The oxidation rate lagged behind the adsorption step rate [16]. As expected, shorter contact time between reactants and catalyst reduced conversions. The most likely reasons for this are correlated with the efficiency of sulfuric acid removal and/or oxygen activation rate. An enhance of catalytic activity has been achieved by doping the internal surface with typical oxidation catalysts, e.g., oxides of cobalt, chromium, and vanadium, or phthalocyanines [14,15].

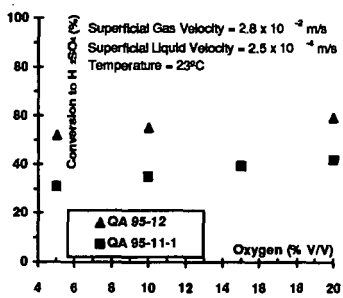

Figure 4. Conversion to $H_2SO_4$ vs. Oxygen Concentration in the Feedstock

It is important to mention that even at the highest gas and liquid flow rates, the pressure drops over the catalytic bed were less than $25 \times 10^{-2}$ kPa.m$^{-1}$. The lowest values were achieved with hydrophobic monoliths.

One of the most important requirements in the oxidation process is to supply sufficient amounts of oxygen onto the active sites. The oxygen adsorption onto the catalytic surface follows a Henry type isotherm; hence an increase in its partial pressure will increase the available active oxygen and will provide an increase in conversion. As shown in Figure 4, an increase in the range of 5 to 20 % $O_2$, led to higher conversion. Further investigations are necessary to develop a better correlation of oxygen concentration with temperature and nature and size of liquid flow rate.

Temperature has a complex effect on the oxidation process. An increase in temperature leads to higher reaction rates and higher concentrations of the sulfuric acid loaded in the pores. However, temperature also determines lower solubilities of reactants in the liquid inside and outside the pores with a subsequent decrease of reaction rate. In our situation, experimental data confirm an enhancement of conversion to sulfuric acid with temperature increase. Values as high as 92% were achieved at 80°C. Experiments in the range of 90 to 120°C are now in progress. The hydrophobic character of the catalytic surface and the continuous alternation of dry and wet surfaces permits easier transfer of reactants to the catalyst surface directly from the gaseous phase, making the contribution of dissolved species less important (Figure 5).

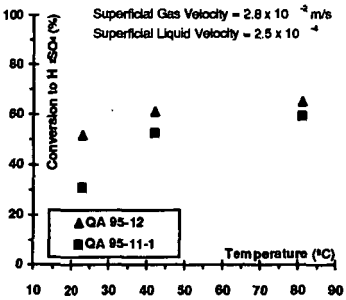

Figure 5. Conversion to $H_2SO_4$ vs. Temperature

## CONCLUSIONS

Centaur activated carbon bound in a thin layer on monolithic or static mixer packings has been used with very good results for $SO_2$ oxidation. Conversions of 92% and productivities relative to a unit weight of carbon were achieved. The high catalytic activity shown by the hydrophobic thin layer catalyst appears to benefit from its hydrophobicity to water and short diffusional paths. Investigations on catalytic system behaviour at higher temperatures (100-120$^{o}$C), using either sulfuric acid solutions or organic substrates, as washing liquids are now in progress. As a consequence of the system features, the use of periodic flushing is expected to enhance catalyst productivity. Very low pressure drops over the catalyst bed, and production of either concentrated solutions of sulfuric acid or sulfated/sulfonated organic substrates make the process very attractive for commercial plants.

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## ACKNOWLEDGEMENTS


The financial support of the Natural Sciences and Engineering Research Council in the form of a Strategic Grant to PLS and RRH is gratefully acknowledged. Sulzer Chemtech has generously provided static mixers for gas-liquid mixing and as catalyst support.

# CONTROL OF MERCURY EMISSIONS IN FLUE GASES BY ACTIVATED CARBON ADSORPTION

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Keywords: Activated Carbon, Mercury Vapors, Flue Gas

## ABSTRACT

The adsorptive capacities of virgin and sulfur impregnated activated carbons (GAC) for gas-phase mercury were evaluated as a function of temperature and influent mercury concentration. The virgin activated carbon showed little adsorptive capacity, especially at temperatures above 90 °C. The pronounced effect of temperature on the adsorptive capacity evidences a physical adsorption mechanism between the mercury and virgin GAC. Sulfur impregnated activated carbons exhibited enhanced mercury removal efficiency over the non-impregnated varieties due to formation of mercuric sulfide on the carbon surface. This chemisorption process is enhanced with increased temperature between 25 and 90 °C. However, at 140 °C a decrease in adsorptive capacity occurs, indicating reduced formation of mercuric sulfide. The method used for impregnating GAC with sulfur had a pronounced effect on mercury removal capacity. The chemical bonding of sulfur and carbon surface at 600 °C provides a more uniform distribution of sulfur throughout the GAC pore structure than achieved by conventional condensation techniques, yielding improved performance.

## INTRODUCTION

Numerous studies have documented the pathways of trace contaminants through coal-fired power plants[1-4]. Lack of mass closure for Hg, Se, Cl, and Br indicates that these elements exist entirely in the gas phase upon exiting the combustion zone, and pass unaffected to the smokestack[1]. Numerous studies have shown that the best available control technology for particulate pollution abatement (high-efficiency electrostatic precipitator) has virtually no impact on the release of vapor-phase trace elements to the atmosphere[1,3-5]. The estimated quantity of mercury released globally from coal combustion is 3000 metric tons per year[5]. Gaseous mercury emissions exist in both the elemental and oxidized ($Hg^{2+}$) forms. Chu and Schmidt[6] have determined that the percent of oxidized mercury in flue gases is a function of the coal type and composition. By quantifying the speciation of mercury in flue gases Prestbo and Bloom[7] reported that particulate forms of mercury generally constitute less than 5% of the total mass of mercury emitted.

The deposition of mercury following discharge to the atmosphere causes some local, but mostly regional impacts. Klein and Russel[8] showed that the soil around a Michigan power plant was enriched with Cd, Co, Cr, Hg and Ni, with contaminant concentration gradients reflecting the prevailing wind patterns. Hall et al.[9] found that the elemental $Hg^0$ will add to the atmospheric background concentration, while the divalent gaseous and particle-associated mercury will have a tendency to deposit within the region where it is emitted.

Increased levels of mercury in the environment are of particular concern due to well documented food chain transport and bioaccumulation of mercury and its forms[10]. Mercury is highly toxic to algae, fungi and seed plants. Mercury tends to accumulate in the lower stem areas rather than in the upper photosynthetic areas. Mercury is a cumulative poison in animals since there is no known homeostatic mechanism for regulating mercury concentration in tissues. Mercury is also a potent neurotoxin that is capable of causing irreversible damage to the central nervous system, or even death. Metabolism and degree of toxicity of mercury to animals is a function of several factors: chemical form, route of entry, duration of exposure, and dietary content of interacting elements, especially selenium. Mercury vapors can cause bronchitis, interstitial pneumonia, circulatory collapse, renal failure and dermatitis, while mercury salts can cause anorexia, memory loss, weight loss and gingivitis. Methylmercury causes paresthesia, hearing loss, ataxia, peripheral vision loss and cerebral disease[11].

Regulatory initiatives and increased public concern regarding elevated levels of mercury in the environment have stimulated research efforts to develop technologies for mercury emission control. Although there are currently no regulations for mercury emissions from electric utilities, the Clean Air Act Amendments of 1990 (Title III, Section 112[b][1]) (CAAA) require major sources to use the best available control technology (BACT), and require the U.S. Environmental Agency (EPA) to perform a study of mercury emissions.

Activated carbon adsorption is a technology that offers great potential for the control of gas-phase mercury emissions. Sinha and Walker[12] demonstrated that the capacity of sulfur impregnated carbons greatly surpassed the virgin carbons at 150 °C due to chemical adsorption of mercury

(through formation of mercuric sulfide) on the carbon surface. Matsumura[13] found that iodized and oxidized activated carbons adsorb 20-160 times more mercury than the untreated variety. Metzger and Braun[15] determined that 5% iodine impregnated activated carbon was an excellent adsorbent for elemental mercury, with the adsorptive capacity greater than 5 mg/g at temperatures ranging from 20 to 180 °C. Otani et al.[14] found that increased sulfur impregnation up to 13.1 wt. %, did not have a detrimental effect on elemental mercury adsorption at low temperatures (36 °C), as reported by Sinha and Walker[12]. Otani et al.[14] suggested that the contradicting results are related to surface area reduction resulting from different impregnation methods and activated carbon types. They also found that a portion of the sulfur impregnated on the activated carbon surface is chemically adsorbed, and not available to react with mercury to form mercuric sulfide. Krishnan et al.[15] demonstrated that the virgin activated carbons adsorbed less mercury with increased temperature, and that heat pretreatment with clean nitrogen at 140 °C destroyed active sites, reducing the adsorptive capacity further still. Livengood et al.[16] showed that the adsorption capacity of sulfur impregnated carbon decreased with an increase in temperature from 55 to 90 °C.

## MATERIALS AND METHODS

Three types of activated carbons were used in this study. Two of the carbons, Filtrasorb-400 (F-400) and HGR were supplied by the manufacturer (Calgon Carbon Corporation, Pittsburgh, PA) in 12x40 and 8x12 U.S. Mesh sizes, respectively. The third type, F-400S, was produced by contacting F-400 carbon with excess amount of sulfur in a pure nitrogen atmosphere at 600 °C. The sulfur contents of F-400, F-400S, and HGR were 0.76, 7.61, and 9.24 wt. %, respectively. The particle size used in this study was 60x80 U.S. Mesh size.

A schematic representation of the experimental setup is shown as Figure 1. By varying temperature of mercury permeation cell and nitrogen flow rate, a wide range of mercury concentrations were generated. The impinger solution used for absorbing gas-phase mercury was prepared with 1.5% potassium permanganate in 10% sulfuric acid as described by Shendrikar et al.[17] Quantification of elemental mercury in the gas phase was performed at a wavelength of 253.7 nm using a Perkin-Elmer Model 403 atomic absorption spectrophotometer (AAS) (Perkin-Elmer, Norwalk, CT) fitted with 18-cm hollow quartz gas cell (Varian Australia Pty. Ltd., Mulgrave, Victoria, Australia). Vapor-phase mercury detection limit for the analytical system used in this study was 1.8 $\mu g/m^3$.

Breakthrough curves were generated using a 3/16 inch stainless steel column charged with 100 mg of activated carbon. The bed was secured in the adsorber by two 200 U.S. Mesh size stainless steel screens. The adsorber was operated in the downflow mode to minimize the potential for fluidization of the packed bed. The influent gas and activated carbon temperatures were regulated by placing the adsorber in a temperature controlled oven. With both the mercury generation device and adsorber off-line, clean nitrogen was passed through the AAS cell for 30 minute warm-up period. Once the lamp output was stabilized and AAS zeroed, the mercury generation device was placed on-line, and the oil bath temperature adjusted to generate the desired mercury concentration. The gas flow rate was adjusted to 0.97 L/min and the absorbance from the AAS was recorded following a 2 hour equilibration period. The adsorber was then placed on-line and the effluent mercury concentrations were continuously monitored until complete breakthrough. Several blank runs with no carbon in the adsorber that were performed at temperatures ranging from 25 -140 °C using an influent mercury concentrations in the range of 25-115 $\mu g/m^3$ revealed that no uptake or transformation of elemental mercury was facilitated by the stainless steel reactor or support screens.

## RESULTS AND DISCUSSION

Figure 2 summarizes the adsorptive capacities measured for F-400 activated carbon at different temperatures. The increase in the slope of the isotherm lines with an increase in temperature shows that bonding of mercury to the carbon surface decreases with an increase in temperature. Only a single data point is shown at 200 °C because no adsorptive capacity was detected at the next lower influent concentration increment of 55 $\mu g/m^3$. The pronounced effect of temperature on the adsorptive capacity of F-400 GAC for elemental mercury indicates that the adsorption mechanism is physical in nature.

A series of experiments was conducted to determine the adsorptive capacity of sulfur impregnated (HGR) activated carbon as a function of adsorber temperature. The influent mercury concentration was maintained at 55 $\mu g/m^3$ in all cases while the adsorber temperature was 25, 50, 90, and 140 °C. Figure 3 indicates that the adsorptive capacity of HGR carbon for mercury increases with an increase in temperature. However, this figure accounts only for the elemental form of mercury in the adsorber effluent as detected by the AAS. A separate experiment was performed to simultaneously monitor the effluent from an adsorber maintained at 90 °C for elemental and total mercury. The elemental form ($Hg^0$) was constantly monitored by AAS output, and the total mercury concentration was determined by trapping the gases in an impinger train at various time increments. As illustrated in Figure 4, complete breakthrough was achieved for total mercury, while

elemental mercury reached equilibrium effluent concentration at $C/C_0$ equal to 0.6. The difference is attributed to the presence of mercuric sulfide in the adsorber effluent. Once a critical concentration of mercuric sulfide is formed on the surface of the GAC, desorption of mercuric sulfide occurs, forcing the product (HgS) into the effluent gas stream with the desorption process being more pronounced at 90 °C than at 20 or 50 °C.

Figure 5 compares the breakthrough characteristics of HGR GAC at 25 and 140 °C. As is apparent from this figure, after 8 hours into the experiment, the effluent from the adsorber operated at 140 °C reached complete breakthrough, while the effluent from the adsorber operated at 25 °C reached equilibrium at $C/C_0$ equal to 0.75. Experimental investigations of sulfur loss from the carbon surface upon exposure to nitrogen gas at various temperatures revealed that the low adsorptive capacity of HGR GAC exhibited at 140 °C can not be the result of sulfur loss form the carbon surface. However, this difference in behavior may be attributed to the fact that both physisorption and reaction with sulfur contribute to mercury uptake at 25 °C while only the reaction with sulfur could be occurring at 140 °C. Another possible explanation for the observed behavior is that the rate of HgS formation on the surface of the sulfur impregnate is much higher at 140 than 25 °C so that the HgS would quickly blind the sulfur surface and prevent any further mercuric sulfide formation, which results in complete breakthrough.

Figure 6 compares the adsorptive characteristics of F-400S to that of HGR and F-400 at 25 °C and an influent mercury concentration of 115 $\mu g/m^3$. As is apparent from this figure, F-400S performed much better than HGR and F-400. The superior adsorptive capacity of F-400S over HGR can not be explained by sulfur content on the GAC surface since F-400S contained 7.61 wt. % sulfur while HGR contained 9.24 wt. % sulfur. It is hypothesized that the higher adsorptive capacity of F-400S is the result of improved sulfur distribution throughout GAC surface. The sulfur in the HGR pore is most likely deposited by condensation as a slug deeply imbedded in the pore. Since the sulfur in the case of F-400S carbon is chemically bonded to the surface, it is more evenly distributed over the entire surface area. Although HGR carbon has higher sulfur content as compared to F-400S, the mercury-sulfur reaction on the surface of the HGR carbon is limited by the rate of diffusion of mercuric sulfide from the surface into the sulfur mass.

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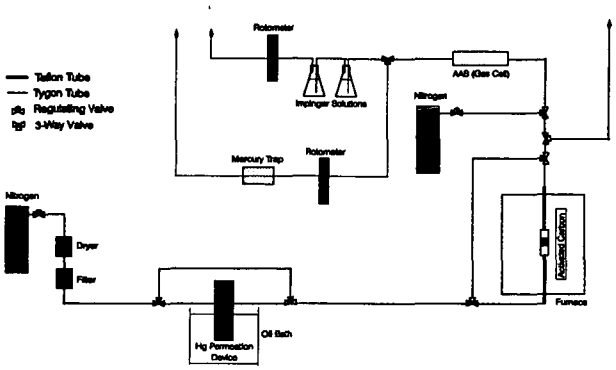


**Figure 1**. Schematic representation of the experimental system

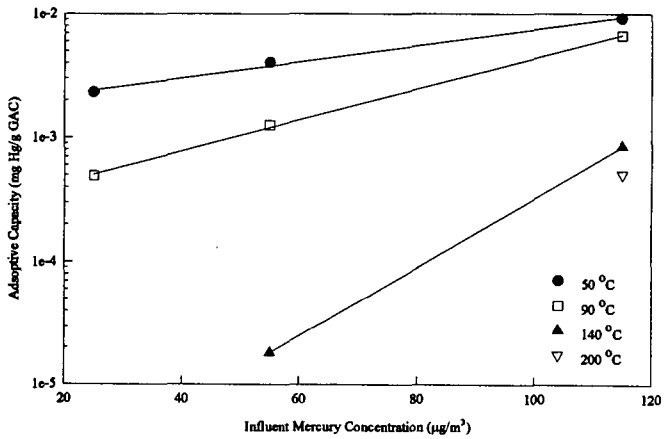


**Figure 2**. Adsorptive capacity of F-400 GAC for vapor-phase mercury

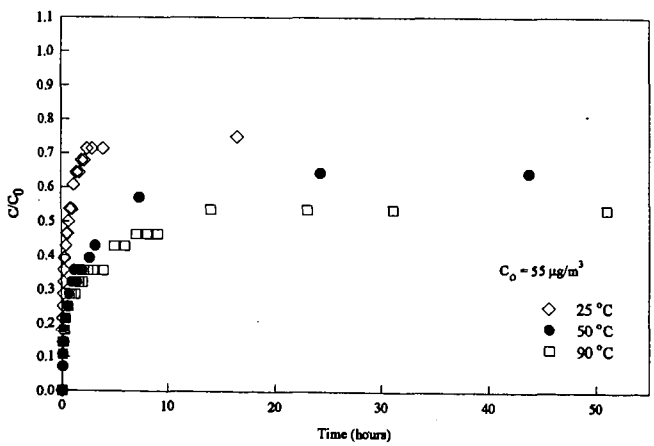


**Figure 3**. Effect of temperature on mercury breakthrough from HGR adsorber

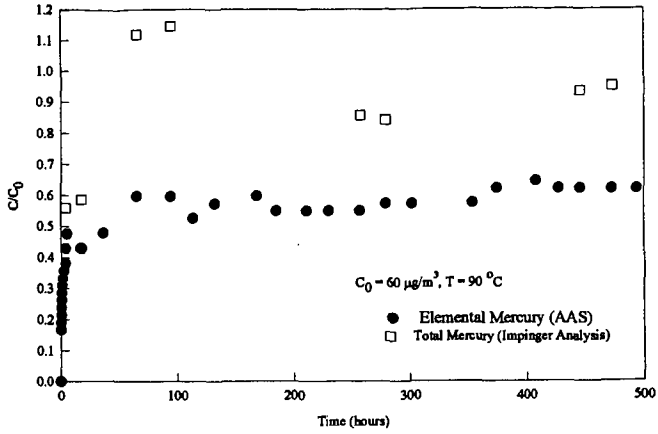


**Figure 4**. Elemental and total mercury breakthrough from HGR adsorber

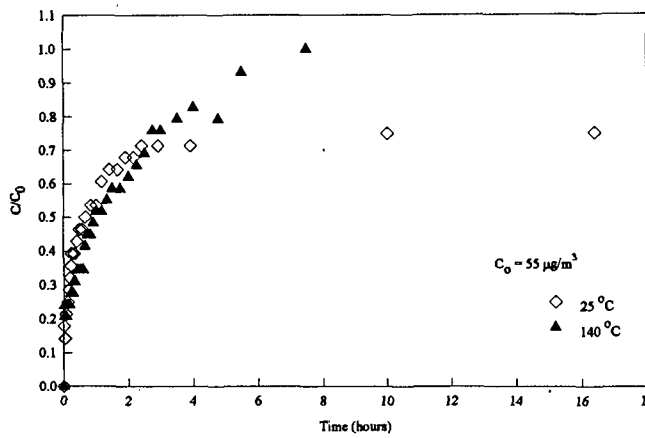


**Figure 5**. Breakthrough of mercury from HGR adsorber at 25 and 140 °C

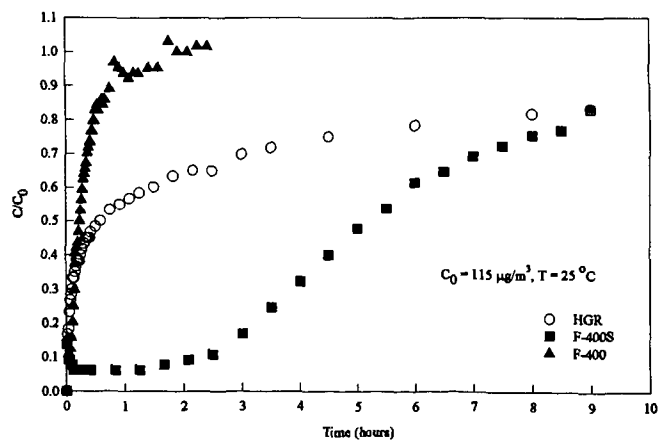


**Figure 6**. Removal of mercury by F-400, HGR and F-400S activated carbons

# MERCURY REMOVAL FROM COMBUSTION FLUE GAS BY ACTIVATED CARBON INJECTION: MASS TRANSFER EFFECTS

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Keywords: Mercury, Activated Carbon, Flue Gas and Mass Transfer

## INTRODUCTION

The Clean Air Act Amendments of 1990 listed 189 substances as hazardous air pollutants, of which 37 substances have been detected in power plant emissions. Of the 37 hazardous air pollutants, 11 are trace metal species. Mercury is trace metal species of greatest concern because of perceived risks from its environmental release and because it is present mainly in the vapor form and is not captured effectively by existing particulate removal systems.

Carbon-based processes (both direct injection and fixed-bed) have been developed for control of mercury emission from municipal- and hazardous-waste incinerators. Existing data from the incinerators provide some insight on mercury control, but these data cannot be used directly for coal-fired utilities because mercury concentration, species, and process conditions differ greatly[1]. For example, municipal solid waste (MSW) mercury concentrations ( 200 to 1000 $\mu g/m^3$) are one to two orders of magnitude higher than for coal combustion sources which contains typically 5 to 10 $\mu g/m^3$.

Injection of activated carbon upstream of a particulate control has the potential of providing a low-cost option for control of mercury emissions from utility flue gas[1]. In several bench[2-7] pilot and full-scale tests[8-10] of the method, the influence of carbon type[2-4,10], carbon structure[3-4] and carbon surface chemistry[2,4,5,7], injection methods (dry or wet)[10], amount of carbon injected[8-10], and flue gas temperatures[8-10] on mercury removal have been examined. The low concentrations of mercury in the flue gas, and limited exposure time (3 seconds) of the sorbent, generally required large amounts of activated carbons in these sorbent injection tests. To achieve high Hg removal (>90%), the required ratio of carbon to mercury (C/Hg) in the flue gas has generally (on weight basis) been found to be 3,000-20,000, depending on the process conditions. Tests have shown that the carbon to mercury ratio in MSW incinerators is more than an order of magnitude lower than that necessary to achieve similar mercury removal in coal combustors.

The high C/Hg ratio could be a result of either mass transfer limitation or low mercury capacity of carbon due to the extremely low concentration of mercury in the flue gas, or the low reactivity of the carbon. To reduce the operating cost of the carbon injection process, either a more efficient sorbent that can operate at a lower C/Hg ratio, or a lower-cost sorbent, or both is required. An understanding of physical and chemical processes that affects mercury removal from flue gas and a systematic sorbent development study would be required to develop an efficient, cost effective carbon injection process for removal of mercury from coal-fired utility flue gas.

The work presented here represents phase 1 of an ongoing EPRI and Illinois Clean Coal Institute funded research program to develop a low-cost, high efficiency sorbent for mercury removal. In this paper the influence of both film and intraparticle mass transfer on mercury removal in the carbon injection process are described.

## MASS TRANSFER CALCULATIONS

### Film Mass Transfer.

In absence of internal (intraparticle) diffusion, the equation describing the transfer of mercury molecules from the bulk flue gas to the surface of carbon per unit interfacial area is:

$$N = k_g (C_g - C^*) \tag{1}$$

where N=mass flux ($g/cm^2 * s$); $k_g$ is mass transfer coefficient (cm/s); $C_g$ are the mercury concentration ($g/cm^3$) in the bulk flue gas and and C* is the mercury concentration in equilibrium with the adsorbed mercury on the carbon surface. Assuming the interfacial area per unit volume in the duct is a/V, the flux per volume of the duct will be:

$$N = k_g \frac{a}{V} (C_g - C^*) \tag{2}$$

where a is the total interfacial area in the duct ($cm^2/cm^3$) and V is the total volume of the duct ($cm^3$) and Cg-C* is considered as the driving force for mass transfer.

The typical mercury concentration in the utility flue gas is about 10 $\mu g/Nm^3$ and usually 90% removal is required. Typically, the particle size of powdered activated carbon ranges between 1 and

60 μm. When injected into the flue gas, the fine carbon particles will suspend and flow with the gas stream. The relative velocity between the particles and the flue gas is practically zero. If the carbon particles are well dispersed and do not agglomerate during the process, the mass transfer coefficient at the gas-solid interface could be calculated by the following equation:

$$\frac{k_g d_p}{D_{Hg}} = 2 \tag{3}$$

where $d_p$ = particle size (cm) and $D_{Hg}$= diffusivity of the mercury molecule in flue gas ($cm^2/s$). Equation (3) shows that the mass transfer coefficient $k_g$ increases with decreasing carbon particle size. Any attempts to introduce turbulence to the flow may not have any significant effects on the mass transfer coefficient.

The value reported in the literature for the diffusivity of mercury in air at 341 °C is $D_{Hg}$= 0.473 $cm^2/s$ which can be corrected to the flue gas temperature (140 °C), $D_{Hg}$= 0.261 ($cm^2/s$). Substituting this value into equation (3) gives :

$$k_g = \frac{2D_{Hg}}{d_p} = \frac{2\times 0.261}{d_p} = \frac{0.522}{d_p} \quad (cm/s) \tag{4}$$

If no strong turbulence or back mixing occurs in the duct, the gas-solid phase can be modeled as a plug flow system. The mass balance equation for a plug flow system is:

$$k_g \frac{a}{V}(C_g - C^*)Sdz = -F_g dC_g \tag{5}$$

where S is the cross section area of the duct ($cm^2$), $F_g$ is the flue gas flow rate ($Nm^3/s$) and dz is the differential length of the duct (cm).

To examine the role of film mass transfer (the maximum mass transfer flux), assume $C^* << C_g$ at all positions in the duct ( this means that mercury adsorption capacity of the carbon and the carbon reactivity are not limiting the mass transfer rate). Equation (6) is obtained by integrating equation(5) using the following boundary conditions:

At the entrance: z=0, $C_g=C_0$

At the outlet: z=L, $C_g=C_g$

$$\ln\left(\frac{C_0}{C_g}\right) = k_g \frac{a}{V} \frac{SL}{F_g} \tag{6}$$

where L is the length (cm) of the duct and $SL/F_g$=t is the residence time of carbon particles in the duct. For 90% mercury removal, $C_g=0.1C_0$ and Equation (6) can be rearranged to solve for the minimum interfacial area:

$$\frac{a}{V} = \frac{2.303}{k_g}\frac{F_g}{SL} = \frac{2.303}{0.522}\frac{d_p}{t} = 4.412\frac{d_p}{t}(cm^2/cm^3) \tag{7}$$

This relationship provides the minimum activated carbon interfacial area required by film mass transfer to remove 90% of the mercury from one $Nm^3$ of utility flue gas.

Because only the external surface area of carbon particles serves as the gas-solid interfacial area the minimum interfacial area needed for mass transfer implies that a certain minimum amount of carbon is required to achieve the desired mercury removal. The minimum amount of carbon and thus the minimum ratio of carbon/mercury can be calculated as follows.

For spherical particles the external surface area per gram of activated carbon is:

$$\frac{\pi d_p^2}{\frac{1}{6}\pi d_p^3 \rho_c} = \frac{6}{d_p \rho_c} \tag{8}$$

where $\rho_c$ is the carbon particle density in g/cm$^3$. The amount of carbon required for mercury removal from one Nm$^3$ of utility flue gas therefore is:

$$(4.412\frac{d_p}{t})/(\frac{6}{d_p\rho_c})=0.7353\frac{d_p^2\rho_c}{t} \tag{9}$$

The carbon /mercury ratio can be calculated from the following relationship:

$$\frac{Carbon}{Mercury}=0.7353\frac{\rho_c d_p^2}{t\ (C_0-C_g)} \tag{10}$$

Assuming carbon particle size of 10 μm, residence time of 3 seconds, carbon particle density of 0.5 g/cm$^3$, inlet mercury concentration of 10 μg/Nm$^3$, and outlet mercury concentration of 1 μg/Nm$^3$, the carbon/mercury ratio is:

$$\frac{Carbon}{Mercury}=0.7353\times\frac{0.5\times(10\times10^{-4})^2}{3\times(10\times10^{-12}-1\times10^{-12})}=13611$$

This analysis indicates that a high C/Hg ratio is required when the carbon particle size is larger than 10 μm.

Equation (10) shows that the C/Hg ratio depends strongly on the particle size. Table 1 represents the carbon/mercury ratios required for 90% mercury removal under mass transfer limited conditions with activated carbon ranging in size from 1 to 10 μm (particle density of activated carbon $\rho_c$= 0.5g/cm$^3$ and contact time of 3 seconds were used).

Table 1 Carbon/mercury ratios for different carbon particle sizes

| Particle size (μm) | $k_g$ (cm/s) | Interfacial area (m$^2$/g) | Ratio of C/Hg * | |
|---|---|---|---|---|
| | | | Utility Flue Gas | MSW Flue Gas |
| 10 | 522 | 1.2 | 13611 | 227 |
| 5.5 | 949 | 2.18 | 4117 | 68 |
| 5 | 1044 | 2.4 | 3402 | 57 |
| 3 | 1740 | 4.0 | 1224 | 20 |
| 1 | 5220 | 12.0 | 136 | 2.3 |

* The inlet mercury concentrations for utility flue gas and MSW flue gas are 10 and 600 μg/Nm$^3$, respectively.

Equation (10) also shows that the C/Hg ratio depends on the mercury concentration in the flue gas ($C_0$-$C_g$). Usually, MSW incinerator flue gas has a mercury concentration of around 200-1000 μg/Nm$^3$ which is almost two orders of magnitude higher than that of utility flue gas. The C/Hg ratio, according to equation (10), for the MSW flue gas will be about two orders of magnitude lower than that of the utility flue gas. The last column of Table 1 lists the C/Hg ratios required for MSW flue gas. For example, the theoretical C/Hg ratio required for a MSW flue gas containing 600 μg/Nm$^3$ mercury is about 60 times lower than that of a utility flue gas containing 10 μg/Nm$^3$ mercury for the same level of mercury removal .

These calculated C/Hg ratios are the minimum needed and assumes mass transfer limitations. At low C/Hg ratios (such as for the MSW flue gas at a C/Hg ratio of 2.3), it is possible that the carbon will actually have reached its equilibrium capacity. Also at higher temperatures, most sorbents have very low capacity for mercury. Under these conditions much more sorbent than that predicted by mass transfer limitation will be needed.

**Intraparticle Diffusion**

Because diffusivities in mircroporous materials vary broadly, depending on the pore structure and pore size, it is difficult to estimate diffusivity when the diffusion is in the configurational range. Configurational diffusion only occurs when the micropore size is comparable to the molecular size of the adsorbate. In this study, calculations were made for a single spherical carbon particle dispersed in a flue gas. The carbon particle is exposed to a step change in mercury concentration at its external surface at t = 0 (corresponding to the injection location). The diffusion of mercury molecules into the carbon, assuming a constant effective diffusivity, can be described by:

$$\frac{\partial q}{\partial t} = D_{Hg}\left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\frac{\partial q}{\partial r}\right) \tag{11}$$

where $D_{Hg}$ is the mercury effective diffusivity in carbon particle and q(r,t) is the adsorbed phase concentration of mercury at position r ( inside the carbon particle) and time t. If the mercury concentration at the external surface of the particle remains constant, the following initial and boundary conditions apply:

$$q(r_c = \frac{1}{2}d_p, t) = q_0 \tag{12}$$

$$q(r,0) = 0, \tag{13}$$

$$\left(\frac{\partial q}{\partial r}\right)_{r=0} = 0 \tag{14}$$

The solution to this problem is given by[11]:

$$\frac{\bar{q}}{q_0} = \frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{4n^2\pi^2 D_{Hg} t}{d_p^2}\right) \tag{15}$$

where $\bar{q}$ , the average concentration of mercury inside the particle, is defined by:

$$\bar{q} = \frac{3}{r_c^3}\int_0^{r_c} q r^2 dr \tag{16}$$

and $m_t$ and $m_\infty$ are the uptakes of mercury at time t and t= ∞. When the fractional uptakes, $m_t/m_\infty$, are larger than 70%, the following simplified equation can be used:

$$\frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2}\exp\left(-\frac{4\pi^2 D_{Hg} t}{d_p^2}\right) \tag{17}$$

For a particle size of $d_p$=10 μm, t=3 s, and 90% mercury uptake ($m_t/m_\infty$=0.90), the mercury diffusivity in activated carbon can be calculated using Equation (17):

$$D_{Hg} = -\frac{d_p^2}{4\pi^2 t}\ln\left(\frac{\pi^2}{6}\left(1 - \frac{m_t}{m_\infty}\right)\right) = -\frac{(10\times10^{-4})^2}{4\times\pi^2\times3}\ln\left(\frac{\pi^2}{6}\times0.1\right) = 1.52\times10^{-8}(cm^2/s) \tag{18}$$

This value of diffusivity is in the range of configurational diffusion. The above calculations indicate that with a 10 μm activated carbon particle, the intraparticle diffusion will be important only when the pore diameter is about 3 Å, i.e., the molecular diameter of mercury.

It should be noted that in the above calculations it was assumed that the mercury concentration at the external surface of the particle remains constant. In the actual process, however, the mercury concentration in the flue gas decreases as the particles flow along the duct. If other conditions remain same, the diffusivity calculated under this situation is $1.32 \times 10^{-8}$ $cm^2/s$ which is comparable to the value calculated using Equation (17).

From the above calculations, it can be concluded that intraparticle diffusion is unlikely to be the controlling step in the carbon injection process so long as the micropore size of the activated carbon is larger than around 3 Å, which is true for most of activated carbon.

## DISCUSSION

Assuming that the adsorption of mercury from flue gas is mass transfer limited provides an indication of the maximum mercury efficiency possible for a specific amount of sorbent injected or an indication of the minimum amount of sorbent needed to achieve a specific mercury removal efficiency. The analysis presented in this paper indicates that under certain carbon injection conditions, mercury removal from coal-fired flue gas is film mass transfer controlled. For example,

Miller et al.[5] used a C/Hg ratio greater than 3000 for an activated carbon with a weight-averaged particle size of 5.5 μm, to remove about 90% mercury from a flue gas. In the same study, for an iodine-impregnated activated carbon with a weigh-averaged particle size of 3 μm, the C/Hg ratio was about 1000. Such C/Hg ratios are comparable to those listed in Table 1.

Full-scale tests of carbon injection process in MSW flue gas also confirm the results shown in Table 1. Licata et al.[9] reported that the equilibrium mercury capacity of an activated carbon used in their tests was about 0.33 gHg/gAC which corresponds to a C/Hg ratio of 3 (temperature was not mentioned). However, in full-scale MSW tests with the same carbon, a C/Hg ratio of more than 300 was used to reduce mercury concentration in the flue gas from 600 to 70 μg/Nm$^3$ at 135 °C. This ratio corresponds to 0.0033 gHg/gAC which is only 1% of the equilibrium capacity of the carbon. In still another field test, White et al.[10] found that carbon injection methods (dry or wet) had a significant effect on the mercury removal while the type and surface chemistry of the activated carbon had not. These data suggested that mass transfer was controlling the mercury removal.

For conditions where mercury adsorption is mass transfer limited, measures should be taken to increase the mercury mass flux (from the bulk gas to the surface of carbon) rather than using a carbon with high capacity. To increase the mass transfer, either the mass transfer coefficient, $k_g$, or the interfacial area, a/V, should be increased. According to equation (3) the mass transfer coefficient increases with decreasing carbon particle size. Reducing carbon particle size also increases the interfacial area, without increasing carbon dosage. The most effective way to reduce the C/Hg ratio is therefore to decrease the carbon particle size. This is clearly shown in Table 1; when the carbon particle size is reduced from 10 μm to 1 μm, the C/Hg ratio is reduced from 13,611 to about 136.

Mass transfer limits only apply when the carbon has sufficiently high reactivity and capacity. When the operating temperature of the process is high, e.g. >180 °C, and the level of mercury removal is high, e.g. 95%, then the mercury capacity of carbon may become limiting. In this case, significantly larger amounts of carbon may be needed unless better carbon (larger capacity and high reactivity) can be produced.

## CONCLUSIONS

- The minimum amount of carbon needed to achieve a specific mercury removal efficiency via sorbent injection can be predicted by assuming mass transfer limitations.
- Mercury removal effectiveness can be increased by decreasing the size of the carbon injected, increasing the residence time, or the amount of carbon injected.
- Intraparticle diffusion is not important because of the small carbon sizes normally used for injection.
- If mercury removal is limited by the reactivity and capacity of the carbon (i.e. not mass transfer limited), then significantly more carbon than predicted by mass transfer limitations may be needed for effective mercury removal unless the reactivity and capacity of the carbon can be improved through structural and surface chemistry changes.

## ACKNOWLEDGEMENT

This research is supported by the Electric Power Research Institute and Illinois Clean Coal Institute.

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