

FIXED BED ACTIVATED COKE FILTERS FOR THE CONTROL OF TOXIC METALS AND ORGANICS FROM WASTE INCINERATORS

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Introduction

In late 1991 the first full-scale activated coke/carbon filter following a waste incineration plant went into operation [1, 2, 3]. After successful start-up the filter has been in continuous operation. In summer and fall 1992 extensive measurements and analysis was done to test the performance of the technology. The flue gas treatment system of the hazardous waste incineration unit of the Rohstoff Rückgewinnungszentrum Ruhr (RZR) in Herten, Germany, consists of an ESP, followed by a two-stage wet scrubbing system operated with lime milk as a neutralizing agent. As reported earlier [1, 2] the system was retrofitted with a two-stage activated carbon filter for flue gas polishing as well as for NO_x reduction. In the first stage hearth oven coke (HOC) made from lignite coal is employed to adsorb all pollutants remaining in the flue gas after the wet scrubbers. In the second stage form activated carbon (FAC) made from hard coal is used as a catalyst. The catalytic capabilities of FAC are utilized to reduce NO_x in the presence of NH₃ at a temperature of around 120°C (250°F). A detailed description of the plant design was presented in earlier papers [1, 2]. - Both units provide a capacity of 125 tpd, generating a flue gas volume flow rate of 65,000-70,000 scm/h.

Operational Parameters During Sampling

During the sampling period about 2.5-3 t/h of solid hazardous waste were burned. Additionally 2.5-3 m³/h of hazardous sludge waste were fed into the rotary kiln. Hence the unit was operated at 100 %-110 % capacity. The burned waste was a mix of halogenated solvents, waste oil sludges, paint sludges, chemical laboratory waste, hospital waste and various solid wastes from industrial production. The metal content of the waste was not determined. The contaminated activated coke and carbon extracted from the filter was added regularly as well. The boiler produced on the average 23 t/h of high pressure steam (320°C, 32 bar). The sampling, as well as the direct measurements, were performed between June 23rd and 26th, 1992, and July 22nd and 23rd, 1992.

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Methods of Sampling and Analysis

The samples were taken from the outlet duct after the ACR-unit. The diameter of the duct is 1.60 m, the cross-sectional area is 2.01 m². The location for sampling was determined to be representative and in compliance with the technical guideline VDI 2066. Isokinetic sampling was performed.

1. Acid Gases and NH₃

In order to measure the acid gases and NH₃ a glass probe of 50 cm length was inserted into the duct. It was fixed and gas tight sealed in the flange and connected to a two-stage impinger apparatus. The impingers were filled with a 3% hydrogen peroxide solution for the absorption of SO₂, Cl⁻, F⁻ and NH₃. After the impingers the gas was led through a demister flask in order to protect the following gas pump and gas meter. The pump was adjusted to a flow rate insuring isokinetic sampling. Each sample taken consisted of 100 liters of flue gas. At the end of each sampling the glass probe was rinsed into the impingers to insure that eventually condensed ammonia salts would be included in the analysis.

For HCl, HF, SO₂ and NH₃ a total of 8 samples were taken and analyzed. The samples were taken on 2 consecutive days, meaning 4 samples per day. The sampling time was 30 minutes per sample.

For the determination of fluoride with an ionsensitive electrode the absorption solution was diluted 1:1 with a buffering solution of pH 5.5. The fluoride content was determined against a calibration curve. The analysis for SO₂ was performed by titration of the solution with barium permanganate solution. Ion chromatography was used to analyze for Cl⁻, Br⁻ and SO₂.

In order to analyze for NH₃ the absorption solution was distilled under alkaline conditions to separate the ammonia. The final analysis for NH₃ was done photometrically. All values given in this paper are corrected to standard temperature (0°C) and pressure (1,013 hPa) (STP).

Table I summarizes the results for inorganic acids and ammonia.

Table I: Results of Analysis for SO₂, HCl, HF, NH₃, Bromine, and Iodide. All values given in mg/m³ at STP corrected to 11% O₂, sampling time was 30 minutes per sample

| | SO ₂ | HCl | HF | NH ₃ | Br | I |
|-------------|-----------------|------|------|-----------------|------|------|
| Sample 1 | 0.11 | 0.45 | 0.03 | 0.12 | 0.07 | 0.1 |
| Sample 2 | 0.20 | 0.63 | 0.02 | 0.11 | 0.07 | 0.1 |
| Sample 3 | 0.14 | 0.79 | 0.03 | 0.17 | 0.15 | 0.22 |
| Sample 4 | 0.47 | 0.84 | 0.02 | 0.33 | 0.13 | 0.19 |
| Average 1-4 | 0.23 | 0.68 | 0.02 | 0.18 | 0.11 | 0.15 |

2. Metals

The same sampling location for acid gases was used to sample metals as well. The sampling train was modified to fit the specific needs. Therefore a titanium probe was connected to the impingers by an unheated glass tube. As a first stage a glass wool filter was added to remove the particulate matter. In order to enhance condensation the impingers were submerged in an ice bath. Again the gas pump was adjusted to insure isokinetic sampling. Two sampling trains were used in parallel. In one train the absorption solution was diluted nitric acid. In the second train potassium permanganate was added to the nitric acid in order to suit the special needs for the absorption of mercury. Again the probe and the glass tube were rinsed to account for possible condensation.

To prepare for the analysis of the particulate matter the collected dust and the quartz wool were homogenized and extracted with hydrofluoric acid, nitric acid and perchloric acid.

Due to the high vapor pressure of mercury the particulate matter of the second train was extracted separately with nitric acid in a thick wall glass flask. The contents of the impingers were also extracted with nitric acid and perchloric acid.

The analysis was performed using either atomic absorption spectrometry (AAS) or inductive coupled plasma atomic emissions spectrometry (ICP-AES).

In order to obtain representative values a total of 4 samples were taken on 2 consecutive days. The sampling time was 60 minutes per sample. The results obtained for the various elements are summarized in Table II.

3. Iodide and Bromide

Sampling and analysis for iodide and bromide was done similar to the method described for HCl and HF. The results of four analyzed samples are given in Table I. The sampling time was 30 minutes per sample.

4. Organics

The different types of organics require different types of analysis and therefore different types of sampling. The volatile halogenated hydrocarbons were sampled according to VDI method 3482. Two activated charcoal tubes were used in-line for the sampling. The activated charcoal was extracted with carbon disulfide. The analysis was done with a gas chromatograph with an electron capture detector (GC/ECD) based on external standards.

This method was modified for aromatics by adding a midjet-impinger prior to the activated charcoal tubes to remove condensate resulting from a high content of water vapor in the flue gas. The condensed aromatics collected in the impinger and the activated charcoal were also extracted with carbon disulfide. A methylsilicone coated quartz capillary column was used in the analysis with high resolution gas chromatography with a mass selective detector (HRGC/MSD). Quantification was also based on external standards.

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Table II: Results of Analysis of Heavy Metals and Other Elements. All values given in $\mu\text{g}/\text{m}^3$ at STP corrected to 11 % O_2 sampling time was 60 minutes per sample; < : actual values were below the given number

| Element | 1 | 2 | 3 | 4 |
|-----------|------|------|------|------|
| Cadmium | <0.5 | 0.9 | <0.8 | <0.7 |
| Thallium | <0.3 | <0.4 | <0.4 | <0.4 |
| Mercury | <0.9 | <1.1 | <0.7 | <0.9 |
| Antimony | <3 | 6 | <4 | <4 |
| Arsenic | <5 | <7 | <8 | <7 |
| Lead | <5 | 8 | <8 | <7 |
| Chromium | <3 | <4 | <4 | <4 |
| Cobalt | <3 | <4 | <4 | <4 |
| Copper | 4 | 5 | 5 | 15 |
| Manganese | <3 | 8 | 5 | <4 |
| Nickel | <3 | <4 | <4 | <4 |
| Vanadium | <3 | <4 | <4 | <4 |
| Tin | <3 | <8 | <4 | <8 |
| Selenium | <5 | <7 | <8 | <7 |
| Zinc | 10 | 23 | 26 | 19 |
| Beryllium | <0.5 | <0.7 | <0.8 | <0.7 |
| Silver | <3 | <4 | <4 | <4 |
| Aluminum | 257 | 97 | 278 | 93 |
| Iron | 22 | 41 | 120 | 52 |
| Boron | 52 | 27 | 46 | 28 |
| Sodium | 279 | 405 | 665 | 321 |
| Potassium | 52 | 104 | 99 | 60 |
| Magnesium | 16 | 29 | 29 | 36 |
| Barium | 6 | 11 | 15 | 10 |
| Silicon | 78 | 45 | 34 | 80 |
| Tellurium | <9 | <13 | <15 | <14 |

Chlorinated and brominated dioxins and furans, benzenes, phenols, biphenyls and PAHs were sampled with a special probe. The titanium probe contained a concentric quartz or glass tube. The sampled gas including the particulate matter and water vapor flowed through the tube. The tube was surrounded by cooling water to enhance condensation. The probe was connected to a glass flask for the collection of condensate followed by a XAD-2-sorbens tube. Following that, a conventional sampling train with a dryer/demister, gas pump, gas meter etc. followed. This sampling method is in compliance with VDI method 3499. The samples were extracted, cleaned and prepared for the HRGC/HRMS analysis following appropriate methods. Table III summarizes the results of the organics analysis from 2 samples. The sampling time was 500 minutes per sample.

Table III: Results of Analyses for Organics. All values at STP corrected to 11% O₂; sampling time was 500 minutes per sample;
<: actual values are below the given number

| Sample | | 1 | 2 |
|-------------------------------------|-------------------|--------|--------|
| PCDD | ng/m ³ | 0.0238 | 0.0261 |
| PCDF | ng/m ³ | 0.0222 | 0.0223 |
| TEQ (I-TEQ, incl. detection limits) | | 0.0009 | 0.0014 |
| PBrDD | ng/m ³ | 0.760 | 0.815 |
| PBrDF | ng/m ³ | 0.760 | 0.815 |
| PAH (EPA 610) | ng/m ³ | 6.282 | 4.146 |
| PCBz (Di-Hexa) | ng/m ³ | 3.2 | 1.8 |
| PCPh | ng/m ³ | 12.3 | 9.2 |
| PCB (Ballschmitter) | ng/m ³ | 10.4 | 10.4 |
| Benzene | µg/m ³ | <95 | <90 |
| Toluene | µg/m ³ | <95 | <90 |
| Ethylbenzene | µg/m ³ | <95 | <90 |
| p- und m-Xylene | µg/m ³ | <95 | <90 |
| o-Xylene | µg/m ³ | <95 | <90 |
| Dichloromethane | µg/m ³ | <160 | <150 |
| 1,1-Dichloroethane | µg/m ³ | <265 | <250 |
| Trichloromethane | µg/m ³ | 2 | 2 |
| 1,1,1-Trichloroethane | µg/m ³ | <1.1 | <1 |
| Tetrachloromethane | µg/m ³ | <1.1 | <1 |
| Trichloroethene | µg/m ³ | <1.1 | <1 |
| Tetrachloroethene | µg/m ³ | <1.1 | <1 |
| 1,1,1,2-Tetrachloroethane | µg/m ³ | <1.1 | <1 |
| 1,1,2,2-Tetrachloroethane | µg/m ³ | <11 | <10 |
| trans-1,2-Dichloroethene | µg/m ³ | <160 | <150 |
| cis-1,2-Dichloroethene | µg/m ³ | <160 | <250 |
| Dichlorobromomethane | µg/m ³ | <1.1 | <1 |
| Dibromochloromethane | µg/m ³ | <1.1 | <1 |

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5. Particulate Matter und Its TOC

The measurements of particulate matter were performed gravimetrically. The sampling was isokinetic. In all cases the particulate matter was below the detection limit ($<1 \text{ mg/m}^3$) thus no TOC could be determined. Considering that nearly 100% of the particulate matter can be expected to be activated carbon dust, the TOC would still be less than 1 mg/m^3 at STP corrected to 11% O_2 . The sampling time was 36 minutes per sample.

Conclusion

Based on the data obtained from the ACR-unit it is obvious that this technology represents the absolute state-of-the-art for flue gas treatment of waste incinerators. It is not in sight that lower emission values can be reached with any other flue gas treatment technology within the near future.

References

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