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Report: New reliable method for the measurement of chlorine in refuse-derived fuels through combustion experiments in a pilot plant

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The calorific values and the chlorine contents of refuse-derived fuels were measured in the pilot combustion plant (PCP) by means of combustion experiments followed by mass and energy balancing. This plant reaches an increased precision by measuring the integrated values throughout the whole experimental period of three hours, based on a fuel capacity of 10 kg per test, allowing a more reliable measurement of pollutants than for experimental analysis of only a few grams of the sample. The combustion experiments are shown for the verification of the quality of the chlorine balancing in the PCP. The test evaluation was carried out by balancing the inputs and outputs of chlorine in the mass streams, and the recovery rates for chlorine were determined. An emission pattern for the chlorine is described by the transfer coefficients and via the temporal fluctuation of the hydrogen chloride concentration in the flue gas. The results of the combustion experiments prove that the balancing via combustion experiments in the PCP provides reliable data on the chlorine concentrations in the fuels, and is a new and reliable method for measuring polluting chlorine in refuse-derived fuels.

Keywords: Waste-to-energy, chlorine, pollutant content, incineration/combustion, solid fuel, refuse-derived fuel (RDF)

Introduction

The laboratory measuring of calorific values and chlorine contents of various types of waste is difficult and imprecise due to the problematic representative sampling of waste, the necessary sample preparation and splitting, and the small amounts of samples taken for analysis. For this reason the *Fachgebiet Abfalltechnik* of the Institute for Water, Waste, Environment has built a pilot combustion plant (PCP) in which calorific values and contents of pollutants were determined by balancing the mass and energy of the combustion. This plant has a fuel capacity of 10 kg per experiment and thereby provides a much increased precision compared to laboratory analysis. The energy balancing has been significantly improved during the last years by modifying the PCP and has been used successfully since then (Friedel 2001, Seeger & Urban 2004).

Various combustion experiments have verified that the balancing via combustion experiments in the PCP is also suited for the measurement of pollutant contents. Flue gas,

flue dust and ashes were the main output streams and therefore had to be measured. Hydrogen chloride concentrations were measured continuously during the experiments and the chlorine contents in the flue gas and the ashes were analysed afterwards. The balancing allows a more reliable measurement of pollutants, especially chlorine. Integrated values are measured throughout the whole experimental period of three hours as opposed to spot sampling. Recovery rates for chlorine were assessed based on analyses of the outgoing mass streams, demonstrating the quality of balancing the combustion process used on different chlorine carriers.

To evaluate the corrosion behaviour of chlorine in the process it is also important to know the emission behaviour of various chlorine compounds, and whether chlorine remains in the combustion chamber, migrates into the flue gas or is transported into the deposit. Chlorine transfer coefficients for the various chlorine carriers in this combustion plant were therefore determined and temporal fluctuation of the

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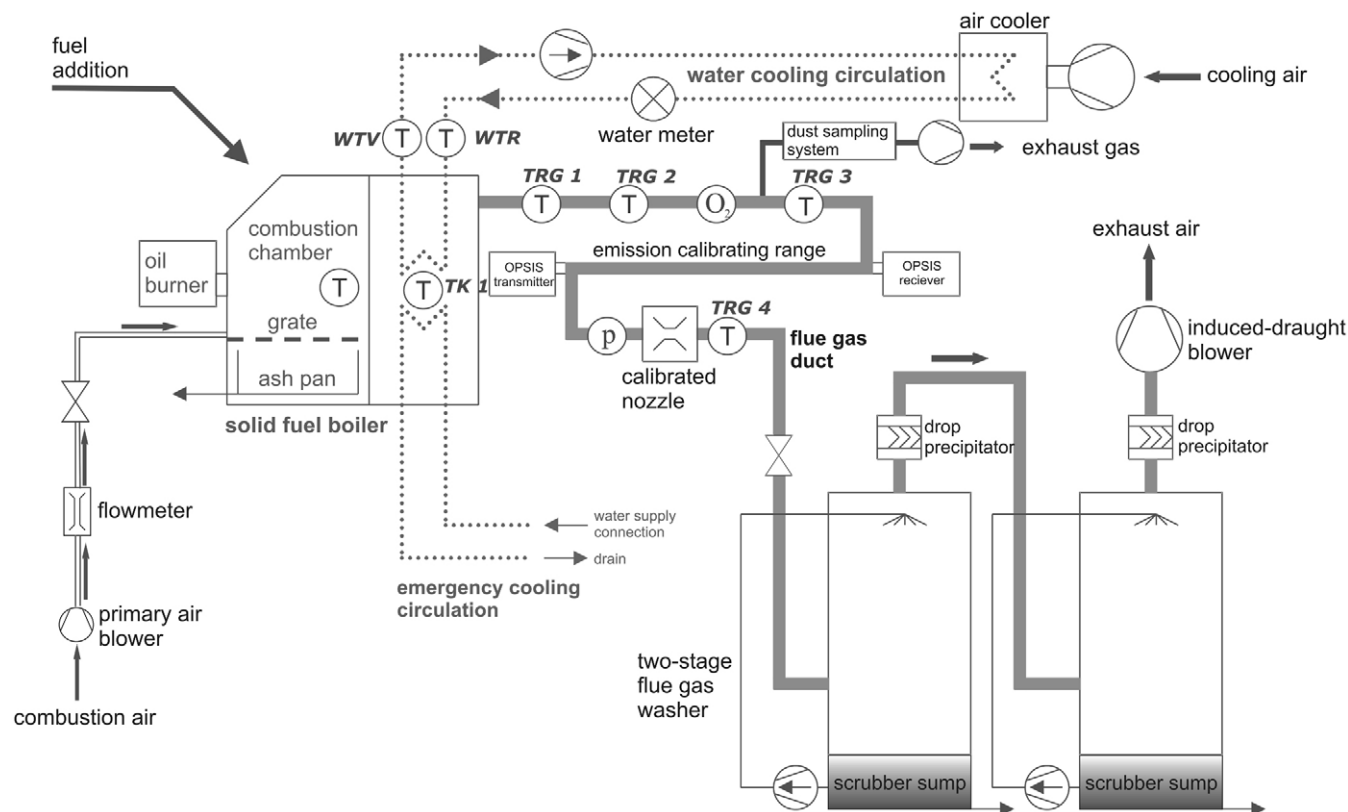


Fig. 1: Current configuration of the pilot combustion plant (PCP).

hydrogen chloride concentration in the flue gas was examined.

Material and methods

Materials

The combustion experiments were executed in the pilot combustion plant (PCP) (Friedel 2001, Seeger & Urban 2004). The current configuration of the PCP is shown in Figure 1.

The main aggregate of the PCP is a solid fuel boiler with a supporting oil burner and a configuration power of 30 kW. The oil burner guarantees a temperature higher than 800°C within the combustion chamber. Fueling takes place semi-continuously at five-minute intervals. The plant contains the emission measuring system OPSIS for the measurement of gaseous pollutant components in the generated flue gas. The flue dust concentration is determined by an automatic dust sampling system. Before the exhaust air is drained over a chimney, the pollutants in the flue gas are removed.

Methods

Predefined fuel mixtures were used in the combustion experiments. PVC or NaCl were used as organic or inorganic chlorine carriers and wood pellets as basic fuel. Chlorine levels were set between 5.2 and 6.0%. The fuel mixtures are shown in Table 1. Fuelling was carried out semi-continuously at five minute intervals with a total fuel mass of 7200 g per experiment.

The test evaluation was made by balancing the ingoing and outgoing chlorine mass streams. The wood pellets, as

Table 1: Mixture of fuel.

	Wood (%)	PVC (%)	NaCl (%)	Cl (%)
Wood/PVC	90.0	10.0	–	6.0
Wood/NaCl	92.3	–	7.7	5.2

well as the PVC and the NaCl, were used to quantify the chlorine input. Flue gas, flue dust and ashes were sampled as the main output streams.

During experiments in the PCP, chlorine was transferred into three output fractions which were examined regarding two aspects: the total chlorine recovery rates of the plant were determined to verify whether the PCP can provide a reproducible and reliable pollutant balance and if the transfer coefficients for the different fractions could be reliably determined and evaluated. In addition, the temporal fluctuations of the HCl concentration in the flue gas were examined.

The chlorine emission into the flue gas during the experiments in the PCP was compared to laboratory tests (Schirmer *et al.* 2003, Schirmer 2005). The transfer coefficients were not compared directly due to different boundary conditions of the experiments in the PCP and in the laboratory plant such as temperature, retention time, chlorine content in the fuel and S/Cl ratio. Instead, forecast transfer coefficients based on the laboratory results were calculated for the experiments in the PCP. These were compared with the transfer coefficients derived from the PCP experiments.

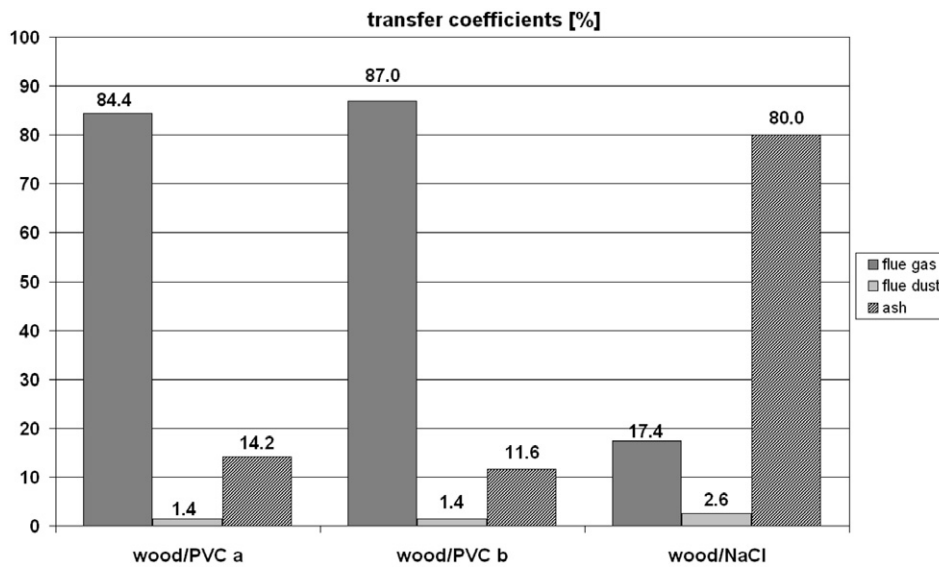


Fig. 2: Chlorine transfer coefficients of the experiments in the PCP.

Table 2: Chlorine recovery rates in combustion experiments in the PCP.

	Wood/PVC a	Wood/PVC b	Wood/PVC average	Wood/NaCl-5
Cl recovery (%)	98.1	92.6	95.4	96.7

Results and discussion

Chlorine recovery rates

The chlorine recovery rates are shown in Table 2. 95.4% of the used chlorine was recovered in the wood/PVC experiments and 96.7% in the wood/NaCl experiment. The high recovery rates of the used chlorine show that a reliable pollutant measurement is possible by balancing the combustion experiments in the PCP. The PCP can therefore be used successfully for the determination of chlorine in refuse-derived fuels of unknown composition.

Fate of chlorine

Figure 2 shows transfer coefficients based on the total output, determined for the three fractions flue gas, flue dust and ashes. During the wood/PVC experiments, 84–87% of chlorine passed into the flue gas and 11–14% of chlorine remained in dust and ashes. Flue gas is therefore the main chlorine output stream. The temperature in the combustion chamber during the experiments in the PCP averaged between 800 and 850°C. Due to the low thermal stability of PVC, the embedded chlorine is readily emitted at lower temperatures than the combustion temperature and a rapid conversion had to be expected in the PCP.

In the wood/NaCl experiment, 89% of the chlorine was derived from the NaCl. During the wood/NaCl experiment, 80% of the chlorine was found in the ashes and only 17% were transferred into the flue gas. Ash is the main output stream for chlorine from NaCl because chlorine from the salt bindings barely migrates into the flue gas at the set experiment temperature.

In Figure 3, the predicted transfer coefficients based on the laboratory tests and the actual determined transfer coef-

ficients in the PCP are shown. The results obviously correlate for the experiments with PVC as chlorine carrier as well as for the experiment with wood/NaCl.

The chlorine emissions over time are shown in Figures 4 and 5. During experiments with PVC addition, clear peaks can be identified for the HCl concentration which can be attributed to the semi-continuous fuel feed. During wood/PVC combustion, the HCl concentration rises immediately after each fuel feed and declines at the end of the interval.

In NaCl experiments, a temporal allocation of the fuel feeds is more difficult. The chlorine level in the flue gas is not con-

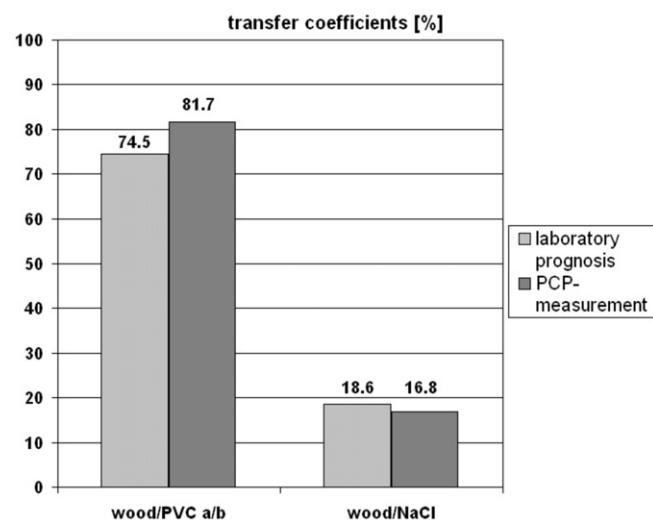


Fig. 3: Comparison of the transfer coefficients for chlorine into flue gas calculated as laboratory prognosis and the transfer coefficients measured during the experiments in the PCP (note: average of the wood/PVC-experiments).

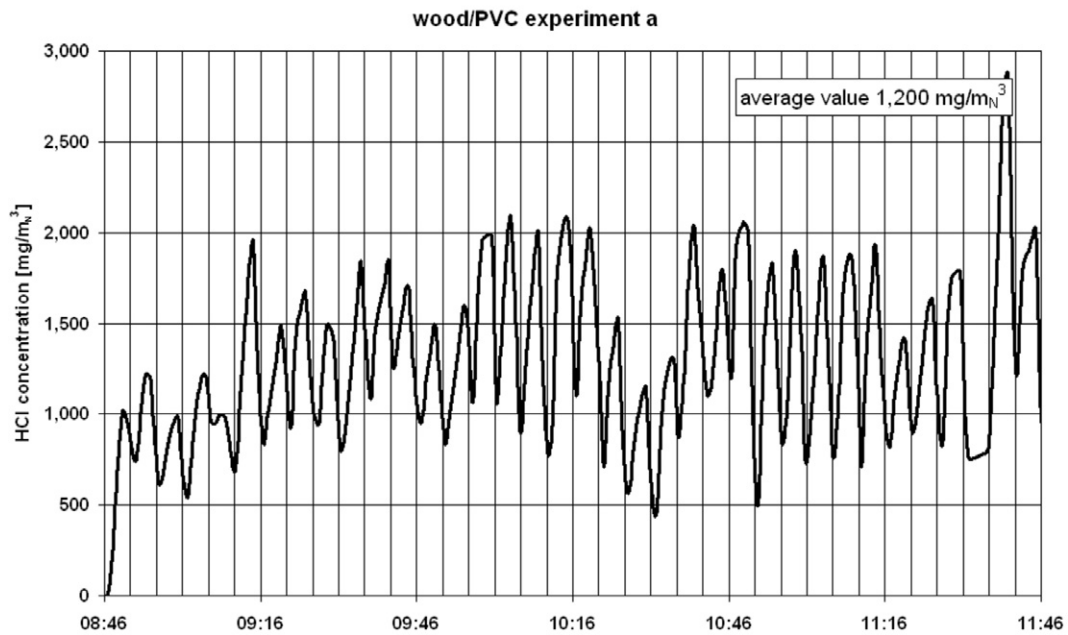


Fig. 4: Temporal fluctuation of the HCl concentration in the wood/PVC experiment (a).

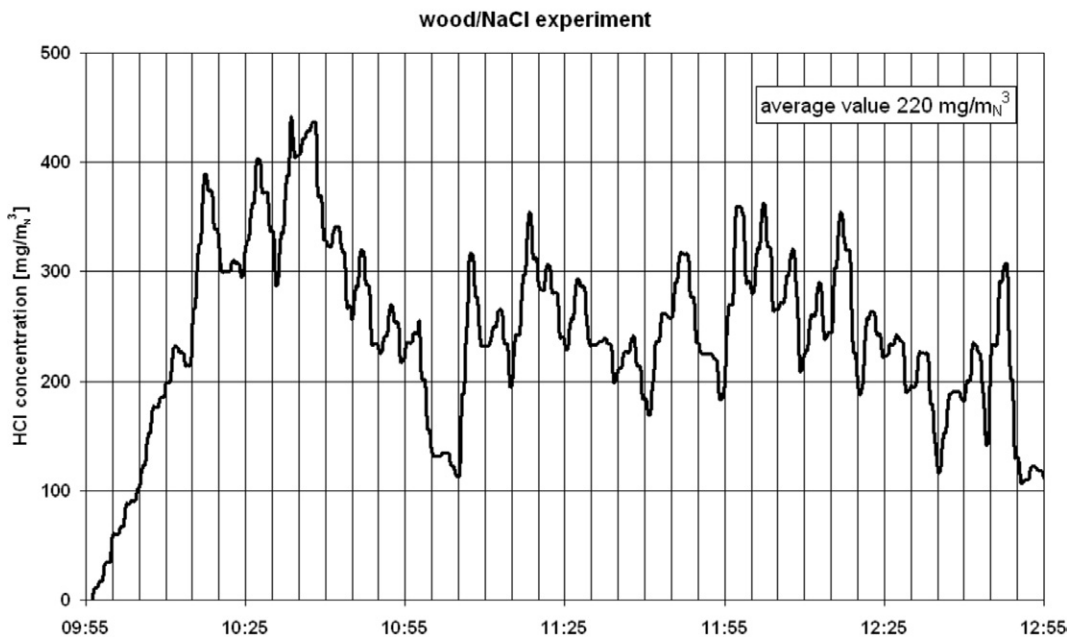


Fig. 5: Temporal fluctuation of the HCl concentration in the wood/NaCl experiment.

sistent throughout the whole test period. The chlorine of the NaCl is marginally mobilized and the HCl derives mainly from the wood pellets as basic fuel.

The fairly diverse emission behaviour of chlorine can also be illustrated by the average concentration of HCl in the flue gases. In the wood/PVC experiment, an average of 1200 mg m_N^{-3} was measured, more than five times higher than the average for wood/NaCl at 220 mg m_N^{-3} . Chlorine content was only about 1.2 times as large, however.

Conclusion

By combining results for the output streams flue gas, flue dust and ashes, high recovery rates for chlorine in fuels can

be achieved. Reasonable chlorine transfer coefficients could be determined using these results.

93–98% of the chlorine input was recovered in flue gas, flue dust and ashes. In the wood/PVC experiments, 84–87% of the chlorine was found in the flue gas, 12–14% in the ashes and only 1.4% in the flue dust. In the wood/NaCl experiment, 80% of the chlorine ended up in the ashes, 17% in the flue gas and less than 3% in the flue dust. The comparison of the PCP measurements with the forecast transfer coefficients from laboratory tests showed a good correlation. The emission behaviour of the chlorine can be described by the temporal fluctuation of the HCl due to intermittent input of fuel.

This research verifies that balancing of pollutants via combustion experiments in the PCP is a reliable method for pollutants measurement. This new method offers the opportunity to examine the pollutant contents of refuse-derived fuels

more precisely. It can therefore yield precious information for producers of refuse-derived fuels and also for plant operators responsible for cement works, coal-fired power plants or incinerators.

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