LUEHR FILTER

Single and multi-stage procedures for the gas treatment downstream incineration plants

Author:
Rüdiger Margraf

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1 Introduction

The dry and semi-dry chemisorption of acid crude gas components such as HF, HCl and SO_x, possibly with separation of dioxins / furans as well as Hg and/or Hg compounds and other heavy metals, gained increasing importance with regard to the range of applications of incineration plants. As a result of the further development of the sorption procedures applied in this connection, this technology became an effective, reliable and cost-effective alternative compared to e.g. the wet scrubbing system. In chapter 5 of the BVT-leaflet concerning the best available technologies for waste incineration (July 2005) these procedures are mentioned as best available technologies.

Table 1 shows the crude gas concentrations to be expected in the flue gas downstream boiler for different types of fuels. The wide range to be covered makes clear, that regarding the plant design and the additive powder selection, the plant constructor has to provide individual concepts that are tailored to the special needs of the corresponding application.

Fuel	approx. range HCl [mg/Nm³ dry]	SO_2 [mg/Nm³ dry]
Wood, grade A I - A IV	100 – 500	100 – 500
Sewage sludge	< 100	800 – 2,000
Domestic waste	750 – 2,500	250 – 1,000
RDF	750 – 4,000	500 – 3,000

Tab. 1: Concentrations of acid crude gases for selected fuels

In the following different process technologies are introduced. Special emphasis lies in this respect on the chemisorption of acid crude gas components. However, it should be mentioned as reservation, that beside the presented variants, further alternative solutions are available on the market, which are realised in practice.

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2 Procedures with utilisation of Ca-containing additive powder qualities
2.1 Dry sorption with gas conditioning
2.1.1 Process description

The base variant is shown in illustration 1. It mainly comprises the units fabric filter and
additive powder injection device. To improve the efficiency, they are often completed by
the component parts reactor with particle re-circulation and evaporative cooler.
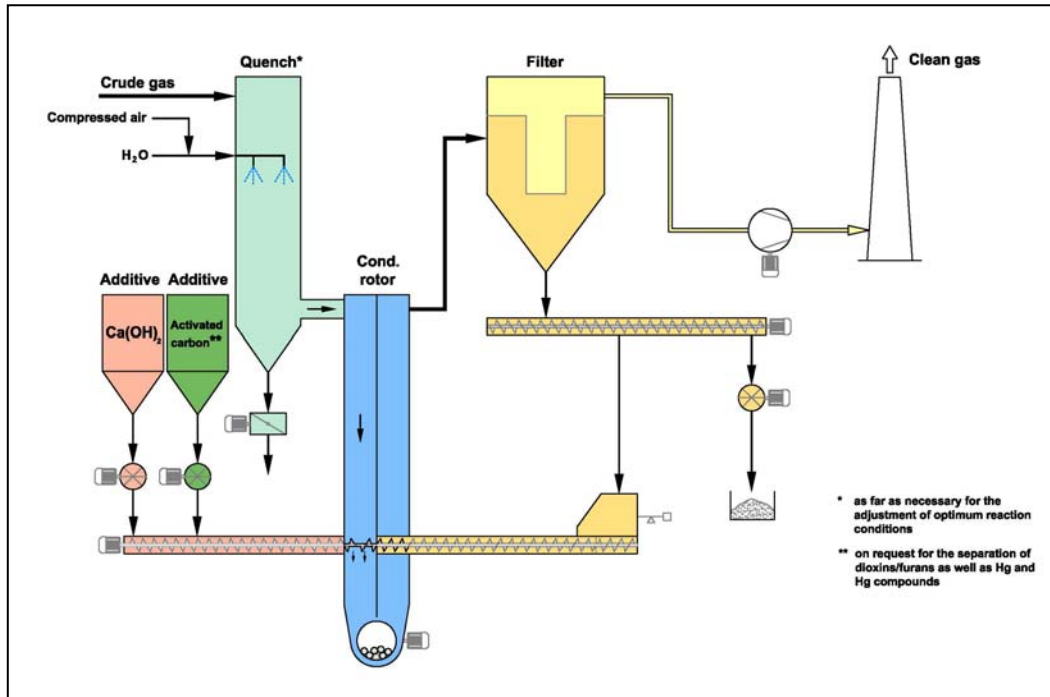

Illustration 1: Dry sorption with gas conditioning

In principle commercially available calcium hydroxide, $Ca(OH)_2$, with a specific surface of
approx. 18 up to 20 m^2/g is injected into the flue gas flow upstream filter. As alternative
high-reactive $Ca(OH)_2$ qualities with a specific surface of up to 40 m^2/g with an at the same
time high pore volume > 0.2 cm³/g are available. The reaction equations as well as the
additive powder injection and remainder quantities at an additive powder efficiency of
100% are listed in table 2 below.

Equations of reaction	$Ca(OH)_2$ - injection quantity related to crude gas at 100% conversion (i=1)	Resulting residual particle quantity (with crystal water content according to experience) related to crude gas
$2HF + Ca(OH)_2 \rightarrow CaF_2 + 2H_2O$	1.85 kg/kg	1.95 kg/kg
$2HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O$	1.01 kg/kg	2.02 kg/kg
$SO_3 + Ca(OH)_2 \rightarrow CaSO_4 + H_2O$	0.93 kg/kg	2.15 kg/kg
$SO_2 + Ca(OH)_2 \rightarrow CaSO_3 + H_2O$	1.16 kg/kg	2.02 kg/kg

Tab. 2: Reaction equations for $Ca(OH)_2$

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In practice the additive powder has to be injected above-stoichiometric (normally 1.5 times up to 3 times) in order to observe reliably the requested emission levels in the clean gas.

It is verifiable that especially in case of high additive powder recycle rates, the particle re-circulation will lead to a clear improvement of the degree of separation for acid crude gas components and/or to a reduction in the additive powder injection quantity.

- The residence time of additive particles in the system is increased
- Near reactor upstream filter there is a higher additive particle density (resulting reaction time in reactor up to > 2 sec.)
- Achievement of a frequent, spatial re-orientation of the re-circulated particulate with re-deposition of the filter cake on the filter fabric

Due to the requested, necessary high particle recycle rates and in order to grant an optimum additive powder efficiency, the utilisation of re-circulation systems becomes necessary which can reliably handle considerable recycling quantities – even if larger quantities of difficult particles, such as $CaCl_2$, are present in the particle spectrum. Illustration 2 shows a technology which has been applied successfully for many years for various fields of application. It is characterised by high reliability and a homogeneous distribution of the re-circulated particulate in the flue gas flow upstream filter. Conveying with pneumatic methods, which is prone to frequent breakdowns, is not used.

Conditioning rotor functions
- Prevention of particle deposits when recycling the descending flow of the crude gas
- Achievement of an homogeneous distribution of particles in the crude gas flow even in the case of high particle concentrations, e.g. up to approx. 200 g/m³
- Break-up of large particle agglomerates with higher settling velocity than the upward gas velocity
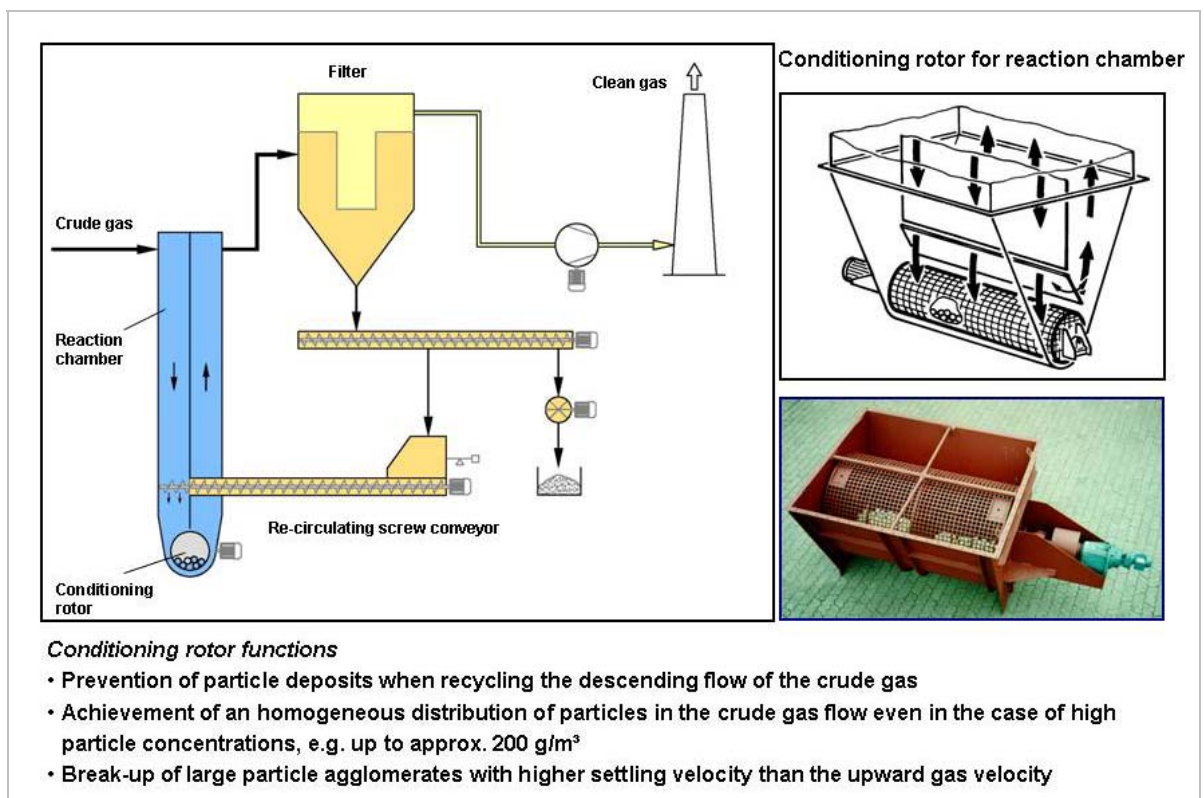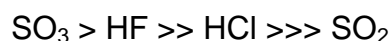
Illustration 2: Conditioning Rotor – Recycle Process (KUV)

The following order of reaction results for the temperature range of 100°C and 220°C typical for fabric filters:

$$SO_3 > HF \gg HCl \ggg SO_2$$

The dry temperature as well as the absolute and relative humidity have a decisive influence on the HCl and SO_2 separation, however, the separation of SO_3 and HF does not present any problems within the stated temperature range. In order to save additive powder, it is often useful to cool down the crude gas temperature upstream reactor to optimal operating temperatures by means of recuperative heat exchange or preferably by using an evaporative cooler. The min. admissible operating temperature has to be chosen that way, that adhesion and blockages especially due to the hygroscopic characteristics of the $CaCl_2$ particles in the plant will be avoided. Illustration 3 shows the preferred temperature range, depending on the dew point temperature.
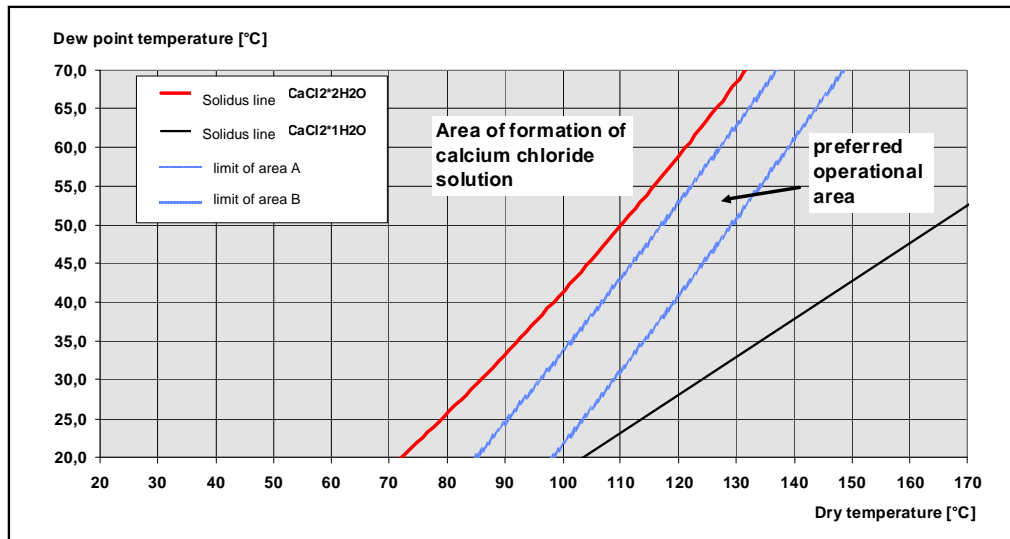
Reference: Dr. Mosch, Karpf

Illustration 3: Phase diagram $CaCl_2 \bullet x \, H_2O$

2.1.2 Application examples

This process variant is especially used for the gas treatment downstream incinerators for wood grade A I – A IV. To support the separation efficiency, high-reactive $Ca(OH)_2$ can be used.

The application example described in illustration 4 clearly shows the evaporative cooler, installed upstream filter. Based on the chosen process technology, a commercially available $Ca(OH)_2$ with low purchase costs can be used for this plant. The particle re-circulation has in addition a positive effect on the consumption rates for activated coke, which is injected for the separation of dioxins/furans and Hg as well as Hg-compounds.

Volume flow: **18.000 Nm³/h humid**

Temperature upstream quench: **210 °C**

Temperature upstream filter: **140 °C**

Crude gas values downstream boiler:

Particles	:	5.000	mg/Nm³ dry
HCl	:	145	mg/Nm³ dry
HF	:	20	mg/Nm³ dry
SO₂	:	195	mg/Nm³ dry
PCDD/PCDF	:	2	ng/Nm³ dry
Hg	:	0,15	mg/Nm³ dry

Guarantee:

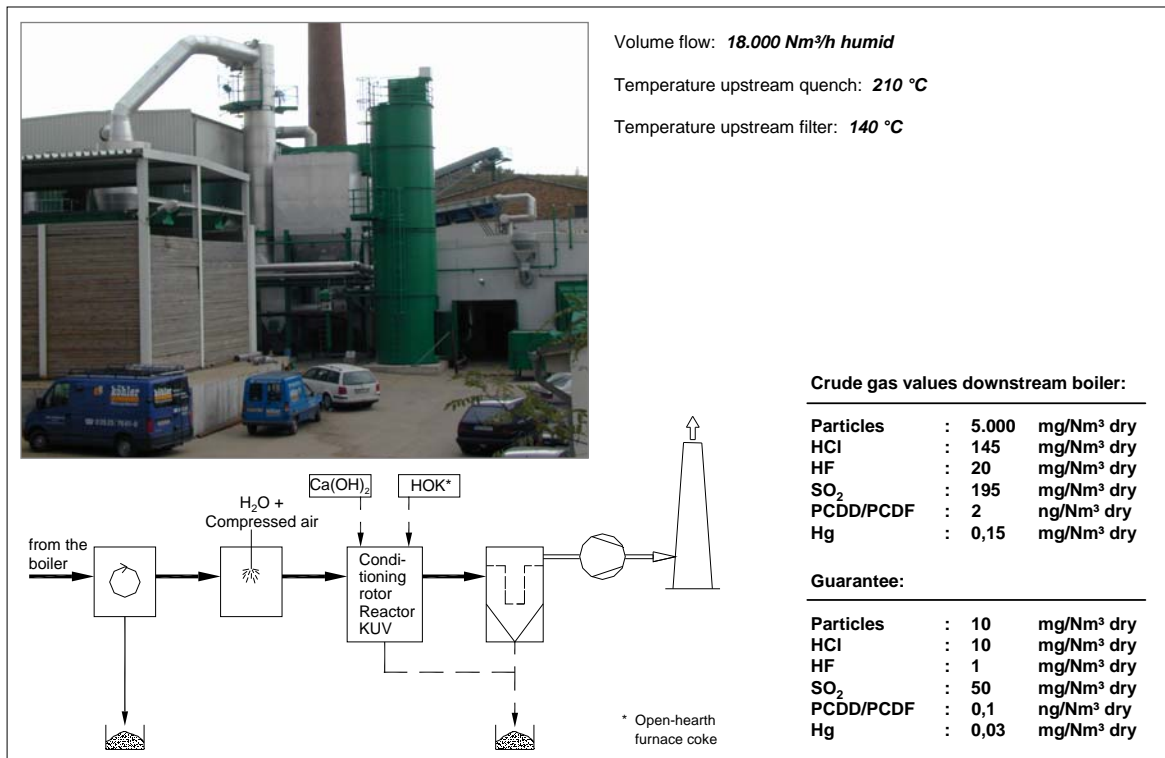| Particles	:	10	mg/Nm³ dry
HCl	:	10	mg/Nm³ dry
HF	:	1	mg/Nm³ dry
SO₂	:	50	mg/Nm³ dry
PCDD/PCDF	:	0,1	ng/Nm³ dry
Hg	:	0,03	mg/Nm³ dry

Illustration 4: Application example: Chemisorption with gas conditioning and particle re-circulation downstream waste wood incinerator with grate bar firing

2.2   Chemisorption with particle conditioning and possibly gas conditioning
2.2.1 Process description

As described before and as a result of the increase in the absolute and relative humidity of the flue gas, the gas conditioning has a positive effect on the sorption output. However, a good additive powder efficiency, especially for the separation of SO_2, can only be achieved if the water steam partial pressure close to the recycled particulate lies at least for a short time in the range of the saturation steam pressure. This will be achieved by using the conditioned chemisorption with particle conditioning (illustration 5). Regarding this type of process, the recycled particulate is wetted prior to reintroduction into the reactor. The wetting causes an increase in the water steam content at the surface of the additive powder particles, thus improving the reactivity in comparison to the acid crude gas components.

Due to the limited proportional wetting of the recycled particulate and depending on the gas temperature upstream reactor, it might be useful to install an upstream located evaporative cooler for the adjustment of optimum reaction conditions.
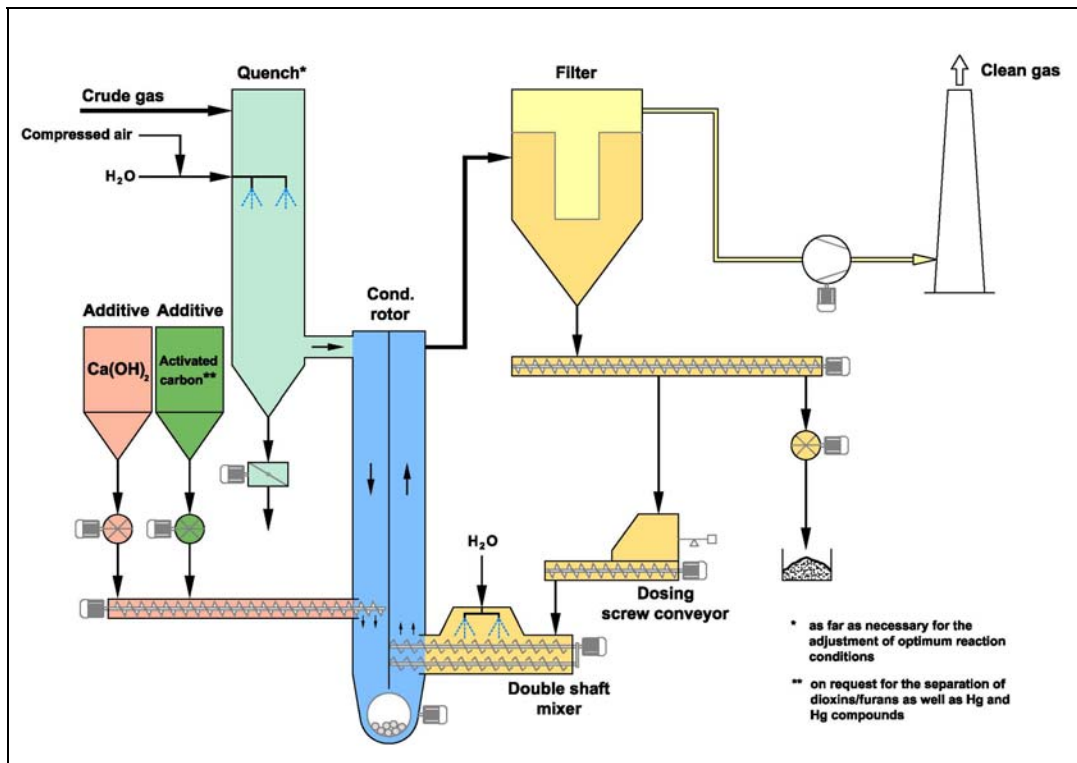
Illustration 5: Chemisorption with particle and gas conditioning

2.2.2 Application examples
2.2.2.1 Sludge incineration

The application example given in illustration 6, shows a sorption stage for the separation of SO_2 and Hg installed downstream of ESP for fly ash separation.
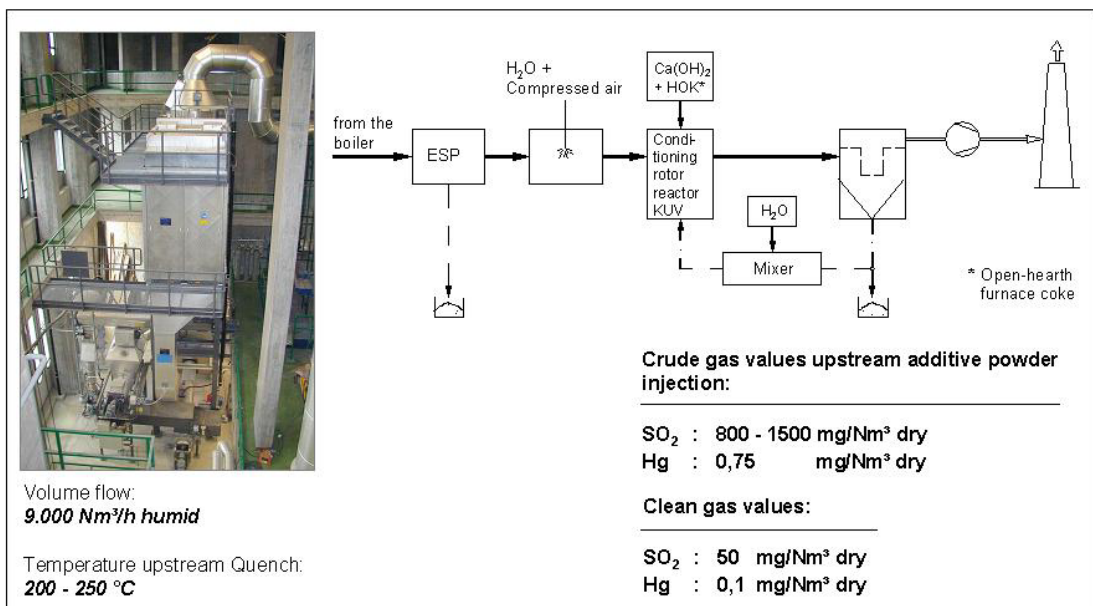

Illustration 6: Application example: Sludge incineration

Illustration 7 reflects the efficiency of the chosen technology on the basis of a record of measuring values of a continuous SO$_2$ crude gas and clean gas measurement over a period of three hours. The indicated results have been achieved due to the utilisation of a particle conditioning at a gas temperature downstream reactor of 120°C. A closer approach of the temperature to the water dew point for the reliable observance of the requested emission levels will not be necessary in this case.
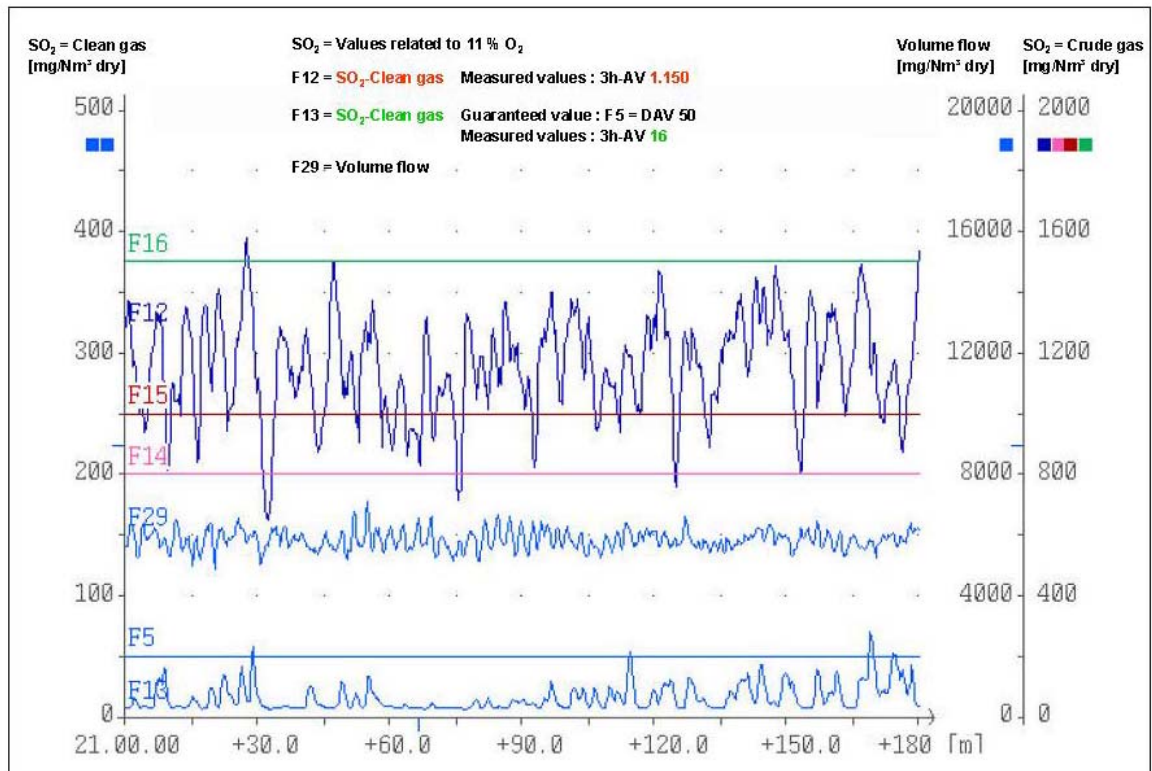

Illustration 7: SO$_2$ separation at sludge incineration

2.2.2.2 Domestic waste incineration

Another example for the efficiency of the chemisorption with particle and gas conditioning is the domestic waste incinerator shown in illustration 8. The requested limit values, mainly in accordance with 17 BImSchV. can reliably be observed even in case of crude gas contents for HCl of up to 2,000 mg/Nm³ and for SO$_2$ up to 1,000 mg/Nm³ - in each case indicated as DAV (illustration 9). The additive powder injection lies in this case at an stoichiometric factor of 2.
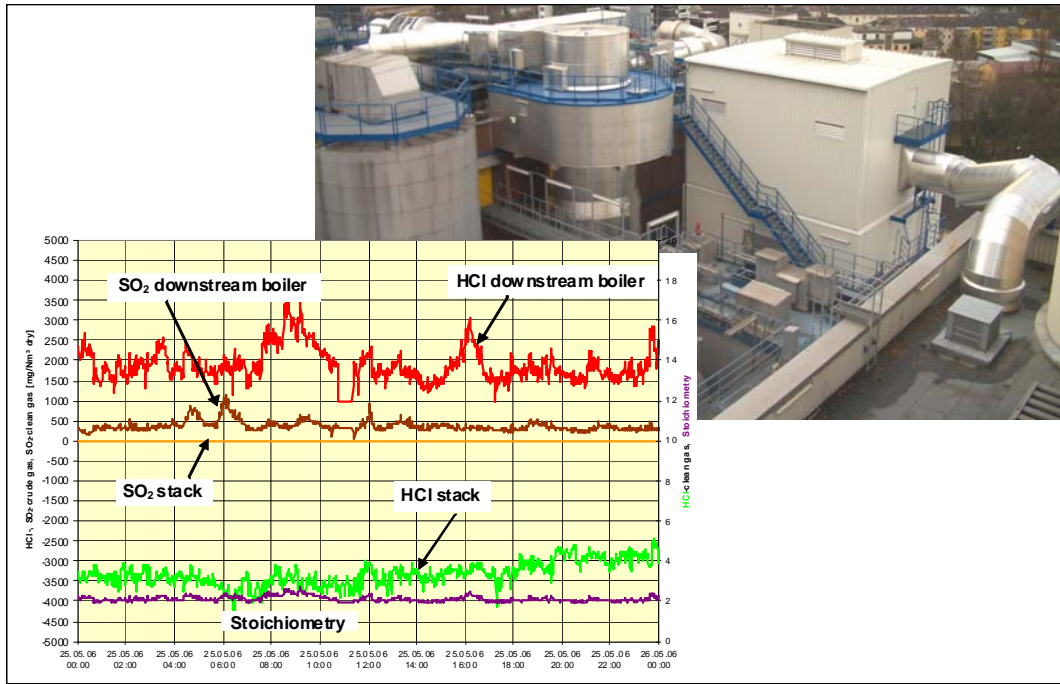
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Illustration 8: Conditioned dry sorption in MHKW Ludwigshafen

The conditioned dry gas cleaning system installed in 2004 replaced a definitely more complex wet process, consisting of spray dryer, electrostatic precipitator, multi-stage scrubber and aerosol separator (illustration 9).
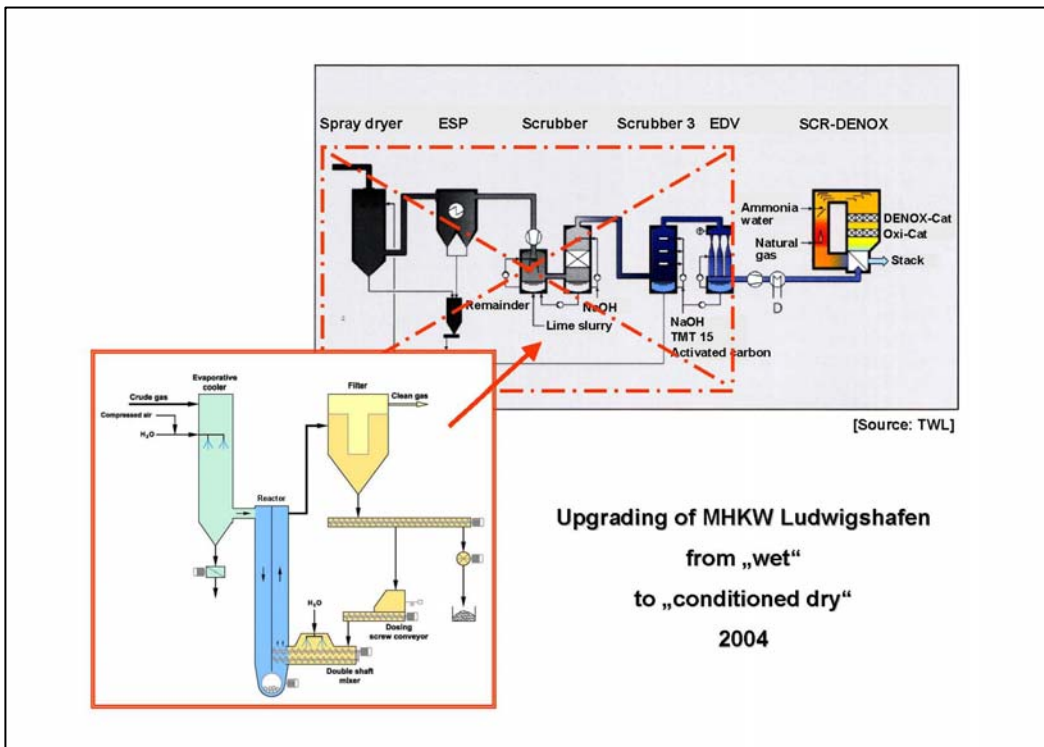

Illustration 9: Upgrading of MHKW Ludwigshafen from „wet" to „conditioned dry"

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downstream incineration plants

Up to the year 2008, another wet flue gas treatment plant had been operated in parallel at the MHKW Ludwigshafen until its conversion in 2008, thus allowing a direct comparison of both installed variants. Illustration 10 shows the average values of the year 2005 for selected substances.
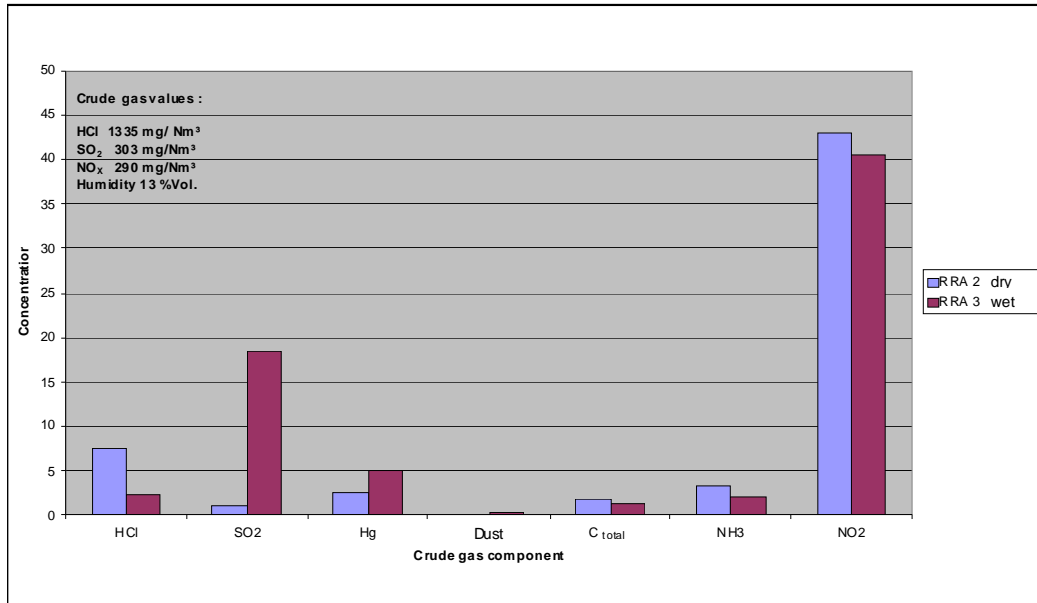

Illustration 10: Comparison of gas cleaning systems „wet" and „conditioned dry" (2005)

The comparison shows that the conditioned dry sorption process is equal to the more complex wet system. The only difference is the reference variable for the separation of the acid crude gas components, i.e. SO_2 for the scrubber and HCl for the conditioned dry sorption.

The high degree of separation of SO_x combined with a nearly 100 per cent SO_3 sorption by means of the conditioned dry sorption process allows the reduction of the operating temperature of the downstream installed SCR plant from 300°C to 230°C.

An additional advantage as to the saving of energy costs is the higher gas temperature upstream SCR stage of approx. 140°C.
It should be mentioned in addition, that compared to the spray sorption, an important advantage of the conditioned dry sorption is the better degree of separation for SO_2. This is especially important in case of downstream installation of SCR plants.

2.3   Conditioned dry sorption with graded additive powder injection
2.3.1 Design variants

In case of increasing crude gas values for HCl and SO_2, the stoichiometry of basic variant of the conditioned dry sorption has to be increased partly definitely above a typical base value of 2 without any additional measures in order to observe reliably the emission limit values. At rising crude gas values it will therefore be advisable to apply a graded additive powder injection, thus using in addition the reaction chamber of evaporative cooler / spray absorber when indicated. Illustration 11 shows different, corresponding process variants. For all concepts, the main quantity of additive powder is injected into the reactor downstream evaporative cooler in the nominal case. The injection of additive powder upstream or within evaporative cooler / spray absorber mainly serves for the corrosion protection as well as for the smoothening of crude gas peaks.
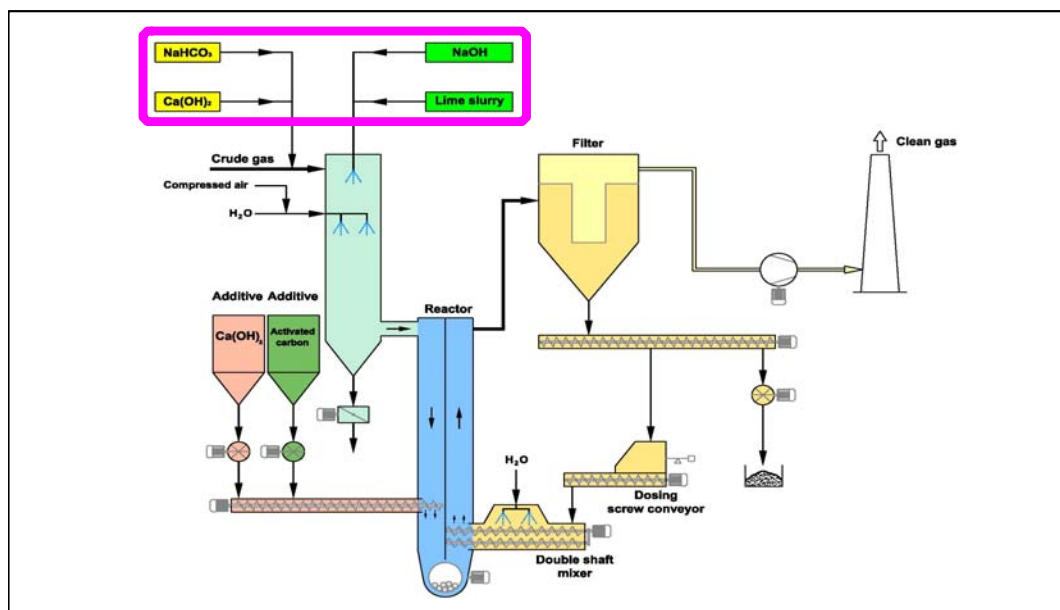

Illustration 11: Conditioned dry sorption with graded additive powder injection

2.3.2 Application examples for RDF incinerations

The separation potential is exemplary shown in illustration 12 by means of a gas cleaning system downstream RDF incinerator. In this case the additive powder injection takes place in steps, using NaOH in the evaporative cooler and $Ca(OH)_2$ in the reactor of conditioned dry sorption. At mean crude gas values for HCl of 1,800 up to 2,500 mg/Nm³ as well as 1,000 up to 1,500 mg/Nm³ for SO_2, combined with definitely higher crude gas peaks for both crude gases, the limit values of 17 BImSchV. will reliably be undercut with at the same time acceptable additive powder consumption.
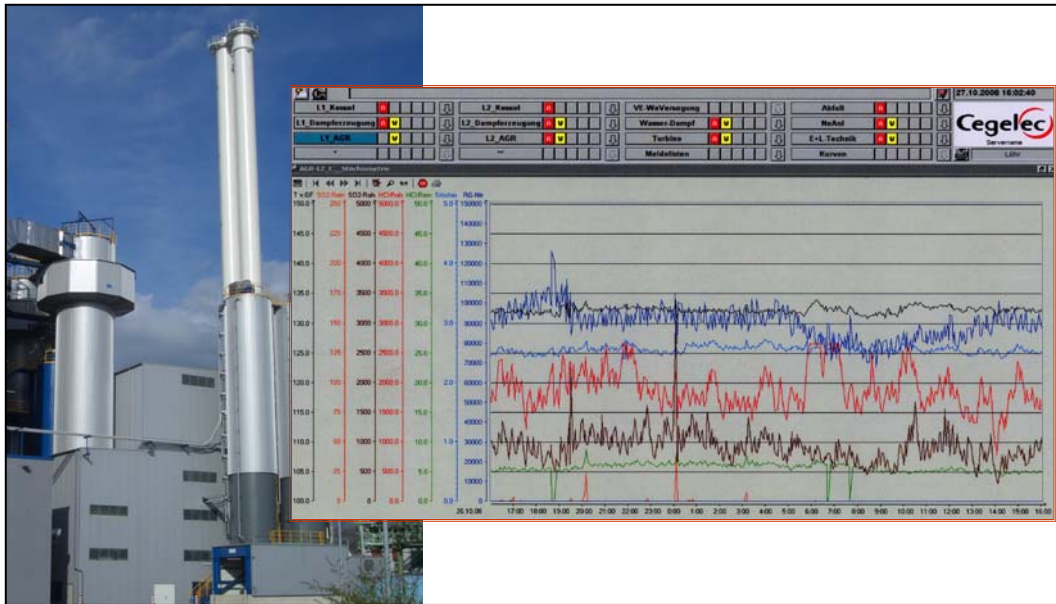
Illustration 12: Gas cleaning with graded additive powder injection downstream RDF incinerator

Illustration 13 shows the RDF heat-and-power-station Stavenhagen as representative for several realised plants and illustration 14 presents some trend curves from the control system of this plant as result for the separation efficiency.

The average stoichiometric factor actually reached in continuous operation has repeatedly been determined by means of remainder analyses. It lies in a range of 1.8 up to 2.0. The chloride content in the remainder totals to approx. 20 up to 22 % thus lying in a range noncritical for the product handling.

Volume flow :
104.000 Nm³/h humid

		DAV nominal	DAV maximal
Particles	mg/Nm³ dry	1,000	1,000
HCL	mg/Nm³ dry	1,300	2,000
HF	mg/Nm³ dry	25	50
SO$_2$	mg/Nm³ dry	1,100	1,900
Hg	mg/Nm³ dry	0.12	0.12
Σ Heavy metals	mg/Nm³ dry	27.5 *	100 *
Cd / Tl	mg/Nm³ dry	1.3 *	6.0 *
PCDD / PCDF	ng/Nm³ dry	3.0 *	4.0 *

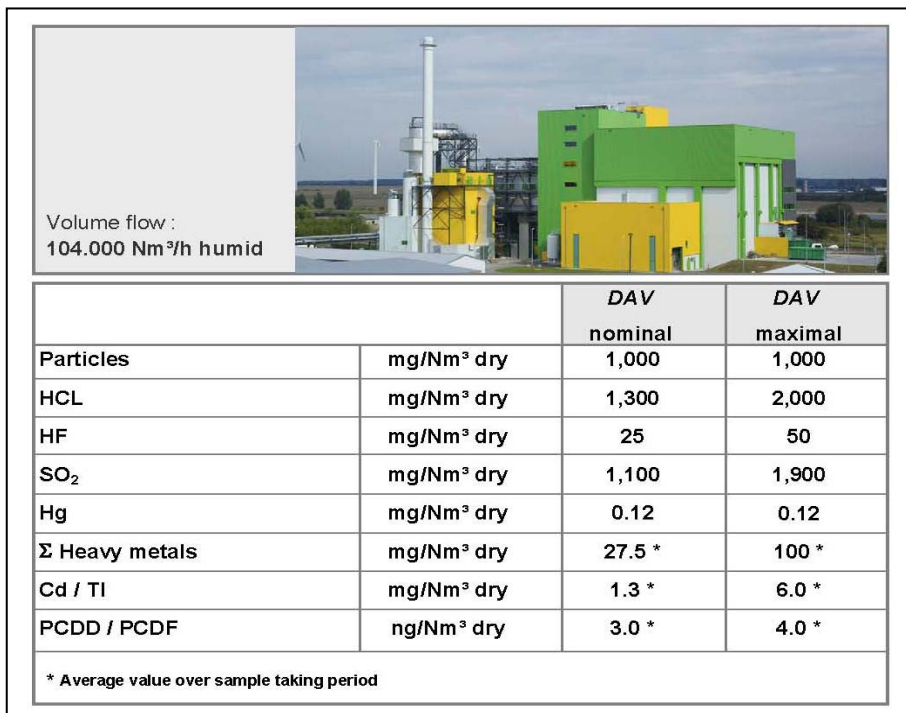* Average value over sample taking period

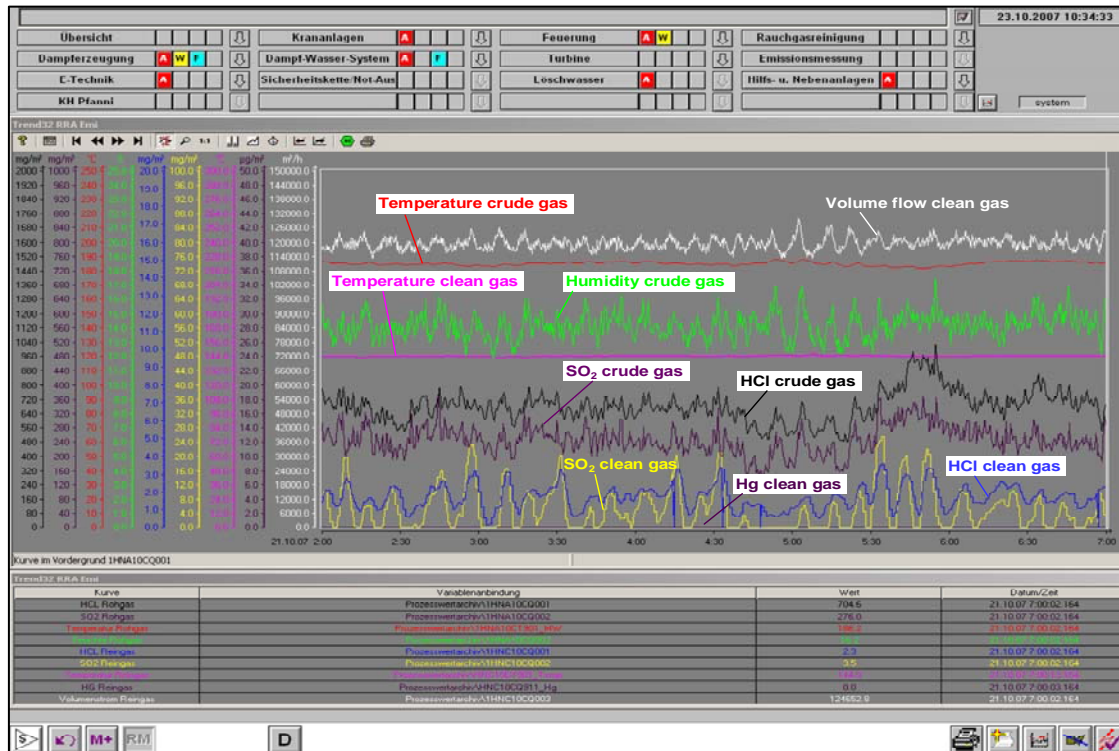*Illustration 13: RDF HKW Stavenhagen*

Illustration 14: Trend curves crude/clean gas values, temperatures, gas humidity and volume flow

2.4 Concepts for low emission limit values, considering NOₓ
2.4.1 Preliminary remark

Since a couple of months, increased discussions are hold on the European scale concerning a tightening of the emission limit values. In this connection, e.g. the request for a NO_x limit value of < 100 mg/Nm³ dry with at the same time limitation of NH_3 slippage is being discussed. Operating results gathered from modern incineration plants with SNCR procedures for the NO_x reduction demonstrated that in most of the cases the reliable observance of the tightened NO_x limit value of 100 mg/m³ will be possible. Even in case of requested lower NO_x emission limit values, the installation of a catalyst is not imperative. Also in this case a SNCR procedure can be applied, but then a further separation stage for NH_3 has possibly to be integrated in the concept, depending on the max. admissible NH_3 slippage.

2.4.2 Application example SNCR with NH_3 separation

Illustration 15 shows an example for a gas cleaning system downstream circulating vortex bed for biomass combustion in the Netherlands. In order to observe the requested NO_x limit value of 70 mg/m³, the constructor of boiler installed a SNCR plant. The NH_3 slippage downstream boiler is limited to max. 15 mg/m³. In addition to this, illustration 15 shows a table with the requested emission limit values to be observed by means of the downstream installed gas cleaning system.

The following concept has been chosen for this gas cleaning system:

- Cyclones for separate fly ash removal
- Conditioned dry sorption at approx. 150° C
- Heat exchanger for cooling down of gases to approx. 100°C
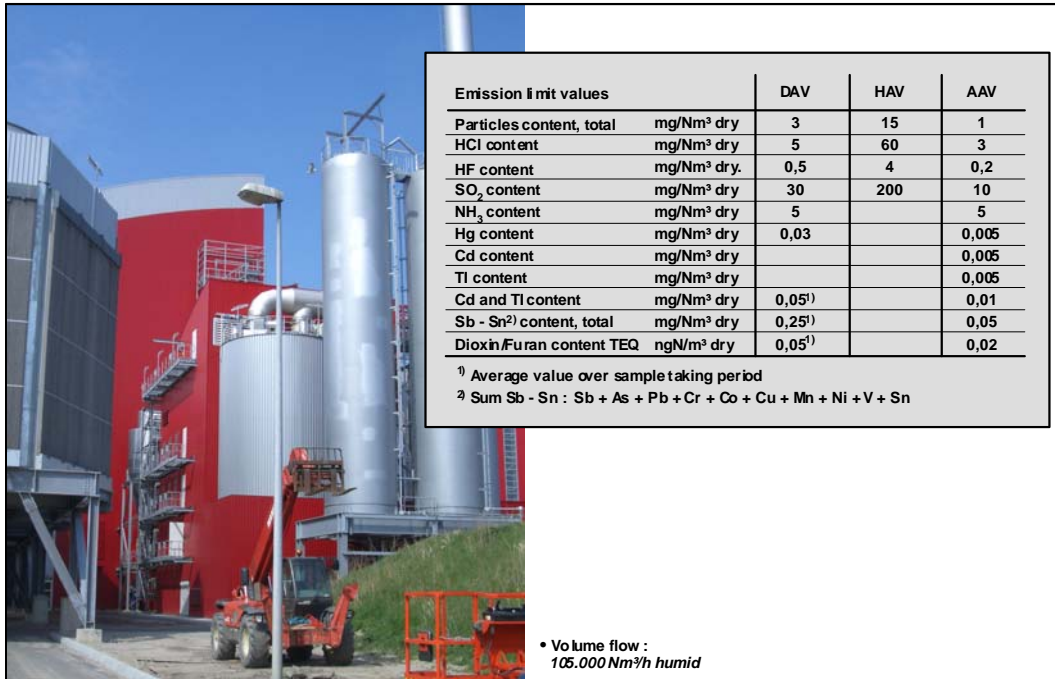- Wet ESP with integrated acid and basic stage

Emission limit values		DAV	HAV	AAV
Particles content, total	mg/Nm³ dry	3	15	1
HCl content	mg/Nm³ dry	5	60	3
HF content	mg/Nm³ dry.	0,5	4	0,2
SO$_2$ content	mg/Nm³ dry	30	200	10
NH$_3$ content	mg/Nm³ dry	5		5
Hg content	mg/Nm³ dry	0,03		0,005
Cd content	mg/Nm³ dry			0,005
Tl content	mg/Nm³ dry			0,005
Cd and Tl content	mg/Nm³ dry	0,05[1]		0,01
Sb - Sn[2] content, total	mg/Nm³ dry	0,25[1]		0,05
Dioxin/Furan content TEQ	ngN/m³ dry	0,05[1]		0,02

[1] Average value over sample taking period
[2] Sum Sb - Sn : Sb + As + Pb + Cr + Co + Cu + Mn + Ni + V + Sn

- Volume flow :
  105.000 Nm³/h humid

Illustration 15: Gas cleaning downstream biomass combustion HVC, Alkmaar/ Netherlands

In addition to an integrated NH$_3$ separation, this concept also offers the reliable observance of extremely low emission values in a cost-effective way

Illustration 16 shows the structure of this plant, based on the scheme taken from the process control system. The wet stage downstream conditioned dry sorption serves for the reliable undercut of all requested emission limit values.
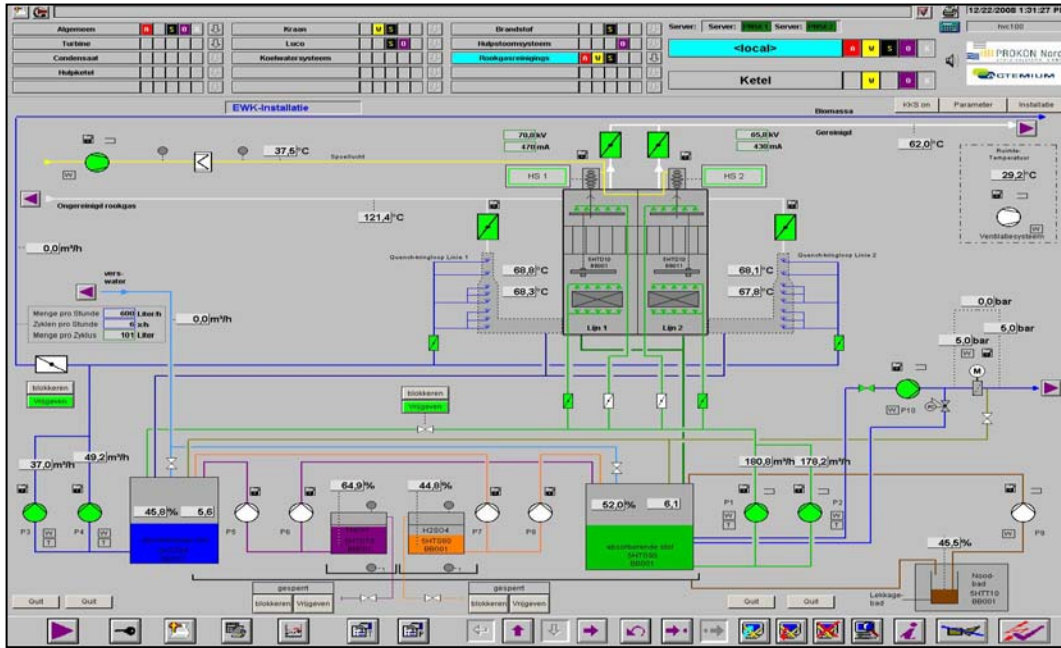
*Illustration 16: Schematic view of gas cleaning system for biomass combustion HVC, Alkmaar/
Netherlands*

The NH$_3$ separation takes place in the acid scrubbing stage (illustration 17) which is installed upstream of wet ESP. The pH-value of this stage is adjusted to approx. 5.6. In order to grant a sufficient SO$_2$ separation, a ph-value of 6.1 has been chosen for the second scrubbing stage.
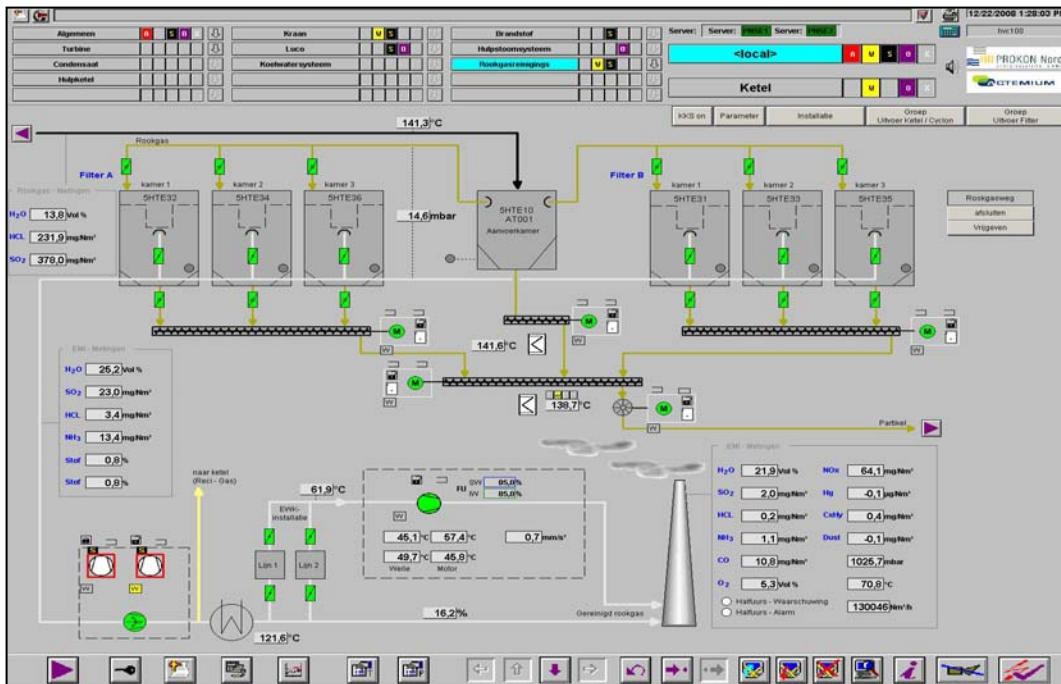

Illustration 17: Schematic view of wet ESP with integrated two-stage scrubbing process

The waste water from the basic scrubbing stage is reused in the humidifying mixers for the conditioned dry sorption. The NH_3-laden water from the acid stage (max. approx. 0.5 m³/h) is directed towards a central water processing of location.

3   Dry sorption with utilisation of $NaHCO_3$
3.1   General design, advantages and disadvantages

The dry sorption with $NaHCO_3$ is competing with process technologies using Ca-containing additive powder qualities. The quite simple process technology of the basic variant is shown in illustration 18. The additive powder is pulverised and injected into the gas flow upstream filter. In case of crude gas temperatures of > 150°C, a thermal activation of sodium hydrogen carbonate will take place which becomes quicker with rising temperatures. The result is a high reactive sodium carbonate. The reaction time from injection point of additive powder until the arrival at the filter fabric should last at least 2 sec.
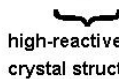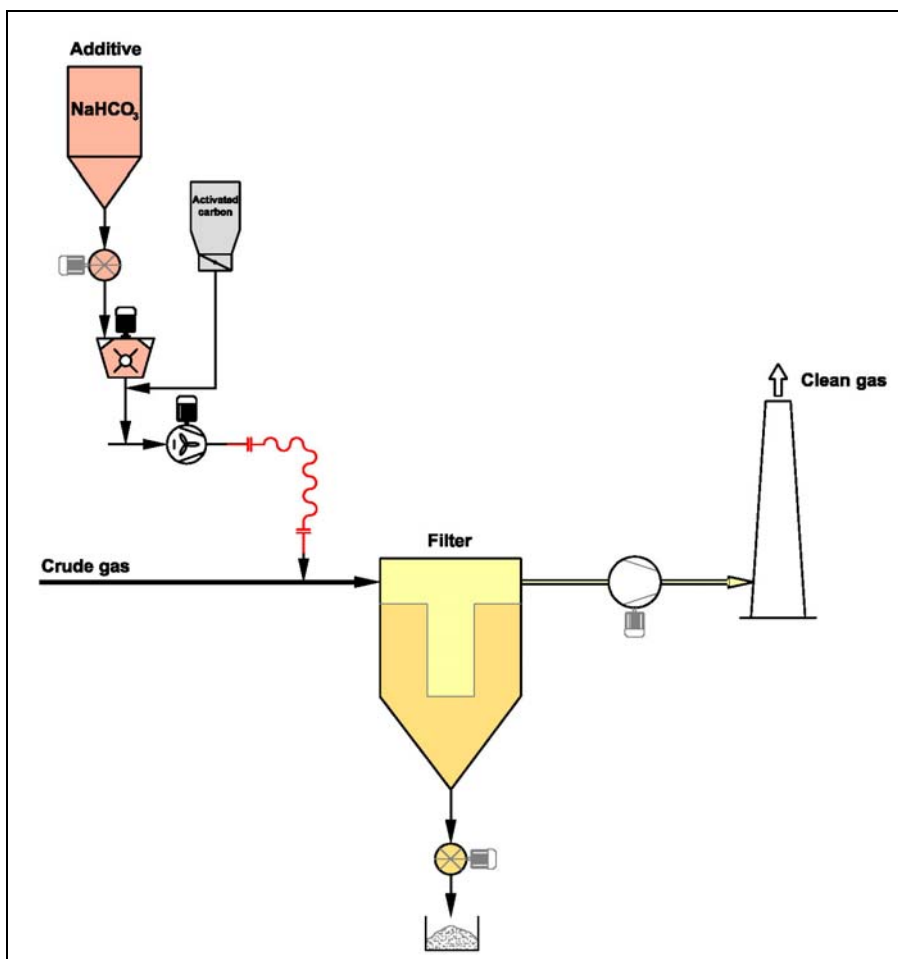

Illustration 18: Basic variant of dry sorption with $NaHCO_3$

Tab.3 shows the chemical reaction equations as well as the injection and remainder quantities on the basis of an additive powder efficiency of 100%. Normally the required emission limit values are reliably achieved in continuous operation with the adequate plant design with an over stoichiometric factor of 1.2 – max. 1.5. Especially in case of temperatures lower than 160°C, the multiple re-circulation of the particles separated in the filter into the flue gas flow upstream filter can be advantageous.

Equations of reaction	$NaHCO_3$ - injection quantity related to crude gas at 100% stoichiometry (i=1)	Resulting residual particle quantity related to crude gas
$HF + NaHCO_3 \circ\ NaF + H_2O + CO_2$	4,2 kg/kg	2,1 kg/kg
$HCl + NaHCO_3 \circ\ NaCl + H_2O + CO_2$	2,3 kg/kg	1,6 kg/kg
$SO_3 + 2NaHCO_3 \circ\ Na_2SO_4 + H_2O + 2CO_2$	2,1 kg/kg	1,77 kg/kg
$SO_2 + 2NaHCO_3 \circ\ Na_2SO_3 + H_2O + 2CO_2$	2,63 kg/kg	2,22 kg/kg

Thermal activation of $NaHCO_3$:

$$2NaHCO_3 \xrightarrow{T \geq 140\,°C} Na_2CO_3 + CO_2 + H_2O$$

high-reactive, porous
crystal structure

Tab. 3: Reaction equations for $NaHCO_3$

The main advantages of this technology are:

- High reactivity of additive powder
- Simple plant design
- Remainder quantity is reduced compared to the additive powder injection (advantage in case of high disposal costs)
- Lower hygroscopic nature of resulting salts

The facing disadvantages are:

- Unfavourable mass ratio of additive powder to crude gas
- Necessary pulverisation of additive powder prior to injection into the flue gas flow
- High specific purchase costs of the additive powder

As alternative there are further additive powder qualities on sodium basis available, such as e.g. Na_2CO_3 or NaOH. These additive powder qualities, however, will not be taken into consideration in the context of this lecture.

3.2   Application examples
3.2.1   Tyre combustion

The plant example shown in illustration 18 demonstrates the advantages of this type of process. The complexity of equipment for achieving a degree of separation of $SO_2 \geq 95$ % is very low. A fabric filter with corresponding additive powder injection has been installed downstream existing filter for fly ash separation. A particle conditioning is not used.
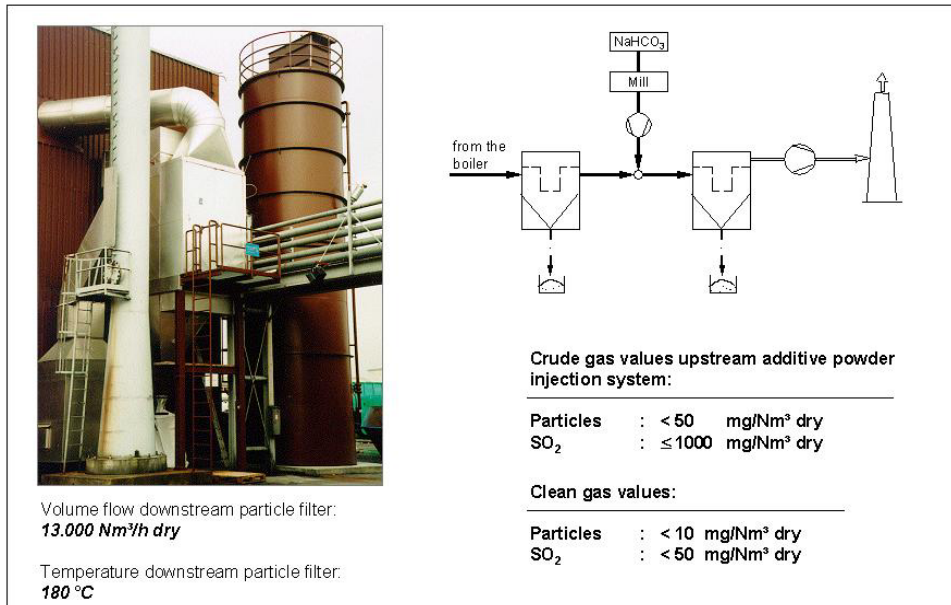

Illustration 19: Application example tyre combustion

3.2.2   Domestic waste incineration

Illustration 20 shows an application example for a gas cleaning plant downstream domestic waste incinerator. Compared to the basic variant shown in illustration 18, this plant is additionally provided with an evaporative cooler for the adjustment of the gas temperature as well as with a particle re-circulation.

In 2009 extensive examinations have been realised at this plant in order to determine the influence of operating temperature and particle re-circulation on the additive powder consumption. Whereas temperatures in a range between 150°C and 180°C do only have a very low, hardly recognisable influence, the operation with and without particle re-circulation shows a considerable difference. Illustration 21 clearly shows the influence of the particle re-circulation. In case of an adequately dimensioned plant and integration of a particle re-circulation system, stoichiometrics of < 1.2 can reliably be kept in continuous operation.
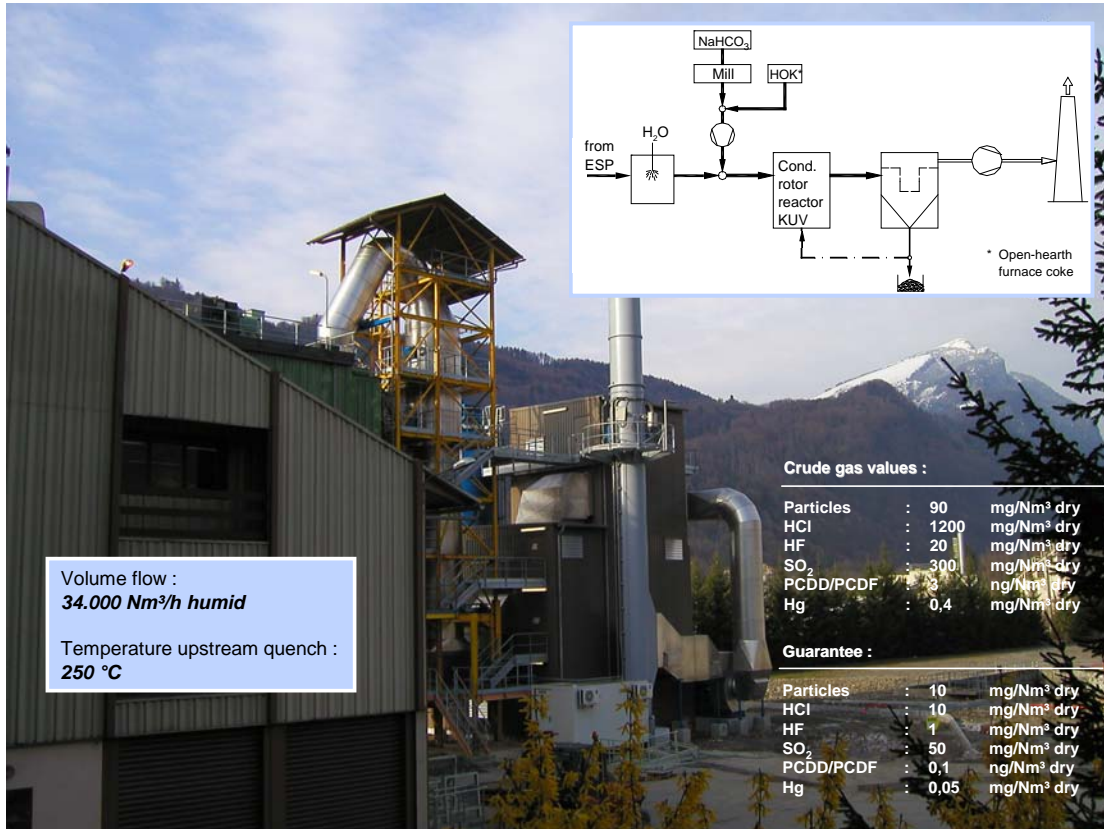
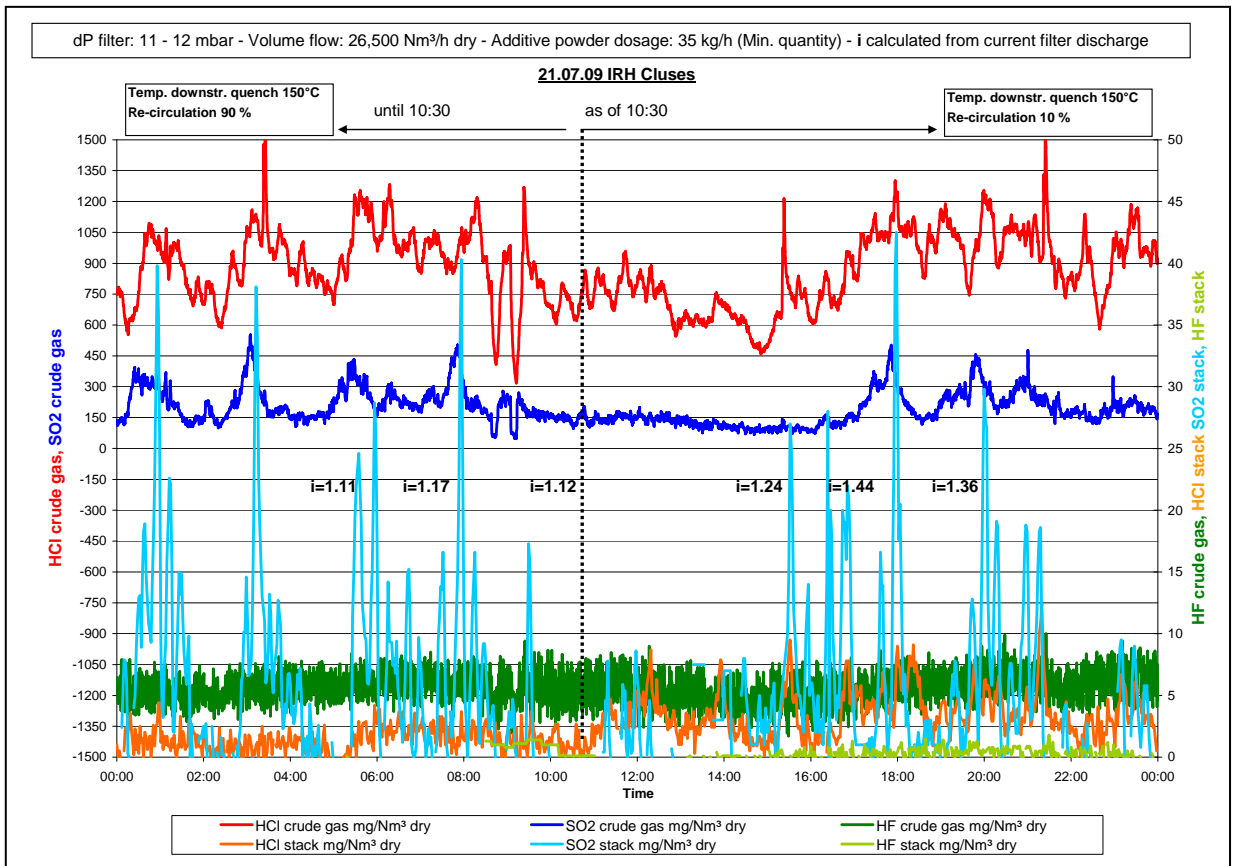Illustration 20: Application example: Domestic waste incinerator

llustration 21: Influence of particle re-circulation on the additive powder consumption

4   Process selection

The introduced examples of process technologies only reflect a selection of concepts that have been realised for the gas treatment downstream incinerators for waste, RDF, sludge or biomass. Independent of this, from the author's point of view, with regard to the design of new plants, the conditioned dry sorption with utilisation of $Ca(OH)_2/CaO$ and the dry sorption with $NaHCO_3$ gained an outstanding position in the last years in Germany and became accepted especially when compared to wet systems. Due to the corresponding requirements and conditions of the separate applications, it will be necessary to adjust the base variant from case to case by means of complementary measures or also by additional separation stages.

This introduction of process technologies did not include a comparative assessment as this has to take place on a project-related basis. All systems have their strengths and weaknesses. There is no most suited procedure for all types of applications.
Each application has to be considered separately. Criterions of choice for the assessment are:

- Requested degrees of separation (nominal and max. values as well as peaks)
- Emission limit values
- Investment costs
- Operating costs as e.g. additive powder supply and disposal as well as energy costs for power and compressed air
- Costs for maintenance and repair
- Plant availability and reliability of operation
- Part load behaviour
- Flexibility with regard to changing crude gas values, emission limit values and specific operating costs

LUEHR FILTER
Air Pollution Control Technology

Enzer Straße 26
31655 Stadthagen
GERMANY

Phone: +49 5721 708 - 200
Fax: +49 5721 708 – 154
E-Mail: info@luehr-filter.com

Internet: www.luehr-filter.com