The aim of this study is to demonstrate such discrepancies or dependencies between attainable emission reductions and the emissions-generating energy input necessarily incurred by flue gas treatment technologies in attaining those reductions.

The study initially focuses on current investigations and assessments related to this issue, as well as on the legal emission requirements. Due to the wide range of components involved in flue gas treatment systems and their consequent numerous combination possibilities, six different system Variants are presented and compared. It is notable in the context of the present study that both single and two-stage or multi-stage systems are considered in the set of Variants, which differ not only in their structure and additive use but also in their separation capacity. These six basic Variants reflect the systems frequently employed in practice and represent non-congruent procedural steps with their respective target emission levels. Based on the fact that each of these Variants is already in operation in thermal waste incineration plants, the assessment draws on many years of existing operative experience.

The individual energy demands for the Variants described are determined on the basis of mass, material and energy balances.

Evaluation criteria for energy demand at the different emission reduction ratios are educed from the formulation of emissions-related energy indicators. This establishes a set of tools with which to assess emissions-generating energy demand in the context of emission reduction ratios.
The BREF revision will present challenging emission limit values. However, our experience will help you to find the optimised solution for your project to achieve future limits.

We guarantee
- reliable performance within the specified emission limits
- high plant availability at low capital and operating costs
- flexible system design modified to the specific application
Dry, Semi-dry or Wet – Which System Fits Best Depending on the Overall Conditions?

Rüdiger Margraf

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Due to the obligation of the European Union member states to supply non-recyclable waste for thermal treatment, numerous waste incineration plants have been constructed in the course of previous years. When selecting the gas cleaning procedure you can currently observe a trend towards dry and especially towards conditioned dry procedures. These procedures allow the simultaneous separation of particles, acid crude gases such as HF, HCl or SO\(_x\), heavy metals and dioxins/furans. Combinations with wet procedures are mainly given preference when the use of condensing heat for e.g. the supply in district heating networks is both feasible and economical.

In particular the criteria below are taken as the basis for the project-related selection of the most suitable procedure:

- Guaranteed performance within specified emission limit values,
- Reliability,
• Economic efficiency with regard to investment and operating costs,
• Public acceptance.

In most of the cases, the values stipulated in the EU Directiv 2000/76/EC are referred to as limit values, but when planning new plants today, the expected stricter emission limit values resulting from the BREF revision are already considered as a precaution. In this regard mainly NO\textsubscript{x}, NH\textsubscript{3} as well as a Hg and Hg compounds have to be mentioned.

The following discusses today’s mainly used procedures, compares the advantages and disadvantages under consideration of the WI BREF revision and indicates some characteristic figures with regard to the operating costs.

1. Influence of the revision of BREF documents

In May 2017 the European IPPC Bureau published the first draft of the WI-BREF [10]. Table 1 compares the BAT-AELs (best available technique associated emission level) of the BREF of 1966 with the current limit values of the EU Directiv 2000/76/EC as well as with the values indicated in the first draft of the new WI BREF. The table in each case only shows the daily average values as well as the average values over sampling periods of some main treated pollutants.

Table 1: BAT-AELs and ELVs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>EU Directive 2000/76/EC</th>
<th>WI BREF 2006</th>
<th>WI BREF D1 2017</th>
<th>Averaging period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emissions to air (mg/Nm\textsuperscript{3} unless stated)</td>
<td></td>
<td>BAT-AEL</td>
<td>BAT-AEL</td>
<td>Averaging period</td>
</tr>
<tr>
<td>Dust</td>
<td>10</td>
<td>1 – 5</td>
<td>2 – 5 (1)</td>
<td>Daily average</td>
</tr>
<tr>
<td>Cd+Tl</td>
<td>0.05</td>
<td>0.005 – 0.5</td>
<td>0.01 – 0.02</td>
<td>Average over the sampling period</td>
</tr>
<tr>
<td>Sb+As+Pb+Cr+Co+Cu+Mn+Ni+V</td>
<td>0.5</td>
<td>0.005 – 0.5</td>
<td>0.05 – 0.3</td>
<td></td>
</tr>
<tr>
<td>HF</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>Daily average or average over sampling period</td>
</tr>
<tr>
<td>HCl</td>
<td>10</td>
<td>1 – 8</td>
<td>2 – 6 (2)</td>
<td></td>
</tr>
<tr>
<td>SO\textsubscript{2}</td>
<td>50</td>
<td>1 – 40</td>
<td>10 – 30</td>
<td></td>
</tr>
<tr>
<td>NO\textsubscript{x}</td>
<td>200</td>
<td>40 – 100 (SCR)</td>
<td>50 – 120 (3)</td>
<td></td>
</tr>
<tr>
<td>NH\textsubscript{3}</td>
<td>–</td>
<td>&lt;10</td>
<td>3 – 10 (3)</td>
<td></td>
</tr>
<tr>
<td>PCDD/F (ng I-TEQ / Nm\textsuperscript{3})</td>
<td>0.1</td>
<td>0.01 – 0.1 ng/m\textsuperscript{3} (non-continuous sample)</td>
<td>&lt;0.01 – 0.04 (4)</td>
<td>Average over the sampling period or long-term sampling average</td>
</tr>
<tr>
<td>PCDD/F + dioxin-like PCBs (ng WHO-TEQ/Nm\textsuperscript{3})</td>
<td>–</td>
<td>No BAT-AEL for PCBs</td>
<td>&lt;0.01 – 0.06 (4)</td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>0.05</td>
<td>0.001 – 0.02</td>
<td>5 – 20 (µg/Nm\textsuperscript{3}) (5)</td>
<td>Daily average, long-term daily average, or average over the sampling method</td>
</tr>
</tbody>
</table>

(1) 2 – 7 for existing plants where a bag filter is not applicable
(2) The lower end of the BAT-AEL range can be achieved when using a wet scrubber; the higher end may be associated with the use of dry sorbent injection
(3) The lower end of the BAT-AEL range can be achieved when using SCR
(4) Either the BAT-AEL for PCDD/F or the BAT-AEL for PCDD/F + dioxin-like PCBs applies
(5) The lower end of BAT-AEL ranges can be achieved when using fixed-bed adsorption or a wet scrubber enhanced with the use of oxidants; the higher end of the BAT-AEL ranges can be achieved when using dry sorbent injection
The BAT-AELs show for the currently valid BREF and the draft of revision, the ranges of actually measured emission values under normal operating conditions. The resulting limit values currently specified in the EU Directiv lie slightly above the BAT-AELs of the BREF 2006. Thus the BAT-AELs have until now not been any binding maximum limit values for emission control. This will change in future. The ranges for the BAT-AELs indicated in the coming BREF will in future represent the legally binding minimum requirements for emission limit values. These, compared to today’s level, lower values will certainly have an effect on the process technology for new plants and will also lead to modifications to existing plants within the stipulated period of max. 4 years. The emission limit values for NO$_x$, NH$_3$ and not least Hg may be considered as especially critical in this connection.

2. Process-related solutions for major gaseous impurities

2.1. Acid crude gases such as HF, HCl and SO$_x$

During chemisorption the acid crude gas components such as HF, HCl and SO$_x$ are reacting with a basic additive powder. The resulting reaction products are salts, which can be separated in a fabric filter.

For improvement of the reaction conditions a part of the reaction products separated in the filter is usually re-circulated in a reactor installed upstream of the filter. The positive influence of particle re-circulation on the separation efficiency combined with reduced additive powder consumption could be proven in a demonstration filter [7].

The used sorption agents are Ca- and Na-based additive powders. While Ca(OH)$_2$/CaO are used for semi-dry/conditioned dry processes, NaHCO$_3$ is used for only dry sorption processes without the use of water for conditioning of gases and/or additive powders.

2.1.1. Ca-based technologies

**Conditioned dry sorption process**

A schematic view of the conditioned dry sorption process is given in Figure 1 using the example of Luehr Filter – Conditioning Rotor – Recycle Process with particle conditioning. It mainly comprises the component parts which are the evaporative cooler, additive powder injection, conditioning rotor reactor, fabric filter as well as particle re-circulation with integrated particle conditioning. Further possible design types are described in [3].

The evaporative cooler (gas conditioning) provides the optimum temperature adjustment for the reaction between the additive particles and the acid gas molecule, combined with an increase in the absolute and relative humidity, for the optimisation of the separation efficiency together with good additive powder utilisation. The evaporative cooler is not needed in cases of the temperatures upstream of the flue gas treatment being in the range of 160 °C or lower.
Whereas in case of use of Ca-based additive powders, the separation of \( \text{SO}_3 \) and HF takes place with a high reaction velocity in the complete temperature range, the dry temperature as well as the absolute and relative humidity in the gas have a considerable influence on the HCl and \( \text{SO}_2 \) separation. Decreasing temperature and increasing humidity will improve the efficiency. Depending on the parameters of an application, the min. admissible operating temperature has to be selected in that way, that deposits and blockages, especially due to the hygroscopic features of \( \text{CaCl}_2 \) particles, will be avoided within the plant. The preferred operating temperature lies approximately 70 K above the water dew point. This corresponds to a temperature range of 130 to 145 °C.

The separation stage composed of the conditioning rotor reactor with additive powder injection, fabric filter and multiple particle re-circulation including particle conditioning, serves for the following:

*Creation of good reaction conditions of up to \( n \times 100 \text{ g/m}^3 \) due to the particle re-circulation*

Especially when achieving high (up to 50fold) additive powder recycle rates, the particle recirculation demonstrably leads to a considerable improvement of the separation capacity, with regards to the acid crude gas components and/or to a reduction in the additive powder injection rate [7].

- Increase in residence time of additive powder particles in the system.
- Higher additive powder density near the reactor upstream filter (the reaction time within reactor amounts to up to > 2 sec.).
• A frequent, spacial new orientation of the re-circulated additive powder particles with rebuild of filter cake on the filter fabric.

It should be noted that the multiple particle recirculation also has an advantageous effect on the reliable achievement of limit values for dioxins/furans and mercury as well as mercury compounds with a corresponding low injection quantity of AC. The large additive powder potential within the system also helps to reliably achieve the limit values during Hg peaks.

* Improvement particularly with regard to the SO₂ separation, due to the wetting of the re-circulated particulate

As described previously, 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 SO₂, can only be achieved if the water steam partial pressure close to the additive particles lies at least for a short time in the range of the saturation steam pressure. This will be achieved by the wetting of the recycled particulate prior to re-injection into the reactor. Up to the evaporation of the water injected into the humidifying mixer, the wetting causes an increase in the water steam content on the surface of additive powder particles, thus improving the reactivity regarding the acid crude gas components.

The following characteristic figures have to be considered for the necessary additive powder injection quantities as well as for the resulting residue quantities:

• Specific injection quantities for Ca(OH)₂
  * HCl: 1.5 up to 1.9 kg Ca(OH)₂/kg HCl
  * SO₂: 1.75 up to 2.2 kg Ca(OH)₂/kg SO₂

• Resulting specific residue quantities
  * HCl: 2.6 up to 3.2 kg residue/kg HCl
  * SO₂: 2.7 up to 3.4 kg residue/kg SO₂

Operating results of numerous installed plants confirm the characteristic figures above [5, 9].

Additionally, it should be mentioned that as an alternative to Ca(OH)₂, CaO may be used as additive powder. Prior to injection in the reactor, CaO will in this connection be converted to Ca(OH)₂ in a dry hydrator by means of water injection. A large number of such systems have previously proven the reliability in continuous automatic operation. The saving of costs lies in an approximate order of 15 EUR/t Ca(OH)₂.

* Comparison of the conditioned dry sorption with the spray sorption process

Today, the conditioned dry sorption as described above has in many cases replaced the spray sorption process with the injection of lime slurry. The corresponding reasons are lower investment and operating costs. The reasons for the higher efficiency of the conditioned dry sorption are explained in the following.
Comparative examinations regarding the additive powder utilisation have been completed at a plant in Germany, provided with both spray sorption and a conditioned dry sorption [2, 11]. The result was a definitely lower additive powder consumption in case of consistent operation of dry sorption compared to the spray sorption. The relevant reasons for this are:

**Formation of CaCO₃ during the aqueous phase**

Compared to the acid crude gases HCl, HF and SO₂, the slightly acid carbon dioxide has a minor affinity to hydrated lime. However, the concentration of CO₂ within the gas is definitely higher. A CO₂ concentration of approximately 10 %-Vol., corresponding to 100,000 ppm, is faced with a HCl concentration of e.g. 1,600 mg/m³, corresponding to 1,000 ppm. During the wet phase a considerable amount of CaCO₃ will be formed which – after drying of lime slurry drops – will have a very limited availability for the reaction.

A disadvantage of incinerators for waste and alternative fuels is, that due to the hygroscopic features of CaCl₂, a temperature reduction to values definitely below 140 °C and by this a possible reactivation of the CaCO₃ during the wet phase will not be possible. In case of a corresponding water injection, the conditioned dry sorption system installed downstream may lead to a partial reactivation of the CaCO₃.

**Formation of agglomerates**

The microscopic photos in Figure 2 show fresh hydrated lime particles compared to calcareous particles extracted downstream of the spray absorber. The freshly slaked hydrated lime has a clearly visible, high outer surface. However, after drying within the spray absorber, this will be reduced, due to the formation of drop shaped agglomerates. Therefore the exchange surface necessary for the chemical reaction will be reduced.

**Influence of particle re-circulation**

As described in section 3.1 of this lecture, the multiple particle re-circulation of the conditioned dry sorption creates a higher particle density within reactor; and increases the residence time of the additive powder. In addition, the separation conditions within the filter will be improved.

---

Figure 2: Surface structure of Ca(OH)₂, upstream and downstream of the spray absorber

Due to the multiple particle re-circulation, the conditioned dry sorption offers advantages regarding the separation of dioxins/furans and mercury. Last but not least, even in case of crude gas peaks, the emission limit values will reliably be achieved with low AC injection.

**Application example**

Some years ago the existing spray sorption system of a waste incinerator in Germany was modified to the conditioned dry sorption process. The reasons for the modification were as follows:

- Reliable achievement of emission limit values for SO₂ and HCl even in the case of arising crude gas peaks.
- Clear reduction in the additive powder consumption rate for the optimisation of operating costs.

![Image](image-url)  
**Figure 3:** Gas cleaning system of MHKW Rothensee after modification

Figure 3 shows the gas cleaning system after modification. The spray absorber was kept as unit but now mainly serves as an evaporative cooler for the adjustment of the optimum reaction temperature. A small quantity of additive powder is still injected as suspension for the reduction of acid dew point and a graded sorption. Depending on the crude gas input values, the main quantity of additive powder is injected into the reactor upstream of the filter in the form of Ca(OH)₂. Ca(OH)₂ is produced on site from CaO by means of a dry hydrator.
Table 2: Results of modification

<table>
<thead>
<tr>
<th>Measuring value</th>
<th>Unit</th>
<th>Prior to modification</th>
<th>After modification</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO\textsubscript{xclean}</td>
<td>mg/m\textsuperscript{3}</td>
<td>31.4</td>
<td>7.1</td>
<td>considerably decreased</td>
</tr>
<tr>
<td>SO\textsubscript{xcrude}</td>
<td>mg/m\textsuperscript{3}</td>
<td>571</td>
<td>597</td>
<td>almost the same</td>
</tr>
<tr>
<td>SO\textsubscript{load}</td>
<td>kg/a</td>
<td>92,455</td>
<td>17,642</td>
<td>considerably decreased</td>
</tr>
<tr>
<td>HCl\textsubscript{clean}</td>
<td>mg/m\textsuperscript{3}</td>
<td>6.4</td>
<td>6.8</td>
<td>almost the same</td>
</tr>
<tr>
<td>HCl\textsubscript{crude}</td>
<td>mg/m\textsuperscript{3}</td>
<td>1,456</td>
<td>1,422</td>
<td>almost the same</td>
</tr>
<tr>
<td>HCl\textsubscript{load}</td>
<td>kg/a</td>
<td>17,842</td>
<td>18,201</td>
<td>almost the same</td>
</tr>
<tr>
<td>(m\textsubscript{CaO, specific})</td>
<td>kg/t\textsubscript{waste}</td>
<td>-7.1</td>
<td>-</td>
<td>considerably decreased</td>
</tr>
<tr>
<td>(m\textsubscript{Ca(OH)\textsubscript{2}, specific})</td>
<td>kg/t\textsubscript{waste}</td>
<td>-2.1</td>
<td>-</td>
<td>completely cancelled</td>
</tr>
<tr>
<td>(m\textsubscript{HOK, specific})</td>
<td>kg/t\textsubscript{waste}</td>
<td>-0.3</td>
<td>-</td>
<td>slightly decreased</td>
</tr>
<tr>
<td>(m\textsubscript{remainder product, specific})</td>
<td>kg/t\textsubscript{waste}</td>
<td>-12</td>
<td>-</td>
<td>considerably decreased</td>
</tr>
<tr>
<td>(m\textsubscript{H\textsubscript{2}O})</td>
<td>kg/t\textsubscript{waste}</td>
<td>+0</td>
<td>-</td>
<td>constant</td>
</tr>
<tr>
<td>Stoichiometry</td>
<td></td>
<td>3.3</td>
<td>&lt;1.8</td>
<td>considerably decreased</td>
</tr>
<tr>
<td>(\Delta p\textsubscript{plant})</td>
<td>mbar</td>
<td>+0</td>
<td>-</td>
<td>constant</td>
</tr>
<tr>
<td>(\eta\textsubscript{plant})</td>
<td></td>
<td></td>
<td></td>
<td>slightly increased</td>
</tr>
<tr>
<td>(Q\textsubscript{electric, specific})</td>
<td>kW/t\textsubscript{waste}</td>
<td>+5.5</td>
<td>-</td>
<td>slightly increased</td>
</tr>
</tbody>
</table>
Figure 4 shows the separation efficiency of the process by means of continuously measured crude gas and clean gas concentrations for HCl and SO₂ over a period of 24 hours. It is clearly visible that not least as a result of the multiple particle re-circulation and the wetting of the re-circulated particulate, the emission limit values can reliably be kept in automatic operation even in case of HCl and SO₂ peaks.

Table 2 shows a summary of the positive results of the modification. The high particle re-circulation combined with the particle wetting results in a significant saving of additive powder costs. The stoichiometry could be reduced from 3.3-fold to < 1.8-fold. Additionally, the SO₂ separation could be improved as a result of the particle conditioning. Based on approximately the same crude gas values, the clean gas value could be reduced from > 30 mg/Nm³ to approximately 7 mg/Nm³ [4].

2.1.2. Dry sorption with NaHCO₃

The dry sorption with NaHCO₃ competes with process technologies using Ca-containing additive powder qualities. The quite simple process technology of the basic variant is shown in Figure 5. The additive powder is milled and injected into the gas flow upstream of the filter. In the case of crude gas temperatures > 140 °C, a thermal activation of sodium hydrogen carbonate will take place, which becomes quicker with rising temperatures. This results in the formation of a highly-reactive sodium carbonate. The reaction time from injection point of additive powder into the ducting until the arrival at the filter fabric should at least total to 2 seconds.

![Diagram of dry sorption with NaHCO₃](image)

Figure 5:
Basic variant of dry sorption with NaHCO₃

Particularly in case of lower temperatures (< approximately 160 °C) the multiple re-circulation of the particles separated in the filter into the flue gas flow upstream of the filter can be advantageous. [6]
The main advantages of this technology are:
- High reactivity of additive powder
- Simple plant structure
- Residue quantity is reduced compared to the additive powder injection (advantage in case of high disposal costs)
- Lower hygroscopic nature of the resulting salts

The opposing disadvantages are:
- Unfavourable mass ratio of additive powder to crude gas
- Necessary pulverisation of additive powder prior to injection into the flue gas flow (pre-milled products are available but present different disadvantages)
- High specific purchase costs of the additive powder

The operation of realised plants results in the following experience-based values for the additive powder consumption.

- Additive powder injection quantities for NaHCO₃
  * HCl: 2.45 up to 2.7 kg NaHCO₃/kg HCl
  * SO₂: 2.75 up to 3.1 kg NaHCO₃/kg SO₂

- Resulting residue quantities
  * HCl: 1.7 up to 1.9 kg residue/kg HCl
  * SO₂: 2.3 up to 2.65 kg residue/kg SO₂

2.1.3. Process comparison

When looking at only the separation of acid crude gases without consideration of further gaseous substances to be separated, there are, referring to the operating costs, clear advantages for conditioned dry sorption. This is demonstrated by the following specific additive powder costs for the separation of HCl and SO₂.

- HCl separation
  * Ca(OH)₂: 0,52 EUR/kg HCl
  * CaO: 0,37 EUR/kg CO₂
  * NaHCO₃: 0,85 EUR/kg HCl

- SO₂ separation
  * Ca(OH)₂: 0,55 EUR/kg SO₂
  * CaO: 0,40 EUR/kg SO₂
  * NaHCO₃: 1,00 EUR/kg SO₂
The indicated values are based on the usual procurement costs for additive powders as well as on the price for the disposal of residues amounting to 100 EUR/t. The higher investment costs for the conditioned dry sorption may certainly not be neglected. In the case of smaller combustion capacities, this results by tendency in an advantage for the dry sorption with NaHCO₃ and in the case of medium and larger combustion capacities there is a clear advantage for the conditioned dry sorption using calcium based additive powders.

2.2. Separation of heavy metals as well as dioxins/furans

As far as heavy metals (except for Hg and Hg compounds) are present in gaseous form due to their steam pressure, they can be converted in particulate compounds by means of chemical reactions with the basic additive powders. In the case of a sufficient quantity of basic additive powders, the separation reliably takes place even in case of temperatures > 200 °C. The separation of Hg and Hg compounds as well as of dioxins/furans is achieved by adsorption to additive powders with large specific surface. Usually, activated coke and/or activated carbon are used for this purpose.

The adjusted gas temperature upstream of the filter is an essential factor for the separation efficiency of especially Hg and Hg compounds. The lower the temperature, the more efficient the separation. This is a clear advantage of the conditioned dry sorption compared to the dry sorption, as generally a lower temperature in a range of 130 °C up to 145 °C is adjusted in the reactor/filter area, whereas the preferred temperature for the dry sorption with NaHCO₃ is > 170 °C. Additionally, the high re-circulation rate of the conditioned dry sorption and the wetting of the re-circulated particulate lead to a very efficient separation. Generally, it may be noted that the dry temperature upstream of the filter should never lie above 200 °C in order to assure a sufficient Hg separation and to exclude as far as possible, the risk of smouldering fires in parts of the plant caused by self-ignition. The usual monitoring devices such as temperature and level measurements have to be considered in any case.

The continuous monitoring of Hg emission values, which is already generally required in Germany and is expected for all other EU countries in future, resulted in the fact that many plants have now been equipped with precautionary measures for the separation of Hg peaks. In this regard, especially the additional injection of doped activated carbon in case of increasing emission limit values may be noted. The injection of additional liquid additives in an evaporative cooler installed upstream of the conditioned dry sorption system may be a further measure [1]. Even acid scrubbing stages installed downstream of a condition dry sorption system can contribute to Hg separation.

The separation of dioxins/furans is reliably possible both by means of a mere dry sorption and by means of a conditioned dry sorption. Operating experience gained from installed plants does not show any dependency on the filter temperature.

The injection quantity of activated coke/activated carbon is, apart from a necessary minimum concentration in the particle spectrum, mainly determined by the Hg concentration in the crude and the requested clean gas value. Furthermore, the particle
re-circulation, the wetting of re-circulated particulate, the filter temperature and the additive powder quality have a determining role. Generally, it can be said that even with regard to heavy metals and dioxins/furans the conditioned dry sorption has clear advantages with regards separation efficiency and additive powder consumption compared to the basic dry sorption with NaHCO₃.

3. Influence of the NOₓ reduction on the selection of process

3.1. Preliminary remark

The BREF dated 2006 specifies two BAT-AEL levels for NOₓ:

- 40 up to 100 mg/Nm³ for SCR processes
- 120 up to 180 mg/Nm³ for SNCR processes

A NH₃ slippage of < 10 mg/Nm³ is indicated for both processes. Depending on the individual countries, often lower values are already specified compared to the emission limit value of 200 mg/Nm³ for NOₓ stipulated in the Directive 2000/76/EC. The 17. BImSchV (dated 2. May 2013) for example states a daily average value of 150 mg/Nm³ at a NH₃ slippage of max. 10 mg/Nm³. As a result of these specifications, SNCR processes were in most cases used for the NOₓ reduction, whereas also the slippage values for NH₃ can be kept without any additional measures.

The BREF revision and the at the same time necessary adoption of emission limit values into national law will lead to significantly stricter regulations. The first draft of the BREF specifies a NOₓ limit value in a range of just 50 up to 120 mg/Nm³ at a slippage of 3 up to 10 mg/Nm³ (Table 1). A footnote points to the fact that the correspondingly stated lower values have to be kept when using a SCR process and the higher values when using a SNCR process. Due to the stricter emission limit values it has to be expected that to achieve NOₓ and NH₃ emission limit values, combined processes will be used in numerous new plants in future. Some process variants are discussed in the following.

3.2. Combined processes for the reliable observance of emission limit values for NOₓ and NH₃

3.2.1. Combination of SNCR – Conditioned dry sorption – Wet scrubber

This process combination especially represents an alternative when the requested NOₓ emission limit values can reliably be kept by means of an SNCR process, however with a higher NH₃ emission. The basic design of this combined process is shown in Figure 6.

In this concept, the conditioned dry sorption is operated in such a way that the crude gas downstream of this stage only contains low residual concentrations of acid crude gas pollutants.
Depending on the application in question, the downstream installed fine cleaning stage serves for the:

- separation of NH₃ in an acid scrubber,
- increased reduction in emission values e.g. for the acid crude gas components,
- heat recovery.

Usually, the wet stage is designed as acid and basic scrubber.

**Acid scrubbing stage**

The acid scrubbing stage serves for the separation of NH₃, HCl and partly of SO₂. To allow this, the gas is cooled down to the saturation temperature by injection of water. In order to ensure a sufficient NH₃ separation, the pH-value in the scrubbing water of the acid stage has to be sufficiently low. In this respect the pH-value will be measured and possibly corrected by injection of H₂SO₄. An example of this is an installed plant that allows a reliable NH₃ reduction in continuous operation from approximately 15 mg/Nm³ dry to < 5 mg/Nm³ at a pH-value of < 5.6. [8]

Due to the fact that the acid scrubber only serves as a fine cleaning stage for the reduction of HCl beside the separation of NH₃, the waste water quantity can be kept on a low level. The injection of water near the conditioned dry sorption system is not possible, as this would release the NH₃ again. It is recommended to inject the low water quantity near the SNCR process in the boiler.

**Basic scrubbing stage**

The basic scrubbing stage mainly serves for a progressing separation of SO₂. In this connection a pH-value of > 6 has to be adjusted in this stage. The pH-value adjustment
is made depending on the requirements by injection of NaOH. The low waste water quantity can usually by injected in the conditioned dry sorption stage without any problems.

It should be noted that this process is preferably used for cases in which the increase in the energy efficiency, by the use of condensation heat of gases can for example be used for district heating networks. NOx values of < 100 mg/Nm³ can reliably be kept with this process with observance of a NH₃ slippage of < 5 mg/Nm³.

### 3.2.2. Combination of conditioned dry sorption with SCR process

As far as NOx emission limit values at the lower end of the value range of 50 up to 120 mg/Nm³ stated in the draft of WI BREF have to be kept, the installation of an SCR process will become necessary. The preferred temperature range for the catalyst in this connection lies in a range of 220 °C up to 240 °C. This temperature range allows a sufficiently good conversion speed. Problems due to the formation of ammonium sulphate can reliably be excluded, as far as the SO₂ content in the gas is < 10 to 25 mg/Nm³ depending on the temperature. Due to the preferred temperature range for the conditioned dry sorption of approximately 130 °C up to 150 °C, a reheating of gases is necessary upstream of the catalyst. It is true that the reheating of gases can to a large extent be realised by the heat recycling around the catalyst. There remains, however, a temperature difference of approximately 30 K which has to be balanced by an external heat input. For this purpose, e.g. natural gas burners or steam/gas heat exchangers are used. A heat exchanger installed downstream can be used for the heat recovery. The resulting quality of the generated heat, however, lies at a low level. Figure 7 shows the scheme of an installed plant.
Dry, Semi-dry or Wet – Which System Fits Best Depending on the Overall Conditions?

Due to the required input of thermal energy and the resulting reduction in the economic efficiency, the combination of conditioned dry sorption with an SCR process is usually only used when the additional energy generated by the downstream installed heat exchanger can for example be used for district heating networks.

3.2.3. Combination of dry sorption with SCR process

As the separation of acid crude gases and especially of $\text{SO}_x$ is very efficiently possible by means of $\text{NaHCO}_3$ in a temperature range of 220 °C up to 240 °C, the reheating can be omitted in case of a combination of a dry sorption with $\text{NaHCO}_3$ and a catalyst installed downstream. Figure 8 shows a possible process variant.

![Figure 8: Combination of 2-stage dry sorption – SCR](image)

The separation of acid crude gases is made in the first dry sorption stage at a temperature of approximately 240 °C by injection of $\text{NaHCO}_3$. The ammonia water injection, the mixing line and the catalyst are installed downstream. In an external economiser installed downstream of catalyst, the gas is cooled down to approximately 120 to 140 °C. By means of the injection of $\text{Ca(OH)}_2$ and activated carbon, a further dry sorption stage serves for the reliable separation of the remaining acid components in the gas, of heavy metals incl. mercury as well as of dioxins/furans. This combination does not only allow the achievement of low $\text{NO}_x$ and $\text{NH}_3$ values, but also assures a very good separation efficiency for all further pollutants with combined low additive powder consumption. When evaluating the profitability, however, one has to consider the specifically high procurement costs for $\text{NaHCO}_3$. 
It may be noted, that it is generally possible to operate catalysts even in case of lower temperatures in a range of for example 190 °C up to 200 °C. This would allow the direct injection of activated carbon in the first dry sorption stage. The second dry sorption stage could then be omitted. In case of this mode of operation, however, an SO₂ content upstream of the catalyst of clearly < 10 mg/Nm³ has to be reliably kept or additional measures for the removal of ammonium sulphate deposits have to be taken. For this purpose, the catalyst is usually divided in several sub-segments. From time to time, one of these elements is heated, the ammonium salts evaporate and are re-injected into the gas cleaning system downstream of the boiler. The additional technical effort should not be neglected.

The direct comparison of the two procedures above shows advantages for the two-stage dry sorption combined with a catalyst. The removal of ammonium salts is not necessary. Furthermore, the two-stage dry sorption offers an excellent separation efficiency even for all further gaseous matters. In energetic terms, this procedure offers advantages in contrast to the combination of conditioned dry sorption with SCR process.

4. Assessment

The requested NOₓ and NH₃ emission limit values play an essential role, when it comes to a comparative assessment of the presented process variants. If these limit values can be kept by means of a SNCR process without any additional measures for reduction of the NH₃ slippage, the dry sorption process offers clear advantages compared to the mere dry process with NaHCO₃. The separation of gaseous matters, such as acid crude gases, heavy metals incl. Hg as well dioxins/furans is efficiently and economically achieved by means of the conditioned dry sorption. The use of well-priced additive powders is possible. These advantages can in most cases not be compensated by the lower investment costs of dry sorption processes.

With regard to investment and operating costs, the conditioned dry sorption even offers advantages compared to the spray sorption technique frequently used in previous times. As far as the selection of the most suitable process is up to the plant constructor, priority will certainly be given to the conditioned dry sorption in nearly all cases.

As far as the emission limit values for NOₓ can be kept by means of a SNCR process, however regardless of a too high NH₃ slippage, one possibility is the combination of the conditioned dry sorption with a wet scrubber. Here, the wet stage at the same time serves as fine cleaning stage for acid components. The plant operates waste water-free. The waste water of the acid scrubber is re-injected in the boiler. The water of the basic stage is injected in the conditioned dry sorption stage. In addition it should also be noted that with this procedure it is possible to use the condensation heat for e.g. district heat, however, only with the provision of a waste water treatment plant.

If the NOₓ emission limit values can only be kept using a catalyst, the graded dry sorption process with NaHCO₃ in the first stage and Ca(OH)₂/activated carbon in the second dry sorption stage offers clear advantages. Very low emission limit values can be achieved for all pollutants with at the same time high energy efficiency.
In summary, it can be said that there is no ideal technology available for all project requirements. The objective is to choose the most suited technology for the corresponding basic conditions of an application, out of the large number of possible process variants, only some of which have been discussed in this lecture.

5. References


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