

LUEHR FILTER

**Reliable and economical –
Replies to the increased requirements on the
emission limit values from the point of view of a
plant constructor**

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1 Introduction

In the course of the past years semi-dry and/or conditioned dry procedures with utilisation of Ca-based additive powders for the gas cleaning downstream waste and RDF incinerators gained outstanding importance especially in Germany. This technology with simple design allows the simultaneous separation of particles, acid crude gas components such as HF, HCl and SO_x, mercury and other heavy metals as well as dioxins/furans in one stage. The requested emission limit values, e.g. in accordance with 17 BImSchV or EU Directive 2000/76/EC, will in case of typical inlet concentrations of components to be separated reliably be observed with at the same time acceptable operating costs.

However, due to the discussion about the tightened emission limit values i.a. for NO_x with consideration of a sufficiently low NH₃ slippage, this process has increasingly been put into question lately. Even for other components such as e.g. the acid crude gases or heavy metals, higher degrees of separation have been requested for many times.

Another challenge is the use of fuels with a high S- and/or Cl-content, particularly in connection with an inhomogeneous feeding in the firing. In order to compensate crude gas peaks in case of conventional plants, an increased additive powder injection has to be provided as a precaution to grant the reliable observance of the requested emission limit values.

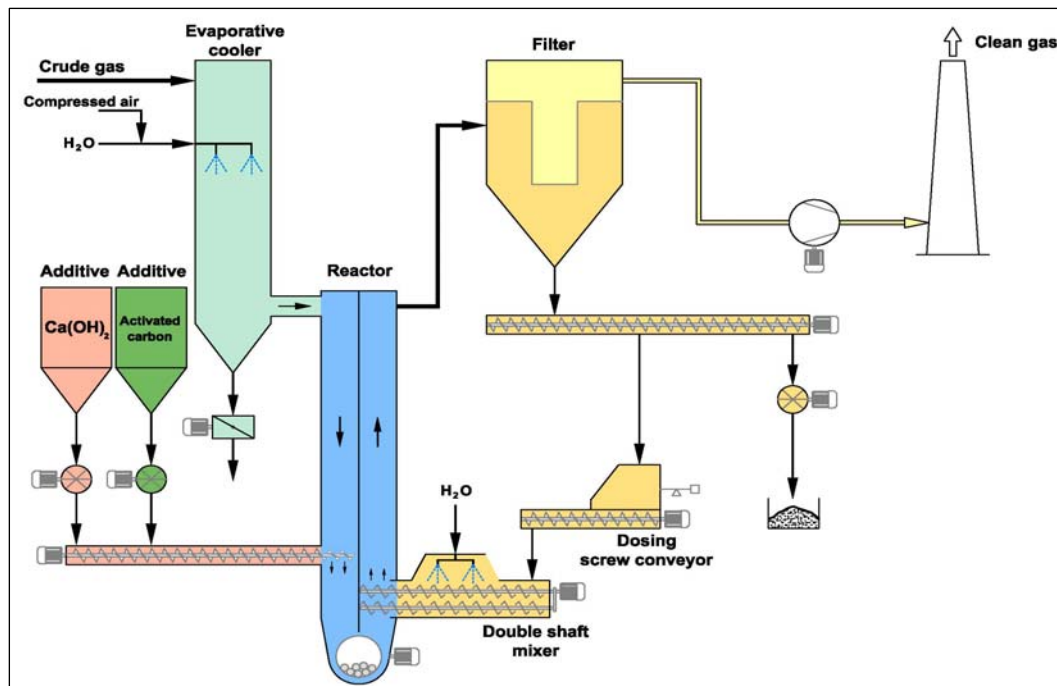
This lecture presents process additions to the conditioned dry sorption, which on one hand allow higher input values for acid crude gases and on the other hand reliably grant the economical observance of emission limit values in continuous operation and which - compared to the typical requirements of today - consider lower values. It also presents a procedure which grants the undershooting of NO_x emission limit values < 100 mg/Nm³ dry without the use of an SCR process.

2 Basic procedure: Chemisorption with gas and particle conditioning

2.1 Process description

Illustration 1 shows a schematic view of this technology which has been introduced and successfully installed since many years downstream waste incinerators for the reliable observance of the emission limit values accord. to 17 BImSchV. It mainly comprises the units evaporative cooler, additive powder injection, reactor, fabric filter as well as particle re-circulation with integrated particle conditioning.

The evaporative cooler (gas conditioning) serves for the optimum adjustment of the reaction temperature, combined with an increase in the absolute and relative humidity in order to optimise the separation and additive powder efficiency. Due to the fact that especially in case of alternative fuel incinerators and as a result of the fuel composition and pre-treatment the gas humidity is often lower than the one of e.g. domestic waste incinerators, the possibility of adjusting an optimum gas temperature gains special importance.



III. 1: Chemisorption with gas and particle conditioning

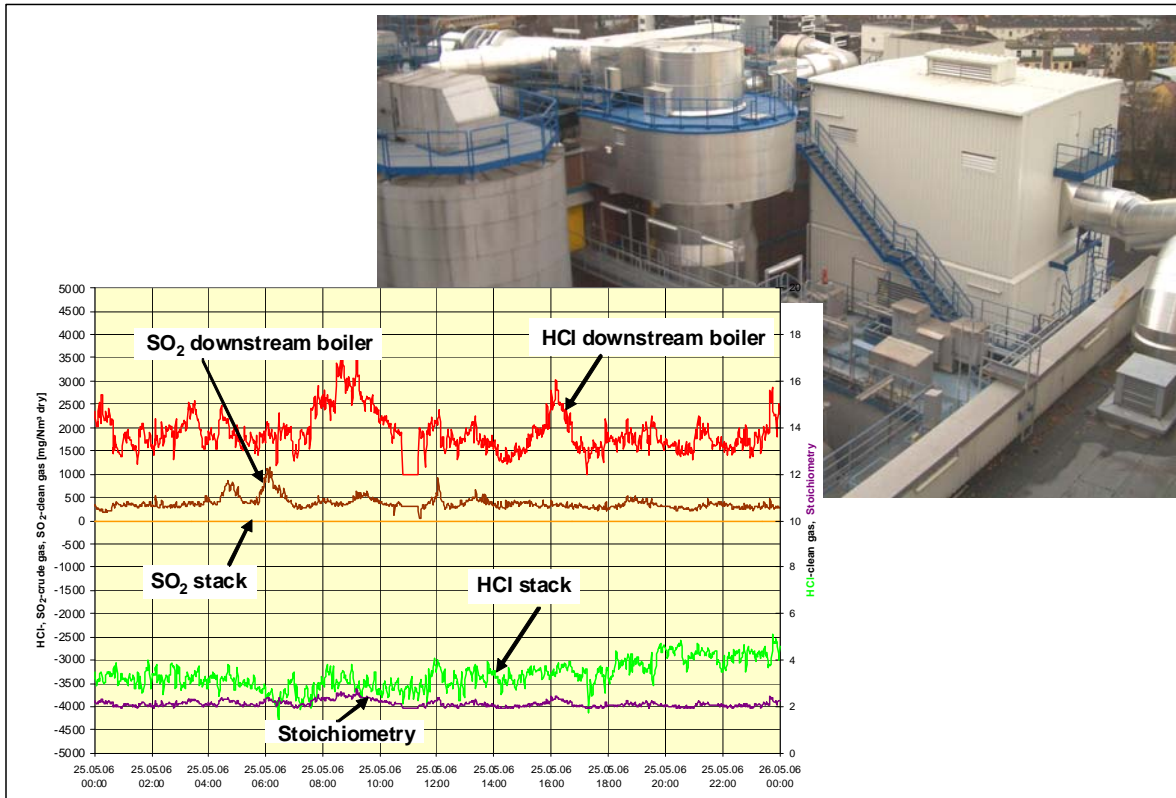
The crude gas sorption and separation of all other relevant components which are not reduced near the boiler and the combustion, takes place in the reactor - filter combination with injection of $\text{Ca}(\text{OH})_2$ and multiple particle re-circulation, including conditioning of re-circulated particulate. Excepted from this is the separation of NH_3 .

The objectives of this stage are:

- Creation of good reaction conditions by means of particle re-circulation up to $n \times 100 \text{ g/Nm}^3$
- Optimisation of SO_2 separation by means of moistening of re-circulated particulate
- Further, even though minor reduction of gas temperature

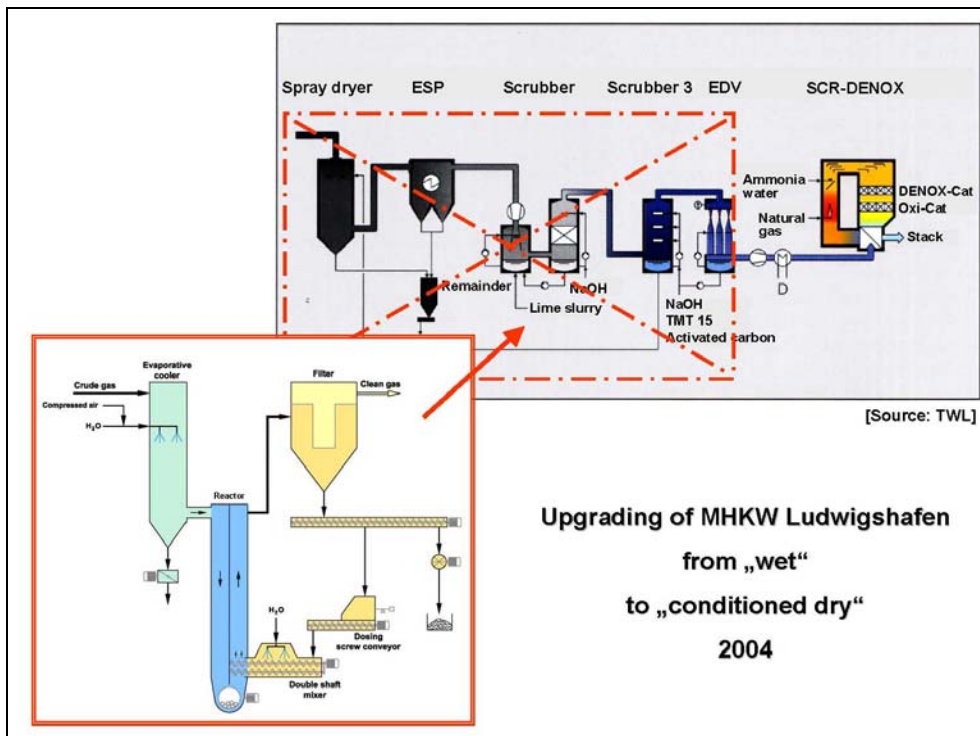
2.2 Application example

The efficiency of the above-described basic variant for the observance of the limit values accord. to 17 BImSchV with crude gas contents of up to approx. $2,000 \text{ mg/Nm}^3$ dry for HCl and up to $1,000 \text{ mg/Nm}^3$ dry for SO_2 is demonstrated by the waste heat generation station MHKW Ludwigshafen (illustration 2).



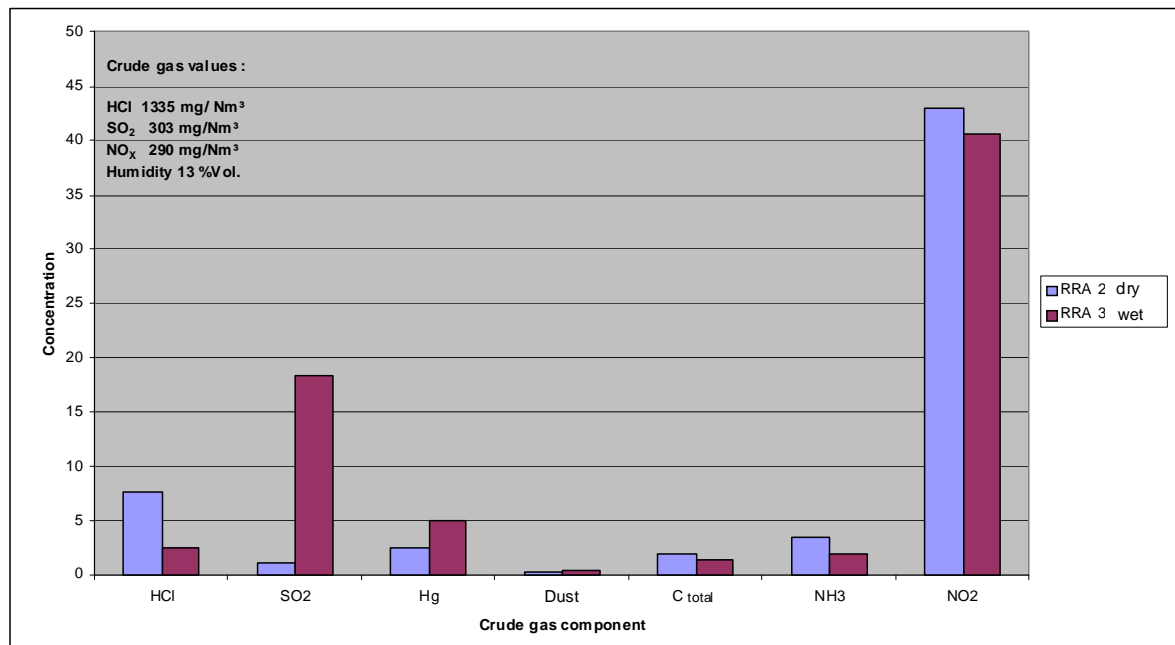
III. 2: Conditioned dry sorption in MHKW Ludwigshafen

The conditioned dry gas cleaning system was installed in 2004 and replaced a definitely more complex wet system, consisting of spray dryer, ESP, multi-stage scrubber and aerosol separator (illustration 3).



III. 3: Upgrading of MHKW Ludwigshafen from "wet" to "conditioned dry"

Up to the year 2008, another wet flue gas treatment system had been operated in parallel with the conditioned dry gas cleaning at the MHKW Ludwigshafen until its conversion in 2008, thus allowing a direct comparison of both installed variants. Illustration 4 shows the average values of the year 2005 for selected substances.



III. 4: 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. SO₂ for the scrubber and HCl for the conditioned dry sorption.

The high degree of SO_x separation combined with a nearly 100% SO₃ sorption by means of the conditioned dry sorption process allowed a reduction in operating temperature of the downstream installed SCR plant in the MHKW Ludwigshafen from 300°C to 230° C. An additional advantage for the saving of energy costs is the higher gas temperature upstream SCR stage of approx. 140°C.

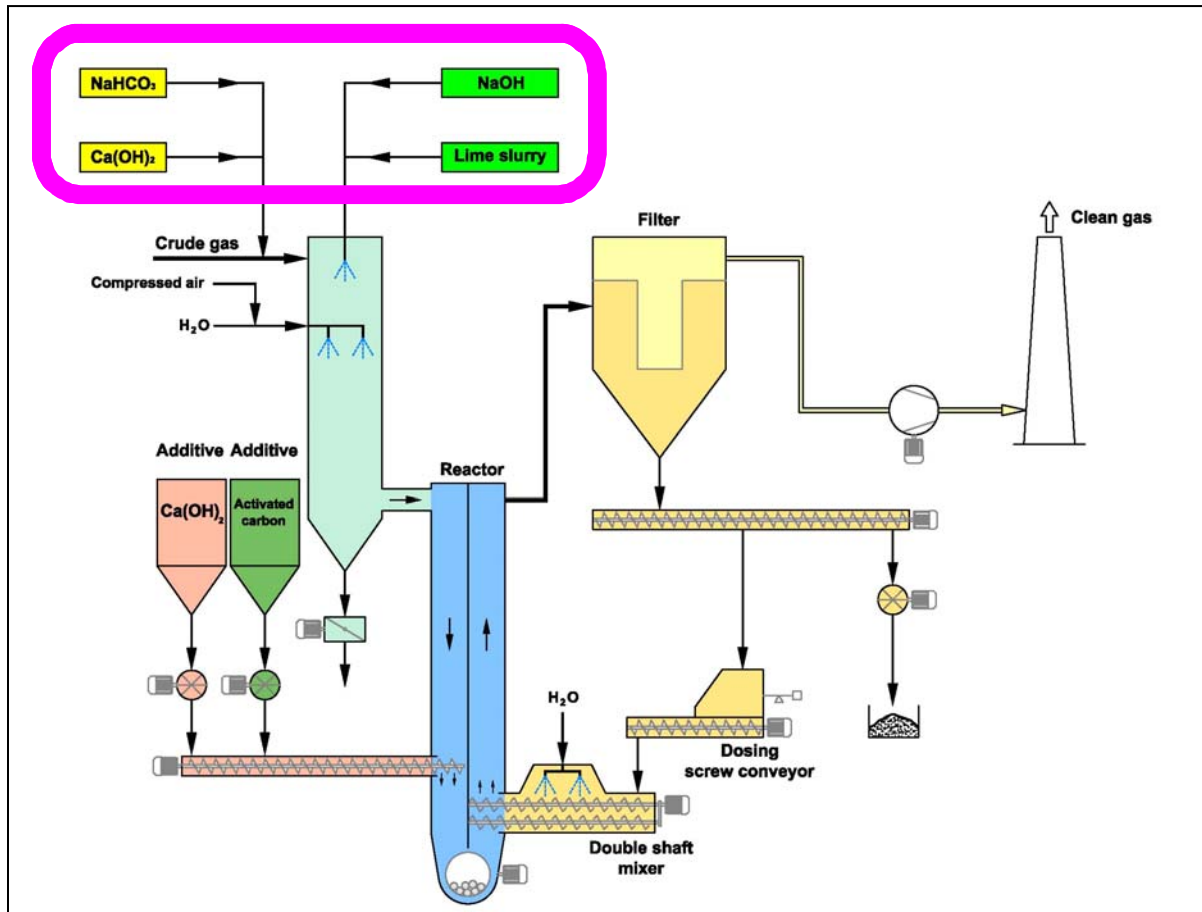
It should be mentioned in addition that compared to the spray sorption, an important advantage of the conditioned dry sorption is the better degree of separation regarding SO₂. This is especially important in case of downstream installation of SCR plants.

3 Conditioned dry sorption with graded additive powder injection

3.1 Process variants

In case of increased requirements on the separation efficiency for the acid crude gas components HCl and/ or SO₂ – mainly due to high input values or in case of need also for the observance of very low emission limit values – it might be reasonable to use the evaporative cooler as upstream installed reaction chamber.

Besides the additional reaction time of more than 2 sec., it offers excellent reaction conditions for the separation of acid crude gas components by means of the cloud of water droplets generated for the gas cooling.



III. 5: Conditioned dry sorption with graded additive powder injection

With regard to the second stage of graded additive powder injection it is not compulsory necessary to use Ca-based additive powders as in the first stage. Illustration 5 shows different process variants.

Not only due to cost reasons, particularly the variants

- graded injection of $\text{Ca}(\text{OH})_2$
- injection of NaOH into evaporative cooler

became accepted in the practice. With regard to all shown concepts, the main quantity of additive powder is in the nominal load case injected as commercially available $\text{Ca}(\text{OH})_2$ into the reactor downstream evaporative cooler. The injection of additive powder upstream or inside of evaporative cooler / spray absorber mainly serves for the corrosion protection as well as for the smoothing of crude gas peaks.

The operating experiences gathered from the use of the above-mentioned concepts are described in the following.

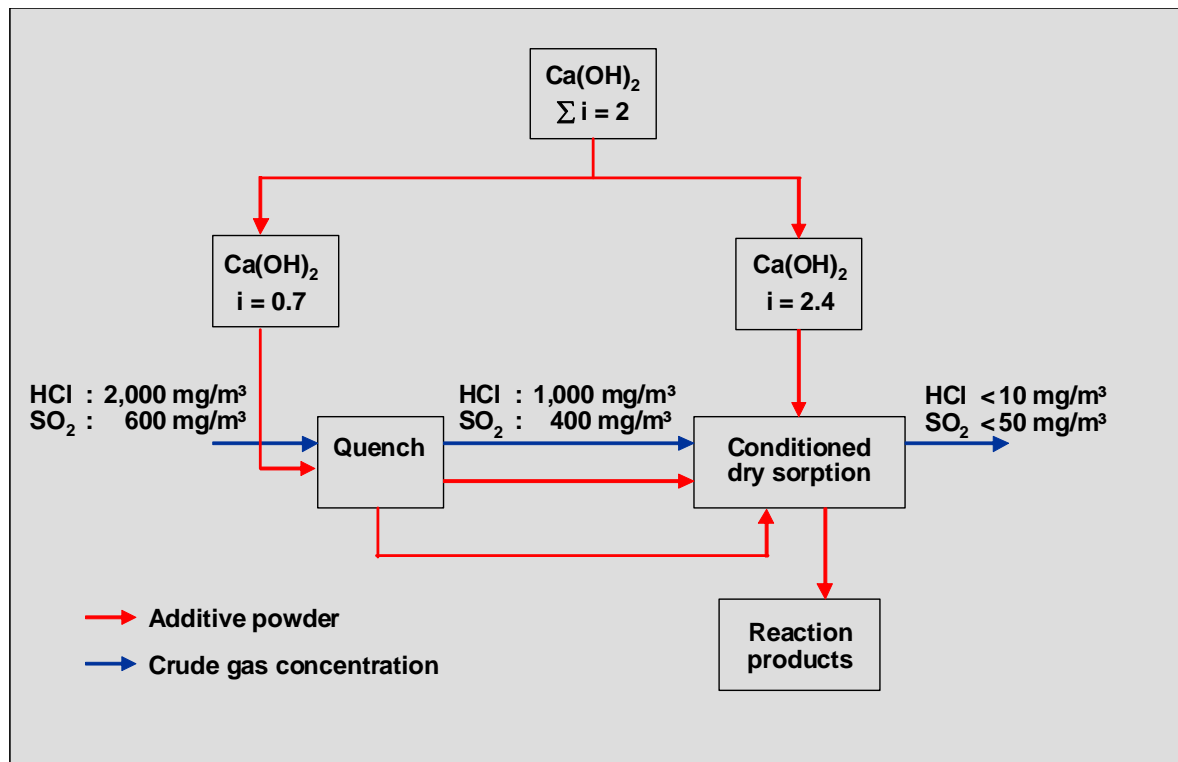
3.2 Graded injection of $\text{Ca}(\text{OH})_2$

This is surely the simplest variant of the graded additive powder injection which has successfully been installed at several realised RDF incineration plants. Reference examples are shown in illustration 6.



III. 6: Reference examples for RDF incinerators

The example shown in illustration 7 presents the advantages of a graded additive powder injection. In the first stage with low stoichiometry related to the crude gas input, a large part of the HCl content (80%) and to a less degree of the SO_2 content are separated. With reference to the crude gas contents to be expected after the first stage and compared to the summarised stoichiometry, a considerably higher stoichiometric injection quantity will be available for the fine cleaning in the second stage.



III. 7: Stoichiometry at graded additive powder injection

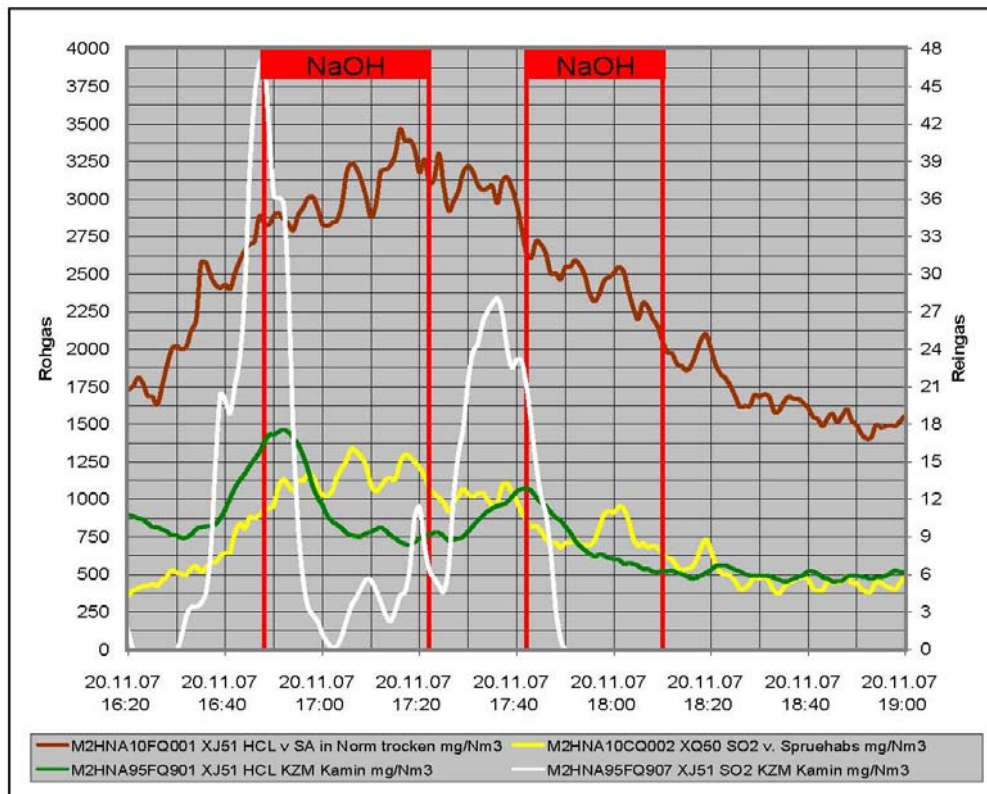
The further advantages of this technology are:

- Simple plant structure
- Long contact time between crude gas molecule and additive powder injected upstream evaporative cooler
- Excellent reaction conditions in the cloud of water droplets within evaporative cooler
- Redundant additive powder injection possible
- No limitation of additive powder injection quantity, as given in case of the spray sorption by the max. lime slurry concentration
- Low maintenance
- Increased formation of CaCO_3 is not expected

The sole disadvantage of this variant is, that depending on the overall concept, long pneumatic conveying routes have partly to be realised, suitable for continuous operation.

3.3. Injection of NaOH inside of evaporative cooler

Due to cost reasons, the adjustment of the control of the additive powder injection of the conditioned dry sorption is often based on an optimised stoichiometry. Regarding the nominal operation, this means a set value for the stoichiometric factor of 2 or less. The clean gas values for HCl then lie in a range of 6 up to 8 mg/Nm^3 dry. As a result of this adjustment the system is prone to HCl crude gas peaks. Without any additional measures, the additive powder injection has - in case of such peaks - to be increased far above-proportional for the reliable observance of the requested emission limit values, thus undoing at least partly the cost advantage of low stoichiometry in the nominal operation.



III. 8: Operating experiences regarding the reduction of HCl peaks with injection of NaOH [1]

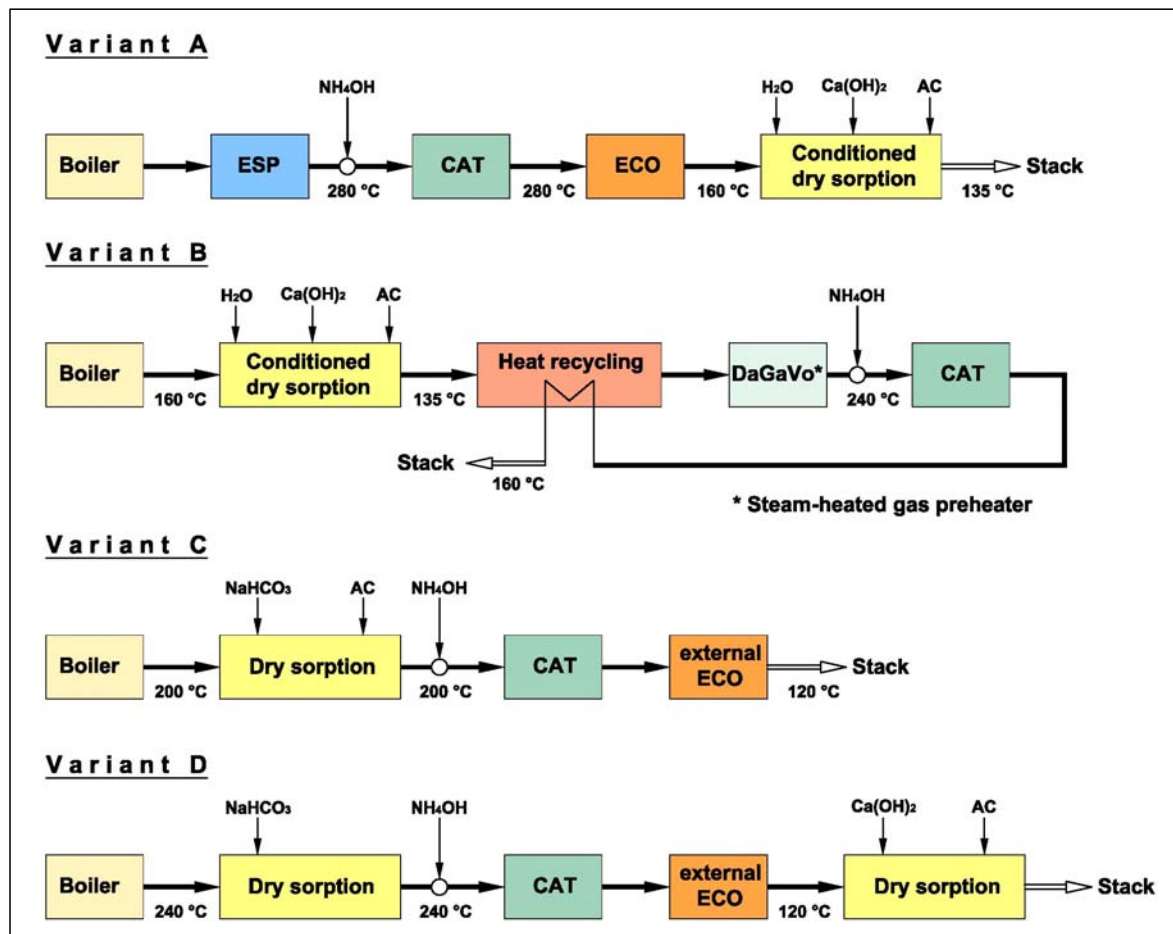
An alternative and in addition well-priced solution is the variable spraying of NaOH into the evaporative cooler depending on the HCl and SO₂ crude gas values. Corresponding examinations have been realised i.a. in the MHKW Ludwigshafen in the year 2007. The efficiency of the NaOH injection in case of crude gas peaks is underlined by the measurements in use shown in illustration 8.

The NaOH injection was started during constant Ca(OH)₂ injection into the reactor of conditioned dry sorption and at rising HCl and SO₂ crude gas values. A spontaneous improvement of the separation efficiency was achieved. To control the efficiency, the NaOH injection was interrupted for a certain time during this test series with still unchanged Ca(OH)₂ injection and was re-started again.

4. Process variants for the observance of tightened emission limit values, i. a. for NO_x clean gas values < 100 mg/Nm³ dry

4.1 Examples of process variants with integration of a catalyst for the NO_x-reduction

Based on the discussion of tightened emission limit values i.a. for NO_x, considering a sufficiently low NH₃ slippage, the conditioned dry sorption was lately increasingly put into question also in connection with a graded additive powder injection. Even for other components such as the acid crude gases or heavy metals, higher degrees of separation have been requested for many times, which cannot be kept reliably without taking additional measures.



III. 9: Flue gas treatment concepts with catalyst for NO_x reduction

Especially the requirement for an improved NO_x reduction involved that increasingly process concepts with integration of an SCR stage have been realised or have been put out to tender for new projects. Illustration 9 exemplary shows some process variants which have been used for incinerators for waste and/or RDF. These concepts do of course only represent a selection of possible variants.

All procedures are characterised by a very good reduction of NO_x in connection with a low NH_3 slippage. However, all variants do also present considerable disadvantages, as shown by trend in illustration 10. The particular disadvantage of variants A and B with utilisation of Ca-based additive powders is that with regard to an improved separation of further gas components beside NO_x , additional process stages will become necessary. In case of use of NaHCO_3 as additive, the high additive powder costs have to be looked upon negatively. Only the variant D shows an improved separation efficiency for further gas components beside NO_x . Detailed information about the advantages and disadvantages of presented variants are included in [2].

	A	B	C	D
Investment costs	-	-	+	-
Operating costs				
• Additive powder	o	o	-	-
• Power ^{*)}	o	-	+	o
Separation efficiency ^{**)}				
• NO _x + NH ₃	+	+	+	+
• HCl, SO ₂	-	-	-	+
• Hg (+SM)	o	o	-	+
^{*)} incl. heat recovery ^{**)} objective: emission values definitely below the typical requirements				

+ advantageous
o average
- disadvantageous

III. 10: Assessment of concepts shown in illustration 9

Due to the fact that all introduced variants show aggravating disadvantages, it was obvious to look for alternative procedures. The essential criteria for the considerations are:

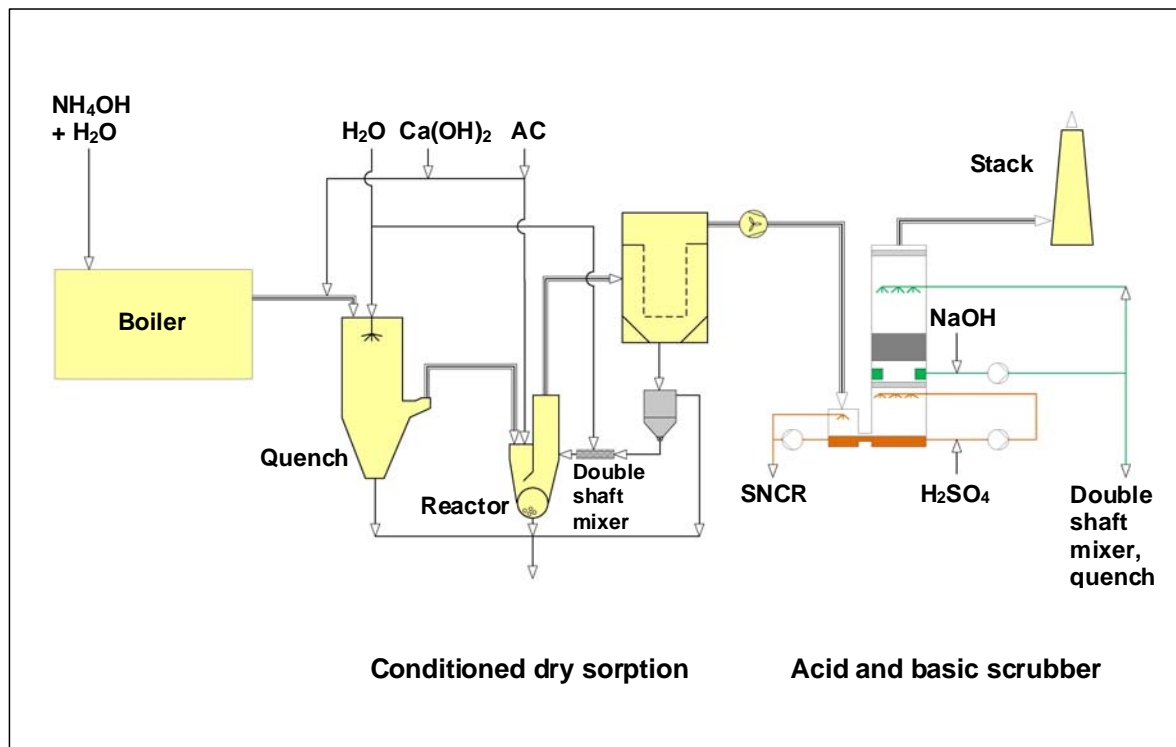
- preferable use of an SNCR - technology
- use of Ca-based procedures for the separation of acid crude gases
- high energy utilisation
- waste water-free operation
- on request, observance of low emission limit values for acid crude gases, mercury and other heavy metals, particles, dioxins/furans

The TwinSorp process developed by LUEHR FILTER is able to fulfil the above-mentioned requirements.

4.2 TwinSorp process

4.2.1 Preliminary remarks and general design

The combination of SNCR with conditioned dry sorption proved to be successful with regard to the requirements accord. to 17 BImSchV or EU Directive 2000/76/EC. The procedure is simple, reliable and economical. The emission limit values accord. to 17 BImSchV are reliably observed. Furthermore, the SNCR technology is nowadays able to observe also NO_x contents definitely below 100 mg/Nm³ dry, however with an increased NH₃ slippage. Following to this, in case of request for lower emission values for NO_x, this well-proven process has only to be extended by one stage for the separation of NH₃. This can be achieved by the installation of a wet fine cleaning stage downstream conditioned dry sorption.



III. 11: *TwinSorp – Basic variant: Combination of conditioned dry sorption - acid and basic scrubbing*

The basic scheme of TwinSorp process is shown in illustration 11.

The conditioned dry sorption of this process variant is operated in that way that the crude gas downstream this stage will as far as possible comply with the requirements of e.g. 17 BImSchV or EU Directive 2000/76/EC. Depending on the application in question, the downstream installed fine cleaning stage serves for the

- separation of NH_3
- progressing reduction in emission values e.g. for the acid crude gas components
- heat recovery

Depending on the requirements, the wet stage of TwinSorp process can be realised as:

- scrubber with acid and basic stage
- acid and basic stage with wet ESP
- measures for heat recovery
 - Heat exchanger between conditioned dry sorption and wet stage
 - Use of heat of condensation inside of scrubber

Below follows a discussion of the separate design types of fine cleaning stage.

4.2.2 Scrubber with acid and basic stage

4.2.2.1 Acid scrubbing stage

The acid scrubbing stage serves for the separation of NH_3 , HCl and partly of SO_2 . To allow this, the gas is cooled down to the saturation temperature by injection of scrubbing water.

In order to ensure a sufficient NH_3 separation, the ph-value in the scrubbing water of the acid stage has to be sufficiently low. Only in case of a definitely acid operating mode, an efficient separation of NH_3 can be achieved. In this respect the ph-value will be measured and possibly corrected by injection of H_2SO_4 . An example of this is a realised plant that allows a reliable NH_3 reduction in continuous operation from approx. 15 mg/Nm^3 dry to $< 5 \text{ mg/Nm}^3$ dry at a ph-value of < 5.6 . Depending on the NH_3 and HCl concentration, a sufficiently low ph-value will temporarily be reached in the water, even without injecting other chemicals.

A high-capacity droplet separator is installed downstream of acid scrubbing stage. This is of considerable importance in order to achieve a clear separation between acid and basic stage. This allows a separate reuse of waste water generated in both stages. In case of a necessary NH_3 separation, a direct injection of purge water from the acid stage into the quench of the conditioned dry sorption or the humidifying mixer of this stage will not be possible. Without a discharge of NH_3 , this will be released again after contact with the basic additive powders in connection with water. With regard to this discharge way, an additional NH_3 stripper has to be installed. This additional unit is complex and energy-intensive in operation.

Due to the fact that the acid scrubber only serves as a fine cleaning stage for the reduction of HCl beside the separation of NH_3 , the waste water quantity can be kept on a low level. With regard to this small amount of water, a much simpler and cost-effective alternative of use is available. During the SNCR process, the NH_4OH solution is normally further diluted, to achieve a homogeneous dispersion of reduction agent over the whole distribution section within boiler. This dilution water can either partly or in total be replaced by the waste water of the acid stage. The NH_3 in the water is at the same time used for the reduction of NO_x . Referred to the HCl mass flow from the fuel, the inlet of HCl is very low. Negative influences on the process, e.g. due to a rise in the HCl concentration upstream crude gas cleaning, have to be excluded.

4.2.2.2 Basic scrubbing stage

The basic scrubbing stage mainly serves for a progressing separation of SO_2 . In this connection a ph-value of > 6 has to be adjusted in this stage. In this connection and depending on the requirements, a corresponding amount of NaOH will be injected into the scrubbing water. Even in this case a droplet separator is installed downstream of stage.

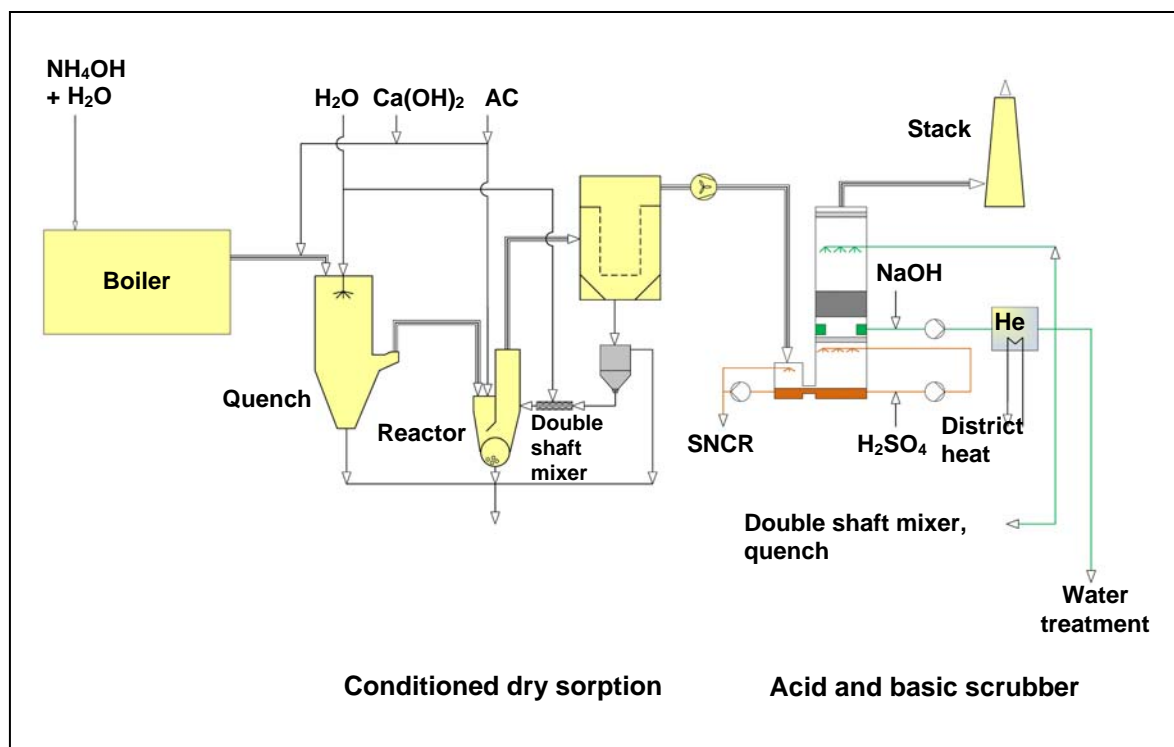
A small amount of waste water has continuously to be extracted. As far as no heat distribution is integrated in this stage, the purge volume can be kept at such a low level that this water in the evaporative cooler of conditioned dry sorption or also in the humidifying mixer of this stage can be used for the cooling of gas downstream boiler and/or for the conditioning of recycled particulate without any further treatment.

Condition for this is of course the the acid crude gases are basically separated in the conditioned dry sorption stage and that the scrubber is operated as fine cleaning stage.

To achieve a progressing separation of particles, heavy metals and/or aerosols, the droplet separator of this stage can be replaced by a high-capacity wet ESP. An emission of sal ammoniac aerosols can reliably be excluded when a wet ESP will be used.

4.2.2.3 Utilisation of heat of condensation

Especially in Northern Europe, the heat of condensation contained in a wet stage is often used as energy input in a district heating network. The heat amounts to be supplied in this connection are not unimportant. Based on the typical general conditions of a waste incinerator, the specific heat amounts can lie in a range of approx. 800 up to 850 kW for a crude gas volume of 10,000 Nm³ humid.



III. 12: Concept for the utilisation of heat of condensation

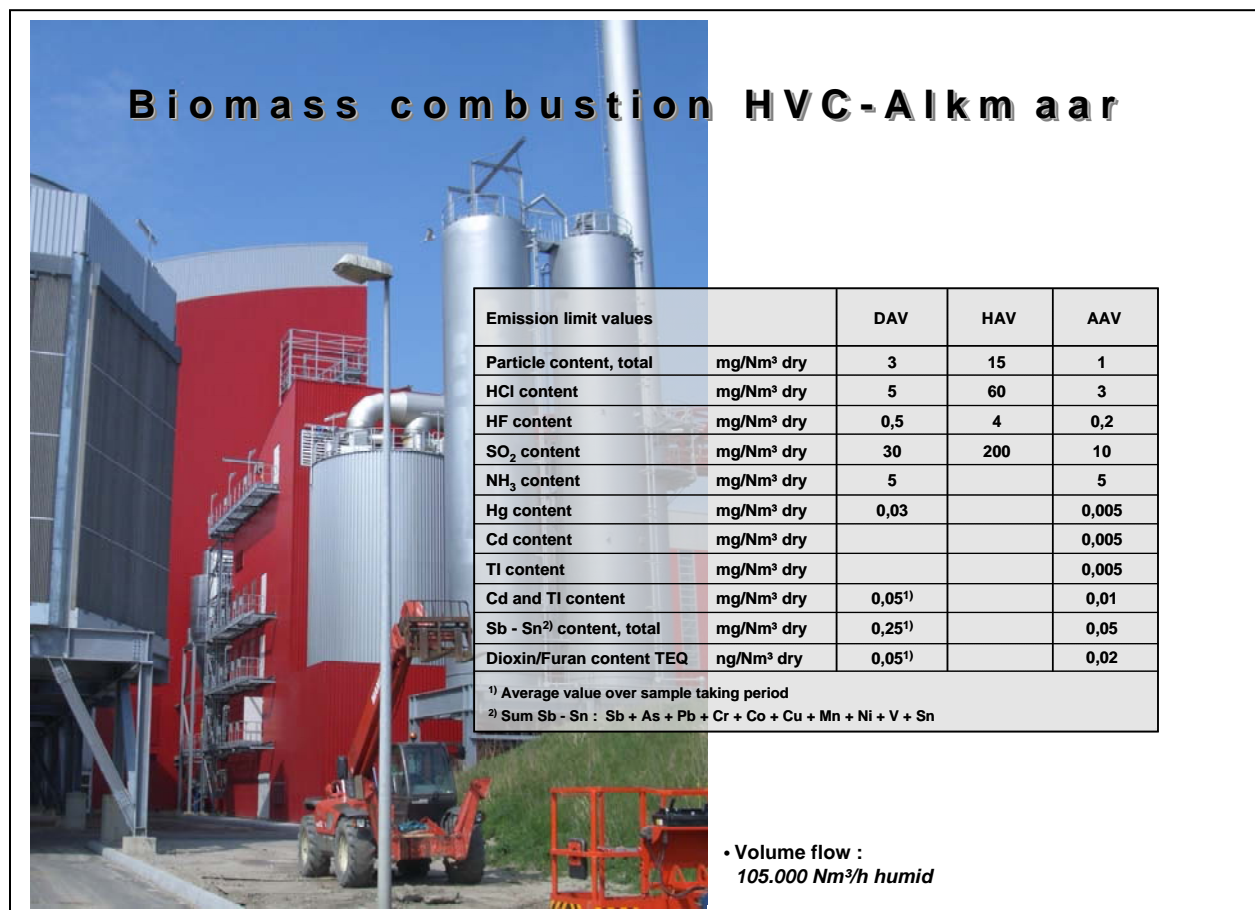
The basic scrubbing stage is in this case realised as packed bed scrubber (illustration 12). The scrubbing water is dispersed on the packed bed by means of nozzles. While trickling through the packed bed the waste water is heated and at the same time the saturated off-gas is cooled down during passage through the packed bed from the bottom to the top. The heated water is directed to an external plate heat exchanger in which the heat is partly transferred to the liquid of district heating network. After that the waste water is re-injected into the scrubber above packed bed. A droplet separator is installed downstream of basic scrubber.

The waste water quantities arising for this application are of course considerably higher and are determined by the cooling down of the gases. A use in the conditioned dry sorption is only possible for a small part. In any case, a waste water treatment has to be installed in accordance with the requirements of location. Due to the separate discharge of water from the acid stage, the use of an NH₃ stripping can in any case be omitted.

This lecture will not go into the design and the possibilities of realisation of such a waste water treatment. However, it may be mentioned that such type of plant will always be connected with comparatively high costs and expenditure.

4.3 Application examples for the TwinSorp process

As an example for a realised plant using the TwinSorp process, illustration 13 shows a gas cleaning system downstream fluidised bed combustion for biomass in the Netherlands.



III. 13: Gas cleaning downstream biomass combustion at HVC in Alkmaar

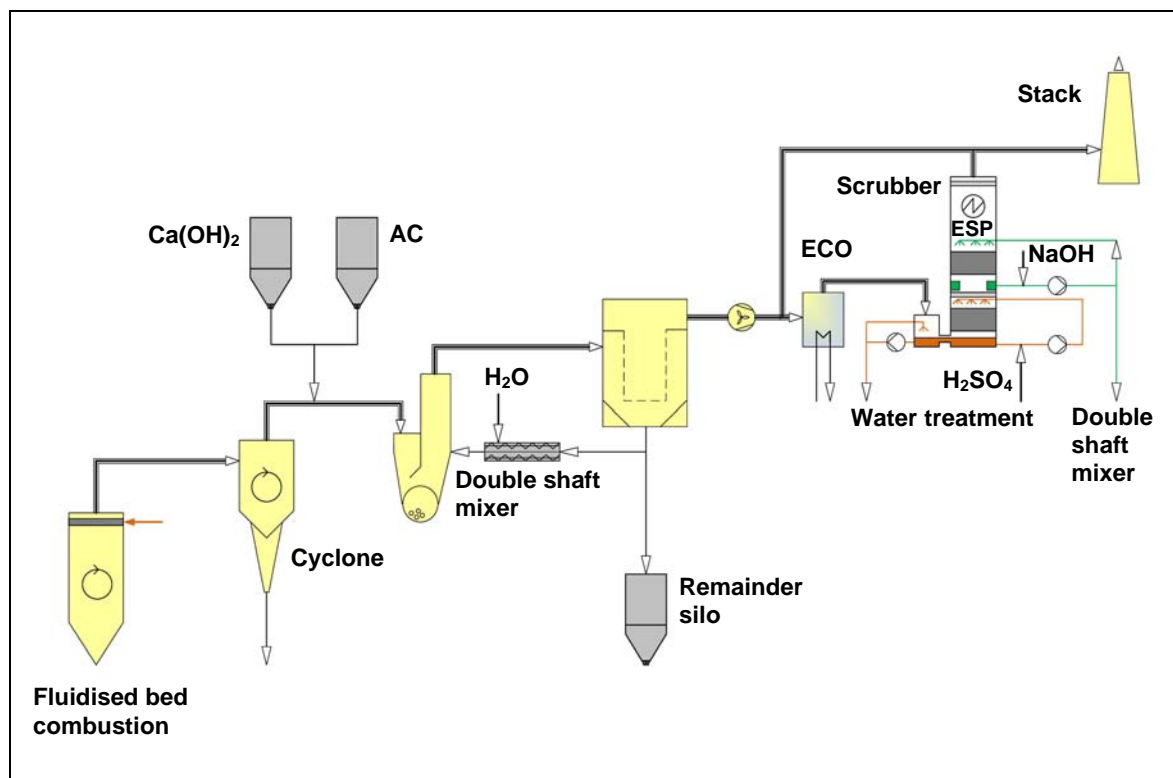
In order to observe the requested NO_x limit value of 70 mg/m³, the boiler manufacturer installed an SNCR plant. The NH₃ slippage downstream boiler is limited to max. 15 mg/m³. Illustration 10 shows also shows a listing of the requested emission limit values to be observed by means of the gas cleaning system installed downstream of boiler.

The requested, extremely low emission limit values especially for the annual average values, make clear that the gas cleaning system - besides a main stage for the observance of the emission limit values in a range of e.g. the EU Directive 200/76/EC - has to be provided with an additional fine cleaning stage, allowing a progressing separation of nearly all requested emission limit values.

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

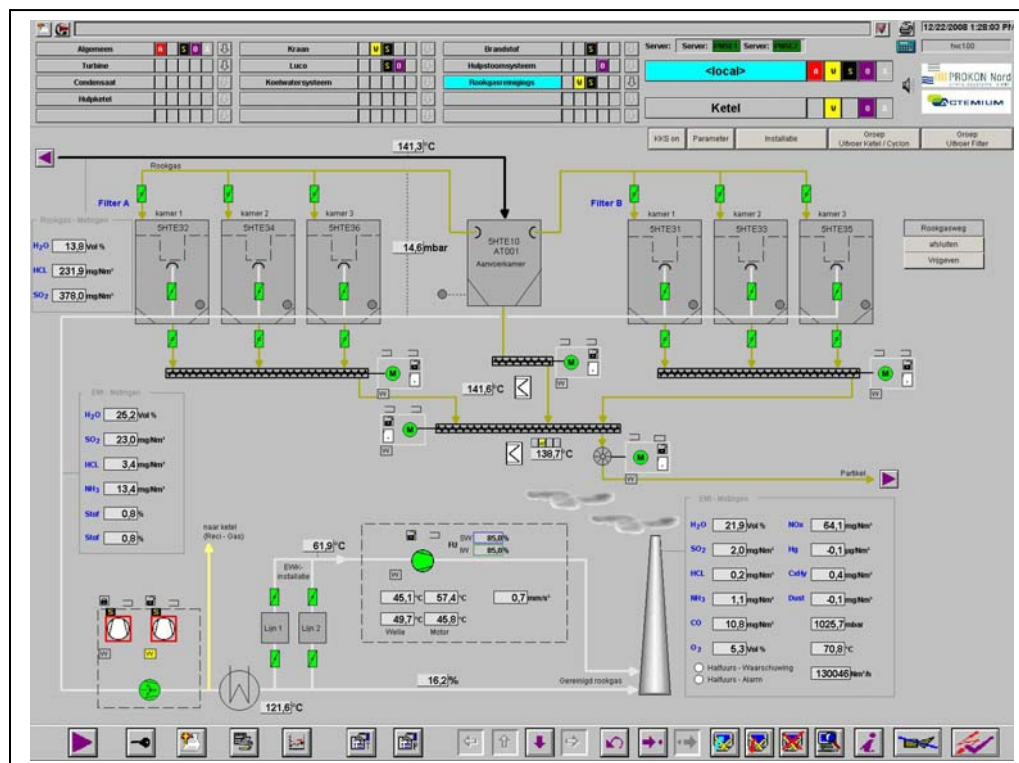
- cyclones for separate fly ash separation
- conditioned dry sorption at approx. 150°C
- heat exchanger for cooling down of gas to approx. 100°C
- wet ESP with integrated acid and basic stage

Besides an integrated NH_3 separation, this concept offers the reliable observance of extremely low emission limit values for all further components in an economical way. As a result of the requested high degrees of separation for particles and heavy metals, the wet ESP had been installed in addition instead of the second droplet separator. The design of the gas cleaning system is shown in the rough scheme in illustration 14.



III. 14: Process concept for gas cleaning system at HVC Alkmaar

This plant has been in operation for more than 2 years. It allows the reliable observance of all relevant emission limit values in continuous operation without any restrictions. Illustration 15 exemplary shows continuously measured emission values at stack as instantaneous values as well as in addition for some components the concentrations in the intermediate gas downstream conditioned dry sorption and/or upstream wet fine cleaning stage.



III. 15: Emission values at HVC Alkmaar

5 Summary of process advantages

As a result of the increasing requirements on the degrees of separation for gas cleaning system downstream incinerators for waste and RDF, a further development and/or completion of the nowadays available, well-proven process technologies became necessary. In addition to the reliable observance of the requested emission limit values, low investment and operating costs have also to be considered, taking into account the heat distribution command.

In many cases the addition of a graded additive powder injection to the basic variant with the conditioned dry sorption already proved to be sufficient to achieve the requested separation efficiency even in case of increased requirements. Particularly regarding the control of input peaks of acid crude gas components, this variant proved of optimal performance in practice.

With regard to a high efficiency separation of nearly all gas components to be treated in the gas cleaning, the discussed TwinSorp process is a comparably simple variant, that can flexibly be adapted to the corresponding requirements. The main advantages are:

- Even in case of emission limit values definitely below 100 mg/Nm³ dry, a simple SNCR process can still be used for the NO_x separation.
- The use of reasonably priced Ca-based additive powder qualities for the separation of acid crude gas components in the main separation stage remains possible even in case of higher requirements on the NO_x reduction and without energetic disadvantages when using a catalyst.
- HCl and/or SO₂ peaks in the off-gas downstream boiler do not have to be compensated by means of a disproportionately high additive powder injection. The reliable observance of the clean gas values is the objective of the wet stage. Resulting from this, the available additive powder quantity in the conditioned dry sorption can be reduced in total. Due to the associated low stoichiometry, savings regarding procurement and disposal costs will result.
- Flexible adjustment of process to the corresponding requirements of an application by means of variation of wet pre-scrubbing stage.
- Cost-efficient and reliable observance of low emission limit values in continuous operation.
- The process works without waste water and without a complex NH₃ stripping.
- Measures for a progressing heat distribution can be integrated.

References:

- [1] Wradatsch, R. (TWL-MHKW Ludwigshafen): "Möglichkeiten der Beherrschung von Schadstoffspitzen mit der Trockensorption des MHKW Ludwigshafen", 5th Symposium in Potsdam – Optimisation of the thermal waste and remainder treatment – Perspectives and possibilities, 21 - 28 February 2008
- [2] Margraf, R. (LUEHR FILTER GmbH): "TwinSorp - a simple process for increased requirements on the emission limit values i.a. for waste and RDF incinerators, considering the energy efficiency command", Haus der Technik e.V. - 6th symposium: Dry flue gas cleaning for firing installations and other thermal processes, 11 - 12 November 2010



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