**Dry and semi-dry crude gas cleaning
downstream incinerators for waste
and other combustibles**

1. Introduction

The utilisation of fabric filters in connection with the dry and semi-dry chemical sorption of acid crude gas components such as HF, HCl and SO_x and, if necessary, including the separation of dioxins / furans as well as Hg and/or Hg compounds and other heavy metals, becomes more and more important with regard to the fields of application of incineration plants. The further development of the sorption procedures used in this connection, proved to be an effective, reliable and cost-effective alternative compared to e.g. wet procedures. In the following this shall be made clearer by means of several application examples. The main focus lies on the chemical sorption of acid crude gas components. As restrictive remark please note, that beside the illustrated variants, further alternative solutions are available on the market which are used in practice.

2. Procedures with utilisation of Ca-containing additive powders

2.1 Dry sorption with gas conditioning

2.1.1 Process description

The fundamental design is shown in illustration 1. It mainly consists of the components fabric filter and additive powder injection device. For increase in efficiency, it is often extended by a reactor with particle re-circulation and an evaporative cooler.
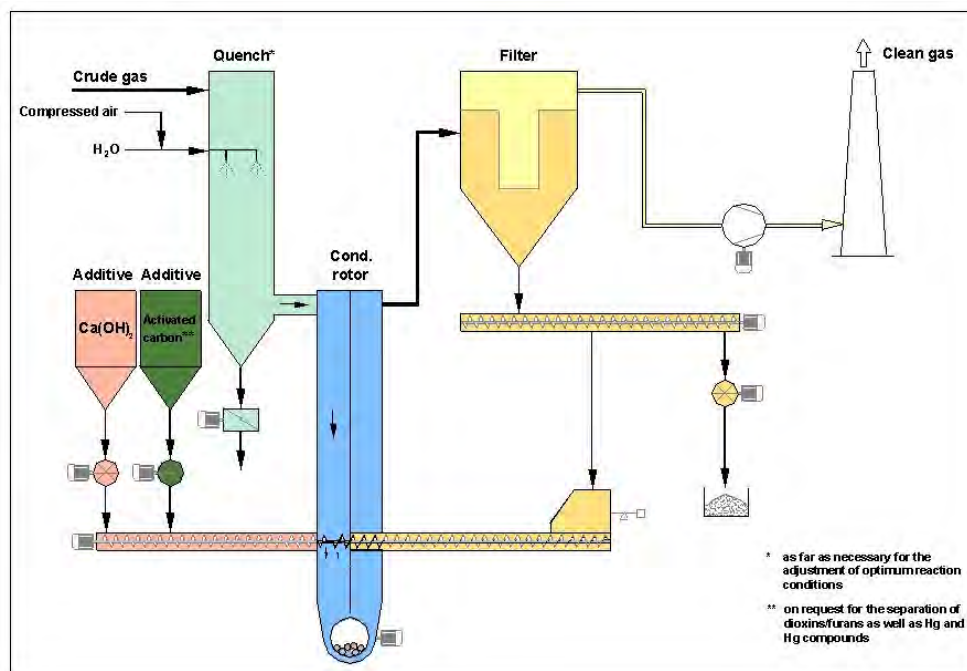

Illustration 1: Dry sorption with gas conditioning

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In general, a commercially available calcium hydroxide, $Ca(OH)_2$, with a specific surface of approx. 18 up to 20 m^2/g is injected into the crude gas flow upstream filter. In special cases $Ca(OH)_2$ qualities with a special surface of up to 40 m^2/g are used. The reaction equations as well as the injection and remainder quantities at an additive powder efficiency of 100% are listed in table 1.

Equations of reaction	$Ca(OH)_2$ - injection quantity related to crude gas at 100% stoichiometric (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. 1: Reaction equations for $Ca(OH)_2$

In order to achieve the reliable observance of the requested emission levels in the practice, the additive powder has to be injected over stoichiometry (normally 1,5- up to 3fold).

It is proven 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 of 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 > 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 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 large 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 a high reliability and a homogeneous distribution of the re-circulated particulate in the crude gas flow upstream filter. Conveying with pneumatic methods, which is prone to frequent breakdowns, is not used.
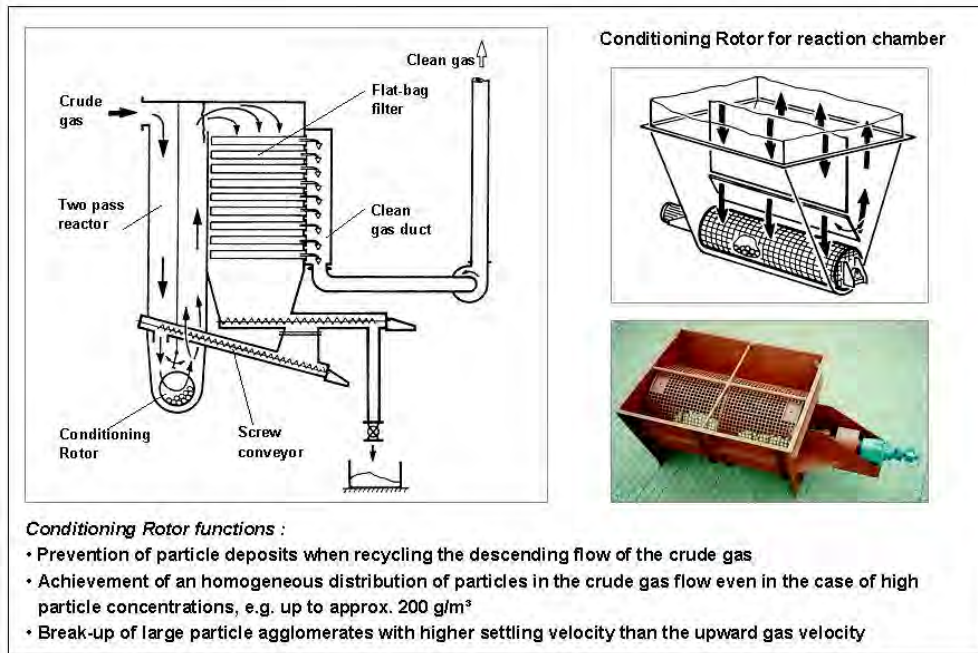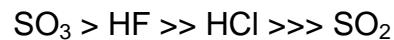
Illustration 2: Conditioning Rotor – Recycle Process (KUV)

The following order of reaction becomes effective for a temperature range
between 100°C and 220°C (this range is usual 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 preferential temperature range, depending on the
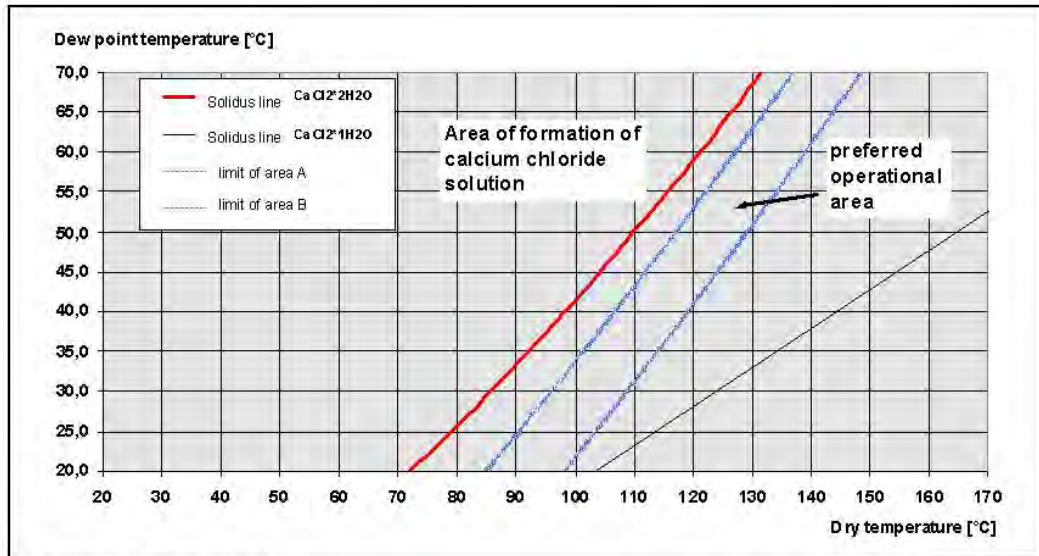dew point temperature.

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Reference: Dr. Mosch, Karpf

Illustration 3: Phase diagram CaCl₂ • x H₂O

2.1.2 Application examples

2.1.2.1 Pyrolysis plant for aluminium recycling of remainders

The application of this pyrolysis plant is the aluminium recycling of remainders. The pyrolysis gas is fed into a thermal post-combustion and a dry sorption plant with gas conditioning and particle re-circulation.
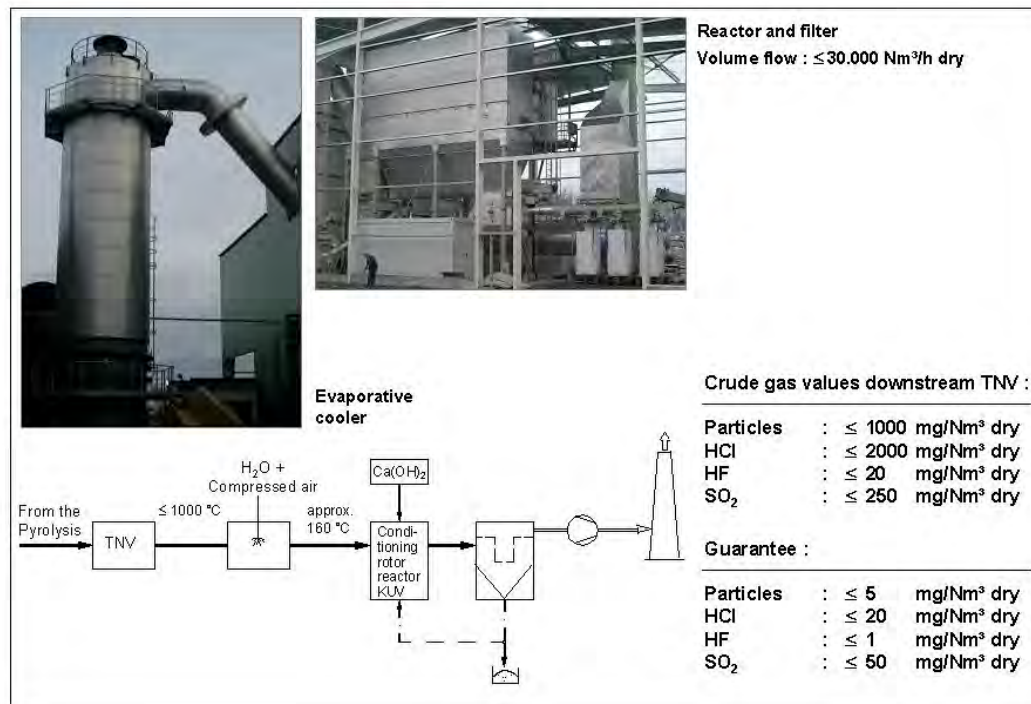

Illustration 4: Application example of a pyrolysis plant for aluminium recycling of remainders

Illustration 4 shows the main plant data as well as the evaporative cooler and the filter with reactor (prior to completion of cladding). Due to the water dew point of > 75°C, the temperature upstream filter is adjusted to min. 160°C. Regarding this application, the basic aim is the separation of HCl. For this purpose, the comparatively simple process technology is quite sufficient.

2.1.2.2   Incineration of industrial waste

Illustration 5 shows another example for a crude gas cleaning downstream an industrial waste incinerator. The plant is executed as pure dry sorption plant. Due to a customer request, the utilisation of water for the conditioning has completely been omitted. Therefore a gas – air heat exchanger has been installed upstream reactor filter plant instead of an evaporative cooler. In order to avoid corrosion in the heat exchanger, a part of the additive powder is injected upstream heat exchanger.

The plant has been designed in two stages in order to

* optimise the additive powder efficiency

* grant the reliable separation of HCl and SO_2 peaks in the crude gas even when using a pure dry sorption

* grant the reliable reduction of the extremely high dioxin crude gas content to values < 0,1 ng/m^3
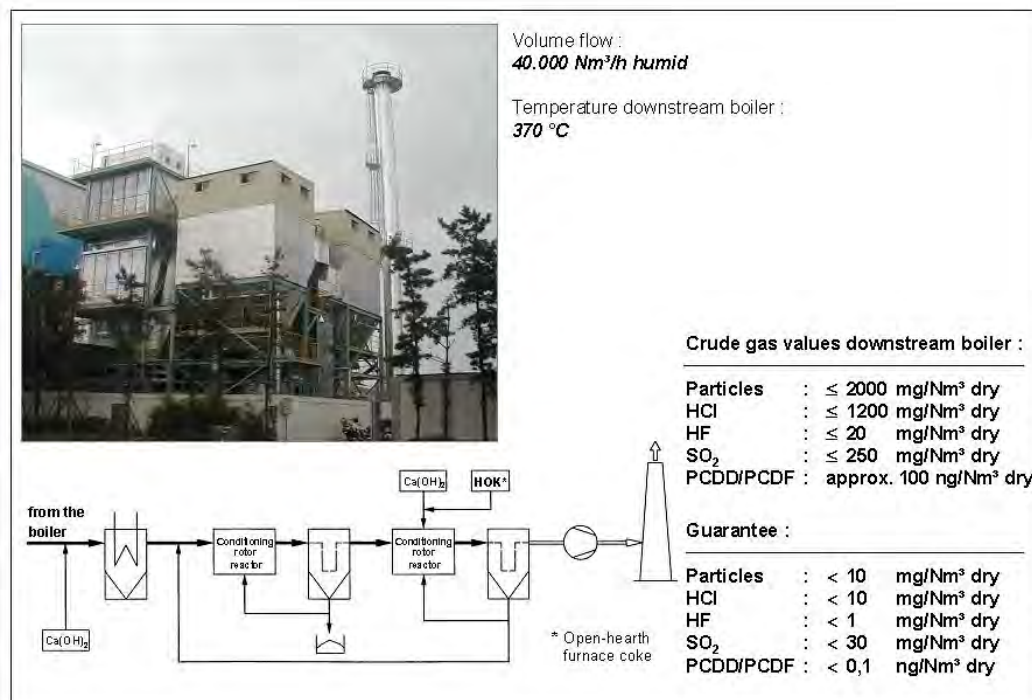

Illustration 5: Application example of a waste incineration

The main advantage of this technology is the counter flow of the used additive powder. Due to the pre-separation of acid crude gas components in the first filter stage and the upstream installed heat exchanger, considerably higher stoichiometric factors are achieved in the second fine cleaning stage than the resulting summarised stoichiometry (illustration 6).

The disadvantage of the chosen technology is the utilisation of two fabric filters installed in sequence. The higher operating costs related to the energy consumption and the filter material have to be taken into consideration when calculating the economic efficiency.
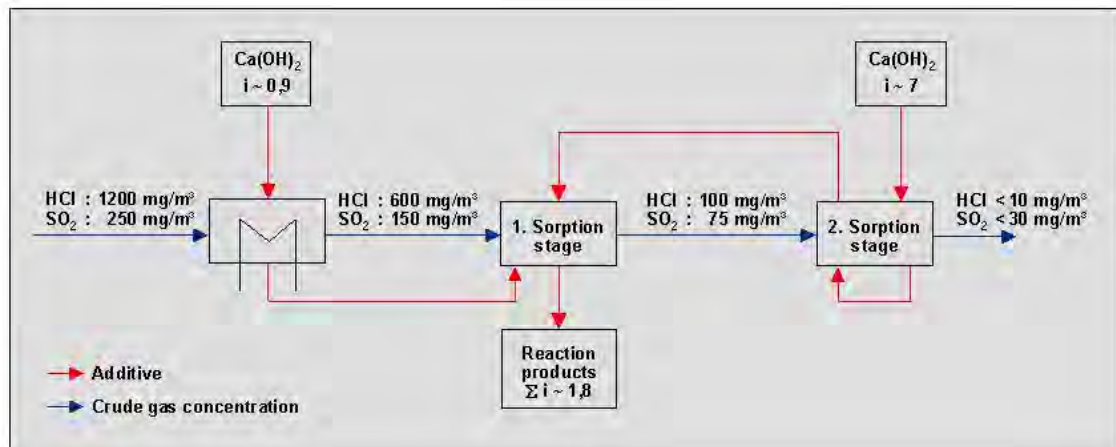

Illustration 6: Stoichiometric fine cleaning stage and summarised stoichiometry

2.2 Chemical sorption with particle conditioning and, if necessary, gas conditioning

2.2.1 Process description

As described before, the gas conditioning has a positive effect on the sorption result by increase in the absolute and relative humidity of the crude gas. 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 dry sorption (illustration 7). Regarding this type of process, the recycled particulate is wettened prior to being reintroduced into the reactor. The wetting causes an increase in the water steam content at the surface of the additive particles, thus improving the reactivity in comparison to the acid crude gas components.
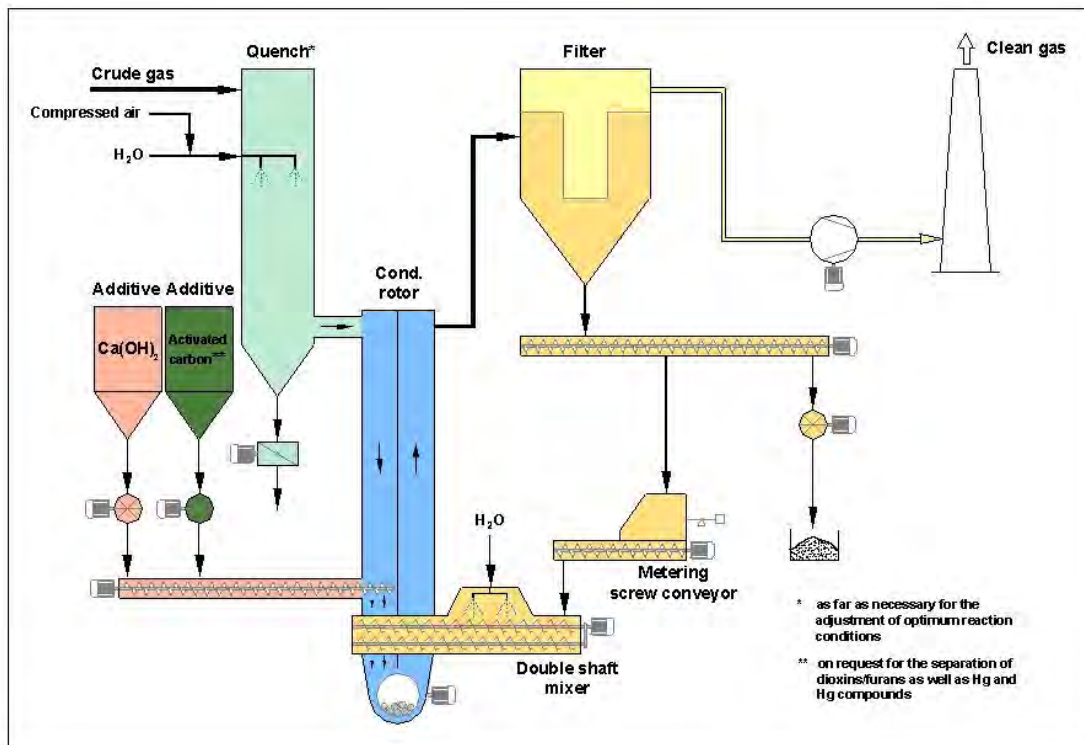
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Illustration *7: Chemical sorption with particle and gas conditioning*

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 evaporation cooler for the adjustment of optimum reaction conditions.

2.2.2   Application examples

2.2.2.1   Sludge incinerator
The plant design shown in illustration 8, demonstrates the installation of a sorption stage for the separation of SO_2 and Hg, located downstream ESP for the separation of fly ash. In this case the chosen technology consists of a gas and particle conditioning.
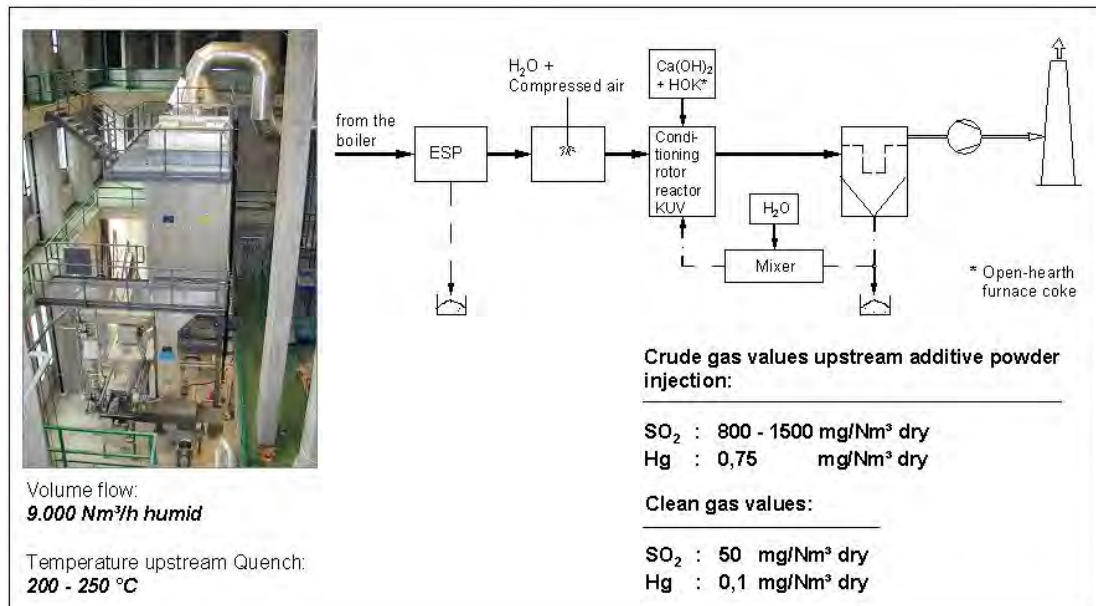
Illustration 8: Application example of a sludge incinerator

Illustration 9 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.
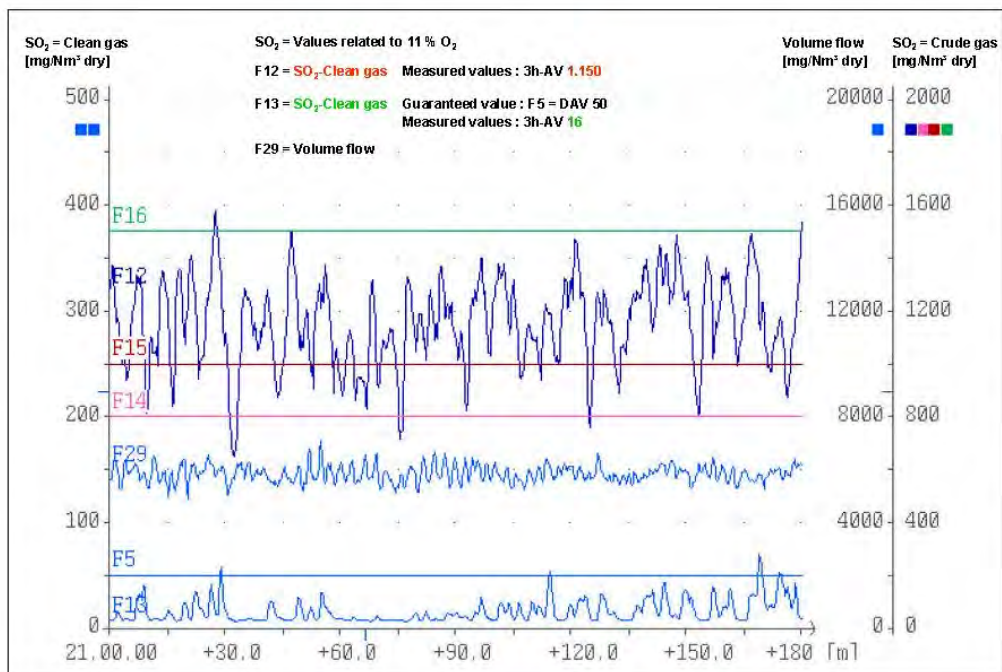

Illustration 9: SO$_2$ separation during sludge incineration

2.2.2.2 Incineration of domestic waste, waste wood, peat and coal in a vortex bed firing

This vortex bed firing, executed for a very variable mixture of combustibles, has been designed for a maximum percentage of waste of 80 %. Peat, coal or waste wood are used as secondary fuels. A rough scheme of the plant as well as the basic data and a photo are shown in illustration 10. Also for this application, an ESP for the separation of fly ash has been installed upstream sorption stage. Due to the low gas temperature of 150°C downstream ESP, the system is working without an additional gas conditioning. Especially because of the unfavourable relation of HCl / SO_2, the utilisation of a dry sorption with particle conditioning is preferable for this type of application.
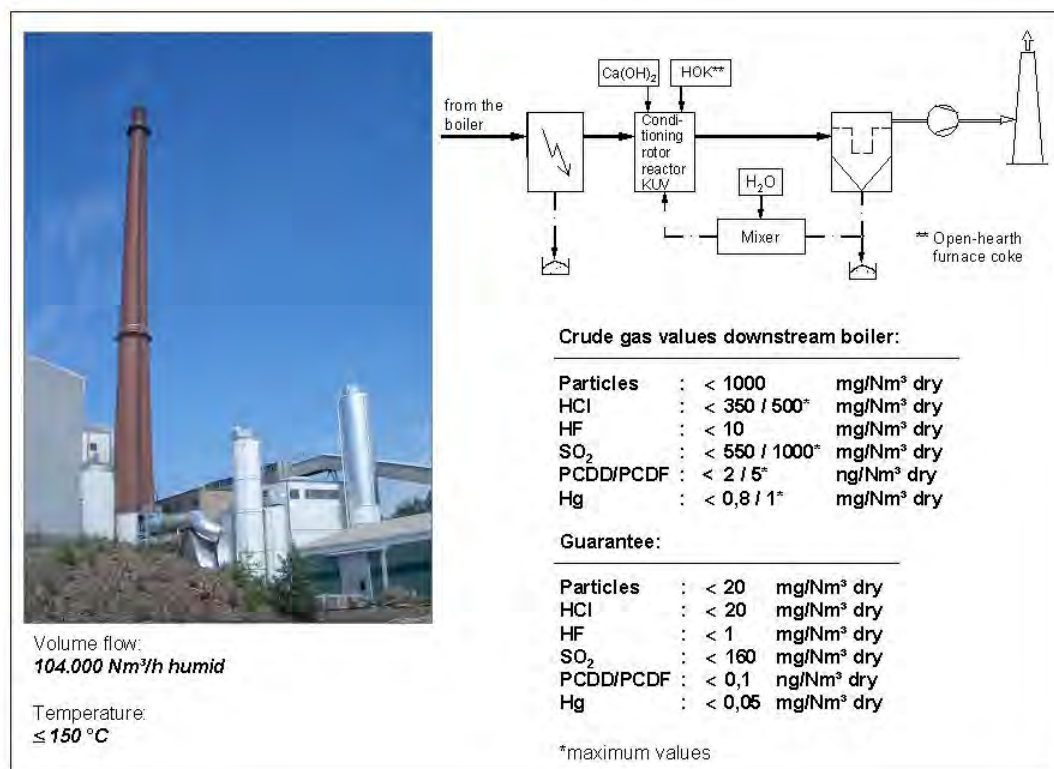
Illustration 10: Circulating vortex bed firing for the incineration of domestic waste, waste wood, peat and coal

2.3 Combination of spray absorption and particle conditioning

2.3.1 Process description

The described conditioned dry sorption process is surely very effective and suitable for most of the applications. However, in case of applications with high crude gas contents in continuous operation and definitely higher short-term peaks in addition to at the same time required high degrees of separation, it will be useful to install an additional pre-sorption stage, e.g.

executed as spray absorber, in order to reduce the additive powder costs of the particle conditioning and to observe the requested emission limit values in all operating phases.

The corresponding technology is shown in illustration 11. The spray absorber (1st stage of separation) serves for the crude gas conditioning (cooling / wetting) and for the spraying of lime slurry. Regarding the production of lime slurry, either CaO or $Ca(OH)_2$ can be chosen.

The 2nd stage of separation is realised in the reactor – filter combination with $Ca(OH)_2$ injection and particle conditioning.
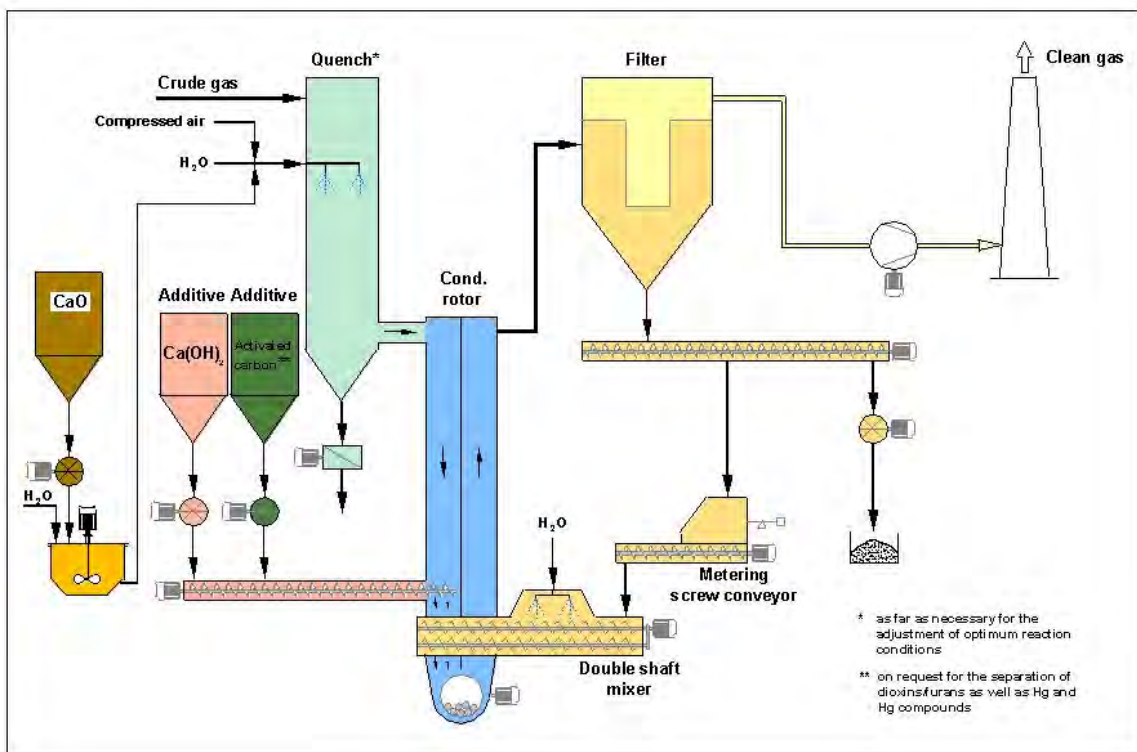

Illustration 11: Combination of spray sorption – conditioned dry sorption

Compared to other dry or semi-dry procedures on the basis of Ca-containing additive powders, the chosen - admittedly a bit more complex - technology offers some advantageous features:

- Graded additive powder injection
  The example shown in illustration 5 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 (80%) and approx. half of the SO_2 content are separated. Referring to the crude gas contents to be expected after the first stage and compared to the summarised stoichiometry, a considerably higher stoichiometry will be available for the fine cleaning in the second stage.
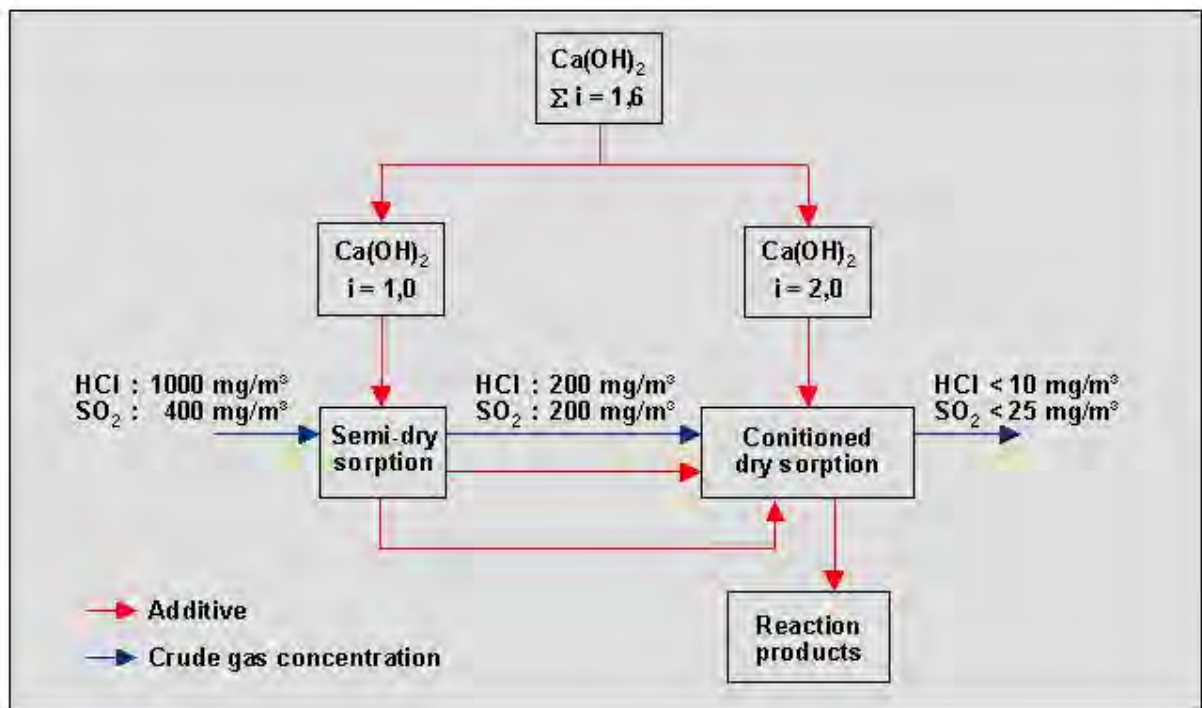
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Illustration 12: Distribution of stoichiometric factor

- Variation limits of crude gas contents
  The overall system is comparatively insensitive with regard to strongly
  fluctuating crude gas components in the flue gas. Assuming a degree of
  separation of 80% for the first stage (as shown in illustration 12) for an HCl
  input value of e.g. 3.000 mg/m³, the input value upstream second stage
  will be reduced to 600 mg/m³.

- Availability / Redundancies
  The highest sorption efficiency is achieved during operation of both
  sorption stages. However, even in case of a failure of part systems, the
  emission values can be observed for all operation conditions by accepting
  a higher additive powder injection quantity.

  - Failure of lime slurry
    → system evaporative cooler, conditioned dry sorption

  - Failure of particle re-circulation
    → system spray absorption and $Ca(OH)_2$ injection upstream fabric
    filter

2.3.2 Application example of a domestic waste incineration

As example for this type of process variant, picture 13 shows the crude gas cleaning of line 2 of MHKW Ludwigshafen and the belonging process scheme is shown in illustration 14.

Pic. 13: Spray absorber head and filter / reactor building

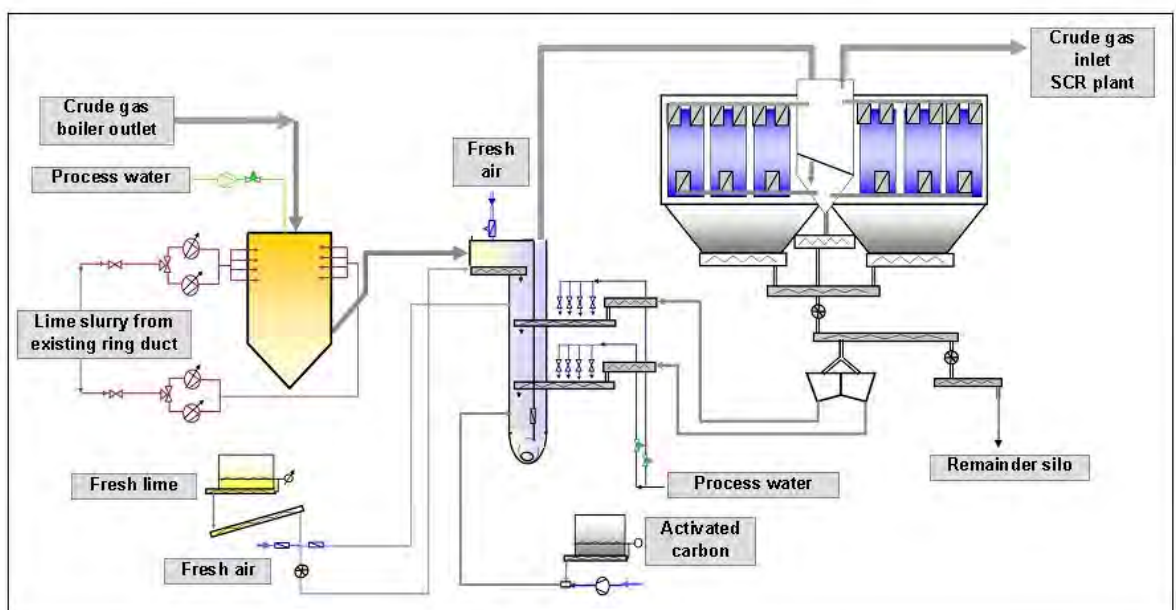*Illustration 14: Simplified process scheme of spray absorption with conditioned dry sorption*

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The crude gas values for HCl and SO_2 at the plant in Ludwigshafen fluctuate in a comparatively wide range. The range for HCl lies between 500 and 4.000 mg/Nm^3 , the one for SO_2 between 100 and 1.500 mg/Nm^3, whereas peaks can exceed these values.

The crude gas values for the stated range are reliably controlled by means of a specific stoichiometric control for the additive powder injection and are reduced to the emission values stated in table 2.

CLEAN GAS	UNIT	DAV	HAV
Overall dust	mg/Nm³ dry	10	20
HCL	mg/Nm³ dry	9	40
HF	mg/Nm³ dry	1	2
SO_2	mg/Nm³ dry	25	150
Cd + Tl	mg/Nm³ dry	0,05[*]	
Hg	mg/Nm³ dry	0,015[*]	0,03[1]
Σ(Sb,As,Pb,Cr,Co, Cu,Mn,Ni,V,Sn)	mg/Nm³ dry	0,5[*]	
Dioxin/Furan	ng TE/Nm³ dry	0,1	

[*] as average value over sample taking period

[1] hourly average value, that may not exceeded at any operating time

Tab. 2: Emission values of crude gas cleaning plant MHKW Ludwigshafen
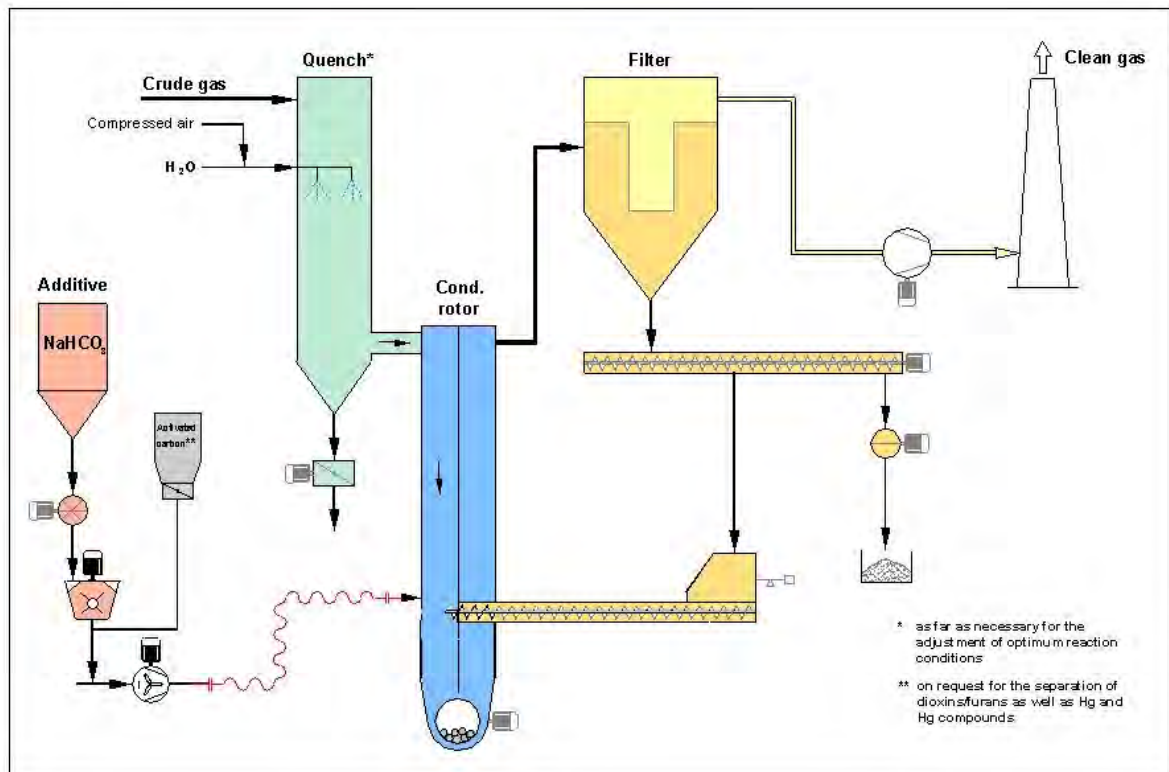
3. Dry sorption process with utilisation of NaHCO₃

Illustration 15: Dry sorption with utilisation of NaHCO₃
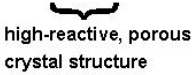
3.1 Process description

The process with a quite simple plant structure is shown in illustration 15. The additive powder is injected into the crude gas flow upstream filter. In case of crude gas temperatures > 140°C, a thermal activation of sodium hydrogen carbonate will take place. The result is a high reactive sodium carbonate. Table 3 states 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 values are reliably achieved in continuous operation with the adequate plant design and an over stoichiometric factor of 1,2 – 1,5. The multiple re-circulation of the particulate separated in the filter into the crude 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$_3$ ° NaF + H$_2$O + CO$_2$	4,2 kg/kg	2,1 kg/kg
HCl + NaHCO$_3$ ° NaCl + H$_2$O + CO$_2$	2,3 kg/kg	1,6 kg/kg
SO$_3$ + 2NaHCO$_3$ ° Na$_2$SO$_4$ + H$_2$O + 2CO$_2$	2,1 kg/kg	1,77 kg/kg
SO$_2$ + 2NaHCO$_3$ ° Na$_2$SO$_3$ + H$_2$O + 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

- the remainder quantity is reduced in contrast to the additive powder injection (advantage in case of high disposal costs)

- lower hygroscopic nature of the resulting salts

The disadvantages are:

- unfavourable mass ratio of additive powder to crude gas

- necessary pulverisation of the additive powder prior to the injection into the crude gas flow

- high specific purchase costs for the additive powder

As alternative there are further additive powder qualities on sodium basis available, such as e.g. Na$_2$CO$_3$ 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 16 reflects 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 16: Application example of a tyre combustion

3.2.2 Thermolysis plant for domestic waste

Illustration 17 shows another plant example. For this application a reactor with particle re-circulation has been installed upstream fabric filter in order to improve the reaction conditions last but not least with regard to the PCDD/PCDF separation.

Illustration 17: Application example of a thermolysis plant for domestic waste

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Within the scope of plant design, a comparing assessment based upon the costs fixed by customer for the additive powder supply and disposal has been carried out between the dry sorption process with $NaHCO_3$ and the conditioned dry sorption process with $Ca(OH)_2$ (illustration 18).
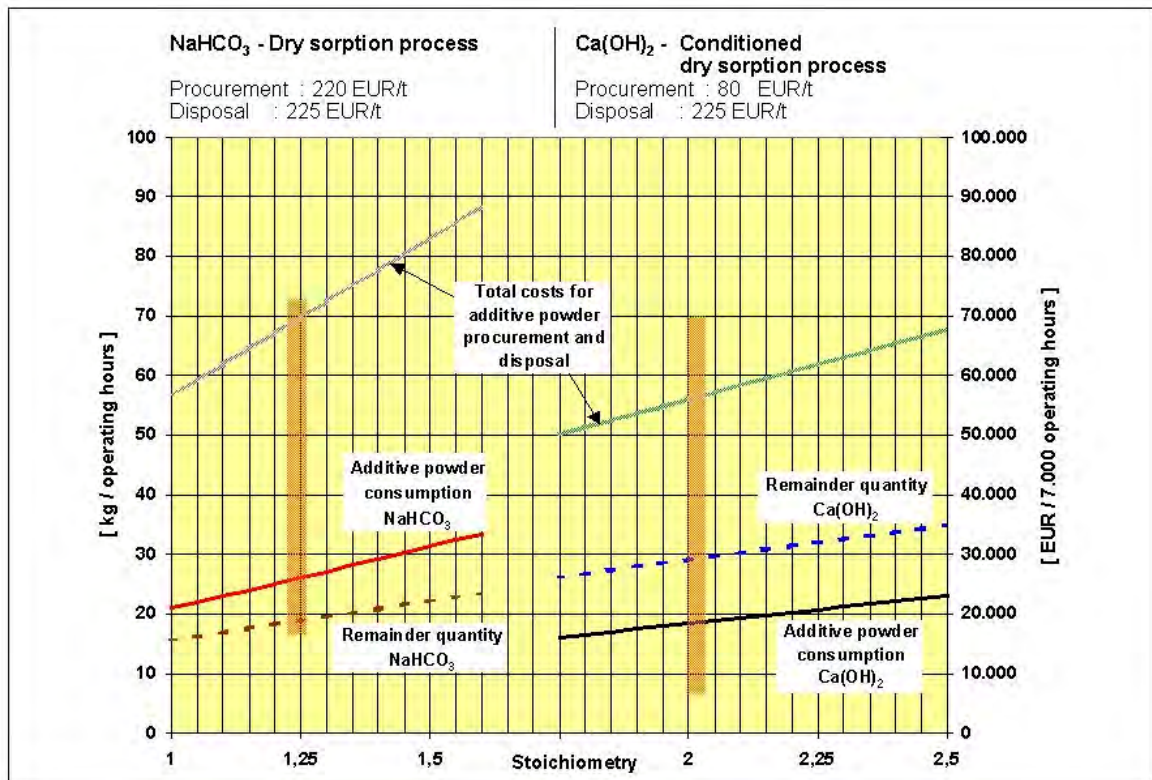

Illustration 18:   Example of assessment regarding thermolysis plant for domestic waste

In spite of the evidently higher additive powder costs for the dry sorption process, the decision was made in favour of this technology. This is justified in the considerably higher costs of capital for the conditioned dry sorption process.

4.   Selection of technology

The examples shown demonstrate that beside the particle separation fabric filters are also able to meet the today's requirements regarding the sorption of acid crude gas components. The current emission values are reliably achieved in continuous operation. In addition it may be remarked that due to the injection of adequate additive powders a reliable, simultaneous separation of dioxins / furans and mercury will be possible.

However, there is no most suited technology available for all fields of application. Each application has to be considered individually.

The criteria of choice for the assessment are:

- Required degrees of separation (average values and max. values as well as peaks)

- Emission values

- Investment costs

- Operating costs such as additive powder supply and disposal as well as energy costs (current and compressed air)

- Costs for maintenance and upkeep

- Plant availability and reliability

- Partial load behaviour

- Flexibility with regard to changing crude gas values, emission values and specific operating costs