

# Basic features of the dry absorption process

for flue gas treatment systems  
in waste incineration

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Ingenieurgesellschaft  
für Energie- und Umweltengineering & Beratung mbH

Hofgut Kolnhausen 12  
35423 Lich (Germany)

Prof. Dr.-Ing. Rudi H. Karpf

☎ 06404 / 65 81 64

☎ 06404 / 65 81 65

✉ [info@ete-a.de](mailto:info@ete-a.de)

🌐 [www.ete-a.de](http://www.ete-a.de)

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## 1 Introduction

The separation of gaseous substances takes place via adsorption over a solid or via absorption into a liquid. Chemical or physical sorption agents are usually brought into contact with the flue gas. Depending on the system, the reaction products accumulate in the form of dissolved or dry salts.

Flue gas treatment for waste and RDF incineration plants may make use of wet and semi-dry/dry systems. The dry and semi-dry systems usually consist of a reaction area with additive supply, possibly a conditioning phase (as in the semi-dry method) and a dust collector (ESP, fabric filter). Wet air pollution control systems for the reduction of HCl, HF and SO<sub>x</sub> emissions operate by means of absorption using scrubbers of varying design, e.g. spray scrubbers, venturi scrubbers or packed scrubbers.

Each of the systems has its own particular advantages and disadvantages as well as legitimacy, depending on location and specific circumstances.

The basic features of both wet and dry systems are compared in Table 1. A consideration of these features facilitates the pre-selection of the most appropriate system.

**Table 1: Characteristics of wet and dry air pollution control systems**

<i><b>Wet system</b></i>	<i><b>Dry system</b></i>
Low sorbent consumption (stoichiometry 1), resulting in low residue volumes	Larger sorbent consumption (stoichiometry SR <sub>II</sub> 1.6 to > 2), resulting in higher residue volumes
Expensive additives (e.g. NaOH)	Less expensive additives (e.g. Ca(OH) <sub>2</sub> )
High separation capacity for HCl and SO <sub>2</sub>	Good separation capacity
Selective deposition	No selective deposition
Multi-stage system	Single-stage system
Complex effluent treatment/disposal	Simple and robust components
Usually requires dust pre-separation	Requires no dust pre-separation
Greater dust/aerosol emissions	Low maintenance demand
PCDD/PCDF separation in conjunction with packed scrubbers and HOK dosage	Very good separation for heavy metals and PCDD/PCDF using HOK
Greater space requirements	No wet stack required, hence no steam plume

## 2 Process Description

The separation of acidic flue gas constituents via the dry absorption system is a simultaneous and absorptive gas/solid-reaction which takes place in the sorbent employed in the process.

In this process, the gaseous pollutants are bound to the surface of the introduced solid. The additives can then be separated from the flue gas together with the dust particles via a fabric filter.

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No pre-dusting is required. The formation of a filter cake is necessary for the dedusting process to function successfully, as it influences the retention time of the additive and, hence, the contact time of additive and pollutant in the flue gas.

Each dry method also allows the dispersal, in dried form, of lignite coke (lc) or activated carbon (ac) into the flue gas stream to separate PCDD/F and heavy metals. These are then likewise separated via the fabric filter.

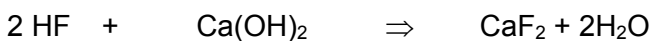
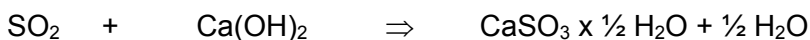
The dry systems are characterised based on the additive applied. They are accordingly referred to as either sodium-based (application of  $\text{NaHCO}_3$ ) or lime-based (application of  $\text{Ca(OH)}_2$ ) systems.

Owing to their single-stage construction and low operative requirements with regard to both space and maintenance, dry flue gas cleaning systems are comparatively inexpensive.

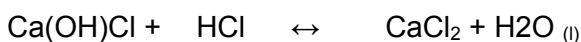
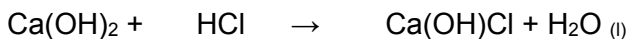
The large quantity of additives that this type of process consumes is counterbalanced by the low purchase price of said additives, and therefore also makes this type of process interesting from an economic point of view. Energy consumption levels are likewise low when compared to the energy levels required for wet flue gas cleaning systems.

## 2.1 Lime-Based Processes

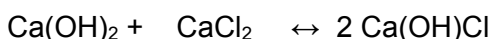
The separation of the pollutants takes place via adsorption on the surface of calcium hydroxide particles. These particles are brought into contact with the flue gas in a variety of forms. The primary reactions take place according to the following equations:



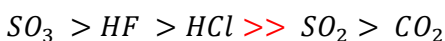
Reaction of lime with HCl in two steps:



Reaction of lime with calcium chloride:



The reactivity sequence between calcium hydroxide and the pollutants can be set out as follows:



The most important calcium-hydroxide-based processes are described in below.

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### 2.1.1 Conditioned Dry Sorption

In this process, separation of the pollutants via deposition on lime is ameliorated by a hydrate shell which is formed around (and inside the pores of) the lime particles and results from the H<sub>2</sub>O contained in the flue gas (Figure 1). This means that the separation is governed by the dissolution rate of the pollutants in aqueous solution. The absorption and adsorption processes run parallel throughout the separation process.

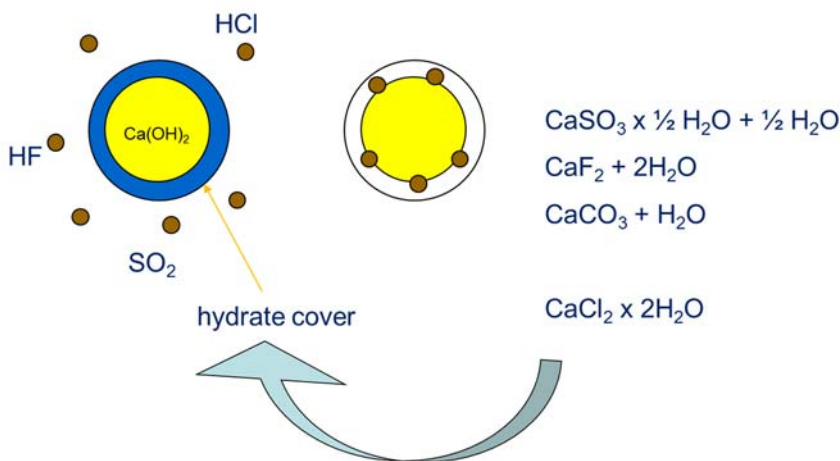
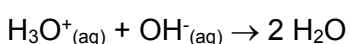
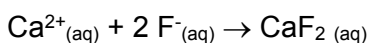
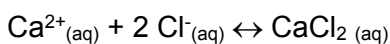
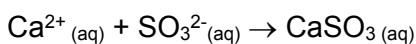
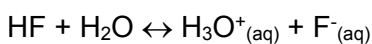
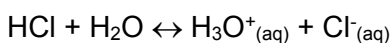
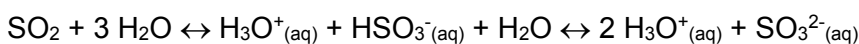
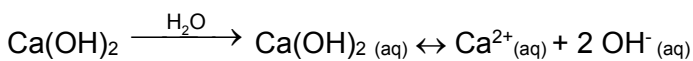


Figure 1: Mechanism forming the hydrate shell/cover

An increased level of relative humidity is required for the capillary condensation and the formation of the hydrate shell on the surface. The flue gas is therefore first conditioned in order to optimize the downstream pollutant separation process. This conditioning consists primarily of a reduction of the gas temperature to approximately 130 – 150 °C in order to achieve a relative humidity of approximately 6 %. Flue gas temperatures below 130 °C should, however, be avoided, as, depending on surface temperature, the salts created during the reaction may increase the risk of corrosion to those parts of the facility in direct contact with the flue gas.

The presence of liquid water allows for the dissolution of the reaction partner (see the following reactions) and for an ionic reaction to take place, the fastest reaction rate at our disposal.



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Reducing the temperature or increasing the relative humidity can be effected via an economizer (ECO) or a cooling tower (CT). However, a combination (Combi) of both the gas cooling and humidifying processes is also possible. The cooling tower allows one to increase the absolute humidity in the system via the amount of injected water. The injected water promotes the separation of pollutants adhering to the hydrate lime particles.

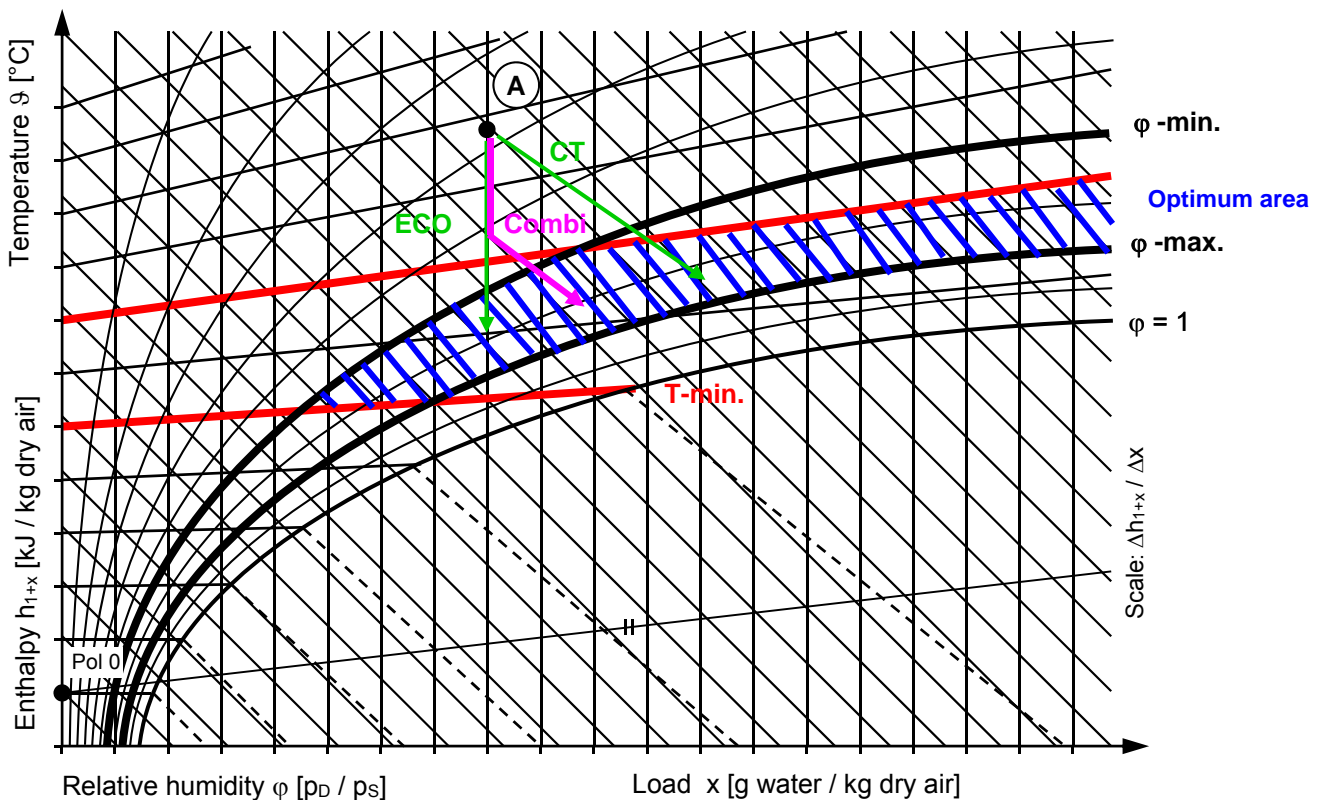
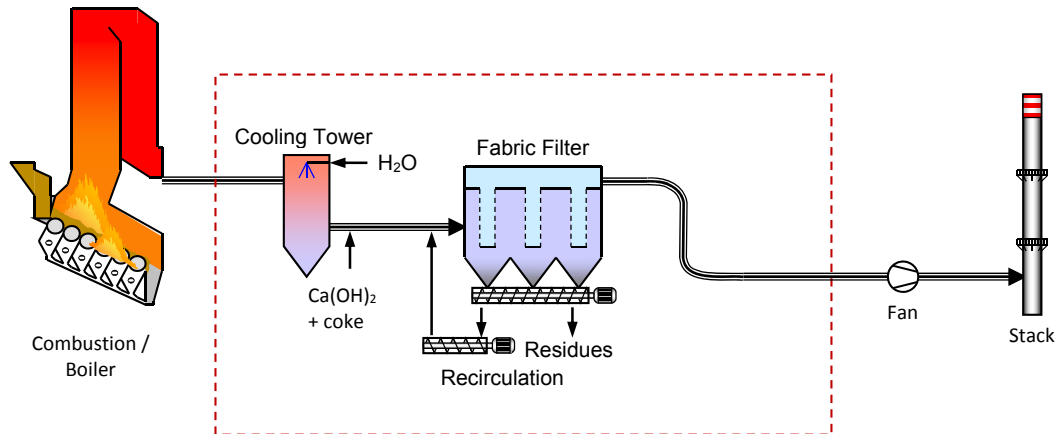


Figure 2: Mollier h-x diagram with optimum temperature-humidity range for conditioned dry absorption with calcium hydroxide. A = starting point

In order to increase the separation efficiency, a part of the residue of the reaction products in the fabric filter should be fed back into the flue gas. This permits the un-reacted contingent to be brought back into contact with the pollutants as well as providing a quantity of chloride to improve separation efficiency, especially that of  $SO_2$ . Concerning the presence of calcium chloride, a quantity of  $HCl/SO_2 > 1$  at the inlet of the flue gas treatment system is necessary.

The higher the fabric filter temperature, the less efficient the  $SO_2$ -separation due to the decrease in relative humidity.

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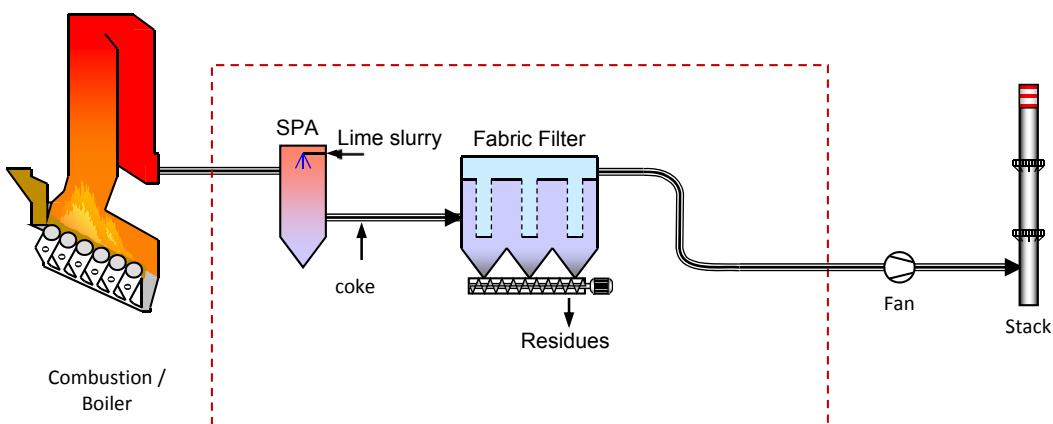


**Figure 3:** Conditioned dry process with hydrated lime

### 2.1.2 Spray Absorption with Lime Slurry

The semi-dry spray absorption process is an alternative method. Here a spray dryer is used to inject a suspension of lime and water (lime slurry) into the flue gas stream.

The suspension is generally created from quicklime (CaO) and water via an on-site slaking process. The fact that this is conducted on-site is of additional benefit to the reactivity of the reagent. When the suspension is injected into the flue gas stream, the water component evaporates and only the solid lime particles remain in the flue gas. The liquid phase of this process has proven to be more efficient concerning HCl-removal than it is by applying slaked lime (calcium hydroxide) in dry form.



**Figure 5:** Spray absorption process with lime slurry (SPA = Spray Absorber)

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Since CO<sub>2</sub> is also an acid gas component, the amount of CO<sub>2</sub>-molecules compared to the amount of the other acid gas molecules such as HCl, HF, SO<sub>2</sub> is much higher. Consequently, the possibility of a reaction between CO<sub>2</sub> and a lime particle is much greater than that of a reaction between the other acid gas components and formed calcium carbonate (CaCO<sub>3</sub>). For the liquid phase, an HCl- or SO<sub>2</sub>-molecule can react with the already formed CaCO<sub>3</sub> and out through the CO<sub>2</sub>-molecule again due to the higher acid state. However, this is only possible in the case of the liquid phase.

Therefore, the spray absorption process will operate with a higher lime consumption (higher stoichiometric ratio (SR)) compared to a conditioned dry absorption process with a dry lime injection. The dosage of lime slurry that is applied is generally too high in cases of a stoichiometric ratio of  $2.3 < SV < 3.5$ . In order for sufficient drying of the particles, an inlet temperature of appr. 200 °C and a certain outlet temperature (mostly > 140 °C) prior to the spray absorber process is desirable, depending on the dimensions of the spray absorber (e.g. residence time). In some cases, the outlet temperature should be lower than 140 °C, especially for SO<sub>2</sub>-removal, except where this is not possible.

If a higher degree of separation efficiency is required, dry calcium hydroxide can be injected upstream of the fabric filter.

### **2.1.3 Retrofit PTU® Process for Optimizing Existing Facilities**

In conditioned dry sorption processes, relative humidity plays a major role with regard to the separation of pollutants – primarily SO<sub>2</sub>. This is why the relative humidity is generally increased by preconditioning the flue gas (lowering of temperature via evaporative cooling and/or adding water to the substances that are to be recirculated).

These procedures for lowering the temperature, however, also increase the risk of corrosion to affected components within the facility. Another point is that the flue gases must be reheated quite considerably in the case of downstream SCR facilities.

It is not however necessary to condition the entire amount of flue gas in order to achieve an efficient degree of pollutant separation. Given the reaction rate of the pollutant separation on hydrated lime, the sorption of HCl, HF and SO<sub>2</sub> on the lime begins immediately after it has been injected into the flue gas stream. Consequently, the separation conditions only need to be optimized at the actual point of injection.

It is with regard to this aspect that the PTU® technique was developed. The PTU® technique uses a special hollow lance to inject a combination of calcium hydroxide and saturated steam into the reaction chamber in order to separate pollutants.

The lance consists of two concentrically arranged pipes. The inner pipe delivers the steam and the outer, larger pipe delivers the lime together with air (see Figure 6). Owing to the comparatively low temperature of the airstream at the exit of the lance (20 – 50 °C), a partial drop below the dew point takes place. The steam condensates preferably in the lime pores / capillaries, but also on the lime surface where they build up the requisite hydrate shell.

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**Capillary condensation** is the process by which multilayer adsorption from the vapour phase into a porous medium proceeds to the point at which pore spaces become filled with condensed liquid from the vapour phase. The unique aspect of capillary condensation is that vapour condensation occurs below the saturation vapour pressure of the pure liquid.

Once condensation has occurred, a meniscus immediately forms at the liquid-vapour interface, which allows for equilibrium below the saturation vapour pressure. A capillary does not necessarily have to be a tubular, closed shape, but can also be any type of confined space with respect to its surroundings.

This promotes the separation of acidic pollutants.

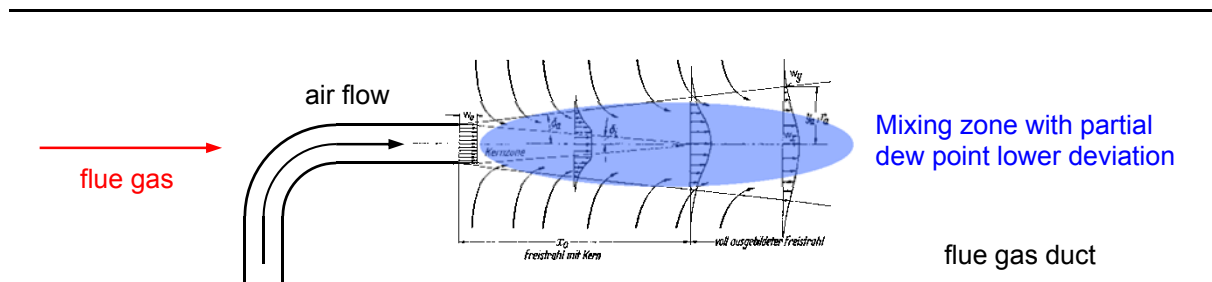


Figure 6: Principle of the PTU®-technique

The advantage of this process is its application in processes where no possibility of increasing the relative humidity or reducing the temperature exists. It is simple to retrofit onto existing facilities. It is not necessary to operate the process near the dew point, thereby reducing the risk of corrosion.

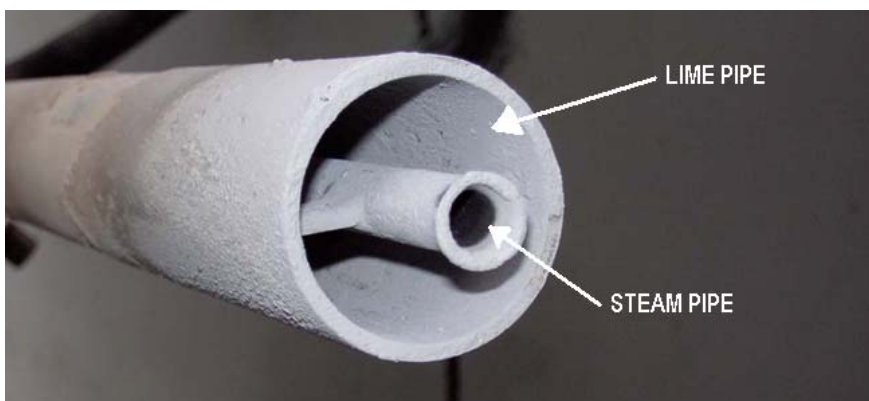


Figure 7: Image showing the front of a steam lance

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Figure 8 illustrates the dry absorption process with steam injection by way of a Mollier h-x diagram for a conveying air system (for the conveyance of hydrated lime), steam and flue gas. Assuming that conveying air, hydrated lime and steam are injected locally in close proximity to each other, the process starts at point L (conveying air prior to entrance into the process). Due to the steam injection and the local mixing of the conveying air with the steam it moves into the fog area to point K. Thereafter, the process follows the line of the fog isotherms to reach point K. Hereby, water condensates until the balance is reached at point S on the saturation line. While mixing with the flue gas (point R), point M is ultimately reached.

The diagram shows the manner in which the hydrate shell can be created over the hydrated lime particles from a different perspective, by passing the fog area.

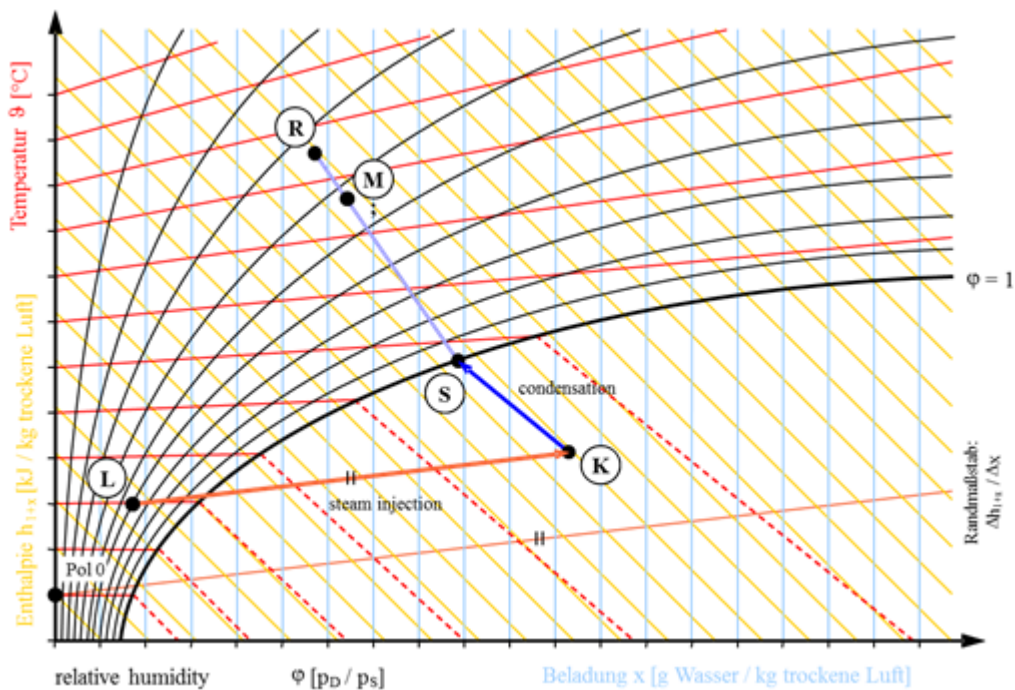
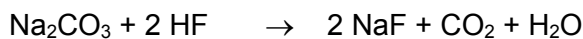
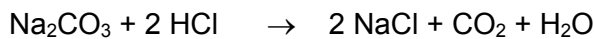
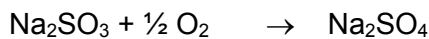
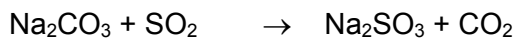
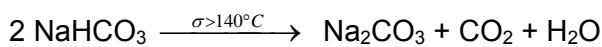


Figure 8: Mollier h-x diagram with the PTU® process [source: R. Karpf; wlb 5/2006]

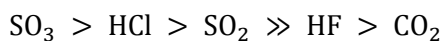
## 2.2 Sodium-Based Process

Sodium hydrogen carbonate allows the implementation of a purely dry technique, as it enables a good dedusting result for HCl and SO<sub>2</sub> at comparatively high temperatures and regardless of the flue gas humidity.

As, in most cases, activated carbon is added to the sodium bicarbonate during the process in order to achieve a better dedusting result with regard to heavy metals and dioxins / furans in the flue gas, the flue gas temperature must be cooled to 140 – 180 °C in order to prevent desorption occurring in the activated carbon. At temperatures > 140 °C, the sodium hydrogen carbonate decomposes into sodium carbonate (NaCO<sub>3</sub>), carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O):



The reactivity sequence can be set out as follows:

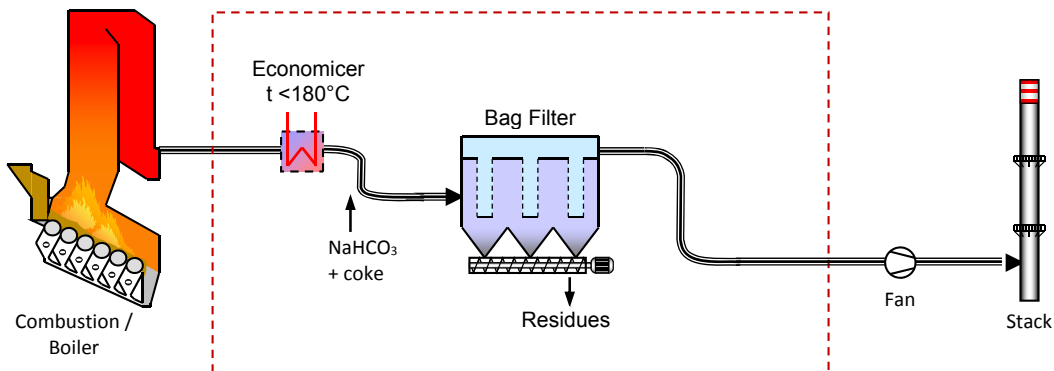


When compared to the application of lime, the chemical decomposition and transition of the gaseous reaction products into the flue gas stream reduces the quantity of residue requiring subsequent disposal.

This decomposition also leads to a greater specific surface. The greater the available reaction surface, the more efficient the separation performance of the sodium carbonate. The removal performance also generally increases in line with a rise in temperature. The temperature must, however, be confined to a specific corridor if activated carbon is also being used to separate mercury.

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**Figure 9:** Conditioned dry process with sodium bicarbonate

### Main Features of the Process:

- Very good reactivity of  $\text{NaHCO}_3$  with  $\text{HCl}$  and  $\text{SO}_2$
- The higher the temperature, the more efficient the separation of  $\text{HCl}$  and  $\text{SO}_2$ . However, limitation of the temperature is advisable due to mercury separation
- The desired temperature corridor should lie between 180 – 190 °C if activated carbon is being used
- Desired bicarbonate grind: the smaller the grain size, the better the separation performance
- No influence of  $\text{HCl}/\text{SO}_2$  ratio on separation performance
- No influence of humidity on separation performance
- Poor reactivity with  $\text{HF}$
- Stoichiometric values of  $1.1 < \text{SV} < 1.4$  are common. A slight improvement in the separation performance if recirculation is applied within the bicarbonate process
- Additives are very expensive
- Low amount of residual substances compared to lime-based process

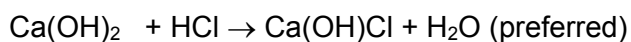
## 2.3 Impact of Recirculation on the Process

The additives used in conditioned dry techniques are not completely spent between the point at which they are introduced into the system and that at which they are separated via the fabric filter. This means that a large quantity of unused reagent remains in the filter following the initial application of the process. This material is passed through the facility unused and then disposed of at great expense.

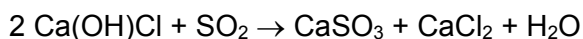
An alternative to this is the recirculation of the unused additive into the flue gas stream. Recirculation allows an increase in the contact frequency between pollutant and unused reagent. It also increases the remaining retention time for the reactions between pollutants and adsorbents on the filter area. This, in turn, greatly increases the utilization efficiency of the applied reagent.

In addition to the more intensive exploitation of the utilized additive, the altered condition of the recirculated material in contrast to freshly introduced material creates effects that further improve dedusting efficiency.

The dry scrubbing process with lime hydrate is implemented primarily to absorb halogen compounds.



Provided the retention period is sufficient, the separation of SO<sub>2</sub> takes place both via a reaction with calcium hydroxide (Ca(OH)<sub>2</sub>) and via a reaction with calcium hydroxide chloride (Ca(OH)Cl), as shown below.



The recirculation process increases the proportion of chloride in the reaction product on the filter area. The conditions for the separation of SO<sub>2</sub> are thereby improved (see Figure 1).

Recirculation can also benefit the separation of heavy metals, PCDD/F, and mercury by increasing the levels of activated carbon / coke adsorption surface made available by means of recirculation.

Summary of benefits:

- Reduction of the surplus proportion of additive, with stoichiometric values reducible to about half the initial amount.
  - Increase in separation efficiency
  - Improved compliance with threshold values for peaks in harmful gas emission
  - Application of normal lime hydrate as opposed to highly reactive lime
  - Low investment and maintenance costs
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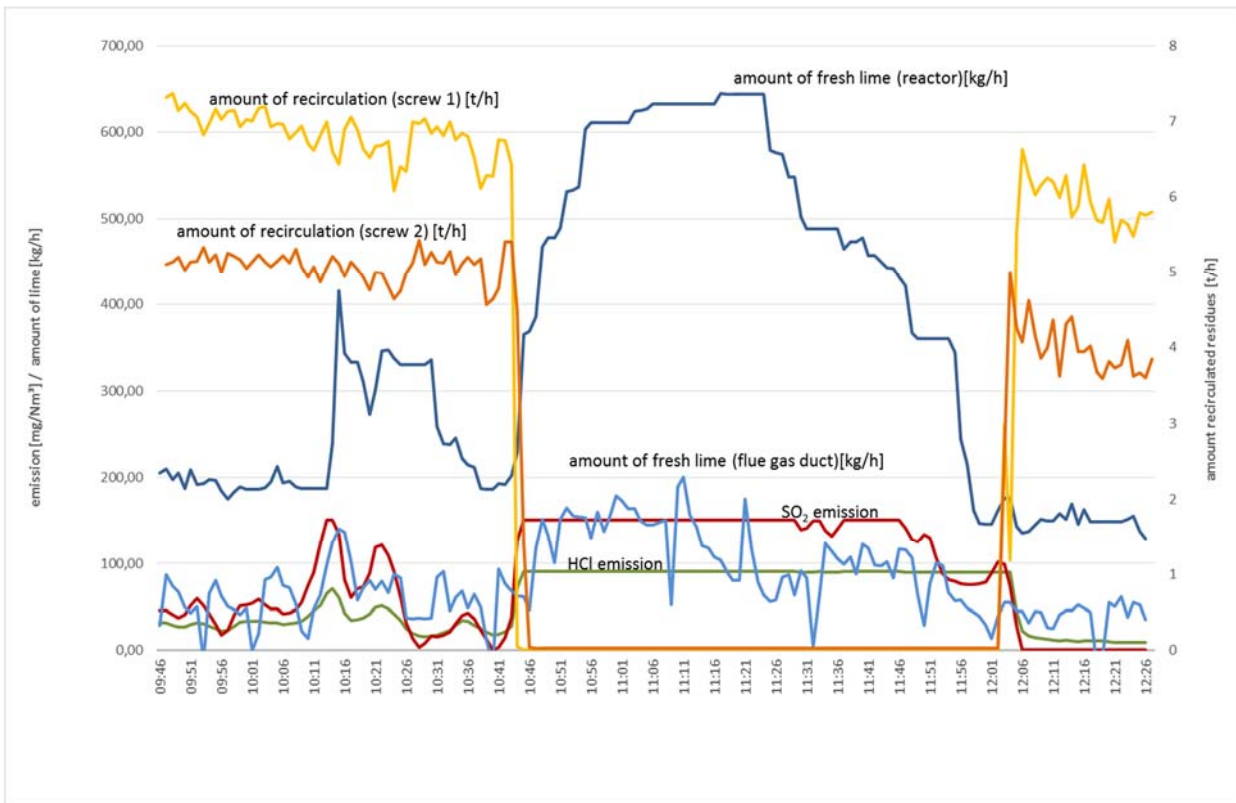


Figure 10: Influence of recirculation on the separation of HCl (MVA Wuppertal)

## 2.4 Filter Design

### Fundamentals

Suitable solid particle filters to be used for dry or semi-dry flue gas scrubbing techniques include dedusting filters with surface filtration in order to separate dust from the added reagent.

The reaction of the pollutant gases in the flue gas with the applied additive takes place primarily at the auxiliary filtration layer. The choice of filter has a direct impact on retention time and thus on dedusting efficiency with regard to harmful acidic gas components.

The surface filtration dedusting filters most frequently used generally consist of bag filter systems, which are particularly useful when coping with high dust loads in the raw gas and large volume flows.

Typical features differentiating the various bag filter systems are the type of dust admission applied and the dedusting method involved. In addition to mechanical dedusting methods, there are also dedusting methods which work with scavenging air.

The dedusting method most commonly used by bag filter systems to clean flue gas emissions in waste incineration plants today is the Pulse Jet method. Here filter hoses are subjected to external streams of flue gas and the dedusting process takes place from the inside out. Compressed air blasts with a duration of 0.1 to 1.0 seconds at an overpressure of 0.5 to 7 bar are fed into the interior of the filter hose.

An air bubble is created which expands in the filter hose and travels from top to bottom. This causes the filter medium, which is admitted from the outside in, to be inflated, and the dust cake falls out.

There is currently no valid model by which to calculate the dimension of fabric filters. The design of the fabric filter is generally based on experience and empirical calculation models. The most important criteria should be established via future research.

### Filter Surface Load

The required filter area ( $A_F$ ) can be established via the volumetric flow rate of moist flue gas in the process ( $\dot{V}_{RG,f,i.B.}$ ) and the specific filter surface load ( $v_F$ ):

$$A_F = \frac{\dot{V}_{RG,f,i.B.}}{v_F}$$

At maximum continuous load the following reference values apply for filter surface load:

Flue gas dedusting	$v_F = 1.0 - 1.2 \left[ \frac{\text{m}^3}{(\text{m}^2 \cdot \text{min})} \right]$
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Dry sorption	$v_F = 0.9 - 1.0 \left[ \frac{\text{m}^3}{(\text{m}^2 \cdot \text{min})} \right]$
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Spray sorption	$v_F = 0.85 - 0.95 \left[ \frac{\text{m}^3}{(\text{m}^2 \cdot \text{min})} \right]$
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Cond. dry sorption	$v_F = 0.75 - 0.85 \left[ \frac{\text{m}^3}{(\text{m}^2 \cdot \text{min})} \right]$
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**Important:**

An even filter allocation is important in order to ensure that dry sorption processes function successfully. Hence, the specific filter surface load for the sorption filter should be comparatively small (approximately 45 - 50 m<sup>3</sup>/(m<sup>2</sup>\*h) in order to ensure that the material is distributed across the entire filter area.

**Dedusting**

The dedusting of the filter medium can be conducted either offline or online. The offline method requires the volumetric flow through the filter to be turned off or diverted. Due to the increased effort involved, this method has decreased in significance in the domain of waste incineration plants and the method now chiefly applied is online dedusting.

The prerequisite for this method is that the dedusted dust cake forms sufficiently large agglomerates on the filter medium. This is why, in this system, the filter media are not pulsed immediately, but at specific time intervals instead. A further factor to be considered in this system is that the individual filter units per dedusting unit that are dedusted should be as small as possible. This ensures that the filter cake required for the pollutant separation process remains intact at all times. The filter hose lines must therefore always be dedusted cyclically – and not sequentially (see figure 9).

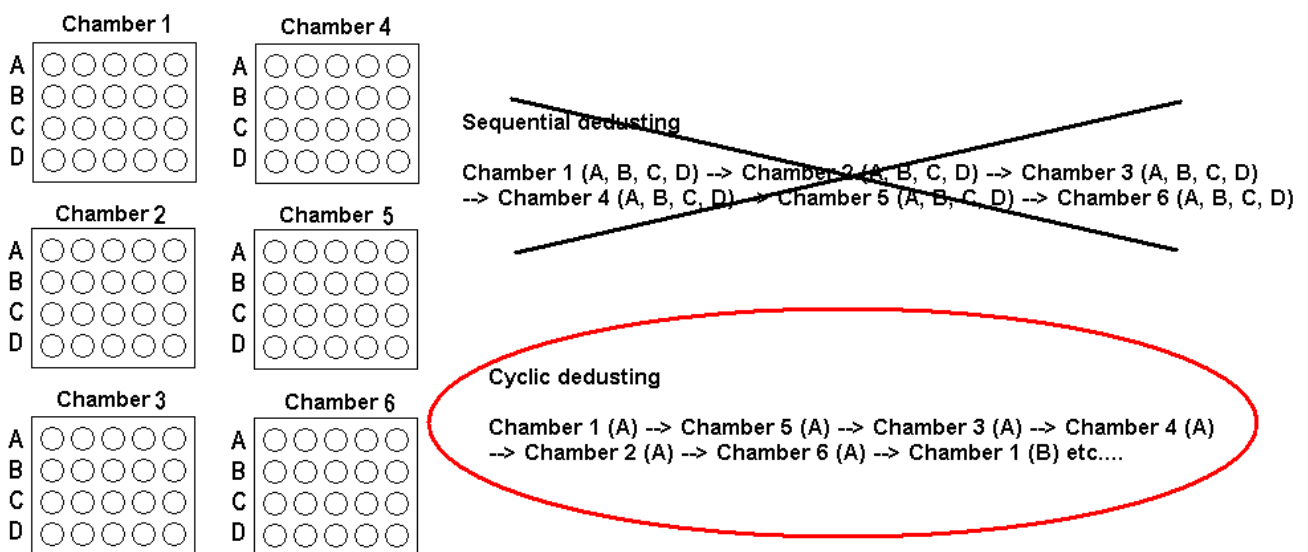


Figure 11: Cleaning method of a fabric filter as sorption filter

### 3 Conclusion

Within the setting of climate protection, waste as a substitute fuel or co-fuel has become an important “primary source of energy” in the energy conversion process. The selection of flue gas cleaning equipment must be carefully considered some basic questions addressed in order that the other pollutants, especially higher concentrations thereof, can also be removed.

Based on experience and developments of the last 20 years, dry, conditioned dry or semi-dry absorption systems have become successful and powerful systems in realizing the low emission figures necessary for economical operation. This has led to most of the new installations across Europe over the last 15 years being either dry or semi-dry systems.

An understanding of the basic features of dry absorption and the interrelationships outlined is reached by means of addressing the basic question of the reduction of pollutants, especially that of their acid components.

The most significant impact on separation efficiency is relative humidity. However, other important factors are the necessary recirculation of residues in the presence of calcium-chloride as well as a suitable filter design capable of accommodating a sufficiently thick filter cake on the bags.

However, the most efficient process must be established on a case by case basis, preferably whilst taking the on-site infrastructure into account. No standard solution for the flue gas purification process exists.

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