

Flue Gas Cleaning Systems

Status and Trends

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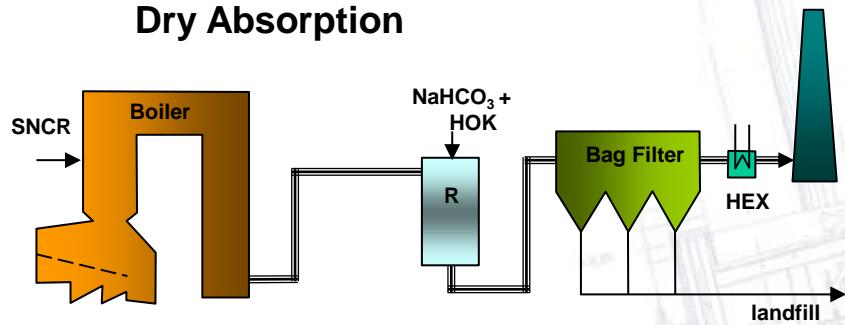


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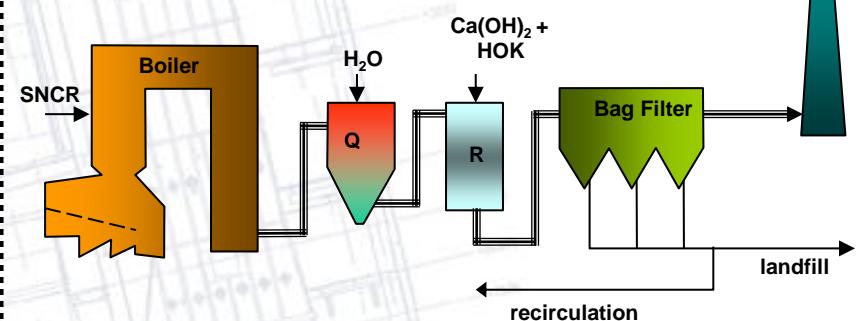
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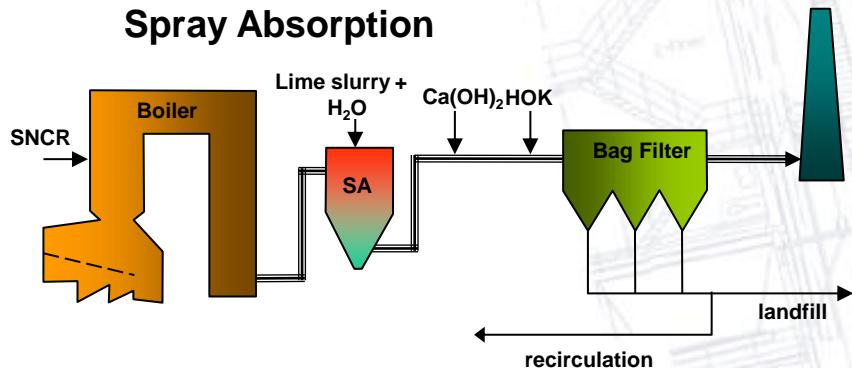
Dry Absorption



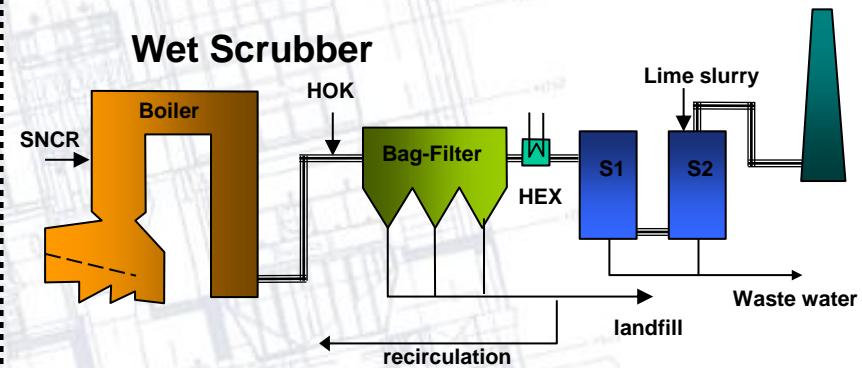
Conditioned Dry Absorption



Spray Absorption



Wet Scrubber



Q = quench
R = reactor

SA = spray absorber
S1/S2 = scrubber
HEX = heat exchanger

Source: fisia-babcock



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Characteristics of dry and wet flue gas treatment systems

<i>Wet systems</i>	<i>Dry systems</i>
Low additive amount (SR 1), respectively low residues amount	Higher additive amount(SR 1,6 up to >2), respectively higher residues amount
Expensive additives (e.g. NaOH)	Cheaper additives(e.g. Ca(OH) ₂)
High removal capacity for HCl and SO ₂	Good removal efficiency
selective removal	non selective removal
multistage System	Single stage system
Waste water treatment	Simple and no sensitive components
Need a pre dust collector	Need not an additional dust collector
Higher dust/aerosol – emission	Low maintenance effort
PCDD/PCDF- removal with ADIOX® grids and AC-injection	Very good removal efficiency for heavy metals and PCDD/PCDF on AC
High space need	No wet stack is necessary ,



requirement for an optimized additive use at a dry system

Characteristics of the plant / Infrastructure	lime	sodiumbicarbonat
Low additive costs	+	-
High residues costs	-	+
Tail-end SCR-DeNOx-plant	+ ¹⁾ /-	+
Maximum need for heat recovery	+ ¹⁾ /0	+
Use of dry fuel (waste)	+/-	+
low HF- and SO ₂ -emission values	+	-
High Hg-removal	+	-
APC-System with puffer capacity (Emission)	+	-

+ good; 0 neutral; - not so good

¹⁾ By using PTU-process

Basics of (conditioned) dry absorption systems

Reactivity of pollutions in respect of

.... Lime



.... Sodiumhydrogencarbonat



Influence of the removal efficiency with lime

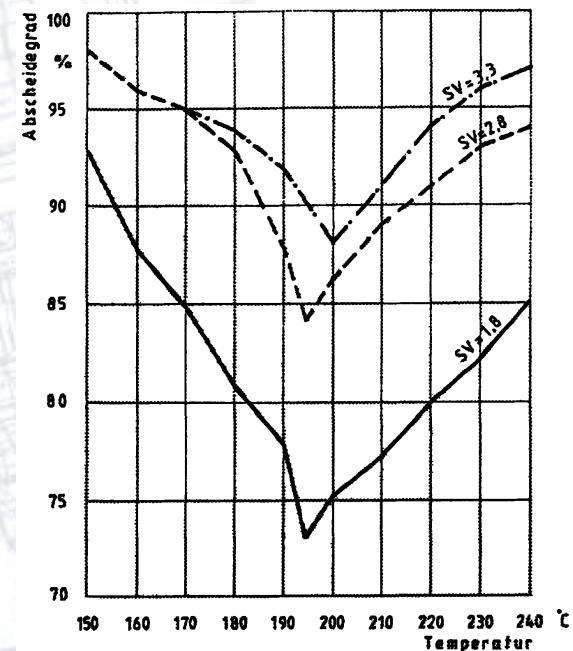
HCl-removal

- relative flue gas humidity ϕ

→ the increase of the relative flue gas humidity occur an increase of the HCl-removal efficiency

- flue gas temperature

→ up to 200°C the HCl-removal efficiency decrease in respect of the lower relative flue gas humidity. >200°C HCl-removal efficiency increase in respect to the higher temperature (kinetics)



Influence of the removal efficiency with lime

SO_2 - removal

- relative flue gas humidity ϕ

→ the relative flue gas humidity has much more influence of the SO_2 -removal as the HCl-removal; that means with an increase of relative flue gas humidity the SO_2 -removal will increase significant

- flue gas temperature

→ in the opposite to the HCl-removal the SO_2 -removal becomes worse with an increase of temperature in respect of the decrease of flue gas humidity

Reactions of the dry absorption system with lime ($\text{Ca}(\text{OH})_2$)



Reaction of lime with Chlorhydrogen in two steps:



Reaction of lime with Calciumchlorid:



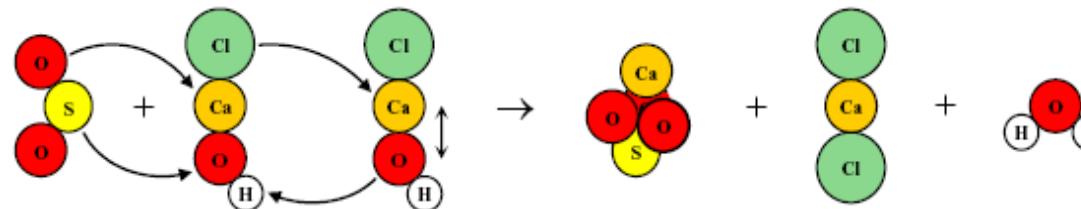
Reactions of the dry absorption system with lime ($\text{Ca}(\text{OH})_2$)

→ the experience shows, that the SO_2 -removal increase with the presents of $\text{Ca}(\text{OH})\text{Cl}$.

possible *reactions can take place*:

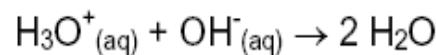
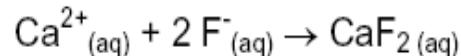
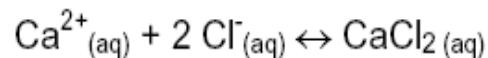
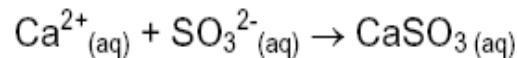
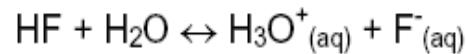
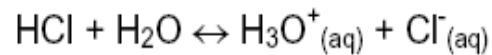
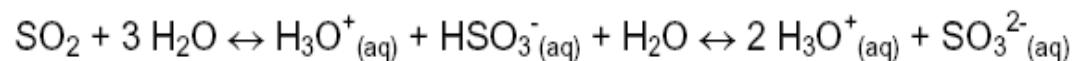
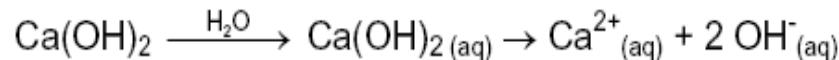


a higher probability is the exchange of anions



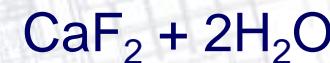
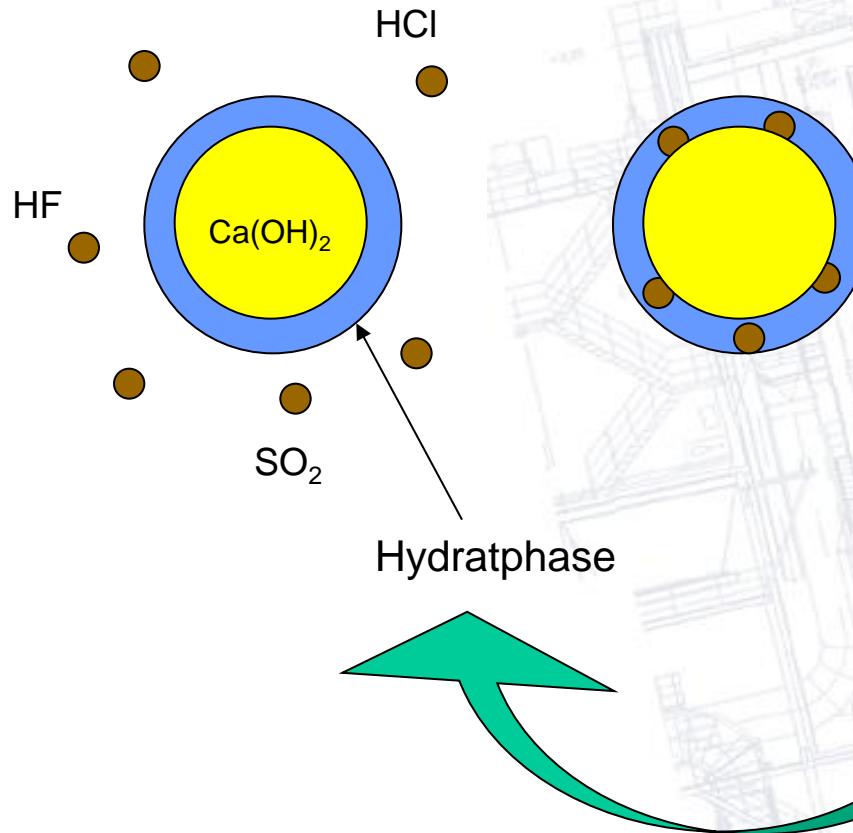
The presence of liquid water increase the reactivity of lime

 The speed of the chemical reactions at a liquid phase are much more higher as at a solid phase in respect of ion formation



Basics for the dry absorption with lime

Mechanism of the gas absorption



Influence of acid gas components removal with lime

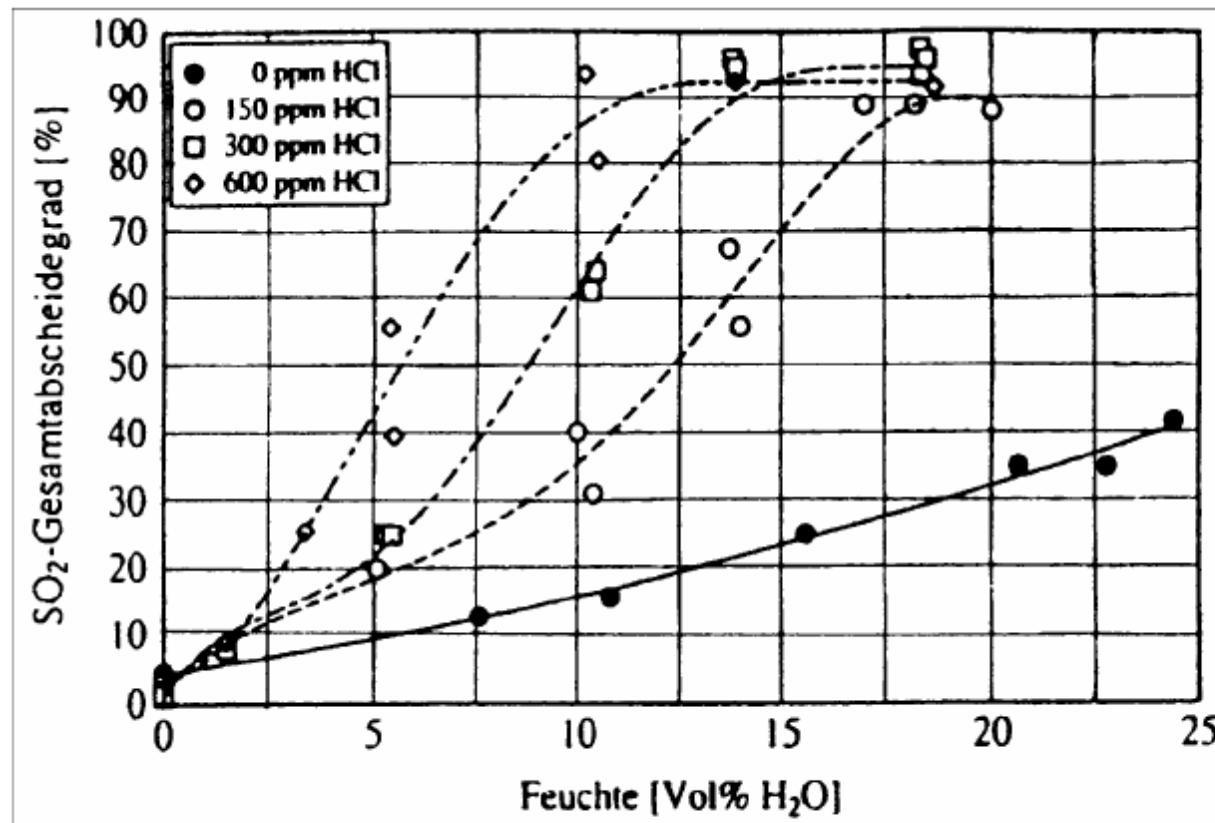
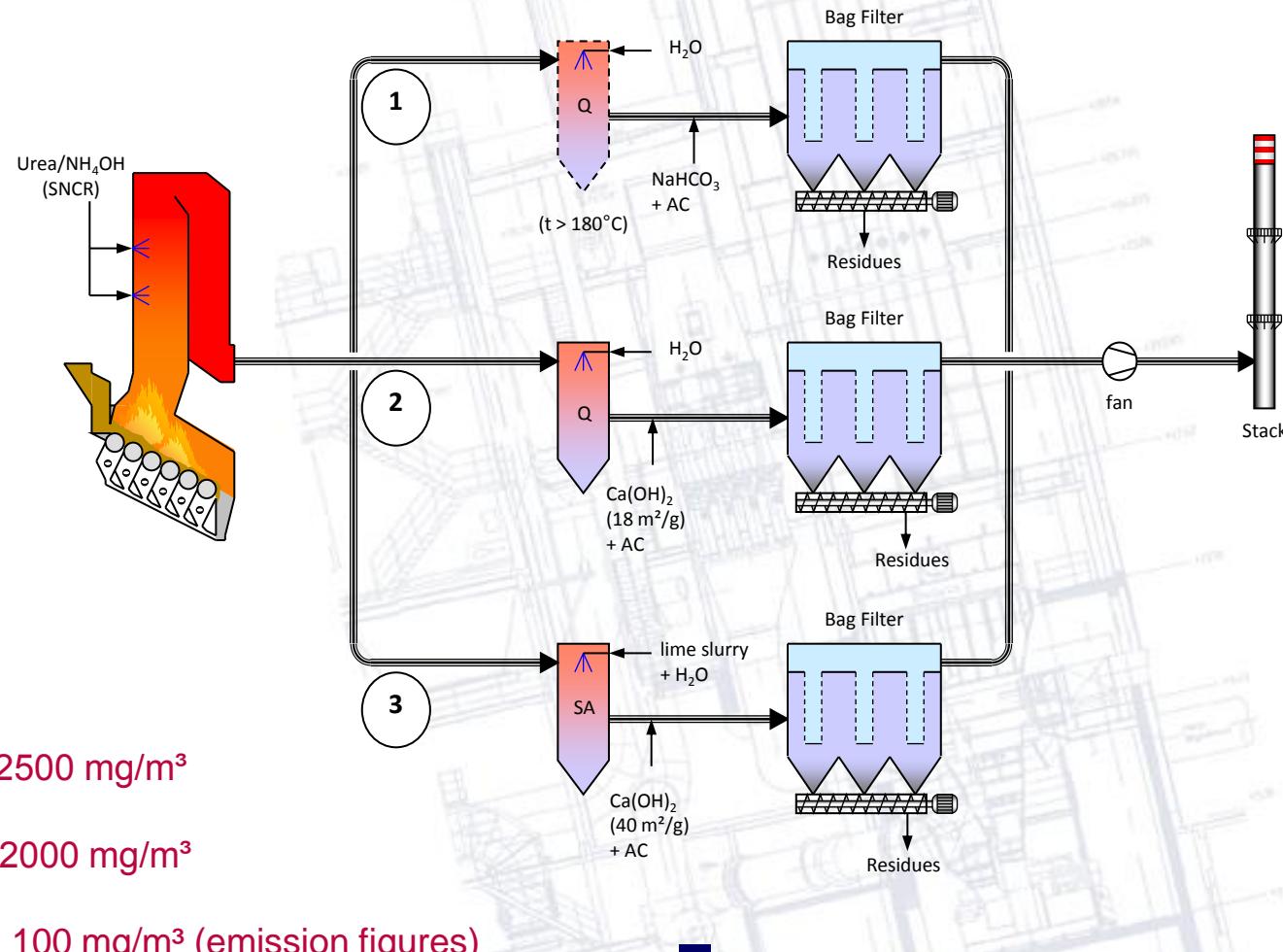


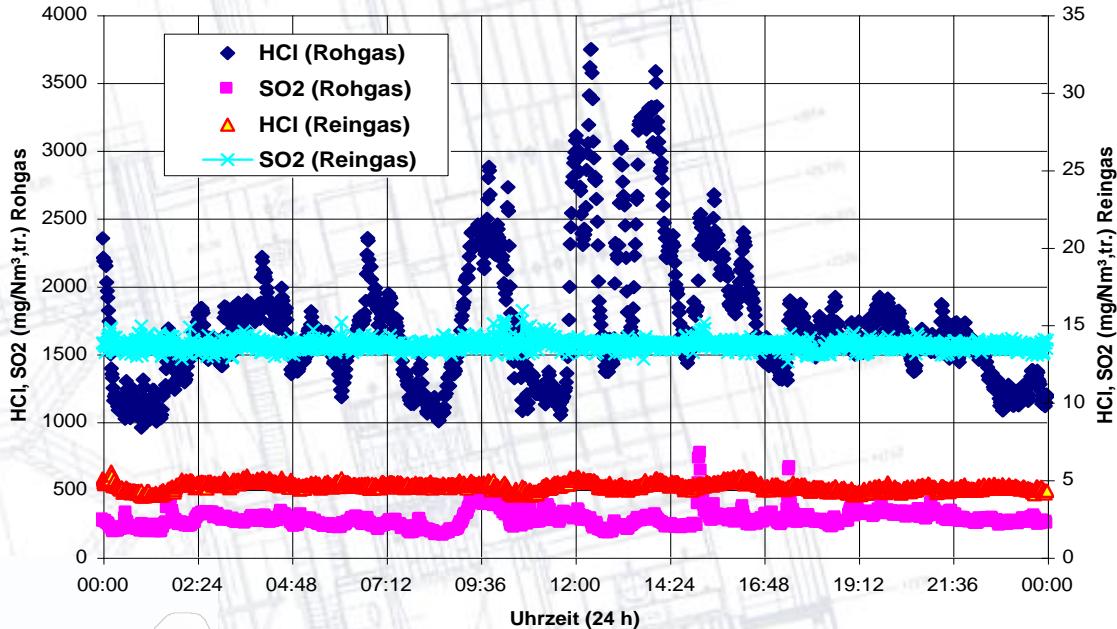
Abb.4 Einfluss der HCl-Konzentration und der absoluten Feuchte auf den SO₂-Gesamtabscheidegrad, Rohgaskonzentrationen: SO₂ = 750 ppm, HCl = 0 bis 600 ppm, Ca/S-Verhältnis = 2 (Quelle: [1] S.507)

Operation range of single stage dry absorption systems

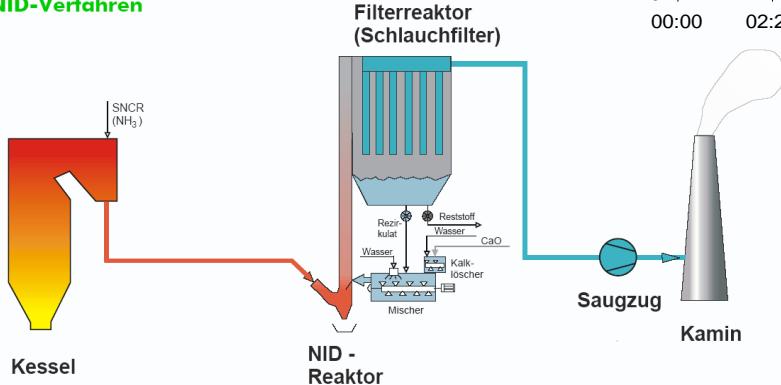


Experience with conditioned dry absorption systems

EBS-plant Romonta



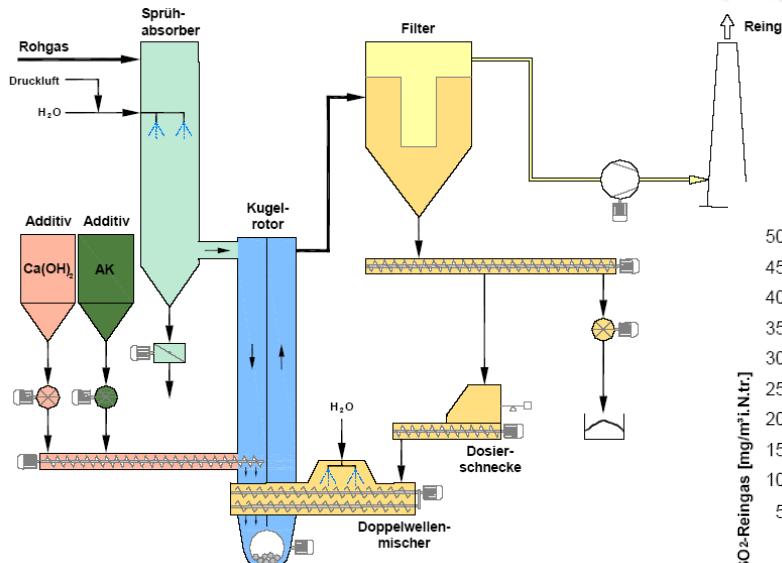
NID-Verfahren



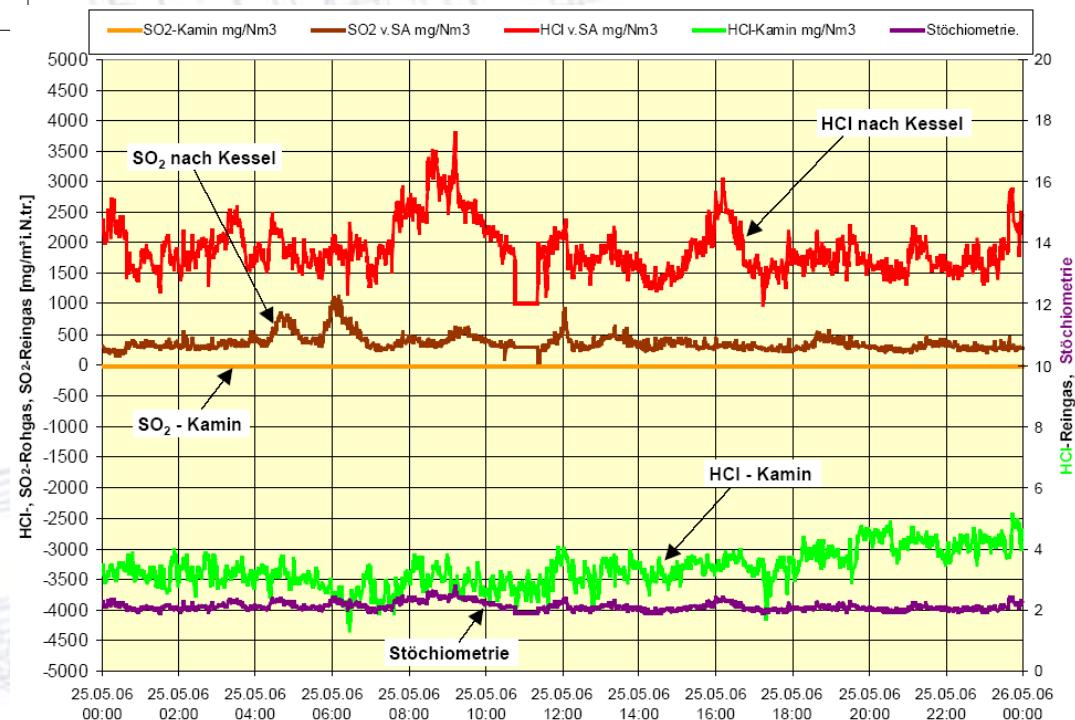
Quelle: ALSTOM Power

Experience with conditioned dry absorption systems

Wte-plant Ludwigshafen



Quelle: Lühr-Filter

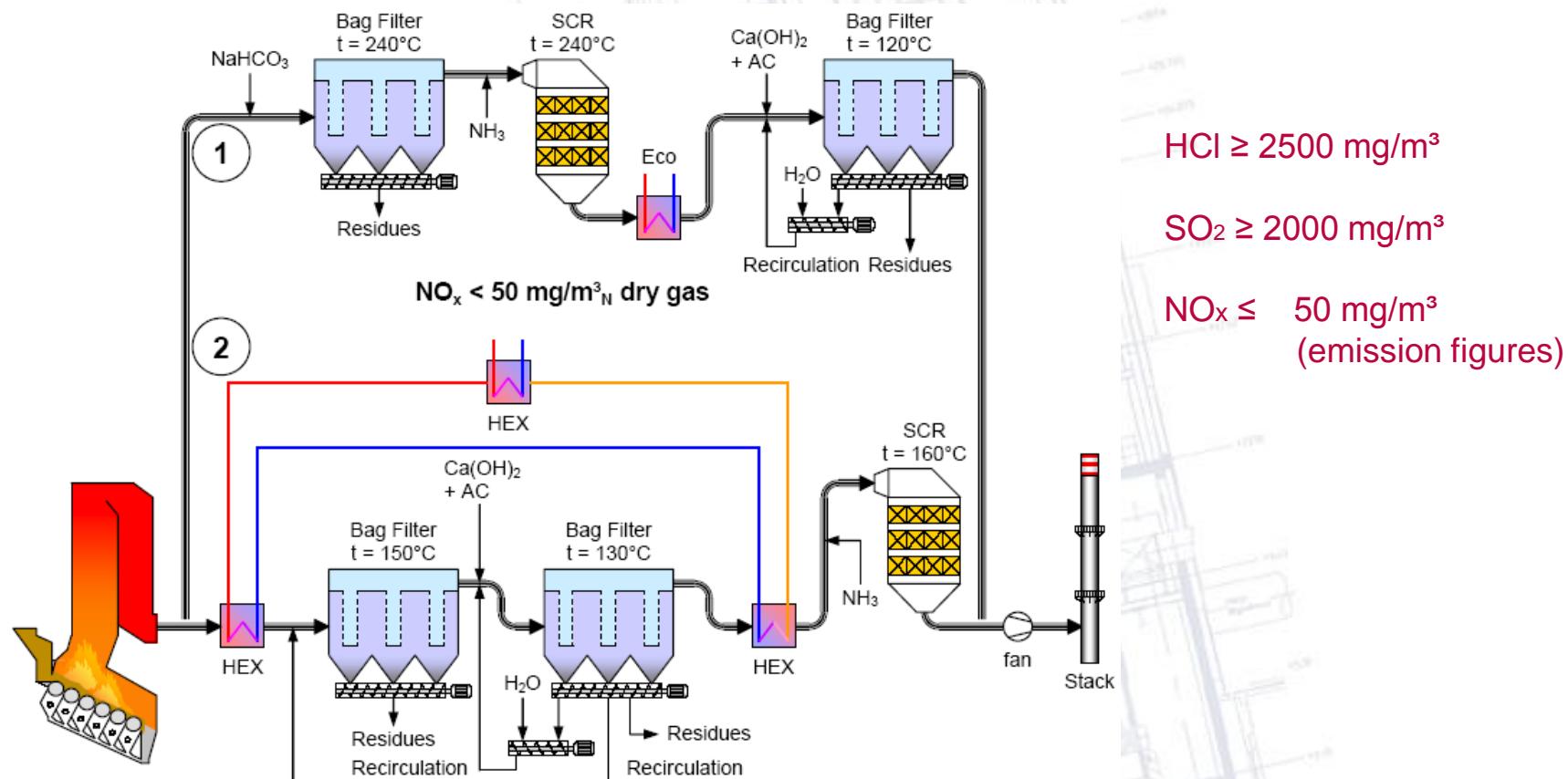


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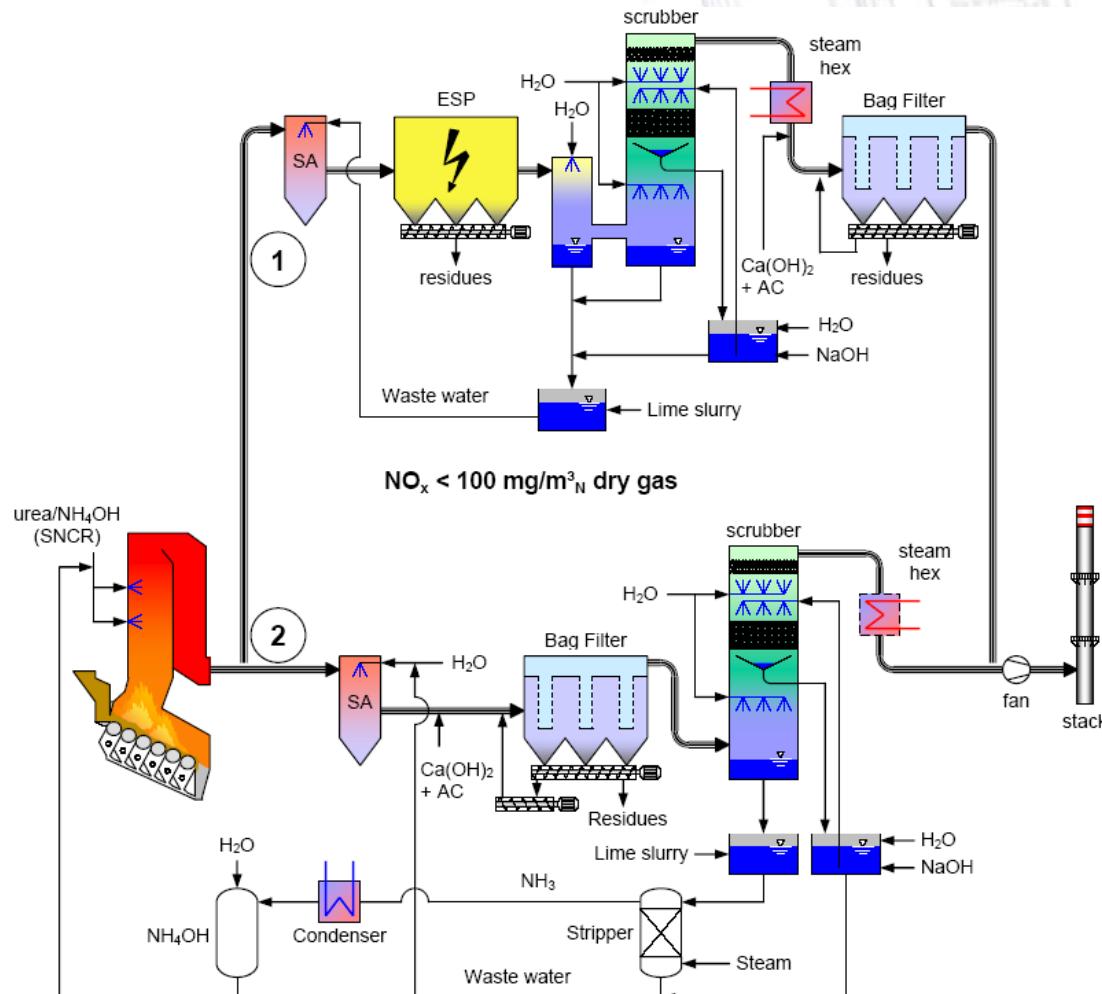
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Operation range of multistage flue gas systems

→ If the HCl-raw gas concentrations as a permanent load is > 2500 mg/m³, a multistage system is necessary



Operation range of multistage flue gas systems



$\text{HCl} \geq 2500 \text{ mg/m}^3$

$\text{SO}_2 \geq 2000 \text{ mg/m}^3$

$\text{NO}_x \leq 100 \text{ mg/m}^3$
(emission figure)

Potential of Optimizing

 **the biggest potential of lime based systems is an increasing of the relative humidity!**

to increase the relative humidity there are several possibilities:

- recuperative gas cooling, for example with a heat exchanger
- about water injection at a cooling tower
- about steam injection

Furthermore for a good removal efficiency it's important to have

- A good flow and dust distribution (filtration velocity & „filter cake“)
- attendance of enough reaction salts, especially Cl-salts

Potential of Optimizing



the biggest potential of sodiumbicarbonate systems is

- keep sure for enough high temperature
- warranty of a homogeneous distribution
- to realize high enough residence time $f(T, \text{Filtersystem})$
- high surface or small particle sizes

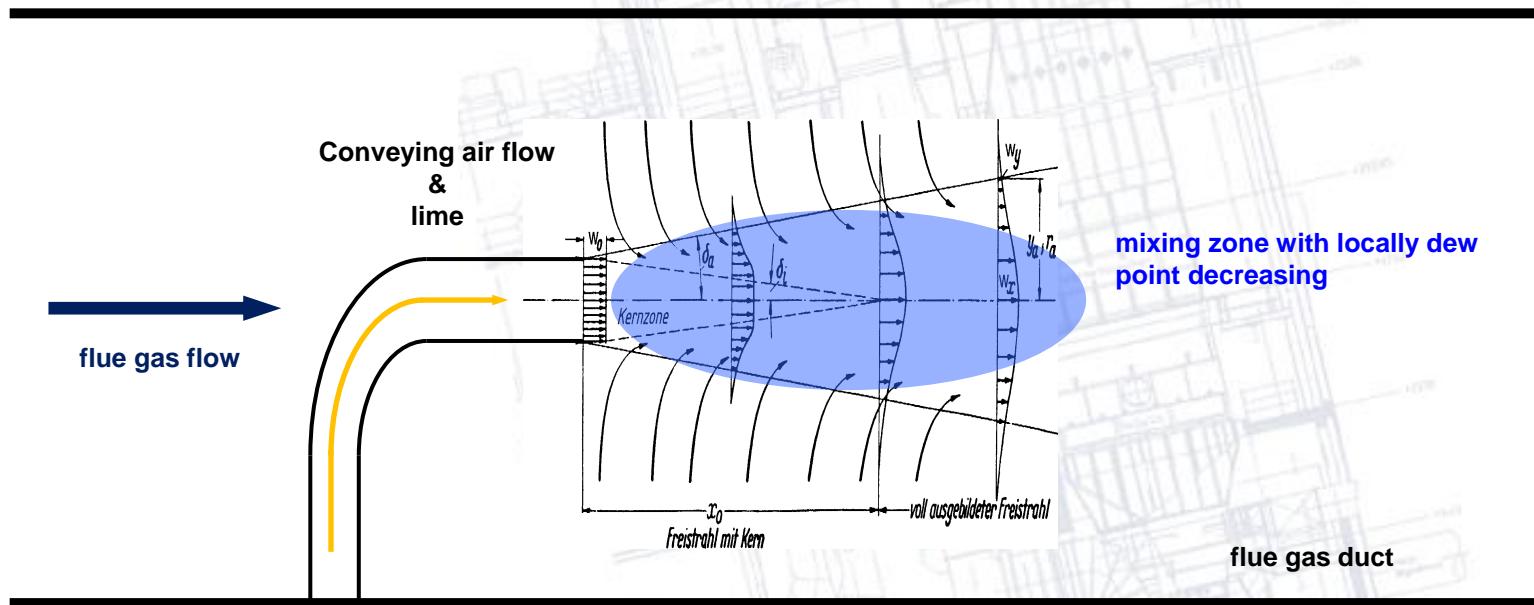
Potential of Optimizing

→ Substitution of spray absorption by a pure water injection

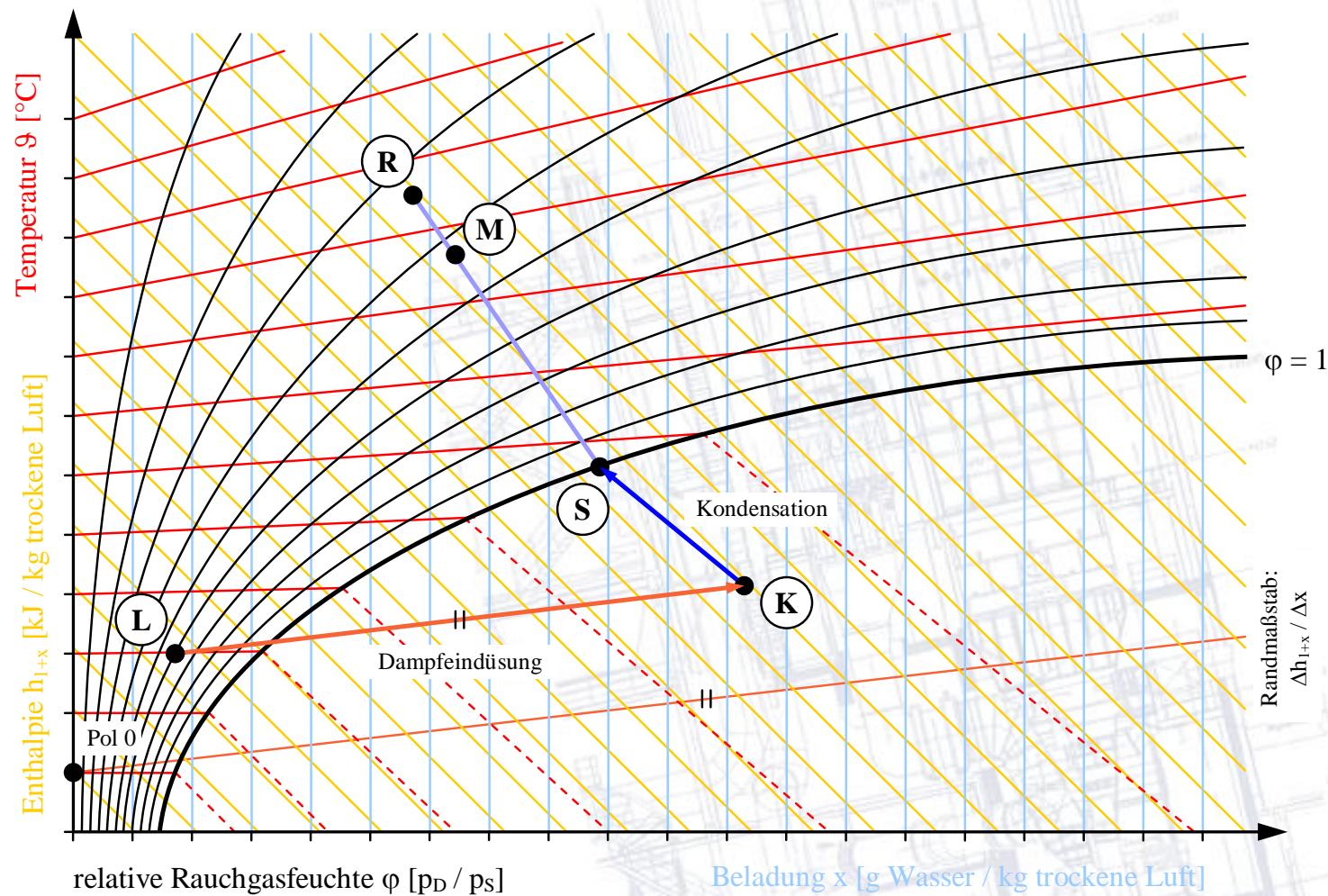
- few calcium carbonate formation and a bigger particle surface for the mass transfer to get a better stoichiometry (it means a more economical system)
- better removal efficiency, because the absorbers are mostly over dimensioned for a pure water injection and in that case the operation temperature can be reduced ($<140^{\circ}\text{C}$)
- a heating system at the bottom area of the absorber is necessary to avoid corrosion

Development / PTU-Process

Principle of “partiellen Taupunktsunterschreitung (PTU-Process)”



h-x diagram



Potential of Optimizing

→ application of PTU-process is ...

- at existing dry absorption systems with lime, when the flue gas humidity is to low or a furthermore temperature reduce is not possible.
- already used at
 - EBS-plants
 - municipal waste incineration plants
 - Hazardous waste incineration plants

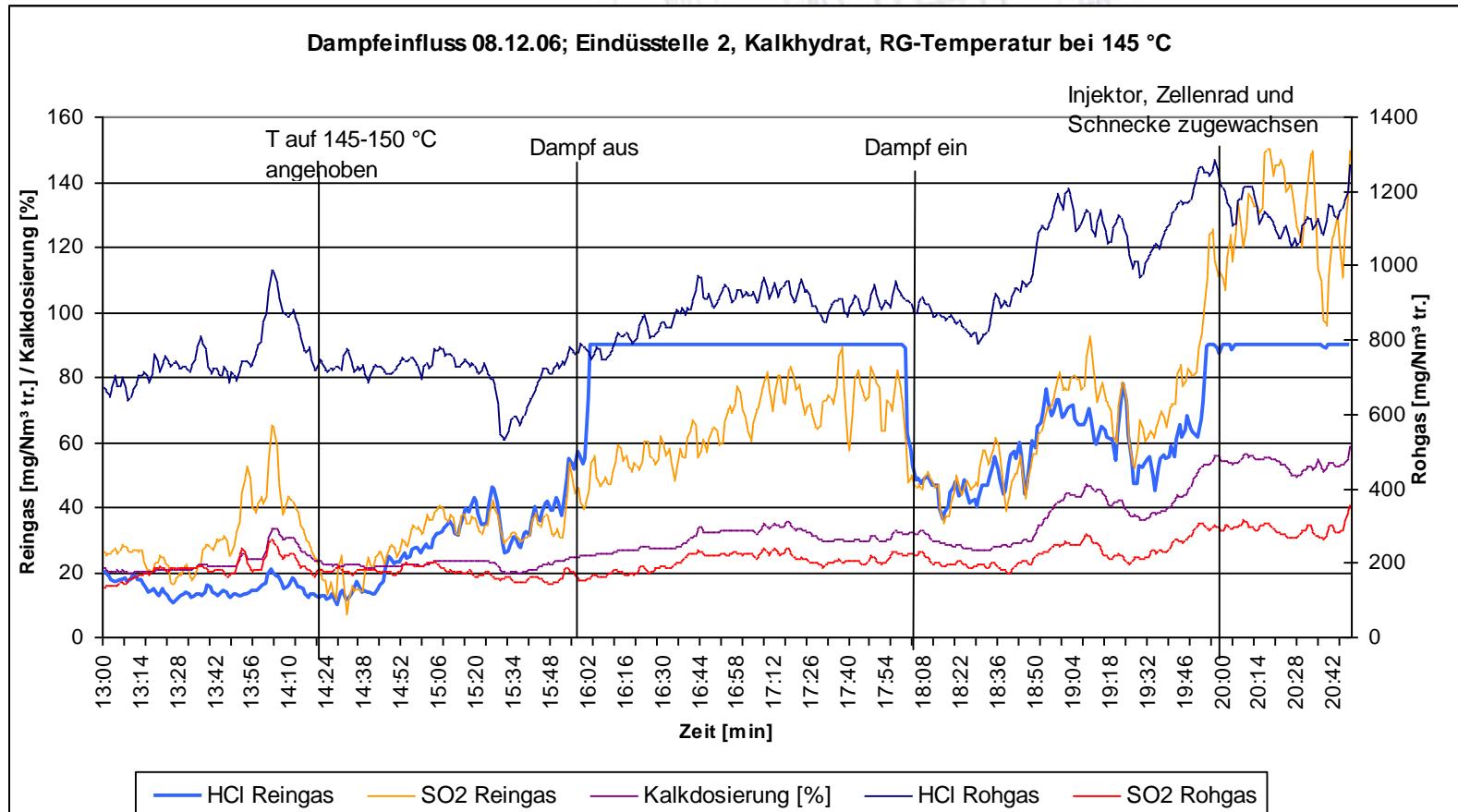
lime / steam lance of PTU-process



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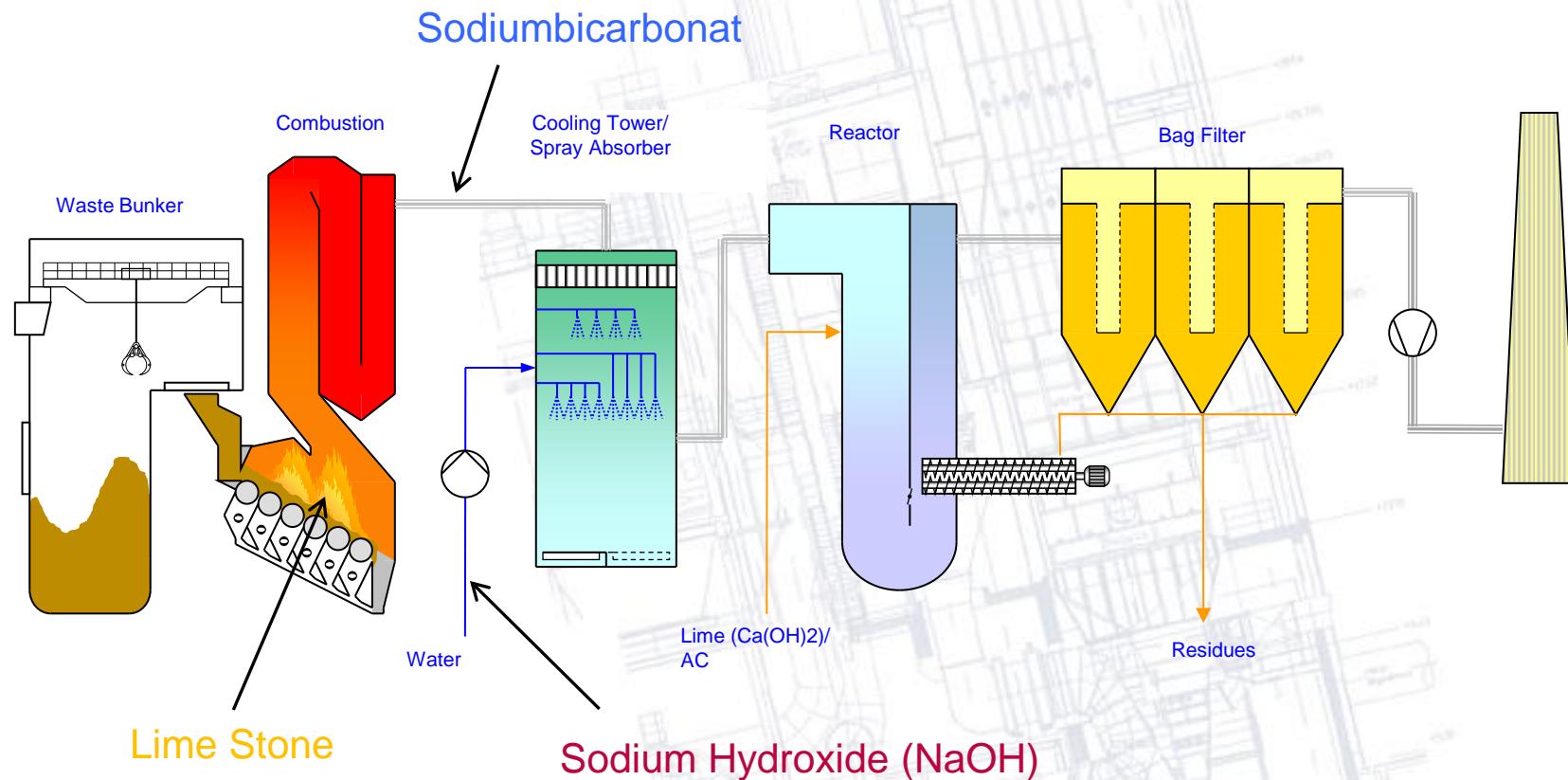
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tests for the steam influence at wte-plant Wuppertal



Potential of Optimizing

Multiple Additiv Injection



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Conclusion

- **conditioned dry absorption systems are high efficient and cheap systems, also for high HCl-concentrations**
- **witch process (wet / dry) or additive have to be use, depend on many factors and must be proved each new plant and location**
- **It is very important to have a optimized process temperature respectively a defined relative flue gas humidity**

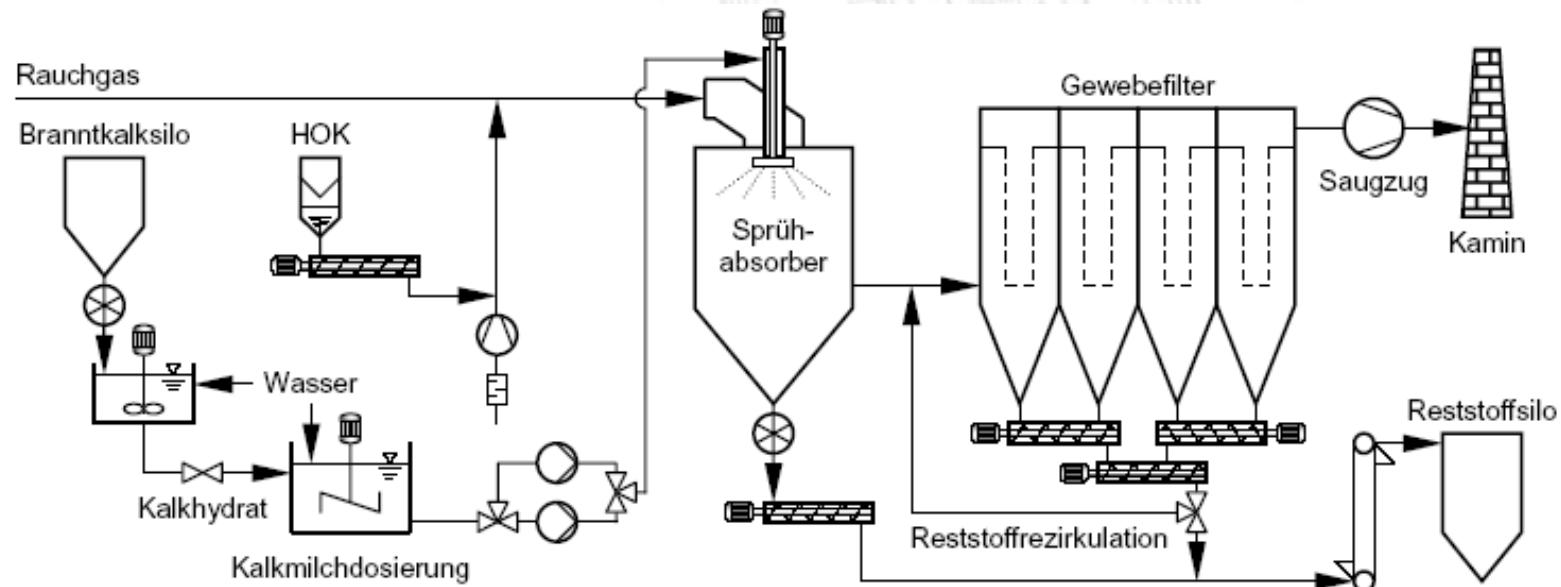
Conclusion

- Spray absorption after waste combustion systems is not so effectively and not economically
 - the rebuilt/shift to a conditioned dry absorption requires not huge retrofit actions
- the development of the flue gas conditioning by steam with the PTU-process has a lot of advantages, especially for retrofit of existing plants
- for high HCl-concentrations $>2500 \text{ mg/m}^3$ (average load) or for lower emission figures like $\text{HCl} < 5 \text{ mg/m}^3$ are multiple stage systems are necessary

If there would be only one truths, it wouldn't be possible
to paint hundred pictures about the same theme.

Pablo Picasso

Besonderheiten der Sprühabsorption



Der Kalk wird in seiner reaktivsten Form, nämlich als Kalkmilch in den Rauchgasstrom eingebracht!



weckt hohe Erwartungen an eine gute und effiziente Abscheideleistung

Besonderheiten der Sprühabsorption

Betriebserfahrungen von ausgeführten Anlagen zeigen jedoch

bei Müllverbrennungsanlagen

- ausreichend gute Abscheideleistungen jedoch bei Stöchiometrien von 2,2 bis $>2,5$ (oftmals unter Zuhilfenahme von einer zusätzlichen Zugabe von hochreaktivem Kalkhydrat)

bei fossil befeuerten Kraftwerken

- ausreichend gute Abscheideleistungen bei Stöchiometrien von $\geq 1,4$



Woher kommt dieser Unterschied?

Besonderheiten der Sprühabsorption

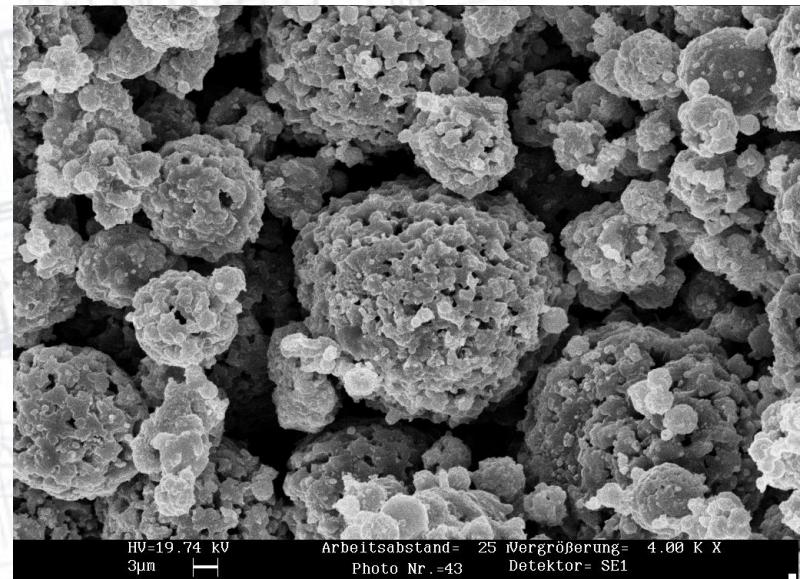
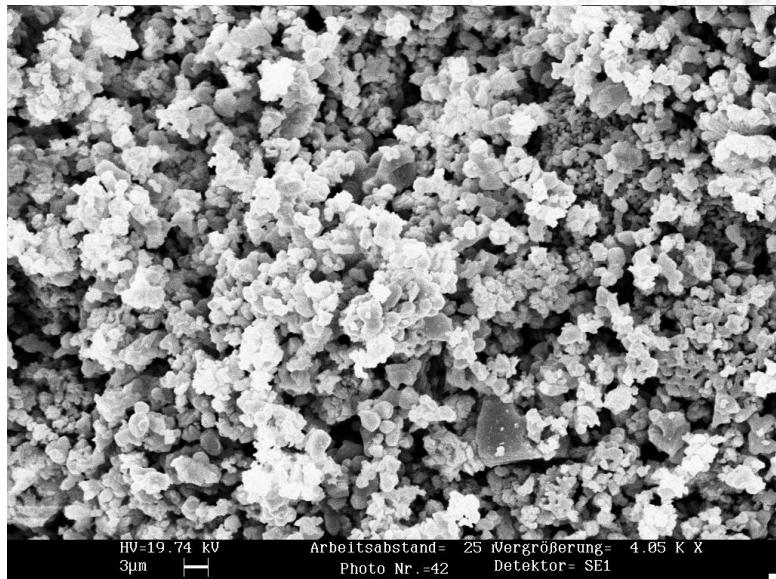
1. Oberflächenstruktur des in Form von Kalkmilch eingebrachten Kalkhydrats

Die erforderliche Stoffaustauschfläche verringert sich infolge der tropfenförmigen Agglomerationen, die bei der Verdampfung der Kalkmilch entstehen

REM-Aufnahmen

von frisch gelöschem Kalkhydrat

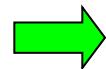
von $\text{Ca}(\text{OH})_2/\text{CaCO}_3$ aus einer
MVA-Sprühabsorption mit Kalkmilch



Besonderheiten der Sprühabsorption

2. Hoher Carbonatanteil / geringere Verweilzeit in der wässrigen Phase
der Kalkmilchtröpfchen (Suspension) stellt ein sehr basisches Milieu dar

Schadstoff	Einheit	CO ₂	HCl	SO ₂	HF
Rohgaskonzentration	[Vol.-%]	10			
	[mg/m ³ _N RG,tr.]		1.000	300	10
Molekülanzahl	[mol/m ³ _N RG,tr.]	4,492	2,74·10 ⁻²	4,68·10 ⁻³	5,00·10 ⁻⁴
Molekülverhältnis	[mol/mol HF]	8.987	55	9	1



Bildung eines hohen Carbonatanteils!



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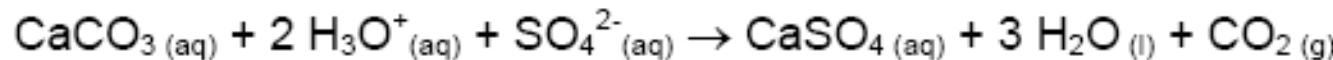
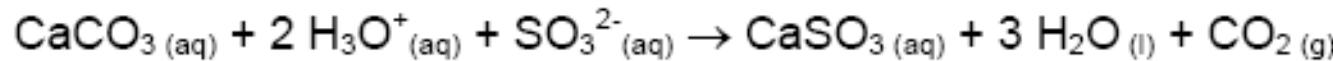
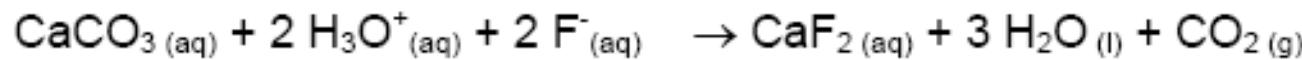
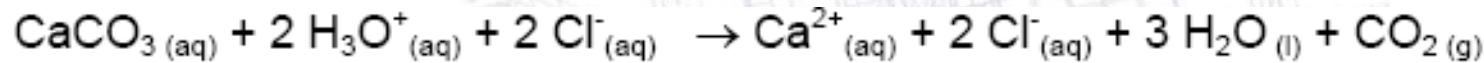
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Besonderheiten der Sprühabsorption

2. Hoher Carbonatanteil / geringere Verweilzeit in der wässrigen Phase

In trockenem Zustand ist das Calciumcarbonat aufgrund seiner hohen Gitterenergie und seiner kompakten Oberflächenstruktur relativ inert (Kalkstein).

Von Säuren wird es jedoch unter Abspaltung von CO₂ zersetzt. Daher kommt es in der flüssigen Phase zu einer Reaktion mit den sauren Schadgasen HCl, HF und SO₂



→ Je länger das Calciumcarbonat in der wässrigen Lösung (Suspension) vorliegt, desto effizienter ist die Abscheidung (wenig Calciumcarbonat)

Besonderheiten der Sprühabsorption

2. Hoher Carbonatanteil / geringere Verweilzeit in der wässrigen Phase

Sprühabsorption hinter fossil befeuerten Kraftwerken

- Prozesstemperatur von ca. 80°C
 - relative Rauchgasfeuchte von ca. 70%
- 

lange Verweilzeit

Sprühabsorption hinter Müllverbrennungsanlagen

- Prozesstemperatur von 135 - 160°C
- relative Rauchgasfeuchte von 4 -7%

Einsatzbereich mehrstufiger Verfahren

Wirtschaftlichkeit im Vergleich einer 2-stufigen Trockensorption(NaHCO₃ u. Ca(OH)₂) und einem Hybridsystem

Grundlagen

Verbrennungskapazität: 25 t/h Abfall oder EBS

Spezifische Kosten:

Betriebsmittel / spezifische Kosten	Einheit	Preis
elektrische Energie	[€/kWh]	0,06
Branntkalk (93,5 Ma.-% CaO)	[€/t]	90
Kalkhydrat (95 Ma.-% Ca(OH) ₂)	[€/t]	95
Natriumhydrogencarbonat (NaHCO ₃)	[€/t]	195
Herdofenkoks (HOK)	[€/t]	480
Ammoniakwasser (25%ig)	[€/t]	94
Natronlauge (50%ig)	[€/t]	260
Wasser	[€/t]	3
Druckluft (tr.)	[€/m ³ _N]	0,03
ND-Dampf (4 bar(a) / 143,6°C)	[€/t]	15
Reststoffentsorgung	[€/t]	110

Wirtschaftlichkeitsbetrachtung:

