

# LÜHR FILTER

## **Dry sorption with sodium bicarbonate – Really a very simple process? – Examinations at a waste incinerator in France**

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Dry flue gas cleaning  
for firing installations and other thermal or chemical processes**

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## 1 Introduction

With regard to gas cleaning systems downstream incinerators for e.g. biomass, waste or RDF, dry and semi-dry procedures for the simultaneous separation of particles, heavy metals, acid crude gas components as well as dioxins and furans became accepted in the past years. The competing additive powder qualities used for the separation of acid crude gases are  $\text{Ca(OH)}_2$  /  $\text{CaO}$  or  $\text{NaHCO}_3$ .

Regarding the dry chemisorption with utilisation of  $\text{NaHCO}_3$ , the following characteristics are often stated as advantageous features:

- High reactivity of additive powder
- Simple and reliable plant design
- Achievement of low stoichiometries
- Low remainder quantities of reaction products compared to Ca-based procedures

However, the influences of

- dry temperature in the gas
- plant design with and without particle re-circulation
- $\text{SO}_2$  /  $\text{HCl}$  ratio

are repeatedly discussed in this connection with reference to the stoichiometries achievable with this process.

To clarify these questions, examinations have been carried out at a flue gas treatment plant downstream waste incinerator in France. The results will be explained in the following and subjected to a final assessment.

This lecture will not go into an explanation of the basic principles regarding the separation of acid crude gases with utilisation of  $\text{NaHCO}_3$ , such as reaction equations, mole weights etc.

## 2 Flue gas cleaning at waste incinerator Cluses/ France

### 2.1 General design

In 2006, the gas treatment system of the waste incinerator in Cluses/France has been upgraded. Illustration 1 shows the plant after reconstruction. Essential data of application are listed in table 1.

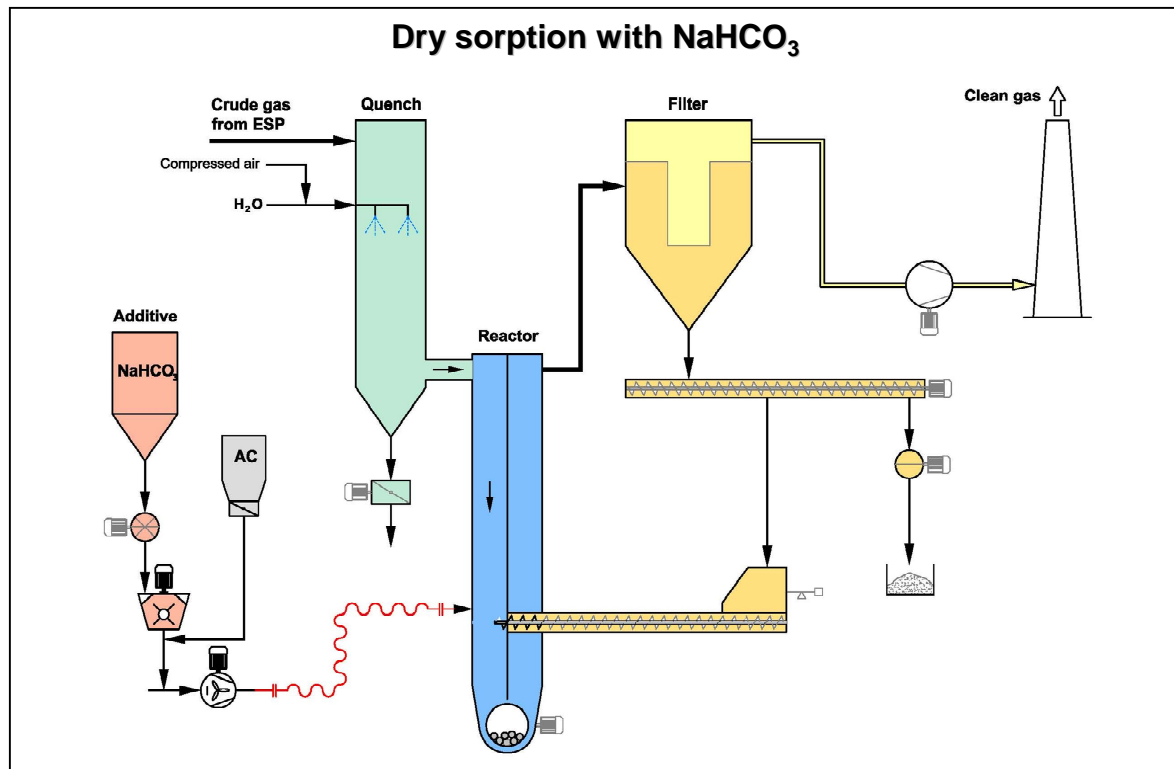


III. 1: MVA Cluses/ France

<b>Volume flow : 34,000 Nm<sup>3</sup>/h humid</b>					
<b>Temperature upstream quench : 250 °C</b>					
<b>Crude gas values :</b>			<b>Guarantee :</b>		
<b>Particles</b>	<b>:</b>	<b>90</b>	<b>mg/Nm<sup>3</sup> dry</b>	<b>Particles</b>	<b>:</b>
<b>HCl</b>	<b>:</b>	<b>1200</b>	<b>mg/Nm<sup>3</sup> dry</b>	<b>10</b>	<b>mg/Nm<sup>3</sup> dry</b>
<b>HF</b>	<b>:</b>	<b>20</b>	<b>mg/Nm<sup>3</sup> dry</b>	<b>10</b>	<b>mg/Nm<sup>3</sup> dry</b>
<b>SO<sub>2</sub></b>	<b>:</b>	<b>300</b>	<b>mg/Nm<sup>3</sup> dry</b>	<b>1</b>	<b>mg/Nm<sup>3</sup> dry</b>
<b>PCDD/PCDF</b>	<b>:</b>	<b>3</b>	<b>ng/Nm<sup>3</sup> dry</b>	<b>50</b>	<b>mg/Nm<sup>3</sup> dry</b>
<b>Hg</b>	<b>:</b>	<b>0.4</b>	<b>mg/Nm<sup>3</sup> dry</b>	<b>0.1</b>	<b>ng/Nm<sup>3</sup> dry</b>
				<b>0.05</b>	<b>mg/Nm<sup>3</sup> dry</b>

Tab. 1: Application of MVA Cluses/ France

The operator chose a dry sorption process with utilisation of NaHCO<sub>3</sub> and activated carbon as additive powders for the new gas treatment system. Illustration 2 shows a rough scheme of the fundamental design of plant.



III. 2: Schematic view of process design of MVA Cluses/ France

The fly ash is separated in an electrostatic precipitator (ESP), installed upstream of sorption stage, thus allowing the separate disposal of fly ash and reaction products.

Due to the boiler-related, comparatively high dry temperature of 230°C up to 250°C at the take-over point downstream ESP, a cooling stage will be necessary, realised as evaporative cooler for the adjustment of an optimum temperature in the sorption stage. When selecting the most suitable operating temperature, not only the separation of acid crude gases has to be considered but also the separation of mercury by means of activated coke injection. Whereas for the separation of  $\text{SO}_x$ , HCl and HF with utilisation of  $\text{NaHCO}_3$  a higher temperature is advantageous, the adsorption of mercury and mercury compounds with injection of activated coke / - carbon requires low temperatures to achieve a better separation efficiency. The evaporative cooler has been designed in such way, that at the inlet of reactor a temperature between 150°C and 180°C can be chosen.

The additive powder qualities are stored separately and dosed independently. The mixing of additives for the additive powder transport into the reactor takes place upstream conveying fan. Classifier mills and conveying fan are realised in redundant execution to ensure the plant availability.

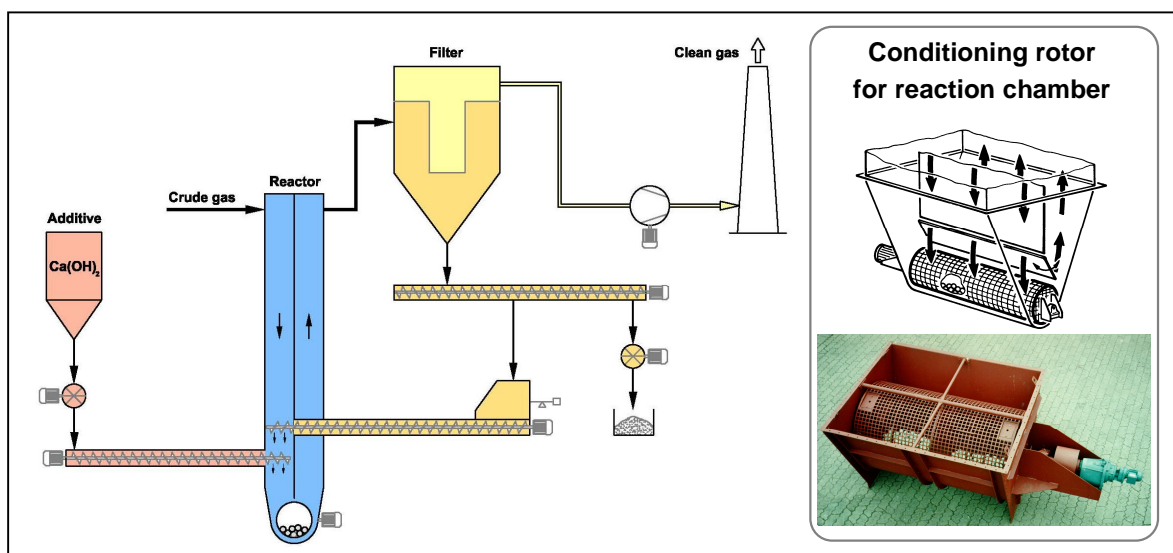
The injection of additive powders in the system takes place downstream evaporative cooler into a reactor, located upstream of filter. The injection quantity of activated coke into the system is adjusted constantly. A continuous measurement of mercury is neither requested for this plant, nor installed. The controlled injection of  $\text{NaHCO}_3$  is based on the continuously measured emission values in the clean gas.

The additive powder and reaction products are separated in a flat-bag filter, executed as a multichamber filter. Prior to their discharge out of the filter, the particles can repeatedly be reintroduced in the reactor.

The average residence time of additive powders in the system is variable. It depends on the chosen cleaning cycle as well as on the adjusted re-circulation rate. The time available for the reaction between the crude gas molecules and the additive powder particles totals to approx. 2 sec. Essential for the efficiency of process is an early, homogeneous distribution of additive powder particles and re-circulated particulate in the gas flow. In order to grant this property, the plant has been provided with the Conditioning Rotor – Recycle Process.

## 2.2 Conditioning Rotor – Recycle Process

A schematic view of the Conditioning Rotor – Recycle Process is given in illustration 3. It mainly comprises the units reaction chamber with conditioning rotor, flat-bag filter and re-circulating screw conveyor.



III. 3: Conditioning Rotor – Recycle Process

The rotor is a hollow cylinder, made of a perforated plate with openings of approx. 30 x 30 mm. Up to 10% of its volume is filled with balls made of heat- and wear-resistant ceramics. The rotor is continuously rotating with approx. 1 rpm by means of a geared motor. The rotation causes the balls to move relatively to each other inside of cylinder and to the perforated shell. The rotor is passed through by the flue gas around its axis of rotation at first in downwards and finally in upwards direction.

The main functions of the conditioning rotor are:

- Avoidance of particle deposits when reversing a particle-laden gas flow
- Achievement of a homogeneous distribution of particles in the flue gas flow even in case of high particle loads (e.g. up to 100 g/m<sup>3</sup>)
- Disintegration of larger agglomerates with a descent velocity higher than the transport velocity in the ascending part of reactor

Prior to being discharged out of the filter, the particles separated in the filter are repeatedly re-introduced in the reactor by means of a conveying screw. The particle recycle rate can be adjusted and, if needed, controlled e.g. subject to the current crude gas volume. With regard to the plant presented in this lecture, the specific recycle rate can be adjusted in a range between 0 and max. 50 gNm<sup>3</sup> humid.

Compared to alternative, e.g. pneumatically working re-circulation systems, the Conditioning Rotor – Recycle Process offers the following advantageous features:

- Mechanical particle transport by means of reliable screw conveyors
- Discharge and possibly intermediate storage of recycled particulate prior to re-circulation is not necessary
- Securing of a homogeneous distribution of recycled particulate during injection in the crude gas flow by using the conditioning rotor
- No increase in O<sub>2</sub> content in the flue gas due to the intake of conveying air

### **3 Influence of dry temperature, particle re-circulation and HCl / SO<sub>2</sub> ratio on the separation efficiency and the stoichiometry**

#### **3.1 Preliminary remarks**

The operator of plant agreed to the test series regarding the examination of the influence of

- dry temperature
- particle re-circulation
- HCl / SO<sub>2</sub> ratio

on the stoichiometry and the separation efficiency. However, some conditions had to be considered for the fixation and realisation of test series.

- The emission values in the clean gas had always to be kept definitely below the corresponding requested limit values (approx. 20% of the limit value).
- The particle re-circulation had to be operated with a min. quantity.

The test series had been carried out with the following setting parameters:

- dry temperature of 150°C and 170°C up to 180°C
- re-circulation rate of 5 g/Nm<sup>3</sup> humid and 45 g/Nm<sup>3</sup> humid



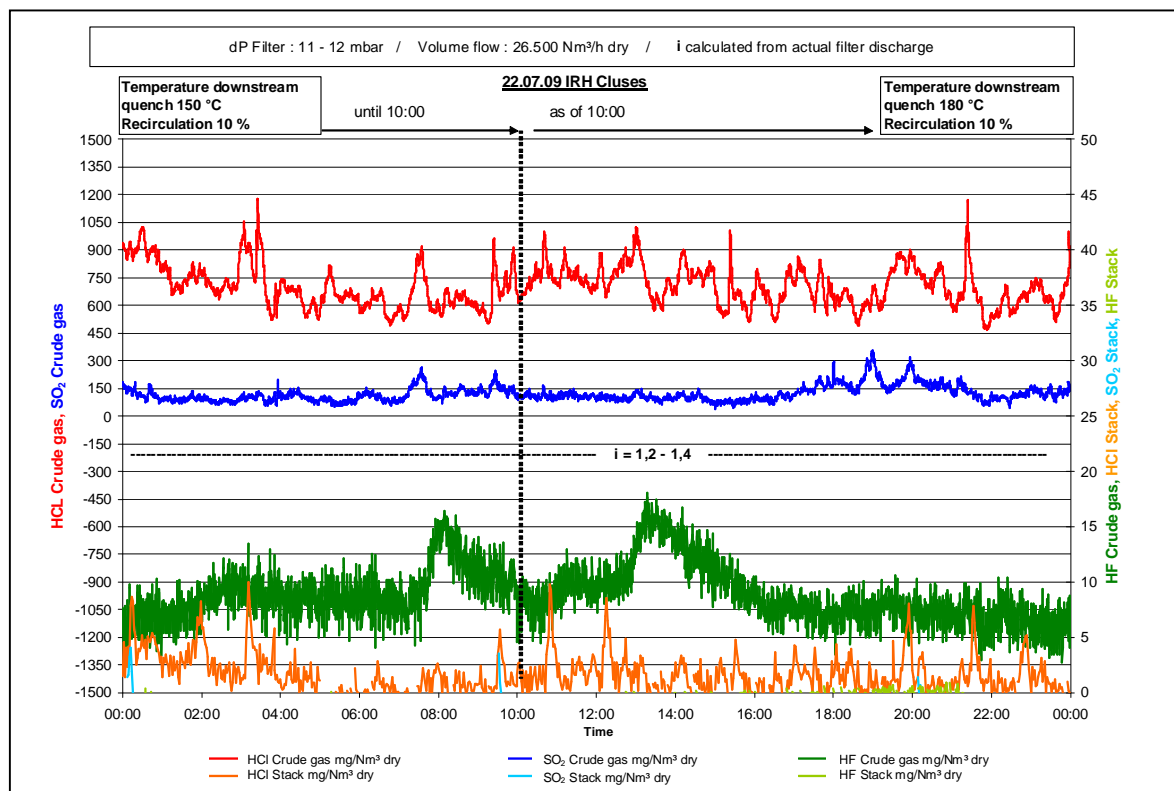
Crude gas and clean gas values for HCl, SO<sub>2</sub> and HF as well as volume flow and dry temperature were continuously measured and records were kept. The stoichiometry was determined on the basis of analyses of discharged reaction products. Mercury measurements were realised on the crude gas and on the clean gas side at several measuring days.

The test series were realised in several campaigns over a couple of weeks. In the following the results will be discussed on the basis of the records of selected days.

## 3.2 Results of examinations

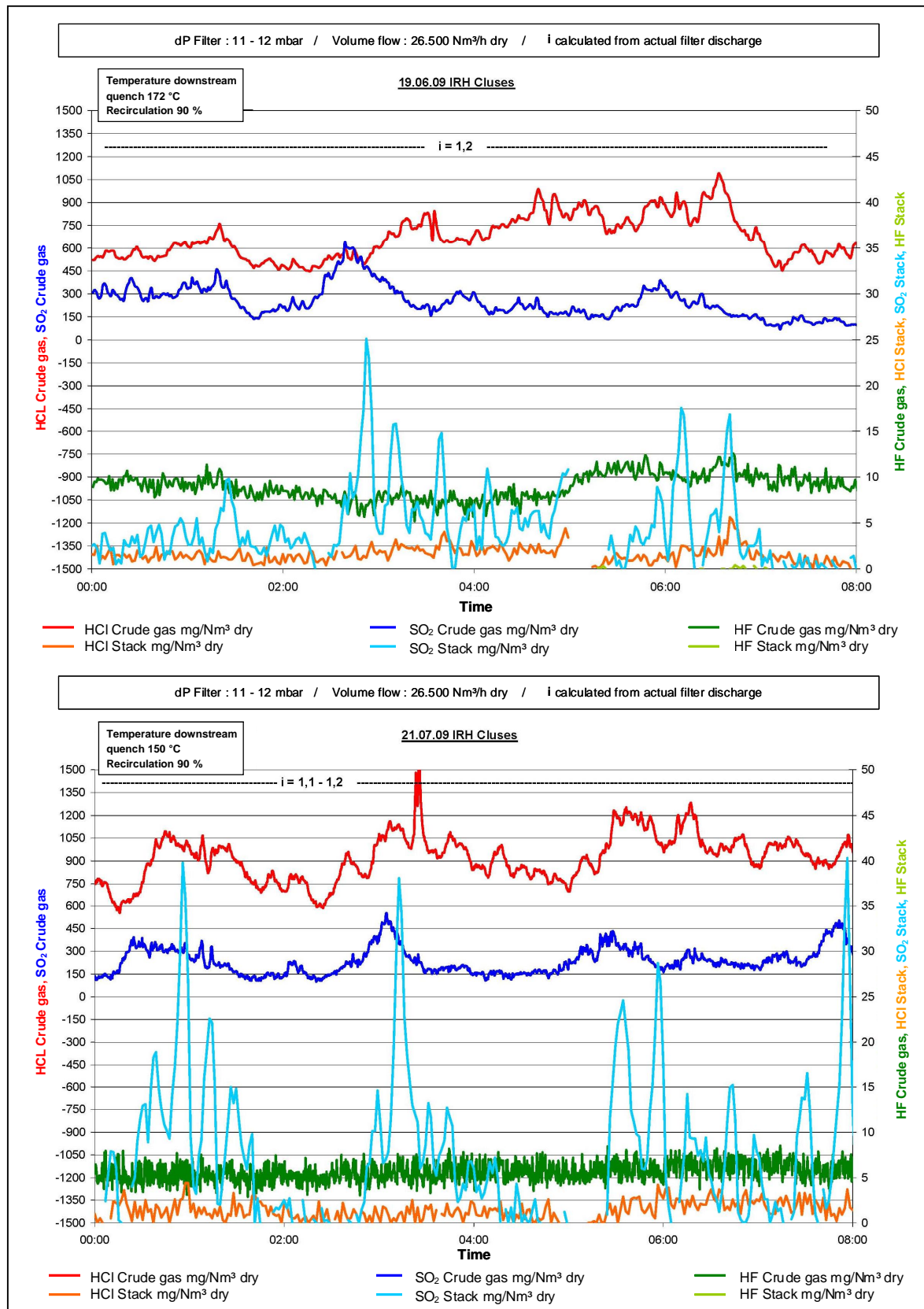
### 3.2.1 Influence of dry temperature on the separation efficiency and the stoichiometry

Normally, when using NaHCO<sub>3</sub> for the separation of acid crude gases, a min. dry temperature in the gas of 140°C is specified. Below this temperature, the reaction for the activation of NaHCO<sub>3</sub> is definitely more inert. The examinations were used to show, to what extent there is a correlation between separation efficiency and temperatures above 140°C. The measurement records shown in illustrations 4 and 5 explain the influence of temperature on the separation of HCl and SO<sub>2</sub>.



III. 4: Influence of temperature on the HCl separation



III. 5: Influence of temperature on the SO<sub>2</sub> separation

On 22.07.2009 (illustration 4) at 10.00 in the morning and at a recycle rate of 5 g/Nm<sup>3</sup> humid, the temperature was increased from 150°C to 180°C. During the whole measuring day, the SO<sub>2</sub> crude gas content was comparatively constant on a quite low level, whereas HCl showed the usual fluctuations of  $\pm 20\%$  around the average value.

No changes in stoichiometry and achieved degree of separation could be detected as a result of the readjustment of temperature.

Another result turns out when comparing the measuring day on 19.06.2009 with the measuring day on 21.07.2009 (illustration 5). On both days

- a high recycle rate of 45 g/Nm<sup>3</sup> humid was chosen,
- the stoichiometric factor totalled to a value  $< 1.2$ ,
- larger fluctuations of crude gas values for HCl and particularly for SO<sub>2</sub> could be noted.

On 19.06.2009 the plant was operated at a temperature of approx. 170°C and on 21.07.2009 at a temperature of 150°C.

Again no influence of temperature on the degree of separation for HCl could be detected. Regarding SO<sub>2</sub> however, the clean gas values tend to be higher in case of an increase of SO<sub>2</sub> crude gas values at the lower operating temperature.

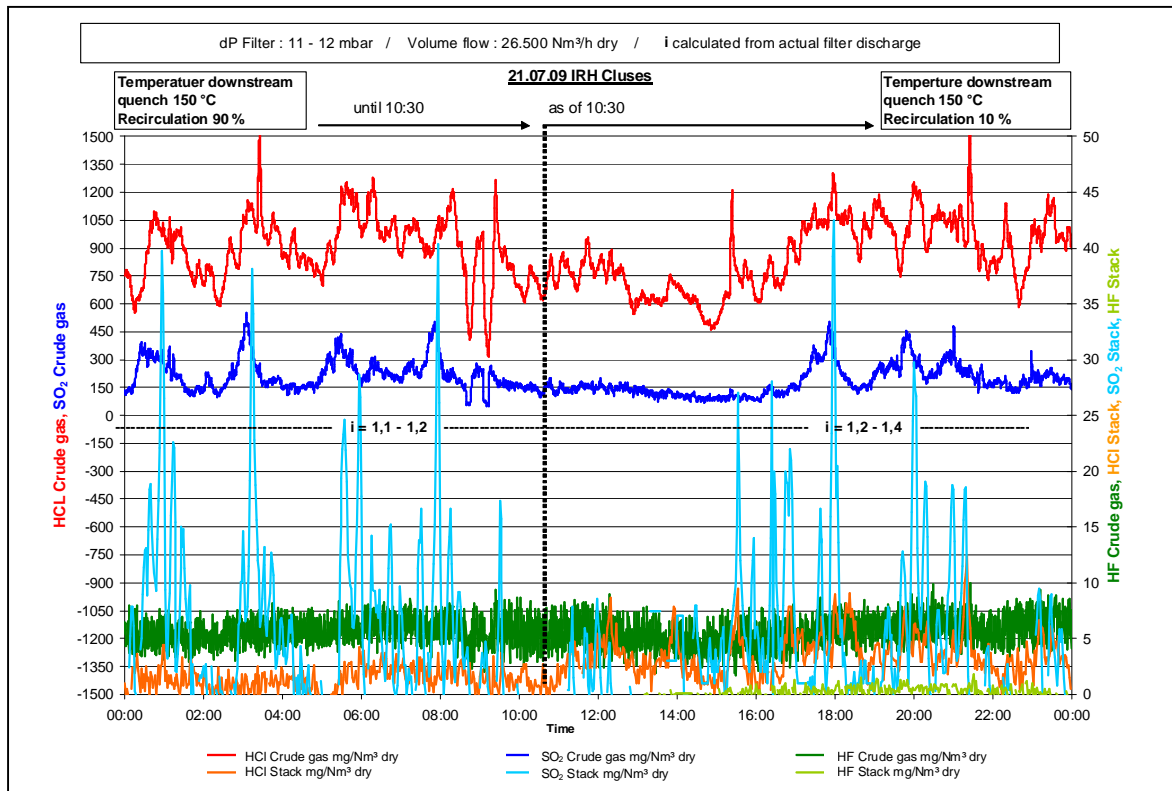
In summary the results show that

- regarding HCl, there is hardly a dependency in the range between 150°C and 180°C
- regarding SO<sub>2</sub>, a dependency could be noted. Higher temperatures improve the separation efficiency.

### **3.2.2 Influence of particle re-circulation on the separation efficiency and the stoichiometry**

Due to the high reactivity of used additive powder, it is often argued that a particle re-circulation will not be necessary for this process and will not lead to any improvement of separation behaviour. Based on the realised examinations, this statement could not be confirmed.

The influence is exemplary shown in illustration 6. On 21.07.2009 the recycle rate has been reduced from approx. 45 g/Nm<sup>3</sup> humid (90%) to 5 g/Nm<sup>3</sup> humid (10%).



### III. 6: Influence of particle re-circulation on the separation efficiency and stoichiometry

The results are as follows:

- The dosing rate was automatically increased to observe the defined max. clean gas values. On average, the stoichiometry rose from approx. 1.1- up to 1.2fold to 1.2- up to 1.4fold.
- The lower recycle rate results in higher clean gas values, especially for HF and HCl.

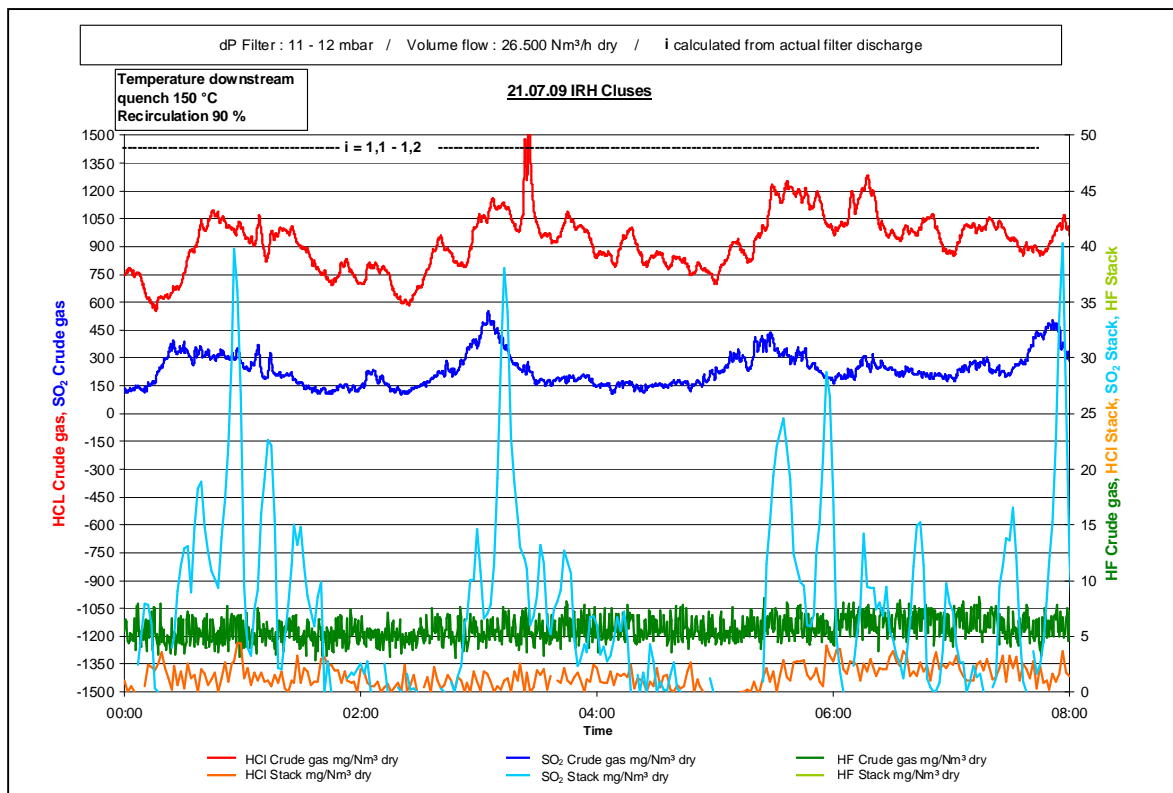
In general, a clear dependency of separation efficiency and/or stoichiometry on the particle re-circulation was detected over the whole measuring period of several weeks. This is partly due to the inertness of the chosen control concept for the  $\text{NaHCO}_3$  dosage. The control is exclusively subject to the clean gas values. This often leads to a temporarily more than stoichiometric additive powder injection. In case of systems without or only inferior particle re-circulation, the additive particles are discharged without utilisation of the complete sorption capacity. At plants with particle re-circulation, as a result of the longer residence time, the additive powder, which is freely available in the system in excessive quantity due to the above-stoichiometric injection, can also be used later for the reaction. In this case, the dosing takes place less than stoichiometric for a limited time.

Apart from this, compared to a system without re-circulation, a system with particle re-circulation generally offers advantages with an influence on the separation efficiency, independent of the used additive powder quality.

- The residence time of additive particles in the system is increased
- There is a higher additive powder density near the reactor upstream filter
- Achievement of a frequent, spatial new orientation of the re-circulated additive powder particles with rebuild of filter cake on the filter fabric.

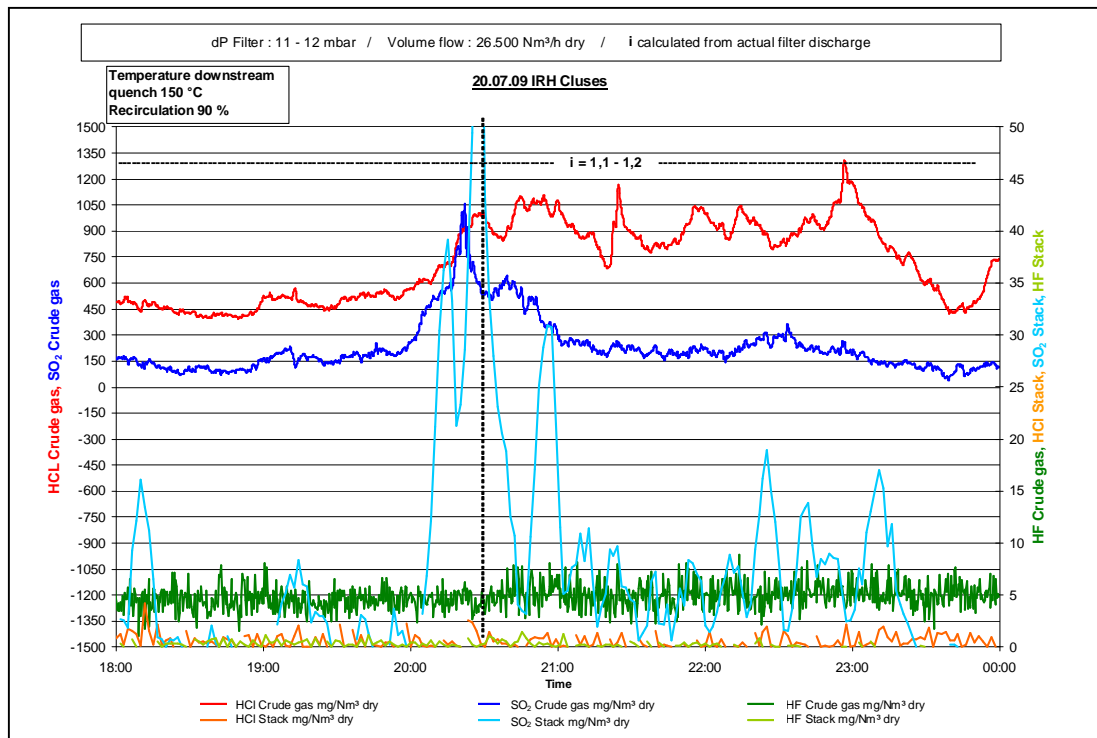
### 3.2.3 Comparison of HCl and SO<sub>2</sub> separation efficiency as well as influence of HCl/ SO<sub>2</sub> ratio on the SO<sub>2</sub> separation efficiency

Over the whole period of measuring campaign, all settings demonstrated, that the affinity of NaHCO<sub>3</sub> towards HCl is definitely higher than in comparison to SO<sub>2</sub>. This is exemplary shown by means of the measuring curves in illustrations 7 and 8.



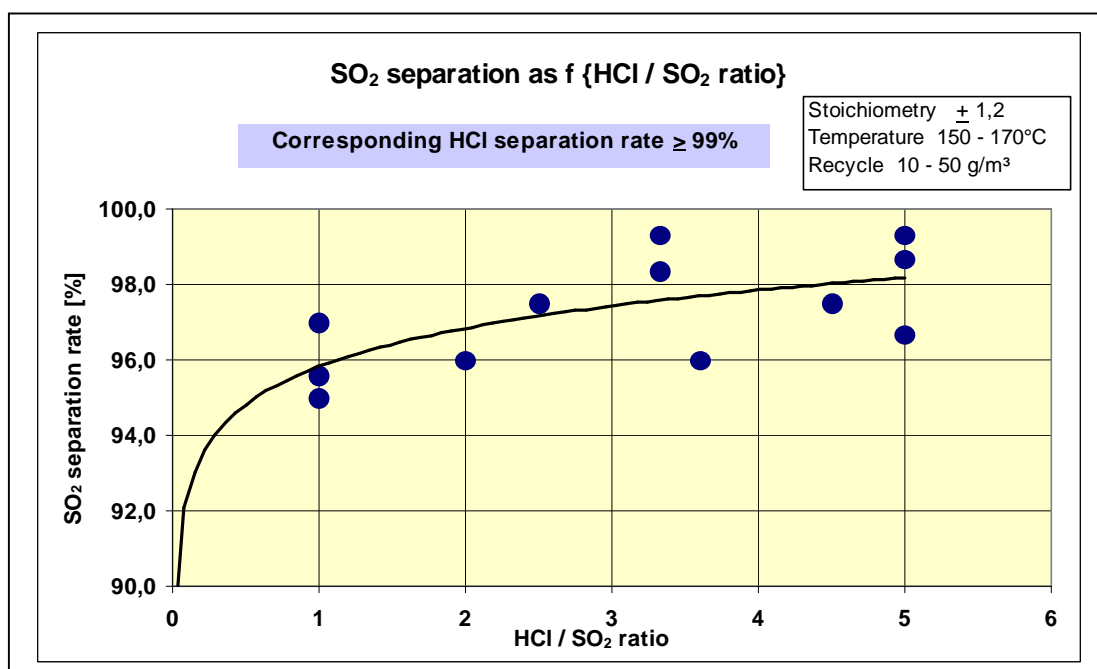
III. 7: Influence of crude gas peaks on the clean gas values

Whereas HCl peaks hardly provoke a noticeable rise in the HCl clean gas values, a spontaneous, considerable increase in the SO<sub>2</sub> clean gas values can be recognised in connection with SO<sub>2</sub> crude gas peaks. Furthermore, a HCl crude gas peak can also cause an increase in the SO<sub>2</sub> clean gas value.



### III. 8: Influence of crude gas peaks on the clean gas values

Illustration 9 shows in addition for different measuring points the SO<sub>2</sub> separation efficiency as function of the HCl / SO<sub>2</sub> ratio. A clear dependency is noticeable. In case of a shifting of the ratio towards SO<sub>2</sub>, the achieved degree of separation for SO<sub>2</sub> will be reduced. This means for applications with preferential SO<sub>2</sub> separation and requested degrees of separation for SO<sub>2</sub> clearly > 90 %, that higher stoichiometric values have to be expected or that the lower speed of reaction has to be compensated by means of a particle re-circulation.



### III. 9: SO<sub>2</sub> separation depending on the HCl/SO<sub>2</sub> ratio

It may be remarked in addition, that an influence of the HCl / SO<sub>2</sub> ratio on the HCl separation efficiency could not be noted.

#### **4 Separation of mercury**

During the measuring campaigns, several mercury measurements have been realised in the crude gas and the clean gas. Independent of the plant operation regarding recycle rates and temperature, very low clean gas values – on average definitely < 5 µg/Nm<sup>3</sup> dry – have been detected. However, the crude gas values with partly clearly < 100 µg/Nm<sup>3</sup> dry were very low and therefore the C / Hg ratio with a factor of approx. 1,000 was very high. Due to the basic conditions, an influence of re-circulation and temperature on the separation efficiency could not be noted.

Variations in the activated coke dosage have not been realised.

#### **5 Assessment and process comparison**

The evaluation of measuring results can be summarised as follows:

- Due to the requirements of plant operator, the clean gas values normally totalled to approx. max. 20% of the requested limit values. The stoichiometry necessary for the observance of these limit values lies on average in a range of 1.1 up to 1.4. This result illustrates the good separation efficiency of the used additive powder.
- As a result of the missing crude gas measurements, fluctuations in the crude gas values lead to emission peaks with temporarily increased stoichiometry. The installation of a HCl and SO<sub>2</sub> crude gas measurement for a prompt additive powder control may be advisable regarding the observance of low stoichiometric values subject to the application.
- The influence of the temperature can only be noted in connection with SO<sub>2</sub>. In case of low temperatures and particularly in case of increased crude gas values, the clean gas values tend to be higher.
- The influence of the particle re-circulation is clearly visible. In order to observe approx. identical clean gas values, the stoichiometric factor with high re-circulation rate has to be increased from 1.1 – 1.2 to 1.2 – 1.4 with low re-circulation rate.
- With regard to the SO<sub>2</sub> separation, there is a dependency on the HCl / SO<sub>2</sub> ratio. Particularly in case of applications with preferential SO<sub>2</sub> separation, this may lead to higher stoichiometric factors.

The results of examinations showed in summary that with regard to the design, the dry sorption process with utilisation of NaHCO<sub>3</sub> is a really simple and reliable process. Depending on the application it may be advisable to complete the basic process, consisting of additive powder injection, reaction line and filter, by the installation of a

crude gas measurement for SO<sub>2</sub> and HCl and / or to install in addition a re-circulation of the particles separated in the filter into a reactor located upstream of filter.

These measures can contribute to the reliable observance of a low stoichiometry in continuous operation and by this to a reduction in operating costs.

The selection of a most suited process in competition between the dry sorption with NaHCO<sub>3</sub> and the dry or semi-dry sorption with Ca-based additive powders for a given application is mainly influenced by the overall costs to be expected. With regard to the waste incinerator in Cluses, table 2 shows the operating costs for the additive powder consumption of the used process compared to a Ca-based process.

Denomination	Dimension	Procedure	
		Cond. dry sorption with hydrated lime	Dry sorption with sodium bicarbonate
Volume flow	Nm³/h dry	24,000	24,000
HCl content	mg/Nm³ dry	1,200	1,200
HF content	mg/Nm³ dry	20	20
SO₂ content	mg/Nm³ dry	300	300
HCl load	kg/h	28.8	28.8
HF load	kg/h	0.5	0.5
SO₂ load	kg/h	7.2	7.2

Absorption agent	----	Ca(OH)₂	NaHCO₃
Necessary stoichiometry		2.00	1.20
Demand for alkaline adsorption agent	kg/h	77	105
Resulting remainder from additive powder injection	kg/h	123	82

Costs / Supply	----			
Alkaline adsorption agent	Unit price	EURO/to	100	220
	Demand	to/a	616	838
	Costs	EURO/a	62,000	184,000
Remainders	Unit price	EURO/to	300	300
	Arisen quantity	to/a	985	656
	Costs	EURO/a	296,000	196,000
Sum of considered costs		EURO/a	358,000	380,000

Tab. 2: Operating costs for additive powders – MVA Cluses/ France

When evaluating the data given in table 2, it has to be considered that with regard to his application especially the comparatively low gas volume and the high specific disposal costs of € 300/t for the reaction products have a considerable influence on the results. Due to the small remainder quantity, the process with NaHCO<sub>3</sub> offers an advantage but in spite of the low stoichiometry, this will be more than used up due to the high purchase costs for the additive powder.



As a result of the higher investment costs and the operating costs for compressed air and energy consumption for the semi-dry process still to be considered, the disadvantage due to the higher costs for the additive powder are more than compensated. For this application, the selection of the dry sorption process with  $\text{NaHCO}_3$  is correct.

In general, two essential influence factors regarding the selection of process on the basis of  $\text{NaHCO}_3$  or  $\text{Ca(OH)}_2/\text{CaO}$  can be named:

- Plant size  
With increasing plant size, advantages for procedures with Ca-based additive powders will arise.
- Specific costs for remainder  
With higher specific costs for the disposal, advantages for  $\text{NaHCO}_3$  will arise.

Beside the separation of acid crude gas components also other aspects of an application have to be considered for the selection of process, e.g. the  $\text{NO}_x$  reduction. Resulting from the currently discussed requirements on  $\text{NO}_x$  emission limit values of partly  $< 100 \text{ mg/Nm}^3$  dry in connection with a limitation of  $\text{NH}_3$  slippage, the combination of dry sorption with  $\text{NaHCO}_3$  at temperatures  $> 200^\circ\text{C}$  combined with a downstream installed catalyst is a possible variant. However, particularly because of the high specific purchase costs for  $\text{NaHCO}_3$ , this variant competes for example with the process chain

SNCR – Semi-dry chemisorption with  $\text{Ca(OH)}_2/\text{CaO}$  – Wet scrubber

i.a. for the separation of  $\text{NH}_3$ . In spite of the definitely more complex design, this combination can be the better variant with regard to the economic efficiency.

For each application it has to be examined separately, which of the processes available on the market will be the most suited one with regard to the used additive powder and the technical equipment. In this respect, the dry sorption with  $\text{NaHCO}_3$  is an interesting alternative.



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