

HDT symposium: Dry sorption

Title: Dipl. – Ing.

First name: Rüdiger

Last name: Margraf

Address: **LÜHR FILTER GmbH & Co. KG**
Enzer Str. 26
31655 Stadthagen
GERMANY

tel.: +49 (0)5721 708-200

fax: +49 (0)5721 708-233200

e-mail: R.Margraf@luehr-filter.de

Title of lecture: Today's and forward-looking concepts for the gas cleaning downstream incinerators for waste and alternative fuels (EBS) with utilisation of additive powder qualities $\text{Ca}(\text{OH})_2$ / CaO or NaHCO_3 from the point of view of a plant constructor

<u>Summary:</u>	Page
1. Introduction	3
2. Dry sorption process with utilisation of Ca-containing additive powders...3	3
2.1 Spray absorption and particle conditioning	3
2.1.1 General structure	3
2.1.2 Advantages and disadvantages of technical procedure	5
2.1.3 Utilisation of CaO instead of Ca(OH) ₂ for the reduction of operating costs	7
2.2 Evaporative cooling and particle conditioning	8
2.2.1 General structure	8
2.2.2 Advantages and disadvantages of technical procedure	9
2.3 Two-stage (conditioned) dry sorption	11
2.3.1 Preliminary remark	11
2.3.2 Process description by means of examples, advantages and disadvantages... 11	11
3. Dry sorption process with utilisation of NaHCO₃.....	16
3.1 General structure, advantages and disadvantages	16
3.2 Influencing figures with regard to the additive powder efficiency	17
3.2.1 Gas temperature and particle re-circulation	17
3.2.2 HF separation	19
4. Comparison of operating costs	19
5. Selection of process technology	22

1. Introduction

Not only due to economic reasons, the operators of thermal waste disposal plants are forced to apply efficient, reliable and favourably priced gas cleaning technologies. In order to observe the emission limiting values according to 17. BImSchV., dry and/or conditioned dry process technologies became more and more accepted during the last years.

These procedures are continuously developed to comply with the growing requirements e.g. in view of increasing contents of crude gas components and/or - with regard to 17. BImSchV. - stronger emission limiting values. The following lecture presents different variants with utilisation of additive powder qualities based on Ca and Na and the corresponding strong and weak points. Plant examples will give indications for the operating costs.

A discussion of the separation technologies is not subject of this lecture.

2. Dry sorption process with utilisation of Ca-containing additive powders

2.1 Spray absorption and particle conditioning

2.1.1 General structure

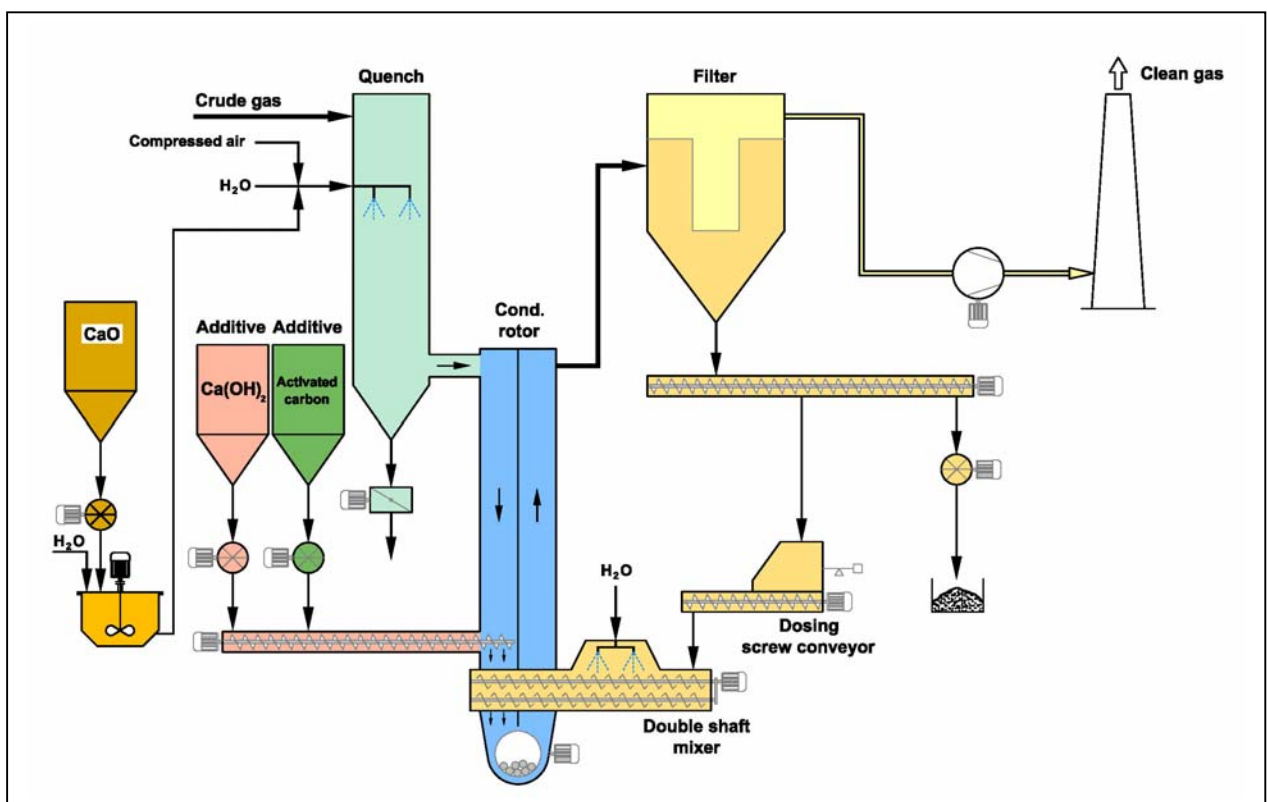


Illustration 1: Combined spray sorption – conditioned dry sorption

This process technology (illustration 1) has been applied for several years for the reliable observance of the emission limiting values according to 17. BImSchV. and has for example been installed during the modification of the gas cleaning system of line 2 at MHKW Ludwigshafen (illustration 2). This process technology has been applied for several incinerators for alternative fuels, being at present in process of installation.



Illustration 2: MHKW Ludwigshafen crude gas cleaning line 2
Spray absorber head and filter / reactor building

The first stage of the combined procedure comprises the spray absorber.
The tasks of this unit are:

- Gas conditioning for adjustment of the optimum reaction temperature and increase in relative and absolute humidity.
- Preliminary sorption by means of injection of lime slurry with at the same time reduction of acid dew point for the avoidance of corrosion.

Due to the fact that especially in case of additional fuel incinerators and as a result of the fuel composition the gas humidity is often lower than the one of e.g. domestic waste incinerators, the possibility of adjusting an optimum gas temperature gains special importance.

The second separation stage comprises the reactor – filter combination with injection of $\text{Ca}(\text{OH})_2$ and multiple particle re-circulation including conditioning of re-circulated particulate. The tasks are the following:

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

2.1.2 Advantages and disadvantages of technical procedure

Compared to other dry and/or semi-dry procedures, based on Ca-containing additive powder qualities, the following advantageous features result from this, admittedly a bit more complex procedure:

- Graded additive powder injection
The example shown in illustration 3 demonstrates the advantages of a graded additive powder injection. In the first stage, with low stoichiometry referred to the crude gas input, a large part of the HCl content (80%) and approx. half of the SO_2 content is separated. Referring to the crude gas contents to be expected after the first stage and compared to the summarised stoichiometry, a definitely higher stoichiometry will be available for the fine cleaning in the second stage.

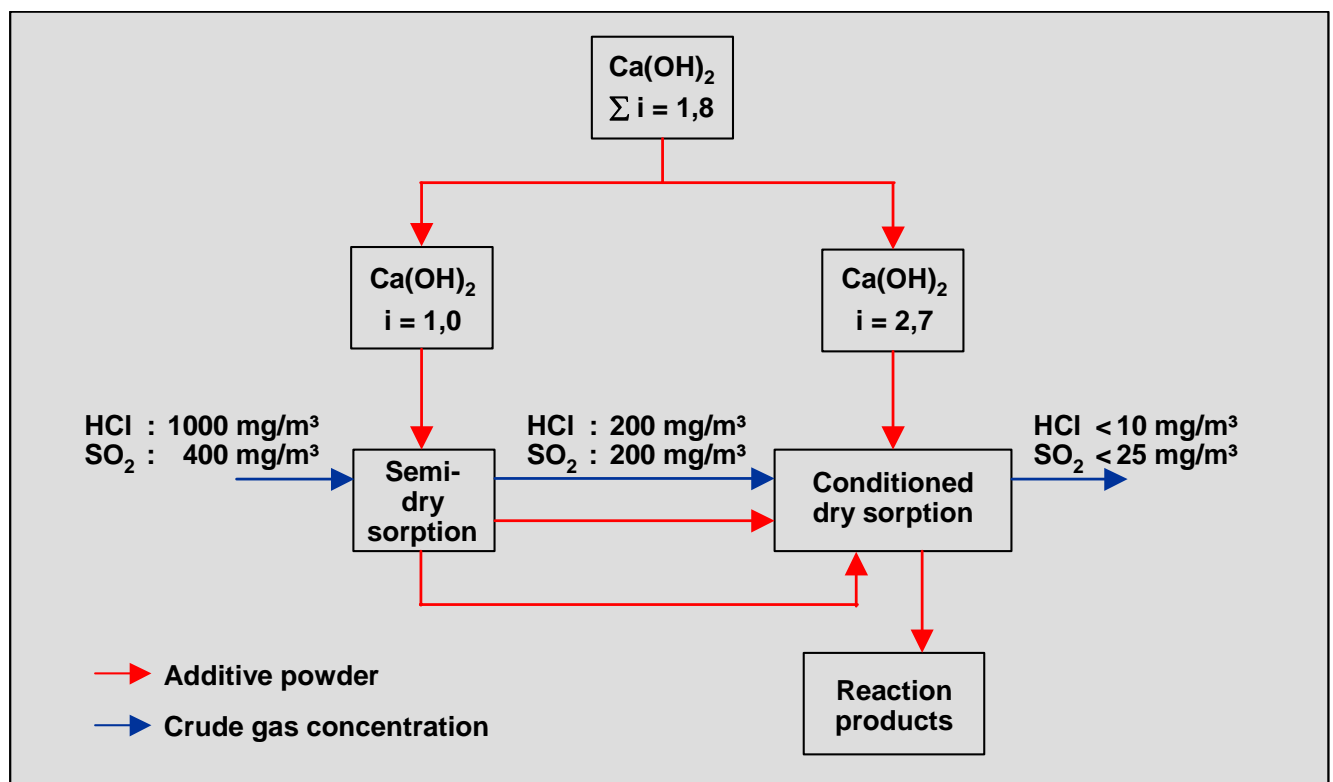
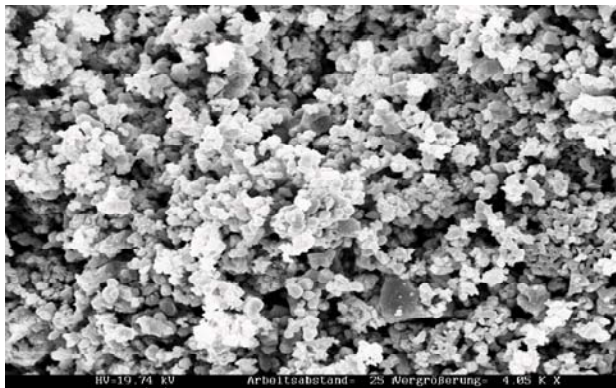


Illustration 3: Graded additive powder injection

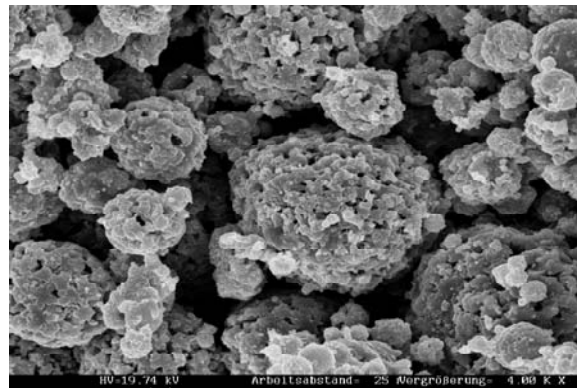
- Variation limits of crude gas contents
The overall system is comparatively insensitive with regard to strongly fluctuating crude gas contents in the crude gas. Assuming a degree of separation in the first stage of 80% as shown in illustration 3 for an input value of HCl of e.g. 3.000 mg/m³ the input value upstream second stage will be reduced to 600 mg/m³.
- Availability / Redundancies
The emission values can reliably be kept even in case of failure of parts of the system.
 - Failure of lime slurry
 - > system evaporative cooler, conditioned dry sorption
 - Failure of particle re-circulation
 - > system spray absorber and Ca(OH)₂ injection upstream fabric filter

However, the described advantages of procedure are confronted with disadvantages, especially resulting from the operating behaviour of spray absorber and thus having a hindering effect on the additive powder efficiency.

- Formation of agglomerates
The microscopic photos in illustration 4 show fresh hydrated lime particles compared to calcareous particles extracted downstream spray absorber. The freshly slaked hydrated lime has a clearly visible high outer surface. However, after drying within spray absorber, this will be reduced due to the formation of drop-shaped agglomerates. The exchange surface necessary for the chemical reaction will be reduced.



Fresh hydrated lime



Calcareous particles from a spray sorption at waste incinerator with lime slurry

Source: Rudi Karpf, etc.a

Illustration 4: Surface structure of the hydrated lime, injected as lime slurry

- **CaCO₃ formation**

Compared to the acid crude gases HCl, HF and SO₂, the slightly acid carbon dioxide has a minor affinity to hydrated lime. However, the concentration of CO₂ within the gas is considerably higher. A CO₂ concentration of approx. 10%Vol., corresponding to 100,000 ppm is faced with a HCl concentration of e.g. 1,600mg/m³, corresponding to 1,000 ppm. During the wet phase a considerable amount of CaCO₃ will be formed which will – after drying of lime slurry drops – be only very limited available for the reaction. With an adequate water supply, the downstream installed conditioned dry sorption could possibly take care for a partial reactivation of CaCO₃.

The before-mentioned disadvantages lead to the fact that with regard to this technical procedure, LÜHR FILTER lays special emphasis on the crude gas sorption in the second stage – the conditioned dry sorption with multiple particle re-circulation. From the author's point of view, the mere spray sorption or also in combination with an additional hydrated lime injection upstream filter presents no effective alternative procedure. Compared to the process variant spray absorber with particle conditioning, the achievable additive powder efficiency is lower.

The author also starts from the point that in normal cases, the adjustment of the optimum reaction temperature should not only be effected by means of particle conditioning without evaporative cooler or spray absorber. In case of a good additive powder efficiency, the material moistened in the mixer and introduced into the reactor contains reaction products which will – in case of a too high proportional moistening – form very large, non floating particle agglomerates and/or lead to hard deposits at the reactor walls, which can only be removed by manual intervention.

2.1.3 Utilisation of CaO instead of Ca(OH)₂ for the reduction of operating costs

In general, during production of lime slurry for the spray absorber and due to cost reasons, CaO in connection with a wet hydrator is used. At approximately equal specific purchase costs per tonne for the materials CaO and Ca(OH)₂ the resulting advantage for CaO lies in the range of 25% whereas the water quantity for hydration still has to be considered. If now the focal point of crude gas sorption is shifted towards the conditioned dry sorption, it will be unavoidable that this cost advantage will be reduced.

To achieve an optimum cost advantage in this respect and to be at the same time independent of the distribution of lime injection to the two sorption systems, a dry hydrator for CaO can – especially in case of higher consumption rates – be used. In this case the complete additive powder quantity will be supplied in form of CaO.

This material will be converted into $\text{Ca}(\text{OH})_2$ in a dry hydrator by means of H_2O injection and is made available as dry additive powder in an intermediate silo for the production of lime slurry and the injection into reactor. The intermediate silo is adequately dimensioned to allow the direct filling of silo with $\text{Ca}(\text{OH})_2$ in case of maintenance or repair works near the dry hydrator.

2.2 Evaporative cooling and particle conditioning

2.2.1 General structure

Based on the consequential consideration of the advantages and disadvantages of the combined procedure spray sorption with conditioned dry sorption mentioned in chapter 2.1.2 it seems to be useful to do completely without the spray sorption. In the MHKW Ludwigshafen (illustration 2) corresponding investigations are made. Since March 2006 the necessary hydrated lime is injected to 100% into reactor upstream filter and the spray absorber is used as evaporative cooler for the adjustment of optimum gas temperature and humidity by means of water injection. The fundamental design of process technology is shown in the schematic view in illustration 5.

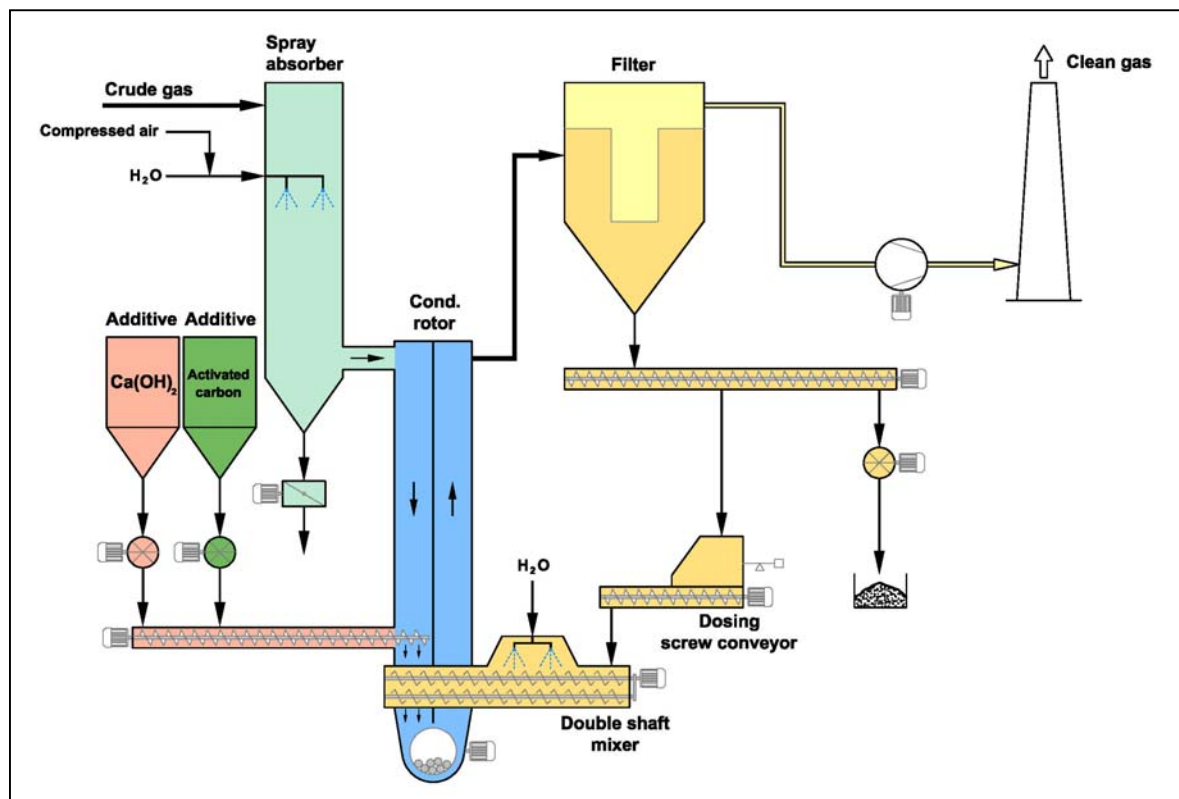


Illustration 5: Chemisorption with particle and gas conditioning

The requested emission limiting values can reliably be kept as shown in illustration 6. In case of HCl concentrations downstream boiler in the range of 1,500 - > 2,500 mg/Nm³ dry, the HCl clean gas value is < 5 mg/Nm³ dry, the SO₂ clean gas value is definitely < 5 mg/Nm³ dry. When using a common hydrated lime with a specific surface of approx. 18 m²/g on average, the additive powder injection quantity corresponds to a stoichiometric factor of 2.0.

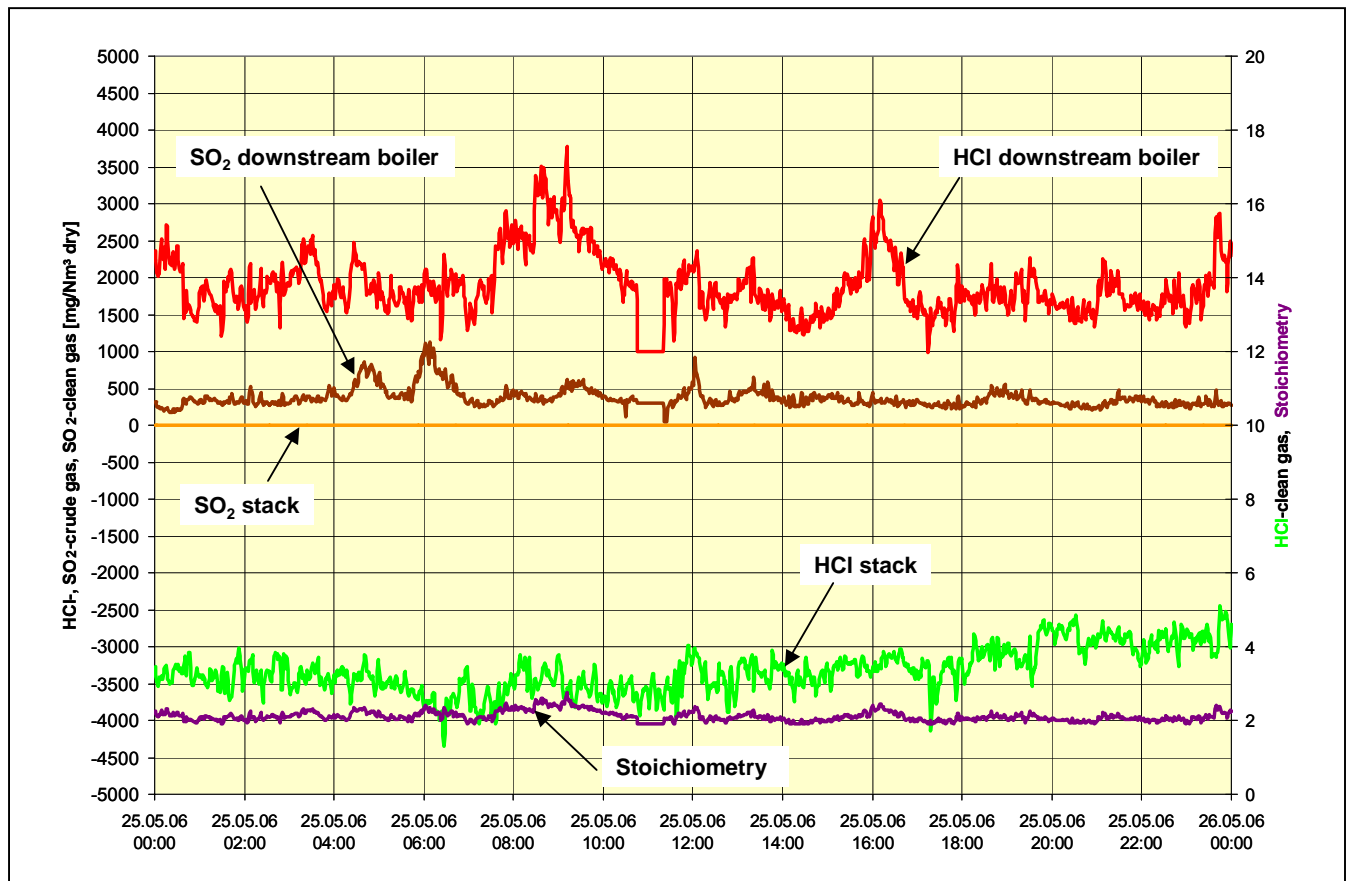


Illustration 6: Trend curves of crude gas and clean gas values and stoichiometry

2.2.2 Advantages and disadvantages of technical procedure

The advantageous features of this procedure are:

- The production and conveyance of lime slurry which is subject to maintenance works can be renounced.
- Compared to a spray absorber, the operating costs related to spare part requirement and maintenance for the evaporative cooler are considerably lower.
- The conversion at Ludwigshafen resulted in a reduction of the portion of calcium carbonate in the re-circulated particulate from approx. 30 weight % to 20 weight %, thus causing a corresponding increase in the free portion of lime. This leads to lower emission values and/or to the reduction of the additive powder injection quantity.
- The requirements regarding the water qualities to be used are reduced. In this respect, e.g. seepage water can be used for the cooling.

The confronting disadvantages are:

- The graded additive powder injection will be cancelled. In doing so, the evaporative cooler with a possible contact time of several seconds will not be used for the crude gas separation.
- The evaporative cooler has additionally to be protected against corrosion by means of corresponding measures.
- The redundancy in the additive powder injection is not given.
- To avoid the loss of the advantage of lower purchasing costs when using CaO, the installation of a dry hydrator instead of the wet hydration device with the related higher investment costs will be necessary

In order to optimise the process variant connected with a compensation of some of the above-mentioned disadvantages, further investigations are planned with the purpose to install an additional additive powder injection between boiler and evaporative cooler (schematic view in illustration 7).

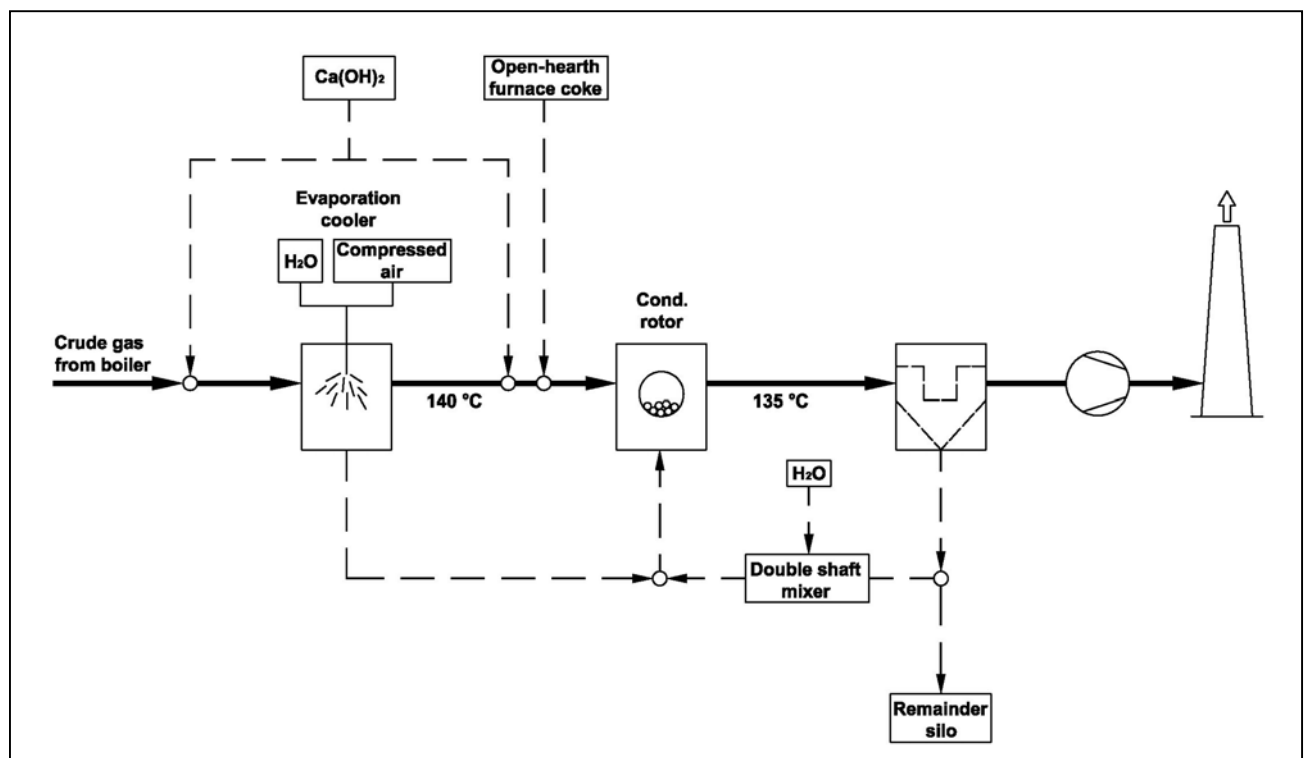


Illustration 7: Process variant: gas and particle conditioning with graded additive powder injection

2.3 Two-stage (conditioned) dry sorption

2.3.1 Preliminary remark

If the requirements on the separation are growing, e.g. with regard to continuously higher chlorine and/or sulphur contents in the fuel and/or regarding the requirement on emission limiting values e.g. according to 50% of the values of 17. BImSchV., the additive powder consumption of both presented variants will increase above average. For a solution of such applications, alternative sorption procedures have to be considered. From the author's point of view, a suitable process variant for this type of application is the two-stage dry sorption and/or two-stage conditioned dry sorption with additive powder guidance in counter-flow. Corresponding operation experiences gathered from this process technology are available at LÜHR FILTER since many years, i.a. also for thermal waste disposal plants.

2.3.2 Process description by means of examples, advantages and disadvantages

Illustration 8 shows an example for the gas cleaning downstream industrial waste incinerator. The plant has been designed as mere dry sorption. Due to a customer request, the utilisation of water for the conditioning had to be omitted. Therefore a gas - air heat exchanger has been installed upstream two-stage 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.

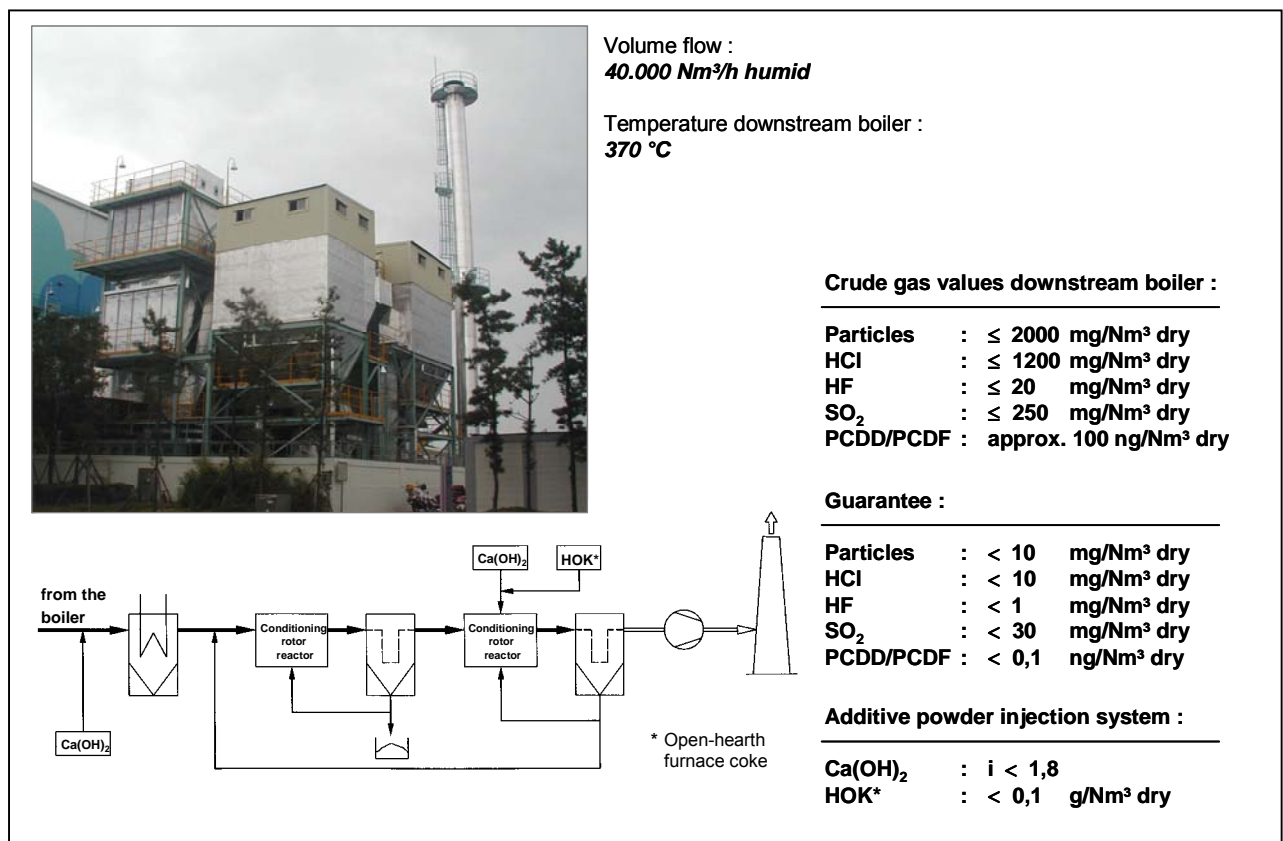


Illustration 8: Application example: industrial waste incinerator

The plant has been designed in two stages in order to

- optimise the additive powder efficiency
- grant the reliable separation of HCl and SO₂ peaks in the crude gas even if using a mere dry sorption
- grant the reliable reduction of the extremely high dioxin content downstream boiler to values < 0.1 ng/m³

The main advantage of this process technology is the additive powder guidance in counter-flow. Due to the pre-separation of acid crude gas components in the first filter stage and in the upstream installed heat exchanger, considerably higher stoichiometric factors than the resulting summarised stoichiometry will be achieved in the second fine cleaning stage, (illustration 9).

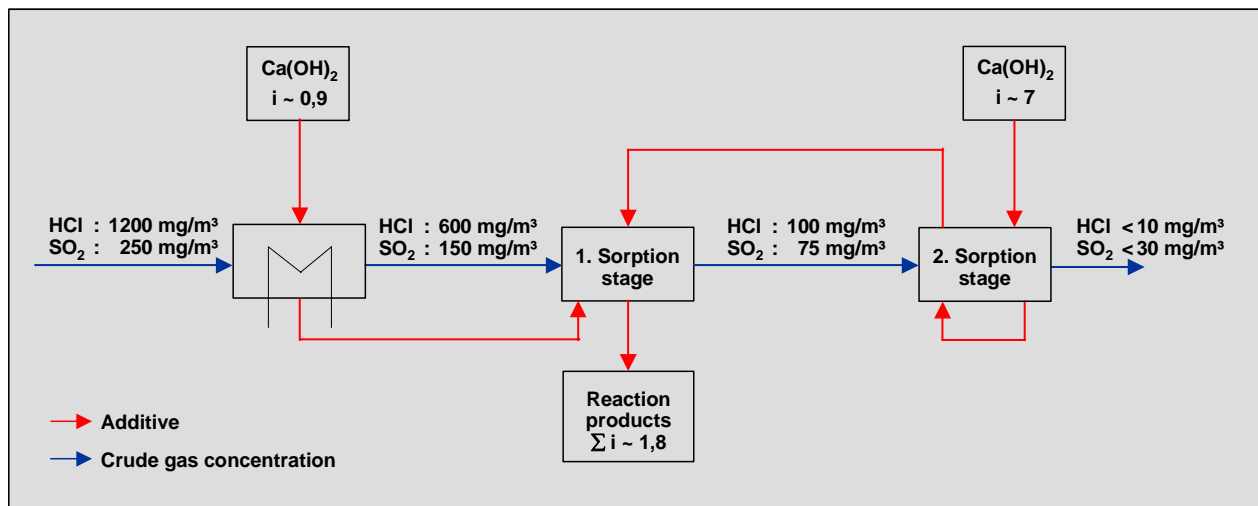


Illustration 9: Stoichiometry fine cleaning stage and summarised stoichiometry

The two-stage design of separation is not only valid for acid crude gas contents but also for all heavy metals as well as for dioxins / furans.

Fluctuations of crude gas contents within the gas downstream boiler will be compensated without increase in stoichiometry.

The disadvantage of the chosen procedure is the utilisation of two fabric filters, installed in series. The higher operating costs referred to the power consumption and filter fabric have to be taken into consideration when calculating the profitability. However, such type of procedure can be compared to e.g. the combination of spray dryer – fabric filter – two-stage scrubber.

A further example is the MVA in Hamelin. Illustration 10 shows a schematic view of the plant, already installed in 1993 and illustration 11 presents the achieved degrees of separation.

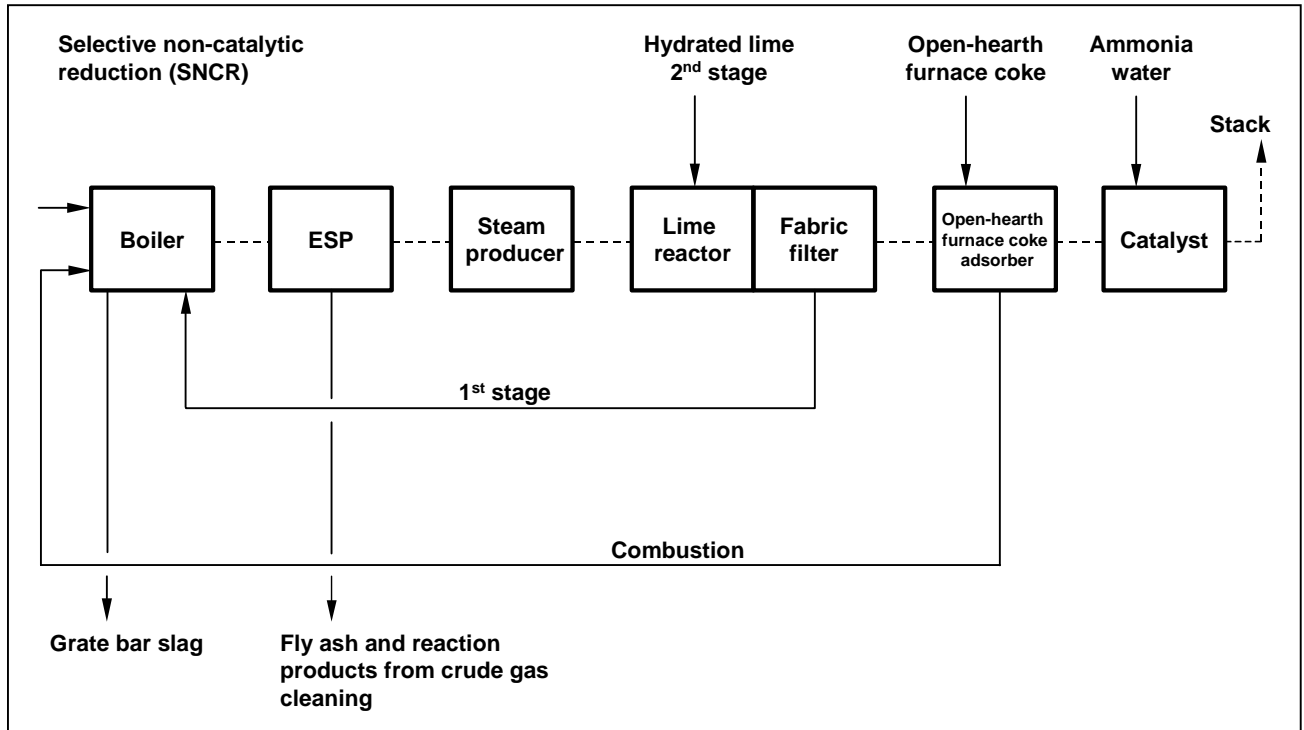


Illustration 10: Process scheme waste incinerator Hamelin

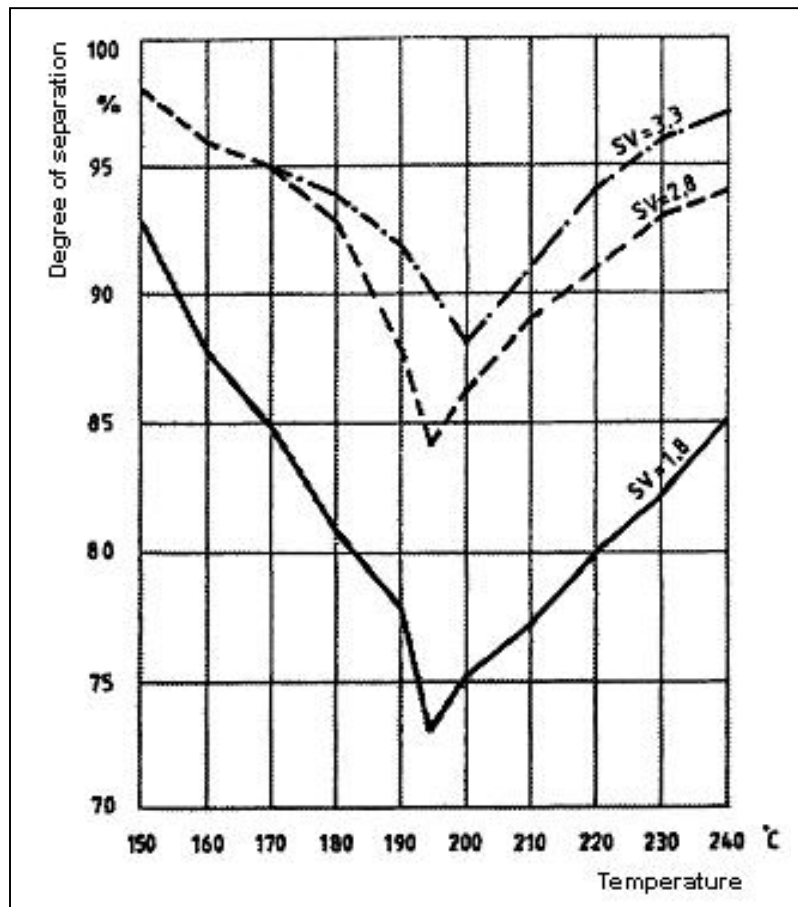
Examples for measured HCl- and SO₂-reductions in the individual process stages

	<i>HCl mg/m³</i>			<i>SO₂ mg/m³</i>		
	After product analysis	Individual measured values	Reduction single stage	After product analysis	Individual measured values	Reduction single stage
In boiler upstream stage1	approx. 950	800 - 1500		approx. 200	300 - 500	
Downstream stage 1 = upstream fabric filter	approx. 250		approx. 70 %	approx. 75	100 - 250	approx. 60 %
Downst. fabric filter = upstream open-hearth furnace coke	8	< - 10	> 95 %	approx. 5	10 - 30	approx. 90 %

Illustration 11: Degrees of separation for two-stage dry sorption

Nowadays we can surely do without the utilisation of a mobile bed adsorber but with regard to the dioxin separation, open-hearth furnace coke/AC has then to be added to the gas in powder form.

The special feature of this process example is the injection of the partly saturated additive powder from the second stage upstream economiser at approx. 300 – 350 °C. The HCl separation in the second stage with a gas temperature of approx. 140°C is supported by the high relative gas humidity and the extremely high stoichiometric factor and the first stage takes advantage of the HCl separation improved by means of the reaction supporting effect of heat (kinetics) (illustration 12).



Source: H. Mosch, ENERGIE SPEKTRUM, Dec. 1987

Illustration 12: Degree of HCl separation as function of temperature

A reduction in the heat transfer within economiser due to the additive powder injection had not been noticed.

3. Dry sorption process with utilisation of NaHCO_3

3.1 General structure, advantages and disadvantages

The dry sorption with NaHCO_3 competes with process technologies using Ca-containing additive powder qualities. The quite simple process technology of the basic variant is shown in illustration 14. The additive powder is injected into the gas flow upstream filter. In case of crude gas temperatures of $> 140^\circ\text{C}$, a thermal activation of sodium hydrogen carbonate will take place. The result is a high reactive sodium carbonate. Usually, based on a proper plant design, the requested emission limiting values can reliably be kept in continuous operation with an above average stoichiometric factor of 1.2 – 1.5.

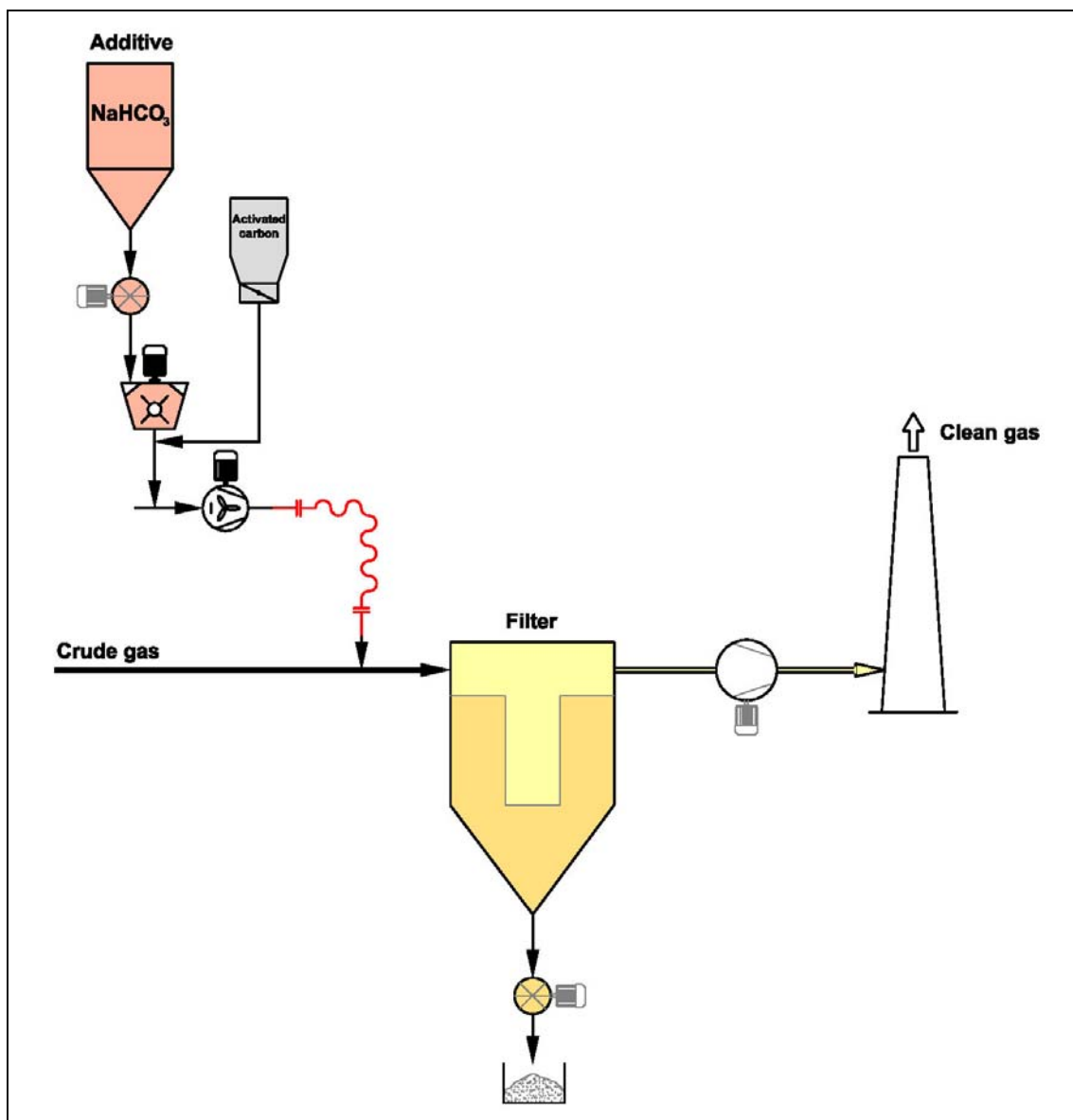


Illustration 14: Basic variant dry sorption with NaHCO_3

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 quantity (advantage in case of high disposal costs)
- lower hygroscopic nature of resulting salts

The disadvantages are:

- unfavourable mass ratio of additive powder to crude gas
- necessary pulverisation of additive powder prior to injection into the gas flow
- higher purchase costs of additive powder compared to Ca-containing additive powders
- low affinity against HF

3.2 Influencing figures with regard to the additive powder efficiency

3.2.1 Gas temperature and particle re-circulation

Illustration 15 shows an application example for a gas cleaning plant downstream domestic waste incinerator. Compared to the basic variant shown in illustration 14, this plant is additionally provided with an evaporative cooler for the adjustment of gas temperature as well as with a particle re-circulation. Within the scope of plant optimisation not only the gas temperature but also the re-circulation rate has been varied.

Illustration 16 demonstrates the influence of the gas temperature on the additive powder consumption. Over a period of 2 hours the temperature has been reduced by 20 Kelvin from 175°C to 155°C. The increase in the clean gas values especially for SO₂ as well as the increase in the additive powder consumption is clearly visible. A similar behaviour could be noticed at plants with and without particle re-circulation. In spite of a contact time of > 2 seconds of the gas and the additive powder particles upstream filter bags, the additive powder consumption can be reduced by means of multiple re-circulation of the particles separated within the filter into the gas flow upstream filter.

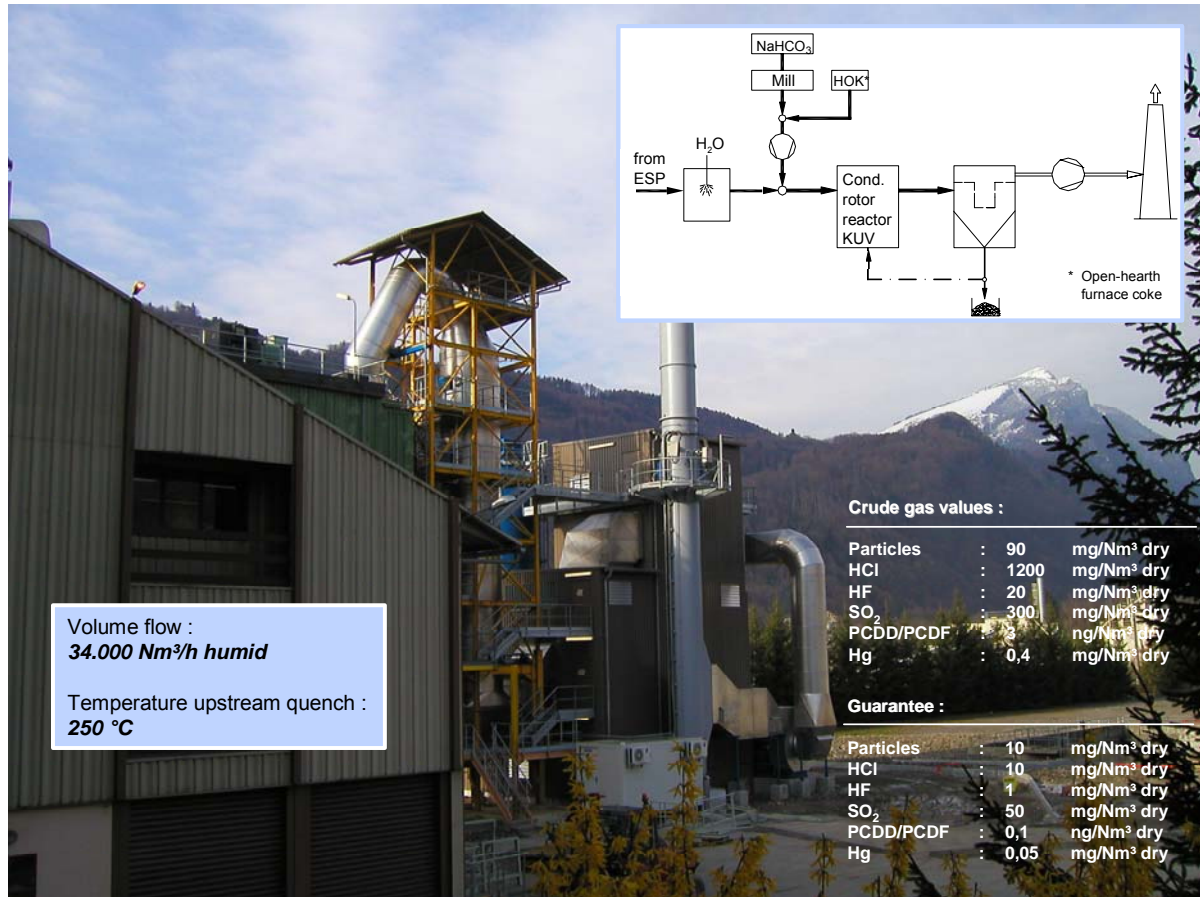


Illustration 15: Application example: Domestic waste incinerator

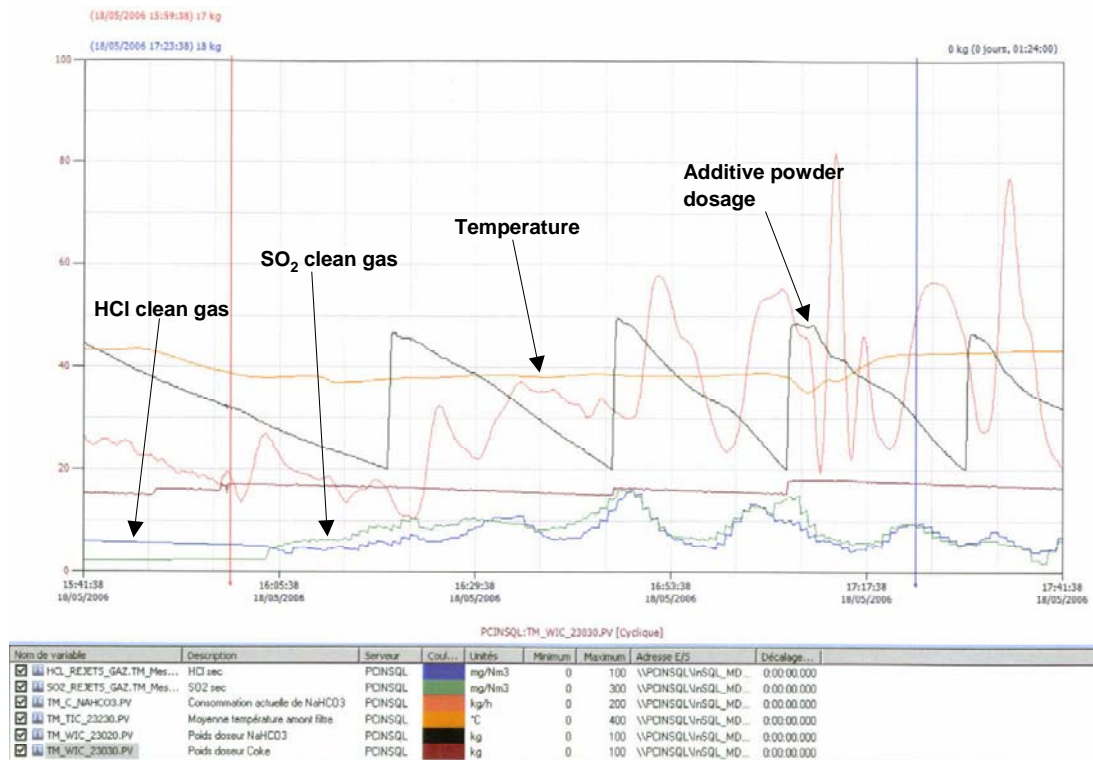


Illustration 16: Trend curves emission values, temperature and additive powder consumption

3.2.2 HF separation

Further investigations have been made with regard to the separation of HF. The result was a correlation between the clean gas content of SO₂ and HF (illustration 17). To grant the reliable observance of a clean gas value for HF of < 1 mg/m³, a SO₂ clean gas value of < approx. 25 mg/m³ will be necessary. A further increase in the additive powder consumption will be necessary if lower HF clean gas concentrations have to be achieved. In addition it may be remarked that the HF concentration in the gas prior to the additive powder injection was in the range of 5 mg/m³.

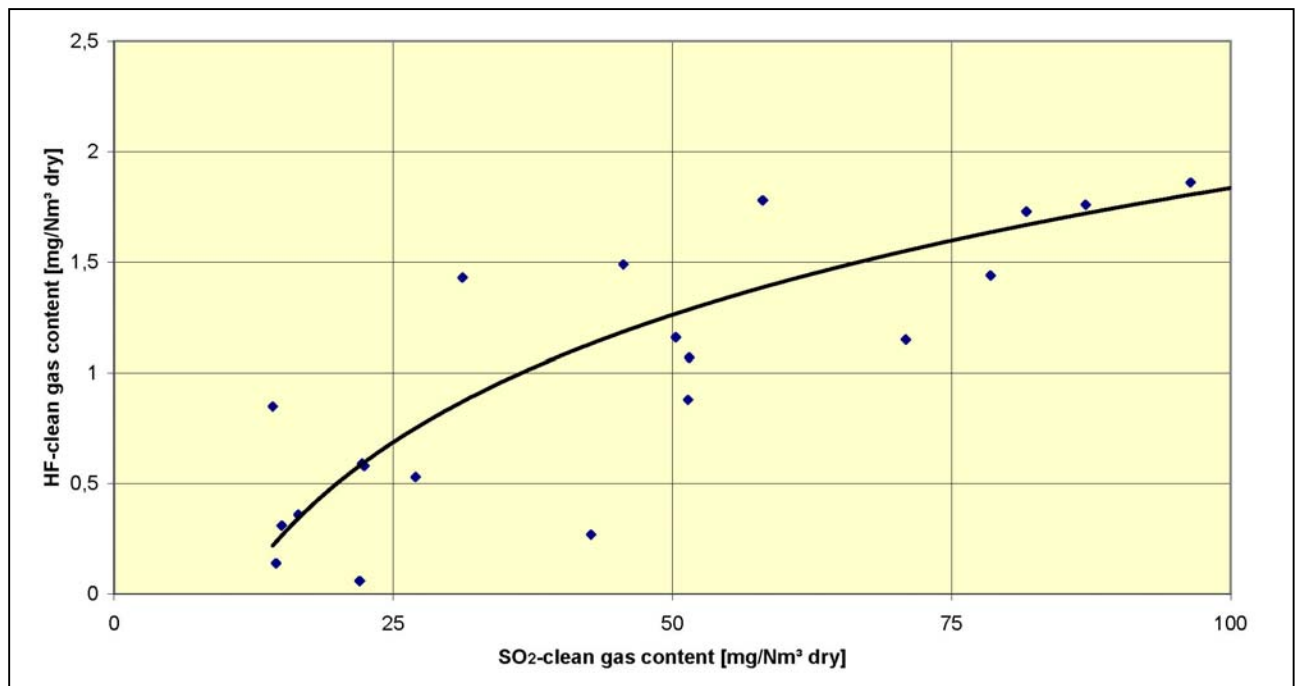


Illustration 17: Correlation HF - SO₂ clean gas values

4. Comparison of operating costs

The selection of the most suitable process technology is mainly influenced by the expected overall costs. In the following 2 examples are given for the estimation of the operating costs resulting from the additive powder consumption.

At first the example given in item 3.2 is considered. During the planning of plant and based on the costs specified by the plant operator for the procurement and disposal of additive powder, a comparative assessment between a dry sorption process with utilisation of NaHCO₃ and a conditioned dry sorption process with utilisation of Ca(OH)₂ has been made out. The results are shown in table 1.

Denomination	Dimension	Process technology	
		cond. dry sorption with hydrated lime	dry sorption with sodium bicarbonate
Volume flow	Nm ³ /h dry	24,0000	24,0000
HCl content	mg/Nm ³ dry	1,200	1,200
HF content	mg/Nm ³ dry	20	20
SO ₂ content	mg/Nm ³ dry	300	300
HCl load	kg/h	28.8	28.8
HF load	kg/h	0.5	0.5
SO ₂ load	kg/h	7.2	7.2
Absorption agent	-----	Ca(OH) ₂	NaHCO ₃
Necessary stoichiometry		2.00	1.25
Need for alkaline absorption agent	kg/h	77	109
Remainder quantity from additive injection	kg/h	123	85
Costs / Supply	-----		
Alkaline absorption agent	Unit price	EURO/to	100
	Need	to/a	616
	Costs	EURO/a	61,567
Remainders	Unit price	EURO/to	300
	Quantity	to/a	985
	Costs	EURO/a	295,521
SUM of considered costs	EURO/a	357,000	384,000

Tab 1: Operating costs from additive powder without open-hearth furnace coke/AC,
example 1

The costs resulting from the additive powder qualities are approx. in the same region for both process variants. Compared to the quality Ca(OH)₂ the purchase costs for NaHCO₃ are definitely higher but this will be compensated by the comparatively high specific disposal costs and the definitely lower remainder quantity as a result of the utilisation of NaHCO₃. Due to the advantages to be expected with regard to the power and water consumption as well as the lower investment costs when using NaHCO₃, the decision was made in favour of the dry sorption procedure with NaHCO₃.

A second example is shown in table 2. The main difference of this plant is the larger combustion output as well as more favourable specific disposal costs for the remainder discharged from the filter. This results in a clear advantage for the conditioned dry sorption process with Ca(OH)₂. Even if a higher power and water consumption has to be taken into account for this procedure, the resulting cost advantage justifies a higher investment. The operating costs can even be reduced when using CaO instead of Ca(OH)₂ with additional installation of a dry hydrator.

Denomination	Dimension	Process technology	
		cond. dry sorption with hydrated lime	dry sorption with sodium bicarbonate
Volume flow	Nm ³ /h dry	90,000	90,000
HCl content	mg/Nm ³ dry	1,600	1,600
HF content	mg/Nm ³ dry	15	15
SO ₂ content	mg/Nm ³ dry	800	800
HCl load	kg/h	144.0	144.0
HF load	kg/h	1.4	1.4
SO ₂ load	kg/h	72.0	72.0
Absorption agent	-----	Ca(OH) ₂	NaHCO ₃
Necessary stoichiometry		2.00	1.30
Need for alkaline absorption agent	kg/h	464	684
Remainder quantity from additive injection	kg/h	743	513
Costs / Supply	-----		
Alkaline absorption agent	Unit price	EURO/to	100
	Need	to/a	3,713
	Costs	EURO/a	371,343
Remainders	Unit price	EURO/to	90
	Quantity	to/a	5,941
	Costs	EURO/a	534,734
SUM of considered costs	EURO/a	906,000	1,355,000

Tab 2: Operating costs from additive powder without open-hearth furnace coke /AC, example 2

Two main influence factors for the selection of a process technology based on NaHCO₃ or Ca-containing additive powders are

- plant size
 - ⇒ increasing plant sizes entail advantages for process technologies using Ca-containing additive powders
- specific costs for remainders
 - ⇒ higher specific costs for the disposal entail advantages for the utilisation of NaHCO₃

5. Selection of process technology

The aforementioned explanations demonstrated that both the conditioned dry sorption procedures with utilisation of Ca-containing additive powder qualities and the dry sorption procedures based on NaHCO_3 are able to meet the today's requirements concerning the sorption of acid crude gas components. The current emission limiting values can reliably be kept in continuous operation. Furthermore, when injecting adequate additive powder qualities, the simultaneous reliable 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 separately. The criteria of choice for the assessment are:

- required degrees of separation (average values and max. values as well as peaks)
- emission limiting values
- investment costs
- operating costs such as additive powder purchase costs and disposal costs as well as power costs (current and compressed air)
- costs for maintenance and upkeep
- plant availability and reliability of operation
- part load behaviour
- flexibility with regard to changing crude gas values, emission limiting values and specific operating costs