First operation experiences after conversion of fume treatment plant line II MHKW Ludwigshafen from wet to conditioned dry

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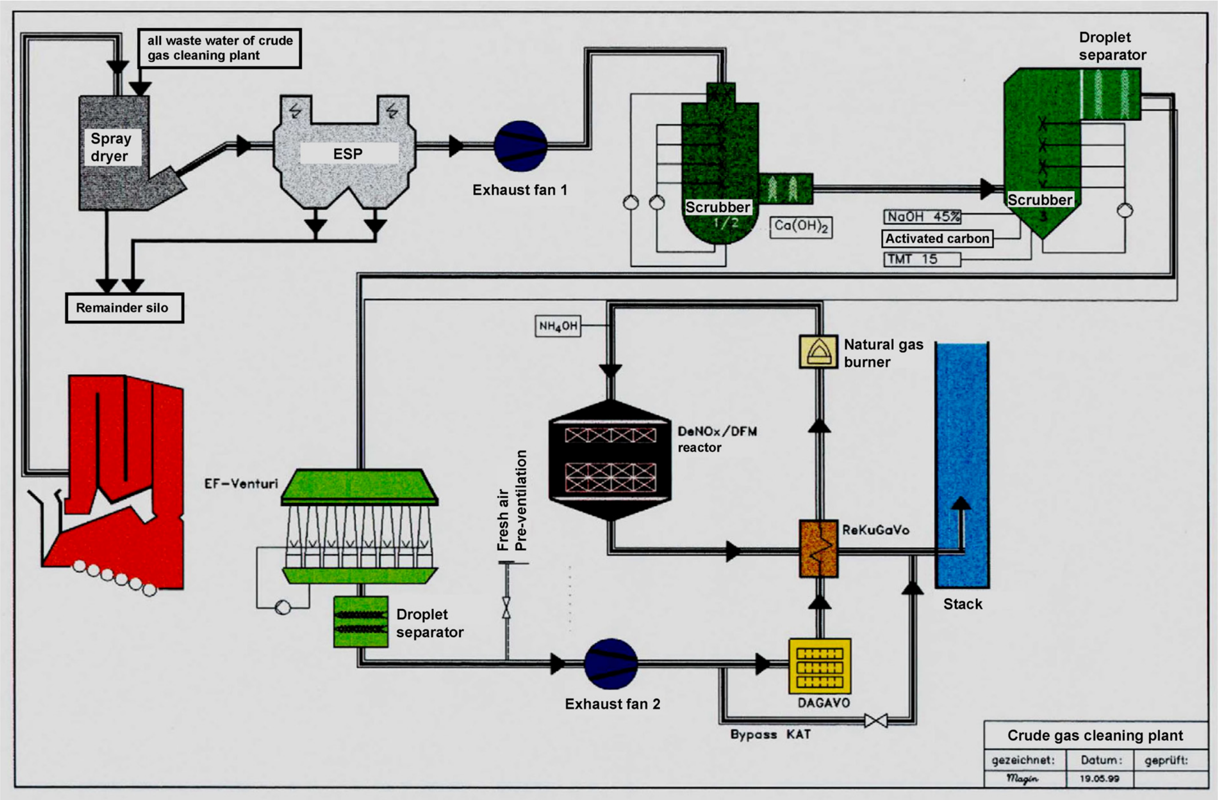
1. Purpose of conversion

Since 1967 the GML Abfallwirtschaftsgesellschaft mbH is running a waste heat generating station (MHKW) in Ludwigshafen. The plant management has been delegated to the Technische Werke Ludwigshafen (TWL).
The MHKW Ludwigshafen comprises three combustion lines with a max. throughput capacity of 12 t/h each and two downstream installed, up to the conversion wet working fume treatment plants (FTP). Prior to the conversion in 2004 the capacity of each of the two FTP has been designed for the take-over of the crude gases of one combustion line. The basic layout is shown in pic. 1. The main components are spray dryer, E-filter, two-stage scrubber, aerosol separator and SCR-plant.



pic. 1: Plant schematic of fume treatment line 2 or 3 of MHKW Ludwigshafen prior to conversion of line 2 [1]

In order to achieve the requested increase in the combustion capacity from 150.000 t/a to 180.000 t/a it had been necessary to modify at least one FTP such that a parallel operation of all three combustion lines could be achieved, with two boilers working in part load operation (max. 8 t/h each). The conversion included the replacement of the wet working fume treatment by a semi-dry working fume treatment procedure with fabric filter.

In October 2003, LÜHR FILTER was put in charge with the installation of the new FTP 2. The commissioning already took place 10 months later, in July 2004.

Relevant crude gas data and the granted emission limit values are given in table 1 and 2.

CRUDE GAS INLET	**UNIT**	**MIN**	**NOMINAL**	**MAX**
Volume flow boiler outlet	Nm³/h dry	38.000	49.000*)	75.000**)
Temperature at boiler outlet	°C	200	250	250
N_2	Vol. %	k. A.	69,4	k. A.
O_2	Vol. %	9,0	9,0	9,0
CO_2	Vol. %	k. A.	8,0	k. A.
Humidity	Vol. %	13,6	13,6	13,6
		DAV	**HAV**	**DESIGN**
Overall dust	mg/Nm³ dry	1.600	5.000	5.000
HCL	mg/Nm³ dry	1.000	2.000	2.000
HF	mg/Nm³ dry	15	30	30
SO_2	mg/Nm³ dry	400	600	600
NO_x	mg/Nm³ dry	350	500	500
Hg	mg/Nm³ dry	0,3	0,3	0,9
Cd + Tl	mg/Nm³ dry	1,0	3,0	3,0
Σ(Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V, Sn)	mg/Nm³ dry	20	50	50
Dioxin / Furan	ng TE/Nm³ dry	3,0	5,0	5,0

*) 65% load one boiler with a waste throughput of 10 t/h

**) 100% load of two boilers with a waste throughput of 8 t/h each

Tab.1: Crude gas data for the new fume treatment plant (all data regarding the concentration refer to 9 Vol. % O_2)

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

*) as average value over the sample taking period

1) hourly average value, may not be exceeded at any operating time

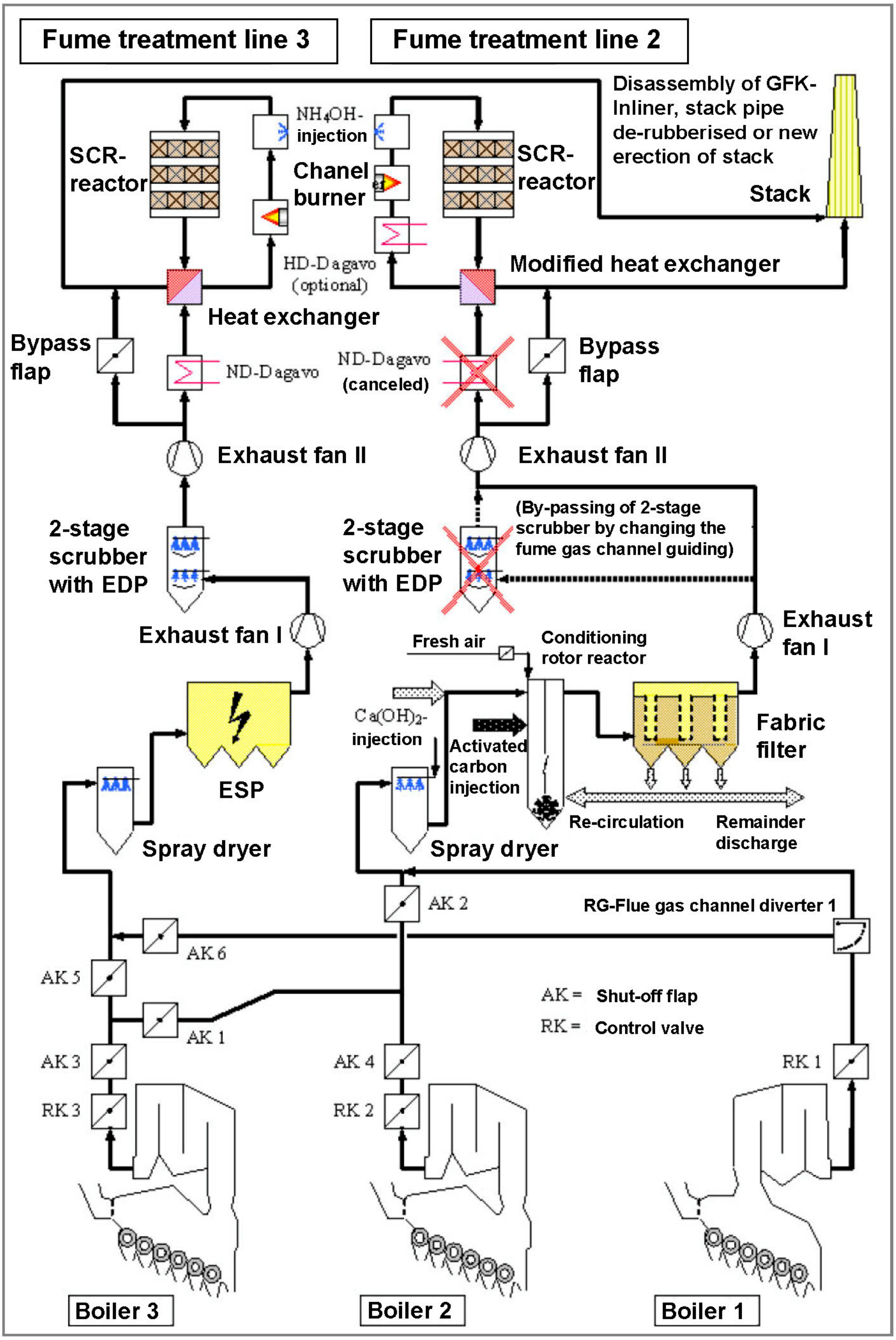
Tab.2: Granted emission limit values of the new FTP

2. Plant description

2.1 Overall plant

The interconnection of the three boiler plants with the old and the new FTP is shown in the simplified plant scheme in pic. 2.
Channel diverters, located downstream the three combustion lines, allow that each boiler can be connected to each FTP. A collective operation will also be possible.

Due to the fact that the SCR-plant disposes of sufficient design reserves and after discussion with the manufacturer of catalyst it was possible to reuse the SCR-plant up to a max. fume volume of 75.000 Nm^3/h dry (corresponds to approx. 2 x 8 t/h waste throughput).

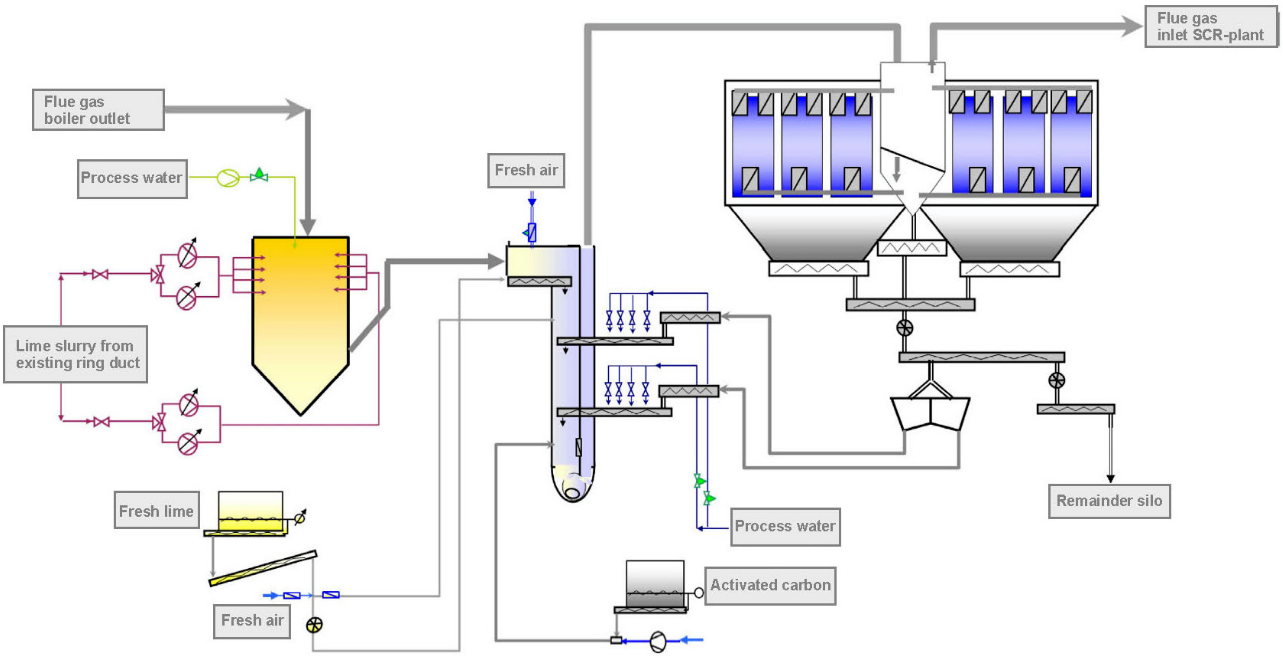


pic. 2: Plant schematic of FTP lines 2 and 3 of MHKW Ludwigshafen [1]

2.2 Combined procedure of semi-dry sorption with conditioned dry sorption

2.2.1 Process description

The new fume treatment is carried out by a combined procedure of semi-dry sorption with conditioned dry sorption by using the LÜHR Conditioning Rotor – Recycle Process (plant integrated particle re-circulation) and a downstream located LÜHR flat-bag filter (pic. 3).



pic. 3: Simplified process scheme of semi-dry sorption and/or dry sorption [1]

The spray absorber (first cleaning stage) is used for the crude gas conditioning (cooling / wetting) and for the spraying of lime slurry. In order to grant the highest possible availability, the spraying of lime slurry is carried out by two separately working supply and spraying units. A water lance which is able to replace the cooling capacity of a lime slurry lance group is installed in addition. The lime slurry is taken from the existing supply system or ring duct. For the compensation of fluctuating lime slurry concentrations in the already long working system, a measurement of density is applied in order to determine the $Ca(OH)_2$ mass flow in connection with a volume measurement.

The system has been designed in such way that the FTP can also be used as pure conditioned dry sorption plant by alternate use of process water instead of lime slurry.

In the second cleaning stage $Ca(OH)_2$ and activated carbon are introduced into the inlet shaft of the reaction chamber upstream fabric filter by means of weight-controlled injection via dosing screws. The conditioning rotor in the lower part of the reaction chamber elbow allows the deposit-free introduction and distribution of the additive powder as well as of the re-circulated reaction product.

In addition to the spray absorber, the adjacent vertical reactor shaft and crude gas inlet area forms a further contact and reaction zone in the flow stream for the physical and chemical conversion between the gaseous crude gas components and the additive powder at high particle density and offers to the crude gas a residence time of 1 – 2 sec.
The re-circulation or recycling of a defined portion of the reaction product separated in the fabric filter is due to several reasons. On one hand the reaction product still contains reactive and uncharged components and on the other hand the calcium chloride, presenting a bigger part of the reaction product, is necessary for an effective separation of SO_2.
The reaction product discharged from the filter hoppers is transported to an intermediate hopper by means of screw conveyors. One screw, serving as skimming device for the intermediate hopper, transports the excessive material to the remainder discharge point. The portion of particles introduced into the intermediate hopper is handed over to a double shaft mixer to which a part of the process water necessary for the crude gas cooling is added. The particle flow into the mixer is controlled by means of a visually working measuring instrument. The wetting of the recycled reaction products causes an increase in the reactivity of the additive particles due to the influence of water as well as an increase in the water steam content on the surface of the additive particles with the positive effect that the sorption efficiency is considerably improved. In order to grant the highest possible availability even in this area, the humidifying mixers are realised in redundant execution.

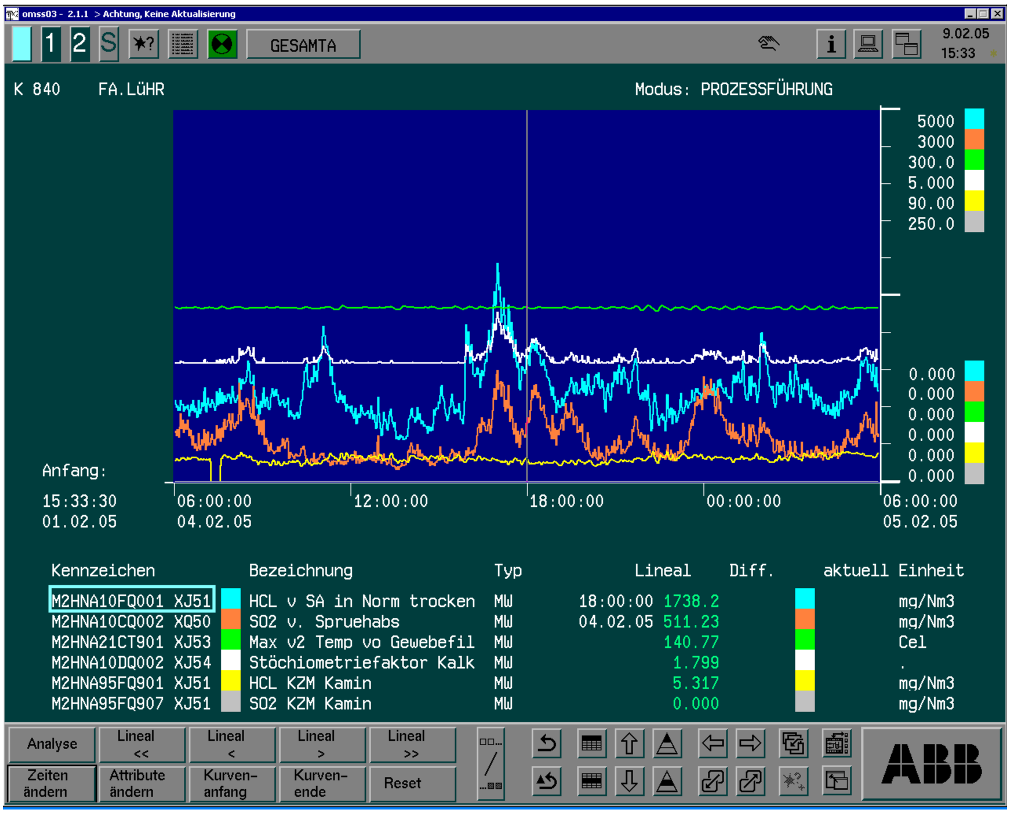
The fabric filter is executed as 6-chamber filter and is provided with vertically installed PTFE flat-bags. The cleaning of the filter bags is carried out by an „Online Pulse Jet Procedure“. Pic. 4 shows a part of the spray absorber as well as the filter and reactor building.

pic. 4: Spray absorber head and filter / reactor building

2.2.2 Control concept for additive powder injection

The injection of the calcium containing additive powder depends on the given stoichiometric factor. The necessary additive powder mass flow according to the adjusted stoichiometric factor is calculated on the basis of the volume flow and the HCl and SO_2 values which are continuously measured in the crude gas upstream spray absorber and the volume flow. In addition to this and in case of increased crude gas values, the stoichiometric factor is automatically increased by means of a superposed adjustment curve. The control of the emission values, combined with an increase in the injection quantity in case the clean gas limit values for HCl and SO_2 are reached, ensures that the emission values (DAV and HAV) will by no means be exceeded.

The control behaviour over a period of 24 hours can clearly be observerd by means of the trend curves shown in pic. 5.



K 840 FA.LüHR

Modus: PROZESSFÜHRUNG

Anfang:
15:33:30
01.02.05

06:00:00
04.02.05

Kennzeichen		Bezeichnung	Typ	Lineal	Diff.	aktuell	Einheit
M2HNA10FQ001 XJ51	🟦	HCL v SA in Norm trocken	MW	18:00:00 1738.2		🟦	mg/Nm3
M2HNA10CQ002 XQ50	🟧	SO2 v. Spruehabs	MW	04.02.05 511.23		🟧	mg/Nm3
M2HNA21CT901 XJ53	🟩	Max v2 Temp vo Gewebefil	MW	140.77		🟩	Cel
M2HNA10DQ002 XJ54	⬜	Stöchiometriefaktor Kalk	MW	1.799		⬜	.
M2HNA95FQ901 XJ51	🟨	HCL KZM Kamin	MW	5.317		🟨	mg/Nm3
M2HNA95FQ907 XJ51	▨	SO2 KZM Kamin	MW	0.000		▨	mg/Nm3

pic. 5: Trend curves for crude / clean gas values, stoichiometry as well as filter temperature

The distribution of the mass flow on the two injection points spray absorber and reaction chamber is pre-selected in the process control system.

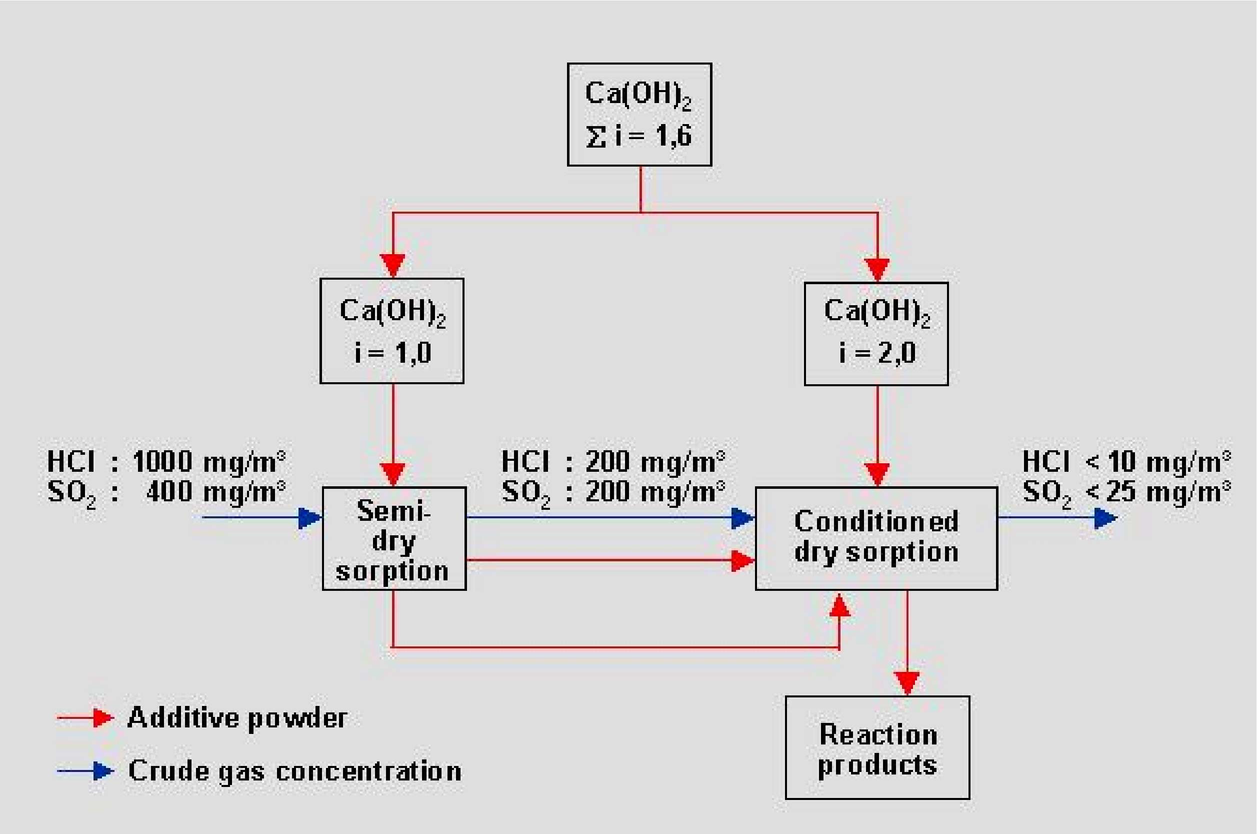
The injection of the activated carbon is effected in accordance with the number of connected boilers.

3. Advantageous features of the procedure

Compared to other dry or semi-dry procedures on the basis of Ca-containing additive powders, the selected process offers some advantageous features. In the following some of them are discussed by means of operation results.

3.1 Graded additive powder injection

The example shown in pic. 5 presents the advantages of a graded additive powder injection. In the first stage with low stoichiometry related to the crude gas input a large part of the HCl (80%) and approx. half of the SO_2 content are separated. Related to the crude gas contents to be expected after the first stage and compared to the summarised stoichiometry, a considerably higher stoichiometric injection quantity as fresh additive powder will be available for the fine cleaning in the second stage.



pic. 6: Distribution of stoichiometric factor

The degrees of separation assumed in the example above have been determined at a domestic waste incinerator in Germany, which is equipped with a continuously working measuring instrument for HCl and SO_2 installed up- and downstream spray absorber.

3.2 Variation limits of crude gas contents

The overall system is comparatively insensitive with regard to strongly fluctuating crude gas components in the flue gas. Assuming a degree of separation of 80% for the first stage (as shown in pic. 6) for an HCl input value of e.g. 3.000 mg/m³, the input value upstream second stage will be reduced to 600 mg/m³.

The crude gas values for HCl and SO_2 at the plant in Ludwigshafen fluctuate in a comparatively wide range. The 1-hour-average values for HCl lie in a range from 500 up to 3.000 mg/Nm^3 dry and for SO_2 from 100 up to 1.000 mg/Nm^3 dry whereas peaks can exceed these values considerably. The crude gas values in the stated range are reliably controlled by means of the stoichiometric control, described under item 2.2.2. The emission values can be observed without manual intervention in the process control system.

3.3 Availability / redundancies

The highest sorption efficiency is achieved during operation of both sorption stages. However, even in case of a failure of part systems, the emission values can be observed for all operation conditions.

- Failure of lime slurry
  → system evaporative cooler, conditioned dry sorption
- Failure of particle re-circulation
  → system spray absorption and $Ca(OH)_2$ injection upstream fabric filter

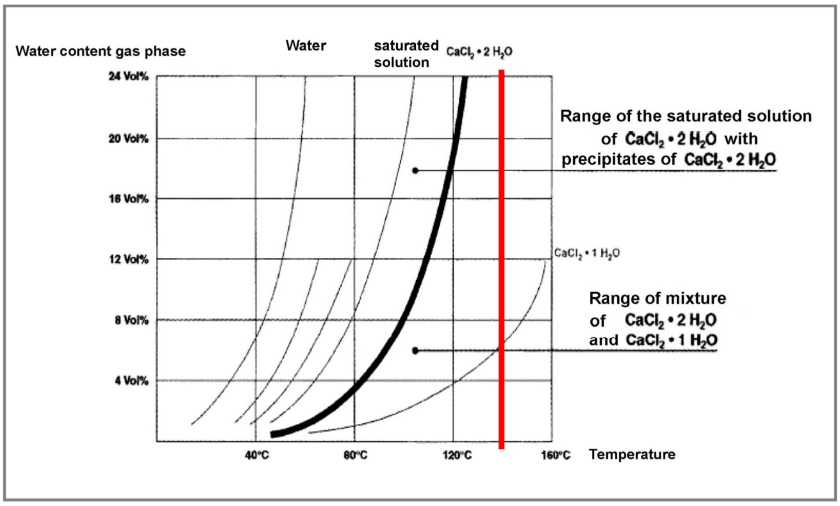
Evidence of the observance of the emission limiting values during plant operation with only one sorption stage could be provided during commissioning of the plant.

In order to ensure a high plant availability of this plant, the following components have been realised in redundant execution:

- Two lime slurry lance groups (lime slurry supply and spraying)
- One water lance as replacement for one lime slurry lance group
- Two conveying pumps per lime slurry station
- Two double shaft mixers for conditioned dry sorption
- Two $Ca(OH)_2$ conveying devices to the dosing station
- Filter in 6 - chamber execution

3.4 Constant filter inlet temperature with sufficient safety distance to the critical temperature

Many procedures require a close approach to the dissociation pressure curve of $CaCl_2$ x $2H_2O$ in order to achieve a sufficient additive powder efficiency. Due to the hygroscopic features of calcium chloride, the reactivity will then be improved especially with regard to the SO_2 separation.
The curve progression is shown in pic. 7.



pic. 7: Extract of phase diagram $CaCl_2$ / H_2O [2]

This operation mode may provoke the risk that during real plant operation an undershooting of this curve due to partial temperature depressions will lead to a wetting of the reaction product. That means that the $CaCl_2 \times 2H_2O$ will be surrounded by free humidity, thus leading to adhesion and deposits in the product charged plant components. The deposits can often only be removed by means of mining measures.

The procedure selected in this case avoids this risk. Due to a well HCl pre-separation in the spray absorber, the FTP can be driven at filter temperatures which are reliably above the critical temperature. The conditioned particle re-circulation grants the SO_2 separation even in case of a higher temperature. The plant in Ludwigshafen is driven at a constant filter inlet temperature of 140°C (see pic. 5). In control mode, the SO_2 clean gas value lies definitely below the guarantee value.
In case of a low emission value (ACTUAL emission value / emission limit value) the filter inlet temperature is automatically increased by up to 5 Kelvin.

4. Adjustment works during commissioning

Apart from the usual problems and adjustments during commissioning of such type of plant, basically two larger problems appeared.

4.1 Blockages near the particle re-circulation

In the intermediate hopper for the re-circulated material, located above the humidifying mixer, a bridge forming and blockages could be detected. The reason was an unsuitable hopper geometry, combined with rough wall surfaces.
The hopper has been replaced by a new one with the following constructional features:

- Inclination of walls ≤ 15°C (preferably negative angles)
- Lining of hopper walls with PTFE - plates
- Discharge of hopper by means of largely dimensioned double screws.

In addition a visually working measuring instrument has been installed in the down-shaft between the dosing screw and the humidifying mixer, serving as control device for the material flow. After installation of the modified intermediate hopper no further problems near the particle re-circulation occurred.

4.2 Lime slurry pump

After extraction from the ring duct the lime slurry is transported to the nozzles of the spray absorber by means of redundant displacement pumps. The pumps installed during commissioning were extremely sensitive to different fluid temperatures. Temperature fluctuations led to a constantly increasing, irreversible reduction in the conveying capacity. The problem was permanently solved by replacing the pumps by pumps of another type. For more than two months the new pumps have now been working without any power loss.

5. Operation experiences

5.1 Lime slurry system

In regular intervals the lime slurry ducts are automatically cleaned be formic acid. Due to this, the maintenance works for this plant area are reduced to a mechanical control of nozzles in the spray absorber. These controls are carried out once a week. Wear of nozzles could not be detected even after six months of operation.

5.2 Additive powder consumption

5.2.1 $Ca(OH)_2$ / CaO

After variation of the different adjustment parameters the plant is now driven as follows:

→ The temperature upstream filter is adjusted to 140°C. This temperature offers a sufficient distance to the critical temperature and also good reaction conditions. In case of clean gas values below the limiting values, the temperature is automatically increased by up to 5 Kelvin.

→ The distribution of the additive powder injection into the spray absorber and the conditioning rotor reactor is effected at the ratio of 50% : 50%.
The $Ca(OH)_2$ concentration in the lime slurry is limited to approx. 12%. The selected injection ratio does also cover crude gas peaks without variation of the distribution.

→ By means of automatic adjustment of the filter cleaning cycle and the particle recycling rate it is granted that the residence time of the additive particles in the system will nearly be constant.
In spite of a low filter differential pressure (< 8 mbar) the chosen cycle time is comparatively short. In case of a longer cleaning cycle and thus longer residence times of the additive powder in a dry condition and low HCl- and SO_2 contents, the $Ca(OH)_2$ will increasingly react with CO_2, i.e. the carbonate formation will increase and the reactivity of the additive powder will decrease.

→ The base value for the stoichiometric control is adjusted to 1,6 whereas in case of increased crude gas values (as described under item 2.2.2), the stoichiometric factor will automatically be re-adjusted by means of a superposed adjustment curve.

All emission limit values are reliably observed in continuous operation by means of the above-mentioned adjustment parameters. Pic. 8 shows the adjustment values as well as the crude and clean gas values for HCl and SO_2 by means of a print out of the process control system.

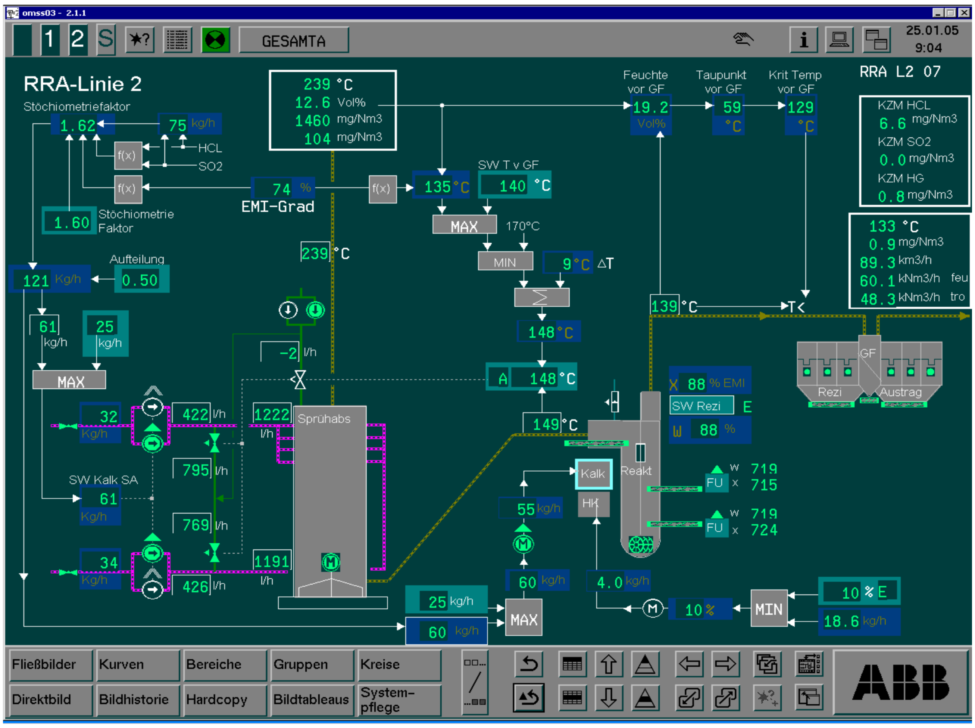


Abb. 8: Adjustment and control scheme (process control system)

In order to control and to confirm an approximately constant additive powder efficiency, the shift staff will carry out a daily chemical control of the product discharged from the filter. The control serves for the determination of the $Ca(OH)_2$, $CaCO_3$ and Cl^- concentration in the material. Pic. 9 shows the measuring results over a measuring period of ten days. In addition it shows the stoichiometric factor, calculated from the values as well as the average value for all components during these ten days.

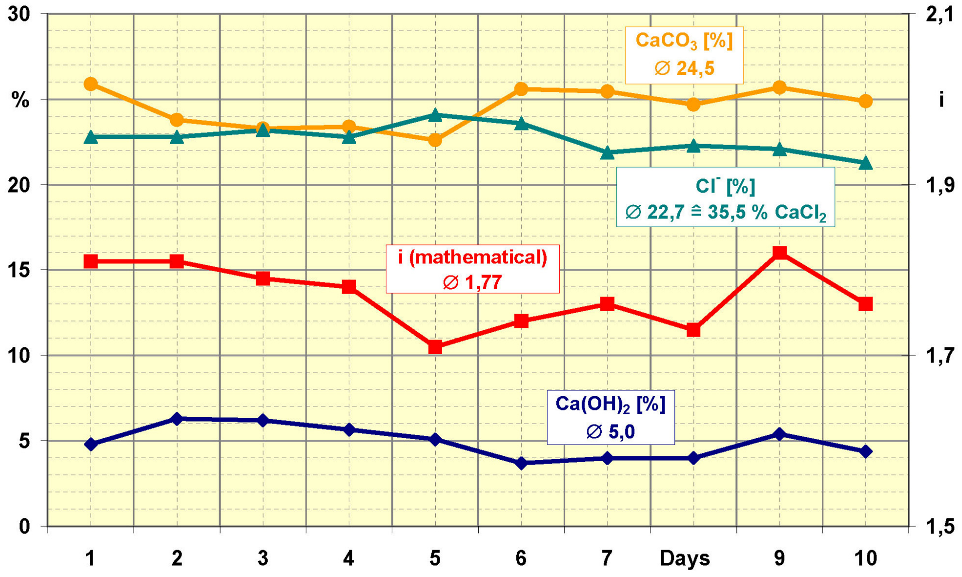


Abb. 9: Graphic presentation of remainder analysis

The quality of the used lime slurry has an essential influence on the additive powder consumption. The reactivity of the CaO is among others given by the kind of combustion procedure during making of this type of additive powder. A measuring method for the evaluation of reactivity is the determination of the time t_{60} (EN459-2). When applying this procedure, a defined quantity of CaO is added to a defined quantity of water at 20°C. While constantly stirring, the time until reaching a temperature of 60°C is determined. The shorter this time, the more reactive is the slaked $Ca(OH)_2$. Table 3 shows the remainder composition of two CaO qualities with different reactivity. The CaO quality with the lower time t_{60} clearly shows the better additive powder efficiency. In this case the $CaCO_3$ content is definitely lower. In addition the table shows the mathematically resulting stoichiometric factors.

	CaO t_{60} = 5 – 10 min	**CaO t_{60} = 3 – 5 min**
Overall Ca	29,70 %	28,40 %
$CaSO_3$	4,88 %	3,65 %
$CaSO_4$	7,44 %	7,40 %
$CaCO_3$	31,20 %	22,70 %
$CaCl_2$ (wl)	28,20 %	32,40 %
CaF_2	0,55 %	0,58 %
$Ca(OH)_2$ ASTM	6,72 %	5,33 %
stoichiometry (mathematical)	2,13	1,78

Tab. 3: Remainder analysis for different CaO qualities

5.2.2 Activated carbon

Activated carbon in commercially used dosing quantities is used as additive powder for the separation of Hg and Hg-compounds and PCDD/-F. The continuously measured Hg-clean gas values are < 10 µg/Nm^3 dry.

The results of a PCDD/-F measurement downstream fabric filter executed in November 2004, show a TE value of < 0,001 ng/Nm^3 dry.

Due to the extremely low emission levels of Hg and PCDD/F, the dosing concentration is gradually reduced after agreement with the operator and observance of the continuously measured Hg clean gas values.

6. Summary

The first operation experiences gathered from the before-described fume treatment plant confirm its potential and reliability. All emission values can reliably be maintained in continuous operation even in case of strongly fluctuating crude gas values. The achieved stoichiometry totals to a value definitely < 2. All start-up and shutdown procedures as well as boiler change-overs over the new FTP had been successful. A by-pass is not existing. The two-stage execution additionally offers a very well plant availability.

An optimisation potential is available by means of a further reduction in the additive powder consumption.

Literature:

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