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Removal of Particles and Acid Gases (SO₂ or HCl) with a Ceramic Filter by Addition of Dry Sorbents

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NaHCO₃, Ca(OH)₂

Introduction

The utilization of biomass as renewable energy source for decentralized production of thermal/electrical energy is growing. It currently does not place emphasis on new gas cleaning technology because available emission control methods suffice for the combustion of clean forestry residues such as saw dust or wood chips. This changes however with other types of feedstocks. Utilization of clean straw will raise e.g. the chlorine content in the flue gas by a factor of up to 100, and the addition of contaminated recycled wood, sludge or other waste would add further contaminants including metals, sulfur or chlorine.

In order to avoid a complex sequence of selective process steps for removing component-by-component particles, acid gases, NO_x, heavy metals etc., an integrated dry gas cleaning concept could offer a low-cost solution. For example, the potential of conventional particle filtration technology includes both very low particulate emissions, variable operating temperatures, and utilization of the filtration unit as a chemical reactor for dry removal of gaseous components. Removal of gaseous sulfur and chlorine species by addition of dry sorbent materials such as NaHCO₃ or Ca(OH)₂ and catalytic reduction of NO_x with NH₃ are examples. The combined dry removal of particulate and gaseous compounds in a single step in a filter unit appear to be an attractive engineering solution for small-scale combustion units operating on biomass or biomass-coal fuels. Not well understood in this context are overall aspects of system performance, such as optimum operating conditions, and stability of the filtration process with added sorbents and chemical reactions ongoing on the particles.

Objectives and Approach

The present investigation intends to add to the fundamental process design know-how for dry flue gas cleaning, especially with respect to process flexibility, in cases where variations in the type of fuel and thus in concentration of contaminants in the flue gas require optimization of operating conditions. In particular, temperature effects of the physical and chemical processes occurring simultaneously in the gas-particle dispersion and in the filter cake/filter medium are investigated in order to improve the predictive capabilities for identifying optimum operating conditions.

Sodium bicarbonate (NaHCO_3) and calcium hydroxide (Ca(OH)_2) are known as efficient sorbents for neutralizing acid flue gas components such as HCl , HF , and SO_2 . According to their physical properties (e.g. porosity, pore size) and chemical behavior (e.g. thermal decomposition, reactivity for gas-solid reactions), optimum conditions for their application vary widely.

The results presented concentrate on the development of quantitative data for filtration stability and overall removal efficiency as affected by operating temperature. Experiments were performed in a small pilot unit with a ceramic filter disk of the type Dia-Schumalith 10-20 (Fig. 1, described in more detail in Hemmer 2002 and Hemmer et al. 1999), using model flue gases containing SO_2 and HCl , flyash from wood bark combustion, and NaHCO_3 as well as Ca(OH)_2 as sorbent material (particle size d_{50}/d_{84} : 35/192 μm , and 3.5/16, respectively). The pilot unit consists of an entrained flow reactor (gas duct) representing the raw gas volume of a filter house and the filter disk with a filter cake, operating continuously, simulating filter cake build-up and cleaning of the filter medium by jet pulse. Temperatures varied from 200 to 600°C, sorbent stoichiometric ratios from zero to 2, inlet concentrations were on the order of 500 to 700 mg/m^3 , water vapor contents ranged from zero to 20 vol%. The experimental program with NaHCO_3 is listed in Table 1. In addition, model calculations were carried out based on own and published experimental results that estimate residence time and temperature effects on removal efficiencies.

Results

Filtration behavior of sorbents and a flyash from wood bark combustion was investigated in three different experimental set-ups: in a small filter house using ceramic filter candles, in the small pilot unit with a ceramic disk, simulating conditions in a real filter house, and in a conventional high temperature dilatometer. As an example, Figure 2 shows the results for NaHCO_3 and bark ash, both in pure form and in two different mixtures (for details see Hemmer 2002). Critical upper temperature limits for these materials lie in the range 300 to 400 °C, although at higher temperatures, operational windows for stable filtration can be found again (which is not shown in Figure 2). Above the critical temperatures shown in Figure 2, filtration (i.e. pressure drop) cycles are not stable in the long run.

As for absorption of SO_2 and HCl with NaHCO_3 and Ca(OH)_2 as sorbents (together with bark ash), Figures 3 to 5 present a selection of experimental results. Figure 3 shows results from a filtration experiment for the combined removal of particles and gaseous pollutants. Bark ash was added to the model gas air, SO_2 as pollutant gas (500 mg/m^3) and NaHCO_3 as sorbent (excess factor $\alpha_{\text{sorb}} = 2$), temperature was 200 °C. In these experiments, the operating behavior of the combined filtration unit is characterized by a low ratio of the surface areas of the filter medium

and all internal surfaces of the unit (gas duct etc.). As a consequence, long operating times are required at some conditions (e.g. at higher temperatures) to achieve stable steady state operation.

The upper part of Figure 3 presents a time period of the experiment by means of the measured SO₂ clean gas concentration behind the filter element versus filtration time. Addition of the pollutant gas was started before feeding any kind of dust particles. After a characteristic time, the inlet concentration of SO₂ was reached in the gas outlet, then addition of the ash/sorbent mixture and thus the normal filtration process was started. After 38 cycles, dust feeding was stopped (ash and sorbent off), but the pollutant gas injection was continued until the maximum SO₂ concentration was reached again. The bottom part of Figure 3 shows a period of time during the normal filtration process. The curve of the SO₂ clean gas concentration follows the curve of the pressure drop. This indicates that although a large portion of SO₂ is absorbed during the residence time in the gas duct (entrained flow reactor), some part of the SO₂ is absorbed in the filter cake, which operates as a fixed bed reactor. The minimum of the SO₂ concentration during each cycle follows the maximum in the pressure drop with a constant delay of about 120 seconds, resulting from the characteristic residence time (before reaching the gas analysis system).

For determining SO₂ or HCl conversion, respectively, average concentration values over a time period of stable filtration are used. The resulting average conversion values correspond to the data points in Figures 4 and 5. The bars are related to the minimum and maximum conversion values during filter cake build-up and cleaning of the filter medium. The hatched area at temperatures above 400 °C indicates the unstable filtration behavior with the kinds of particles used in these experiments.

Measured SO₂ conversion with a sorbent excess ratio of 2.0 exhibits values of about 90 % at 200 °C, whereas at 300 and 400 °C, the removal efficiency is close to 100 % with NaHCO₃ as sorbent. With a reduced excess ratio (0.9), the efficiencies were only 45 % at 200 °C, 55 % at 300 °C and close to 100 % at 400 °C. The latter value indicates that bark ash also contributes to the removal of SO₂ in these experiments. Therefore, the behavior of pure bark ash was investigated in a separate experiment. Here, the removal efficiency is close to 10 % at 200 °C, 15 % at 300 °C and again close to 100 % at 400 °C. The latter can be contributed to the large amounts of bark ash present with a relatively high content of available Calcium in the ash. The formal stoichiometric ratio of the bark ash Calcium available for SO₂ is about 2.6. However, according to the results found, the Calcium in the bark ash needs high temperatures for being active as a sorbent.

The experiments with Ca(OH)₂ as sorbent show lower removal efficiency compared to the experiments with NaHCO₃ as sorbent. At 400 °C, one can observe a nearly complete SO₂ removal, which again is partly due to the content of additional Calcium in the bark ash. Further experiments show a negative effect of CO₂ (as it is present in flue gases from combustion) on removal efficiencies with Ca(OH)₂ as sorbent, possibly due to competing CO₂ sorption effects.

Figure 5 gives a comparison of SO₂ and HCl conversion as affected by temperature. In addition, the effect of water vapor on SO₂ removal efficiency can be seen. The empty data points correspond to the results with $\alpha = 0.9$ and NaHCO₃ as sorbent, as shown in Figure 4. An increasing amount of water vapor present in the model gas (up to 20 vol%) leads to a slightly

higher removal efficiency for SO₂. In addition, the removal efficiency values for HCl are significantly higher than for SO₂.

Based on the experimental results from the combined filtration unit, a simple kinetic model was developed for absorption of SO₂ with NaHCO₃ and Ca(OH)₂ as sorbents in an entrained flow reactor. In the case of NaHCO₃, this model includes the consecutive reactions of (1) activation (leading to a porous, high activity Na₂CO₃ sorbent), (2) sorption of SO₂, (3) deactivation of active Na₂CO₃ sorbent, and (4) absorption of SO₂ with deactivated Na₂CO₃ species (Figure 6). In the present case, only the reactions in the entrained flow part of the reactor were considered, because due to the long residence times (30 s), high SO₂-conversion was achieved also directly after clean-up of the filter medium (Figure 3). The model assumes pseudo-homogeneous reactions, steady-state conditions, simple first- or second-order rate equations, kinetic constants for r1 from Hu et al. (1986). Rate constants for r2 were determined from the own experiments, reactions r3 and r4 can be considered not to be significant for the conditions of an entrained flow reactor. In the case of Ca(OH)₂ as sorbent, sorption reaction was modeled only as one reaction, and reaction of Ca in the bark ash applied was treated in the same way.

Validation of the model was done with own experimental data (τ gas 30s). The validated model then can be used for case studies. An example is given in Figure 7, where the situation in an entrained flow absorption reactor is shown. In technical applications, this entrained flow reactor is usually followed by a gas-particle filter, where additional sorption reactions occur in the gas duct, in the inlet gas volume of the filter house and in the filter cake. SO₂ conversion and available molar fraction of activated Na₂CO₃ values as calculated with the model are shown for two temperatures. Curves for activated Na₂CO₃ fraction reflect the typical behavior of an intermediate product. Very high SO₂ conversion can be achieved in time scales of a few seconds.

The results from the present study (i.e. sorption of SO₂ and HCl with caustic sorbents) were placed in the context of other potential removal processes in a combined filter reactor. Figure 8 shows as a result an overview of calculated temperature effects on SO₂ absorption with NaHCO₃, catalytic NO_x-reduction with NH₃, and adsorption of dioxins/furanes (as examples for VOCs). The NO_x-reduction curves are based on a kinetic analysis of experimental data with a ceramic filter element impregnated with SCR catalyst (Hübner et al. 1996, Schaub et al. 2002). Adsorption of dioxins/furanes was studied by means of a simple equilibrium calculation based on Langmuir's theory and a selectivity calculation regarding the adsorption parameters (Wang 2002).

Temperature effects on the different removal processes for gaseous compounds are very different. In a given situation with specific removal requirements, it is obvious that a detailed information is required for optimization of the overall process. Conflicts may arise when high adsorption removal efficiencies and high NO_x-conversion are desired at the same time.

Conclusion and Future Activities

It was possible to establish a temperature window for stable filter operation as well as satisfactory removal of gaseous species. For the kind of particles used (mixture of bark ash and sorbent products), 400 °C represent a critical limit, above which no stable filtration was possible. Within this window, removal efficiencies of up to 99 % for HCl and SO₂ can be achieved at emission levels of below 25 mg/m³.

Main conclusions for the combined removal are: a) sorption of SO₂ for a given stoichiometry is better with NaHCO₃ than with Ca(OH)₂, in particular at lower temperature, due to the transient presence of a porous and chemically very active Na₂CO₃ species, formed in-situ by thermal decomposition of NaHCO₃, b) high SO₂ conversion values can be achieved at higher temperature with bark ash alone, due to a significant Ca content of the fly ash, c) higher amounts of water vapor in the raw gas improve SO₂ conversion. This is especially of interest in biomass combustion where H₂O is always present in larger quantities.

Temperature effects on SO₂ and HCl absorption with caustic sorbents must be seen in the context of other removal processes of gaseous compounds in a filter reactor. Combining SO₂ and HCl absorption with catalytic NO_x-reduction should in principle be possible, according to the characteristic temperature effects. However, if adsorption is desired to occur simultaneously (e.g. of VOCs or volatile Hg), conflicting temperature requirements may arise. In the context of the present study, optimization of catalytic reactions in ceramic filter materials are being continued.

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References

- Hemmer, G., 2002. Die kombinierte Abscheidung von Stäuben und gasförmigen Schadstoffen nach Biomasseverbrennungsanlagen. *Dissertation Universität Karlsruhe*.
- Hemmer, G., Wang, J., Schaub, G., Kasper, G., 2001. Combined Dry Removal of Particles and Gaseous Pollutants from Biomass Combustion Off-Gases. *Partec 2001 in Nürnberg, Germany, International Congress for Particle Technology, Proceeding, Session: Gas Cleaning, Internal Number 110*.
- Hu, W., Smith, J.M., Dogu, T., Dogu, G., 1986. Kinetics of Sodium Bicarbonate Decomposition. *AIChE Journal* 32: 1483-1490.
- Hübner, K., Pape, A., Weber, E.A., 1996. Simultaneous Removal of Gaseous and Particulate Components from Gases by Catalytically Ceramic Filters. *Conf. Proc. High Temperature Gas Cleaning: 267-277*.
- Schaub, G., Unruh, D., Wang, J., Turek, T., 2002. Kinetic Analysis of Selective Catalytic NO_x Reduction (SCR) in a Catalytic Filter. *Chemical Engineering and Processing* (in press).

VDI-Richtlinie 2040, 1991. Berechnungsgrundlagen für die Durchflussmessung mit Blenden, Düsen und Venturirohren. *VDI/VDE-Gesellschaft Mess- und Automatisierungstechnik GMA*.

VDI-Wärmeatlas, 1994.

Wang, J., 2002. Gas-Partikel-Oberflächenfilter als chemischer Reaktor in der Rauchgasreinigung - Sorption und katalytische Umsetzung. *Dissertation Universität Karlsruhe* (in preparation).

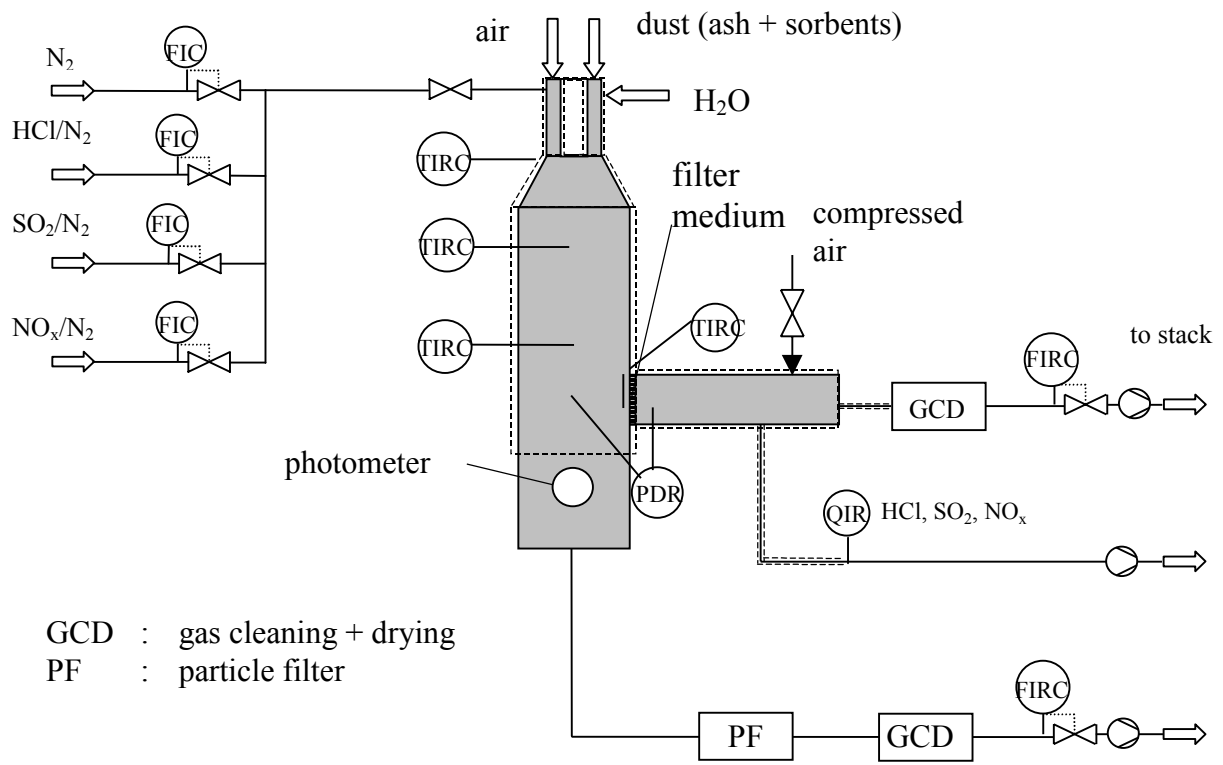


Fig. 1: Combined filtration unit for simultaneous removal of particles and gaseous pollutants

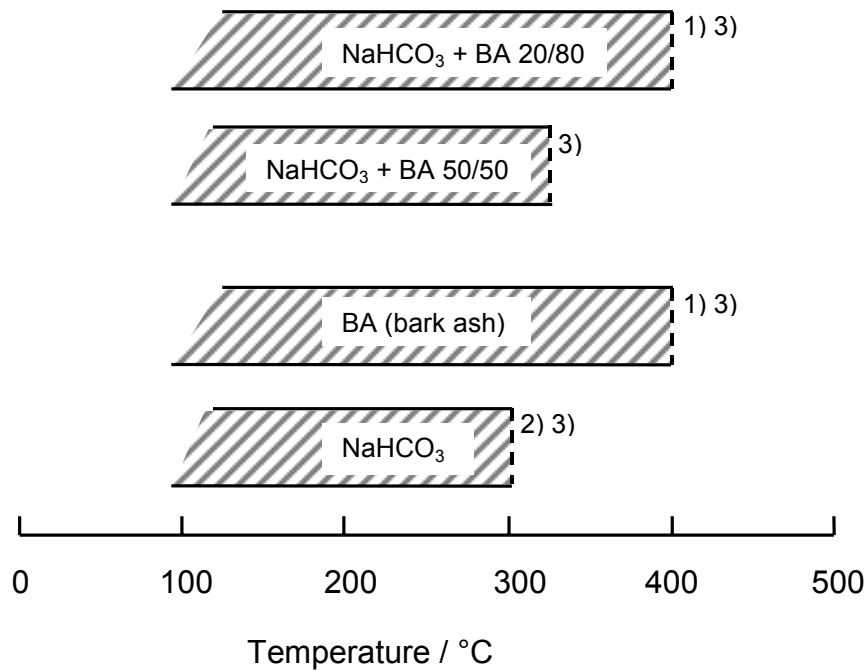


Fig. 2: Temperature ranges for stable filtration behaviour of NaHCO₃ sorbent and ash from bark combustion (based on Hemmer 2002)
 1) filtration with ceramic candles in air 2) filtration with disk in air
 3) dilatometer experiments

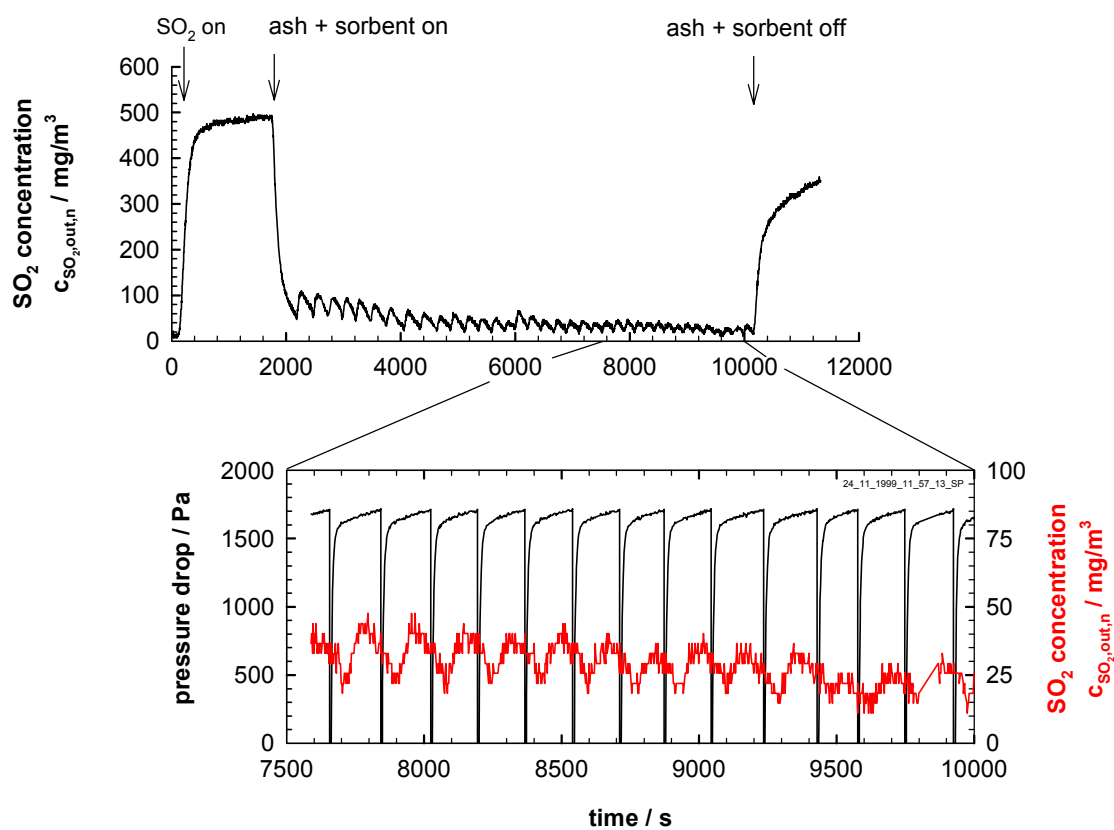


Fig. 3: Measured pressure drop and SO₂ concentration versus filtration time, sorbent: NaHCO₃, T: 200 °C, model gas: air/SO₂ (500 mg/m³), sorbent excess factor: 2.0, other conditions see Table 1

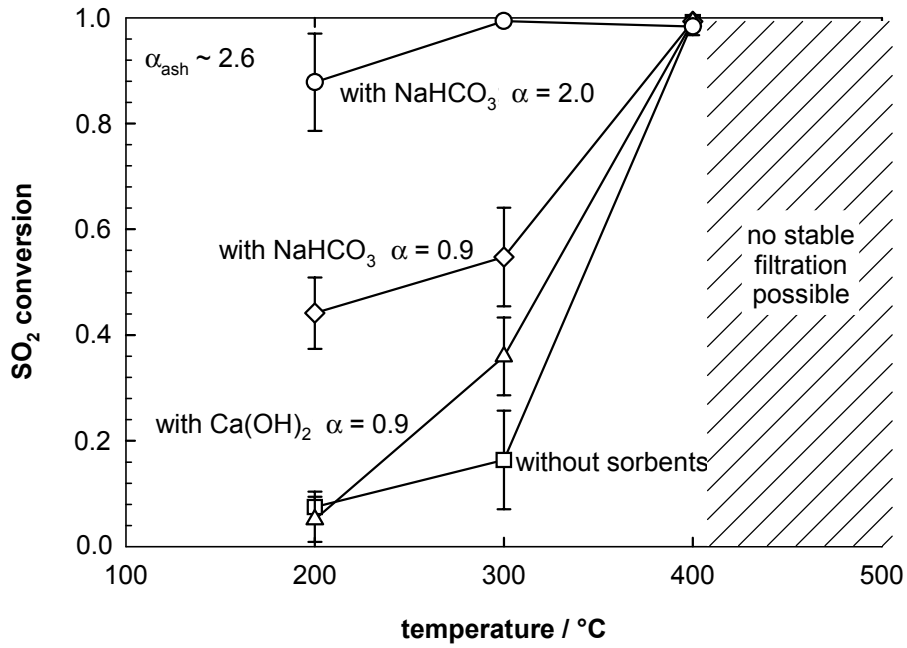


Fig. 4: Measured SO₂ conversion with NaHCO₃ and Ca(OH)₂ as sorbents in the presence of wood bark ash versus temperature. Signs: mean values, bars: minimum or maximum values, model gas: air, other conditions see Table 1

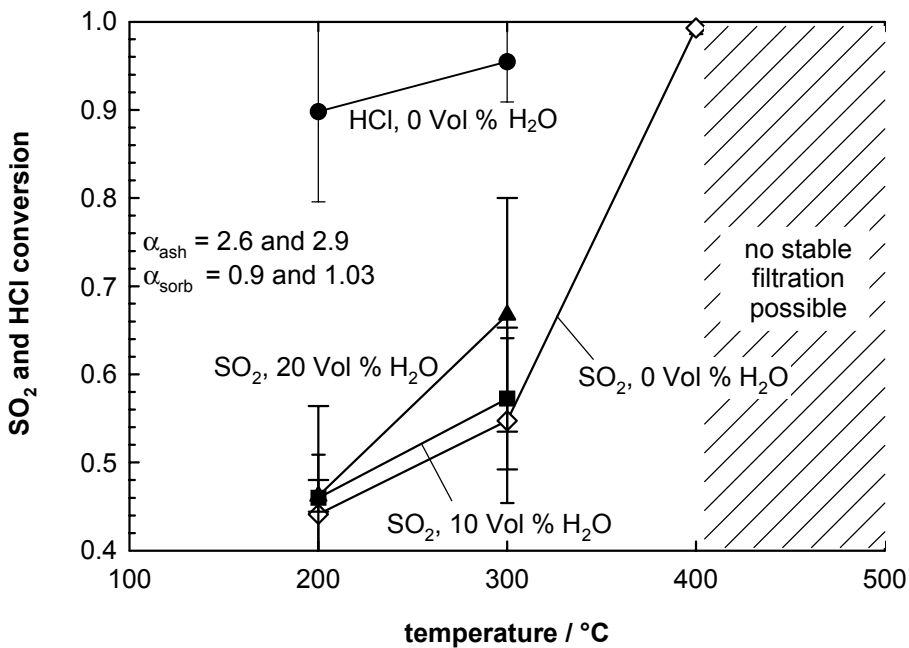


Fig. 5: Measured SO₂ and HCl conversion with NaHCO₃ as sorbent versus temperature, effect of water vapour. Signs: mean values, bars: minimum or maximum values, model gas: air, other conditions see Table 1

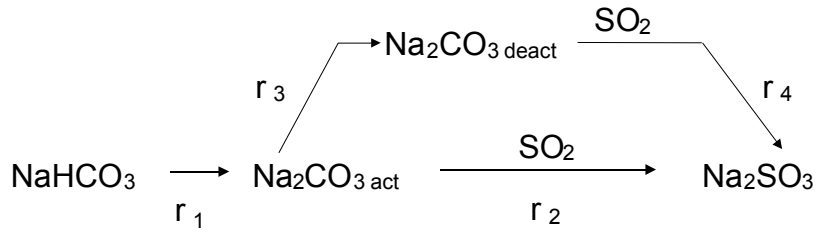


Fig. 6: Reactions occurring in SO₂/NaHCO₃ system

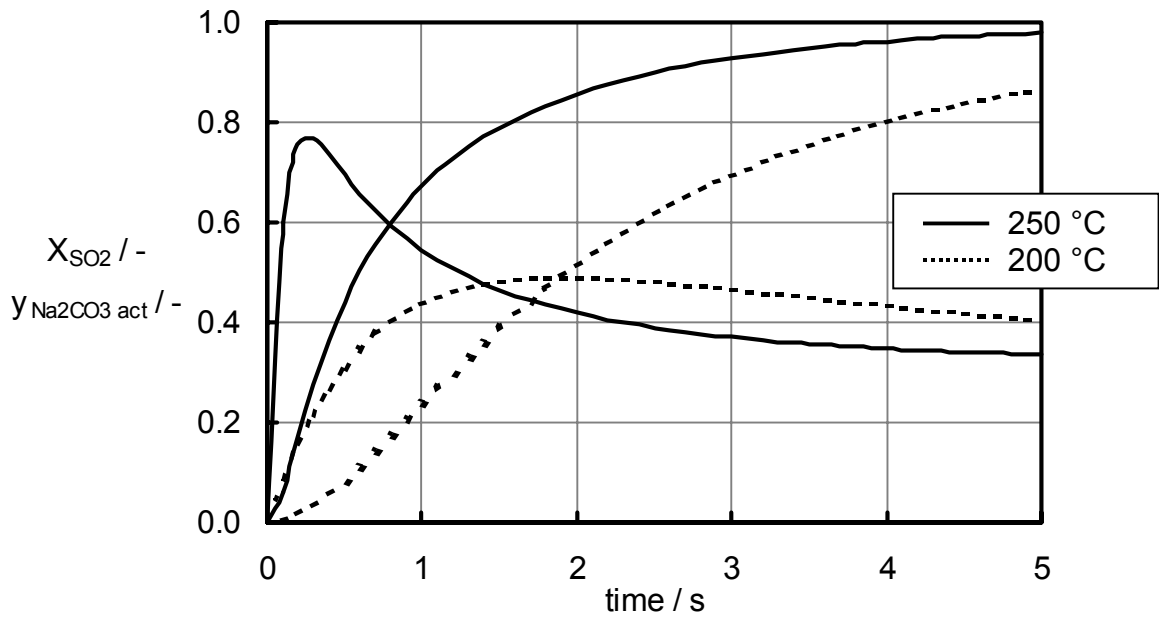


Fig. 7: Calculated residence time effect on SO₂ conversion X_{SO₂} and on available molar fraction of activated Na₂CO₃ y_{Na₂CO₃ act} in an entrained flow reactor with NaHCO₃ as sorbent, c_{SO₂} in eff: 500 mg/m³, α_{sorb}: 1.5

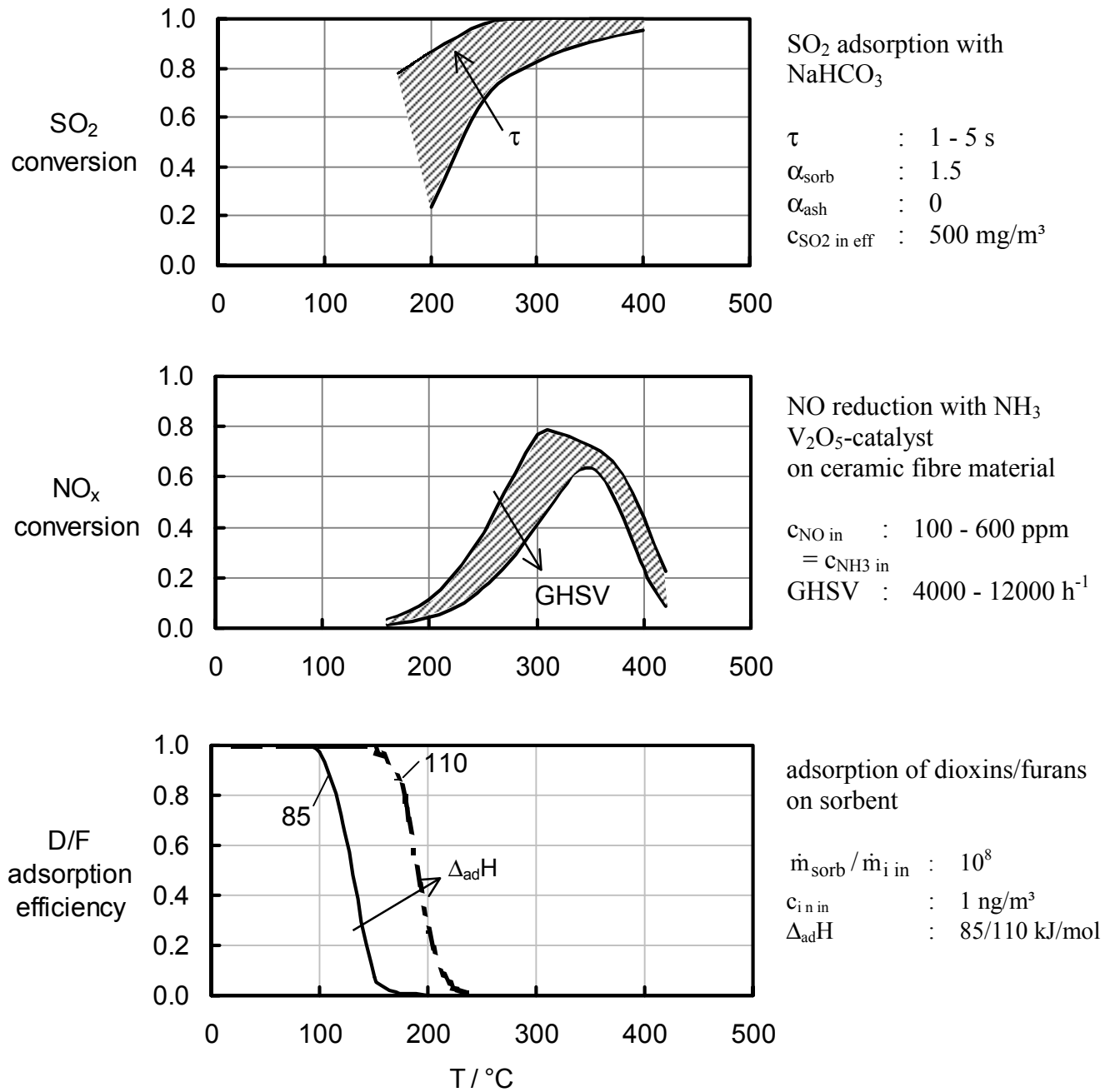


Fig. 8: Summary of calculated temperature effects during sorptive and chemical removal of gaseous compounds in a dry combined process, based on different information, top: own experiments, middle: kinetic analysis of published data (Hübner et al. 1996), bottom: estimate based on adsorption equilibrium analysis (Langmuir)

Table 1: Overview of measurements with SO₂ and HCl as gaseous pollutant and NaHCO₃ as sorbent

| temperature | °C | 200 | 300 | 400 |
|---|-------------------|--------------------|--------------------|--------------------|
| $\dot{V}_{g,eff}$ | m ³ /h | 18.8 | 18.8 | 18.8 |
| c _{SO2 in n} , c _{HCl in n} | mg/m ³ | 500 | 600 | 700 |
| x _{H2O} (for SO ₂) | vol% | 0, (10, 20) | 0, (10, 20) | 0, (10, 20) |
| balance | | air | air | air |
| sorbent | | NaHCO ₃ | NaHCO ₃ | NaHCO ₃ |
| excess factor (for SO ₂) | | 0.9, 2.0 | 0.9, 2.0 | 0.9 |
| excess factor (for HCl) | | 1.03 | 1.03 | - |
| c _{ash,eff} | g/m ³ | 5 | 5 | 5 |
| c _{sorbent,eff} | g/m ³ | 0.68 | 0.68 | 0.68 |
| u _{gas,eff} ¹ | cm/s | 5 | 5, 7 | 5 |

¹ vertical duct and filter cake