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Flue gas treatment in the ceramic industry

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Abstract

Various flue gas cleaning processes are used in the ceramic industry. In most cases dry sorption systems are used due to low invest and maintenance costs and a high performance in operation. These processes run with lime based sorbent materials.

In the ceramic industry emissions of fluorides (HF), sulfuroxides (SO_2 / SO_3) and Hydrogen Chloride (HCl) must be removed. Most important processes are the fixed bed filter and dry sorption with fabric filter. In this presentation, processes, sorbents and performances of existing plants are presented.

Keywords: flue gas treatment FGT, dry absorption, specific surface, SO2, HF and HCl removal, fixed bed filter, fabric filter, emission control, limestone, hydrated lime, high surface area hydrated lime.

1. Processes

Flue-gas treatment (FGT) processes can be roughly classified into three categories:

1. Wet flue-gas cleaning processes,

2. Semi-dry flue-gas cleaning processes,

3. Dry flue-gas cleaning processes.

Wet FGT processes are primarily used in power stations for flue-gas desulphurisation (FGD). Small units for industrial applications are available, but due to high invest and maintenance costs with rare examples not established in the ceramic industry. In semi-dry processes, a lime milk suspension is introduced into the stream of flue gas so that the flue gas is cooled by evaporation of the water to a temperature of 130 – 180 °C. The reaction products are separated as a dry powder by a downstream filter. In the case of dry processes, the sorbent is injected as a powder into the flue gas (Fabric filter process) or the gas is led through a fixed bed of the sorbent (Packed Bed Filter process -PBF) at temperatures of 120 - 240°C. Dry processes have become standard in modern flue-gas cleaning in industrial Processes since they offer to the user decisive advantages. In addition to the safe compliance with mandatory limiting values and high flexibility, they also lead to lower investment and operating costs, low personnel expenditures as well as a simple concept and space-saving design. The reaction products are dry.

Depending on the raw materials and fuels used in the brick and tile industry different pollutants are released. In different temperature zones of the tunnel kiln, fluorides (HF), sulfuroxides (SO_2 / SO_3) and hydrochloric acid (HCl) are released and must be removed by a FGT-installation.

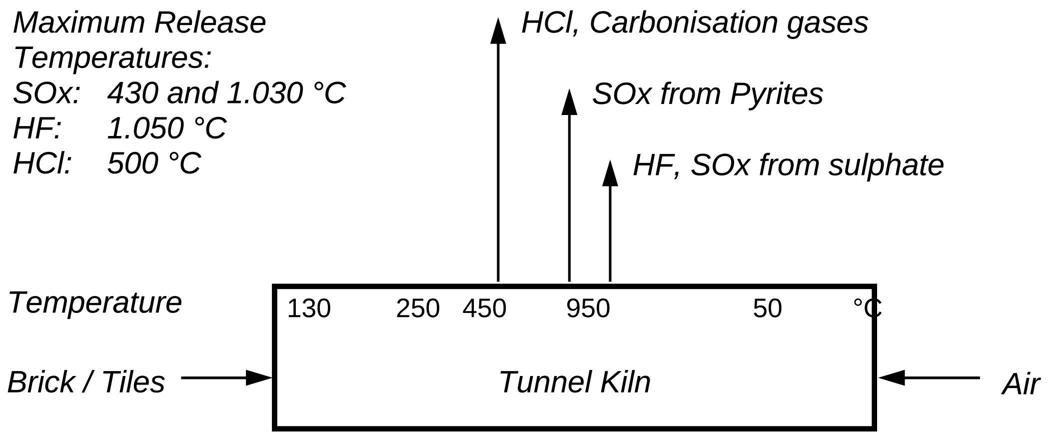

Fig 1: Release of pollutants in the ceramic process.

First the carbonisation gases are released. These organic compounds are treated in thermal units. In this temperature range also HCl is released, if Chlorides are in the raw material or applicator to it. Second the SOx from pyrites (Fe_2O_3) in the raw material are released. At last the sulphates and fluorides release SOx and HF. The Maximum release temperatures are 430 and 1.030°C for SO_2 and SO_3, 1.050°C for HF and 500°C for HCL[1].

In some cases it is possible to influence the release of SOx by increasing the raw materials calcium content. Mixing the clay with milled Limestone is practiced. This method is just suppressing the release of SOx. It has a very low effect on the other acid compounds of the raw gas.

In the next figure the application temperatures for reduction of different acid gases in dry sorption processes are shown.

The high (850 – 1000 °C), medium (300 – 450 °C) and low (80 – 220 °C) temperature ranges are used for this. In particular for flue gas treatment in the ceramic industry the high temperature range is used for direct reduction of SO_2 and the low temperature range is used in dry sorption processes. Dry processes have become very successful in modern flue-gas cleaning since they offer the user decisive advantages.

The medium temperature range offers very good application conditions for hydrates, particularly those to remove SO_2. For example, in the glass industry, flue-gas cleaning widely use Sorbacal® *A at 350 – 500 °C[2]. In the high-temperature range at approx. 850 –1000 °C, products with high surface areas that were specially developed for flue-gas cleaning (e.g. Sorbacal® A or Sorbacal® SP) have also been used successfully.

In the production of Bricks and Tiles, direct removal of SO_2 is possible by using powderderised limestone (PL) products in the preparation of raw material (Primary reduction process)[3]. These PL must in particular have a defined grain structure to avoid losses in brick and tile product quality. Shrinkage behaviour, drying properties and sintering behaviour are essentially influenced by the grain size distribution[4]. The use of powderderised Limestone with > 97% $CaCO_3$ and a grain size distribution with 1% residue on 45 µm reduces the sulphur oxide concentration in the raw gas and improves considerably the quality of the brick and tile products. This process is already used in the production of clay roofing tiles in a number of cases .

* Sorbacal® is a brand name of the Groupe Lhoist. Sorbacal® SP, Sorbacal® A and Sorbacal® G are patented product property of the Lhoist Group

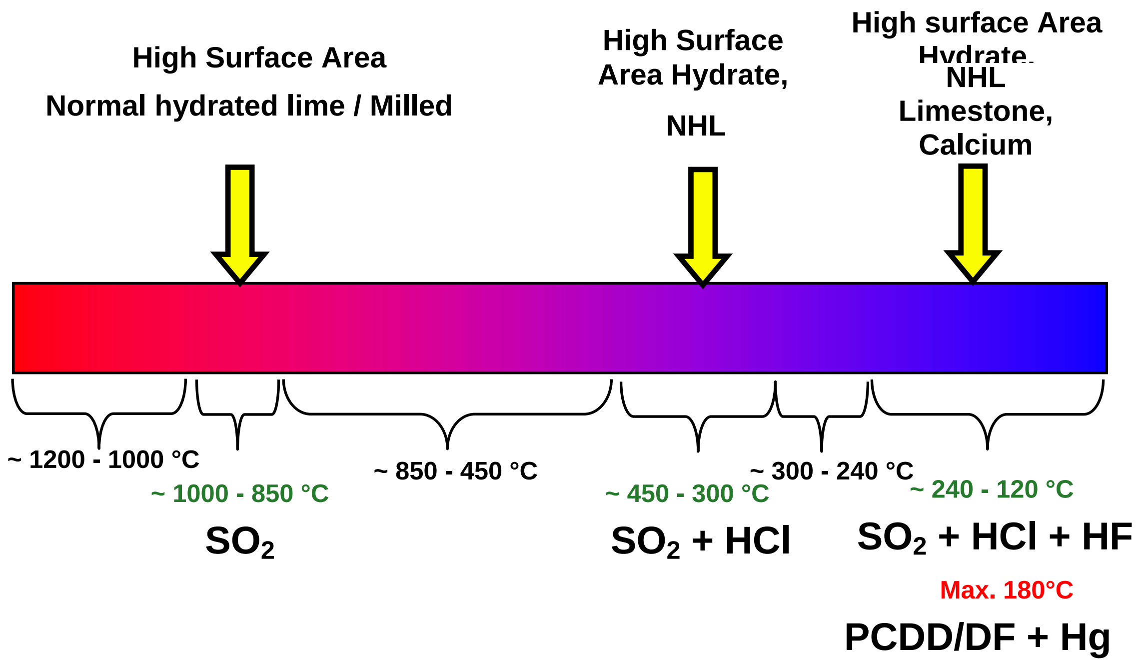

Fig 2: Temperature application range of FGT with lime based products

In addition to the temperature a number of other factors influence the removal of pollutant gases. They can be summarised under the headings gas properties (given), process engineering (can be influenced) and adsorbent (can be influenced). The influence of absorbent for the use of limestone, granulated materials, normal hydrated lime and high surface area hydrated limes in dry process is discussed here, in particular.

2. Sorbents

The common factor in all processes is the general use of lime-based products (milled limestone - $CaCO_3$, lime - CaO, hydrated lime – $Ca(OH)_2$) to neutralise the acid forming pollutants (HCl, SO_2, HF). Criteria for the application of these products to scrub gases are, in addition to chemical purity (CaO content and secondary components), for:

· **Limestone** and **Granulated sorbents** : specific surface area, porosity.

· **Hydrated limes:** grain-size distribution, specific surface area, pore volume.

2.1. HYDRATED Limes specificities:

The Lhoist Group has been a driving force since the mid-1980s in the development of products for use in semi-dry and dry processes (Sorbacal® SP, Sorbacal® A, Sorbacal® G), in particular. The result of this intensive research was the first hydrated lime with a high surface area (High Surface Hydrated lime-HSH), namely Sorbacal® A. While standard hydrated lime usually has a specific surface area of approx. 18 m^2/g (according to BET), the specific surface area of Sorbacal® A is approx. 38 m^2/g. In this way, the surface area available for the gas-solid reactions in the dry sorption process is, in principle, more than doubled. Furthermore, the number of particles and dispensability is markedly increased owing to the fineness of the product (d_{50} approx. 3 µm compared to 6 µm for standard commercial hydrated lime). The intensive development to improve the standard hydrated lime by the Lhoist research department led to the product Sorbacal® SP. Here, in addition to a further increase in the specific surface area to approx. 45 m^2/g, the pore volume, which is particularly important for the difficult removal of SO_2, was decisively increased. While standard hydrated lime has a pore volume of approx. 0.08 cm^3/g, the corresponding value for Sorbacal® SP is higher than 0.2 cm^3/g (N2 adsorption).

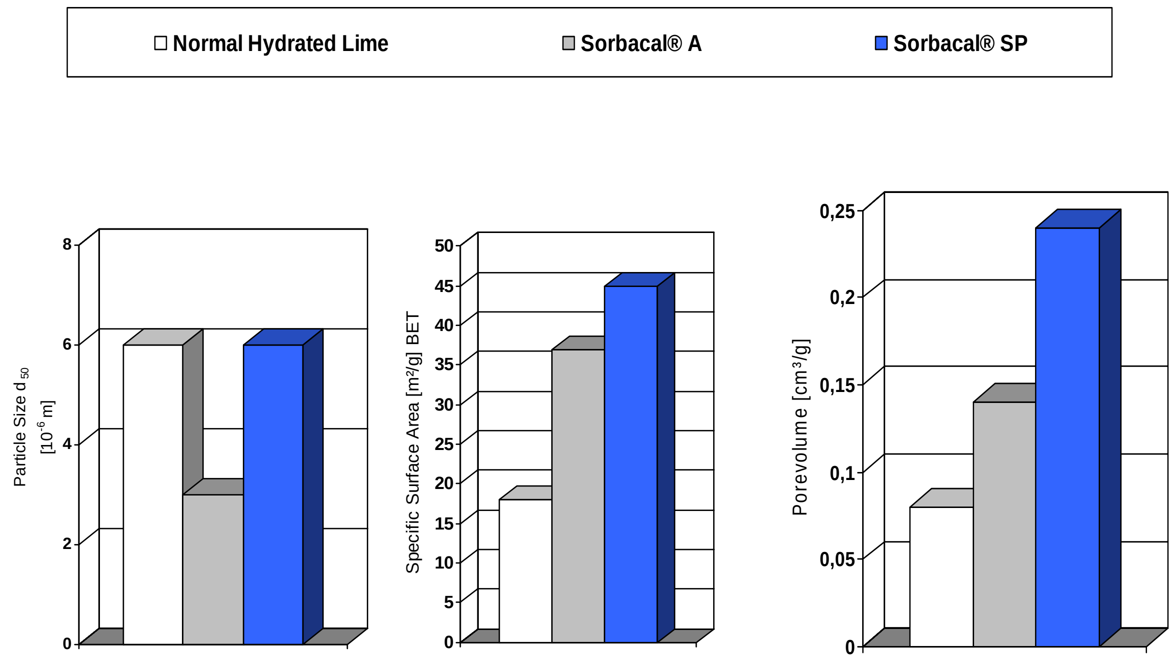

Fig. 3: Comparison of different Hydrated Limes

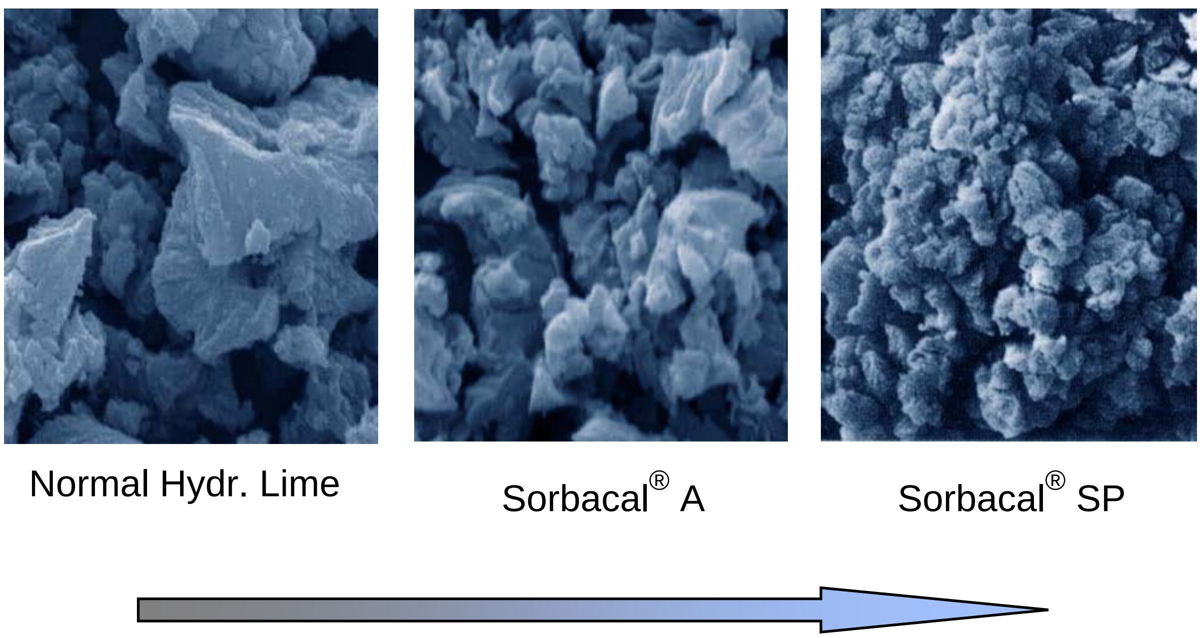

Fig. 4: Development of hydrated limes

2.2. LIMESTONE and GRANULATED Sorbent

In packed bed filters (PBF) appropriate ground limestone ($CaCO_3$) or granulated sorbents are used. Limestone is relatively inert in reaction with acid gases. Therefore the required reduction rates – particularly if SO_2 is present besides HF, or also HCl are very often not obtainable. If limestone chippings are used, often a very high consumption occurs in operation. By use of granulated materials modified for the process of PBF the performance of a conventional filter is increased on a very high level.

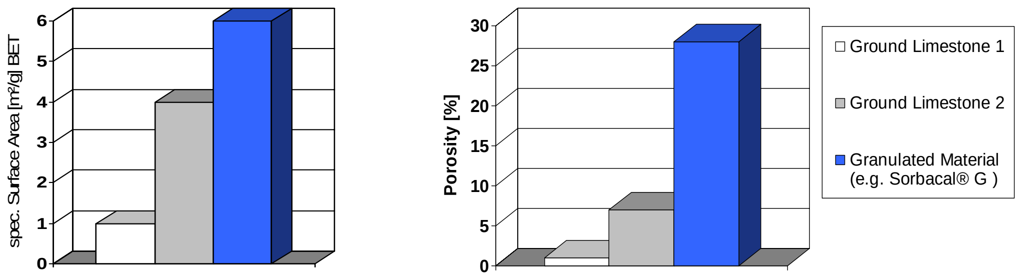

Fig. 5: Specific surface area and porosity of ground limestone and granulated sorbent

Granulated materials with app. 6 m²/g have a 2-5 times higher specific surface area than ground limestone and with 28% a 5-20 times higher porosity. The most important factor for the higher performance is the porosity. The porosity makes the sorbent available for the reaction with acid gas compounds and the sorbent can not be covered with a mantle of reaction products as gypsum or calcium fluoride. Just a few deposits of ground Limestone provide sufficient qualities that can be used in packed bed filters.

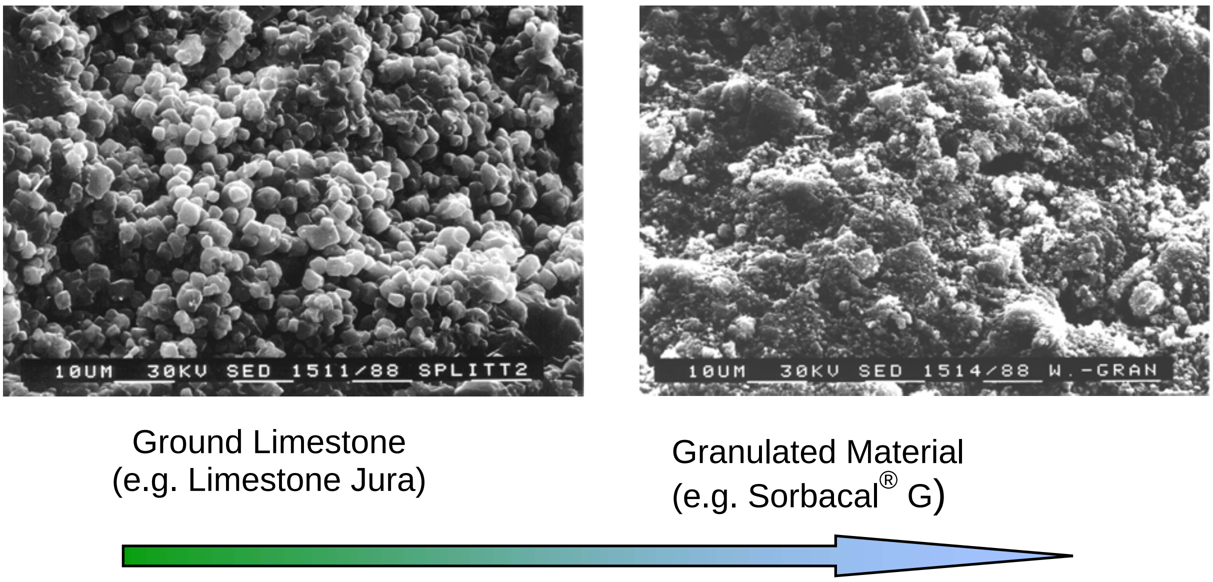

Fig. : 6: Scanning electron microscope pictures of ground limestone and granulated sorbent

2.3. DRY Hydrated lime and/or DRY limestone ?

The use of products that are optimally customised to the process provide particular advantages for the operator of dry processes. Therefore, HSH lime is generally used since this:

- Minimises the consumption of operating materials.

- Allows a safe compliance with mandatory limiting values.
- Reduces the amount of residual waste (requirement to minimise residual waste!).

In the low-temperature range, HSH lime products or granulated sorbents for PBF are used successfully in many cases. Results and operating experience are discussed on the basis of practical examples from the field of ceramic industry.

3. Examples for dry sorption in the ceramic industry

Dry sorption process in ceramic industry is mostly implemented for reduction of acid gas compounds. Namely packed bed filter and fabric filter systems are successfully in operation. The driving force for this is the national regulation (e.g. in Germany TA-Luft 2002)**,** which is transferred from European legislation (1999/30/EU), which moreover also affects the other industrial fields. The emission limits resulting from the 1999/30/EU legislation will have to be fulfilled latest in 2010.

Pollutant		**1999/30/EU**	**Comment**
SO_2	mg/m³	350 - 500	
HCl	mg/m³	< 30	
HF	mg/m³	< 3-5	
Dioxins	ngTE/m³	< 0,1 - 0,4	
Heavy Metals eg. Hg	mg/m³	< 0,05	
year to be fullfilled		2005 - 2010	Existing Plants

Fig. 7: Legislation and regulations in EU

These Regulations are converted into National Law in most countries of EC. The release of pollutants can not be avoided in the ceramic process. The EC-Air Quality Regulation 1999/30/EG has to be put into Practice for all members of EC.

3.1 Dry sorption with packed bed filters

This technique is mainly applied in flue gas treatment of the ceramic industry. The PBF technology is proven and offers a cheap and perfectly on the ceramic industry adopted process. In many cases if only HF has to be removed and SOx / HCl are only on low concentrations this Filters can be run with limestone.

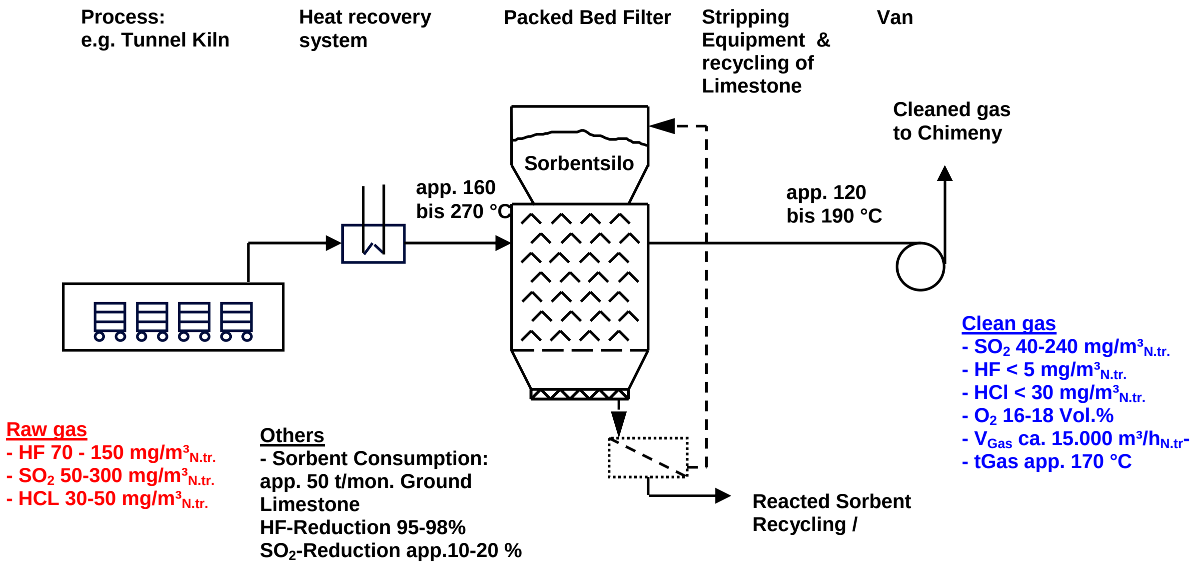

Fig. 8: Conventional packed bed filter with ground limestone

The degree of utilisation of the limestone and ability of reduction can be increased by stripping the reacted limestone. These systems reach their limit if SOx increases above a concentration of app. 300 mg/Nm³ dry , or if besides SOx, also HCl has to be removed[5].

The removal capacity and utilisation rate of the sorbent increase when granulated materials with a high porosity are used.

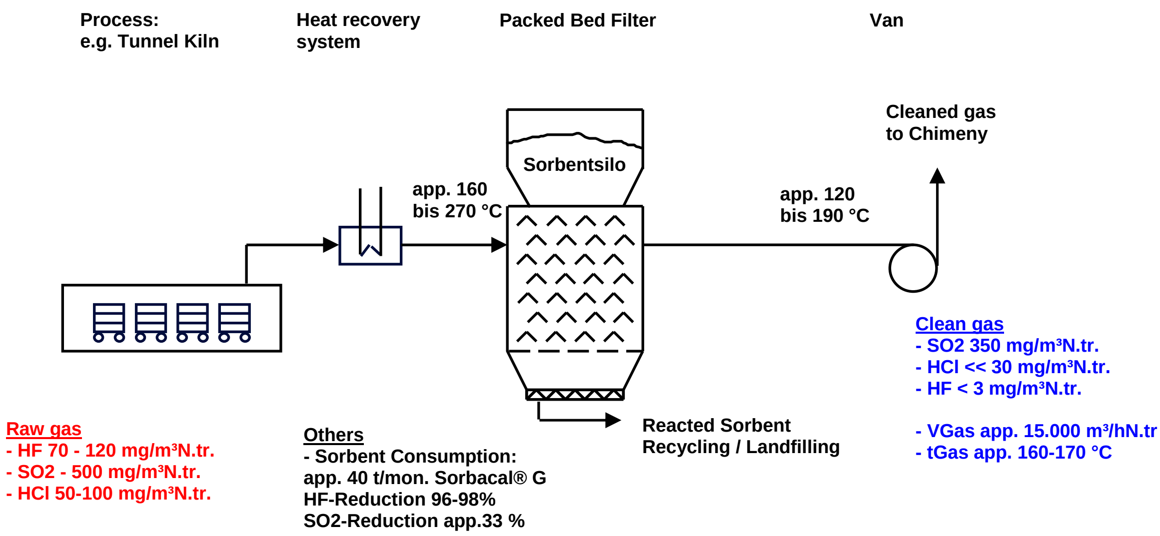

Fig. 9: Conventional packed bed filter with granulated sorbent

In this example HF is removed < 3 mg/m³N though SOx and HCl are represented with high concentrations in the raw gas. Also HCl that reaches a level of 50-100 mg/m³N in the raw gas of this tile producing plant is removed far below 30 mg/m³N. The reduction of SO_2 reaches its limit in this simple single step PBF with an app. 33% removal rate.

The capacity of the PBF system operating with granulated sorbents of high porosity can be considerably improved by using multistage systems of this technique. Such systems where installed for high performance reduction of SOx. They lead to a performance that made reduction of Sulfuroxides below 500 and even 300 mg/m³N possible!

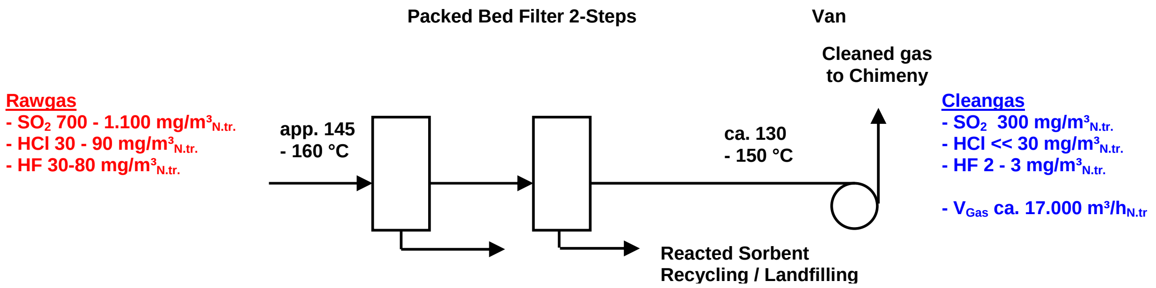

Fig. 10: Multistage packed bed filter systems (2-stage)

In Figure 10 the performance of a 2-stage system operating in France is shown. Reduction rates of app. 55-75% are reached in daily operation. The emission limit of 300 mg SO_2 /m³N is met safely. HF is removed below 2 mg/m³N. The consumption of this filter is 80-100 kg/h granulated sorbent.

At another plant a 4-stage System with internal heat management is in operation since many years. The removal of SO_2 is controlled continuously. A level of < 400 mg SO_2 is mandatory. The consumption is 170 – 250 kg/h granulated sorbent Sorbacal® G, depending on the load of SO_2 in the raw gas. The consumption is daily adjusted to the mandatory emission limit. This guaranties an optimal load of acid gas on the sorbent.

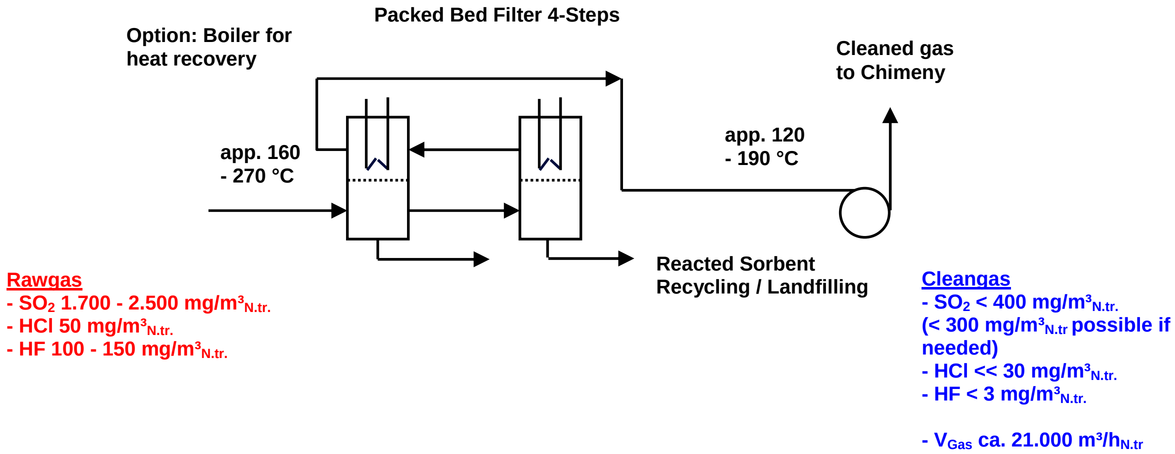

Fig. 11: 4-stage packed bed filter system with temperature management

With this PBF system reductions of 76-84 % of SO_2 and 97-98% of HF are realised. Such systems are in operation for several years now. They are very reliable and allow a safe and stabile process.

3.1 Dry sorption with fabric filters

In cases of very high removal rates needed a dry sorption system with a fabric filter may be the best solution in commercial aspects. Those systems require a higher invest and maintenance than PBF, but lead in some cases to a better performance of reduction – especially for SO_2 - compared to PBF systems. A number of plants like are in operation in different countries. The case shown here is a plant in France with an optimised process.

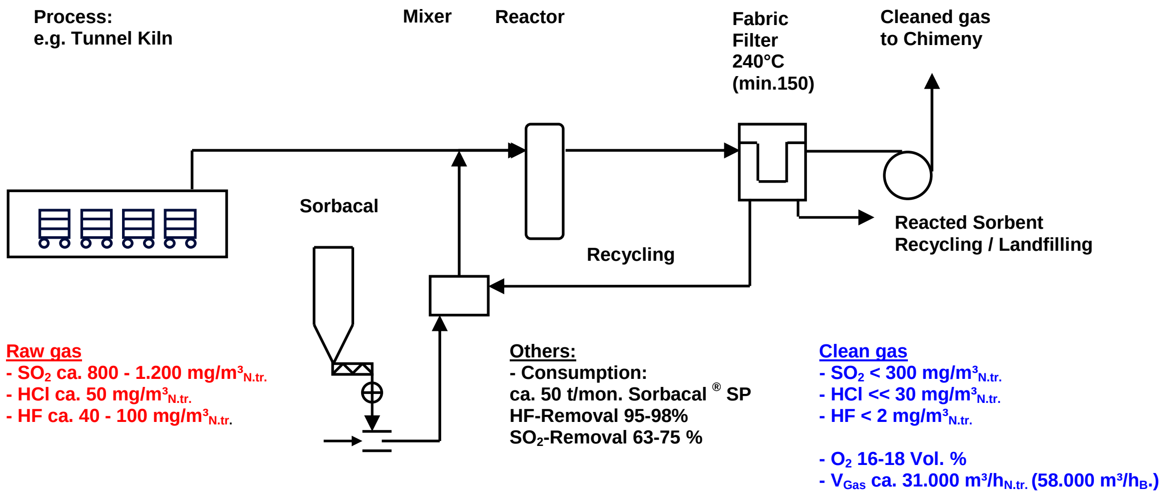

Fig. 12: Dry sorption with fabric filter.

The plant operates with injection of the high surface area and large porosity hydrated lime Sorbacal® SP in the duct. In the reactor the contact time of sorbent and acid gas compounds is extended and turbulences lead to high contact plausibility. Recirculation increases the load of reaction products on the sorbent. The filter is running at app. 240°C. By this process a consumption of only app. 75 kg/h Sorbacal® SP is needed. With this fabric filter sorption system reductions of 63 - 75 % of SO_2 and 95-98% of HF are realised.

A trial with normal hydrated lime was conducted and led to much higher consumption and a considerable loss of removal capacity.

4. Conclusions

Dry flue gas treatment processes have a long and successful story in processes of the ceramic industry. In particular the packed bed (or kiesbed-) filter represents a technique outstandingly adapted to the needs of the operators in the ceramic industry. These systems can be run with ground limestone in many cases if demanded removal rates and load of other compounds than HF, e. g. sulfuroxides or HCl are low. Just a few deposits provide Limestone that can be utilised for this application. The PBF systems can be increased in their performance by using optimised granulated sorbents, synthetic limestone. If higher standards have to be fulfilled modification of PBF by using multi stage systems and management of reaction conditions (e. g. temperature of the gas) leads to solutions perfectly adapted to the ceramic process.

Dry sorption processes with fabric filters provide a higher removal level and can meet higher standards of flue gas treatment.

Both systems, PBF and fabric filter are used successfully in practice and lead to good solutions in a commercial sense. In both processes advanced lime products like granulated sorbent or high surface area hydrate improve considerably the efficiency. Those sorbents are often used as these:

- Increase the removal efficiency and ability of dry sorption (Safe operation)
- Permit the installation of less expensive flue gas treatment technique (Low invest)
- Minimise consumption of sorbent and mass of residues (Low costs of operation).

In practice this means in technical terms:

- Even in the temperature ranges previously regarded as being unfavourable for the use of dry sorption techniques, the removal of acid-forming pollutants, such as HCl and SO_2, by means of a highly reactive additive tailored to the application case, was highly effective.
- The limiting values of the 1999/30/EC are observed.
- Practice, shows that the use of optimised sorbents for the flue gas treatment (e. g. Sorbacal®) gives reductions of more than a half in the consumption of operating materials.
- This gives corresponding reductions in the amount of residual waste.

- According to currently available operating experience, the use of granulated sorbent (e.g. Sorbacal® G) in a PBF a single or multi-stage dry sorption plant can safely comply with the limiting values for SO_2, HF and HCl. This means that complicated flue-gas cleaning processes are not necessary. It also ensures an economically viable operation on a long-term basis with low expenditures of personnel, equipment and materials.

- If high contents in the raw gas occur frequently, the use of the fabric filter process with its high effectiveness and low consumption of additives allows compliance with mandatory limiting values, even under conditions that were previously considered to be unfavourable. Moreover, this process allows operation with low expenditures of personnel, equipment and materials.

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