APPLICATION CONDITIONS FOR HIGHLY REACTIVE LIME HYDRATES IN DRY SORPTION

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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 investment and maintenance costs and high performance in operation. These processes run with lime based sorbent materials. Dry flue gas treatment processes have a long and successful history in ceramic industry processes. In the ceramic process, emissions of fluorides (HF), sulphur oxides (SO_2/ SO_3) and hydrogen oxide (HCl) have to be removed. The mostly used processes are dry sorption processes with the packed bed filters (PBF or Kiesbedfilter) and fabric filters.

Both systems, PBF and fabric filter are used successfully in practice and lead to good solutions in a commercial sense. In both processes advanced products on a lime base as granulated sorbents or high surface area hydrates improve considerably the efficiency. Sorbents of this type are often used, as they:

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

In this presentation processes, sorbents and performances of existing plants are presented.

1. PROCESSES

Flue gas treatment (FGT) processes can be roughly classified in 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). Because of the process technology, flue gas temperatures of approx. 60 - 70°C in the scrubbing stage are achieved. In the case of 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 reaction material is introduced as a powder into the flue gas (Baghouse filter process) or the gas is led through a fixed bed of the sorbent (Packed Bed Filter process) at temperatures of 120 - 240°C.

Dry processes have become standard in modern flue gas cleaning in industrial processes since they offer 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 produced in the dry state. Examples for its use can be found in almost all fields of application, e.g.:

- wood and biomass-fired power stations,
- municipal waste incineration plants,
- hazardous waste incineration plants,
- conventional power stations,
- non-ferrous metal processing,
- glassworks,
- ceramics industry,
- process firing.

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), sulphur oxides (SO_2/SO_3) and hydrogen oxide (HCl) are released and have to be removed.

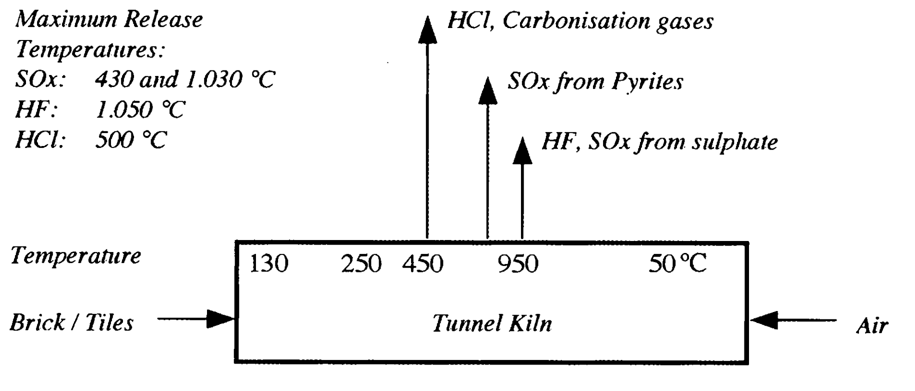

Figure 1. Release of pollutants in the ceramic Process.

First the carbonisation gases are released. These organic compounds are treated in thermal units. In this temperature range HCl can also be released. Second, the SOx from pyrites in the raw material are released. Finally, the sulphates and fluorides release SOx and HF. The maximum release temperatures are 430 and 1030°C for SO_2 and SO_3, 1050°C for HF and 500°C for HCl[12].

In some cases it is possible to influence the release of SO_x by increasing the raw materials calcium content by mixing the clay with powdered limestone. This method has only 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 standard 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 has been very successful using WÜLFRAsorp® A at 350 – 500°C[3] . In the high-temperature range at approx. 850 –1000°C, products with high surface areas that were specially developed for flue gas cleaning have also been used successfully.

In the production of bricks and tiles direct removal of SO_2 is possible by using powdered limestone (PL) products in the preparation of raw material (primary reduction process)[4]. 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[5]. The use of powered 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 considerably improves 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.

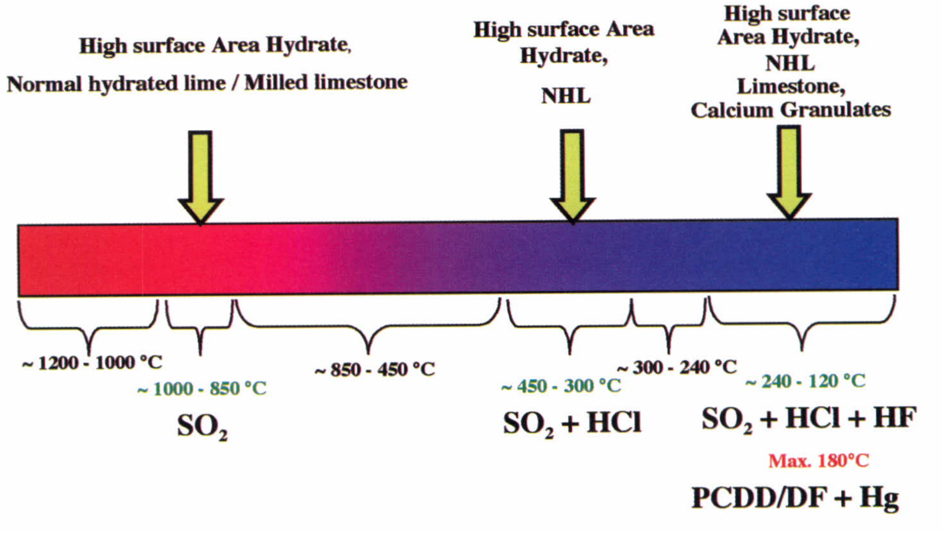

Figure 2. Temperature application range of FGT with lime based products.

In addition to 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 sorbentes (can be influenced). The influence of the sorbent in 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 the 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, SO2, HF). Criteria for the application of these products to scrub gases are, in addition to chemical purity (CaO content and secondary components), for

- **limestone:** specific surface area, porosity,
- **granulated sorbents** specific surface area, porosity,
- **hydrated limes:** grain-size distribution, specific surface area, pore volume.

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, in particular. The result of this intensive research was the first hydrated lime with a high surface area (HSH lime), namely WÜLFRAsorp® 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 WÜLFRAsorp® 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 dispersibility 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 Spongiacal® (brand name in Germany: WÜLFRAsorp® D SP and in France: Captacal® 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 Spongiacal® is greater than 0.2 cm^3/g (N_2 desorption).

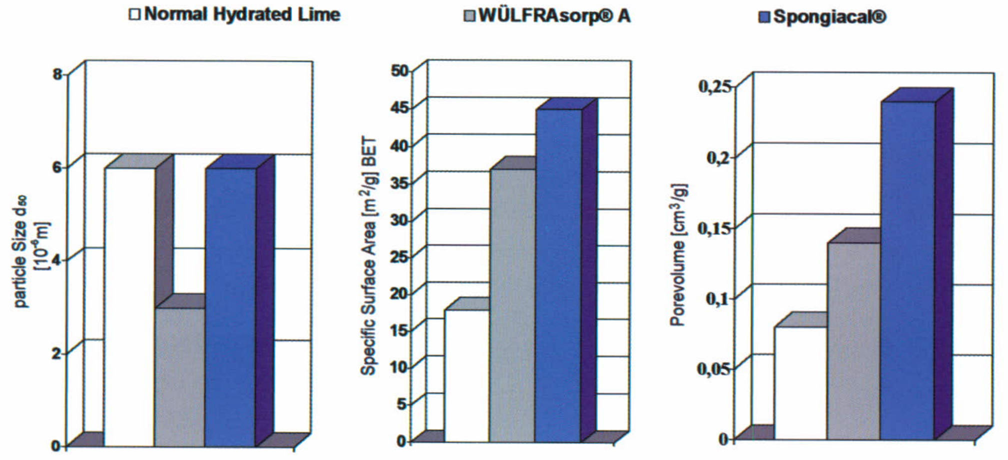

Figure 3. Comparison of different hydrated limes

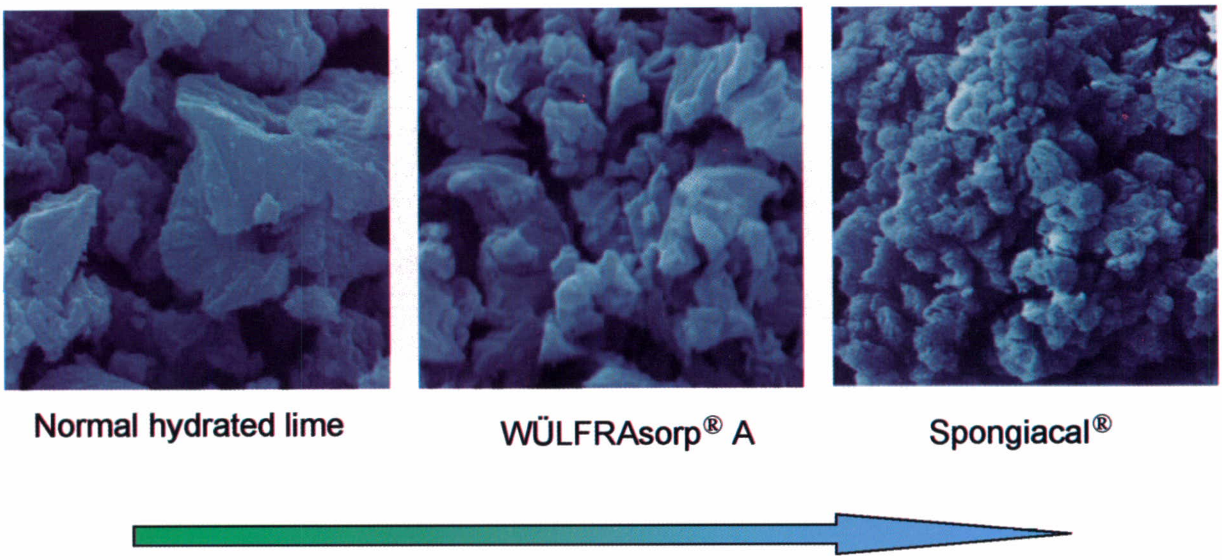

Figure 4. Development of hydrated limes

In packed bed filters, appropriately 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 HCl also has to be removed – are in many cases 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 to a very high level.

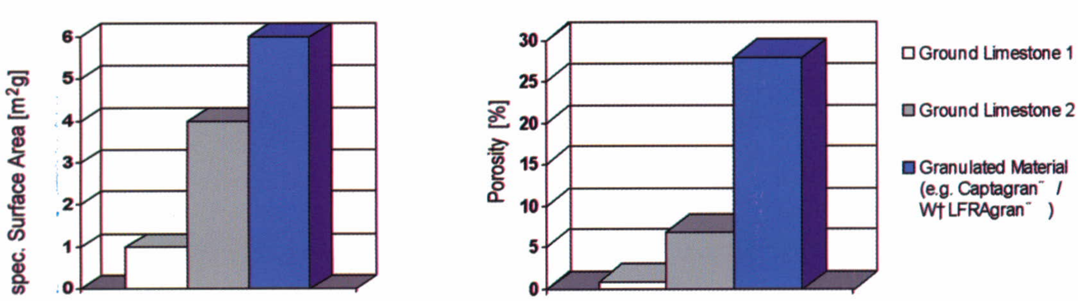

Figure 5. Specific surface area and porosity of ground limestone and granulated sorbent

Granulated materials with approx. 6 m^2/g have a 2-5 times higher specific surface area than ground limestone, and with 28% porosity, 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 like gypsum or calcium fluoride.

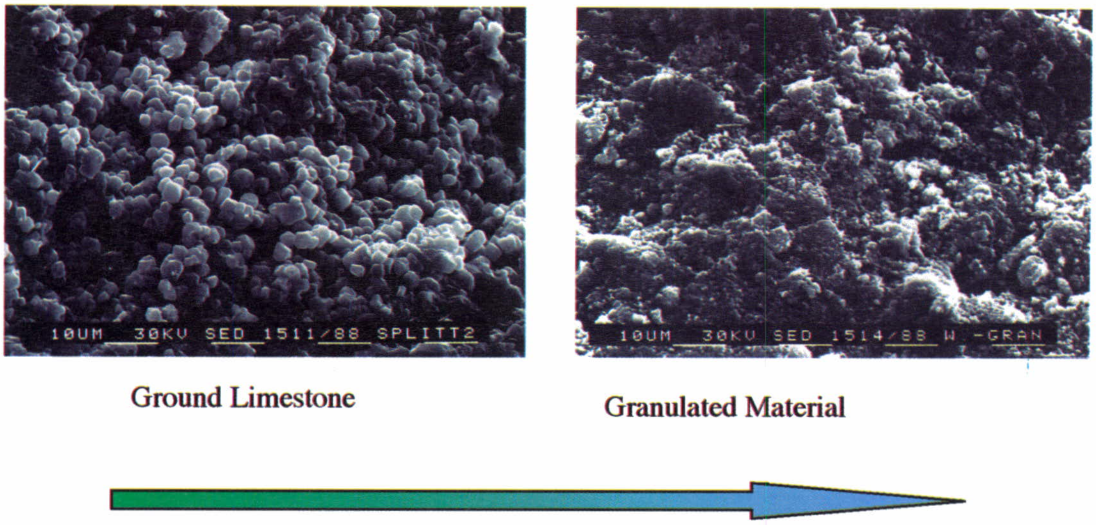

Figure 6. Scanning electron microscope pictures of ground limestone and granulated sorbent

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 safe compliance with mandatory limiting values,
- reduces the amount of waste (requirement to minimise waste!).

In the low-temperature range, HSH lime products (e. g. High surface area Hydrates 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 processes in the ceramic industry are mostly implemented for the reduction of acid gas compounds. Specifically, packed bed filter and fabric filter systems are successfully in operation. The driving forces for this are the national regulations (e.g. in Germany TA-Luft 2002, in France …., in Spain….) which are transferred from European legislation (1999/30/EC), which moreover also affects the other industrial fields. The emission limits resulting from the 1999/30/EC legislation will have to be fulfilled by the latest in 2010.

These Regulations have been transposed to National Law in most EC countries. The release of pollutants can not be avoided in the ceramic process. The EC Air Quality Regulation 1999/30/EC has to be put into Practice for all EC Member States. In Germany with TA-Luft 2002 the regulation of TA Luft 1986 had to be reviewed and led to more restricted emission limits.

Pollutant / Limit value		1999/30/EC	Comment
SO_2	mg/m³	350 - 500	
HCl	mg/m³	< 30	
HF	mg/m³	< 3-5	
Dioxinas	ngTE/m³	< 0,1 - 0,4	
Heavy metals e.g. Hg	mg/m³	< 0,05	
Name of regulation		e.g. TA Luft 2002	German regulation
Year to be fulfilled		2005 - 2010	Existing plants

Figure 7. Legislation and regulations in 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 adapted process to the ceramic industry. In many cases, if only HF has to be removed and SOx/HCl is only present in low concentrations, these filters can be run with 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 approx. 300 mg/m³Ntr., or if besides this, HCl also has to be removed. [6]

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

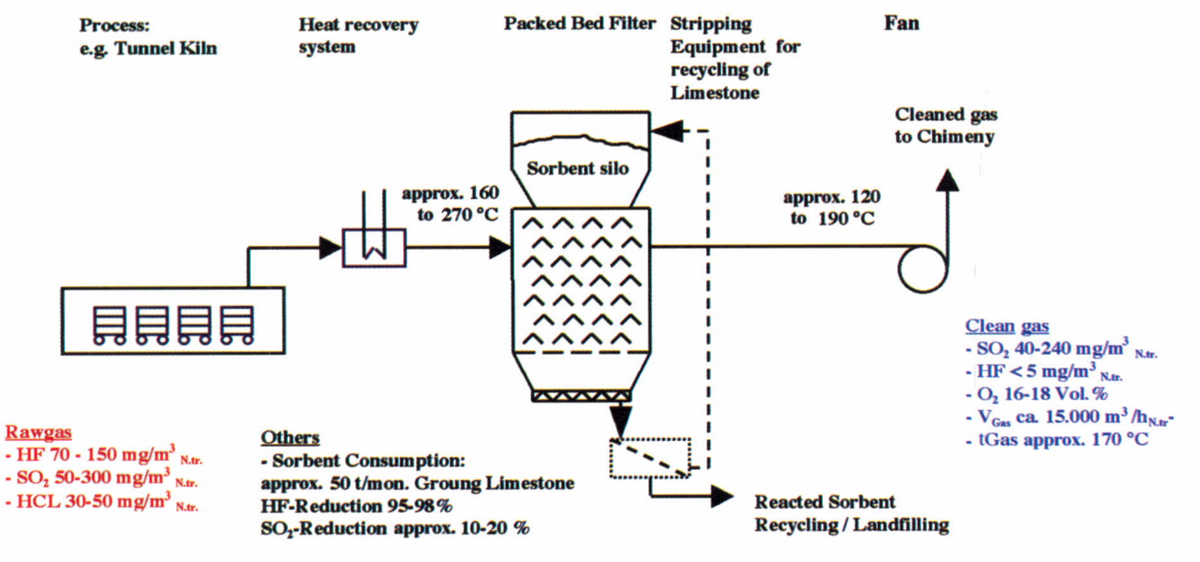

Figure 8. Conventional packed bed filter with ground limestone

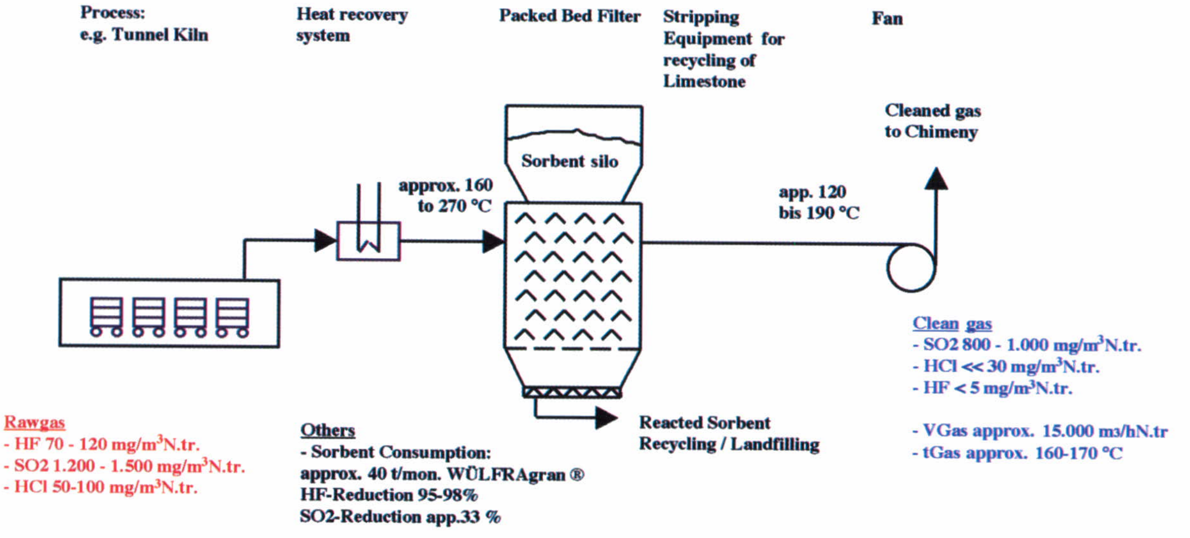

Figure 9. Conventional packed bed filter with granulated sorbent

In this example, HF is removed <5 mg/m³N though SOx and HCl are present with high concentrations in the raw gas. Also HCl, which 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 approx. 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 have been installed for high performance reduction of SO_x. They have enabled reducing sulphur oxide below 500 and even 300 mg/m³N!

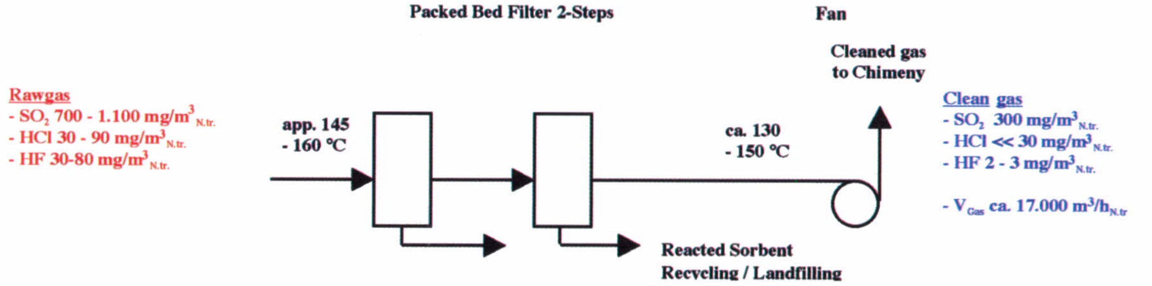

Figure 10. Multistage packed bed filter systems (2-stage)

Figure 10 shows the performance of a 2-stage system operating in France. Reduction rates of approx. 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 has been operating for 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

WÜLFRAgran, depending on the load of SO_2 in the raw gas. The consumption is adjusted daily to the mandatory emission limit. This guaranties an optimal load of acid gas on the sorbent.

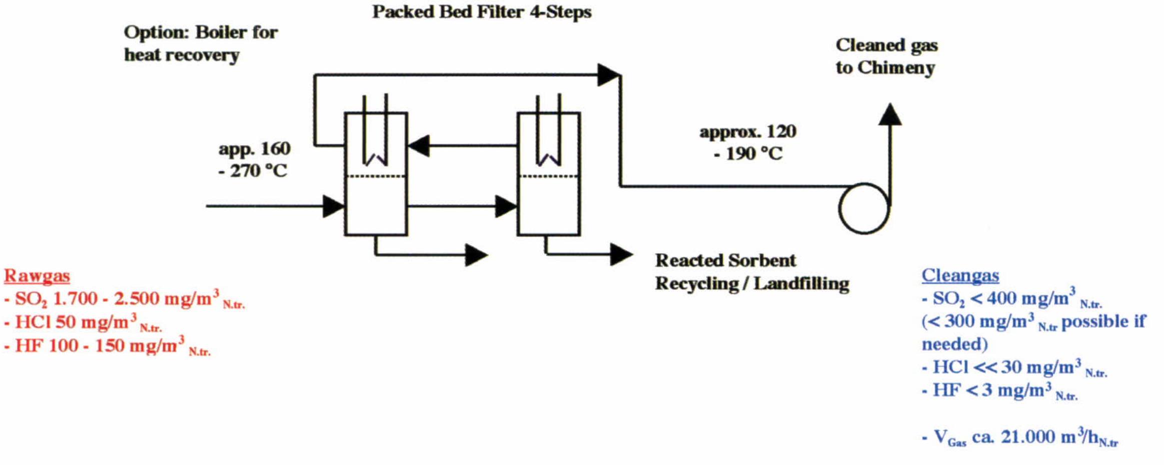

Figure 11. 4-stage packed bed filter system with temperature management

With this PBF system, reductions of 76-84 % of SO_2 and 97-98% of HF are achieved. These systems are very reliable and allow a safe and stable process.

3.2 DRY SORPTION WITH BAGHOUSE FILTERS

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

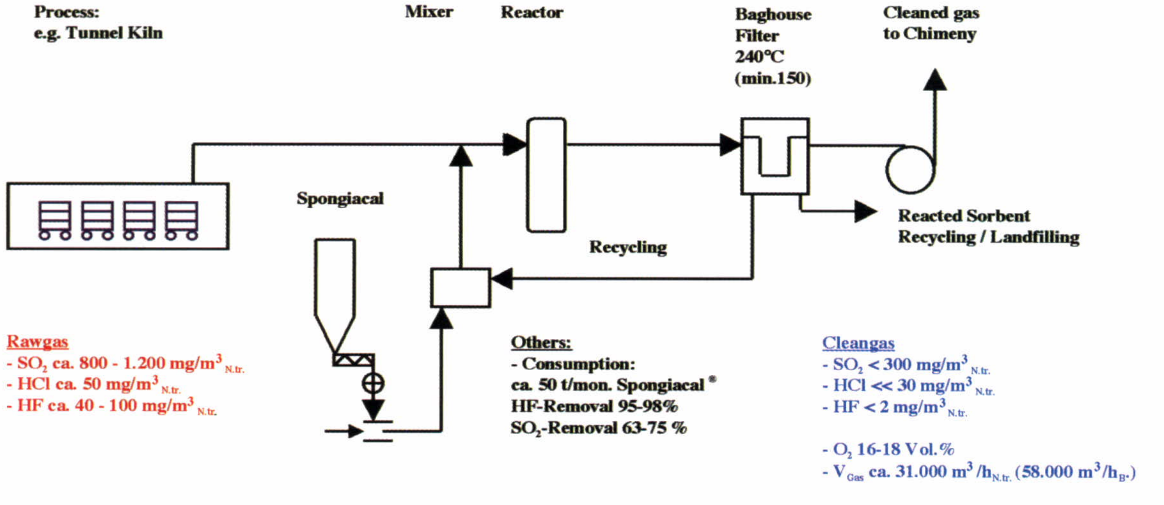

Figure12. Dry sorption with fabric filter Type KHD-R

The plant operates with injection of the high surface area hydrate Spongiacal in the duct. In a 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 approx. 240°C. By this process, a consumption of only approx. 75 kg/h Spongiacal is needed. With this baghouse filter sorption system, reductions of 63 - 75% of SO_2 and 95-98% of HF are achieved.

A trial with normal hydrated lime was carried out and this 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 filter (PBF or Kiesbedfilter) represents a technique outstandingly adapted to the needs of the operator. These systems can be run with ground limestone in many cases, if the demanded removal rates and load of other compounds than HF, e. g. sulphur oxide or HCl are low. The PBF systems can be increased in their performance by using optimised granulated sorbents. 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 filters, are used successfully in practice and lead to good solutions in a commercial sense. In both processes advanced products on a lime base as granulated sorbents or high surface area hydrates considerably improve the efficiency. These types of sorbents are often used, as they:

- Increase the removal efficiency and ability of dry sorption (Safe operation)
- Permit the installation of less expensive flue gas treatment technique (Low investment)
- Minimise sorbent consumption 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 Directive are observed.
- In practice, it has been demonstrated that the use of optimised sorbents for flue gas treatment reduces operating materials consumption by more than half.
- This gives corresponding reductions in the amount of waste.

- According to currently available operating experience, the use of granulated sorbent 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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