OPTIMIZATION OF SNAP

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Abstract

The SO_2, NOx Adsorption Process (SNAP) is a dry combined SO_2 and NOx removal process using a regenerable sorbent. The only products from SNAP is nitrogen and sulfur. Removal of SO_2 and NO_x from the flue gas is performed in the riser type adsorber. The regenerable sorbent is composed of a high surface area γ-alumina impregnated with sodium. Regeneration of the sorbent include heating the sorbent to approximately 600°C and treating it with a reducing gas and steam. The objective of this project is to optimize the SNAP with respect to the performance of the adsorption and regeneration processes.

Investigation of the adsorption chemistry and kinetics in a fixed bed plug flow reactor system using step experiments concluded in a proposed mechanistic model for the simultaneous adsorption of SO_2 and NOx. A window of SOx/NOx ratios is found in which the simultaneous adsorption of SO_2 and NOx is the most effective. This can be explained by the character of the NO adsorption, that, at the same time, is both sequential and competitive with the SO_2 adsorption.

10 different reducing gasses is tested at different temperatures in a laboratory scale fluid bed regenerator. The tests revealed that the regeneration consist of two separate mechanisms leading to SO_2 and H_2S respectively. Good regeneration performance was obtained using CO and hydrogen/CO mixtures, but these reducing gasses rely heavily on the steam treatment step.

Testing of different methods for production of sodium impregnated sorbents lead to the conclusion that impregnating a bulk alumina with Na-acetate to approximately 5 % Na lead to a sorbent that was fully comparable to commercial available sorbents.

For optimal design and operation of the GSA a 3-D simulation taking the adsorption into account must be performed. The equation for this is defined and programmed. For the simulation of the riser adsorber a Eulerian-Eulerian approach is taken. The particles are handled as a continuous phase, the solid phase, which interacts with the gas phase through three mechanisms: gas-solid drag plus mass and heat transfer between phases. A dual time stepping method and a finite volume technique are used for the integration in time and space, respectively. The integration scheme is based on point Gauss-Seidel relaxation.

1 Project partners

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2 Objectives of the project

2.1 Description of the SNAP process

The $\underline{S}O_2$, $\underline{N}$Ox $\underline{A}$dsorption $\underline{P}$rocess (SNAP) is a dry combined SO_2 and NOx removal process using a regenerable sorbent. The only products from SNAP is nitrogen and sulfur. Removal of SO_2 and NO_x from the flue gas take place on a sorbent in the adsorber. The regenerable sorbent is composed of a high surface area γ-alumina substrate impregnated with sodium. In this sorbent γ-alumina provides the structural strength essential for attrition resistance, while sodium increases adsorption capability.

The major components of SNAP are shown schematically in Figure 1 and include the Gas Suspension Adsorber (GSA), sorbent heater, regenerator, sorbent cooler and Claus unit.

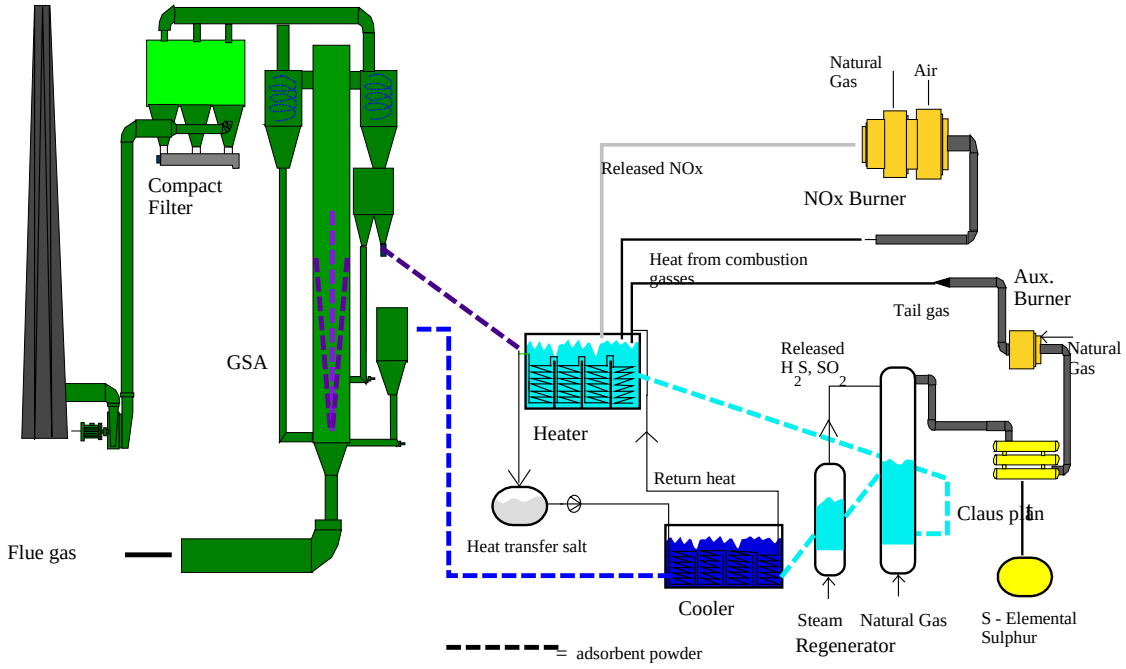

Figure 1: Schematic process description of the SNAP

2.1.1 Gas Suspension Adsorber (GSA)

The flue gases from a coal burning power plant are introduced into the GSA reactor downstream of the plant's particulate control unit. The GSA reactor comprises a riser with a conical inlet, cyclones for primary gas-solid separation and means for solid recirculation to the bottom of the riser. Flue gas enters the reactor through the conical inlet at the bottom and gets into contact with suspended sorbent which adsorbs SO_2 and NO_x. The GSA reactor design allows for a high flue gas velocity, a high gas-solid contact time at a relatively low pressure drop. The sorbent entrained in the flue gas is separated in the cyclones and is recycled to the bottom of the reactor. The recirculation of the sorbent allows its relatively high concentration in the reactor which together with high flue gas velocity results in high mass transfer rates.

Fine sorbent entrained in the flue gas exiting the GSA cyclones are removed in a particulate control unit and returned to the process. Clean flue gas proceeds to the stack from where it is released into the ambient air.

2.1.2 Sorbent heater/cooler

The sorbent heater and cooler represent the first and last stage of the sorbent regeneration system. A slip stream of loaded sorbent from the GSA cyclone recycle loop and sorbent collected in the particulate control unit are introduced to the heater via a pneumatic transporter. The amount of sorbent entering the heater depend on the amount of SO_2 and NO_x adsorbed in the GSA.

The sorbent heater is a multistage fluidized bed where sorbent is heated by indirect heat transfer from heating coils immersed in the fluidized bed. The heat added in the heater is taken from the sorbent in the sorbent cooler which also is a multistage fluidized bed, with cooling coils immersed in the fluidized bed, for cooling the regenerated sorbent.

During the process of sorbent heating to the regeneration temperature (app. 550^{o}C-620°C), all NO_x adsorbed on the sorbent is released. Since the fluidized bed sorbent heater is operated at low air velocity, the total volume of this NO_x bearing stream is relatively small. The NO_x in this air stream is reduced to N_2 and O_2 by staged combustion in the NO_x destruction burner.

2.1.3 Regenerator

The sorbent regenerator is a two-stage fluidized bed. In the first stage the heated sorbent is contacted with a reducing gas, which also serves as the fluidization medium. The chemisorbed SO_2 on the sorbent reacts with methane and is released in the form of SO_2 and H_2S. Some sulfur compounds produced in the first stage of the regeneration is afterwards released by steam hydrolysis in the second stage to regain the original active adsorption sites for reuse in the GSA.

2.1.4 Claus unit

The first step in the Claus process is cooling of gases from the regenerator to about 220^{o}C so that sulfur can be produced in the catalyst bed. The stoichiometry in the catalyst bed is controlled by air addition while the outlet temperature is controlled by recycle. The sulfur produced in this catalytic stage is condensed by cooling. The gases are then re-heated and passed to a second catalyst bed. If the H_2S content is too low, part of the gas is passed through the hydrogenation step where reducing a gas is introduced in front of the hydrogenation reactor.

The tail gas from the Claus process is passed through an incinerator to convert all remaining sulfur compounds to SO_2. The gas is then cooled and recycled to the flue gas stream entering the GSA.

2.2 Project objectives

The overall objective of the project was to optimize the SNAP process with respect to performance and thus economic profitability. Five areas of potential improvement was specified. These five areas are each covered in one of the work packages that the project was divided into:

Work package 1: Sorbent chemistry and kinetics
Work package 2: Sorbent loading
Work package 3: Alternative regeneration gasses
Work package 4: SO_2/NOx removal model
Work package 5: Riser and fluid bed hydrodynamic model

2.2.1 Work package 1: Sorbent chemistry and kinetics

The main objective in this work package is to obtain a better understanding of the adsorption chemistry in the process. The increased knowledge can be used for optimization of the adsorber process conditions and as a basis for structured studies regarding construction of an improved sorbent. Finally the sorbent chemistry and kinetics will be used in the fluid dynamic modeling of the GSA adsorber in work package 5.

2.2.2 Work package 2: Sorbent loading

The sorbent used in the process is a mayor economic factor in the SNAP process. Improving the potential sulfur loading capacity will both decrease the cost of the sorbent load, but will

also decrease the size of the equipment in the regeneration cycle. The objective of this work package is therefore to improve the sorbent with respect to sulfur loading capacity under the constraint that the NOx adsorption must be maintained.

2.2.3 Work package 3: Alternative regeneration gasses

Regeneration of the spent sorbent is another mayor cost in the SNAP process. This is due to the high regeneration temperature (above 600°C) of the sorbent when natural gas is used. The objective of this work package is to obtain a relation between the regeneration gas and the temperature at which the regeneration do occur. This must be done by performing experiments using different regeneration gases at different regeneration temperatures.

2.2.4 Work package 4: SO_2/NOx removal model

The removal efficiency of SO_2 and NOx in the GSA depend upon several process operational parameters such as pressure drop across the adsorbed (= sorbent load in the adsorber), temperature, gas flow rate, solid recirculation rate, SO_2/NOx concentration ratio and others. It is of great importance that a good empirical model for estimation of the removal efficiencies are known in order to optimize the process control of the adsorber operation. This work package has the objective to develop an empirical model for the SO_2 and NOx removal efficiencies for the SNAP.

2.2.5 Work package 5: Riser and fluid bed hydrodynamic model

The objective of this work package is to develop a hydrodynamic model for the riser adsorber in the SNAP process. The model should incorporate the gas and solid flow in the reactors and can be used in the optimization of the design of the reactors.

3. Technical description

The technical description presented in this chapter is divided based on the work packages already described in this report.

3.1 Work package 1: Sorbent chemistry and kinetics

The adsorption is studied by means of step experiments in a fixed bed plug flow reactor. The concentration of all components are measured in time immediately up and downstream of the sorbent bed. A quadrupole mass spectrometer is used. The inlet step is created by switching a four-way valve. The pressure at both inlets of the four-way valve are equalized using a metering valve.

The principle of the experimental setup is shown in figure 2.

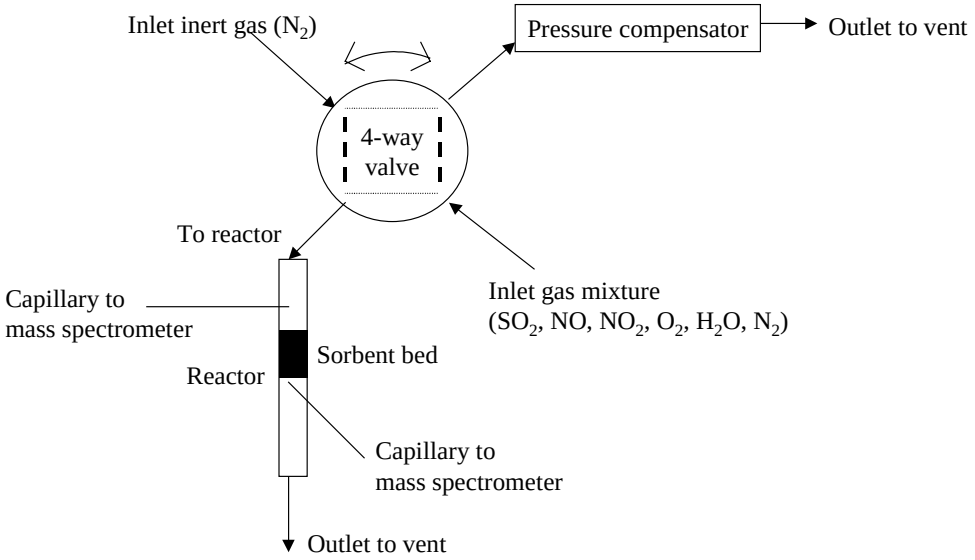

Figure 2: Experimental setup.

The experimental setup consists of a feeding system, the reactor section, and the analysis section. The feeding system includes pressure-regulators, a flushing system, mass flow controllers, safety valves, a mixer, a water feeding pump, an evaporator, and the four-way step-valve. This four-way valve is equipped with the High Speed Switching Accessory activated by Helium, allowing very fast switches of the valve. The reactor is build into an air-circulated oven together with the step-valve. The oven and the reactor are equipped with several thermocouples. The reactor is build in boro-silicate-glass, an inert material, and a thin quarts filter is build in to serve as a carrier for the sorbent bed. The feeding lines from the step valve to the reactor are also in inert material. The reactor is equipped with two sample points for the capillary of the mass spectrometer: one before the sorbent bed, and another right after the bed. For the analysis a fast Balzers Thermostar mass spectrometer is used. It allows a fast measurement of the concentration of several selected components in time. The outlet parallel to the reactor outlet is equipped with a metering valve used to compensate the pressure drop over the sorbent bed.

3.2 Work package 2: Sorbent loading

This work package was divided into two sub tasks. The first task was to produce and evaluate a number of sorbents in to find the best impregnation method, whereas the second task was to test commercial available aluminas using the production method found in the first part.

The sorbents are produced using the following procedure.

- An impregnation salt is dissolved in water. The amount of impregnation salt used is calculated in order to result in the target load of the impregnation agent.
- High quality laboratory grade γ–alumina is added to the liquid and the mixture is stirred until a slurry is formed.
- The slurry is dried in the oven at 110°C for 5 hours.
- The dried slurry is afterwards calcined at 450-650°C for approximately 5 hours.

All adsorption performance tests are performed in a fluid bed laboratory reactor. The temperature in the tests is 100°C and the gas concentrations are approximately 2500 ppm SO_2, 300 ppm NO , 3 % O_2, 3 % CO_2, 15 % H_2O and balance of nitrogen. The gas concentrations were before each experiment measured through a bypass of the reactor so that the gas inlet concentrations were known for the specific experiment. All gas analysis is performed using a Mass Spectrometer.

3.3 Work package 3: Alternative regeneration gasses

An experimental setup consisting of a fluid bed regenerator is constructed including complete downstream gas analysis using mass spectrometry to evaluate the sorbent regeneration performance. The data analysis consist of sulfur reduction profiles that are based on the actual realized sulfur reduction combined with the distribution of sulfur reduction over time. This sulfur reduction distribution is estimated based on the measured off-gas profile and the off-gas flows. 76 regeneration experiments were performed in order to evaluate 10 different regeneration gasses at varying temperatures.

3.4 Work package 4: SO_2/NOx removal model

Control of the process operating parameters in the adsorption unit of the SNAP is important in order to operate the SNAP plant as efficient as possible. The operating parameters must be determined based on several input variables regarding flue gas flow and composition etc. The first step in this work is to develop a good empirical model that ties the input variables, the process operating parameters and the process output (Removal efficiencies) together. It was decided that the model should be approached based on two separate parts:

A) Investigation of the physical flow of sorbent particles in the GSA based on flow experiments in the pilot scale GSA

B) Investigation of the adsorption performance under altering chemical process conditions based on laboratory scale adsorption experiments.

Experiments performed at the SNAP pilot plant in order to gain knowledge about the flow of sorbent particles in the GSA include:

1. Tracer tests
2. Batch loading of sorbent
3. Clean gas pressure measurements
4. Measurement of particle densities in the GSA
5. Continuos collection of pressure profiles along the vertical axis of the GSA at different operating conditions.

Experiments performed in a laboratory scale reactor to investigate the effect of the input variables on the adsorption behavior of SO_2 and NOx included testing of the following parameters:

1. Temperature
2. SO_2/NOx concentrations
3. Oxygen content
4. Water content

3.5 Work package 5: Riser and fluid bed hydrodynamic model

Adsorption of SO_2 and NOx is performed in a Gas Suspension Adsorber (GSA). For optimal design and operation of this GSA, a 3-D simulation taking the adsorption into account must be performed.

The objective of this work package is to perform a complete simulation of the GSA. The GSA reactor is shown in Figure 3. The reactor has a conical bottom part. Gas is fed through a bottom inlet pipe. Sorbent particles are fed from three inlet pipes at the reactor wall. Two of them feed sorbent recycled from the reactor outlet. One inlet tube feeds fresh regenerated sorbent.

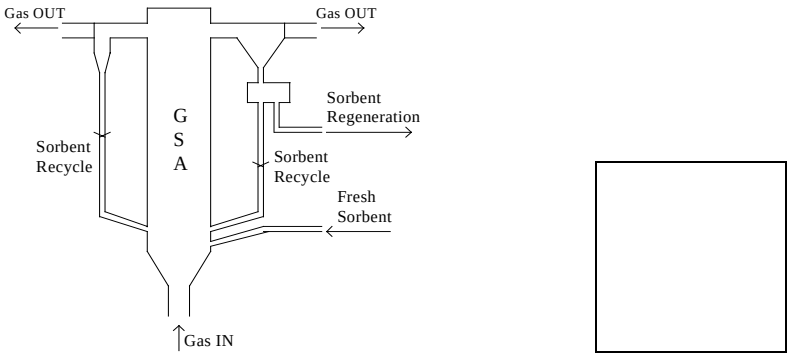

Figure 3 The GSA reactor

For scale-up and optimization of the reactor, a detailed simulation is required. The positioning and character of the different feeding pipes explicitly requires a 3-D simulation. Furthermore,

flow field and adsorption reaction influence one another. Therefore flow field and composition calculations are coupled.

This work do include setting up all the equations that describe the physical phenomena in the GSA, but also finding an appropriate integration scheme that can solve the equations.

4. Results and discussion

The following pages will summarize the conclusions from each of the work packages.

Work package 1: Sorbent chemistry and kinetics

The main objectives of this work package was to investigate the chemistry and kinetics of the simultaneous adsorption of SO_2 and NOx. An experimental technique has been developed for the determination of the mechanism and kinetics of the simultaneous adsorption of SO_2 and NOx. Experiments have been performed for several SO_2/NOx-ratios and the influence of O_2 has been investigated. A mechanism is proposed that is able to explain the experimental results. A window of SOx/NOx ratios is found in which the simultaneous adsorption of SO_2 and NOx is the most effective. This can be explained by the character of the NO adsorption, that, at the same time, is both sequential and competitive with the SO_2 adsorption. A simulation program for the experimental reactor was written and coupled to a Marquard optimization procedure. The estimation of the kinetic parameters and the model discrimination has started.

Work package 2: Sorbent loading

The main objective of this work package was to develop a new or cheaper sorbent to be used in the SNAP. For this purpose 14 sorbents were produced from pure γ-alumina and they were all tested for adsorption performance. The studied sorbent preparation parameters are: impregnation load, sodium counter ion, calcination time and calcination temperature

Testing of these sorbents revealed that the best performance was obtained by impregnating to approximately 5 % Na using Na-acetate as impregnation chemical, while the calcination procedure, that was found to be without effect on the adsorption performance, was fixed at 550°C for 5 hours.

Testing was then directed towards an inexpensive bulk alumina carriers in order to investigate the performance of these materials. This carrier was impregnated using the above mentioned method and tested for three cycles of adsorption and regeneration. This testing showed a performance that is comparable with the commercial available sorbents, mainly because the deactivation of the impregnated bulk alumina was not seen in the first three cycles.

Work package 3: Alternative regeneration gasses

The regeneration constitute a large part of the cost in the SNAP due to the high temperature required to obtain a good regeneration. The objective of this work package was to investigate the use of different regeneration gasses.

The experimental work was performed in a laboratory batch scale regenerator that strongly differed from the actual flow reactor, and it has not been possible to obtain results that exactly match the data from the pilot scale regenerator. The trend in the experiments do however simulate start up gas profiles from the SNAP pilot plant , which validates that the same reactions do occur.

There seem to be 2 distinct mechanisms. An initial mechanism that lead to SO_2 followed by a second mechanism that is characterized by a high CO_2 production that lead to H_2S.

10 different gases were all tested in the experimental setup. The following conclusions are drawn form the experiments.

Methane, Ethane and propane show very similar behaviors including the above mentioned double mechanism. The regeneration rates increased in the row methane-ethane-propane, but the activation energies seem to be similar for the three gasses. The results from butane regeneration was very limited by the fact that the gas-cylinder used only contained 10 % butane, and no estimation of the regeneration rates are determined for butane. Heavy coking stop the regeneration for octane and decane, and even burning of the coke cannot restart the regeneration. These components are therefore considered to be without interest for the regeneration in the SNAP.

Hydrogen also show a two mechanism behavior. Comparing the hydrogen regeneration rates with the rates of the hydrogen/CO mixtures show that the hydrogen/CO mixture behave like the second hydrogen mechanism, but that the rates are considerable higher for the mixture which proves high performance of CO present in the gas. CO seem to be a very interesting reducing agent, but using CO seem to leave a large part of the sulfur on the sorbent as H_2S or Sulfur that only can be removed by steam treatment.

Based on the above findings no conclusion regarding the optimal regeneration gas is found. The investigation did however led to the conclusion that hydrogen/CO mixtures from reforming or gasification seem to be a very attractive regeneration gas mainly due to the CO content.

Work package 4: SO_2/NOx removal model

The main objective of this work package was to develop an empirical model for the determination of the adsorption performance given the process conditions. No total model is predicted due to limited results from the SNAP pilot plant. A model is derived based on particle flow experiments for the particle density in the GSA based on the gas flow rate, the pressure drop across the GSA, the GSA dimensions and the gas properties. Chemical testing in a laboratory scale reactor have shown that the main affecting parameter is the sulfur load on the sorbent, which implies that the main parameter that can be controlled in future adsorption units is the feeding rate of fresh sorbent to the GSA. An increased ratio of SO_2/NO strongly increases the NO adsorption performance up to a SO_2/NO ratio of about 4 to 5, which is in good agreement with the results in work package 1.

An increase in the water concentration also lead to a higher adsorption performance and seem to result in stronger binding of especially NO to the surface of the sorbent. The effect of temperature upon the adsorption performance is difficult to determine since the SO_2 adsorption performance is strongly affected by the presence of the NO break through that vary great with temperature. It can however be found that the NO adsorption performance do decrease by an increased temperature, and that basically no NO removal will occur for temperatures above 200°C.

Work package 5: Riser and fluid bed hydrodynamic model

For the simulation of the riser adsorber a Eulerian-Eulerian approach is taken. The particles are handled as a continuous phase, the solid phase, which interacts with the gas phase through three mechanisms:

- gas-solid drag
- mass transfer between phases, and
- heat transfer between phases.

Because SO_2 and NOx adsorption influences the physical properties that govern the flow, the continuity equations for all components are considered in the equation set. A dual time stepping method and a finite volume technique are used for the integration in time and space, respectively. The integration scheme is based on point Gauss-Seidel relaxation. The inviscid fluxes are split into convective terms which are treated upwind following the value of the advective velocity, and pressure flux terms which are governed by the acoustic wave speeds of the gas phase and split using weight factors based on the polynomial expansion of the characteristic speeds. The viscous fluxes are calculated following a central scheme. The source terms in the turbulence equations are split into a positive and a negative part, calculated at different iteration levels. The gas-solid interaction and reaction terms are treated similarly.

5. Exploitation plans and anticipated benefits

No new items for exploitation have directly been developed, however a possible exploitation is using an inexpensive bulk alumina sorbent impregnated to 5 % Na as SNAP sorbent if the sorbent proves to be attrition resistant. This can have a large economic impact on the SNAP.