Evaluation of Concepts for secondary SO$_x$ and NO$_x$ Removal from the Oxy-Fuel Process

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The oxy-fuel process is a promising technology for capture of CO_2 from coal fired power plants. This work investigates and compares two concepts for secondary SO$_x$ and NO$_x$ removal in their application in flue gas treatment for oxy-fuel combustion: Absorption based removal utilizing the Lead-chamber-process (LCP) and removal by distillation. Since these concepts are not suitable for flue gas treatment in air combustion, there is little information available in the literature. The LCP concept is modelled as a plug flow reactor implementing known reaction rates and the distillation concept is evaluated with an equilibrium based model applying the Peng-Robinson equation of state. Theoretically, both concepts achieve high removal efficiencies of SO$_x$ and NO$_x$ from the flue gas in the oxy-fuel process, but a high removal efficiency of SO$_x$ by distillation is associated with large energy requirements. The NO$_x$ removal in the LCP concept is limited by its absorption mechanism with a possible reduction of about 80-85%. In the distillation concept 3-8 % of all NO$_x$ is lost in form of NO as non-condensable gas. In comparison to the LCP concept, the distillation concept has a higher power demand and a lower SO$_x$ removal efficiency. Yet, beside a higher NO$_x$ removal rate, distillation has the advantage of being a mature technology.

Introduction

The oxy-fuel (O_2/CO_2) combustion process is a technology for carbon capture from coal fired power plants. Figure 1 shows the basic principles of the oxy-fuel process with a wet and low-dust flue gas recycle. In the boiler, coal is combusted in a mixture of high-purity oxygen, (>95%) produced in an air separation unit (ASU), and recirculated flue gas to achieve combustion and heat transfer conditions similar to air combustion [1]. Typically, about ⅔ of the total flue gas volume is recirculated after particle removal (A in Figure 1).

The flue gas stream consists mainly of CO_2 and has about ¼ of the volume flow in air combustion, due to the separation of airborne N_2 in the ASU. The main part of the water is removed by condensation during the first compression step, which is part of the liquefaction process (B). The water concentration is further decreased by absorption (C) to avoid acid formation. The dry flue gas is cooled to liquefy the CO_2 and separate the non-condensable gases O_2, N_2 and Ar (plus NO) (D). SO$_x$ and NO_2, which is the major NO$_x$ species under the present process conditions, stay, if not removed before, with the CO_2.
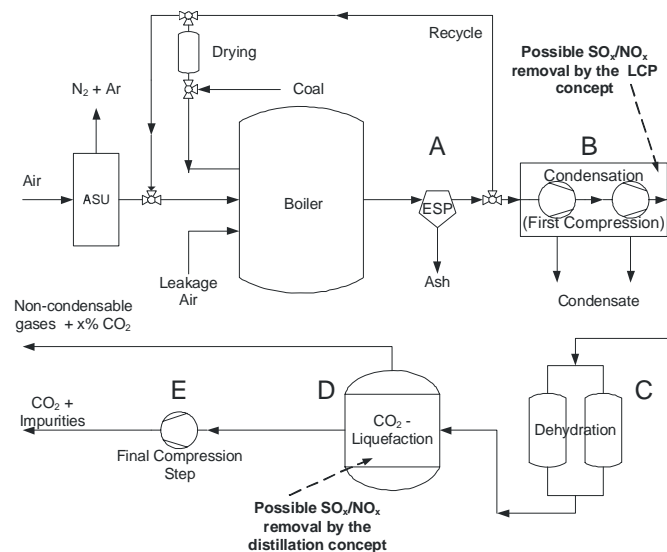

Figure 1: The oxy-fuel process with positions for SO$_x$/NO$_x$ removal concepts.

The removal of SO_x and NO_x is the focus of this work. The concentrations of SO_x and NO_x in oxy-fuel flue gas are higher than in an air-fired plant, due to decreased flue gas volume [2]. However, the emissions of SO_x and NO_x are lower per unit energy supplied [2, 3] due to an observed reduction associated with the recycling of those components together with the main recycling flow. Different process designs have been proposed for removal of SO_x and NO_x in the oxy-fuel process. Kather et al. [1] suggest a conventional selective catalytic reduction (SCR) unit and the installation of a conventional limestone scrubber as flue gas desulfurization unit (FGD) to reach the EU emission limits of 200 mg/m_N^3 NO_x (180 ppm) and 200 mg/m_N^3 SO_x (85 ppm) [4]. These numbers for air combustion are used here, since there is yet no consensus on future legislative regulations for the higher concentrations in the reduced flue gas volume from CO_2-capture by oxy-fuel combustion. Taking the reduction in flue gas volume into account, future regulations based on absolute emissions (in mg/MJ) might be expected, which would correspond to higher concentration limits.

However, the elevated pressure and low temperature of the CO_2 conditioning train in the oxy-fuel process enable two other possibilities for flue gas cleaning of SO_x and NO_x: Absorption, based on the Lead-chamber-process (LCP), and, removal based on distillation. Both processes are indicated in Figure 1 with their respective position in the process.

In combination with the oxy-fuel combustion process, the LCP concept was first proposed by Allam et al. (2007) [5]. The main idea originates from the former Lead-chamber-process for production of sulfuric acid from gases containing relatively high concentrations of SO_x. The process employs three reactors, operating at ambient pressure. Such a process is proven for flue gas flows in the scale of 10,000 m_N^3/h and with SO_x concentrations down to 0.5 mol% [6]. With the conditions in the flue gas treatment of the oxy-fuel process, the absorption process of SO_x can be simplified and performed in a single absorption column [5]. According to Allam et al., almost all SO_x in the flue gas can be removed as sulfuric acid (H_2SO_4) together with the condensation of water in the flue gas treatment (B in Figure 1), whereas ~90% of the NO_x can be removed as nitric acid (HNO_3).

The concept of SO_x and NO_x removal, based on distillation, was first presented in [7]. According to the authors, SO_x and NO_2 can be removed as liquid product in a distillation column downstream the removal of non-condensable gases (D in Figure 1). In a cost analysis of CO_2-capture by oxy-fuel combustion, the International Energy Agency (IEA) [8] mentions that, in future work, the distillation concept should be further evaluated, since the concept has not yet been experimentally tested. In [9], ongoing construction of a pilot plant is indicated.

Independent of the open questions of legislative or technical necessity for SO_x and NO_x removal, this work evaluates the performance of the LCP and the distillation concept for SO_x and NO_x emission control in the oxy-fuel process. In order to compare the two concepts by modeling, information on the reaction rates behind the LCP concept had to be gathered from different literature sources, since in previous work [5] a complete quantitative description of the reaction mechanism was not presented. For the distillation concept, recently published thermodynamic property data has been used to describe the phase equilibria between CO_2 and its impurities in the process modeling. Thus, the new models that have been employed in the present work reveal the influence of changes in pressure, temperature and concentrations on the performance of the processes in both concepts. Furthermore the separation efficiency, the energy requirement, the influence on CO_2 capture rate and critical or limiting factors in the processes are identified, making it possible to compare the concepts on a technical level.
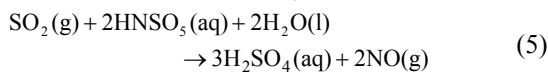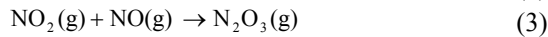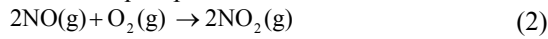
Theory

The LCP Absorption Mechanisms

In the flue gas from combustion processes, SO_2 is the major SO_x species. The solubility of SO_2 in water-based liquids is low, but it is significantly higher for higher oxidized sulfur species. The reaction mechanism for SO_2-absorption in the LCP concept is described by the overall reaction [6, 10]:

$$2NO_2(g) + 2SO_2(g) + 2H_2O(l) + O_2(g) \rightarrow 2H_2SO_4(aq) + 2NO_2(g) \quad (1)$$
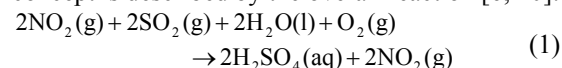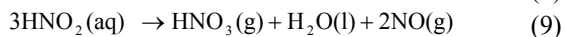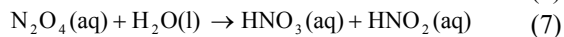
The direct gas-phase oxidation of SO_2 by O_2 is slow [11] (typically about 1% of SO_2 is converted to SO_3 in flue gas from air combustion [12]). Reaction 1 shows that NO_2 acts as a catalyst in the oxidation and absorption of SO_2, but this effect can not be

explained with the gas-phase oxidation of SO_2 by NO_2, which has a slow reaction rate [13], not sufficient to complete the SO_2-absorption process at a reasonable residence time. Previous experimental work [14, 15] has shown that SO_2, slightly dissolved in sulfuric acid, oxidizes in a fast liquid phase reaction since the available dissolved nitric oxides act as catalyst. This reaction path is represented by Reactions 2 to 5, including both gas-phase and liquid-phase reactions.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \qquad (2)$$

$$NO_2(g) + NO(g) \rightarrow N_2O_3(g) \qquad (3)$$

$$N_2O_3(g) + 2H_2SO_4(aq)$$
$$\rightarrow 2HNSO_5(aq) + H_2O(l) \qquad (4)$$

$$SO_2(g) + 2HNSO_5(aq) + 2H_2O(l)$$
$$\rightarrow 3H_2SO_4(aq) + 2NO(g) \qquad (5)$$

In Reaction 2, NO is oxidized to NO_2. The latter reacts with NO in Reaction 3 to yield N_2O_3. In sulfuric acid with a concentration higher than 52 wt%, the absorption of N_2O_3 starts to increase due to the immediate reaction with the sulfuric acid to $HNSO_5$ (nitrosulfuric acid) (Reaction 4) [14]. The nitrosulfuric acid oxidizes the partially dissolved SO_2 in the fast liquid phase Reaction 5, with H_2SO_4 as final product [15]. A concentration of 70-80 wt% H_2SO_4 is desirable [6, 10]. At lower concentrations, $HNSO_5$ is unstable and reactive and at H_2SO_4 concentrations above 80 wt% problems with crystallization start to occur [6]. The concentration of the produced acid is adjusted by the amount of water entering the SO_2-absorption column with the flue gas.

In the NO_x-absorption column the absorption mechanism [16] starts with oxidation of NO to NO_2, Reaction 2. N_2O_3 and N_2O_4 are formed in the gas phase via Reactions 3 and 6, and are absorbed in the liquid phase. Nitric acid (HNO_3) and nitrous acid (HNO_2) are then formed by the hydrolysis Reactions 7 and 8. The formed nitrous acid reacts in a dissociation reaction to yield nitric acid and NO, according to Reaction 9.

$$2NO_2(g) \rightarrow N_2O_4(g) \qquad (6)$$

$$N_2O_4(aq) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq) \qquad (7)$$

$$N_2O_3(aq) + H_2O(l) \rightarrow 2HNO_2(aq) \qquad (8)$$

$$3HNO_2(aq) \rightarrow HNO_3(g) + H_2O(l) + 2NO(g) \qquad (9)$$

Absorption paths of minor importance are the direct absorption of NO and NO_2, gaseous nitrous acid (HNO_2) and nitric acid (HNO_3 (g)) in nitric acid. As long as the absorption of SO_2 is active, only small amounts of NO_x are absorbed [5].

Phase behavior in the distillation column

The gases involved in the flue gas distillation can be classified into three fractions according to the boiling point of the pure substances at ambient pressure, see Table 1. In the flue gas distillation, non-condensable gases (Fraction I) are separated as gases by condensation of CO_2, whereas SO_x and NO_2 are retrieved as liquid product.

Table 1: Flue gas components and their respective boiling temperatures (T_b) ([11, 16]) (I, II, III: non-condensable gases, main product (CO_2) and condensable oxides respectively)

	T_b [°C]	Fraction
N_2	-195.8	
Ar	-185.9	I
O_2	-183.0	
NO	-151.8	
CO_2	- 78.4	II
SO_2	- 10.0	
SO_3	+ 44.8	III
NO_2	+ 21.9	

Method

The reaction rates for the LCP concept are applied in two plug flow reactor models in Matlab [17]. The distillation concept is evaluated in connection with the removal of the non-condensable gases: O_2, N_2 and Ar, in an integrated purification section. For this, the process simulation software Aspen Plus [18] is used, applying the Peng-Robinson equation of state for equilibrium based modeling. In both simulations, a flue gas stream of 125 m_N^3/s (corresponding to an oxy-fuel power plant with about 520 MW gross electricity output) is used. The main components of the flue gas (besides NO_x and SO_x) are CO_2 (89 mol%), N_2 (5 mol%), O_2 (5 mol%) and Ar (6000ppm) (on dry basis). The concentrations correspond to recirculation of ⅔ of the flue gas, a stoichiometric ratio (λ) of 1.15 and an air leakage of 1% [1]. The LCP concept is investigated at SO_x concentrations between 100 ppm, and 10000 ppm while the distillation concept is examined for 700 to 3000 ppm SO_2. The concentration of NO_x is in all simulations of the distillation concept 1000 ppm, as SO_2 concentration is, as discussed later on in this paper, the more decisive factor. In the LCP concept, the inlet NO_x concentration is optimized with respect to residence time in the absorption columns. The SO_x and NO_x concentration in oxy-fuel combustion will depend on the coal type as well as on combustion conditions.
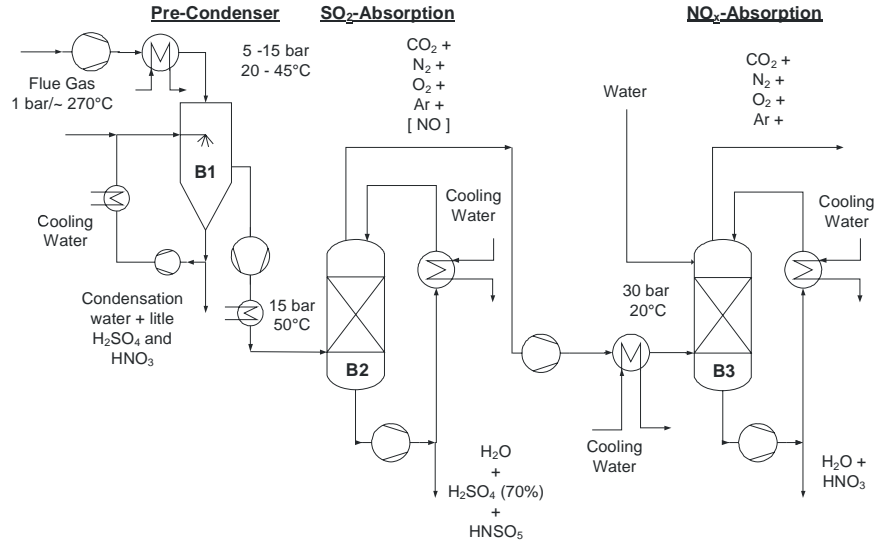
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Figure 2: Absorption of SO_2 and NO_x in packed columns at elevated pressure and low temperature. Based on the process suggested in [5].

Model of the LCP concept

Figure 2 shows the process scheme for the LCP concept investigated in this work, based on the process in [5]. The flue gas enters the purification section at ambient pressure and with a temperature of about 270°C. After adjusting the water balance in a direct contact cooler (B1 in Figure 2), the dried flue gas is further compressed and enters the SO_2-absorption column (B2). The product is concentrated sulfuric acid (70 wt%) including a small fraction of nitrosulfuric acid ($HNSO_5$), *cf.* Reactions 2 to 5. This product is used as absorber and is partly recycled to the top of the column. The recycle is cooled to control the temperature of the exothermic absorption process. The production of a mixture of sulfuric and nitric acids is avoided by adjusting the residence time in this column (B2). Thus, the flue gas leaving the SO_2-absorption column contains almost all initial NO and enters the NO_x-absorption column (B3), after possible further compression with inter-cooling. In this reactor, NO_x is absorbed in a mixture of cooled recirculated nitric acid and water.

The required residence times in the absorption columns are used as measures of the efficiency of the removal processes. In the model of the SO_2-absorption column, the concentrations of $H_2SO_4(aq)$ and $HNSO_5(aq)$ are assumed to be constant, since the liquid to gas ratio is high and the concentrations in the gas phase are relatively low. The concentration of O_2 in the gas phase is assumed to be constant, since it is high compared to the

concentration of NO and SO_2. Table 2 presents the boundary conditions of the simulations.

Table 2: Boundary conditions for feed and liquid recycle in the SO_2-absorption column.

	Feed	Recycle
Flow	125 m_N³/s; 2m/s*	40 l/s; 0.02 m/s*
SO_2	0.01-1 mol%	-
O_2	3 mol%	-
H_2O	1–1.25 mol%**	30 wt%
H_2SO_4	-	70 wt%
$HNSO_5$	-	~ 0.027 wt% [10].

Further varied parameters: NO_x, T and p
* for a surface area a = 100 m²/m³
** adjusted according to the SO_2 inlet concentration (see [19])

Reaction 2 is the rate limiting reaction [20]. It is exothermic and the equilibrium is favored at lower temperature. According to Tsukahara et al. [21] the reaction rate (mol/(l·s)) is expressed by,

$$-\frac{\partial[NO]}{\partial(t)} = 2 \cdot (1200)e^{\frac{530}{T}} [NO]^2[O_2] \qquad (10)$$

where t is the time (s) and T the temperature (K). The reaction rate for Reaction 3 is expressed by,

$$\frac{\partial[N_2O_3]}{\partial(t)} = k_p\left([NO_2]\cdot[NO] - \frac{[N_2O_3]}{K_p \cdot R \cdot T}\right) \quad (11)$$

where k_p is the reaction rate constant (4.75×10^{12} l/(mol·s) [11]) and K_p is the equilibrium constant (Pa^{-1}), which according to [16] is defined as,

4

$$K_p = \frac{pN_2O_3}{pNO \cdot pNO_2} = 65.3 \cdot 10^{-9} e^{\frac{4740}{T}} \qquad (12)$$

The absorption of N_2O_3 is modeled using the two-film theory for mass transfer followed by a subsequent fast surface reaction. The absorption rate of N_2O_3 per unit surface area (mol/(m²·s)), is described as

$$J_{(N_2O_3)} = k_{ag}(pN_2O_3) \qquad (13)$$

where k_{ag} is the mass-transfer coefficient (8.3×10^{-6} (mol/(m²·s·Pa)) of absorption in concentrated H_2SO_4 [22]). Absorption of N_2O_4, NO_2 and NO in H_2SO_4 is insignificant [14] and therefore neglected.

Only a small fraction of the SO_2 is dissolved in the sulfuric acid according to the Henry constant of 1 mol/(l·Pa) (at 70 wt% H_2SO_4) [23]. In the liquid phase, this dissolved SO_2 is immediately oxidized by nitrosulfuric acid according to the reaction rate presented in Martin et al. [15]:

$$\frac{\partial [H_2SO_4]}{\partial (t)} = k_S [H^+]^{1/2} [HNSO_5][SO_2(aq)] \quad (14)$$

where k_S is the reaction rate constant and the product of $k_S \cdot [H^+]^{1/2}$ is 9400 mol/(l·s). Here, it is assumed that in 70 wt% H_2SO_4 all HNO_2 exists as $HNSO_5$.

The reaction rates of the absorption mechanism in the NO_x-absorption column are obtained from [16]. All NO_x entering the NO_x-absorption column is assumed to be NO. This assumption is a worst case scenario for the NO_x-absorption efficiency. The absorption is assumed not to be influenced by anything but the concentrations of nitric species. The liquid flow is sufficiently high for the concentration of nitric acid to be constant at about 45 wt%. A more detailed description of the models used and the reactions mechanisms implemented is available in [19].

Model of the Distillation Concept

On each theoretical plate in the distillation column, equations for mass balance, equilibrium conditions, summation terms and heat balance are solved simultaneously. The system has two degrees of freedom, the reflux-ratio and the reboiler duty. These parameters are adjusted in order to achieve the desired CO_2 and the SO_x/NO_2 capture rate.

The equilibrium concentration in the gas phase is described by the Peng-Robinson (PR) equation of state. The Mathias-Copeman Alpha Function (MC α-function) provides, especially for polar compounds (as SO_2 and NO_2), an accurate fit of the PR equation of state to real phase behavior [24] in the temperature range between the triple point and the critical point. The necessary empiric parameters are taken from Hernández-Garduza et al. [24]. The data for NO_2 was obtained from the model library of Aspen [18]. The empiric binary parameters implemented in the Aspen simulations are presented in Table 3. The remaining binary coefficients are assumed to be zero.

Figure 3 shows the process scheme investigated in this work, which is based on the principle design presented in [7], but with a different heat integration. The temperatures in the process are partly below ambient temperature. The temperature in the first condenser is -55°C to minimize CO_2 losses and to avoid formation of dry ice, which is formed at -56.2C [8]. In the distillation process proposed in [8], the final CO_2 product stream is expanded to achieve the low temperatures required. However, the simulations done in the present work show that the distillation concept is more energy efficient if the gaseous distillates of both columns are pressurized above the initial 30 bar and after inter-cooling expanded in order to get sufficient cooling capacity.

The flue gas enters the purification section at a pressure of 30 bar and a temperature of 20°C (Stream 1 in Figure 2) [8]. The operating parameters for removal of non-condensable gases (D1 in Figure 3) are not varied, because it is not the main focus of this work. D1 has three stages and the temperature of the feed, the reflux and the boil-up (which is the gaseous reflux from the bottom reboiler) is -31°C, -55°C and -27°C, respectively [8].

The CO_2 rich stream leaves D1 as liquid bottom product (Stream 3). It enters the column for SO_x/NO_2 removal (D2) close to the dew point of the mixture. The pressure in D2 is 30 bar in accordance with the conditions suggested in the work on CO_2-capture by oxy-fuel combustion presented by the IEA [8]. The gaseous stream at the outlet of D2 (mainly CO_2) is compressed and condensed. The liquid CO_2 is expanded to the initial pressure of 30 bar, resulting in a temperature of -24°C (Stream 9) close to the dew point. A fraction of the CO_2 product stream is lead back to D2 as liquid reflux. The split fraction or reflux ratio defines the SO_x/NO_2 removal efficiency. The CO_2 product stream is used to cool the incoming flue gas and leaves the purification section at the initial pressure and temperature (30 bar and 20°C).

Table 3: Binary equation of state parameters used.

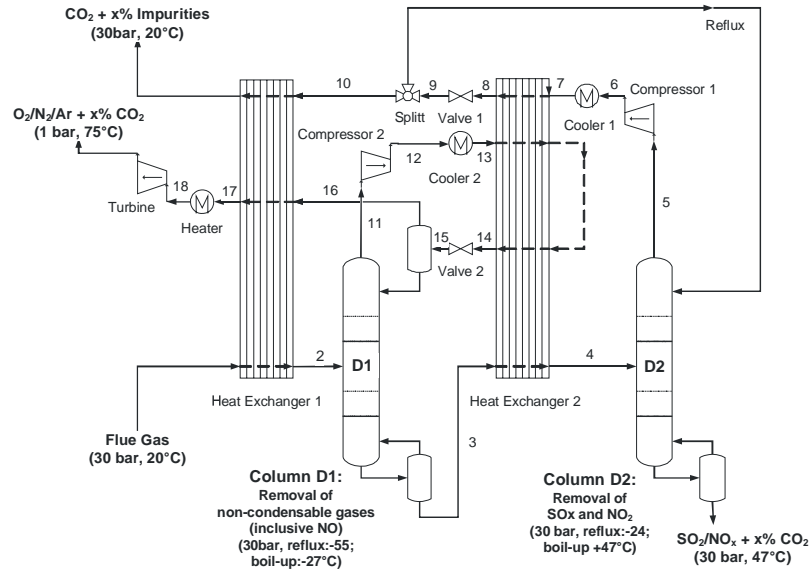|	CO$_2$-N$_2$	CO$_2$-O$_2$	CO$_2$-Ar	CO$_2$-SO$_2$	N$_2$-O$_2$	N$_2$-Ar	N$_2$-SO$_2$	O$_2$-Ar
k$_{ij}$	-0.01493	-0.04838	+0.1427	+0.05585	-0.0119	-0.0026	+0.08	+0.0104
[Ref.]	[25]	[26]	[27]	[27]	[18]	[18]	[18]	[18]

Figure 3: Flow sheet of the distillation based flue gas treatment. The basic concept is based on work presented in [7].

Results

LCP concept

The pressure in the SO$_2$-absorption column (B1 in Figure 2) is an important factor influencing the absorption process. Figure 4 shows that a pressure of 15 bar to 30 bar is sufficient to absorb nearly all SO$_2$ in a residence times below 10 seconds.
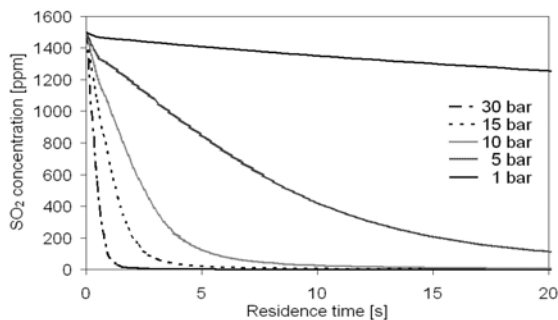

Figure 4: Decrease in SO$_2$ concentration as a function of the residence time in the SO$_2$-absorption column (B2 in Figure 2), (50°C).

At lower pressures, the absorption efficiency is significantly decreased, due to the lower oxidation rate of NO (Reaction 2). The absorption efficiency increases at lower temperature, but temperature is not as important as pressure. The decomposition temperature of HNSO$_5$ (73.5°C) is the upper temperature limit for the absorption process and the lower temperature limit is 19°C where crystallization of HNSO$_5$ starts to occur [14].

Figure 5 shows the required residence time to absorb near all SO$_2$ (rest concentration < 10 ppm). For the different conditions chosen, efficient absorption of SO$_2$ is achieved for 500 ppm and 1000 ppm inlet concentration of NO$_x$ depending on pressure.
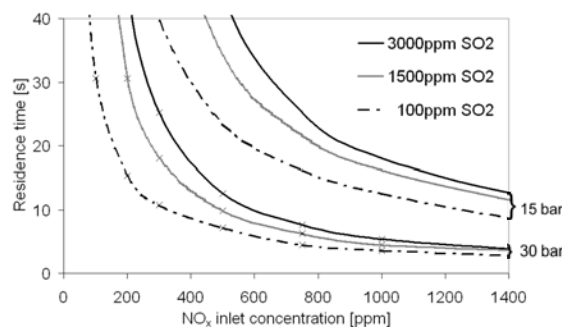

Figure 5: Required residence time in the column for SO$_2$-absorption (B2 in Figure 2) to absorb near all SO$_2$ at different inlet concentrations of NO$_x$ and 15 bar and 30 bar pressure respectively, (50°C).

At lower initial partial pressure of NO the rate of NO oxidation (Reaction 2) is significantly lower and the residence time required increases

correspondingly. The required residence time has also a weak dependence on HNO_3 concentrations.

Figure 6 shows the decrease of NO_x concentration in the gas phase throughout the NO_x-absorption column (B3) for different pressure levels. The NO_x absorption efficiency increases with pressure, but the maximum pressure level is 30 bar because it is the favorable pressure for the downstream removal of non-condensable gases [28].
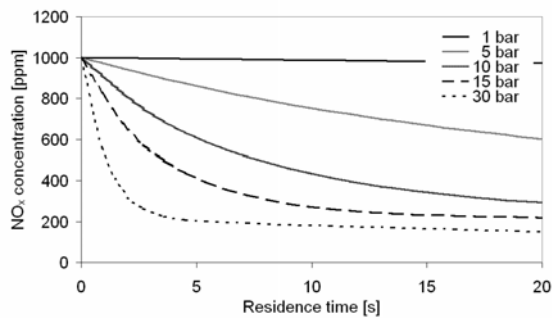

Figure 6: Decrease in NO_x concentration as a function of the residence time in the NO_x-absorption column (B3 in Figure 2), (20°C).

Complete NO_x-absorption is not achievable due to the limiting oxidation rate of Reaction 2, which is to the second power dependent on the NO concentration, but also due to the equilibrium of the absorption as NO is re-emitted in the gas phase by Reaction 9. Figure 7 gives the required residence time to reach the 180 ppm target, for different initial NO_x concentrations (worst case assumption: only NO is available initially).
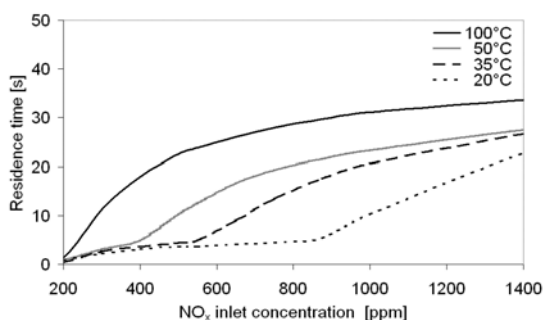

Figure 7: Required residence time in the NO_x-absorption column (B3 in Figure 2) to reach the 180 ppm target at different NO_x inlet concentrations and temperatures, (30 bar).

Increasing temperature leads to increased residence time. With a temperature of 20°C, residence times well below 10 seconds

(corresponding to a reactor volume of 41.5 m³ for 125 m^3_N/s) are possible.

Figure 8 shows the total residence time for both, NO_x- and SO_2-absorption column, as an indication of the investment costs. Higher NO_x concentration leads to an increased residence time for NO_x absorption, but to a decreased residence time for SO_2 absorption. A minimum residence time is reached for an initial NO_x concentration of 750 to 1000 ppm. Absorption of 1000 ppm NO_x to 180 ppm corresponds to a 75-80% reduction and gives about 700 l/h nitric acid while SO_2 is absorbed to almost 100% and gives, in the case of 1500 ppm SO_2, 2500 l/h of sulfuric acid for an oxy-fuel power plant with 520 MW gross electricity output.
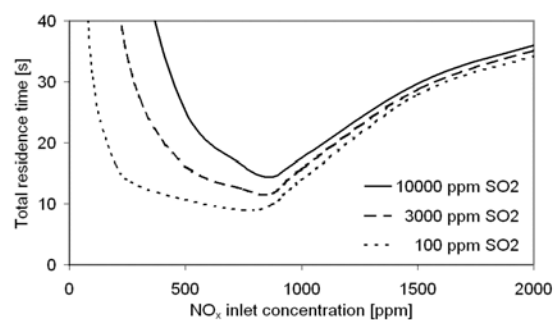

Figure 8: Total residence time for NO_x and SO_2 absorption (at 30 bar, 50°C in column B2; and 30 bar, 20°C in column B3) depending on initial NO_x and SO_2 concentration.

The power consumption of the LCP concept is low: mechanical energy is only needed for the recirculation pumps and to compensate the pressure losses in the columns. Additional cooling is needed at temperatures of 50°C and 20°C to reject the heat of reaction in the absorption columns. Concerning the CO_2 capture rate, simulations of CO_2 solubility performed in the present work, show that the CO_2 losses in the condensation water in the pre-condenser and in the acid streams in the absorption columns are in the order of 0.01 % of the initial CO_2 flow.

Distillation Concept
Simulations of the distillation concept show that a decreased pressure in the distillation column for SO_x/NO_2 removal (D2 in Figure 3) is favorable with respect to the phase equilibria between NO_2 and SO_x and CO_2. Nevertheless, in accordance with the results presented in [8], a pressure of 30 bar is chosen, because reduction in pressure would rise the need for more energy intensive compression for the liquefaction of the final CO_2 stream. The

temperatures in the column are -7°C, 47°C and -24°C in the gaseous inlet, the boil-up and the liquid reflux respectively.

SO_2 is more difficult to separate from CO_2 than NO_2. In order to limit the energy consumption, a SO_x removal target of 85 ppm (200 mg/Nm³) is employed, as discussed previously. With an inlet concentration of 700, 1500 and 3000 ppm SO_x, this corresponds to a SO_x reduction of 87.9%, 94.3% and 97.2% (see Figure 8). At this SO_x removal rate, all NO_2 is removed. But, since the boiling temperature of NO is higher than that of CO_2, all NO, which is not oxidized to NO_2, remains in the gas-phase together with the non-condensable gases in the first distillation column (D1). Thus, the same oxidation reaction, which limits the LCP concept, is also limiting the distillation concept. An important difference to the LCP concept is that no other equilibrium limitation is active and that the oxidation reaction rate is favored by the lower temperatures. Thus, the theoretical NO_x removal by distillation is slightly higher than in the LCP concept. However, the actual NO_x recovery rate will depend on the residence time before the first distillation. NO_x recovery is 92 % or 97 % for an initial NO concentration of 1000 ppm and a residence time of 20 or 50 seconds (at 30 bar and -30°C) before entering the first distillation.

As the columns are integrated with each other, the power consumption of a flue gas treatment with the same CO_2-capture rate, but not including the SO_x/NO_2 removal column, is used as a reference. The reference process consumes about 0.6 % of the power plants gross electricity output, including recovered power by expansion of the stream of separated non-condensable gases in a turbine. The energy consumption of the distillation concept is evaluated for a CO_2-capture rate of 97.5%. Almost all CO_2-losses are due to the distillation column for removal of non-condensable gases. The gaseous distillate of both columns is compressed (to 275 and 62 bar) to condense the reflux. The power consumption in the compressors depends on the desired purity of the CO_2, which is a function of the respective reflux ratio. In Figure 9, the relative energy consumption for SO_x/NO_2 removal with different initial SO_x concentrations and 1000 ppm initial NO_x are presented.

The operational condition chosen for the column for SO_x/NO_2 removal are 15 theoretical plates and a reflux ratio of about 0.17, 0.20 and 0.23 for 700, 1500 and 3000 ppm SO_2 respectively. Figure 10 gives the influence of the number of plates (N) in the SO_x/NO_2 removal column on the energy consumption. For lower numbers of N, the reflux ratio and the compressor duty necessary for the separation increase strongly. For larger values of N the relative savings in energy consumption are low and the necessary value of N increases drastically.
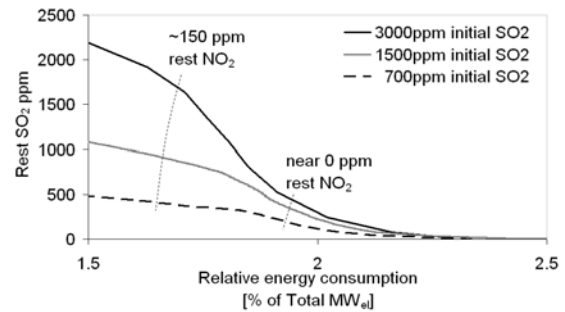

Figure 9: Relative energy consumption for removal of SO_x/NO_2 (15 stages) for different initial SO_x concentrations and 1000 ppm NO_x (CO_2 capture rate: 97.5%). The 3-8 % NO_x lost as NO are not included in the figure.
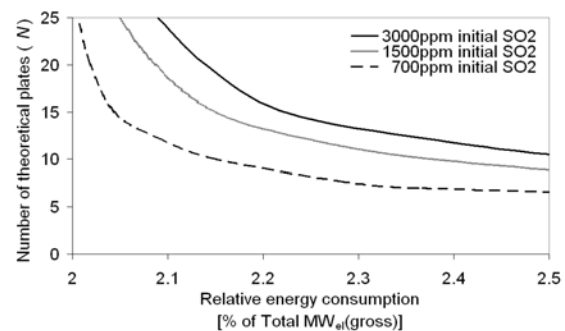

Figure 10: Relation between N and the relative energy consumption for the SO_x/NO_x removal column at the evaluated conditions

Table 3: Composition of the major inlet and outlet streams of the proposed scheme (Figure 3) in molar fractions (97.5 % CO_2-capture rate; 1500 ppm SO_2 case).

	Initial flue gases	CO_2-stream	$O_2/N_2/Ar$-stream	SO_x/NO_x-stream
Flow*	1	0.906	0.091	0.003
CO_2	0.89	0.960	0.23	0.22
N_2	0.05	0.013	0.42	-
O_2	0.05	0.025	0.30	-
Ar	0.006	0.001	0.05	-
SO_x	$1500 \cdot 10^{-6}$	$83 \cdot 10^{-6}$	-	0.47
NO	$\sim 50 \cdot 10^{-6}$	$22 \cdot 10^{-6}$	$333 \cdot 10^{-6}$	-
NO_2	$\sim 950 \cdot 10^{-6}$	-	-	0.31

* relative mol flow

At the chosen operational condition of the distillation column, the SO_x and NO_x removal requires 2.0 % to 2.2 % of the gross electricity output of the oxy-fuel power plant. The liquid product stream, containing the separated sulfur and nitrogen oxides, is in the case of 1500 ppm SO_2 and for an oxy-fuel power plant with 520 MW gross electricity output, about 2600 l/h with the composition given in Table 3.

Discussion

Comparison of the two concepts

Table 4 summarizes and compares the results for both concepts as obtained from the simulations of the present work. Both concepts have the potential for an efficient removal of SO_x and NO_x without any chemical additives. Yet, from Table 4 it can be seen that the LCP has the clear advantages of low CO_2 loss, low energy requirements and total SO_2 removal, at a NO_x removal rate satisfying current emission limits (as discussed previously).

In the LCP concept, SO_x and NO_x are removed in two separate absorption columns. The NO_x removal is limited by the rate of oxidation of NO to NO_2 and the phase equilibrium of the absorption processes. The emission limit of 180 ppm NO_x (corresponding to today's regulation in the EU) is however reached within a reasonable residence time. The required residence time for absorption of SO_x is decreased with a high initial NO_x concentration and with pressure.

For 30 bar pressure in both columns, the minimum in the total residence time for both NO_x and SO_x removal is reached with a NO_x concentration of about 1000 ppm in the flue gas. However, such a concentration is relatively high, compared to observed NO_x concentrations in the oxy-fuel process [2]. If the proposed treatment process is applied to an oxy-fuel combustion process, no primary NO_x reduction is needed. Instead, it could be favorable to adjust the combustion conditions to increased NO_x formation. The only additional power consumption of the LCP is used in the recycle pumps and for the compensation of the pressure loss over the columns. The LCP concept has the advantage that it can be adjusted to yield separate product streams of sulfuric (with nitrosulfuric acid as impurity) and nitric acid.

In the distillation concept, NO_x and SO_x are removed by distillation downstream of the distillation column for removal of non-condensable gases. NO_x removal is slightly higher than in the LCP concept, but the performance is closely related to the residence time before the first distillation column. High SO_x removal is correlated with high power consumption so that a removal target of 85 ppm (corresponding to today's regulation in the EU) has been introduced. A stream of SO_x, NO_2 and CO_2 is produced, which could be solved in water to yield a mixture of sulfuric and nitric acid.

Table 4: Comparison of the evaluated concepts for SO_x and NO_x removal from oxy-fuel combustion (initially 1500 ppm SO_x and 1000 ppm NO_x)

	LCP concept	Distillation concept
SO_x removal	~100 %	88 - 97 %
NO_x removal *	80 - 85 %	92 - 97 %
CO_2 losses	<< 1 %	~2.5 %
Energy requirements**	low	2.0 - 2.2 %
Maturity	uncertain	mature technology

   * for 20 and 50 seconds residence time

   ** percent of total gross electricity output

Conclusions

Two concepts for SO_x and NO_x removal in the treatment of flue gases from oxy-fuel combustion have been investigated by process simulations: The Lead-chamber-process (LCP) concept and the distillation concept. Both concepts are only feasible at the elevated pressure in the flue gas treatment of the oxy-fuel process. Beside absorption mechanisms and phase equilibria, pressure is strongly influencing the gas phase oxidation of NO to NO_2; this is the main limiting reaction rate for NO_x separation in both concepts and for the SO_2 separation in the LCP concept.

The LCP has the clear advantages of small CO_2 losses, low energy requirements and a complete SO_x removal, with a NO_x removal rate satisfying current emission limits. However, distillation is the more mature technology, and may therefore on short term be easier to implement on a large scale.

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