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Modeling and Parametric Analysis of Nitrogen and Sulfur Oxide removal from Oxy-Combustion Flue Gas

Using a Single Column Absorber

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Abstract

Oxy-coal combustion has great potential as one of the major CO₂ capture technologies for power generation from coal. In oxy-coal combustion, the oxygen source is a high concentration oxygen stream and the product flue gas consists primarily of CO₂ and H₂O with contaminants like nitrogen oxides (NOₓ), sulfur oxides (SOₓ) and non-condensable gases like argon, oxygen and nitrogen. NOₓ and SOₓ removal can be achieved via traditional selective catalytic reduction (SCR) and flue gas desulfurization (FGD). These traditional methods however result in relatively high capital cost and energy requirement and face complex material handling challenges. White et al proposed a different approach to NOₓ / SOₓ removal based on the nitric acid and lead-chamber chemistry process [1]. This two-column design utilizes an intermediate and a high-pressure reactive absorption column connected in series to respectively remove SOₓ and NOₓ from the high CO₂-concentration flue gas. In this study, we propose a modification to this two-column process that achieves the complete removal of SOₓ and NOₓ from the CO₂ stream in a single column. We demonstrate by means of pressure sensitivity studies that this new design can meet the same separation targets as the two-column process in fewer column stages and half the feed water requirement by exploiting the pressure dependence of the rate determining NO oxidation reaction. Furthermore, we make use of parametric studies to analyze the dependence of NOₓ / SOₓ removal on key design and operating parameters for the proposed system: pressure, vapor hold-up per stage and water flow rate. Results show that the process is strongly pressure dependent, with a 3-order of magnitude decrease in required residence time when the operating pressure is varied from 4 bars to 30 bars. Vapor holdup volume and feed water flow rate have a significant impact on NOₓ / SOₓ removal up to a point - about 20m³ and 2kg/sec respectively for the case analyzed. Beyond these values, column performance shows substantially less sensitivity to increasing holdup volume or water flow rate. The analysis presented in this paper also shows that recycling bottoms liquid can reduce the feed water requirement by up to 40% without significantly affecting the exit gas purity.
1. Introduction

Coal is set to remain a dominant energy source for electricity generation in the world because of its abundance and low costs. Coal currently accounts for over 40% of global electricity generation and is projected to remain above 38% by 2035 [2]. However, coal combustion for power generation releases a significant amount of CO$_2$ to the environment, which will be at odds with current global efforts to cut back on atmospheric CO$_2$ levels by 80-95% below 1990 levels by 2050 [3,4]. Carbon dioxide capture from coal fired power plants provides a means of utilizing the world’s abundant coal resource while staying on track to meet these short-to-medium term emission targets. Oxy combustion technology has great potential as one of the major CO$_2$ capture technologies for power generation from coal and other fossil fuels [5]. The distinguishing feature of oxy-coal combustion is that the oxygen source is a high concentration oxygen stream and the product flue gas consists primarily of CO$_2$ and H$_2$O with contaminants like NO$_X$, SO$_X$, and non-condensable gases like argon, oxygen and nitrogen. Table 1 shows the typical composition of oxy-coal combustion flue gas downstream of the power island after water has been condensed out. For carbon sequestration or Enhanced Oil Recovery (EOR) applications, pipeline transport standards as well as storage specifications impose concentration limits on these contaminants. Impurities like NO$_X$, SO$_X$, need to be removed to ensure that the transported CO$_2$-rich stream stays within specified purity limits. These specifications are typically determined by technical, economic and environmental considerations. Table 2 shows typical CO$_2$ transport NO$_X$/SO$_X$ purity specifications as well as the purity specs selected for this study.

Nitrogen and sulfur oxides can be removed from the flue gas stream using traditional processes like selective catalytic reduction (SCR) and flue gas desulfurization (FGD) [6, 7]. However, Traditional FGD and SCR strategies significantly add to the complexity and cost of the power plant, requiring a range of equipment from limestone silos and slurry tanks to gas heaters, pumps and catalyst beds. An alternative strategy involves technologies that utilize the sulfuric acid (lead chamber) and nitric acid chemistry processes for the removal of SO$_X$ and NO$_X$ respectively as sulfuric and nitric acid from the flue gas of industrial plants. Keilin & Wallit, [8] proposed the first important configuration in this category. The schematic of the Keilin process is represented in
figure 1. In this process, the SO$_2$ in the flue gas is first oxidized with NO$_2$ to form SO$_3$, which is removed as sulfuric acid by contact with water. Recycled sulfuric acid is used to scrub the flue gas of the NO, then sent to the catalytic stripper, where NO is oxidized to NO$_2$ and separated from the sulfuric acid stream. Some of the NO$_2$ produced is recycled to the SO$_2$ oxidation reactor while the rest is removed as nitric acid in the HNO$_3$ absorber. More recently, White et al [1] proposed a modification of the lead chamber process that removes nitrogen oxides and sulfur oxides as nitric and sulfuric acid respectively in two high pressure reactive absorber columns (figure 2). It was specifically proposed for oxy-coal combustion. Unlike the Keilin configuration, this is a low temperature process and replaces the catalytic oxidation of NO with a pressure enhanced, direct oxidation to NO$_2$ by oxygen in the flue gas stream. In this reference design, the first column is maintained at 15 bars and is primarily responsible for SO$_2$ removal while the second column removes the remaining NO$_2$ at 30bar.

In this study, we propose a modification to this two-column process. This modified design (figure 3) uses a single reactive column at high pressure to achieve similar separation efficiencies as the reference two-column design, by exploiting the pressure dependence of the rate determining reactions in the NO$_X$ / SO$_X$ removal process. We discuss the underlying chemistry of the process, describe the methodology for modeling this purification unit in Aspen Plus and provide justification for important modeling assumptions. Having identified pressure, vapor holdup and water flow rate as key design parameters for the absorber column, we carry out a sensitivity analysis to determine their impact on the extent of removal of the NO$_X$ and SO$_X$ pollutant species, as well as the state and composition of the exit streams. We also analyze the impact of, bottoms liquid recycle and flue gas composition on the overall performance of the system. These studies are used to determine the optimal specifications for the column design and operation, and to identify design modifications that improve overall performance, energy consumption and water use.

Section 2 presents a discussion on the underlying chemistry of the removal process and provides a basis for justifying the key modeling assumptions. Section 3 describes the methodology for developing the purification system models used in this study. Sections 4 and 5 present the base case simulation results and the results from the parametric studies.
2. Process Chemistry

2.1. Nitric Acid Chemistry

NO\textsubscript{X} absorption columns are used extensively in industry for production or recovery of nitric acid. Reactions 1-5 represent the key reaction steps describing the process.

\[ 2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g) \] (1)

\[ 2\text{NO}_2(g) \leftrightarrow \text{N}_2\text{O}_4(g) \] (2)

\[ \text{N}_2\text{O}_4(g) \leftrightarrow \text{N}_2\text{O}_4(l) \] (3)

\[ \text{N}_2\text{O}_4(l) + \text{H}_2\text{O}(l) \leftrightarrow \text{HNO}_3(l) + \text{HNO}_2(l) \] (4)

\[ 3\text{HNO}_2(l) \leftrightarrow \text{HNO}_3(l) + \text{H}_2\text{O}(l) + 2\text{NO}(g) \] (5)

This reaction scheme has been studied in detail and is relatively well understood, with properly documented reaction rates. Reaction 1 is the tri-molecular gas phase oxidation of NO [9-11] with rate given by

\[ R_1 = k_1 \left( p_{\text{NO}}^2 * p_{\text{O}_2} / K_1 \right) \frac{[kPa]}{[sec]} \] (6a)

\[ k_1 = \exp \left( \frac{1.468}{T} - 10.9043 \right) \frac{1}{[kPa^2/sec]} \] (6b)

\[ K_1 = \exp \left( -8.002 + 1.75 \ln(T) - 0.000217T - \frac{2.496}{T} \right) \frac{1}{[kPa^2]} \] (6c)

Where \( k_1 \) is the reaction rate constant, \( K_1 \) is the equilibrium constant, \( T \) is the temperature in Kelvin, and \( p \) is the partial pressure in kPa. This reaction is the rate determining step in the process; its rate is highly dependent on pressure and correlates negatively to the reaction temperature. Reaction 2 is the dimerization of nitrogen dioxide with equilibrium constant given by

\[ K_2 = \frac{p_{\text{N}_2\text{O}_4}}{p_{\text{N}_2\text{O}_2}} \frac{1}{[kPa]} \] (7)

Where \( p_i \) refers to the partial pressure of component \( i \). Miller [11] combined the mass transfer reaction 3 and the liquid phase reactions 4 and 5 into a single overall reaction step (8a) with an effective rate that accounts for both the kinetic and transport processes:
\[3N_2O_4 + H_2O \leftrightarrow HNO_3 + H_2O + 2NO\] \hspace{1cm} (8a)

\[R_{8a} = H_{N_2O_4} \sqrt{(K_{4.5} D_{N_2O_4}) A \left( \frac{P_{N_2O_4}}{K_0} \right)^{\frac{3}{2}}} \left( \frac{kmol}{s} \right)^{\frac{3}{2}}\] \hspace{1cm} (8b)

\[K_{4.5} = \frac{p_{NO} \cdot a_{HNO_3}}{p_{NO_2} \cdot a_{H_2O}} \left( \frac{kmol}{m^3 kPa} \right)^2\] \hspace{1cm} (8c)

Where \( K_0 \) is an exponential function of the weight fraction of \( HNO_3 \) in \( kPa^{-\frac{1}{2}} \) [11], \( A \) is the interfacial area in \( m^2 \), \( H \) is the Henry coefficient in \( \frac{kmol}{m^3 kPa} \), \( D \) is the effective diffusivity in \( m^2/sec \) and \( \alpha \) is the activity, \( \frac{kmol}{m^3} \).

### 2.2. Sulfuric acid chemistry

The process for the removal of \( SO_2 \) as sulfuric acid in countercurrent reactive absorber columns is known to proceed based on chemistry associated with the lead chamber processes. The overall reaction is represented in reaction 9.

\[SO_2 + NO_2 + H_2O \leftrightarrow H_2SO_4 + NO\] \hspace{1cm} (9)

The exact pathway for this process is yet unsettled mainly because the design of the process had been highly empirical and also due to waning interest since the development of the contact process for the manufacture of sulfuric acid. The overall chemical reaction scheme involves the oxidation of \( SO_2 \) by \( NO_2 \) in the presence of water to produce \( H_2SO_4 \). These reactions are known to take place in the gas phase, at the gas-liquid interface and in the liquid phase.

#### 2.2.1. Gas Phase Reaction

According to this mechanism, \( NO_2 \) oxidizes or catalyzes the gas phase oxidation of \( SO_2 \) to \( SO_3 \). Once \( SO_3 \) is formed, it quickly condenses, pulling water with it into the liquid phase to form sulfuric acid. This process is represented in reactions 10 and 11.

\[SO_2 + NO_2 \rightarrow SO_3 + NO\] \hspace{1cm} (10)

\[SO_3 + H_2O \leftrightarrow H_2SO_4\] \hspace{1cm} (11)

Falgout studied gas phase reactions between \( NO_2 \) and \( SO_2 \) in some detail [12]. The study reported a 4-order of magnitude increase in \( SO_2 \) removal rate from dry gas reactions (0.02%/hr) to reactions with the gas initially
at 100% relative humidity (715%/hr). Falgout also observed that as water vapor increased, NO₂ consumption reduced, suggesting that in these conditions, NO₂ may also catalyze the oxidation of SO₂ by atmospheric oxygen. A more recent study by Torrente-Murciano et al [13] reported a one-to-one fractional conversion of SO₂ by NO₂ in the absence of oxygen and a larger SO₂ conversion when oxygen is present. Unlike Falgout however, they believe that the real driver for enhanced SO₂ oxidation is the presence of highly acidic liquid droplets, and not water vapor. From this perspective, it is possible that the enhanced reaction rates observed by Falgout were caused in part by rapid reactions on the surface of suspended liquid droplets initially present in the saturated gas stream or formed on the condensation of the first sulfuric acid droplets. While this view may not be conclusive, it does suggest the importance of reactions at the gas-liquid interface in the SO₂ removal process.

2.2.2. Reactions at the gas-liquid interface

Ernst Berl [14], building on the work of George Lunge [15, 16], proposed one of the most widely accepted reaction steps for the lead chamber process. This proposed overall mechanism involve reactions at the gas-liquid interface and fast liquid phase reactions, with violet acid (H₂SO₄.NO) and nitrosyl sulfuric acid (SO₅NH) as the key reaction intermediates. Compared to the traditional lead chamber process, the conditions in the oxy-combustion flue gas purification process are marked by much lower NOₓ and SOₓ fractions, lower gas temperatures and very dilute acid concentrations. Since these key intermediates are unstable in dilute acid, they will decompose rapidly to form sulfuric acid and nitrogen oxides, reducing the interfacial reactions to the overall step in equation 9.

Since these reactions take place at the gas-liquid interface, the reaction rate is also influenced by the gas-liquid contact surface area, and consequently, by pressure, as pressure increases the effective gas-liquid interfacial area [14, 17]. In his analysis of the pressure dependence of H₂SO₄ production in the lead chamber, Berl showed a 6000-fold increase in H₂SO₄ output from 3kg/m³/day at 1 atm to over 9000kg/m³/day at 25atm. This is due the effect of pressure on both the rate-limiting NO oxidation reactions and on the reactions at the gas-liquid interface.
2.2.3. Liquid phase reactions:

One of the earliest studies on lead chamber chemistry by Raschig [18], suggested that SO$_2$ and NO$_2$ are absorbed separately in the sprayed liquid film and react independently with water to form H$_2$SO$_3$ and HNO$_2$; these then combine to eventually form sulfuric acid and NO. This model was mostly criticized for predictions that deviated from lead chamber experience [14-16]. A more recent work by Ellison and Eckert studied the impact of NO$_X$ on the aqueous phase oxidation of SO$_2$ [19]. They reported that the catalytic effect of NO$_2$ on SO$_2$ oxidation observed in the gas phase kinetics does not occur in the liquid phase. Rather, direct reaction takes place, which involves the two compounds and their aqueous species. What remained unresolved, though, is whether the chief oxidant is NO$_2$ at the gas-liquid interface, the absorbed NO$_2$ or the hydrolyzed nitrous acid. They however concluded from their experiments that it is more likely that the absorbed NO$_2$ hydrolyzes to nitrous acid (HNO$_2$) before reacting with dissolved SO$_2$. Nitric acid (HNO$_3$) is also formed with the absorption of NO$_2$ but unlike nitrous acid, which quickly oxidizes the aqueous SO$_2$, nitric acid indirectly inhibits the oxidation by increasing the ionic strength of the liquid phase.

To put this in perspective, let us assume typical gas phase compositions for NO$_2$ and SO$_2$ of 300ppm and 2000ppm. From Henry’s law,

\[ S = K_H \times P_{gas} \]  

(12)

Where $S$ represents solubility; $K_H$ is Henry’s constant; $P_{gas}$ is the partial pressure of the gas species. Though the solution is non-ideal, the low gas phase concentrations make Henry’s law adequate for an order of magnitude estimate. Taking typical values of 1.4 and 0.012 for SO$_2$ and NO$_2$ Henry constant respectively [20], we find that the equilibrium solubility of SO$_2$ is about 3 orders of magnitude higher than that for NO$_2$. Therefore, in the absence of some other catalyst, or oxidizing medium, the aqueous phase oxidation of sulfur dioxide to sulfuric acid by hydrolyzed NO$_2$ will be relatively low, and other mechanisms have to be included to account for the significant production of sulfuric acid observed in experimental investigations.
2.3. Assumption on SO$_2$ removal Rate:

The key modeling assumptions for SO$_2$ removal in the counter current absorption column is that the rate of the SO$_2$ reaction is sufficiently faster than that of the rate-limiting NO oxidation reaction such that it can be modeled as equilibrium relative to NO oxidation. Since we did not find any explicit documentation of the kinetic information for this reaction, we would use estimates based on experimental and process measurements to assess this assumption. We have shown in the preceding discussion that SO$_2$ is oxidized via the gas phase, interfacial and liquid phase routes. We would therefore estimate the rate SO$_2$ removal via each of these routes and compare it to NO oxidation rates in conditions expected in oxy-combustion flue gas treatment unit.

2.3.1. Gas phase route

If we assume that Falgout’s measurements capture the rate of the gas phase SO$_2$/NO$_2$ reaction, then the gas phase reaction rate is given by

$$ R_{gas} = 715 \left[ \%_{HR} \right] = 3.19 \times 10^{-3} \left[ \frac{mol}{litre \ HR} \right] $$  \hspace{1cm} (13)

Assuming a second order rate, and that we could extrapolate the SO$_2$ conversion rate to elevated pressures by multiplying by the square of the pressure ratio, then

$$ R'_{gas} = R_{gas} \times \left( \frac{P}{P_0} \right)^2 \left[ \frac{mol}{litre \ HR} \right] $$  \hspace{1cm} (14)

Where $P$ is the operating pressure and $P_0$ is the ambient pressure (at which the measurements were taken).

Interfacial Route

As a rough estimate, we shall use the data from the graph by Ernst Berl [14] relating H$_2$SO$_4$ production in a lead chamber as a function of pressure and convert it to appropriate units as follows

$$ R_{int} = \frac{M}{MM_{H_2SO_4}} \times \left( \frac{1000}{24+1000} \right) \left[ \frac{mol}{litre \ HR} \right] $$  \hspace{1cm} (15)

Where $M$ = H$_2$SO$_4$ production rate in $\frac{kg}{m^3 \ day}$, $MM_{H_2SO_4}$ is the molar mass of H$_2$SO$_4$ in g/mol.
2.3.2. Liquid phase route

Assuming that there is enough nitrous acid or dissolved nitrogen oxides to oxidize SO\(_2\) in the liquid phase, the controlling process for this route would be the rate of transfer of SO\(_2\) from the gaseous to the liquid phase. This is given by the following expression

\[
R_{LIQ} = \frac{A \Delta C}{R_m} \left[ \frac{\text{mol}}{\text{Litre HR}} \right] \tag{16}
\]

Where \(A\) is the interfacial area in \(\frac{dm^2}{L}\), \(\Delta C = \text{gas to liquid concentration difference in } \frac{\text{mol}}{L}\) and \(R_m\) is the mass transfer resistance in \(\frac{HR}{dm}\). \(A\) is estimated using extrapolated data from the study by Benadda et al[17]; liquid SO\(_2\) concentration is assumed to be zero therefore \(\Delta C\) is equal to the gas phase concentration (1000ppm); \(R_m\) is estimated using the method by Liss [21], which is based on Dankwerts resistance equation[22]. The mass transfer resistance is a strong function of pH, increasing asymptotically at lower pH values. Though liquid phase pH found in the absorber column is typically less than 1, we choose a mass transfer resistance at pH of 2 to avoid extrapolating the results presented by Liss. Results at lower pH values can be found in [23].

2.3.3. NO oxidation

NO oxidation proceeds by the well known third order reaction whose rate is given by

\[
R_{NO} = k [NO]^2[O_2] \quad \tag{17}
\]

Where \(k\) is the reaction rate constant in \(\frac{L^2}{\text{mol HR}}\) [9, 10], [NO] is the gas phase NO concentration in \(\frac{\text{mol}}{L}\) and [O\(_2\)] is the gas phase oxygen concentration in \(\frac{\text{mol}}{L}\). For these estimates, we assume gas phase compositions of SO\(_2\), NO and O\(_2\) to be 1000ppm, 200ppm and 5% respectively.

2.3.4. Discussion

The results from these estimates are shown in figure 4 and table 3. We see that both the gas phase and interfacial removal routes are 3-orders of magnitude faster than the NO oxidation at 1bar, and at least an order of magnitude faster at 30 bar. Note that the gas phase and interfacial rate estimates were determined from measurements that did not necessarily discriminate between gas phase and interfacial reactions. Figure 4 also suggests that the liquid phase SO\(_2\) removal route has the slowest rate and is therefore not the most important
pathway for sulfuric acid production, given the impact of pH on NOX solubility. Adding a buffer that raises the pH from 2 to 7 would increase this absorption rate by at least an order of magnitude [23]. Liu et al have analyzed in detail the dependence of SO2 absorption on pH value [24 - 26]. Their studies also demonstrate a positive correlation, with a stronger dependence in the lower pH range.

In practice, SO2 oxidation is expected to proceed via all three routes, and the estimates show that the average SO2 removal rate is faster than the NO oxidation rate within the range of operating conditions expected in the NOX/SOX column. The usefulness of this result is that in the absence of kinetic information for the SO2 removal reaction steps, we can model the overall reaction as equilibrium relative to the NO oxidation reaction. For this reason, knowing the exact SO2 removal pathway becomes less relevant from a thermodynamic point of view.

3. Modeling and Methodology

3.1. Two-column unit:

The reference two-column configuration for the removal of nitrogen and sulfur oxides from oxy-combustion flue gas is based on the process suggested by White et al (figure 2). The flue gas from the oxy-combustion power island is first compressed to 15 bar, then fed into a reactive absorber column where sufficient residence time and contact with water is provided to remove all the sulfur dioxide as sulfuric acid and some nitrogen oxides as nitric acid. The sulfur dioxide-free flue gas is then further compressed up to 30bar and enters the second reactive absorber column where most of the nitrogen oxides are removed as nitric acid.

3.2. Proposed single column unit

In this configuration, the flue gas is compressed up to 30 bars, then fed into a single, multistage countercurrent reactive absorber column which removes NOX and SOX as nitric acid and sulfuric acid respectively (figure 3). The flue gas leaving this column will subsequently be dried in a molecular sieve dryer and sent to the non-condensable gas removal unit, where gases like oxygen, nitrogen and argon are removed.
from the flue gas. High pressure operation speeds up the rate limiting NO oxidation reaction, reducing the required residence time in the reactive column.

### 3.3. Overall Reaction Scheme

The combined reaction scheme adopted in the model is shown in table 4. Reactions (i), (ii), (iii) represent the sulfuric acid process while reactions (i), (iv), (v) represent the nitric acid process. We already showed by means of order of magnitude estimates that the SO$_2$ oxidation to sulfuric acid is fast enough to be considered equilibrium relative to the NO oxidation reaction for the range of operating conditions considered. Thus, the selected scheme is good enough for estimating how rapidly SO$_2$ is removed from the gas phase and can provide a good estimate of the composition of the acidic liquid discharged from the removal equipment.

The absorber columns are modeled using Radfrac blocks in Aspen Plus™. The sulfuric acid and nitric acid reactions are provided as inputs to the simulation. Reactions ii and iii are handled directly in Aspen Plus™. The rest are implemented using a Radfrac User-Kinetic model which links to an external subroutine that calculates the required reaction rates as well as the rate of generation for each species per stage using Miller’s model as described in equations 1-8.

### 3.4. Thermodynamic Property Method

The ELECNRTL property method is specified in Aspen Plus™ to describe liquid phase solution equilibrium in the RadFrac columns. This method has been determined to be accurate for the dilute acid conditions that we expect in the absorber columns. Dissociation reactions for the acids are also included as part of the chemistry defined for the absorber column block and associated with the ELECNRTL method. The coefficients for the Henry constant correlation for CO$_2$-H$_2$O binary pair were updated to improve prediction accuracy for CO$_2$ absorption in the liquid phase.

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1 RadFrac is a rigorous model in Aspen for simulating all types of multistage vapor-liquid fractionation operations and facilitates the simulation of tray and packed columns.
3.5. Design Specifications

The base power cycle for which the Purification train model was developed has been described in detail by Hong et al [5]. It is a pressurized oxy-coal plant designed with coal flow rate of 30 kg/s (HHV: 874.6MWth, LHV: 839.1MWth) with flue gas flow rate of 87.4kg/s, typical flue gas composition as shown in table 1 and combustor pressure of about 10 bar.

Table 5 lists the specifications for the absorber columns used in the model. The column sizing parameters shown here are based on results from earlier simulations designed to achieve the <15ppm purity targets by providing sufficient residence time for the rate limiting reactions. Figure 5 shows the stage-labeling convention for the absorber column.

4. Results

4.1. Performance comparison

4.1.1. Two Column Absorber

Table 6 shows the composition of the exit streams for the two-column and single column designs for the same inlet stream composition. For the two-column model, SO2 is completely removed in the 15 bar absorber column and more of the unconverted NOX is removed in the 30bar column down to about 12ppm, which is below the transport specifications of table 2. The NOX and SOX gas phase composition profile in the 15 bar column (figure 6) shows that between stages 1 and 4, while SO2 concentration dropped, NO and NO2 fraction remained fairly constant. Since equation (i) is the rate limiting reaction and any NO2 formed is quickly consumed by the SO2 reaction, the rate of production of NO from (ii) is approximately balanced by the rate of consumption of NO in equation (i). However, in stage 5, since most of the SO2 has been removed, there is a slight decrease in the amount of NO2 consumed in (ii) and a corresponding drop in the amount of recycled NO produced from (ii). This explains the slight increase in NO2 concentration and the slight decrease in NO concentration in figure 6. At 30 bar, the NO oxidation rate increases, speeding up the removal of NOX from the gas phase as shown in figure 7. The liquid phase profiles in figures 8 and 9 show that sulfuric acid formation dominates in the 15 bar
column while nitric acid formation mostly takes place in the 30 bar column. One of the motivations for the two-column design is to separate sulfuric acid from nitric acid production. However, figure 8 shows that some nitric acid is still formed in the lower pressure - sulfuric acid dominant - column.

4.1.2. Single Column Absorber

The single column absorber achieves similar NO$\text{X}$ and SO$\text{X}$ removal as the two-column design with fewer stages with half the demand for water as shown in tables 5 and 6. Operating at 30 bar speeds up the rate limiting, pressure dependent NO oxidation reaction (reaction (i), table 4), leading to a faster overall conversion process. Faster NO oxidation reaction enables the complete removal of SO$_2$ within the bottom stage, freeing up the rest of the stages for NO$\text{X}$ removal via the nitric acid process reactions, as illustrated in the gas and liquid phase profiles of figures 10 and 11. Halving the fresh water requirement improves water conservation in operating the purification system. Using a single column instead of two reduces the material requirement for the column, which translates to savings in capital cost. In addition, using a single column avoids the need for a second compressor in-between the two columns and reduces the energy requirement associated with column pressure drop.

4.2. Sensitivity Studies

In section 4.1, we presented a modified reactive absorber NO$\text{X}$ and SO$\text{X}$ removal design that takes advantage of the pressure dependence of the rate limiting reaction to improve performance. Thus, pressure is an important design parameter that affects the operation of the absorber column. Other important parameters include the vapor hold up volume per stage and the water flow rate. Understanding how these factors impact performance is key to determining an optimal design for the process as well as gaining useful insight into the behavior of the system under various operating conditions. In this section we present parametric study results that show how these factors impact the extent of removal of the major pollutant species in the gas stream, and where
applicable, their impact on required residence time. We also study the feasibility of bottoms liquid reuse for better fresh water conservation.

4.2.1. Pressure Sensitivity Analysis

**NO\textsubscript{X} Removal:** For this study, the operating pressure of the system is varied from 2 bars to 40 bars while other design parameters remained at the single column design base case values, except when stated otherwise. For the simulations that show the variation of required residence time with pressure, the diameter of the column remained constant while the total volume was allowed to vary until the target exit gas composition specifications are reached. Figure 12 shows the variation of NO and NO\textsubscript{2} fraction in the absorber exit flue gas stream with pressure. The plot can roughly be divided into two sections. In the first section (below 10 bars), the NO\textsubscript{X} composition stays almost constant because in this range, there is sufficient SO\textsubscript{2} in the flue gas to ensure lead chamber reactions (ii) and (iii) remain dominant. Therefore, any NO\textsubscript{2} produced from reaction (i) is quickly consumed by reaction (ii), which is faster than both the NO oxidation reaction (i) and the nitric acid reactions (iv) and (v). In the second section (above 10 bars), the SO\textsubscript{2} in the gas phase gets depleted before the flue gas leaves the column. Initially, there is not sufficient time for the nitric acid chemistry to use up the NO\textsubscript{2} produced, which explains the initial spike in NO\textsubscript{2} composition. As pressure increases, SO\textsubscript{2} is removed more quickly, allowing more time for the NO\textsubscript{X} removal chemistry to take place, as shown in the gradual decay of the NO\textsubscript{X} fraction in the flue gas. The shape of the graph also shows that at low ppm levels, the incremental improvement in NO\textsubscript{X} removal per unit pressure increase becomes less significant.

**SO\textsubscript{X} Removal:** The impact of pressure on SO\textsubscript{2} removal is even more remarkable. SO\textsubscript{2} composition in the exit gas stream decreases rapidly with pressure and the minimum pressure required for complete SO\textsubscript{2} removal in a 3-stage, 6-stage and 9-stage column is 18 bars, 14 bars and 12 bars respectively (figure 13). To appreciate the implication of this result, keep in mind that the total residence time required in the NO\textsubscript{X} / SO\textsubscript{X} removal column is determined by the amount of time needed to completely remove the NO\textsubscript{X} down to transport specifications.
However, the NO\textsubscript{X} removal chemistry (iv) and (v) do not really kick in until the SO\textsubscript{2} in the flue gas - which outcompetes it for NO\textsubscript{2} supplied by reaction (i) - is sufficiently depleted. Therefore, increasing the column pressure increases the rate of SO\textsubscript{2} removal, thereby allowing more time for NO\textsubscript{X} removal to take place. For example, if a 9-stage column is operated at 30 bar, all the SO\textsubscript{2} is removed while the gas is still the first stage, leaving the remaining stages for NO\textsubscript{X} removal.

Residence Time: figures 14 and 15 relate the NO\textsubscript{X} composition and the column pressure to the residence time. Residence time is determined from the ratio of the vapor holdup volume to the volumetric flow rate and provides a handle to the required column size that meets design purity specifications (<15ppm). Figures 14a and 14b show the variation of NO\textsubscript{X} composition with residence time for 10, 20, 30 and 40 bar operation. The profiles for the four cases are similar. The initial stages are marked by a slower NO\textsubscript{X} removal rate which represent the phase when the SO\textsubscript{X} chemistry dominates the process. Afterwards we observe a sharp increase in the rate of NO\textsubscript{X} depletion rate, followed by a gradual flattening out as NO\textsubscript{X} concentration in the flue gas becomes very small. The total residence time required for the purification process is highly pressure dependent, requiring 1780 seconds at 10 bars compared to 72 seconds at 40 bars. Figure 15 provides a summary view of the relationship between required residence time and operating pressure in the range of 4 bars to 40 bars. The time is represented on a log scale for convenient viewing. The total residence time correlates to the total volume of the absorber vessel and indirectly to the cost of the equipment. It follows then that there is considerable incentive to operate the column at elevated pressures.

4.2.2. Holdup Sensitivity Analysis

The vapor holdup volume is a design parameter used to provide sufficient residence time for the rate-limited reactions to take place. In this study, the operating pressure of the absorber column is kept constant at 30 bar while the vapor holdup volume per stage is varied from 2 to 100m\textsuperscript{3}. All other design specifications for the column remain unchanged for this simulation. Figure 16 shows the impact of increasing stage vapor holdup on NO\textsubscript{X} removal from the flue gas stream. The impact of holdup volume on SO\textsubscript{2} removal is not shown because all
the SO$_2$ is completely removed at 30 bar for the range of holdup values investigated. Increasing holdup per stage from 2 m$^3$ up to 20 m$^3$ results in significant increase in the extent of NO$_X$ removal. Above this range, the slope of the curve changes such that increasing the holdup volume further does not result in commensurate improvement in NO$_X$ removal.

4.2.3. Water flow rate sensitivity analysis

The impact of varying the water flow rate on the performance of the absorber column is shown in figure 17. To obtain these results, the water flow rate into the top of the column was varied from 1 kg/s to about 12 kg/s while other design parameters were kept constant. It can be seen from figure 17 that increasing the water flow rate beyond 2 kg/s did not have a considerable impact on the composition of the exit flue stream. As a matter of fact, beyond 2 kg/s, much of the reduction in NO$_X$ concentration in the flue gas is due to direct dissolution of the NO$_X$ in the liquid phase. This is possible because there is more water and also because increasing water flow slightly increases the pH of the liquid stream. One argument that favors larger water flow rates is to reduce the acid resistance requirement of the absorber column material. However, simulation results show that even with 12 kg/s flow rate, the liquid pH still remains below 1 and acid resistance will remain an important consideration in material selection.

4.2.4. Bottoms recycle

Figure 18a illustrates the impact of bottoms liquid recycle on the exit gas stream composition from the absorber column. The plot was created by keeping the total top stage liquid supply constant and gradually replacing the fresh water supply with recycled liquid from the bottoms stream. Bottoms liquid recycle up to 40% by mass had very little effect on the purity of the exhaust stream. However, beyond 40%, increasing liquid recycle significantly deteriorates column performance. An important phenomena that explains this behavior is the change in the pH of the bottoms liquid stream. Increasing recycle reduces pH, increases the ionic strength of the liquid phase and thus inhibits NO$_X$ solubility, as shown in figure 18b. Therefore, to sustain high recycle ratios without changing column dimensions, a neutralizing agent will need to be added to the system to raise pH.
5. Conclusion

In this paper we presented the underlying theory and the methodology for developing a novel process for the removal of NO\textsubscript{X} and SO\textsubscript{X} from oxy-combustion flue gas stream as nitric and sulfuric acid respectively. This process utilizes a reactive absorber column operating at elevated pressure which favors the removal chemistry. By taking advantage of the pressure dependence of the key rate limiting NO oxidation reaction, we proposed a modification that replaces the two-column design of White et al [1] with a single, high pressure reactive absorber column. This new design meets the same purity targets in fewer stages and with a lower feed water requirement. This advantage also translates to lower energy requirement – for overcoming pressure drop – and lower capital cost – fewer columns and gas compressors.

This study also analyzed the effect of pressure, vapor holdup volume, water flow rate and bottoms recycle on overall performance of the column. Pressure has the most significant impact on column performance, as the study showed an order of magnitude reduction in required residence time for a change in operating pressure from 10 bar to 30 bar. Increasing the design holdup volume per stage increases the effective residence time of the flue gas in the column, leading to lower NO\textsubscript{X} and SO\textsubscript{X} fractions in the exhaust gas for same operating pressure and feed water rate. Column performance is less sensitive to water flow rate than to pressure or holdup volume. This is because for a fixed operating pressure and holdup volume (and assuming gas/liquid interfacial area does not change), the most important factor that drives NO\textsubscript{X} removal is the liquid phase pH and increasing water flow has only a mild effect on pH. Bottoms liquid reuse was considered as a means of improving water management and the sensitivity study showed that the system can support up to 40% bottoms liquid recycle without significantly reducing the exit gas purity.

An important consideration for implementing this NO\textsubscript{X} and SO\textsubscript{X} removal system is the selection of appropriate acid resistant material. Simulation results show very low pH values for the bottoms liquid. In addition, since both sulfuric and nitric acid are produced, we expect to see local oxidizing and reducing conditions in some parts of the absorber column, requiring a material with resistance to both oxidizing and
reducing agents. On the other hand, there may be some advantage to having both acids present since the acid mixture could create a passivation of the metallic surface, increasing overall corrosion resistance [27]. Whatever the case, there is need to balance cost with adequate acid resistance when selecting appropriate materials. A feasible recommendation is to use carbon steel for the absorber column shell material and Inconel® Alloy 686 as cladding material. Carbon steel is relatively cheap and therefore provides cost control. Inconel® has high nickel and chromium content which provide protection from highly reducing and oxidizing media respectively [28]. These material properties will also improve resistance to corrosion due to trace amounts of mercury present in the bottoms liquid. However, when the feed coal has high mercury content, it may be worthwhile to consider additional mitigation measures like thermal pretreatment to reduce the mercury fraction in the feed coal [29]. A more detailed discussion on material selection for this system can be found in [23].

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Notes

The authors declare no competing financial interest

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Figures
Figure 1: Schematic diagram of the Keilin & Wallit Process
Figure 2: Double Column (Base Case) NO\textsubscript{X} & SO\textsubscript{X} Removal Process
Figure 3: Single Column (Modified) NO\textsubscript{X} & SO\textsubscript{X} Removal Process
Figure 4: Log-scale plot comparing SO$_2$ removal rate via the different possible routes to the rate of NO oxidation. In the operating range covered, SO$_2$ removal rate is sufficiently faster than NO oxidation rate to be assumed equilibrium relative to the NO reaction.
Figure 5: absorber column schematic showing stage-labeling convention
Figure 6: Vapor phase profile in the lower pressure (15 bar) column of the two-column reactive absorber unit.

All the SO$_2$ is removed from the flue gas across the 5 stages.
Fig 7: Vapor phase profile in the higher pressure (30 bar) column of the two-column reactive absorber unit
Figure 8: Liquid phase profile in the lower pressure (15 bar) column of the two-column reactive absorber unit
Figure 9: Liquid phase profile in the higher pressure (30 bar) column of the two-column reactive absorber unit
Figure 10: Vapor phase profile in the 30 bar single column reactive absorber unit. All the SO$_2$ is removed within the initial stage (bottom stage 9) of the absorber column.
Figure 11: Liquid phase profile in the 30 bar single column reactive absorber unit. At this pressure, practically all the sulfuric acid is formed in the bottom stage (stage 9) of the column. Values are taken at the exit of each stage.
Figure 12: Impact of pressure on NO$_x$ removal (9-stage column). Below 10 bar, reaction 2 in table 4 is dominant, consuming any NO$_2$ produced and replenishing the NO. Above 10 bar, most SO$_2$ is removed, allowing the nitric acid reactions (1, 4, 5 in table 4) to kick in.
Figure 13: Impact of pressure on SO$_2$ removal. All the SO$_2$ in the flue gas is removed at around 18 bars, 14 bars and 12 bars for the 3-stage, 6-stage and 9-stage columns respectively.
Figure 14a: NO\textsubscript{x} mole fraction vs required residence time profile at 10 and 20 bar column operating pressures
Figure 14b: NO\textsubscript{X} mole fraction vs required residence time profile at 30 and 40 bar column operating pressures
Figure 15: Impact of Pressure on required overall gas residence time in the column for NO\textsubscript{X} removal down to about 12 ppm
Figure 16: Impact of water holdup volume (per stage) on NO$_X$ removal for a 9-stage absorber column
Figure 17: Impact of water flow rate on NO\textsubscript{X} removal from the flue gas
Figure 18a: Impact of bottoms recycle on NO\textsubscript{X} removal from the flue gas
18b: Impact of bottoms recycle on bottoms liquid pH: Lower pH reduces NO\textsubscript{X} solubility and hence deteriorates NO\textsubscript{X} removal from the gas phase, as seen in figure 18a.
Tables

Table 1: Typical flue gas composition for a pressurized oxy-coal combustion system

<table>
<thead>
<tr>
<th>Component</th>
<th>CO₂</th>
<th>H₂O</th>
<th>O₂</th>
<th>N₂</th>
<th>Ar</th>
<th>CO</th>
<th>NO</th>
<th>NO₂</th>
<th>SO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole fraction</td>
<td>0.86</td>
<td>0.015</td>
<td>0.057</td>
<td>0.015</td>
<td>0.047</td>
<td>4E-4</td>
<td>3E-4</td>
<td>8E-5</td>
<td>.002</td>
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Table 2: Pipeline Specifications

<table>
<thead>
<tr>
<th>Component</th>
<th>Gulfaks*</th>
<th>Target Specs for this study</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOₓ</td>
<td>&lt; 50ppm</td>
<td>&lt; 15ppm</td>
</tr>
<tr>
<td>SOₓ</td>
<td>&lt; 10ppm</td>
<td>&lt; 1ppm</td>
</tr>
</tbody>
</table>


Table 3: Comparing SO₂ removal rate to NO oxidation rate

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>SO₂ liquid phase absorption (mol L⁻¹ hr⁻¹)</th>
<th>SO₂ Gas Phase Route (mol L⁻¹ hr⁻¹)</th>
<th>SO₂ interfacial Route (mol L⁻¹ hr⁻¹)</th>
<th>NO oxidation (mol L⁻¹ hr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.6E-04</td>
<td>3.2E-03</td>
<td>1.3E-03</td>
<td>4.6E-06</td>
</tr>
<tr>
<td>15</td>
<td>8.4E-03</td>
<td>7.2E-01</td>
<td>1.5E+00</td>
<td>1.6E-02</td>
</tr>
<tr>
<td>30</td>
<td>2.3E-01</td>
<td>2.9E+00</td>
<td>6.0E+00</td>
<td>1.3E-01</td>
</tr>
</tbody>
</table>

Table 4: combined reaction scheme implemented in model

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>i NO+½O₂ → NO₂</td>
<td>Rate limited, 3rd order gas phase reaction</td>
</tr>
<tr>
<td>ii NO₂+SO₂ ↔ NO+ SO₃</td>
<td>Fast equilibrium reaction</td>
</tr>
<tr>
<td>iii SO₃ + H₂O ↔ H₂SO₄</td>
<td>Fast equilibrium reaction</td>
</tr>
<tr>
<td>iv 2NO₂ ↔ N₂O₄</td>
<td>Fast equilibrium dimerization reaction</td>
</tr>
<tr>
<td>v 3N₂O₄ + 2H₂O ↔ 4HNO₃ + 2NO</td>
<td>Mass transfer limited reaction</td>
</tr>
</tbody>
</table>
Table 5: Design Specifications for the Absorber Columns

<table>
<thead>
<tr>
<th>Design Specification</th>
<th>2-Column Design</th>
<th>Single Column Design</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Column 1</td>
<td>Column 2</td>
</tr>
<tr>
<td>Top stage pressure</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>Number of stages</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>Flue gas feed stage</td>
<td>Bottom (5)</td>
<td>Bottom (8)</td>
</tr>
<tr>
<td>Water Feed stage</td>
<td>Top (1)</td>
<td>Top (1)</td>
</tr>
<tr>
<td>Condenser/Reboiler</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>On-stage cooling</td>
<td>Bottom Stage</td>
<td>Bottom Stage</td>
</tr>
<tr>
<td>Vapor holdup per stage</td>
<td>20 m$^3$</td>
<td>20 m$^3$</td>
</tr>
<tr>
<td>Water flow rate</td>
<td>2kg/s</td>
<td>2kg/s</td>
</tr>
<tr>
<td>Flue gas flow rate</td>
<td>87kg/s</td>
<td>87kg/s</td>
</tr>
<tr>
<td>Column diameter</td>
<td>4.5m</td>
<td>4.5m</td>
</tr>
</tbody>
</table>

Table 6: Stream Results

<table>
<thead>
<tr>
<th>Component</th>
<th>Flue Gas In</th>
<th>Flue Gas Out</th>
<th>Flue Gas Out</th>
<th>Flue Gas Out</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Two-Column Absorber</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15 bar column</td>
<td>30 bar column</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Flow kg/sec</td>
<td>86.91</td>
<td>86.64</td>
<td>86.51</td>
<td>86.52</td>
</tr>
<tr>
<td>Temperature K</td>
<td>298.15</td>
<td>305.62</td>
<td>293</td>
<td>298</td>
</tr>
<tr>
<td>Mole Fraction</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>2.62E-04</td>
<td>2.35E-04</td>
<td>8.03E-06</td>
<td>9.08E-06</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>7.58E-05</td>
<td>3.16E-05</td>
<td>2.19E-06</td>
<td>2.75E-06</td>
</tr>
<tr>
<td>N$_2$O$_4$</td>
<td>-</td>
<td>5.57E-08</td>
<td>1.21E-09</td>
<td>1.29E-09</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>1.79E-03</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>5.06E-03</td>
<td>3.67E-03</td>
<td>1.08E-03</td>
<td>1.45E-03</td>
</tr>
<tr>
<td>N$_2$</td>
<td>1.51E-02</td>
<td>1.52E-02</td>
<td>1.52E-02</td>
<td>1.52E-02</td>
</tr>
<tr>
<td>O$_2$</td>
<td>5.73E-02</td>
<td>5.66E-02</td>
<td>5.66E-02</td>
<td>5.66E-02</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>8.73E-01</td>
<td>8.77E-01</td>
<td>8.79E-01</td>
<td>8.79E-01</td>
</tr>
<tr>
<td>AR</td>
<td>4.70E-02</td>
<td>4.72E-02</td>
<td>4.73E-02</td>
<td>4.73E-02</td>
</tr>
</tbody>
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