Modeling and parametric analysis of nitrogen and sulfur oxide removal from oxy-combustion flue gas using a single column absorber

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Chukwunwike Iloeje [a],*, Randall Field [b], Ahmed F. Ghoniem [a]

[a] Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139-4307, United States
[b] MIT Energy Initiative, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139-4307, United States

ABSTRACT

Oxy-coal combustion has great potential as one of the major CO_2 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 CO_2 and H_2O with contaminants like nitrogen oxides (NO_X), sulfur oxides (SO_X) and non-condensable gases like argon, oxygen and nitrogen. NO_X and SO_X 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 NO_X/SO_X removal based on the nitric acid and lead-chamber chemistry process (White et al., 2010). This two-column design utilizes an intermediate and a high-pressure reactive absorption column connected in series to respectively remove SO_X and NO_X from the high CO_2-concentration flue gas. In this study, we propose a modification to this two-column process that achieves the complete removal of SO_X and NO_X from the CO_2 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 NO_X/SO_X removal on key design and operating parameters for the proposed system: pressure, vapor hold-upper 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 NO_X/SO_X removal up to a point – about 20 m^3 and 2 kg/s 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_2O 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

* Corresponding author. Tel.: +1 857 5000928; fax: +1 615 253 5981.
  E-mail address: nwike@mit.edu (C. Iloeje).

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

Component	CO_2	H_2O	O_2	N_2	Ar	CO	NO	NO_2	SO_2
Mole fraction	0.86	.015	.057	.015	.047	4E−4	3E−4	8E−5	.002

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 and Wallit [8] proposed the first important configuration in this category. The schematic of the Keilin process is represented in Fig. 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 NO from the flue gas, 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 (Fig. 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 30 bar.

In this study, we propose a modification to this two-column process. This modified design (Fig. 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 on the overall performance
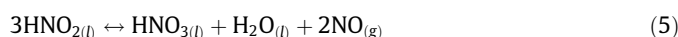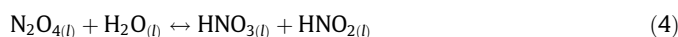
of the system. These studies are used to determine the optimal specifications for the column design and operation, and to identify design modifications that improve overall performance, energy consumption and water use.

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_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.

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)} \tag{1}$$

$$2NO_{2(g)} \leftrightarrow N_2O_{4(g)} \tag{2}$$

$$N_2O_{4(g)} \leftrightarrow N_2O_{4(l)} \tag{3}$$

$$N_2O_{4(l)} + H_2O_{(l)} \leftrightarrow HNO_{3(l)} + HNO_{2(l)} \tag{4}$$

$$3HNO_{2(l)} \leftrightarrow HNO_{3(l)} + H_2O_{(l)} + 2NO_{(g)} \tag{5}$$

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

$$R_1 = k_1 \left(p_{NO}^2 * p_{O_2} - \frac{p_{NO_2}}{K1} \right), \left[\frac{kPa}{s} \right] \tag{6a}$$
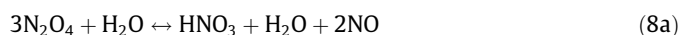
$$k_1 = \exp\left(\frac{1468}{T} - 10.9043 \right), \left[\frac{1}{kPa^2 \, s} \right] \tag{6b}$$

$$K_1 = \exp\left(-8.002 + 1.75\ln(T) - 0.000217T - \frac{2,496}{T} \right), \left[\frac{1}{kPa^2} \right] \tag{6c}$$

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

$$K_2 = \frac{p_{N_2O_4}}{p_{NO_2}}, \left[\frac{1}{kPa} \right] \tag{7}$$

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:

$$3N_2O_4 + H_2O \leftrightarrow HNO_3 + H_2O + 2NO \tag{8a}$$

Table 2
Pipeline specifications.

Component	Gulfaks[a]	Target specs for this study
NO_X	<50 ppm	<15 ppm
SO_X	<10 ppm	<1 ppm

[a] *Source:* Dynamis CO_2 quality recommendations, International Journal of Greenhouse Gas Control 2 (2008).