Nitrogen and sulphur chemistry in pressurised flue gas systems: A comparison of modelling and experiments

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A B S T R A C T

The nitrogen and sulphur chemistry is more significant during compression of flue gases than they are under atmospheric conditions. This fact became apparent during the development of oxy-fuel power plant technology to capture carbon dioxide (CO_2). In the oxy-fuel power plant, the CO_2-rich flue gas stream is compressed to enable efficient transport and storage. During this process, NO_x and SO_x are removed as acids in the condensed water. However, the chemistry of these steps is not understood well enough to allow for control and design of the process.

In the present work, the gas- and liquid-phase chemistry of NO_x and SO_x at elevated pressures were evaluated by comparing a state-of-the-art reaction mechanism to the results of experimental investigations. The model used confirms previous observations of substantial absorption of NO_x and SO_x and subsequent formation of acids in pressurised flue gas systems. The results of the modelling show that the oxidation of NO into NO_2 governs the absorption of NO_x. The complex chemistry of the liquid phase, which includes reactions between HNO_2, H_2SO_3, and possibly H_2SO_4, is critical for the rate of absorption of NO_x and SO_x from the gas to the liquid phase. This process is heavily dependent upon the pH level. The modelling suggests that N_2O is formed as a stable product through the liquid-phase reactions.

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1. Introduction

As part of efforts to counteract global warming, various technologies for carbon capture and storage have been proposed, which can be grouped into the general categories of pre-combustion, post-combustion, and oxy-fuel combustion technologies. A feature shared by all of these capture processes is that N_2 is removed from the flue gases (either before or after combustion), to create a CO_2-rich stream, which is compressed and purified to enable efficient transport and storage. During combustion the CO_2 stream is contaminated by various gases that require control measures. The focus of the present work is on the NO_x and SO_x components, whose chemistry are changed during the compression of the CO_2-rich flue gas. The flue gas conditioning in oxy-fuel combustion systems is highlighted in the present work, although the results are also applicable to other capture processes in which NO_x and SO_x species are present during flue gas compression. Depending

on the fuel and combustion conditions used, oxy-coal combustion generates a flue gas that typically contains 1000–10,000 ppm SO_x and 100–1000 ppm NO_x. During combustion, SO_2 and NO are the thermodynamically favoured species and they make up most of the total SO_x and NO_x contents. However, at ambient temperature, SO_3 and NO_2 are thermodynamically favoured. Under atmospheric conditions, the reactions are too slow for oxidation to occur during the residence time in a conventional flue gas cleaning process (maximally, a couple of minutes). However, in the oxy-fuel flue gas cleaning process, the increased pressure increases the volumetric gas-phase concentrations (mol/m^3), with the consequence that the reaction rates are increased. The solubility of NO_2 in water is high and it is absorbed by the water that is condensed during CO_2 compression. The NO_x-related gas-phase reactions, as well as the absorption and liquid phase reactions, are well-understood, the latter having HNO_2 and HNO_3 as the main products. However, in the presence of SO_x, the numbers of possible products and reaction routes increase dramatically (Chang et al., 1982; Siddiqi et al., 2003). In the liquid phases of such systems, the absorbed NO_2 will participate in a series of reactions that involve both dissolved NO_x and SO_x.

The initial practical and modelling experiences with oxy-fuel systems have shown that nitric and sulphuric acid form in the high-pressure parts of the flue-gas train (Kühnemuth et al., 2008; Liémans et al., 2011; Thébault et al., 2009; Torrente-Murciano

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et al., 2011a). The acid-forming reactions, which are active in the lead-chamber process (an industrial process for sulphuric acid production), are usually implicated the formation of sulphuric acid. However, to ensure efficiency, the lead-chamber mechanism requires that SO_2 is absorbed in highly concentrated sulphuric acid (70–80 wt%) (Meyer and Erich Pietsch, 1963), which is not the case in the process discussed here. Therefore, this mechanism is not likely to be the major route for acid formation in pressurised flue gas systems, although it could have some impact on the outcome. Previous studies of SO_x and NO_x absorption in flue-gas cleaning systems at atmospheric pressure (i.e., conventional air-fired power plants; Hüpen and Kenig, 2005; Pires and Rossi, 1997; Siddiqi et al., 2003) have emphasised the complexity of simultaneous NO_x and SO_x absorption, which has to be represented as a two-phase, multi-component reaction system.

To date, studies of the detailed reaction chemistry using relevant kinetic and equilibrium data and studies of flue-gas systems using only experimental observations (mainly focusing on the gas-phase components) have been conducted. The present investigation combines these two types of investigations and evaluates the reaction kinetics relevant to NO_x and SO_x chemistry during flue-gas compression in light of the results of the experimental studies. To compare these studies, a reactor model that describes the experimental reactors is created in which the proposed reaction kinetics is applied. The main objectives are to expand current knowledge of pressurised flue-gas systems and to elucidate the crucial reactions in this system. Understanding the SO_x and NO_x chemistry in pressurised flue gas systems is especially important, not only with respect to the development of technical solutions for emission control, but also for predicting conditions in which there is strong formation of acid and risk of corrosion.

2. Methodology

The present work investigates the nitrogen and sulphur chemistry of pressurised flue gas systems by modelling the relevant experimental data generated previously. Descriptions of the mixing and mass transfer characteristics of the model are provided below. It needs to be pointed out that the main focus in the present work is not mass transfer, which is highly dependent upon equipment design, but rather the chemistry of the system (described in Section 3). The following experimental studies, identified as pertaining to the current investigation, are compared to the modelling results: (1) experiments performed at Imperial College London (ICL), London, UK (Torrente-Murciano et al., 2011a,b); and (2) experimental work performed at the l'Université Henri Poincaré (UHP), Nancy, France (Pétrissans et al., 2005). The experimental setups are briefly presented in this chapter.

2.1. Reactor description

The modelled absorption column consists of two sections oriented in a series: (a) an initial gas–liquid section, which consists of gaseous bubbles and a liquid phase; and (b) an ending gas section, which consists of a pure gas phase. The liquid is prefilled and modelled as a perfectly mixed batch-reactor, while the gas is introduced continuously to the gas–liquid section and modelled as a series of perfectly mixed tank reactors. The composition of the inlet stream is derived from the experiments (inlet composition is presented in connection with the results). The gas–liquid and gas section are represented by five reactors each. The gas phase in the gas–liquid section in reactor j is described by:

$$\frac{dC_{A,j}^g}{dt} = \frac{1}{V_\varepsilon}(\dot{V}C_{A,j-1}^g - \dot{V}C_{A,j}^g) + \sum r_{A,j} + J_{A,j}a \tag{1}$$

The expression for the gas section is similar, but without the interfacial mass-transfer term ($J_{A,j}a$). The liquid phase is described by:

$$\frac{dC_{A,k}^l}{dt} = \sum r_{A,k} - \frac{\varepsilon}{1-\varepsilon}J_{A,k} \tag{2}$$

The liquid concentration and temperature are assumed to be constant in the reactor, owing to the high concentrations of inert gases (mainly N_2) and good mixing. Initially (at time = 0), the gas consists of pure N_2 and the liquid is pure water of pH 7. The gas phase is assumed to be saturated with water vapour throughout the reactor. The retention of gas in the bottom section is of short duration due to the low velocities of the experiments, which means that the gas residence time is longer in the gas section.

The interfacial mass transfer is described by the two-resistance theory. The gas-phase resistance (k_ga) is highly dependent upon system conditions (superficial gas velocity, type of disperser, pressure) and is difficult to estimate for specific experimental conditions. In the model, the correlation described by Cho and Wakao (1988) was used (Eq. (4)). The effect of pressure on mass transfer is not fully understood. However, it has been shown that bubble size decreases as the pressure increases, thereby affecting the contact area between the gas and the liquid (Oyevaar and Westerterp, 1989). It has also been shown that k_g decreases with pressure in gas–liquid reactors (Oyevaar and Westerterp, 1989). Eq. (4) does not rely on pressure and therefore must be adjusted for the present conditions. An initial evaluation of the experiments showed that the value on k_ga proposed by Cho and Wakao (1988) needed to be adjusted by a factor of approximately 3 at 5 bar and by a factor of 0.3 at 15 bar.

$$k_ga = 2.6 \times 10^3 D_{AB}{}^{0.5}v_{sg}{}^{0.76} \tag{4}$$