A METAL CHELATE PROCESS FOR REMOVAL OF NITRIC OXIDE FROM FLUE GAS

David Littlejohn
Eric K. Pham
S. G. Chang
Energy & Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Key words: nitric oxide, flue gas clean-up, metal chelates

INTRODUCTION

Control of sulfur dioxide (SO_2) in flue gases has been achieved by utilization of its high solubility in aqueous solutions. Unlike sulfur dioxide, nitric oxide (NO) has low solubility in aqueous solutions. Consequently, achieving simultaneous control of sulfur dioxide and nitric oxide in flue gas has been difficult to achieve. Nitric oxide can be oxidized to nitrogen dioxide (NO_2), which is more soluble. However, many oxidants are expensive and some of the oxidant material may consumed by the oxidation of dissolved sulfur dioxide. Much of the effort of research for the control of nitric oxide has focused on the development of additives that enhance the solubility of nitric oxide in aqueous solutions. Of the additives investigated, the most promising compounds appear to be metal chelates which are capable of reacting with nitric oxide to form nitrosyl complexes. In particular, many ferrous ion complexes have a high affinity for nitric oxide [1]. Some of the ferrous ion complexes that have been studied have some shortcomings. In particular, ferrous ion-polyaminocarboxylic acid complexes, such as Fe^{2+}(EDTA), are susceptible to oxidation by residual oxygen in the flue gas. The nitrosyl complexes they form react with dissolved sulfur dioxide to form nitrous oxide (N_2O) and nitrogen-sulfur compounds [2]. In recent years, we have investigated thiol-based ligands complexed with ferrous ions that have superior oxidation resistance and NO absorbing capacity [3]. We report here the results of our study of a new thiol-based iron complex using 2,3-dimercapto-1-propane sulfonate (DMPS). It is superior to Fe^{+2}(EDTA) chelate in three aspects: (a) the ability to reduce Fe^{+3} to Fe^{+2}, (b) the absence of nitrogen-sulfur byproducts, and (c) the ease of regeneration using electrochemical reduction. We present here results of the NO removal chemistry of $Fe^{+2}(DMPS)_2$ and the electrochemical regeneration of $Fe^{+2}(DMPS)_2$. Also presented are results of NO thermal desorption studies, which is an alternative regeneration method.

EXPERIMENTAL

NO Absorption Experiments The absorption of NO by $Fe^{+2}(DMPS)_2$ was studied by flowing the gas mixture through a frit at the bottom of a Pyrex column (5cm dia. x 42cm). The $Fe^{+2}(DMPS)_2$ solution was adjusted to pH 5-7 and the temperature of the solution was maintained at 55°C. Simulated flue gas (N_2 with 300-600 ppm NO and 5% O_2) was bubbled through the solution at a flow rate of about 1 L/min, providing a contact time of about 6 seconds. The NO concentration was monitored with a Thermoelectron 14A chemiluminescent NO_x analyzer. The gases were flowed until the NO concentration in the outlet gas matched that of the inlet gas.

Cyclic Voltammetry The electrolytic cell consisted of two flasks separated by an anion-exchange membrane. The cell contained a 0.7 cm dia. glassy carbon working electrode and a platinum foil counter electrode. A saturated calomel electrode was used as reference and 1M Na_2SO_4 was used for the supporting electrolyte. The experiments were performed with a Princeton Applied Research Model 173 potentiostat and a EG&G Model 175 universal programmer. The output was recorded on an XY recorder. All potentials reported are versus SCE.

Electroregeneration of $Fe^{+2}(DMPS)_2$ A somewhat larger electrochemical cell was used for regeneration of the solutions. The cell contained a 11 cm dia. glassy carbon working electrode and a platinum counter electrode separated by an anion exchange membrane. To increase current flow, a barium titanate ultrasonic

transducer was attached to the glassy carbon electrode. During the electroreduction, the solutions in both compartments were agitated with a flow of nitrogen. Under these conditions, the observed current was consistently in the range of 1.5 - 2.0 A for a 0.025 M $Fe^{+2}(DMPS)_2$ solution. Ammonia produced by the reduction was collected in a trap containing 100mL sulfuric acid connected to the electroreduction cell gas outlet. A Dionex 2010i ion chromatograph with a conductivity detector and a CS12 cation column was used to determine the concentration of NH_4^+ in the trap following electroreduction.

Thermal Regeneration of $Fe^{+2}(DMPS)_2$ In these experiments, solutions of 50 mM $Fe^{+2}(DMPS)_2$ were saturated with nitric oxide at 55°C. For thermal desorption, the flow of NO (only) was stopped and the temperature of the $Fe^{2+}(DMPS)_2NO$-containing solution was raised to 95°C. After a fixed amount of time (5 min - 2 h) at 95°C, the solution was cooled down to 55°C. The nitric oxide flow was then restarted to assess the NO removal efficiency of the regenerated solution.

RESULTS AND DISCUSSION

To determine the absorption capacity of $Fe^{+2}(DMPS)_2$ solutions, NO was bubbled through a 10 mM $Fe^{+2}(DMPS)_2$ solution, and the NO absorption capacity was measured with the NO_x analyzer. The NO absorption profile for $Fe^{+2}(DMPS)_2$ exposed to 580 ppm NO at 55°C and pH 6.6 is shown in Figure 1a. By graphically integrating the absorption trace, the amount of NO absorbed was determined, and the concentration of $Fe^{+2}(DMPS)_2NO$ was found to be 7.5 mM in the absence of oxygen. NO absorption under the same conditions except for the addition of 5% oxygen to the gas stream is shown in Figure 1b. It was found that the introduction of 5% O_2 reduces the NO absorption capacity of the solution by 44%. For comparison, a nitric oxide absorption by a 10 mM $Fe^{+2}(EDTA)$ solution under similar conditions is shown in Figure 1c. The solution formed only 2.6 mM of the NO adduct. Introducing 5% O_2 into the gas stream results in a 83% reduction in NO absorption by the $Fe^{+2}(EDTA)$ solution, as shown in Figure 1d. From these measurements, we find that $Fe^{+2}(DMPS)_2$ has 2.5 times larger NO absorption capacity than $Fe^{2+}(EDTA)$ at typical scrubber conditions in the absence of oxygen. Its performance in the presence of oxygen is even better, absorbing 7.5 time more NO than $Fe^{+2}(EDTA)$ in the presence of 5% O_2.

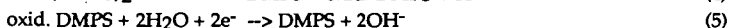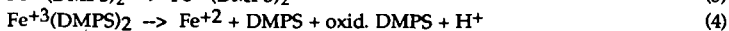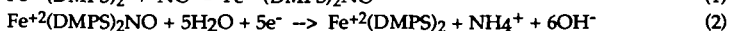The efficient removal of the NO group from the $Fe^{+2}(DMPS)_2NO$ complex to regenerate $Fe^{+2}(DMPS)_2$ for sustained NO absorption is important in the development of a practical flue gas scrubbing system. Chemical reduction of the coordinated nitric oxide is one such approach that has been used with a number of ferrous nitrosyl complexes. The nitrosyl group of many ferrous ion complexes will react with sulfite ion. However, unlike $Fe^{+2}(EDTA)NO$ and other complexes, the coordinated NO in the $Fe^{+2}(DMPS)_2NO$ complex does not react with SO_3^{2-}/HSO_3^-, even at temperatures up to 95°C. This is advantageous in that no undesirable products such as N_2O and nitrogen-sulfur compounds are formed [2]. At present, no suitable chemical agent has been found to regenerate the $Fe^{+2}(DMPS)_2$ complex due to the relative inertness of the NO group.

In an earlier study, the addition of SH-containing compounds, such as penicillamine, or ß,ß'-dimethylcysteine, had been found to enhance the NO removal ability of ferrous cysteine solutions, resulting in an increase in its NO absorption capacity [4]. However, addition of excess thiolated reagents such as cysteamine, cysteine, or DMPS, showed no notable increase in the NO absorption of $Fe^{+2}(DMPS)_2$. This is illustrated in Figure 2 which shows the effect of excess DMPS on the NO absorption capacity of a 10 mM $Fe^{+2}(DMPS)_2$ solution. There is no appreciable increase in NO absorption beyond a 2:1 complex, $Fe^{+2}(DMPS)_2$.

Since flue gas typically contains 2-8% O_2, it can oxidize Fe^{2+} to Fe^{3+}. DMPS rapidly reduces Fe^{3+} back to Fe^{2+} by electron transfer. However, the resulting oxidation of the SH moiety in DMPS leads to a disulfide (S-S) linkage. To maintain its activity, oxidized DMPS must be reduced to its original form. Electrochemical reduction of the disulfide bond to a thiol has been used to convert cystine to cysteine [5]. We have found that oxidized DMPS can be reduced electrolytically to its original state. Electroreduction can also be used to eliminate the nitrosyl group of the

Fe^{+2}(DMPS)$_2$NO complex. Cyclic voltammograms of Fe^{+2}(DMPS)$_2$NO were taken at pH 6 with a scan rate of 50 mV/s using glassy carbon and platinum electrodes. They showed a wave due to the reduction of NO at -0.75 V vs. SCE, in addition to waves associated with the reversible Fe(II)/Fe(III) redox couple. Reduction of S-S linkages has been reported to occur at about -1 V [5], where there is interference from hydrogen evolution with the electrodes. Measurements in our laboratory suggest that the potential that is needed may be somewhat lower.

The fate of the coordinated NO following electroreduction is of interest. Results from our analysis of the reduction products by ion chromatography indicate that the NO is reduced to NH$_3$ with quantitative yield. There is no evidence, based on gas chromatography analysis, of either N$_2$ (2-electron reduction) or N$_2$O (1-electron reduction) being formed. Controlled-potential bulk electrolysis of Fe^{+2}(DMPS)$_2$NO solutions indicates that current densities of 15-20 mA/cm^2 can be routinely achieved using ultrasound vibration and nitrogen bubbling. Under these conditions, the NO desorption rates, as measured from NO absorption experiments on the electroregenerated Fe^{+2}(DMPS)$_2$ solutions, are 6 x 10^{-5} mol/min and 1.2 x 10^{-5} mol/min, in the absence and presence of 5% O$_2$, respectively. More importantly, there is no attenuation in the NO removal capacity of the electroregenerated Fe^{+2}(DMPS)$_2$ after repeated electroreduction cycles. This indicates that electrolytic decomposition of the chelate is unlikely. Therefore, electrolysis of Fe^{+2}(DMPS)$_2$NO solutions accomplishes dual tasks in the regeneration of Fe^{+2}(DMPS)$_2$: (1) it electrochemically removes bound NO, and (2) it electroreduces the S-S linkage to reform the S-H groups. This is illustrated in the following scheme:

$$Fe^{+2}(DMPS)_2 + NO = Fe^{+2}(DMPS)_2NO \qquad\qquad (1)$$
$$Fe^{+2}(DMPS)_2NO + 5H_2O + 5e^- \longrightarrow Fe^{+2}(DMPS)_2 + NH_4^+ + 6OH^- \qquad (2)$$
$$Fe^{+2}(DMPS)_2 \overset{O_2}{\longrightarrow} Fe^{+3}(DMPS)_2 \qquad\qquad (3)$$
$$Fe^{+3}(DMPS)_2 \longrightarrow Fe^{+2} + DMPS + oxid.\ DMPS + H^+ \qquad (4)$$
$$oxid.\ DMPS + 2H_2O + 2e^- \longrightarrow DMPS + 2OH^- \qquad (5)$$

Thermal desorption of NO from Fe^{+2}(DMPS)$_2$NO represents a simple and attractive method for the regeneration of Fe^{+2}(DMPS)$_2$. We have determined the extent of NO desorption by heating a 50 mM Fe^{+2}(DMPS)$_2$ solution, under anaerobic conditions: the NO-saturated solution containing the resulting 37 mM Fe^{+2}(DMPS)$_2$(NO) was subjected to several cycles of heating to 100°C for fixed amounts of time followed by NO absorption experiments at 55°C to quantify the amount of NO desorbed. The results are shown in Figure 3 which plots the percentage of Fe^{+2}(DMPS)$_2$ recovered as a function of heating time (from 55°C to 100°C to 55°C). Up to 7.5% of the 37 mM of absorbed NO can be removed by heating the spent solution to 100°C for 2h. Heating times of more than 2h become impractical due to significant water evaporation. There is also no evidence of a linear increase in the amount of NO removed following more than 2h of 100°C heat. These results are reproducible over additional thermal cycles, thus precluding the possibility of thermal decomposition of Fe^{+2}(DMPS)$_2$ and its NO adduct.

In the presence of 5% O$_2$ and under similar experimental conditions, a 50 mM Fe^{+2}(DMPS)$_2$ solution absorbs 17 mM of NO. Of this amount, only 5% could be desorbed in the presence of 5% O$_2$ after 2h of heat treatment at 100°C. However, there is a rapid drop off to negligible NO desorption in the second thermal cycle due to the oxidation of DMPS. Thus, to make the process recyclable, electrochemical regeneration of DMPS which is needed to reduce Fe^{+3} to Fe^{+2} for sustained NO absorption must still be used. Even so, a comparison of the NO removal efficiencies in the absence of oxygen clearly indicates that thermal desorption is not as efficient as electroreduction in regenerating Fe^{+2}(DMPS)$_2$.

REFERENCES

1. Littlejohn, D. and S.G. Chang, Kinetic Study of Ferrous Nitrosyl Complexes. *J. Phys. Chem.*, **1982**. *86*, 537-540.

2. Littlejohn, D. and S.G. Chang, Reaction of Ferrous Nitrosyl Chelates with Sulfite and Bisulfite Ions. *I&EC Res.*, **1990**. *29*, 10-14.

3. Chang, S.G., D. Littlejohn, and D.K. Liu, Use of Ferrous Chelates of SH-Containing Amino Acids and Peptides for Removal fo NO_x and SO_2 from Flue Gases. *I&EC Res.*, **1988**. *27*, 2156-2161.

4. Liu, D.K., L.P. Frick, and S.G. Chang, A Ferrous Cysteine Based Recyclable Process for the Combined Removal of NO_x and SO_2 from Flue Gas. *Environ. Sci. Technol.*, **1988**. *22*, 219-223.

5. Zagal, J.H. and P. Herrera, Electrochemistry of Cysteine and Cystine on Metal-Phthalocyanines Adsorbed on a Graphite Electrode. *Electrochim. Acta*, **1985**. *30*, 449-454.
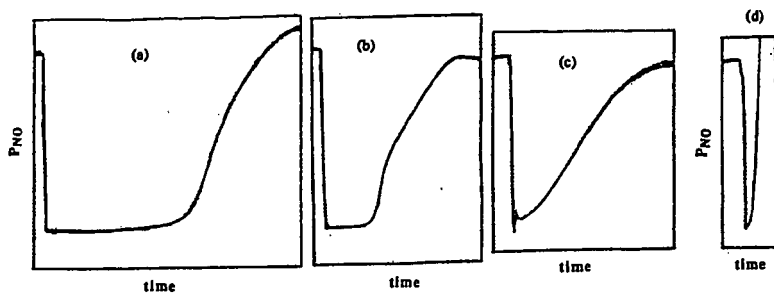
Figure 1. Comparison of NO absorption by $Fe^{+2}(DMPS)_2$ and $Fe^{2+}(EDTA)$ solutions, with and without the presence of 5% oxygen.

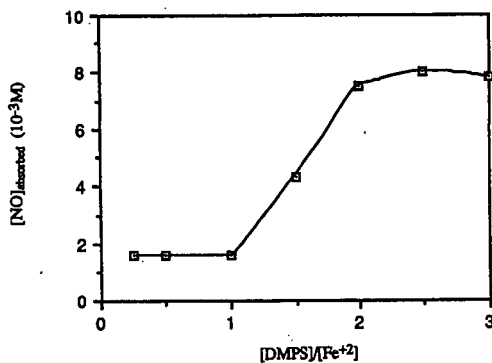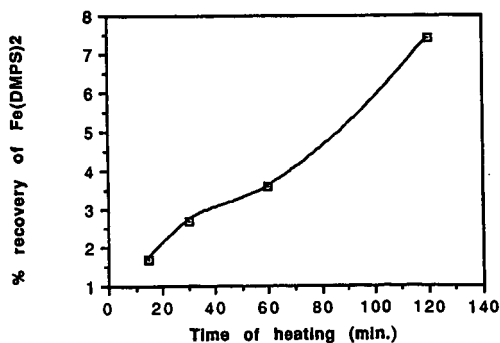Figure 2. Effect of Fe^{2+}:DMPS ratio on the absorption of nitric oxide.

Figure 3. Percent recovery of $Fe^{+2}(DMPS)_2$ as a function of time of heat treatment (55°C --> 100°C --> 55°C) of a 37mM $Fe^{+2}(DMPS)_2(NO)$ solution generated from 50mM $Fe^{+2}(DMPS)_2$ + 550ppm NO (pH 6, 55°C).