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NO$_x$ and SO$_2$ Removal From Flue Gas
by Ferrous Ion-Peptide Solutions

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SO₂ and NOₓ generated by combustion are believed to oxidize in the atmosphere to form H₂SO₄ and HNO₂/HNO₃. The main removal mechanism of these acids from the atmosphere is precipitation, popularly referred to as acid rain. Considerable research is being done to develop efficient, cost-effective procedures to remove SO₂ and NOₓ from power plant flue gases (1). SO₂ can be removed more readily than NOₓ since it is highly soluble in aqueous solutions and can be oxidized to form SO₄²⁻. The sulfate ion can then be precipitated with calcium ions, if desired. Most of the NOₓ is in the form of NO, which has limited solubility in water. Many control strategies for NOₓ have focused on compounds which enhance the solubility of NO. These systems are usually based on ferrous ion-chelate compounds which readily form nitrosyl complexes (2). Early systems used aminocarboxylic acid chelates such as EDTA, because of their large equilibrium constants for the formation of nitrosyl complexes. However, these systems were very sensitive to the presence of oxygen. In oxygen-free systems, solutions of these compounds can remove significant amounts of NO (3). With oxygen present, the ferrous ion is rapidly oxidized to ferric ion, which does not absorb NO. The oxidized metal ion must then be chemically or electrically reduced to the +2 state. This adds to the cost and complexity of processes using these compounds. The recovery or removal of the absorbed NO is not straightforward in these systems, and it would be desirable to develop a chemical system in which this could be done more easily.

In a search for more suitable iron-chelate combinations, the ferrous ion-cysteine combination was studied (4). It was found that cysteine would readily reduce ferric ion to ferrous ion, and in so doing, keep most of the iron in the ferrous state when exposed to oxygen. The ferrous ion-cysteine system was found to be capable of absorbing significant amounts of NO, with or without the presence of oxygen. Cystine, the oxidized form of cysteine, can be reduced back to cysteine by the appropriate application of HS⁻ and SO₄²⁻ (5). These compounds can be obtained from the SO₂ removed from the flue gas.

Various cysteine derivatives have been studied to determine if they would be superior to cysteine in removing NO from flue gas. These include glutathione (a tripeptide) and glycylcysteine (a dipeptide) which are the subject of this study. Glutathione (glutamylcysteinylglycine, abbreviated GSH) is a thiol compound that is abundant in living cells. It is composed of the amino acids glutamic acid, cysteine and glycine linked by peptide bonds. Cysteine is the central amino acid. In a manner similar to cysteine, GSH can be oxidized to the disulfide (noted as GSSG).

Glycylcysteine is readily produced by the acid hydrolysis of GSH (6). It also forms a disulfide when oxidized.

**EXPERIMENTAL**

Glutathione (Sigma Chemical, 99%) was used without further purification. Glycylcysteine was prepared by hydrolyzing glutathione in 1.2N HCl at 95 °C for 60-90 min. under a nitrogen atmosphere. Yield was in excess of 95%. Pyrrolidone carboxylic acid (pyroglutamic acid) is a co-product of the hydrolysis. It was prepared independently by heating glutamic acid with an equal amount of water in a sealed tube to 140 °C for 3 hours (7). The compounds used for preparing the acetate and borate, as well as the ferrous ammonium sulfate, were of reagent grade quality.

Two types of experiments were done with the ferrous ion - peptide systems in aqueous solutions to study their effectiveness in removing NO from the gas phase. In the first set of experiments, buffered ferrous ion - peptide solutions were prepared on a vacuum line. A bulb of known volume was filled with NO and expanded into the evacuated bulb.
with the ferrous ion - peptide solution. The pressure was noted and vigorous stirring of
the solution was initiated. Once the pressure stabilized, the pressure drop was used to
calculate the amount of NO absorbed by the solution. Corrections were made for water
vapor pressure and the solubility of NO in water. Runs were done with the pH of the
solution ranging from acidic to alkaline. All runs were done with the peptide concentra-
tion four times that of the ferrous ion concentration.

The second type of experiment is designed to determine the ability of ferrous ion -
peptide to remove NO from the gas phase under realistic conditions. Simulated flue gas
was prepared by mixing nitrogen, oxygen, nitric oxide and, in some cases, sulfur dioxide.
The gas mixture was passed through the buffered ferrous ion - peptide solution, which had
been heated to 55°C. NO removal was determined by measuring the fraction of NO not
absorbed by the solution using a chemiluminescent NO\(^2\) analyzer. The plot of NO
absorbed vs. time, was graphically integrated to obtain the total quantity of NO removed
by the solution. When SO\(_2\) was used, the amount of SO\(_2\) removed was obtained in a
similar manner using a pulsed fluorescent SO\(_2\) analyzer.

The solutions were saved for analysis after the experiments were complete. Ferrous
ion was analyzed by the 1,10 phenanthroline method. Nitrate and nitrite ions were
analyzed by ion chromatography. An amino acid analyzer was used to measure the
amounts of the reduced and oxidized forms of the peptides that were present.

RESULTS AND DISCUSSION

The NO absorption experiments with glutathione were done over a pH range from
3.0 to 8.5. The ferrous ion concentrations were 0.02M. The NO:Fe stoichiometry was 2:1
or higher over the pH range studied. The stoichiometric ratio increased as the pH
increased. In solutions with pH <7, the nitrosyl complex formed a rust-colored precipi-
tate. This is similar to what is observed in ferrous cysteine solutions when treated with
NO. In alkaline solutions, no precipitate was observed.

NO absorption by ferrous ion - glyclycysteine solution was studied over a pH range
from 4 to 9. Again, a NO:Fe stoichiometry in excess of 2:1 was found. With glyclycysteine,
a solid nitrosyl complex formed at all pH conditions. The appearance of the precipi-
tates was similar to the solids obtained with GSH.

To confirm that glyclycysteine, not pyroglutamic acid, was responsible for the NO
absorption observed, separate experiments were run with glutamic acid and pyroglutamic
acid. Solutions of these compounds mixed with ferrous ions absorbed NO only marginally
better than solutions of ferrous ions alone. This suggests that the peptide forming the
complex with the ferous ion needs to contain cysteine to efficiently bind NO.

The NO absorption experiments discussed above were done with approximately one
atmosphere of NO. The second set of experiments, in which the NO-containing gas was
bubbled through the heated solution, were done at much lower concentrations. The gas
mixture was typically 96% N\(_2\), 4% O\(_2\) and 500 ppm NO. SO\(_2\), when included, was typi-
cally at 2500 ppm. The ferrous ion concentration used in these experiments was 0.01M,
and the peptide concentration was four times higher. The ferrous ion - GSH solutions
were studied over a pH range of 4.3 to 10.9, and the ferrous ion - glyclycysteine solutions
were studied at pH 4.3 to 9.2.

Essentially no NO was absorbed by the Fe(II)-GSH solution at pH 4.3, suggesting
the equilibrium constant for the formation of the nitrosyl complex is small under these
conditions. At slightly less acidic conditions (pH 5.4), the best NO removal was found.
An NO:Fe stoichiometry of 0.54:1.0 was obtained. This stoichiometry decreased as the
pH rose, ending with NO:Fe = 0.17:1.0 at pH 10.9. The decrease with increasing pH is presumably due to the increasing role of oxidation of GSH and Fe(II) with the increase in pH. The rate of NO absorption was found to be highest in neutral and slightly alkaline solutions, and the rate was slowest in the acid solutions. SO₂ was less difficult than NO to remove. It was removed most efficiently by alkaline solutions.

In the alkaline solutions, almost all the NO absorbed was converted to nitrite and nitrate ions. Almost all of the iron in the solution precipitated out in Fe(III) form. Much of the GSH was oxidized to GSSG. Under very alkaline conditions, there was some decomposition of the GSH.

The ferrous ion - glycylcysteine solutions absorbed NO at all conditions studied. The NO:Fe stoichiometry was about 0.3:1.0 in acidic conditions and rose to 0.87:1.0 at pH 7.3. It then dropped off rapidly as the pH increased, falling to 0.05:1.0 at pH 9.2. The rate of NO absorption was slowest under acidic conditions. In neutral or alkaline conditions, the rate of NO absorption was considerably higher than with the corresponding GSH solutions. It appears that oxidation of the Fe(III) and glycylcysteine is significant in alkaline conditions, and this limits how much NO can be absorbed. In acidic conditions the oxidation is slower, but the NO absorption is also slow.

A rust-colored precipitate formed in all of the solution, apparently containing most of the iron as Fe(III). Most of the glycylcysteine was oxidized to the disulfide form.

Both GSH and glycylcysteine are capable of reducing Fe(III) to Fe(II) in solution. Thus, they enhance the NO removal capabilities of an Fe(II) solution not only by forming an effective ferrous nitrosyl complex, but also by maintaining the iron in the ferrous state. Of course, the peptides will be oxidized as a result. The oxidized peptides can be reduced to their original form by several methods. These include the technique developed for cysteine in which the oxidized material is sequentially treated with H₂S and SO₂ (5).

These compounds have been found to be considerably more effective than cysteine in ferrous ion - based NO removal systems operating at pH 5 to 7. Other cysteine-based peptides might be equally effective. To be commercially useful, however, the compounds must not be excessively expensive and capable of being regenerated without large losses.
REFERENCES


