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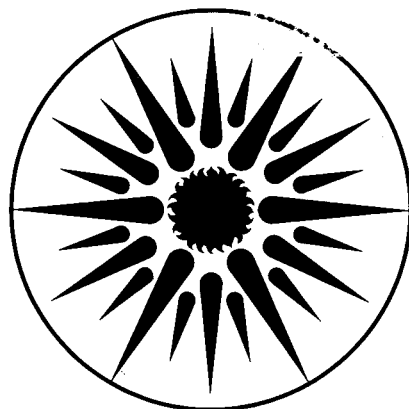
USE OF FERROUS CYSTEINE AND CYSTEINE DERIVATIVES FOR THE REMOVAL OF NO_x AND SO₂ FROM FLUE GAS

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March 1987

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**Use of Ferrous Cysteine and Cysteine Derivatives
for the Removal of NO_x and SO₂ from Flue Gas**

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ABSTRACT

The use of ferrous complexes of cysteine and its derivatives for the removal of NO and SO₂ in wet flue gas clean-up systems is reported. Compared to conventional chelates such as EDTA, these thioamino acids not only can stabilize ferrous ion in alkaline solutions to promote the absorption of NO, but are also capable of rapidly reducing any ferric ions formed during the scrubbing process back to ferrous ions so that continual absorption of NO can be achieved. In the case of ferrous cysteine, the absorbed NO is further reduced to form N₂. The disulfide form of the thioamino acids produced upon oxidation can be conveniently reduced by SO₂ and H₂S to regenerate the starting thioamino acids, thus making possible the recycling of the reagents. The effects of pH, O₂, SO₂, and S₂O₃²⁻ on the absorption of NO by ferrous thioamino acid complexes will also be discussed.

Introduction

The wet lime/limestone system is currently the most widely used flue gas desulfurization scrubber in the utility industry. This system is very efficient in SO_2 removal; however, it removes only a little NO_x . This is because most of the NO_x in flue gas is NO , which is only slightly soluble in aqueous solution. Work has been conducted at several institutions to modify the system such that NO_x can be removed simultaneously [1-3]. One approach that has been developed involves the addition of ferrous chelates such as Fe^{2+} (EDTA) in scrubbing liquor to promote the solubility of NO by forming Fe^{2+} (EDTA)(NO). The absorbed NO is then chemically converted to N_2O , N_2 and nitrogen-sulfur compounds [2-5] by reacting with dissolved SO_2 . One problem associated with this approach is that these nitrogen-sulfur compounds, including hydroxylamine sulfonates and amine sulfonates have to be removed from the scrubbing liquors. Another complication is that residual oxygen in the flue gas in the range of 3-5% will oxidize ferrous chelates into ferric chelates, which are inactive in complexing with NO . As a result, NO removal efficiency cannot be sustained. Therefore, an efficient and cost-effective way for reducing ferric chelates back to ferrous chelates is necessary.

Several conventional methods for reducing ferric chelates to ferrous chelates have been tested, including electro- and chemical reductions. The electroreduction method is not effective if applied in-situ in the absorber because excess electrical energy is then required for reducing other species, such as dissolved O_2 , which have lower reduction potentials than ferric chelates. The most well-tested chemical method is the reduction of ferric chelates by bisulfite ions, which come from dissolution of SO_2 in flue gas. However, the reaction rate is slow and therefore a big holding tank is required. Furthermore, dithionate ion is produced, which is very soluble, and cannot be easily removed from the scrubbing liquors [3]. Finally, the reduction of ferric chelates to ferrous chelates by H_2S

may be a viable approach [6]. This technology has been applied in the control of H₂S emission, but has not been well developed for the purpose of controlling NO_x or SO₂ emissions. It appears that fine tuning of reaction conditions is required to prevent pyrite formation.

This paper reports the use of a new type of ferrous chelate for simultaneous removal of NO_x and SO₂ from flue gas. The new chelating agents are cysteine and cysteine derivatives which include acetylcysteine, penicillamine, and glutathione. These chelating agents are amino acids or peptides containing a thiol (-SH) group and collectively will be called thioamino acids. The molecular structures of ferrous thioamino acid complexes are shown in Figure 1. The use of these new ferrous chelates creates different and simpler chemistry in scrubber systems, compared to those using Fe²⁺ (EDTA). A system using ferrous thioamino acid complexes produces little or no dithionate or nitrogen-sulfur compounds. Other advantages include the ability of thioamino acids to reduce Fe³⁺ to Fe²⁺ and that the oxidation products (the dimers of corresponding thioamino acids) can be conveniently converted back to thioamino acids, thus making the process recyclable.

Experimental Section

The effects of oxygen, pH of the solution, chemical additives, and the molar ratio of chelates to ferrous ion, $n_{\text{chelate}}/n_{\text{Fe}^{2+}}$, on the reaction of ferrous thioamino acid complexes with NO have been studied. The amount of NO which can be absorbed into the solutions at different conditions were determined using a bench-scale gas scrubber and a Thermolectron Model 14A chemiluminescent NO_x analyzer [7]. The experiments were carried out at 55° C and between pH 6.8-12.0 by bubbling a gaseous mixture of NO (P_{NO} = 500 ppm), O₂ (0 % or 4%) and N₂ (balance) into an absorber containing about 250 ml of an aqueous solution of ferrous salt (0.005-0.05 M) and cysteine (0.02-0.75 M) or

cysteine derivatives (0.02-0.04 M). The gas flow rates were about 750 ml/min.

The identification of reaction products after the absorption of NO by solutions containing ferrous thioamino acid complexes was accomplished by the use of an amino acid analyzer for chelates, a Dionex 2010i ion chromatograph for $[\text{NO}_2^-]$ and $[\text{NO}_3^-]$, and a 1,10-phenanthroline photometric method for the Fe^{2+} and Fe^{3+} analysis.

For the reduction of cystine to cysteine, the following procedure was used. 0.2 l of a cystine solution (0.04 M) buffered with sodium borate (0.05 M Na^+) at pH 10.0 was allowed to equilibrate at 60° C. H_2S and SO_2 (6.11% in N_2) were bubbled through the cystine solution for 20 min. at flow rates of 0.01 l/min and 0.9 l/min, respectively. Aliquots of the reaction mixture were taken at designated time intervals and monitored by amino acid analysis.

Results and Discussion

When oxygen is absent from the simulated flue gas, ferrous cysteine is more effective in absorbing NO than the corresponding penicillamine and N-acetylcysteine (Figure 1). The presence of 4% O_2 in the simulated flue gas significantly reduces the NO absorption capacity of all ferrous thioamino acid complexes, with ferrous cysteine being the most adversely affected (Figure 2). The decrease in the NO absorption capacity in the presence of O_2 is attributed to the rapid oxidation of thioamino acids to their corresponding dimers by O_2 , catalyzed by the Fe^{2+} in solutions. It is important to point out that while the capacity for NO absorption for the ferrous thioamino acid complexes in the presence of 4% O_2 follows the order $\text{Fe}(\text{glutathione}) > \text{Fe}(\text{penicillamine}) > \text{Fe}(\text{N-acetylcysteine}) \geq \text{Fe}(\text{cysteine})$, the rate of NO absorption follows a more or less reversed order, i.e., $\text{Fe}(\text{cysteine}) > \text{Fe}(\text{penicillamine}) > \text{Fe}(\text{N-acetylcysteine}) > \text{Fe}(\text{glutathione})$. The reaction rates were not quantitatively determined, but the relative reaction rates were

estimated from the NO absorption curves. It has been suggested [8] that the two β -methyl groups in penicillamine serve to inhibit oxidation-reduction reactions. Therefore, steric factors appear to play an important role in the capacity and the kinetics of NO absorption by ferrous complexes of SH-containing amino acids.

While the NO absorption capacity of ferrous cysteine is fairly pH independent in the presence of 4% O₂, the ferrous penicillamine, N-acetylcysteine and glutathione systems are more efficient as the solutions become more acidic, up to pH \sim 5 (Figure 3). The effect of pH on the NO absorption is attributed to the pH dependence of the ionization constants of thioamino acids, stability constants of ferrous thioamino acid complexes and ferrous hydroxide, and the oxidation rate of thioamino acids by O₂ catalyzed by Fe²⁺. The complexation of ferrous thioamino acids can be achieved only when the pH of the solutions is higher than the pKa of the -COOH and -SH groups for a particular thioamino acid. However, the higher the pH of the solution, the larger the stability constant of ferrous hydroxide and the less the fraction of ferrous ion is in the form of ferrous thioamino acid complexes. The thioamino acids appear to be more stable towards oxidation by O₂ at lower pH.

The fate of the absorbed NO has been studied in some detail. Previous results [9] have shown that reaction products depend very much on the pH of the solution in the absence of oxygen in the ferrous cysteine system. Infrared spectroscopic and elemental analyses of the solid residue revealed that if the reaction was carried out at pH \sim 7, part of the NO absorbed was bound to the metal chelate to form a dinitrosyl complex with the empirical formula [Fe(CySSCy)(NO)₂], where CySSCy represents cystine. The coordinated NO could be released when the solid was subjected to heating (\sim 155° C) or placed under vacuum (\leq 10⁻² torr). Gas phase products were determined by mass spectral analysis to contain N₂ and N₂O. The latter could be produced from the reaction of NO

with ferrous cysteine and/or the thermal decomposition of NO in the reaction chamber. However, the same reaction at $\text{pH} \geq 8$ yielded no nitrosyl complex; most of the NO absorbed was reduced to N_2^- .

In the presence of 4% oxygen, an analogous dinitrosyl metal complex was not detected. Most of the NO was either reduced to N_2 and N_2O in the gas phase or converted to NO_2^- (about 6%) in solutions for systems using ferrous cysteine [10]. In the ferrous glutathione system, all of the absorbed NO was converted to a mixture of NO_2^- (> 90%) and NO_3^- at $\text{pH} > 7$. When the same absorption reaction was carried out at $\text{pH} \sim 5$, < 10% $\text{NO}_2^-/\text{NO}_3^-$ and no $\text{N}_2\text{O}/\text{N}_2$ were detected, which suggested the formation of an iron nitrosyl complex. In all cases, iron (II)/(III) hydroxide and the oxidized (dimeric) form of the thioamino acids were formed at $\text{pH} > 9$. The fact that a greater fraction of NO was reduced to N_2 and N_2O , and a lesser fraction of NO was oxidized to NO_2^- and NO_3^- in the ferrous cysteine than ferrous glutathione systems implies that cysteine is a stronger reducing agent than glutathione.

The effects of several additives on the NO removal efficiency were examined, and the results are summarized in Table I. Power plant flue gas typically contains several thousand ppm SO_2 , which dissolves in scrubbing liquors to form primarily SO_3^{2-} at $\text{pH} > 9$. The effect of SO_2 on the NO absorption capacity can therefore be studied by the addition of SO_3^{2-} to the ferrous cysteine solution. Addition of SO_3^{2-} to the scrubbing solution increases the number of moles of NO absorbed per mole of ferrous salt added ($n\text{NO}/n\text{Fe}^{2+}$). The SO_3^{2-} additive can improve the NO removal efficiency via two routes: (i) by its reaction with O_2 to form SO_4^{2-} ; and (ii) by its reaction with CySSCy to form CySH and cysteine sulfonate (vide infra). High concentrations of $\text{S}_2\text{O}_3^{2-}$ also appear to enhance NO removal, probably because $\text{S}_2\text{O}_3^{2-}$ can serve as an oxidation inhibitor. It is

expected that SO_3^{2-} and $\text{S}_2\text{O}_3^{2-}$ will also improve the NO removal efficiency for systems using ferrous cysteine derivatives. The extent of the improvement may not be as much as that in the ferrous cysteine system because the effect of O_2 is not as pronounced.

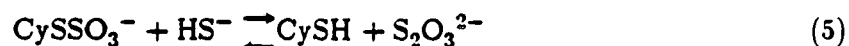
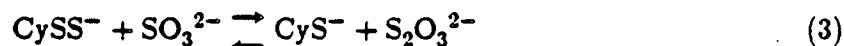
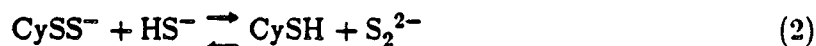
As mentioned earlier, residual O_2 in flue gas can oxidize cysteine (CySH) to cystine (CySSCy) in the presence of Fe^{2+} catalyst. Therefore, the use of excess CySH should improve the performance of ferrous cysteine. As shown in Figure 4, increasing [CySH] at a fixed $[\text{Fe}^{2+}]$, increases $n\text{NO}/n\text{Fe}^{2+}$ from 0.01 at $[\text{CySH}]/[\text{Fe}^{2+}] = 1$ to 0.065 at $[\text{CySH}]/[\text{Fe}^{2+}] = 16$. However, the number of moles of NO absorbed per mole of CySH, $n\text{NO}/n\text{CySH}$, decreases from 0.01 at $[\text{CySH}]/[\text{Fe}^{2+}] = 1$ to 0.004 at $[\text{CySH}]/[\text{Fe}^{2+}] > 4$. Therefore, the exact ratio of CySH to Fe^{2+} to be used would depend on whether the NO removal efficiency of the ferrous cysteine system is to be maximized with respect to Fe^{2+} or CySH.

In our previous papers [9,10], we demonstrated that cysteine was oxidized to cystine in the reaction of ferrous cysteine with both NO and O_2 under most experimental conditions used. We have recently found that cysteine derivatives undergo similar oxidation processes to form corresponding dimers when their ferrous complexes react with O_2 , but not with NO in the case of glutathione. It is therefore necessary to reduce the dimeric thioamino acids back to monomeric forms in order to make the process recyclable. We have developed a simple and potentially cost-effective method for the regeneration of cysteine from cystine using H_2S (or sulfide/hydrogen sulfide ion) and SO_2 (or sulfite/bisulfite ion). In principle, this method may also be applied to the regeneration of cysteine derivatives.

The regeneration of cysteine from cystine has been performed under several experimental conditions [10]. The best result obtained so far was from the reaction of CySSCy

with H₂S at pH 10 and 60 °C (Table II, Method I). The concentrations of HS⁻ and SO₃²⁻ are estimated to be 0.04 M and 0.22 M, respectively. In this case, a 90% yield of CySH was obtained together with small amounts of cysteine sulfonate (CySSO₃⁻) and unreacted CySSCy. The yield of CySH was increased to 95% upon neutralization of the reaction mixture to pH ~ 7. The concentration-time profile of this reaction is shown in Figure 5. When H₂S and SO₂ were applied simultaneously under the same conditions (Method IIa), CySH was obtained in 85% yield. The slightly lower yield could be attributed to the slow reaction between HS⁻ and SO₃²⁻ to form S₂O₃²⁻ at 60 °C.

The effects of temperature and pH on this CySH regeneration were examined. Raising the reaction temperature to 80 °C did not affect the yield of CySH (Method IIb), although the equilibrium was achieved in ~ 15 min. Finally, increasing the pH to 12 also had no effect on the CySH yield (Method IIc). The mechanism for the conversion of CySSCy to CySH is summarized by the following equations:

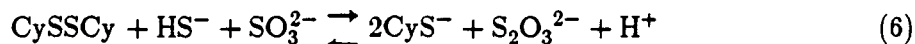


where CySS⁻ represents S-thiocysteine.

We have recently completed a kinetic study [11] of reactions (1) and (2). The reaction between CySSCy and SO₃²⁻, reaction (4), is also well established [12]. Preliminary

experiments in our laboratory have provided evidence for reactions (3) and (5). Therefore, the conversion of both CySSCy and CySSO_3^- to CySH is possible using the above procedure.

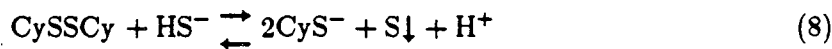
The overall reaction for the regeneration of CySH from CySSCy using HS^- and SO_3^{2-} can be expressed as



In an acidic medium, thiosulfate decomposes to form HSO_3^- (and/or SO_2) and colloidal sulfur, as shown in equation 7.



By adding equations 6 and 7 and taking into account the equilibrium between SO_3^{2-} and HSO_3^- , we obtain the net equation



Thus the only reagent consumed in the conversion of CySSCy to CySH is HS^- , and elemental sulfur is formed as a product. The latter can be converted back to H_2S by reaction with H_2 , which can be derived from CO and H_2O (water-gas shift reaction) [13]. Therefore, in essence, the reducing agent consumed in this CySH regeneration scheme is CO , which can be easily obtained from the incomplete combustion of coal. It can be inferred from equation 8 that one mole of CO is required for the regeneration of two moles of CySH .

Conclusion

The scrubber chemistry using ferrous thioamino acid complexes depends on the reducing strength of the particular thioamino acid used. A strong reducing agent such as cysteine can reduce not only Fe^{3+} to Fe^{2+} but also NO to N_2 and possibly N_2O , whereas a

weak reducing agent such as glutathione reduces Fe^{3+} to Fe^{2+} , but not NO in any significant quantity. In the latter case, NO is probably complexed and then oxidized by O_2 to form NO_2^- , especially at alkaline conditions. The NO_2^- is expected to react with HSO_3^- to produce N-S compounds, which can be precipitated out of the scrubbing liquors as potassium salts. Because the reduction rate of Fe^{3+} to Fe^{2+} by thioamino acids is very rapid, it not only prevents the formation of dithionate ion resulting from the reduction of Fe^{3+} by HSO_3^- , but also maintains the Fe^{2+} concentration in the absorber and sustain the NO removal efficiency if the thioamino acid can be continually refurbished. It is therefore desirable to release a side stream of scrubbing liquors from the absorber so that the thioamino acids can be regenerated from their oxidized (dimeric) form for recycling. The regeneration method developed appears to be simple and potentially cost-effective. The chemicals consumed in this regeneration method are water and CO, which can be obtained from the incomplete combustion of coal.

Based on the chemistry discussed, it appears that ferrous thioamino acid complexes will provide several advantages over Fe^{2+} (EDTA), when used as additives in wet lime/limestone systems for combined control of NO_x and SO_2 emissions. The fact that there is a specific pH range where each ferrous thioamino acid complex operates (Figure 3) implies that ferrous thioamino acid additives may be more suitable for the integration with a double alkaline system for the simultaneous removal of NO_x and SO_2 from flue gas.

It is very desirable to develop additives for use with alkaline solutions or slurries in spray drying systems for combined removal of NO_x and SO_2 from flue gas. Ferrous cysteine can rapidly absorb NO and reduce NO to N_2 and/or N_2O , and thus appears to be suitable for use in spray drying systems. However, the stoichiometric ratio of ferrous cysteine to NO (Figure 3) required for obtaining the desired NO removal efficiency appears

to be to large to be practical.

ACKNOWLEDGEMENT

We appreciate the support and encouragement of Charles Drummond, Gilbert McGurl and Michael Perlsweig. This work was supported by the Assistant Secretary for Fossil Energy, U.S. Department of Energy under Contract No. DE-AC03-76SF00098 through the Pittsburgh Energy Technology Center, Pittsburgh, PA.

Additive	Concentration, M	nNO/nFe ²⁺
none	—	0.023
Na ₂ SO ₃	0.05	0.040
	0.10	0.050
	0.50	0.068
Na ₂ S ₂ O ₃	0.05	0.030
	1.00	0.080

^aThe concentrations of Fe²⁺ and CySH were 0.01M and 0.04M, respectively. The reaction was carried out at pH 9.5 (borate buffer) and 55 ° C using a gas mixture of 500 ppm NO, 4% O₂ and the balance N₂.

Method*	pH	T °(°C)	CySH, %	CySSO ₃ ⁻ , %	CySSCy, %
I	10.0	60	90	5	4
IIa	10.0	60	85	8	6
IIb	10.0	80	84	10	6
IIc	12.0	60	84	6	5

*See text for description of experimental methods.

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Figure Captions

Fig. 1 The molecular structures of ferrous complexes of cysteine, penicillamine, N-acetylcysteine and glutathione.

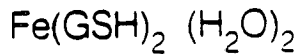
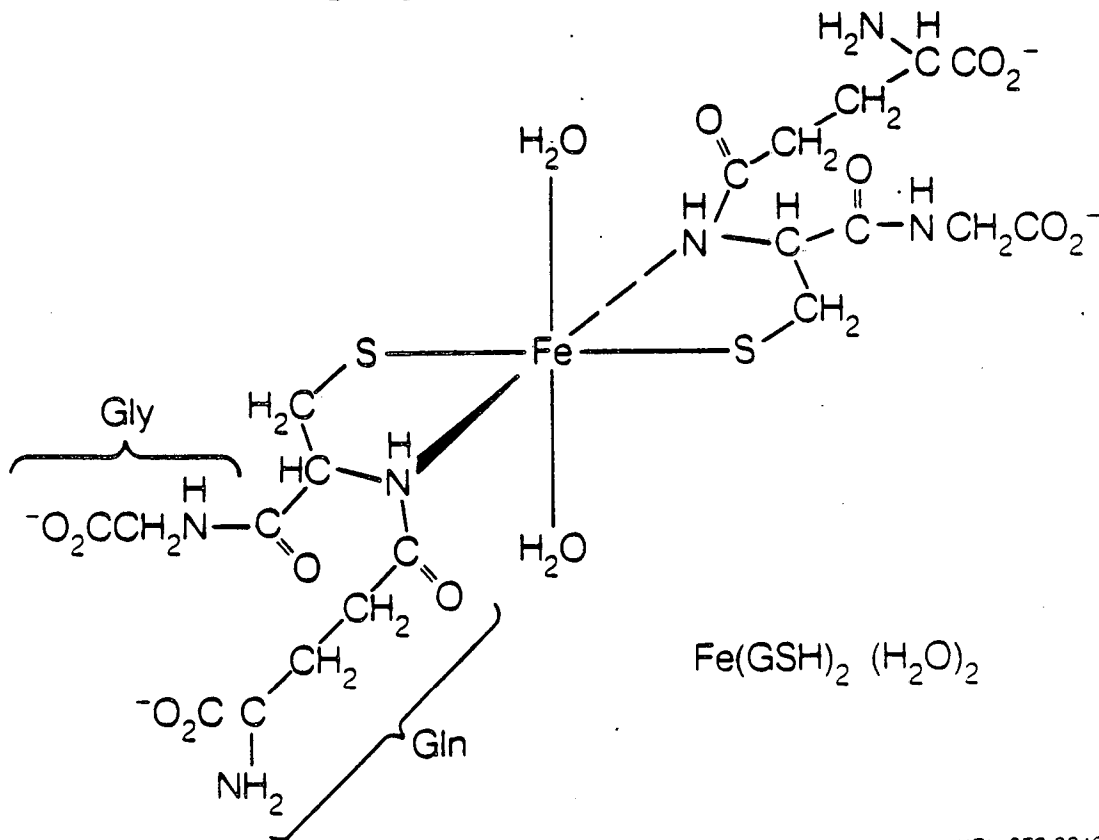
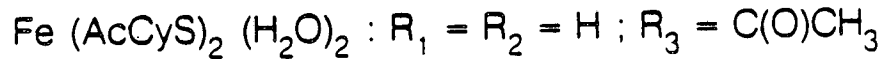
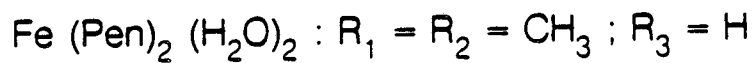
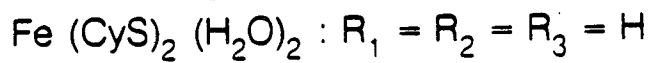
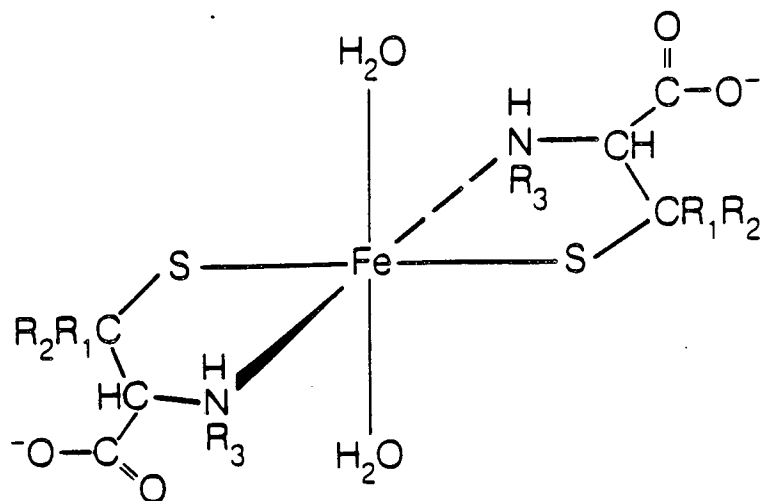
Fig. 2 The NO Removal Efficiencies of ferrous thioaminoacid complexes in the absence of O_2 . Reaction conditions were: $[Fe^{2+}] = 0.005$ M; [thioamino acid] = 0.02 M; $[B_4O_7^{2-}] = 0.18$ M; $P_{NO} = 980$ ppm; $pH = 7.0$; $T = 55$ °C.

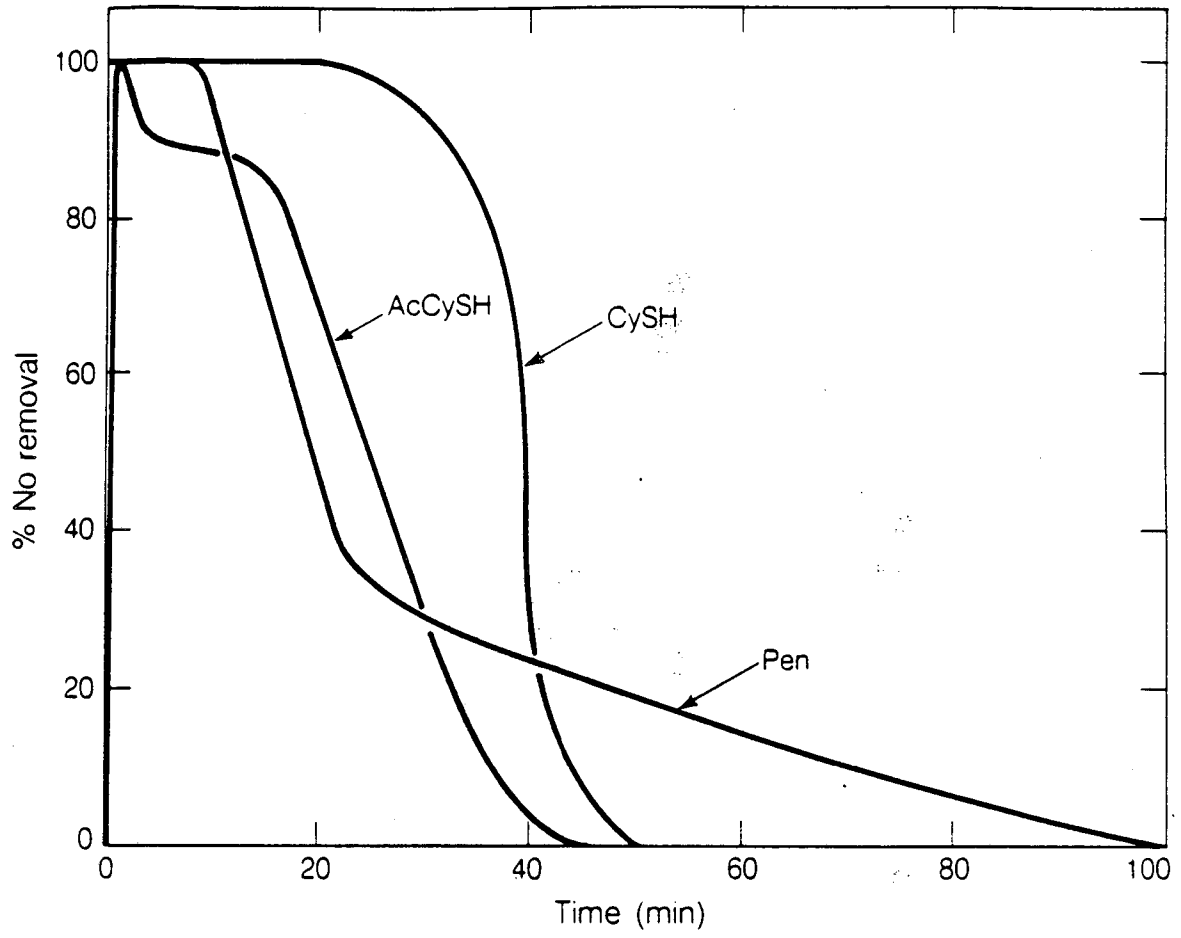
Fig. 3 The NO Removal Efficiencies of ferrous thioaminoacid complexes in the presence of 4% O_2 . Reaction conditions were: $[Fe^{2+}] = 0.01$ M; [thioamino acid] = 0.04 M; $[B_4O_7^{2-}] = 0.18$ M; $P_{NO} = 500$ ppm; $pH = 7.0$; $T = 55$ °C.

Fig. 4 The NO absorption capacity of ferrous thioaminoacid complexes as a function of pH. Reaction conditions were: $[Fe^{2+}] = 0.01$ M; [thioamino acid] = 0.04 M; $[B_4O_7^{2-}] = 0.18$ M; $P_{O_2} = 4\%$; $P_{NO} = 500$ ppm; $pH = 7.0$; $T = 55$ °C.

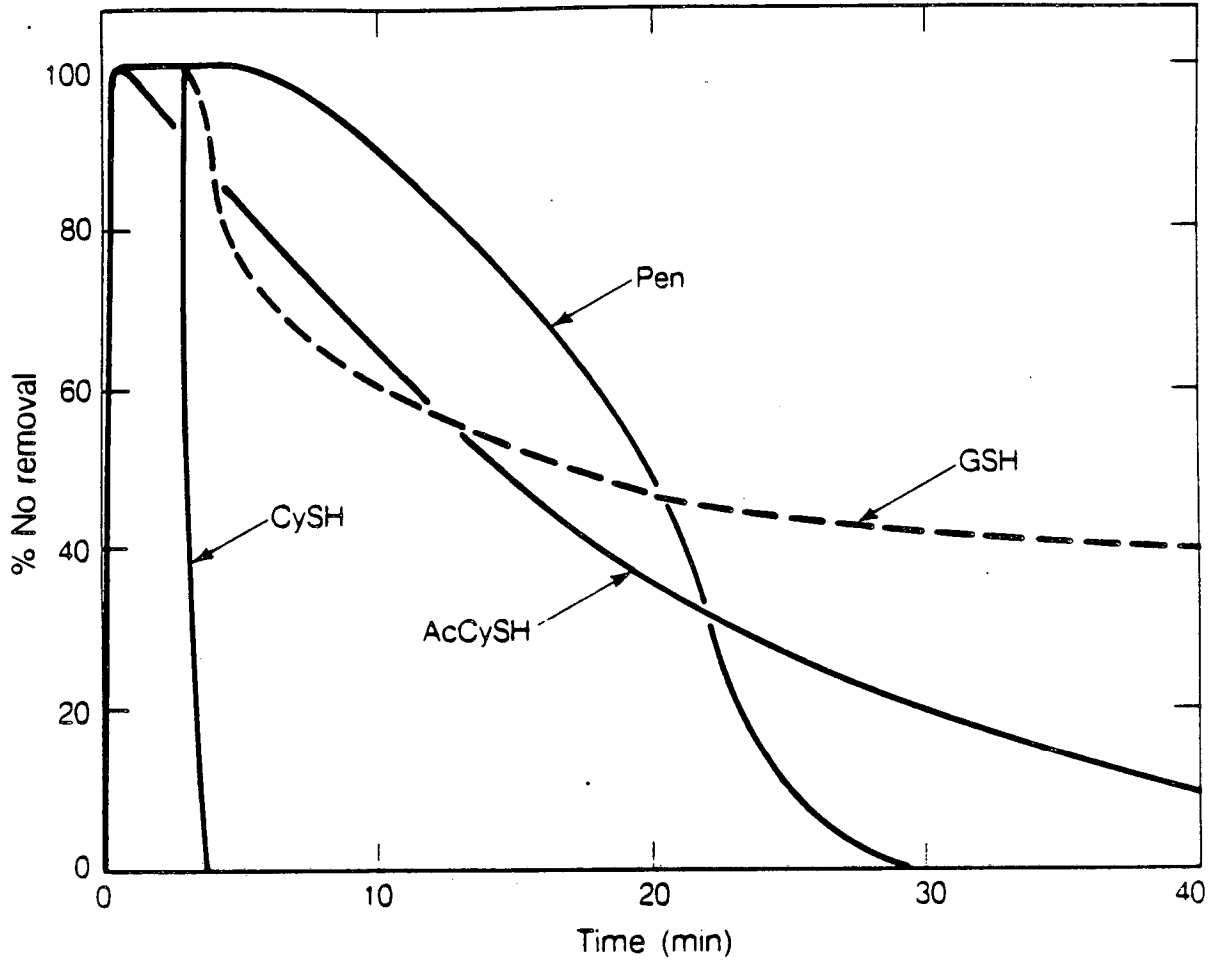
Fig. 5 The NO absorption capacity of ferrous cysteine as a function of $[CySH]/[Fe^{2+}]$. Reaction conditions were: $[Fe^{2+}] = 0.05$ M; $[B_4O_7^{2-}] = 0.18$ M; $P_{O_2} = 4\%$; $P_{NO} = 500$ ppm; $pH = 9.5$; $T = 55$ °C.

Fig. 6 The concentration-time profile of the regeneration of CySH from CySSCy at pH 10 and 60 °C by the reaction of CySSCy first with H_2S and then SO_2 , followed by neutralization to $pH \sim 7$.

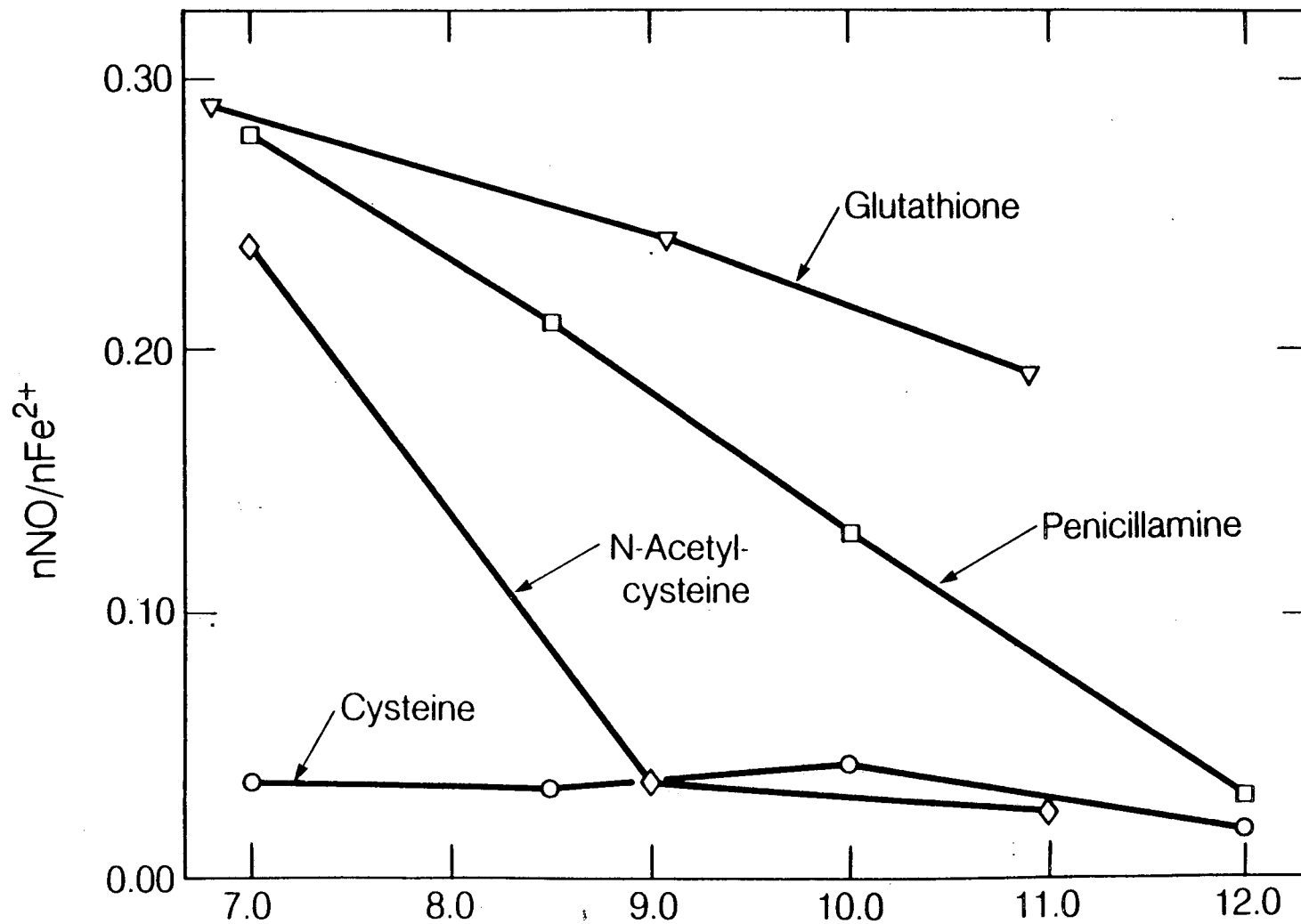


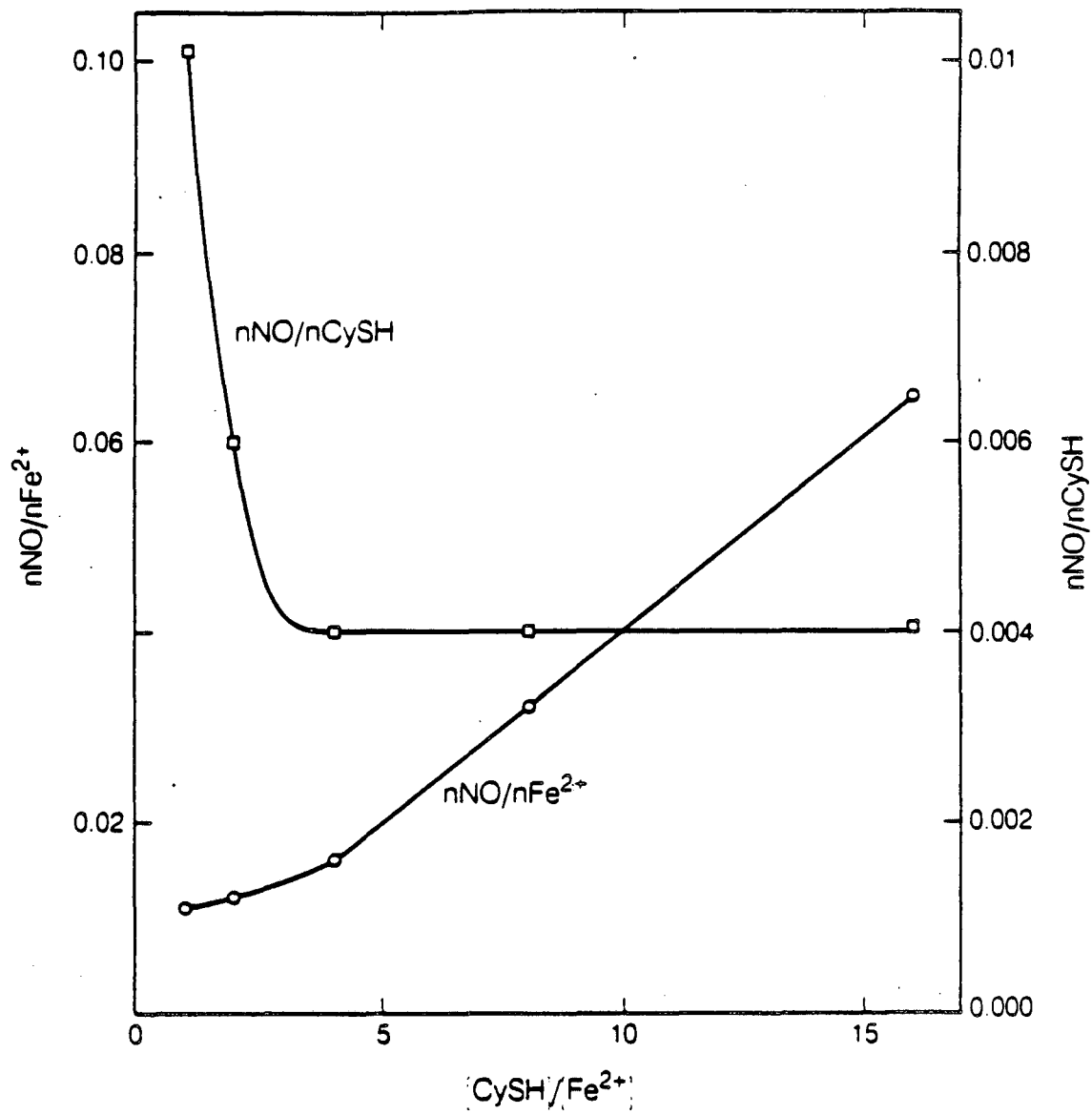


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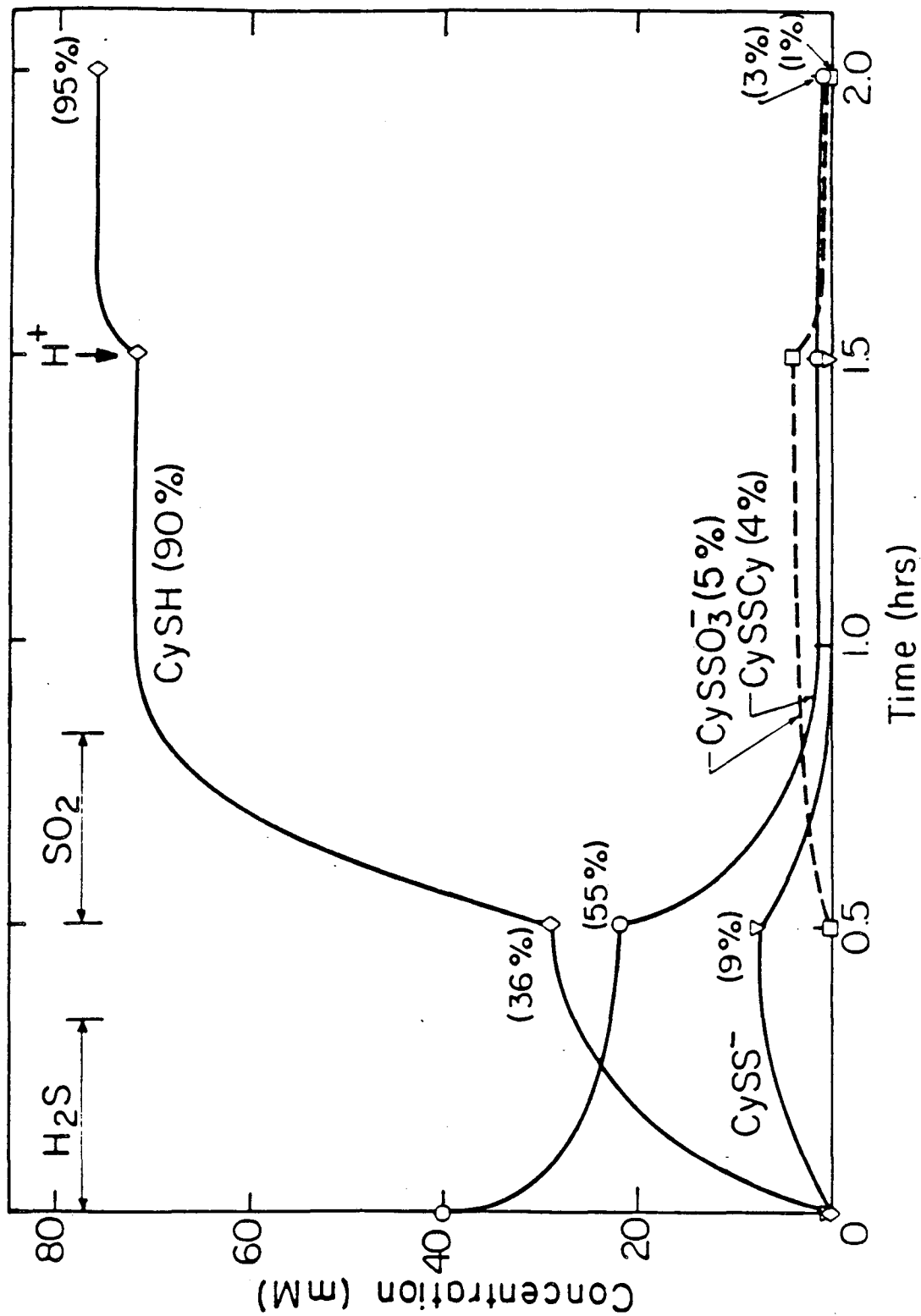


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