

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

USE OF FERROUS CYSTEINE AND CYSTEINE DERIVATIVES FOR THE REMOVAL OF NO<sub>x</sub> AND SO<sub>2</sub> FROM FLUE GAS

### Permalink

<https://escholarship.org/uc/item/7j874532>

### Authors

Chang, S.G.

Liu, D.K.

Littlejohn, D.

### Publication Date

1987-03-01

2



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

APPLIED SCIENCE  
DIVISION

RECEIVED  
LAWRENCE  
BERKELEY LABORATORY

MAY 12 1987

LIBRARY AND  
DOCUMENTS SECTION

Presented at the AIChE 1987 Spring National Meeting,  
Houston, TX, March 29-April 2, 1987, and to be  
published in Environmental Progress

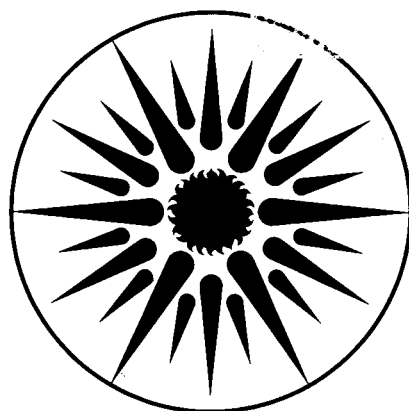
## USE OF FERROUS CYSTEINE AND CYSTEINE DERIVATIVES FOR THE REMOVAL OF NO<sub>x</sub> AND SO<sub>2</sub> FROM FLUE GAS

S.G. Chang, D.K. Liu, and D. Littlejohn

March 1987

**TWO-WEEK LOAN COPY**

*This is a Library Circulating Copy  
which may be borrowed for two weeks.*



APPLIED SCIENCE  
DIVISION

LBL-23198  
2

## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

**Use of Ferrous Cysteine and Cysteine Derivatives  
for the Removal of NO<sub>x</sub> and SO<sub>2</sub> from Flue Gas**

S. G. Chang, David K. Liu, and D. Littlejohn

Applied Science Division  
Lawrence Berkeley Laboratory  
University of California  
Berkeley, CA 94720

**ABSTRACT**

The use of ferrous complexes of cysteine and its derivatives for the removal of NO and SO<sub>2</sub> 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 N<sub>2</sub>. The disulfide form of the thioamino acids produced upon oxidation can be conveniently reduced by SO<sub>2</sub> and H<sub>2</sub>S to regenerate the starting thioamino acids, thus making possible the recycling of the reagents. The effects of pH, O<sub>2</sub>, SO<sub>2</sub>, and S<sub>2</sub>O<sub>3</sub><sup>2-</sup> 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  $\text{SO}_2$  removal; however, it removes only a little  $\text{NO}_x$ . This is because most of the  $\text{NO}_x$  in flue gas is  $\text{NO}$ , which is only slightly soluble in aqueous solution. Work has been conducted at several institutions to modify the system such that  $\text{NO}_x$  can be removed simultaneously [1-3]. One approach that has been developed involves the addition of ferrous chelates such as  $\text{Fe}^{2+}$  (EDTA) in scrubbing liquor to promote the solubility of  $\text{NO}$  by forming  $\text{Fe}^{2+}$  (EDTA)( $\text{NO}$ ). The absorbed  $\text{NO}$  is then chemically converted to  $\text{N}_2\text{O}$ ,  $\text{N}_2$  and nitrogen-sulfur compounds [2-5] by reacting with dissolved  $\text{SO}_2$ . 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  $\text{NO}$ . As a result,  $\text{NO}$  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  $\text{O}_2$ , 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  $\text{SO}_2$  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  $\text{H}_2\text{S}$

may be a viable approach [6]. This technology has been applied in the control of H<sub>2</sub>S emission, but has not been well developed for the purpose of controlling NO<sub>x</sub> or SO<sub>2</sub> 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<sub>x</sub> and SO<sub>2</sub> 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 Fe<sup>2+</sup> (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 Fe<sup>3+</sup> to Fe<sup>2+</sup> 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<sub>x</sub> 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<sub>NO</sub> = 500 ppm), O<sub>2</sub> (0 % or 4%) and N<sub>2</sub> (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  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  analysis.

For the reduction of cystine to cysteine, the following procedure was used. 0.2  $\ell$  of a cystine solution (0.04 M) buffered with sodium borate (0.05 M  $\text{Na}^+$ ) at pH 10.0 was allowed to equilibrate at 60° C.  $\text{H}_2\text{S}$  and  $\text{SO}_2$  (6.11% in  $\text{N}_2$ ) were bubbled through the cystine solution for 20 min. at flow rates of 0.01  $\ell/\text{min}$  and 0.9  $\ell/\text{min}$ , 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%  $\text{O}_2$  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  $\text{O}_2$  is attributed to the rapid oxidation of thioamino acids to their corresponding dimers by  $\text{O}_2$ , catalyzed by the  $\text{Fe}^{2+}$  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%  $\text{O}_2$  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  $\beta$ -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% O<sub>2</sub>, 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 O<sub>2</sub> catalyzed by Fe<sup>2+</sup>. 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 O<sub>2</sub> 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)<sub>2</sub>], 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<sup>-2</sup> torr). Gas phase products were determined by mass spectral analysis to contain N<sub>2</sub> and N<sub>2</sub>O. 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  $\text{N}_2^-$ .

In the presence of 4% oxygen, an analogous dinitrosyl metal complex was not detected. Most of the NO was either reduced to  $\text{N}_2$  and  $\text{N}_2\text{O}$  in the gas phase or converted to  $\text{NO}_2^-$  (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  $\text{NO}_2^-$  (> 90%) and  $\text{NO}_3^-$  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  $\text{N}_2$  and  $\text{N}_2\text{O}$ , and a lesser fraction of NO was oxidized to  $\text{NO}_2^-$  and  $\text{NO}_3^-$  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  $\text{SO}_2$ , which dissolves in scrubbing liquors to form primarily  $\text{SO}_3^{2-}$  at  $\text{pH} > 9$ . The effect of  $\text{SO}_2$  on the NO absorption capacity can therefore be studied by the addition of  $\text{SO}_3^{2-}$  to the ferrous cysteine solution. Addition of  $\text{SO}_3^{2-}$  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  $\text{SO}_3^{2-}$  additive can improve the NO removal efficiency via two routes: (i) by its reaction with  $\text{O}_2$  to form  $\text{SO}_4^{2-}$ ; and (ii) by its reaction with  $\text{CySSCy}$  to form  $\text{CySH}$  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  $\text{SO}_3^{2-}$  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  $\text{O}_2$  is not as pronounced.

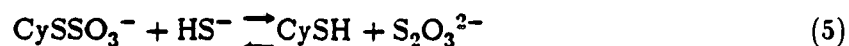
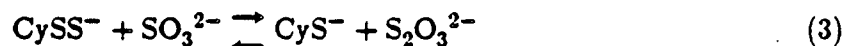
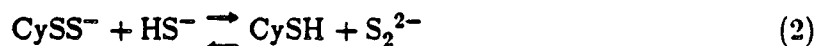
As mentioned earlier, residual  $\text{O}_2$  in flue gas can oxidize cysteine (CySH) to cystine (CySSCy) in the presence of  $\text{Fe}^{2+}$  catalyst. Therefore, the use of excess CySH should improve the performance of ferrous cysteine. As shown in Figure 4, increasing [CySH] at a fixed  $[\text{Fe}^{2+}]$ , 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  $\text{Fe}^{2+}$  to be used would depend on whether the NO removal efficiency of the ferrous cysteine system is to be maximized with respect to  $\text{Fe}^{2+}$  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  $\text{O}_2$  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  $\text{O}_2$ , 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  $\text{H}_2\text{S}$  (or sulfide/hydrogen sulfide ion) and  $\text{SO}_2$  (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 H<sub>2</sub>S at pH 10 and 60 °C (Table II, Method I). The concentrations of HS<sup>-</sup> and SO<sub>3</sub><sup>2-</sup> 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 (CySSO<sub>3</sub><sup>-</sup>) 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 H<sub>2</sub>S and SO<sub>2</sub> 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<sup>-</sup> and SO<sub>3</sub><sup>2-</sup> to form S<sub>2</sub>O<sub>3</sub><sup>2-</sup> 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:

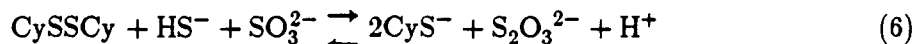


where CySS<sup>-</sup> represents S-thiocysteine.

We have recently completed a kinetic study [11] of reactions (1) and (2). The reaction between CySSCy and SO<sub>3</sub><sup>2-</sup>, 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  $\text{CySSCy}$  and  $\text{CySSO}_3^-$  to  $\text{CySH}$  is possible using the above procedure.

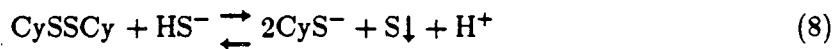
The overall reaction for the regeneration of  $\text{CySH}$  from  $\text{CySSCy}$  using  $\text{HS}^-$  and  $\text{SO}_3^{2-}$  can be expressed as



In an acidic medium, thiosulfate decomposes to form  $\text{HSO}_3^-$  (and/or  $\text{SO}_2$ ) and colloidal sulfur, as shown in equation 7.



By adding equations 6 and 7 and taking into account the equilibrium between  $\text{SO}_3^{2-}$  and  $\text{HSO}_3^-$ , we obtain the net equation



Thus the only reagent consumed in the conversion of  $\text{CySSCy}$  to  $\text{CySH}$  is  $\text{HS}^-$ , and elemental sulfur is formed as a product. The latter can be converted back to  $\text{H}_2\text{S}$  by reaction with  $\text{H}_2$ , which can be derived from  $\text{CO}$  and  $\text{H}_2\text{O}$  (water-gas shift reaction) [13]. Therefore, in essence, the reducing agent consumed in this  $\text{CySH}$  regeneration scheme is  $\text{CO}$ , which can be easily obtained from the incomplete combustion of coal. It can be inferred from equation 8 that one mole of  $\text{CO}$  is required for the regeneration of two moles of  $\text{CySH}$ .

### 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  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  but also  $\text{NO}$  to  $\text{N}_2$  and possibly  $\text{N}_2\text{O}$ , whereas a

weak reducing agent such as glutathione reduces  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ , but not NO in any significant quantity. In the latter case, NO is probably complexed and then oxidized by  $\text{O}_2$  to form  $\text{NO}_2^-$ , especially at alkaline conditions. The  $\text{NO}_2^-$  is expected to react with  $\text{HSO}_3^-$  to produce N-S compounds, which can be precipitated out of the scrubbing liquors as potassium salts. Because the reduction rate of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  by thioamino acids is very rapid, it not only prevents the formation of dithionate ion resulting from the reduction of  $\text{Fe}^{3+}$  by  $\text{HSO}_3^-$ , but also maintains the  $\text{Fe}^{2+}$  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  $\text{Fe}^{2+}$  (EDTA), when used as additives in wet lime/limestone systems for combined control of  $\text{NO}_x$  and  $\text{SO}_2$  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  $\text{NO}_x$  and  $\text{SO}_2$  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  $\text{NO}_x$  and  $\text{SO}_2$  from flue gas. Ferrous cysteine can rapidly absorb NO and reduce NO to  $\text{N}_2$  and/or  $\text{N}_2\text{O}$ , 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.

Table I. Effects of Various Additives on NO Absorption Capacity of Ferrous Cysteine <sup>a</sup>		
Additive	Concentration, M	nNO/nFe <sup>2+</sup>
none	—	0.023
Na <sub>2</sub> SO <sub>3</sub>	0.05	0.040
	0.10	0.050
	0.50	0.068
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	0.05	0.030
	1.00	0.080

<sup>a</sup>The concentrations of Fe<sup>2+</sup> 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% O<sub>2</sub> and the balance N<sub>2</sub>.

Method*	pH	T °(°C)	CySH, %	CySSO <sub>3</sub> <sup>-</sup> , %	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.



Literature Cited

1. Faucett, H.L., J.D. Maxwell, and T.A. Burnett, "Technical Assessment of NO<sub>x</sub> Removal Processes for Utility Application," EPRI AF-568, March (1978).
2. Chang, S.G., D. Littlejohn, and N.H. Lin, ACS Symp. Ser 188, 127 (1982).
3. Chang, S.G., ACS Symp. Ser. 319, 159 (1986).
4. Littlejohn, D. and S.G. Chang, *Environ. Sci. & Tech.* 18, 305 (1984).
5. Littlejohn, D. and S.G. Chang, *Anal. Chem.* 58, 158 (1986).
6. Chang, S.G., D. Littlejohn, and S. Lynn, *Environ. Sci. & Tech.* 17, 649 (1983).
7. Lin, N., D. Littlejohn, and S. Chang, *ISEC Proc. Design & Develop.* 1, 725 (1982)
8. Stadtherr, L.G. and R.B. Martin, *Inorg. Chem.*, 11, 92 (1972).
9. Tu, M.D. and S.G. Chang, *AIChE Environ. Progr.* 6, 51 (1987).
10. Liu, D.K., P.F. Lawrence, and S.G. Chang, "A ferrous cysteine based recyclable process for the combined removal of NO<sub>x</sub> and SO<sub>2</sub> from flue gas," Lawrence Berkeley Laboratory Report LBL-22855, submitted to *Environ. Sci. & Tech.* for publication.
11. Liu, D.K. and S.G. Chang, *Can. J. Chem.* 1987, in press.
12. Stricks, W. and I.M. Kolthoff, *J. Am. Chem. Soc.* 73, 4569 (1951).
13. Kent, J.A., Ed., Riegels Handbook of Industrial Chemistry, 7th Ed., Van Nostrand Reinhold, New York, 1974, p. 87.

Figure Captions

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

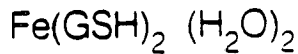
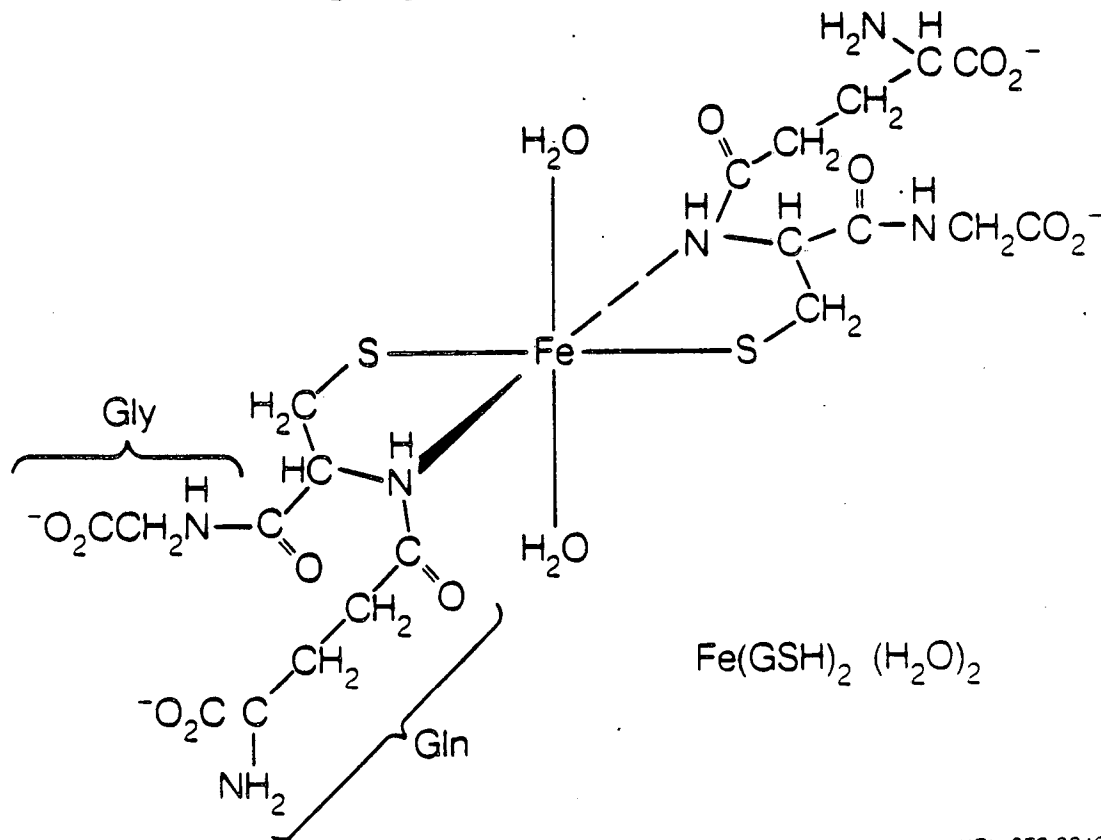
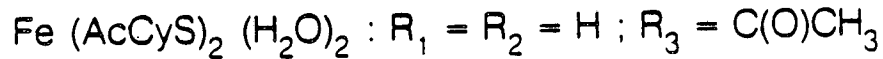
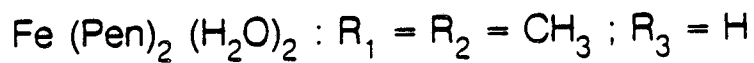
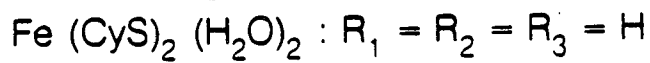
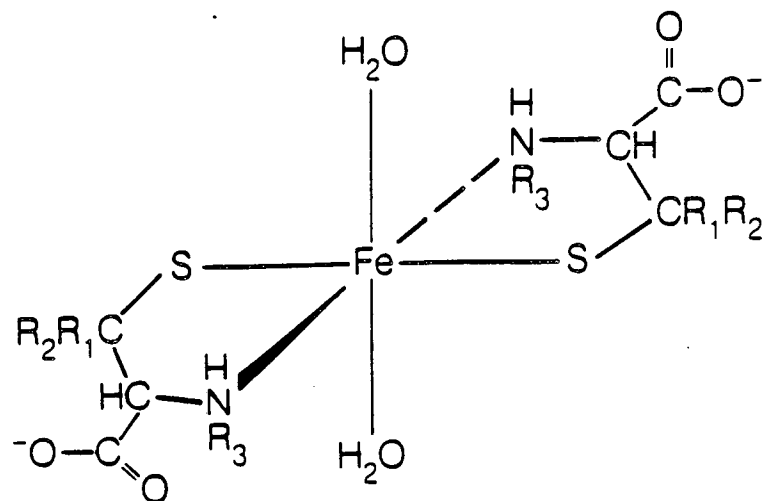
**Fig. 2** The NO Removal Efficiencies of ferrous thioaminoacid complexes in the absence of  $O_2$ . Reaction conditions were:  $[Fe^{2+}] = 0.005$  M; [thioamino acid] = 0.02 M;  $[B_4O_7^{2-}] = 0.18$  M;  $P_{NO} = 980$  ppm; pH=7.0;  $T^\circ = 55^\circ C$ .

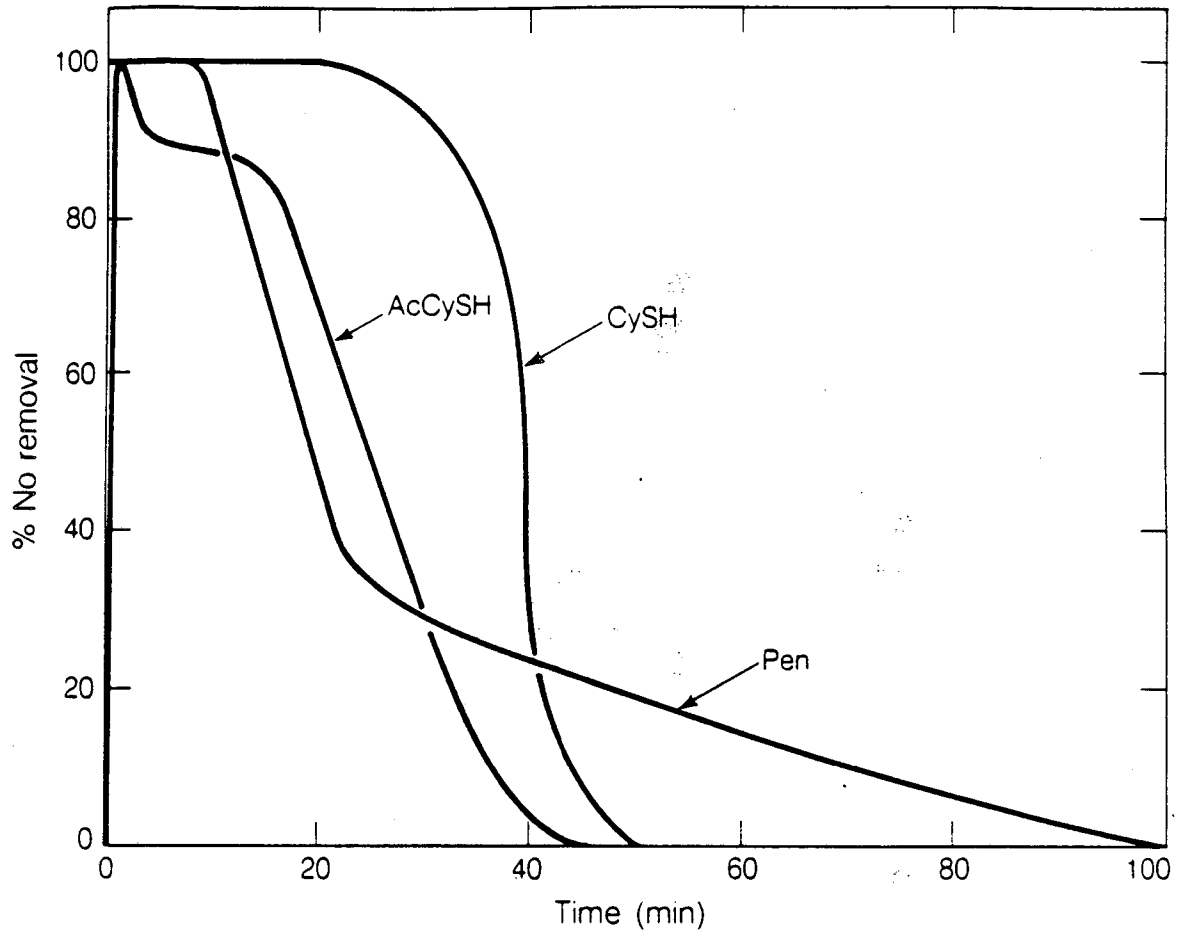
**Fig. 3** The NO Removal Efficiencies of ferrous thioaminoacid complexes in the presence of 4%  $O_2$ . Reaction conditions were:  $[Fe^{2+}] = 0.01$  M; [thioamino acid] = 0.04 M;  $[B_4O_7^{2-}] = 0.18$  M;  $P_{NO} = 500$  ppm; pH=7.0;  $T^\circ = 55^\circ C$ .

**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;  $T^\circ = 55^\circ C$ .

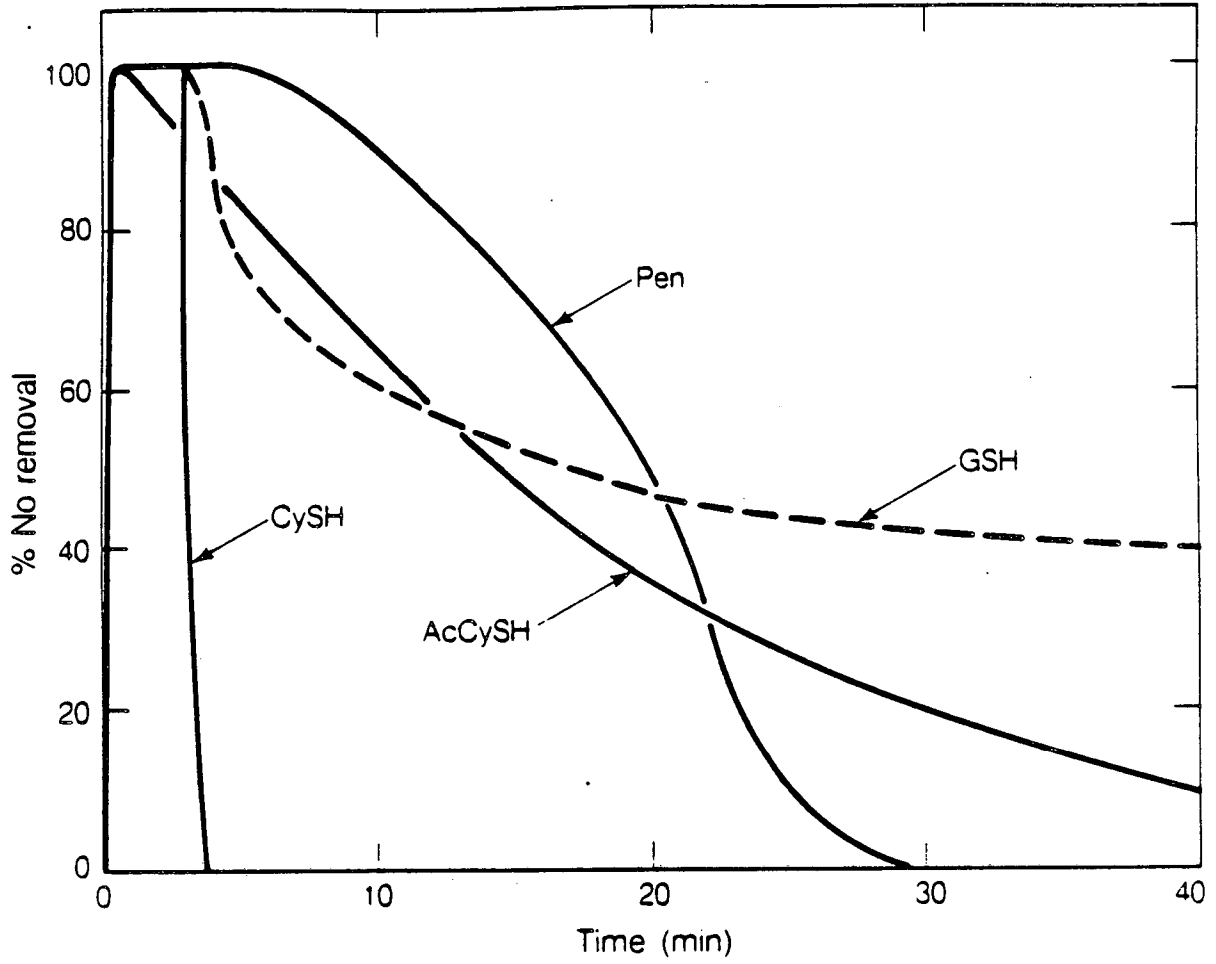
**Fig. 5** The NO absorption capacity of ferrous cysteine as a function of  $[CySH]/[Fe^{2+}]$ . Reaction conditions were:  $[Fe^{2+}] = 0.05$  M;  $[B_4O_7^{2-}] = 0.18$  M;  $P_{O_2} = 4\%$ ;  $P_{NO} = 500$  ppm; pH=9.5;  $T^\circ = 55^\circ C$ .

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

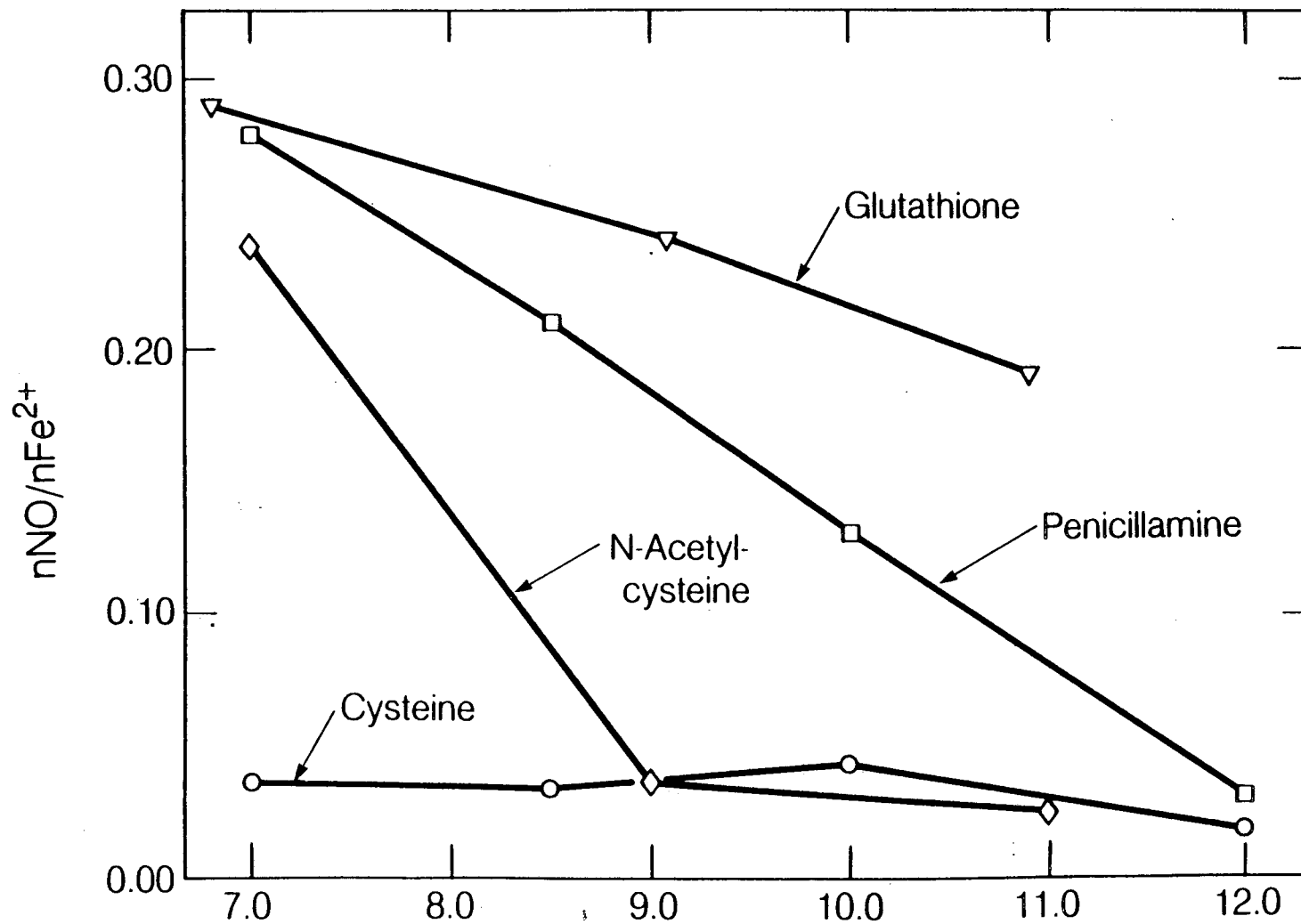


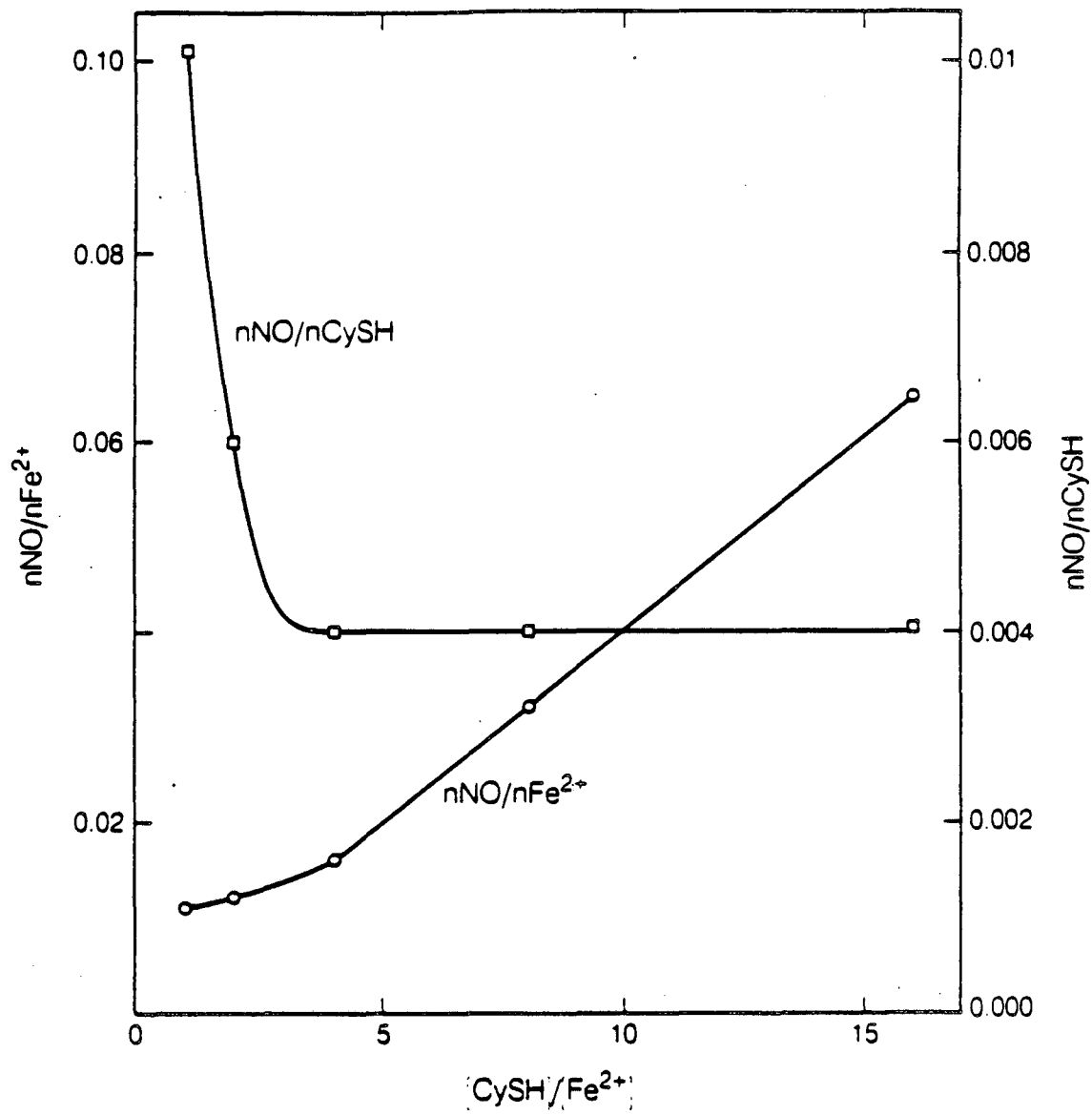


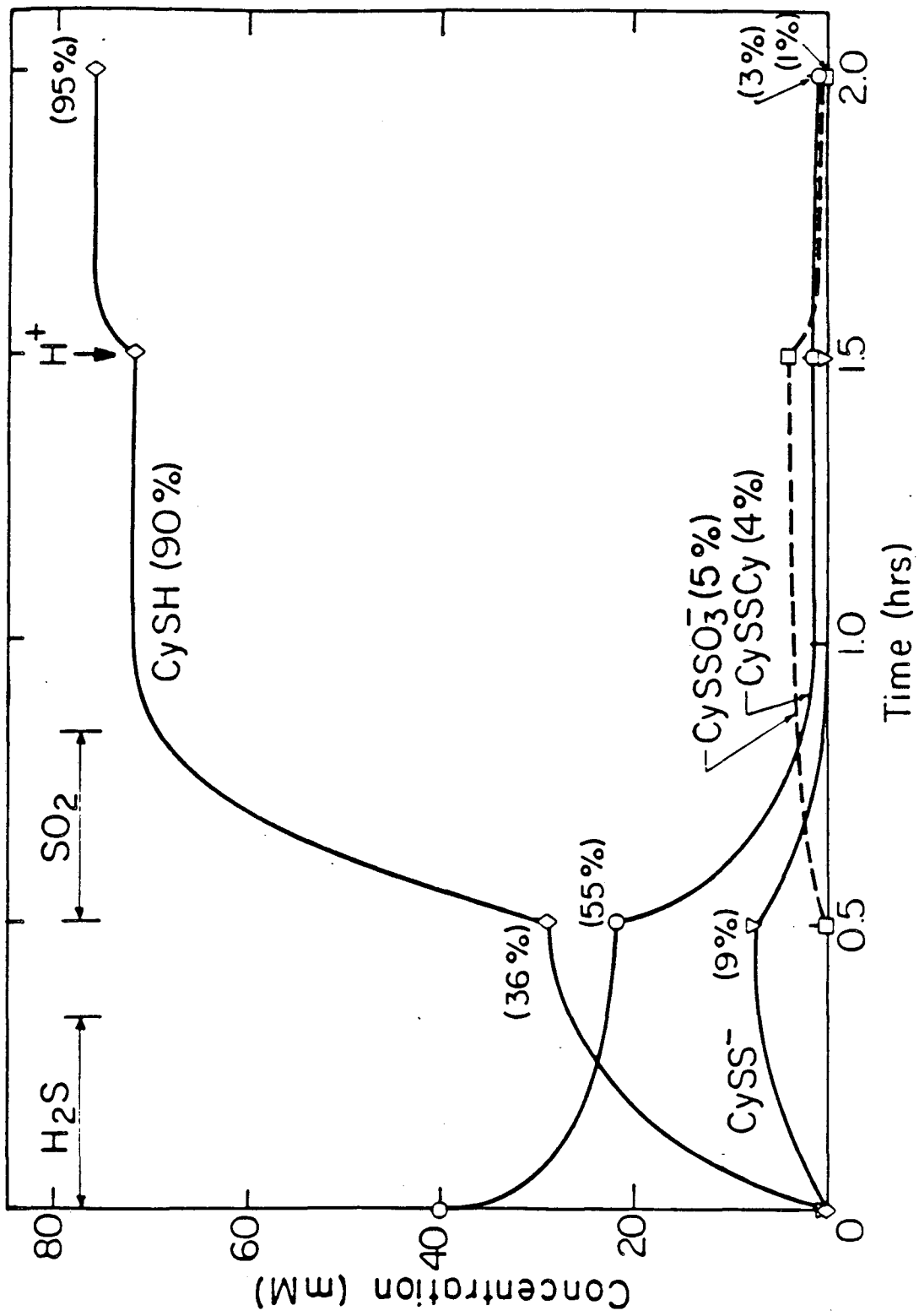
xBL 373-9238



XBL 873-9236







XBL 864 - 7598



This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

*LAWRENCE BERKELEY LABORATORY  
TECHNICAL INFORMATION DEPARTMENT  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720*