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ENHANCED NOx REMOVAL
IN WET SCRUBBERS
USING METAL CHELATES

DOE CONTRACT DE-AC22-90PC90362

FINAL REPORT

VOLUME 1 OF 2

PREPARED FOR THE

U.S. DEPARTMENT OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER

SUBMITTED BY

DRAVO LIME COMPANY

DLC-5237

DECEMBER, 1992

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Glossary

GLOSSARY OF TERMS

ACFM	- actual cubic feet per minute.
ADS	- amine disulfonate.
ATS	- amine trisulfonate.
BNA	- base neutral acid.
BSAP	- bisulfate addition product.
CLP	- contract lab program.
DP	- differential pressure.
EDTA	- ethylenediaminetriacetic acid.
EP	- extraction procedure.
Fe+2 or Fe(II)	- ferrous form of iron.
Fe+3 or Fe(III)	- ferric form of iron.
FGD	- flue gas desulfurization.
FGV	- flue gas velocity.
FPS	- feet per second.
GPM	- gallons per minute.
HA	- hydroxylamine.
HADS	- hydroxylamine monosulfonate.
HAMS	- hydroxylamine monosulfonate.
kW	- kilowatt.
L/G	- liquid to gas ratio.
MCL	- maximum containment levels.
MEL	- magnesium enhanced lime.
mM	- millimolar.
NO (or NOx)	- forms of nitrogen oxide.
NTU	- number of transfer units.
PSD	- particle size distribution.
RCRA	- Resource Conservation and Recovery Act.
SAM	- sulfamate.
SCR	- selective catalytic reduction.
SEM	- scanning electron microscope.
SNC	- sulfur nitrogen compounds.
TCLP	- Toxic Characteristic Leaching Procedure.
Thiosorbic	- Dravo registered trade name for magnesium enhanced lime FGD.
WC	- water column.
XRF	- x-ray flouresence spectroscopy.

Section I

ENHANCED NOx REMOVAL IN WET SCRUBBERS USING METAL CHELATES

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FINAL REPORT

SUBMITTED DECEMBER, 1992

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EXECUTIVE SUMMARY

SIMULTANEOUS REMOVAL OF SO_2 AND NOx IN WET SCRUBBERS USING METAL CHELATES

Successful pilot plant tests of simultaneous removal of SO_2 and NOx in a wet lime flue gas desulfurization system were concluded in December. The tests, at up to 1.5 MWe capacity, were conducted by the Cincinnati Gas and Electric Company and Dravo Lime Company for the U.S. Department of Energy at a pilot facility at the Miami Fort station of CG&E near Cincinnati, Ohio. The pilot plant scrubbed a slipstream of flue gas from Unit 7, a 530 MW coal-fired electric generating unit. Tests were conducted in three phases between April and December. Perry Bergman was the Technical Project Officer and Gary Miller and Bruce Lani of Dravo Lime were the Project Managers.

The pilot tests followed laboratory-scale research supported by DOE/PETC at Argonne National Laboratory, Lawrence Berkeley Laboratory, and in-house research by Dr. Richard Walker with guidance from Dr. Mildred Perry. Pilot tests of this NOx removal technology had been conducted in Japan and Germany, but these tests were the first at this scale in the U.S. utilizing flue gas from high-sulfur coal.

The technology tested was wet scrubbing with Thiosorbic^R magnesium-enhanced lime for SO_2 removal and simultaneous NO scrubbing with ferrous EDTA, a metal chelate. Magnesium-enhanced lime-based wet scrubbing is used at 20 full-scale high-sulfur coal-fired electric generating units with a combined capacity of 8500 MW. Ferrous EDTA reacts with nitric oxide, NO, which comprises about 95% of NOx from coal-fired boilers. In this report, although not precise, NO and NOx are used interchangebly. A major objective of the tests was to combine NOx removal using ferrous EDTA, a developing technology, with SO_2 removal using wet lime FGD, already in wide commercial use. If successful, this could allow wide application of this NOx removal technology.

In the pilot tests, flue gas was scrubbed in a 3 foot diameter, 40 foot high, absorber tower. In a 216-hour test which simulated application of this process to a scrubber built specifically for simultaneous removal of SO_2 and NO, 99.9% SO_2 removal and up to 60% NO removal were achieved. In a test which simulated retrofit of NOx removal to an existing wet scrubber of similar duration, SO_2 removal was above 99.5% and NO removal was about 30%. These tests were conducted using fine sprays and packings to increase gas-liquid contact.

Another objective of pilot testing was to determine dependence of NO removal on absorber operating conditions. A mathematical model that describes the dependence of NO removal efficiency on absorber flue gas velocity, absorber liquid rate, ferrous EDTA concentration, absorber length, and gas-liquid contact time was derived and used to guide test conditions and correlate NO removal data. NO removal data obtained was well correlated by the model. The model will allow better prediction of NO removal that could be achieved in existing full-scale wet scrubbers and also provide a guide to design new scrubbers to achieve higher levels of NO removal.

Although the pilot tests confirmed earlier laboratory findings that showed that NO can be removed from flue gas using ferrous EDTA, the tests also confirmed that ferrous EDTA is deactivated (oxidized to ferric (Fe^{+3}) EDTA) by oxygen in flue gas and other reactions. Means to reactivate it, such as subsequently, addition of reducing agents and antioxidants during the test program, were required. Sodium dithionite ($Na_2S_2O_4$) and ascorbic acid, used in the pilot tests, were very effective in reactivating ferrous EDTA, but they are too expensive to be practical. Lower cost chemical reducing/antioxidants are required for the combined NOx/SO_2 removal process to be applied at commercial scale. A nonchemical method which utilizes an electrochemical cell for reduction of ferric EDTA to ferrous EDTA is projected to be practical in cost and is the most promising means at present but requires further development.

Another reducing agent/antioxidant tested, glyoxal (HOC=COH), was effective and significantly less expensive, but interfered with process chemistry. Additional laboratory study of use of glyoxal would be required before additional tests should be conducted at this scale.

A 10 day test using very high ferrous EDTA concentrations along with thiosulfate, a sulfite oxidation inhibitor, showed promise that some ferrous EDTA could be reactived by a mild reducing agent, sulfite ($SO_3^{=}$), that is naturally present in FGD process liquid. This approach has the advantage that the cost of reducing agents/antioxidants is avoided at the expense of a higher, though practical, cost for makeup ferrous EDTA. Thiosulfate appears to improve solids dewatering, which allows high ferrous EDTA concentrations to be used practically. Though promising, the tests conducted were too brief to conclude that this approach would succeed in long-term commercial operation. Additional laboratory research is suggested to further study this approach.

NO removal using ferrous EDTA would be suitable following low-NOx combustion as a combination of NOx removal technologies that can achieve higher levels of NOx removal than either technology alone. NO removal using ferrous EDTA was found in the pilot tests to be independent of flue gas NO concentration. Overall NOx removal of 75% would be achieved by combination of 50% removal with low-NOx combustion and 50% removal using ferrous EDTA.

Solids produced as a by-product of removal of SO_2, dewatered extremely well to levels unprecedented for magnesium-enhanced lime FGD systems. An increase in solids content reduces the weight and volume of solids that must be placed in a landfill and reduces transportation and placement costs. Solids content of filter cake averaged between 65 to 77 weight percent during the test program, compared with 35-45 weight percent for a magnesium-enhanced lime FGD system operated without simultaneous NO removal. An increase in solids content from 40 wt.% to 70 wt.% results in a 42.8% reduction in weight of solids disposed.and likely a similar reduction in disposal cost.

Physical properties of the solids were measured, and their chemical analyses determined. Particle size and shape of the solids were determined. Elemental analyses were performed using wavelength-dispersive X-ray fluorescence. Moisture and residual EDTA were also measured.

Laboratory tests were conducted to determine if solids produced by the system, including entrained NOx-capture products, could be treated and made inert using the treatment method used at present in commercial FGD systems. Tests were conducted to determine if the solids could be stabilized, that is, treated to increase bearing strength and decrease permeability, using current treatment for stabilizing FGD solids before placement in a landfill. Tests were conducted with addition of various amounts of flyash and lime. The results showed the solids were easily stabilized using current technology.

Tendency for heavy metals to leach from the stabilized solids and their toxicity were determined. TCLP tests for heavy metals were performed on the solids both before and after stabilization. TCLP results after stabilization were well below TCLP limits for heavy metals and also below limits for drinking water. Toxicity tests using Daphnia simplex and fat-head minnows were performed on solids both before and after stabilization.

Attempts to balance the amount of NO removed from flue gas with the amount of NO-capture products found in liquid and solids in the system were only partly successful. The NO-capture products found were among those which had been found in earlier laboratory scale tests. Amine disulfonate ($N(SO_3)^=$) and sulfamate ($NH_2SO_3^=$) were the major capture products of NO absorption. Little hydroxylamine disulfonate ($HON(SO_3)^=$) was found, though it was found in greater amounts in earlier laboratory tests. Addition of reducing agents/antioxidants during the pilot tests could have had an effect on the amount of hydroxylamine disulfonate formed.

Nitrous oxide (N_2O) was not found in scrubbed flue gas during pilot tests. Scrubbed flue gas was sampled and analyzed for N_2O during several test periods, including one where NO removal was highest, about 60%. Gas samples were analyzed using gas chromatography with a thermal conductivity detector. The detection limit was 10 ppmv. Absorber liquid was maintained at a pH of 6.5 throughout almost all tests, which was probably responsible for lack of N_2O production. A prominent researcher in this area, Dr. Chang at Lawrence Berkeley Laboratory, found N_2O in much greater amounts, especially at higher pH levels.

Little effect of a higher ratio of flue gas SO_2 to NOx on NO removal efficiency was found in pilot tests. A higher ratio reduces the concentration of NOx-capture products that form in the absorber liquid and in liquid that is discharged from the process.

Areas for further research in this area were identified. Additional laboratory research is required to find less expensive means to maintain iron EDTA in the ferrous form. Chemical reducing agents and antioxidants whose potential cost is under $12 per lb-mole of ferric EDTA reduced (or per lb-mole of ferrous EDTA protected from oxidation) should be screened in laboratory tests for reducing/antioxidant efficiency and checked to see if their presence interferes with either NO removal chemistry or with SO_2 removal chemistry. An important interference would be reaction with sulfite which is required both to promote SO_2 removal and to regenerate ferrous EDTA from the ferrous EDTA-NO complex formed when NO is absorbed.

Additional study of electrochemical reduction of ferric EDTA to the ferrous form is recommended. Though it was not tested in the pilot program, tests of an electrochemical cell at similar scale by DOW Chemical Company and at bench scale at Dravo Lime Company's Research Center showed great promise that this approach was workable. Operating costs projected in this report, $1-3 per lb-moles of ferric EDTA reduced, would make the electrochemical cell a very low cost means to maintain ferrous EDTA.

The results of this work have implications for electric utility engineers considering options for SO_2 and NOx removal to comply with the 1990 Clean Air Act and for researchers studying wet NOx removal processes.

I. SUMMARY

A. INTRODUCTION

Several groups have conducted research and development to use ferrous iron-based complexes, called ferrous chelates, to absorb nitrogen oxides (NOx) in wet scrubbers designed to remove sulfur dioxide (SO_2). PETC has sponsored laboratory work at Argonne National Laboratory by Drs. David Livengood, John Harkness, and Marshall Mendelsohn, at Lawrence Berkeley Laboratory by Dr. S. G. Chang, David Littlejohn and others, and in-house laboratory work by Dr. Richard Walker, Mildred Perry, Charles Drummond and Henry Pennline. Dow Chemical Company has developed a technique for regeneration of ferrous chelates using an electrochemical cell and tested it at laboratory and small pilot scale. Researchers in Japan and Germany have also studied use of ferrous chelates for NO_x removal.

Dravo Lime Company worked with Argonne beginning in 1987 to determine how use of ferrous chelates, primarily ferrous ethylenediaminetetraacetate ($[Fe^{+2}EDTA]^{=}$) for NOx removal could be combined with the Thiosorbic^R magnesium-enhanced lime wet scrubbing process for SO_2 removal. Dr. Y. Joseph Lee and Lewis Benson of Dravo Lime also conducted laboratory research to study use of ferrous EDTA and additional means to maintain a sufficient concentration of ferrous EDTA to achieve a practical process. Their judgement was that 15 millimolar (mM) ferrous iron in absorber liquid would be practical.

Most of the wet flue gas desulfurization (FGD) systems operating on flue gas from high sulfur coal in Pennsylvania, Ohio, West Virginia and Kentucky use the magnesium enhanced lime process. Laboratory analysis suggested ferrous chelates would perform best when scrubbing flue gas from high-sulfur coal where the FGD chemistry produced absorber liquid with high sulfite and bisulfite concentrations ($SO_3^{=}$ and HSO_3^{-}) as occurs in magnesium-enhanced lime systems.

Use of ferrous chelates for NOx control when wet FGD is required has potential advantages over some other processes for NOx removal. Scrubbing equipment used to remove SO_2 also removes NOx, thereby eliminating most capital costs for NOx control equipment. This compares favorably with selective catalytic reduction (SCR) which requires a separate reactor and a relatively expensive catalyst. Ferrous chelate scrubbing could be retrofitted to existing wet scrubbers. New wet FGD systems could also use this NOx control technology.

Use of ferrous chelates may be better suited to treating flue gas from burning high-sulfur coal than is SCR. NOx removal with ferrous chelates requires a molar ratio of absorbed SO_2 to absorbed NOx of at least 2, and the process likely benefits from higher amounts of SO_2 because sulfite formed from absorbed SO_2 reacts with absorbed NO to form sulfur-and-nitrogen-containing capture products (so-called sulfur-nitrogen compounds) and helps regenerate the ferrous chelate. SCR catalysts, while proven on low-sulfur coals in Germany and Japan, may be poisoned and deactivated by flue gas from high-sulfur coals in the U.S.

In 1988, Dravo Lime Company committed itself to design and construction of a 3 MWe pilot plant for tests of advanced wet lime scrubbing concepts, including simultaneous SO_2 and NOx removal using ferrous EDTA. Dravo Lime, the Cincinnati Gas and Electric Company and the Ohio Coal Development Office co-sponsored the project. The pilot plant is located at the Miami Fort station of CG&E near North Bend, Ohio, west of Cincinnati. The pilot plant scrubs a slipstream of flue gas from Unit 7, a 530 MW coal-fired electric generating unit. Flue gas from the unit normally contains 1000-2000 ppmv SO_2 and 400-700 ppmv NOx. Operation began in September of 1989 and continued until March of 1991. The test program included four weeks in November and December of 1990 to test addition of ferrous chelate to the system and determine NOx removal.

In May of 1989, Dravo Lime proposed to DOE that additional tests of ferrous EDTA in the pilot plant be conducted. In the first phase, testing was to be conducted using ferrous EDTA prepared by a technique developed at Argonne that was claimed to make the chelates resistant to oxidation. It was expected from the earlier tests conducted under Ohio Coal Development Office co-sponsorship that addition of chemical reducing agents and antioxidants would be required to maintain 15 mM ferrous EDTA. In the second phase, testing was to be conducted using an iron chelate maintained in the active ferrous form by an electrochemical reduction cell supplied by Dow Chemical Company.

During these tests, the effect of gas-liquid contact and ferrous EDTA concentration on NOx removal efficiency was to be determined. The effect of SO_2 to NOx ratio would also be investigated.

The third phase of testing was to consist of sustained operation of the test facility using the most promising ferrous EDTA maintenance technique and operating conditions found in the earlier tests. Testing was to focus on effects that require a longer time to be observed such as the type and amount of NOx capture compounds produced and the effect of these compounds on the FGD system.

DOW Chemical Company withdrew from the project in February of 1991, citing the concern that pilot-size electrochemical cells they had available for the tests would not have sufficient capacity for the larger pilot tests planned in this program. In place of the electrochemical cell tests, tests were planned to study the effect on NOx removal of flue gas velocity, absorber liquid rate, use of packings and fine sprays to increase gas-liquid contact, and absorber pH. These tests resulted in significantly higher NOx removal than in the earlier tests and allowed a mathematical model that described their effects on NOx removal to be confirmed. These tests were among the most productive in the program.

An objective of the test program was to achieve an overall NOx removal of 88%. A promising combination of technologies to achieve this is low-NOx combustion modification followed by ferrous chelate-based scrubbing. A key to this combination was to determine the effect of inlet flue gas NOx concentration on percentage NOx removal. The combination offers to reduce several of the potential problems in application of ferrous chelate NOx scrubbing.

NOx removal tests were conducted in a 35.5 inch diameter, 40 foot high, absorber tower with various internal configuration. These included combinations of spray headers, trays and packings.

Technical personnel from Argonne participated in the project with Dravo Lime Company. An economic evaluation of ferrous chelate NOx scrubbing integrated with wet FGD was performed using leading studies of the costs of SCR and wet FGD by the Electric Power Research Institute, report GS-7193 and the Integrated Air Pollution Control System cost model, version 4.0, by the U.S. EPA.

The test program was conducted at modest cost for work at this scale. The only significant equipment installed at the pilot site was an SO_2 injection system to increase the SO_2 concentration of the flue gas.

B. PROJECT OBJECTIVES

Objectives of the pilot-scale (3 foot diameter, 0.75-1.5 MWe scale) tests were:

1. Determine what is the dependence of NOx (NO) removal on absorber operating conditions (liquid-to-gas ratio (L/G), degree of gas-liquid contact, ferrous EDTA concentration) for application of this technology for both retrofit and new wet SO_2/NOx removal systems.

2. Obtain a better understanding of absorber operating conditions required for higher levels of NOx removal.

3. Study chemical reduction and electrochemical reduction of ferric EDTA to active ferrous EDTA. Test promising chemical reductants and antioxidants as schedule permits.

   Successful maintenance of most of the iron in the ferrous form, in an economical way, is a key step toward commercialization of this technology.

4. Study the effect of the ratio of flue gas SO_2 to NOx. Higher ratios are expected to cause some improvement in NOx removal and to reduce the concentration of NOx-capture products that form in the absorber liquid and in liquid that is discharged from the process.

5. Attempt to balance the amount of NOx removed from the flue gas with the amount of NOx-capture products in absorber liquid. Determine what are the primary products formed in absorber liquid and verify that nitrous oxide (N_2O) is not formed and evolved in substantial amounts. Conduct laboratory study of stabilization prior to discharge and disposal of by-product solids (calcium sulfite) containing NOx-capture products.

6. Evaluate the NOx scrubbing with ferrous chelates following low-NOx combustion as a combination of NOx removal technologies that can achieve higher levels of NOx removal than either technology alone.

7. Evaluate the economics of NOx removal with this technology.

8. Identify areas for future research.

C. MAJOR RESULTS AND CONCLUSIONS

1. Dependence of NOx Removal on Absorber Operating Conditions

a. Model of NO Removal

The first two objectives of pilot testing were to determine dependence of NO removal on absorber operating conditions and to obtain better understanding of conditions required to achieve higher levels of NOx removal. These objectives were met very well through testing which led to development of a mathematical model that describes the dependence of NO removal efficiency on absorber flue gas velocity, absorber liquid rate, ferrous EDTA concentration, absorber length, and gas-liquid contact time. The model equation is:

$$NTU = -\ln(1 - \%\ removal/100)$$

$$= \frac{(k_2\ [Fe^{++}]\ D_{NO})^{1/2}}{H/p_T} \qquad \frac{a\ \ Z}{p_M\ \ v}$$

where:

NTU = NO removal as number of transfer units, dimensionless

k_2 = reaction rate constant for second-order reaction between dissolved (but not yet reacted) NO and ferrous EDTA = 2.2445 x 10^{12} ft^3/lb mole-sec @ 122°F.

$[Fe^{++}]$ = ferrous EDTA concentration in absorber liquid, mM 6.2362 x 10^{-5} = lb mole/ft^3.

D_{NO} = diffusivity of dissolved NO in absorber liquid = 4.4 x 10^{-8} ft^2/sec @ 122°F.

a = gas-liquid interfacial area per volume of contact zone, ft^2/ft^3

Z = length of gas-liquid contact zone, ft

p_M = molar density of flue gas = 0.00235 lb-moles/ft^3 @ 122^{o}F

v = flue gas velocity in absorber, ft/sec

p_T = total pressure = 1 atm

H = Henry's law constant for NO in water = 11383.25 ft^3-atm/(lb-mole) @ 122^{o}F (if flue gas is saturated with water vapor, the effective solubility of NO in water is 12813.56 ft^3/lb-mole.)

NO absorption was found to be controlled by liquid film resistance. This is expected to hold at low ferrous EDTA concentrations with moderate to high absorber gas velocities (e.g.,> 4 feet/sec).

The liquid film mass transfer coefficient, $(k_2\ [Fe^{++}]\ D_{NO})^{0.5}$, is based on the assumption of pseudo-first-order irreversible fast reaction between ferrous EDTA and NO with bulk liquid concentration of ferrous EDTA much greater than concentration of dissolved NO at the gas-liquid interface. This coefficient would also nearly apply for the reversible reaction between ferrous EDTA and NO since the equilibrium constant is very large, about 10^6 M^{-1}.

The surface area "a" is a function of liquid rate and packing type for packings, so "a" contains the dependence of removal on liquid rate. It is expected for each packing that:

a = constant * (liquid rate, gpm)^b where b is a constant. "b" is expected to be <0.5.

"a" depends on liquid rate and nozzle type for spray nozzles, but also on gas velocity and absorber diameter. It is expected to be more difficult to predict or correlate.

The model was derived during Phase I and used to guide test conditions and correlate NO removal data in Phases II and III. NO removal data were very well correlated by the model. A detailed derivation is given in Section II A and correlations of NO removal data are given in Section III B. The model will allow better prediction of NO removal that could be achieved in existing full-scale wet scrubbers and could provide a guide to design of new scrubbers to achieve higher levels of NO removal.

2. NOx and SO_2 Removals Achieved

a. Retrofit Mode

In the third phase of the pilot tests, a 216 hour test was conducted to simulate retrofit of combined SO_2 and NO removal to an existing absorber built only for SO_2 removal. Twelve feet of Munters PN Fill structured packing was installed in the 3 foot diameter tower as shown in Figure 1. Flue gas velocity in the tower was maintained at 8 feet per second, typical for existing SO_2 absorbers, and absorber liquid rate was about 110 gpm. About 30% NO removal and 99.5% SO_2 removal was achieved. Addition of reducing agent/antioxidant sodium dithionite and ascorbic acid was required to maintain about 15 mM ferrous EDTA.

b. New Plant Mode

Following the retrofit tests described above, a 216-hour test was conducted which simulated application of this process to a new wet scrubber built for simultaneous removal of SO_2 and NO. Twelve feet of Munters PN Fill structured packing was used in the tests. Flue gas velocity was about 4 feet per second and absorber liquid rate was about 250 gpm and 99.9% SO_2 removal and up to 60% NO removal were achieved.

3. Effect of Inlet NOx Concentration on NOx Removal

Percent NO removal was found to be independent of inlet flue gas NO concentration, as shown in Figure 2. Percent removal is independent of inlet NO concentration because the concentration of absorbed, but not yet reacted, NO in the bulk of absorber liquid is very low, due to the very rapid rate at which absorbed NO reacts with ferrous EDTA. Since the concentration of absorbed NO is essentially zero, its rate of absorption is proportional to the concentration of NO in the flue gas, and percentage removal is independent of inlet flue gas NO concentration.

NO removal was also independent of inlet flue gas oxygen concentration. Although the oxygen concentration in part determines the steady state concentration of ferrous EDTA, once the ferrous EDTA concentration is determined, NO removal would be expected to be independent of flue gas oxygen.

4. Effect of Ferrous EDTA Concentration on NOx Removal

As expected from earlier laboratory testing by Dr. Walker and from the mathematical model described above, NO removal as number of transfer units (NTU) increased as about the square root of ferrous EDTA concentration. The data from Phase I testing in Figure 3 shows that NTU increased as the 0.56 power of ferrous EDTA concentration. During tests in Phase III to confirm the earlier finding, NTU increased as the 0.58 power.

There were periods when removal as NTU increased as a lesser power of ferrous EDTA concentration, especially during testing of an alternative reducing agent, glyoxal. The effects of glyoxal on system chemistry are described in Section III B.

5. Effect of Inlet SO_2 To NOx Ratio on NOx Removal

Little effect of a higher ratio of flue gas SO_2 to NOx on NO removal efficiency was found in pilot tests. System operation benefits from a higher ratio primarily because it reduces the concentration of NOx-capture products that form in the absorber liquid and in liquid that is discharged from the process.

6. Fate of Absorbed NOx

a. Sulfur-Nitrogen Anions Formed

The NO-capture products found were among those which had been found in earlier laboratory scale tests. Amine disulfonate ($N(SO_3)=$) and sulfamate ($NH_2SO_3=$) were the major capture products of NO absorption. Little hydroxylamine disulfonate ($HON(SO_3)=$) was found, though it was found in greater amounts in earlier laboratory tests. Addition of reducing agents/antioxidants during the pilot tests could have had an effect on the amount of hydroxylamine disulfonate formed. The sulfur-nitrogen compounds that would be expected to form are discussed in Section II A.

b. Lack of Formation of N_2O

Nitrous oxide (N_2O) was not found in scrubbed flue gas during pilot tests. Scrubbed flue gas was sampled and analyzed for N_2O during several test periods, including one where NO removal was highest, about 60%. Gas samples were analyzed using gas chromatography with a thermal conductivity detector; the detection limit was 10 ppmv. Absorber liquid was maintained at a pH of 6.5 throughout almost all tests, which was probably responsible for lack of N_2O production. A prominent researcher in this area, Dr. Chang at Lawrence Berkeley Laboratory, found N_2O in much greater amounts, in laboratory tests especially at higher pH. Subsequently, the findings here should be checked in future laboratory and pilot testing before one can be assured that N_2O will not form.

c. Balance between Absorbed NOx and Sulfur-Nitrogen Anions Formed

Attempts to balance the amount of NO removed from flue gas with the amount of NO-capture products found in liquid and solids in the system were only partly successful. Because of the large volume of liquid in the pilot system, about 8000 gallons, compared with the rate at which liquid left the system with filter cake (about 0.125 gpm when the absorber was operated at 8 feet per second gas velocity and proportional to this value for lower velocity) the concentration of sulfur-nitrogen compounds could not approach its steady state value in the shorter test periods. For example, the time to reach steady state for operation at 8 feet per second is about 19 weeks.

7. Study of Alternate Reducing Agents to Reduce Ferric EDTA

Although the pilot tests confirmed earlier laboratory findings that showed that NO can be removed from flue gas using ferrous EDTA, the tests also confirmed that ferrous EDTA is deactivated (oxidized to ferric (Fe^{+3}) EDTA) by oxygen in flue gas. Means to reactivate it, such as addition of reducing agents or antioxidants during the test program, is required. Sodium dithionite ($Na_2S_2O_4$) and ascorbic acid, used in the pilot tests, were very effective in reactivating ferrous EDTA, but they are too expensive to be practical. Lower cost chemical reducing agents/antioxidants are required for the combined NOx/SO_2 removal process to be applied at commercial scale. Also, though not tested here, use of an electrochemical cell for reduction of ferric EDTA to ferrous EDTA is projected to be practical in cost and is the most promising means at present.

Another reducing agent/antioxidant tested, glyoxal (HOC=COH), was effective and significantly less expensive, but interfered with process chemistry. Additional laboratory study of use of glyoxal would be required before additional tests should be conducted at this scale.

A 10 day test using very high ferrous EDTA concentrations along with thiosulfate, a sulfite oxidation inhibitor, showed promise that some ferrous EDTA could be reactived by a mild reducing agent, sulfite ($SO_3^=$), that is naturally present in FGD process liquid. This approach has the advantage that the cost of reducing agents/antioxidants is avoided at the expense of a higher, though practical, cost for makeup ferrous EDTA. Thiosulfate appears to help improve solids dewatering, which allows high ferrous EDTA concentrations to be used practically. Though promising, the tests conducted were too brief to conclude that this approach would succeed in long-term commercial operation. Additional laboratory research is suggested to further study this approach.

D. PROGRESS OF PROJECT COMPARED TO EXPECTED RESULTS

Substantial progress was made toward understanding how NO removal is determined by absorber operating conditions. The NO removal model equation will provide a guide to researchers conducting further work in this area to allow NO removal obtained at small scale to be reasonably scaled up to large systems.

E. IMPLICATION OF RESULTS FOR COMMERCIAL USE

The NO model will allow better prediction of NO removal that could be achieved in existing full-scale wet scrubbers and could provide a guide to design of new scrubbers to achieve higher levels of NO removal.

Low-cost means to maintain about 15 mM ferrous EDTA in absorber liquid remains as the major hurdle to commercialization of this technology. As recommended in section H below, additional research in this area is required. The electrochemical approach appears most promising.

Another concern regarding use of EDTA is potential for solubilization of heavy metals. The results of the waste characterization studies showed that heavy metals were not leached from EDTA-containing solids produced by the pilot plant that has been treated using the current FGD stabilization method.

F. COST OF SO_2, NOx REMOVAL

Cost projections for several combined SO_2 and NOx removal systems are discussed at length in Section V.

G. WASTES AND BY-PRODUCTS AND THEIR DISPOSAL

Solids produced as a by-product of removal of SO_2 dewatered extremely well to solids concentrations unprecedented for magnesium-enhanced lime FGD systems. An increase in solids content reduces the weight and volume of solids that must be placed in a landfill, and reduces transportation and placement costs. Solids content of filter cake was 65 to 77 weight percent during the entire test program, compared with 35-45 weight percent for a magnesium-enhanced lime FGD system operated without simultaneous NO removal. An increase in solids content from 40 wt.% to 70 wt.% results in a 42.8% reduction in weight of solids disposed and likely a similar reduction in disposal cost.

Physical properties of the solids were measured, and their chemical analyses determined. Particle size and shape of the solids were determined. Elemental analyses were performed using wavelength-dispersive X-ray fluorescence, and moisture and residual EDTA were determined.

Laboratory tests were conducted to determine if solids produced by the system, including entrained NOx-capture products, could be treated and made inert using the treatment method used at present in commercial FGD systems. Tests were conducted to determine if the solids could be stabilized, that is, treated to increase bearing strength and decrease permeability, using current treatment for stabilizing FGD solids before placement in a landfill. Tests were conducted with addition of various amounts of flyash and lime. The results showed the solids were easily stabilized using current technology.

Tendency for heavy metals to leach from the stabilized solids and their toxicity were determined. TCLP tests for heavy metals were performed on the solids both before and after stabilization. TCLP results after stabilization were well below TCLP limits for heavy metals and also below limits for drinking water. Toxicity tests using Daphnia simplex and fat-head minnows were performed on solids both before and after stabilization.

Detailed results of the characterization of the solid waste produced from this process appear in Section IV.

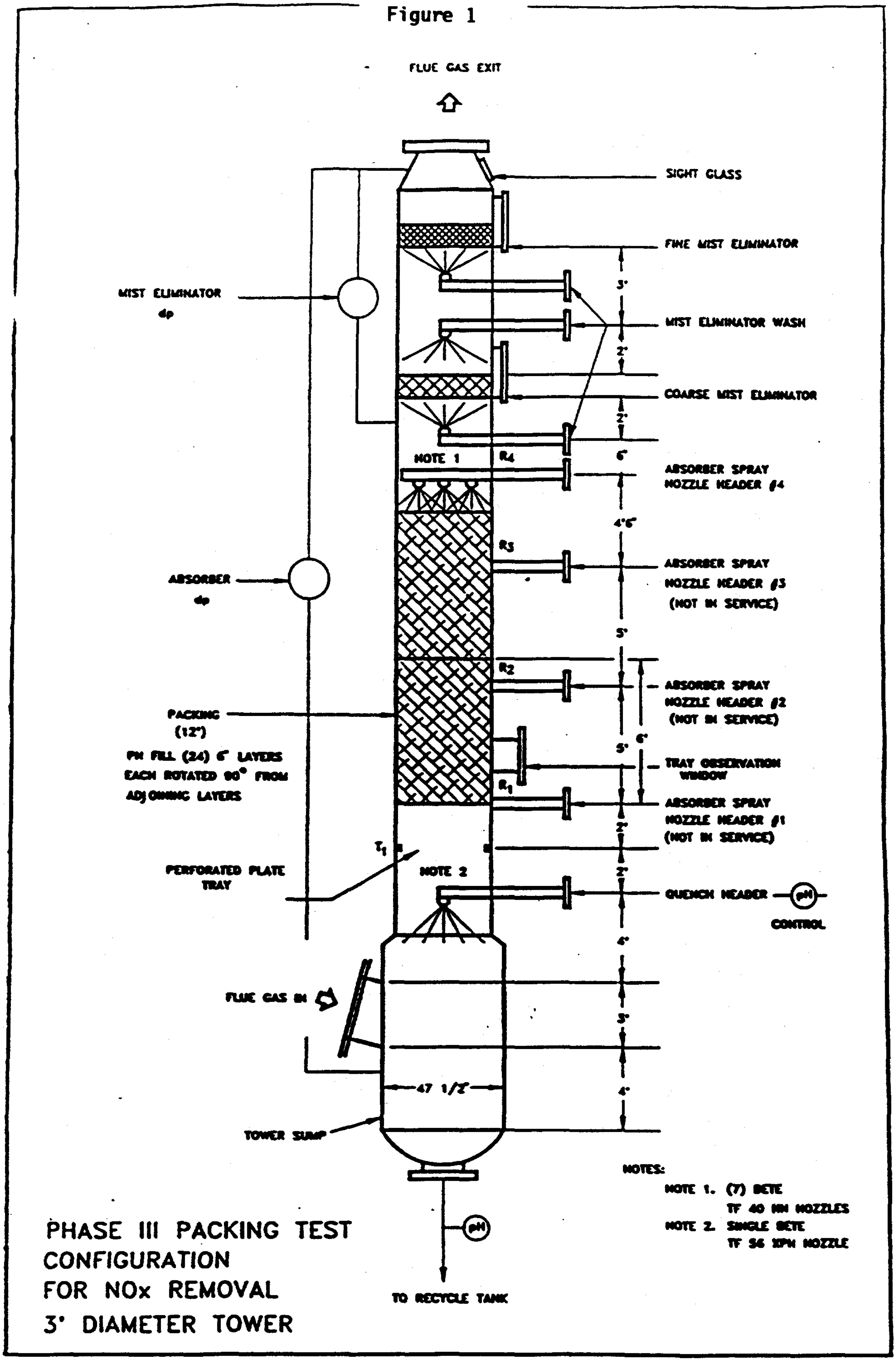
H. SUGGESTIONS FOR FUTURE RESEARCH

Additional laboratory research is required to find less expensive means to maintain iron EDTA in the ferrous form. Chemical reducing agents and antioxidants whose potential cost is under $12 per lb-mole of ferric EDTA reduced (or per lb-mole of ferrous EDTA protected from oxidation) should be screened in laboratory tests for reducing/antioxidant efficiency and checked to see if their presence interferes with either NO removal chemistry or with SO_2 removal chemistry. An important interference would be reaction with sulfite, which is required both to promote SO_2 removal and to regenerate ferrous EDTA from the ferrous EDTA-NO complex formed when NO is absorbed.

Additional study of electrochemical reduction of ferric EDTA to the ferrous form is recommended. Though it was not tested in the pilot program, tests of an electrochemical cell at similar scale by DOW Chemical Company showed great promise that this approach was workable, and operating costs projected in this report, $1-3 per lb-moles of ferric EDTA reduced, would make it a very low cost means to maintain ferrous EDTA.

Additional research would be to test use of an electrochemical cell at laboratory scale to optimize current efficiency.

Figure 1



PHASE III PACKING TEST CONFIGURATION FOR NOx REMOVAL 3' DIAMETER TOWER

Figure 1

NOx Removal Corrected to Fe+2=15 mM to Eliminate Effect of Ferrous Concentration

	NOx NTU(corr.) = f(O2)		
	m1	b	
	0.0029	0.1524	
Std. Err. Coef.	0.0027	0.0238	Std. Err. Coef.
r^2	0.02	0.03	Std. Err. of Y Est.
F	1.15	62.00	d.f.
SSreg.	0.0009	0.05	SSresid.

	NOx NTU(corr.) = f(NOx In)		
	m1	b	
	0.0000	0.1989	
Std. Err. Coef.	0.0000	0.0257	Std. Err. Coef.
r^2	0.01	0.03	Std. Err. of Y Est.
F	0.71	62.00	d.f.
SSreg.	0.0006	0.05	SSresid.

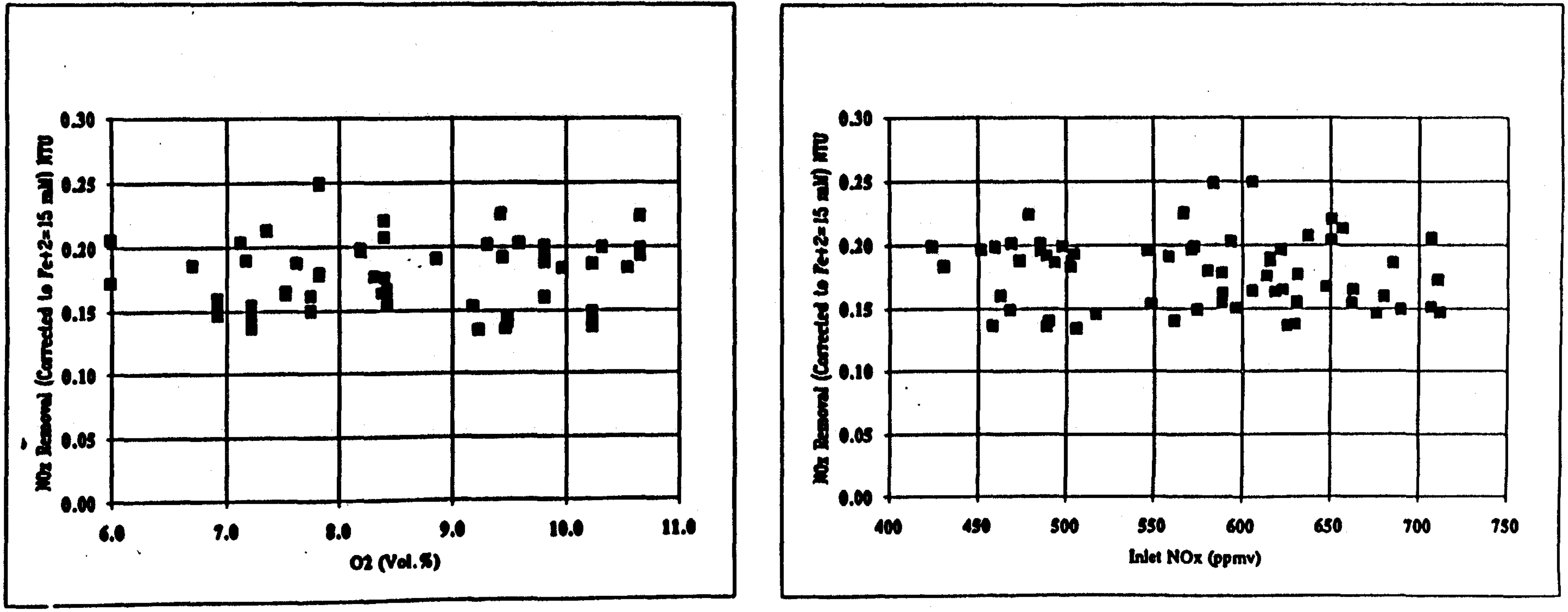


Figure 2

Figure 2

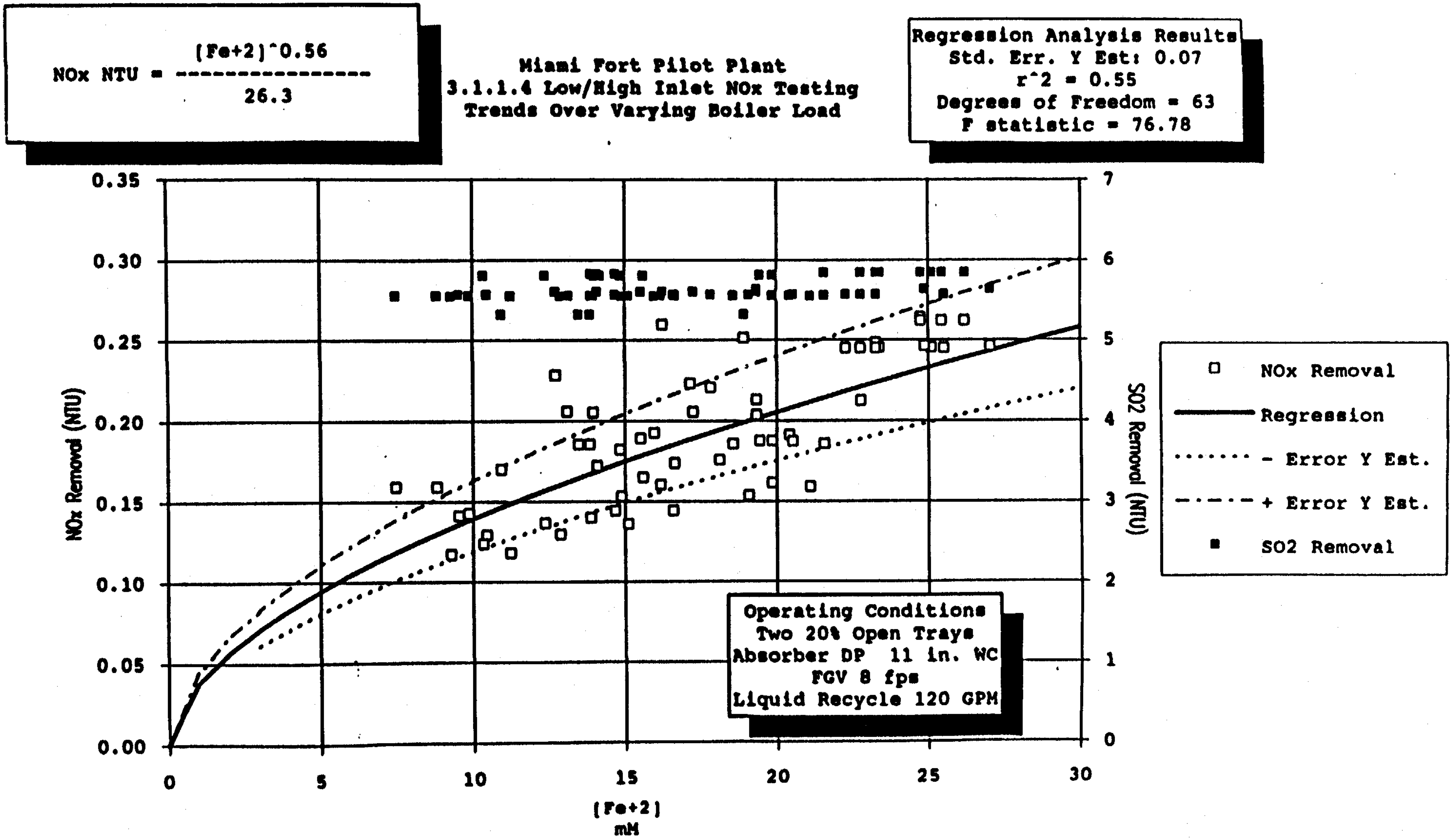


Figure 3

Figure 3

Section II

II. BACKGROUND OF PROJECT AND TECHNOLOGY

A. DESCRIPTION OF PROCESSES - NOx REMOVAL AND SO_2 REMOVAL

1. Chemistry of NOx Removal Using Ferrous EDTA

Nitrogen oxides in flue gas from coal-fired utility boilers are typically more than 95% nitric oxide (NO), with the balance nitrogen dioxide (NO_2). Nitric oxide is only slightly soluble in water, about 2300 times less soluble than sulfur dioxide (SO_2), based on their Henry's law constants[1]. The solubility of NO in water at 50^oC, normal wet scrubber operating temperature, is 0.03152 liters of NO gas (at 1 atm and 0^oC) per liter of water[2], equivalent to a Henry's law constant of 710.65 atm/M. Once dissolved in water, NO does not react with alkali as does SO_2. Nitrogen dioxide is about 21 times more soluble in water than NO[3] and can react directly with alkali and with sulfite, so it is absorbed more readily than NO.

Because of the low solubility of NO in water and its inability to react with alkalies like lime, essentially no NO is removed in a normal wet flue gas desulfurization (FGD) system.

Addition of ferrous chelate, particularly ferrous ethylenediaminetetraacetic acid ($Fe^{+2}EDTA$), to absorber liquid in a wet FGD system allows absorption of NO. NO gas first dissolves in absorber liquid, then reacts with ferrous EDTA:

$$NO\ (in\ gas) \longleftrightarrow NO\ (in\ liquid) \qquad (1)$$

$$NO\ (in\ liquid) + [Fe^{+2}EDTA]^{=} \longleftrightarrow [Fe^{+2}EDTA\text{-}NO]^{=} \qquad (2)$$

Reaction 2 is reversible as indicated, second order with respect to the forward reaction (first order in NO and Fe^{+2}EDTA, respectively) and first order with respect to the reverse reaction [4]. The forward rate is fast with a second order rate constant of about 1.2×10^8 liters/g mole-sec at pH 7 and 25°C and is thought to reach a maximum at this ph [5]. The large equilibrium constant of reaction 2, 1.2×10^7 liters/g mole at 25°C [6], greatly favors formation of the adduct.

Reaction 2 is irreversible when sulfite ($SO_3^=$) is present in absorber liquid. The rate constant was found to be 1.4×10^8 liters/g mole-sec, about the same as the forward rate when sulfite is absent[7]. This fast reaction with dissolved NO allows absorption of NO from flue gas at a practical rate, even with its low solubility in water.

The low solubility of NO in water causes the rate of NO removal to be controlled by conditions in the liquid, or be "liquid-film controlled", even though NO reacts rapidly with ferrous EDTA once it dissolves. This is discussed further in the section "Control of NO Absorption Rate" below.

EDTA forms a strong chelation complex with ferrous ion and an even stronger complex with ferric ion (Fe^{+3}) with equilibrium (formation) constants of 2.1×10^{14} and 1×10^{25}, respectively [8]. While free ferrous ion has some affinity for NO, chelation by EDTA greatly increases the tendency of ferrous iron to bind NO over ferrous ion alone [9]. Ferric EDTA has little affinity for NO. Chelation by EDTA also serves to keep ferric iron in solution in the pH range typical of lime-based flue gas desulfurization (FGD) systems. Free ferric ion is very insoluble at pH greater than 5 and all of the iron would be rapidly precipitated as hydroxides ($Fe(OH)_3$ and $Fe(OH)_2$) in the absence of a chelating agent like EDTA.

Other chelating agents, for example, nitrilo triacetic acid (NTA) and hydroxyethylenediaminetriacetic acid (HEDTA), have been used to chelate ferrous ion for NO removal, but neither has been found as effective as EDTA for promoting absorption of NO by ferrous ion [10, 11]. Several new chelating agents specifically designed to promote absorption of NO by ferrous ion have been synthysized and tested at a laboratory scale and show promise to be superior to EDTA [12,13, 14]. They have yet to be produced in amounts sufficient for testing at pilot scale.

The ferrous EDTA-NO adduct reacts irreversibly with dissolved sulfite present from absorption of SO_2 to regenerate ferrous EDTA and form primarily hydroxylamine disulfonate (HADS) which further reacts to form other nitrogen-and-sulfur-containing products:

$$[Fe^{+2}EDTA\text{-}NO]^{=} \text{ (ferrous EDTA-NO adduct)} + 2\ SO_3^{=} + H_2O$$

$$\text{--->} [Fe^{+3}EDTA\text{-}NO]^{-} + HON(SO_3)^{=} + OH^{-} \qquad (3)$$

The rate of reaction 3 has been studied [15,16], but its mechanism is complex. The rate is proportional to sulfite concentration and to ferrous EDTA-NO concentration and inversely proportional to ferric EDTA concentration.

The rate of disappearance of ferrous EDTA-NO via reaction 3 is thought to be fast at high sulfite concentrations compared to its formation by reaction 2, the rate-controlling reaction. If the sulfite concentration in absorber liquid is reduced, the rate of NO removal might decrease even at constant ferrous EDTA concentration since in this case reaction 3 would also begin to control the overall rate.

Several compounds are formed from further reaction of HADS with sulfite and from its hydrolysis [17]. Some of the HADS formed can react with sulfite to form amine trisulfonate (ATS) which rapidly hydrolyzes to form amine disulfonate (ADS) and sulfate. HADS can also hydrolyze to form hydroxylamine monosulfonate (HAMS) and sulfate. HAMS can hydrolyze to form sulfamate (SAM) or hydroxylamine (HA). Ammonium ion (NH_4^+) and sulfate can form by hydrolysis of sulfamate at very low pH.

Nitrite (NO_2^-) and nitrate (NO_3^-) ions are not expected to be major products of absorption of NO with ferrous EDTA. Nitrate would be present in absorber liquid in substantial amounts only if a large amount of NO_2 were also absorbed from the flue gas:

$$2\ NO_{2(gas)} + H_2O \text{ ---> } NO_3^- + NO_2^- + 2\ H^+ \qquad (4)$$

Since flue gas from coal-fired boilers usually contains little NO_2 (<5% of NOx), little nitrate would be expected.

Nitrite can form from absorption of NO_2 as above and from absorption of N_2O_3 formed in the gas phase from NO and NO_2:

$$NO_{(gas)} + NO_{2(gas)} \text{ ---> } N_2O_{3(gas)} \qquad (5)$$

$$N_2O_{3(gas)} + H_2O \text{ ---> } 2\ NO_2^- + 2\ H^- \qquad (6)$$

NO_2 can also react directly and rapidly with sulfite in absorber liquid to form nitrite.

Nitrite formed in these ways would be rapidly converted to HADS by reaction with sulfite. Nitrite can also react with several other of the sulfur-nitrogen compounds, so that little would remain in solution as free nitrite.

Minimal amounts of the gases nitrogen (N_2) and nitrous oxide (N_2O) are expected to form in this process when absorber liquid pH is 6 to 7, the normal range for magnesium-enhanced lime (MEL) based flue gas desulfurization (FGD) systems, though there is some disagreement in published laboratory work. Substantial amounts of nitrogen and nitrous oxide have been formed under laboratory conditions at pH greater than 7 [18, 19]. N_2O is formed first and in greater amount. Sada et. al. found no N_2O at pH 6, while Chang et. al. found substantial amounts of N_2O at pH 6.

Hydroxylamime ($HO-NH_2$) can form by hydrolysis of HAMS, but its presence has not been reported in laboratory work because it is difficult to measure in the presence of other similar compounds. Hydroxylamine is unlikely to be present when high sulfite concentrations are present in absorber liquid since HAMS reacts more rapidly with sulfite to form ADS and sulfamate [20]. Hydroxylamine also reacts slowly with sulfite to form sulfamate [21]. Hydroxylamine may be toxic.

Oxidation of Ferrous EDTA

Ferrous EDTA is rapidly oxidized to ferric EDTA by oxygen absorbed from the flue gas:

$$4\ [Fe^{+2}{*}EDTA]^{=} + O_2 + 2\ H_2O \dashrightarrow 4\ [Fe^{+3}{*}EDTA]^{-} + 4\ OH^{-} \qquad (7)$$

Ferric EDTA does not form a strong complex with NO, so it is essentially inactive for NO removal.

Studies have determined the rate of oxidation of ferrous EDTA by oxygen was first order in dissolved oxygen and one-half order in ferrous EDTA [22]. Oxidation was suppressed by excess EDTA; a 20% molar excess of EDTA over iron suppressed the rate of oxidation by about 30%.

Chelation of ferrous ion with EDTA increases the strength with which it binds NO, but it also makes it easier to be oxidized to ferric ion. The half-cell oxidation potential, a measure of the ease with which ferrous is oxidized, increases from -0.77 volts to 0.117 volts when ferrous ion is chelated by EDTA [23]. A loosely-held electron in the ferrous ion is what gives it its ability to bind NO. Apparently, the more weakly held this electron is, the more tendency chelated ferrous has to bind NO, but also the more easily the electron is lost (i.e., ferrous is oxidized).

If the electron is held more tightly, ferrous will be more difficult to oxidize, but NO will be less strongly bound. An example is the ferrous 1,10-phenanthroline chelate. Its half-cell potential is -1.14 volts, meaning that it is far less easily oxidized than ferrous EDTA, but it has little tendency to bind NO [24].

Some of the ferrous EDTA is also oxidized when the ferrous EDTA-NO adduct reacts with sulfite to form the sulfur-nitrogen compounds discussed earlier. Ferrous EDTA is not oxidized by NO alone, but only also in the presence of sulfite. The mechanism of this oxidation is not well understood.

Although ferrous EDTA is oxidized rapidly by oxygen and during regeneration of the ferrous EDTA-NO adduct by sulfite, the ferrous EDTA concentration in absorber liquid is not expected to fall to zero because sulfite reduces ferric EDTA back to ferrous EDTA at a slow rate at 50°C:

$$2\ [Fe^{+3}*EDTA]^{-1} + 2\ SO_3{}^{=}$$

$$\text{--->}\ 2\ [Fe^{+2}*EDTA]^{-2} + S_2O_6{}^{=} \qquad (8)$$

Sulfite is present in absorber liquid in magnesium-enhanced lime based FGD systems at concentrations of 50-100 mM.

Although some reduction of ferric EDTA is accomplished by sulfite that is naturally present in the MEL FGD system, and this reduction is very desirable because it is accomplished without additional cost, the amount of reduction is expected to be too little to be practical under normal coal-fired flue gas scrubber conditions. Less than 10% is expected to remain in the ferrous form under flue gas scrubbing conditions. The percentage of iron EDTA that remains in the ferrous form at flue gas scrubbing conditions depends on the concentration of sulfite and the ferrous oxidation rate.

Sulfite reduces ferric EDTA faster at higher temperature. The rate of reduction has been determined[25] and processes based on reduction by sulfite at higher temperature have been proposed[26]. A patent assigned to DOE claims a ferrous EDTA-based NO removal process with reduction by sulfite at about 80°C [27]. The hurdle for application of these processes is to provide the very large amounts of heat and heat interchange equipment required to increase absorber liquid temperature from 50 to 80°C for the reduction step.

The rate of reduction by sulfite also depends on pH and appears to be faster at higher pH. An earlier study noted above appeared to show that bisulfite (HSO_3^-) rather than sulfite is the species that reduces ferric EDTA and therefore reduction should be faster at lower pH [28]. A later study by the same group and other studies by Walker at PETC[29] and in-house tests by Dravo Lime[30] indicated that reduction was faster at higher pH at the conditions tested.

Although a small concentration of ferrous EDTA is maintained by reduction by sulfite, a practical ferrous EDTA concentration can be maintained only by providing additional means to reduce ferric EDTA. These means include addition of chemical reducing agents, such as sodium dithionite (NaS_2O_4). Dithionite rapidly reduces ferric EDTA:

$$2\ [Fe^{+3}*EDTA]^{-1} + S_2O_4^{=} + 2\ H_2O$$

$$\text{--->}\ 2\ [Fe^{+2}*EDTA]^{-2} + 2\ SO_3^{=} + 4H^+ \qquad (9)$$

Another approach is to add antioxidants, compounds which react with dissolved oxygen before it can oxidize ferrous EDTA. Examples are ascorbic acid [31] and polyphenolic compounds [32]. Antioxidants often also reduce ferric EDTA directly. For example, in laboratory experiments by Dravo Lime, one mole of ascorbic acid reduced 10 moles of ferric EDTA. (The distinction between antioxidants and reducing agents is somewhat artificial. It is convenient to compare agents on the basis of moles of ferric EDTA reduced, whether ferric was actually reduced by a reducing agent or oxidation was prevented by an antioxidant.)

Another approach is to reduce ferric EDTA using an electrochemical cell. DOW Chemical has conducted development work in this area, and has reported results of both laboratory and pilot-scale tests [33]. A cell consists of cathode and anode compartments, separated by a membrane that is permeable for some ions. Ferric EDTA is reduced at the cathode:

$$[Fe^{+3}*EDTA]^{-1} + e^{-} \text{--->} [Fe^{+2}*EDTA]^{-2} \qquad (10)$$

At the anode, water is oxidized to produce oxygen gas and acidity:

$$1/2\ H_2O \text{--->} 1/4\ O_2 + H^{+} + e^{-} \qquad (11)$$

The overall reaction in the cell is:

$$\begin{aligned}&[Fe^{+3}*EDTA]^{-1} + 1/2\ H_2O \text{--->}\\ &\ [Fe^{+2}*EDTA]^{-2} + 1/4\ O_2 + H^{+}\end{aligned} \qquad (12)$$

The catholyte solution is a sodium carbonate solution maintained at a pH of 7 or above by addition of caustic. Since a mole of acidity is produced for each mole of ferric reduced, caustic or another compatible alkali must be regularly added to the catholyte to neutralize it. This regular addition of alkali would represent an operating cost for the cell in addition to electricity.

(Pilot tests using an electrochemical cell had been planned for this project, but DOW decided that further cell mechanical design and development was required before further pilot tests would be productive.)

Cost to Reduce FERRIC EDTA to FERROUS EDTA

The cost to either prevent the oxidation of ferrous EDTA or to reduce ferric EDTA back to ferrous EDTA is the largest cost identified for this process. Table 1 shows a comparison of cost among several agents and electrochemical reduction. Cost for electricity and make-up alkali to operate a cell to reduce ferric EDTA is lower than the cost of chemical reducing agents or antioxidants to reduce ferric EDTA. The cost for electricity is about $1/lb-mole ferric EDTA reduced, and the cost of make-up sodium hydroxide is about $2.5/lb-mole reduced. This compares with a cost for sodium dithionite of about $54/lb-mole reduced as shown in Table 1. Cost for glyoxal depends on how completely it reacts, but even at 67% utilization, it is far less costly than dithionite. Ascorbic acid is very effective at maintaining ferrous EDTA, but it is too costly to be practical.

Relative costs of the various agents and electrochemical reduction are shown graphically in Figures 1 and 2.

Finding means to economically reduce ferric EDTA to ferrous EDTA is the key step in commercializing this process.

Control of NO Absorption Rate

In a countercurrent absorber, as shown for the pilot plant in Figure 3, the rate of absorption of NO into liquid containing ferrous EDTA is:

$$N_{NO} = K_g \, a \, S \, Z \, (p_{NO})_{\ln \text{ mean}} \qquad (13)$$

where:

N_{NO} = rate of absorption of NO, lb-moles/hr

K_g = overall mass transfer coefficient, defined based on the gas phase, lb-moles/hr-ft^2-atm

a = gas-liquid interfacial area per volume of contact zone, ft^2/ft^3

$(p_{NO})_{ln\ mean}$ = logarithmic mean of absorber inlet and outlet partial pressures (concentration)

S = horizontal cross-sectional area of absorber, ft^2

Z = length of gas-liquid contact zone, ft

It is helpful to recognize that the above expression is a simple rate equation like Ohm's law, i.e., the rate is equal to a driving force divided by a resistance to flow. The equation can be written as:

$$N_{NO} = \frac{1}{1/K_g} a\ S\ Z\ (p_{NO})_{ln\ mean} \qquad (14)$$

where the mass transfer coefficient K_g is shown in the form of a resistance, $1/K_g$.

For NO to be absorbed, it has to pass first through both a gas film and then through a liquid film on each side of the gas-liquid interface, as shown in Figure 4. These two films and their resistances to mass transfer are in series, so the overall resistance $(1/K_g)$ is the sum of the individual gas and liquid film resistances:

$$(1/K_g) \text{ (overall resistance)} = (1/k_g) \text{ (gas film resistance)} + H/k_l \text{ (liquid film resistance)} \qquad (15)$$

where: k_g = gas-film mass transfer coefficient, lb-moles/hr-ft^2-atm

k_l = liquid-film mass-transfer coefficient, ft/hr

H = Henry's law coefficient, atm/(lb-mole/ft^3)

As seen from the equation, a large value of H increases the liquid side resistance compared to the gas-side resistance and decreases the overall mass transfer coefficient. Since NO is only slightly soluble in water (i.e., a large value of H), the resistance of the liquid film is large compared to the gas-side resistance. Subsequently the liquid-side resistance controls the rate of NO removal. This compares with absorption of SO_2 which is about 2000 times more soluble in water than NO and which has a much lower liquid-side resistance to absorption of SO_2. Harriott estimated the relative gas-side and liquid-side resistances for absorbing NO with ferrous EDTA in a spray tower. The liquid-side resistance was about 99% of the total, making it the controlling resistance [34].

When the liquid-side resistance accounts for almost all of the resistance, as when NO is absorbed, absorption is said to be liquid-film controlled and the resistance of the gas film can be neglected.

The gas-side film coefficient depends only on the hydrodynamics of the system, for example, relative velocity between flue gas and liquid drops. The liquid-side coefficient can depend on both hydrodynamics and on chemical reaction of the absorbed gas in the liquid. The extent to which the liquid-film coefficient is increased over its value for physical absorption only is expressed by an "enhancement factor", E:

$$k_l \text{ (liquid-film coefficient)} = E\, k_l^{o} \qquad (16)$$

where: E = enhancement factor for absorption with chemical reaction, dimensionless

k_1^0 = liquid-film mass-transfer coefficient for physical absorption only (i.e., unenhanced by chemical reaction), ft/hr

The expression for the overall mass transfer coefficient then becomes:

$$(1/K_g) \text{ (overall resistance)} = (1/k_g) \text{ (gas film resistance)} + H/(E\ k_1^0) \text{ (liquid film resistance)} \qquad (17)$$

As seen from the equation, an increase in E decreases the liquid side resistance and increases the overall mass transfer coefficient.

The enhancement factor depends on the order of reaction, the diffusibility of NO in absorber liquid, the second order rate constant (of reaction 2 above), and whether reaction 2, the rate controlling reaction, is reversible or irreversible[35]. The expression for reversible second order reactions is complicated while the expression for irreversible reactions is simple [36,37]. For the simple case where reaction 2 is irreversible and where the concentration of ferrous EDTA in the bulk liquid is greatly in excess of the concentration of NO dissolved at the gas-liquid interface (which is almost always the case because of the low solubility of NO in water), the enhancement factor for absorption of NO by ferrous EDTA is expected to be:

$$E = (k_2\ [Fe^{++}]\ D_{NO})^{1/2}/k^o_1 \qquad (18)$$

where: k_2 = reaction rate constant for second-order reaction between dissolved (but not yet reacted) NO and ferrous EDTA = 2.2445×10^{12} ft^3/lb-mole-sec. @ 122^{o}F.

$[Fe^{++}]$ = ferrous EDTA concentration in absorber liquid, lb-moles/ft^3

D_{NO} = diffusibility of dissolved NO in absorber liquid = 4.4×10^{-8} ft^2/sec @ 122°F.

Substitution of E into equation 17 and allowing that the gas side resistance is negligible yields the following expression for the overall mass transfer coefficient for removal of NO:

$$K_g = (k_2\ [Fe^{++}]\ D_{NO})^{1/2}/H \qquad (19)$$

Dependence of NO Removal Efficiency on Absorber Operating Conditions

The rate of absorption of NO by the liquid was written earlier in equation (13) as:

$$N_{NO} = K_g\ a\ S\ Z\ (p_{NOin} - p_{NOout})_{ln\ mean}$$

where: N_{NO} = rate of absorption of NO, lb-moles/hr

K_g = overall mass transfer coefficient, defined based on the gas phase, lb-moles/hr-ft^2-atm

a = gas-liquid interfacial area per volume of contact zone, ft^2/ft^3

$(p_{NO})_{ln\ mean}$ = logarithmic mean of absorber inlet and outlet partial pressure (concentration)

S = horizontal cross-sectional area of absorber, ft^2

Z = length of gas-liquid contact zone, ft

The logarithmic mean concentration difference is equal to:

$$(p_{NO})_{ln\ mean} =$$

$$(p_{NOin} - p_{NOout})/\ln\ (p_{NOin}/p_{NOout}) \qquad (20)$$

The rate of NO absorption by the liquid must be equal to the rate at which NO is lost from the gas, which is:

$$N_{NO} = p_M \, v \, S \, (p_{NOin} - p_{NOout})/p_T \tag{21}$$

where: N_{NO} = rate of absorption of NO, lb-moles/hr

p_M = molar density of flue gas, lb-moles/ft^3

v = flue gas velocity in absorber, ft/hr

$(p_{NOin} - p_{NOout})$ = difference in flue gas NO concentration between absorber inlet and outlet, atm

p_T = total pressure, atm

S = horizontal cross-sectional area of absorber, ft^2

Combining equations 13 and 2 to eliminate N_{NO} and solving for $\ln(p_{NOin}/p_{NOout})$ yields:

$$\ln (p_{NOin}/p_{NOout}) = K_g \; a \, P_T \, Z \,/\, (p_M \, v) \tag{22}$$

The term on the left-hand side is the number of transfer units, or NTU, which is related to percent removal by:

$$\begin{aligned} NTU &= \ln (p_{NOin}/p_{NOout}) = -\ln(p_{NOout}/p_{NOin}) \\ &= -\ln(1 - \%\ \text{removal}/100) \end{aligned} \tag{23}$$

(It is convenient to note that for % removal of 20% or less, fractional removal (%removal/100) and NTU are about equal. For example, 10% removal = 0.105 NTU and 20% removal = 0.22 NTU. Figures 5 and 6 show the relationship between NTU and percent removal up to 95%.)

Combining this equation with the expression for K_g from equation 19 for removal of NO with ferrous EDTA yields a single equation that describes the dependence of NO removal on ferrous EDTA concentration, flue gas velocity in the absorber, the length of the absorption zone, and the effective interfacial area between flue gas and absorbing liquid.:

$$NTU = -\ln(1 - \%\ \text{removal}/100) = \frac{(k_2\ [Fe^{++}]\ D_{NO})^{1/2}}{H/p_T}\ \frac{a\ Z}{p_M\ v} \qquad (24)$$

Implication of Equation for NO Removal Efficiency for Pilot Plant Testing and For Full-Scale Design

Once it is verified in pilot tests, equation 24 could be used for scale-up of pilot results to existing absorbers and for design of large absorbers, assuming that the interfacial area, a, can be predicted. Prediction of "a" is a major challenge in scale-up of gas absorption. When packings are used, "a" depends primarily on absorber liquid flow rate. Subsequently "a" is a function of absorber liquid flow rate. (Therefore, the effect on removal of absorbing liquid flow rate is contained in "a".) For absorption using spray nozzles, "a" depends on the size and type of nozzle, on absorber liquid flow, and on flue gas velocity prediction of interfacial area is uncertain when spray nozzles are subsequently used.

Equation 24 also provides a basis for correlation of pilot plant data and a guide to means to increase NO removal efficiency.

Removal efficiency is expected to increase with the square root of the ferrous EDTA concentration. For example, if NO removal is 15% (0.163 NTU) at 15 mM ferrous EDTA, an increase in ferrous EDTA concentration to 25 mM would be expected to increase removal by $(25/15)^{0.5}$, or by 1.29, to 0.210 NTU or 19%.

This modest increase in NO removal efficiency with increased ferrous EDTA concentration suggests that it would likely be more effective and less costly to increase NO removal efficiency by increasing gas-liquid interfacial area since removal is expected to increase directly with an increase in interfacial area.

Removal efficiency is expected to increase in direct proportion to gas-liquid interfacial area and to absorber height. If a packing is installed in the absorber which triples gas-liquid interfacial area, then NO removal as NTU would be expected to triple. For example, if NO removal is 15% before installing packing, and the packing triples the interfacial area, removal would be expected to increase to 0.488 NTU or 38.6 % removal.

Removal efficiency is expected to increase in inverse proportion to a decrease in absorber gas velocity. If NO removal is 15% at a gas velocity of 10 feet per second and velocity is decreased to 5 feet per second, removal would be expected to increase to 0.326 NTU or 27.8 %.

Combination of these individual factors would be expected to substantially increase NO removal. If interfacial area is tripled and gas velocity is halved, removal would be expected to increase six-fold. For example, if removal is 15% prior to these changes in conditions, removal would be expected to increase to 0.975 NTU or 62.3% removal. This increase is based on the assumption that the liquid side resistance is still the controlling resistance. It is possible for the gas side resistance to become larger and begin to contribute significantly to the overall resistance when gas velocity is reduced since the gas film mass transfer coefficient decreases with decreased gas velocity. If the gas side resistance becomes significant, NO removal will not increase as much as expected. For example, if the gas film coefficient increased to equal 20% of the overall resistance when the gas velocity is halved in the example above, then NTU would increase instead to 80% of 0.975 NTU or to 0.780 NTU or 54.1 % removal.

However, at practical flue gas velocities, 4 to 10 feet per second, the liquid film coefficient for NO is so low compared to the gas film coefficient that the gas film coefficient is essentially negligible. Only at very low flue gas velocities as would be tested in a laboratory absorber (e.g., less than 1 foot/second) or at very high ferrous EDTA concentrations, would the gas film coefficient be significant.

2. Contrast Between Removal Efficiencies of SO_2 and NO

As shown above, absorption of NO with ferrous EDTA is expected to be liquid-film controlled. In contrast, SO_2 absorption is expected to be gas-film controlled. The solubility of SO_2 is about 2000 times greater than that of NO (that is, the Henry's law constant for SO_2 is about 2000 times less than that for NO). The presence in absorber liquid at pH 6.5 of 50-100 mM sulfite, which can react with absorbed SO_2, produces a large enhancement factor (see equation 16 above) for SO_2. These two factors combine (see equation 17 above) to reduce the liquid side resistance for absorption of SO_2. The gas-side resistance then becomes the controlling resistance for absorption of SO_2.

The difference in control mechanisms between absorption of NO and SO_2 has several implications. The expressions for the removal efficiencies for both NO and SO_2 can be written as:

For NO removal:

$$NTU = -\ln(1 - \%\ removal/100) = \frac{(k_2\ [Fe^{++}]\ D_{NO})^{1/2}}{H/p_T} \quad \frac{a\ Z}{p_M\ v} \qquad (24)$$

For SO_2 removal:

$$NTU = -\ln(1 - \%\ removal/100) = k_g \quad \frac{a\ p_T\ Z}{p_M\ v} \qquad (25)$$

where the terms in both equations are as defined earlier.

One implication of these equations is that the ratio of NTU for NO to NTU for SO_2 will not be constant but would be expected to depend on the concentration of ferrous EDTA and on k_g, which in turn depends on flue gas velocity. This ratio is:

$$\frac{\text{NTU, NO}}{\text{NTU, } SO_2} \approx \frac{(k_2 \, [Fe^{++}] \, D_{NO})^{1/2}}{H \, k_g} \qquad (26)$$

Another important implication is that removals of NO and SO_2 will vary differently with flue gas velocity. For NO, removal should clearly increase as flue gas velocity is decreased, since the mass transfer coefficient (the first term on the right-hand side of equation 24) does not depend on gas velocity. In contrast, for SO_2 removal, the gas-side mass transfer coefficient k_g depends strongly on gas velocity. The mags transfer coefficient would be expected to vary with the 0.5 to 1.0 power of gas velocity, so that a decrease in gas velocity would also decrease k_g, and SO_2 removal would increase only slightly (since the decrease in k_g in the numerator of equation 25 partially compensates for the decrease in v in the denominator). Similarly, SO_2 removal would decrease only slightly as flue gas velocity is increased. In contrast, NO removal clearly would be expected to decrease with an increase in gas velocity.

Effect of SO_2 Concentration in Flue Gas

Coals burned by electric utilities in the Eastern U.S. generally have sulfur contents greater than 2 weight percent. Coals produced in Ohio average 3.5% sulfur.

As discussed earlier, absorption of NO with ferrous EDTA depends on the presence of sulfite in absorber liquid. Sulfite is present from absorption of SO_2 which reacts with water to form sulfurous acid.

Sulfurous acid in turn dissociates to form sulfite and bisulfite. When magnesium-enhanced lime is used for flue gas desulfurization or some of the sulfite remains in solution as magnesium sulfite, which is available to react with absorbed NO.

Removal of NO using ferrous EDTA simultaneous with removal of SO_2 with magnesium-enhanced lime is expected to be practical only from flue gases containing a high ratio of SO_2 to NO. Since most of the sulfur-nitrogen compounds, for example, ADS and sulfamate, contain two moles of sulfur per mole of nitrogen, formation of sulfur-nitrogen compounds requires a minimum of two moles of absorbed SO_2 per mole of absorbed NO. However, use of a calcium-containing alkali like lime will cause most of the absorbed SO_2 to precipitate as calcium sulfite. If only two moles of SO_2 were absorbed per moles of NO absorbed, all of the calcium from the lime would remain in solution in absorber liquid as for, example, calcium ADS. The very high calcium concentration in absorber liquid that would result would cause severe calcium sulfate scale to form inside the absorber. This effect can be reduced by increasing the fraction of magnesium oxide to calcium oxide contained in the lime and by increasing the ratio of absorbed SO_2 to absorbed NO. The molar ratio of soluble magnesium oxide to calcium oxide in the lime should be at least the ratio of absorbed NO to absorbed SO_2. For example, when flue gas contains 600 ppmv NO and 2500 ppmv SO_2, and 50% NO removal is required (300 ppmv NO removed), the lime should contain at least 6 weight percent MgO and 90 weight percent CaO.

Laboratory tests on NO removal with iron EDTA by Argonne National Laboratory showed that higher flue gas SO_2 concentration caused an increased NO removal[38,39]. These results were likely due to higher ferrous EDTA concentration caused by higher sulfite concentration when greater amounts of SO_2 were absorbed into absorbing liquid that was rich in sodium.

Effect of Ratio of SO_2 to NO in Flue Gas

The primary effect of flue gas SO_2 to NO ratio is expected to be on absorber liquid composition and on the concentration of sulfur-nitrogen compounds formed from absorption of NO. A higher ratio of SO_2 to NO is expected to prevent build up of very high concentrations of sulfur-nitrogen compounds in absorber liquid. Very high concentrations of sulfur-nitrogen compounds could cause scale formation inside the absorber, through an increase in absorber liquid calcium concentration necessary to balance the increase in sulfur-nitrogen compounds.

The concentration of sulfur-nitrogen compounds in absorber liquid is determined by the NO removal rate and the rate at which liquid is carried out with calcium sulfite solids formed. If the absorbed SO_2 to absorbed NO ratio is higher, more calcium sulfite solids are produced and more liquid is carried out with the solids relative to the amount of NO absorbed, which decreases the steady-state concentration of sulfur-nitrogen compounds in absorber liquid.

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B. OVERALL AND SPECIFIC OBJECTIVES

Overall and specific objectives of the pilot-scale (3 foot diameter, 0.75-1.5 MWe scale) tests were:

1) Determine what is the dependence of NOx (NO) removal on absorber operating conditions (liquid-to-gas ratio (L/G), degree of gas-liquid contact, ferrous EDTA concentration) for application of technology for retrofit and for new wet SO_2/NOx removal systems.

   One uncertainty in laboratory scale testing of NO removal using ferrous EDTA is in projection of NO removal obtained at laboratory scale to those which would be obtained at large scale. Tests at pilot scale would allow more realistic projections of NO removal that would be obtained in a full-scale system.

   Earlier laboratory tests had suggested that NO removal as NTU would increase as the square root of ferrous EDTA concentration. It was important to confirm this finding in the pilot tests, since it suggests that an attempt to greatly increase ferrous EDTA concentration would not be a very effective or economical means to increase NO removal. For example, doubling ferrous EDTA concentration from 15 mM to 30 mM, likely at double the cost to maintain the higher concentration, would result in an increase of only 41% in number of transfer units.

2) Obtain a better understanding of absorber operating conditions required for higher levels of NOx removal.

   It was clear from earlier laboratory tests that absorption of NO is slower than absorption of SO_2. In order to determine what operating conditions would allow greater than 60% NO removal to be achieved, a more complete model that described the dependence of NO removal on all operating conditions would allow one to design a scrubber to achieve the maximum removal practical.

3) Study chemical reduction and electrochemical reduction of ferric EDTA to active ferrous EDTA. Test promising chemical reductants and antioxidants as schedule permits.

   Finding a low-cost means to maintain about 15 mM ferrous EDTA in absorber liquid is the key step to develop a practical process.

4) Study the effect of the ratio of flue gas SO_2 to NOx.

   Higher ratios are expected to cause some improvement in NOx removal and to reduce the concentration of NOx-capture products in absorber liquid and in liquid that is discharged from the process.

5) Attempt to balance the amount of NOx removed from the flue gas with the amount of NOx-capture products in absorber liquid. Determine what are the primary products formed in absorber liquid and verify that nitrous oxide (N_2O) is not formed and evolved in substantial amounts. Conduct laboratory study of stabilization prior to discharge and disposal of by-product solids (calcium sulfite) containing NOx-capture products.

6) Evaluate NOx scrubbing with ferrous chelates following low-NOx combustion as a combination of NOx removal technologies that can achieve higher levels of NOx removal than either technology alone.

7) Evaluate the economics of NOx removal with this technology.

8) Identify areas for future research.

C. ACKNOWLEDGMENT OF PARTICIPANTS

1. Cincinnati Gas & Electric Company (CG&E) - provided use of the pilot plant site at their Miami Fort Power Station and served as liaison for receiving chemicals and other bulk commodities. During pilot plant operations, CG&E supplied flue gas for scrubbing from Unit #7, power to operate the pilot plant, service water for plant operations, pilot plant effluent water treatment and disposal, and by-product calcium sulfite disposal at their East Bend Station landfill. In addition, they provided maintenance and instrumentation personnel in support of testing activities and in the start-up of the SO_2 injection system.

2. Argonne National Laboratory - served as consultants during the entire NOx removal project and were especially valuable in setting up the iron chelate addition scheme and adding their expertise to the solid waste characterization studies conducted.

3. Dravo Lime Company - functioned as overall project management. Dravo Lime was responsible for the initial design and construction of the pilot plant facility as well as the modifications made in support of NOx removal activities. Included in the range of activities managed by Dravo Lime at the site were "day to day" pilot plant operations, running of tests, generation of operational data, chemical analyses, and supply and slaking of magnesium-enhanced lime for simultaneous SO_2/NOx removal. Project activities conducted at Dravo's Research Center in Pittsburgh included development of test plans, data analysis, technical supervision, and report generation.

4. Individual Project Personnel - involved in either the pilot plant modification, support activities, or NOx testing program included:

Cincinnati Gas & Electric Company:

Vice President - Stephen G. Salay
Liasion Engineering - Daniel T. Horn
Site Liaison - Howard J. Klosterman
- Mike Hoffman

Argonne National Laboratory:

Project Manager - C. David Livengood

Dravo Lime Company:

Research Director - Manyam Babu
Project Manager - Gary Miller/Bruce Lani
Technical Director - Lewis B. Benson/Kevin Smith
Process Engineer - Kevin Smith
Test Engineer - Bruce Lani
Analytical Services - William Carlson
Technical Services - Jerome Hoffman
- William Biles
- Daniel W. Berisko
Waste Characterization - Steve Tutokey
Pilot Plant Site Supervisor - Casey Schulz
Pilot Plant Operations - Donald Kerivan
- Harry Sovel
- Larry McLean
Pilot Plant Analytical Lab - Mario Panella
- Charles French
- Richard Bozian

Consultant - Dr. Peter Harriott
Cornell University

D. DESCRIPTION OF MIAMI FORT PILOT FACILITIES

The pilot plant is located at the Cincinnati Gas & Electric Company's Miami Fort Station in North Bend, Ohio. Construction of the plant was funded by Cincinnati Gas & Electric company, The Ohio Coal Development Office and Dravo Lime Company. The facility went into operation at the end of 1989.

Figure 7 details the components of the facility which are available for FGD studies. A slipstream from Miami Fort Unit No. 7 downstream of the precipitator supplies the flue gas to the pilot plant. The facility includes all components of a typical wet lime FGD system, including flue gas scrubbing and dewatering equipment, thickeners and a belt filter, lime reagent preparation equipment and various other equipment for preparing and metering chemical additives for the scrubbing system.

The plant has two 40 foot tall scrubbing towers, one 4 foot and the other 3 foot in diameter. Aside from enabling the capability to simulate various flue gas velocities within the scrubbers, the towers allow testing of both countercurrent and cocurrent modes of gas-liquid contact. Varying degrees of contact/between the flue gas and the scrubbing liquor can be accomplished by operating any number of the three available recycle pumps, changing the location of the spray nozzles within the tower, or by installing sieve trays or packing. Liquid to gas ratios of 15 to 225/1000 ACFM can be achieved. The 3-foot scrubber tower detailed in Figure 8 was utilized for the Ferrous-Chelate NOx removal tests in order to minimize costs associated with reagents and FGD waste disposal.

The booster fan utilized for moving the slipstream is located between the access point downstream of the utility's precipitator and the inlet to the pilot plant scrubber modules. Flue gas flow rates of 2000 to 15000 ACFM at 300°F, equivalent to 0.6 to 4.5 MW, can be achieved by a controlling damper on the inlet to the fan and by sheave modifications to the drive mechanism of the fan. A venturi flow meter immediately downstream of the fan is utilized to monitor the gas flow rate for automatic damper control. Boiler load changes between 260 to 530 MW as well as the type of coal being fired influence the composition of the flue gas. Typical volumetric concentration ranges are:

5.5-10.5% for O_2, 700 to 2800 ppm for SO_2 and 500 to 750 ppm for NOx. An on-site SO_2 spiking system, capable of vaporizing up to 150 lb SO_2/hour, enables control of the SO_2 concentration to the inlet of the scrubber. This concentration was maintained at 2500 ppmv during the NOx removal studies.

A continuous emissions monitoring system, shown in Figure 9, analyzes the flue gas entering and leaving the scrubber. Vacuum pumps are utilized to extract the sample gas from the process stream through heated sample probes which are maintained at 350^{o}F. Heat traced sample lines transport the gas from the probe to the precooler which reduces the gas temperature to 40^{o}F. Upon exiting the precooler, the gas sample passes through a vacuum pump into a refrigerated dryer system. The dry gas is divided into three streams for analysis of O_2, SO_2 and NOx concentrations. A matched set of gas analyzers are maintained for the inlet and outlet gas analysis. Servomex - Sybron/Taylor Model 540A Paramagnetic Analyzers, ranged 0-25% vol.% monitor the O_2 concentrations. Western Research & Development, Model 721AT2 Ultraviolet Analyzers, ranged 0-1000, 0-3500 ppmv on the inlet and 0-500, 0-1000 ppmv for the outlet determine SO_2 concentrations. Thermo Environmental Instruments, Inc., Model 44 Chemiluminescent Analyzers, ranged 0-1000 ppmv analyze for both NO and NOx. Due to the low concentrations of NO_2, typically less than 10 ppm, these analyzers remained in the NOx monitoring mode. During the calibration of the analyzers, the zero and calibration gases passed through the sample conditioning system before entering the analyzers. Mid-span gases were utilized to verify the linearity of the analyzers between the zero and span calibration gases.

The scrubber recycle tank design enables operation with slurry suspended solids concentrations far lower than present designs. These concentrations were typically in the 2-4 wt% range. A variable speed agitator provides a more gentler agitation than present designs and allow variations in agitation level.

Various auxiliary equipment for producing chelate solutions and metering reducing/anti-oxidant additives for the scrubber system supplement the pilot plant. Varying concentrations of the Ferrous-EDTA solution were produced in a batch mode utilizing the agitated reaction make tank. Typically 800 gallons of scrubber liquor was transferred from the thickener overflow tank into the make tank. Sufficient quantities of Sodium EDTA and Ferrous Sulfate were added in a 2:1 wt. ratio to achieve the desired concentration of iron within the scrubber system. Upon complete mixing of the solution, the contents of the make tank were emptied into either the recycle tank or the thickener overflow weir.

The mode of supplying the reducing/anti-oxidant additives for maintaining Ferrous EDTA concentrations was determined by the physical state of the additive being utilized. A dry powder feed system incorporating a day bin located above a screw feeder was used to meter the mixture of Sodium Hydrosulfite and Ascorbic Acid into the recycle tank. A Sodium Hydrosulfite to Ascorbic Acid weight ratio of 250:55 was vacuumed periodically into the day bin. Glyoxal, a liquid reducing/anti-oxidant additive, was pumped directly for its storage drum into the recycle tank via a metering pump. In both additive cases, regular analysis of the Ferrous content within the scrubbing liquor was utilized in determining the rate of addition. Periodic calibrations of the metering equipment were conducted to verify consumption rates of the additives.

The dewatering system includes two thickeners, 8 foot and 12 foot in diameter, respectively. Total unit area is 51 ft^2/TPD of dry sludge when operating at 3 MW of flue gas from a 2.75% sulfur coal. The 8 foot thickener had sufficient capacity to be utilized as the sole settling vessel during the chelate studies. The thickener underflow is periodically pumped for storage in the filter feed tank. From this tank, the slurry is filtered on a horizontal belt filter with an active filter area of 10 sq. ft. The filter has provisions for three countercurrent cake washes. For the cake generated during the NOx removal tests, only the first wash utilizing filtrate was operated. All filtrate collected from the belt was returned to the scrubber system via the thickener overflow tank.

Analysis of the pilot plant performance is accomplished through an on-site analytical lab and a computerized data acquisition system. Liquid chemistry data is obtained around the clock by technicians which staff the plant's analytical lab. A data base of the lab analysis is maintained on one of the three on-site computers. Scrubber operating data is displayed continuously on a computer with 30 second updates. Various menu driven display screens enable operators to monitor sub-systems of the pilot plant as well as the overall process. The 30 second updates are stored in a process data base as 5 minute averages. Both the lab and process data bases are transferred electronically to Dravo Lime Company's Research Center in Pittsburgh, where additional analysis and evaluation are performed.

E. OUTLINE OF PILOT TESTING PHASES AND SCHEDULE

In order to familiarize the reader with the scope and context of the testing program, attached is a brief synopsis of the testing performed at the Miami Fort Pilot Plant during the project. Organized by Phases and emphasizing weekly activities, the summary serves as an overview of testing activities for the project. It provides a useful reference guide for the detailed study of NOx removal testing presented in Section III.

PHASE 1
DOE Contract DE-AC22-90PC90362
Miami Fort Pilot Plant - Enhanced NOx Removal in Wet Scrubbers Using Metal Chelates

TEST WEEK TEST DATES	#1 4/1-4/5	#2 4/8-4/12	#3 4/15-4/19	#4 4/22-4/26	#5 4/29-4/30	#5 5/1-5/3	#6 5/6-5/10	#7 5/13-5/17	#8 5/20-5/24	#9 5/28-5/31
Test Description	Startup & baseline NOx removal w/o additives	Transfer Units Tests Simple Retrofit Mode	Transfer Units Tests New Plant Mode	Transfer Units Tests New Plant Mode	Fe++ Oxid Rate Study	Startup SO2 Spiking System	SO2/NOx Ratio Tests Wk 1	SO2/NOx Ratio Tests Wk 2	Low NOx Burner Simulation Runs	Glyoxal Testing
Scrubber Configuration	Tray @ location #2 R2 & R3 headers active 3 ft dia. @ 10 FPS	Tray @ loc. #2 R2 & R3 headers active 3 ft dia. @ 10 FPS	Trays @ loc. #1,2,3,4&5 R2,R3&R4 Hdrs active 3 ft dia. @ 10 FPS	Tray @ loc. #1,2,3,4&5 R2 & R3 Hdrs active 3 ft dia/ @ 10 FPS	Trays @ loc. #2, 5 R2 & R3 Hdrs active 3 ft dia. @ 8 FPS	Trays @ loc. #2, 5 R2 & R3 Hdrs active 3 ft dia. @ 8 FPS	Trays @ loc. #2, 5 R3A & R3B Hdrs active 3 ft dia. @ 8 FPS	Trays @ loc. #2, 5 R3A & R3B Hdrs active 3 ft dia. @ 8 FPS	Trays @ loc #2, 5 R3A & R3B Hdrs active 3 ft dia. @ 8 FPS	Trays @ loc. #2, 5 R3A & R3B Hdrs active 3 ft dia. @ 8 FPS
Plant Configuration	8 ft thickener active	8 ft thickener active	8 ft thickener active	8 ft thickener active	8 ft thickener active	8 ft thickener active	8 ft thickener active 2500 ppm SO2 spike	8 ft thickener active 2500 ppm SO2 spike	8 ft thickener active 2500 ppm SO2 spike	8 ft thickener active 2500 ppm SO2 spike
Test Chemicals:										
Chelates	Iron Sulfate & NaEDTA	Iron Sulfate & NaEDTA	Iron Sulfate & NaEDTA	Iron Sulfate & NaEDTA	Iron Sulfate & NaEDTA	Iron Sulfate & NaEDTA	Iron Sulfate & NaEDTA	Iron Sulfate & NaEDTA	Iron Sulfate & NaEDTA	Iron Sulfate & NaEDTA
Additives	None	Sodium Dithionite Ascorbic Acid	Sodium Dithionite Ascorbic Acid	Sodium Dithionite Ascorbic Acid	Sodium Dithionite Ascorbic Acid	Sodium Dithionite Ascorbic Acid	Sodium Dithionite Ascorbic Acid	Sodium Dithionite Ascorbic Acid	Sodium Dithionite Ascorbic Acid	Glyoxal
Addition points:										
EDTA & Ferrous Sulfate	Recycle Tank	Recycle Tank	Recycle Tank	Recycle Tank	Recycle Tank	Recycle Tank	TOF Tank	TOF Tank	TOF Tank	TOF Tank
Additives	N/A	Recycle Tank	Recycle Tank	Recycle Tank	Recycle Tank	Recycle Tank	Recycle Tank	Recycle Tank	Recycle Tank	Recycle Tank
Target Concentrations	Total Iron = 35 mM	Total Iron = 35-40 mM Fe++ Iron=15 mM	Total Iron = 35-40 mM Fe++ Iron=15mM	Total Iron = 35-40 mM Fe++ Iron=15mM	Total Iron - 35-40 mM Fe++ Iron=25mM to End	Total Iron - 35-40 mM Fe++ Iron=15 mM	Total Iron = 35-40 mM Fe++ Iron=15 mM	Total Iron = 35-40 mM Fe++ Iron=15 mM	Total Iron = 35-40 mM Fe++ Iron=15 mM or 25	Total Iron = 35-40 mM Fe++ Iron uncontrolled

PHASE 2
DOE Contract DE-AC22-90PC90362
Miami Fort Pilot Plant - Enhanced NOx Removal in Wet Scrubbers Using Metal Chelates

TEST WEEK TEST DATES	#1 7/8 - 7/12	#2 7/15 - 7/19	#3 7/22 - 7/26	#4 7/29 - 8/2	#5 8/5 - 8/9	#6 8/12 - 8/16	#7 8/19 - 8/23	#8 8/26 - 8/30
Test Description	Rebuild Chelate Chemistry Glyoxal Testing	Glyoxal Testing	pH vs NO Removal Tests	Fine Spray Tests	Packing Testing 2" and 3" Saddles	Packing Testing 2" Saddles	Packing Testing Snowflake	Packing Testing PN Fill WK 1
					6' Packing Installed	6' Packing Installed		
Scrubber Configuration	Tray @ locations #2 & 5 R2 & R3 Hdrs active 3 ft dia. @ 8 FPS	Tray @ locations #2 & 5 R3A & R3B Hdrs active 3 ft dia. @ 8 FPS	Tray @ locations #2 & 5 R3A & R3B Hdrs active 3 ft dia. @ 8 FPS pH 6, 7 & 8	Tray @ location #1 R3A & R3B Hdrs active 7 nozzles / header 3 ft dia. @ 5,7.5,10 FPS	Tray @ location #1 R3 & R4 Hdrs active 7 nozzles / header 3 ft dia. @ 5,7.5,10 FPS	Tray @ location #1 R3 & R4 Hdrs active 7 nozzles / header 3 ft dia. @ 4,6,8 FPS	No Trays, R3 header Active. Nominal 6 ft packing installed 3 ft dia. @ 4,6,8 FPS	No Trays, R3 header Active. TF28XPN nozzles 7 nozzles / header 3 ft dia. @ 5,7.5,10 FPS
Plant Configuration	8 ft thickener active 2500 ppm inlet SO2 spike	8 ft thickener active 1500 - 2500 ppm inlet SO2 spike	8 ft thickener active 2500 ppm inlet SO2 spike	8 ft thickener active 2500 ppm inlet SO2 spike	8 ft thickener active 2500 ppm inlet SO2 spike	8 ft thickener active 2500 ppm inlet SO2 spike	8 ft thickener active 2500 ppm inlet SO2 spike	8 ft thickener active 2500 ppm inlet SO2 spike
Test Chemicals: Chelates Additives	Iron Sulfate & NaEDTA Glyoxal, Mg(OH)2	Iron Sulfate & NaEDTA Glyoxal	Iron Sulfate & NaEDTA Glyoxal, Mg(OH)2	Iron Sulfate & NaEDTA Dithionate/Ascorbic Acid	Iron Sulfate & NaEDTA Dithionate/Ascorbic Acid	Iron Sulfate & NaEDTA Dithionate/Ascorbic Acid	Iron Sulfate & NaEDTA Dithionate/Ascorbic Acid	Iron Sulfate & NaEDTA Dithionate/Ascorbic Acid
Addition points: EDTA & Ferrous Sulfate Additives	TOF Tank Recycle Tank	TOF Tank Recycle Tank	TOF Tank Recycle Tank	TOF Tank Recycle Tank	TOF Tank Recycle Tank	TOF Tank Recycle Tank	TOF Tank Recycle Tank	TOF Tank Recycle Tank
Target Concentrations Fe++ Iron=15mM all tests	Total Iron = 35-40 mM EDTA = 43 mM	Total Iron = 35-40 mM EDTA = 43 mM	Total Iron = 35-40 mM EDTA = 43 mM	Total Iron = 35-40 mM EDTA = 43 mM	Total Iron = 35-40 mM EDTA = 43 mM	Total Iron = 35-40 mM EDTA = 43 mM	Total Iron = 35-40 mM EDTA = 43 mM	Total Iron = 35-40 mM EDTA = 43 mM
Supplemental Tests	Filtercake samples w/ & w/o Iron Sulfate/NaEDTA; Glyoxal	Vary L/G, SO2/NOx rati Test 2 Ferrous levels 15 & 25 mM Ferrous			Dynamic Oxidation Rate Tests Vary L/G	Dynamic Oxidation Rate Tests 3 vels /3 L/G's each week	Dynamic Oxidation Rate Tests 3 vels /3 L/G's each week	Dynamic Oxidation Rate Tests
Filter Cake Samples DLC Research Center Argonne National Labs	6 gals per belt run 10 gals per belt run	6 gals per belt run 10 gals per belt run	6 gals per belt run 10 gals per belt run	6 gals per belt run 10 gals per belt run		6 gals per belt run 10 gals per belt run	6 gals per belt run None	6 gals per belt run 10 gals per belt run

TEST WEEK TEST DATES	#9 9/2 - 9/6	#10 9/9 - 9/12	#10 9/12 - 9/13
Test Description	Packing Testing PN Fill WK 2	Fine Spray Tests Revisited	pH vs NO Removal Tests Revisited
Scrubber Configuration	No Trays, R3 & R4 headers Active. Nominal 6 ft packing installed 3 ft dia. @ 4,6,8 FPS	Tray @ location #1 R3A & R3B Hdrs active 7 nozzles / header 3 ft dia. @ 5,7.5,10 FPS	Tray @ locations #2 & 5 R3A & R3B Hdrs active 3 ft dia. @ 8 FPS pH 6, 7 & 8
Plant Configuration	8 ft thickener active 2500 ppm inlet SO2 spike	8 ft thickener active 2500 ppm inlet SO2 spike	8 ft thickener active 2500 ppm inlet SO2 spike
Test Chemicals: Chelates Additives	Iron Sulfate & NaEDTA Dithionate/Ascorbic Acid	Iron Sulfate & NaEDTA Dithionate/Ascorbic Acid	Iron Sulfate & NaEDTA Dithionate/Ascorbic Acid
Addition points: EDTA & Ferrous Sulfate Additives	TOF Tank Recycle Tank	TOF Tank Recycle Tank	TOF Tank Recycle Tank
Target Concentrations Fe++ Iron=15mM all tests	Total Iron = 35-40 mM EDTA = 43 mM	Total Iron = 35-40 mM EDTA = 43 mM	Total Iron = 35-40 mM EDTA = 43 mM
Supplemental Tests	Dynamic Oxidation Rate Tests 3 vels /3 L/G's each week		
Filter Cake Samples DLC Research Center Argonne National Labs	6 gals per belt run None	6 gals per belt run 10 gals per belt run	6 gals per belt run 10 gals per belt run

PHASE 3
DOE Contract DE-AC22-90PC90362
Miami Fort Pilot Plant – Enhanced NOx Removal in Wet Scrubbers Using Metal Chelates

TEST WEEK TEST DATES	#1 10/14 – 10/18	#2 10/21 – 10/25	#3 10/28 – 11/1	#4 11/4 – 11/8	#5 11/11 – 11/15	#6 11/18 – 11/22	#7 12/02 – 12/06	#8 12/09 – 12/13
Test Description	Model Confirmation Tests WK 1	Model Confirmation Tests WK 2	Retrofit Mode Week #1	Retrofit Mode Week #2	New Construction Mode Week #1	New Construction Mode Week #2	High Iron Content Testing WK #1	High Iron Content Testing WK #2
Scrubber Configuration	12' PN Fill Packing No Trays R4 Header Active 3 ft dia. @ 4 & 8 FPS	6'PN Fill + 6'SnowFlake Tray @ location #1 R4 Header Active 3 ft dia. @ 4 & 8 FPS	12' PN Fill Packing Tray @ location #1 R4 Header Active 3 ft dia. @ 8 FPS	12' PN Fill Packing Tray @ location #1 R4 Header Active 3 ft dia. @ 8 FPS	12' PN Fill Packing Tray @ location #1 R4 Header Active 3 ft dia. @ 4 FPS	12' PN Fill Packing Tray @ location #1 R4 Header Active 3 ft dia. @ 4 FPS	12' PN Fill Packing Tray @ location #1 R4 Header Active 3 ft dia. @ 8 FPS	12' PN Fill Packing Tray @ location #1 R4 Header Active 3 ft dia. @ 8 FPS
Plant Configuration	8 ft thickener active 2500 ppm inlet SO2 spike	8 ft thickener active 2500 ppm inlet SO2 spike	8 ft thickener active 2500 ppm inlet SO2 spike	8 ft thickener active 2500 ppm inlet SO2 spike	8 ft thickener active 2500 ppm inlet SO2 spike	8 ft thickener active 2500 ppm inlet SO2 spike	8 ft thickener active 2500 ppm inlet SO2 spike	8 ft thickener active 2500 ppm inlet SO2 spike
Test Chemicals:								
Chelates	Iron Sulfate & NaEDTA	Iron Sulfate & NaEDTA	Iron Sulfate & NaEDTA	Iron Sulfate & NaEDTA	Iron Sulfate & NaEDTA	Iron Sulfate & NaEDTA	Iron Sulfate & NaEDTA	Iron Sulfate & NaEDTA
Additives	Dithionate/Ascorbic Acid	Dithionate/Ascorbic Acid	Dithionate/Ascorbic Acid	Dithionate/Ascorbic Acid	Dithionate/Ascorbic Acid	Dithionate/Ascorbic Acid	NO ADDITIVES	NO ADDITIVES
Addition points:								
EDTA & Ferrous Sulfate	TOF Tank	TOF Tank	TOF Tank	TOF Tank	TOF Tank	TOF Tank	TOF Tank	TOF Tank
Additives	Recycle Tank	Recycle Tank	Recycle Tank	Recycle Tank	Recycle Tank	Recycle Tank	N/A	N/A
Target Concentrations	Total Iron = 35–40 mM EDTA = 43 mM Fe++ Iron = 15 mM	Total Iron = 35–40 mM EDTA = 43 mM Fe++ Iron = 15 mM	Total Iron = 35–40 mM EDTA = 43 mM Fe++ Iron = 15 mM	Total Iron = 35–40 mM EDTA = 43 mM Fe++ Iron = 15 mM	Total Iron = 35–40 mM EDTA = 43 mM Fe++ Iron = 15 mM	Total Iron = 35–40 mM EDTA = 43 mM Fe++ Iron = 15 mM	Total Iron = 70-105 mM EDTA = 86 - 129 mM Fe++ Iron level varied	Total Iron = 85 - 105 mM EDTA = 105 - 129 mM Fe++ Iron level varied

F. BUDGET SUMMARY

The project was initially funded for $1,787,345.00 to cover 36 weeks of project activity including 8 weeks of plant modifications and 22 weeks of process testing in three phases. Actual testing effort expended covered 25 weeks for these three phases without additional cost to DOE. In addition, contract modification 004 was submitted and approved for performance of two additional weeks of testing for $106,092.00. Additional effort was also expended in the preparation of a Waste Characterization Study on the generated solids from all phases of testing, the scope of which far exceeded that as defined in the original project proposal. Work for each phase was completed substantially on projected schedule with all goals for each phase successfully completed.

Early in the project definition phase, DOW Chemical Company, originally a project co-participant for Phase II, declined to participate due to a corporate realignment of spending priorities. Subsequently, the goals for Phase II were renegotiated with DOE personnel and testing conducted by Dravo Lime Company alone to DOE's satisfaction. In addition Dr. Peter Harriott, a recognized authority in the field of NOx removal and metal chelate scrubbing, was involved in the review of the phase results as well as participating in the phase review meetings.

As part of the plant modification effort, installation of an SO_2 injection system was budgeted as a modular skid mounted unit supplied by a major national vendor of such equipment. The system was subsequently designed and supplied by a local small business and installed at the pilot plant in a structurally permanent configuration. The use of small business entities, both from the Pittsburgh and Cincinnati areas, was extensive and as such the project far exceeded its goals for small business utilization.

The project testing was completed on time and within budget despite the unforeseen cost of chemical additives used throughout the test program (due to the presence of high oxygen content in the test flue gas) and the realignment of the Phase II test effort. Approximately $107,000.00 of unanticipated chemical additive cost was successfully absorbed by the project budget without requesting additional funds from the DOE.

TABLE 1

COST OF CHEMICAL REDUCING AGENTS/ANTIOXIDANTS

COUMPOUND	FORMULA	COST PER POUND	FORMULA WEIGHT	REDUCTION STOICHIOMETRY (NOTE 1)	RELATIVE COST, $ PER LB-MOLE FERRIC EDTA REDUCEI (NOTE 2)	REDUCTION COST IN MILLS/kW-HR (NOTE 2)
SODIUM DITHIONITE (ANHYDROUS)	Na2S204	0.62	174	2	53.94	18.0
ASCORBIC ACID		5.50	176	10	96.80	32.3
GLYOXAL (NOTE 3) AT 100% UTILIZATION	C202H2	1.43	58	6	13.78	4.6
GLYOXAL AT 66.7% UTILIZATION	C202H2	1.43	58	4	20.66	6.9

ELECTROCHEMICAL REDUCTION REAGENT AND ELECTRICITY COST

ELECTRICITY COST, MILLS/kW-HR	CAUSTIC COST, $/LB	COST OF ELECTRICITY, $ PER LB-MOLE FERRIC EDTA REDUCED	COST OF CAUSTIC, $ PER LB-MOLE FERRIC EDTA REDUCEI	TOTAL REDUCTION COST IN MILLS/kW-HR (NOTE 2)
25	0.125	0.68	2.5	1.06

NOTE 1: STOICHIOMETRY IS NUMBER OF MOLES OF IRON REDUCED PER MOLE OF COMPOUND

NOTE 2: COST IS BASED ON REDUCTION RATE 0.5 LB-MOLES FERRIC EDTA
REDUCED PER HOUR IN PILOT PLANT OPERATING AT 1.5 MWe CAPACITY.
FOR THE ELECTROCHEMICAL CELL, IT IS ALSO BASED ON CELL VOLTAGE OF 2 VOLTS
AT 90% CURRENT EFFICIENCY.

NOTE 3: GLYOXAL IS SOLD AS A 40 WT.% SOLUTION AT $0.57/LB SOLUTION
(CHEMICAL MARKETING REPORTER, JUNE 1991)

FIGURE 1

ABSOLUTE COSTS OF FERRIC EDTA REDUCING AGENTS

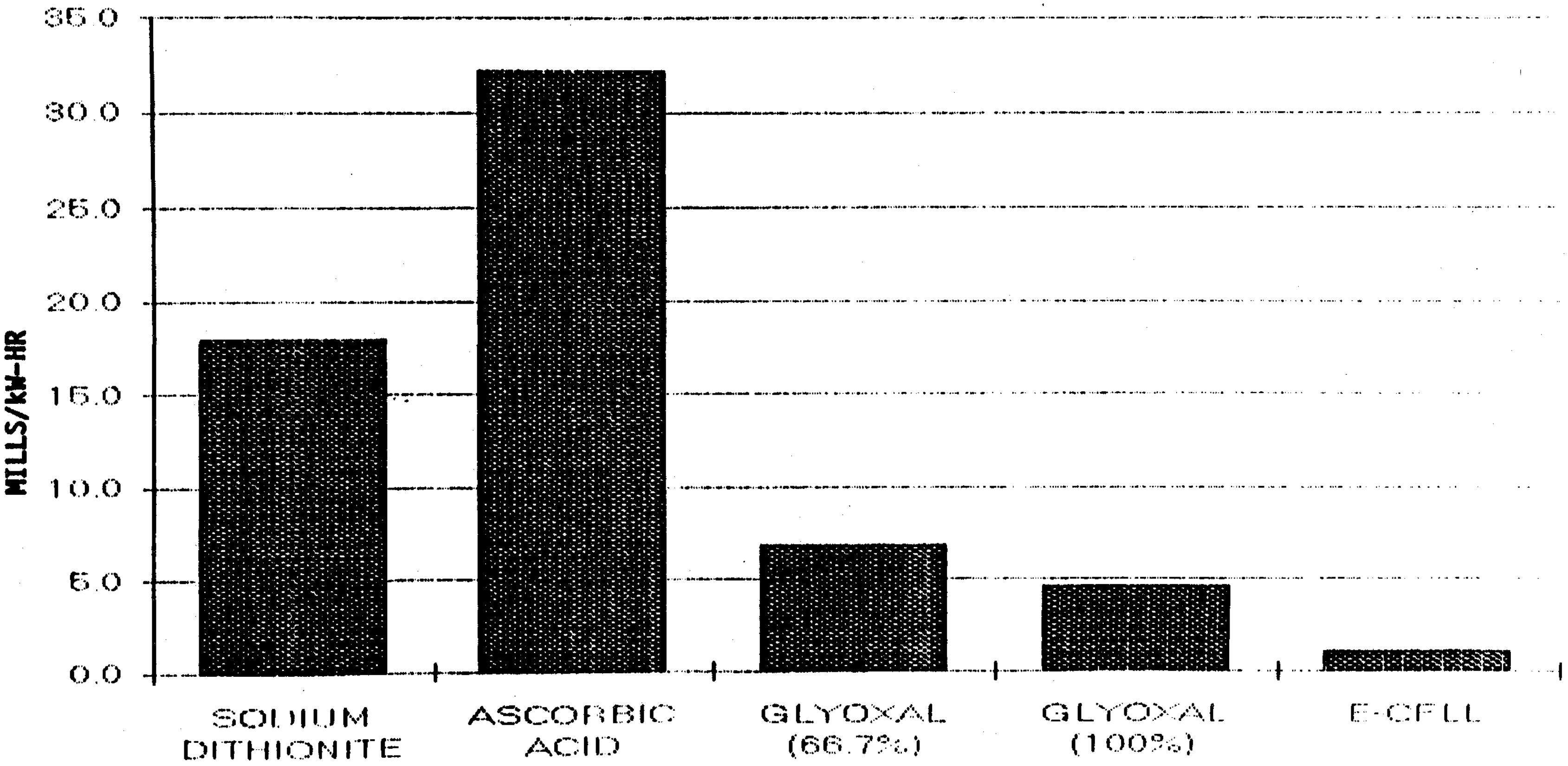


Figure 1

Figure 1

FIGURE 2

RELATIVE COSTS OF FERRIC EDTA REDUCING AGENTS

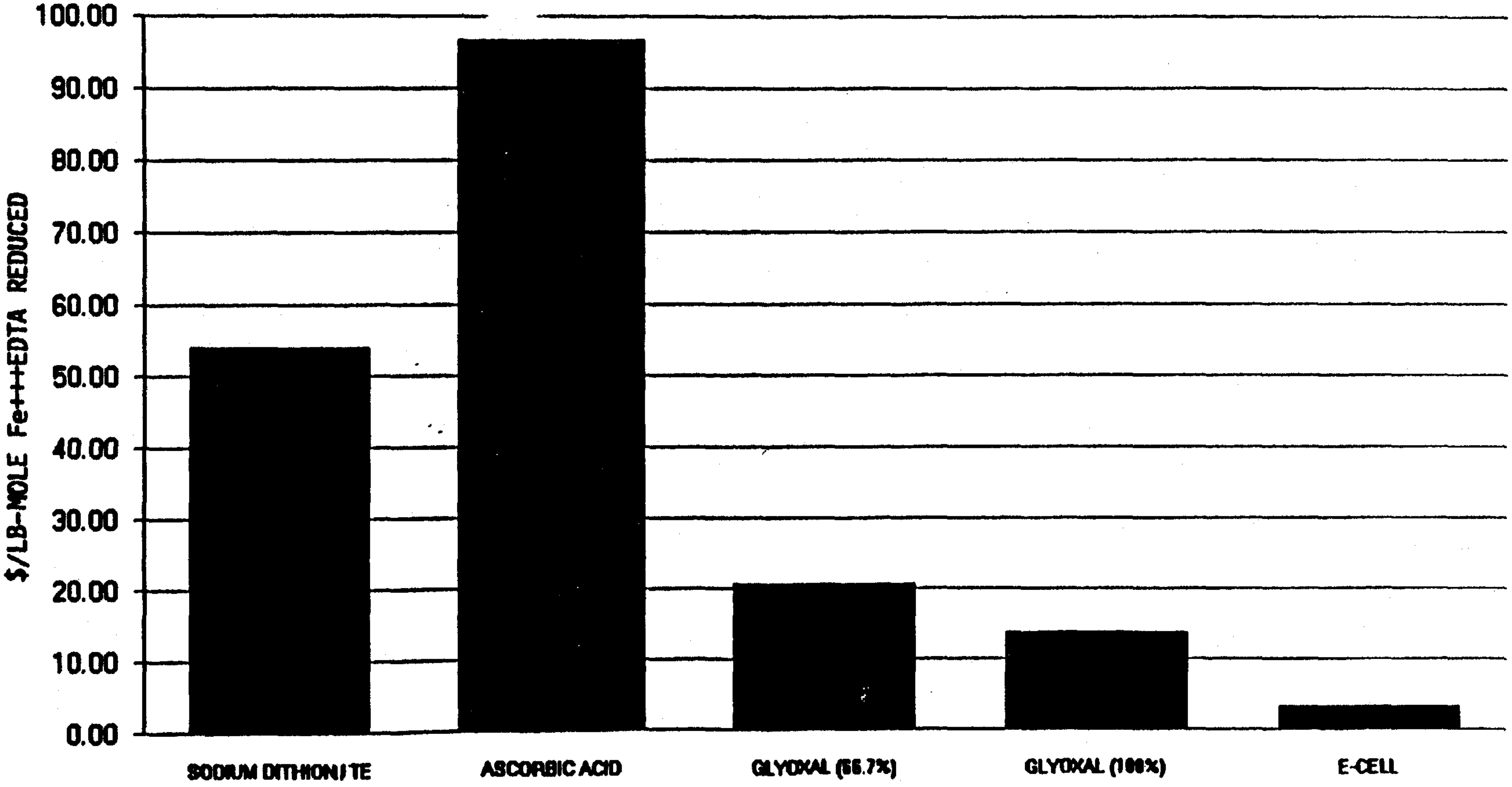
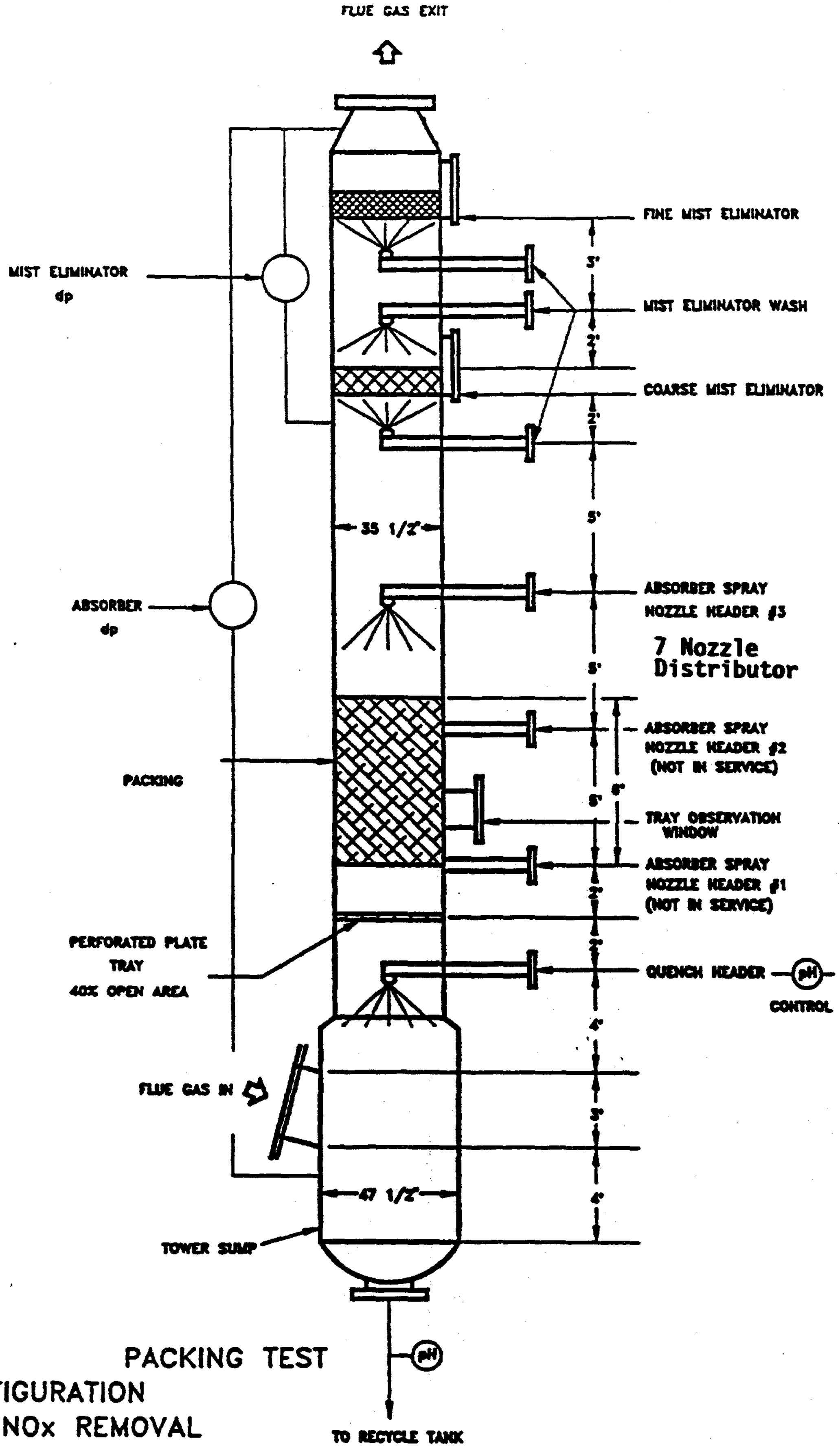


Figure 2

Figure 2

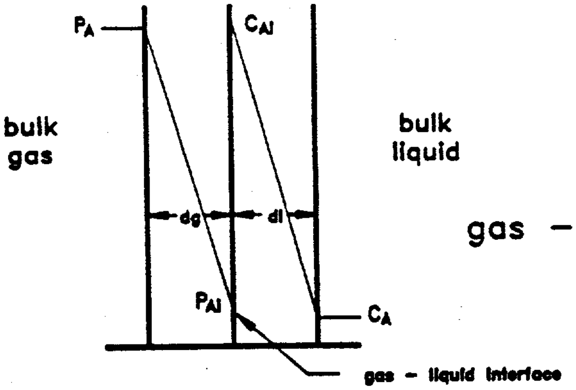
Figure 3

:GURE 3

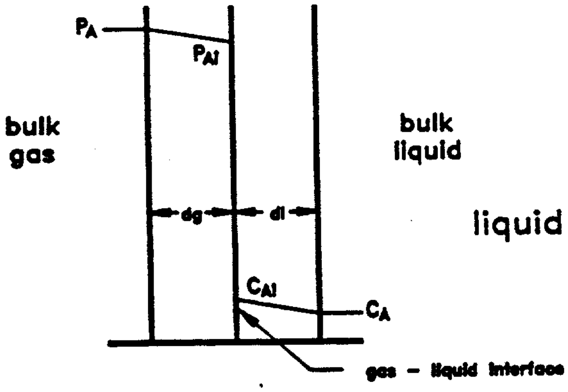


PACKING TEST
CONFIGURATION
FOR NOx REMOVAL
3' DIAMETER TOWER

Transfer through gas and liquid films



gas - film controlled



liquid - film controlled

Figure 4

FIGURE 5

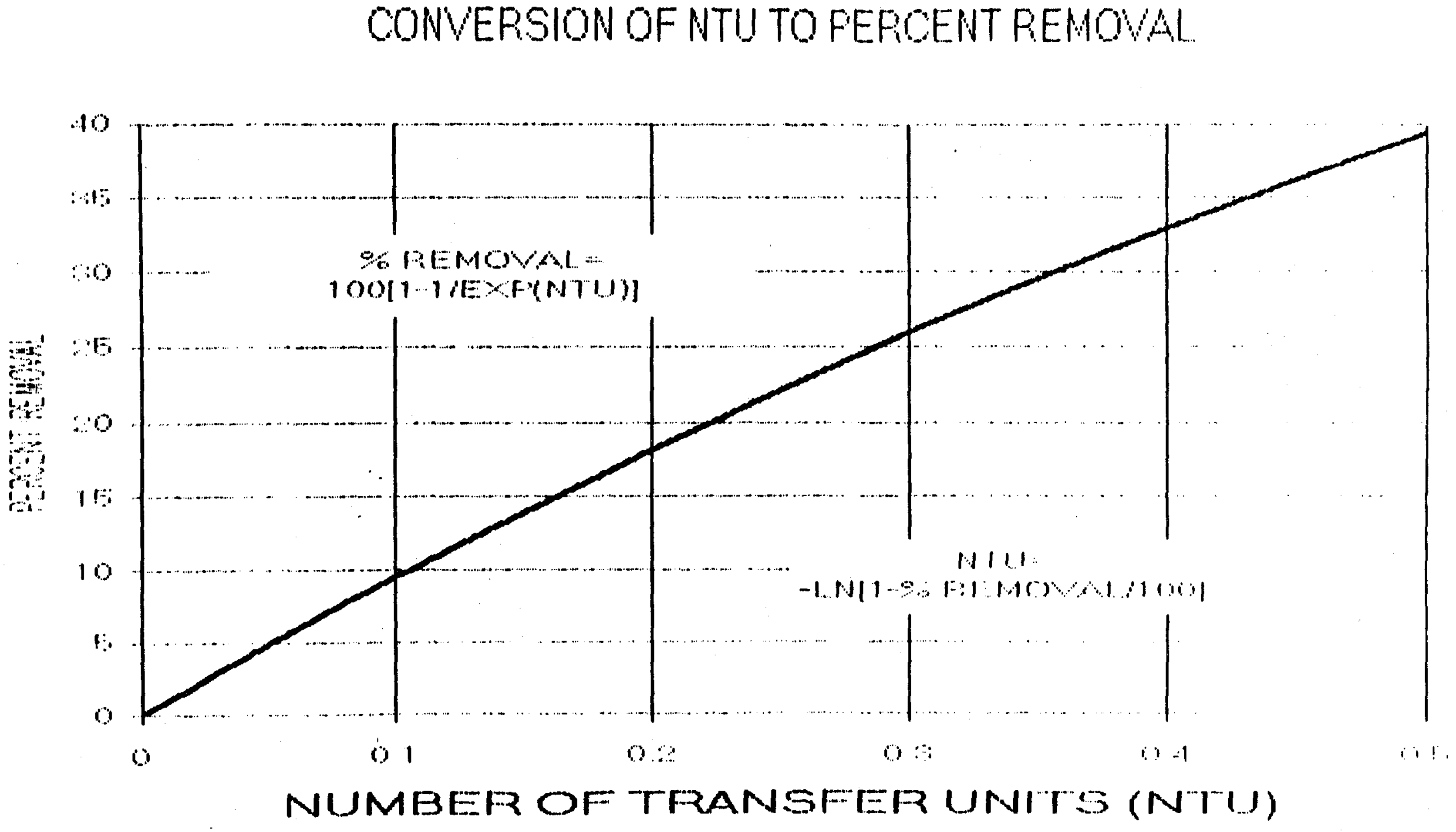


Figure 5

Figure 5

FIGURE 6

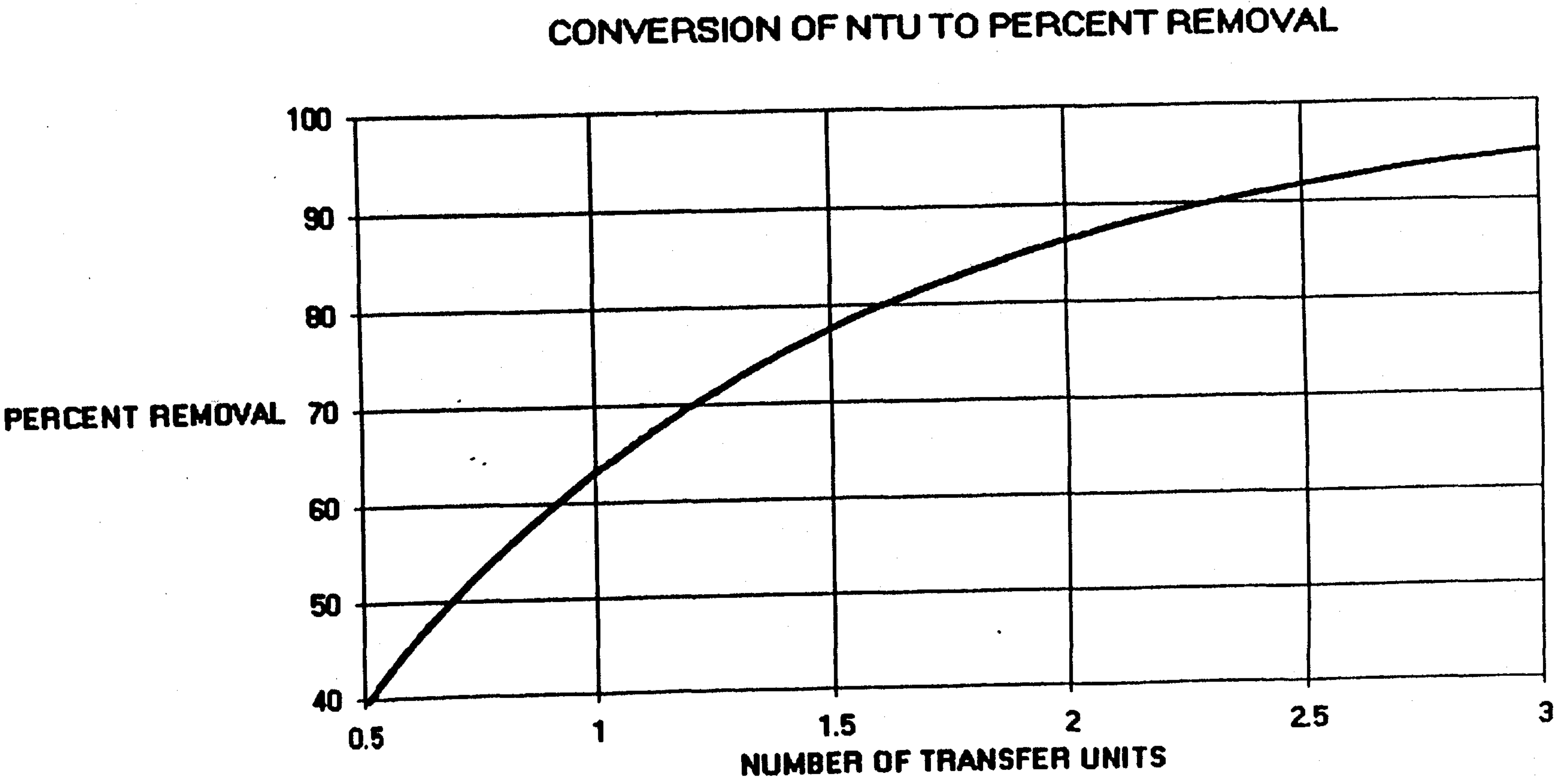
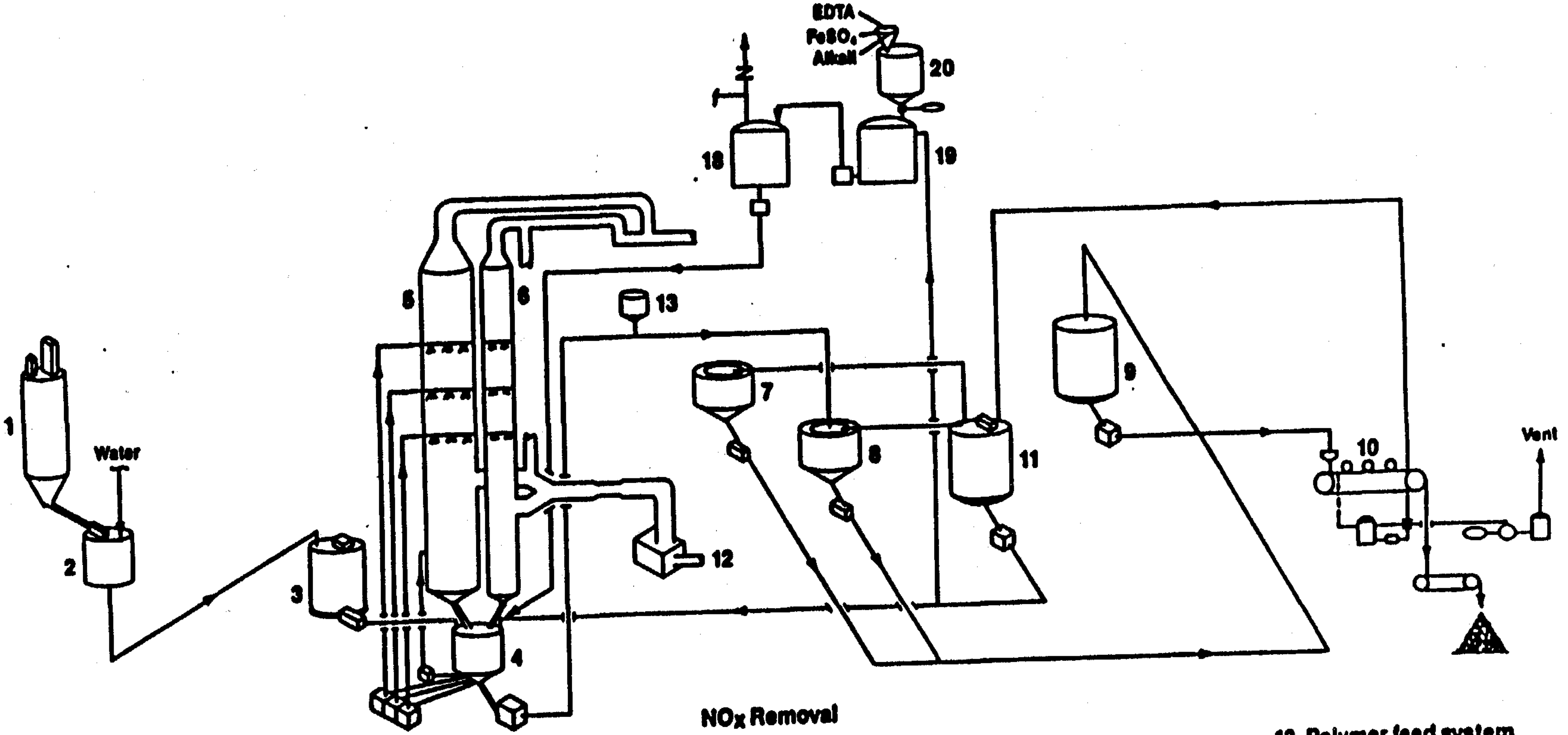

CONVERSION OF NTU TO PERCENT REMOVAL

Figure 6

Miami Fort Station Pilot Plant



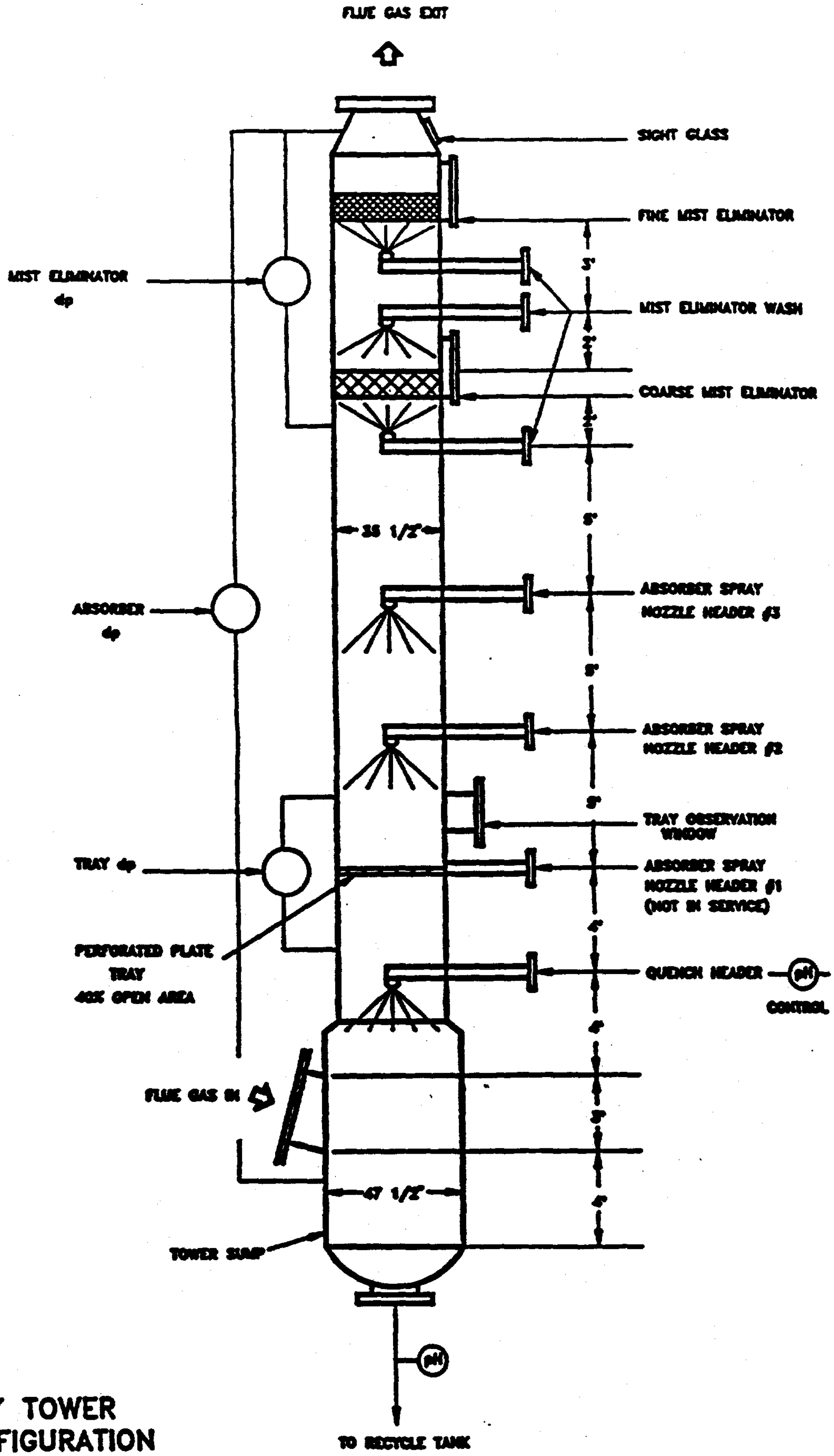
NOx Removal

1. Lime silo
2. Lime slaker
3. Lime slurry tank
4. Recycle slurry tank
5. Upflow scrubber
6. Upflow/downflow scrubber
7. Thickener
8. Thickener
9. Filter feed tank
10. Sludge filter system
11. Thickener overflow tank
12. Flue gas fan
13. Polymer feed system
18. Reaction make tank
19. Reaction day tank
20. Additive bin

Dravo Lime Company

Figure 7

Figure 7



TRAY TOWER
CONFIGURATION
3' DIAMETER TOWER

Figure 8

Figure 9

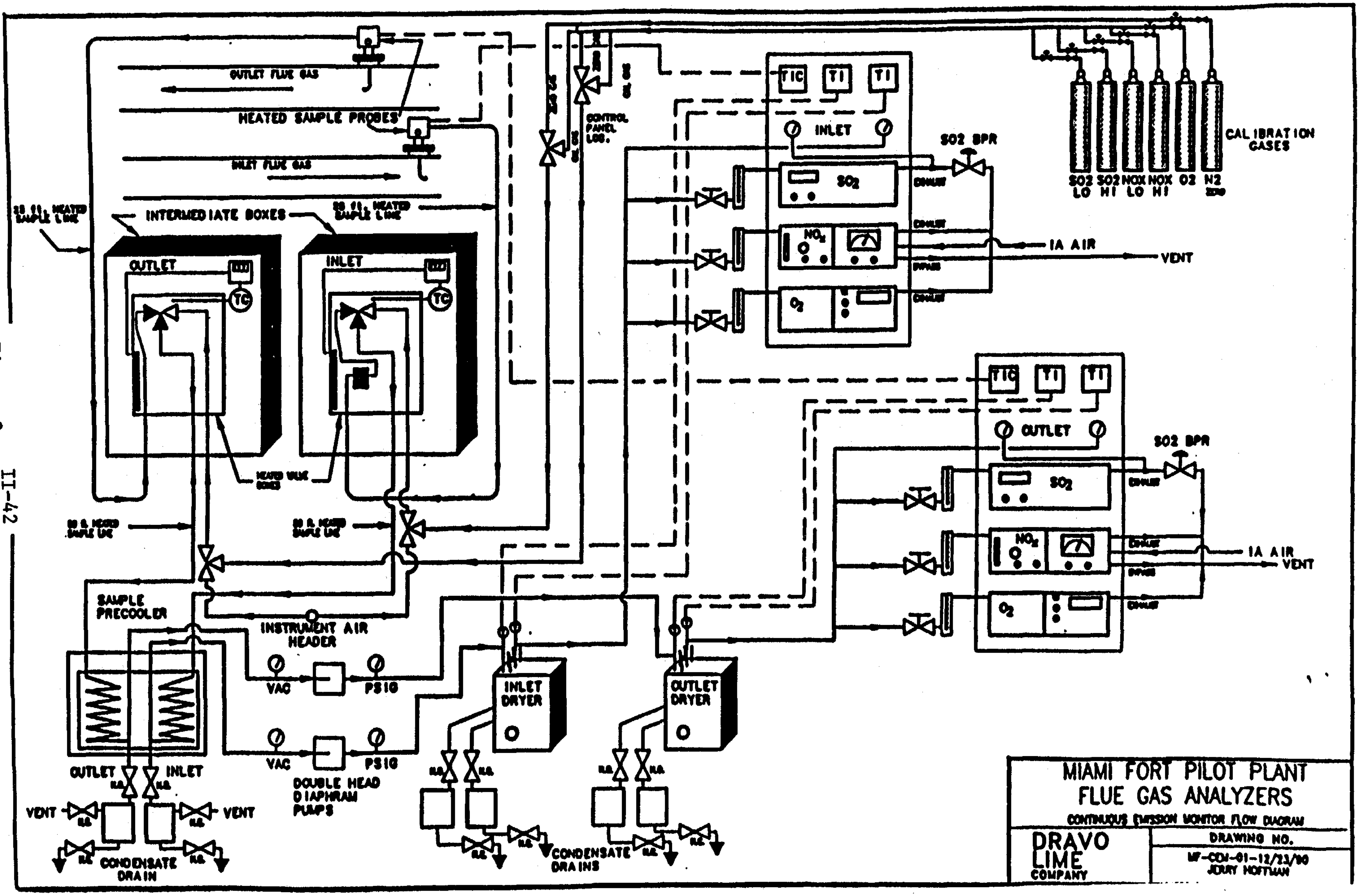


Figure 9