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**Simultaneous SO₂ / NO_x Removal Testing
and Toxics Characterization**

Phase 1

Milestone Report

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SIMULTANEOUS SO₂ / NO_x REMOVAL TESTING AND TOXICS CHARACTERIZATION

This report describes the work completed in the first phase of the Simultaneous SO₂ / NO_x Removal Testing and Toxics Characterization test program. Tasks covered in this report as specified in the Statement of Work included:

- Task 1.2.0 Equipment Modification and Reagents Procurement
- Task 1.3.0 Testing at the 5 kW Scale
- Task 1.3.1 Temperature Enhanced Fe(III)EDTA Reduction
- Task 1.3.2 Electrolytic Cell Fe(III)EDTA Reduction
- Task 1.3.3 Chemical Regeneration Agents Testing
- Task 1.3.4 Combination of Strategies
- Task 1.4.0 Data Analysis and Phase I Report

Proposed in Task 1.3.4 are combinations of regeneration methods (based on data generated in Tasks 1.3.1 to 1.3.3) that gave the best results at the lowest possible cost. The Test Plan approval (Task 1.1.0) was previously submitted under separate cover. The proposed project timeline for potential Phase II operations is shown in Figure 1.

I. OBJECTIVES OF PHASE 1

The Clean Air Act Amendments (CAAA) introduced in 1990 require more stringent control on SO₂ and NO_x emissions from coal-fired electric generating units in the US. Sixteen percent of the units effected by the Clean Air Act are located in Ohio where their primary source of coal is in-state. Replacement of this high sulfur coal with out-of-state low sulfur coal to lower SO₂ emissions will result in a continued decline in Ohio coal production. To maintain high coal production in the state of Ohio, it is therefore important to develop near term post combustion technologies which achieve strict emission reductions on SO₂ and NO_x. The ThioNO_x process, using Dravo Lime Company's Thiosorbic lime, was developed to simultaneously remove SO₂ and NO_x. This

SIMULTANEOUS SO₂ / NO_x REMOVAL TESTING AND TOXICS CHARACTERIZATION

MIAMI FORT PILOT PLANT OPERATION

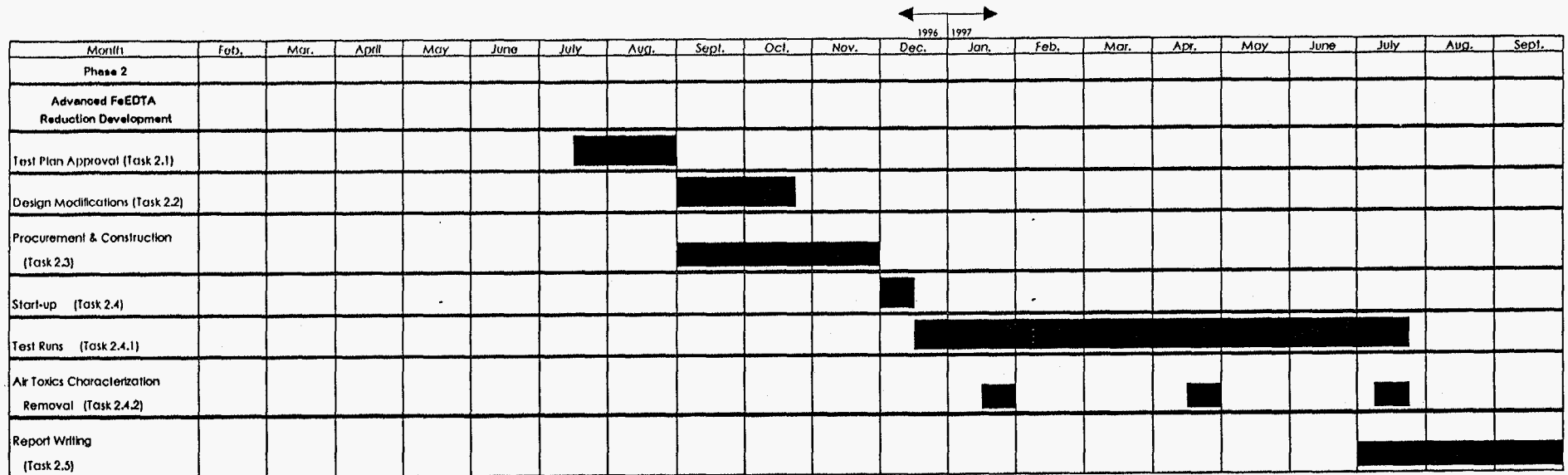


Figure 1. Phase 2 Timeline

technology could be readily incorporated into new or retrofit flue gas desulfurization (FGD) systems and is especially suitable for boilers burning high-sulfur Ohio coals. The ThioNO_x technology integrates the SO₂ / NO_x removal process which may be more cost-effective than a combination of control schemes.

The overall project objective is to achieve commercialization of the ThioNO_x process. In order for this technology to develop commercially, certain goals must be met. The percentage removal of SO₂ should exceed 99% and NO_x removal should exceed 60%. In addition, retrofit costs to existing wet scrubbing FGD systems using this proposed technology should be less than that associated with currently available NO_x removal technologies. Other goals which must be met but can not be adequately achieved by 5 kW testing include removal of air toxics utilizing the condensing heat exchanger, establishing that current stabilization techniques can be used to safely dispose of the by-products, and showing that the disposal cost for these materials is less than the current cost involved in disposal of by-products from wet FGD systems. These concepts will be tested at Miami Fort pilot plant once a ferrous ion regeneration method for NO_x removal has been deemed successful by meeting the operating objectives at the 5 kW level.

There are several unresolved technical issues which must be addressed during the 5 kW and Miami Fort pilot plant test program.

- The regeneration of ferrous ion must be lower in cost than competitive SO₂ / NO_x removal technologies.
- In previous Miami Fort pilot plant testing conducted in 1991, DOE Contract No: DE-AC22-90PC90362, sodium based regeneration agents have been used which allow high concentrations of sulfite / bisulfite ions to accumulate in the liquor. Additional sodium ions can contaminate the leachate from the landfill, increasing costs associated with disposal. Therefore avoiding the introduction of sodium ions into the process

chemistry will have to be evaluated as to its impact on SO₂ removal and solids dewatering.

- Air toxics emission data from FGD systems needs to be collected to determine if further abatement measures would be necessary when pending regulations are issued.

It was the goal during Phase 1 to examine different methods of ferrous ion regeneration to determine the most effective method for NO_x removal. For the ThioNO_x process, the ferrous ion concentration determines the NO_x removal. It was also important that the regeneration method not adversely affect the system chemistry. Tests which satisfy these criteria were subjected to a detailed economic analysis for cost comparison with competitive SO₂ / NO_x removal technologies. The specific objectives of Phase I are given below.

- a. ThioNO_x tests will be conducted at various conditions without application of a regeneration method. This will establish the baseline ferrous ion concentration and NO_x removal. This will allow the effect of flue gas oxygen concentration and absorber packing on SO₂ and NO_x removal to be observed. Any NO_x removal above that observed for the baseline tests when carrying out different regeneration methods will be due strictly to the regeneration method used.
- b. A series of regeneration agents will be examined for their ability to maintain a high concentration of ferrous ion and associated NO_x removal. The chemical agents selected are listed below:
 - iron
 - iron using a digestion tank
 - zinc
 - aluminum
 - hydroxylamine

- hydrazine hydrate
- hydrazine sulfate
- sodium sulfide hydrate
- sodium tetrasulfide
- sulfide / polysulfides
- ammonium thiosulfate

The evaluation will consist of monitoring key parameters given below:

- SO₂ removal as a function of test time.
- NO_x removal as a function of test time.
- Ferrous ion concentration maintained after steady state established.
- Analysis of system chemistry and filtercake solids content.
- Adherence of the NO_x removal to the proposed model.
- Economic analysis based on reactivity of regeneration agent.

These evaluation parameters will determine the suitability of the regeneration agent.

- c. The thermal regeneration method will incorporate a vessel equipped with a heating rod. The heating rod will maintain an elevated liquor temperature which could greatly improve the ferrous ion regeneration rate. This hypothesis will be verified by conducting test runs. The factors evaluated will be the same as those for the chemical regeneration agents. The values of these factors will determine the effectiveness of thermal regeneration as a method for high NO_x removal.
- d. An electrochemical cell will be introduced into the 5 kW system to determine its ability to maintain a high ferrous ion concentration. The evaluation method will consist of the same parameters as that used for the chemical regeneration agents and thermal regeneration method. Factors influencing the performance of the electrochemical cell will be identified and their operating values found. The

economics for the electrochemical cell will be compared with the cost of the regeneration agents.

- e. A combination of regeneration methods will be carried out pending the results of the different regeneration methods. The method of evaluation will involve the same criteria as that used for the regeneration agents, thermal regeneration, and electrochemical cell.
- f. A detailed economic analysis of the method possessing the highest NO_x removal with no adverse affect on system chemistry will be performed. A comparison of the results of this analysis with alternative SO_2 / NO_x removal processes will be made to determine if Thio NO_x is lower in cost.

II. DISCUSSION, TEST RESULTS, ECONOMIC ANALYSIS, ATTAINMENT OF OBJECTIVES

A. Baseline Tests

Baseline tests were carried out to determine the ferrous ion concentration and NO_x removal with no regeneration method used. Several different configurations were tested and include packing and non-packed modes in the absorber module, and variable flue gas oxygen content. This includes a test conducted with exhaust gas blanket over the recycle tank. The packing and non-packed tests were further subdivided into 100 mM and 50 mM initial total iron concentration.

Figure 2 illustrates a schematic flow diagram of Dravo Lime Company's 5 kW scale test unit. The facility consists of a scrubber, recycle tank, thickener, heat exchangers, tubing, pumps, pH controllers, temperature indicators, analyzers for SO_2 , NO_x and O_2 , data acquisition system, and gas cylinders. The scrubber body consists of a 5.5" I.D. x 24" long plastic column. Up to five pieces of perforated trays can be installed inside this column with or without packing.

The recycle tank is constructed on one 7.5" I.D. x 18" long plastic column capable of holding up to 12 liters of liquor. The nominal amount of liquor kept in the recycle tank is ~9L. Lime can be added to this tank to neutralize the acidified liquor from the downcomer of the scrubber. A mixer is installed in the tank to insure adequate mixing and to prevent solids from settling. The thickener is made of a piece of 11.5" I.D. plastic column with four overflow ports. The volume of the liquor collected at the downcomer is measured to determine the liquor circulation rate through the scrubber. The liquid-to-gas ratio or L/G is then calculated based on the circulation rate and the total gas flow rate.

To maintain the temperature of the recirculated liquor entering the scrubber at ~50°C, a portion of the recycle tank liquor is pumped through a heat exchanger via two 3/8" O.D.

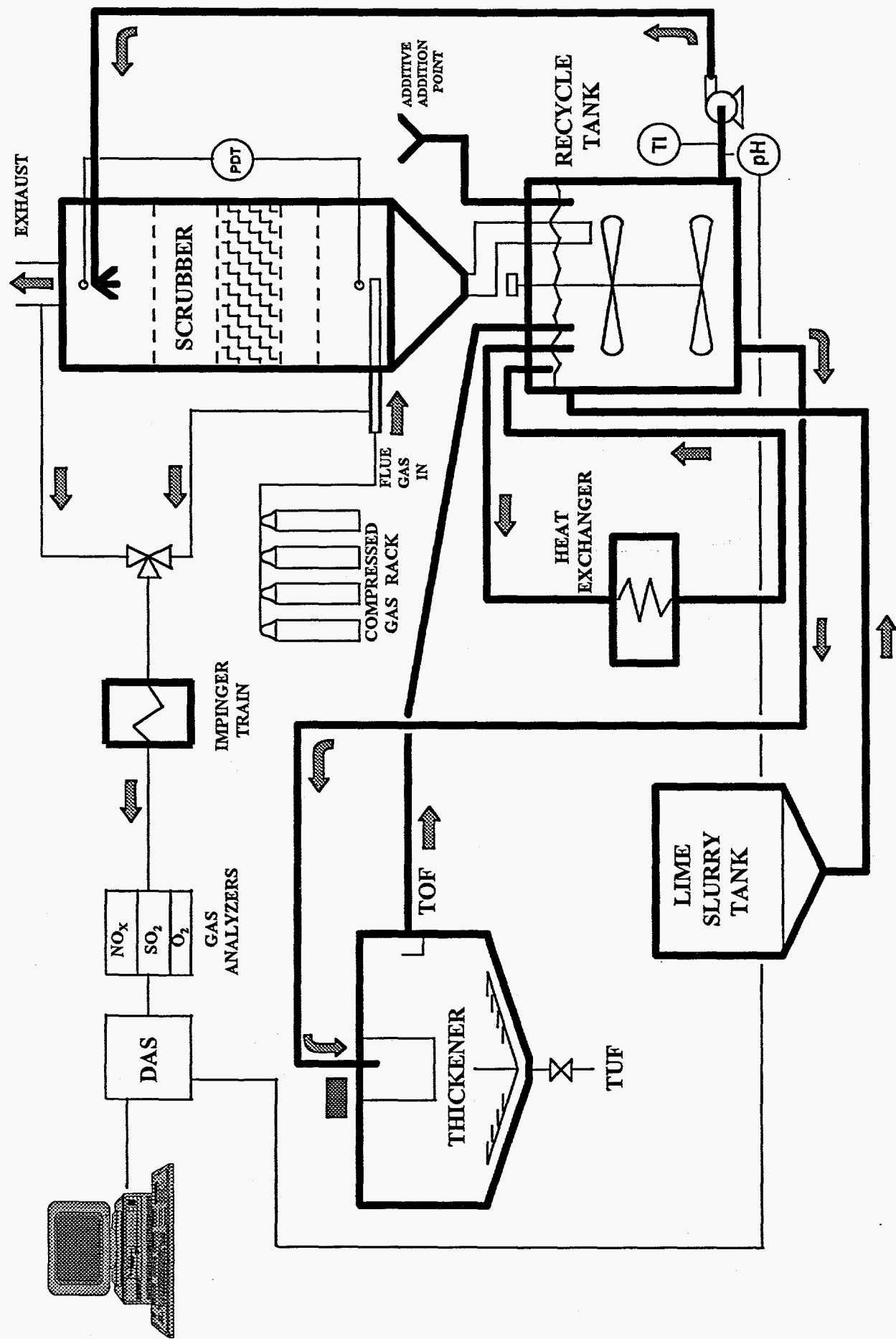


Figure 2. The 5 kW Bench Scale Scrubber Test Facility

stainless steel coils submerged in hot water controlled at $\sim 75^{\circ}\text{C}$. All the pumps used to move the liquor from one vessel to another are Peristaltic pumps.

The flue gas is synthesized by blending nitrogen and CO_2 with the in-house compressed air. The mixture is then doped with SO_2 and NO_x to get the desired inlet concentrations for O_2 , SO_2 and NO_x . The flow of each gas stream is monitored and controlled by its respective rotameter. The flue gas from either the inlet or the outlet of the scrubber is pulled by a vacuum pump through a three-impinger train in ice water baths. The moisture condensed inside the first impinger is then pumped out continuously through a dip tube inserted in this impinger. The gas leaving the impinger train then runs through a heat-traced 1/4" O.D. stainless steel tubing and the O_2 , SO_2 , and NO_x concentrations are then measured by their respective analyzers. The inlet concentrations are monitored at least twice per run to insure that the concentrations are not drifting. Immediately before a test, the O_2 , SO_2 and NO analyzers are zeroed by nitrogen. Calibrations are then performed by flowing standard gases with different O_2 , SO_2 and NO_x concentrations into the analyzers. After a test is completed, the above procedures are repeated to insure that the analyzers are not drifting.

Two Signet pH controllers are available to control the pH of the recirculated liquor. The SO_2 concentration is monitored on-line by a Western Research Model 721 AT SO_2 analyzer, O_2 by a Servomex Series 1400 O_2 analyzer, and the NO_x (NO and NO_2) concentration by a Thermo Environmental Instruments Inc. Model 10 chemiluminescent analyzer.

The values of the pH's, SO_2 , NO_x , and O_2 are recorded by an IBM compatible PC equipped with a LabtechTM (trademark of Laboratory Technologies Corporation) Notebook real time data acquisition and control software. Up to eight signals can be received and acquired simultaneously. The monitor can display values of any two of the eight signals.

1. Non-packed Tests

a) 5 kW Configuration

For the non-packed tests, the 5 kW was configured as shown in Figure 3. The objective was to determine the NO_x removal and ferrous ion concentration when no packing was present in the absorber. This would provide the baseline data necessary for determining the enhancement to NO_x removal provided by a regeneration method.

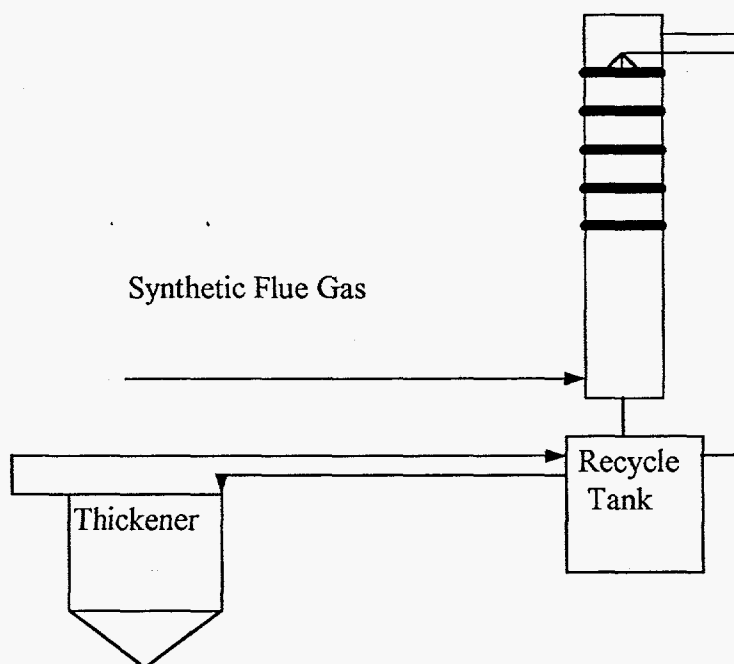


Figure 3. Flow Diagram for the Standard 5 kW Test Facility

b) Test Results

For test DT031094 (non-packed mode, ~100 mM initial total iron concentration, recycle tank pH = 6.4, L/G = 44, 6.5 vol.% O₂) SO₂ removal reached greater than

98% after 20 minutes of testing. There was only one excursion below 95%. Other than this excursion, SO₂ removals remained above 98%. The SO₂ removal is depicted in Figure 4. During the first hour of testing the largest drop in NO_x removal occurred. After this, NO_x removal declined only gradually. By the end of testing the steady state NO_x removal was at 20%. This is illustrated in Figure 5. The ferrous ion concentration determines the NO_x removal. After three hours of testing, the ferrous ion concentration dropped from 45.1 mM to 8.6 mM. Afterwards the ferrous ion concentration decreased slowly to 6.5 mM by the end of testing. The steady state ferrous ion concentration averaged to ~ 7.7 mM. Even without a regeneration method, there is still a small concentration of ferrous ion in the system after the chemistry has attained equilibrium.

On examination of the system chemistry shown in Table 1 the sodium ion concentration was found never to exceed 100 ppm, which is typical for a ThioNO_x system. The sulfite ion concentration increased from 2,824 ppm at the beginning of testing to 7,890 ppm by the end of testing. The magnesium ion concentration followed the same increasing trend. As a result of the increasing trend of these ions, the alkalinity increased from 2,102 ppm to 4,587 ppm. At this alkalinity, SO₂ removal should be high. The solids content of the filtercake reached 80 wt.%.

The adherence to the NO_x removal model was high with a correlation coefficient of 0.8695. This suggests the effective ferrous ion concentration closely approximates the concentration of ferrous ion. This is illustrated in Figure 6.

For test DT030994 (non-packed mode, ~50 mM initial total iron concentration, 6.5 vol.% O₂), SO₂ removals reached greater than 98% after 5 minutes of testing. Figure 7 shows the SO₂ removal curve. Figure 8 illustrates the decrease in NO_x removal from 46% initially to 17% by the end of testing. The ferrous ion concentration had the usual trend of decreasing as testing progressed, where the most rapid change occurred at the beginning of testing. The ferrous ion

concentration was initially at 15.5 mM but decreased to a steady state value of ~2.8 mM. This is shown in Figure 9. This test had a high correlation to the NO_x removal model which was found to be 0.7552 as shown in Figure 10.

The system chemistry shown in Table 2 reveals a low average sodium concentration of 43.8 ppm. Unlike test DT031094, the sulfite ion concentration was high throughout the test resulting in high alkalinities and magnesium ion concentration. Despite the high sulfite levels, the calcium ion concentration averaged only 154 ppm. The filtercake solids content did not increase during the test. The final solids content was 57.9 wt.%.

c) Attainment of Objectives

A baseline ferrous ion concentration was established without any regeneration method for a non-packed mode. This is necessary for the evaluation of ferrous ion concentration when regeneration methods are applied. The baseline NO_x removal at 6.5 vol.% O₂ in the non-packed mode was 20%.

Figure 4. SO₂ concentration and removal vs. time

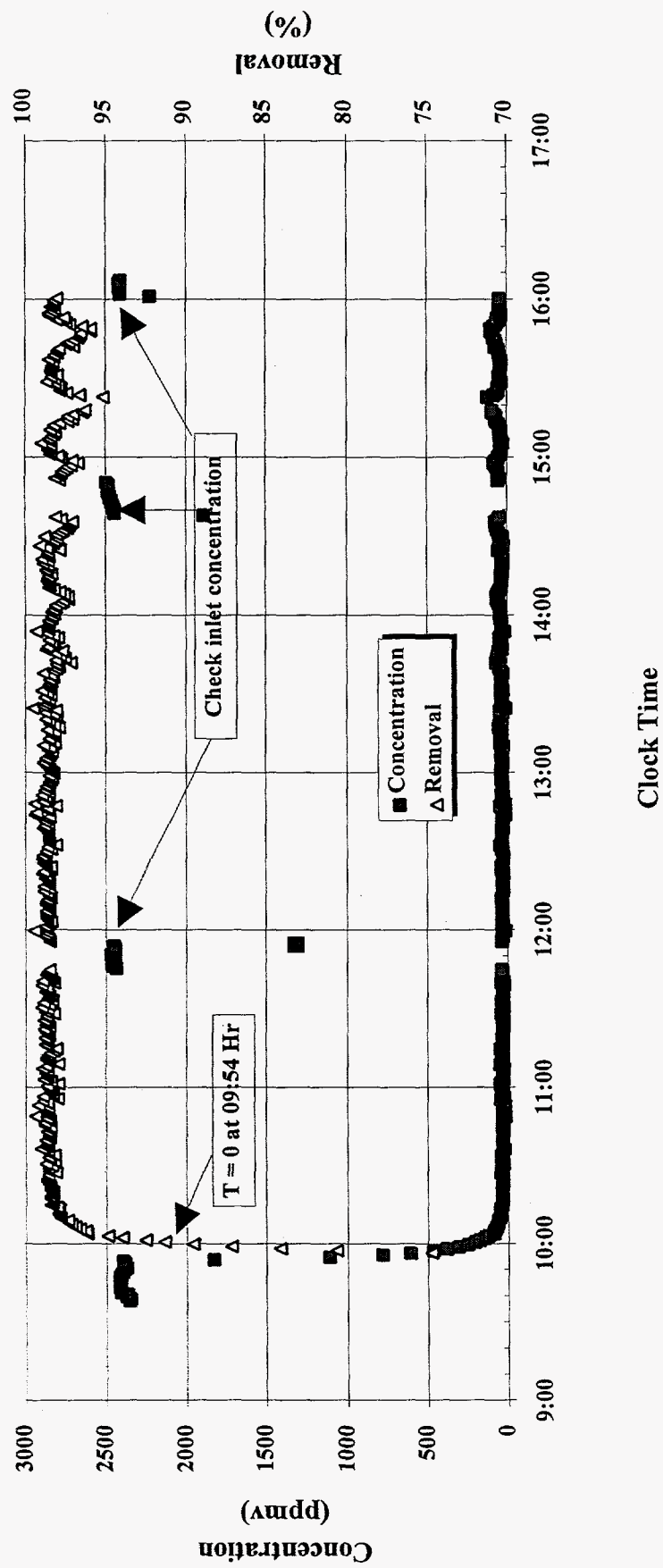
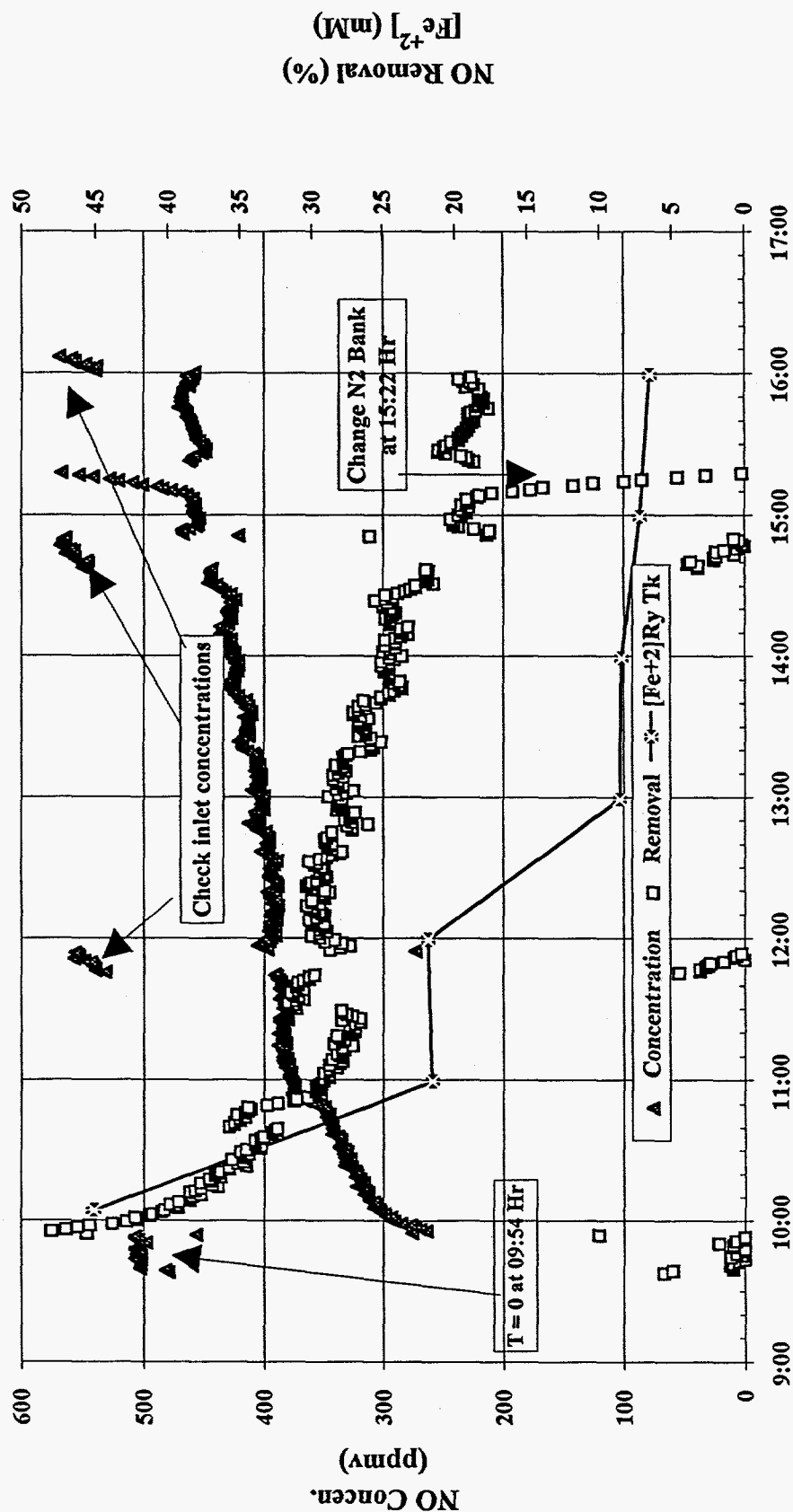


Figure 5. NO concentration, NO removal, and $[\text{Fe}^{+2}]$ vs. time



Clock Time

Figure 6. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

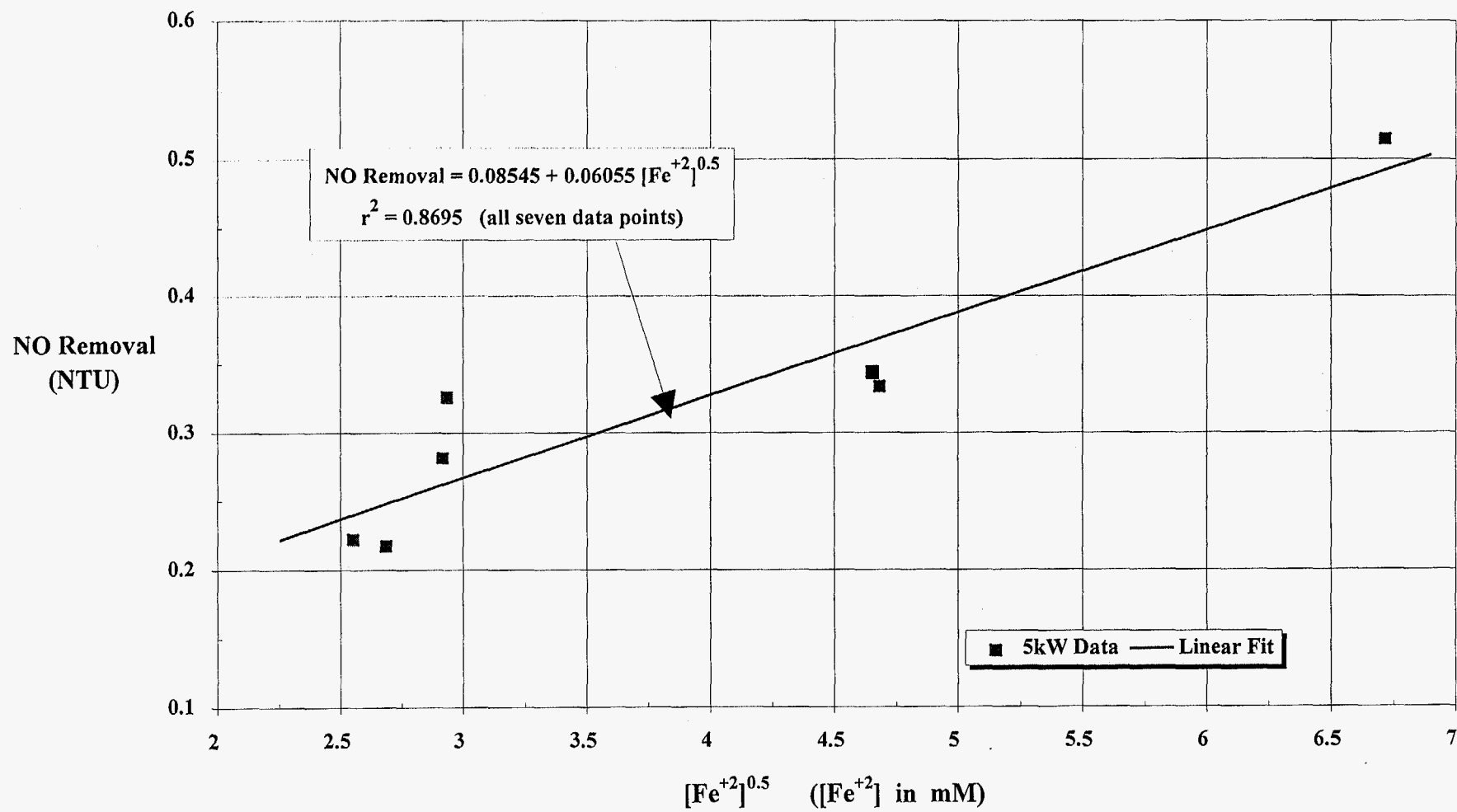


Figure 7. SO₂ concentration and removal vs. time

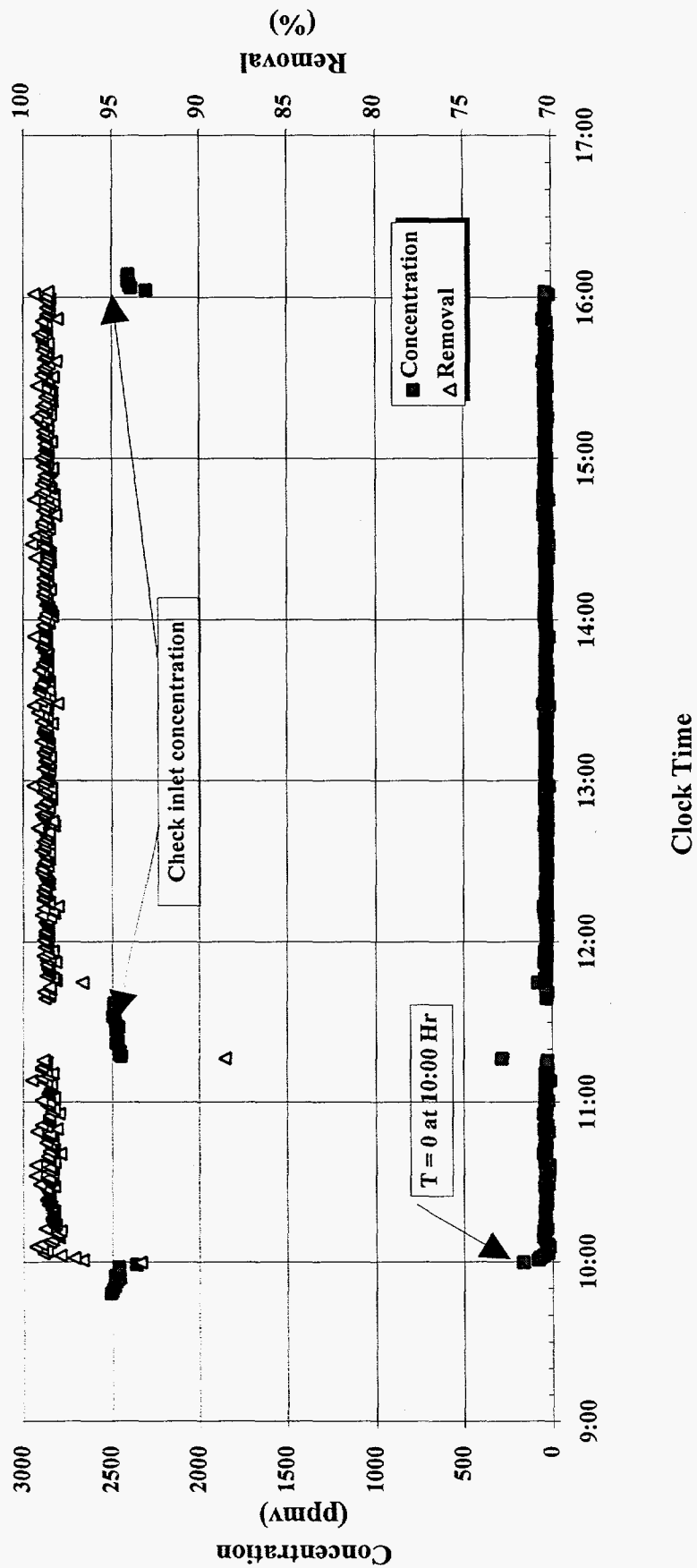


Figure 8. NO concentration and NO removal vs. time

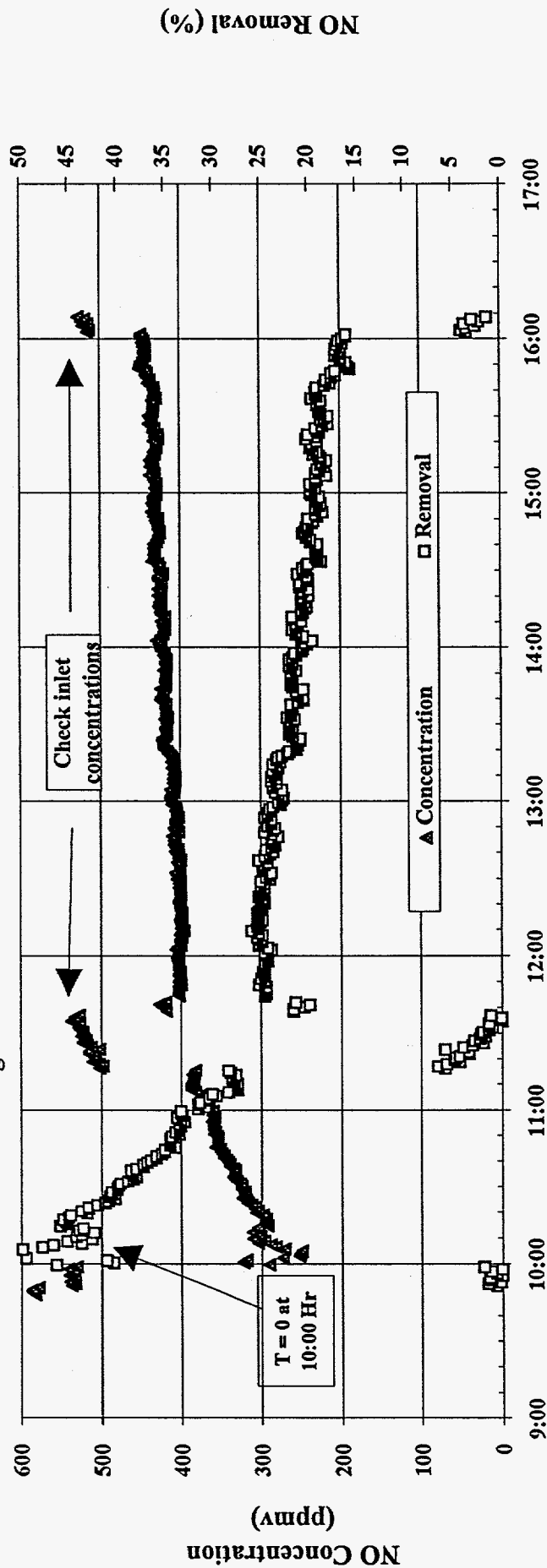


Figure 9. Change of recycle tank liquor $[\text{Fe}^{+2}]$ with respect to time

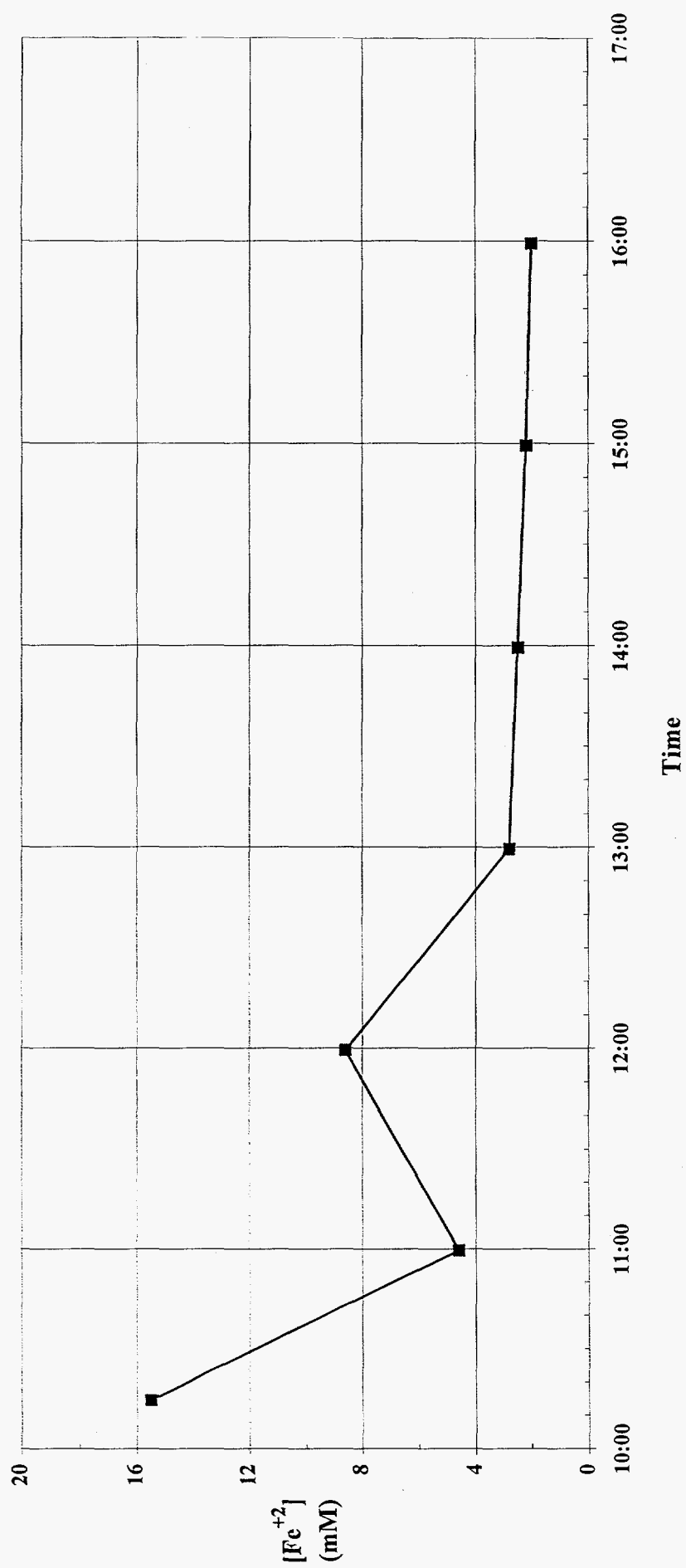


Figure 10. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

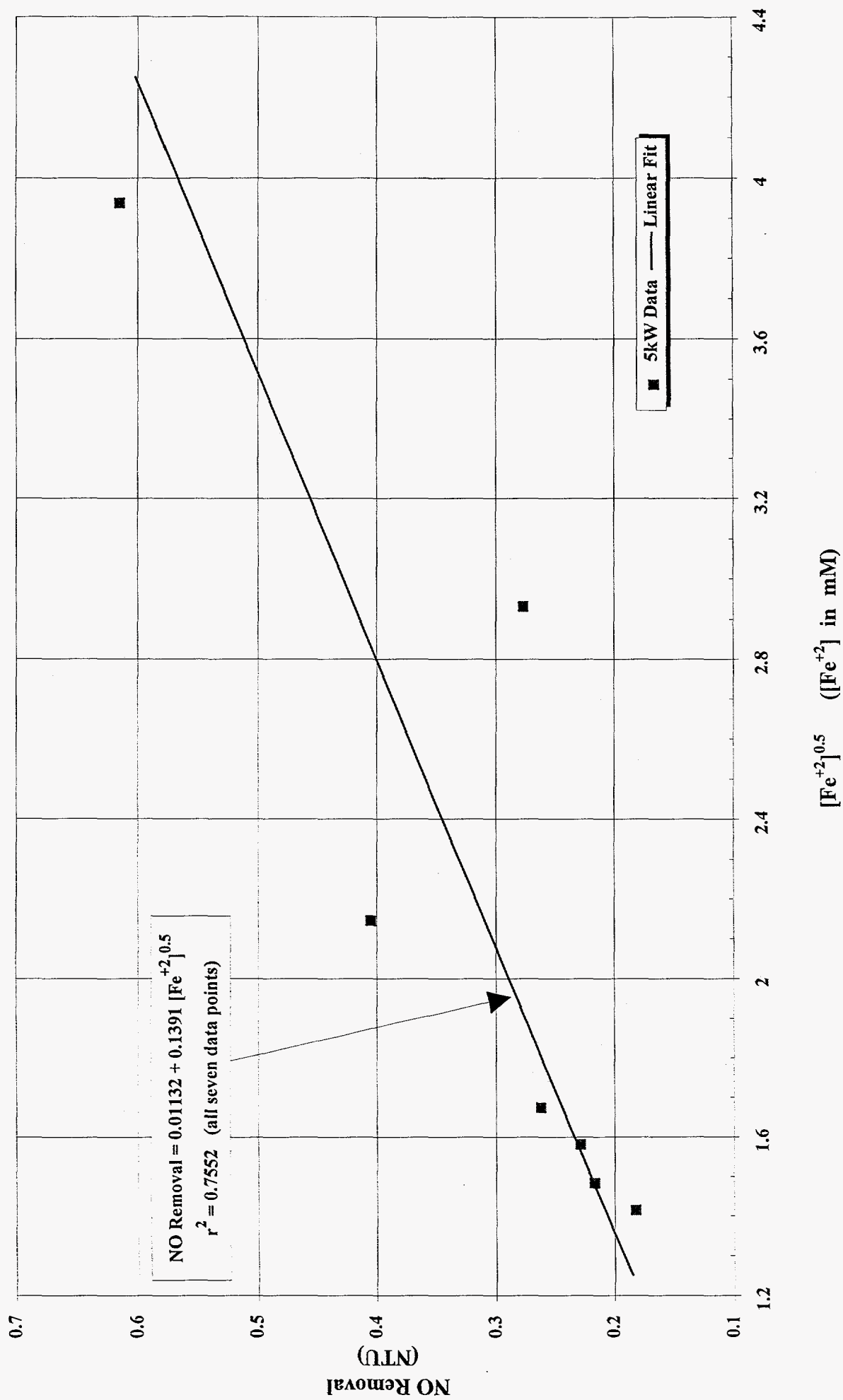


Table 1. Chemistry Data

Clock Time	Recy Tank	Alkalinity	[SO ₃ ²⁻] as	[Fe ⁺²] _{RY Tk}	[SO ₃ ²⁻]	[ADS]	[Mg ⁺²]	[Ca ⁺²]	Total Fe] _{RY T}	[Na ⁺¹]	Filtercake
(Hr: Min)	Liquor pH	(ppm)	analyzed	(mM)	corrected for	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	Solids
			(ppm)		[Fe ⁺²] _{RY Tk}						(wt %)
					(ppm)						
10:05	6.4	2102	4628	45.1	2824	15.66	6044	1733	5252	75.7	69.1
11:00	6.4	3069	4275	21.6	3411	15.42	6145	1623	4790	53.7	71.5
12:00	6.4	3353	4451	21.9	3575	16.69	6643	1172	4907	70.4	72.7
13:00	6.4	4387	4948	8.6	4604	24.34	7238	1533	5143	52.7	75.3
14:00	6.4	4453	6581	8.5	6241	36.7	7646	832	4986	54.4	80.5
15:00	6.4	4537	8230	7.2	7942	43.65	8218	1373	4906	52.9	83
16:00	6.4	4587	8150	6.5	7890	55.02	8716	731	4949	53.5	85.4
avg:	6.4	3784			5212		7236	1285	4990	59.0	78.1

Table 2. Chemistry Data

Clock Time	Recy Tank	Alkalinity	[SO ₃ ⁻²] as	[Fe ⁺²] _{Ry Tk}	[SO ₃ ⁻²]	[ADS]	[Mg ⁺²]	[Ca ⁺²]	Total Fe] _{Ry}	[Na ⁺¹]	Filtercake
(Hr: Min)	Liquor pH	(ppm)	analyzed	(mM)	corrected for	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	Solids
			(ppm)		[Fe ⁺²] _{Ry Tk}						(wt %)
					(ppm)						
10:15	6.4	2035	5644	15.5	5024	1.00	3592	251	2067	54.2	
11:00	6.5	3570	7590	4.6	7406	1.00	4700	92.2	1971	22.3	59.5
12:00	6.4	4120	8839	8.6	8495	2.02	5122	116	1856	26.4	65.9
13:00	6.4	4837	8943	2.8	8831	3.77	5371	106	1958	58	60.4
14:00	6.4	4654	9255	2.5	9155	4.38	5566	145	1852	47.9	60.6
15:00	6.4	4753	9299	2.2	9211	6.47	5881	174	1711	52	59.8
16:00	6.4	4837	9327	2	9247	8.8	6107	193	1882	45.8	57.9
avg:	6.41	4115			8196		5191	154	1900	43.8	60.7

2. Packing Test

a) 5 kW Configuration

For the packing test, the 5 kW apparatus was configured the same as for the non-packed mode except for packing inserted between trays 1 and 2, 2 and 3, 3 and 4, and 4 and 5. Between trays 1 and 2, 2 and 3, and 3 and 4, 1/8" ceramic berl saddles were used extending to a height half the distance between the trays. Between trays 4 and 5, 3/8" ceramic berl saddles were used extending to a height half the distance between the trays. The general configuration is shown in Figure 11. The tests were conducted at 100 mM and 50 mM initial total iron concentration.

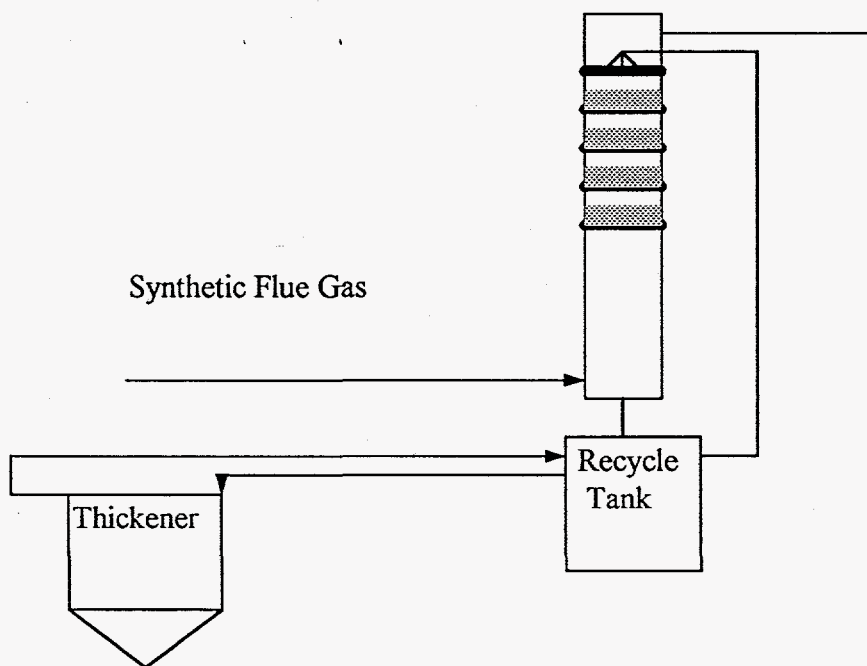


Figure 11. Flow Diagram for Packing Test

b) Test Results

For test DT030394 (packing mode, ~100 mM initial total iron concentration recycle tank pH = 6.5, L/G = 44, 6.5 vol.% O₂), SO₂ removal reached greater than 98% after 20 minutes of testing. For a good part of the test, SO₂ removal was above 99%. The SO₂ removal curve is shown in Figure 12. During the first hour of testing the largest drop in NO_x removal was observed. After this period, the NO_x removal gradually declined to a steady state removal of 16%. This is similar to the final NO_x removal achieved without packing. It should be pointed out that even without a ferrous ion regeneration method, there is NO_x removal in the 5 kW system. This is shown in Figure 13. After 45 minutes of testing, the ferrous ion concentration dropped from 20.8 mM to 7.4 mM. After this, the ferrous ion concentration slowly dropped from 7.4 mM to 3 mM by the end of testing. The steady state ferrous ion concentration averaged ~3 mM as shown in Figure 14.

On examination of the system chemistry, shown in Table 3, the sodium ion concentration never exceeded 100 ppm. The sulfite and magnesium ion concentrations both gradually increased during testing reflecting the steady increase in alkalinity from 3,086 ppm to 6,205 ppm. With packing, a higher alkalinity resulted. This is not surprising since SO₂ removal is enhanced. The filtercake solids achieved levels higher than 80 wt.%. This level of filtercake solids is the goal of the ThioNO_x process.

The correlation coefficient of the data points to the NO_x removal model was 0.9381 suggesting the concentration of ferrous ion closely follows the effective ferrous ion concentration. The NO_x removal model curve is shown in Figure 15.

For test DT030294 (packing mode, ~50 mM initial total iron concentration, recycle tank pH = 6.6, L/G = 44, 6.5 vol.% O₂), the SO₂ removal did not reach 99% until later in the testing. This is shown in Figure 16. The NO_x removal was

initially at 36% but decreased to a steady state value of 17% by the end of testing. This is similar to the NO_x removal obtained for test DT030394. The NO_x removal curve is shown in Figure 17. The ferrous ion concentration was 11.8 mM initially before dropping off to a steady state value of 2.4 mM. This curve is shown in Figure 18.

The system chemistry shown in Table 4 was low in sodium ion concentration averaging only 45 ppm. The sulfite ion concentration was high and steady leading to alkalinities above 5,000 ppm. Because of the high sulfite ion concentrations, the calcium ion concentration averaged above 200 ppm. Because the pH was maintained above 6.5, it is not unusual to see this high a sulfite ion concentration. The filtercake solids content increased from 59.7 wt.% to 65.7 wt.%. This is not unusual in the absence of a regeneration technique. The correlation to the NO_x removal model is shown in Figure 19 and was found to be high at 0.8655.

c) Attainment of Objectives

A baseline ferrous ion concentration was determined without any regeneration method for a packing mode at both 100 mM and 50 mM initial ferrous ion concentration. This is necessary for the baseline evaluation of ferrous ion concentration and NO_x removal when regeneration methods are applied to a packing configuration. The baseline NO_x removal was found to be 17%.

Figure 12. SO₂ concentration and removal vs. time

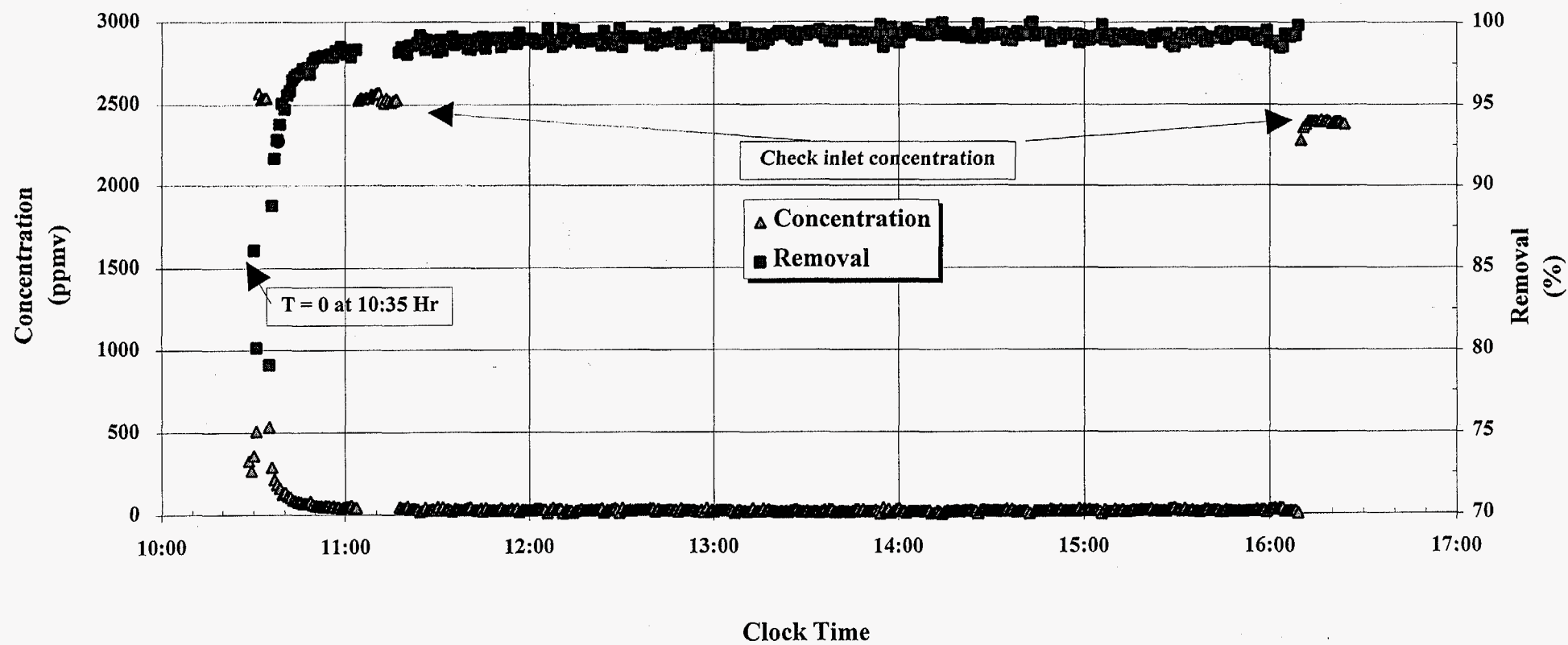


Figure 13. NO concentration and removal vs. time

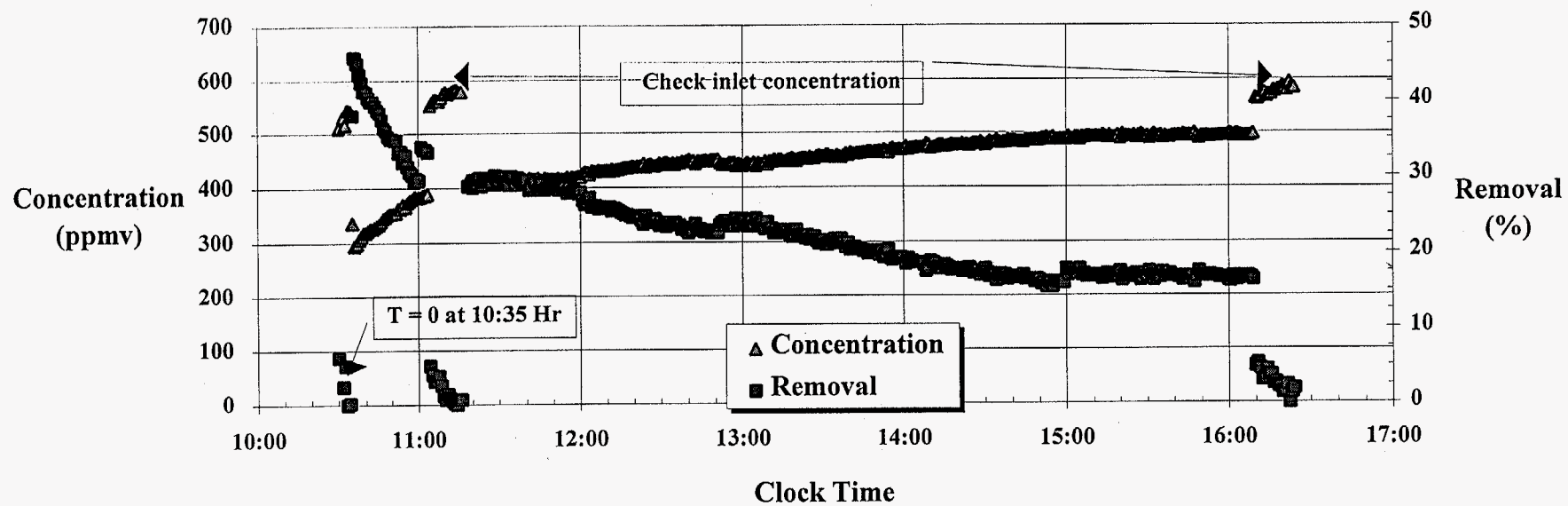


Figure 14. Change of recycle tank liquor $[\text{Fe}^{+2}]$ with respect to time

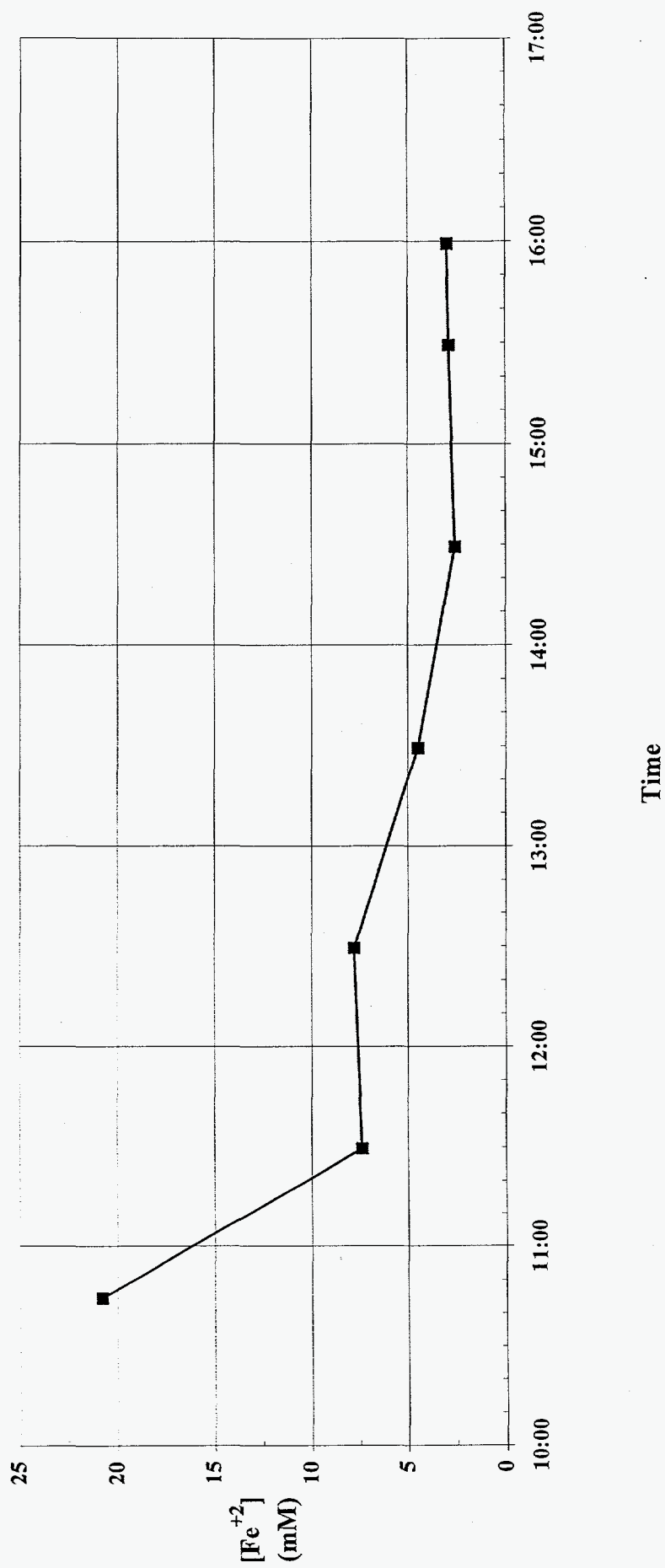


Figure 15. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

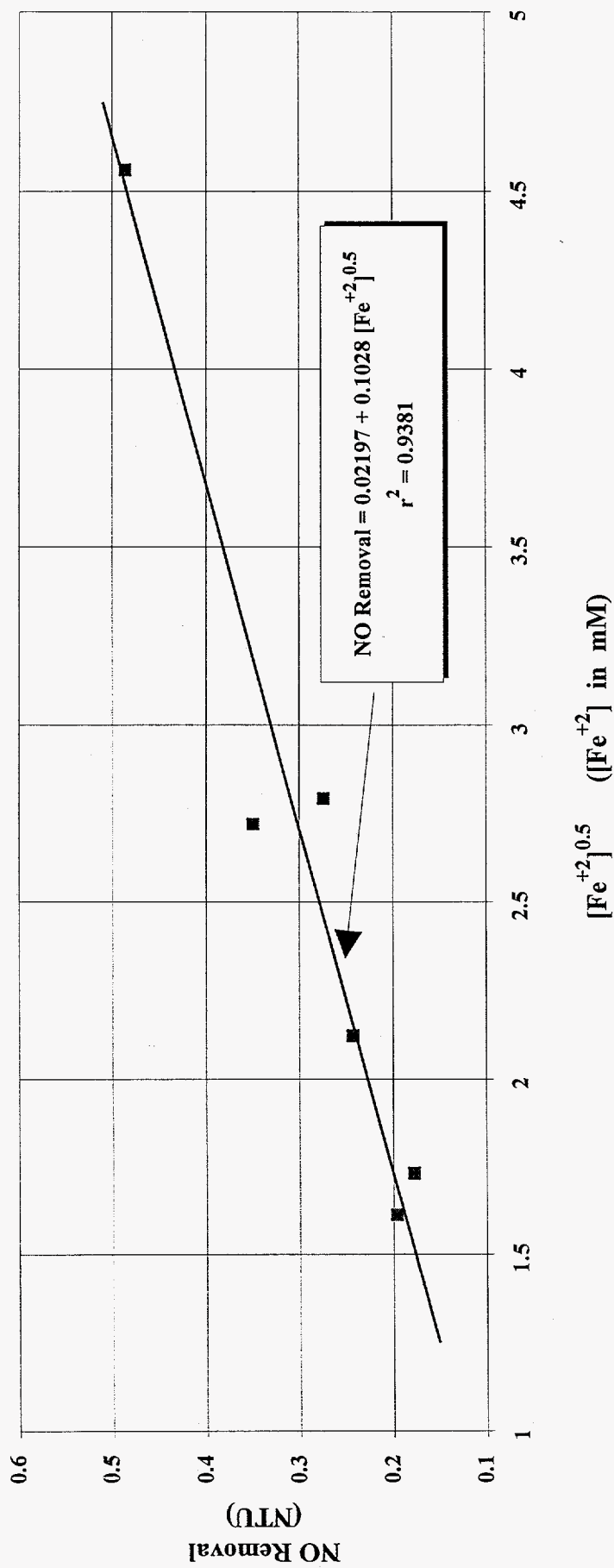


Figure 16. SO₂ concentration and removal vs. time

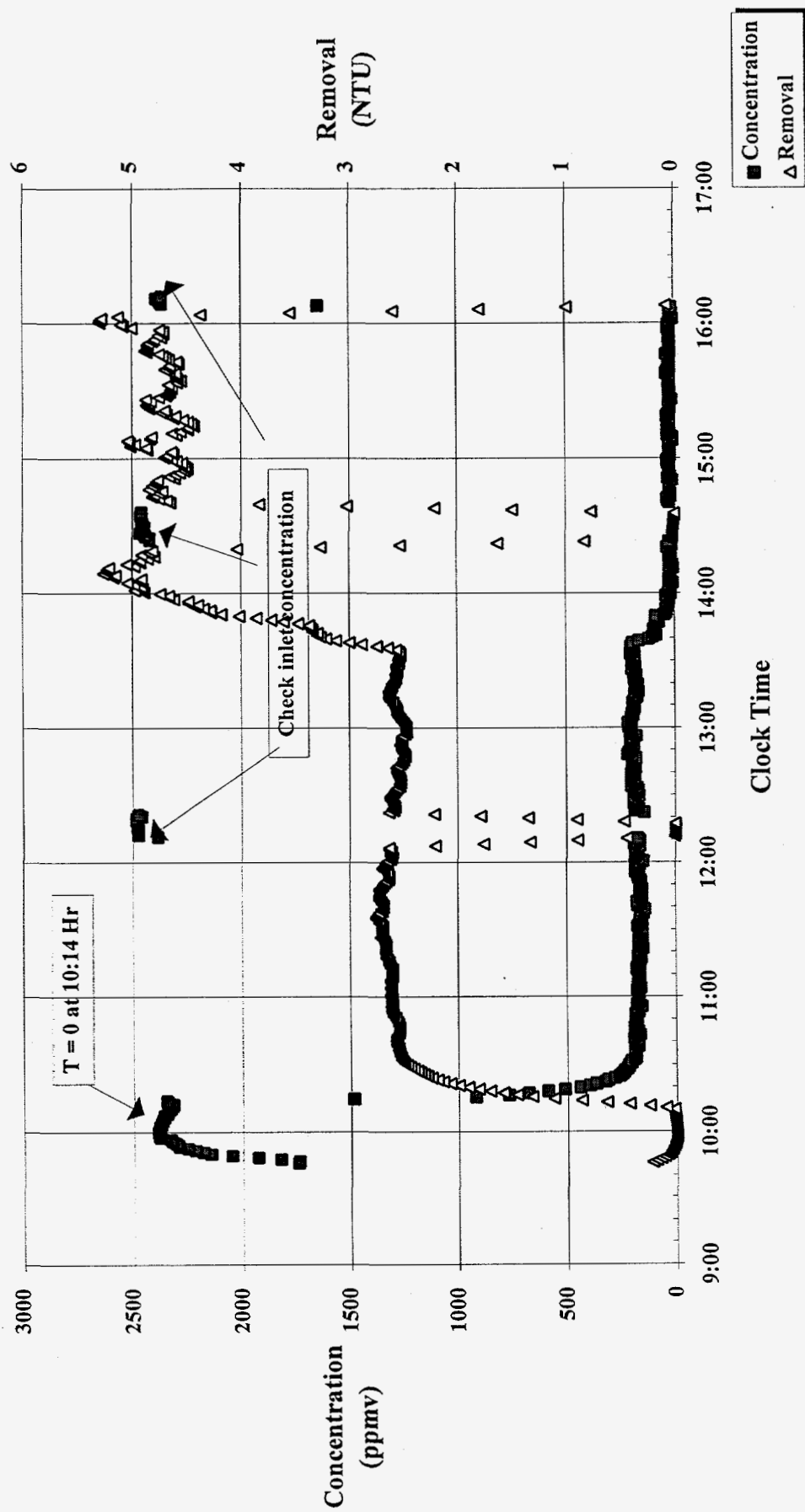


Figure 17. NO concentration and NO removal vs. time

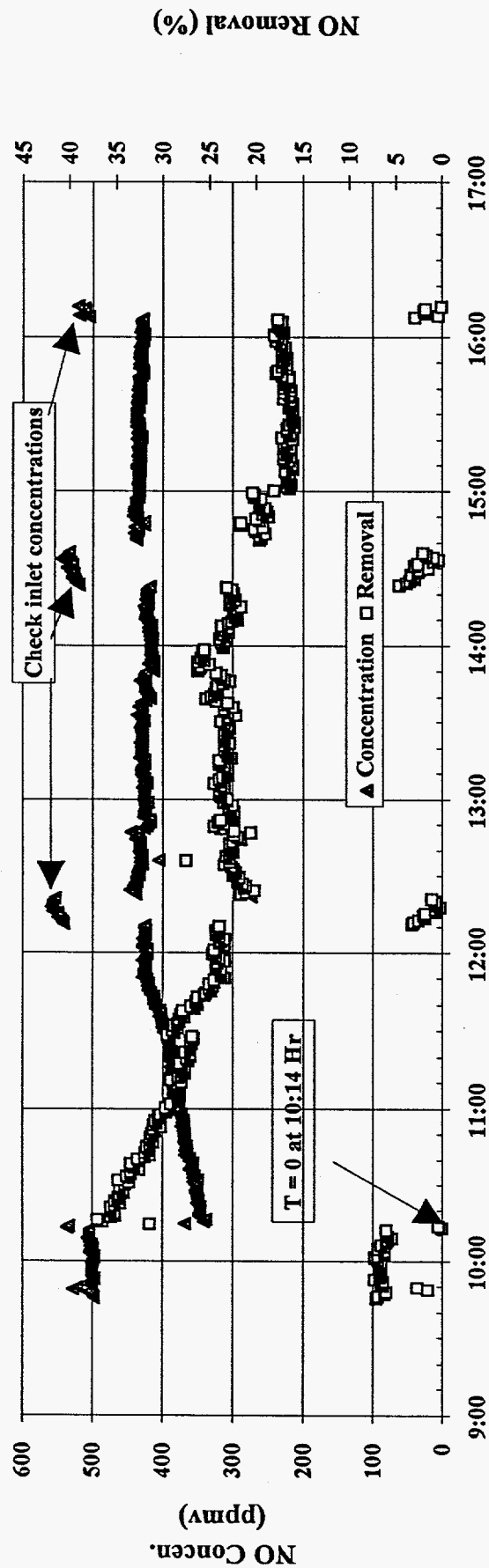


Figure 18. Change of recycle tank liquor $[\text{Fe}^{+2}]$ with respect to time

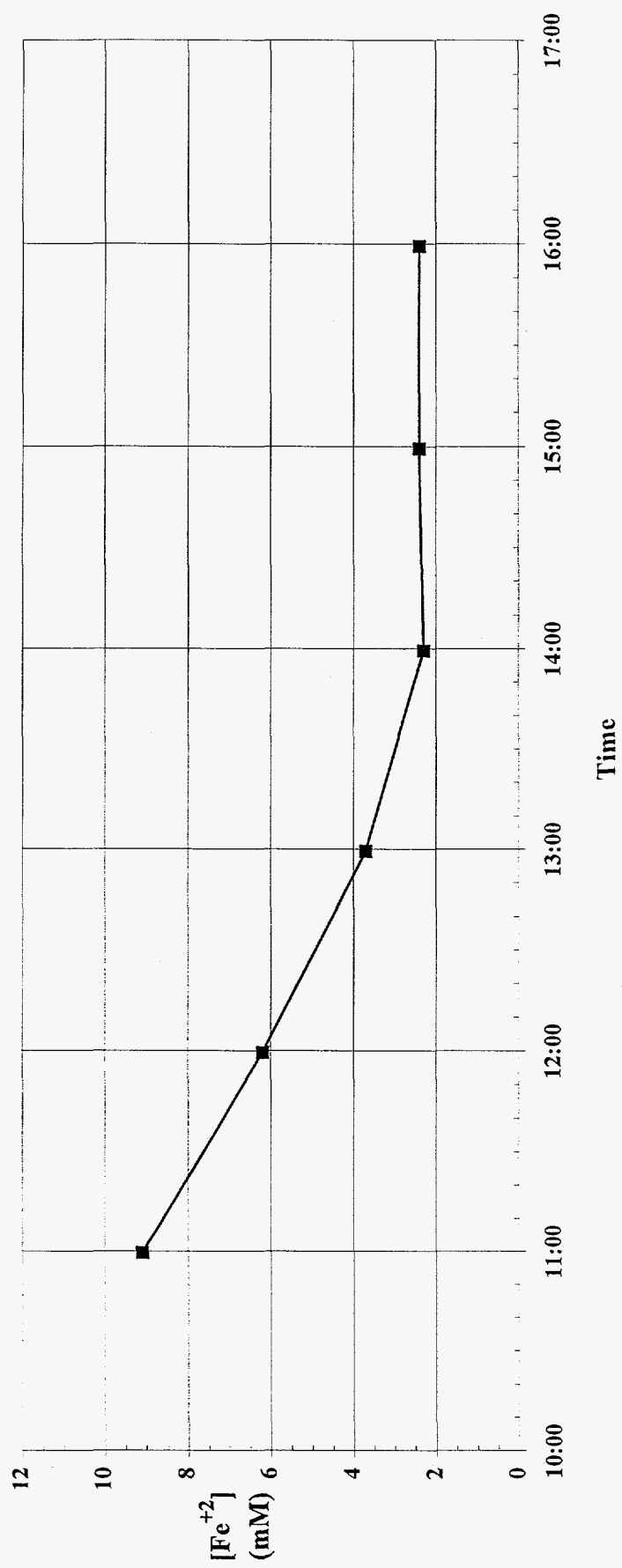


Figure 19. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

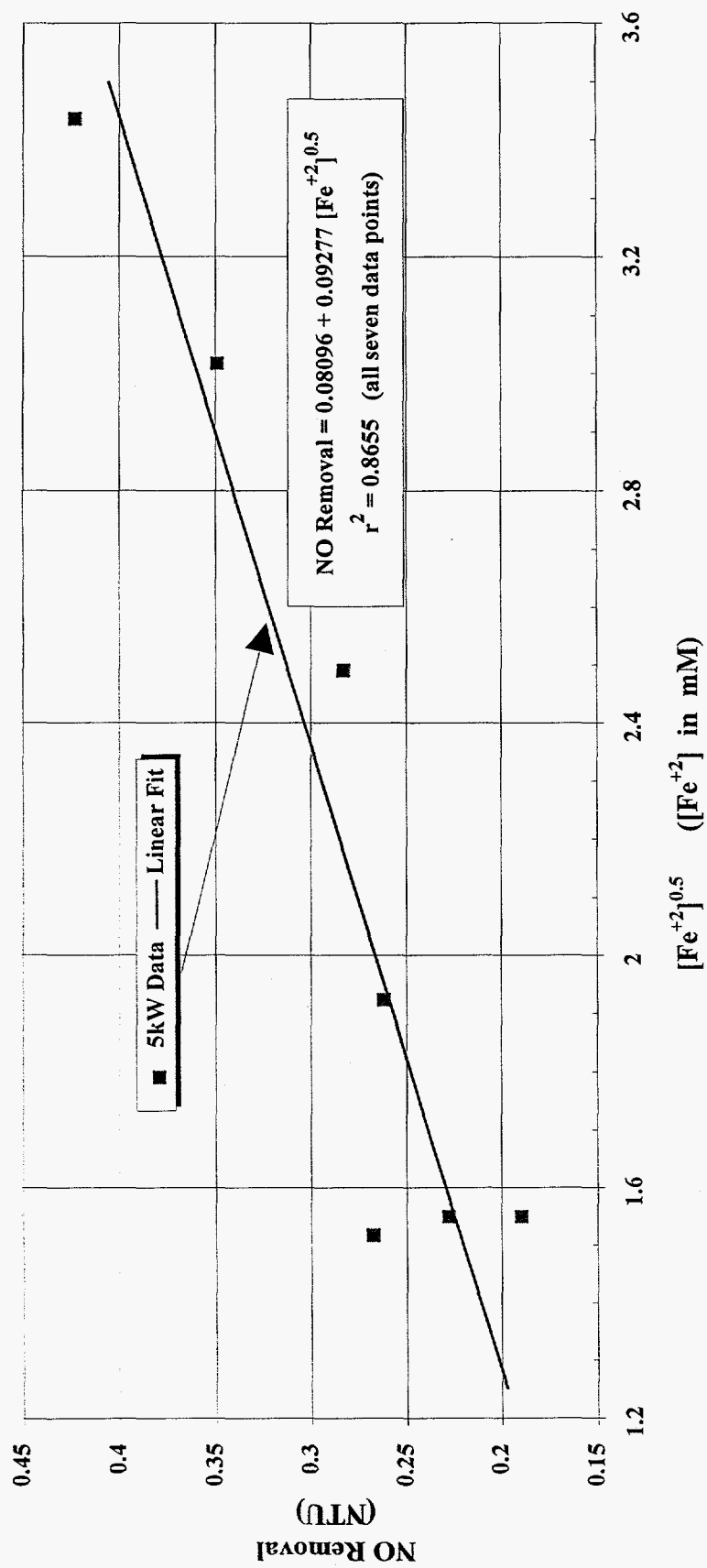


Table 3. Chemistry Data

Clock Time	Recy Tank	Alkalinity	[SO ₃ ⁻²] as	[Fe ⁺²] _{Ry Tk}	[SO ₃ ⁻²]	[ADS]	[Mg ⁺²]	[Ca ⁺²]	[Total Fe] _{Ry Tk}	[Na ⁺¹]	Filtercake
(Hr: Min)	Liquor pH	(ppm)	analyzed	(mM)	corrected for	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	Solids
			(ppm)		[Fe ⁺²] _{Ry Tk}						(wt %)
					(ppm)						
10:45	6.5	3086	3739	20.8	2907	16.12	6499	2309	5287	61.6	71.2
11:30	6.6	4120	3307	7.4	3011	17.58	6742	1973	5015	72.4	76.3
12:30	6.6	4754	3347	7.8	3035	22.04	6973	1909	5184	63.8	78.7
13:30	6.6	5254	3347	4.5	3167	26.44	7249	1646	5268	67.3	80.7
14:30	6.5	5838	3860	2.6	3756	34.11	7668	1422	5509	69.2	82.2
15:30	6.5	6088	3907	2.9	3791						83.1
16:00	6.6	6205	4067	3	3947	43.98	8518	1038	5332	63.1	84.3
avg:	6.56	5049			3373		7275	1716	5266	66.2	79.5

Table 4. Chemistry Data

Clock Time	Recy Tank	Alkalinity	[SO ₃ ⁻²] as	[Fe ⁺²] _{RyTk}	[SO ₃ ⁻²]	[ADS]	[Mg ⁺²]	[Ca ⁺²]	[Total Fe] _{RyTk}	[Na ⁺¹]	Filtercake
(Hr: Min)	Liquor pH	(ppm)	analyzed	(mM)	corrected for	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	Solids
			(ppm)		[Fe ⁺²] _{RyTk}						(wt %)
					(ppm)						
10:30	6.6	4220	8591	11.8	8119	1	4985	188	2926	48.1	
11:00	6.6	4787	8094	9.1	7730	1	5293	167	2901	38.9	59.7
12:00	6.7	5171	8022	6.2	7774	1.9	5238	245	2620	33.8	64.2
13:00	6.7	4954	8230	3.7	8082	2.7	5123	159	2721	55.8	66.1
14:00	6.6	5421	8206	2.3	8114	3.47	6039	225	2550	46	67.9
15:00	6.6	5504	8863	2.4	8767	5.2	5859	211	2405	45.4	67.9
16:00	6.6	5688	8711	2.4	8615	6.43	5975	276	2501	49.3	65.7
avg:	6.63	5106			8172		5502	210	2661	45	65.3

3. Exhaust Gas Blanket Test

a) 5 kW Configuration

The 5 kW was set-up the same as for the non-packed modes except a bleed from the exhaust synthetic flue gas line was directed to the recycle tank to provide an atmosphere over the recycle tank liquor. In this manner, the effect of oxidation of ferrous ion could be analyzed. The general set-up is shown in Figure 20.

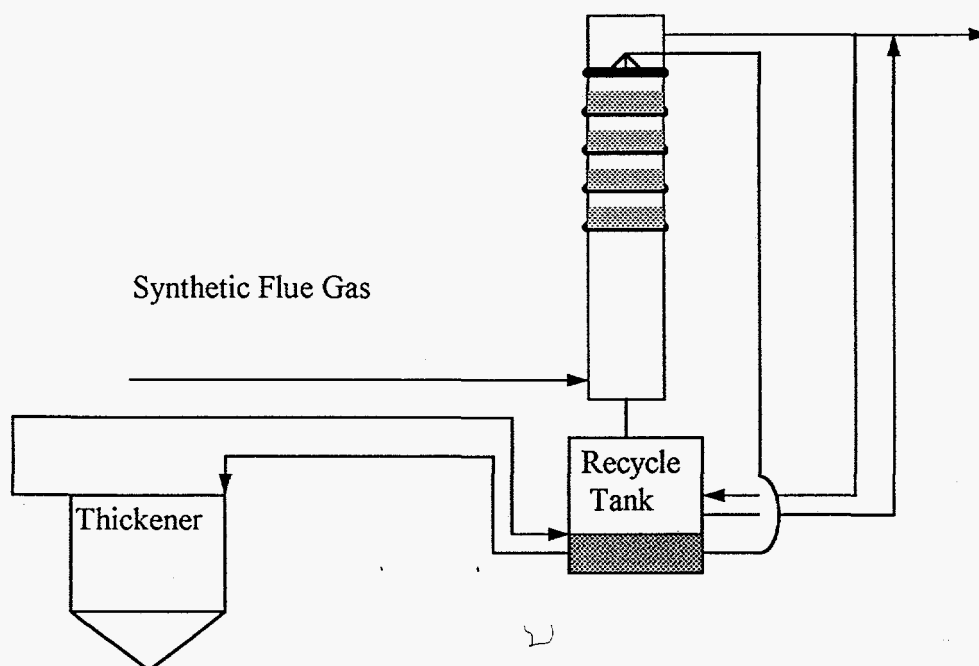


Figure 20. 5 kW Exhaust Gas Blanket Configuration

b) Test Results

For test DT041394 (non-packed mode, ~50 mM initial total iron concentration recycle tank pH = 6.2, L/G = 44, 6.5 vol.% O₂) SO₂ removal reached greater than 96% after 10 minutes of testing. SO₂ removal exceeded 98% after 90 minutes of testing and remained above this value for the duration of the run as shown in

Figure 21. The NO_x removal dropped much less rapidly during the first hour of testing than the baseline tests run without the exhaust gas blanket. During the test run, the NO_x removal gradually declined to reach a final steady state value of 15%. The final value for NO_x removal is actually less than the final removals obtained in the other four baseline tests run without an exhaust gas blanket. The NO_x removal curve is shown in Figure 22. There was a significant drop in the ferrous ion concentration during the first two hours of testing from 33.8 mM to 8.2 mM. After this there was only a gradual decline from 8.2 mM to 4.3 mM at the end of testing. The steady state ferrous ion concentration was ~6.05 mM which is similar to the baseline results without an exhaust gas blanket. The recycle tank ferrous ion concentration is shown in Figure 23. This suggests that exhaust gas blanketing has no effect on the ferrous ion oxidation rate except for possibly decreasing the rate at which steady state NO_x removal is achieved.

The sodium ion concentration was well below 100 ppm during the test run while the sulfite ion concentration increased from 5,185 ppm initially to a final value of 8,564 ppm. The increase in sulfites resulted in high SO_2 removals during the test. The magnesium ion concentration followed the same increasing trend. At these sulfite concentrations, the alkalinity averaged 3,283 ppm. The solids content of the filtercake reached 62.5 wt.%. This is typical for a process in which no regeneration agent is used. These values are shown in Table 5. The correlation coefficient of the data points to the NO_x removal model is shown in Figure 24 and was found to be 0.9166.

c) Attainment of Objectives

It was determined that the oxygen concentration in the head space over the recycle tank had little effect on the baseline steady state ferrous ion concentration. For this test the baseline NO_x removal was 15%. This was a surprise since the oxidation rate of ferrous ion should decrease with lower oxygen content in the

recycle tank. This indicated that oxidation of ferrous ion occurs primarily in the absorber.

Figure 21. SO₂ concentration and removal vs. time

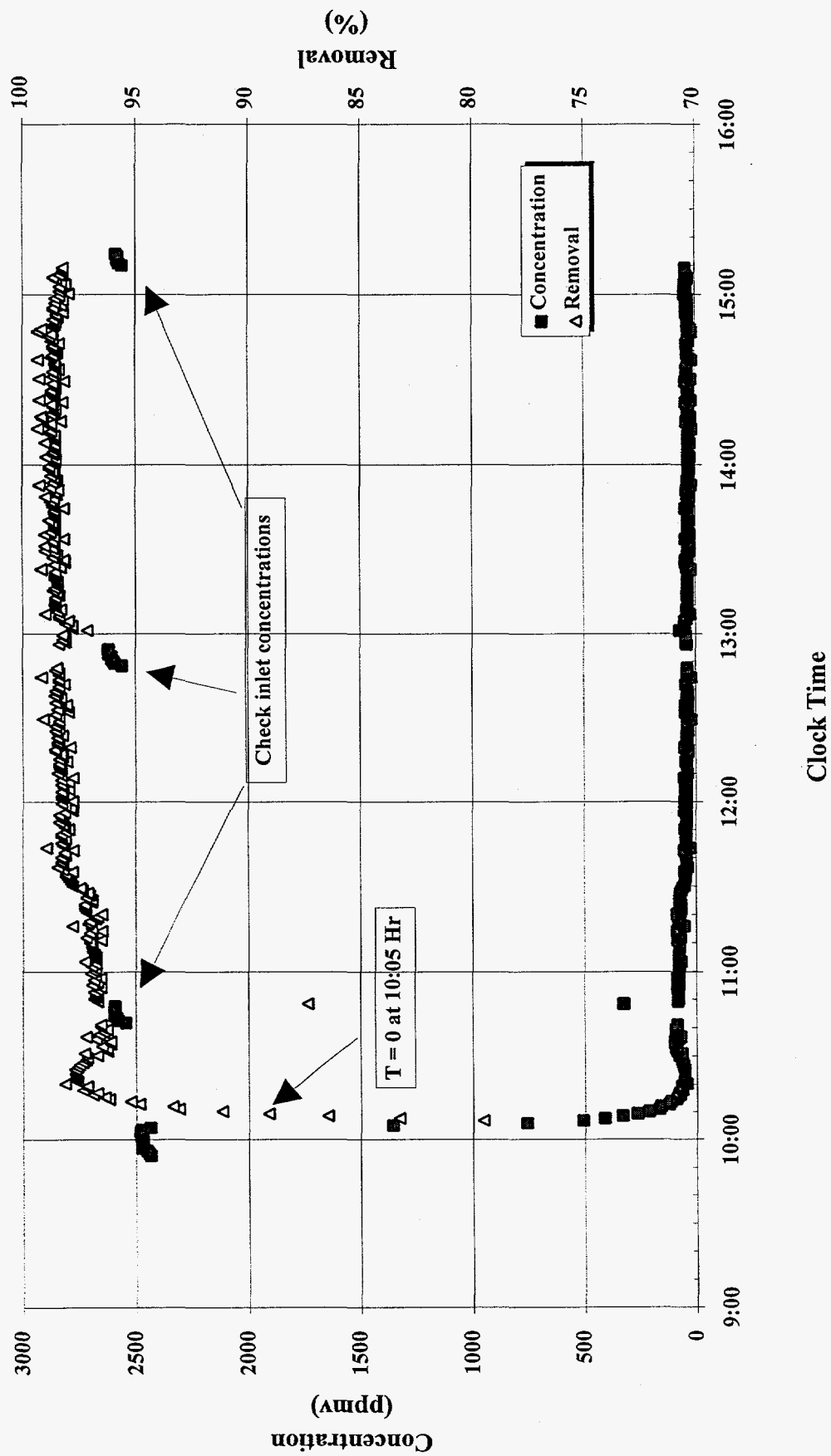


Figure 22. NO concentration and removal vs. time

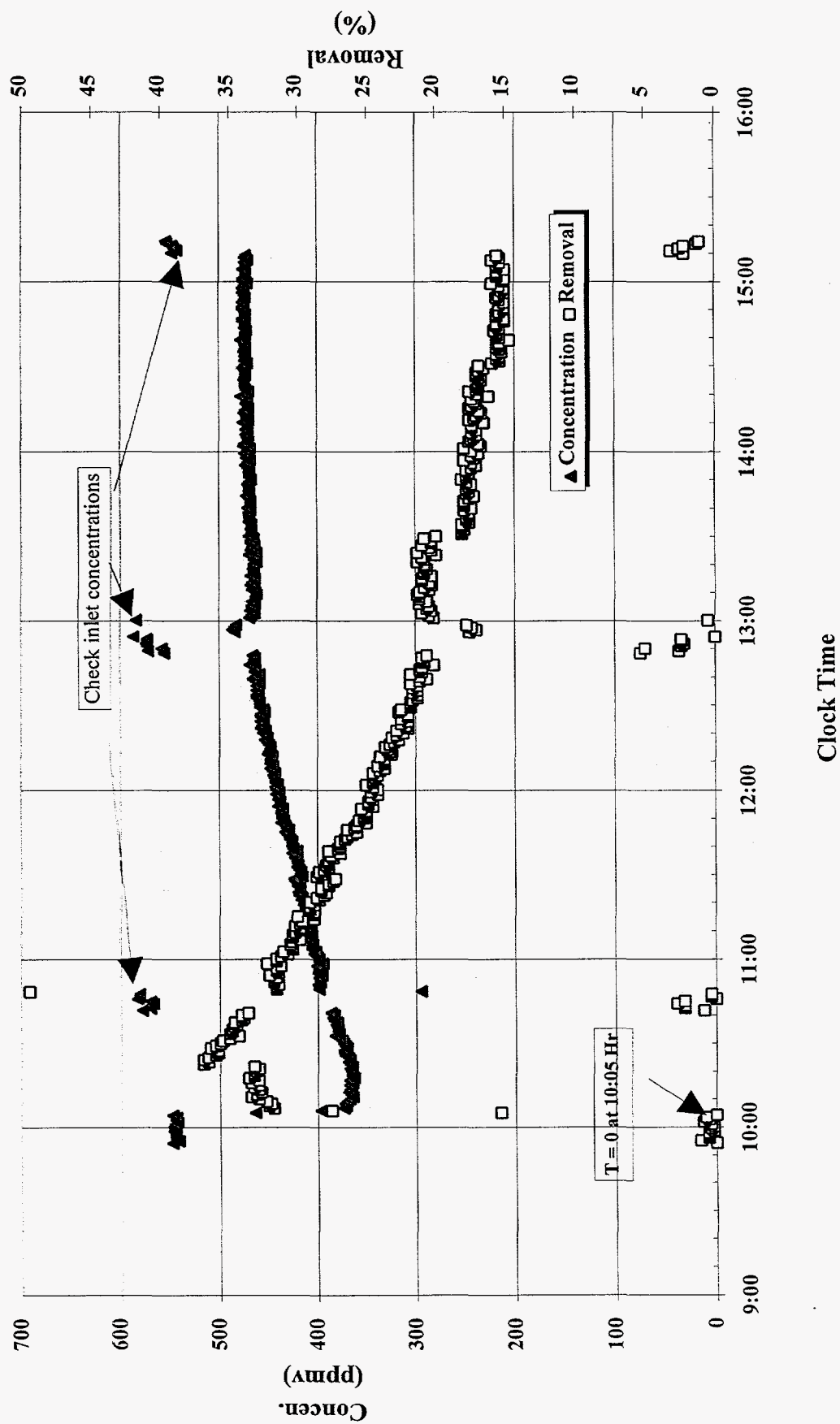


Figure 23. Change of recycle tank liquor $[\text{Fe}^{+2}]$ with respect to time

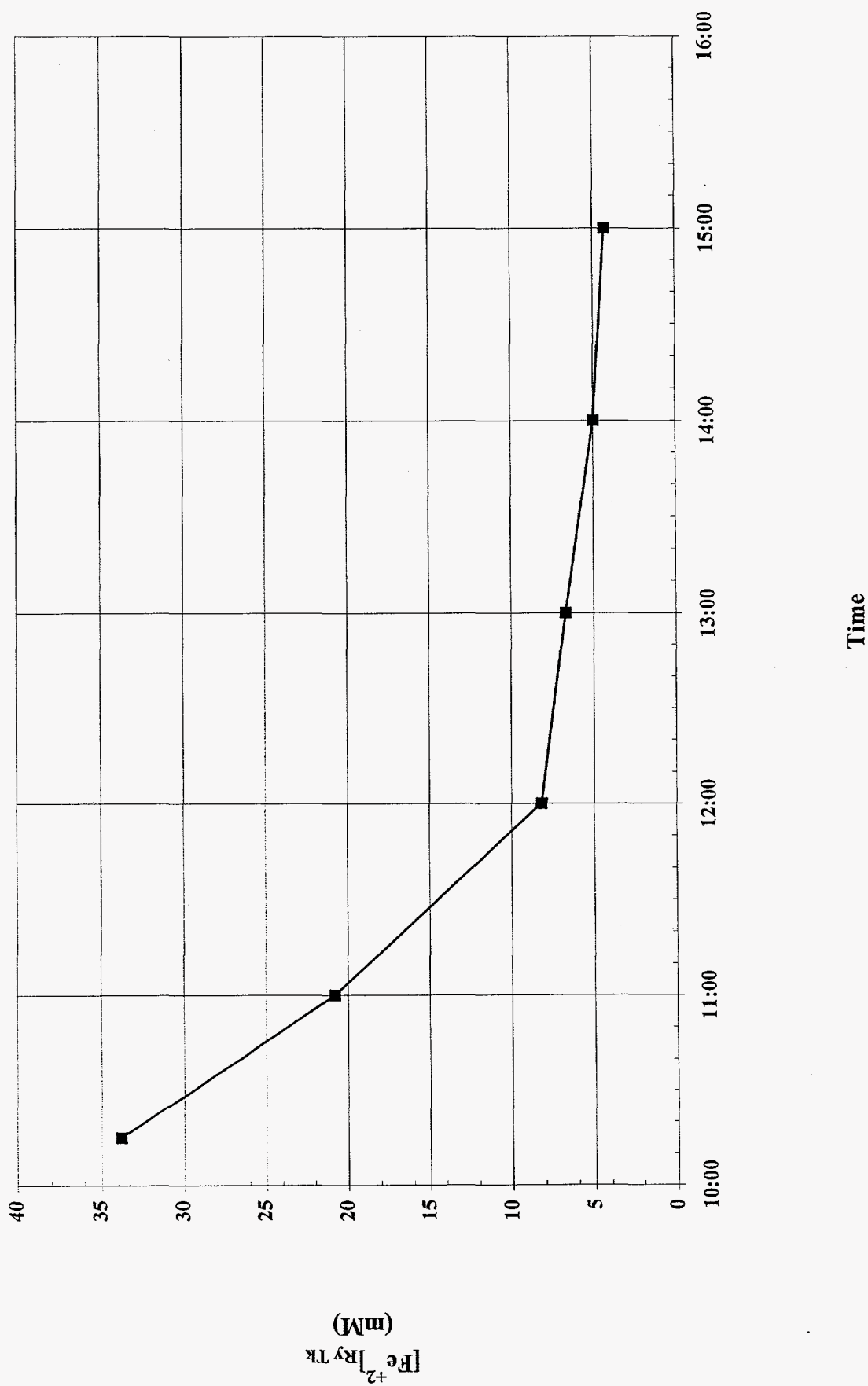


Figure 24. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

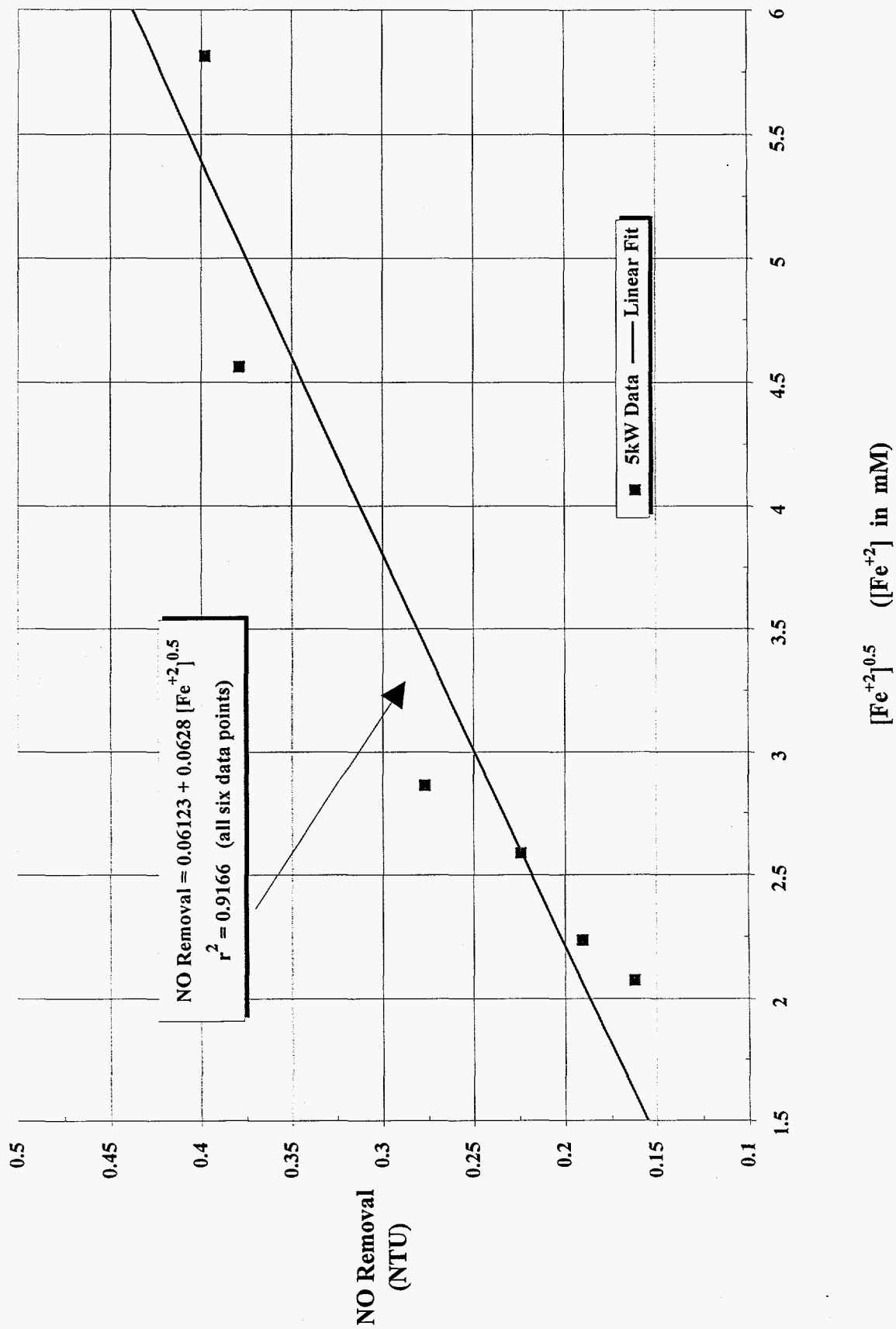


Table 5. Chemistry Data

Clock	L/G	Recycle	Alkalinity	[SO ₃ ⁻²]	[Fe ⁺²]	[SO ₃ ⁻²]	[ADS]	[SA]	[Mg ⁺²]	[Ca ⁺²]	[Total Fe]	[Na ⁺¹]	[SO ₃ ⁻²]	[SO ₄ ⁻²]	[Cl ⁻¹]	Filtercake
Time		Tank	(ppm)	as analyzed	(mM)	adjusted for	by IC	by IC	by ICP	by ICP	by ICP	by ICP	by IC	by IC	by IC	Solids
(Hr: Min)		Liquor		(ppm)		[Fe ⁺²] _{Rxn}	(mM)	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(wt %)
		pH				(ppm)										
10:15	44	6.4	3369	7574	33.8	6222		0.12	3707	108.0	1909	70.5	5185	4605	80	
11:00	44	6.3	3153	9896	20.8	9064	2.27	0.75	4482	88.6	2327	21.0	7790	4540	580	
12:00	44	6.1	3019	10072	8.2	9744	2.57	1.86	4452	79.6	2282	39.8	8836	4556	202	66.1
13:00	44	6.2	3303	9904	6.7	9636	4.61	2.70	4557	77.9	2242	36.9	8938	4482	162	61.3
14:00	44	6.2	3403	9832	5.0	9632	7.02	3.31	4849	82.1	2319	36.7	9158	4826	116	62.0
15:00	44	6.1	3453	9671	4.3	9499	9.73	3.52	5075	106.4	2338	45.8	8564	4688	80	60.7
Six pts. avg:		6.22	3283			8966			4520	90.4	2236	41.8	8079	4616	203	

4. Variable Flue Gas Oxygen Content

a) 5 kW Configuration

The 5 kW was configured identical as the non-packed mode runs with the flue gas oxygen concentration at 3 and 12 vol.% respectively. The layout is shown on Figure 3.

b) Test Results

For test DT120194 (non-packed mode, ~50 mM initial total iron concentration, recycle tank pH = 6.9, L/G = 44, 3 vol.% O₂) SO₂ removals were greater than 99% after 20 minutes of testing and remained high throughout the test run. SO₂ removal for test DT120594 (non-packed mode, ~50 mM initial total iron concentration, recycle tank pH = 6.9, L/G = 44, 12 vol.% O₂) was greater than 99% after 15 minutes and remained at this level for the duration of the test. The SO₂ removal curves for both tests are shown in Figures 25 and 26. It is interesting that the overall drop in NO_x removal for the run with low O₂ concentration was 10% compared with a 28% drop in NO_x removal for the test with an O₂ concentration of 12 vol.%. This is shown in Figures 27 and 28. The final NO_x removal was 38% at 3 vol.% O₂ with the NO_x removal curve leveling off the last 30 minutes of testing. For the test conducted at 12 vol.% O₂ concentration the final NO_x removal was 16% with the NO_x removal curve leveling off the last 20 minutes of testing. The higher oxygen concentration in the synthetic flue gas leads to a more rapid decay of the NO_x removal curve than that observed with a lower oxygen concentration. For this reason it is not surprising that the drop in ferrous ion concentration was more significant for test DT120594 (12 vol.% O₂ level) than for test DT120194 (3 vol.% O₂ level). The drop in ferrous ion concentration was nearly 14% during the first hour of testing for test DT120194 and 17% during the first hour for run DT120594. After the first hour of testing for

run DT120194, the decrease in ferrous ion concentration was slow with time. The decrease in ferrous ion concentration for run DT120594 was also gradual after the first hour of testing. The final ferrous ion concentration was 18 mM for DT120194 and 2.1 mM for test DT120594. These results are illustrated in Figures 29 and 30. This result suggests that the oxygen concentration in the flue gas increases the decay rate of ferrous ion in solution.

The sodium ion concentration was higher for test DT120194 (>100 ppm) than for test DT120594 (<50 ppm) as shown in Tables 6 and 7. The sulfite concentration averaged nearly 7,000 ppm for test DT120194 and approximately 5,416 ppm for test DT120594. Both these concentrations are in the range of normal ThioNO_x operation. For each of the tests, the sulfite concentrations were fairly constant. The magnesium concentration was fairly steady for test DT120194 averaging 5,227 ppm. For test DT120594, the magnesium concentration slowly increased averaging 5,000 ppm. The alkalinities were similar for each test averaging 4,400 ppm. Both tests exhibited standard chemistries for a ThioNO_x system. Because no regeneration methods were used for these tests, the filtercake solids content was below 70% for both tests. This is not unusual for a baseline test. The correlation coefficients of the data points to the NO_x removal model was 0.8100 for test DT120194 and 0.99014 for test DT120594. This is shown in Figures 31 and 32.

c) Attainment of Objectives

The goal of determining whether the flue gas oxygen concentration had an effect on ferrous ion decay was met. The ferrous ion decays more slowly as the flue gas oxygen concentration decreases. It was anticipated before testing that the oxygen concentration would play a role in influencing the ferrous ion decay rate. During regeneration methods testing control of the oxygen concentration in the flue gas will have to be exercised to eliminate its control on the steady state NO_x removal. This will make comparisons between test results more accurate.

Figure 25. SO₂ concentration and removal vs. time

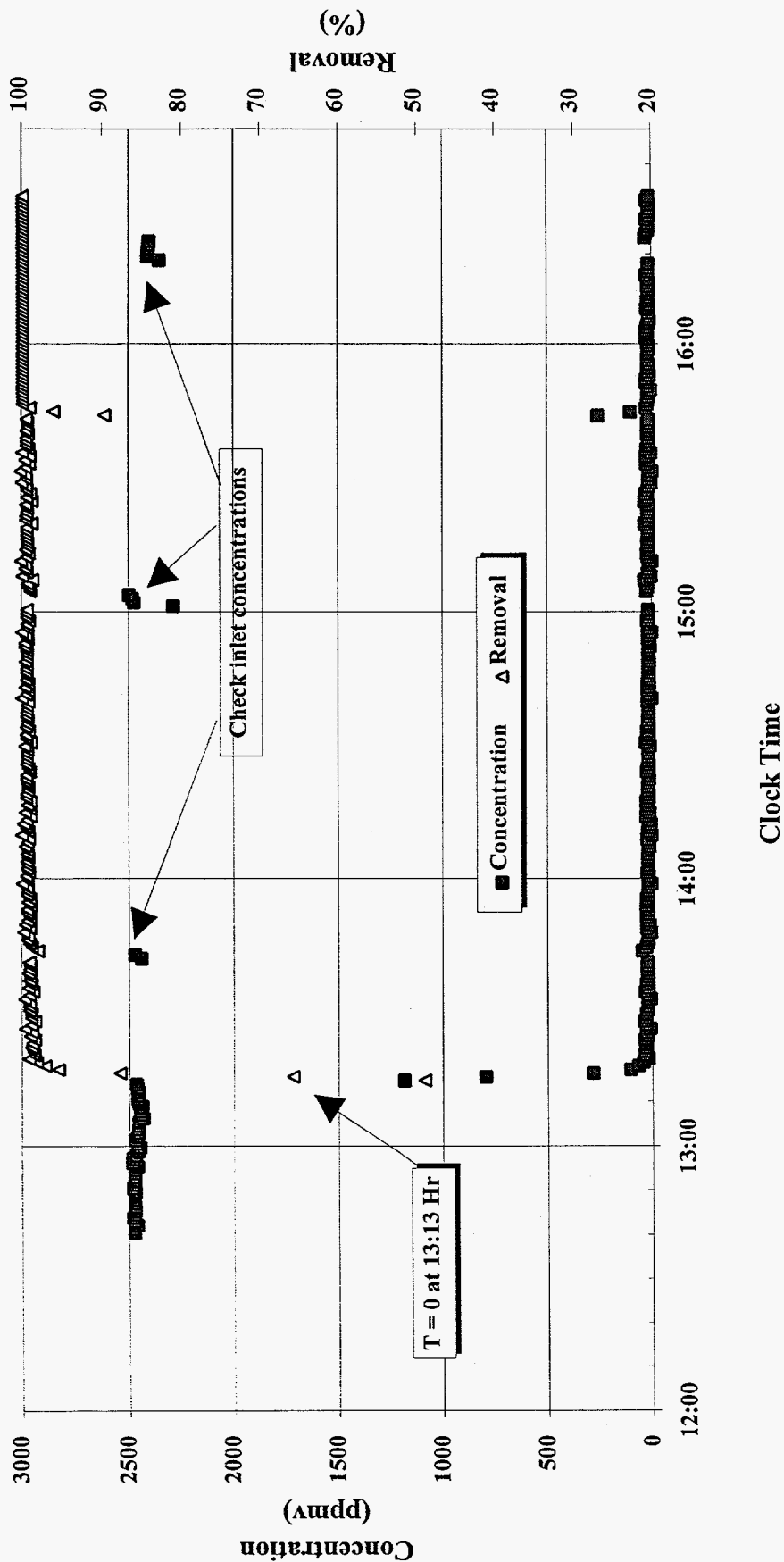


Figure 26. SO₂ concentration and removal vs. time

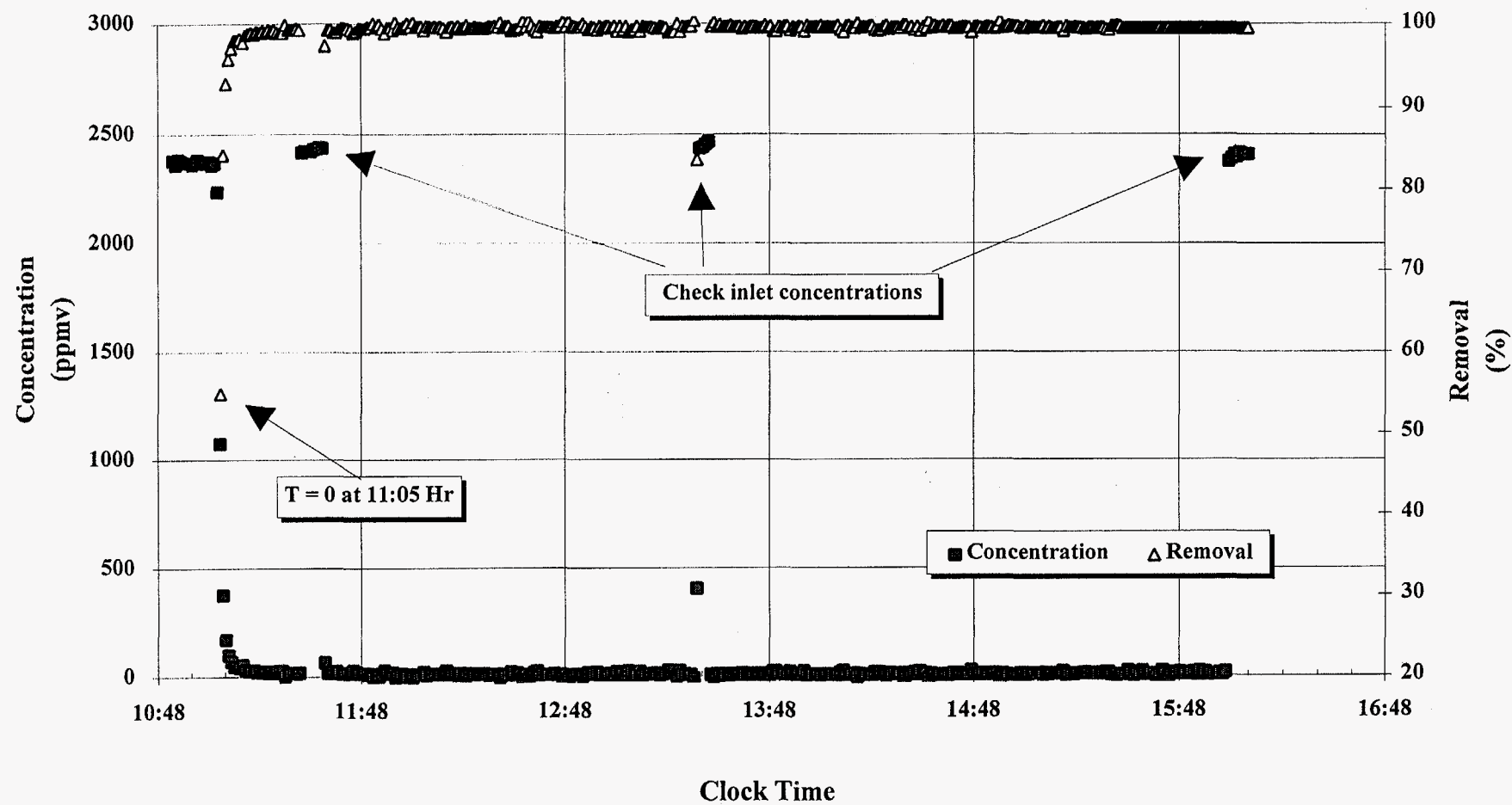


Figure 27. NO concentration and removal vs. time

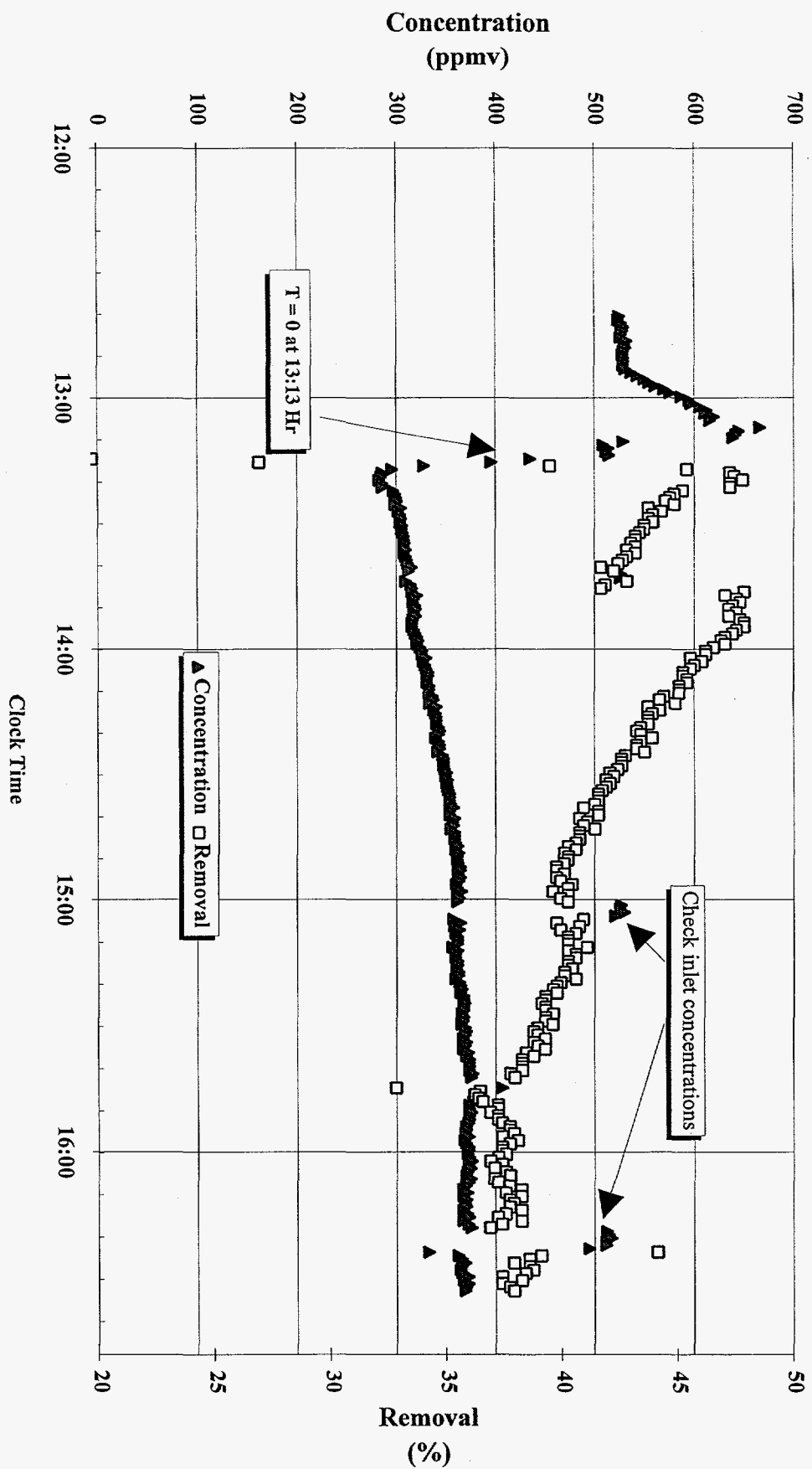


Figure 28. NO concentration and removal vs. time

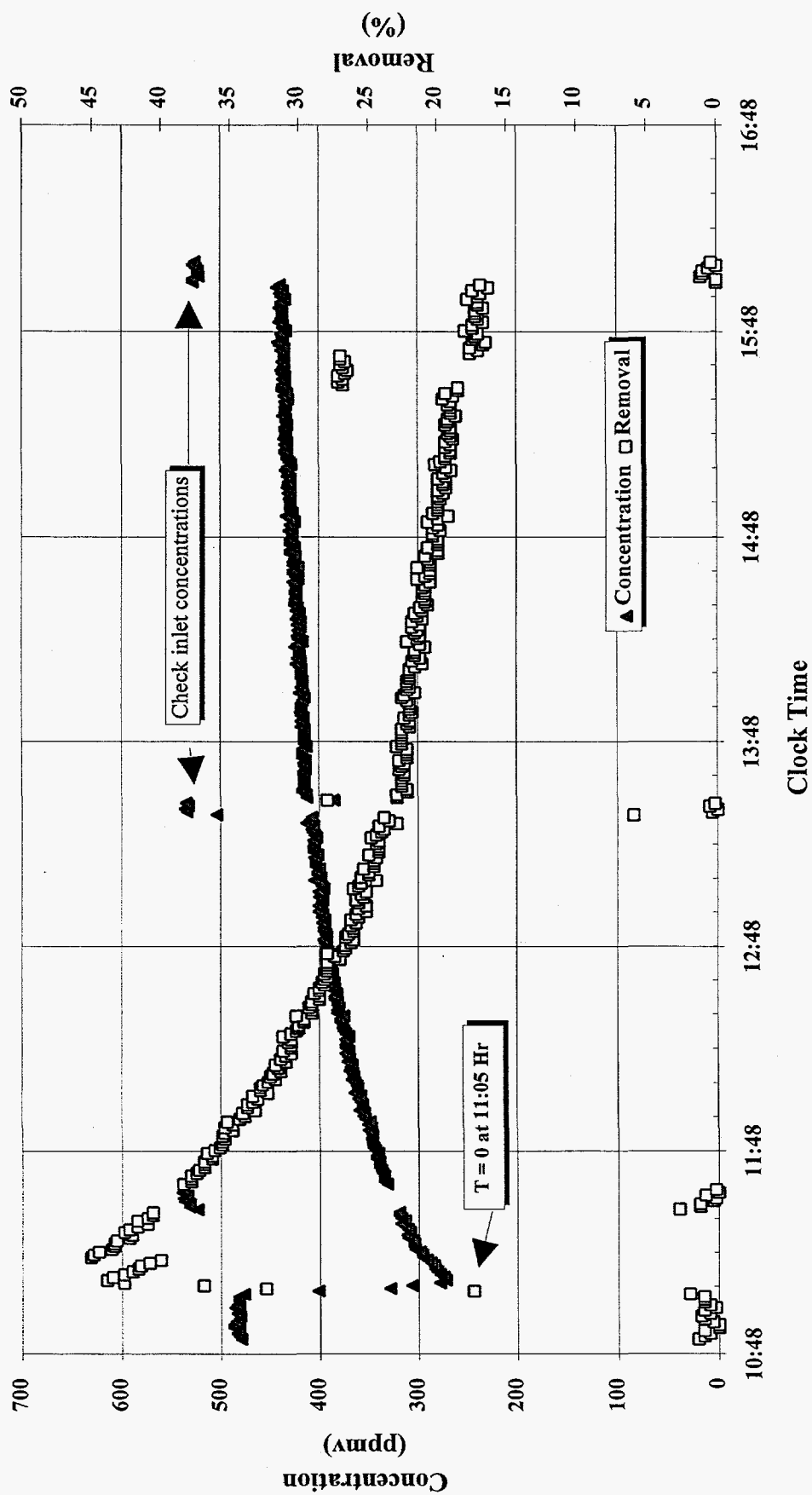


Figure 29. Change of recycle tank liquor $[\text{Fe}^{+2}]$ with respect to time

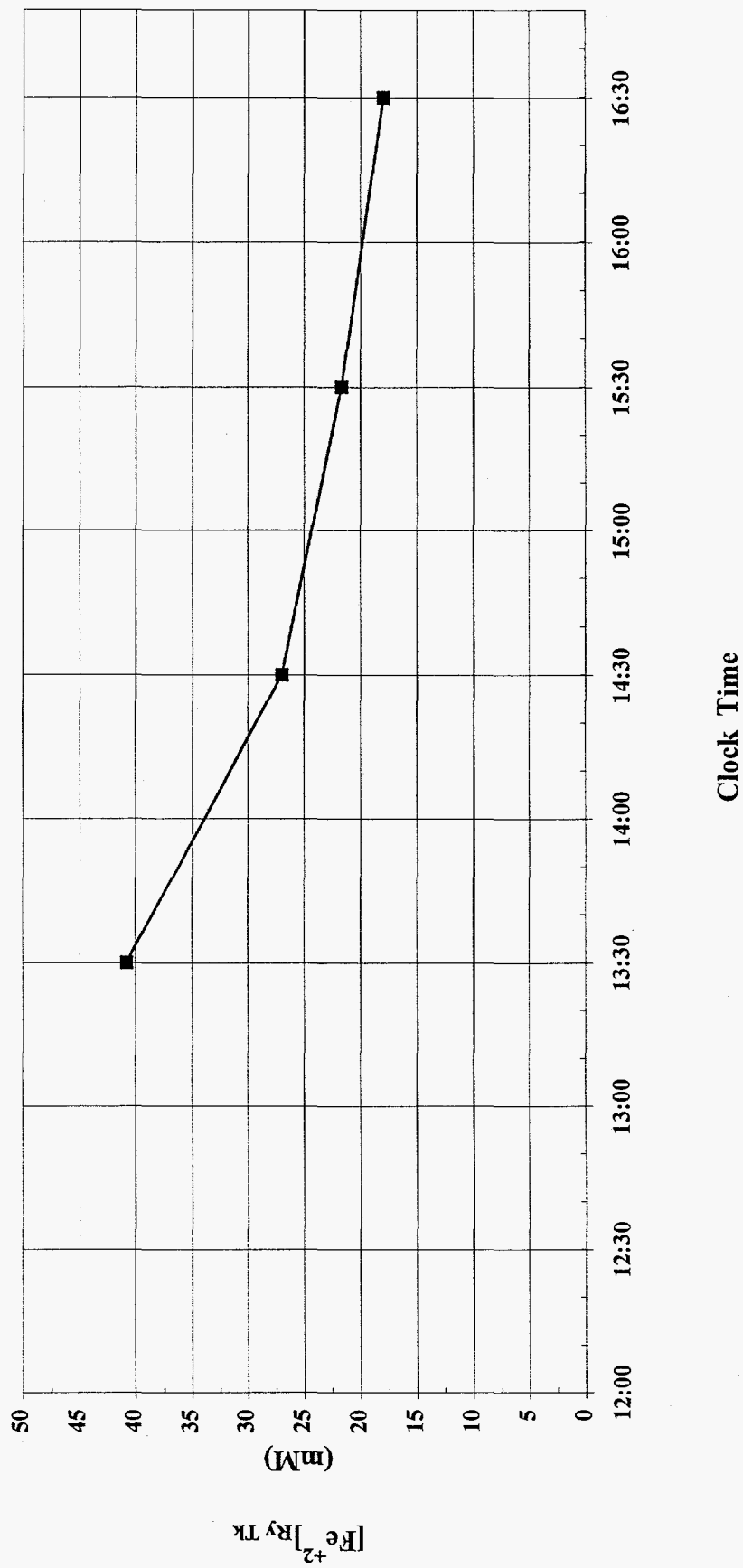


Figure 30. Change of recycle tank liquor $[\text{Fe}^{+2}]$ with respect to time

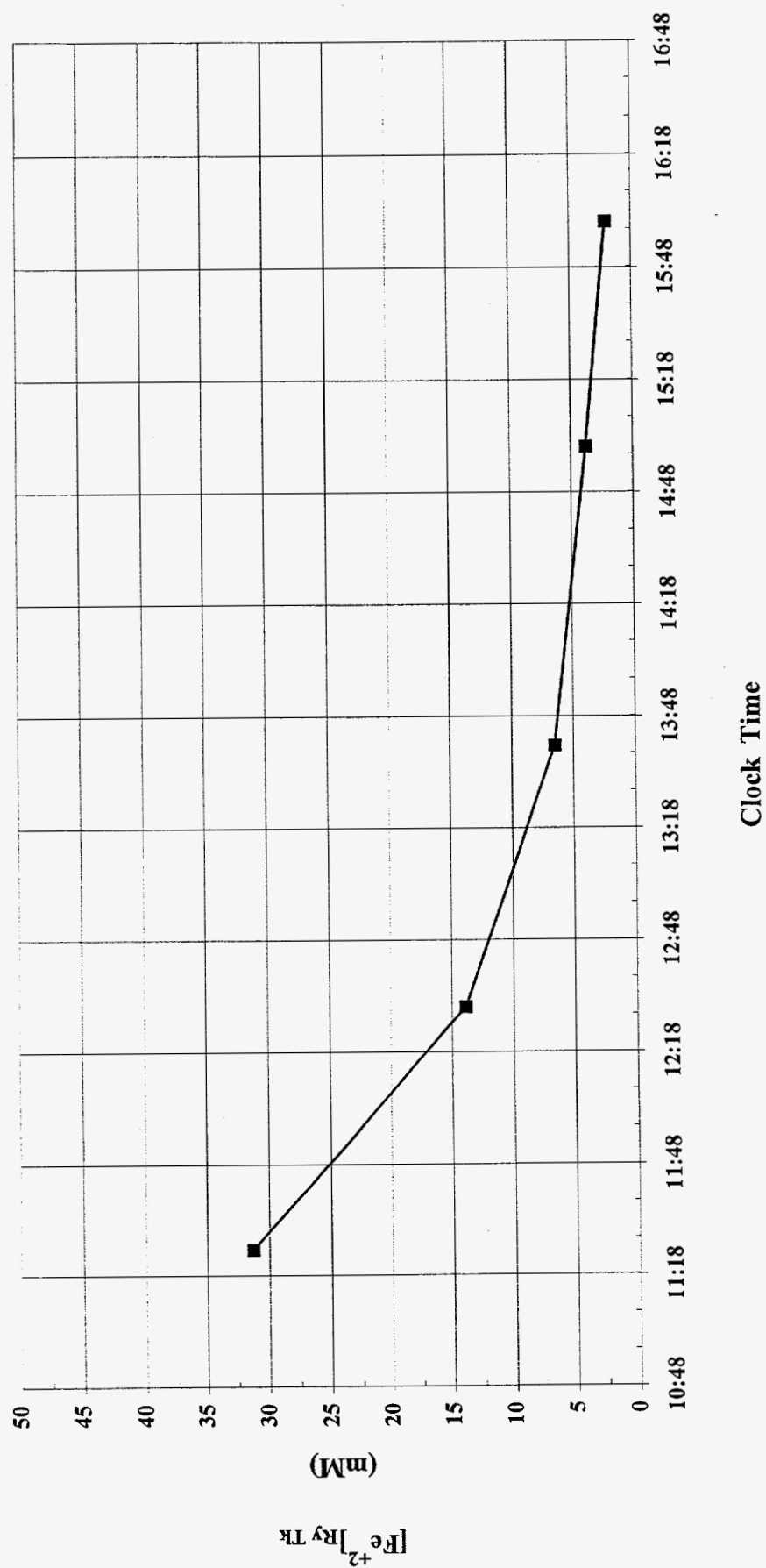


Figure 31. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

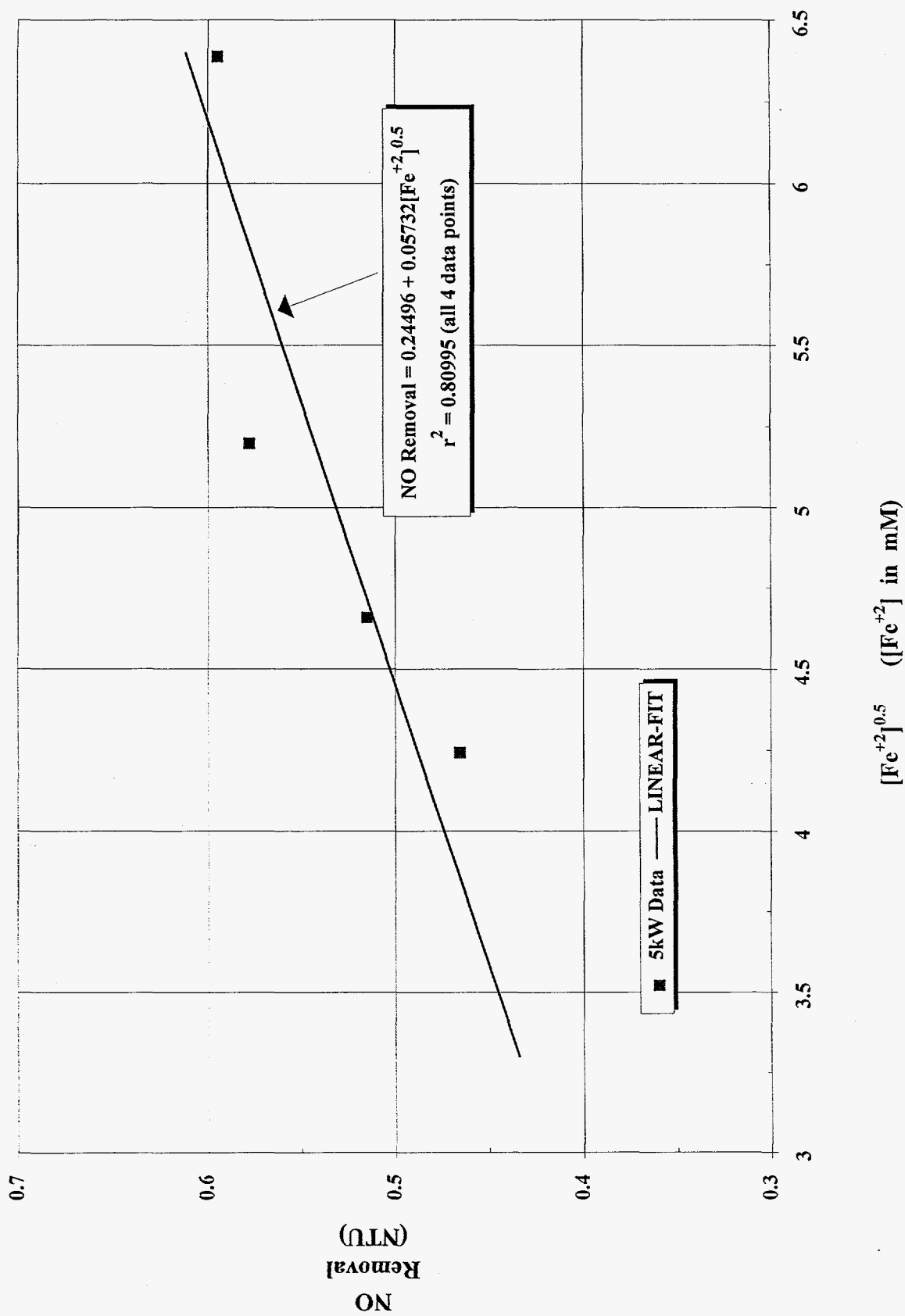


Figure 32. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

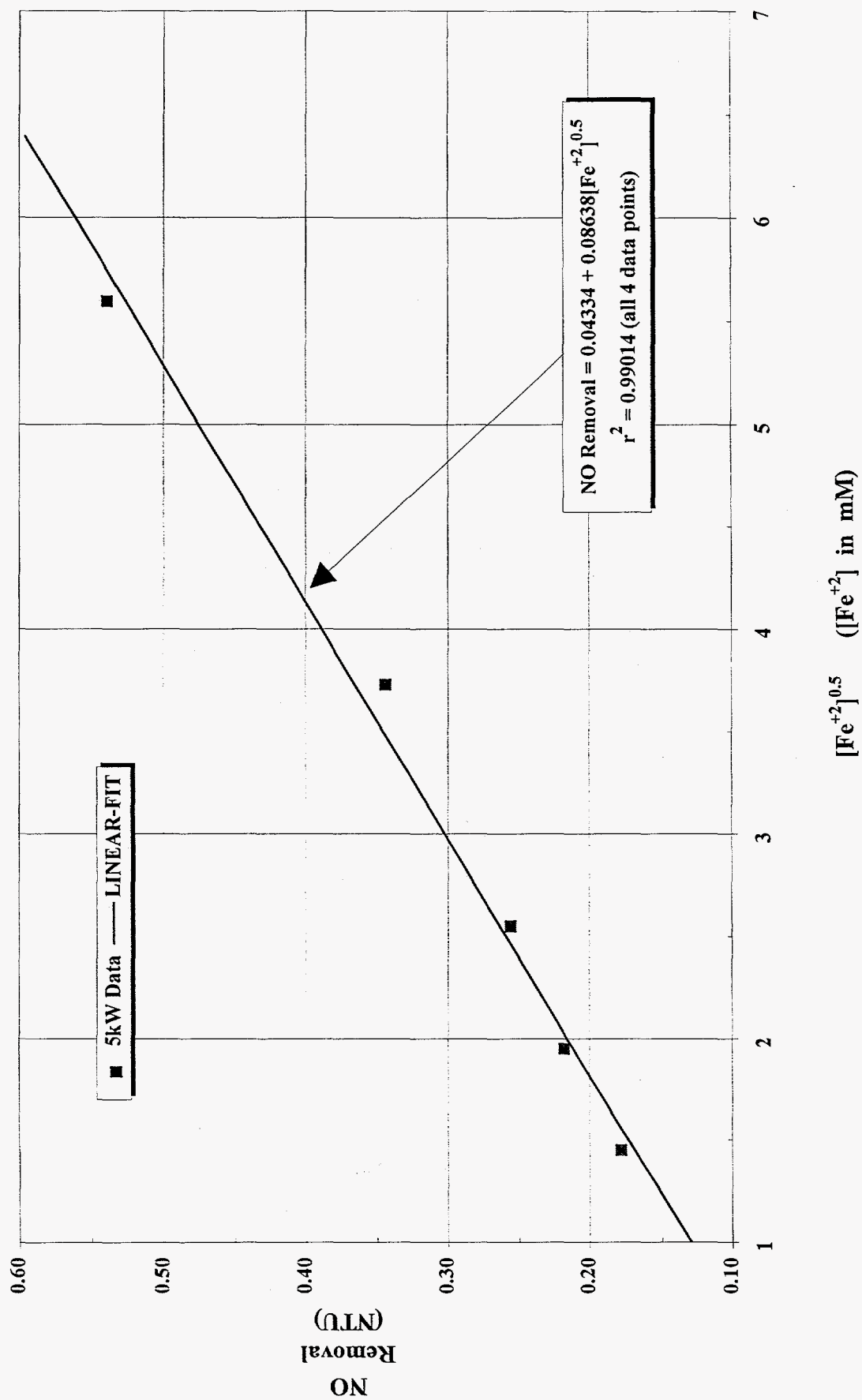


Table 6. Chemistry Data

Clock	L/G	Recycle	Alkalinity	[S ₂ O ₃ ²⁻] by	[SO ₃ ²⁻] by	[Fe ²⁺] _{by tit}	[SO ₃ ²⁻]	[ADS]	[SA]	[S ₂ O ₃ ²⁻]	[Mg ²⁺]	[Ca ²⁺]	[Total Fe]	[Na ⁺]	[SO ₃ ²⁻]	[SO ₄ ²⁻]	[Cl ⁻]	Filtercake
Time		Tank	(ppm)	I ₂ -titration	I ₂ -titration	by Spec 20	adjusted for	by IC	by IC	by IC	by ICP	by ICP	by ICP	by ICP	by IC	by IC	by IC	Solids
(Hr. Min)		Liquor		(ppm)	(ppm)	(mM)	[S ₂ O ₃ ²⁻] &	(mM)	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(wt %)
		pH					[Fe ²⁺]											
							(ppm)											
13:30	44	6.90	4237	202	8503	40.8	5095	n.d.	1.66	64	5088	208	2992	124	7132	5663	80	n.d.
14:30	44	7.10	4454	75	8006	27.0	5792	0.32	1.16	51	5059	128	3064	131	6539	5272	78	65.0
15:30	44	7.00	4570	1456	8210	21.7	5434	1.27	1.71	56	5338	107	3198	142	6664	4963	88	68.6
16:30	44	6.80	4737		8334	18.0	6894	1.94	2.19	59	5422	108	3101	114	7485	5504	93	62.5
4-pt avg:							5804								6955			

Table 7. Chemistry Data

Clock	L/G	Recycle	Alkalinity	[SO ₃ ⁻²] by	[Fe ⁺²]	[SO ₃ ⁻²]	[ADS]	[SA]	[S ₂ O ₃ ⁻²]	[Mg ⁺²]	[Ca ⁺²]	[Total Fe]	[Na ⁺¹]	[SO ₃ ⁻²]	[SO ₄ ⁻²]	[Cl ⁻¹]	Filtercake
Time		Tank	(ppm)	I ₂ -titration	by Spec 20	adjusted for	by IC	by IC	by IC	by ICP	by ICP	by ICP	by ICP	by IC	by IC	by IC	Solids
(Hr: Min)		Liquor		(ppm)	(mM)	[Fe ⁺²]	(mM)	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(wt %)
		pH				(ppm)											
11:25	44	7.3	3936	9125	31.3	6621	0.64	n.d.	n.d.	4658	116	2654	31				
12:30	44	7.0	4470	8990	13.9	7878	1.43	0.18	n.d.	4768	163	2700	21	5175	4281	134	55.4
13:40	44	6.8	4237	8668	6.5	8148	3.67	0.31	n.d.	4917	127	2697	35	5904	4880	147	61.1
15:00	44	6.7	4470	8265	3.8	7961	6.31	0.33	n.d.	5129	140	2690	35	5341	5070	139	60.9
16:00	44	6.8	4620	7740	2.1	7572	8.74	0.41	n.d.	5373	158	2730	36	5244	5476	165	61.8

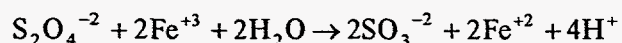
B. Chemical Regeneration Agents

1. Sodium Dithionite / Ascorbic Acid

a) 5 kW Configuration

The screening tests conducted under project 5253 were anticipated to be potentially less expensive on a mM ferrous ion concentration and NTU removal basis than this mixture of regeneration agents. To accurately assess the consumption economics for the regeneration methods, the consumption economics for sodium dithionite / ascorbic acid had to be well defined. Hence, two tests were carried out at different oxygen concentrations in the synthetic flue gas to ascertain a typical cost on a mM ferrous ion concentration and NTU removal basis.

Tests DT021496 (packing mode, ~100 mM initial total iron concentration, recycle tank pH = 6.0, L/G = 90, 10.3 vol.% O₂) and DT021696 (packing mode, ~100 mM initial total iron concentration, recycle tank pH = 6.0, L/G = 90, 6.0 vol.% O₂) were carried out with the mixture sodium dithionite / ascorbic acid. The agent was added directly to the recycle tank in ~5:1 weight mixture sodium dithionite to ascorbic acid. The consumption rate of sodium dithionite was 60 g/hr and 13.2 grams ascorbic acid/hr for test DT021496. For test DT021696, the consumption rate was 40 grams sodium dithionite/hr and 8 grams ascorbic acid/hr. Because many of the regeneration tests were run with packing in the absorber, both these tests were conducted with packing. A schematic of the process flow is shown in Figure 33. The ascorbic acid acts as an ferrous ion oxidation inhibitor while the reaction believed to occur with dithionite is as follows:



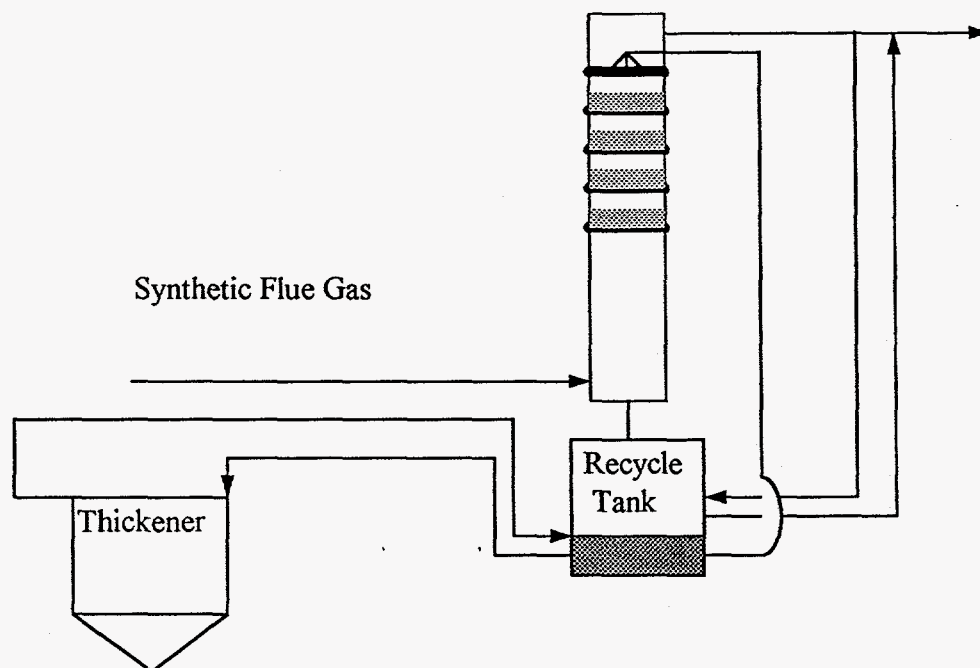


Figure 33. Solids Addition 5 kW Configuration

b) Test Results

Test DT021496 shows the SO_2 removal reached after 60 minutes of testing. The SO_2 removal continued to increase after this period. The removal curve is shown in Figure 34. The NO_x removal was between 50% and 60% the last 3 hours of testing demonstrating the regeneration ability of this mixture. As expected, the steady state ferrous ion concentration was high averaging ~ 70 mM. At ferrous ion concentrations this high, the NO_x removal should be high. The NO_x removal and ferrous ion concentration curves are shown in Figures 35 and 36.

Not surprisingly, the sodium ion displayed an increasing trend as testing progressed, as shown in Table 8. High sodium ion concentrations can result in an interference in the operation of the recycle tank pH probe. The magnesium ion concentration was in the normal range for a Thio NO_x process while the calcium ion concentration was slightly elevated. However, the calcium ion concentration displayed a decreasing trend with run time so that by the end of testing the calcium

ion concentration was less than 250 ppm. One of the benefits from adding dithionite is that one of the products of the regeneration reaction is sulfite which helps maintain high alkalinity. The sulfite ion concentration exhibited an increasing trend from 8,011 ppm at the beginning of testing to 10,925 ppm by the end of testing. The solids content of the filtercake increase from 72.2 wt.% at the beginning of testing to 77.0 wt.% at the end of testing. This is a typical solids content when a regeneration agent is used. The correlation of the data points to the NO_x removal model was low for this test ($r^2 = 0.03533$). This is depicted in Figure 37.

The SO_2 removal for test DT021696 increased rapidly to 99% and stayed at this level for the duration of testing. This is shown in Figure 38. The high SO_2 removal can be attributed to a liquid to gas ratio of 90. The steady state NO_x removal was between 50% and 60%. This high NO_x removal can be explained by a high ferrous ion concentration at steady state. The steady state ferrous ion concentration was ~45 mM. The NO_x removal and ferrous ion concentration curves are shown in Figures 39 and 40.

Like test DT021496, the sodium ion concentration increased significantly during testing as shown in Table 9. This is not surprising since sodium ion was added to the system. A continued increase in sodium ion concentration will lead to increased sulfite ion concentrations since the positive charge associated with sodium ion must be balanced by the negative charge of the sulfite ion. In addition, sulfite ion is one of the products of the regeneration reaction with dithionite. Thiosulfate ion exhibited an increasing trend since dithionite and sulfite ion react to form thiosulfate. Because of the increasing anion concentration the calcium ion concentration is slightly elevated with values above 200 ppm. The solids content of the filtercake increased from 68.8 wt.% at the beginning of testing to 76.4 wt.% at the end of the test. During the initial part of testing, the solids content displayed a rapid increase followed by a steady solids content, for the remainder of the test.

The solids content of 75.6 wt.% achieved during steady state represents a typical value when a regeneration method is employed.

The correlation to the NO_x removal model was low (<0.500) as depicted in Figure 41. The mathematical model for NO_x removal does not account for regeneration of ferrous ion. The activity coefficient for ferrous ion concentration can not be taken as unity in this particular case.

c) Economics

These two tests were performed in order to compare the consumption economics of other regeneration methods to the cost associated with the sodium dithionite / ascorbic acid mixture since one of the principle goals is to find regeneration methods more cost effective than sodium dithionite / ascorbic acid. A 5:1 weight mixture of sodium dithionite / ascorbic acid is an expensive agent at \$1.78/lb_m. The cost of a 5:1 weight mixture of sodium dithionite / ascorbic acid on a mM ferrous ion concentration and NTU removal basis was found to be \$0.01332/day·mM Fe^{2+} ·vol.% O_2 and \$0.9954/day·NTU·vol.% O_2 , respectively. Obviously, it was hoped that regeneration methods could be found which were more economical than this mixture.

d) Attainment of Objectives

The economics associated with a 5:1 weight mixture of sodium dithionite / ascorbic acid was determined. This would allow a comparison with other regeneration methods. Ideally, the selection of a regeneration method would depend primarily if it was more cost effective than sodium dithionite / ascorbic acid. The liquor chemistry would also have to exhibit typical ion concentrations. For sodium dithionite / ascorbic acid, sulfite and sodium ion concentrations were becoming elevated. Sulfite ion concentration increases could lead to precipitation

if calcium ion concentration increases. Sodium ion may cause erroneous measurements indicated by the pH probes of the process liquor.

Figure 34. SO₂ concentration and removal vs. time

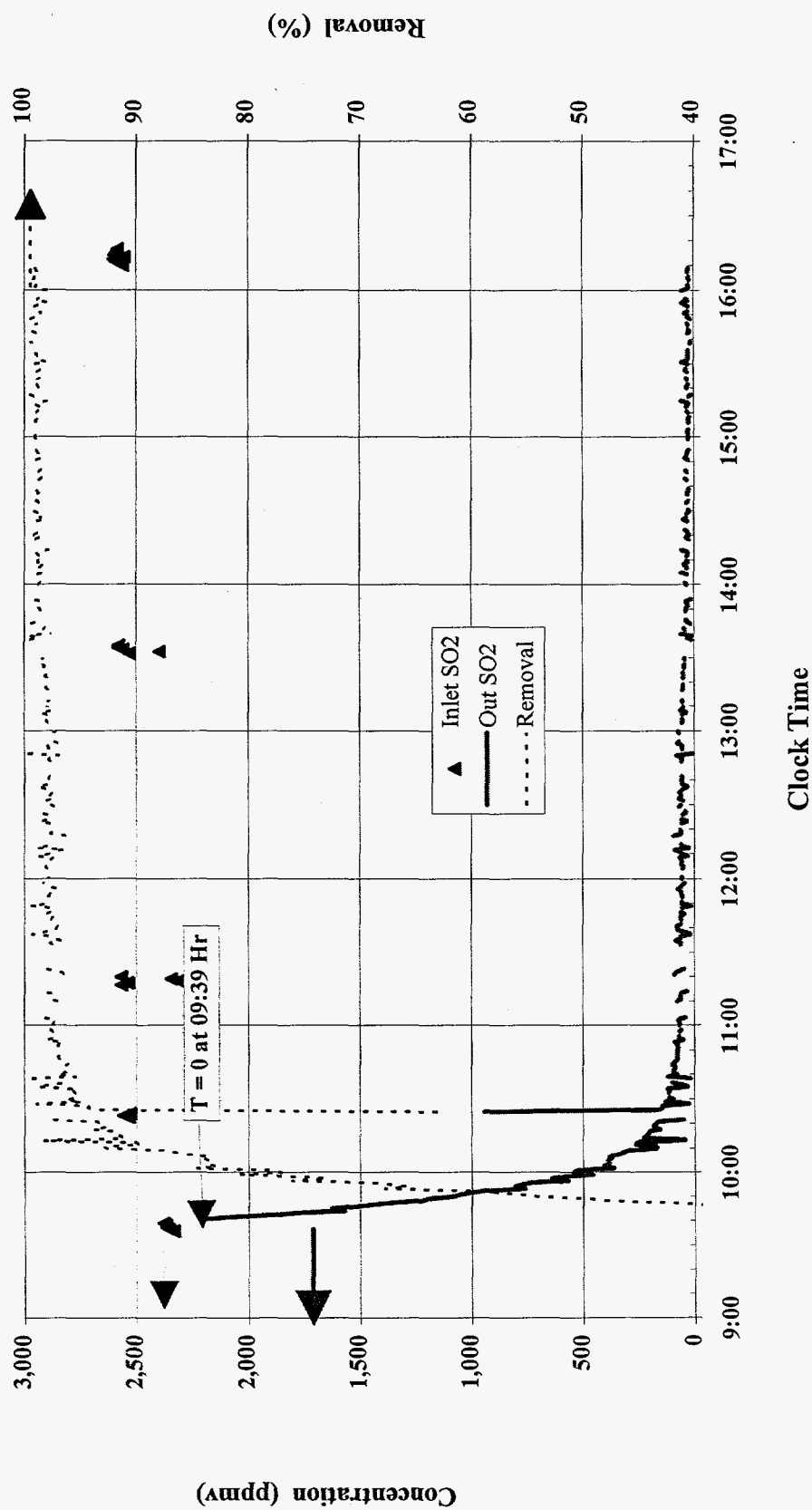
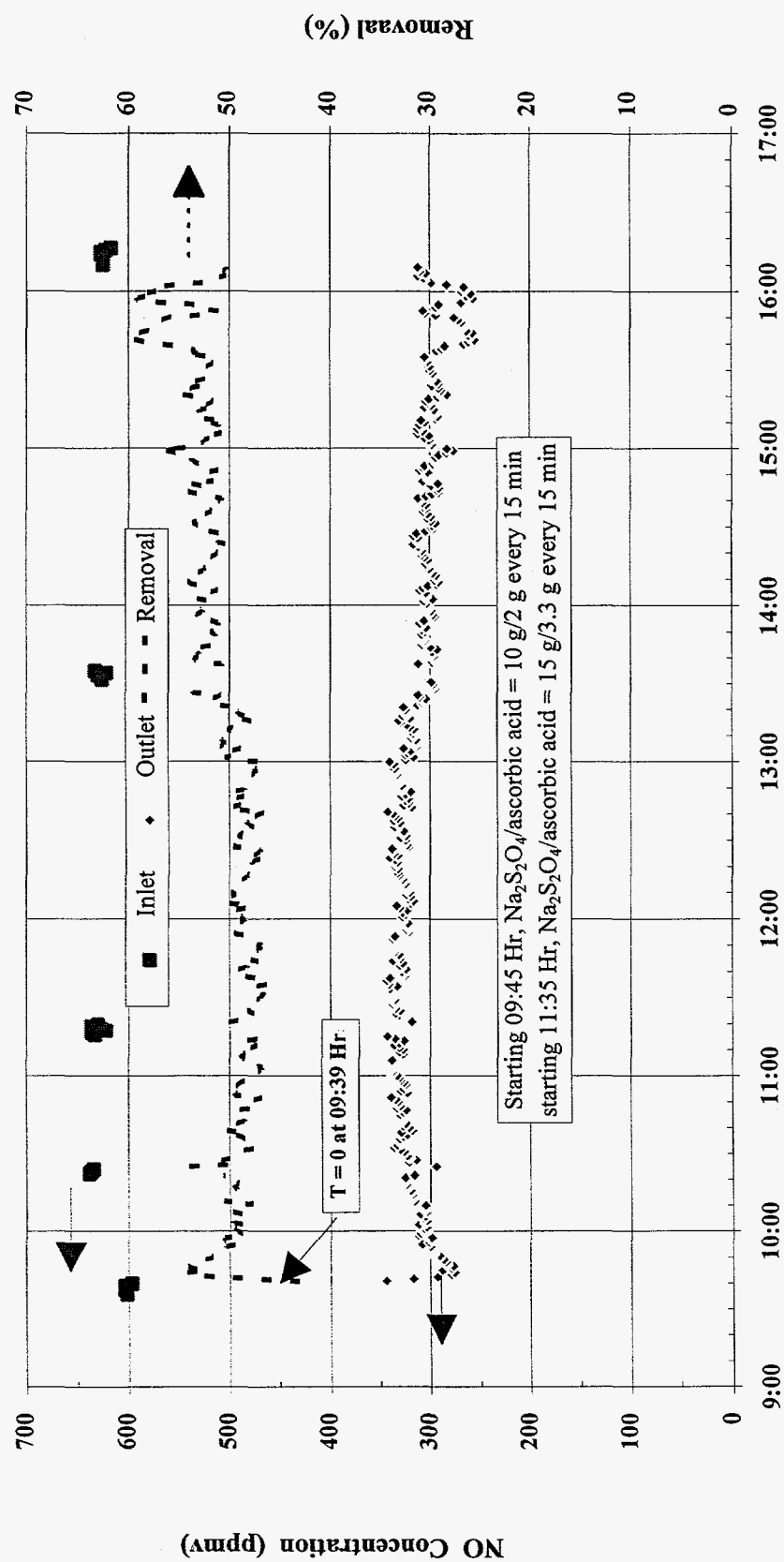


Figure 35. NO concentration and removal vs. time



Clock Time

Figure 36. Change of recycle tank liquor $[\text{Fe}^{+2}]$ and NO removal

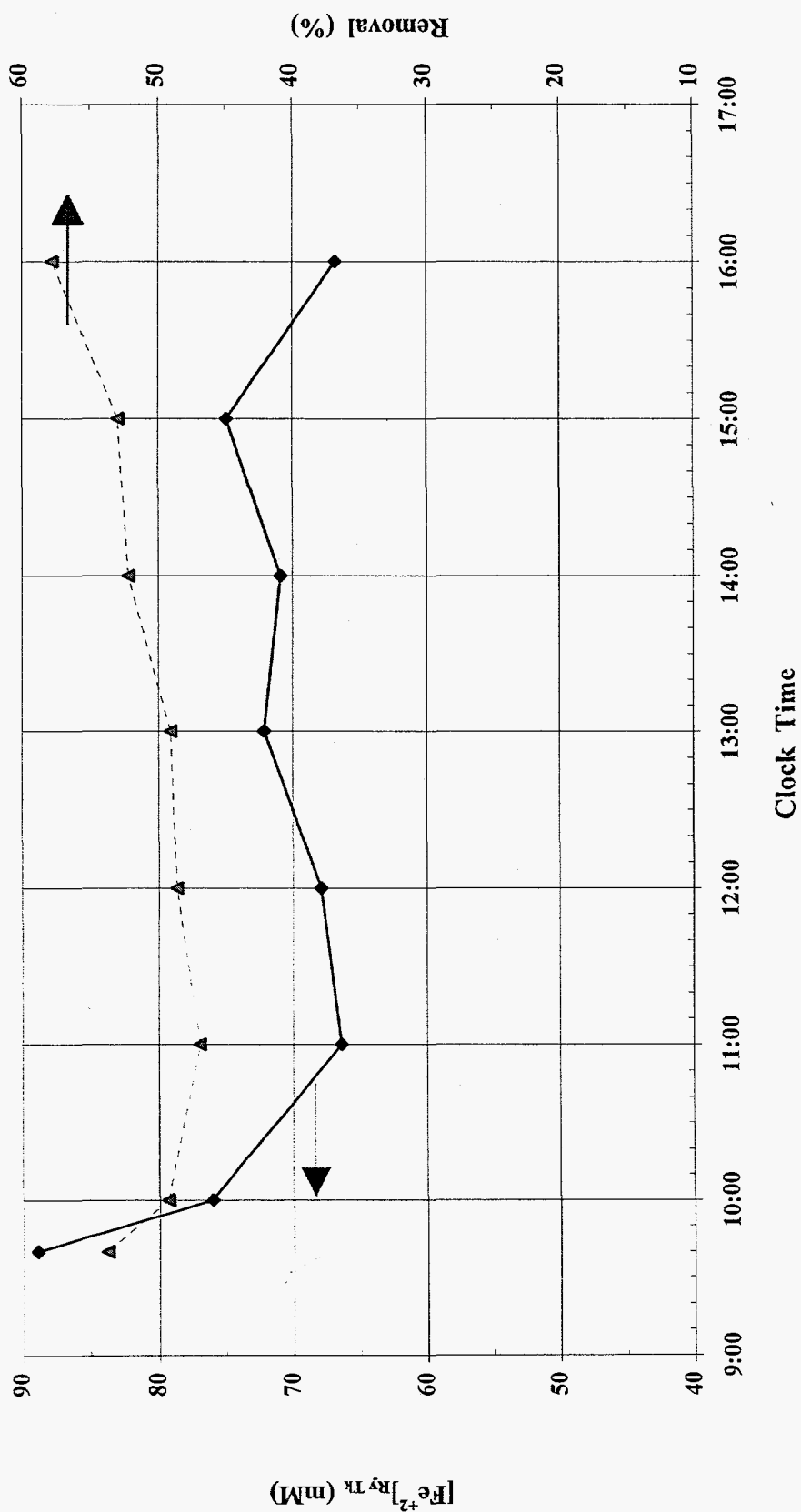


Figure 37. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

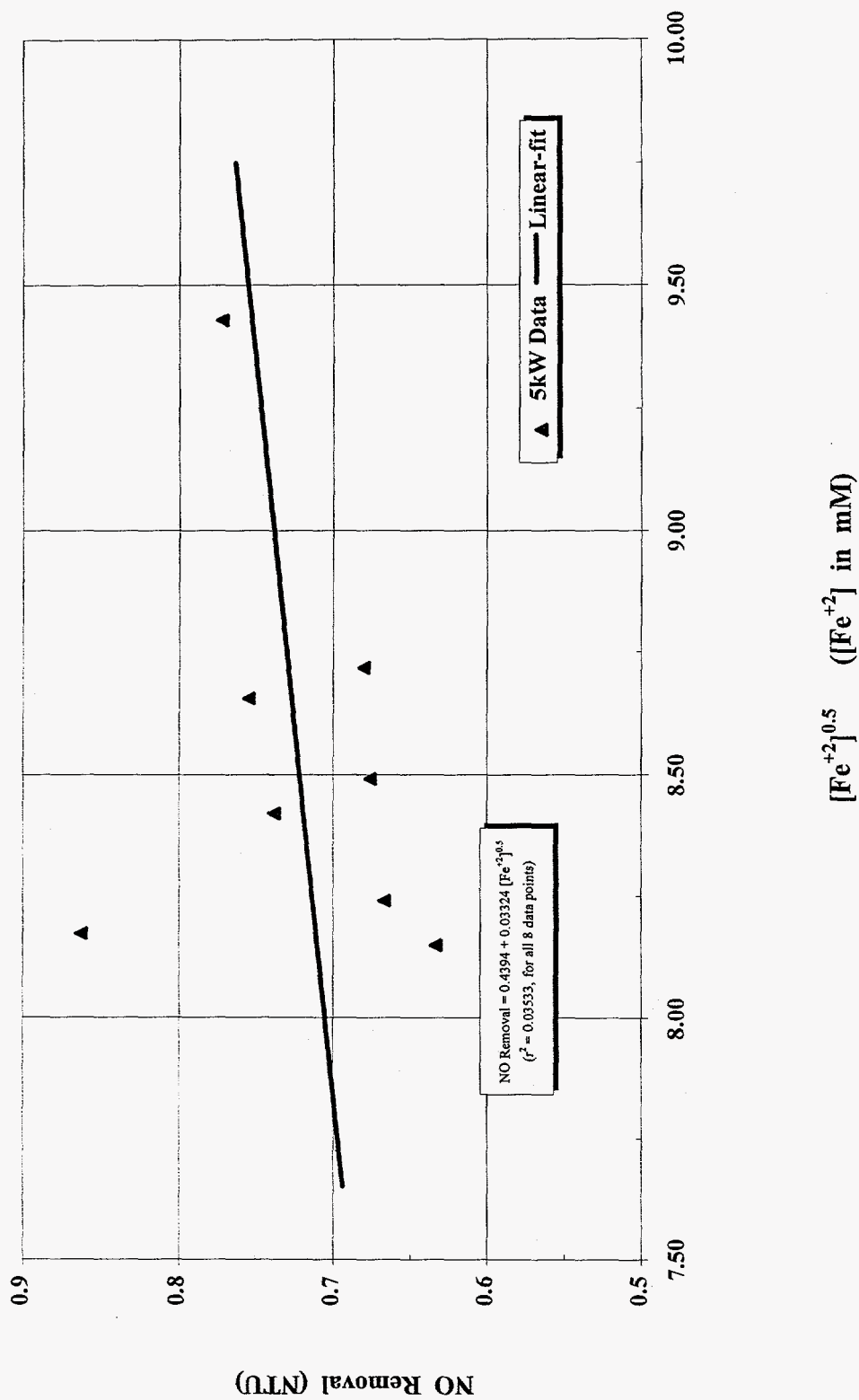


Figure 38. SO₂ concentration and removal vs. time

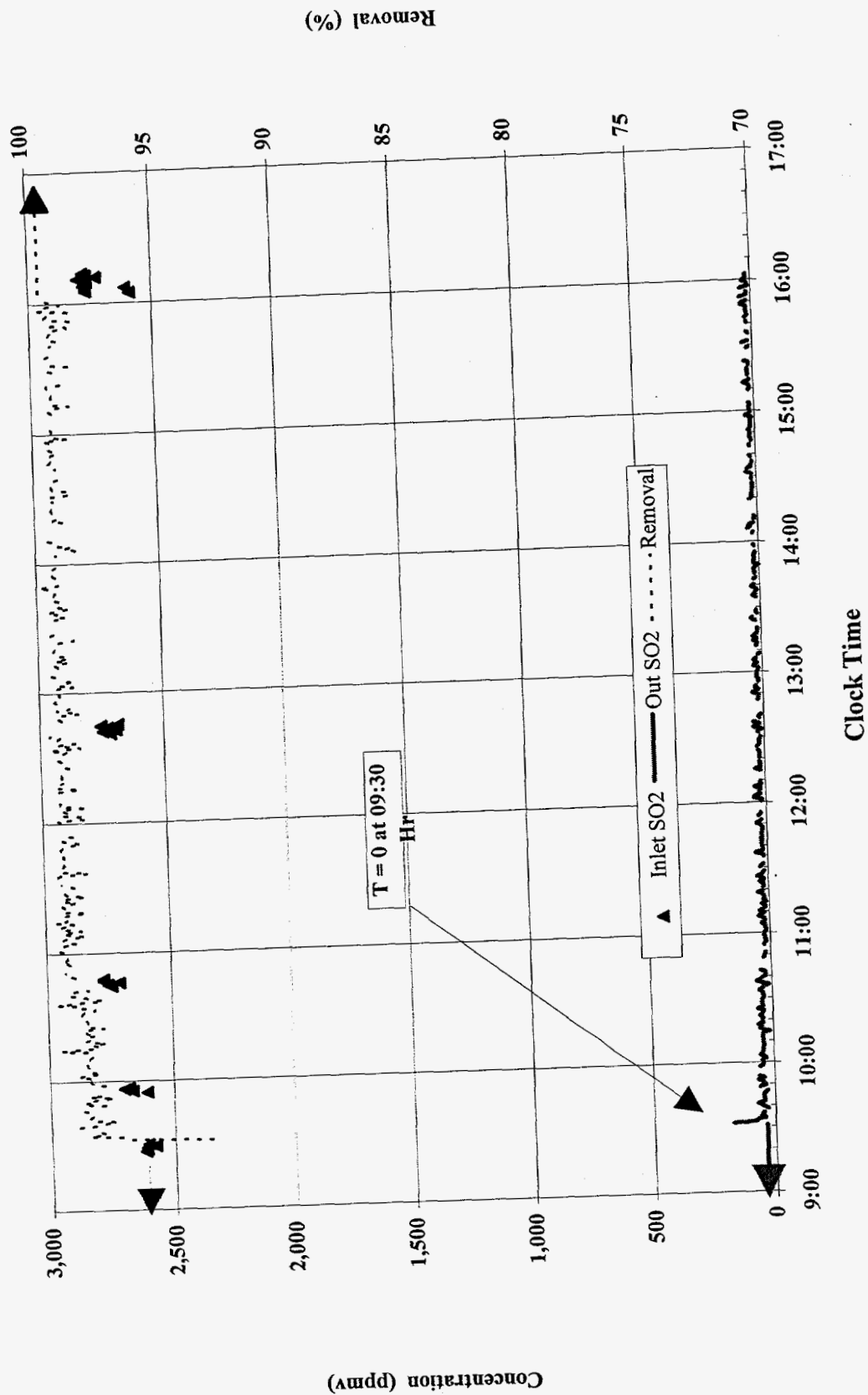
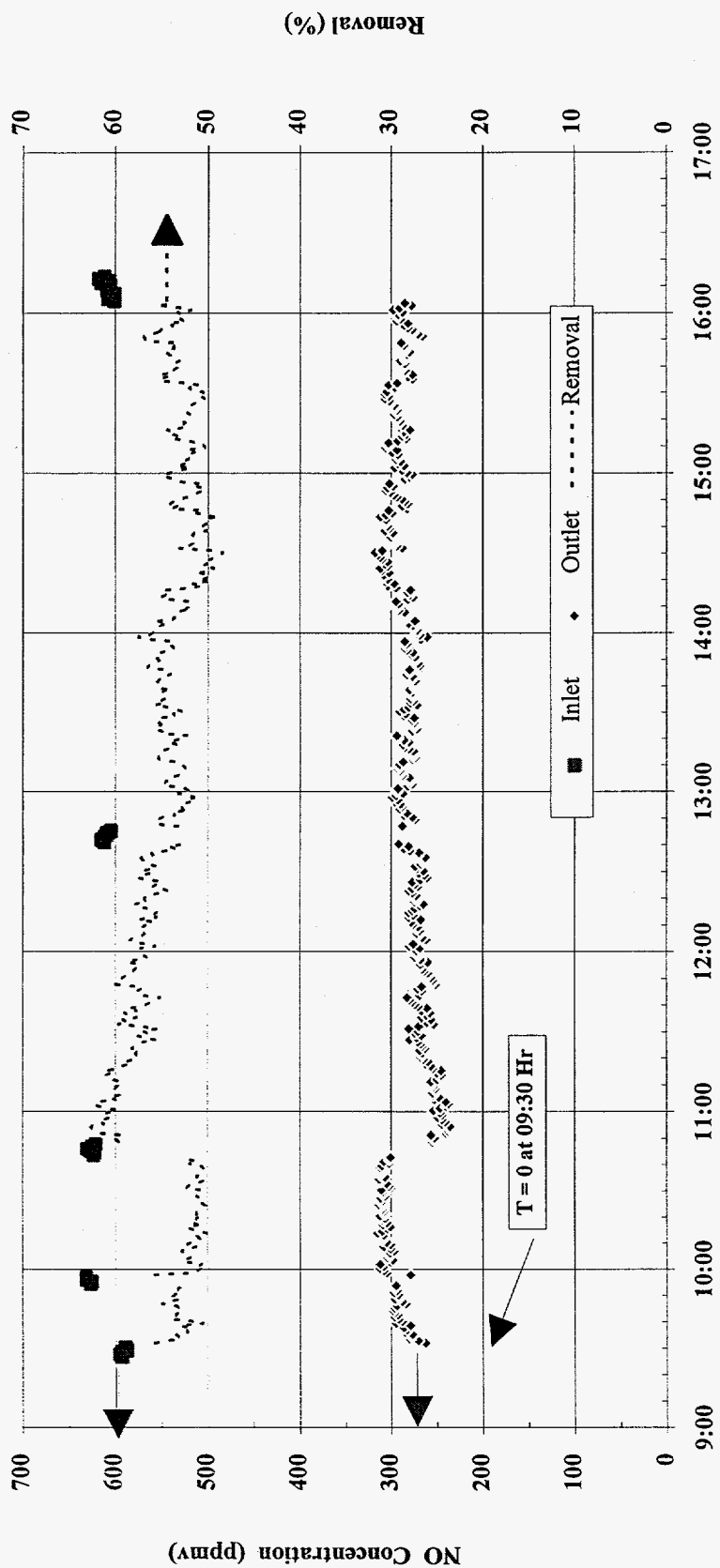


Figure 39. NO concentration and removal vs. time



Clock Time

Figure 40. Change of recycle tank liquor $[\text{Fe}^{+2}]$ and NO removal

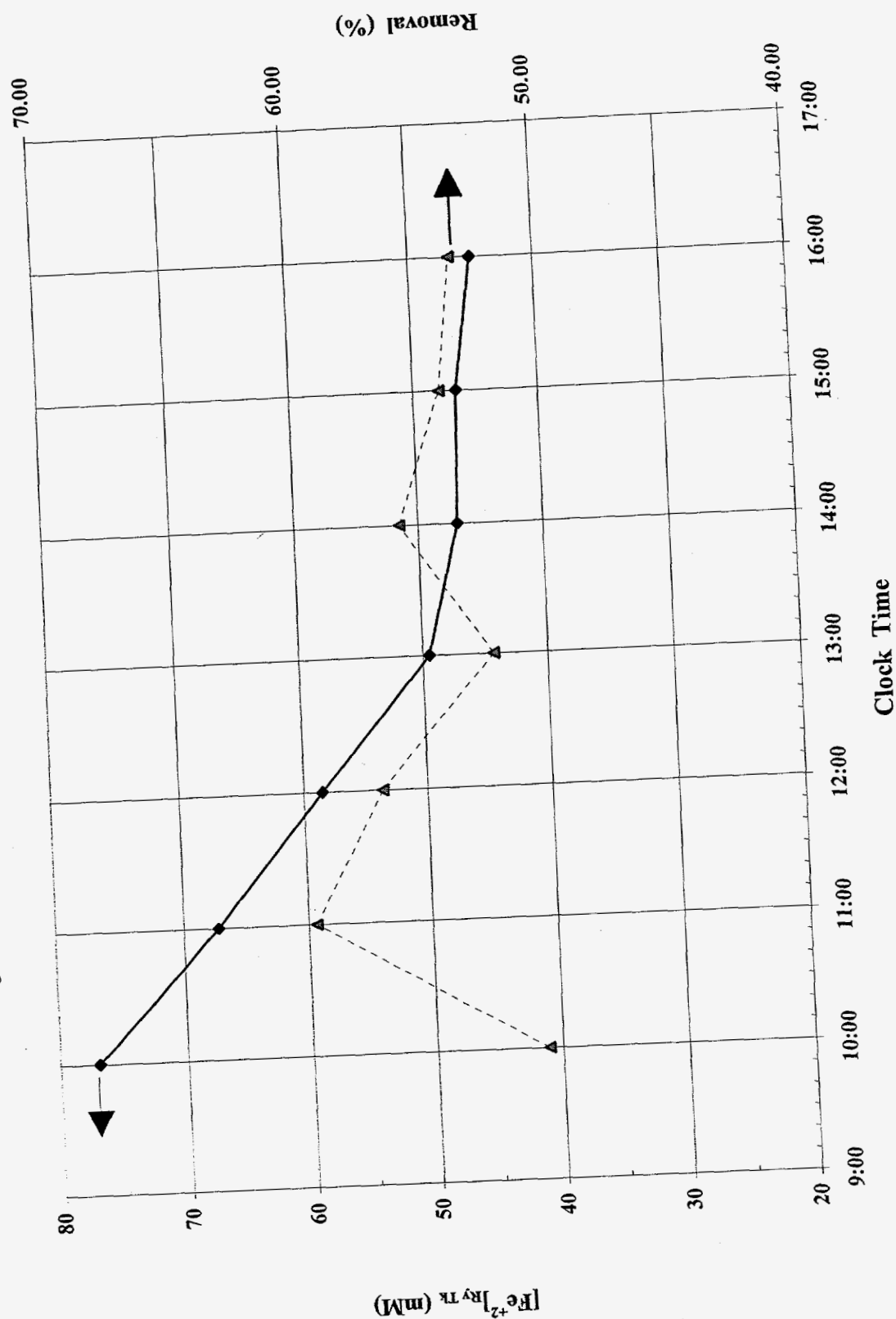


Figure 41. NO removal in $[\text{Fe}^{+2}]^{0.5}$

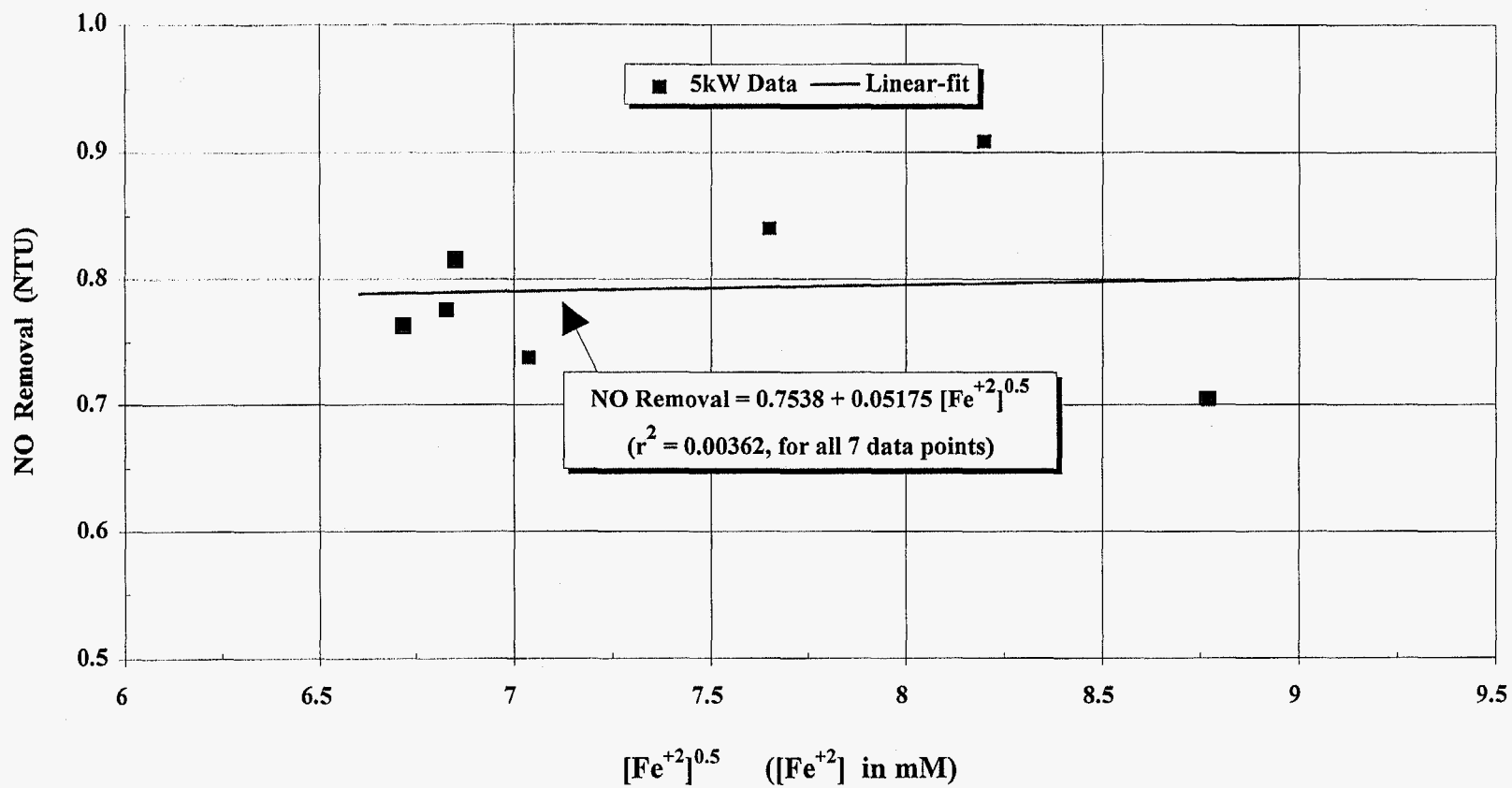


Table 8. Chemistry Data

Clock	Recycle	Alkalinity	[Fe ²⁺] _{by TK}	[SO ₄ ²⁻] by	[SO ₄ ²⁻]	[ADS] _{calculated}	[SA]	[SA] _{acidified}	[Mg ²⁺]	[Ca ²⁺]	[Total Fe]	[Na ⁺]	[S ₂ O ₃ ²⁻]	[SO ₃ ²⁻]	[SO ₄ ²⁻]	[Cl ⁻]	Filtercake
Time	Tank	(ppm)	by Spec-601	I ₂ titration	adjusted for	(mM)	by IC	by IC	by ICP	by ICP	by ICP	by ICP	by IC	by IC	by IC	by IC	Solids
(Hr: Min)	Liquor pH		(mM)	(ppm)	[Fe ²⁺] _{by TK}		(mM)	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(wt %)
					(ppm)												
9:40	5.3	1,668	88.9	12,746	9,190	0.91	0.64	1.55	7,899	640	5,601	27	n.d.	8,011	7,938	3,482	
10:00	5.8	2,786	76.0	10,584	7,544	1.35	0.30	1.65	7,704	384	5,397	149	n.d.	6,730	8,449	3,822	
11:00	6.1	4,370	66.4	10,968	9,497	2.06	3.50	5.56	7,857	456	5,425	651	n.d.	7,289	8,444	3,981	72.2
12:00	6.25	5,154	67.9	12,153	10,382	4.46	1.07	5.53	7,991	432	5,417	1,279	n.d.	7,782	7,497	3,122	72.4
13:00	6.3	5,187	72.1	13,098	11,706	4.45	5.19	9.64	7,671	403	5,361	2,001	n.d.	7,369	6,056	2,444	73.4
14:00	6.3	5,438	70.9	14,590	11,535	2.05	8.31	10.36	7,467	260	5,267	2,583	n.d.	10,003	6,870	2,495	76.0
15:00	6.3	5,671	74.9	14,371	10,780	5.96	10.77	16.73	7,500	219	5,292	3,361	n.d.	9,616	5,903	2,154	75.9
16:00	6.3	6,021	66.8	15,220	11,101	11.98	10.04	22.02	7,430	223	5,179	4,045	n.d.	10,925	6,053	2,264	77.0

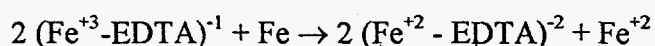
Table 9. Chemistry Data

Clock	Recycle	Alkalinity	[Fe ⁺²] _{by Tn}	[SO ₃ ⁻²] by	[SO ₃ ⁻²]	[ADS] _{solid}	[SA]	[SA] _{solid}	[Mg ⁺²]	[Ca ⁺²]	[Total Fe]	[Na ⁺¹]	[S ₂ O ₃ ⁻²]	[SO ₃ ⁻²]	[SO ₄ ⁻²]	[Cl ⁻¹]	Filtercake
Time	Tank	(ppm)	by Spec-601	I ₂ titration	adjusted for	(mM)	by IC	by IC	by ICP	by ICP	by ICP	by ICP	by IC	by IC	by IC	by IC	Solids
(Hr: Min)	Liquor pH		(mM)	(ppm)	[Fe ⁺²] _{by Tn}		(mM)	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(wt %)
					(ppm)												
10:00	6.1	4,170	76.9	11,041	7,965	-0.11	1.57	1.46	8,822	327	5,963	440	n.d.	7,095	8,855	4,634	68.8
11:00	6.35	5,271	67.2	11,937	9,249	-0.04	2.10	2.06	8,744	338	5,788	950	100	9,123	9,252	4,563	71.3
12:00	5.8	4,337	58.5	13,482	11,142	5.26	2.52	7.78	8,291	233	5,675	1,636	80	9,766	7,651	3,496	75.1
13:00	6.0	5,504	49.5	13,210	11,230	6.63	3.86	10.49	8,493	232	5,583	2,055	269	11,740	8,893	4,069	74.8
14:00	6.0	5,738	46.9	13,186	11,310	8.83	5.51	14.34	8,334	215	5,511	2,646	354	12,504	8,513	4,178	74.9
15:00	6.1	5,871	46.6	13,691	11,827	15.39	7.03	22.42	8,148	280	5,432	3,034	442	12,921	8,239	3,778	76.8
16:00	6.3	6,605	45.1	14,107	12,303	7.51	14.42	21.93	8,309	379	5,265	3,458	600	13,161	8,048	3,779	76.4

2. Iron

a) 5 kW Configuration

Tests were conducted using the chemical regeneration agent iron. The 5 kW configuration was that of the baseline tests with 4 gram quantities of 100 mesh iron powder added manually to the recycle tank every 30 minutes. The reaction believed to occur with iron is as follows:



It should be cautioned that this reaction involving ferric ion has not been substantiated. No modifications from the baseline set-up were required. Figure 33 depicts the 5 kW configuration.

b) Test Results

Test DT031794 (non-packed mode, ~50 mM initial total iron concentration, recycle tank pH = 5.3, L/G = 44, 6.5 vol.% O₂) and test DT032294 (non-packed mode, ~50 mM initial total iron concentration, recycle tank pH = 5.3 to 5.8, L/G = 44 to 88, 6.6 vol.% O₂) were performed using iron as the regeneration agent. For test DT032294, an L/G of 44 was used for the first five hours followed by a L/G of ~88 for the remainder of the run. Also during this test run, the pH was initially set at 5.3 but raised to 5.8 after 8 hours.

SO₂ removal curves for each test are given in Figures 42 through 43. SO₂ removal was poor at the beginning of test DT031794 run but increased to reach 95% by completion of the test. The SO₂ removal for test DT032294 followed the same trend as observed for the first test. The highest removal for this test was observed at L/G of 88 and pH of 5.8. At these conditions the SO₂ removal was 98% to

100%. The low initial SO_2 removals indicate the need to maintain a pH above 5.3 in the recycle tank. The initially low SO_2 removals for both tests could be the result of a non-packed mode. SO_2 absorption into the liquid stream will increase with greater gas-liquid contacting resulting from packing. NO_x removal averaged 25% to 30% for test DT031794 as depicted in Figure 44. The increasing and decreasing patterns in NO_x removal is due to the periodic addition of iron to the recycle tank. Shortly, after the addition of iron, the NO_x removal would rapidly decrease until the next addition of iron where the NO_x removal would increase again before dropping. The fact that NO_x removal immediately decreased after addition of iron without leveling off suggests that greater additions of iron (greater than 8 grams 100 mesh iron/hr) will result in higher initial removals followed by a rapid drop in ferrous ion concentration until the next addition of iron. Unfortunately, not all of the iron was utilized. Some of the iron settled to the bottom of the thickener, recycle tank, and heat exchanger tubing. It also accumulated on the trays of the absorber. There is a point beyond where additional amounts of iron powder will not be utilized because the excess iron will settle out in the system. The NO_x removal averaged 25% to 30% for test run DT032294, as illustrated in Figure 45. The low NO_x removals can be explained by the ferrous ion concentration. The ferrous ion concentration in the recycle tank dropped from the beginning of test DT031794 until three hours after testing when the ferrous ion concentration began to increase to eventually reach 20 mM by the end of the test. This is depicted in Figure 46. The ferrous ion concentration for test DT032294 dropped rapidly for the first two hours then increased to an average concentration of 15.4 mM for the next 4.5 hours as shown in Figure 47. For the last three hours, the ferrous ion concentration decreased to an average concentration of 9.1 mM. The ferrous ion concentration never recovered after its initial drop in value.

The sodium ion concentration averaged below 50 mM for both tests. This is shown in Tables 10 and 11. The sulfite ion concentration increased throughout

both the runs. The sulfate ion concentration also elevated significantly in concentration during test run DT032294. With this increase in sulfite and sulfate ion concentrations, the magnesium and calcium ion concentrations became larger. The increase in these species can lead to scaling if the condition continues. The filtercake solids content averaged below 65 wt.% for both tests. The solids content was thus lower than typically achieved with a regeneration method. The correlation to the NO_x removal model was poor for both test runs (<0.650) indicating that the ferrous ion concentration and effective ferrous ion concentration differ substantially from each other. The NO_x removal model curves are shown in Figures 48 and 49.

c) Economics

Iron is an inexpensive agent at \$0.15/lb. The cost of iron on a mM ferrous ion concentration and NTU removal basis was found to be \$0.000691 / day·mM Fe^{2+} ·vol.% O_2 and \$0.0295 / day·NTU·vol.% O_2 . The cost on both scales is shown in Figures 50 and 51. Regeneration using iron powder with and without a digester represents the most economical chemical regeneration agent examined so far. The operating costs are comparable to those of the electrochemical cell. It is evident that iron with and without a digester is more cost effective than a 5:1 weight mixture of sodium dithionite and ascorbic acid. The cost of this mixture is \$0.01332/day·mM Fe^{2+} ·vol.% O_2 and \$0.99541/day·NTU·vol.% O_2 which makes this agent prohibitive for consumption in a scaled-up process. This is what initially prompted the investigation into alternative regeneration methods. The low cost of this regeneration agent makes this agent an attractive choice for scaled-up testing.

d) Attainment of Objectives

The suitability of iron as a chemical regeneration agent was determined. The effect on process chemistry was also determined. The addition of 4 gram of iron every

30 minutes was moderately successful for NO_x removal since both tests displayed a NO_x removal recovery after an initial drop. The final removals were within 10% of the initial NO_x removals for both test runs. The ferrous ion concentration also increased after an initial drop in concentration for both tests representing the regeneration ability of iron powder. The maximum NO_x removal of 35% was well below the target stated in the test plan. During these tests, SO₂ removal reached 98% to 100% only after the pH was increased from 5.5 to 6.0 coupled with an L/G increased to 88. Unfortunately, after the pH was increased for test run DT032294, the NO_x removal and ferrous ion concentration dropped. The pH was kept low initially to help dissolve the iron. For test DT031794, the sulfite ion concentration was observed to increase in concentration as testing continued. A similar trend was observed for the sulfite and sulfate ion concentrations for test DT032294. This will pose a problem for long term testing because calcium ion will increase in concentration to maintain charge balance. This will eventually lead to scaling in the scrubber and recycle tank. The low solids content was a surprise and poses a question to the suitability of this agent for a NO_x removal process. This was especially the case for test DT032294 where the filtercake solids content averaged less than 60 wt.% during the course of the test run.

Figure 42. SO₂ concentration and removal vs. time

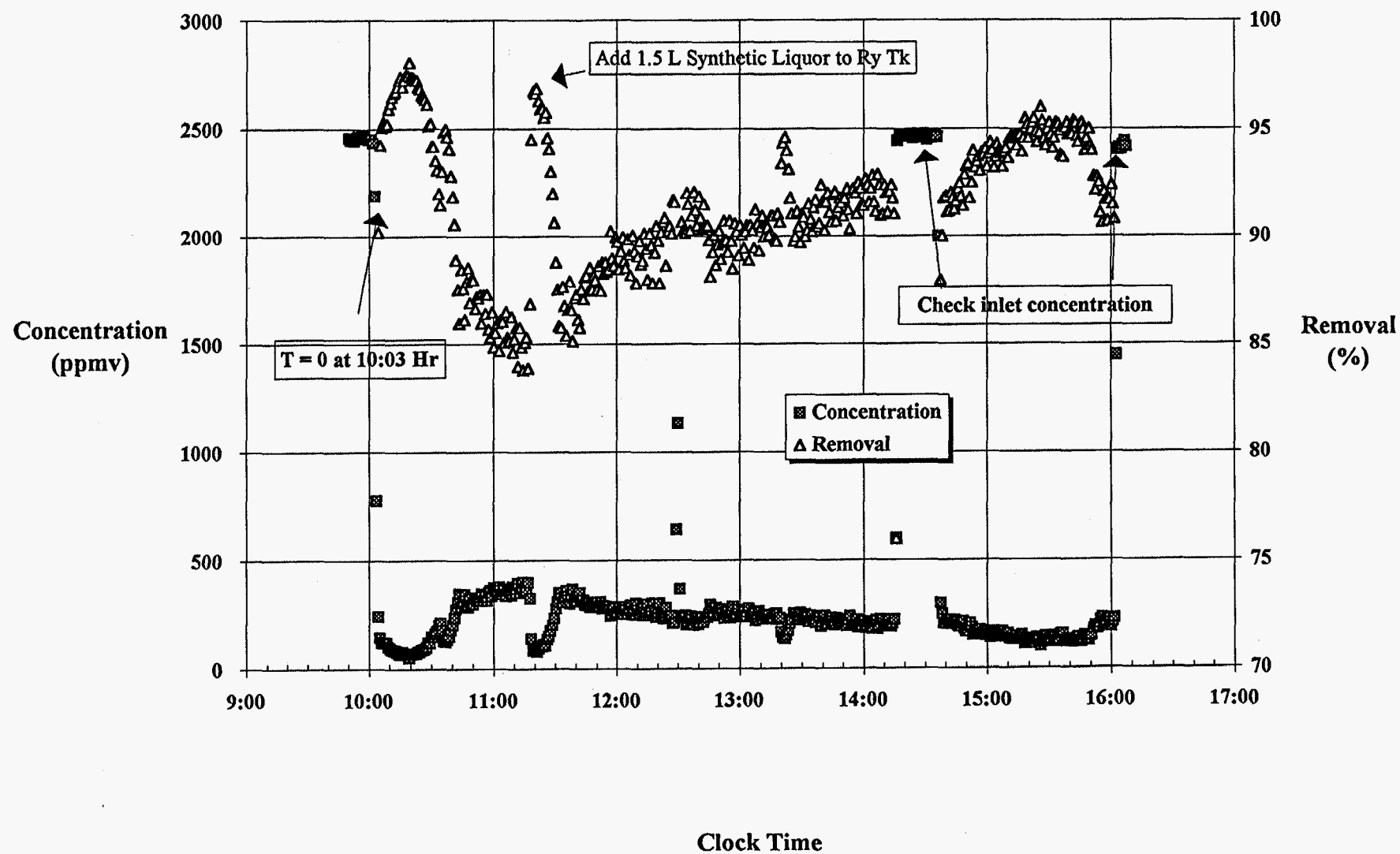


Figure 43. SO₂ concentration and removal vs. time

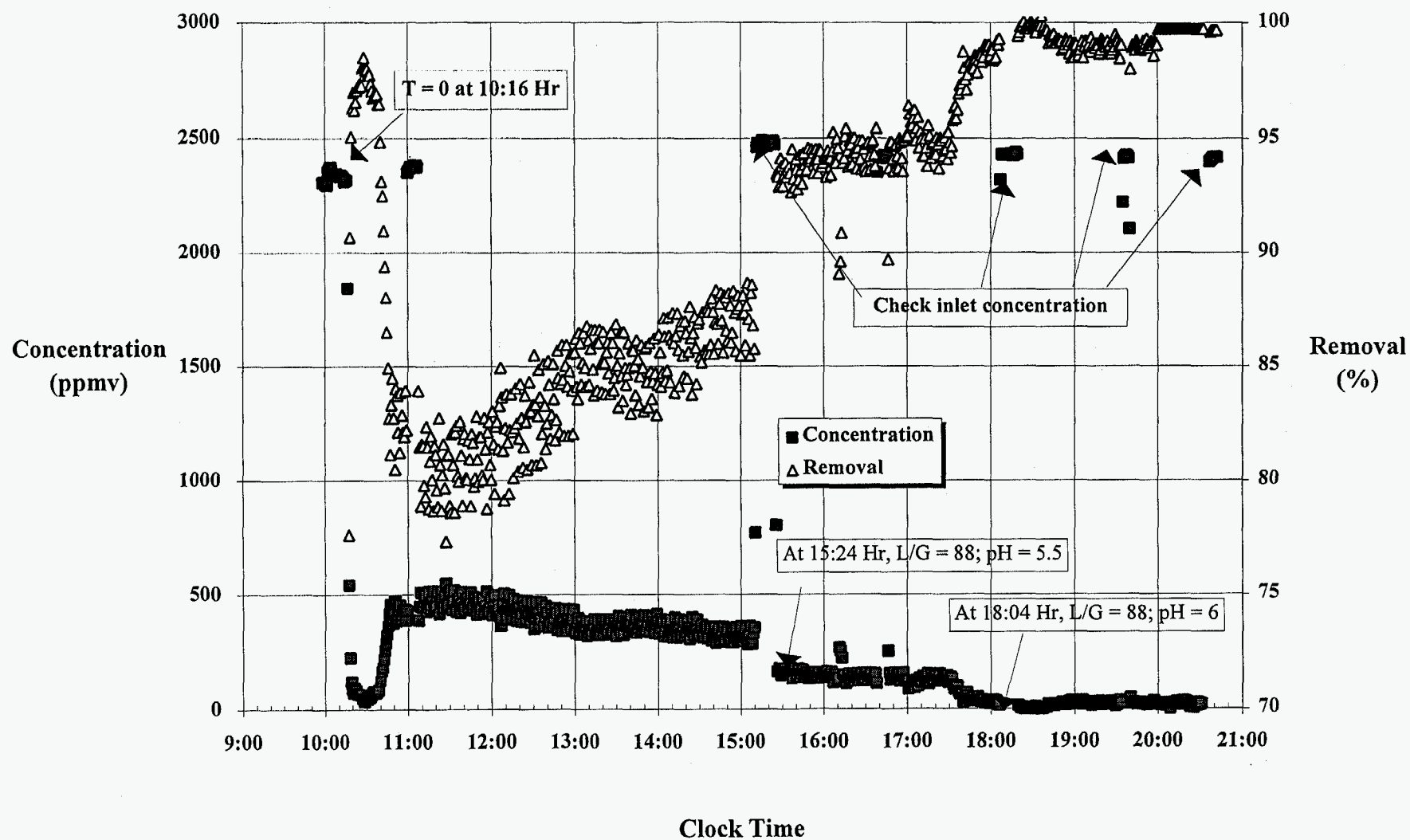


Figure 44. NO concentration, NO removal, and $[\text{Fe}^{+2}]$ vs. time

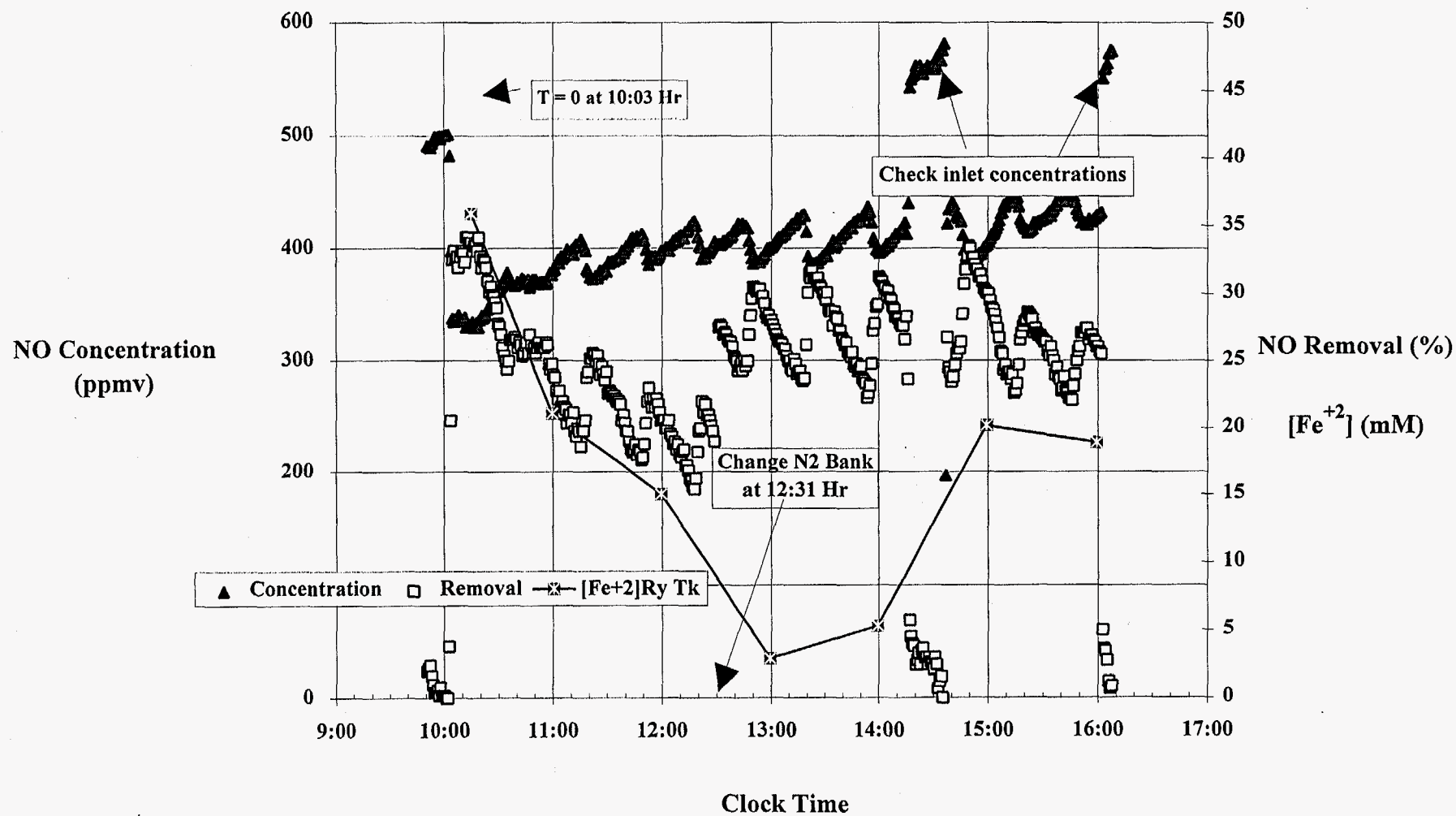


Figure 45. NO concentration and removal vs. time

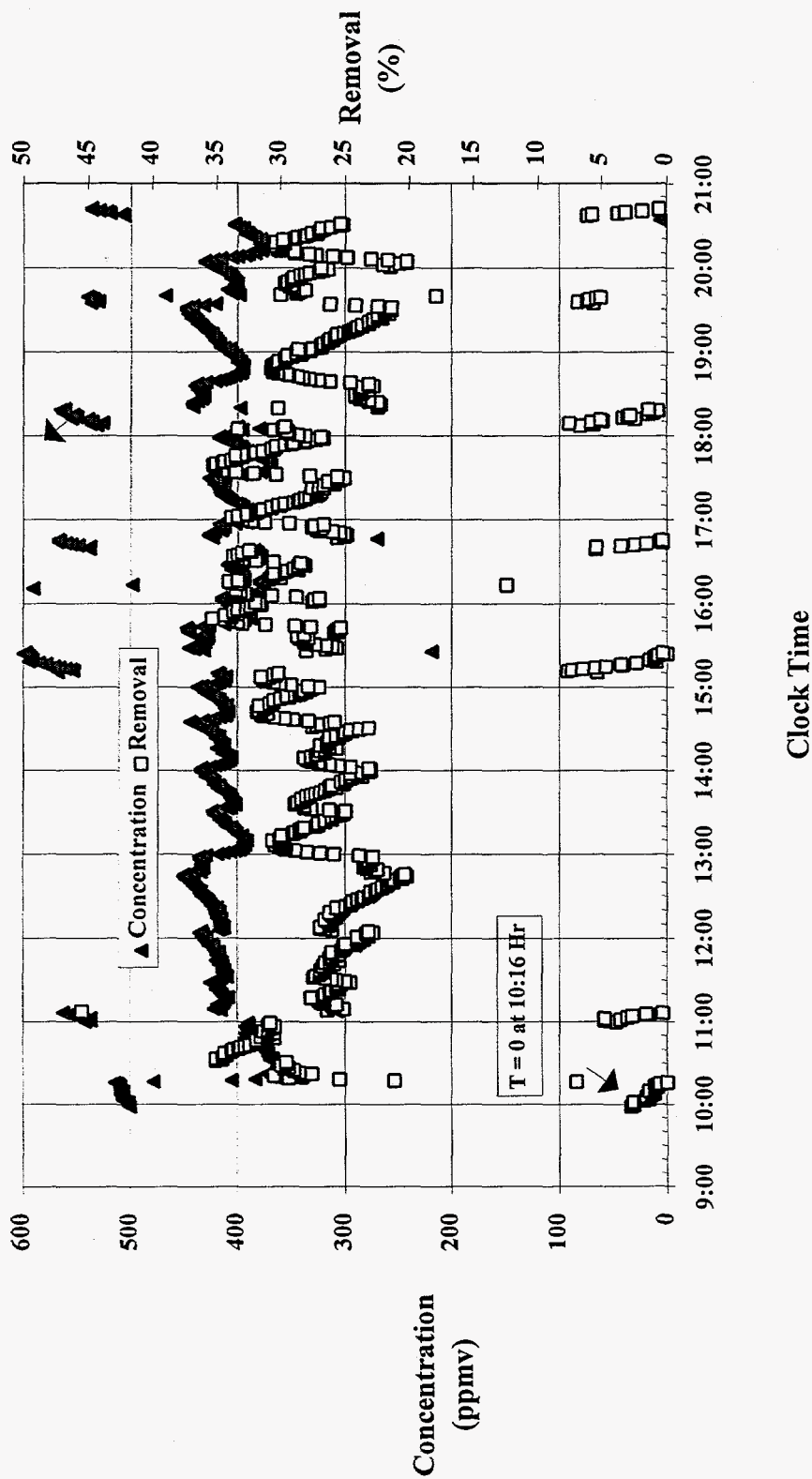


Figure 46. NO removal and $[\text{Fe}^{+2}]$ vs. time

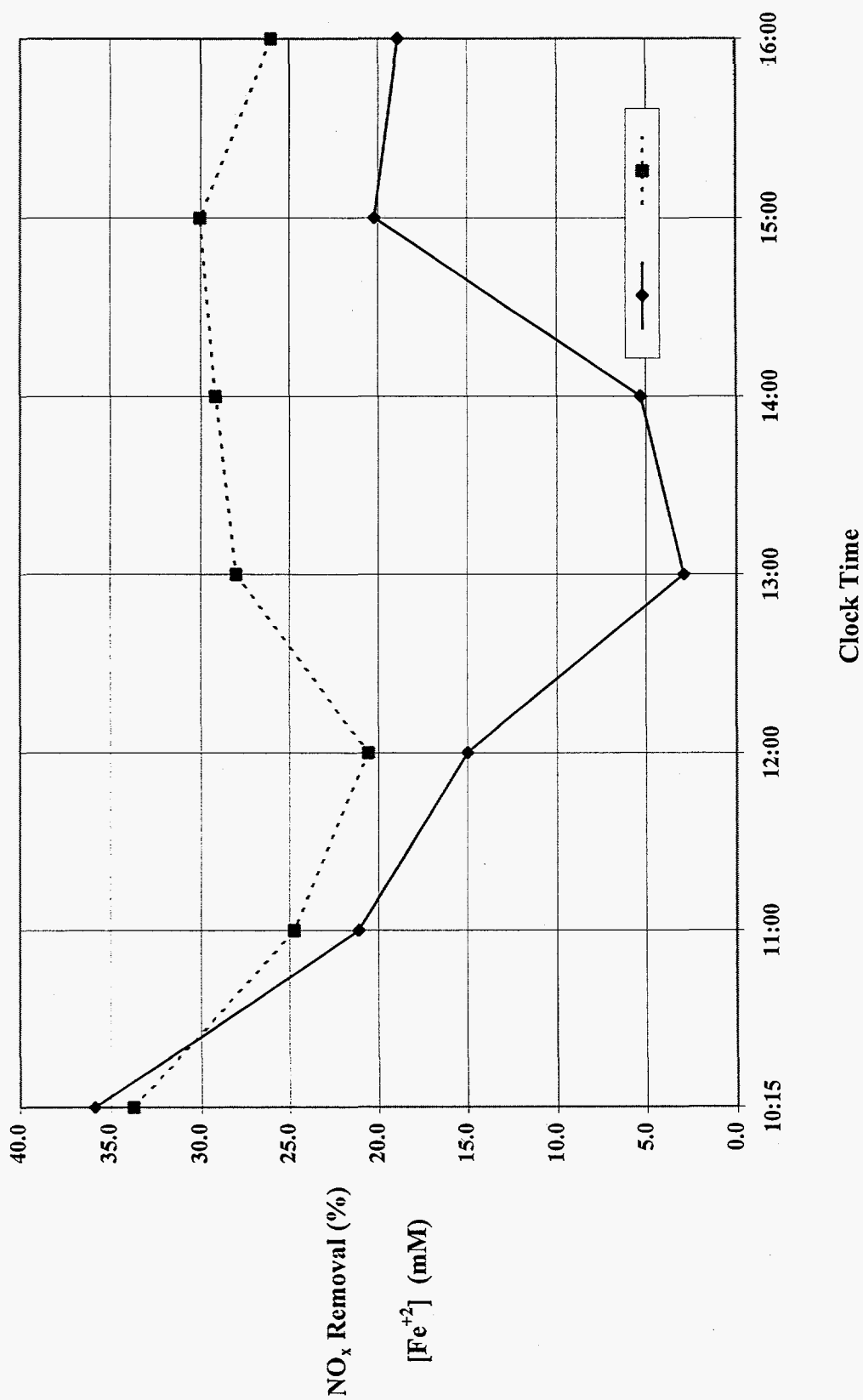
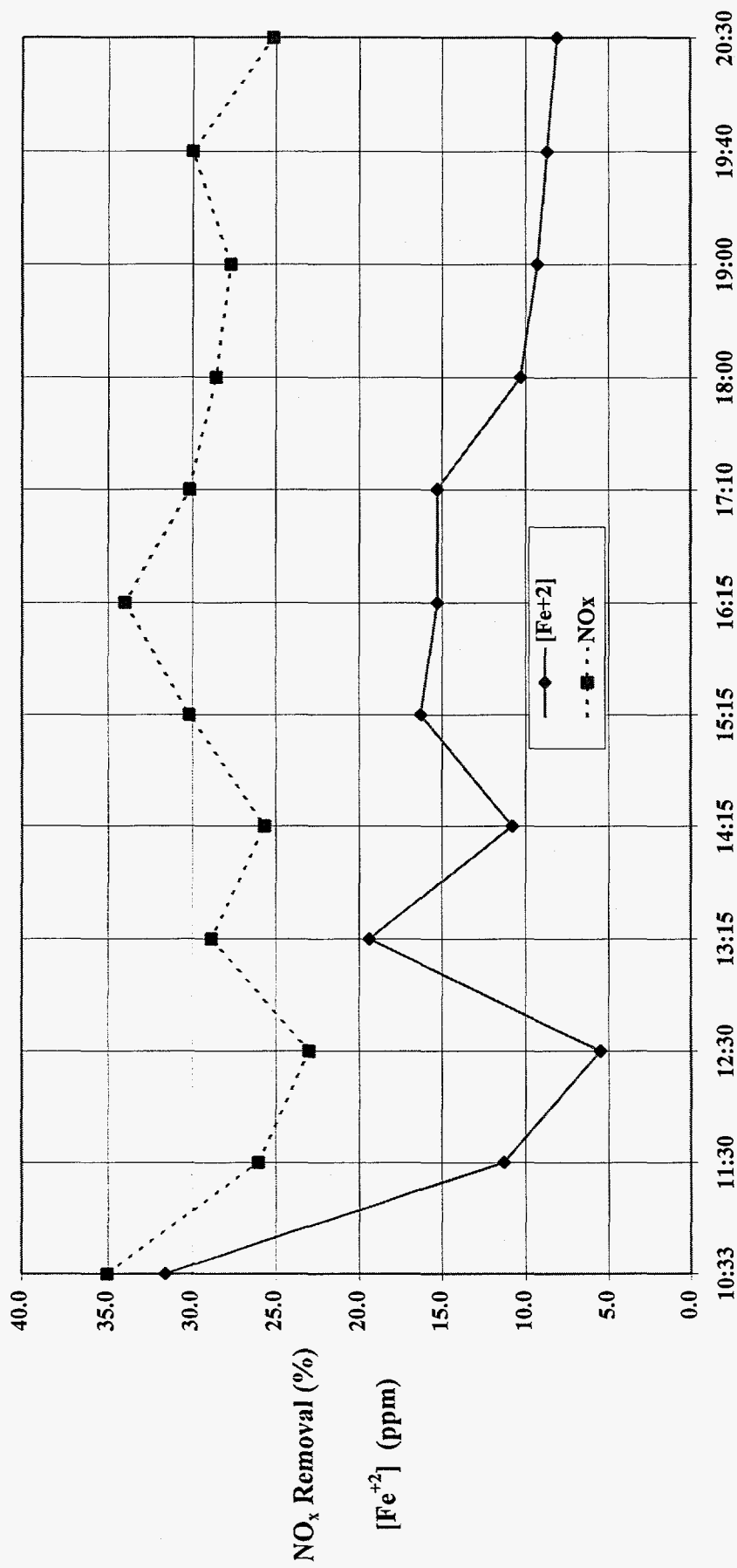


Figure 47. NO removal and $[\text{Fe}^{+2}]$ vs. time



Clock Time

Figure 48. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

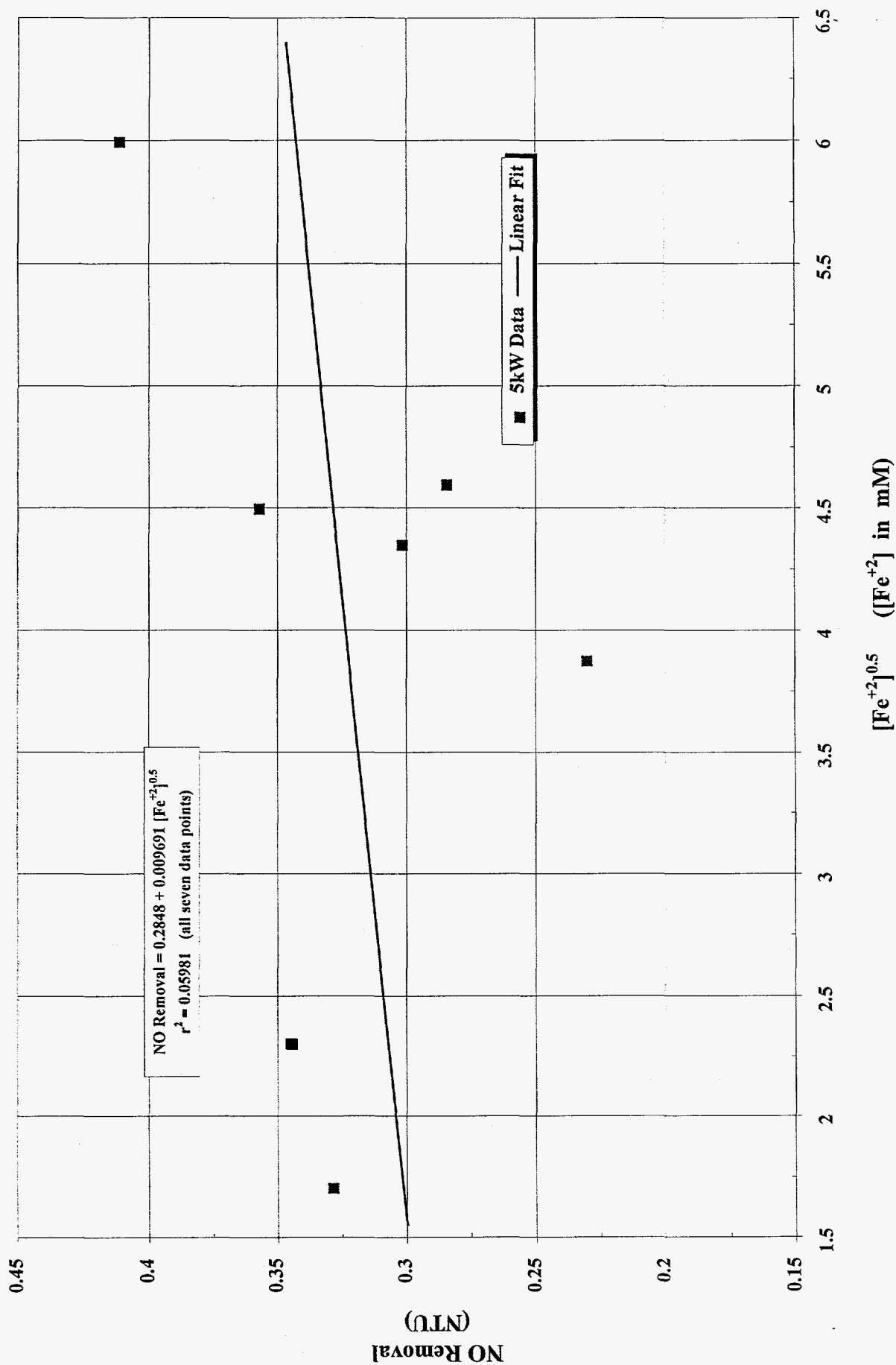


Figure 49. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

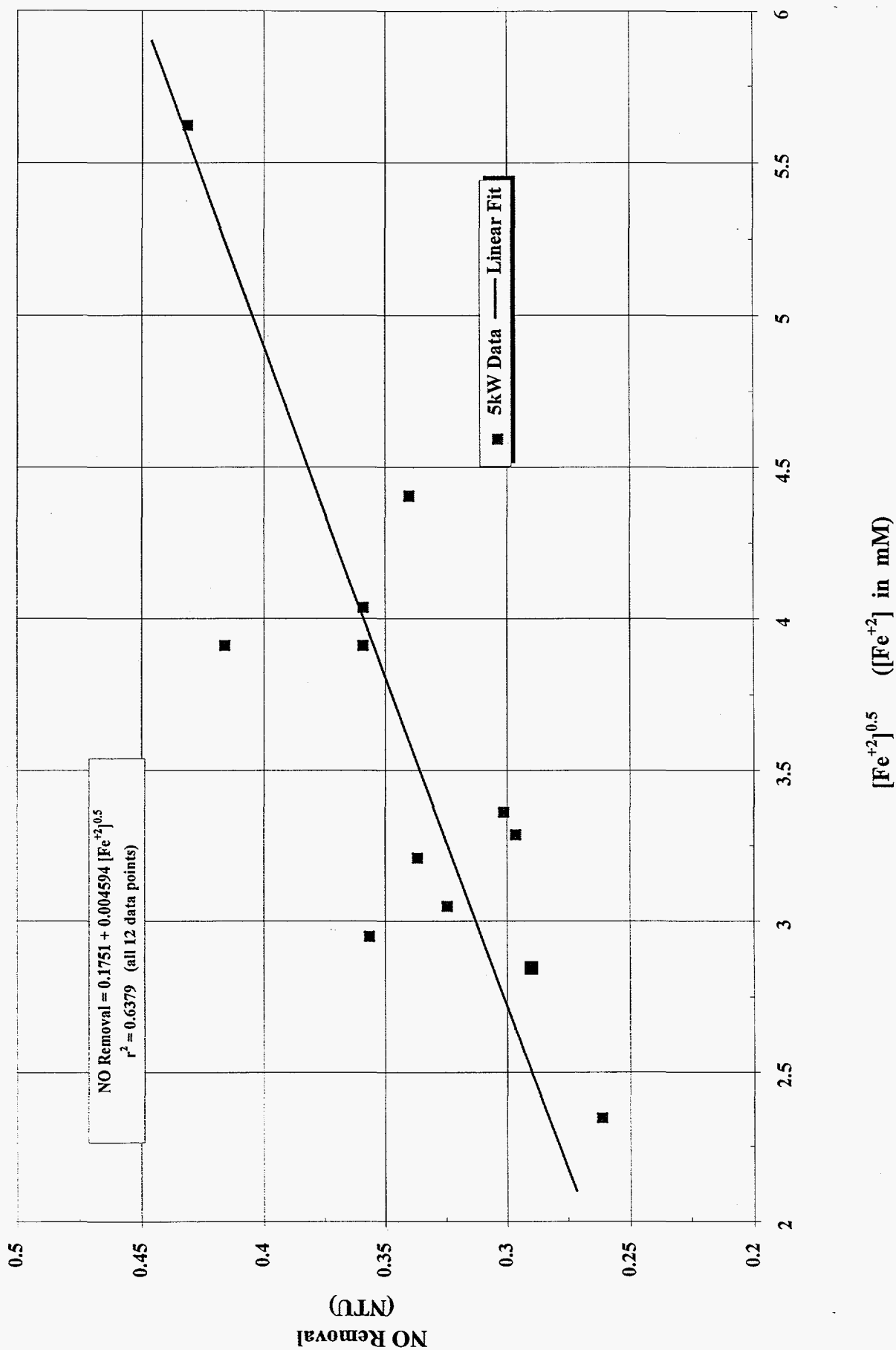


Figure 50. Consumption Economics (mM Fe⁺² concentration basis)

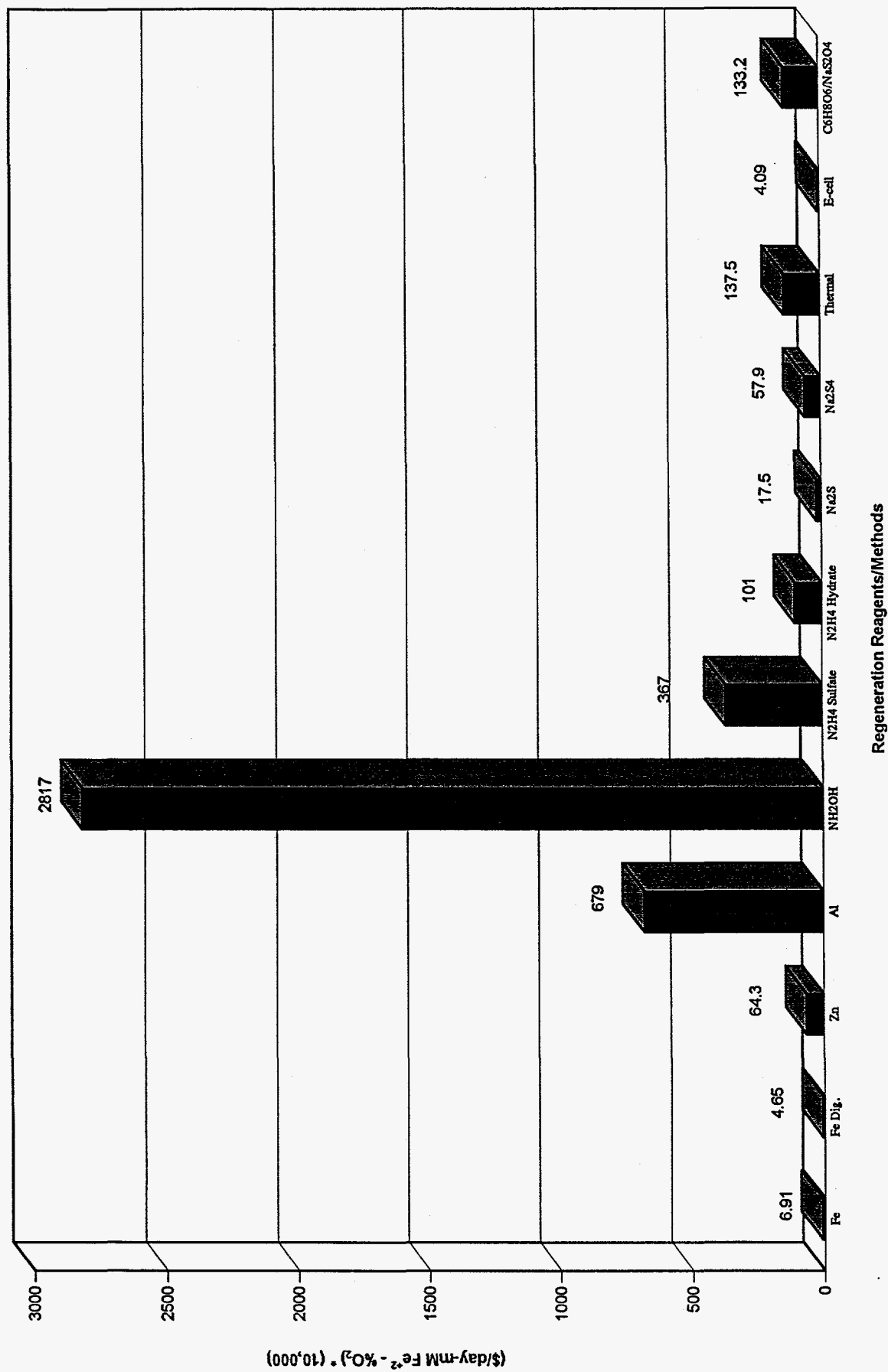


Figure 51. Consumption Economics (NTU Removal Basis)

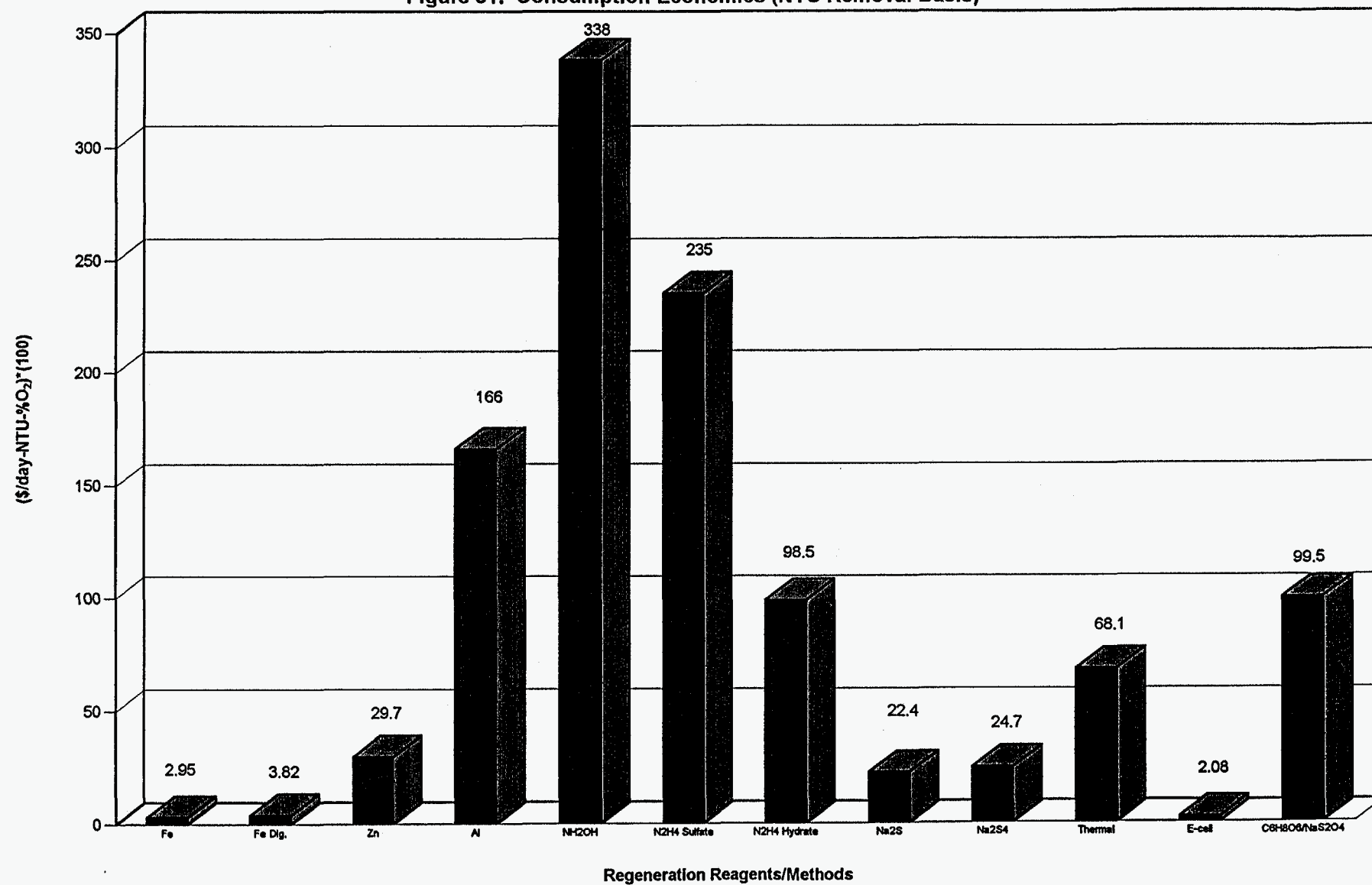


Table 10. Chemistry Data

Clock Time	Recy Tank	Alkalinity	[SO ₃ ⁻²] as	[Fe ⁺²] _{RY TK}	[SO ₃ ⁻²] corrected for [Fe ⁺²] _{RY TK}	[ADS]	[Mg ⁺²]	[Ca ⁺²]	[Total Fe] _{RY TK}	[Na ⁺¹]	Filtercake
(Hr: Min)	Liquor pH	(ppm)	analyzed (ppm)	(mM)		(mM)	(ppm)	(ppm)	(ppm)	(ppm)	Solids (wt %)
10:15	5.7	2118	8150	35.9	6714	0.39	3408	234	1763	42.8	
11:00	5.3	884	10008	21.1	9164	1.53	3847	301	2061	32	
12:00	5.2	834	12185	15.0	11585	4.13	4506	220	2287	73.7	54
13:00	5.2	1051	12241	2.9	12125	6.55	4681	244	2420	39.1	61.3
14:00	5.2	1084	12209	5.3	11997						64.2
15:00	5.3	1200	12129	20.2	11321	15.4	5350	351	2850	53.5	65.1
16:00	5.2	1251	12385	18.9	11629	17.27	5456	289	2871	42.3	68.3
avg:	5.30	1203			10648		4541	273	2375	47.2	62.6

Table 11. Chemistry Data

Clock Time	L/G	Recy Tank	Alkalinity	[SO ₃ ⁻²] _{Ry Tk}	[Fe ⁺²] _{Ry Tk}	[SO ₃ ⁻²] _{Ry Tk}	[ADS] _{Ry Tk}	[Mg ⁺²] _{Ry Tk}	[Ca ⁺²] _{Ry Tk}	[Total Fe] _{Ry Tk}	[Na ⁺¹] _{Ry Tk}	[SO ₃ ⁻²] _{Ry Tk}	[SO ₄ ⁻²] _{Ry Tk}	[Cl ⁻¹] _{Ry Tk}	Filtercake
(Hr. Min)		Liquor pH	as analyzed	as analyzed	by Spec-20	corrected for	by IC	by ICP	by ICP	by ICP	by ICP	by IC	by IC	by IC	Solids
			(ppm)	(ppm)	(mM)	[Fe ⁺²] _{Ry Tk}	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(wt %)
						(ppm)									
			Alkalinity		[Fe ⁺²]										
10:33	44	5.80	1685	7318	31.6	6054	0.61	3431	145	1691	32.3	5860	5720	122	
11:30	44	5.35	784	8967	11.3	8515	3.5	3630	181	1570	24.1	8980	5725	71	
12:30	44	5.30	767	9920	5.5	9700	5.99	4174	171	1683	25.2	10333	6189	74	52.4
13:15	44	5.35	984	10449	19.4	9673	5.02	4409	191	1846	31.4	10206	6993	76	54
14:15	44	5.35	1050	10784	10.8	10352	10.22	4929	188	1753	39.1	10730	7936	78	53.6
15:15	44	5.30	1134	11337	16.3	10685	10.36	5583	184	1710	37.5	11391	9133	88	52.5
16:15	88	5.30	1485	12962	15.3	12350	16.18	6065	224	1793	39.8	12125	10721	295	50.4
17:10	88	5.30	1384	12714	15.3	12102	21.47	6888	270	1739	39.7	12864	12450	332	52.5
18:00	88	5.30	1651	13490	10.3	13078	16.67	7111	413	1738	37.6	14008	13210	106	56.5
19:00	88	5.80	2185	10192	9.3	9820	17.18	6922	160	1253	37.2	9190	13230	100	61.6
19:40	88	5.80	2352	10312	8.7	9964	27.02	7378	153	1298	39.5	9382	14058	102	59.3
20:30	88	5.80	2467	10824	8.1	10500	32.33	8089	174	1369	47.3	10220	15374	110	59.9

3. Iron Using a Digestor

a) 5 kW Set-up

Three tests DT071795 (packing mode, ~150 mM initial total iron concentration, recycle tank pH = 5.5 - 5.9, L/G = 44, 10 vol.% O₂), DT072595 (packing mode, ~100 mM initial total iron concentration, recycle tank pH = 5.6, L/G = 44, 10 vol.% O₂), and DT072795 (packing mode, ~100 mM initial total iron concentration, recycle tank pH = 5.7, L/G = 44, 10 vol.% O₂) were conducted using iron as the chemical regeneration agent and a process modification incorporating a digestor and settling tank. This process design modification was intended to increase the ferrous ion concentration and subsequent NO_x removal. It was of concern that not all of the iron added was going into solution when added directly to the recycle tank. A digestor was added to the process scheme to alleviate this concern. The key to fulfilling the objective of the digestor was to maintain the digestor liquor in the pH range from 4.0 to 4.5. Twenty percent by volume sulfuric acid solution was used to control the digestor pH. The temperature of the digestor liquor was maintained at 95°C to enhance the dissolution of iron powder. In addition to the digestor, a settling tank was used where any undissolved iron would settle to the bottom of the vessel preventing iron from settling in any of the other vessels associated with the 5 kW. The settling tank overflow would be directed to the recycle tank. If the settling tank was operating properly, the overflow would be clear of iron particles. A schematic of the process flow is shown in Figure 52.

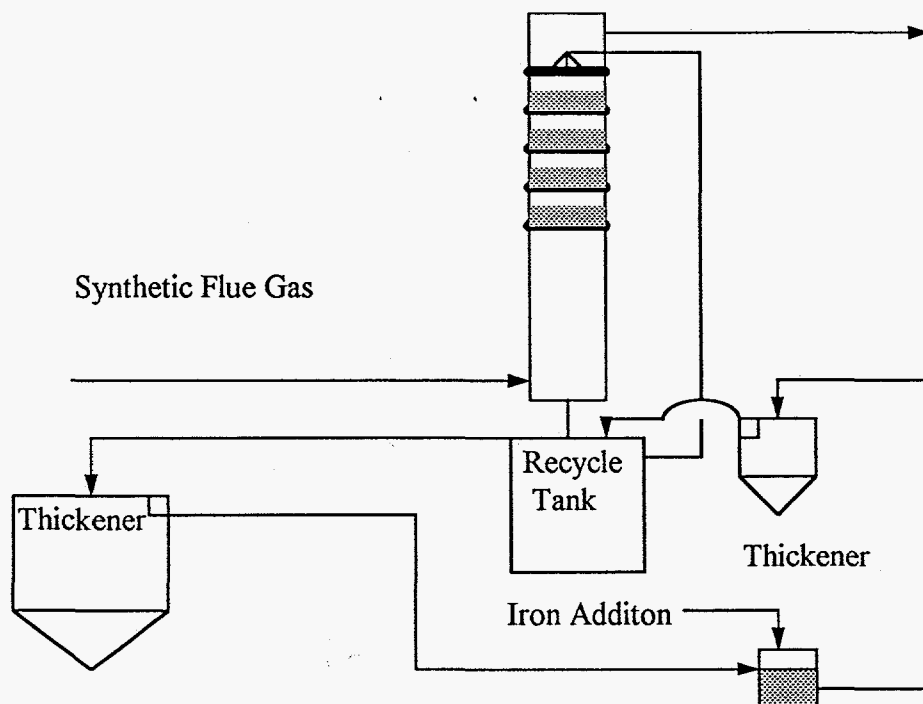


Figure 52. Flow Diagram for Iron using a Digestor

b) Test Results

Tests DT072595 and DT072795 were short term tests each lasting a little longer than six hours. For both of these tests SO_2 removals of 99% were achieved. Results were particularly promising for test DT072595 where SO_2 removals reached 99% and stayed at this level for the entire test period. The SO_2 removal curves are shown in Figures 53 and 54. The method of addition of the regeneration agent was 5 grams of 100 mesh iron powder added to the digester every 15 minutes.

During extended periods of the 60 hour long term test DT071795 99% SO_2 removal was realized. This is shown in Figure 55. The pH of the recycle tank liquor was initially 5.5 before being raised to ~5.9 for the remainder of the run. It was after the pH was increased to 5.9 that SO_2 removals averaged 99%. The method of iron addition was changed several times during testing. To start with,

5 grams of iron was added to the digester every 15 minutes and 25 grams of Na_4EDTA was added to the digester every 30 minutes. This was then changed to 5 grams of iron added to the digester every 15 minutes and 20 grams of EDTA acid added every 30 minutes. The final regeneration agent addition made was 10 grams of iron added to the digester every 15 minutes with no EDTA addition.

The process modification had a positive impact on NO_x removal for the removal attained levels of 50% before dropping to 40% for test DT072595. Similar results were achieved for test DT072795 where the NO_x removal attained levels of 50% removal before dropping late in the testing to 40% removal. For both these short term tests, NO_x removal was between 40% and 50%. The NO_x removal curves are shown in Figures 56 and 57. This is a significant improvement in NO_x removal over that obtained by adding iron directly to the recycle tank. For the 60 hour run (DT071795), the NO_x removal exceeded 50% at various times. The NO_x removal seldom dropped below 45%. The high NO_x removals attained during the long term test are very promising. The NO_x removal curve for this long term test is shown in Figure 58.

For test DT072595, the ferrous ion concentration dropped in the first couple hours of testing then increased above 20 mM in concentration. This is higher than the ferrous ion concentration observed when iron was added directly to the recycle tank. The ferrous ion concentration did not drop significantly during test DT072795 with the ferrous ion concentration staying above 25 mM during the course of testing. This is an improvement over those tests with iron addition directly to the recycle tank. The ferrous ion concentration varied from 40 mM to 70 mM for test DT071795. The ferrous ion concentration was cyclical in variation demonstrating that iron added to the digester regenerated the ferrous ion concentration over the run time. The ferrous ion concentration curves are depicted in Figures 59 through 61.

Sodium ion concentrations were below 60 ppm as illustrated in Tables 12 and 13 for tests DT072595 and DT072795 respectively. For a ThioNO_x system the sodium ion level should be low. The sodium level was high for the long term test (DT071795) but this is because Na₄EDTA was added to the digester for the first 6.5 hours of testing. After discontinuing the addition of Na₄EDTA, the sodium ion concentration began to decline as shown in Table 14. At 10 vol.% O₂ in the synthetic flue gas, the sulfites oxidized to form sulfate. This occurred for both tests DT072595 and DT072795 where the sulfites dropped in concentration while the sulfates increased in concentration. A similar trend was not observed for test DT071795 where both the sulfite and sulfate concentrations decreased. The decrease in sulfite ion concentration is a concern since the absorption of SO₂ is facilitated by the sulfites present in the ThioNO_x liquor. Although the sulfite concentration decreased for each test run, the alkalinity was sufficient for high SO₂ removals. The magnesium ion concentration was approximately 7,000 ppm for runs DT072595 and DT072795. For the long duration run, the magnesium ion concentration was higher due to higher anion concentrations.

The major problem that developed for this test series was the low solids content of the filtercake. For tests DT072595 and DT072795, the solids content of the filtercake was initially above 60% but continuously decreased during testing to below 50%. This significant decrease in solids content can be explained by the presence of a constituent in the filtercake which lowers the dewatering ability. The iron powder is believed to participate in a side reaction where an iron compound is formed due to the reaction of ferrous ions and anionic species in solution. The amount of iron which can be added to the digester is limited by this side reaction. It was postulated that ferrous hydroxide could be formed which is a gelatinous colloidal material with crystal size on the order of 5-15 µm. For the long term test the average solids content of the filtercake was 58.6 wt.% which is also low. One of the economic advantages of the ThioNO_x process is the high solids content that can be achieved. This translates into a saving in disposal cost of landfill material.

Since the ThioNO_x process is capable of producing 80% solids in the filtercake, this series of tests was unsuccessful in achieving the high solids content that can be obtained in this process.

The correlation to the NO_x removal model was low for both tests DT072595 and DT072795. The same poor correlation to the NO_x removal model exists for test DT071795. The correlation curves to the NO_x removal model are shown in Figures 62 through 64.

c) Economics of Iron Digestion

The agent used in this process is iron but there is a process modification in the method of addition that alters the economics from that of iron addition directly to the recycle tank. The cost of iron digestion on a mM ferrous ion concentration and NTU removal basis was found to be \$0.000465/day·mM Fe⁺²·vol.% O₂ and \$0.0382/day·NTU·vol.% O₂, respectively. This process is comparable to iron addition directly to the recycle tank and the electrochemical cell. Economically, this represents an attractive technique for NO_x removal. The use of iron powder incorporating a digester is nearly as cost effective as iron powder without a digester. Its comparison with sodium dithionite and ascorbic acid is presented in the economics section of iron powder.

d) Attainment of Objectives

The effectiveness of iron as a regeneration agent using a digester in the 5 kW system was determined along with changes in process chemistry resulting from its use. The addition of 5 to 10 grams of iron every 15 minutes led to NO_x removals ranging from 40% to 50%. The long term test was even more promising since NO_x removals seldom went below 45%. SO₂ removal reached 99% at different times for all three tests satisfying the SO₂ removal objective stated in the test plan.

The high solids content which can be achieved in this process was not fully realized for this series of test runs. In all cases, the average solids content was below 60wt.%. The removal of the gelatinous iron hydroxide from the filter cake is necessary in order to make the iron digestion technique more attractive.

Figure 53. SO₂ concentration and removal vs. time

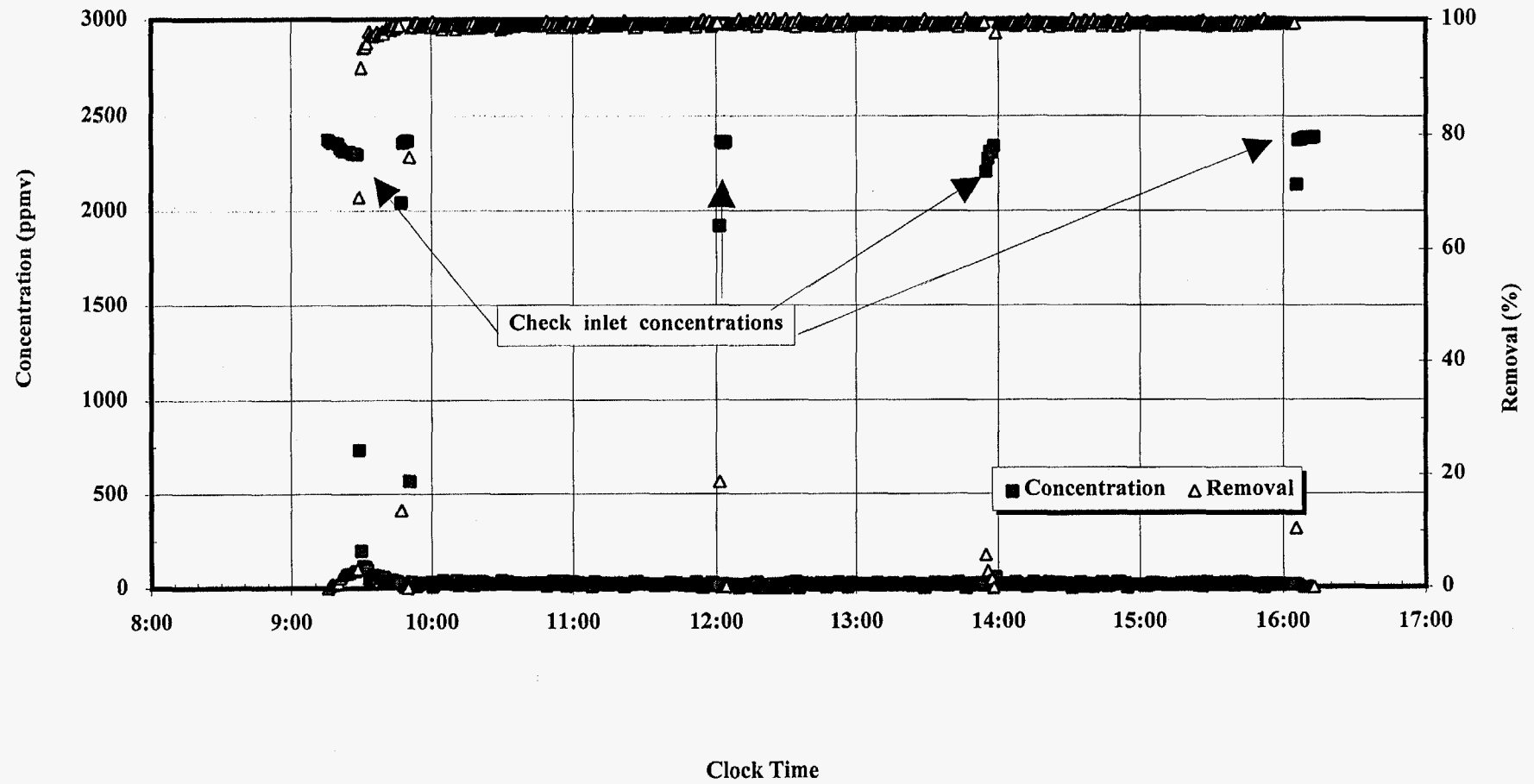
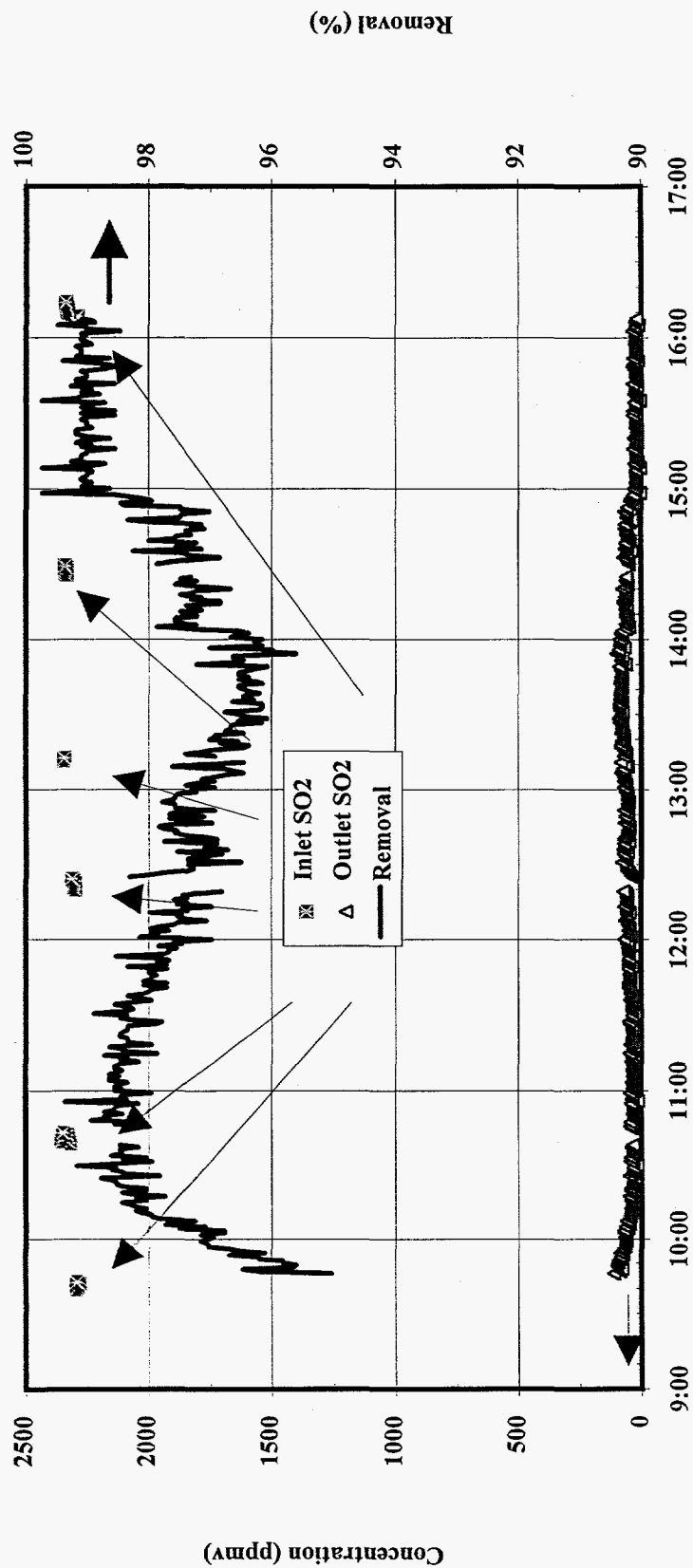
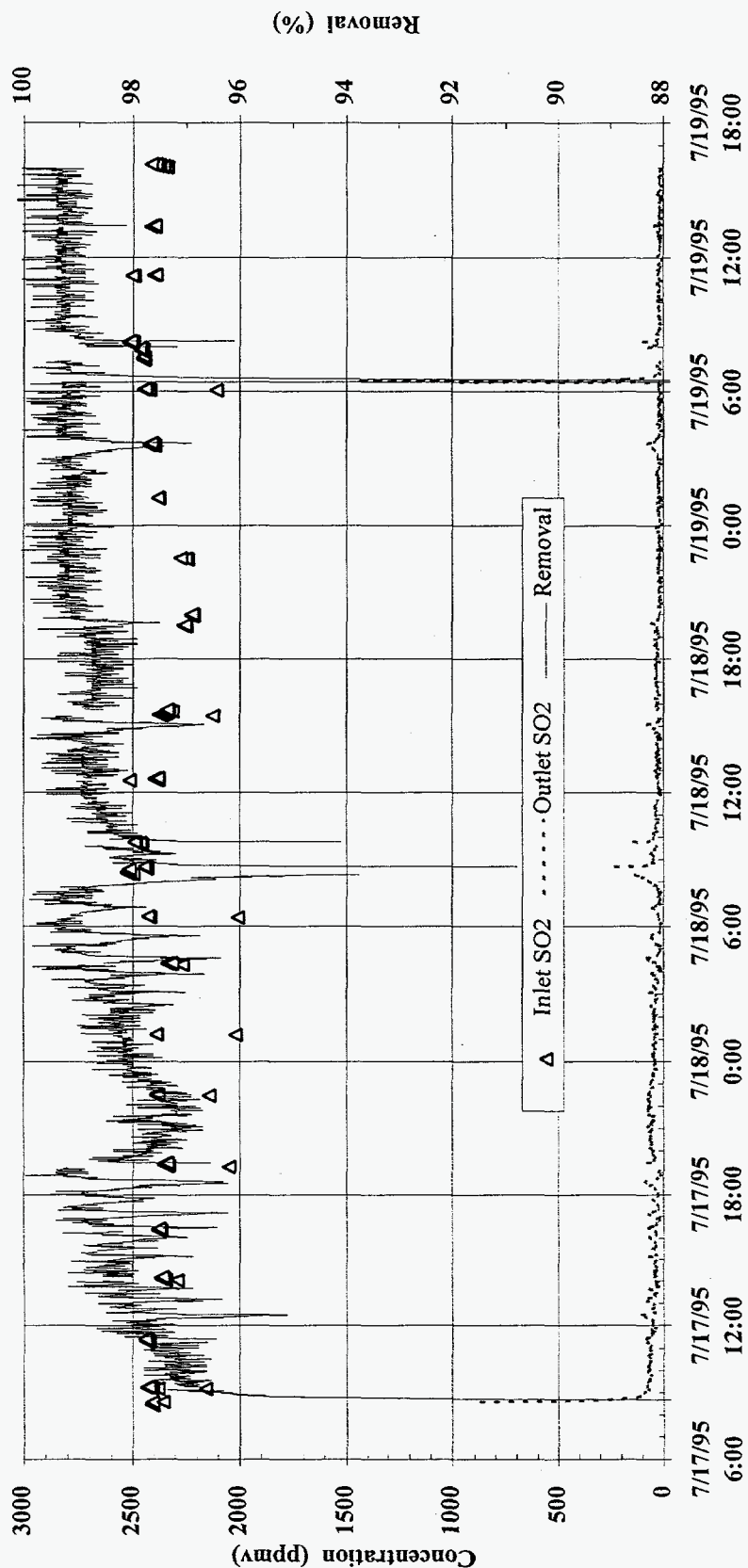


Figure 54. SO₂ concentration and removal vs. time



Clock Time

Figure 55. SO₂ concentration and removal vs. time



Clock Time

Figure 56. NO concentration and removal vs. time

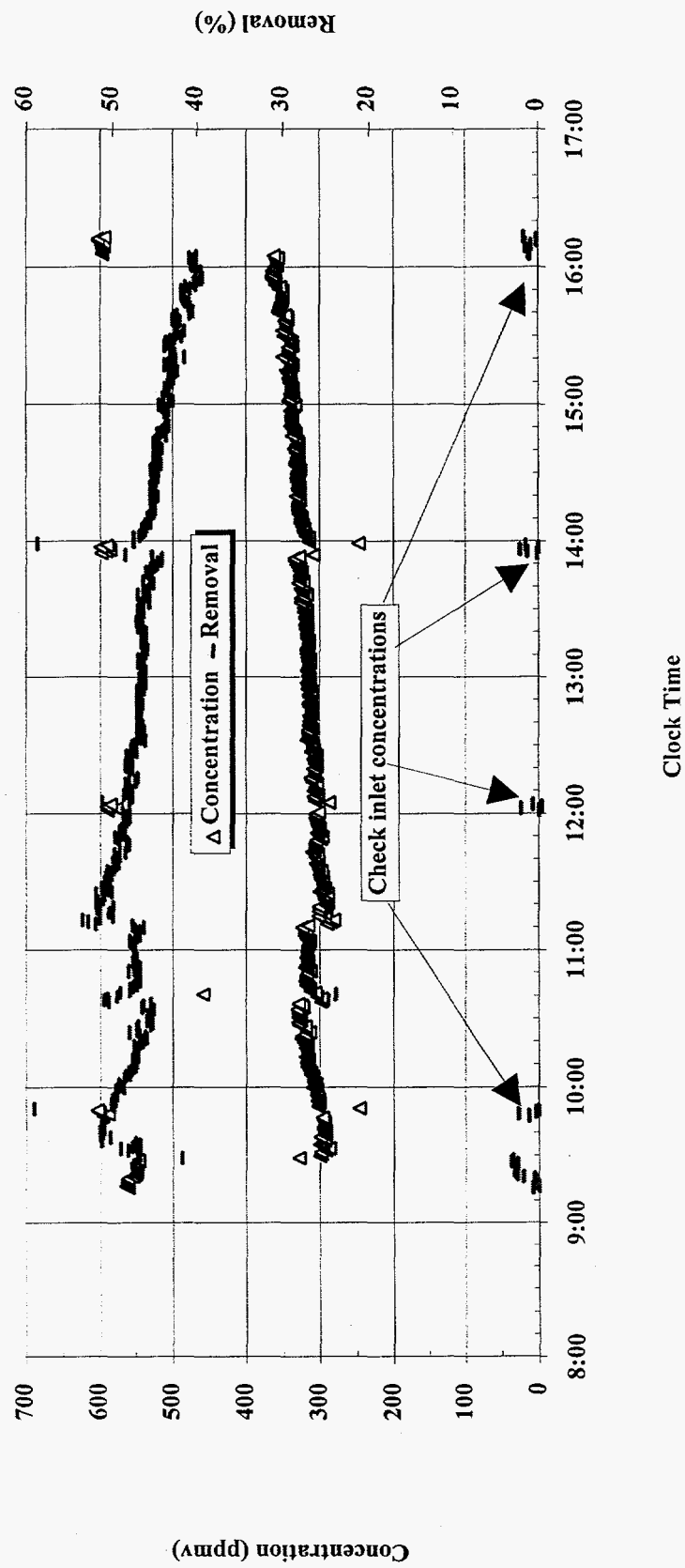


Figure 57. Inlet and outlet NO concentrations and removal vs. time

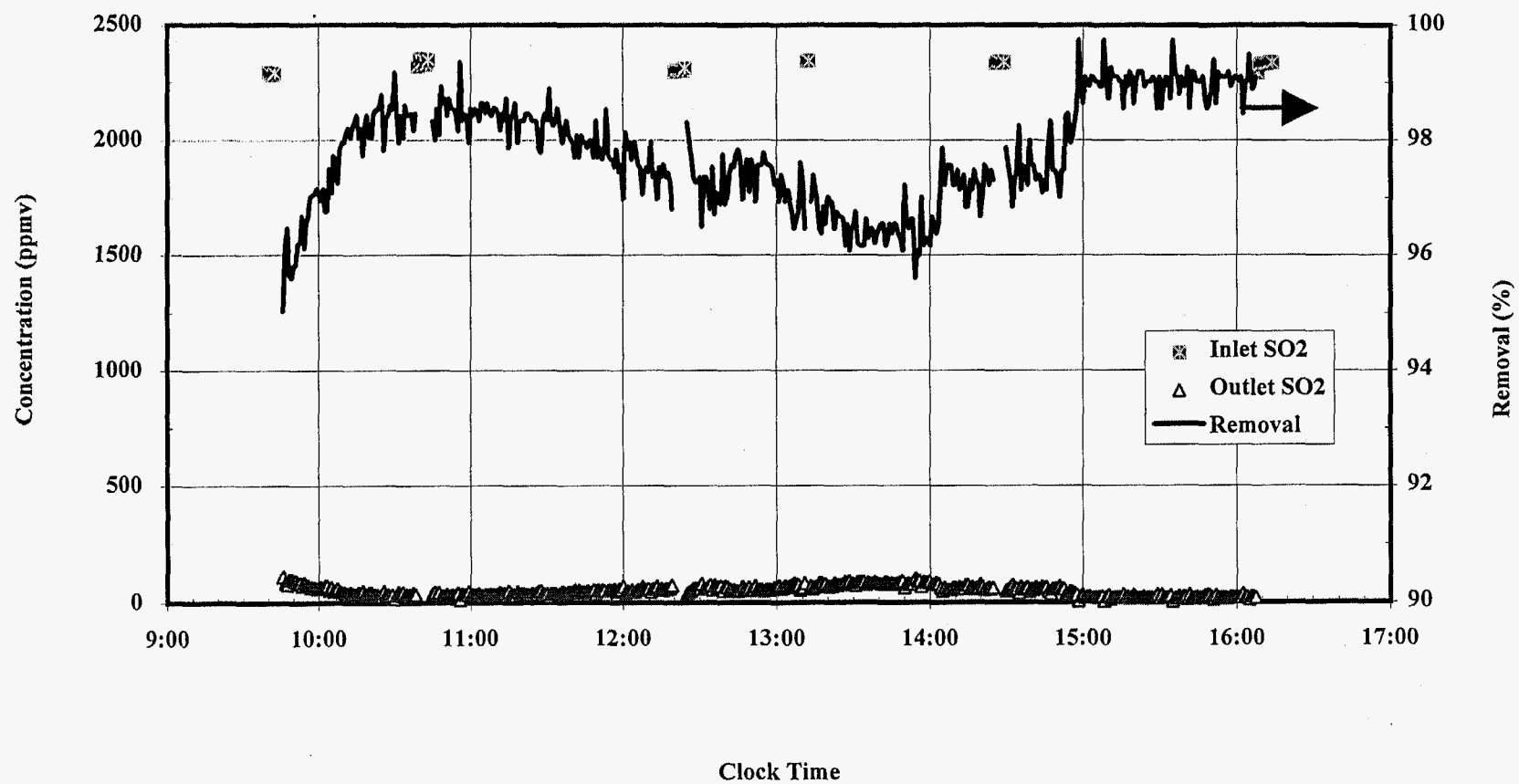
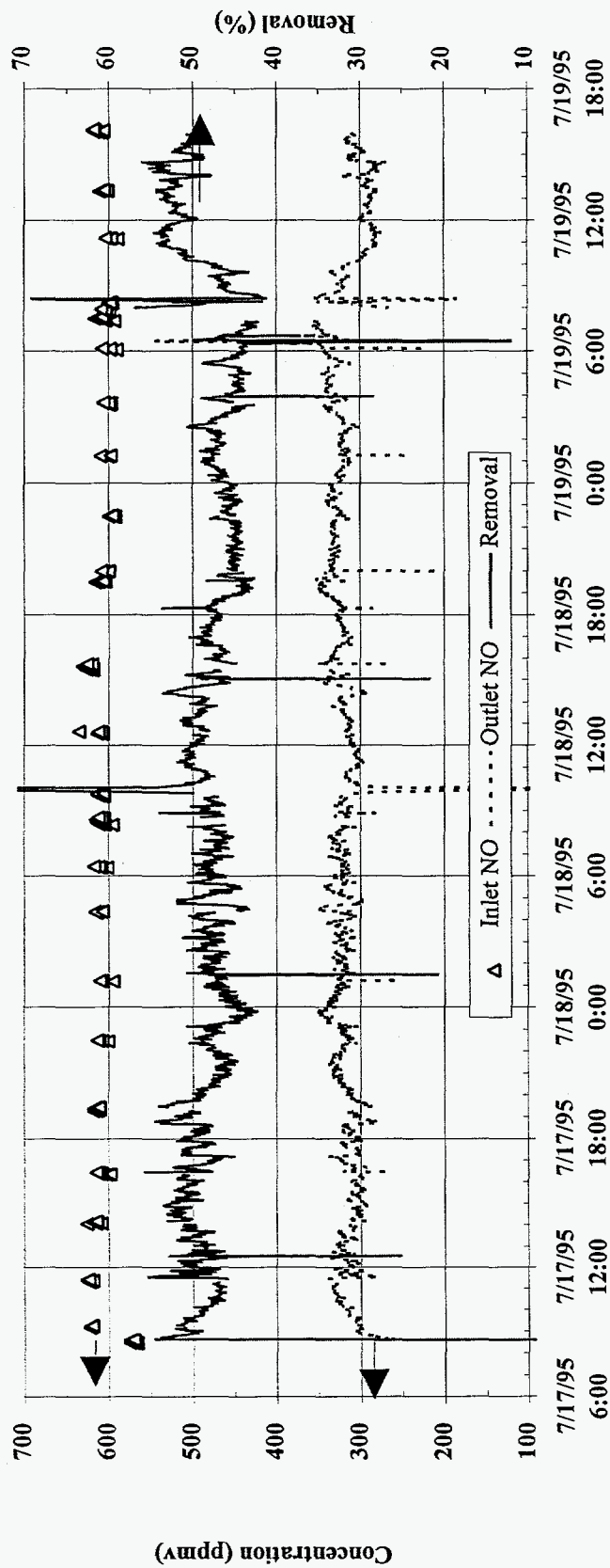


Figure 58. NO concentration and removal vs. time



Clock Time

Figure 59. Measured $[\text{Fe}^{+2}]$ in the recycle tank, downcomer, and digester

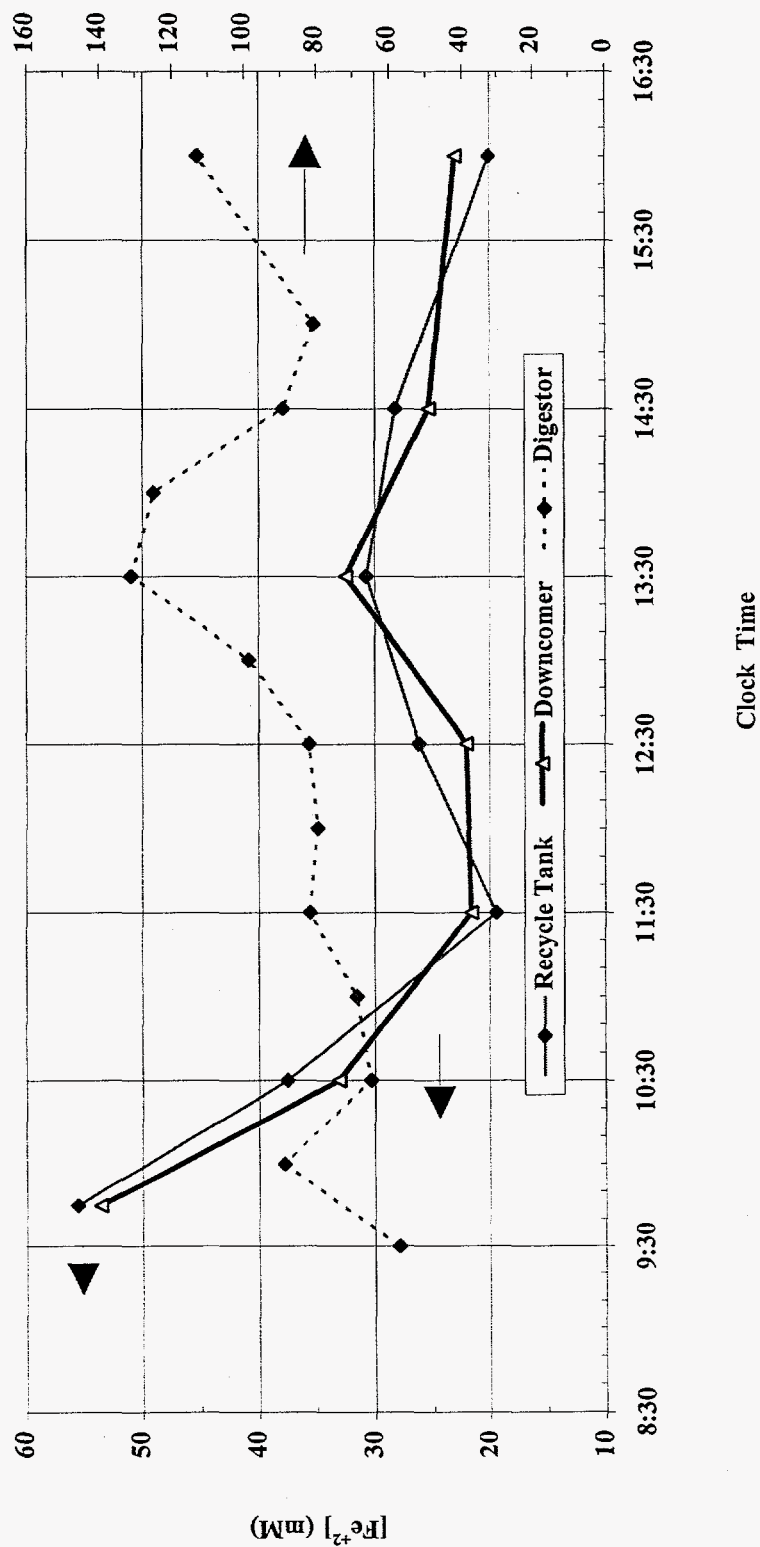


Figure 60. Measured $[\text{Fe}^{+2}]$ in the recycle tank, downcomer, and digester

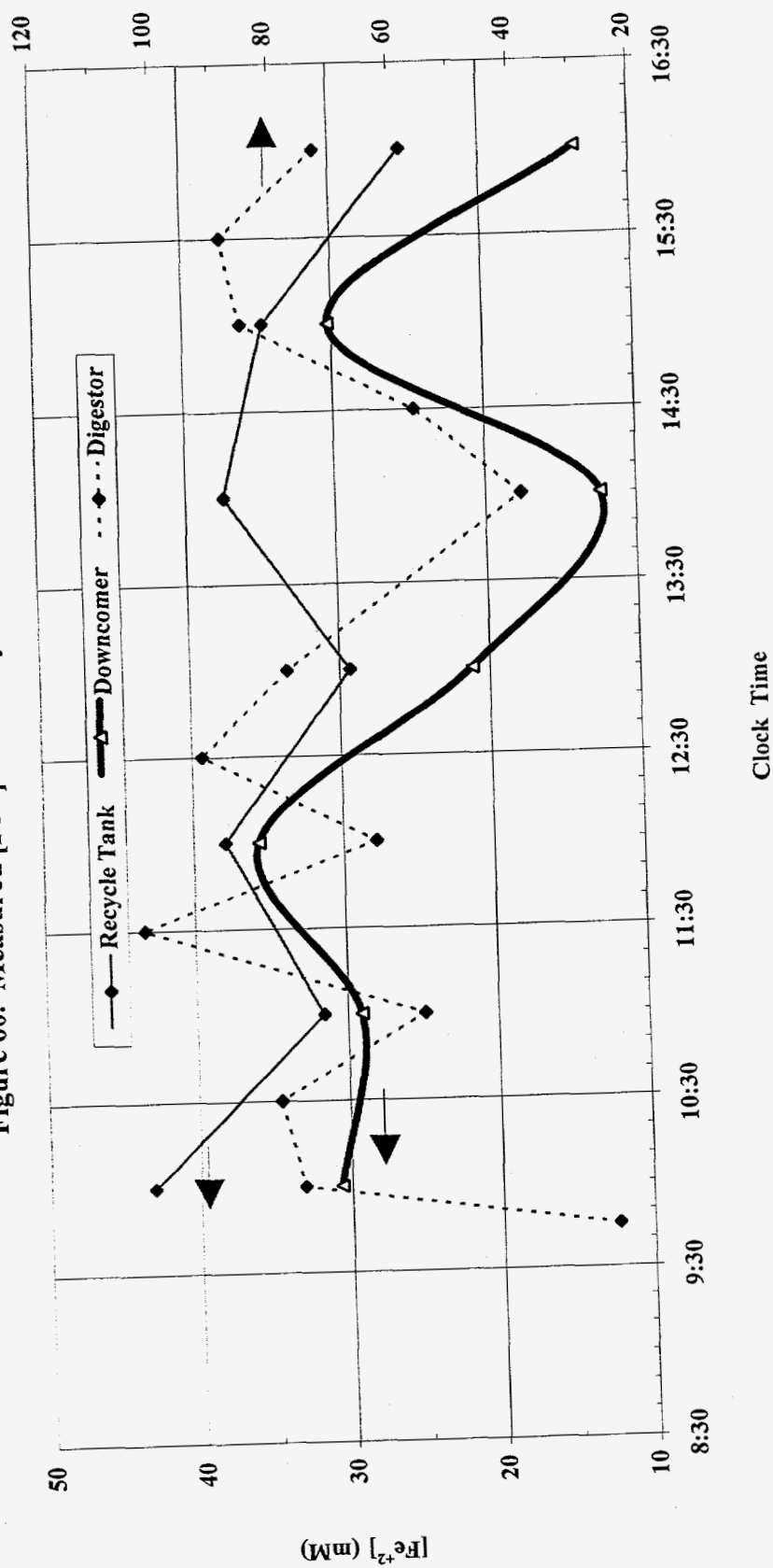


Figure 61. Change of recycle tank liquor $[\text{Fe}^{+2}]$ and NO removal with time

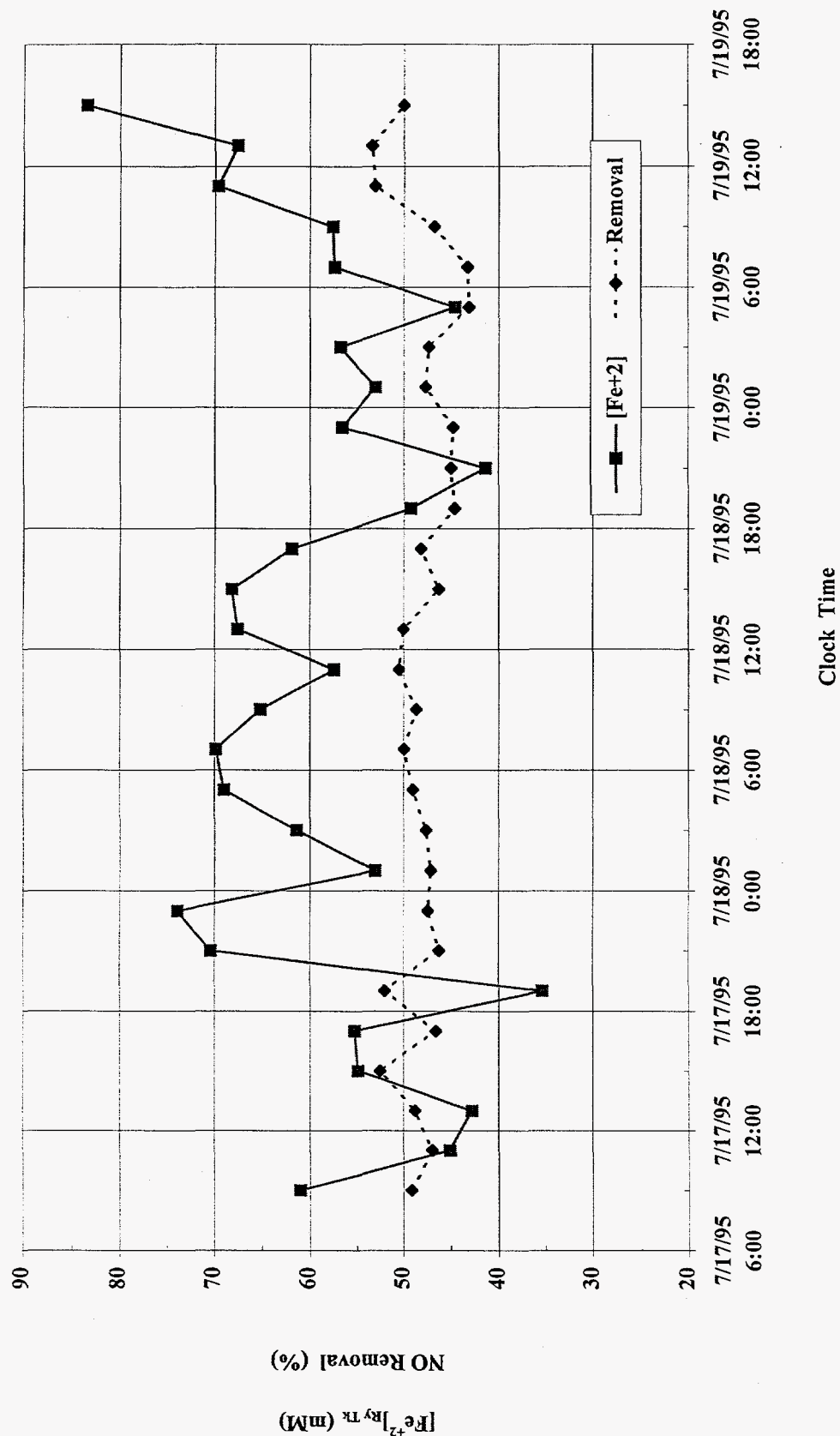


Figure 62. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

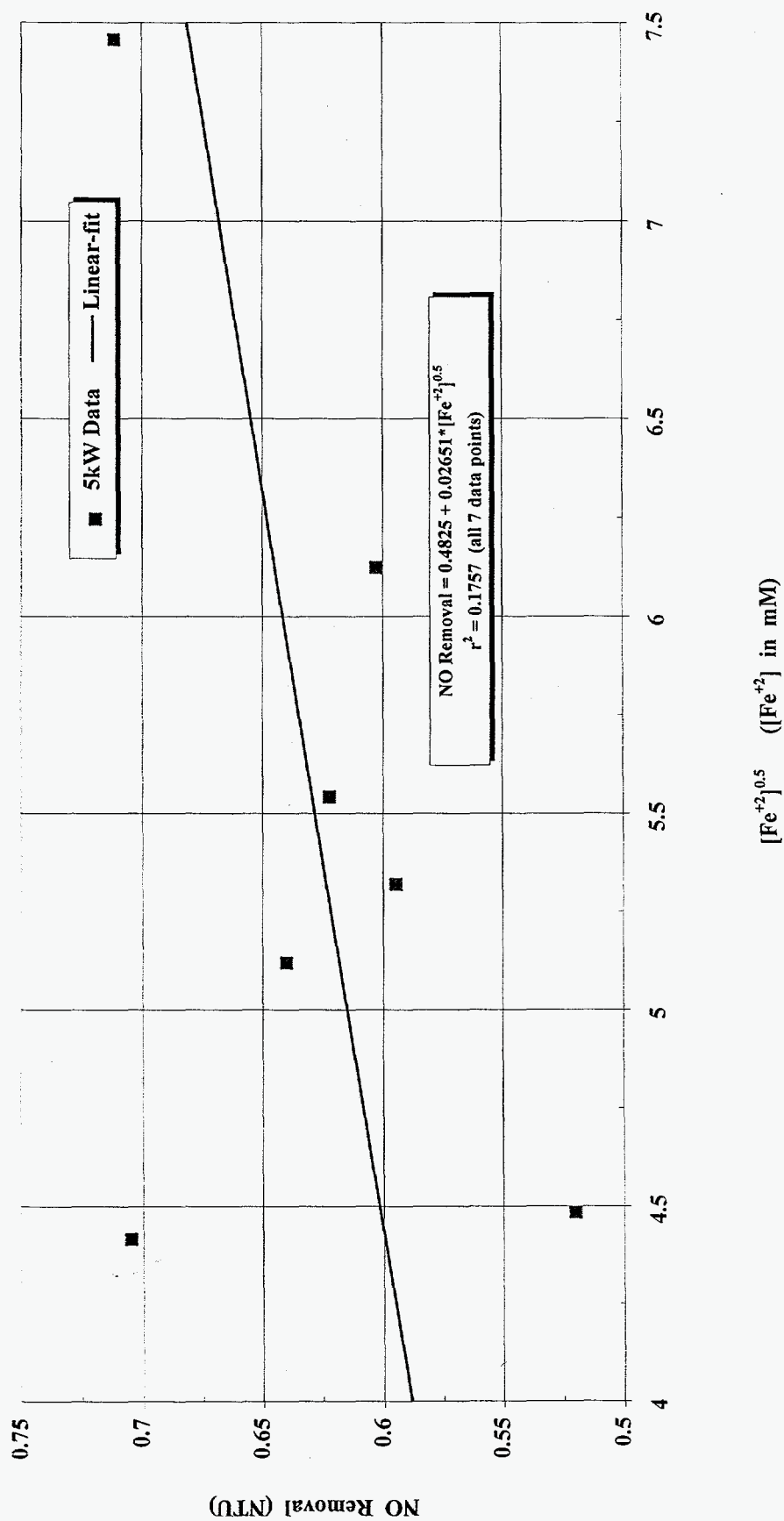


Figure 63. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

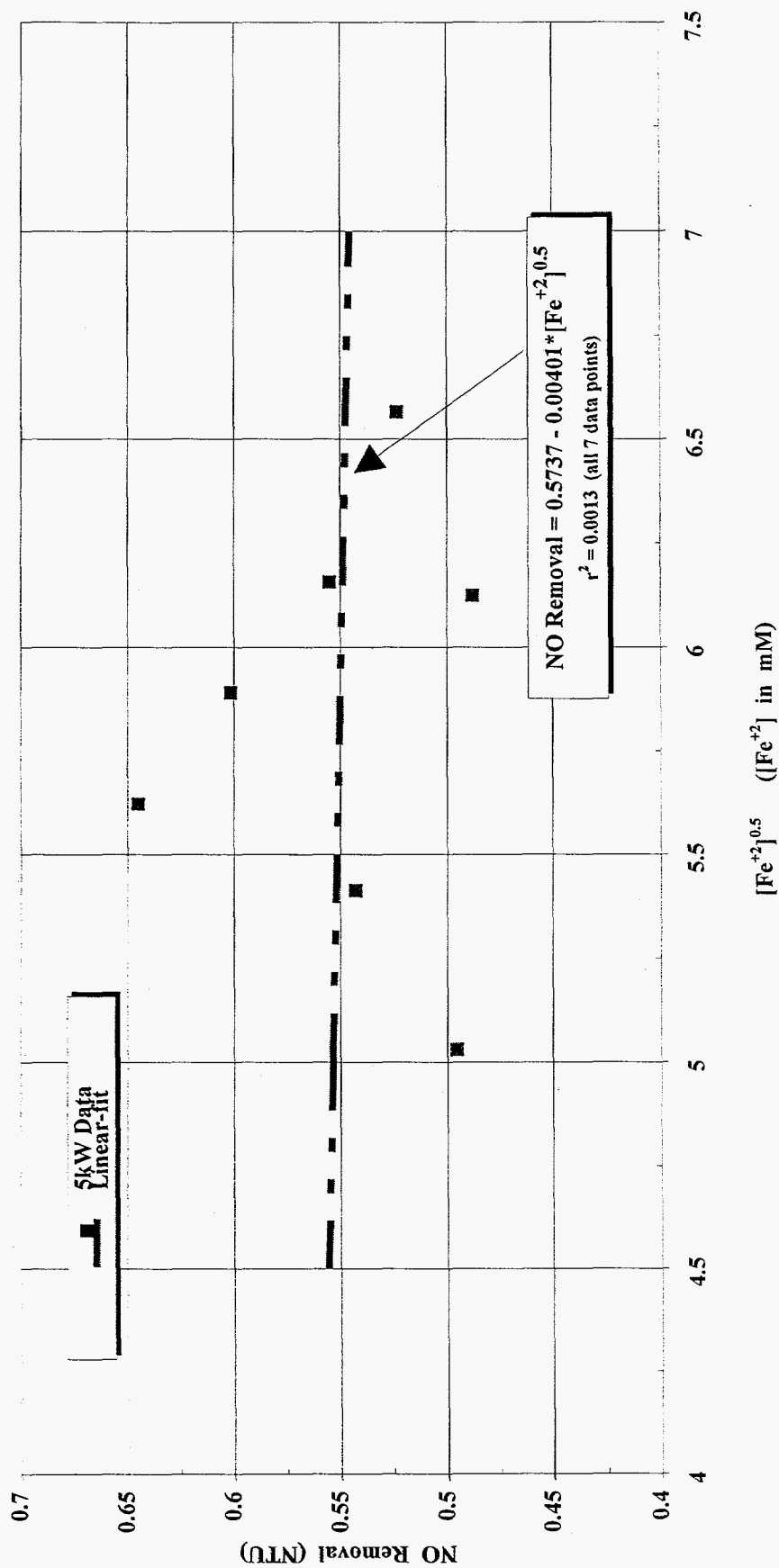


Figure 64. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

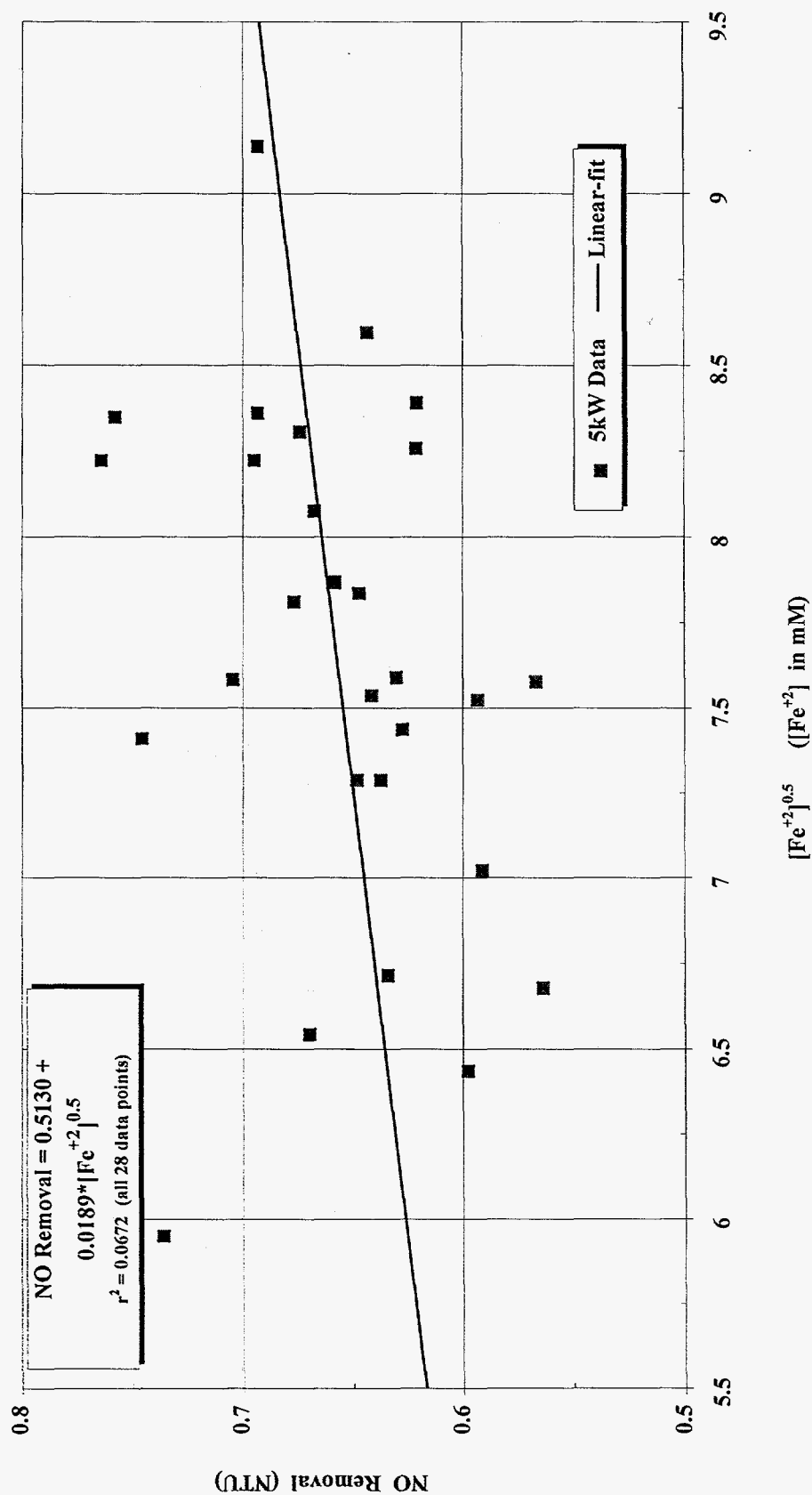


Table 12. Chemistry Data

Clock	Recycle Tank	Alkalinity (ppm)	[Fe ²⁺] by Spec-60 (mM)	[SO ₃ ²⁻] by I ₂ titration (ppm)	[SO ₃ ²⁻] adjusted for [Fe ²⁺] _{by rx} (ppm)	[SA] by IC (mM)	[SA] _{adjusted} (mM)	[ADS] _{adjusted} (mM)	[Mg ²⁺] by ICP (ppm)	[Ca ²⁺] by ICP (ppm)	[Total Fe] by ICP (ppm)	[Na ⁺] by ICP (ppm)	[S ₂ O ₃ ²⁻] by IC (ppm)	[NO ₃ ⁻] by IC (ppm)	[SO ₃ ²⁻] by IC (ppm)	[SO ₃ ²⁻] by IC (ppm)	[Cl ⁻] by IC (ppm)	Filtercake Solids (wt %)
	Liquor																	
	pH																	
9:45	5.5	1,851	55.6	7,622	5,398	0.93	2.1	1.2	6,863	346	4,850	41	n.d.	trace	5,393	7,441	3,881	
10:30	5.5	2,652	37.5	8,150	6,650	0.71	13.3	12.6	7,257	331	5,205	33	100	trace	6,659	9,214	4,734	69.8
11:30	5.6	2,252	19.5	7,029	6,249	1.76	24.7	22.9	7,264	368	4,995	50	136	trace	5,676	9,364	4,670	64.5
12:30	5.55	2,035	26.2	6,285	5,237	3.54	41.2	37.7	7,206	518	5,047	49	256	trace	4,209	9,459	4,339	58.4
13:30	5.8	2,068	30.7	5,500	4,272	5.98	53.6	47.6	7,441	848	4,988	50	314	trace	3,024	11,146	4,495	57.3
14:30	5.7	1,952	28.3	5,124	3,992	6.08	73.3	67.2	7,509	1,061	4,958	56	494	trace	2,795	11,396	4,475	56.5
16:00	6.0	2,285	20.1	4,323	3,519	10.1	116	105.9	7,552	1,904	4,563	54	742	trace	1,989	13,416	4,662	49.7

Table 13. Chemistry Data

Clock	Recycle	Alkalinity	[Fe ⁺²]	[SO ₃ ⁻²] by	[SO ₃ ⁻²]	[SA]	[SA] _{acidified}	[ADS] _{calculated}	[Mg ⁺²]	[Ca ⁺²]	[Total Fe]	[Na ⁺¹]	[S ₂ O ₃ ⁻²]	[NO ₃ ⁻¹]	[SO ₃ ⁻²]	[SO ₄ ⁻²]	[Cl ⁻¹]	Filtercake
Time	Tank	(ppm)	by Spec-601	I ₂ titration	adjusted for	by IC	by IC	(mM)	by ICP	by ICP	by ICP	by ICP	by IC	by IC	by IC	by IC	by IC	Solids
(Hr: Min)	Liquor		(mM)	(ppm)	[Fe ⁺²] _{by tx}	(mM)	(mM)		(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(wt %)
	pH				(ppm)													
10:00	5.60	2,352	43.1	7,214	5,490	1.56	2.88	1.32	6,644	431	4,494	40	n.d.	trace	5,133	6,814	4,090	
11:00	5.60	2,685	31.6	7,614	6,350	1.72	6.38	4.66	7,017	305	5,280	48	106	trace	5,558	8,217	4,724	62.8
12:00	5.75	2,469	37.9	6,805	5,289	2.47	8.49	6.02	6,615	349	4,936	44	140	trace	4,005	7,250	3,823	57.8
13:00	6.00	3,036	29.3	5,604	4,432	4.16	14.60	10.44	6,656	605	4,835	45	150	trace	3,066	8,328	3,962	56.0
14:00	5.70	2,018	37.5	5,596	4,096	5.36	15.70	10.34	6,783	707	4,863	49	201	trace	3,188	9,620	4,306	57.4
15:00	5.80	5,135	34.7	4,620	3,232	7.96	23.5	15.54	6,596	856	5,488	50	203	trace	2,406	9,334	3,989	59.5
16:00	6.00	2,652	25.3	4,115	3,103	8.92	31.70	22.78	6,525	1,318	4,348	51	194	trace	2,267	9,672	3,834	49.7

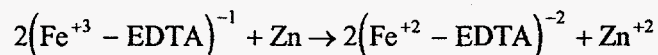
Table 14. Chemistry Data

Clock	Recycle	Alkalinity	[Fe ²⁺] _{Ry Th}	[SO ₃ ²⁻] by	[SO ₃ ²⁻]	[SA]	[SA]acidified	[ADS] _{calculated}	[Mg ²⁺]	[Ca ²⁺]	[Total Fe]	[Na ⁺]	[S ₂ O ₃ ²⁻]	[NO ₃ ⁻]	[SO ₃ ²⁻]
Time	Tank	(ppm)	by Spec-601	I ₂ titration	adjusted for	by IC	by IC	(mM)	by ICP	by ICP	by ICP	by ICP	by IC	by IC	by IC
(Hr: Min)	Liquor		(mM)	(ppm)	[Fe ²⁺] _{Ry Th}	(mM)	(mM)		(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
	pH				(ppm)										
7/17/95 9:00	5.1	984	61	12,025	9,585	1.56	4.26	2.7	8,544	1,062	6,070	174	45	tr	9,036
7/17/95 11:00	5.1	2,085	45.1	11,761	9,957	3.26	9.93	6.7	8,748	608	6,810	837	60	tr	9,317
7/17/95 13:00	5.2	2,685	42.8	11,729	10,017	13	24.6	11.6	9,119	788	7,966	1,519	245	tr	8,669
7/17/95 15:00	5.15	2,085	54.9	11,793	9,597	14.5	39.2	24.7	9,598	838	8,866	2,361	328	tr	9,614
7/17/95 17:00	5.05	2,218	55.3	10,368	8,156	18.8	44.8	26.0	9,951	879	9,557	2,497	492	tr	8,270
7/17/95 19:00	6.5	4,770	35.4	6,165	4,749	22.8	49.4	26.6	9,788	1,436	9,319	2,269	192	tr	2,696
7/17/95 21:00	5.1	2,235	70.4	14,275	11,459	19.5	53.9	34.4	10,950	1,649	12,300	2,591	624	tr	10,707
7/17/95 23:00	5.2	4,370	73.9	13,234	10,278	27.5	55.8	28.3	10,660	1,849	12,670	2,391	931	tr	12,267
7/18/95 1:00	5.05	2,969	53.1	11,481	9,357	37.5	49.7	12.2	10,090	2,889	11,210	1,634	851	tr	6,800
7/18/95 3:00	5	2,652	61.4	10,985	8,529	27.1	59	31.9	10,810	2,315	12,130	1,662	448	tr	7,428
7/18/95 5:00	5.6	5,171	69	8,102	5,342	32.4	68.6	36.2	10,840	2,698	11,790	1,506	584	tr	4,920
7/18/95 7:00	6	7,656	69.9	8,166	5,370	32.4	70.6	38.2	10,970	3,433	11,980	1,522	771	tr	4,728
7/18/95 9:00	4.85	3,069	65.2	11,473	8,865	23.4	60.2	36.8	9,795	2,152	10,920	1,051	452	tr	7,362
7/18/95 11:00	4.9	3,570	57.5	10,832	8,532	27.2	69.7	42.5	9,510	2,315	11,260	1,036	423	tr	7,563
7/18/95 13:00	4.85	3,169	67.6	10,792	8,088	28.5	68.2	39.7	10,460	2,862	12,380	1,087	331	tr	6,644
7/18/95 15:00	4.6	1,418	68.2	11,785	9,057	37.1	91.8	54.7	11,400	2,895	13,630	1,113	373	tr	7,221
7/18/95 17:00	5.05	3,603	61.9	10,448	7,972	30.2	78.5	48.3	10,060	2,420	11,920	1,099	334	tr	6,684
7/18/95 19:00	5.1	3,536	49.3	9,623	7,651	29.7	72.2	42.5	10,280	3,017	12,300	1,071	367	tr	6,560
7/18/95 21:00	5.6	5,254	41.4	7,382	5,726	32.1	83.5	51.4	9,918	3,598	11,770	1,010	379	tr	3,788
7/18/95 23:00	5.6	5,254	56.6	7,790	5,526	29.4	81.2	51.8	9,884	3,879	11,850	945	410	tr	4,228
7/19/95 1:00	5.6	4,220	53.1	7,462	5,338	32.2	131	98.8	9,617	3,127	10,720	1,051	287	tr	3,762
7/19/95 3:00	5.2	3,169	56.8	7,646	5,374	33.7	134	100.3	9,798	3,051	11,290	1,064	324	tr	4,190
7/19/95 5:00	6	6,672	44.6	5,756	3,972	37.9	155	117.1	9,484	4,099	11,170	999	221	tr	2,960
7/19/95 7:00	5.8	6,972	57.4	7,037	4,741	39	164	125.0	9,397	4,270	10,800	925	318	tr	3,491
7/19/95 9:00	5.65	5,054	57.6	5,532	3,228	40.5	130	89.5	8,547	3,582	9,973	925	254	tr	3,196
7/19/95 11:00	5.35	4,237	69.7	7,822	5,034	40.4	141	100.6	8,602	3,953	9,691	905	232	tr	3,066
7/19/95 13:00	5.3	3,570	67.6	6,637	3,933	51	162	111.0	8,702	4,417	9,510	861	498	tr	3,502
7/19/95 15:00	6.2	5,738	83.5	6,397	3,057	46.6	149	102.4	8,791	5,569	8,217	849	669	tr	2,584
7/19/95 16:00	5.4	2,902	86.1	6,917	3,473	59.8	205	145.2	9,044	4,325	9,163	871	664	tr	4,401

4. Zinc

a) 5 kW Configuration

No process modifications were required using zinc as a chemical regeneration agent. The configuration of the 5 kW is illustrated in Figure 33. The regeneration reaction believed to occur with zinc is as follows:



For test DT031694, (non-packed mode, ~50 mM initial total iron concentration, recycle tank pH = 5.3, L/G = 44, 6.5 vol.% O₂) the zinc was added manually to the recycle tank every 30 minutes. The addition rate was 12 grams/hr. To facilitate dissolution of the zinc, the liquor in the recycle tank was maintained at a pH of 5.3.

b) Test Results

The SO₂ removal was less than 90% for most of the test run. The average pH of 5.3 for the recycle tank liquor is low for achieving high alkalinities essential for high SO₂ removals. The SO₂ removal curve is shown in Figure 65. The NO_x removal was initially between 35% and 40% as illustrated in Figure 66 before decreasing to less than 20% by the end of the test run. The NO_x removals would show a sudden increase with zinc addition followed by a rapid decrease. The NO_x removal would probably increase with larger additions of zinc. Like iron, however, not all of the zinc is utilized. Some of the zinc settles to the bottom of the thickener, recycle tank, and heat exchanger tubing. The addition of more zinc would not be utilized because the excess would settle out in the system. The low NO_x removal can be explained by the low ferrous ion concentration after steady state was achieved. The average ferrous ion concentration was 10.2 mM well

below that necessary to obtain high NO_x removals. The ferrous ion concentration is illustrated in Figure 67.

Table 15 shows the sodium ion concentration was low, averaging 50.1 ppm. The sulfite ion concentration displayed an increasing trend which may have resulted from zinc ion concentration increasing as the test progressed. The accumulation of zinc ion indicates the zinc was acting as a regeneration agent. There was a drop in total iron concentration as testing continued. The drop in total iron concentration could be associated with the displacement of iron in iron-EDTA by zinc to form zinc-EDTA. The loss in total iron presents a problem since this also indicates a loss in ferrous ion. Calcium ion concentrations averaged 398 ppm. The solids content of the filtercake displayed an increasing trend during the run. The final solids content was 72.1 wt.%. This represents a solids content that is typically achieved in the ThioNO_x process. The correlation to the NO_x removal model is shown in Figure 68. The correlation coefficient is 0.9007, indicating a good fit.

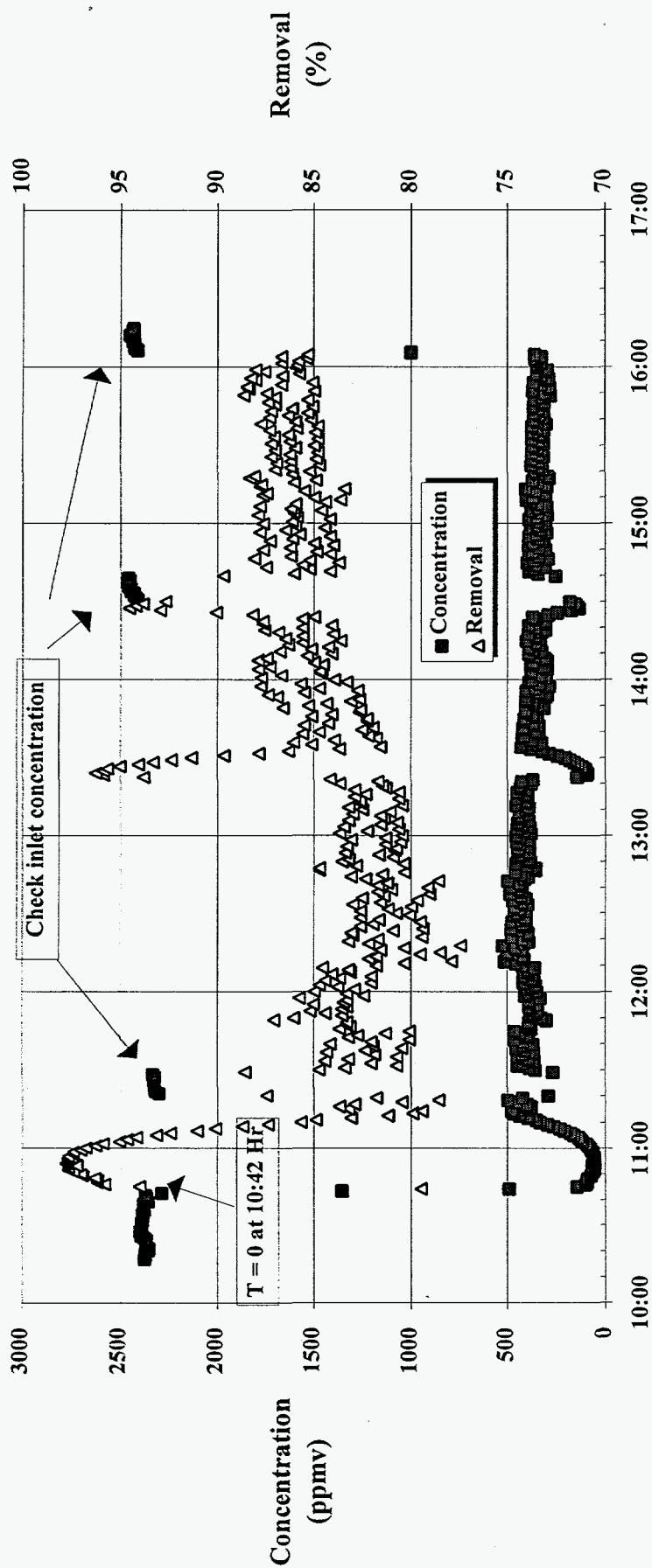
c) Economics of Zinc Addition

The cost of this regeneration agent is \$0.53/lb_m. On a mM ferrous ion concentration and NTU removal basis the cost was found to be \$0.00643/day·mM Fe⁺²·vol.% O₂ and \$0.297/day·NTU·vol.% O₂, respectively. This was a less expensive agent than aluminum, hydroxylamine sulfate, and both hydrazine compounds. The use of zinc was also found to be more economical than the thermal regeneration method. The comparative economics of this regeneration agent is displayed on Figures 50 and 51. Zinc was a member of a class of regeneration agents consisting of zinc, hydrazine, sodium tetrasulfide, thermal regeneration method, and sodium dithionite/ascorbic acid ranging from \$0.0005 to \$0.0200/day·mM Fe⁺²·vol.% O₂. This group of agents represented the middle ground in terms of cost effectiveness. A second group was more economical while a third group was less.

d) Attainment of Objectives

The objective of testing zinc to determine its suitability as a regeneration agent was satisfied. The SO₂ removal objective was not met. The SO₂ removal for this test was low averaging less than 90%. NO_x removals were below 30% for all but the beginning of the test run. Obviously NO_x removals were not high enough to justify its use. There is also evidence that zinc is stripping iron from EDTA resulting in a drop in ferrous ion concentration. High ferrous ion concentrations are essential for high NO_x removal.

Figure 65. SO₂ concentration and removal vs. time



Clock Time

Figure 66. NO concentration and NO removal vs. time

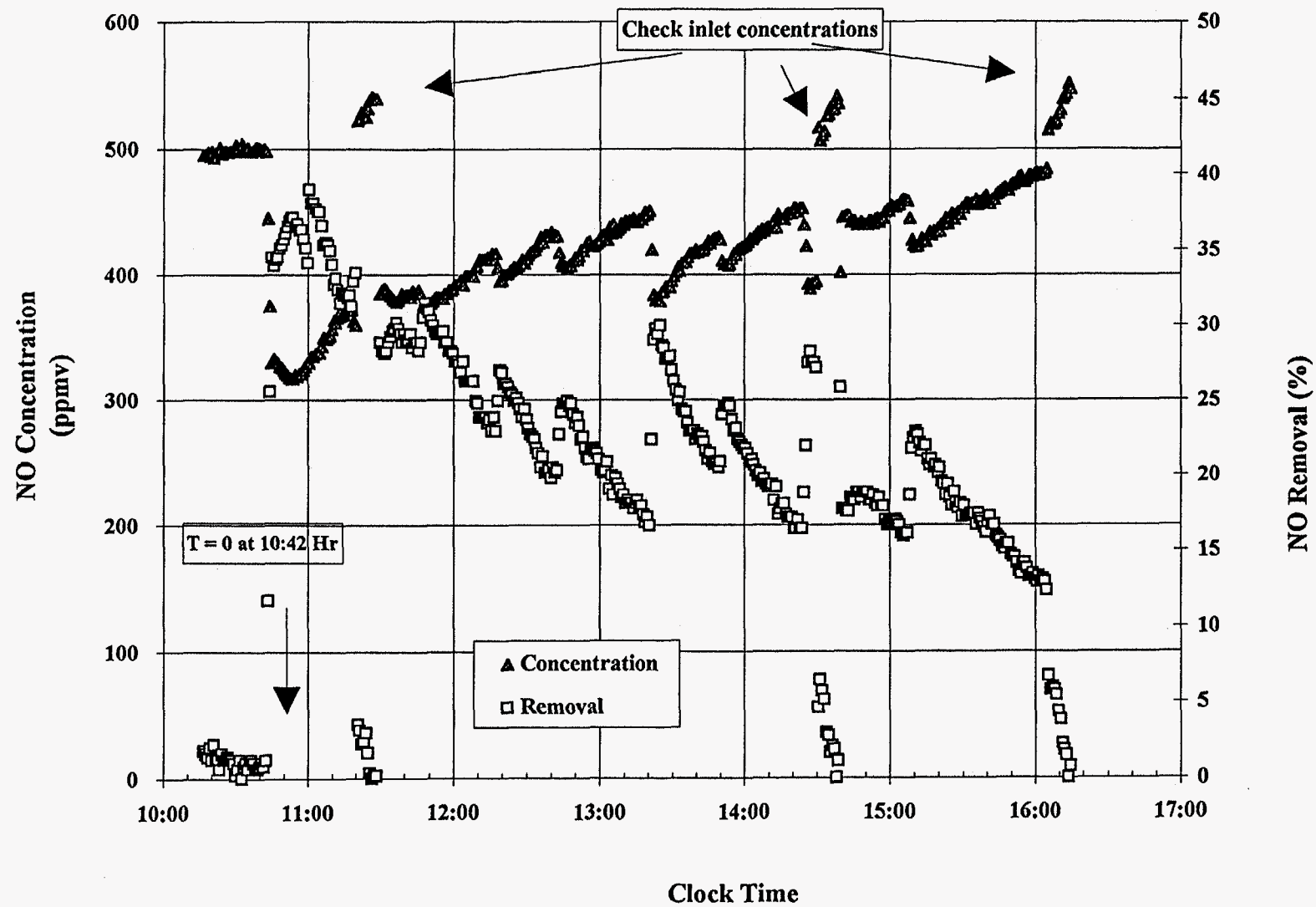


Figure 67. Change in recycle tank $[\text{Fe}^{+2}]$ with time

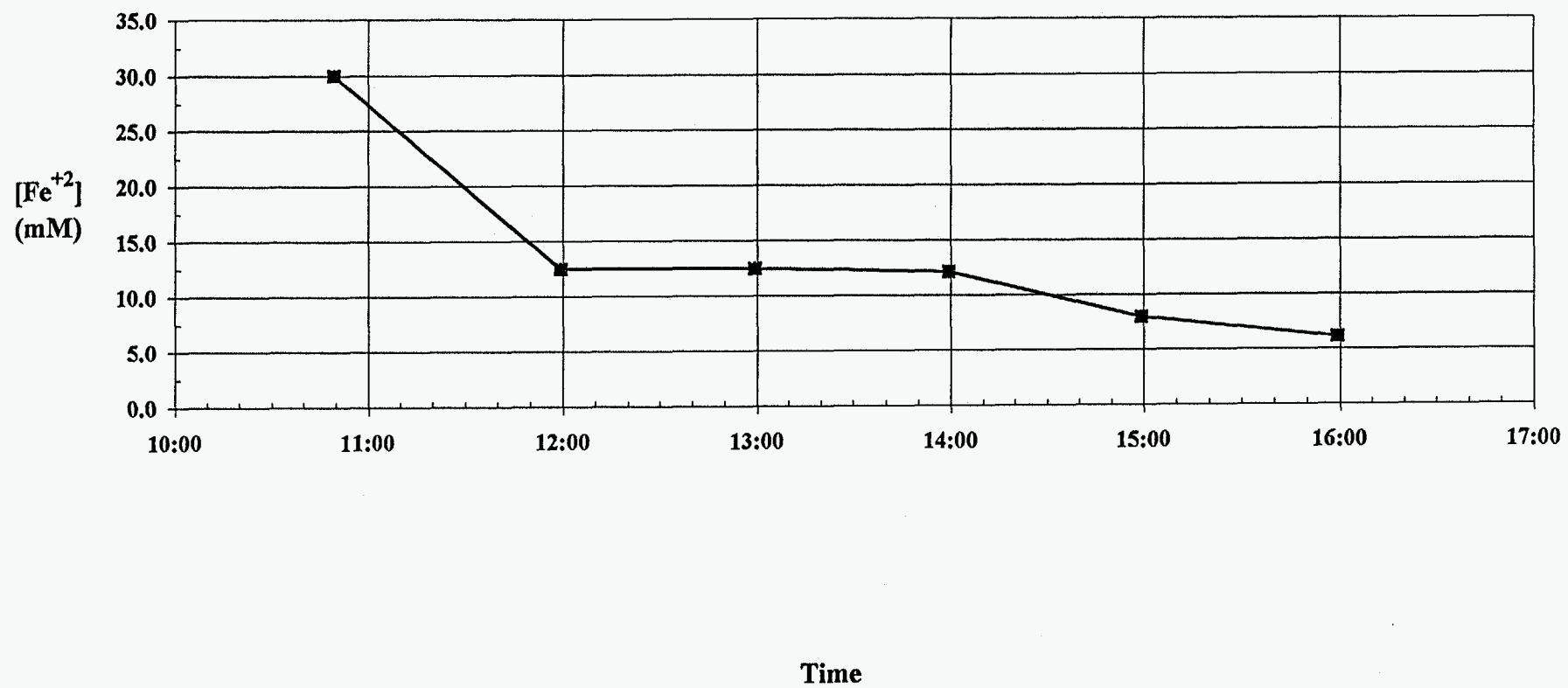


Fig 68. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

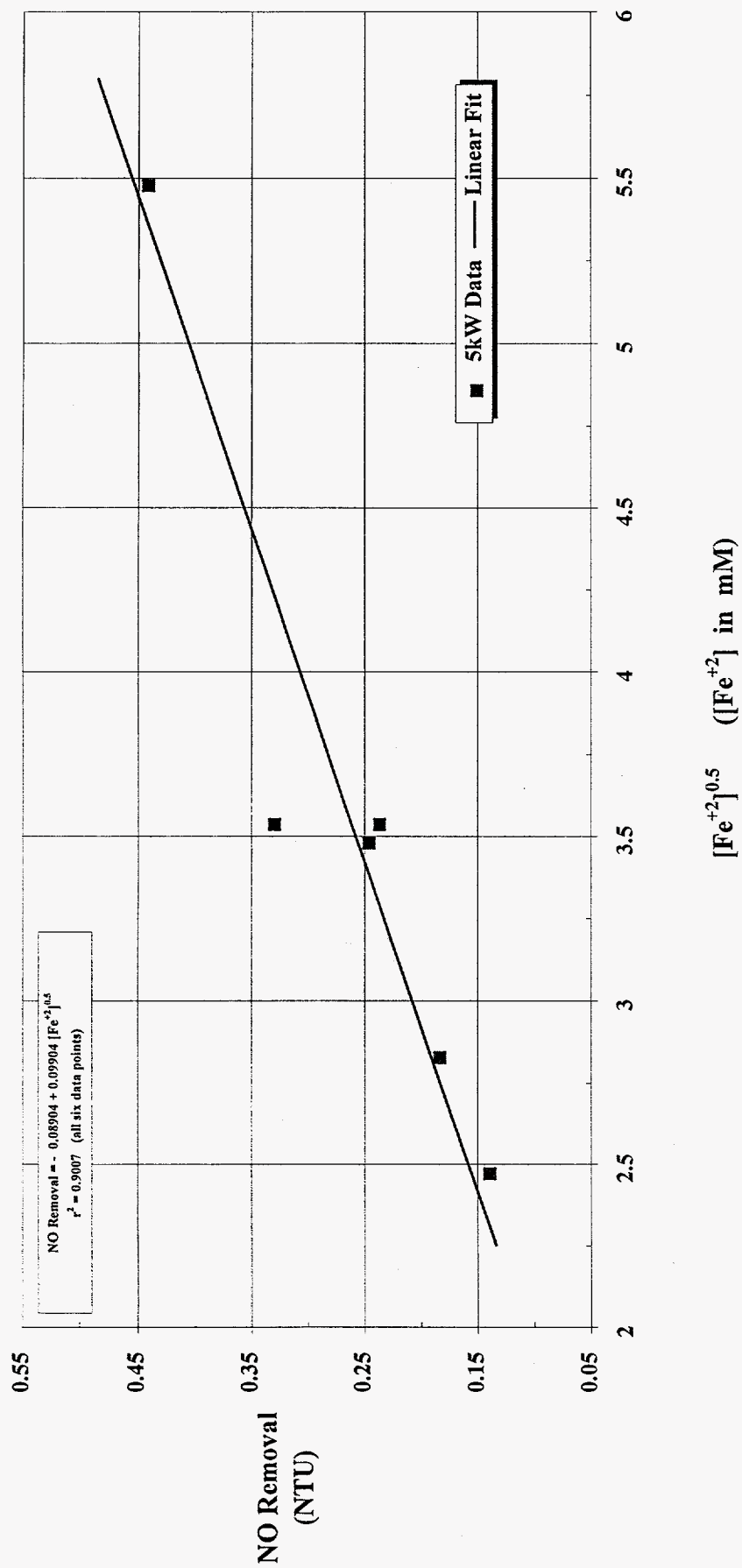


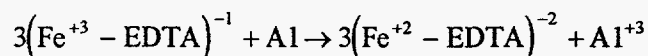
Table 15. Chemistry Table

Clock Time	Recy Tank	Alkalinity	[SO ₃ ⁻²] as	[Fe ⁺²] _{Ry Tk}	[SO ₃ ⁻²]	[ADS]	[Mg ⁺²]	[Ca ⁺²]	[Total Fe] _{Ry Tk}	[Zn ⁺²]	[Na ⁺¹]	Filtercake
(Hr: Min)	Liquor pH	(ppm)	analyzed	(mM)	corrected for	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	Solids
			(ppm)		[Fe ⁺²] _{Ry Tk}							(wt %)
					(ppm)							
10:30	6.3	1751	5596	30.0	4396	0.58	3540	211	1940	12.7	84.2	
12:00	5.3	1051	10256	12.5	9756	2.85	4286	445	1910	758	43	
13:00	5.2	867	10696	12.5	10196	5.73	4124	467	1534	1213	51.3	61.8
14:00	5.3	851	12378	12.1	11894	9.88	4780	452	1345	1775	40.5	67.3
15:00	5.3	1151	12001	8.0	11681	12.24	5197	391	1197	1890	38.6	70.1
16:00	5.3	1518	12025	6.1	11781	15.04	5455	423	1097	2092	42.7	72.1
avg:	5.5	1198			9951		4564	398	1504	1290	50.1	67.8

5. Aluminum

a) 5 kW Configuration

No process modifications were necessary with aluminum as the regeneration agent. The configuration of the 5 kW is illustrated in Figure 33. The regeneration reaction believed to occur with aluminum is as follows:



For test DT092094 (non-packed mode, ~50 mM initial total iron concentration, recycle tank pH = 5.7, L/G = 44, 6.5 vol.% O₂), aluminum was added manually to the recycle tank at a rate of 8 grams/hr. To facilitate dissolution of the aluminum, the liquor in the recycle tank was maintained at a pH of 5.7.

b) Test Results

The SO₂ removal was between 90% and 95% for most of the run. This is illustrated in Figure 69. This low SO₂ removal exists because of the low average pH of the recycle tank liquor. The NO_x removal, as shown in Figure 70, declined from 35% to less than 15% by the end of the test. NO_x removals did not show sudden increases with aluminum addition. This is comparable to the removals achieved with the baseline tests. Aluminum is therefore not thought to have any regeneration ability. The low NO_x removal was the result of the ferrous ion concentration dropping continuously during the initial part of the test. By the end of the test run, the ferrous ion concentration was less than 5 mM. With such low ferrous ion concentrations, high NO_x removals were never achieved. The ferrous ion concentration curve is also shown in Figure 70.

The sodium ion concentration was low averaging 43.3 ppm as shown in Table 16. The sulfite ion concentration was fairly constant averaging 5,948 ppm. The sulfate ion was also relatively steady averaging 4,425 ppm. The magnesium ion concentration was 2,890 ppm. These are standard chemistries for a ThioNO_x system. The solids content of the filtercake decreased from 75.7 wt.% to 67.6 wt.%. This decreasing trend indicates that with continued testing the filtercake solids content would decrease even more. This is far below the maximum dewatering capability exhibited by the ThioNO_x process. Subsequently, the dewatering criteria as outlined in the test plan were not met. The aluminum ion concentration was monitored during the run and found to increase in amount only sparingly. This suggests aluminum may not be highly reactive when it comes to regenerating ferrous ion.

The correlation of the data points to the NO_x removal model was found to be 0.989. The curve to the removal model is shown in Figure 71.

c) Economics of Aluminum Addition

Aluminum is an expensive reagent costing \$3.23 / lb_m. This represents a cost over twenty times that of iron. The cost on a mM ferrous ion concentration and NTU removal basis was determined to be \$0.0679/day·mM Fe⁺²·vol.% O₂ and \$0.297/day·NTU·vol.% O₂, respectively. Only hydroxylamine sulfate costs more than this agent. The comparative economics of this regeneration agent is shown in Figures 50 and 51. Aluminum, hydroxylamine sulfate, and hydrazine sulfate form a class of agents representing the highest cost on a mM ferrous ion concentration and NTU removal basis. These agents form an economically unfavorable class ranging in cost from \$.0300 to \$.3000/day·mM Fe⁺²·vol.% O₂.

d) Attainment of Objectives

The objective of testing aluminum to determine its suitability as a regeneration agent was satisfied. The SO_2 removal was more than 5% below the criteria established in the test plan. NO_x removals were below 30% for all but the beginning of the test run. NO_x removal was not high enough to justify the use of this chemical agent. The small increase in aluminum ion concentration suggests that aluminum was not reactive in the ferric ion reduction. The solids content of the filtercake is also below the criteria established for the Thio NO_x process as set forth in the test plan.

Figure 69. SO₂ concentration and removal vs. time

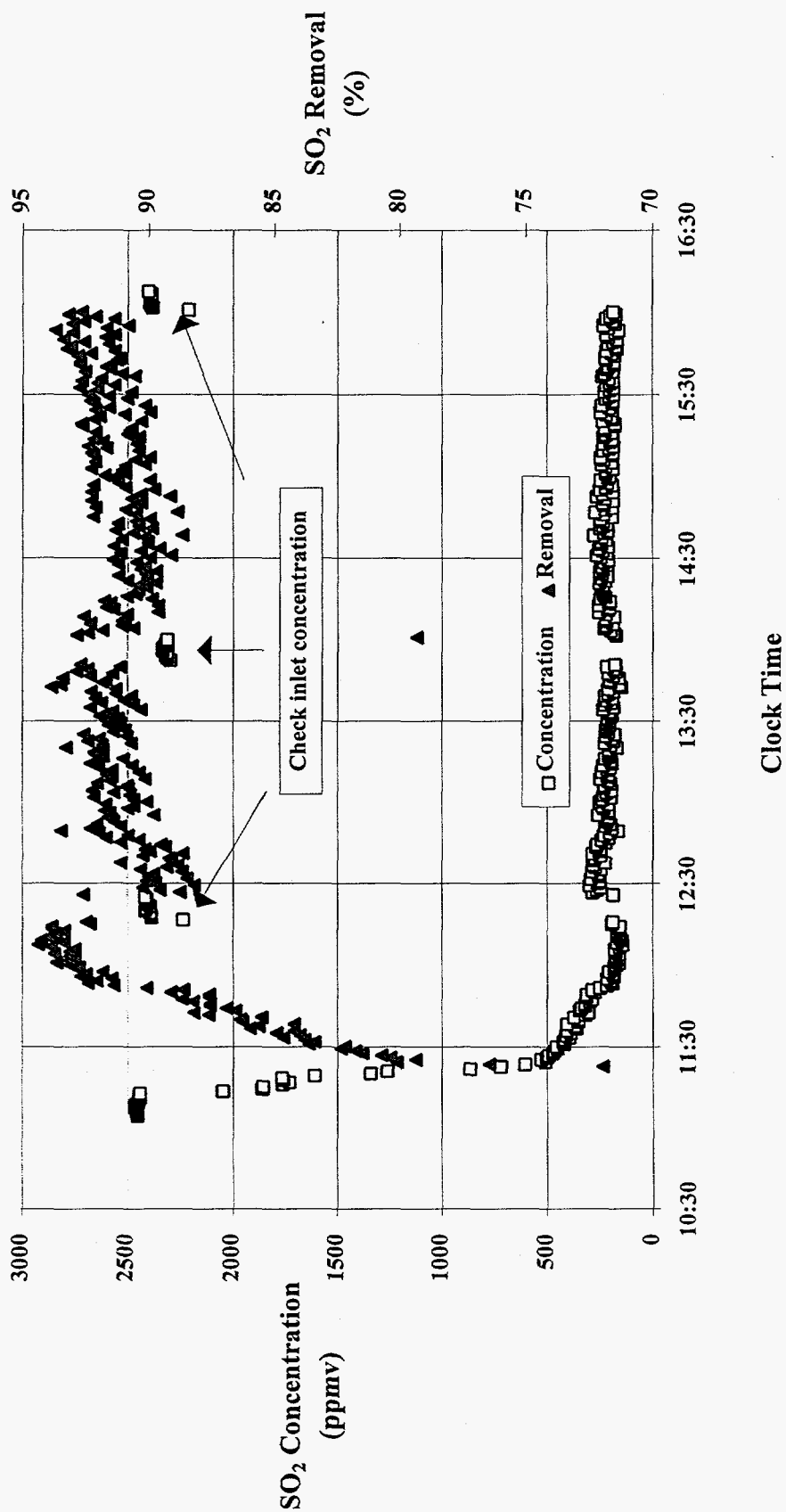


Figure 70. NO concentration, NO removal, and $[\text{Fe}^{+2}]$

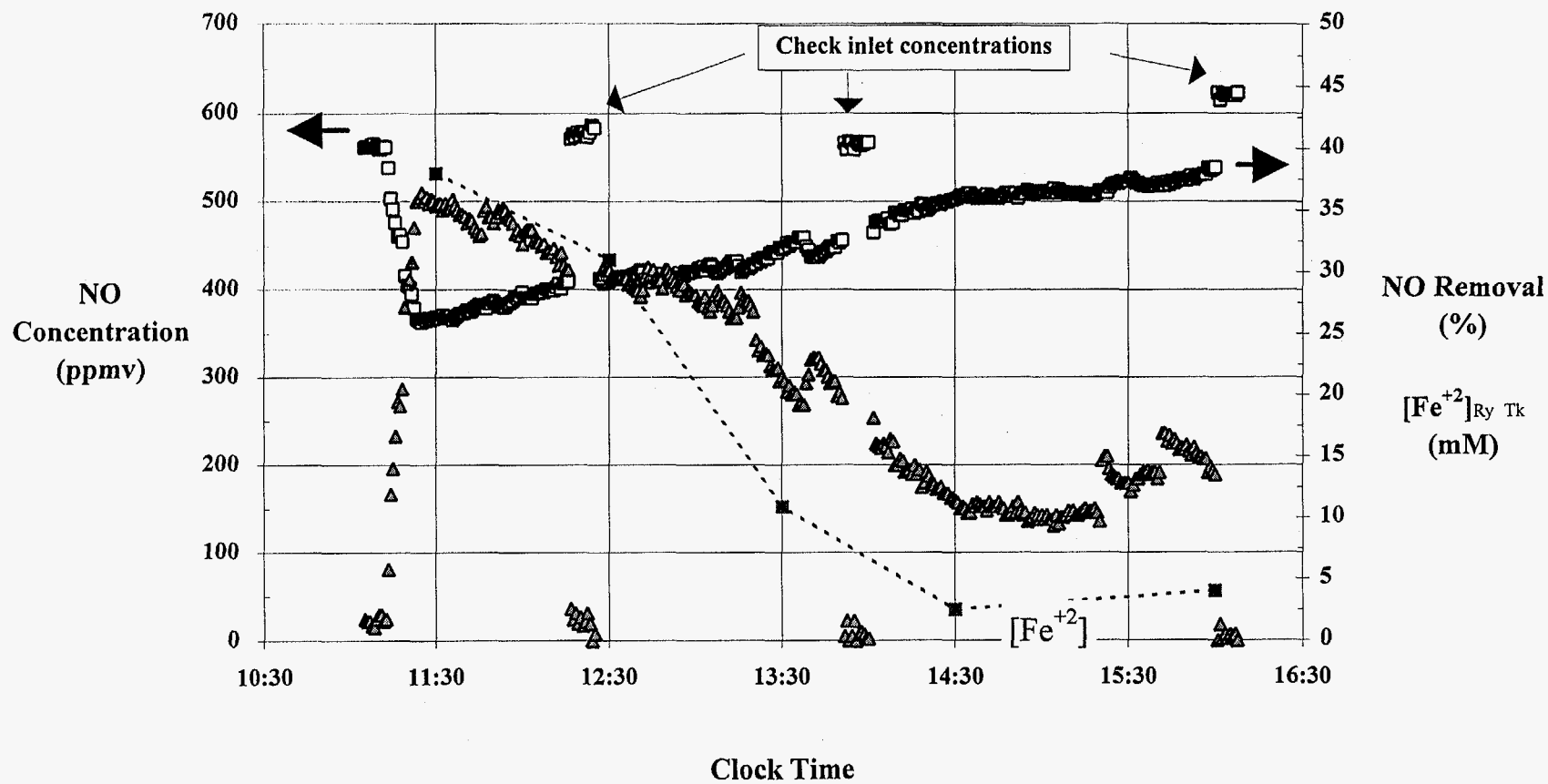


Figure 71. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

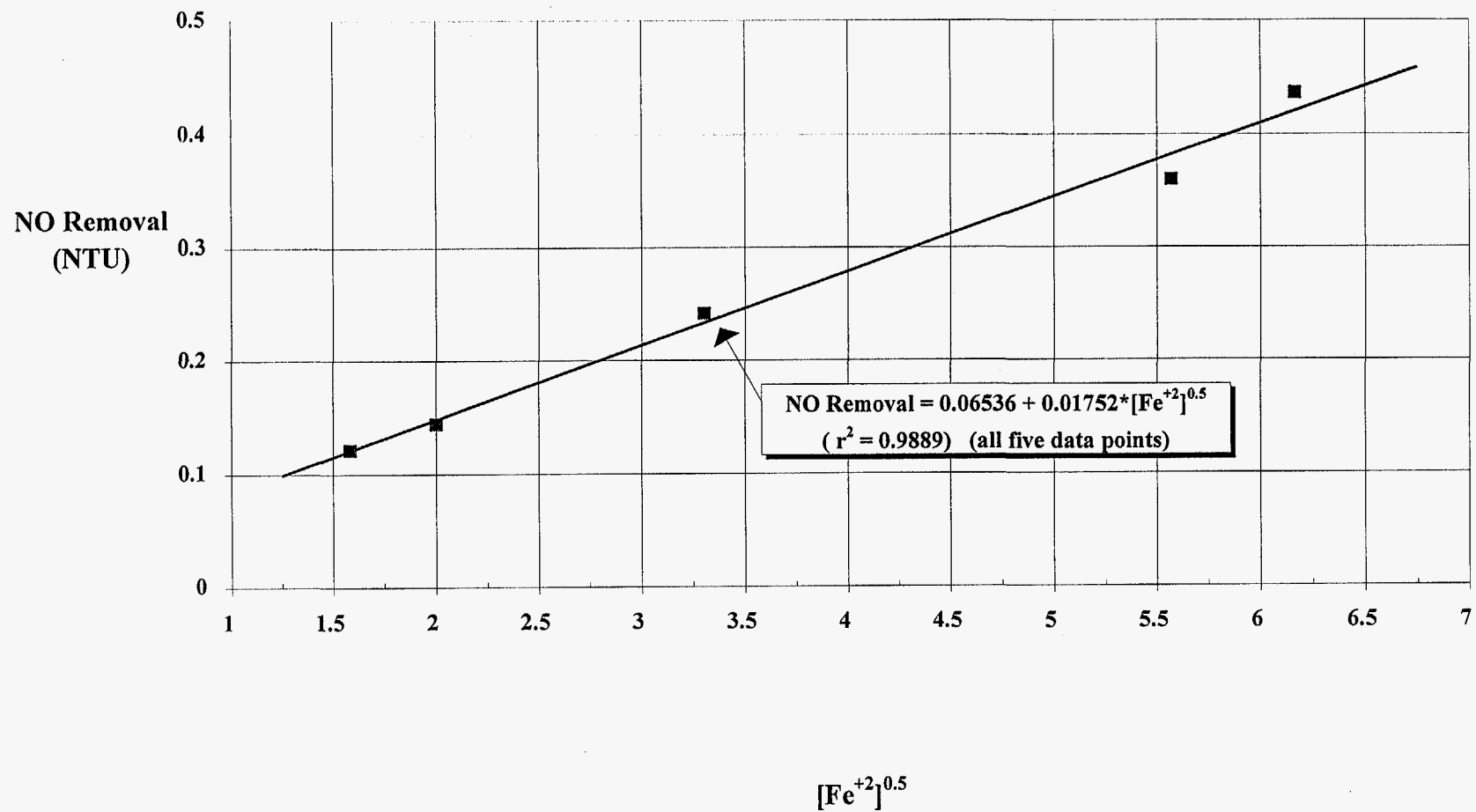


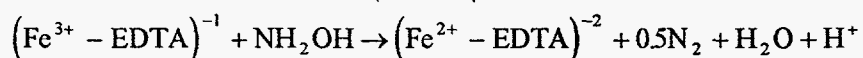
Table 16. Chemistry Data

Clock Time	Recy Tank	Alkalinity	[SO ₃ ⁻²] as	[Fe ⁺²]	[SO ₃ ⁻²]	[Mg ⁺²]	[Ca ⁺²]	[Total Fe]	[Na ⁺¹]	[Al ⁺³]	[ADS]	[SA]	[SO ₃ ⁻³]	[SO ₄ ⁻²]	[S ₂ O ₃ ⁻²]	[Cl ⁻¹]	Filtercake
(Hr: Min)	Liquor pH	(ppm)	analyzed	(mM)	corrected	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(mM)	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	Solids
			(ppm)		for [Fe ⁺²]												(%)
					(ppm)												
11:30	5.8	1,184	7,286	38.0	5,766	2,783	366	2,534	44.05	2.85	0.68	n.d.	5,968	4,705	n.d.	286	
12:30	5.8	1,101	5,660	31.0	4,420	2,849	408	2,565	44.50	3.82	0.37	0.76	5,134	4,503	n.d.	234	
13:30	5.6	1,051	5,829	10.9	5,393	2,751	228	2,333	42.02	4.26	1.68	3.23	5,876	4,438	n.d.	303	75.7
14:30	5.65	1,218	5,788	2.5	5,688	3,043	239	2,442	42.90	5.10	10.79	1.97	6,260	4,295	n.d.	230	72.5
16:00	5.75	1,301	5,973	4.0	5,813	3,022	194	2,298	42.84	8.52	6.47	4.66	6,504	4,186	n.d.	285	67.6

6. Hydroxylamine Sulfate

a) 5 kW Configuration

No process modifications were necessary with hydroxylamine sulfate as the regeneration agent since this chemical was added as a solid directly to the recycle tank. The configuration of the 5 kW is illustrated in Figure 33. The regeneration reaction believed to occur with hydroxylamine sulfate is as follows:



Two tests were conducted with this agent DT032494 (non-packed mode, ~50 mM initial total iron concentration, recycle tank pH = 6.3, L/G = 44 to 88, 6.5 vol.% O₂) and DT032594 (non-packed mode, ~25 mM initial total iron concentration, recycle tank pH = 5.8, L/G = 44 to 88, 6.5 vol.% O₂).

For both tests 60 grams per hour of agent were added. Running two tests at different recycle tank liquor pH values enabled a comparison to be made with the SO₂ and NO_x removal of both tests

b) Test Results

The SO₂ removal reached greater than 99% after increasing the L/G from 44 to 88 for test DT032494 meeting the SO₂ removal criteria. This is illustrated in Figure 72. The SO₂ removal reached 98% to 99% for test DT032594 after increasing the L/G from 44 to 88 also meeting the SO₂ removal goal as shown in Figure 73. The NO_x removal for test DT032494 was fairly constant but averaged below 20%. The NO_x removal was also fairly constant for test DT032594 averaging slightly below 15%. Comparing these NO_x removals with those obtained for the baseline tests revealed no improvement in NO_x removal. The final steady state NO_x

removal for the baseline tests was between 15% and 20%. This implies that hydroxylamine sulfate has low regeneration ability of ferrous ion. If 60 grams of hydroxylamine sulfate per hour is ineffective as a regeneration agent, then it is believed that no addition rate will elevate the ferrous ion concentration to a level where 50% to 60% NO_x removal is obtained. The NO_x removal curves for both tests are shown in Figures 74 and 75. The low NO_x removals resulted from a rapid decrease in ferrous ion concentration after the test was initiated. The average ferrous ion concentration after steady state was achieved was 2.1 mM for test DT032494 while for test DT032594 the ferrous ion concentration averaged 1.6 mM after steady state. The ferrous ion concentration curves are shown in Figures 76 and 77. Obviously with ferrous ion concentrations below 2.5 mM, NO_x removal will be low.

Tables 17 and 18 shows the sodium ion concentration averaged 33 mM for test DT032494 and 23.5 mM for test DT032594, both of which were within the sodium ion range for a ThioNO_x system. For both tests the sulfite ion concentrations decreased during the test run although SO₂ removals were high once the L/G was increased from 44 to 88. The filtercake solids content averaged 51.0 wt.% for test DT032594. For test DT032494, the filtercake solids content decreased continuously as testing progressed. By the end of the test period, the solids content of the filtercake was 52.4 wt.%. In both instances the solids content was below that typically achieved in a ThioNO_x process. For both cases, the correlation to the NO_x removal model were high. The correlation coefficients of both sets of data were above 0.950. The NO_x removal model curves are shown in Figures 78 and 79.

c) Economics of Hydroxylamine Sulfate Addition

The cost of this agent was \$1.00 / lb_m. The economic analysis performed for this agent revealed that it was the most expensive means for ferrous ion regeneration. The cost on a mM ferrous ion concentration and NTU removal basis was found to be \$0.282/day·mM Fe⁺²·vol.% O₂ and \$3.38/day·NTU·vol.% O₂ respectively. Its cost relative to other ferrous ion regeneration methods is depicted in Figures 50 and 51. Based on the economics of this agent, it should be ruled out as an effective ferrous ion regeneration agent.

d) Attainment of Objectives

The objective of determining whether hydroxylamine sulfate was a suitable chemical regeneration agent was met. The SO₂ removal was found to meet the criteria established for percentage removal. However, the NO_x removal fell short of reaching the 60% NO_x removal targeted in the test plan. The chemistry for these test runs was typical for a ThioNO_x test except for the solids content of the filtercake which was lower than normally observed. The consumption economics indicate the agent is ineffective to reduce ferric ions.

Figure 72. SO₂ concentration and removal vs. time

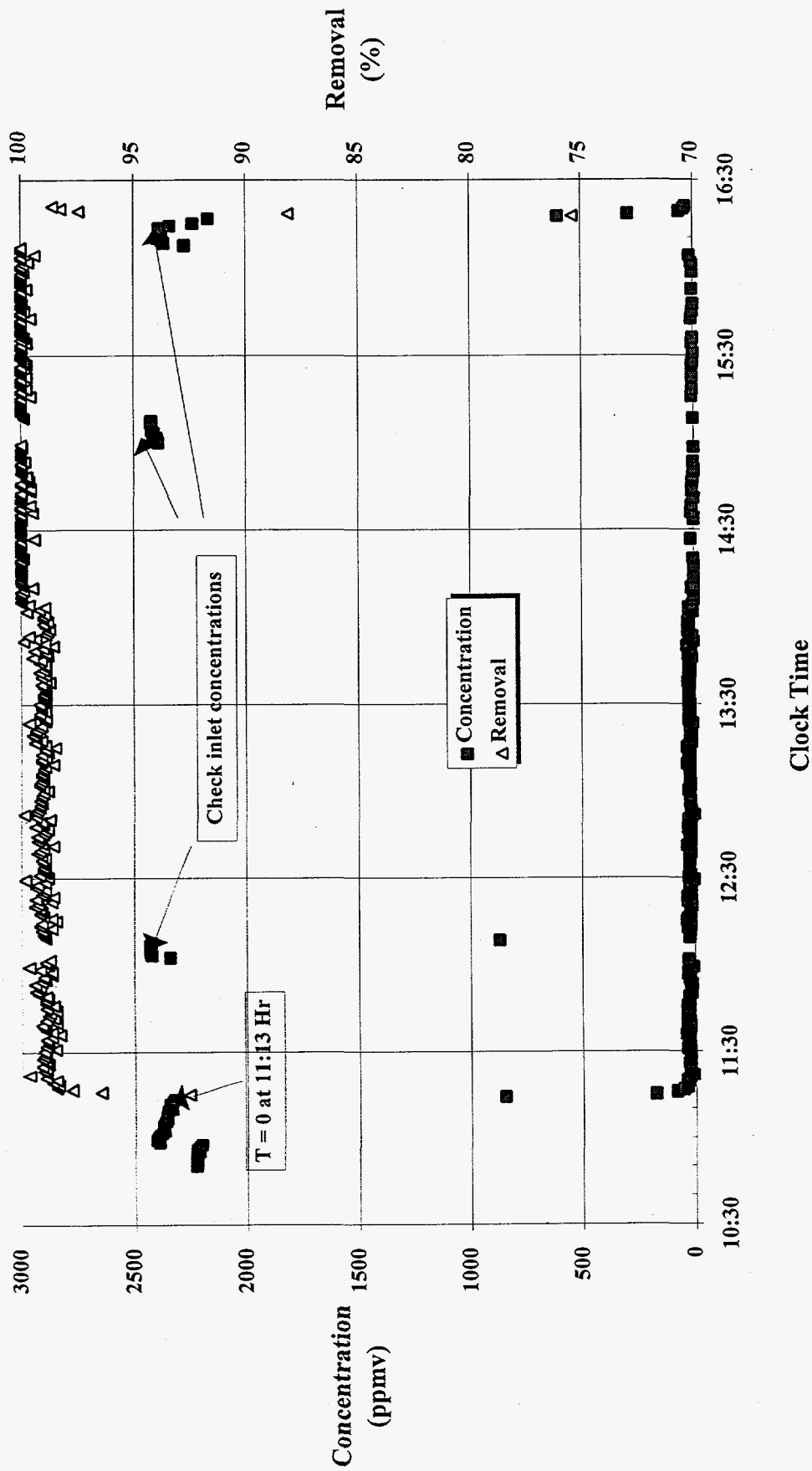


Figure 73. SO₂ concentration and removal vs. time

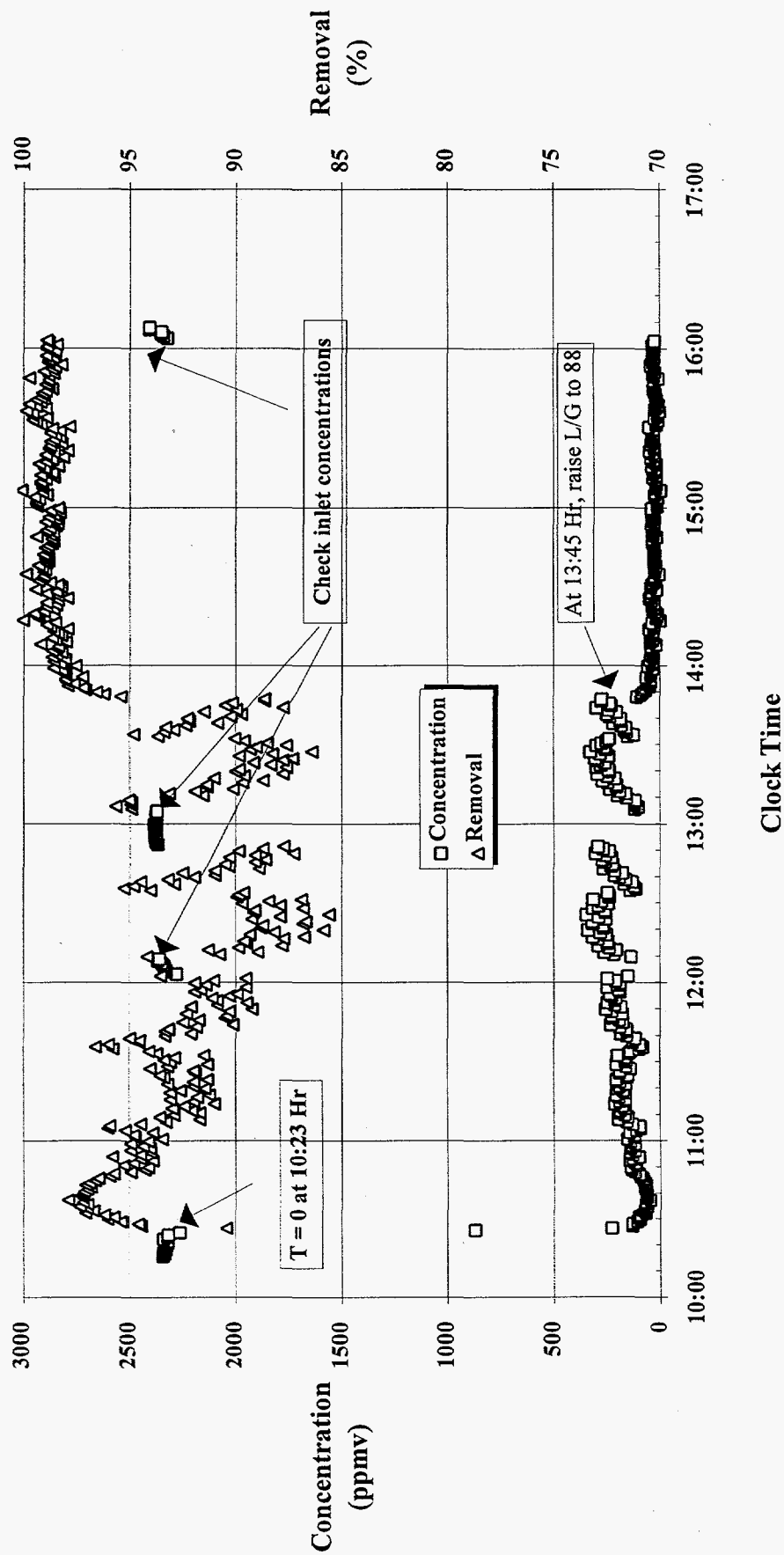


Figure 74. NO concentration and removal vs. time

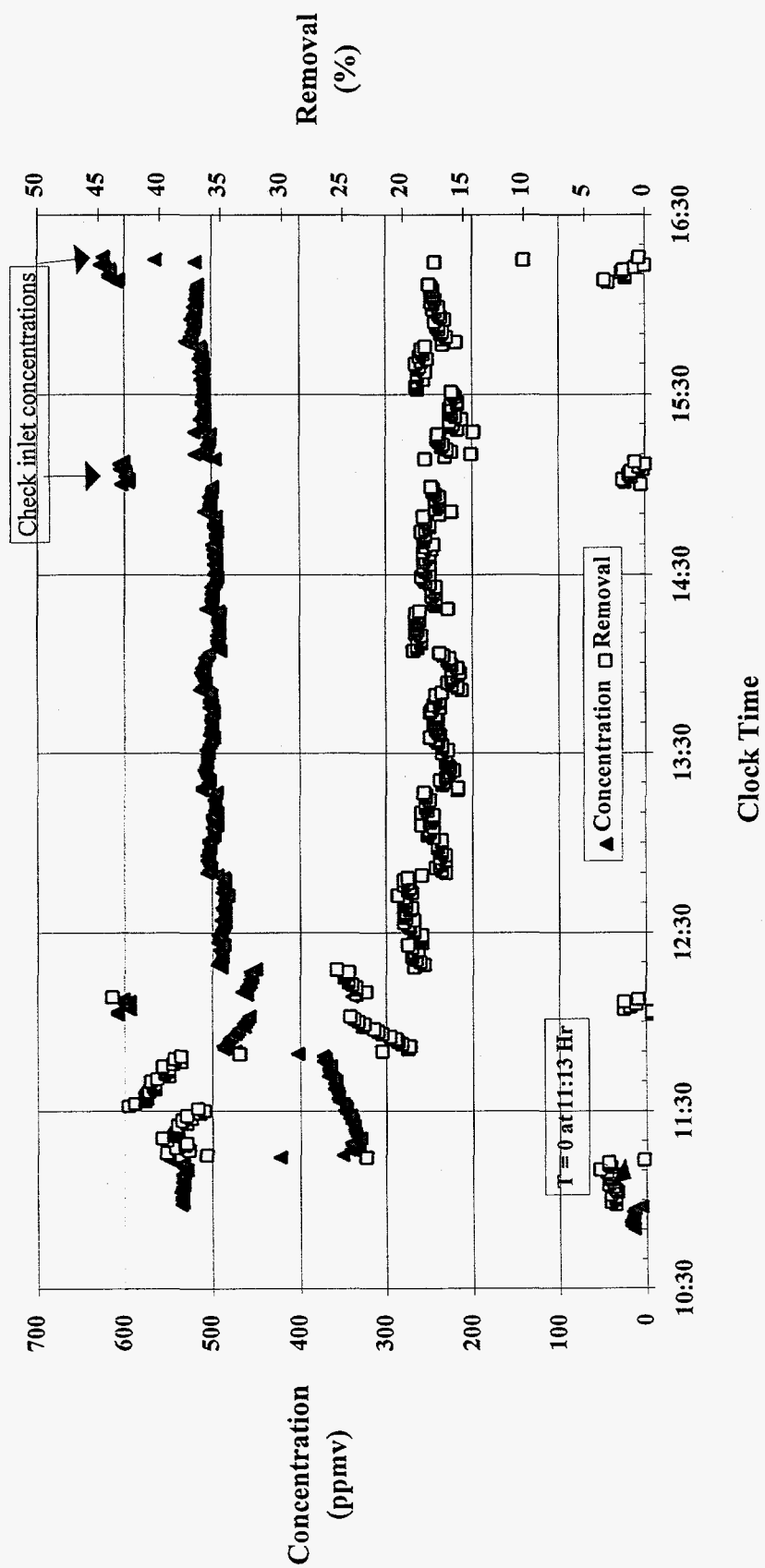


Figure 75. NO concentration and removal vs. time

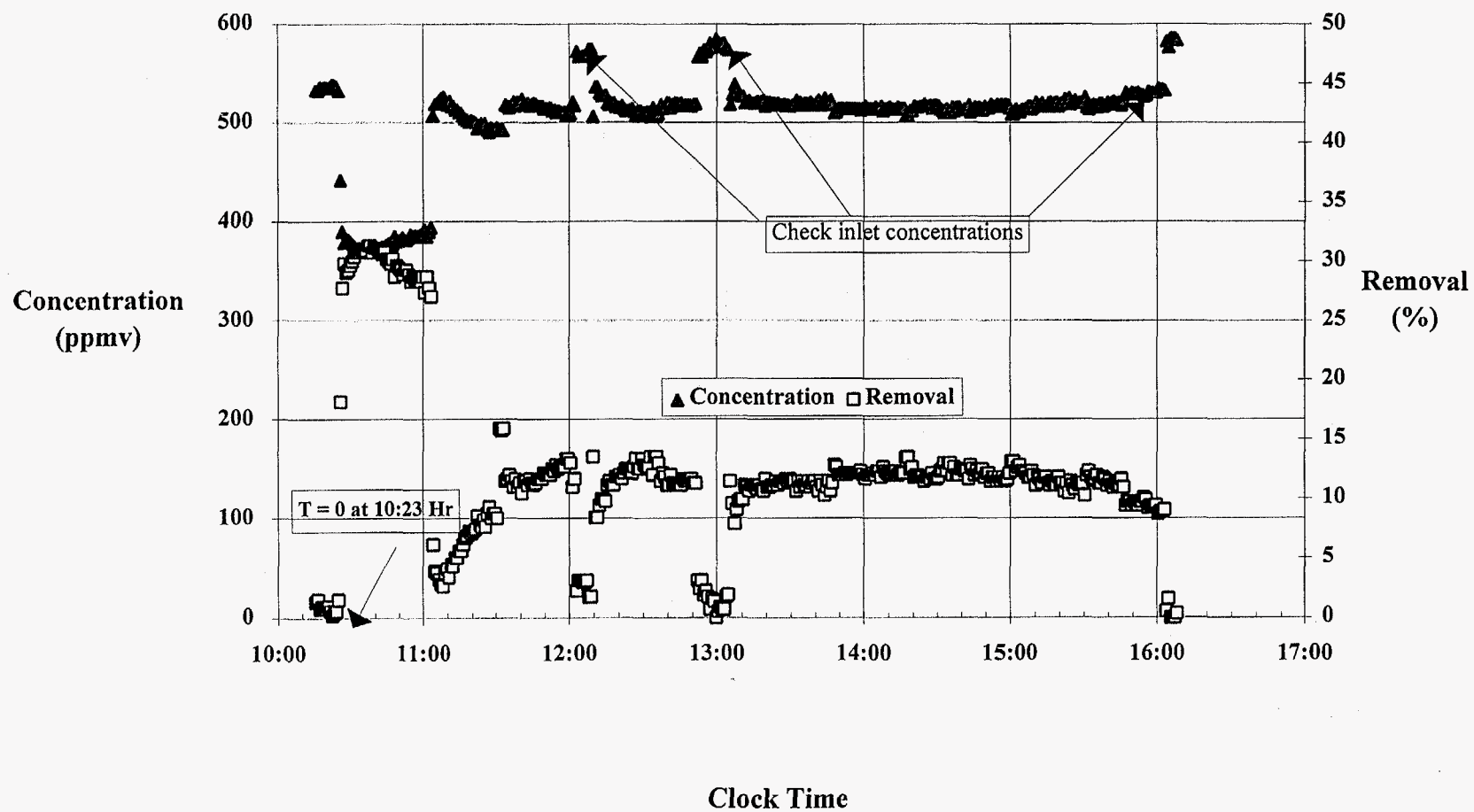


Figure 76. Change of recycle tank liquor $[\text{Fe}^{+2}]$ with respect to time

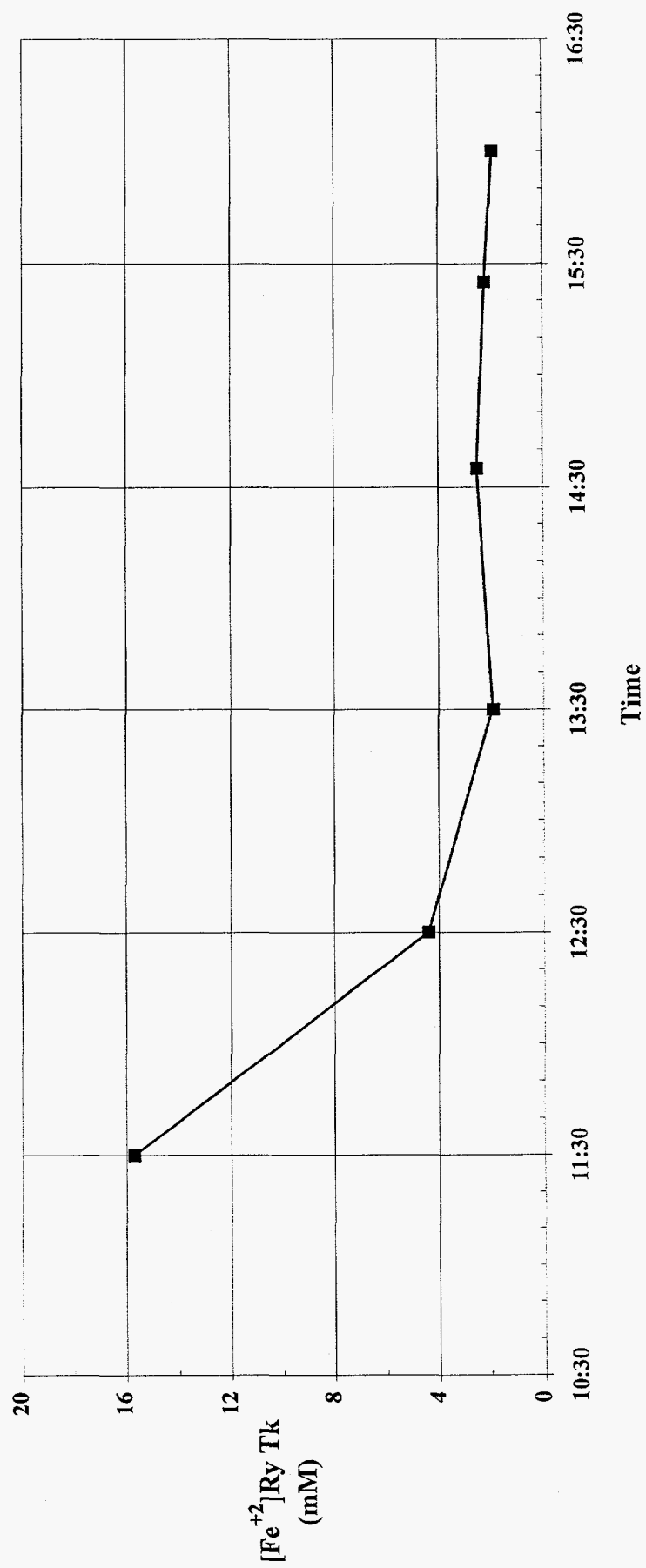


Figure 77. Change of $[\text{Fe}^{+2}]$ with respect to time

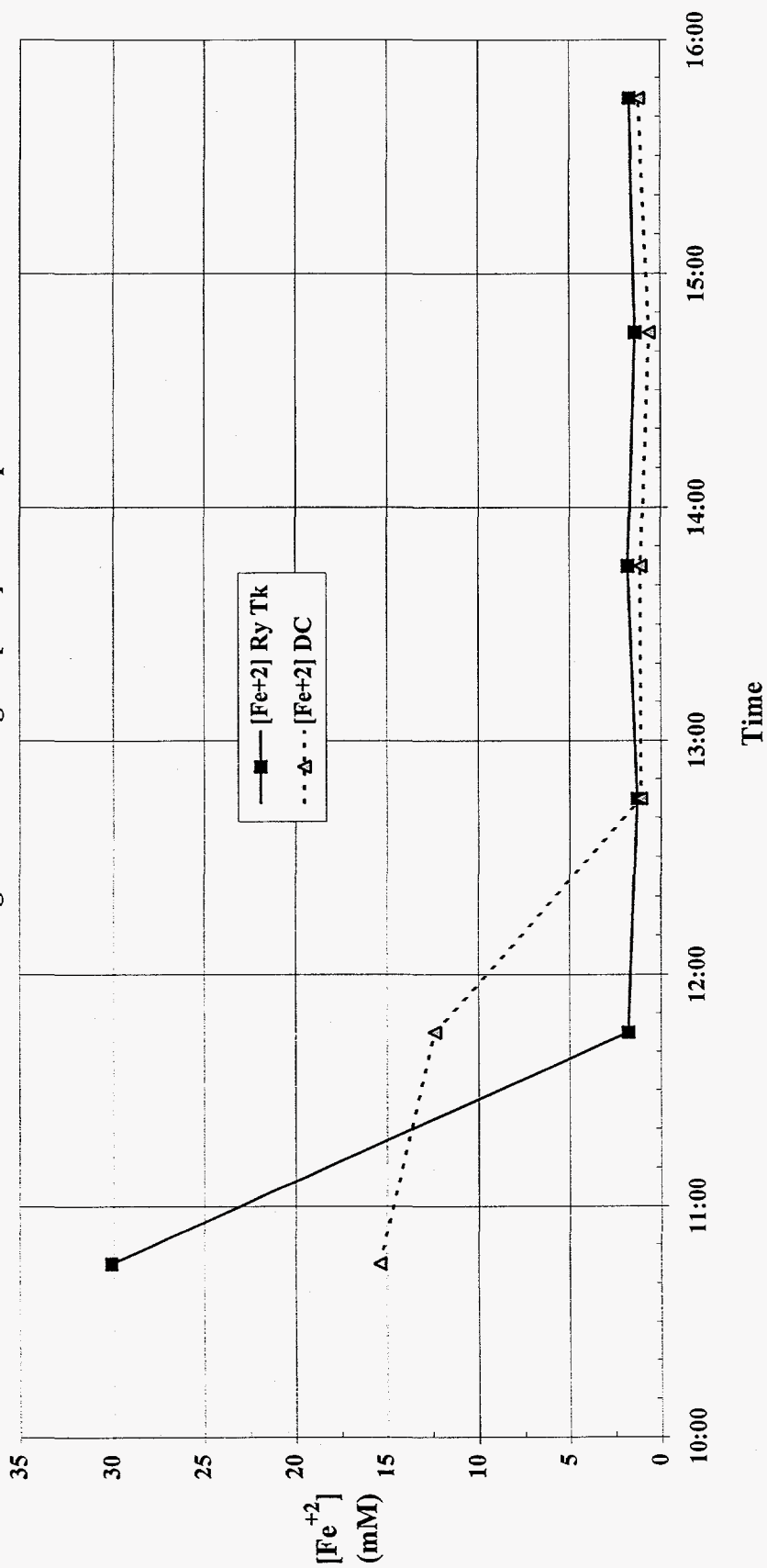


Figure 78. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

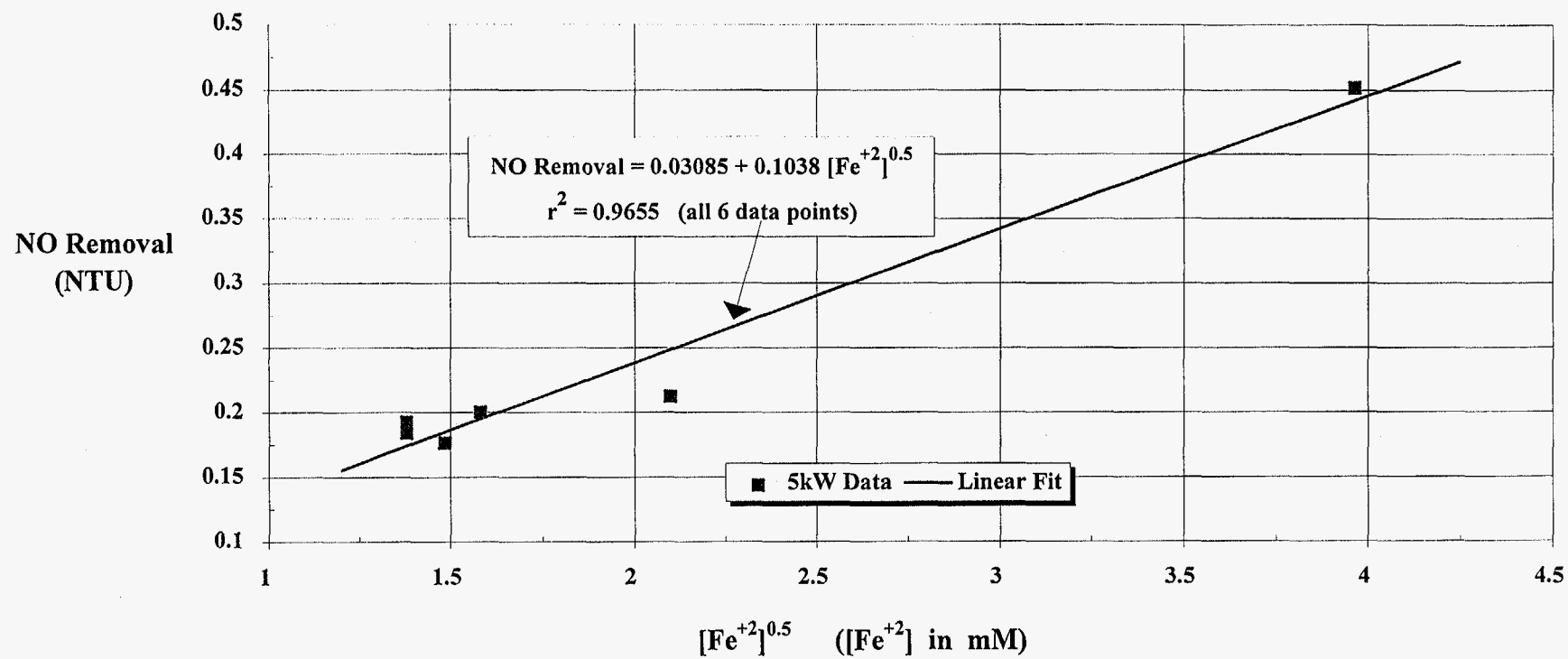


Figure 79. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

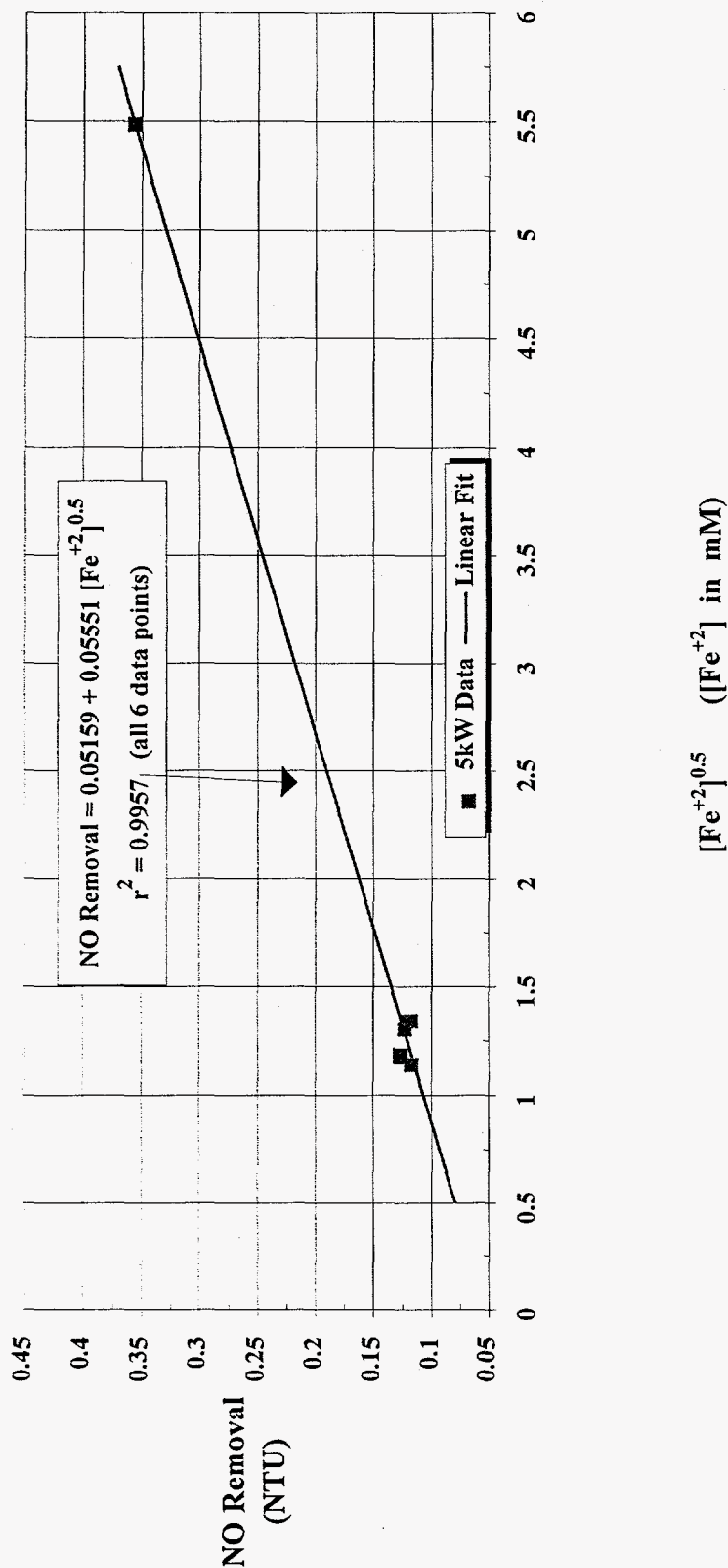


Table 17. Chemistry Data

Clock Time	L/G	Recy Tank	Alkalinity	[SO ₃ ⁻²] as	[Fe ⁺²] _{Ry Tk}	[SO ₃ ⁻²]	[ADS]	[Mg ⁺²]	[Ca ⁺²]	[Total Fe] _{Ry Tk}	[Na ⁺¹]	Filtercake
(Hr: Min)		Liquor pH	(ppm)	analyzed	(mM)	adjusted for	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	Solids
				(ppm)		[Fe ⁺²] _{Ry Tk}						(wt %)
						(ppm)						
11:30	44	6.35	2852	8511	15.7	7883		4608	110	2601	38.3	
12:30	44	6.30	3036	6309	4.4	6133	1.37	4678	162	2379	27.3	67.96
13:30	44	6.30	2042	4419	1.9	4343	2.55	5200	228	2271	33.3	64.29
14:35	88	6.30	2369	4099	2.5	3999	3.73	5688	430	2381	32.5	59.74
15:25	88	6.30	1918	3122	2.2	3034	5.04	5614	633	2278	32.8	58.77
16:00	88	6.30	1902	2962	1.9	2886	7.6	6091	742	2359	33.9	52.4

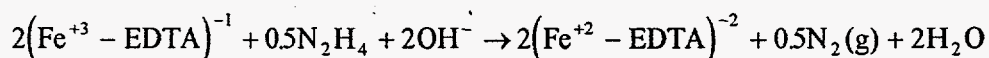
Table 18. Chemistry Data

Clock Time	L/G	Recy Tank	Alkalinity	[SO ₃ ⁻²] _{Ry Tk}	[Fe ⁺²] _{Ry Tk}	[SO ₃ ⁻²] _{Ry Tk}	[ADS] _{Ry Tk}	[Mg ⁺²] _{Ry Tk}	[Ca ⁺²] _{Ry Tk}	[Total Fe] _{Ry Tk}	[Na ⁺¹] _{Ry Tk}	[SO ₃ ⁻²] _{Ry Tk}	[SO ₄ ⁻²] _{Ry Tk}	[Cl ⁻¹] _{Ry Tk}	Filtercake
(Hr: Min)		Liquor pH	(ppm)	as analyzed	by Spec-20	corrected for	by IC	by ICP	by ICP	by ICP	by ICP	by IC	by IC	by IC	Solids
				(ppm)	(mM)	[Fe ⁺²] _{Ry Tk}	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(wt %)
						(ppm)									
10:45	44	6.1	1918	3282	30.1	2078	1.44	3528	169	1457	24.4	5856	5844	57	
11:45	44	5.8	884	4876	1.8	4804	3.92	3581	209	1419	17.3	4560	8158	142	50.9
12:45	44	5.8	851	4147	1.3	4095	5.81	4126	350	1410	20.1	3197	12136	540	52.79
13:45	88	5.8	734	3283	1.8	3211	8.06	4455	451	1307	23.1	3127	15196	572	52.53
14:45	88	5.8	1067	4524	1.4	4468	10.9	5310	468	1322	22.6	3690	15550	950	50.1
15:45	88	6.0	1200	4387	1.7	4319	11.44	5811	772	1291	33.7	2700	21326	472	48.81

7. Hydrazine Sulfate

a) 5 kW Configuration

No modifications were made to the 5 kW system with hydrazine sulfate as the regeneration agent since the chemical was in solid form. The configuration of the 5 kW is illustrated in Figure 33. The regeneration reaction believed to occur with hydrazine is as follows:



It was added directly to the recycle tank at 60 gram/hr. One test, DT011095 (non-packed mode, ~50 mM initial total iron concentration, recycle tank pH = 6.8, L/G = 44, 6.3 vol.% O₂) was run with this agent. This elevated pH enabled high SO₂ removals to be achieved in the scrubber.

b) Test Results

The SO₂ removal reached 99% and stayed at this level for the duration of the test run. The SO₂ removal curve is shown in Figure 80. The NO_x removal declined from an initial 45% to a steady state level of 35% for the remainder of testing. The NO_x removal curve is shown in Figure 81. Higher dosages of hydrazine sulfate (60 grams/hr) is prohibited by the accumulation of sulfate in the 5 kW system. If the sulfate is accompanied by an increase in calcium ion concentration, calcium sulfate scale formation will rapidly occur. The constant NO_x removal can be explained by the constant ferrous ion concentration after steady state was achieved. The average concentration was ~26.8 mM as shown in Figure 82.

As shown in Table 19, the sodium ion concentration averaged 47.5 ppm which is typical for a ThionO_x system. The sulfite ion concentration was fairly steady

during the test averaging 5,412 ppm. Obviously the sulfate level increased with hydrazine sulfate addition. Surprisingly the magnesium and calcium ion concentrations did not increase to a significant extent. In addition, the filtercake solids content was 71.9 wt.% by the end of testing meeting the dewatering goal of the filtercake solids.

The correlation to the NO_x removal model was high ($r^2 = 0.9464$). This is illustrated in Figure 83.

c) Economics of Hydrazine Sulfate

The cost of hydrazine is \$1.85/lb_m. Based on the steady state ferrous ion concentration achieved after several hours of testing and a flue gas oxygen content of 6.3 vol.%, the cost on a day basis was found to be \$0.0367/day·mM Fe^{2+} ·vol.% O_2 . The cost on an NTU removal basis was found to be \$2.35/day·NTU·vol.% O_2 . Relative to the other chemical regeneration agents tested, hydrazine sulfate was an expensive agent on both a mM ferrous ion concentration and NTU removal basis (refer to Figures 50 and 51).

d) Attainment of Objectives

The testing of hydrazine sulfate to determine whether this agent was a viable regeneration agent was performed. The SO_2 removal met the goal established in the test plan while the NO_x removal of 35% to 45% was below the goal set in the test plan. An imbalance in the chemistry was present with high sulfate ion concentrations in the Thio NO_x liquor. This could lead to gypsum scaling in the system if testing were extended. The filtercake met the dewatering standards established in the test plan.

Figure 80. SO₂ concentration and removal vs. time

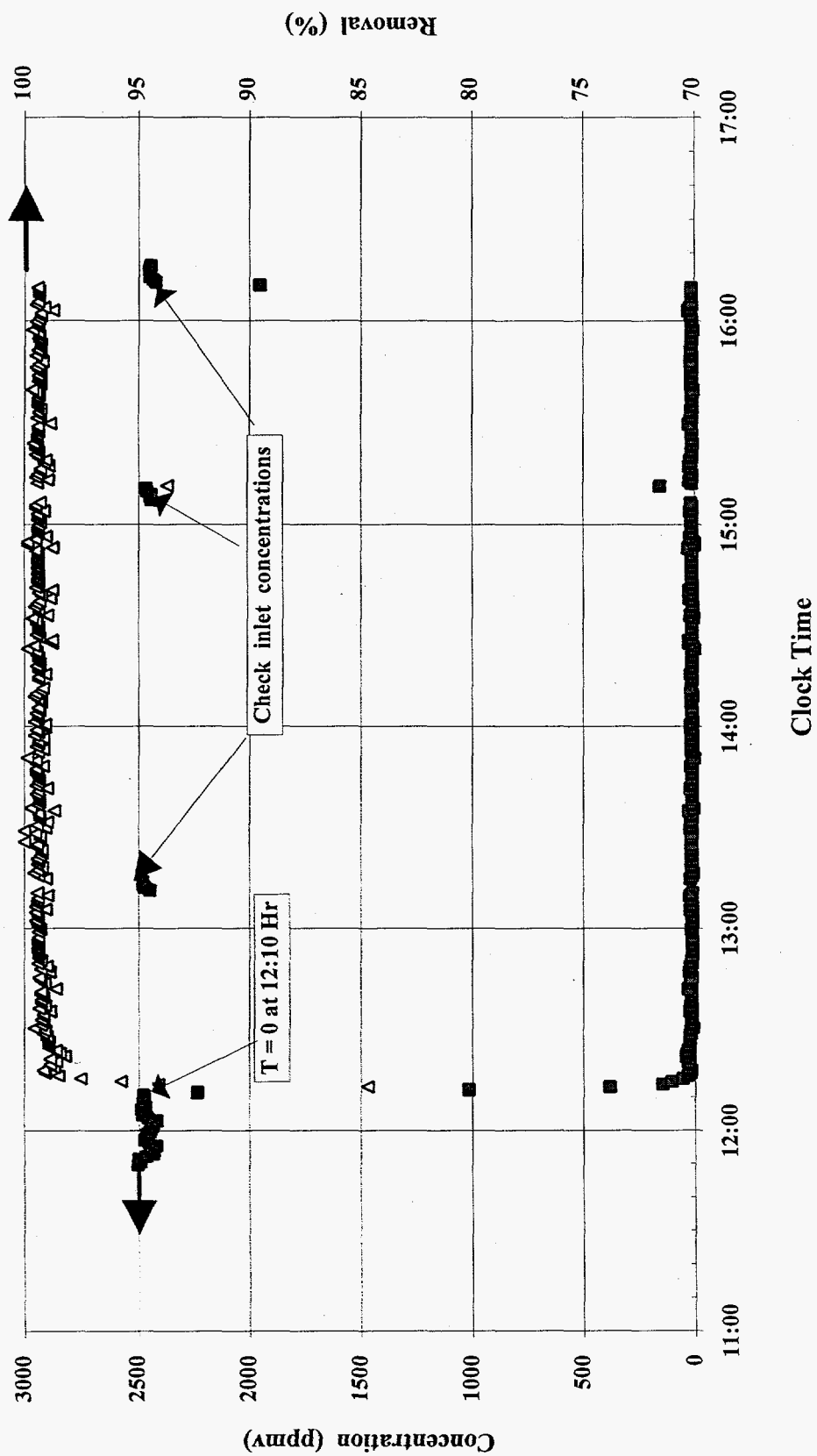


Figure 81. NO concentration and removal vs. time

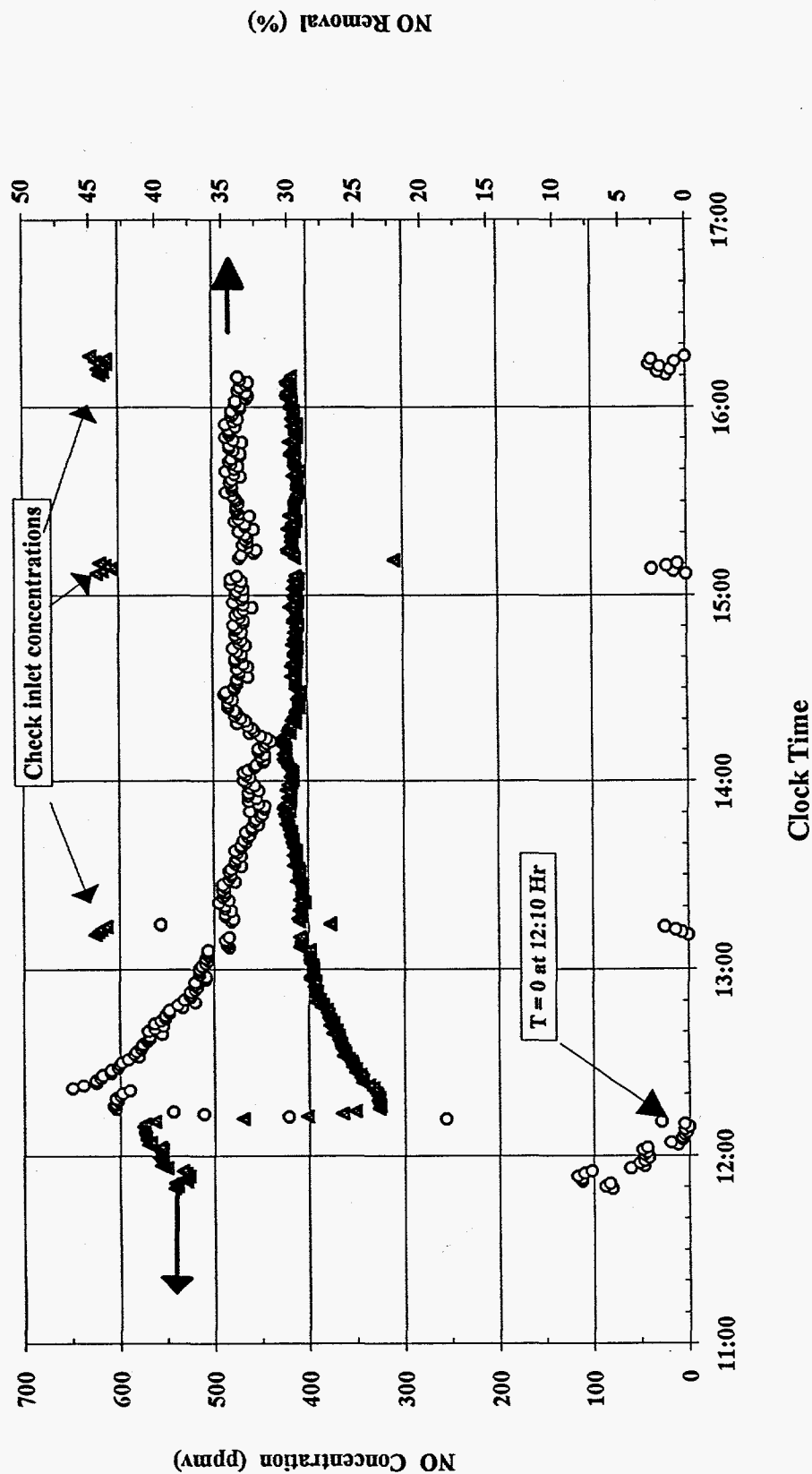


Figure 82. Change of recycle tank liquor $[\text{Fe}^{+2}]$ and NO removal.

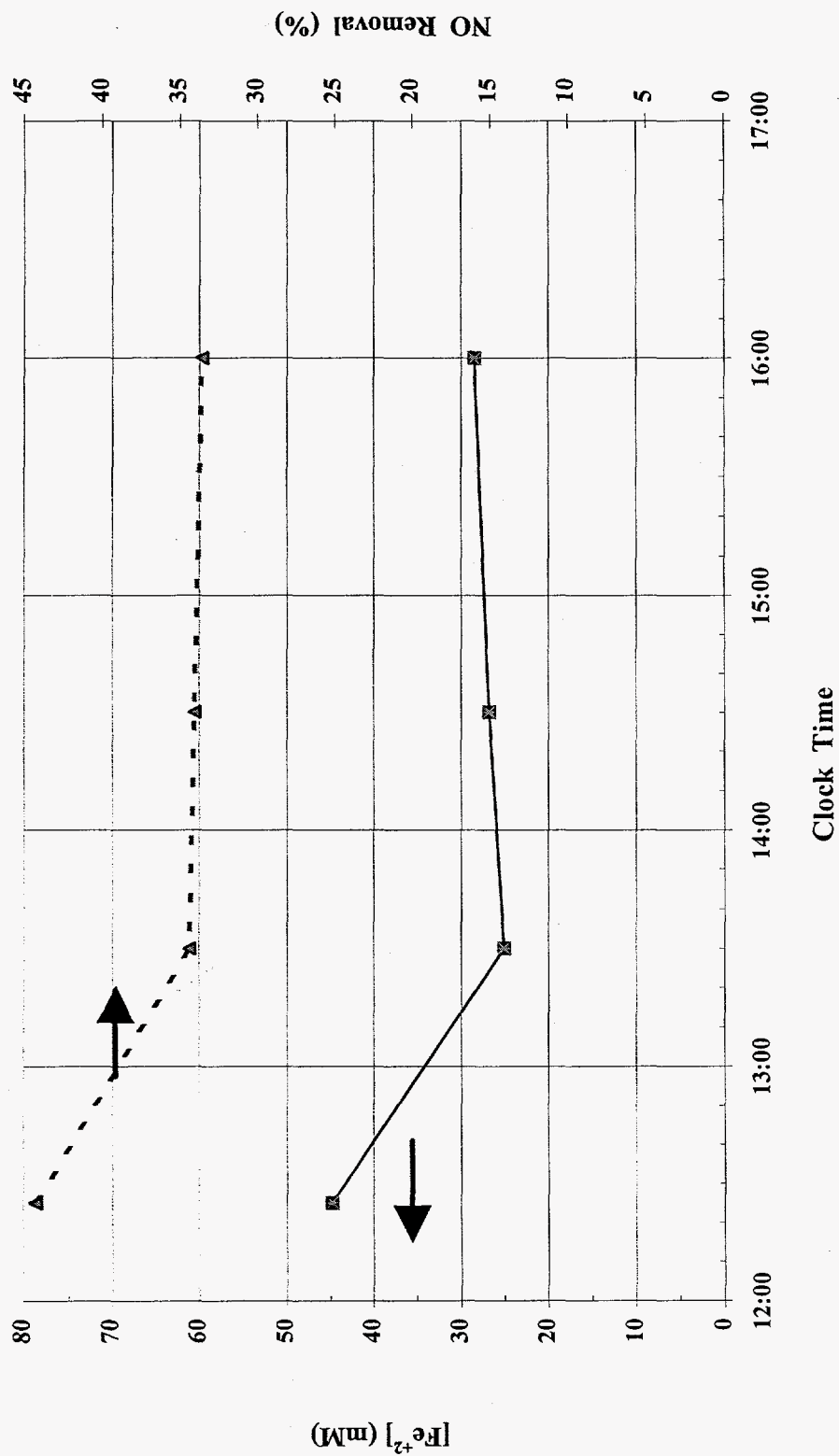


Figure 83. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

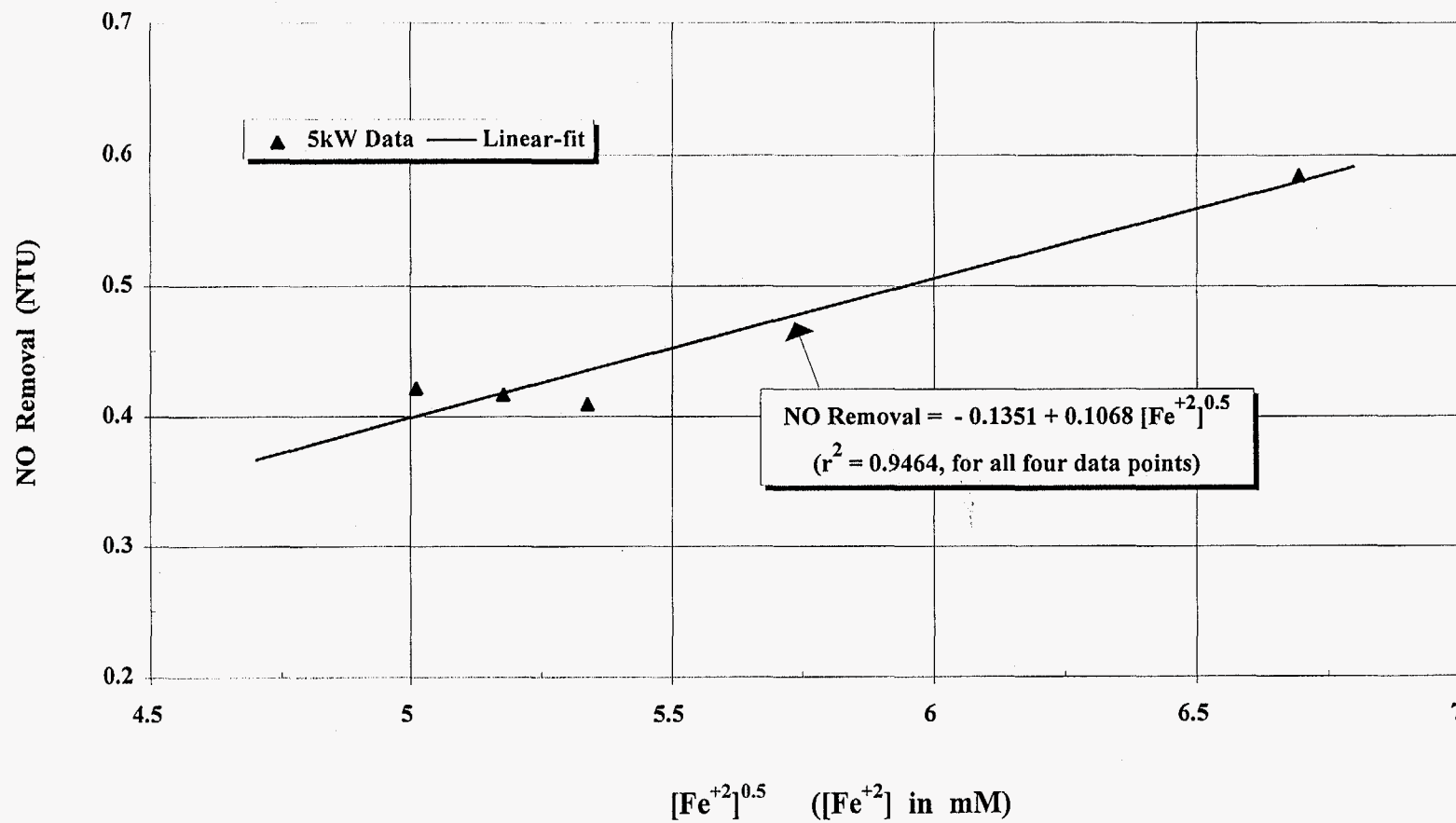


Table 19. Chemistry Data

Clock	L/G	Recycle	Alkalinity	[Fe ²⁺] _{by tit}	[S ₂ O ₃ ²⁻] by	[SO ₃ ²⁻] by	[ADS]	[SA]	[Mg ²⁺]	[Ca ²⁺]	[Total Fe]	[Na ⁺]	[S ₂ O ₃ ²⁻]	[SO ₃ ²⁻]	[SO ₄ ²⁻]	[Cl ⁻]	Filtercake
Time		Tank	(ppm)	by Spec-601	I ₂ titration	I ₂ titration	by IC	by IC	by ICP	by ICP	by ICP	by ICP	by IC	by IC	by IC	by IC	Solids
(Hr: Min)		Liquor pH		(mM)	(ppm)	(ppm)	(mM)	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(wt %)
12:25	44	7.3	4,420	44.8	3,136	7,774	1.11	n.d.	4,981	133	2,771	71	n.d.	5,682	4,502	82	
13:30	44	6.9	4,770	25.1	2,240	11,265	2.58	n.d.	5,113	202	2,630	42	n.d.	6,643	7,688	78	67.12
14:30	44	6.8	4,620	26.8	1,307	13,210	8.86	0.96	5,164	284	2,581	39	n.d.	4,987	9,280	96	71.79
16:00	44	6.7	4,120	28.5	2,203	15,068	16.28	1.79	5,595	280	2,633	38	n.d.	4,336	9,818	102	71.92

8. Hydrazine Hydrate

a) 5 kW Configuration

A holding tank serving as a hydrazine reservoir was incorporated into the 5 kW configuration. The hydrazine in this holding tank was then pumped to the recycle tank for 4 minutes at a rate of 10 ml/min. This was performed every 30 minutes. The 5 kW set-up is shown in Figure 84. Only one test, DT060195 (packing mode, ~100 mM initial total iron concentration, recycle tank pH = 6.0, L/G = 44, 10 vol.% O₂), was run with this regeneration agent.

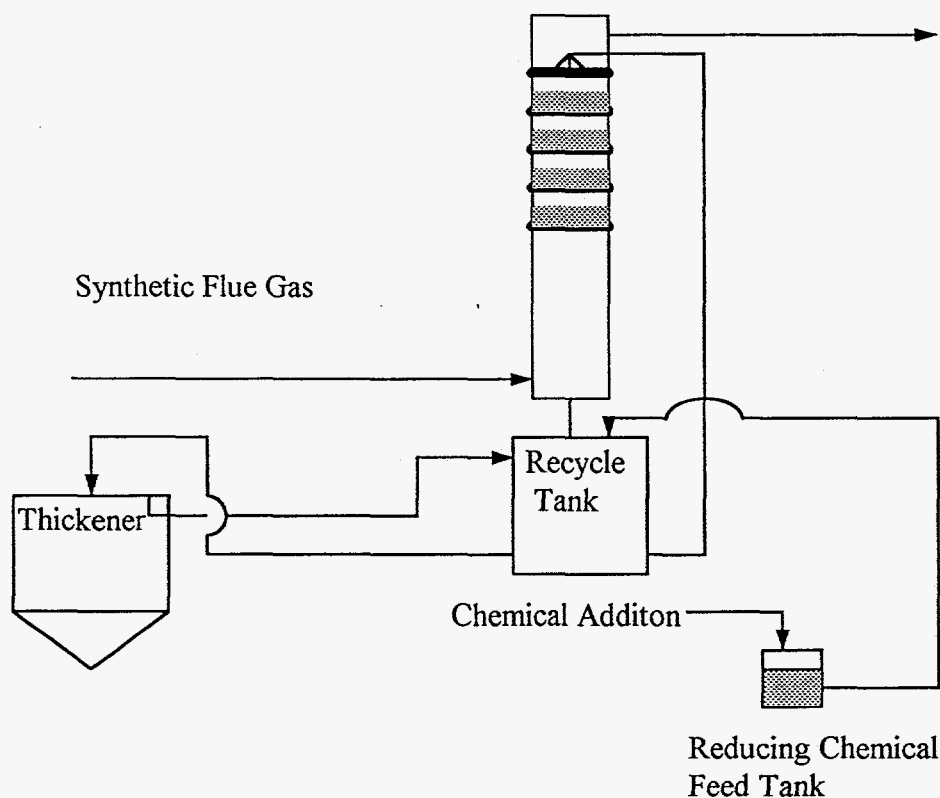


Figure 84. Flow Diagram for Liquid Addition Regeneration

b) Test Results

The SO₂ removal reached between 98% to 99% as shown in Figure 85 for the entire test run which meets the stated objective for SO₂ removal in the test plan. NO_x removal actually increased from 50% early in the run to 60% by the end of the run. Only on few occasions did the NO_x removal drop below 50% and this occurred at the beginning of the test run. This is illustrated in Figure 86. The high NO_x removal can be explained by the increasing trend in ferrous ion concentration. This is substantially different from the results of other regeneration agents where the ferrous ion concentration rapidly dropped during the first part of the test run before achieving a low steady state value. The initial ferrous ion concentration was 50.9 mM while the final ferrous ion concentration was 88.1 mM. The ferrous ion concentration is shown in Figure 87.

Table 20 shows the sodium ion concentration averaged 73.4 ppm, typical for a ThioNO_x system. The sulfite ion concentrations were fairly constant averaging 10,408 ppm. The sulfate ion concentration followed an increasing trend for this test run with 10,163 ppm sulfate ion concentration at the beginning of the test and 22,975 ppm sulfate ion concentration by the end of the test run. The increasing anion charge must be balanced by an increasing cation charge. This explains why magnesium ion increased in concentration. Although calcium ion does not increase in concentration, the high concentrations of magnesium and sulfite could lead to precipitation of magnesium sulfite throughout the system.

Hydrazine accumulated with test time. Because hydrazine is a suspected carcinogen, the levels of this chemical in the landfill material must be carefully controlled to prevent the filtercake solids from being classified as hazardous waste material. The accumulation of hydrazine in the system as the test progressed prohibited higher addition rates since this would only increase the concentration of

residual hydrazine in the 5 kW liquor. This test suggested that lower addition rates of hydrazine hydrate could lower, or perhaps eliminate, the concentration of hydrazine in the liquor. Unfortunately, adding less hydrazine will result in lower NO_x removals falling short of the target removal. The solids content of the filtercake steadily increased to 79.1 wt.% by the end of the test period. Correlation to the NO_x removal model was poor as shown in Figure 88.

c) Economics of Hydrazine Hydrate Addition

Hydrazine is listed as \$1.85/lb_m. Because the ferrous ion concentration and removal of NO_x in NTU displayed an increasing trend even at the end of testing, the cost of hydrazine hydrate is based on the last ferrous ion and NO_x removal measurement. Based upon these measurements, the cost of hydrazine hydrate was \$0.0101/day·mM Fe^{2+} ·vol.% O_2 and \$0.985/day·NTU·vol.% O_2 . Hydrazine hydrate was similar to the thermal regeneration method and sodium dithionite/ascorbic acid mixture in cost. It was less expensive on a mM ferrous ion and NTU level than aluminum, hydroxylamine sulfate, and hydrazine sulfate. However, it was more expensive than the electrochemical cell and the remainder of the chemical regeneration agents. The cost of this regeneration agent is shown in Figures 50 and 51.

d) Attainment of Objectives

The goal of testing hydrazine hydrate to determine whether it satisfied the criteria outlined in the test plan was met. The SO_2 removal was close to 99% meeting the stated goal of SO_2 removal. The NO_x removal approached 60% during the last part of testing. The NO_x removal satisfied the criteria for NO_x removal laid out in the test plan. The increasing sulfite and magnesium ion concentrations raised a concern for precipitation of magnesium sulfite in the 5 kW system. The increasing levels of hydrazine in the system presented the possibility that hydrazine would

accumulate in the filtercake solids, introducing an environmental concern of the landfill material. Hydrazine does not meet the goal as stated in the proposal of producing an environmentally safe landfill material.

Figure 85. SO₂ concentration and removal vs. time

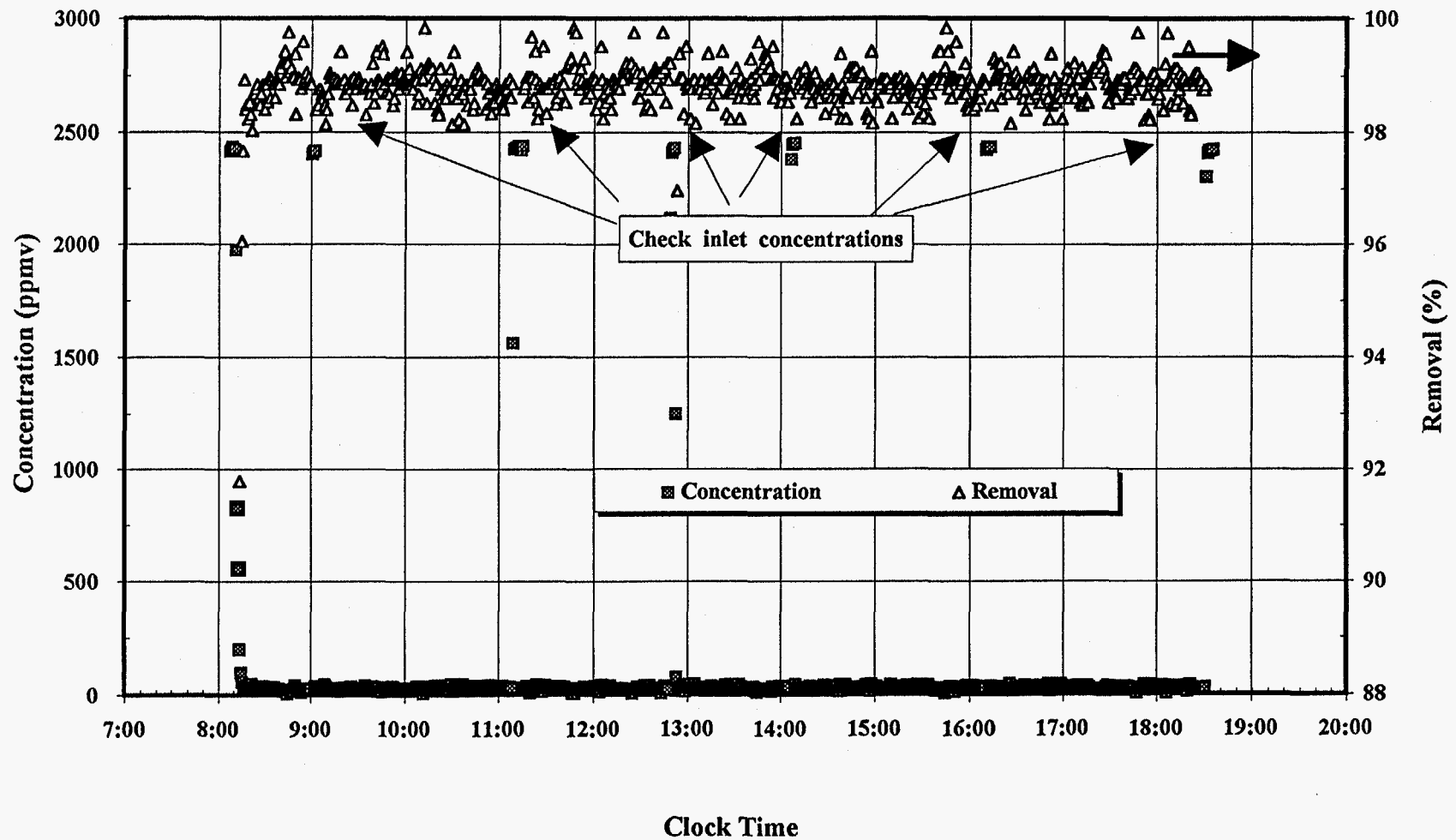


Figure 86. NO concentration and removal vs. time

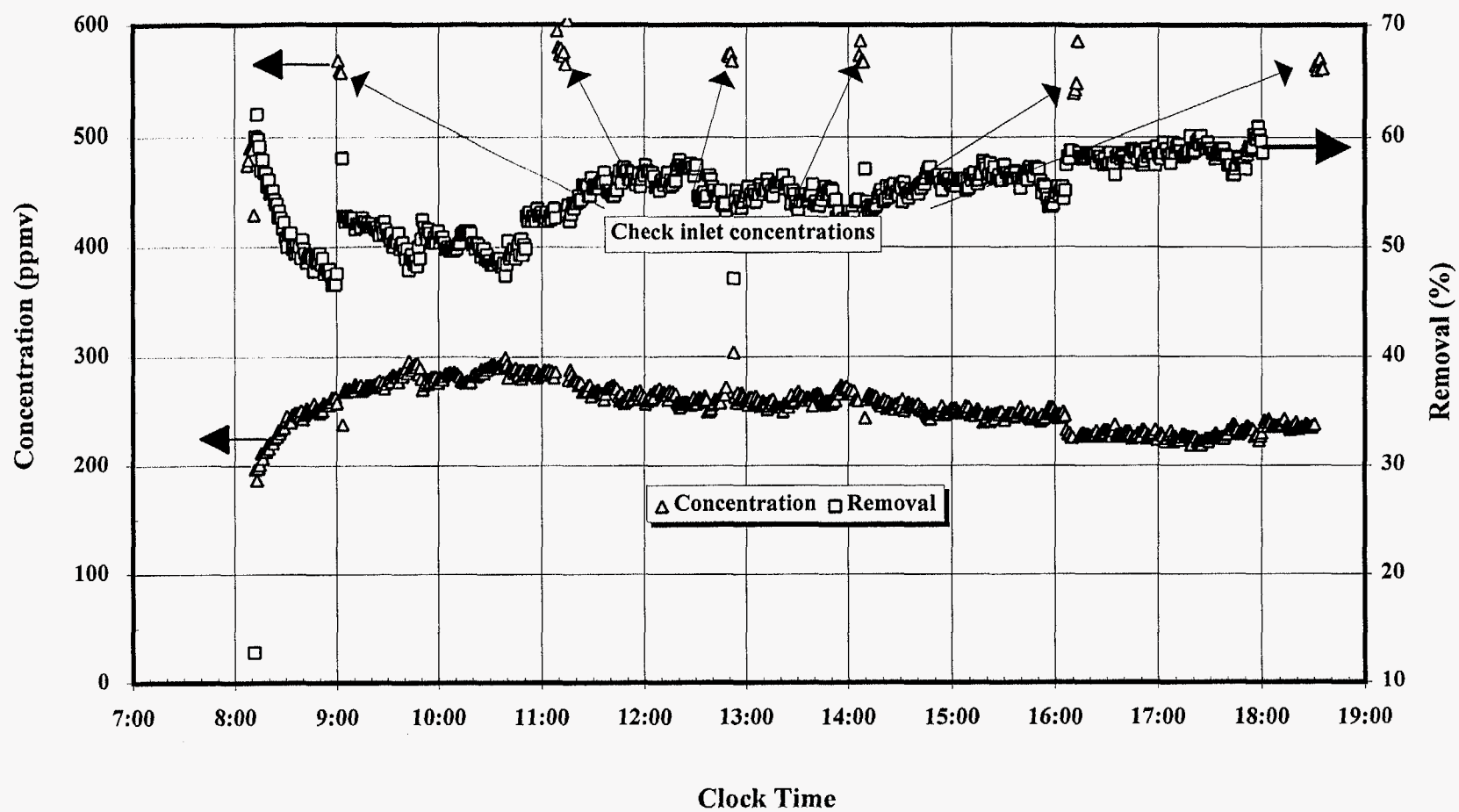


Figure 87. Recycle tank liquor $[\text{Fe}^{+2}]$ and NO removal vs. time

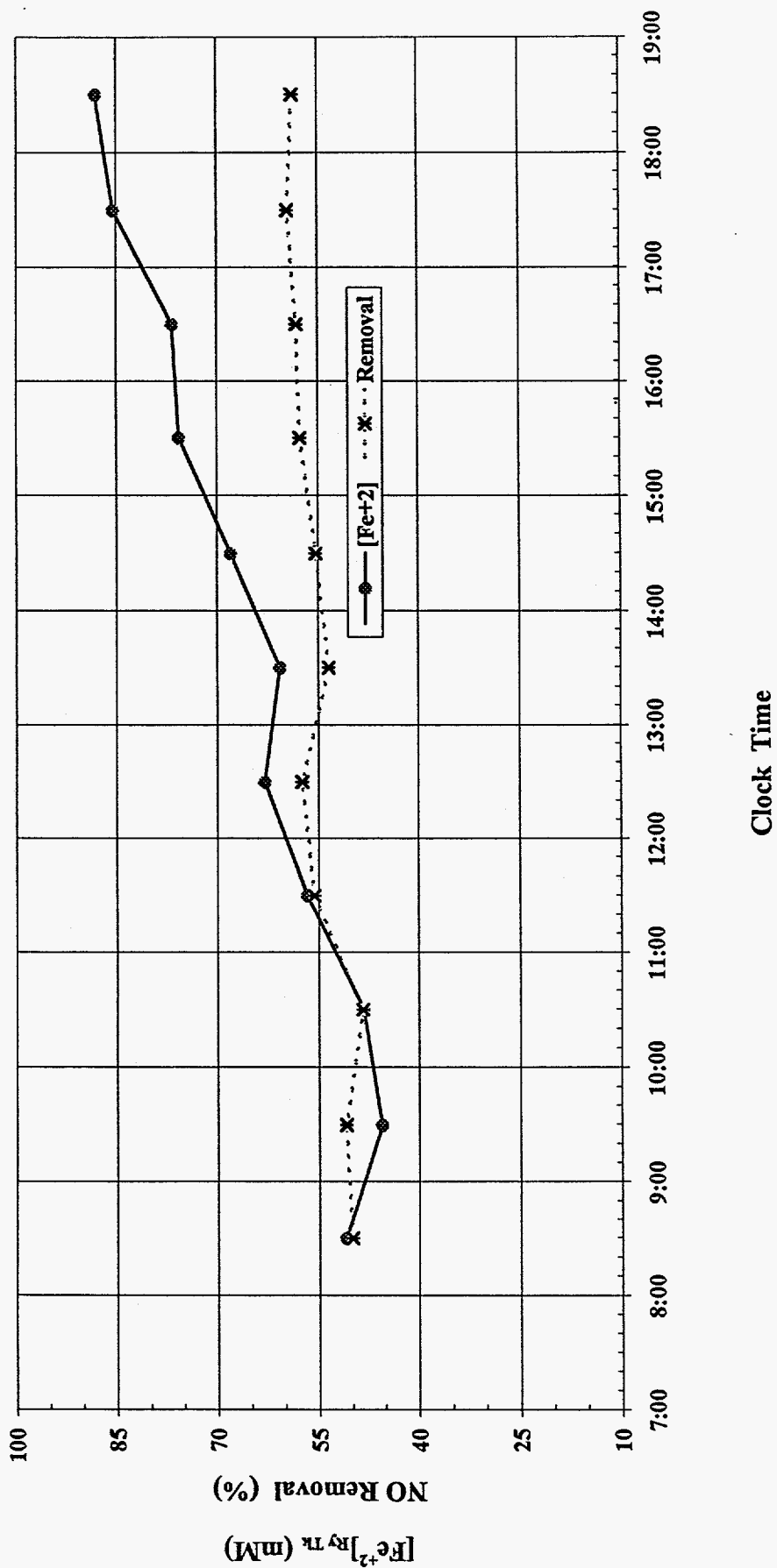


Figure 88. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

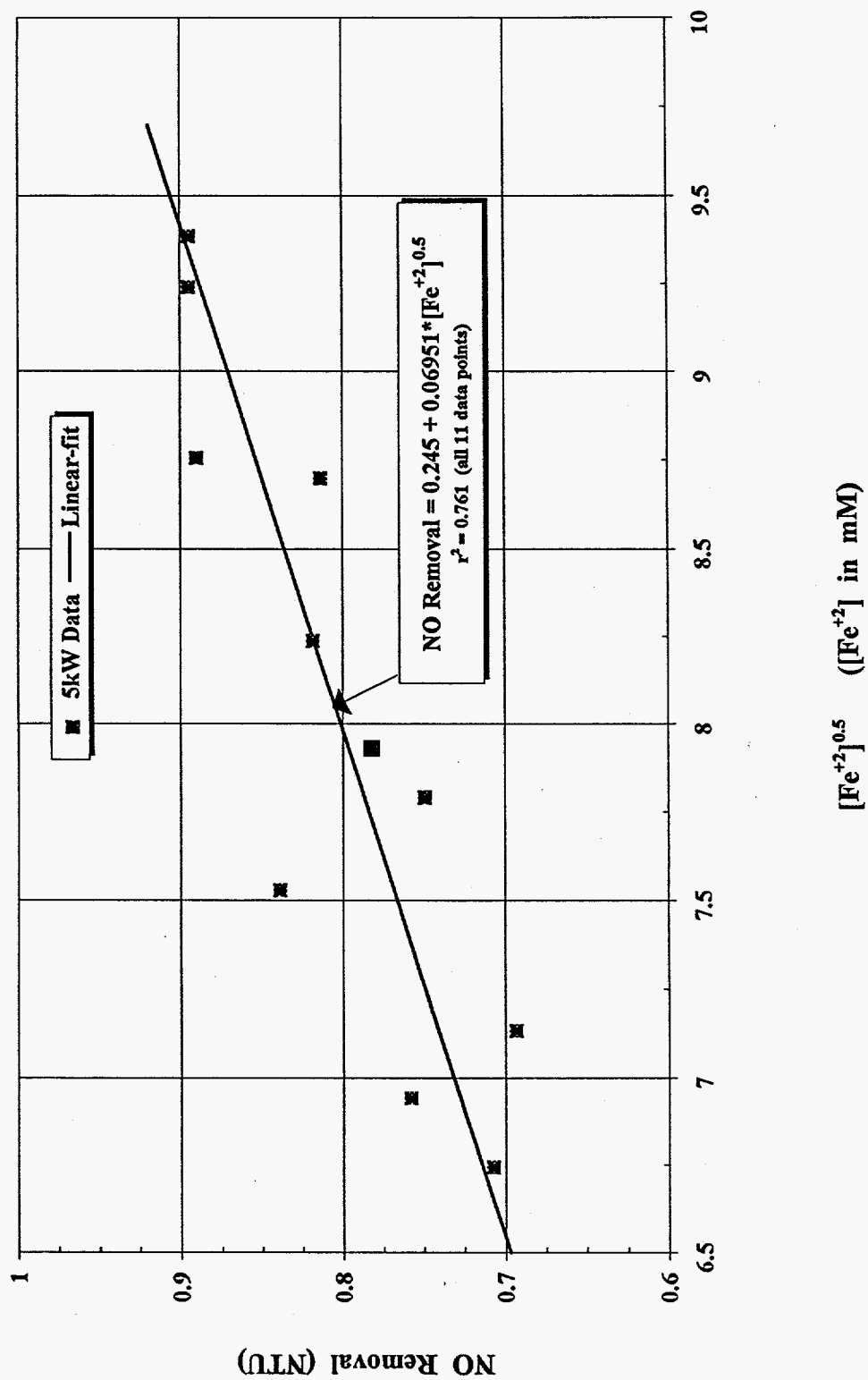


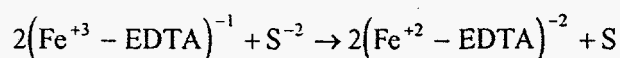
Table 20. Chemistry Data

Clock	Recycle Tank	Alkalinity (ppm)	[Fe ²⁺] _{h,n} by Spec-601 (mM)	[Total Fe] (mM)	[SO ₄ ²⁻] by I ₂ titration (ppm)	[SO ₄ ²⁻] adjusted to [Fe ²⁺] _{h,n} (ppm)	[SA] by IC (mM)	[SA] _{adjusted} by IC (mM)	[ADS] _{h,n} (mM)	[Mg ²⁺] by ICP (ppm)	[Ca ²⁺] by ICP (ppm)	[Total Fe] by ICP (ppm)	[Na ⁺] by ICP (ppm)	[S ₂ O ₃ ²⁻] by IC (ppm)	[NO ₃ ⁻] by IC (ppm)	[SO ₄ ²⁻] by IC (ppm)	[SO ₄ ²⁻] by IC (ppm)	[Cl ⁻] by IC (ppm)	Filtercake Solids (wt %)
Time (1hr: Min)	Liquor																		
	pH																		
8:30	5.9	2,635	50.9	115.2	10,200	8,164	0.12	6.83	6.71	6,844	407	6,035	70.2	n.d.	trace	7,423	10,163	95	
9:30	5.9	3,469	45.5		19,191	17,371	1.18	28.27	27.09	7,066	322	6,210	72.3	n.d.	trace	10,421	10,758	176	69.6
10:30	6	4,170	48.2	120.2	26,087	24,159	3.49	52	48.51	7,511	336	6,473	64.1	n.d.	trace	11,273	10,984	316	73.3
11:30	6	4,620	56.7		32,865	30,597	6.2	80.34	74.14	7,592	312	6,614	64.1	n.d.	trace	11,427	12,464	562	75.2
12:30	6.1	5,154	62.9		40,912	38,396	9.12	120.5	111.38	7,986	296	6,857	67.9	n.d.	trace	11,513	17,864	256	
13:30	6	5,388	60.7		48,157	45,729	11.63	149	137.37	8,320	313	6,846	71.0	n.d.	trace	10,717	14,885	545	78
14:30	6.1	5,671	67.9		52,681	49,965	14.92	184.8	169.88	8,584	267	7,091	84.4	n.d.	trace	11,271	19,700	252	
15:30	5.95	5,338	75.7		58,445	55,417	18.53	215.3	196.77	8,705	208	7,195	76.3	n.d.	trace	11,086	21,680	176	79.2
16:30	6.1	6,272	76.7		63,489	60,421	22.08	251.4	229.32	8,849	262	7,202	80.9	n.d.	trace	11,245	24,209	182	76.1
17:30	6	5,938	83.4	227	74,296	68,880	30.41	300.9	270.49	9,416	133	7,590	77.3	n.d.	trace	10,203	29,207	183	78.5
18:30	6.1	6,355	88.1	144.1	66,291	62,767	34.39	322.2	287.81	9,575	247	7,656	78.7	n.d.	trace	7,913	22,975	150	79.1

9. Sodium Sulfide Hydrate

a) 5 kW Configuration

For sodium sulfide hydrate a holding tank was incorporated into the 5 kW system. A diagram of the set-up is shown in Figure 84. The sodium sulfide solution was stored in the holding tank where it was pumped into the recycle tank at 10 ml/min. The reaction believed to occur with sodium sulfide is as follows:



Four short term tests and one long term test were run. For one of the short term tests an exhaust gas blanket was maintained over the recycle tank. This meant the atmosphere over the recycle tank was low in oxygen concentration. The other tests were conducted with an ambient air blanket over the recycle tank. The short term tests were DT041494 (non-packed mode, ~50 mM initial total iron concentration, recycle tank pH = 6.0, L/G = 44, 6.5 vol.% O₂), DT041594 (non-packed mode, ~40 mM initial total iron concentration, recycle tank pH = 6.5, L/G = 44, 6.3 vol.% O₂), DT042094 (non-packed mode, ~25 mM initial total iron concentration, recycle tank pH = 6.5, L/G = 44, 6.5 vol.% O₂), and DT042194 (non-packed mode, ~29 mM initial total iron concentration, recycle tank pH = 6.5, L/G = 44, 6.5 vol.% O₂). The long term test was DT052395 (packing mode, ~100 mM initial total iron concentration, recycle tank pH = 6.1 to 6.5, L/G = 44, 10 vol.% O₂).

Based upon the low cost steady state operations for ferrous regeneration achieved during the short term tests, provisions were made to evaluate sodium sulfide hydrate at the Miami Fort pilot plant. During these studies which are detailed in the appendix of this report, long term effects of the use of this reagent were noted.

Subsequently, the 5 kW test unit was utilized to reevaluate sodium sulfide hydrate on a long term basis to confirm the findings of the pilot plant studies.

b) Test Results

The SO₂ removal was between 98% to 99% for most of the run for the four short term tests. This is shown in Figures 89 through 92. These tests met the goal for SO₂ removal established in the test plan.

During the long term test, however, there were significant periods where the SO₂ removal fell below 97% as shown in Figure 93. Long term testing is very informative for predicting removals for a scaled-up operation. A possible reason for the discrepancy between the results of the short term tests and the long term test was the higher recycle tank liquor pH for the short term tests except for test DT041494 where the recycle tank liquor pH was 6.0. A higher recycle tank liquor pH results in higher alkalinity and subsequently, higher SO₂ removals. Scale formation in the absorber could also lower absorption of SO₂ into the liquid phase decreasing SO₂ removal. Scale formation in the absorber was observed for the long term test. As shown in Figures 94 through 97, for the short term tests NO_x removal never climbed above 30%. Once 25% NO_x removal was reached, the removal curve would begin to level off. The NO_x removal initially dropped from greater than 50% to 20% for the long term test. After this period, the NO_x removal increased to 40%. For most of the test NO_x removal was below 45% as shown in Figure 98. Because of the scale that formed throughout the system for the long term test, higher amounts of sodium sulfide addition were prevented. The low NO_x removal can be explained by the low ferrous ion concentrations present during the short term tests. For the tests conducted with ambient air over the recycle tank, the average ferrous ion concentration after steady state was achieved was 9.57 mM. For the test conducted with the exhaust gas blanket, the average ferrous ion concentration was 17.3 mM. The additional ferrous ion concentration

over that obtained with ambient air over the recycle tank helped maintain the NO_x removal between 25% to 30%. The exhaust gas blanket obviously helped lower the oxidation rate of ferrous ion. This lower oxidation rate was balanced by the regeneration activity of sodium sulfide to produce a higher ferrous ion concentration. The ferrous ion concentrations for the short term tests are given in Figures 99 through 102. For the long term test, the NO_x removal was generally higher than for any of the short term tests. A higher NO_x removal implies higher ferrous ion concentration which was observed for this test compared with the short term tests. The average ferrous ion concentration was 102 mM. The ferrous ion concentration for the long term test is given in Figure 103.

Tables 21 through 25 show the addition of sodium sulfide to the 5 kW system introduced high concentrations of sodium ion to the liquor. This was observed for all the short term tests where the sodium ion concentration accumulated throughout the test period. To maintain charge balance, the concentration of anions will increase. The sodium ion concentration rose dramatically during the long term test to reach levels of 20,000 ppm. For only one short term test did the sulfites exceed 10,000 ppm. Not surprisingly, this result occurred with the exhaust gas blanket in the recycle tank where oxidation of sulfite ion to sulfate ion was at its lowest. For the long term test the sulfite ion concentration was usually less than 6,000 ppm. The sulfate ion concentration exceeded 10,000 ppm for one short term test in which there was an exhaust gas blanket over the recycle tank. For the long term test, the sulfate ion concentration was greater than 10,000 ppm for much of the test period. The calcium and magnesium ion concentrations were generally below 200 ppm and 6,000 ppm, respectively, for the short term tests which are fairly typical chemistries for a Thio NO_x system. The long term test displayed an increasing trend in calcium and magnesium ion concentrations. The elevation of both these concentrations of ions raises the concern of calcium sulfite/calcium sulfate/or magnesium sulfite precipitation. Of additional concern, the thiosulfate ion also increased in concentration for both the long and short term tests. Sulfide

ion reacts with sulfite ion to form thiosulfate. This condition will also lead to increasing calcium ion concentrations which furthers the likelihood of precipitation. Among the short term tests, there was no discernible trend in the filtercake solids. The solids usually varied between 55 wt.% to 65 wt.%. There was also no trend in the filtercake solids for the long term test. The solids varied from 62 wt.% to 75 wt.% meeting the dewatering goal stated in the proposal.

The correlation to the NO_x removal model varied for both the short term and long term tests as Figures 104 through 108. For two short term tests, the correlation to the NO_x removal model was below 0.75. The long term test had a correlation coefficient of less than 0.1.

c) Economics of Sodium Sulfide Hydrate Addition

Sodium sulfide hydrate has a cost of \$0.32 lb_m. The steady state ferrous ion measurement was achieved for the tests conducted. However, the ferrous ion measurements at the end of testing were substantially different from each other. Therefore an average cost had to be calculated for sodium sulfide hydrate. The cost of sodium sulfide hydrate on both a mM ferrous ion concentration and NTU removal basis was less than zinc, aluminum, hydroxylamine, hydrazine sulfate, hydrazine hydrate, sodium tetrasulfide, and thermal regeneration. The cost of sodium sulfide hydrate on a mM ferrous ion concentration was found to be \$0.00175/day·mM Fe^{2+} ·vol.% O_2 and \$.224/day·NTU·vol.% O_2 on an NTU removal basis. The cost on both a ferrous ion concentration and NTU removal basis was higher than iron, with and without a digester.

d) Attainment of Objectives

The objective of determining whether sodium sulfide met the criteria outlined in the proposal was performed. The SO₂ removal goal was not satisfied using this regeneration agent. The SO₂ removal fell short of 99% during the long term test. In all tests performed, the NO_x removal was almost always below 45%. The increase in thiosulfate concentration represents a potential problem since calcium ion concentration will eventually increase to maintain charge balance. The increase in calcium ion concentration can lead to precipitation of calcium sulfite/calcium sulfate. The formation of large concentrations of thiosulfate makes sodium sulfide less attractive as a regeneration agent. Black scale also formed in the system during the long term test which poses a problem since SO₂ and NO_x removal will eventually be adversely effected by the presence of this material. The dewatering characteristics met the goal outlined in the proposal.

Figure 89. SO₂ concentration and removal vs. time

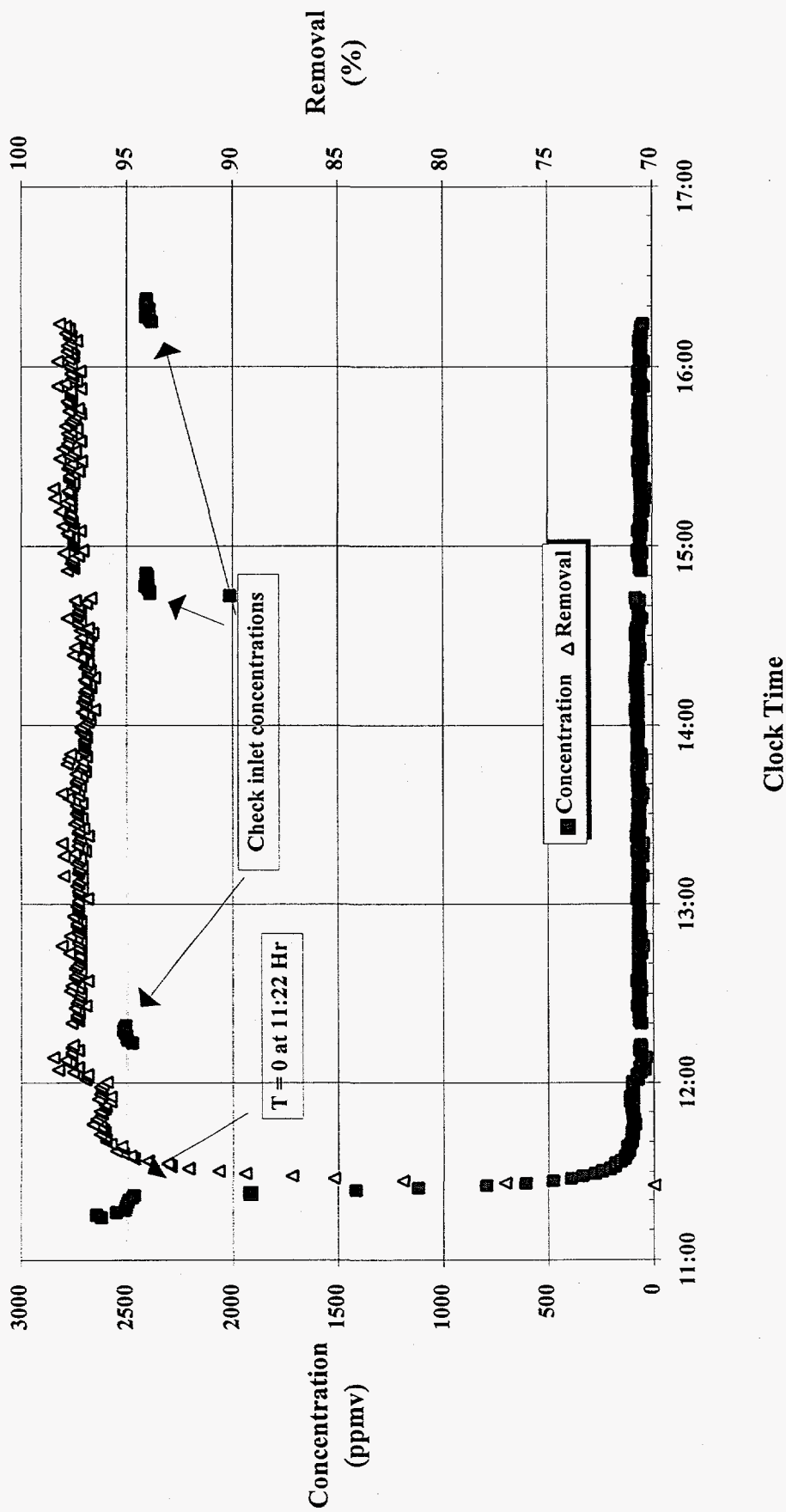


Figure 90. SO₂ concentration and removal vs. time

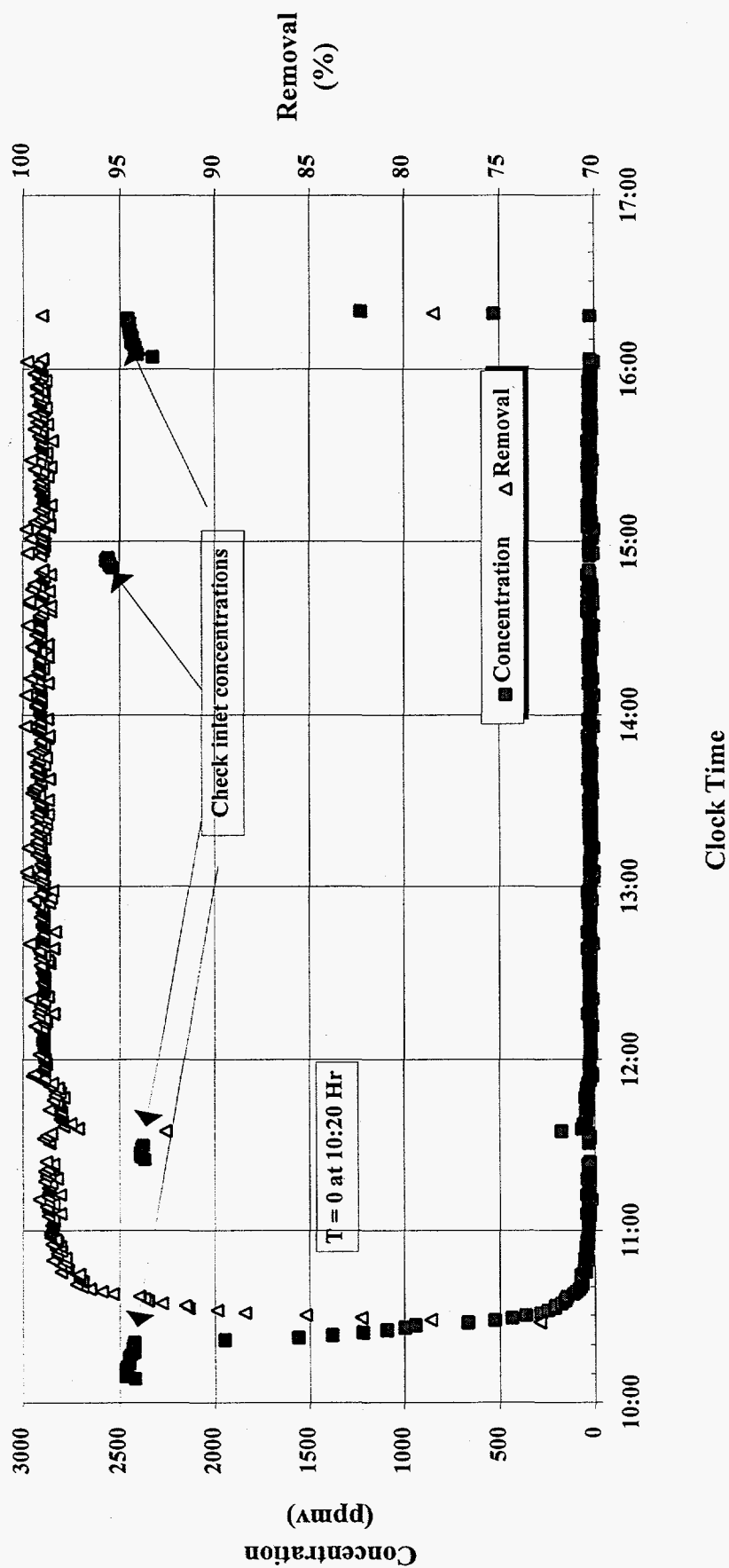


Figure 91. SO₂ concentration and removal vs. time

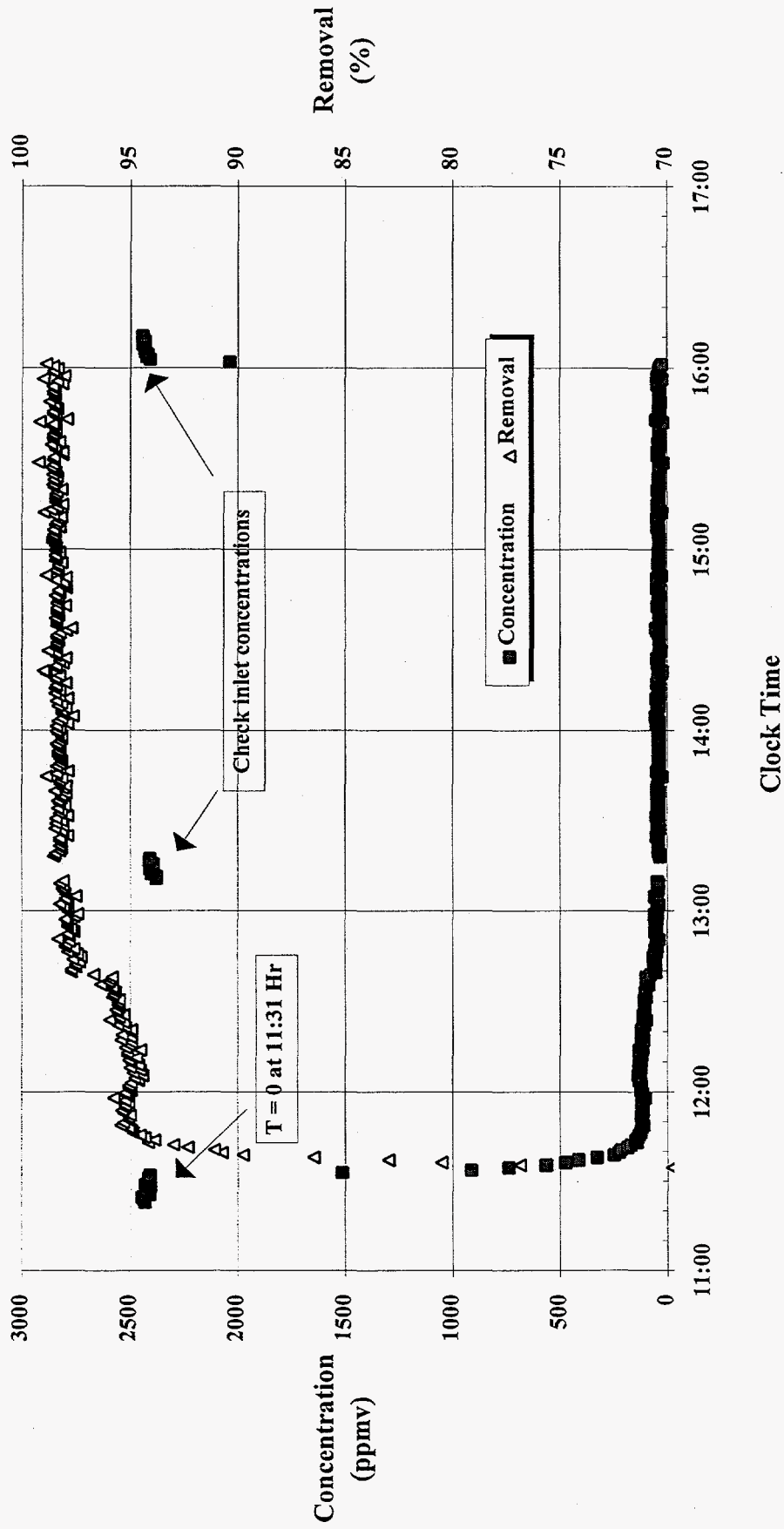


Figure 92. SO₂ concentration and removal vs. time

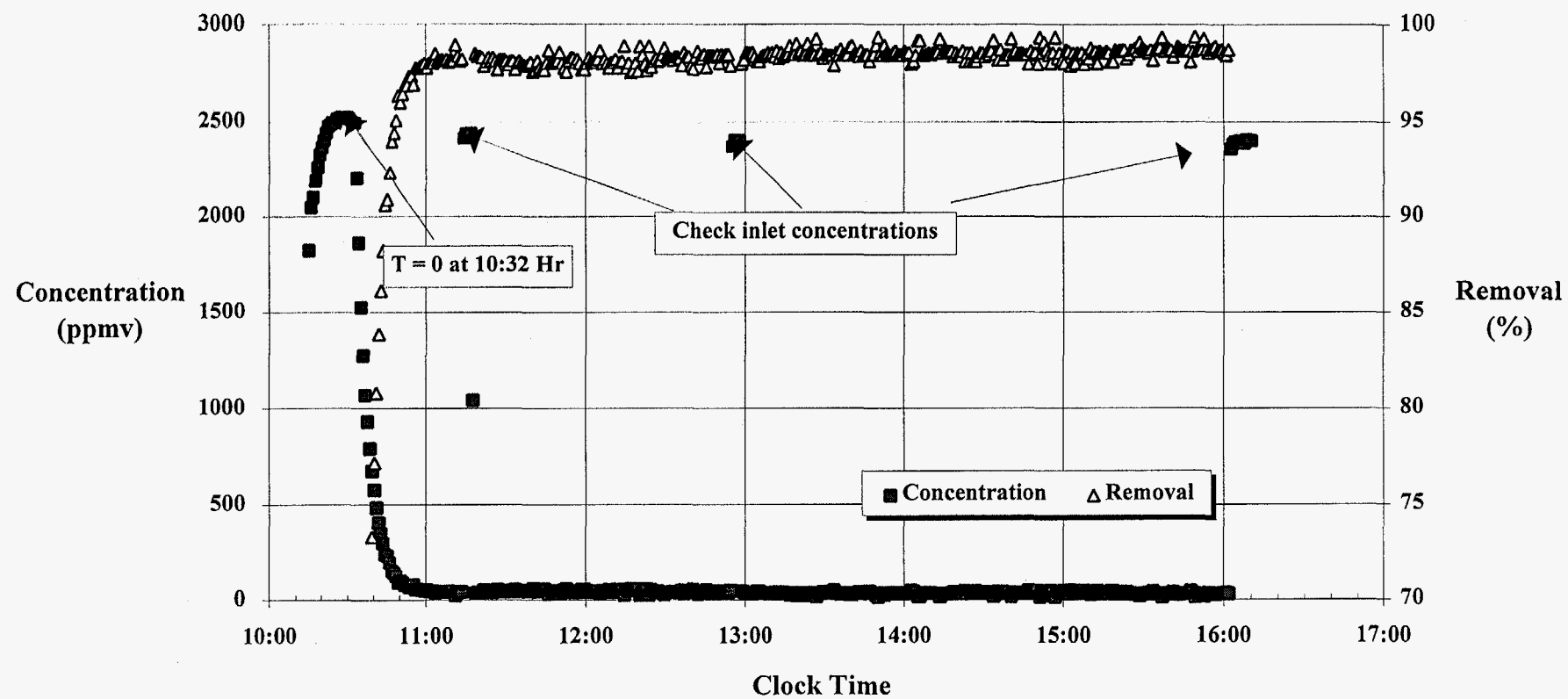
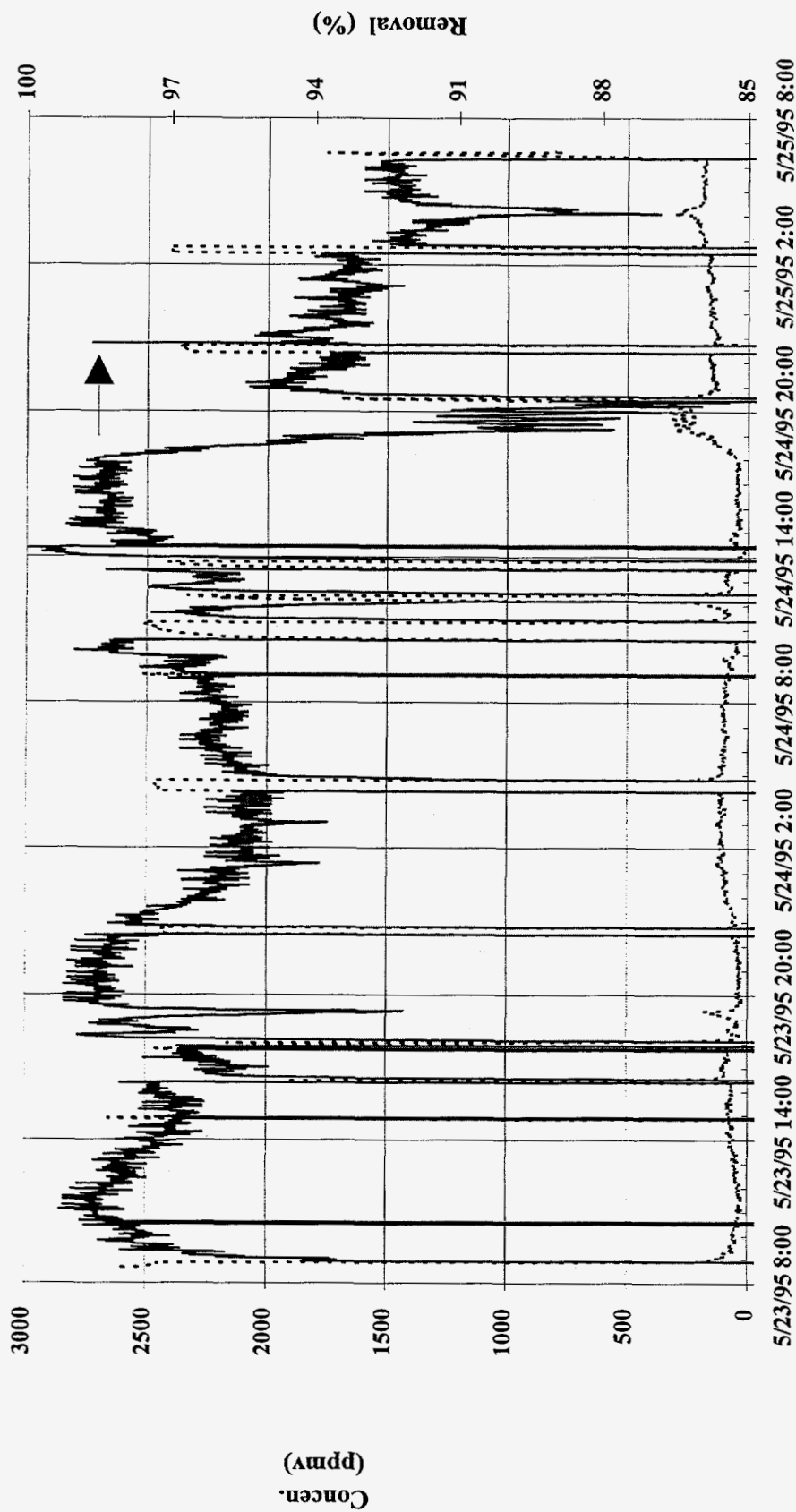
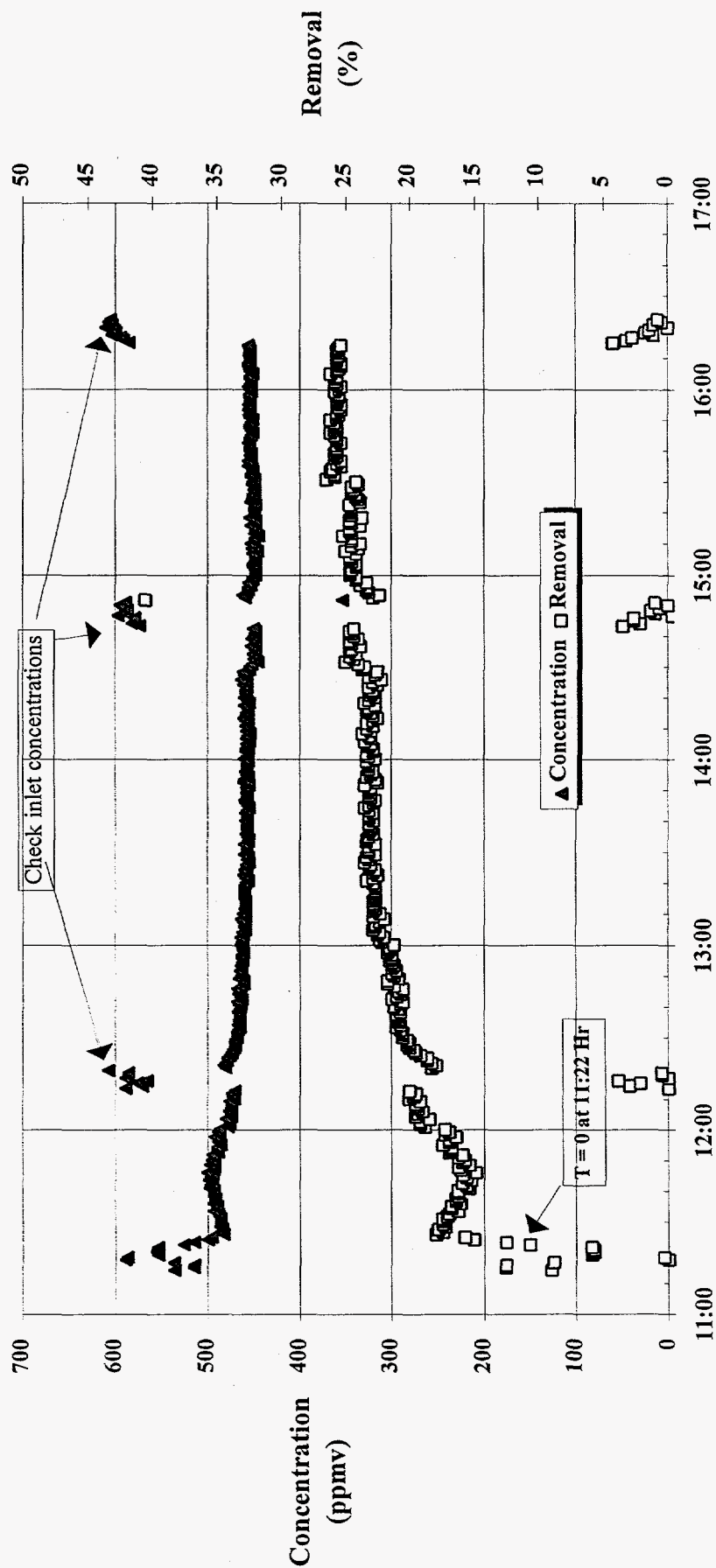


Figure 93. SO₂ concentration and removal vs. time



Clock Time

Figure 94. NO concentration and removal vs. time



Clock Time

Figure 95. NO concentration and removal vs. time

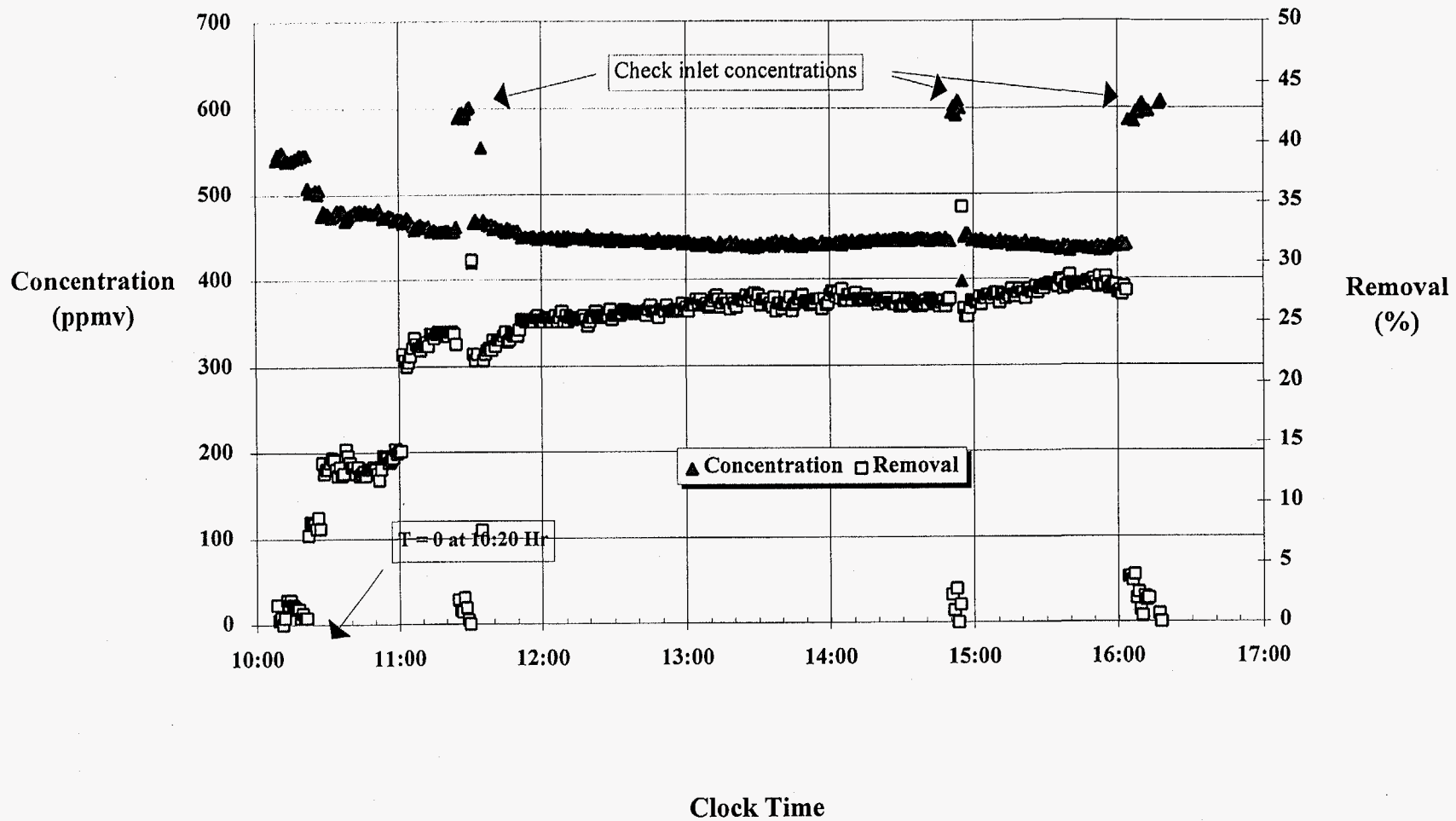


Figure 96. NO concentration and removal vs. time

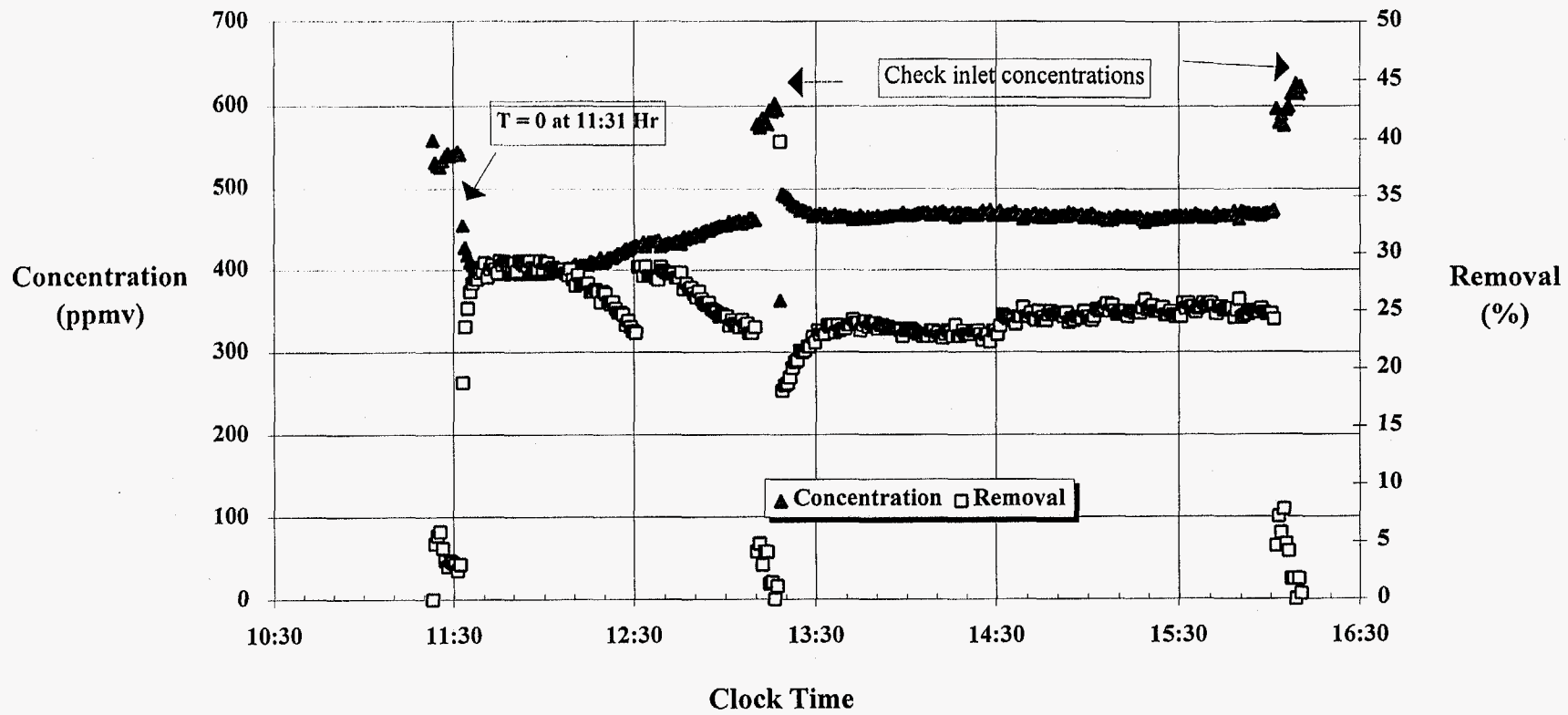


Figure 97. NO concentration and removal vs. time

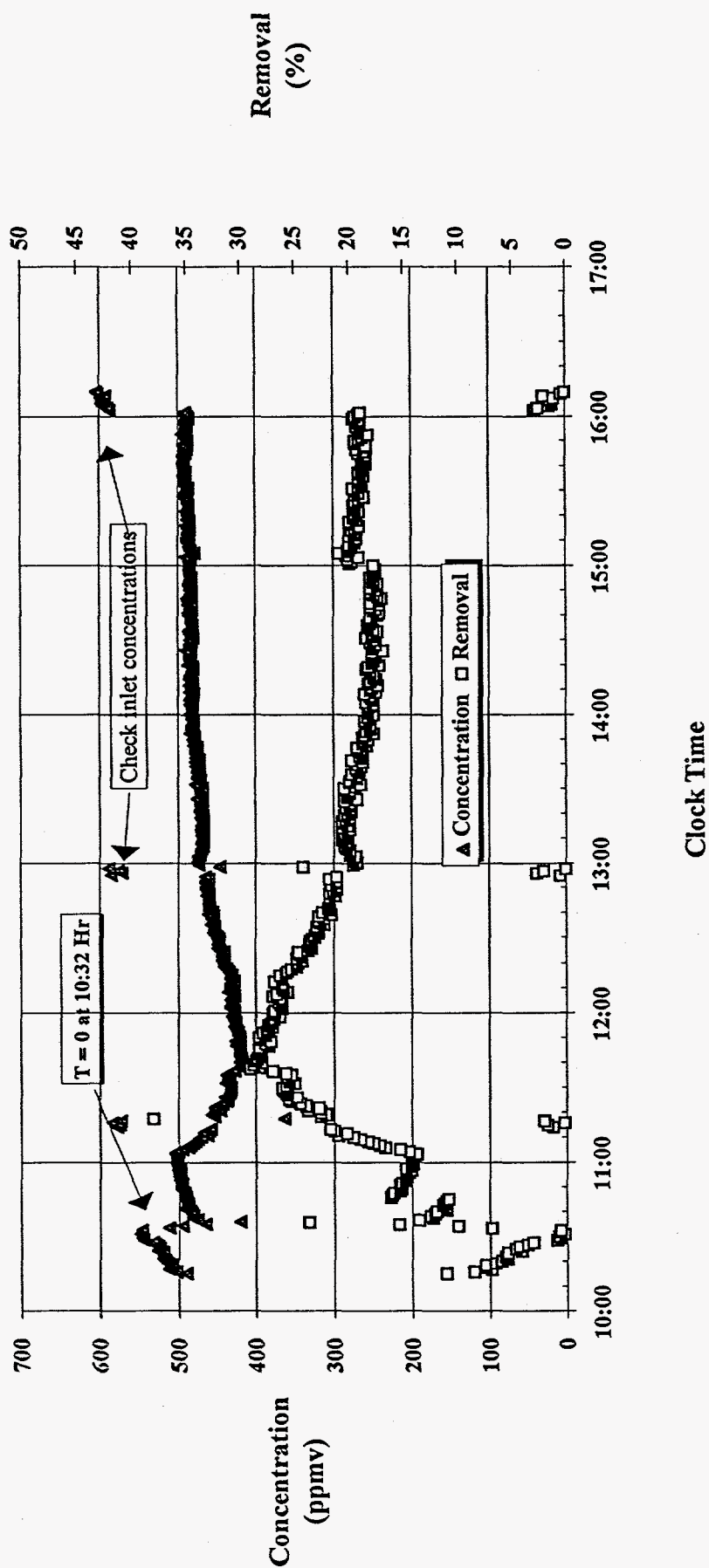
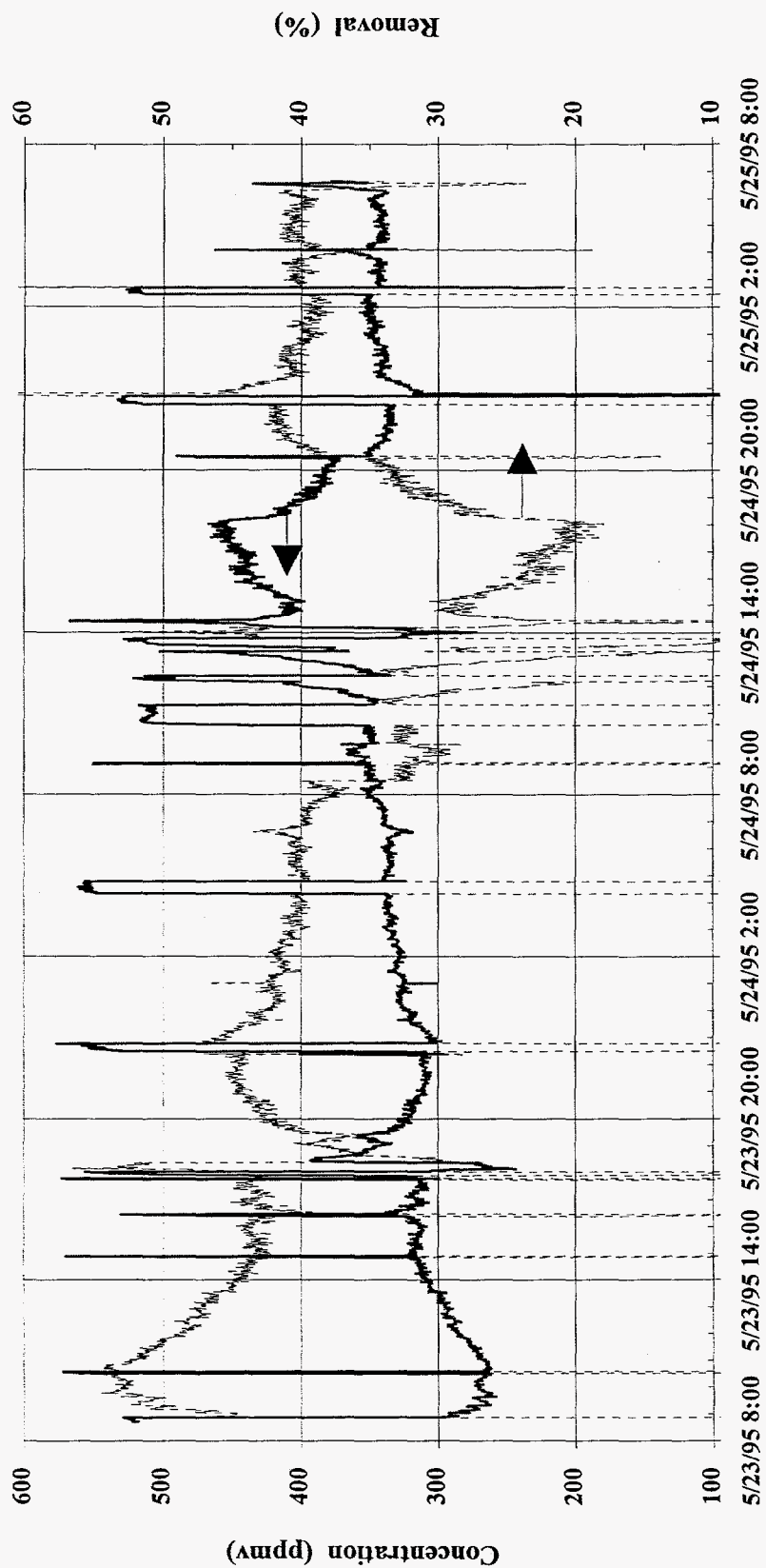


Figure 98. NO concentration and removal vs. time



Clock Time

Figure 99. Change of recycle tank liquor $[\text{Fe}^{+2}]$ with respect to time

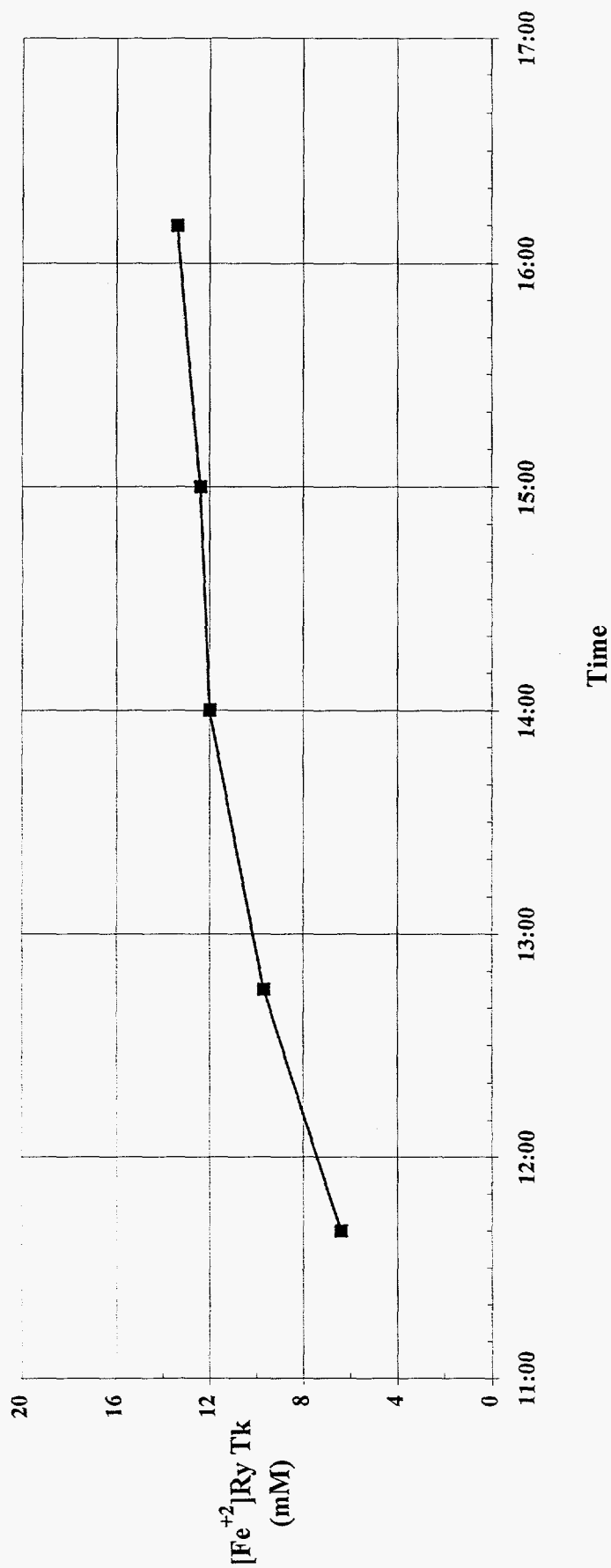


Figure 100. Change of recycle tank liquor $[\text{Fe}^{+2}]$ with respect to time

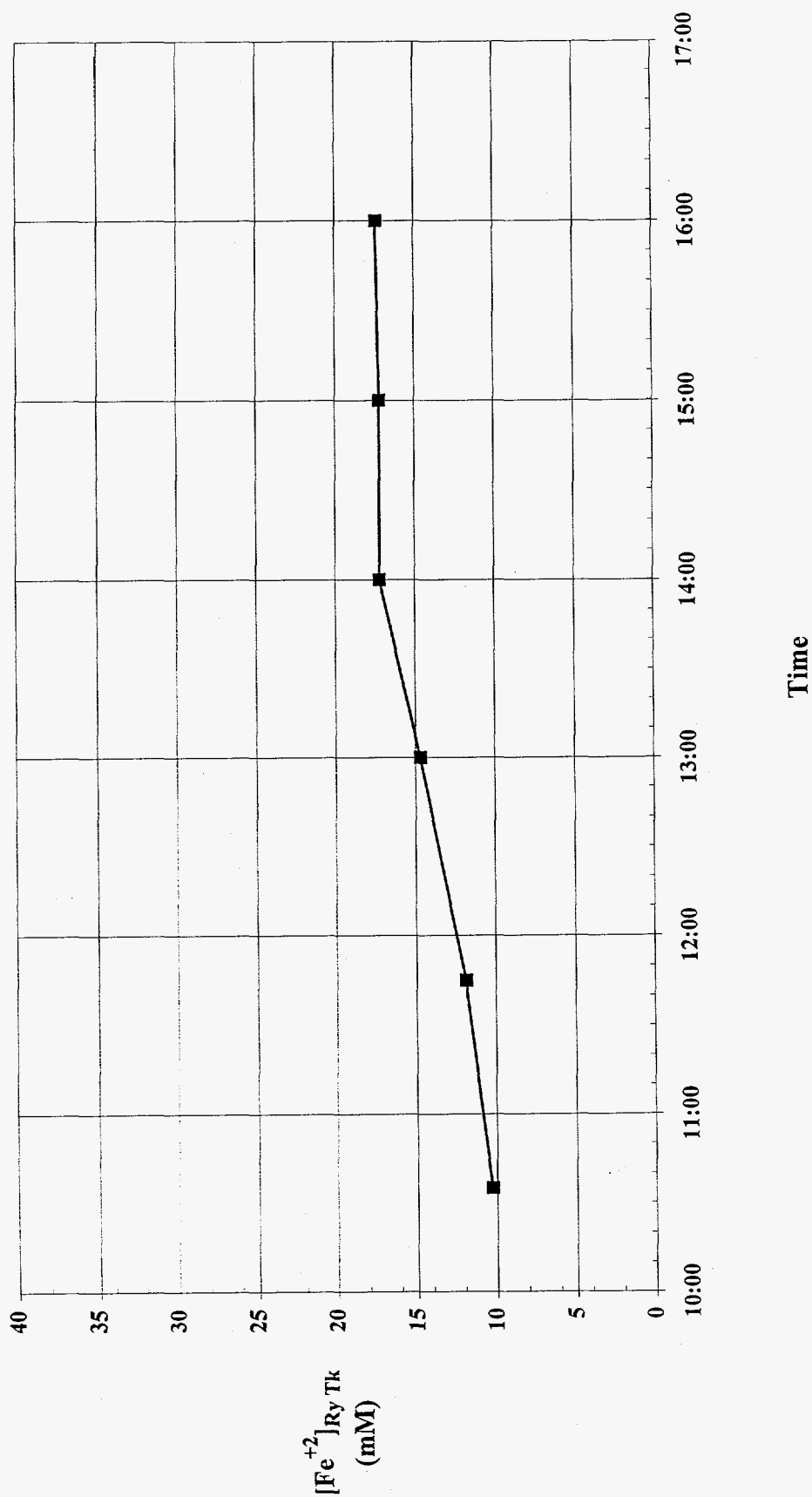


Figure 101. Change of recycle tank liquor $[\text{Fe}^{+2}]$ with respect to time

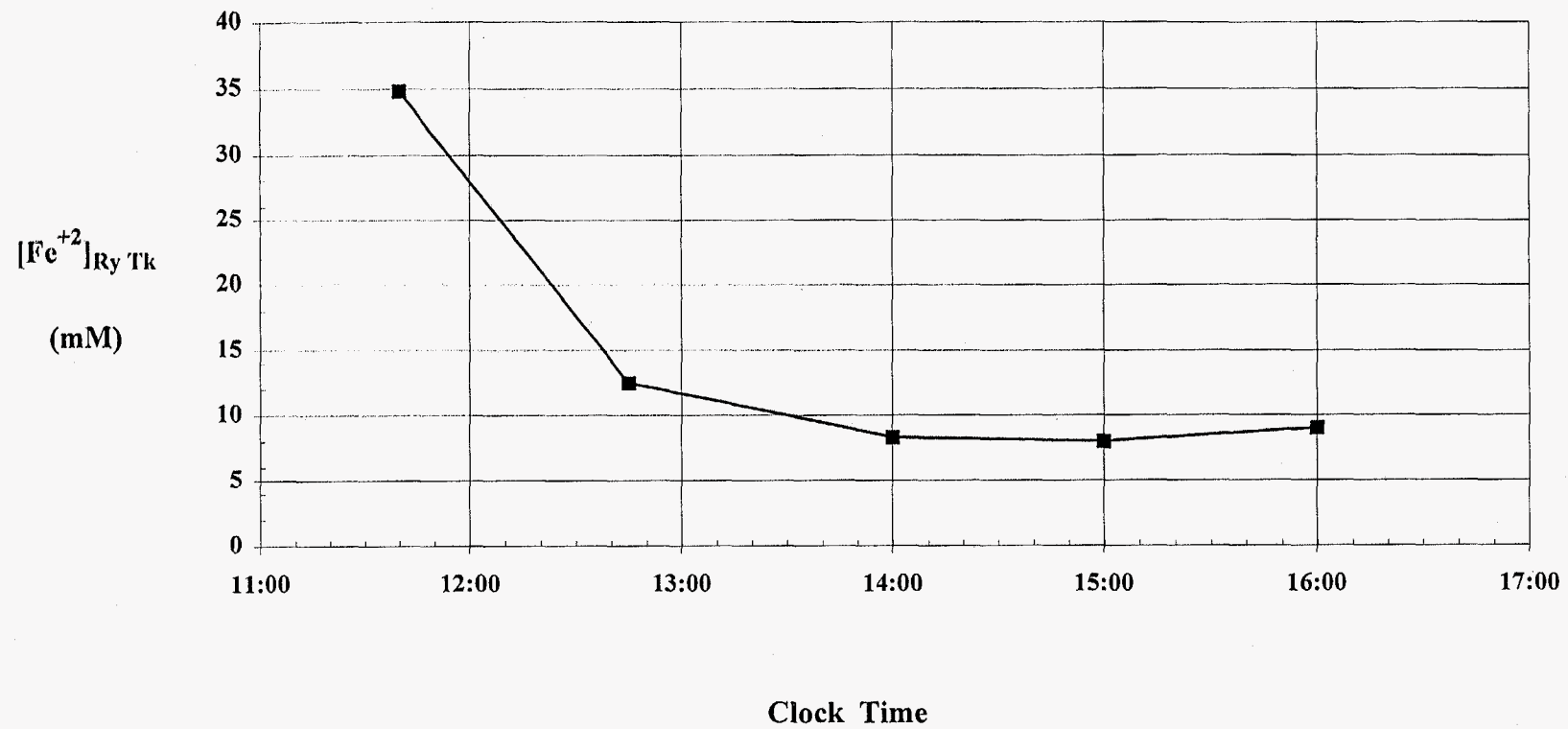


Figure 102. Change of recycle tank liquor $[\text{Fe}^{+2}]$ with respect to time

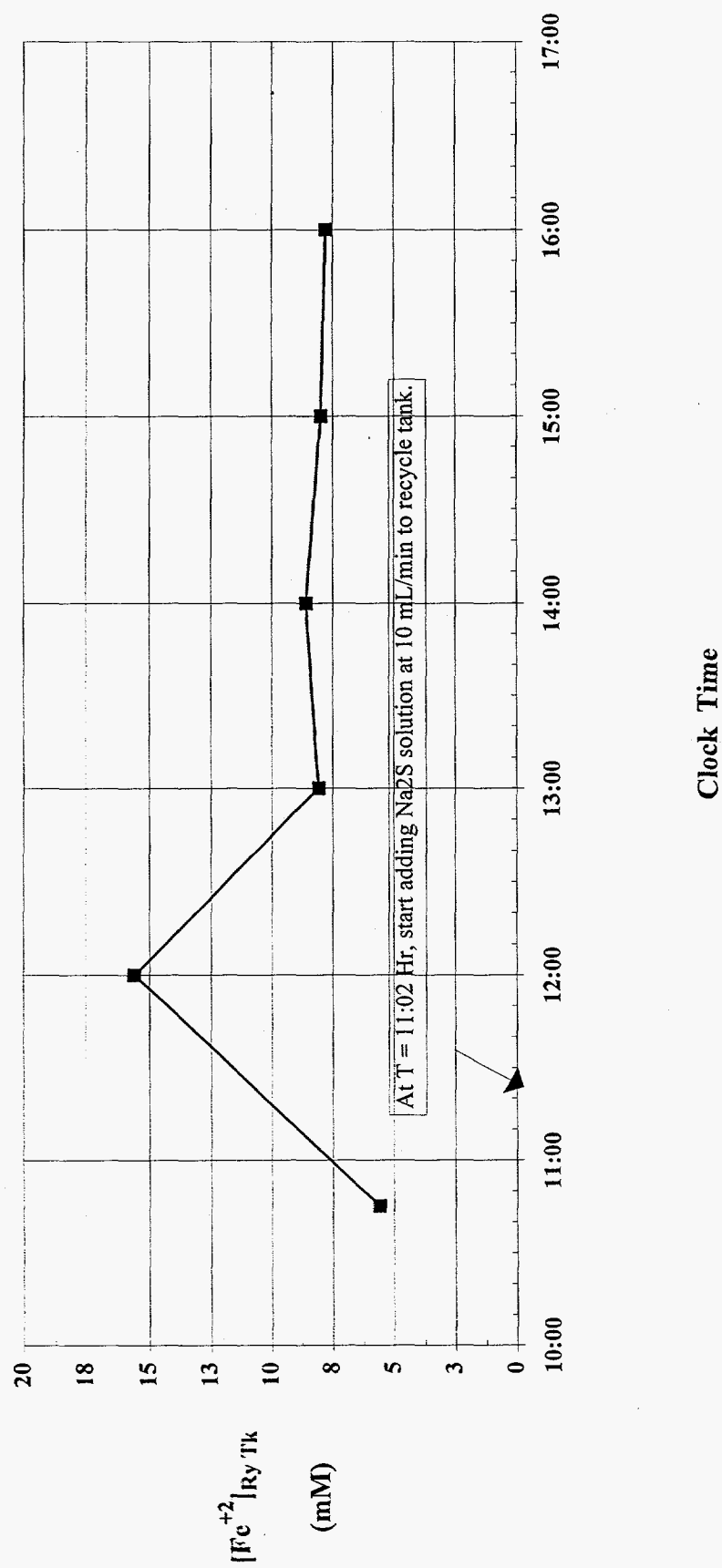


Figure 103. $[\text{Fe}^{+2}]$ and NO removal vs. time

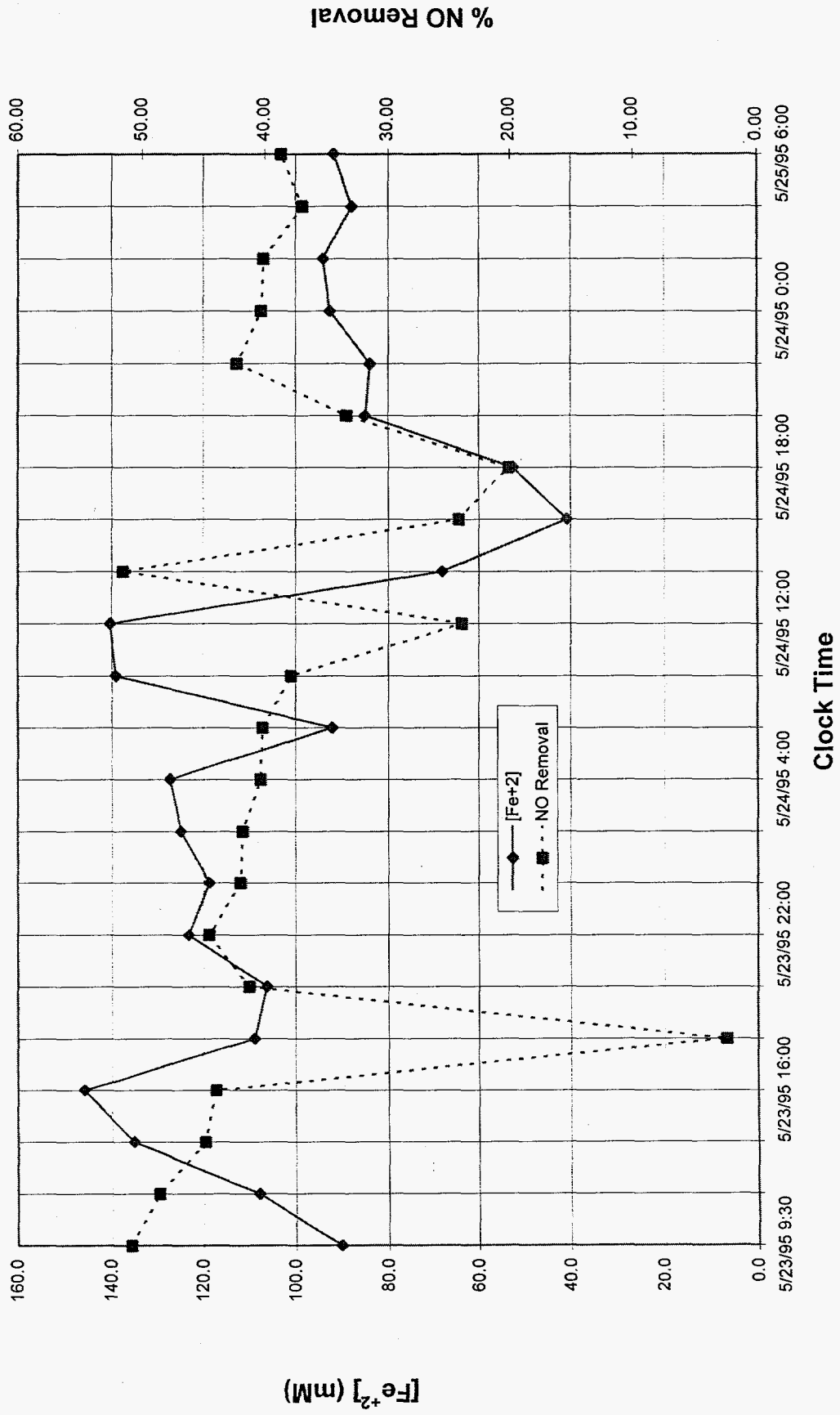


Figure 104. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

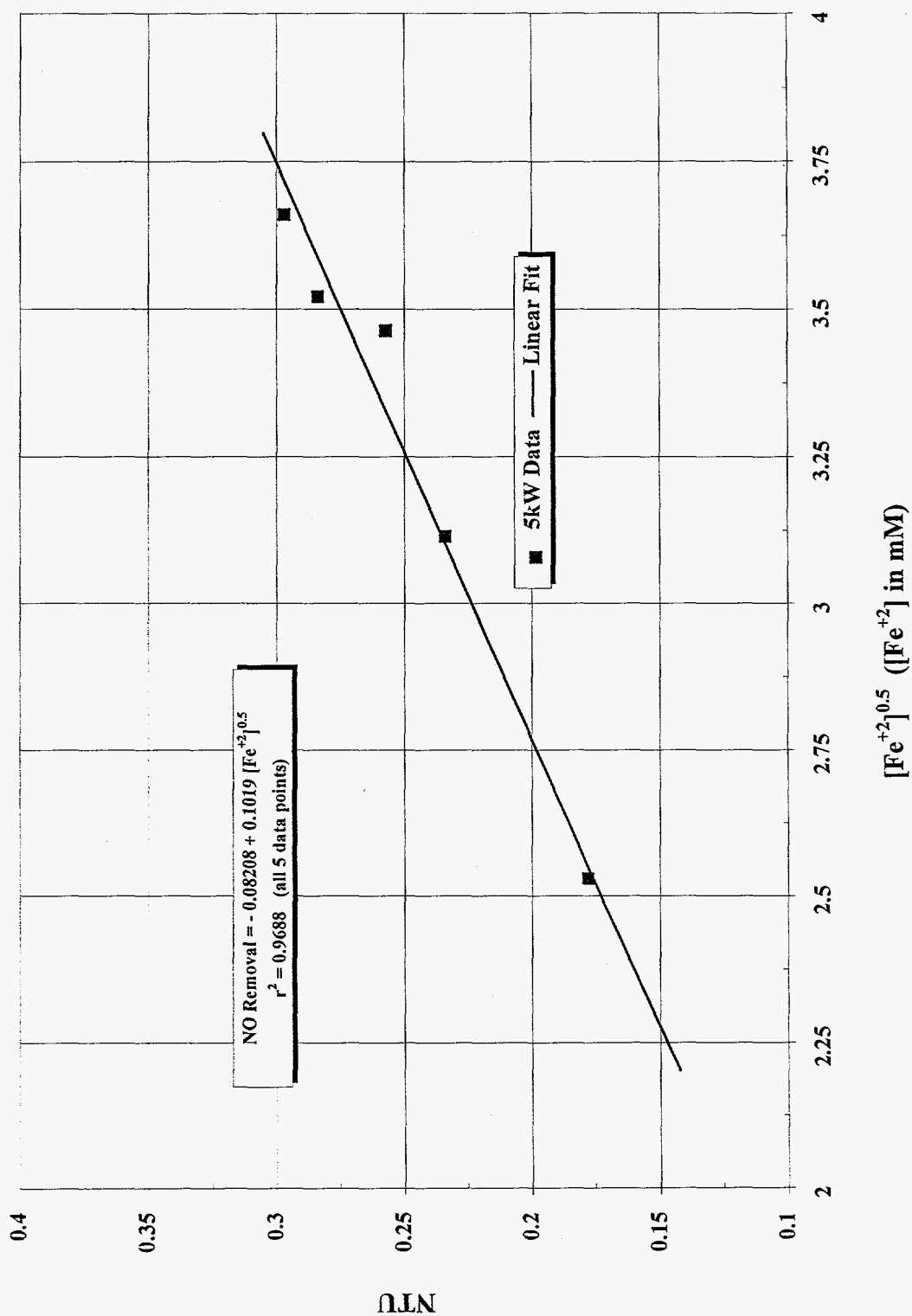


Figure 105. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

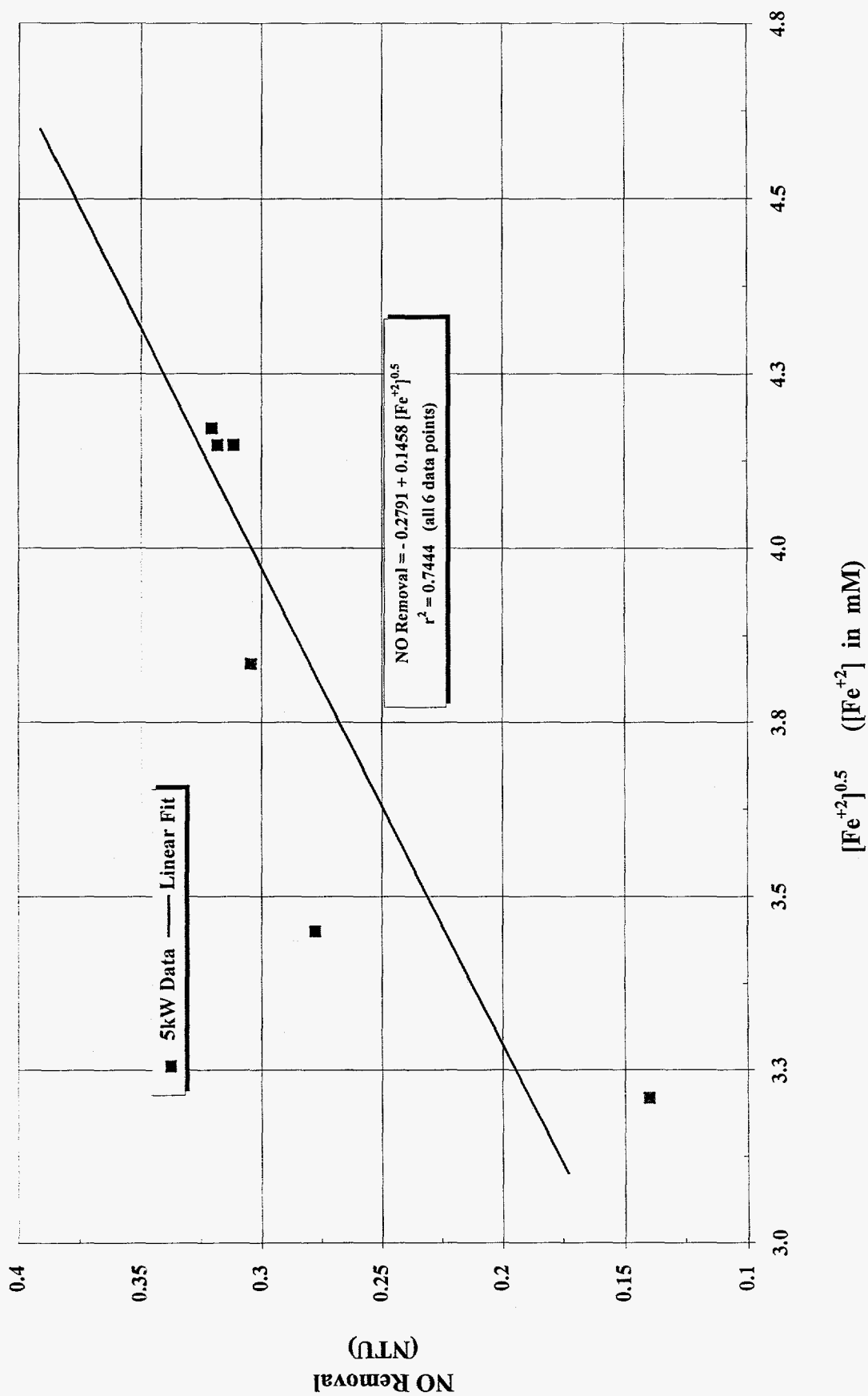


Figure 106. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

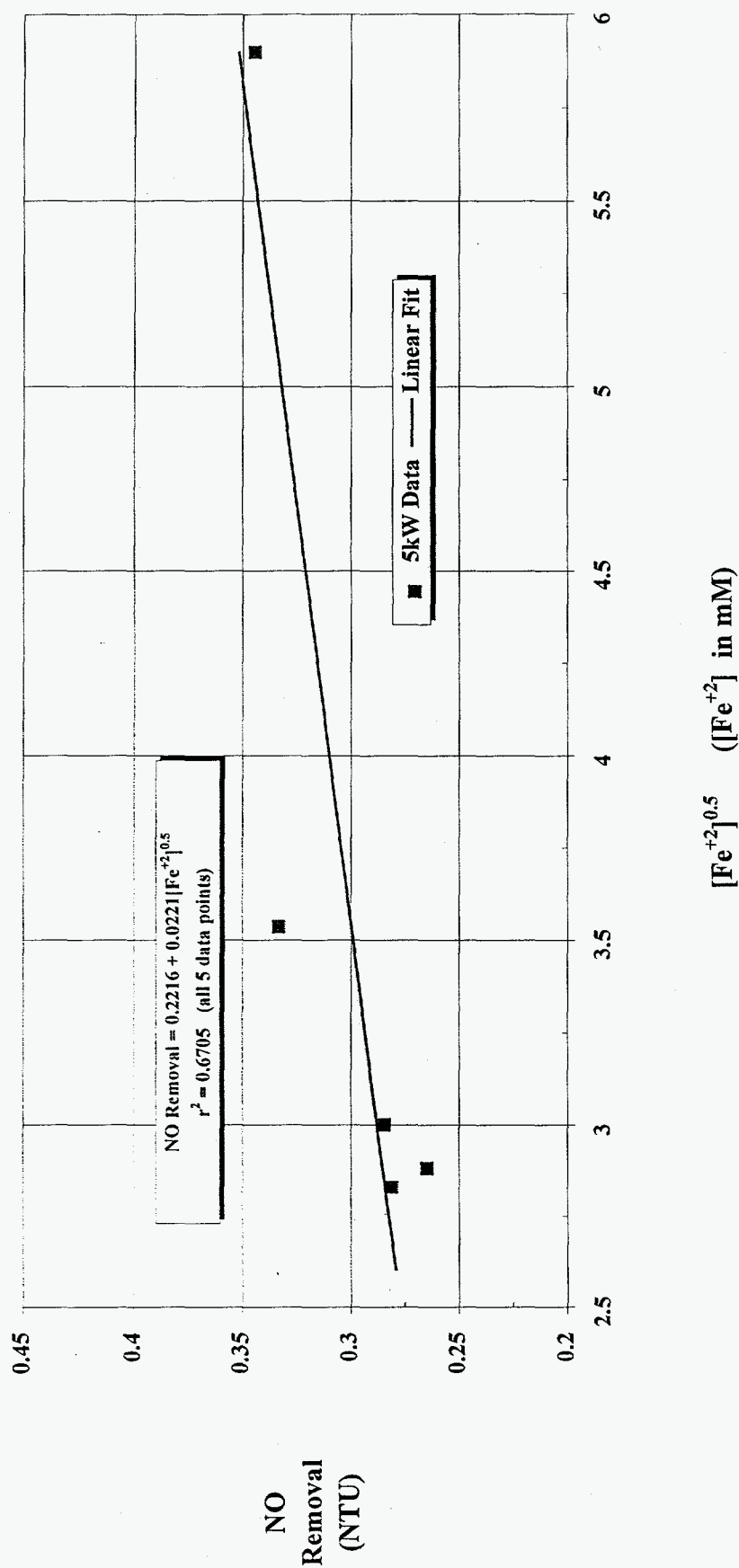


Figure 107. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

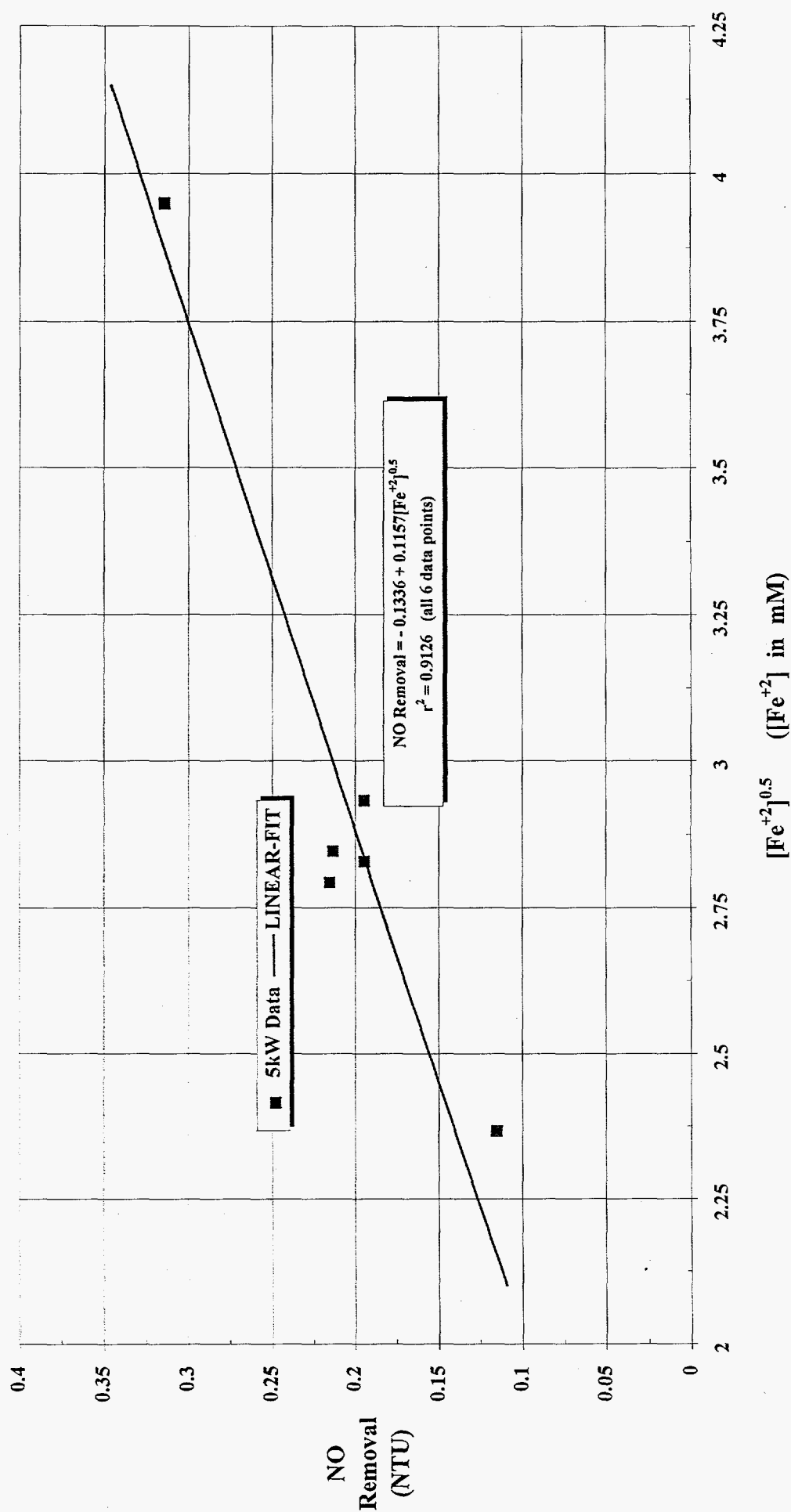


Figure 108. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

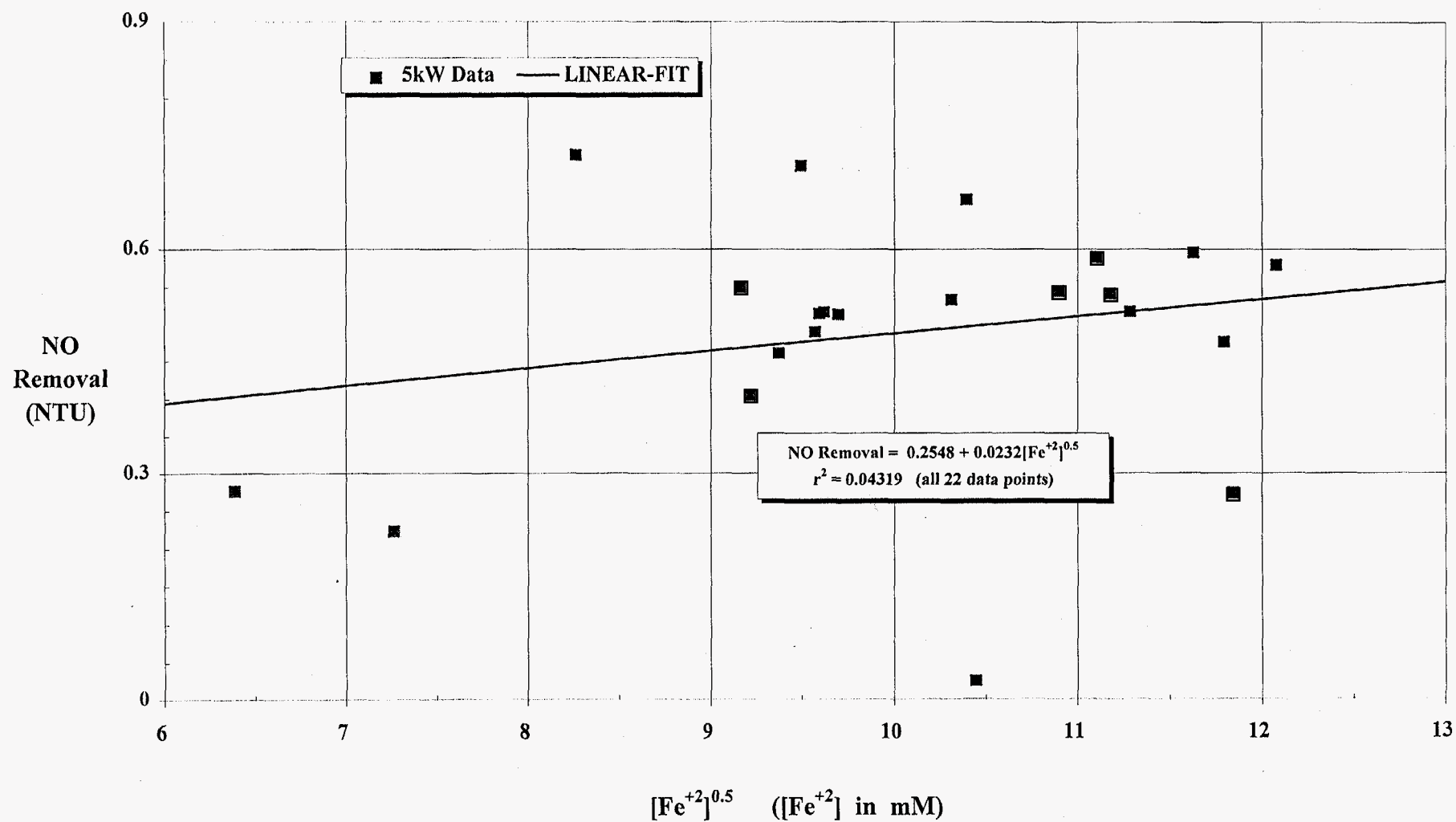


Table 21. Chemistry Data

Clock	L/G	Recy Tank	Alkalinity	[SO ₃ ⁻²]	[Fe ⁺²]	[SO ₃ ⁻²]	[ADS]	[SA]	[Mg ⁺²]	[Ca ⁺²]	[Total Fe]	[Na ⁺¹]	[SO ₃ ⁻²]	[SO ₄ ⁻²]	[Cl ⁻¹]	Filtercake
Time		Liquor pH	(ppm)	as analyzed	(mM)	adjusted for	by IC	by IC	by ICP	by ICP	by ICP	by ICP	by IC	by IC	by IC	Solids
(Hr: Min)				(ppm)		[Fe ⁺²]	(mM)	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(wt %)
						(ppm)										
11:40	44	6.25	3620	7366	6.4	7110	21.35	3.9	5360	149	2657	948	6826	8458	65	56.19
12:45	44	6.10	2736	8390	9.7	8002	21.49	4.04	5011	130	2386	1118	7425	7126	87	59.18
14:00	44	6.00	2502	9343	12.0	8863	25.70	4.75	5130	121	2319	1436	8020	6900	59	59.68
15:00	44	6.00	2836	9647	12.4	9151	29.54	6.37	5490	135	2364	1824	8142	7246	92	62.43
16:10	44	6.00	2969	10136	13.4	9600	37.29	7.96	5791	135	2433	2206	3710	10702	210	63.38
Five points avg:		6.07	2933						5356	134	2432	1506	6825	8086	103	

Table 22. Chemistry Data

Clock	L/G	Recycle	Alkalinity	[S ₂ O ₃ ⁻²] as	[SO ₃ ⁻²] as	[Fe ⁺²]	[SO ₃ ⁻²]	[ADS]	[SA]	[Mg ⁺²]	[Ca ⁺²]	[Total Fe]	[Na ⁺¹]	[SO ₃ ⁻²]	[SO ₄ ⁻²]	[Cl ⁻¹]	Filtercake
Time		Tank	(ppm)	analyzed	analyzed	(mM)	adjusted for	by IC	by IC	by ICP	by ICP	by ICP	by ICP	by IC	by IC	by IC	Solids
(Hr: Min)		Liquor pH		(ppm)	(ppm)		[Fe ⁺²]	(mM)	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(wt %)
							(ppm)										
10:35	44	6.40	3119	3136	7374	10.3	5842	27.15	6.01	5865	223	2036	1563	5986	9922	80	68.34
11:45	44	6.50	3586	3061	8246	11.9	6677	27.80	6.44	6321	143	2013	1793	6718	10270	183	65.01
13:00	44	6.50	3736	4629	9079	14.7	6838	30.90	6.98	6466	161	2005	2186	8934	11276	92	61.67
14:00	44	6.55	3970	5637	9423	17.2	6722	33.13	7.74	6740	185	2021	2529	10112	12040	79	60.09
15:00	44	6.55	4003	6011	9976	17.2	7141	37.00	8.49	6775	182	2018	2898	10344	13040	101	58.89
16:00	44	6.55	4070	8624	10416	17.4	6640	39.42	9.29	7081	165	2022	3192	9830	13756	84	60.55
avg (last 3 pts.)		6.55	4014	6757	9938	17.3	6834	36.52	8.51	6865	177	2020	2873	10095	12945	88	59.84

Table 23. Chemistry Data

[illegible]

Table 24. Chemistry Data

[illegible]

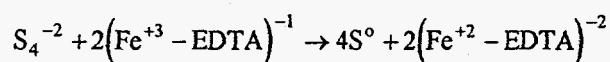
Table 25. Chemistry Data

Clock	L/G	Recycle	Alkalinity	[S ₂ O ₃ ²⁻] as	[Fe ²⁺]	[S ₂ O ₃ ²⁻]	[SO ₃ ²⁻] as	[SO ₃ ²⁻]	[ADS]	[SA] _{Adjusted}	[Mg ²⁺]	[Ca ²⁺]	[Total Fe]	[Na ⁺]	[S ₂ O ₃ ²⁻]	[SO ₃ ²⁻]	[SO ₄ ²⁻]	[Cl ⁻]	[NO ₃ ⁻]	Filtercake
Time		Tank	(ppm)	analyzed	(mM)	adjusted for	analyzed	adjusted for	by	by IC	by ICP	by ICP	by ICP	by ICP	by IC	by IC	by IC	by IC	by IC	Solids
(Hr: Min)		Liquor		(ppm)		[Fe ²⁺] _{by TK}	(ppm)	[S ₂ O ₃ ²⁻] _{&}	calculation	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(wt %)
		pH				(ppm)		[Fe ²⁺] _{by TK}	(mM)											
								(ppm)												
5/23/95 9:30		6.05	1134	17509	90.1	7417.8	12890	6637	1.181	1.56	7419	441	6577	4080	11014	4292	11000	256	nd	NA
5/23/95 12:00		6.10	2485	29381	108.0	17285	18694	8201	14.28	18.20	7473	1501	6521	10020	26408	3745	11340	435	nd	NA
5/23/95 14:00		6.15	1701	35504	135.2	20361.6	22986	10306	19.55	25.70	7898	1791	6695	13170	35504	4370	11493	723	nd	NA
5/23/95 16:00		6.20	2018	33488	145.8	17158.4	25356	13396	42.22	48.40	7904	1688	6573	16280	41660	4394	10998	911.0	nd	NA
5/23/95 18:00		6.20	2385	42896	109.0	30688	28142	12822	65.72	77.30	7845	1783	6451	16940	47163	6016	9890	980	nd	62.5
5/23/95 20:00		6.20	2002	43680	106.3	31774.4	28102	12502	62.72	97.80	8462	1877	6738	19970	53320	4786	10518	1108	nd	71.6
5/23/95 22:00		6.4	2152	50624	123.2	36825.6	32025	13945	79.97	123.2	8677	1942	6847	22910	61028	4817	10514	1093	nd	70.3
5/23/95 0:00		6.4	2218	45024	118.7	31729.6	33786	17706	91.12	144.5	8671	2344	6626	25500	69783	4747	10136	1365	nd	68.8
5/24/95 2:00		6.5	2052	56000	124.9	42011.2	37589	17589	84.38	153.5	8920	2502	6603	28600	78804	4981	10327	1281	nd	67.7
5/24/95 4:00		6.4	2068	60480	127.3	46222.4	41032	19432	103.58	174	9132	2826	6515	31880	85417	4487	10299	1400	nd	74.4
5/24/95 6:00		6.4	2185	72800	92	62496	42873	16873	120.32	194.9	9225	3347	6242	33800	97767	4632	10512	1704	nd	69
5/24/95 8:00		6.45	2302	74816	139.1	59236.8	42233	15513	109.42	194	9083	3424	6024	35930	104832	3347	9875	1266	nd	65
5/24/95 12:00		6.7	3203	84224	140.3	68510.4	59126	29046	40.2	160	9755	4579	5822	45700	117603	13455	10275	346	trace	67.9
5/24/95 14:00		6.25	3736	56224	68.2	48585.6	32025	11945	14.43	98.6	8246	2625	5583	27270	73591	9504	9688	1101	trace	65.8
5/24/95 16:00		6.3	4687	45696	40.8	41126.4	32785	16465	30.68	85.6	8040	1452	5420	22430	61858	9755	8075	689	trace	62.3
5/24/95 18:00		6.4	4704	47488	52.7	41585.6	27862	10902	34.03	80.2	7769	1227	5254	20210	53520	7410	7058	742	trace	NA
5/24/95 20:00		7.4	3586	50176	84.9	40667.2	28382	10462	64.65	110.4	8270	1602	5409	22920	61290	4760	7162	740	trace	64.9
5/24/95 22:00		6.5	2602	44352	83.9	34955.2	31184	15344	69.73	120.6	8863	1601	5721	23950	66183	5606	7633	917	trace	73.1
5/24/95 0:00		6.5	2068	56000	92.5	45640	33706	13706	68.42	120	8331	2159	4988	27300	80265	4873	7607	964	trace	47
5/25/95 2:00		6.35	2285	70784	94	60256	38830	13550	81.07	142.8	8836	3182	5107	31000	87828	6958	7866	1120	trace	62.5
5/25/95 4:00		6.3	2052	45472	87.8	35638.4	36148	19908	67.69	132.8	8535	3058	5023	29680	82747	5949	7398	1538	trace	67.6
5/25/95 6:00		6.3	2118	68768	91.6	58508.8	40111	15551	73	148	8796	3472	5016	33320	94651	5849	7357	488	trace	73

10. Sodium Tetrasulfide

a) 5 kW Configuration

A holding tank was incorporated into the 5 kW system for sodium tetrasulfide addition. A schematic of the set-up is shown in Figure 84. The chemical reaction believed to occur with sodium tetrasulfide is given by the equation below:



Three tests were performed, DT050394 (non-packed mode, ~27 mM initial total iron concentration, recycle tank pH = 6.5, L/G = 44, 6.5 vol.% O₂), DT050594 (non-packed mode, ~33 mM initial total iron concentration, recycle tank pH = 6.9, L/G = 44, 6.5 vol.% O₂), DT050694 (non-packed mode, ~40 mM initial total iron concentration, recycle tank pH = 7.0, L/G = 44, 6.5 vol.% O₂) where sodium tetrasulfide solution in the holding tank was pumped to the recycle tank at 10 ml/min. The regeneration solution was 3.4 wt.% sodium tetrasulfide for test DT050394 and DT050594 while for test DT050694, the solution was 1.7 wt.% sodium tetrasulfide.

b) Test Results

The SO₂ removal reached 99% for only test DT050394. For tests DT050594 and DT050694 the SO₂ removal was at or below 95% for much of the run. The low removal achieved with test DT050694 could be due to solids build up, which was observed for this test, on the trays of the absorber. The SO₂ removal curves which were lower than expected are shown in Figures 109 through 111. Figures 112 through 114 show the NO_x removal was highest for test DT050394 where it decreased from 40% to between 20% and 25% at steady state. For the other two tests, NO_x removal seldom exceeded 20%. The use of 3.4 and 1.7 wt.% sodium

tetrasulfide solution added at 10 ml/min did not result in any enhancement in NO_x removal over that of the baseline tests. Due to the ineffectiveness of sodium tetrasulfide as a ferrous ion regeneration agent, the level of NO_x removal is invariant to the quantity of sodium tetrasulfide added to the 5 kW system. The low NO_x removal is due to the low ferrous ion concentration which was observed throughout testing. The ferrous ion concentration was highest for test DT050394 where the steady state ferrous ion concentration was 15 mM. For the other two tests, the average ferrous ion concentration was less than 15 mM. The graphs of the ferrous ion concentration with test time is given in Figures 115 through 117.

As seen from Tables 26 through 28, one problem with sodium tetrasulfide addition is the accumulation of sodium ion in the system. This will result in an increase in the anion concentration to maintain charge balance. The sulfite and sulfate ions were not observed to increase with test time except for run DT050594 where the sulfite ion concentration exhibited an increasing trend during the test period. The anion which increased most in concentration was thiosulfate. Thiosulfate is the product of an undesirable side reaction which occurs between sulfur and sulfite anion. The magnesium ion concentration varied from 4,000 to 6,000 ppm typical of Thio NO_x chemistry. The calcium ion concentrations were elevated for tests DT050594 and DT050694 causing concern for precipitation of calcium sulfite/calcium sulfate if the sulfite or sulfate ion concentrations were to further increase. The filtercake solids content displayed an increasing trend for both tests DT050594 and DT050694. By the end of testing, the filtercake solids content was between 70 wt.% and 80 wt.%, meeting the solids dewatering goal stated in the proposal.

Correlation to the NO_x removal model was highest for test DT050394. (Figures 118 through 120). The value of the correlation coefficient was 0.7003. For tests DT050594 and DT050694, the correlation was less indicating a difference between the effective ferrous ion concentration and actual ferrous ion concentration.

c) Economics of Sodium Tetrasulfide Addition

The cost of sodium tetrasulfide was found to be \$0.40/lb_m. One test did not reach steady state so the final ferrous ion concentration and NO_x removal was used to calculate the cost of this agent for this test. It was averaged with those tests which did reach steady state near the end of testing in the calculation of cost. This agent was found to be slightly more expensive than sodium sulfide hydrate. The cost on a mM ferrous ion concentration and NTU removal basis was found to be \$.00579/day·mM Fe²⁺·vol.% O₂ and \$.0247/day·NTU·vol.% O₂, respectively. These values are depicted in Figures 50 and 51.

d) Attainment of Objectives

During this testing, it was determined if sodium tetrasulfide met the goals outlined in the test plan. 99% SO₂ removal was not achieved for tests DT050594 and DT050694. For the first test, the NO_x removal was highest ranging from 20% to 25% after achievement of steady state. This does not meet the requirement for NO_x removal. The solids content of the filtercake met the goal set in the proposal.

Figure 109. SO₂ concentration and removal vs. time

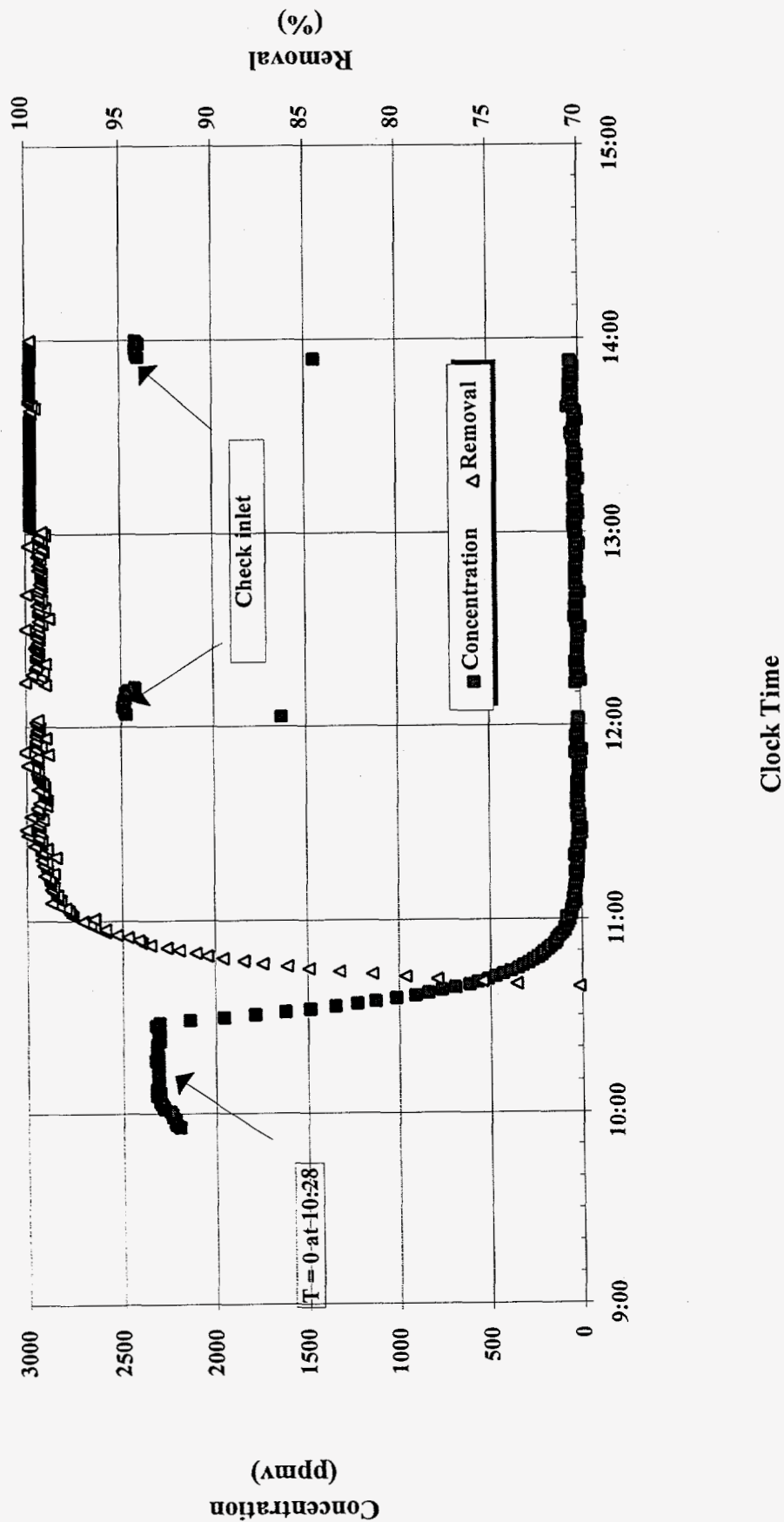


Figure 110. SO₂ concentration and removal vs. time

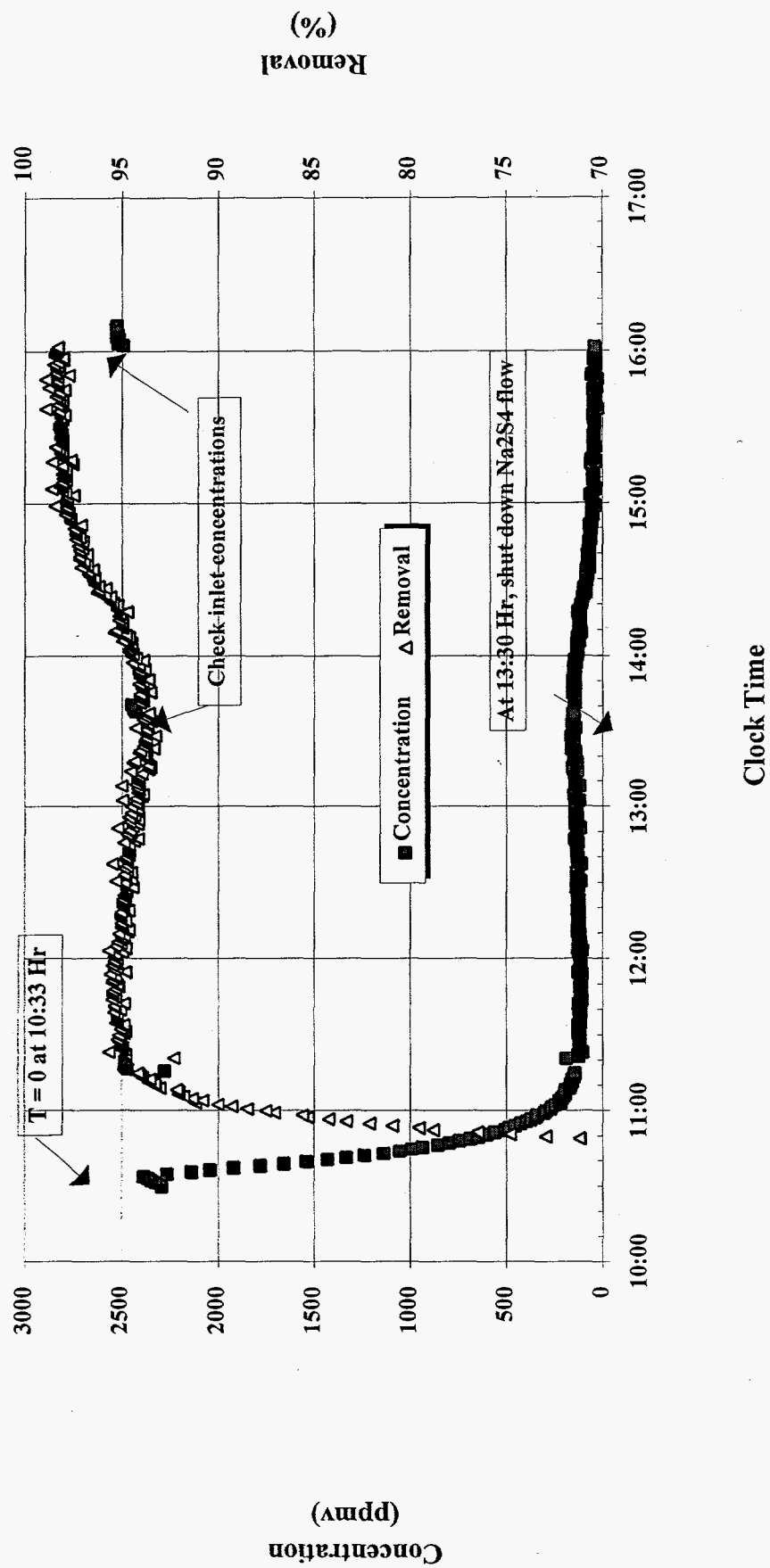


Figure 111. SO₂ concentration and removal vs. time

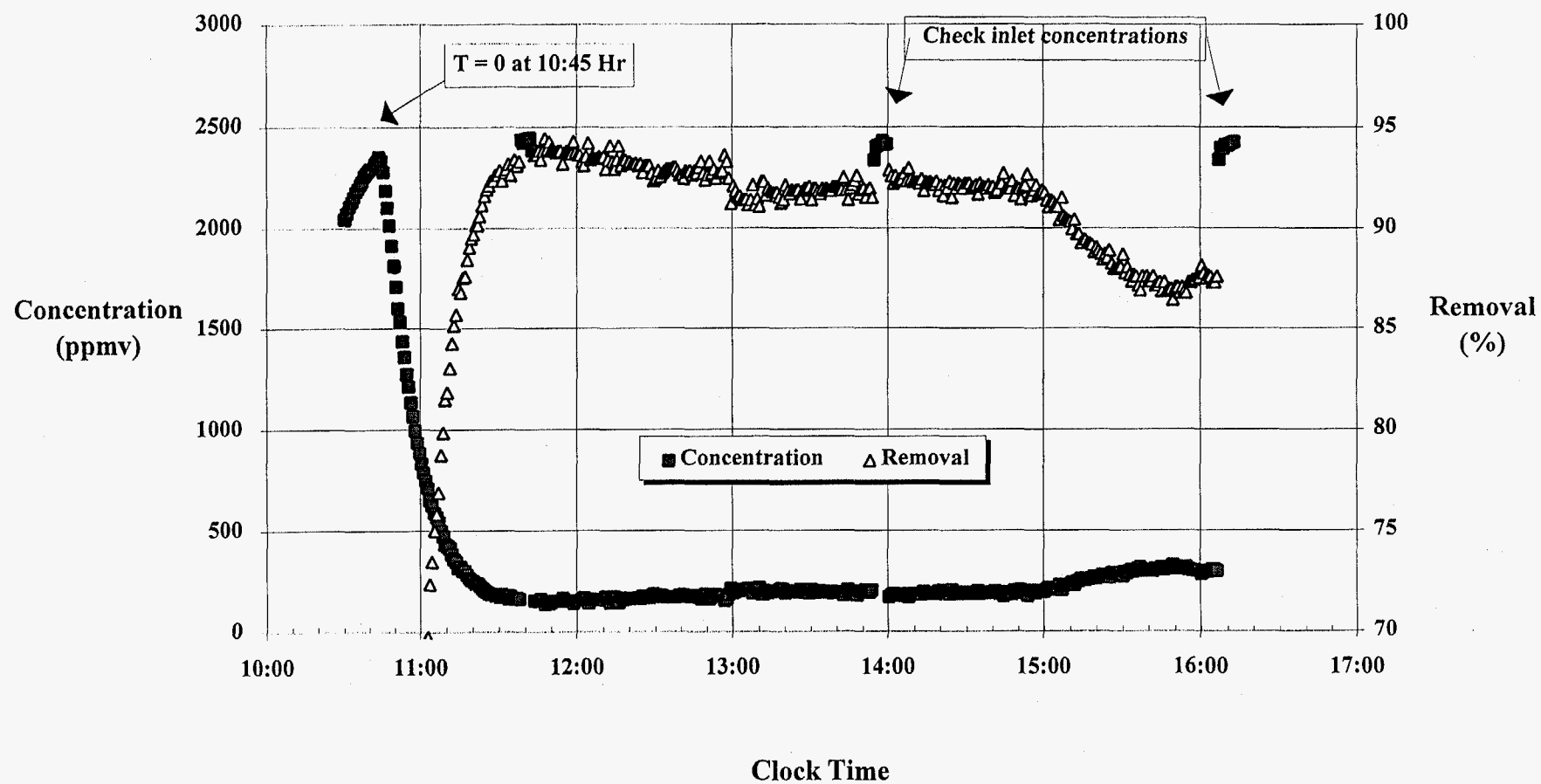


Figure 112. NO concentration and removal vs. time

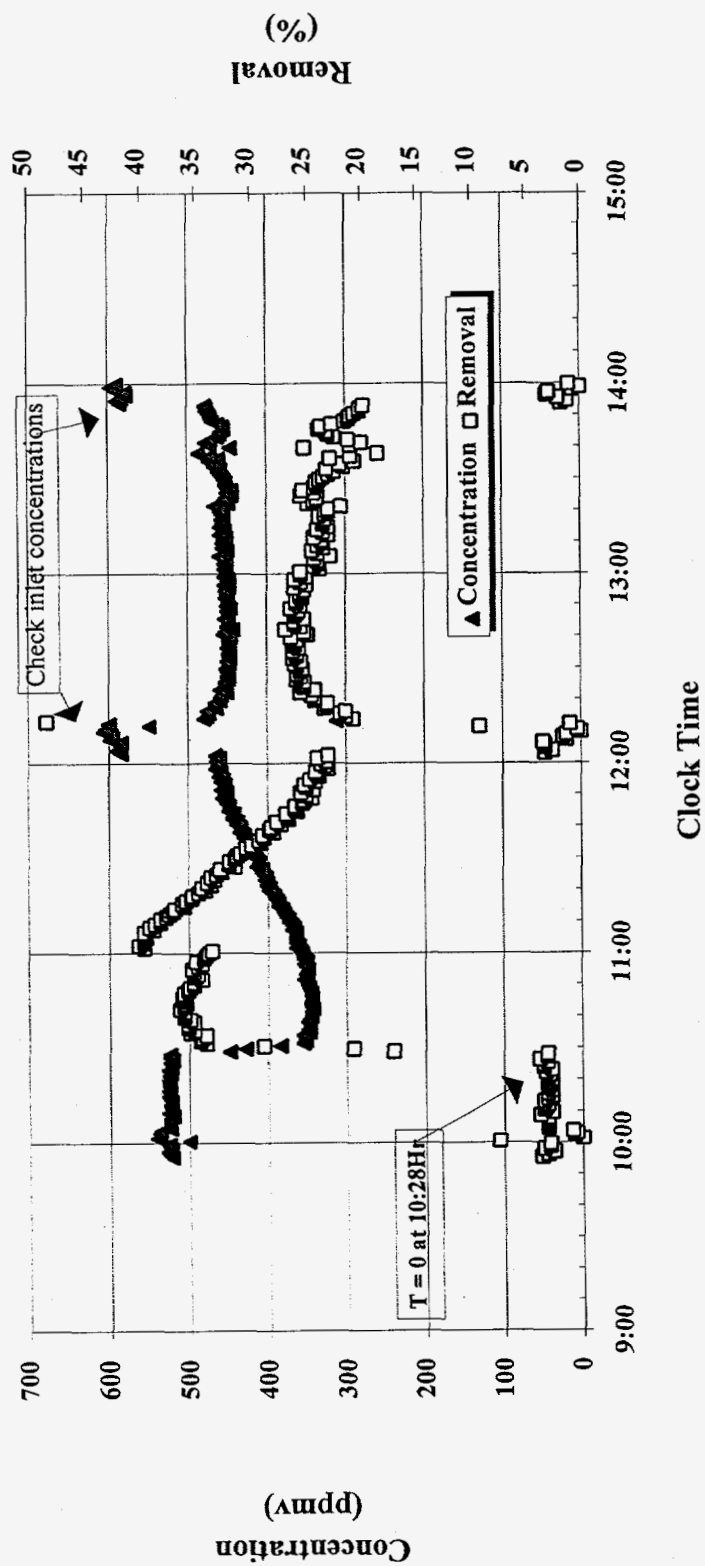


Figure 113. NO concentration and removal vs. time

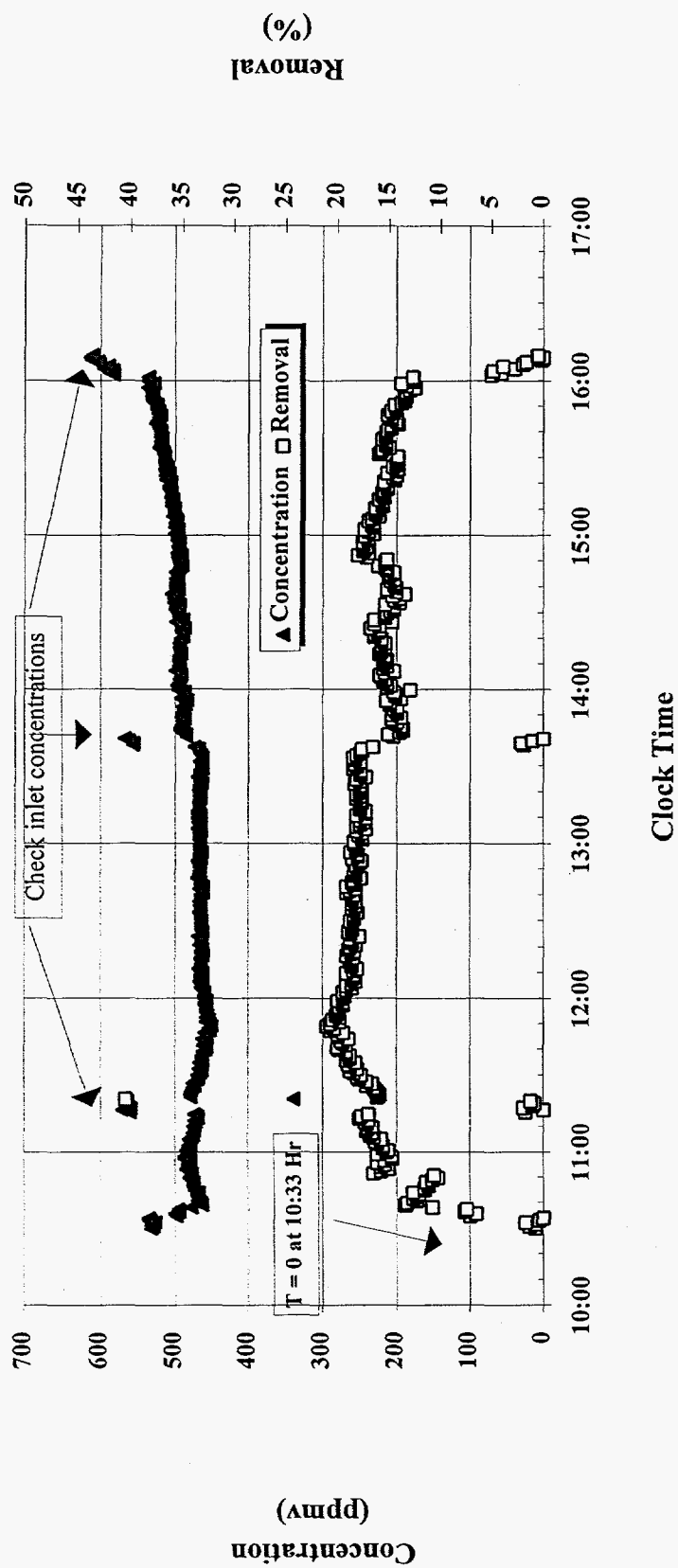
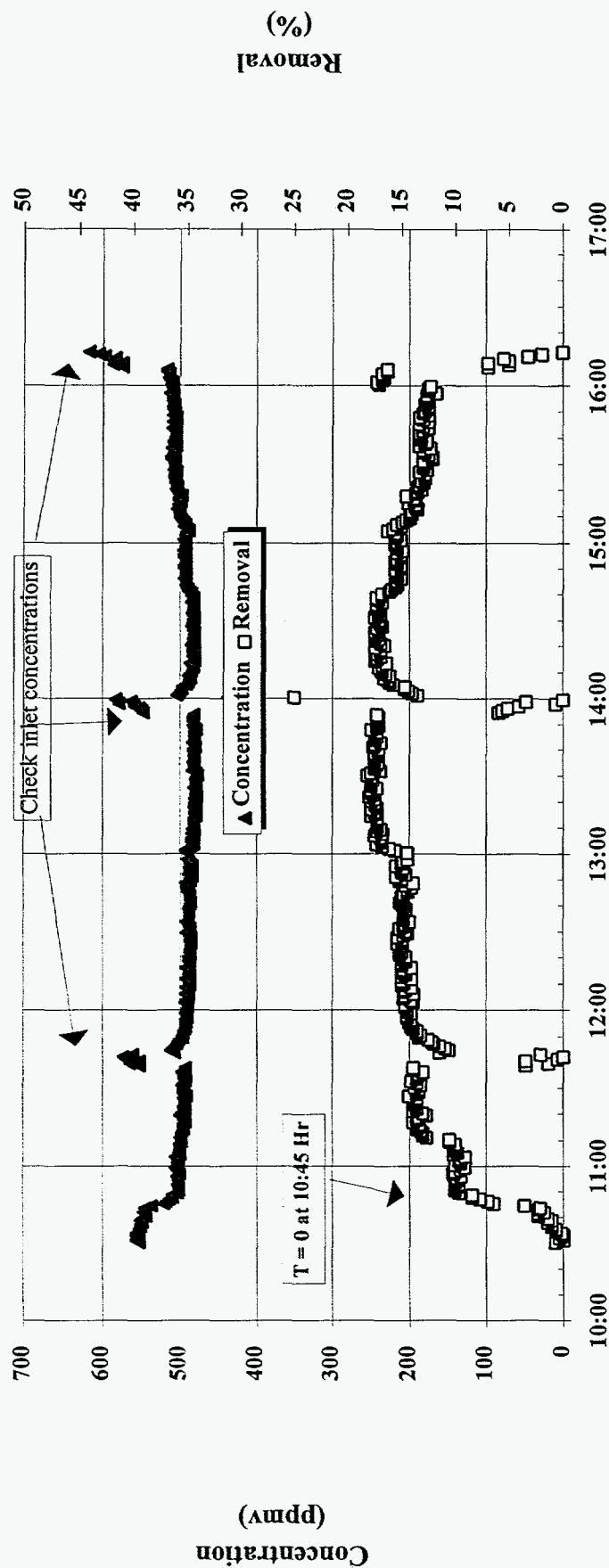
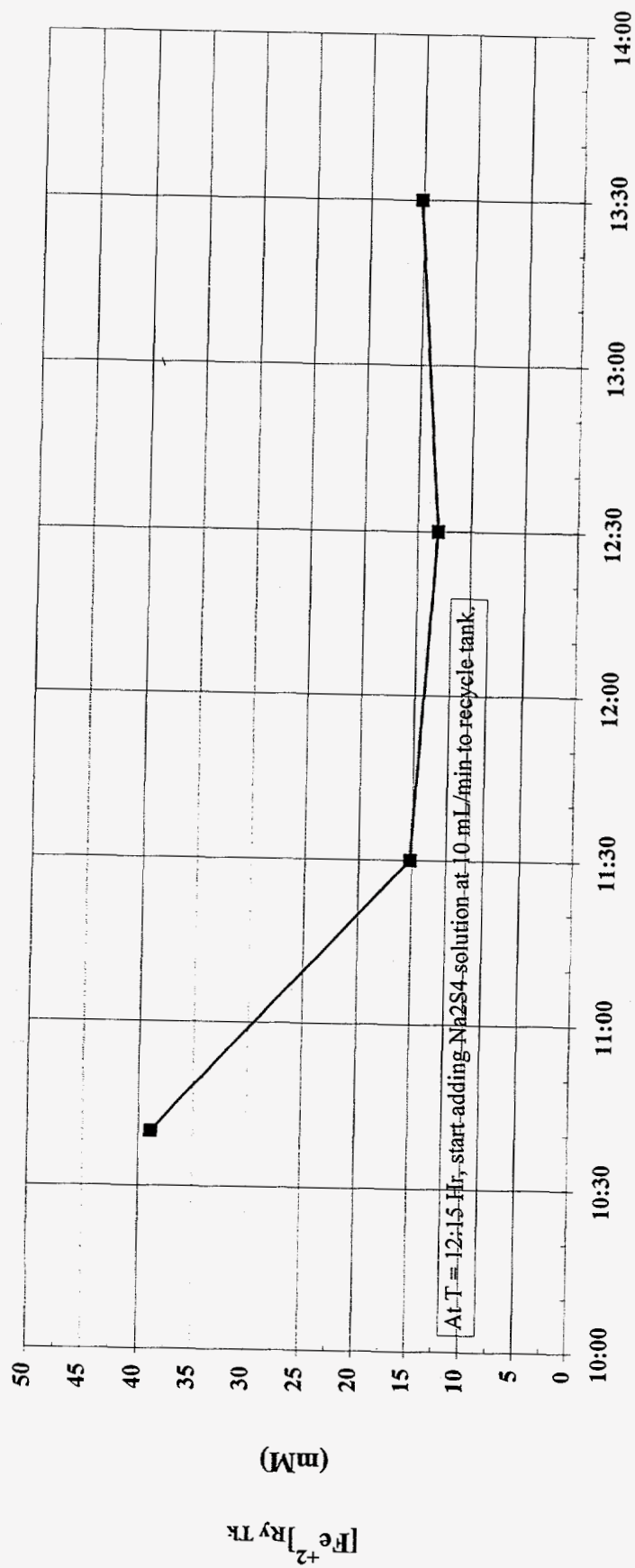


Figure 114. NO concentration and removal vs. time



Clock Time

Figure 115. Change of recycle tank liquor $[\text{Fe}^{+2}]$ with respect to time



Clock Time

Figure 116. Change of recycle tank liquor $[\text{Fe}^{+2}]$ with respect to time

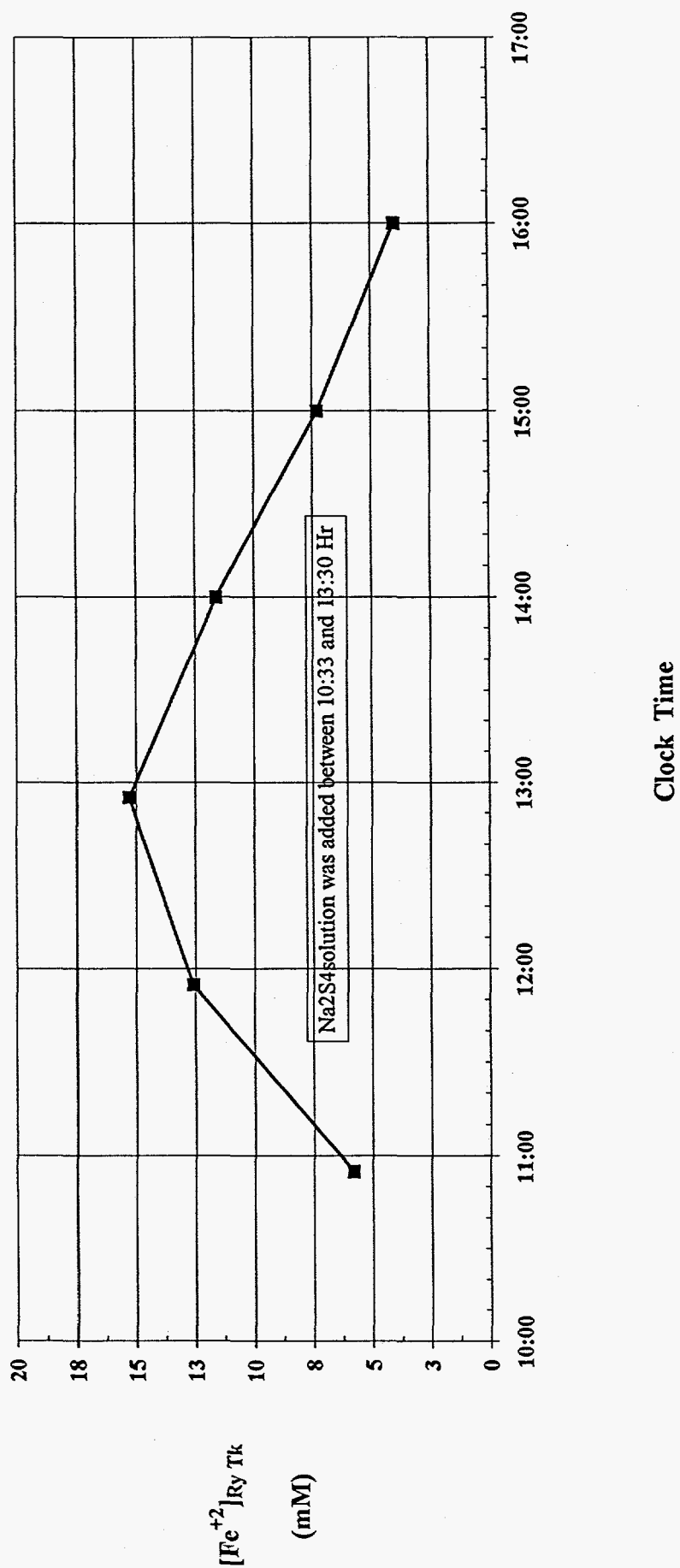
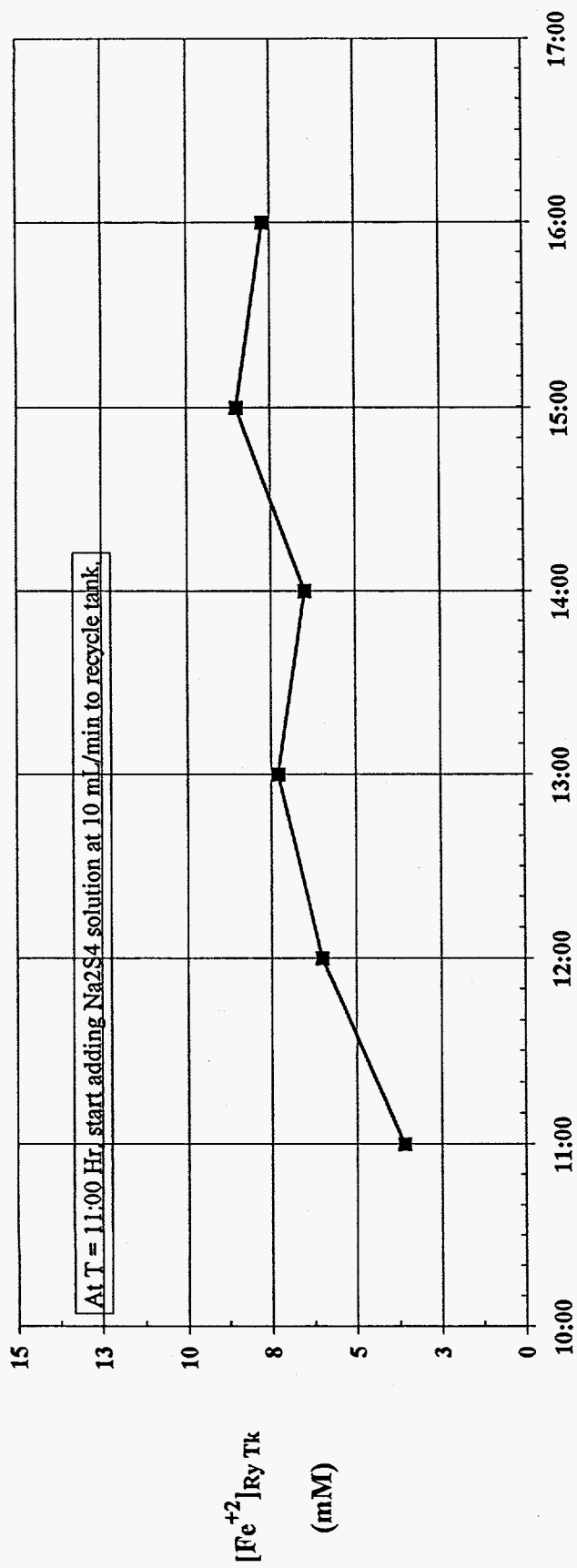


Figure 117. Change of recycle tank liquor $[\text{Fe}^{+2}]$ with respect to time



Clock Time

Figure 118. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

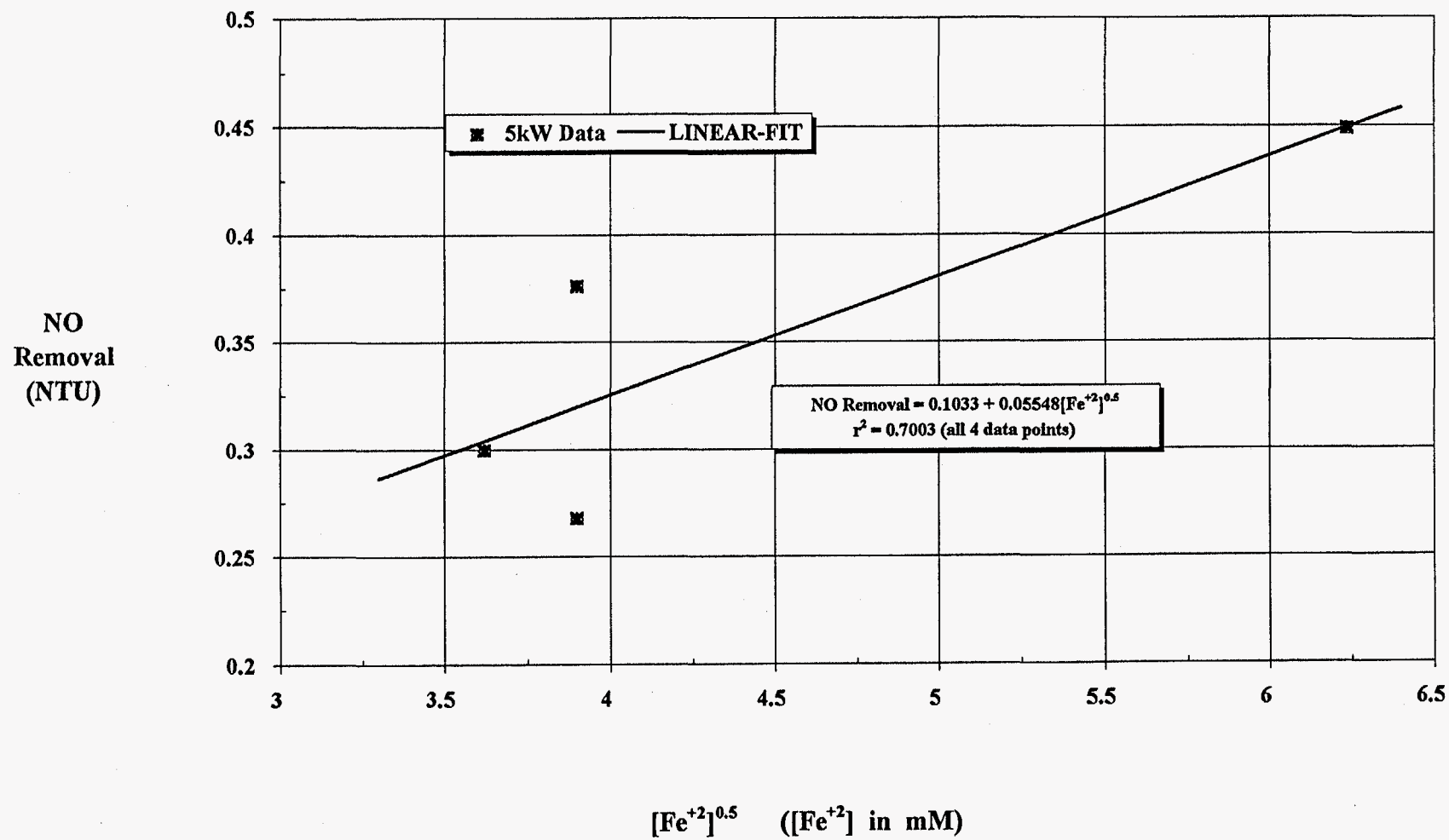


Figure 119. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

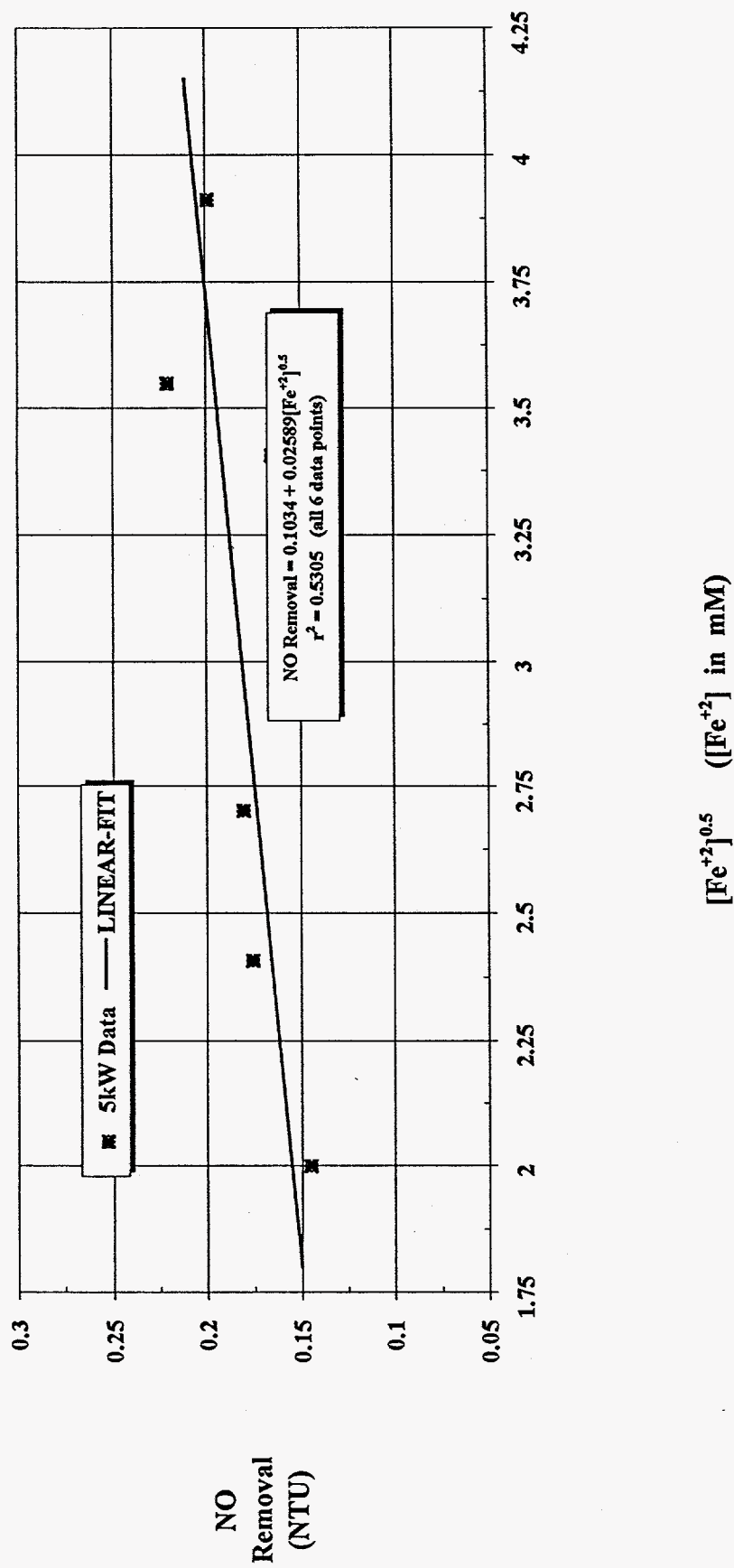


Figure 120. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

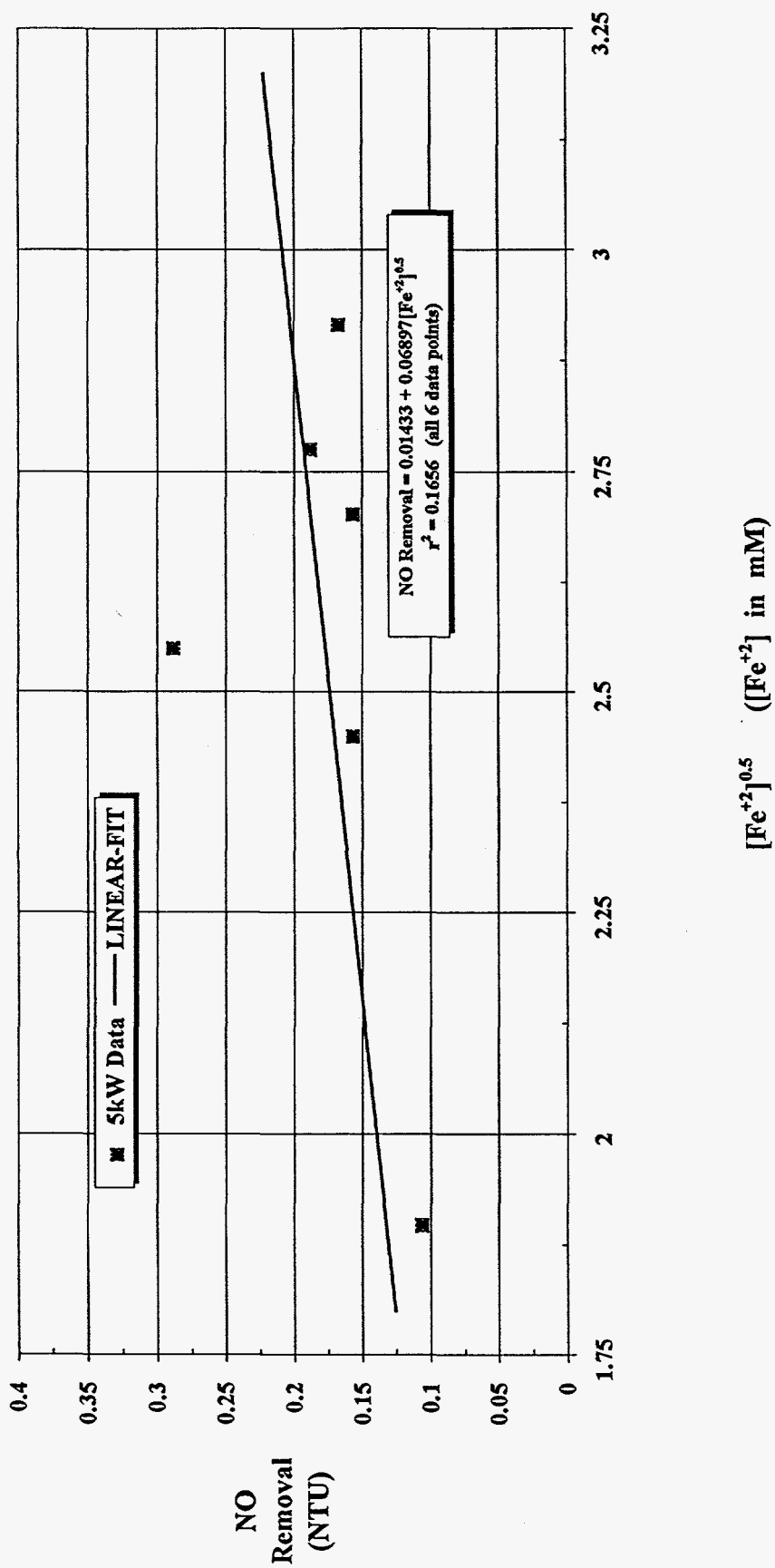


Table 26. Chemistry Data

[illegible]

Table 27. Chemistry Data

[illegible]

Table 28. Chemistry Data

[illegible]

11. Sulfide / Polysulfide

Previous testing with emulsified sulfur added to the recycle tank displayed NO_x removals less than 30%. The difficulty associated with adding excess sulfur to the recycle tank is that thiosulfate ion will accumulate in the system. This causes the calcium ion concentration to increase. With high calcium ion concentrations, the possibility of calcium sulfite/calcium sulfate precipitation increases. As a consequence of these test results, it was decided not to test sulfide / polysulfide, due to the low NO_x removals, as part of the screening tests for regeneration agents for Phase I.

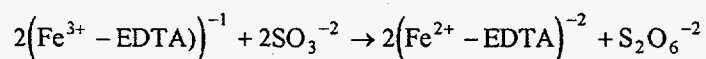
12. Ammonium Thiosulfate

Because of the low NO_x removals achieved adding emulsified sulfur to the recycle tank, it was decided not to test ammonium thiosulfate as part of the screening tests for Phase I. The emulsified sulfur is believed to react with calcium hydroxide to form thiosulfate and polysulfide anion. Since most of the reducing activity is thought to be derived from the polysulfide anion, ammonium thiosulfate should not function as an effective regeneration agent if emulsified sulfur is ineffective in NO_x removal.

C. Thermal Regeneration

1) 5 kW Configuration

A thermal regeneration vessel was added to the 5 kW system where the thickener overflow was directed to the thermal regeneration vessel and the liquor in the thermal regeneration tank was pumped back to the recycle tank. The liquor in the thermal regeneration vessel was heated to elevated temperatures by a heating rod. A diagram of the set-up is shown in Figure 121. Two tests were conducted, DT121294 (non-packed mode, ~50 mM initial total iron concentration, recycle tank pH = 7.2, L/G = 44, 6.5 vol.% O₂, thermal regeneration vessel = 76°C) and DT011995 (non-packed mode, ~100 mM initial total iron concentration, recycle tank pH = 6.8, L/G = 44, 11.5 vol.% O₂, thermal regeneration vessel = 90°C), using the thermal regeneration vessel. It was the goal to determine if natural reduction of ferric EDTA by sulfite ion would be significantly increased with a temperature elevation. The regeneration reaction believed to occur in the thermal regeneration vessel is as follows:



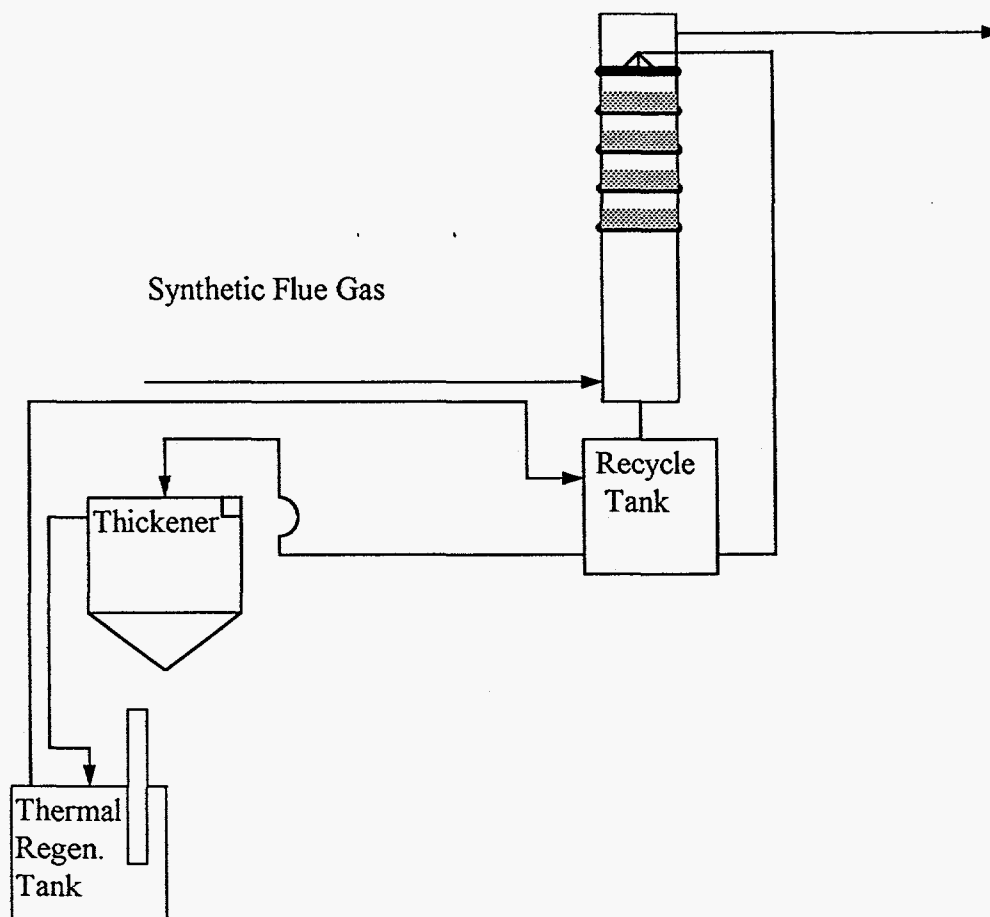


Figure 121. Flow Diagram for Thermal Regeneration

2) Test Results

The SO_2 removal reached between 98% and 99% for most of test DT121294. This is shown in Figure 122 depicting SO_2 removal. For test DT011995, the SO_2 removal was greater than 97% after 10 minutes of testing. It eventually reached 98% and stayed at this level for the duration of testing. The SO_2 removal curve is shown in Figure 123. NO_x removal was initially above 40% but continuously decreased to 25%. The NO_x removal curve is shown in Figure 124. The NO_x removal also decreased in a continuous fashion for test DT011995 until the end of

testing when the removal began to level off. Initially, the NO_x removal was 48% but leveled off to 26% by the end of testing. This is illustrated in Figure 125. The low NO_x removals for both tests can be explained by the decreasing ferrous ion concentration. DT121294 reveals 40.7 mM at the beginning of testing dropping to 9.7 mM by the end of testing. The large drop in ferrous ion concentration indicates that NO_x removal will be low. The ferrous ion concentration with time for test DT121294 is given in Figure 126. The ferrous ion concentration also declined for test DT011995 from 78.5 mM initially to a final value of 21.0 mM. Figure 127 depicts the drop in ferrous ion concentration explaining the decrease in NO_x removal with test time.

Table 29 shows the sodium, sulfite, and sulfate ion concentrations were in the usual range for a Thio NO_x process for test DT121294. Magnesium and calcium ions were also in normal concentration ranges. The magnesium ion concentration varied from 4,000 to 6,000 ppm while the calcium ion concentration varied from 100 ppm to 400 ppm. The solids content of the filtercake averaged 71.2 wt.%. The dewatering characteristics of the filtercake satisfied the goal of the test plan. Table 30 displays the system chemistry for test DT011995. The sodium ion concentration was low throughout the test averaging 30.6 ppm. The high flue gas oxygen concentration and temperature in the thermal regeneration vessel may have increased the rate of oxidation of sulfite ion to sulfate ion explain the high concentrations of sulfate ion in the system. This is also the reason for the high calcium ion concentration. The magnesium ion concentration was typical for a Thio NO_x system averaging 6,303 ppm.

The correlation to the NO_x removal model was high. The curve depicting the NO_x removal model is given in Figure 128 and 129.

3) Economic Analysis

The cost of thermal regeneration was based on an absorber bleed flow of 200 ml/min and energy cost of \$0.07/kw-hr. Making these assumptions in calculating the cost of a thermal regeneration method using the final ferrous ion concentration and NO_x removal since steady state was not achieved, the cost was found to be \$0.0138/day·mM Fe²⁺·vol.% O₂ and \$0.592/day·NTU·vol.% O₂. These values represent an average of two thermal regeneration tests carried out. Thermal regeneration on a mM ferrous ion concentration was similar to the regeneration agent combination sodium dithionite/ascorbic acid. The cost of thermal regeneration on a NTU basis was less than hydrazine hydrate. Based on these approaches, thermal regeneration was more expensive than sodium sulfide hydrate, sodium tetrasulfide, iron, with and without a digester, zinc, and the electrochemical cell. It is therefore economically unattractive as a regeneration method.

4) Attainment of Objectives

The objective of finding the suitability of the thermal regeneration method was met. The SO₂ removal goal was satisfied using this regeneration technique. The target for NO_x removal was not obtained using thermal regeneration. The dewatering goal stated in the test plan was achieved. In addition, the chemistry was standard for a ThioNO_x system.

Figure 122. SO₂ Concentration and Removal vs. Time

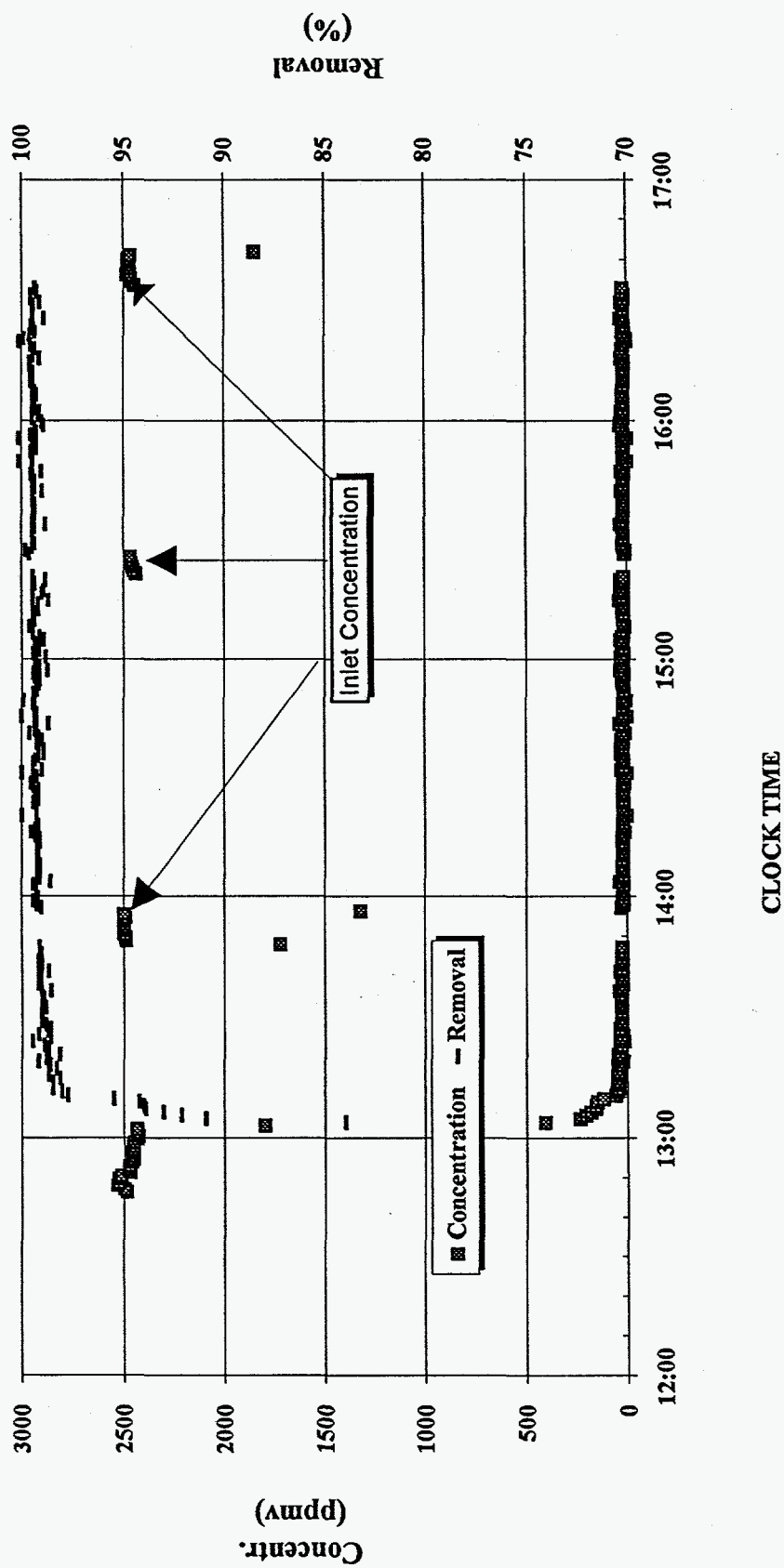


Figure 123. SO₂ concentration and removal vs. time

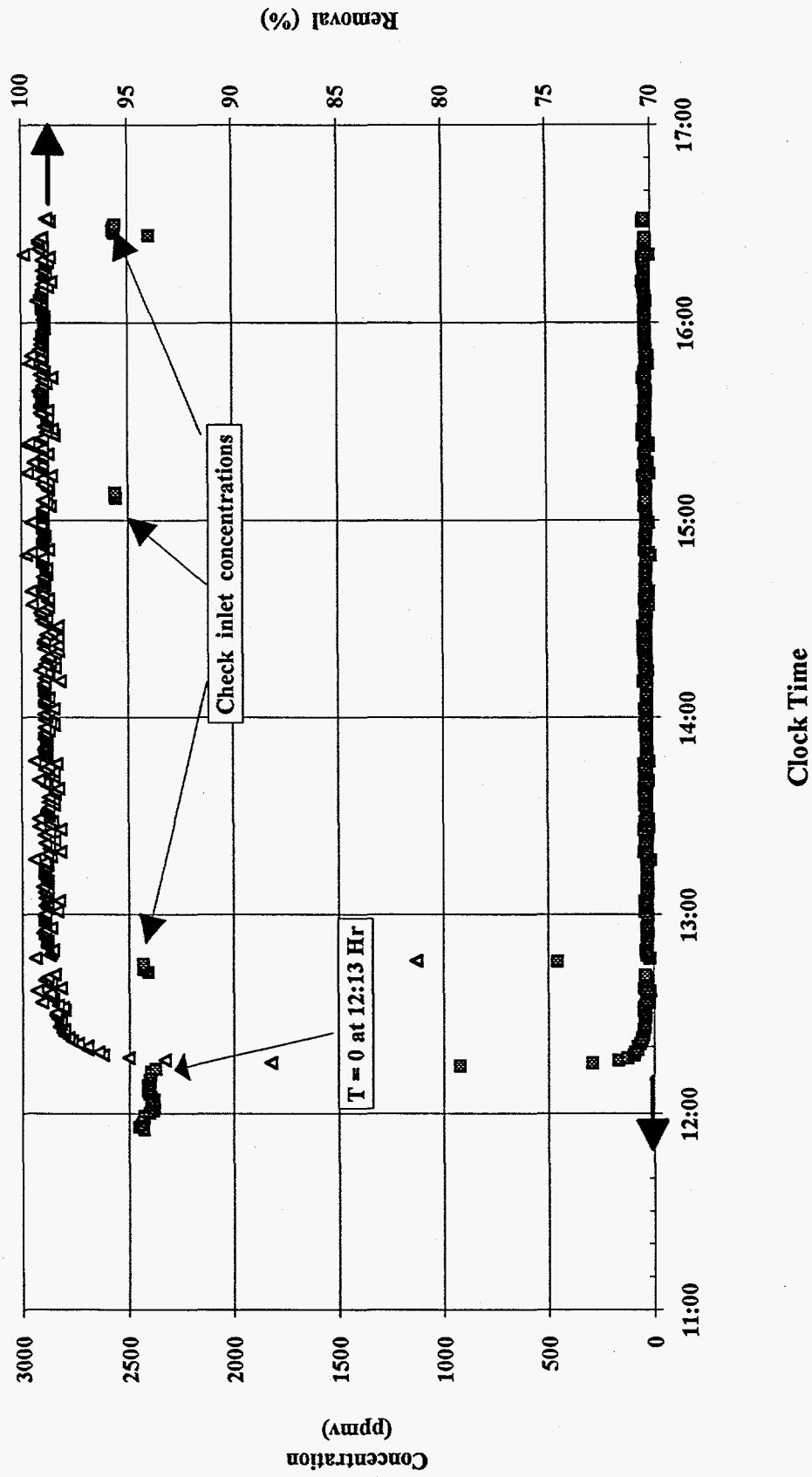


Figure 124. NO concentration and removal vs. time

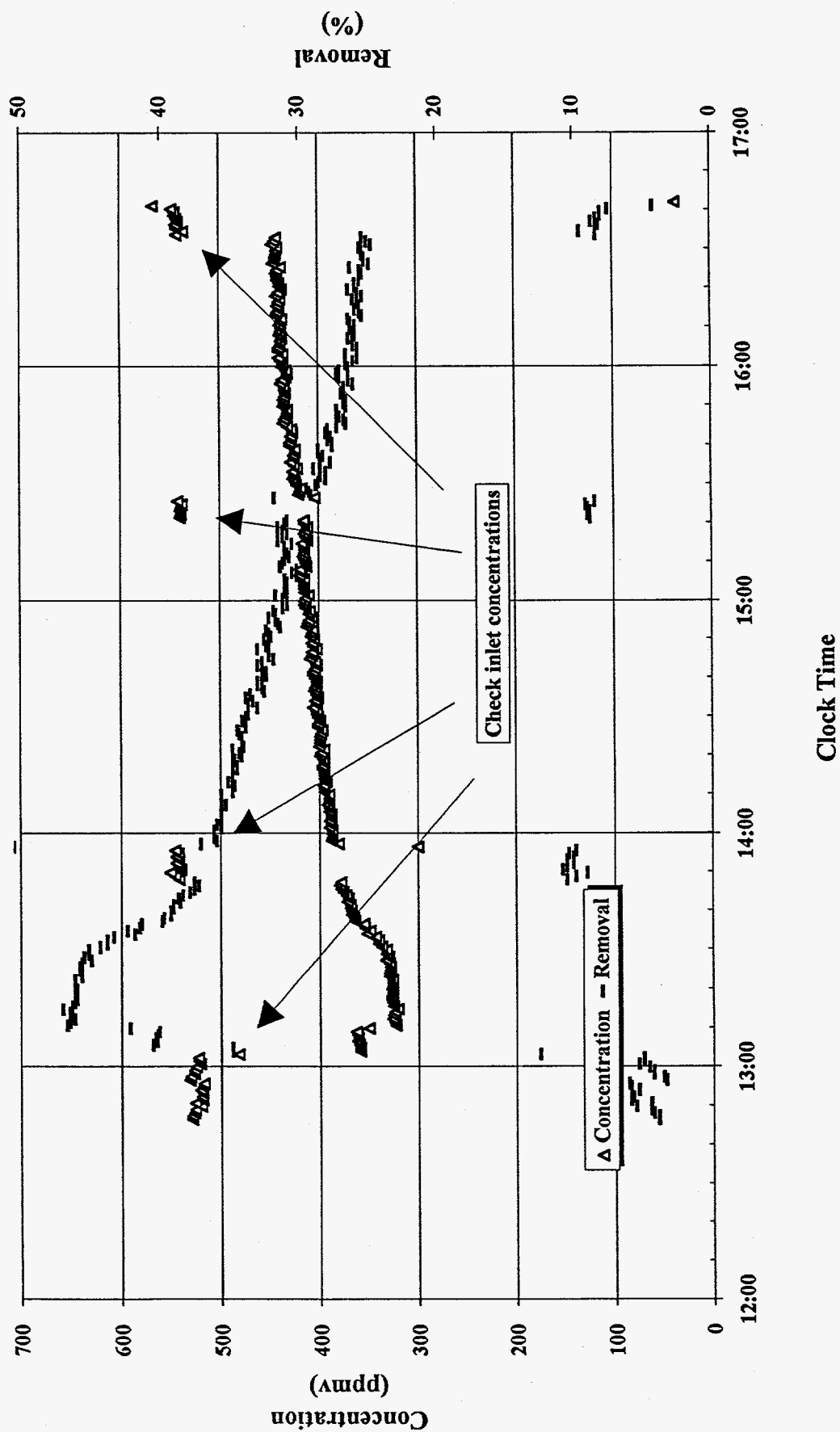
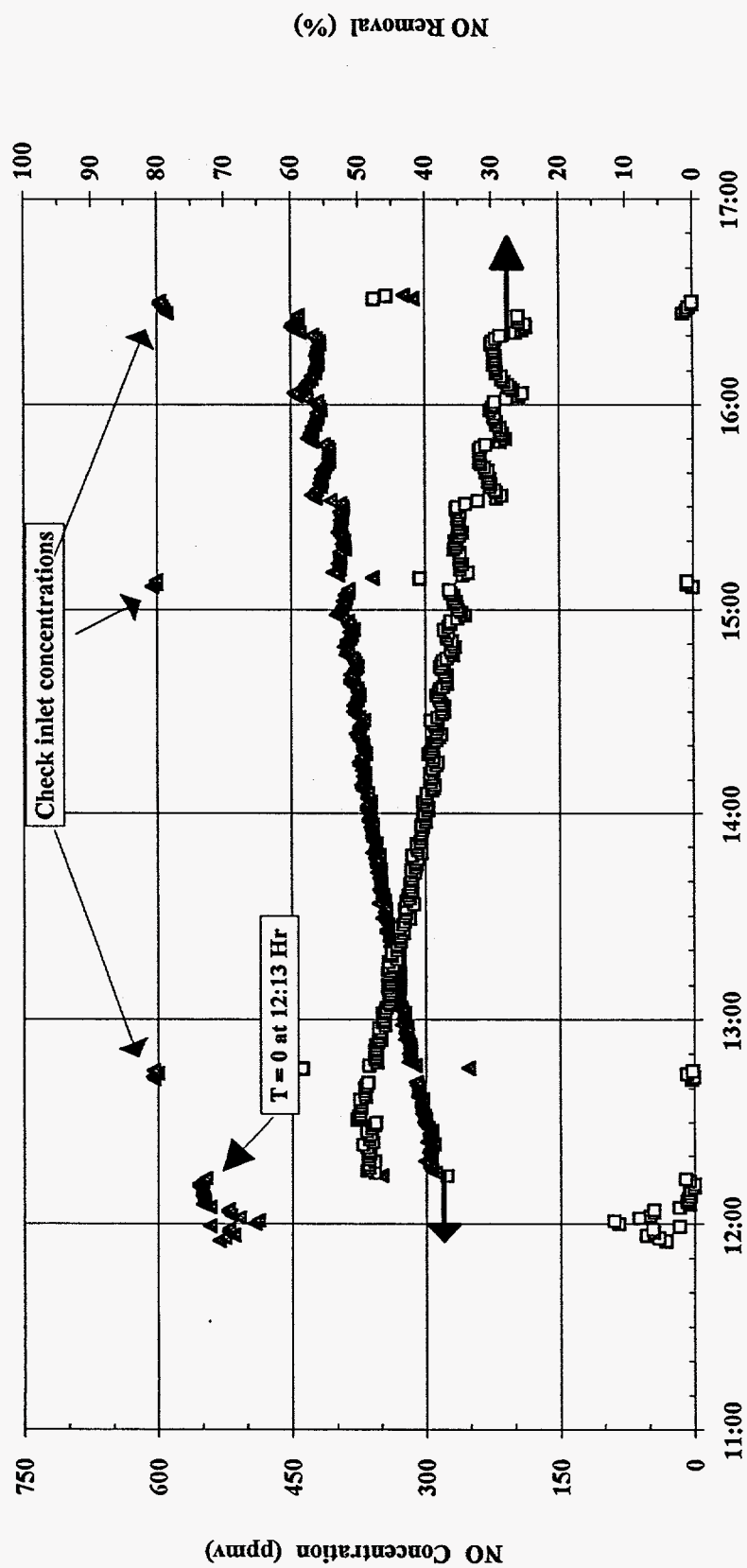
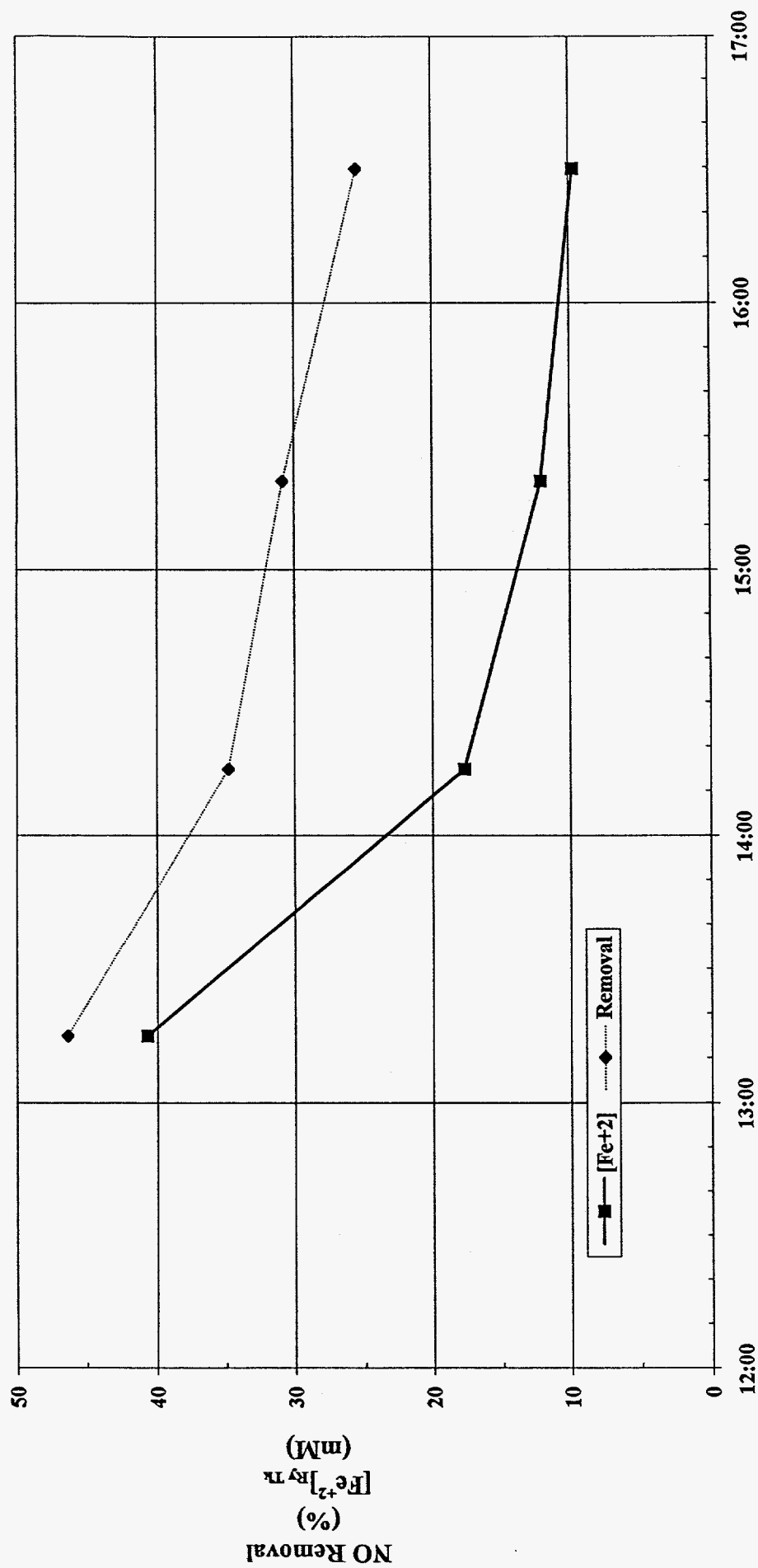


Figure 125. NO concentration and removal vs. time



Clock Time

Figure 126. Change of recycle tank liquor $[\text{Fe}^{+2}]$ and NO removal with time



Clock Time

Figure 127. Change of $[\text{Fe}^{+2}]$ and NO removal

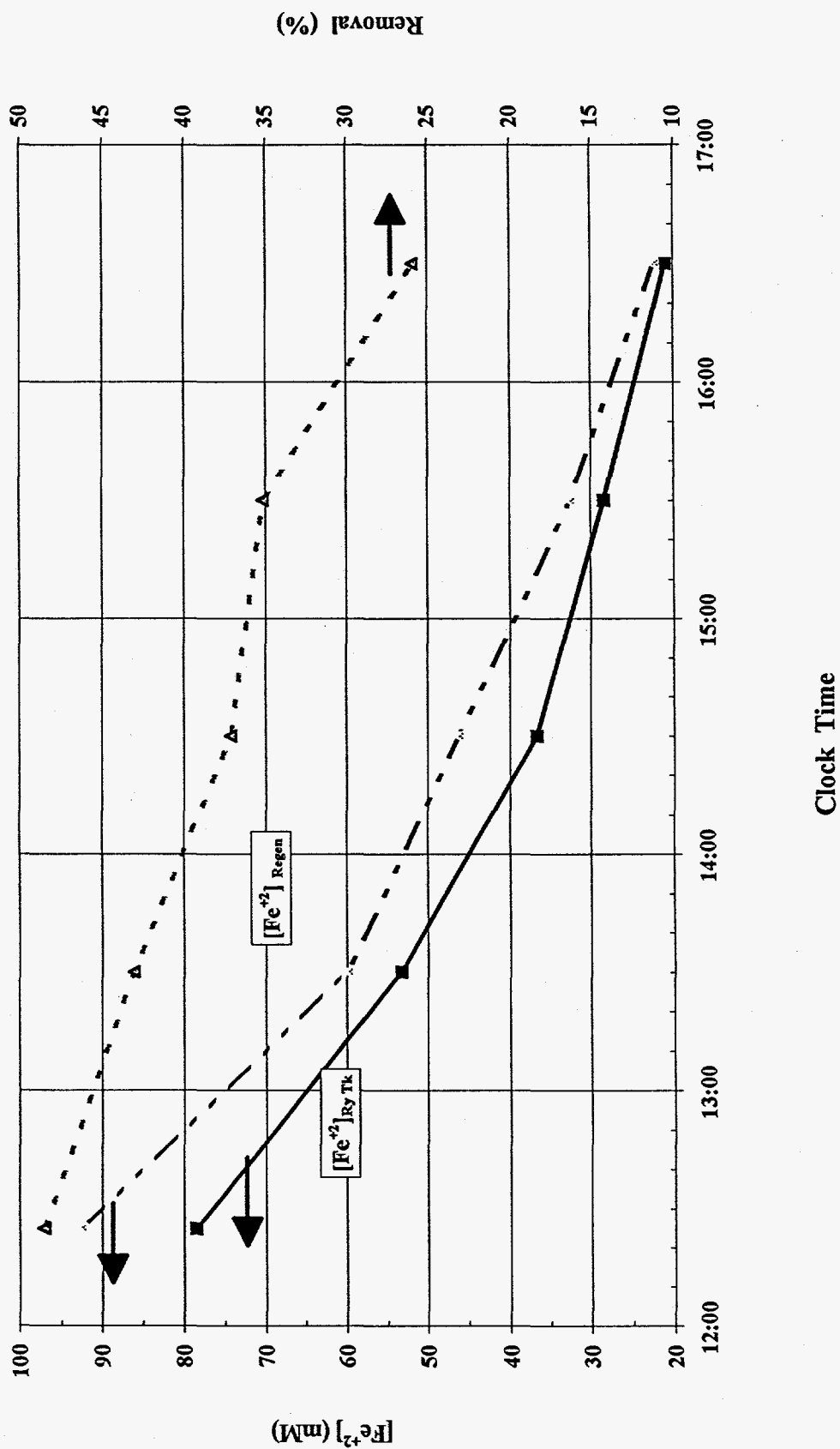


Figure 128. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

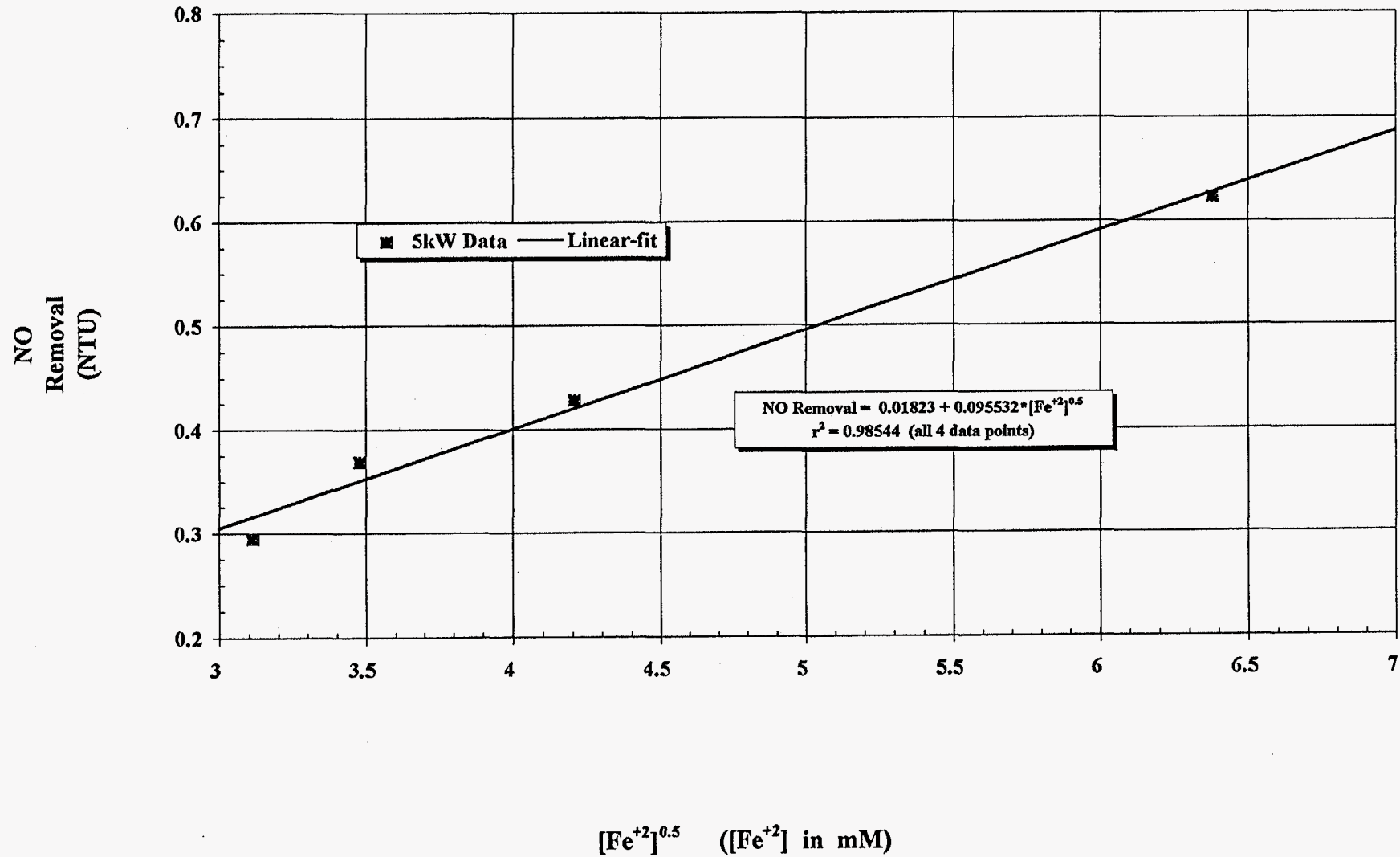


Figure 129. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

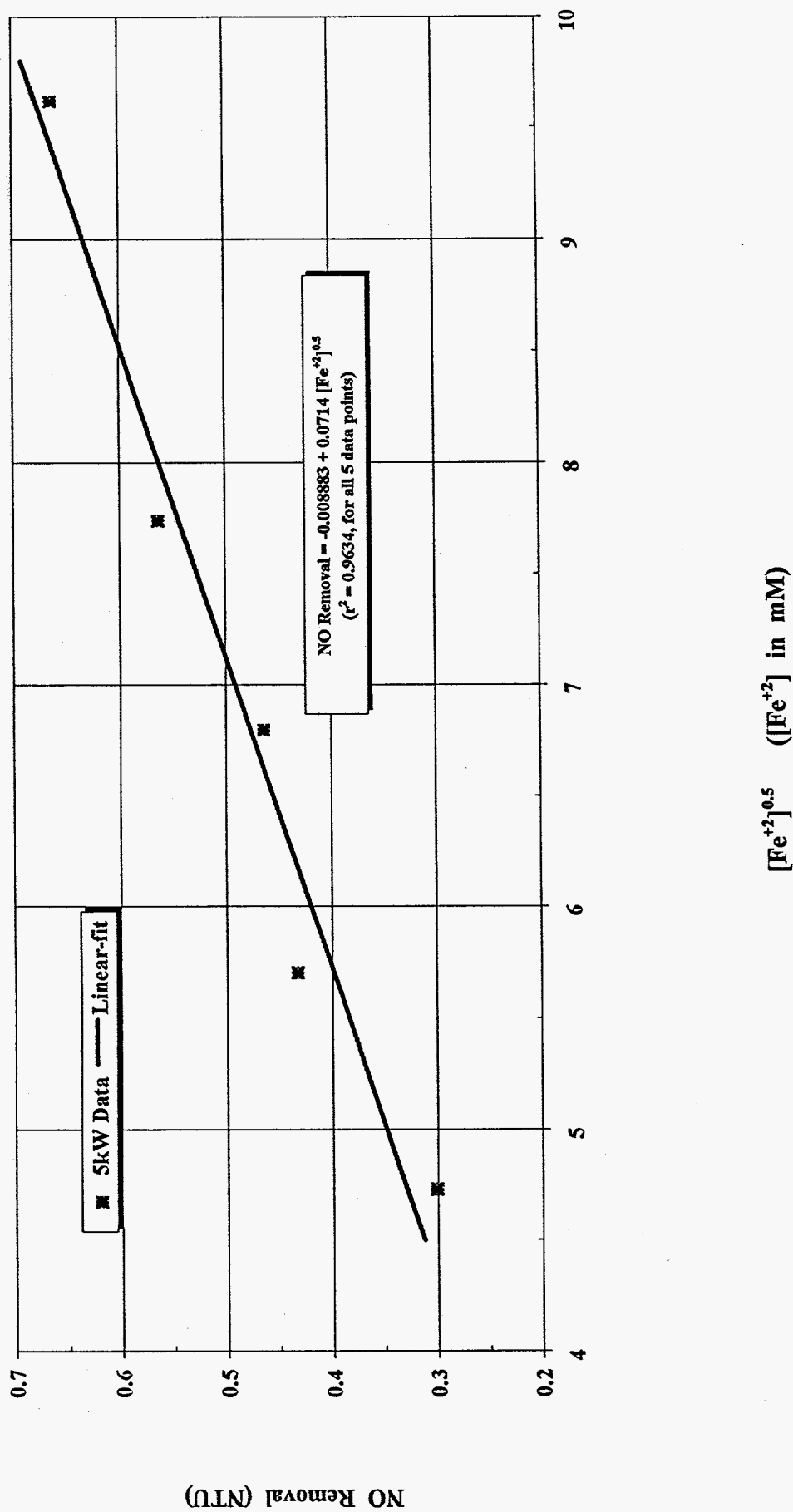


Table 29. Chemistry Data

Clock	L/G	Recycle	Alkalinity	[Fe ²⁺]	[SO ₃ ⁻²]	[ADS]	[SA]	[Mg ²⁺]	[Ca ²⁺]	[Total Fe]	[Na ⁺]	[S ₂ O ₃ ⁻²]	[SO ₃ ⁻²]	[SO ₄ ⁻²]	[Cl ⁻]	Filtercake
Time		Tank	(ppm)	by Spec-20	[SO ₃ ⁻²]	by IC	by IC	by ICP	by ICP	by ICP	by ICP	by IC	by IC	by IC	by IC	Solids
(Hr: Min)		Liquor		(mM)	(ppm)	(mM)	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(wt %)
		pH														
13:15	44	7.5	3,686	40.7		0.60	1.10	4,642	140	2,900	32	n.d.	6,984	6,210	95	
14:15	44	7.4	4,487	17.7		7.01	6.65	5,856	431	2,598	86	n.d.	5,785	7,374	148	
15:20	44	6.9	4,370	12.1		9.08	6.98	5,857	290	2,566	97	n.d.	6,896	8,366	155	73.4
16:30	44	7.0	4,670	9.7		11.36	7.68	6,394	270	2,684	103	n.d.	6,109	7,608	156	68.9
Last 4 pts average:			4,303	20				5,687	283	2,687	80	0	6,444	7,390	139	71.2

Table 30. Chemistry Data

Clock	L/G	Recycle	Alkalinity	[Fe ³⁺] _{by n}	[SO ₃ ²⁻] _{by I₂ titration}	[SO ₃ ²⁻] _{adjusted for [Fe³⁺]_{by n}}	[ADS]	[SA]	[Mg ²⁺] by ICP (ppm)	[Ca ²⁺] by ICP (ppm)	[Total Fe] by ICP (ppm)	[Na ⁺] by ICP (ppm)	[S ₂ O ₃ ²⁻] by IC (ppm)	[SO ₃ ²⁻] by IC (ppm)	[SO ₄ ²⁻] by IC (ppm)	[Cl ⁻] by IC (ppm)	Filtercake
Time		Tank	(ppm)	by Spec-601 (mM)	(ppm)	(ppm)	(mM)	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	Solids
(Hr: Min)		Liquor pH															by IR lamp (wt %)
12:25	44	7.0	1,968	78.5	6,093	2,953	n.d.	n.d.	5,351	304	4,791	28	n.d.	3,230	10,279	335	
13:30	44	6.7	2,519	53.3	5,957	3,825	n.d.	n.d.	6,159	365	4,988	30	n.d.	3,499	9,838	358	61.6
14:30	44	6.6	2,769	36.7	5,020	3,552	n.d.	n.d.	6,396	437	4,828	31	n.d.	2,986	8,487	291	64.3
15:30	44	6.4	3,069	28.4	5,292	4,156	n.d.	n.d.	6,953	431	4,876	29	n.d.	4,708	11,099	346	67.3
16:30	44	7.2	3,620	21.0	2,770	1,930	n.d.	n.d.	6,657	1,266	3,554	35	n.d.	2,060	9,932	184	54.1

D. Electrochemical Cell

1) 5 kW Configuration

The electrochemical cell consisted of titanium cathodes and a corresponding number of anodes provided by Eltech Research Corporation in Fairport Harbor, OH. The cell membrane was also provided by Eltech. A rectifier capable of delivering 50 amps at 20 volts provided the current to the electrochemical cell.

A series of tests were initially conducted at the Eltech research facility for evaluation of the prototype electrochemical cell. The evaluation consisted of determining whether the designed current density could be imposed on the cell. The suitability of the current density was established by the cell current efficiency. To calculate the current efficiency, the initial and final ferrous ion concentrations were determined from a linear fit of the ferrous ion data. Because the volume of catholyte used in the test was known, the total amount of ferrous ion regenerated could be calculated. The amount of electricity can be determined by the current and the duration of the test quantity of electricity required measured in moles of electrons delivered to the cathode. The ratio of the moles of ferrous ion regenerated to the moles of electricity consumed gives the current efficiency. For two of the tests, the design current density (23.9 amp/ft^2) was met with greater than 85% efficiency. This is very promising since a high current density decreases the size of the cell required for reduction of ferric EDTA. The general operating conditions for the series of tests were a charge density of 15 to 24 amp/ft^2 , cell voltage of 2.5 to 4.5 volts, catholyte feed drum pH of 5 to 7, catholyte temperature of 60°C , catholyte flow rate of 3.5 ml/min to 3.6 ml/min, anolyte temperature of 45°C , and anolyte flow rate of 0.85 ml/min.

Several performance parameters were identified and their operating values determined. It was found out during testing, that using diluted sulfuric acid

solution as the anolyte caused the cell voltage to exceed the capabilities of the rectifier used at Eltech. An excessive voltage causes the electrolysis of water forming hydrogen gas. The formation of hydrogen bubbles at the cathode increases mass transfer resistance of ferrous ion to the surface of the cathode. A thin layer of EDTA also formed on the diaphragm. Other tests conducted under a different project have also shown EDTA coated on the diaphragm when diluted sulfuric acid solution was used as the anolyte. Sulfuric acid solution has a lower conductivity than a 20 wt.% magnesium sulfate solution. A sulfuric acid solution at pH of 1.5 is ~31.6 mM hydrogen ions and ~15.8 mM sulfate ions while a 20 wt.% magnesium sulfate heptahydrate solution is ~812 mM of magnesium and sulfate ions. For these reasons, magnesium sulfate solution is preferable to the use of sulfuric acid solution as anolyte. It was found that increasing the catholyte flowrate helped reduce the electrochemical cell voltage. This could be the result of reduced mass transfer resistance at the cathode surface. In addition, in cases where the catholyte flow rate was 3.5 l/min, it was observed that iron was deposited on the diaphragm and cathode.

The pH of the catholyte was reduced to help maintain iron in its chelated form. At higher pH values EDTA will also chelate with calcium and magnesium. The pH should be kept below 6.5 where 90% of the EDTA in solution is still chelated with ferrous ion. Maintaining ferrous ion in its chelated form is critical since the mechanism for NO_x removal is dependent on EDTA chelation with iron.

Two batch tests, D060595A and D060595B were also conducted at the Dravo Research facility. The anolyte solution was made of 20 wt.% magnesium sulfate solution. The acidified anolyte exiting the electrochemical cell was neutralized by diluted magnesium hydroxide slurry to maintain the pH of the anolyte in the feed bucket at 3.0. The pH of the catholyte in the feed beaker was 5.5 and no attempt was made to control or adjust the pH in the beaker. The temperature of the catholyte in the beaker was targeted at ~50°C. The charge density supplied to the

cathode was 24 amps/ft². The current efficiency for test D060595A was found to be 72.05% and the current efficiency for test D060595B was greater than 100%.

Based on the Eltech series of experiments and the batch tests conducted at Dravo Research facility the electrochemical cell was found suitable for integration into the 5 kW system along with a thickener overflow surge tank. The thickener overflow was directed to the thickener overflow surge tank. The catholyte for the electrochemical cell was supplied by the thickener overflow surge tank. The catholyte flow rate was maintained at 2 L/min. The anolyte pH was controlled between 3.0 and 4.0 using 20 wt.% Maysville lime slurry or magnesium hydroxide. The flow rate of the anolyte, which consisted of dissolved magnesium sulfate, through the anode chamber was ~50 mL/min. A filter was also present between the thickener and thickener overflow surge tank to prevent solids reaching the electrochemical cell and depositing on the cathode. A process flow diagram is shown below in Figure 130.

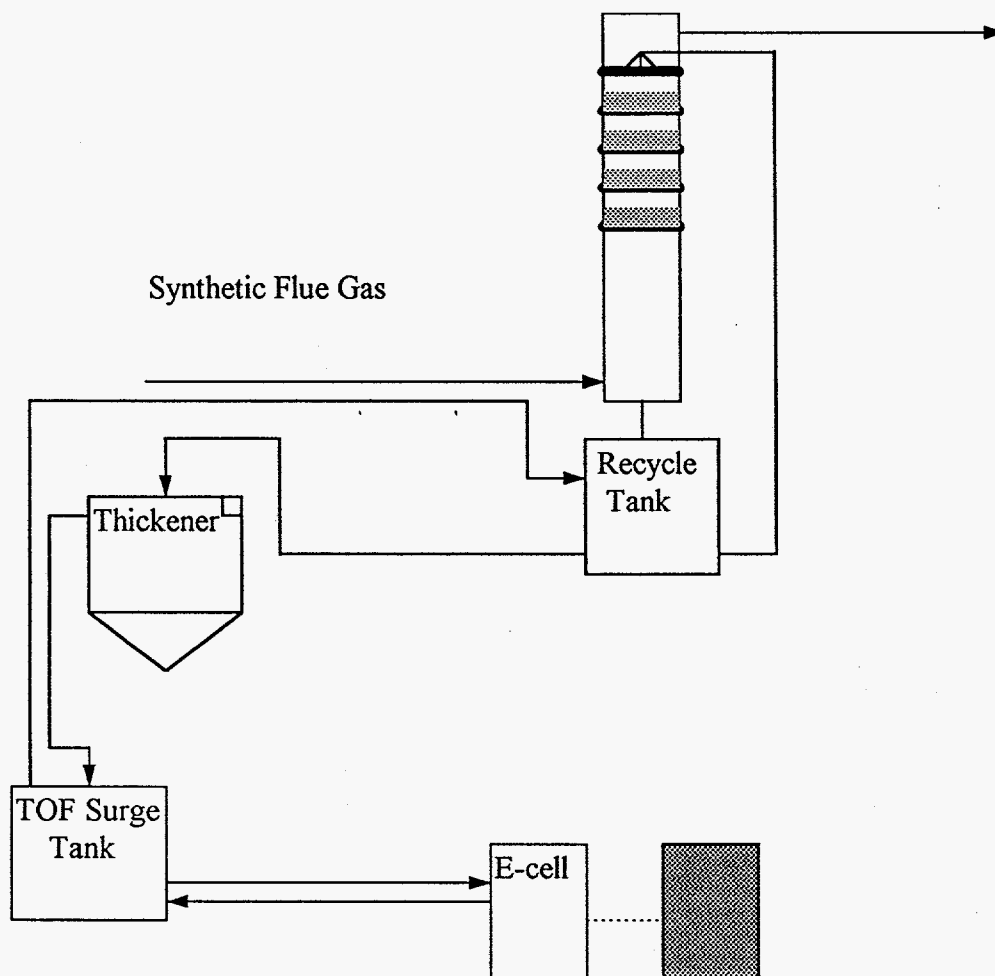


Figure 130. Flow Diagram Incorporating the E-cell into the 5kW

2) Test Results

The SO₂ removal reached between 98% to 99% for two short term tests, DT060695 (packing mode, ~120 mM initial total iron concentration, recycle tank pH = 6.1, L/G = 44, 10.0 vol.% O₂, 3 amps/cathode), and DT011395 (non-packed mode, ~100 mM initial total iron concentration, recycle tank pH = 6.4, L/G = 44, 5.9 vol.% O₂, 3 amps/cathode). For the 48 hour long term test, DT060795 (packing mode, ~120 mM initial total iron concentration, recycle tank pH = 5 to

5.8, L/G = 44, 6-10 vol.% O₂, 3 amps/cathode), the SO₂ removal reached levels of 98% to 99% as shown in Figures 131 through 133. The SO₂ removals achieved for the different tests met the goal for the test plan concerning SO₂ removal. For test DT101094 (non-packed mode, ~100 mM initial total iron concentration, recycle tank pH = 6.4, L/G = 44, 6-10 vol.% O₂, 3 amps/cathode) the flue gas oxygen content was held at 6 vol.% during part of the test and 10 vol.% for the remainder of the test. By changing the flue gas oxygen content, the effect of oxygen on the ferrous ion regeneration rate could be examined. SO₂ removal was above 98% after one hour of testing and remained at this level for the duration of the run. The SO₂ removal curve is shown in Figure 134. Test DT101194 (non-packed mode, ~82 mM initial total iron concentration, recycle tank pH = 6.6, L/G = 44, 6 vol.% O₂, 3-5 amps/cathode) was carried out with the current delivered to the electrochemical cell varied during the test. The first current selected was 3.0 amps. The next current chosen was 4.0 amps then 5.0 amps. Accompanying the increase in current was an increase in the temperature of the process liquor in the thickener overflow surge tank. At 3.0, 4.0, and 5.0 amps, the temperature in the thickener overflow surge tank was 27°C, 52°C, and 74°C respectively. During the run, it was found that the flow to the absorber was less than expected. In addition, later during the test run it was observed that not all of the trays were fully wetted. A reduction in liquid to gas (L/G) ratio and poor gas liquid contacting both functioned to lower SO₂ removal. This was observed for particular periods where the SO₂ removal fell below 95%. The SO₂ removal curve is shown in Figure 135. Tests DT101494 (non-packed mode, ~100 mM initial total iron concentration, recycle tank pH = 6.5, L/G = 44, 6.0 vol.% O₂, 3 amps/cathode) and DT102094 (non-packed mode, ~100 mM initial total iron concentration, recycle tank pH = 6.4, L/G = 44, 6.1 vol.% O₂, 3 amps/cathode) were run at similar conditions to acquire some consistency in the level of NO_x removal. For test DT101494, the SO₂ removal was greater than 98% after 30 minutes of testing and remained high throughout the duration of the test run. The SO₂ removal for test DT102094 was greater than 98% after 13 minutes of testing and greater than 99% after 128

minutes of testing. The removal remained high throughout the duration of the test run. The SO_2 removal curves are shown in Figures 136 and 137.

The NO_x removal was not very promising for test DT011395 as the maximum removal of 40% dropped slowly to 30% where it remained for the duration of testing. The NO_x removal curve is shown in Figure 138. Greater success was achieved for NO_x removal for test DT060695. The NO_x removal was greater than 50% before gradually dropping to less than 40% by the end of testing. After dropping to 40% NO_x removal the curve was fairly constant for the remainder of testing. The NO_x removal curve is shown in Figure 139. For most of testing for run DT060795, the NO_x removal was below 35%. The NO_x removal curve is shown in Figure 140. NO_x removal ranged from 30% to 40% after leveling off for the three tests. The NO_x removal for test DT101094 decreased from greater than 40% to less than 25% by the end of testing. The NO_x removal was level after reaching 25% removal. The NO_x removal curve is shown in Figure 141. NO_x removal was fairly steady during the course of test DT101194 averaging 25% initially then dropping to 20% by the end of testing. The NO_x removal was highest when 4.0 amps was sent to the electrochemical cell. The projected surface area of the cathode used at 4.0 amps was $.125 \text{ ft}^2$ making the current density 32 amps/ft^2 at maximum NO_x removal. The NO_x removal curve at the different current settings is shown in Figure 142. Tests DT101494 and DT1022094 run under similar conditions gave similar NO_x removals of 30%. Both curves are shown in Figures 143 and 144.

For test DT011395, the ferrous ion concentration leveled off to 26.2 mM after steady state was achieved. This is shown in Figure 145. This is much lower than the 88.1 mM final ferrous ion concentration achieved with hydrazine hydrate. The NO_x removal with hydrazine hydrate was 60% by the end of the run. For test DT060695, the ferrous ion concentration dropped from 53.7 mM at the beginning of testing to 36.6 mM by the end of testing. The NO_x removal was highest for this

short term test. The lowest ferrous ion concentration for this group of tests was observed for the long term test. The ferrous ion concentration fluctuated between 10 mM and 20 mM. Because of the low ferrous ion concentration, it is not surprising that NO_x removal fell below 35% for most of testing. The ferrous ion concentration graphs are given in Figures 146 and 147. The low removal for test DT101094 can be explained by the low ferrous ion concentration in the recycle tank throughout the test. The ferrous ion concentration was at its highest levels near the end of testing where it averaged ~15 mM. High NO_x removals can not be achieved with such low ferrous ion levels. The ferrous ion curve is shown in Figure 148.

Not surprisingly for test DT101194, the ferrous ion concentration was highest at 4.0 amps averaging ~15 mM. Although, the removal was highest at 4.0 amps, the ferrous ion concentration was too low to obtain high NO_x removals. The ferrous ion concentration curve is shown in Figure 149. The steady state ferrous ion concentrations for the tests run under similar conditions was 30 mM. This is similar to test DT060695. The ferrous ion concentrations are given in Figure 150 and 151.

Table 31 shows the sodium ion concentrations were below 100 ppm at all times for each test except one analysis for test DT011395. The sulfite and sulfate ion concentrations were high for the long term test and run DT060695 as shown in Tables 32 and 33 raising concern for precipitation of calcium sulfite/calcium sulfate with increasing calcium ion concentrations. For test DT060795, the calcium ion concentration reached a point where scale would form in the scrubber. Magnesium ion concentration was also elevated for test DT060795. This is expected due to the high concentrations of sulfite and sulfate ions. For the long term test, the filtercake solids reached a level quickly between 70 wt.% and 80 wt.% solids. This meets the requirement set forth in the test plan for solids dewatering. Table 34 for test DT101094 shows the liquor chemistry was low in

sodium ion concentration with a level averaging ~48 ppm. The corresponding sulfite concentration was 5,499 ppm which is typical for a ThioNO_x system. The sulfate ion concentration was higher than usual for a ThioNO_x system, possibly from using sulfuric acid solution as the anolyte. The high sulfate ion concentrations lead to high calcium ion concentrations in the ThioNO_x liquor. As is the case with solutions containing a high concentration of calcium and sulfate ions precipitation will occur if supersaturation is reached. The high SO₂ removals can be explained by the alkalinity averaging greater than 3,000 ppm. The solids content of the filtercake was 76.4 wt.% at the beginning of testing and 82.9 wt.% by the end of testing. This is the desired filtercake solids content for the ThioNO_x process.

The sodium ion concentration was low throughout testing averaging 54.5 mM for test DT101194. This is shown in Table 35. The sulfite ion concentrations were normal for ThioNO_x system averaging 5,574 ppm. However, the sulfate ion concentration was high averaging 7,934 ppm. The high sulfate ion concentration was most likely due to using sulfuric acid solution as anolyte. The calcium ion concentration was high as a result of high sulfate ion concentrations. The magnesium ion concentration was also typical for a ThioNO_x system averaging 6,614 ppm.

The filtercake solids content averaged 82.2 wt.% which is normal for a ThioNO_x system when a ferrous ion regeneration method is used. The sodium ion concentration became elevated for test DT101494 exceeding values of 300 ppm. For test DT102094, the sodium ion concentration averaged 45 ppm. The sulfite ion concentration was low for test DT104494 while it was slightly elevated for test DT102094. This is reflected in the alkalinities which are higher for test DT102094 than for test DT101494. Even with this difference in liquor chemistries, the NO_x removal for both tests were very similar. The solids content of the filtercake for test DT102094 was typical of a ThioNO_x process in which a ferrous ion

regeneration method is used averaging 82.3 wt.%. The chemistry for both systems is depicted in Tables 36 and 37.

The correlation to the NO_x removal model was low for all the tests carried out with the electrochemical cell. The correlation coefficients of the different tests averaged 0.4476. The curves showing the correlation of the NO_x removal model are given in Figures 152 through 158.

Test DT052296 (non-packed mode, ~ 100 mM initial total iron concentration, recycle tank pH = 5.8, L/G = 44, 6 vol.% O_2 , 25 amps/ft² cathode) a 48 hour duration test, was run with the electrochemical cell / 5 kW combination in an effort to determine if the cathode would exhibit material build-up after several days of operation. The absence of deposits on the cathode was deemed critical to the success of this phase of the project. Obtaining the desired NO_x removal and ferrous ion concentration provided a strong indication of whether deposition was occurring on the cathode although periodic removal and photographing of the cathode was also performed. The electrochemical cell consisted of one titanium wire mesh cathode and one anode with the cathode having a surface area of 1.0 ft². The current density delivered to the cathode surface was 25 amps/ft².

Figure 159 illustrates the SO_2 removal during testing. From 5/22/96 19:12 to 5/23/96 4:48 and from 5/23/96 19:12 to 5/24/96 2:24, the SO_2 removal was below 96%. Pressure drops below 2.0" H_2O were observed indicating a shorter liquid hold-up time which changed the mass transfer properties within the absorber. A higher pressure drop across the absorber implied longer liquid hold-up with higher SO_2 removals. For instance, Figure 159 shows the SO_2 removal from 5/22/96 9:36 to 5/22/96 18:00 was above 97% with a pressure drop greater than 2.5" H_2O . Liquid hold-up probably increases as material build-up occurs along the surface of the packing decreasing the void volume.

Figure 160 shows the NO_x removal was between 45 and 55% with lower removals toward the end of testing. The ferrous ion concentration is also shown in Figure 160. The ferrous ion concentration declines from the beginning of testing at 60 mM to a level of 30 mM by the end of testing. Although the ferrous ion concentration exhibits a decreasing trend, the NO_x removal stays fairly constant after reaching 45%. The increased liquid hold-up near the end of testing may have offset the negative effect of the low ferrous ion concentration. The decrease in ferrous ion concentration is believed to result from material build-up on the cathode. The cathode was inspected at 12 hour intervals and found to possess some deposits even after the first 12 hours. This would explain the decrease in ferrous ion concentration representing a major drawback to this technology.

Table 38 shows the sulfite and sulfate ion concentrations were both high for this test averaging over 10,000 ppm. The calcium ion concentration ranged from 200 to 500 ppm which is also elevated for a Thio NO_x system. These conditions would be undesirable on a larger scale due to deposition of calcium compounds throughout the system. The magnesium ion concentration was higher than usually observed for a Thio NO_x system averaging ~10,000 ppm. The sodium ion concentration was also high at 10,000 ppm. The high sodium ion concentration was established to maintain high solution conductivity. However, with high solution conductivity also comes higher concentrations of sulfite and sulfate ions. This would eventually lead to scaling conditions in a scaled up process. The filtercake solids averaged ~70 wt.% which is a typical result for the Thio NO_x system.

A linear correlation of NO_x removal in NTU units versus the square root of ferrous ion concentration was made with a resulting correlation coefficient of 0.1806. This is shown in Figure 161. The low correlation coefficient is due to changing conditions in the absorber which alters the mass transfer of NO_x gas into the liquor. Since NO_x removal is dependent upon the conditions in the absorber as

well as the ferrous ion concentration changes in both these parameters will yield low linear correlation coefficients when removal is plotted against the square root of ferrous ion concentration.

Determining operating conditions for the electrochemical cell / 5 kW system which will not result in material build-up on the cathode remains an elusive challenge. Because of the inability to eliminate material build-up on the cathode an alternative NO_x removal technology is being explored. Cathode material build-up prohibits the electrochemical cell / 5 kW technology from going to Miami Fort Pilot plant.

3) Economics of Electrochemical Cell

The economics was based on the steady state results of the tests carried out. An average cost was calculated based on the seven tests performed where the results indicated that the electrochemical cell had the lowest cost compared with all other regeneration methods except for iron with and without a digester. Figures 41 and 42 show the cost of the electrochemical cell on a mM ferrous ion concentration and NTU removal basis was \$0.000409/day·mM Fe^{+2} ·vol.% O_2 and \$0.0208/day·NTU·vol.% O_2 , respectively. Economically, the electrochemical cell is one of the best methods available. It belongs to a group of regeneration agents (iron with and without a digester and the electrochemical cell) that represents the most cost effective means of NO_x removal determined from these screening tests.

4) Attainment of Objectives

The goal of testing the electrochemical cell was to determine whether the criteria established in the test plan was realized. The SO_2 removal was close to 99% meeting the goal for SO_2 capture appearing in the test plan. The NO_x removal ranged from 30% to 40% for the tests with highest removal at steady state.

Performance factors were identified and solutions to their proper functioning were addressed. The solids dewatering criteria was met.

E Combination of Strategies

For all of the tests conducted with the electrochemical cell, the thickener overflow surge tank was operated at an elevated temperature. The reason for conducting the tests in an integrated fashion (thermal regeneration mode/electrochemical cell) was the ease with which the thermal regeneration mode could be utilized with the electrochemical cell. Because all electrochemical cell tests conducted utilized a heated thickener overflow surge tank, the tests carried out with an electrochemical cell / heated thickener overflow surge tank are covered in the electrochemical cell section.

The thermal regeneration technique was not combined with any chemical regeneration agent because few agents displayed high enough NO_x removal to justify its use. Only hydrazine hydrate, sodium sulfide hydrate, and iron using a digester displayed NO_x removals high enough to warrant a thermal regeneration vessel. Due to the liquor chemistry problems associated with each agent (hydrazine hydrate resulted in residual hydrazine in the liquor, sodium sulfide resulted in accumulation of thiosulfates in the liquor and black scale throughout the system, and iron using a digester resulted in a low solids content of the filtercake), combination testing using these agents was ruled out.

Only hydrazine hydrate, sodium sulfide hydrate, and iron using a digester had high enough NO_x removals to consider combination with the electrochemical cell. Because of the previous chemistry problems with these agents, combination tests with the electrochemical cell were not carried out.

Figure 131. SO₂ concentration and removal vs. time

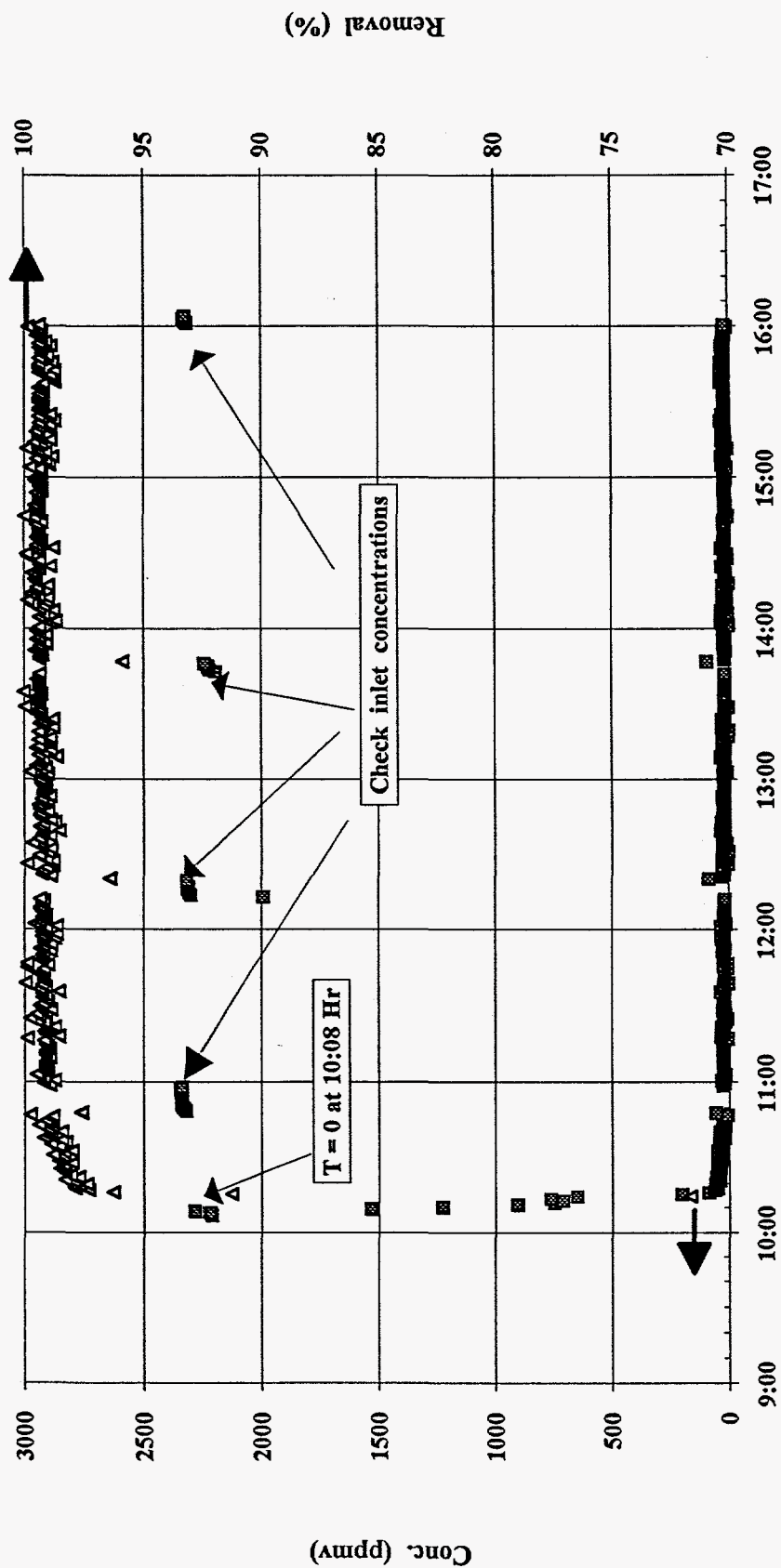
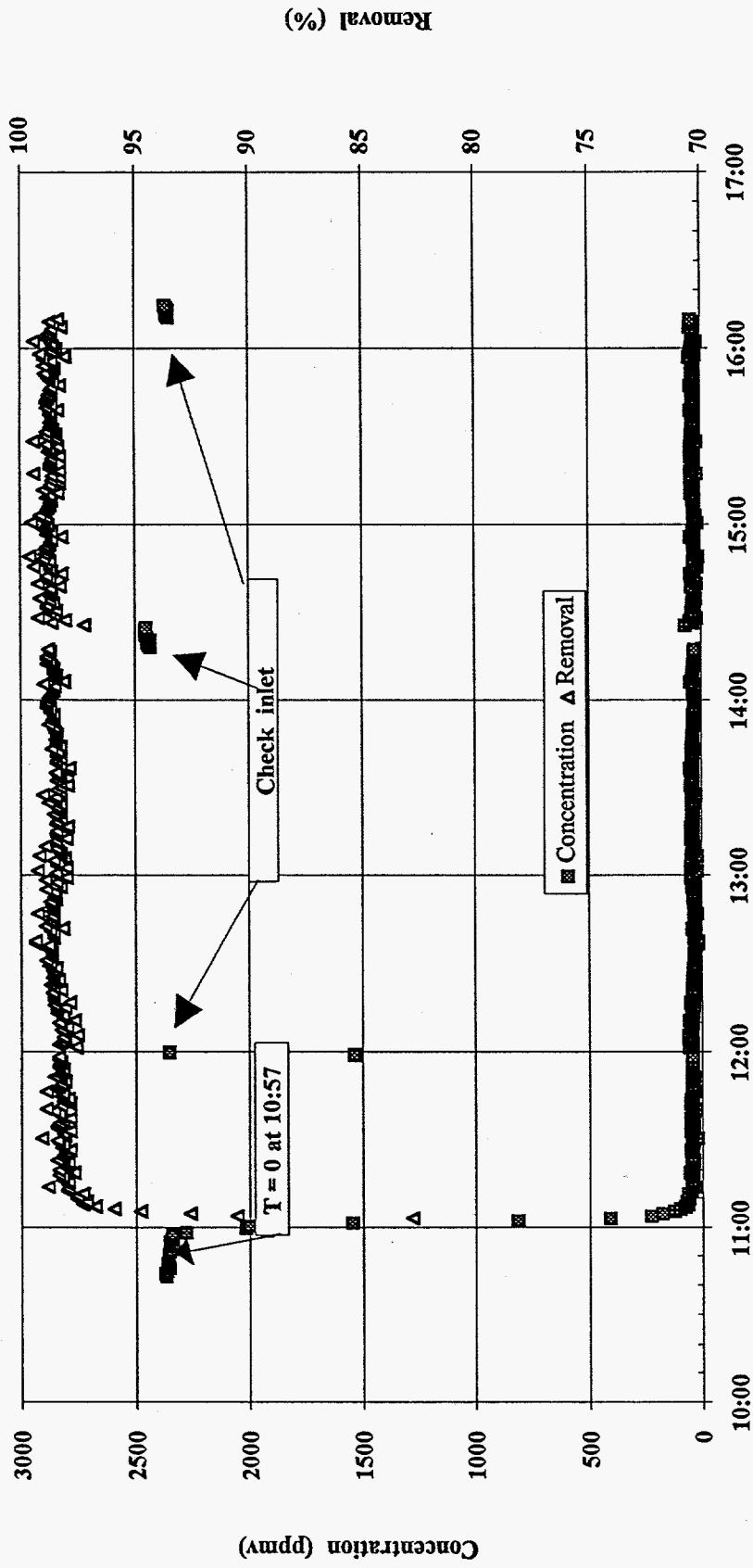


Figure 132. SO₂ concentration and removal vs. time



Clock Time

Figure 133. SO₂ concentration and removal vs. time

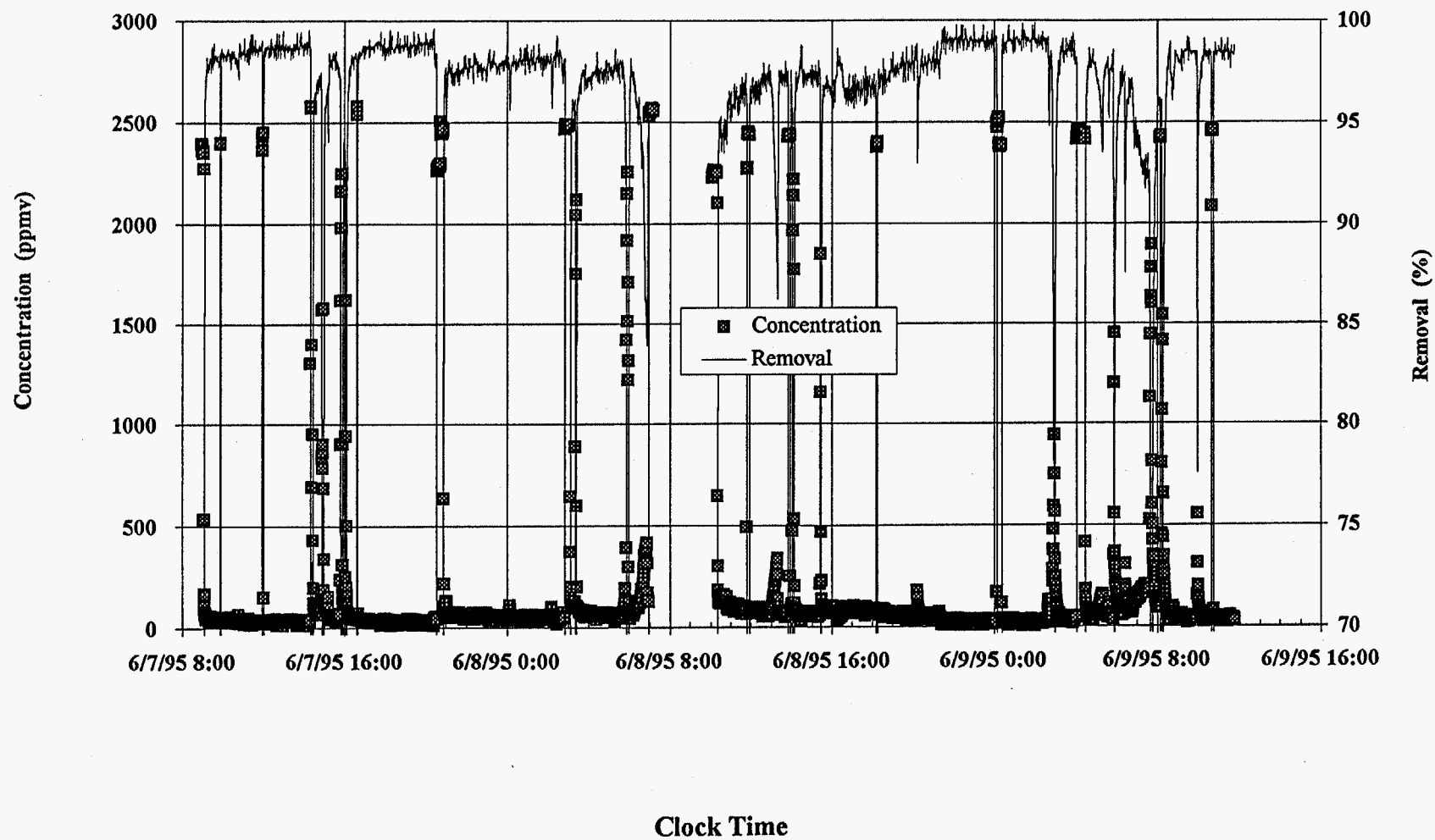


Figure 134. SO₂ concentration and removal vs. time

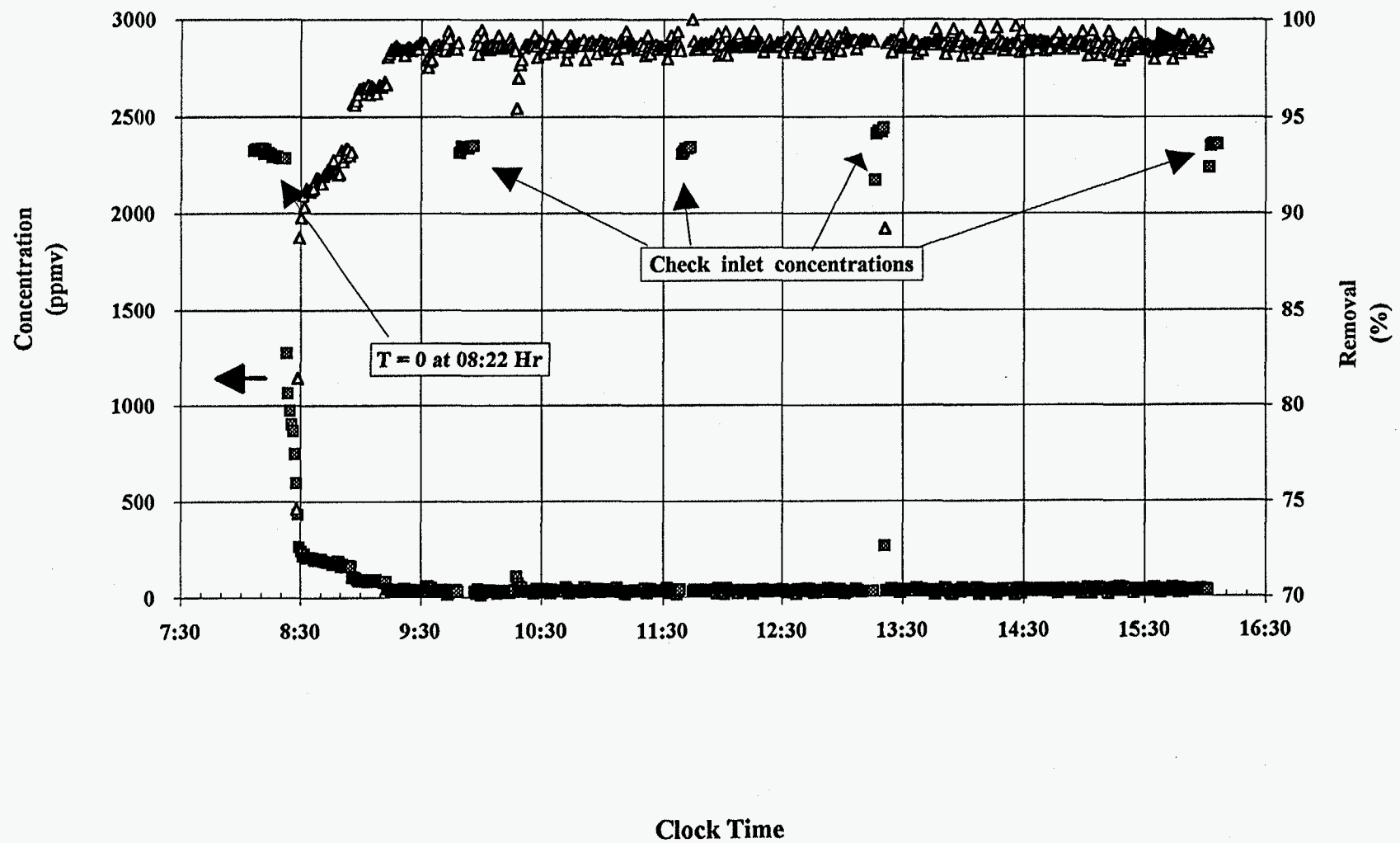


Figure 135. SO₂ concentration and removal vs. time

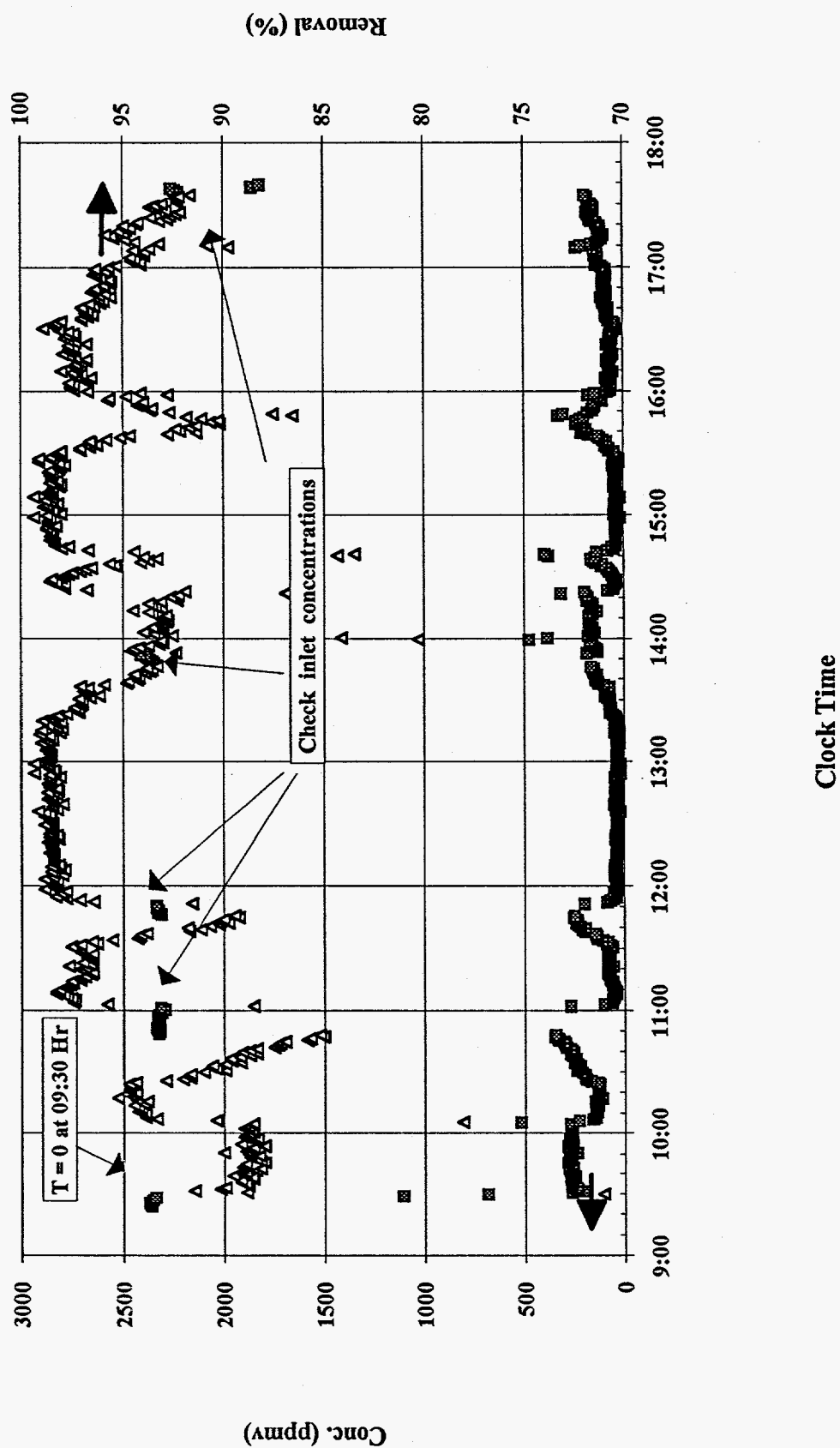
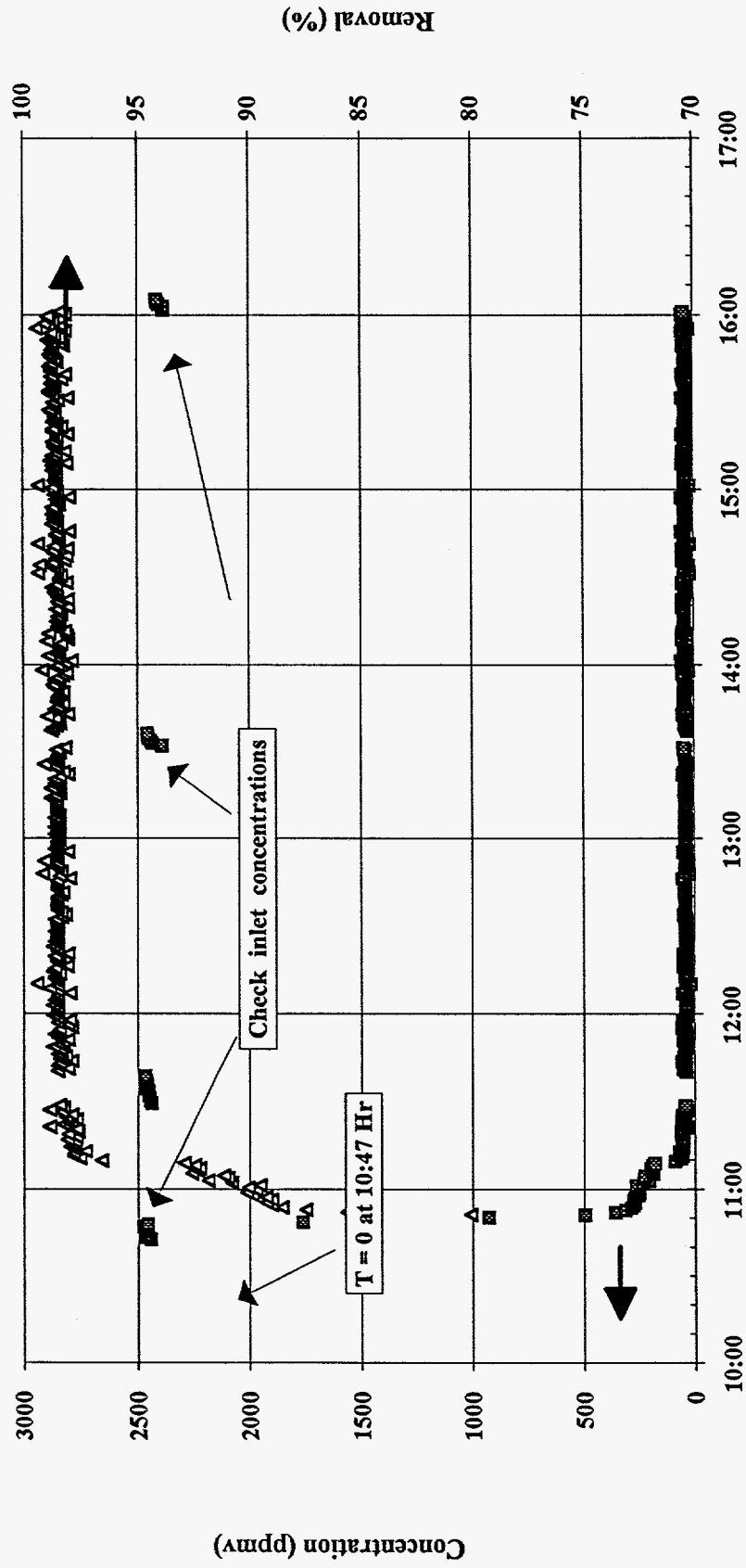


Figure 136. SO₂ concentration and removal vs. time



Clock Time

Figure 137. SO₂ concentration and removal vs. time

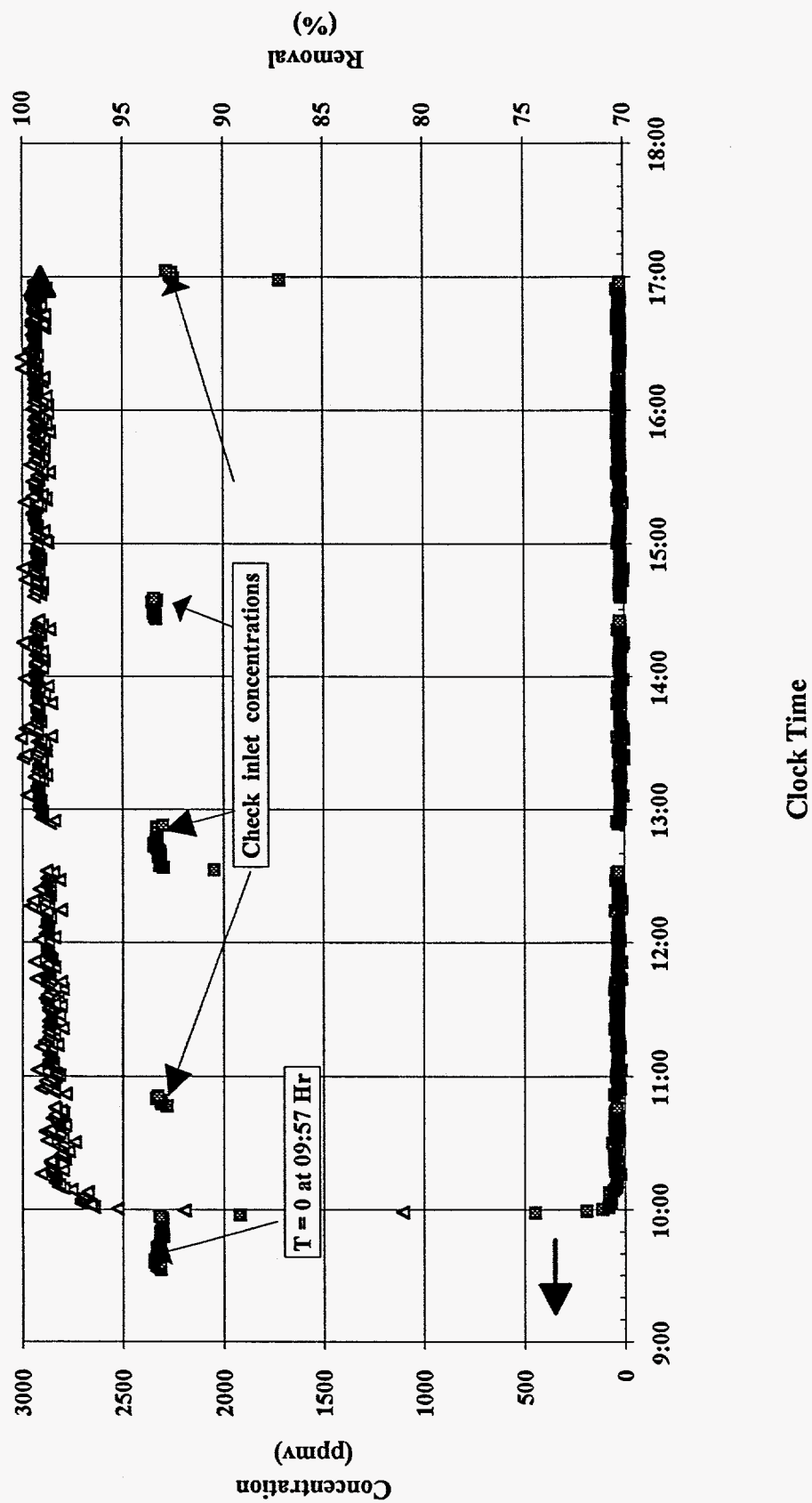


Figure 138. NO concentration and removal vs. time

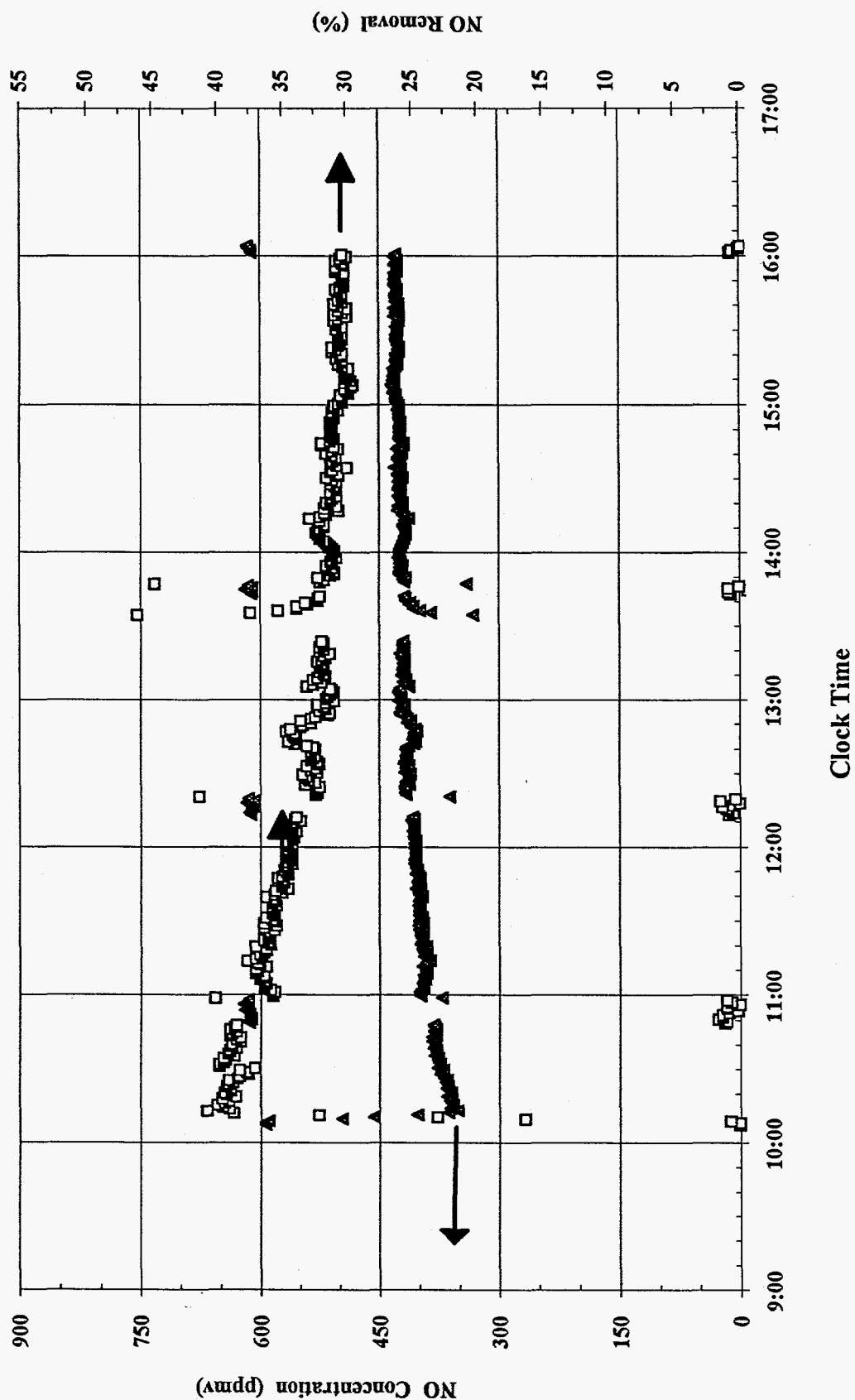
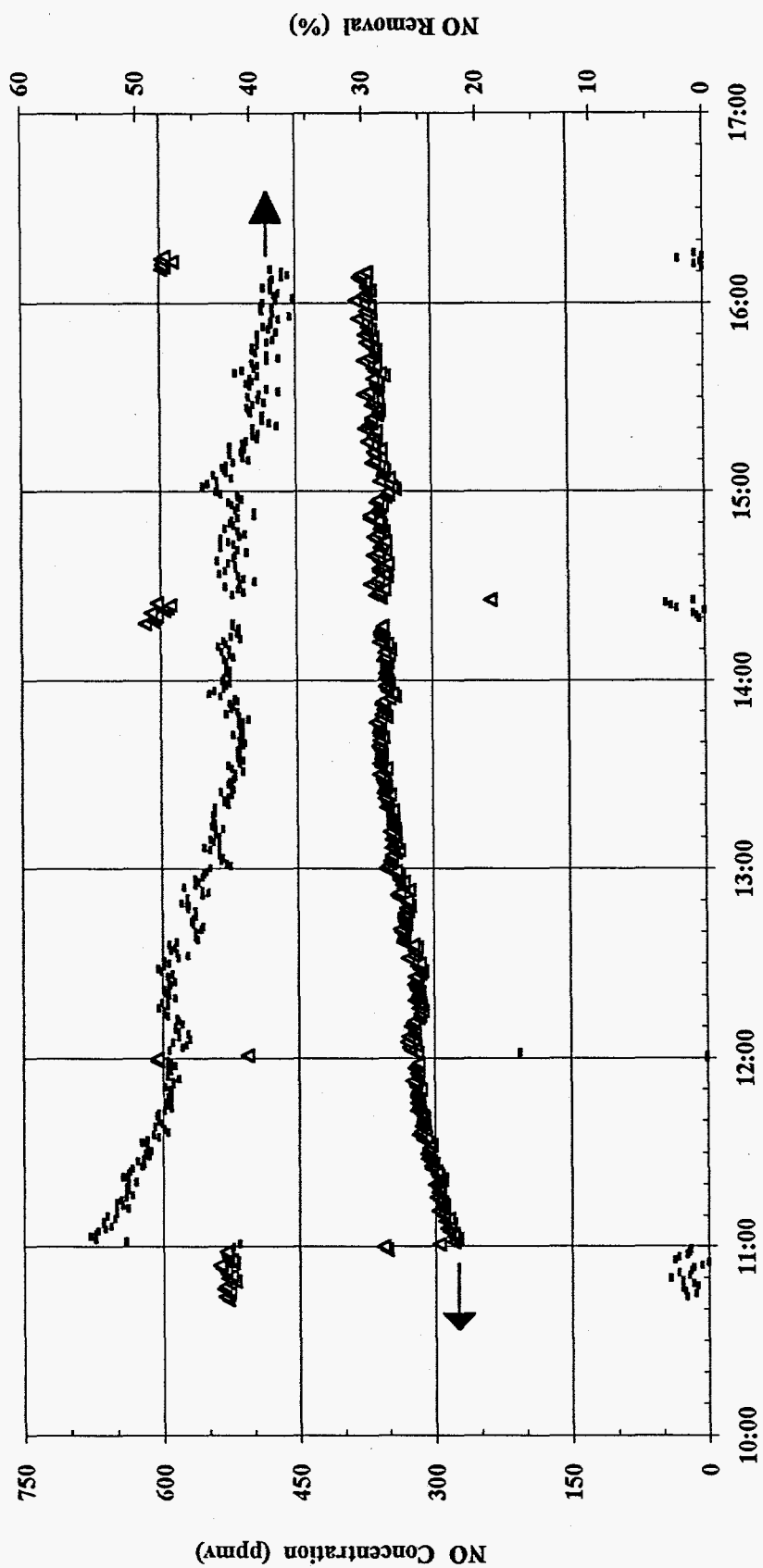
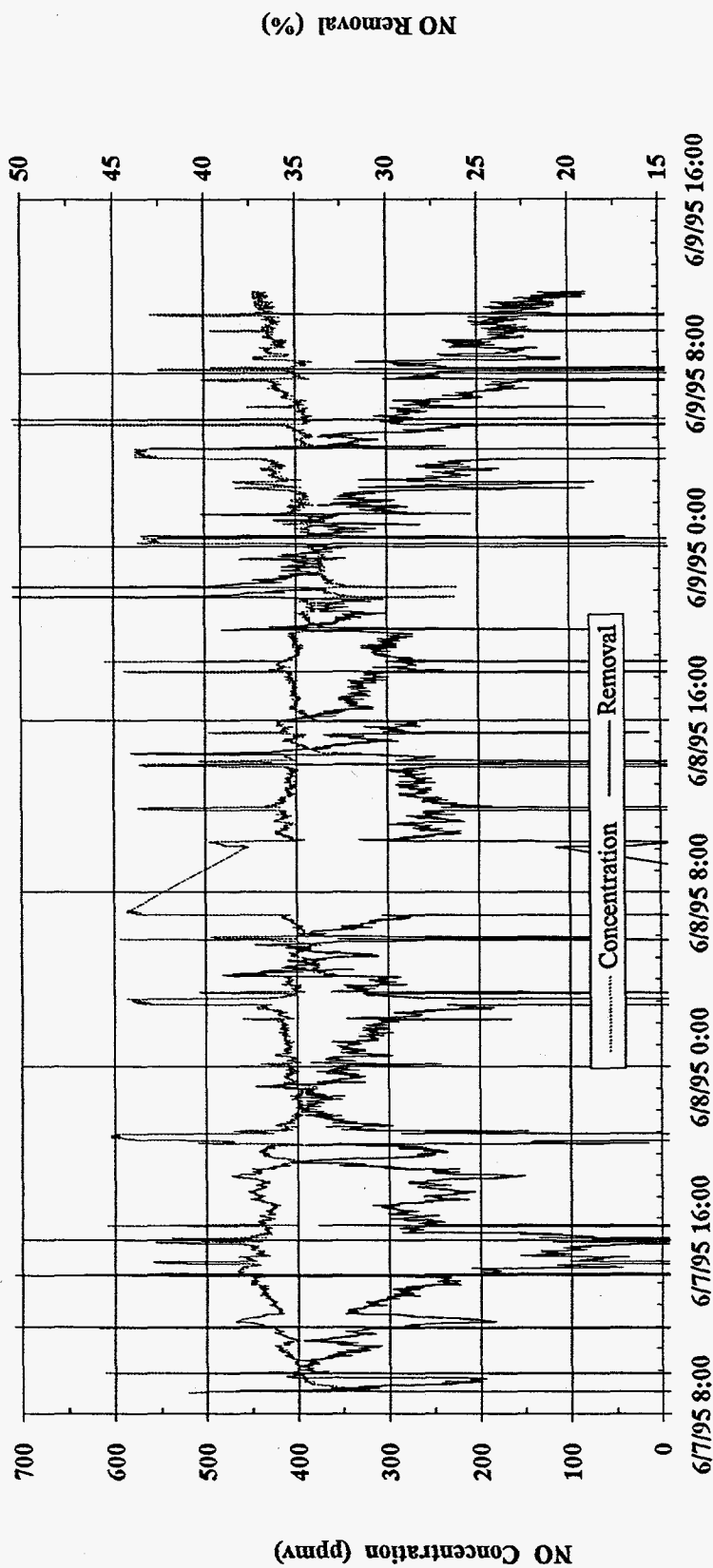


Figure 139. NO concentration and removal vs. time



Clock Time

Figure 140. NO concentration and removal vs. time



NO Concentration (ppmv)

NO Removal (%)

Concentration — Removal

Clock Time

Figure 141. NO concentration and removal vs. time

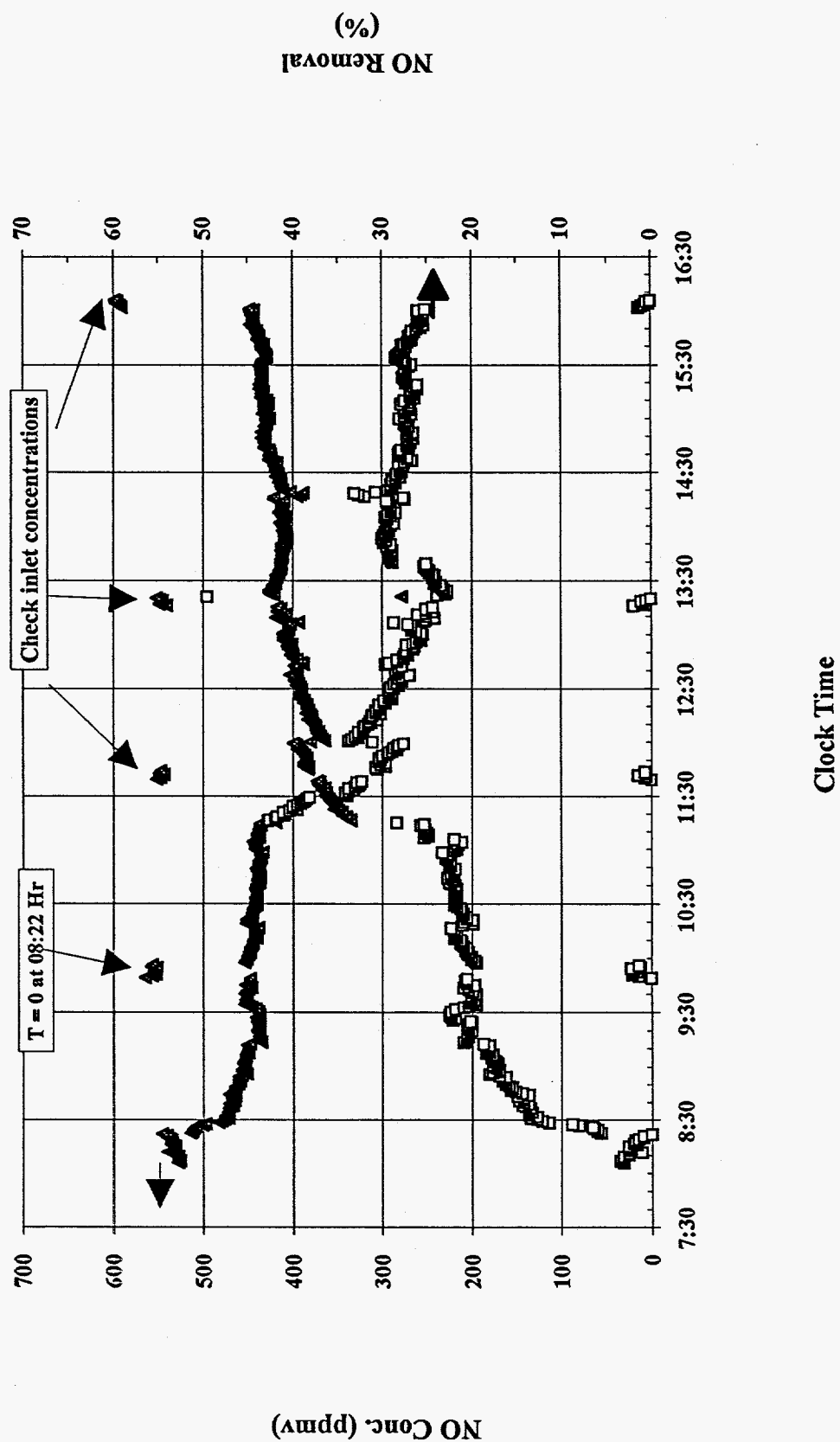


Figure 142. NO concentration and removal vs. time

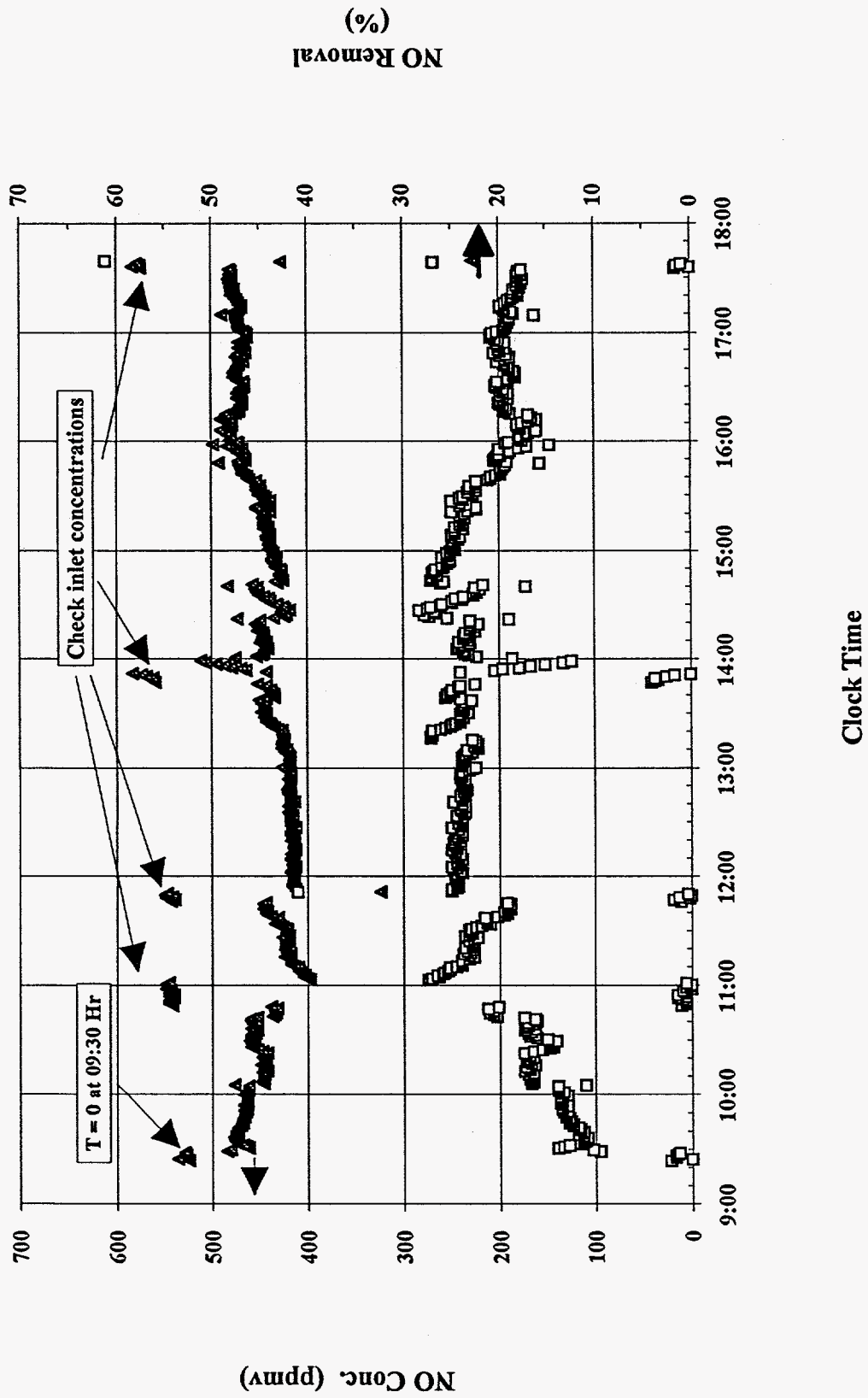


Figure 143. NO concentration and removal and $[\text{Fe}^{+2}]$ vs. time

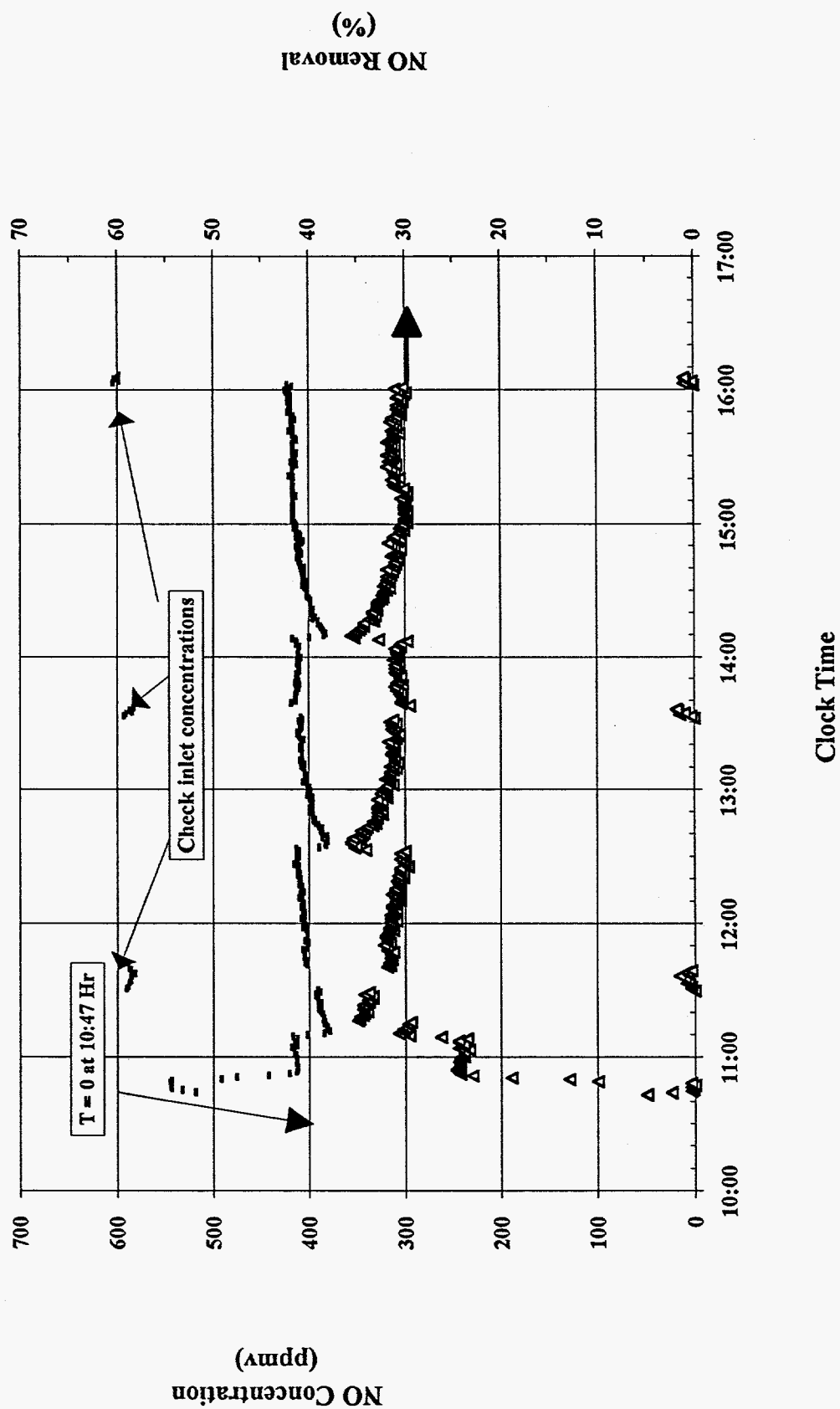


Figure 144. NO concentration and removal vs. time

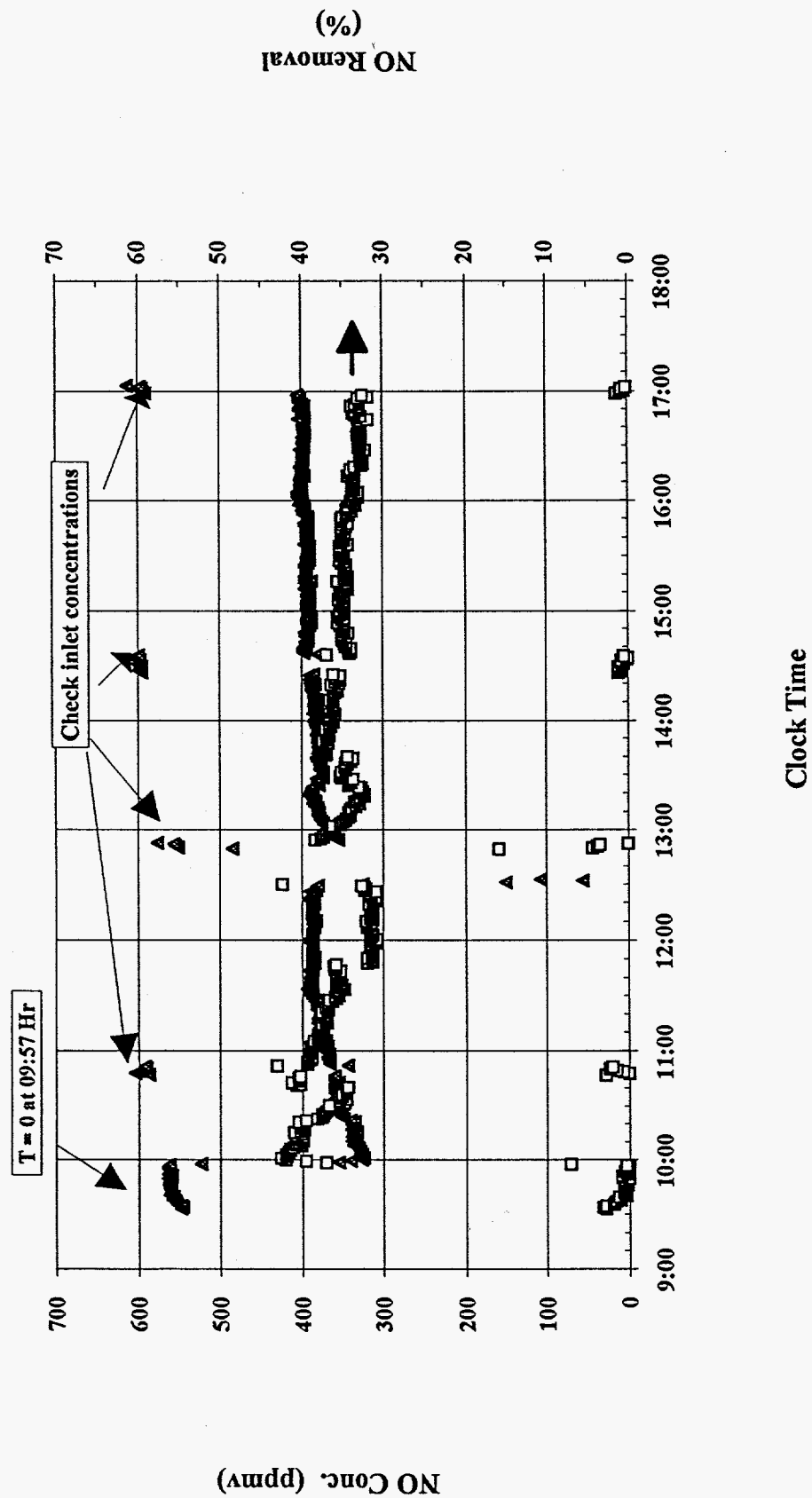
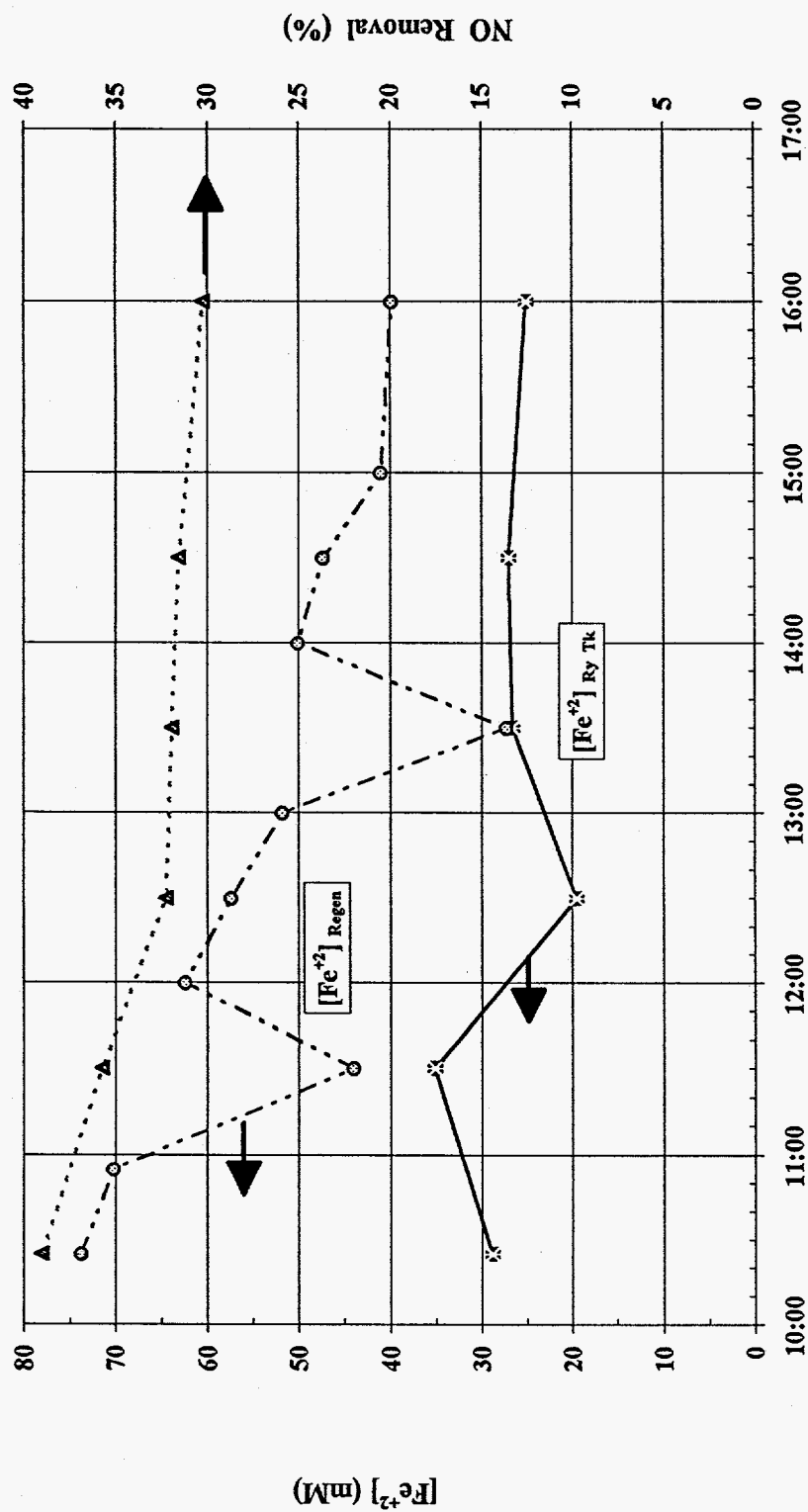


Figure 145. Change of recycle tank liquor $[\text{Fe}^{+2}]$ and NO removal



Clock Time

Figure 146. Change of recycle tank liquor $[\text{Fe}^{+2}]$ and NO removal

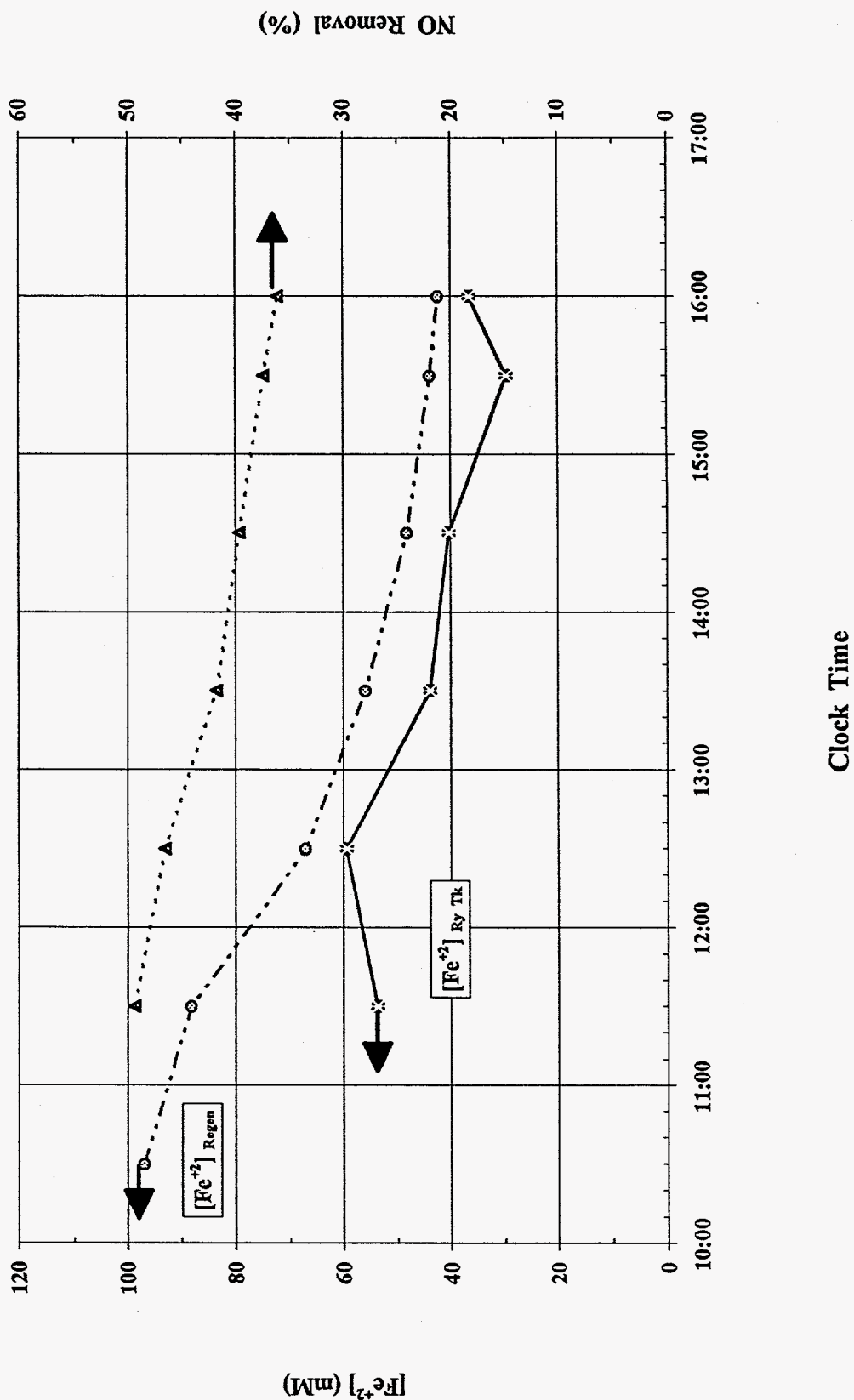
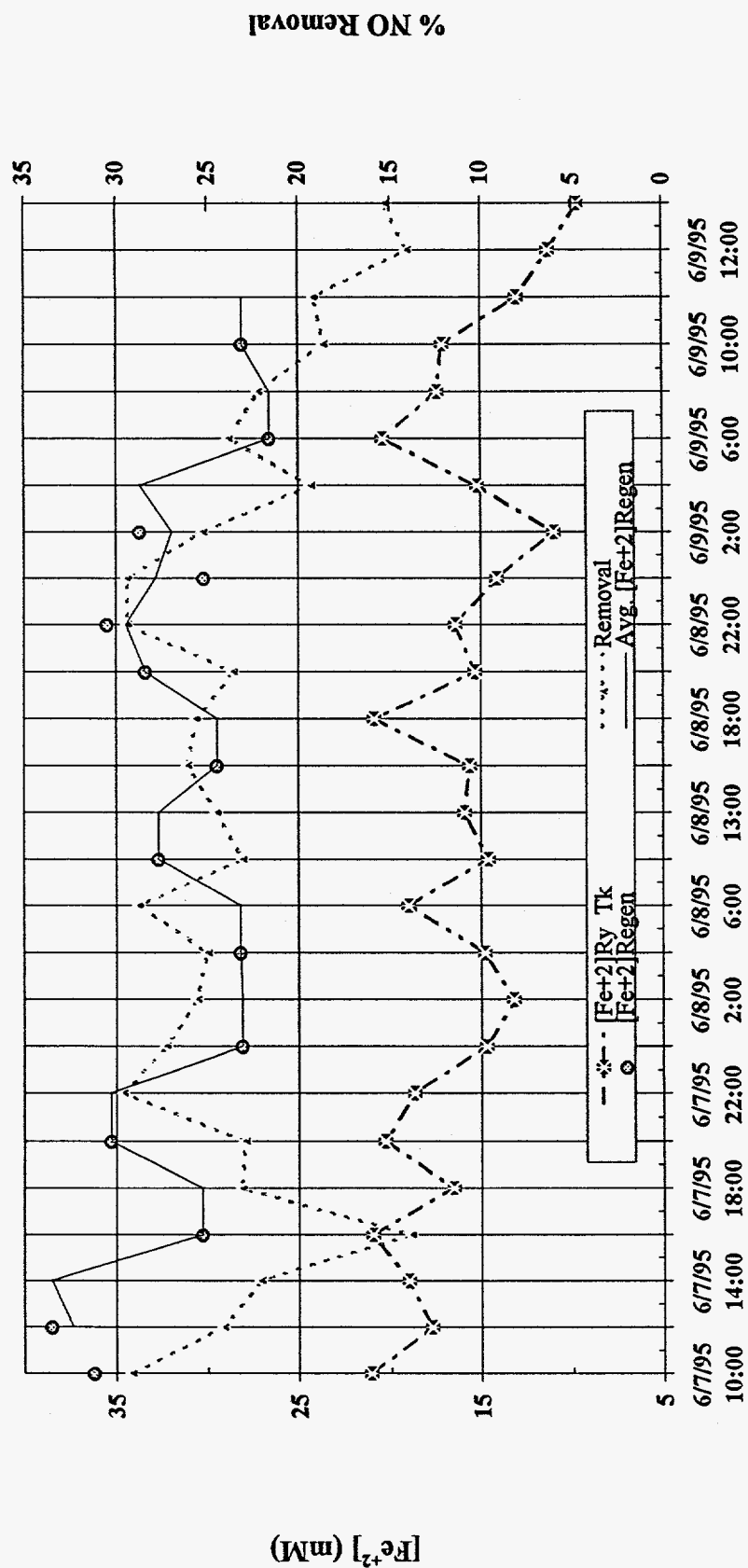


Figure 147. Change of recycle tank liquor $[\text{Fe}^{+2}]$ and NO removal



Clock Time

Figure 148. Measured $[\text{Fe}^{+2}]$ in recycle tank

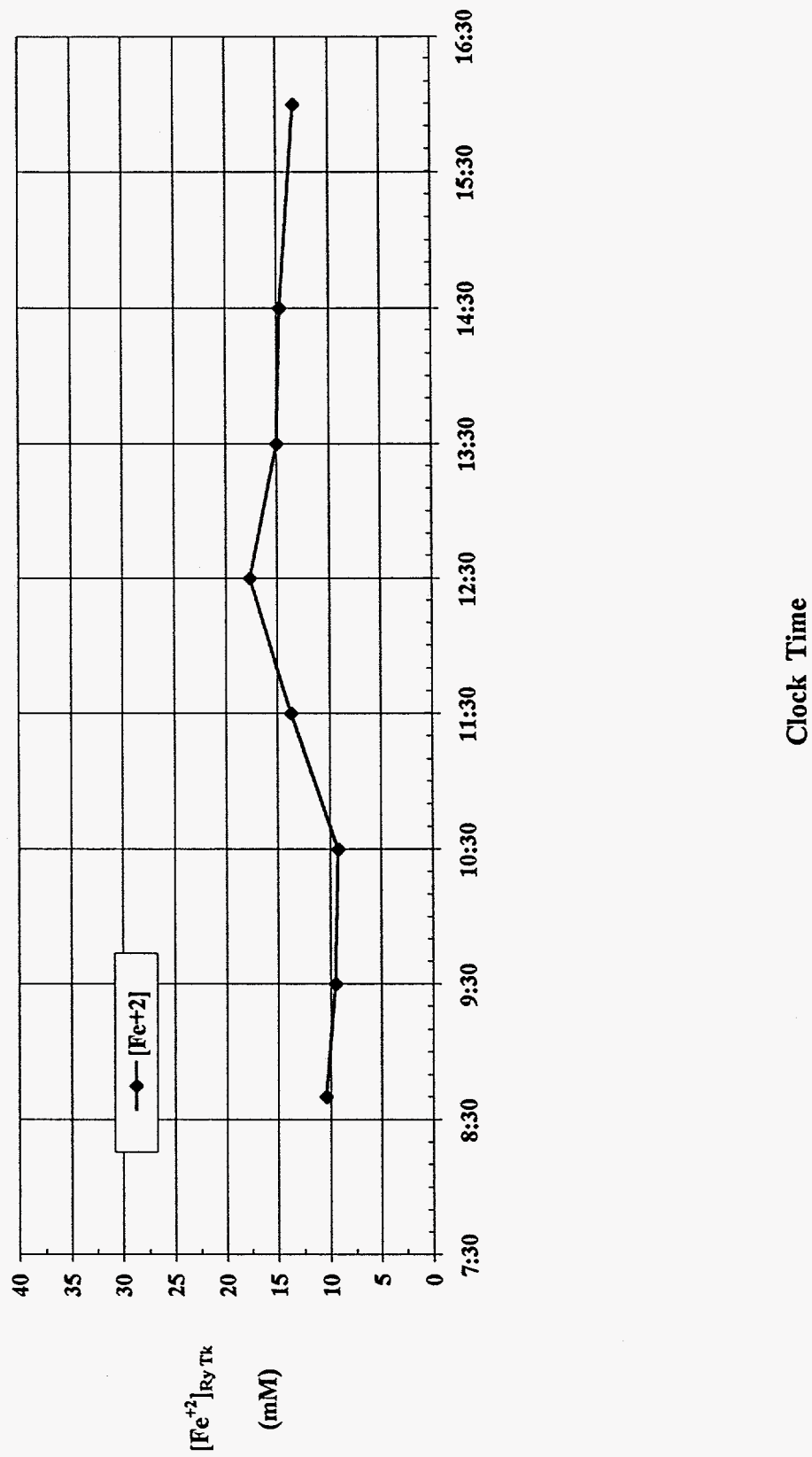
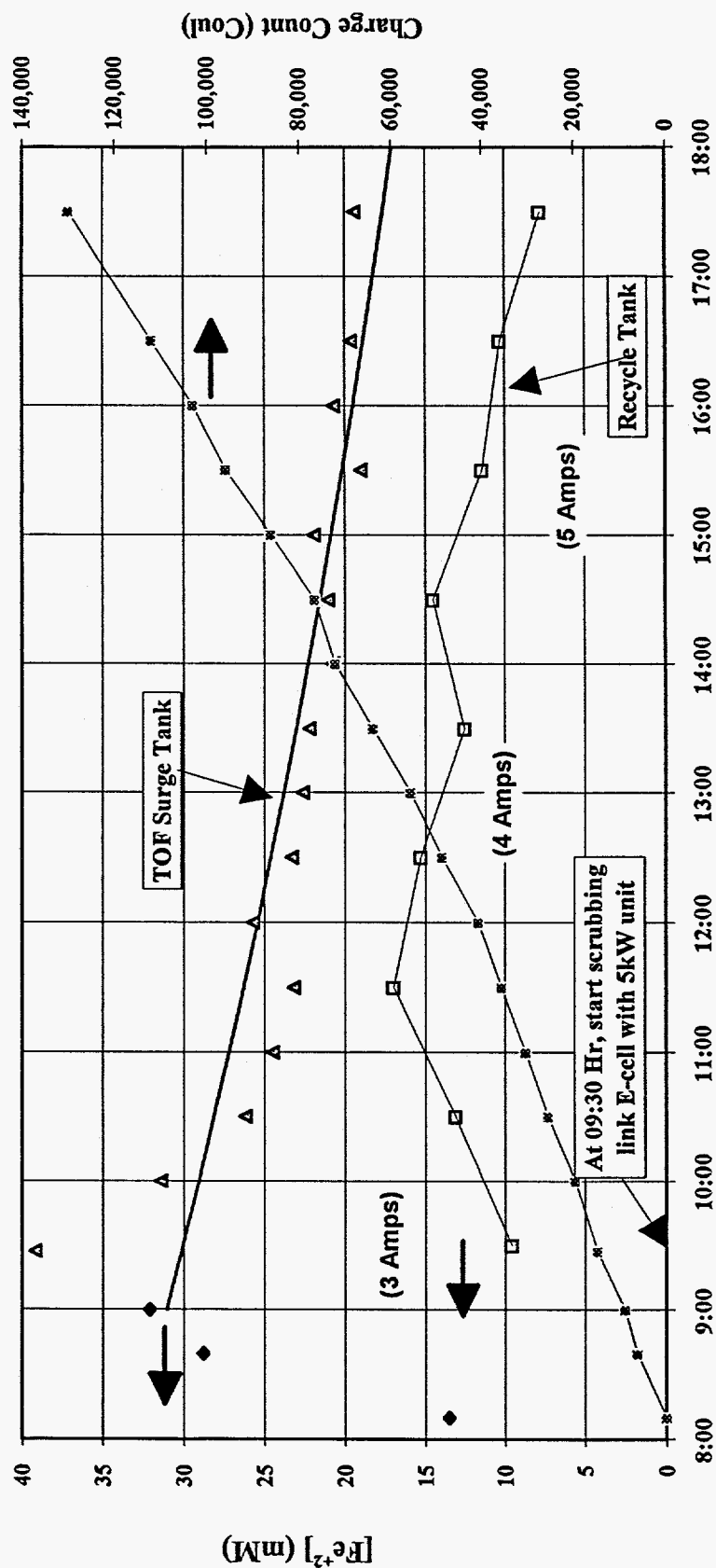


Figure 149. $[\text{Fe}^{+2}]$ measured in recycle and surge tank.



Clock Time

Figure 150. Measured $[\text{Fe}^{+2}]$ in recycle tank.

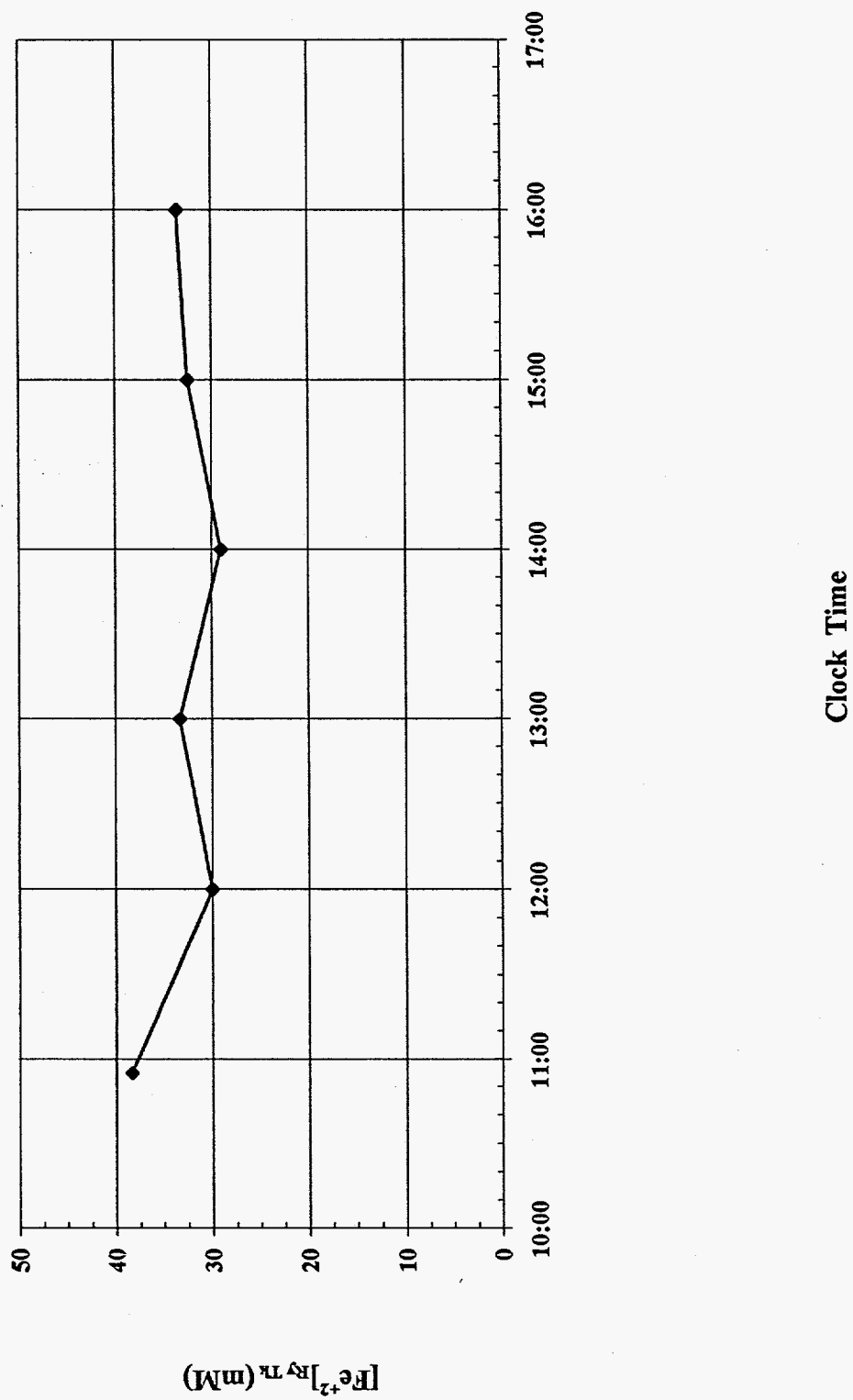
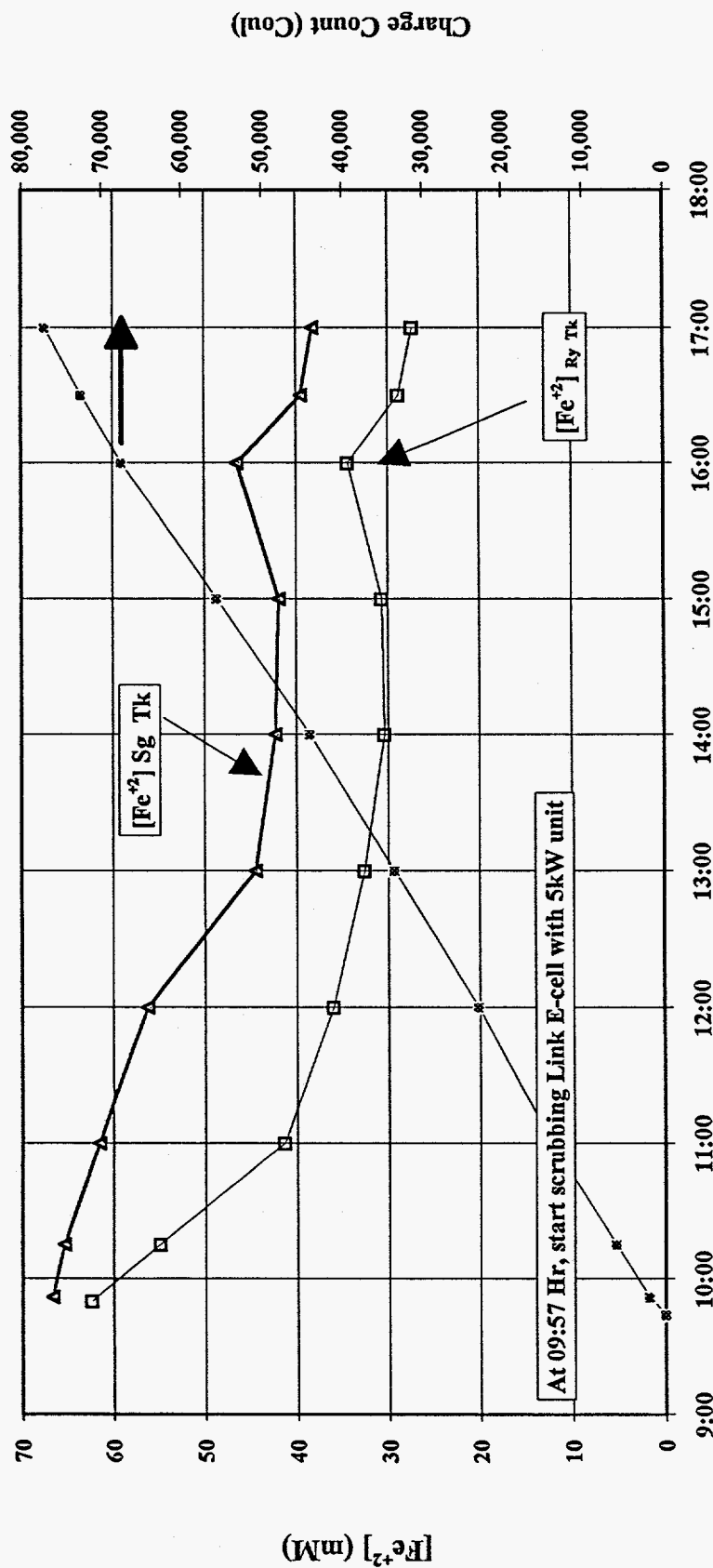


Figure 151. Measured $[\text{Fe}^{+2}]$ in Recycle and Surge Tank.



Clock Time

Figure 152. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

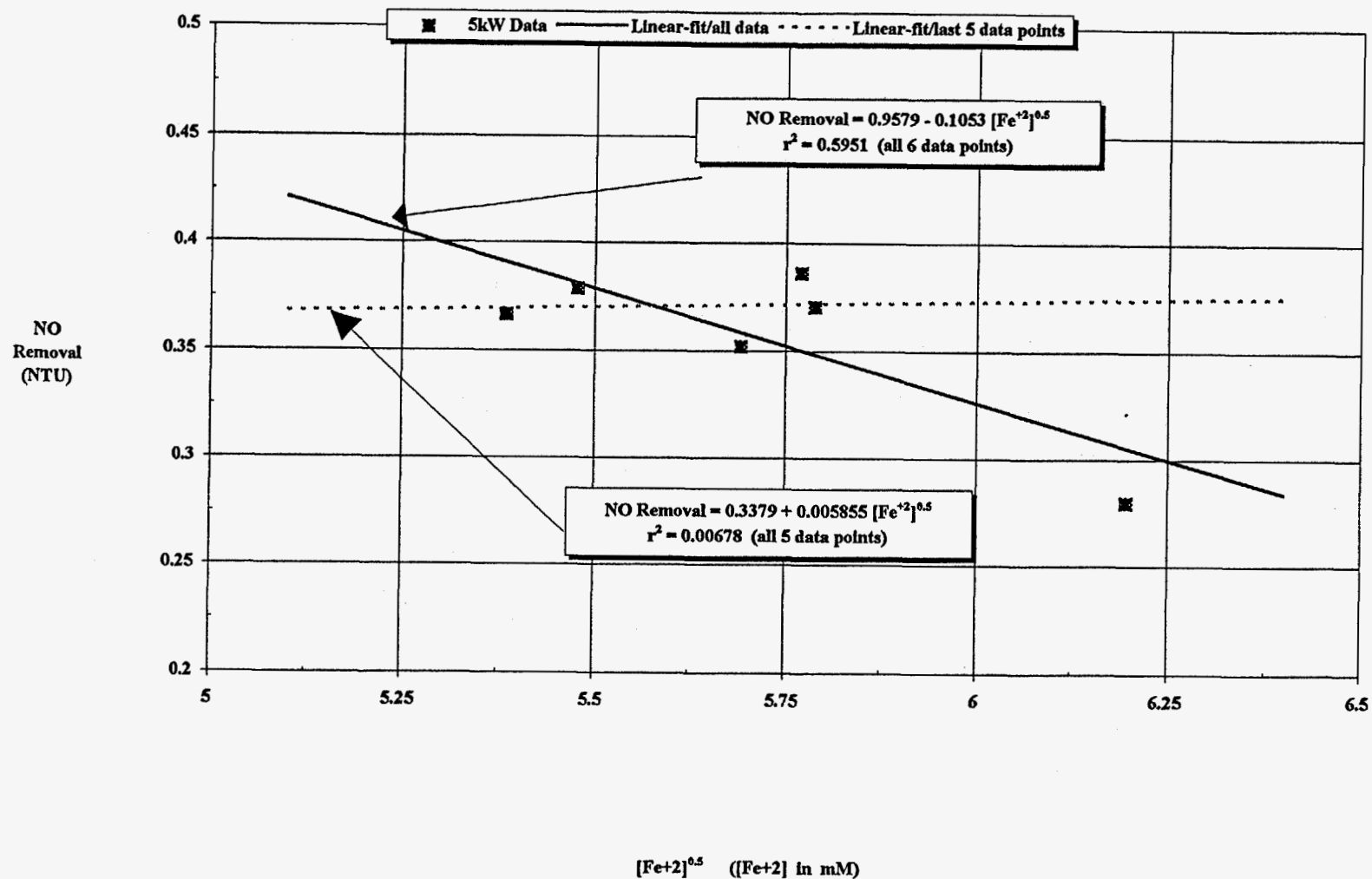


Figure 153. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

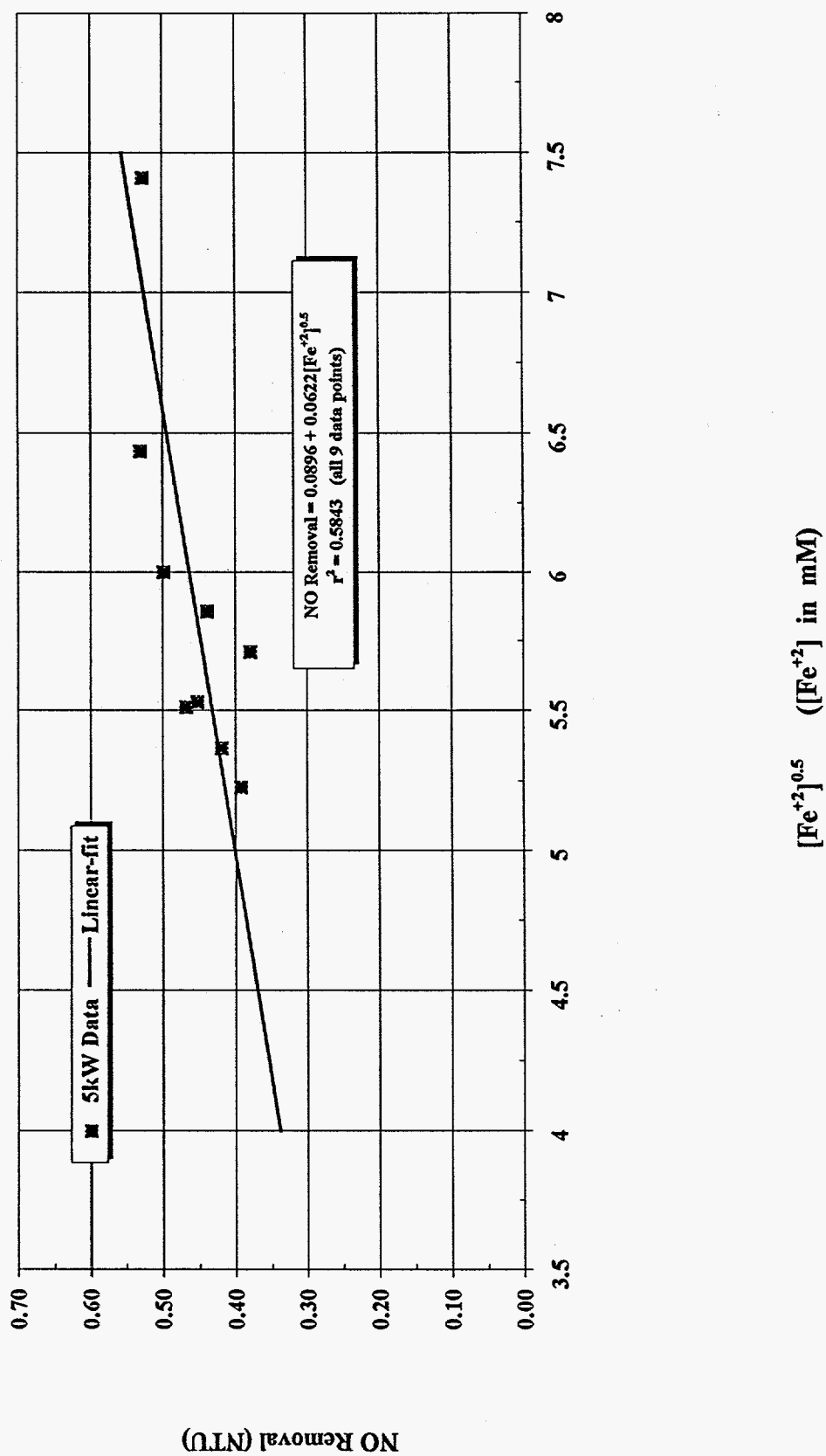


Figure 154. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

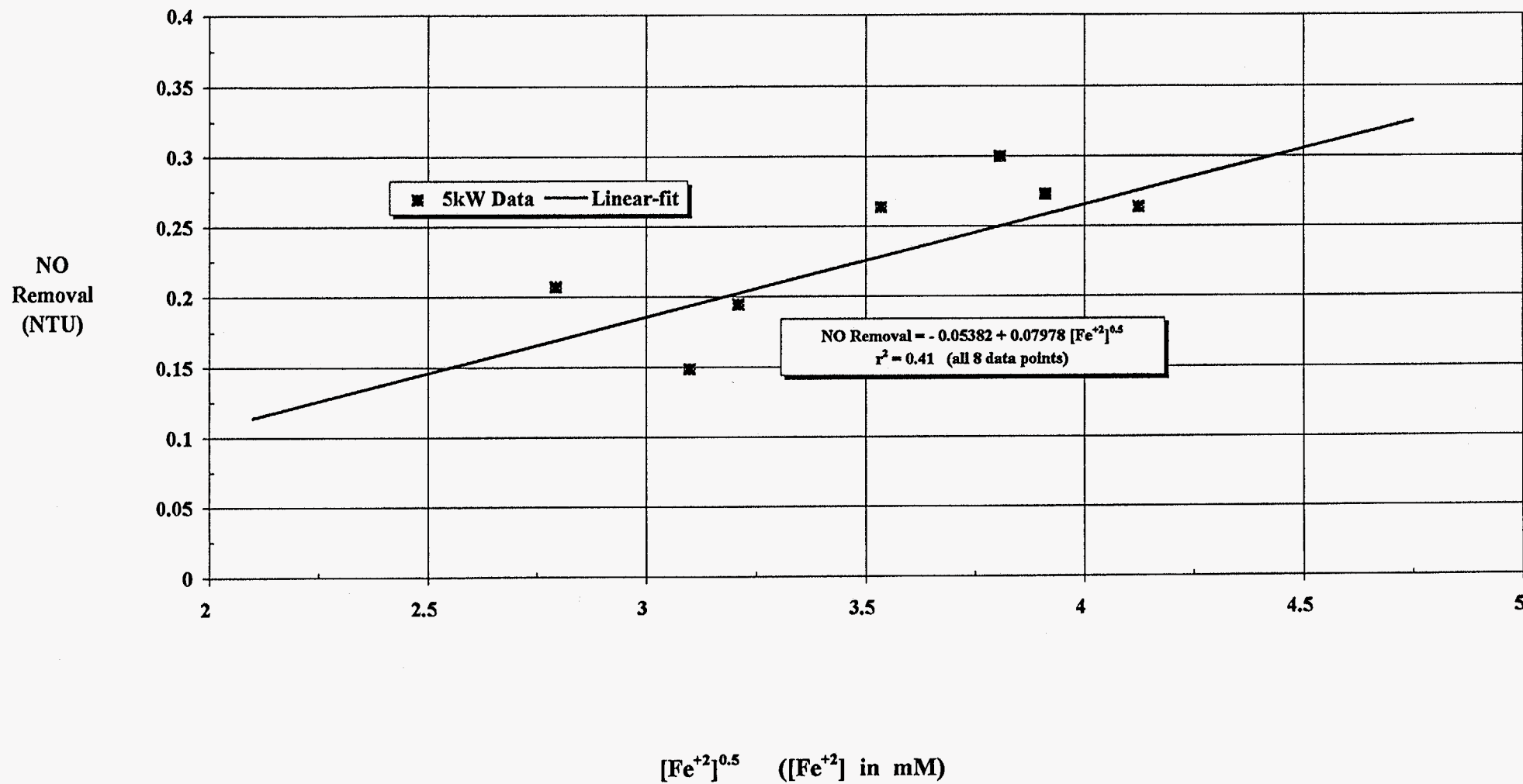


Figure 155. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

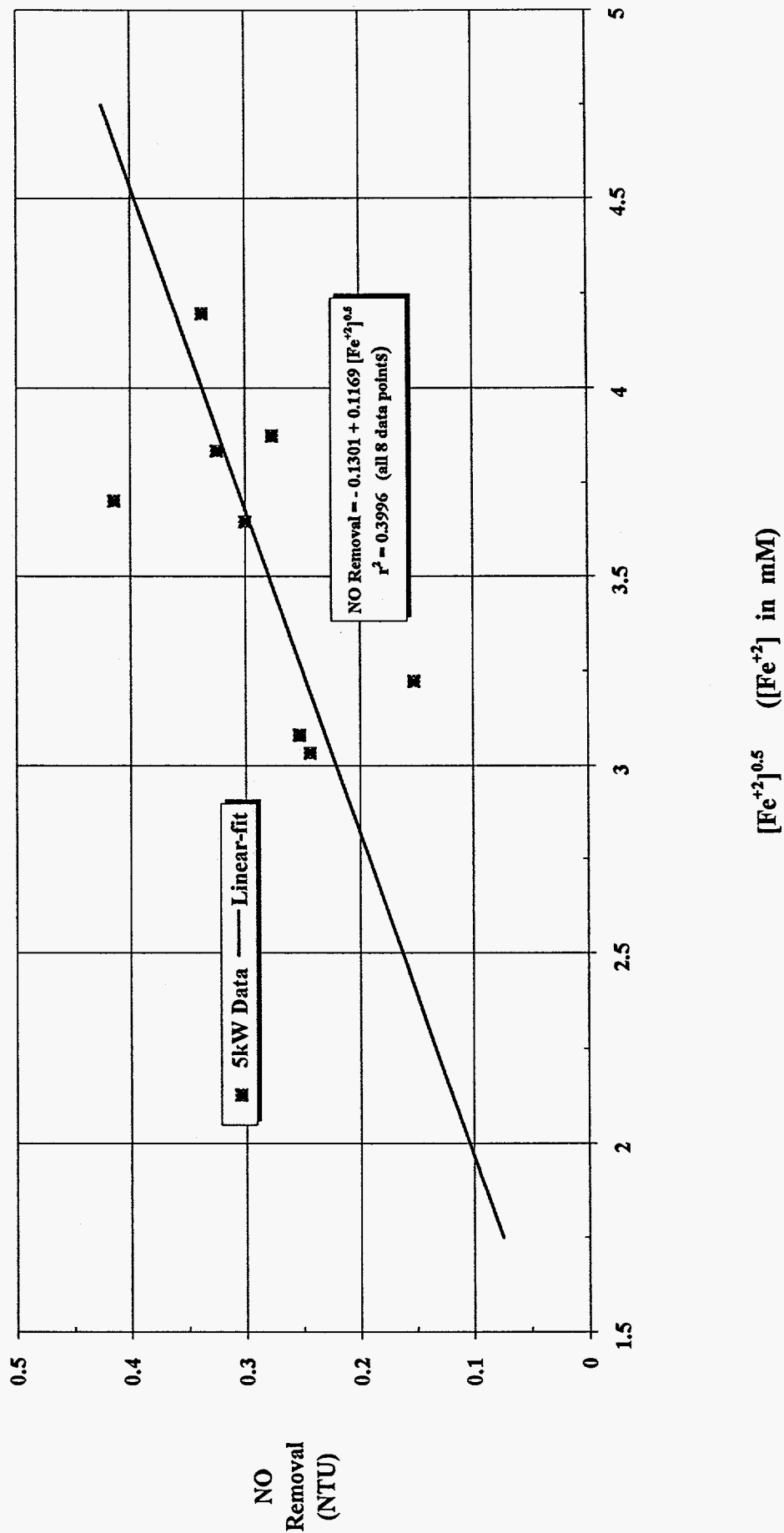


Figure 156. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

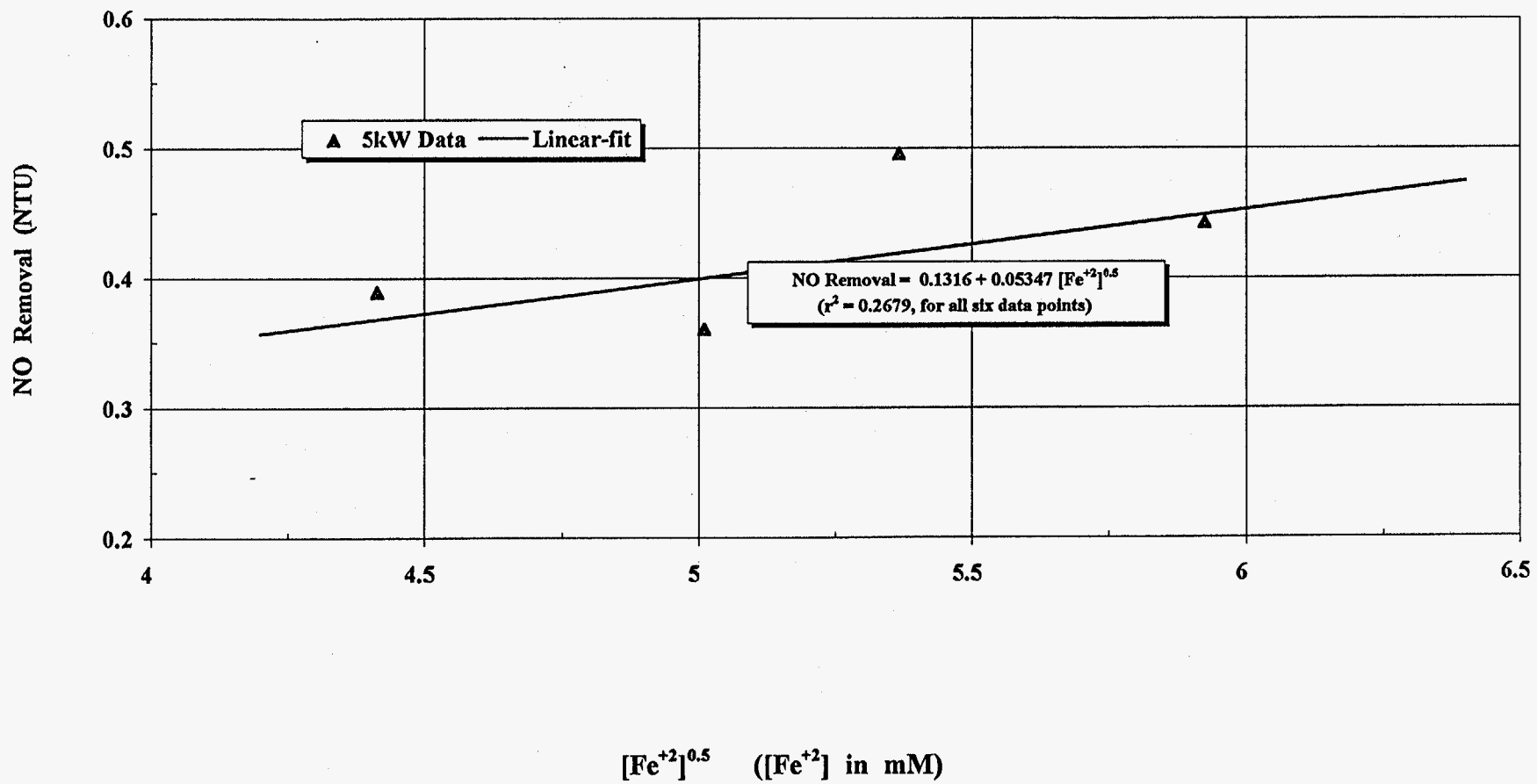


Figure 157. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

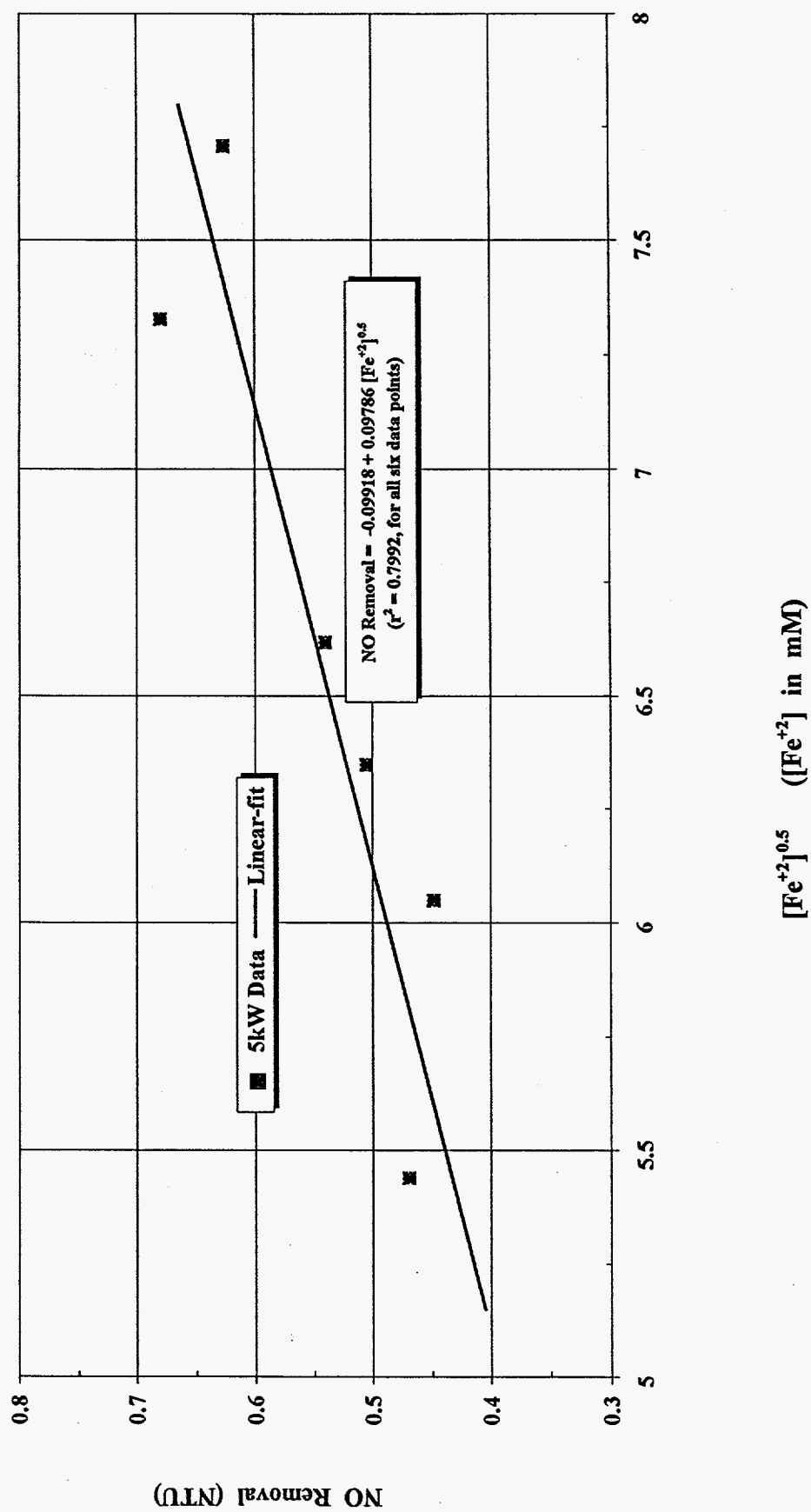


Figure 158. NO removal vs. $[\text{Fe}^{+2}]^{0.5}$

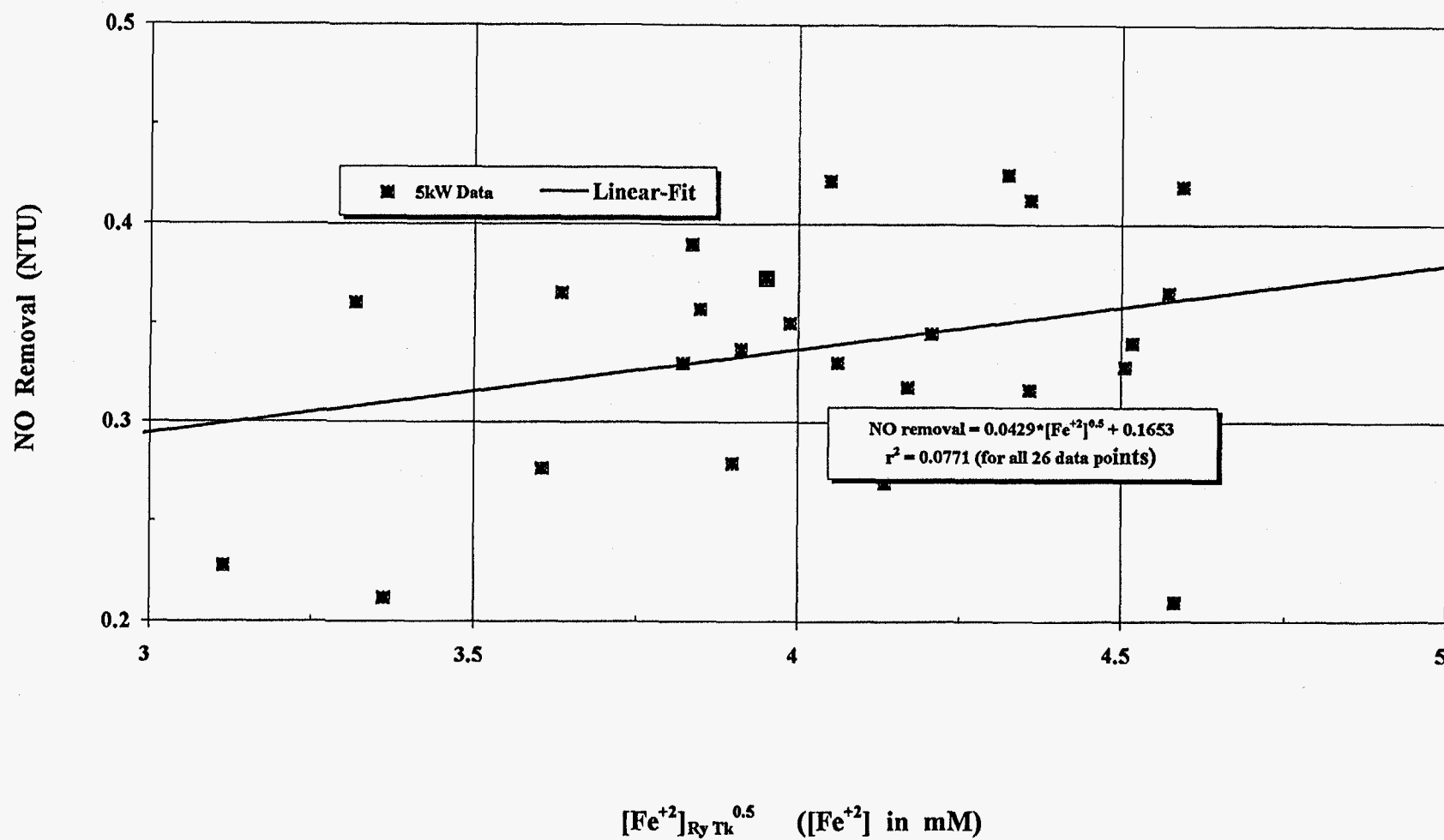
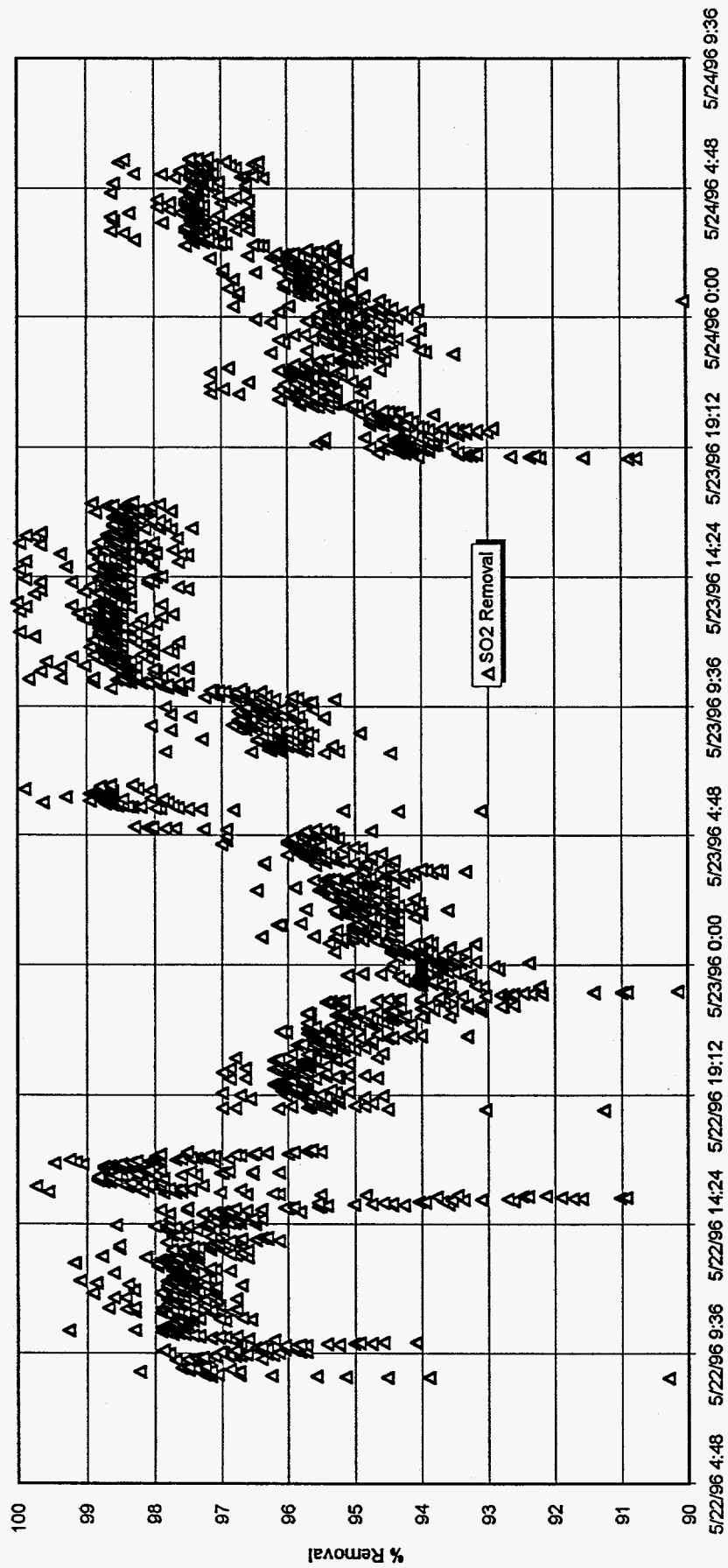
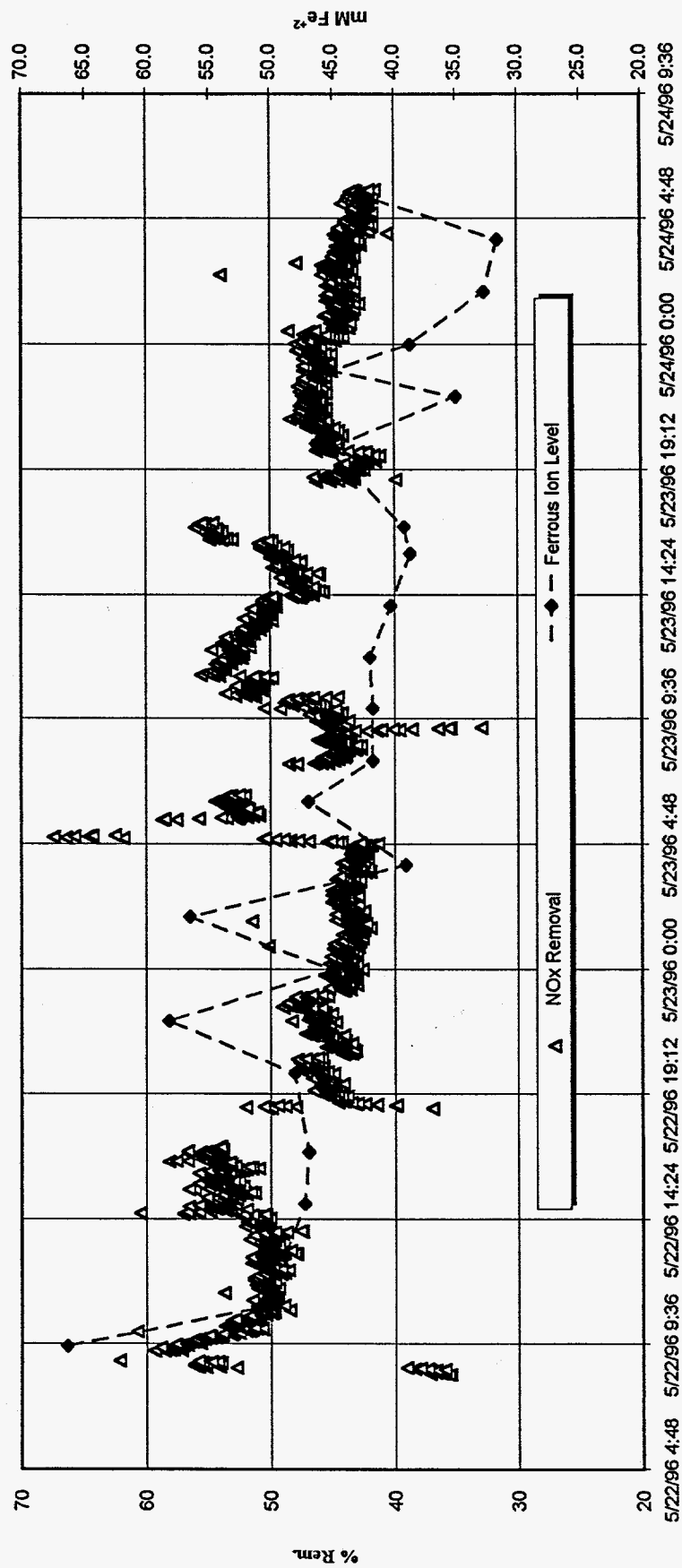


Figure 159. SO₂ removal vs. time



Date and Time

Figure 160. NO_x removal and [Fe⁺²] vs. time



DATE AND TIME

Figure 161. NOx Removal vs. $[\text{Fe}^{+2}]^{0.5}$

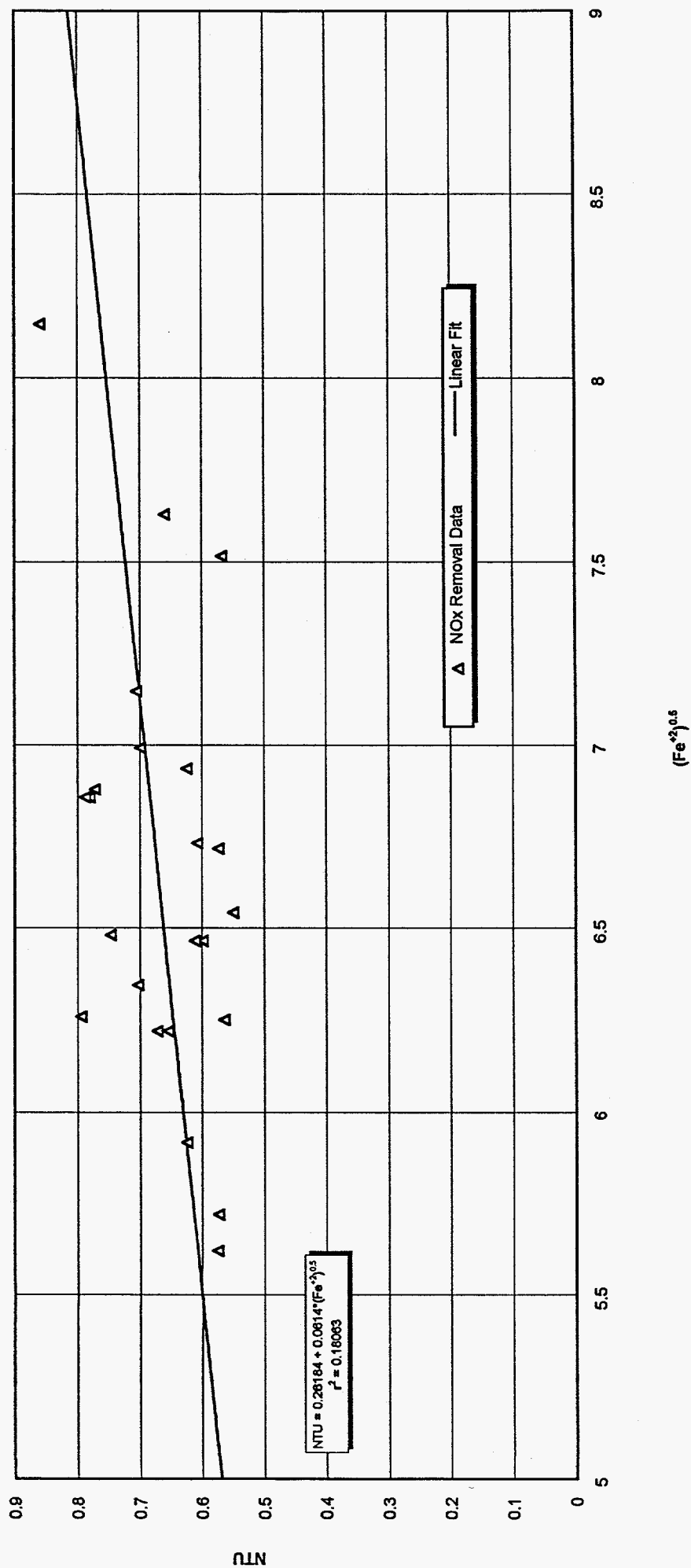


Table 31. Chemistry Data

Clock	L/G	Recycle	Alkalinity	[Fe ⁺²] _{Ry Tk}	[SO ₃ ⁻²] by	[SO ₃ ⁻²] _{Ry Tk}	[Mg ⁺²] _{Ry Tk}	[Ca ⁺²] _{Ry Tk}	[Total Fe] _{Ry Tk}	[Na ⁺¹] _{Ry Tk}	[S ₂ O ₃ ⁻²]	[SO ₃ ⁻²]	[SO ₄ ⁻²]	[Cl ⁻¹]	Filtercake
Time		Tank	(ppm)	by Spec-610	I ₂ titration	adjusted for	by ICP	by ICP	by ICP	by ICP	by IC	by IC	by IC	by IC	Solids
(Hr: Min)		Liquor pH		(mM)	(ppm)	[Fe ⁺²] _{Ry Tk}	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(wt %)
						(ppm)									
10:25	44	6.35	3,219	28.8	6,157	5,005	5,512	210	5,106	53	n.d.	3,887	7,560	187	
11:30	44	6.5	3,936	35.1	6,189	4,785	5,740	207	4,834	58	n.d.	4,360	6,860	164	58.25
12:30	44	6.4	4,787	19.5	6,149	5,369	6,140	235	4,916	68	n.d.	4,655	6,747	220	64.33
13:30	44	6.35	4,737	26.6	6,301	5,237	6,327	211	4,795	56	n.d.	5,132	7,716	173	60.47
14:30	44	6.35	4,704	27.0	6,461	5,381	6,374	173	4,917	59	n.d.	5,982	8,550	255	62.52
16:00	44	6.45	4,754	25.1	6,493	5,489	6,608	201	5,200	320	n.d.	6,238	9,633	344	61.18

Table 32. Chemistry Data

[illegible]

Table 33. Chemistry Data

Clock Time	Recycle Tank	Alkalinity (ppm)	[Fe ²⁺] _{spn} by Spec-601 (mM)	[SO ₄ ²⁻] by I ₂ titration (ppm)	[SO ₄ ²⁻] adjusted for [Fe ²⁺] _{spn} (ppm)	[ADS] by calculation (mM)	[SA] _{unox} by IC (mM)	[SA] by IC (mM)	[Mg ²⁺] by ICP (ppm)	[Cu ²⁺] by ICP (ppm)	[Total Fe] by ICP (ppm)	[Na ⁺] by ICP (ppm)	[S ₂ O ₃ ²⁻] by IC (ppm)	[SO ₃ ²⁻] by IC (ppm)	[SO ₄ ²⁻] by IC (ppm)	[Cl ⁻] by IC (ppm)	Filtercake Solids (wt %)
(hr: Min)	Liquor pH																
6/7/95 10:00	5.6	6,522	21.1	14,075	13,231	18.27	23.4	5.13	9,936	676	6,920	61	n.d.	13,284	12,535	103	63.3
6/7/95 12:00	5.6	5,354	17.7	13,883	13,175	30.34	35.0	4.66	10,480	680	7,027	65	n.d.	15,800	15,536	178	75.9
6/7/95 14:00	5.6	5,254	19.0	14,147	13,387	29.55	34.6	5.05	11,440	508	7,526	64	n.d.	13,708	14,470	137	85.38
6/7/95 16:00	5.6	4,887	21.0	13,555	12,715	33.84	39.2	5.36	11,000	560	6,955	66	n.d.	14,784	15,544	139	77.04
6/7/95 18:00	5.4	4,720	16.5	14,627	13,567	38.55	44.6	6.05	11,440	602	7,221	58	n.d.	13,433	13,025	131	82.75
6/7/95 20:00	5.5	5,087	20.3	14,571	13,759	40.16	45.7	5.54	11,030	720	6,987	63	n.d.	14,402	14,249	137	82.68
6/7/95 22:00	5.2	3,920	18.7	16,893	16,145	42.55	48.5	5.95	11,070	715	6,977	57	n.d.	15,750	13,864	118	74.17
6/8/95 0:00	5.3	3,836	14.7	15,516	14,928	48.7	61.8	13.10	10,500	679	6,366	64	n.d.	18,093	12,648	212	79.84
6/8/95 2:00	5.4	4,670	13.2	14,898	14,370	43.5	57.7	14.20	10,700	615	6,221	61	n.d.	15,924	11,406	222	76.03
6/8/95 4:00	5.2	3,503	14.8	16,773	16,181	43.8	60.2	16.40	10,730	776	6,143	65	n.d.	19,872	12,516	167	67.86
6/8/95 6:00	6.2	5,871	19	9,277	8,767	42.3	56.5	14.20	9,753	276	6,043	56	n.d.	10,333	11,396	207	60.1
6/8/95 11:00	5.1	2,852	14.6	13,587	13,003	43.9	60.1	16.20	10,120	625	6,338	60	n.d.	15,274	12,692	212	58.56
6/8/95 13:00	5	5,354	15.9	14,675	14,039	38	55.1	17.10	11,180	732	6,617	68	n.d.	21,393	18,211	212	70.7
6/8/95 15:00	5.1	3,052	15.6	15,196	14,572	45.3	62.9	17.60	11,530	684	6,645	69	n.d.	18,136	16,160	203	78.33
6/8/95 18:00		3,386	20.9	15,220	14,384	57.6	77.1	19.50	11,820	591	6,706	68	n.d.	19,402	17,218	320	78.3
6/8/95 20:00	5.2	4,687	15.3	15,932	15,320	64.5	87.9	23.40	12,740	630	7,067	69	n.d.	20,905	19,272	256	72.55
6/8/95 22:00	6	7,406	16.4	12,634	11,978	63.2	86.5	23.30	12,630	537	7,086	71	n.d.	12,404	14,087	228	71.35
6/9/95 0:00	5.6	7,623	14.1	12,986	12,422	64.8	76.4	11.60	12,660	427	7,299	69	n.d.	15,732	16,431	171	80.54
6/9/95 2:00	5.8	4,837	11	12,834	12,394	47.8	57.2	9.40	12,830	435	7,179	66	n.d.	13,340	15,079	129	71.7
6/9/95 4:00	5.6	6,222	15.2	14,051	13,443	56.7	66.5	9.80	13,030	484	7,136	64	n.d.	14,765	14,564	138	78.98
6/9/95 6:00	5.2	4,303	20.4	16,629	15,813	67.4	76.6	9.20	12,700	773	7,032	61	n.d.	21,034	17,330	194	57.11
6/9/95 8:00	5.1	4,037	17.4	17,141	16,445	78.2	88.4	10.20	13,510	652	6,942	60	n.d.	18,811	14,722	247	74.87
6/9/95 10:00	5.8	6,605	17.1	11,993	11,309	66.5	75.5	9.00	12,650	493	6,374	58	n.d.	11,514	12,017	118	76.43
6/9/95 11:00	5.9	7,089	13	11,361	10,841	65.5	75.1	9.60	12,940	503	6,463	59	n.d.	14,546	15,576	178	71.4
6/9/95 12:00	5.8	6,522	11.3	11,705	11,253	75.4	84.7	9.30	12,540	532	6,262	52	n.d.	12,684	13,134	167	73.33
6/9/95 13:00	5.9	6,655	9.7	10,977	10,589	71.1	80.5	9.40	12,830	400	6,330	52	n.d.	14,121	15,036	197	69.35
																	73.40576923

Table 34. Chemistry Data

Clock	L/G	Recycle	Alkalinity	[Fe ⁺²]	[SO ₃ ⁻²] by	[SO ₃ ⁻²]	[ADS]	[SA]	[Mg ⁺²]	[Ca ⁺²]	[Total Fe]	[Na ⁺¹]	[SO ₃ ⁻²]	[SO ₄ ⁻²]	[Cl ⁻¹]	Filtercake
Time		Tank	(ppm)	by Spec-20	I ₂ titration	adjusted for	by IC	by IC	by ICP	by ICP	by ICP	by ICP	by IC	by IC	by IC	Solids
(Hr: Min)		Liquor pH		(mM)	(ppm)	[Fe ⁺²]	(mM)	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(wt %)
						(ppm)										
8:40	44	6.40	3,036	10.4	4,588	4,172	*	*	6,295	481	4,212	48.07	4,551	8,655	102	
9:30	44	6.45	3,603	9.5	5,460	5,080	*	*	6,641	602	4,303	47.49	5,923	8,930	89	76.39
10:30	44	6.50	3,553	9.2	4,708	4,340	*	*	6,665	1,612	4,092	49.17	4,877	7,061	98	81.42
11:30	44	6.40	3,086	13.7	5,829	5,281	*	0	6,837	798	5,719	48.85	5,236	9,945	88	81.24
12:30	44	6.40	3,620	17.6	6,261	5,557	*	*	6,658	789	5,293	46.97	5,647	8,098	98	82.93
13:30	44	6.40	3,586	15.0	6,021	5,421	*	0	6,680	716	4,977	45.47	5,040	6,946	96	81.29
14:30	44	6.30	3,586	14.7	6,549	5,150	*	*	6,874	750	5,037	49.89	6,622	8,176	99	83.78
16:00	44	6.35	3,369	13.3	5,981	5,449	*	*	6,924	482	4,918	52.62	6,097	7,635	114	82.86

Table 35. Chemistry Data

Clock	L/G	Recycle Tank	Alkalinity (ppm)	[Fe ⁺³] by Spec-20 (mM)	[SO ₄ ⁻²] by I ₂ titration (ppm)	[SO ₄ ⁻²] adjusted for [Fe ⁺²] (ppm)	[ADS] by IC (mM)	[SA] by IC (mM)	[Mg ⁺²] by ICP (ppm)	[Ca ⁺²] by ICP (ppm)	[Total Fe] by ICP (ppm)	[Na ⁺¹] by ICP (ppm)	[SO ₃ ⁻²] by IC (ppm)	[SO ₄ ⁻²] by IC (ppm)	[Cl ⁻¹] by IC (ppm)	Filtercake Solids (wt %)
Time (Hr: Min)		Liquor pH														
9:30	44	6.7	3,920	9.6	3,763	3,379	*	*	6,577	524	4,627	51.45	4,584	7,382	112	
10:30	44	6.8	4,387	13.1	4,267	3,743	*	*	6,287	648	4,410	46.27	5,652	7,562	110	84.35
11:30	44	6.65	4,120	17.0	4,700	4,020	*	*	6,690	524	4,895	58.40	6,540	8,351	111	80.32
12:30	44	6.6	4,353	15.3	4,844	4,232	*	*	6,719	528	4,794	49.26	7,071	8,027	118	79.95
13:30	44	6.6	4,504	12.5	5,084	4,584	*	*	6,630	644	4,709	52.25	5,712	7,840	139	84.27
14:30	44	6.6	4,037	14.5	4,179	3,599	*	*	6,653	542	4,674	56.21	4,746	8,412	145	81.34
15:30	44			11.4			*	*							115	
16:30	44	6.55	3,803	10.3	4,243	3,104	*	*	6,409	454	4,457	59.84	4,883	7,810	162	80.16
17:30	44	6.55	4,153	7.8	4,716	4,404	*	*	6,944	369	4,753	61.93	5,405	8,090	101	84.88

Table 36. Chemistry Data

Clock Time	L/G	Recycle Tank	Alkalinity (ppm)	[Fe ⁴⁺] by Spec-20 (mM)	[SO ₃ ²⁻] by I ₂ titration (ppm)	[SO ₃ ²⁻] adjusted for [Fe ⁴⁺] (ppm)	[ADS] by IC (mM)	[SA] by IC (mM)	[Mg ²⁺] by ICP (ppm)	[Ca ²⁺] by ICP (ppm)	[Total Fe] by ICP (ppm)	[Na ⁺] by ICP (ppm)	[SO ₃ ²⁻] by IC (ppm)	[SO ₄ ²⁻] by IC (ppm)	[Cl ⁻] by IC (ppm)	Filtercake Solids (wt %)
(Hr: Min)		Liquor pH														
10:55	44	6.5	3,002	38.4	4,548	3,012	1.82	*	6,130	1,341	5,942	79	3,038	14,695	42	
12:00	44	6.5	3,436	30.0	4,227	3,027	3.40	*	6,350	1,047	5,979	184	3,145	14,684	39	
13:00	44	6.55	3,269	33.3	4,259	2,927	4.85	*	6,473	1,015	5,888	232	3,067	14,717	45	50.37
14:00	44	6.5	3,786	29.0	4,499	3,339	6.45	*	6,795	950	6,067	237	3,584	14,546	35	
15:00	44	6.5	3,536	32.4	4,692	3,396	8.22	*	7,084	879	6,080	333	3,588	14,722	30	59.38
16:00	44	6.4	3,653	33.5	4,908	3,568	10.40	*	7,177	785	6,200	331	3,995	14,746	33	62.48

Table 37. Chemistry Data

Clock	L/G	Recycle	lkalinit	[Fe ⁺²]	[SO ₃ ⁻²] by	[SO ₃ ⁻²]	[ADS]	[SA]	[Mg ⁺²]	[Ca ⁺²]	[Total Fe]	[Na ⁺¹]	[SO ₃ ⁻²]	[SO ₄ ⁻²]	[Cl ⁻¹]	Filtercake
Time		Tank	(ppm)	by Speco-20	I ₂ titration	adjusted for	by IC	by IC	by ICP	by ICP	by ICP	by ICP	by IC	by IC	by IC	Solids
(Hr: Min)		Liquor pH		(mM)	(ppm)	[Fe ⁺²] _{RyTk}	(mM)	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(wt %)
						(ppm)										
10:15	44	6.30	3469	54.9	9,135	6,939	*	*	6265	382	5693	51	10183	10909	88	N.A.
11:00	44	6.40	4020	41.4	8,022	6,366	*	*	6395	413	5638	46	7842	10426	98	76.97
12:00	44	6.40	4353	36.0	8,158	6,718	*	*	6741	449	5861	45	7676	10506	120	N.A.
13:00	44	6.20	4187	32.6	8,695	7,391	*	*	7065	330	6134	43	8068	10882	95	82.59
14:00	44	6.35	4720	30.4	8,599	7,383	*	*	7362	406	6314	40	7919	10962	121	82.20
15:00	44	6.40	5721	30.6	8,510	7,286	*	*	7563	399	6349	42	8035	10982	91	82.66
16:00	44	6.40	4187	34.3	7,830	6,458	*	*	7514	397	6186	45	7582	10543	106	82.41
16:30	44	6.50	4937	28.8	8,702	7,550	*	*	7813	464	6451	48	8208	11002	119	83.29
17:00	44	6.55	5438	27.3	7,550	6,458	*	*	7632	436	6239	43	7855	10393	95	85.85

Table 38. Chemistry Data

Clock	L/G	Recycle	Alkalinity	[Fe ³⁺] _{by n}	[SO ₄ ²⁻] by	[SO ₄ ²⁻]	[SA] _{adjusted}	[SA]	[Mg ²⁺]	[Ca ²⁺]	[Total Fe]	[Na ⁺]	[SiO ₂ ³]	[SO ₄ ²⁻]	[SO ₄ ²⁻]	[Cl ⁻]	Filtercake
Time		Tank	(ppm)	by Spec-601	titration	adjusted for	by IC	by IC	by ICP	by ICP	by ICP	by ICP	by IC	by IC	by IC	by IC	Solids
(Date, Hrs Min)		Liquor pH		(mM)	(ppm)	[Fe ³⁺] _{by n}	(mM)	(mM)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(wt %)
						(ppm)											
5/22/96 9:30	44	5.3	2302	66.4	11097	8,441	3.9	1.8	9,002	464	6,652	9,902	n.d.	9,264	11,630	4,696	
5/22/96 11:00	44	5.6	3503	51.1	10993	8,949	7.0	3.5	9,253	568	6,392	9,253	n.d.	9,551	11,495	4,529	67.63
5/22/96 13:00	44	5.6	2769	48.9	11705	9,749	13.4	3.4	9,750	463	6,460	9,750	n.d.	10,454	12,213	4,250	62.3
5/22/96 15:00	44	5.0	1701	47.3	13603	11,711	20.7	8.1	10,320	401	6,286	10,320	n.d.	10,997	13,392	3,437	64.1
5/22/96 17:00	44	5.1	2002	47.0	12546	10,666	28.2	14.6	10,460	446	6,104	10,460	n.d.	11,542	15,788	4,250	64.72
5/22/96 20:00	44	5.7	4353	48.1	11233	9,309	22.2	8.0	9,939	247	5,610	9,939	n.d.	9,805	15,116	3,890	65.81
5/22/96 22:00	44	5.3	3370	58.2	13370	11,042	27.8	12.4	10,820	370	5,744	10,820	n.d.	11,907	14,438	3,590	65.65
5/23/96 0:00	44	5.85	5171	45.1	13754	11,950	32.5	13.6	11,130	430	5,614	11,130	n.d.	12,892	15,068	3,554	70.11
5/23/96 2:00	44	5.7	4803	56.5	14675	12,415	37.6	14.7	11,160	260	5,436	11,160	n.d.	14,236	14,501	3,365	71.59
5/23/96 4:00	44	5.8	5554	39.1	15524	13,960	39.4	15.9	11,610	336	5,456	11,610	n.d.	15,666	14,774	3,281	71.12
5/23/96 6:25	44	5.65	5120	47	13546	11,666	28.0	12.1	10,020	332	5,042	10,020	n.d.	12,778	12,278	3,285	65.48
5/23/96 8:00	44	5.5	3503	41.8	12330	10,658	24.6	17.5	9,726	496	5,020	9,726	n.d.	11,784	11,734	3,818	68.74
5/23/96 10:00	44	5.9	5021	41.8	13394	11,722	33.3	14.2	10,310	489	5,058	10,310	n.d.	13,124	11,821	3,783	76.59
5/23/96 12:00	44	5.8	5187	42	14595	12,915	39.9	17.5	10,690	261	5,009	10,690	n.d.	14,220	11,587	3,597	74.35
5/23/96 14:00	44	5.9	5121	40.3	15604	13,992	46.7	17.1	10,770	250	4,902	10,770	n.d.	15,467	11,451	3,385	63.6
5/23/96 16:00	44	5.8	5338	38.7	16669	15,121	55.7	18.1	11,110	205	4,846	11,110	n.d.	17,030	11,705	3,190	68.68
5/23/96 17:00	44	5.7	5004	39.2	18102	16,534	55.0	21.3	11,510	182	4,977	11,510	n.d.	18,756	11,843	3,154	71.39
5/23/96 20:00	44	5.85	3820	45.3	12265	10,453	23.1	8.6	8,672	223	4,374	8,672	n.d.	11,406	10,116	3,509	65.84
5/23/96 22:00	44	5.7	3986	35	12970	11,570	33.1	9.9	9,223	159	4,243	9,223	n.d.	12,339	11,064	3,544	78.86
5/23/96 23:00	44			45.1													
5/24/96 0:00	44	5.5	3636	38.7	14228	12,680	35.9	12.5	9,753	275	4,108	9,753	n.d.	14,709	12,147	3,951	70.26
5/24/96 2:00	44	5.5	4253	32.7	14819	13,511	40.6	13.6	10,010	237	4,077	10,010	n.d.	15,635	11,803	3,375	73.62
5/24/96 4:00	44	5.8	5054	31.6	15644	14,380	44.6	14.0	9,868	270	3,999	9,868	n.d.	16,512	12,132	3,111	74.98
5/24/96 5:45	44	5.7	4854	42.8	16724	15,012	47.7	13.8	10,560		1,302	10,560		17,887	12,293	3,404	74.6

III. SIGNIFICANT PROBLEMS ENCOUNTERED

A. Baseline Tests

No major operating problems developed for the baseline tests conducted. As part of maintenance for the continued operation of the system, synthetic liquor occasionally had to be added to the recycle tank as make-up for evaporative losses in the absorber where liquor would evaporate and exit with the flue gas.

B. Chemical Regeneration Agents

1. Sodium Dithionite / Ascorbic Acid

The high sulfite ion concentrations for both tests near the end of their respective runs could result in scaling if the calcium ion concentration increased further. The calcium ion concentration was 640 ppm for test DT021496 but displayed a decreasing trend to 223 ppm by the end of the test. At 223 ppm calcium ion concentration precipitation of calcium sulfite will not occur. For test DT021696, the calcium ion concentration was steady at 286 ppm. If the calcium ion concentration for either of these two tests were to further increase, precipitation would occur. The long term chemistry associated with the use of this regeneration mixture could lead to scaling in the system.

2. Iron

Besides low NO_x removal, the tests ran smoothly with no unusual occurrences in regard to equipment operation such as problems with tubing pluggage. The concentration of ions in the liquor were typical for a ThioNO_x process except for the sulfate ion concentration. For test DT032294, the sulfate ion concentration increased from 5,720 ppm initially to 15,374 ppm by the end of testing. If calcium ions increase in concentration then precipitation of calcium sulfate will occur throughout the system. For test DT031794, the

average solids content of the filtercake was 62.6 wt. % while for test DT032294, the average solids content of the filtercake was 55.3%. It is believed that iron is participating in a side reaction where an iron compound is formed that lowers the dewatering characteristics of the filtercake.

3. Iron Using a Digestor

The filtercake solids content decreased as testing continued for both short term tests DT072595 and DT072795. For test DT072595, the filtercake solids content was 69.8 wt.% at the beginning of testing and 49.7 wt.% by the end of testing. Similar results were observed for test DT072795 where the solids content was 62.8 wt. % at the beginning of testing and 49.7 wt. % by the end of testing. During previous ThioNO_x tests, the solids content usually increased with test time but for these two runs the solids content decreased by an average of 16.6 wt.%. The filtercake solids content was also low for the long term test averaging 58.6 wt.%. At the beginning of testing, the filtercake solids was 70.5 wt.%. This significant decrease in solids content can be rationalized by the presence of a constituent in the filtercake which lowers the dewatering ability. The iron is believed to participate in a side reaction where iron hydroxide is formed due to the reaction between ferrous ions and lime in the recycle tank. Ferrous hydroxide is known to be gelatinous colloidal material which is known to be difficult to dewater. The formation of such a material would substantially lower the dewatering characteristics of the filtercake.

4. Zinc

During this test, DT031694, the calcium ion concentration was higher than normally observed for a ThioNO_x system. The average concentration was 398 ppm. The increase in calcium ion concentration could result in gypsum precipitation if the sulfate concentration became too large.

The total iron concentration in the system decreased during the test. Specifically, the total iron dropped ~850 ppm in the course of the run. The drop in total iron is associated with the displacement of iron in iron-EDTA by zinc to form zinc-EDTA. The displaced iron then reacts with a free ion in the liquor and precipitates out of solution accounting for the decrease in total iron concentration. This decrease presents a problem in the system in that a loss in total iron means a loss in ferrous ion, which is necessary for NO_x removal.

5. Aluminum

There were no unusual occurrences in regards to equipment operation and the run was basically clean in terms of undesirable side reactions causing problems in the system. The sulfites, sulfates, calcium, and magnesium ion concentrations were typical for the ThioNO_x process. Although there were no unusual occurrences with the 5 kW chemistry, the aluminum ion concentration remained very low throughout the test indicating the poor ferrous ion regeneration capability of this agent.

6. Hydroxylamine Sulfate

Operation of the 5 kW with the addition of hydroxylamine sulfate as the regeneration agent proved to be relatively routine. There were no unusual occurrences in regards to equipment operation. However, the system chemistry was effected by the addition of hydroxylamine sulfate since this regeneration agent served as a source of sulfate anion. As an example, the sulfate ion concentration increased from 5,844 ppm at the beginning of testing to 21,326 ppm at the end of testing for DT032594. This explains why the calcium ion concentration increased from 169 ppm initially to 772 ppm finally. The cation concentration must increase to balance the increase in anion concentration. The increase in calcium concentration and sulfate concentration will lead to gypsum scaling throughout the system if testing is extended in time.

The filtercake solids content averaged 60.6 wt. % solids for test DT032494 and 51.0 wt. % solids for test DT032594. This is a low solids content for the ThioNO_x process. One of the economic advantages of ThioNO_x is the increase in percent solids represents a cost savings in the waste disposal cost. For instance, an increase from 55 wt. % solids to 80 wt % solids represents a 47% reduction in the mass of water sent to the landfill

7. Hydrazine Sulfate

The sulfate ion increased in concentration as testing continued along with the calcium ion concentration. This could be a potential problem since extended testing would result in scale formation.

8. Hydrazine Hydrate

As hydrazine hydrate was added to the system, it began to accumulate in the scrubbing liquor. Initially residual hydrazine was calculated at 2.32 mM but increased by the end of testing to 171.4 mM. Hydrazine is a suspected carcinogen so it is critical that high levels do not accumulate in either the waste or the absorber liquor. The ability to control residual hydrazine in the absorber liquor will be the deciding factor in using hydrazine as a regeneration agent. There was no problem with clogging in the tubing as observed in other 5 kW tests using different chemical regeneration agents.

9. Sodium Sulfide Hydrate

For the long term tests there were several difficulties encountered in operating the 5 kW using sodium sulfide as the regeneration agent. Due to the black liquor accompanied by the black scale coating the equipment, continuous operation of all equipment was impossible. Buildup of the black scale in the tubing caused many clogs, resulting in leaks which required immediate attention. Many of these leaks occurred in the tubing between the heat exchanger and recycle tank. These leaks required shutting down the flow

between the heat exchanger and recycle tank for periods of time while the tubing was being changed or cleaned. Often the tubing between the recycle tank and the top of the scrubber had to be cleaned as well, requiring shutting down the recycle flow. Since the black liquor made it impossible to view the activity inside the scrubber, operators were unable to see the flooding occurring in the column at one point during testing. This flooding caused the liquor to foam out of the scrubber column. This problem was corrected by reducing the liquid feed rate to the column.

One possible explanation for the formation of the black liquor and scale is the formation of iron sulfide which is the product of a reaction between the added sulfide ions and iron in the system.

The thiosulfate and sodium ion concentrations increased as testing progressed for each test run. It has been reported by Ellis and DeBerry (Radian Corporation) that thiosulfate in combination with chloride can cause corrosion of metals that may be used in scrubber equipment. Excessive sodium ion may also poison the pH probes. It also represents a potential filtercake contaminant material.

10. Sodium Tetrasulfide

There were several difficulties encountered in operating the 5 kW using sodium tetrasulfide as the regeneration agent. During test DT050394, plugging occurred in the heat exchanger tubing which caused the loss of 4.5 liters of liquor from the recycle tank. For test DT050694 SO₂ removals were lower than for tests DT050394 and DT050594 most likely due to solids build-up in the recycle lines.

In addition to plugging, thiosulfate continuously increased for all three tests. For test DT050594, sodium tetrasulfide addition had to be terminated due to high levels of thiosulfate ion. Sodium ion levels increased as well.

11. Sulfide/Polysulfide

No tests were conducted in Phase I with emulsified sulfur addition to the recycle tank. Testing of this agent under a different project revealed that NO_x removal was well below the target NO_x removal established in the test plan.

12. Ammonium Thiosulfate

No tests were conducted in Phase I with ammonium thiosulfate addition to the recycle tank. Ammonium thiosulfate is believed to be a less effective regeneration agent than sulfide/polysulfide. Because sulfide/polysulfide was not found to have ferrous ion regeneration ability, tests with ammonium thiosulfate were not carried out.

C. Thermal Regeneration

Operation of the 5 kW with the addition of the thermal regeneration vessel provided a normal ThioNO_x chemistry. The magnesium, calcium, sodium, sulfate, and sulfite ion concentrations were within the normal range for the ThioNO_x process. There were also no unusual occurrences in regards to equipment operation. However, the NO_x removal increase was only 10% higher than that observed for the baseline tests.

D. Electrochemical Cell

There were several difficulties encountered in operating the 5 kW using an electrochemical cell as the regeneration method. Because of the short time scale of the 5.5 hour test, few major difficulties were observed. On the other hand, due to either build-up of scale or solids in the system, continuous operation of all equipment was impossible for the 51 hour test. On several occasions, the recycle pump became plugged and had to be shut down and cleaned or the tubing had to be changed. This was an unusual occurrence because solids do not usually build up in the recycle tubing. The heat exchanger was shut down

and flushed with hydrochloric acid due to clogging trouble. Solids also built up in the electrochemical cell on at least one occasion, requiring a reduction in power supplied to the electrochemical cell and periodic flushing of the cathode with hydrochloric acid.

For the short term test, DT011395, the liquor chemistry was standard and no problems with plugging or equipment occurred. Synthetic liquor was added to the recycle tank to replenish evaporative losses in the scrubber. The electrochemical cell functioned without problems except for the formation of yellow solids in the anolyte solution 3.5 hours into the test run.

For the electrochemical cell tests conducted at Eltech, the volume of catholyte solution was reduced for tests 6 through 7 to ensure higher changes in ferrous ion concentration. This improved the accuracy of the calculated current efficiency of the electrochemical cell.

During tests 2 and 3 bubbles were observed forming between the cathode and cell wall. These bubbles were hydrogen gas and were due to the electrolysis of water. The hydrogen bubbles function as an insulator for the cathode, further increasing the voltage. Elevations in the voltage lead to undesirable side reactions. One such reaction is the reduction of ferrous ion to form metallic iron. This was observed for tests 1 through 4 where iron was deposited on the diaphragm and cathode. To alleviate these problems, the catholyte flow rate was increased for tests 6 through 8 to flush out hydrogen bubbles on the cathode screen. This helped decreased the mass transfer resistance to the cathode surface.

In test 5 use of diluted sulfuric acid solution as an anolyte increased the cell voltage beyond the capability of the rectifier used at Eltech. This might be explained by the coating of H_4EDTA observed on the diaphragm. A similar coating was observed for tests DT101094, DT101194, DT101494, and DT102094 where sulfuric acid was used as anolyte. Subsequently, magnesium sulfate solution was chosen as the anolyte because of its higher conductivity.

E. Combination of Strategies

Problems occurring with the electrochemical cell/heated thickener overflow surge tank are outlined in the electrochemical cell section. No tests were carried out with any other combination of regeneration techniques.

IV SUMMARY

A. Baseline Tests

For the baseline tests where the initial total iron concentration varied between 100 mM and 50 mM with and without packing inserted in the absorber along with variable flue gas oxygen contents, SO₂ removals were usually above 98% after a short time period. The steady state NO_x removal was 15% to 20% for all tests except that conducted at low flue gas oxygen content. At 3 vol.% oxygen in the flue gas, the steady state NO_x removal was above 20%. This indicated that lower oxygen concentrations in the flue gas decrease the oxidation rate of ferrous ion resulting in higher ferrous ion concentrations. As a result of these baseline tests, it was found that any removal above 20% was due solely to the regeneration method employed.

B. Chemical Regeneration Agents

1. Sodium Dithionite / Ascorbic Acid

The cost of a 5:1 weight mixture sodium dithionite / ascorbic acid was determined. The cost of sodium dithionite / ascorbic acid on a mM ferrous ion concentration basis was found to be \$0.01332/day·mM Fe⁺²·vol.% O₂. On an NTU removal basis, the cost was determined to be \$0.9954/day·NTU·vol.% O₂. The cost was considered economically unfavorable and a search was carried out for lower cost regeneration methods. This experiment served as an important measuring stick on which to base all other testing.

2. Iron

SO₂ removal in the range of 98% to 100% was achieved with L/G of 88 and recycle tank liquor pH of 6.0. NO_x removal ranged from 25% to 30% for both tests. Economically, it is one of the most effective regeneration methods that were examined. For test

DT032294, the filtercake solids content averaged 55.3 wt. % while for test DT031794 the filtercake solids content averaged 62.6 wt. %. This was a low solids content for a ThioNO_x process. Consequently, iron does not meet all the criteria established in the test plan.

3. Iron Using a Digester

SO₂ removals reached 99% at various times for the test runs. The NO_x removal varied between 40% and 50% for the test runs carried out. This is higher than the NO_x removals obtained with iron additions directly to the recycle tank. Unfortunately, if the iron is added in larger quantities the fraction of iron utilized will decrease. The undissolved iron settles to the bottom of the settling tank. The solubility of iron would increase at lower pH values but the SO₂ removal in the absorber would be lower. The economics of iron with a digester is similar to that without a digester forming one of the most cost effective methods for NO_x removal. The filtercake solids content was low for each of the tests. For the short term tests the final solids content was below 50 wt.% while for the long term test, the average solids content was 58.6 wt. %. The poorer dewatering ability of the filtercake can be attributed to the presence of an iron compound present in the solids. The iron compound presumably formed in a side reaction in which iron participates as iron hydroxide. Even with this process modification, the dewatering of the landfill material is not met.

4. Zinc

Due to the low pH of 5.5 in the recycle tank, necessary for dissolution of zinc, SO₂ removal did not meet the target expressed in the test plan. NO_x removal was not significantly higher than that observed for the baseline tests. The total iron concentration declined during testing which could be due to zinc replacing iron in iron-EDTA to form zinc-EDTA. A loss in total iron implies there is a loss in ferrous ion as well. As a result of these findings, zinc was deemed inappropriate as a regeneration agent.

5. Aluminum

The SO₂ removal was below the criteria declared in the test plan. Similar to the zinc experiment, the recycle tank pH averaged 5.7 which lowered SO₂ absorption into the ThioNO_x liquor. After the NO_x removal leveled off, it was no higher than the removals observed for the baseline tests. The dewatering criteria outlined in the proposal and test plan were also not met. Clearly, aluminum is inappropriate as a regeneration agent. This is demonstrated in the consumption economics which shows aluminum to have one of highest costs for NO_x removal.

6. Hydroxylamine Sulfate

The SO₂ removal criteria was met with this regeneration agent after increasing the L/G from 44 to 88. No improvement was observed in NO_x removal compared with the removal obtained for the baseline tests indicating no ferrous ion regeneration ability. The economics of this agent reveal that it is the most expensive method available for NO_x removal. The filtercake solids content averaged 51.0 wt. % for one test and 60.7 wt.% for another test. The dewatering characteristics do not meet the goal of the test plan. Subsequently, hydroxylamine sulfate has been discarded as a potential regeneration agent.

7. Hydrazine Sulfate

The SO₂ removal criteria was met for this agent. However, the NO_x removal goal was not met with the steady state NO_x removal averaging 35%. Hydrazine sulfate had the second highest cost for NO_x removal. The solids content of the filtercake met the criteria established in the test plan. Higher additions of hydrazine sulfate are limited by accumulation of this material in the ThioNO_x liquor and filtercake. Because of the accumulation of sulfate ions to the system with addition of hydrazine sulfate, this agent will not be further tested for its ferrous ion regeneration abilities.

8. Hydrazine Hydrate

The SO₂ removal was between 98% and 99% for the duration of the test. For this agent, the NO_x removal target was met which is substantially different from the results of other chemical regeneration agents. Residual hydrazine accumulated in the 5 kW liquor as testing progressed suggesting that lower addition rates of hydrazine hydrate should be made to lower the amount of residual hydrazine in the liquor and landfill material. The toxicity of hydrazine prevents this agent from being a suitable regeneration agent. This agent met all the criteria in the test plan except for the toxicity requirement for the waste material.

9. Sodium Sulfide Hydrate

During the long term test, there were many times when the SO₂ removal dropped below 97%. Consequently, the SO₂ removal objective was not met for this agent. The NO_x removal curve was highest for the long term test where NO_x removal was between 35% and 45% for much of testing showing promise as a regeneration method. Unlike previous tests, the NO_x removal was low for the high concentration of ferrous ion observed in the system. The thiosulfate ion concentration accumulated in the liquor due to the reaction of sulfide with sulfite ion. This could pose a problem if calcium ion levels displayed an increase to maintain charge balance.

The dewatering goals in the proposal were met. For instance, the solids varied from 62 wt. % to 75 wt. % for the long term test. Because of the formation of black scale in the scrubber for the long term test, sodium sulfide hydrate is not suitable as a chemical regeneration agent.

10. Sodium Tetrasulfide

The SO₂ removal was lower than expected for several of the runs. For one run, it never exceeded 95%. The highest steady state NO_x removal achieved was between 25% and 30%. The quantity of sodium tetrasulfide added to the system did not affect the level of NO_x removal. In fact, no enhancement to NO_x removal over that of the baseline tests was observed. The solids dewatering goal stated in the test plan was met. Due to the low NO_x removal, sodium tetrasulfide is considered ineffective as a regeneration agent.

11. Sulfide/Polysulfides

Prior testing with emulsified sulfur containing polysulfides gave NO_x removals less than 30%. As a consequence of this testing, screening tests were not performed with emulsified sulfur added to the recycle tank.

12. Ammonium Thiosulfate

In the proposal, for Phase 1, ammonium sulfate was selected as one of the chemical regeneration agents to be examined. Because of the low regeneration ability that emulsified sulfur was found to possess, it was felt that ammonium sulfate would not be an effective regeneration agent for ferrous ion. For emulsified sulfur, the sulfur reacts with calcium hydroxide to form thiosulfate and polysulfide ion. The polysulfide ion is believed to have a much higher regeneration activity than thiosulfate ion. Therefore, if emulsified sulfur exhibited low regeneration activity, then ammonium sulfate should have even a lower regeneration ability of ferrous ion.

C. **Thermal Regeneration**

The SO₂ removal target was met as set forth in the test plan. The final NO_x removal was 25% which is below the target established in the test plan. The dewatering characteristics

of the filtercake also met the goal outlined in the test plan. Because of the ease with which the thermal regeneration mode could be incorporated in the 5 kW system it was decided to implement this concept to the electrochemical cell. This could be performed by heating the thickener overflow surge tank. This technique is ideal in that the ThioNO_x chemistry is not effected by elevated temperatures in the surge tank. However, the thermal regeneration mode by itself does not meet the NO_x removal goal.

D. Electrochemical Cell

The SO₂ removal reached between 98% and 99% many times during the 48 hour long term test. This indicates the SO₂ removal goal was met for this regeneration method. NO_x removal ranged from 30% to 40% after steady state was achieved for the tests conducted. Although NO_x removal was not as effective with the electrochemical cell as with hydrazine hydrate, sodium sulfide hydrate, or iron using a digester, the chemical problems associated with these agents eliminated them from further testing. With the long term test, the filtercake solids was usually between 70 wt. % and 80 wt. % solids, meeting the solids dewatering goal set forth in the test plan. The electrochemical cell offers the best chance for meeting the stated objectives in the test plan. This is demonstrated by the favorable economics of the electrochemical cell (\$.000409/day·mM Fe⁺²·vol.% O₂ and \$.0208/day·NTU·vol.% O₂) against other regeneration methods examined.

Several performance parameters were identified and their operating values determined. It was discovered that a high catholyte liquid flow rate (>5.0 l/min) helps maintain a low voltage across the electrochemical cell. Magnesium sulfate solution functioned well as an anolyte also helping to maintain a low voltage across the electrochemical cell.

E. Combination of Strategies

All results of the combination of electrochemical cell/thermal regeneration vessel are reported in the electrochemical cell section. The other combination strategies outlined in

the test plan were not feasible due to chemical problems associated with hydrazine hydrate, sodium sulfide, and iron using a digester.

F. Discussion

The goals of Phase 1 of this project were to develop a wet scrubbing process based on iron chelate chemistry which could achieve +98% SO₂ removal and +60% NO_x removal, easily retrofitted to existing scrubbers, and be cost competitive with other NO_x removal technologies. In prior testing sponsored by the Department of Energy at the Miami Fort pilot plant, the combination of the Thiosorbic lime process for SO₂ removal and the iron chelate process for NO_x removal was demonstrated to be effective in removing these pollutants within the same scrubbing tower. Dravo Lime Company designated this process as the ThioNO_x process. The shortcoming of this pilot plant testing was a method for economically regenerating the iron chelate to the ferrous form. Ferrous chelate is the active form of the iron chelate required for NO_x removal.

Phase I of this project focused on evaluating various methods of regeneration at the bench scale level on Dravo Lime Company's 5-kW test scrubber apparatus. As detailed in this report, each of the methods investigated could not achieve the goals set forth at the beginning of the project. Methods utilizing iron, sulfates, sodium, hydrazine, and sulfides introduced new chemical species into the process chemistry which degraded the dewatering of the calcium sulfite filter cake, increased scale formation, or contaminated the by-products to be landfilled. Chemical additions of zinc, aluminum, and ammonium thiosulfate and thermal regeneration were ineffective in regenerating sufficient quantities of ferrous iron required for the NO_x removal process.

However, the potential of the electrochemical cell appeared to overcome the shortcomings of these other regeneration methods and considerable effort was spent in its development for this application. The generation of electrons by the electrochemical cell to convert ferric iron to ferrous iron had virtually no other detrimental impact on the process

chemistry. Electricity consumption would be minimal because the efficiency of the cell for the conversion was over 90%. But through the continued development of the electrochemical cell, other cell related constraints became apparent. The combination of deposition and crystallization of calcium sulfite and EDTA decreased the efficiency of the cell as the electrode surface area was lost as a result of these two phenomena. To minimize these problems, the cell current density was lowered to 25 amps/ft² and the catholyte flow rate was increased to 7 l/ft². These actions minimized but did not eliminate the deposition. Significant increases in both the capital and operating costs resulted from these actions due to the increase in the number of cells required and the associated pumping costs. The preliminary cost analysis based on the best performance of the electrochemical cell estimated capital costs of 263 \$/kW and levelized operating costs of 3413 \$/ton NO_x removed for a 300 MW generating station.

As a result of the findings of this report based on the failure of Phase I testing to achieve the project goals, it is recommended that the efforts as outlined for Phase II of this project not be pursued.

V. APPENDIX

A. Miami Fort Pilot Plant Operation

1. Objectives

Four weeks of testing were conducted at the Miami Fort Pilot Plant Facility (3/13/95 - 4/7/95). The objectives for this phase of testing varied with each week of operation. The overall goal was to prepare the pilot plant for long term SO_2/NO_x removal testing based on the results of sodium sulfide regeneration of iron chelates from the bench scale 5 kW scrubber evaluations. The objectives for each week of operation are covered below.

There were three objectives for the first week of testing. The first goal was to shakedown the pilot plant equipment which had been inactive during the winter. Immediately following shakedown, the second goal would be to establish a Thiosorbic scrubbing liquor chemistry which would be utilized for the Thio NO_x NO_x removal process. The liquor chemistry targets were a magnesium ion concentration of 4,500 ppm and a minimum alkalinity of 1,500 ppm (measured as carbonate). The third objective was to establish a total iron concentration of 45 mM in the process chemistry in preparation for the following week of testing.

For the second week of operation, NO_x removal studies using a sodium sulfide solution as the ferrous ion regeneration agent were initiated. The objective of these studies was to reestablish baseline NO_x removal conditions at 15 mM ferrous ion which could be compared to prior studies funded by the Department of Energy which were conducted at the same ferrous ion concentration while utilizing sodium dithionate/ascorbic acid as the regeneration agent. Such studies will indicate whether the regeneration agent utilized to achieve the desired ferrous ion concentration has an impact on the corresponding NO_x removal.

The objective for the third week of process testing was to achieve 60% NO_x removal. This was to be accomplished by establishing liquor chemistry targets of 115 mM total iron and 75 mM ferrous ion. The total iron concentration was required to be increased to 115 mM to ensure sufficient iron was available for conversion to the ferrous form. The ferrous ion target would be achieved by incremental increases in the sodium sulfide additions until the desired target was achieved.

The last week of operation was devoted to investigating the conversion efficiency of the reducing agent mixture of sodium dithionate/ascorbic acid as compared to sodium sulfide which was introduced into the process both as a dry powder and a solution. As a result of the by-products of sodium sulfide decomposition within the system increasing in concentration, it was important to verify the original baseline NO_x removal results at the ferrous ion concentration of 15 mM utilizing the sodium dithionate/ascorbic acid mixture. To ensure that the utilization of sodium sulfide for regeneration of the ferrous ion was not compromised by dissolving the sodium sulfide in water before entering the process, this regeneration agent was added to the process in its original powder form so as to determine the amount required to maintain 15 mM ferrous ion and the corresponding NO_x removal.

2. Discussion, Test Results, and Attainment of Objectives

a) Discussion

To build the Thiosorbic liquor chemistry, magnesium hydroxide was added to the system to quickly increase the alkalinity, magnesium, and sulfite ion concentrations. The system chemistry was observed to strengthen the most the last day of operation where the alkalinity reached 4,000 ppm, magnesium ion concentration 7,500 ppm, and sulfite ion concentration 4,000 ppm. The added magnesium hydroxide also controlled the pH of the mix tank solution which was a combination of ferrous sulfate and EDTA added to prepare the liquor for the NO_x removal process. In the absorber, 12 feet of PN-FILL packing was inserted to aid

in mass transfer of NO_x into the scrubbing solution. Other operating conditions associated with the absorber were a liquid to gas ratio with quench spray of 45.5 with scrubber velocity of 8 ft/sec. The absorber conditions were kept similar to the scrubber conditions used for 5 kW testing in order to produce comparable data with the 5 kW results.

On the fourth day of operation ferrous sulfate and EDTA were added to the liquor to produce high levels of total iron. The reagents were combined in a mix tank and dissolved in 600 gallons of liquor provided by the thickener overflow tank. The composition consisted of two 50 lb bags of magnesium hydroxide, 4 bags of EDTA, and three 50 lb bags of ferrous sulfate. Although the total iron concentration was 45 mM, the ferrous ion concentration was negligible since ferric ion was not being reduced to ferrous ion by a chemical regeneration agent. If a chemical regeneration agent such as sodium sulfide had been added the ferrous ion concentration would have shown an increase. The building up of ferrous ion was observed later during testing.

The second week was characterized by regeneration agent addition. This occurred on the third day of process testing where the addition of the regeneration agent was observed to have a positive impact on the ferrous ion concentration in the system as it reached 15 mM. This provides unequivocal evidence of the ability of sodium sulfide to maintain ferrous ion. In this manner, it is similar to the testing conducted in 1991 where addition of sodium dithionate/ascorbic acid was also added to maintain 15 mM ferrous ion concentration. In order to maintain a target ferrous ion concentration of 15 mM, a minimum of 15.0 lbs/hr of sodium sulfide was added to the recycle tank. The 15.0 lbs of sodium sulfide/hr corresponds to 87.2 g-moles of sodium sulfide/hr which is higher than the g-moles of sodium dithionate/ascorbic acid required to maintain 15 mM ferrous ion concentration. This indicates that sodium sulfide has a lower ferrous ion regeneration activity than sodium dithionate/ascorbic acid. The increasing ferrous ion concentration

translated into higher NO_x removals which were in the range 25% to 35%. During the first week of testing with no ferrous ion in solution the NO_x removal was below 10% which demonstrates NO_x removal depends on the ferrous ion concentration.

The target total iron concentration and ferrous ion concentrations were increased the third week of testing in order to obtain a NO_x removal of 60%. The target levels were 115 mM total iron and 75 mM ferrous ion. Sodium sulfide additions varied during the week from 20 to 63 lbs/hr in an effort to achieve 75 mM ferrous ion. NO_x removal was 46% at 63 lbs/hr sodium sulfide addition with a ferrous ion concentration of 65 mM. Even at 63 lbs/hr sodium sulfide addition, a ferrous ion concentration of 75 mM could not be reached. At 20 lbs/hr sodium sulfide addition, NO_x removal was 35% with a ferrous ion concentration of 20 mM demonstrating that the greater the ferrous ion concentration the higher the NO_x removal. The inability of ferrous ion to reach 75 mM even with a total iron concentration of 115 mM further supports the hypothesis that sodium sulfide possesses a low regeneration activity.

It was during this week that the filter cake solids content displayed a significant rise to 60 wt.%. This is believed to be the by-product of NO_x removal since this was the first full week in which a regeneration agent was added. This enhancement in the filtercake solids content with the ThioNO_x process is an attractive feature to this technology since landfill cost of the sludge is reduced.

The thiosulfate ion concentration increased to 27,500 ppm by the end of the week without showing signs of levelling off during this testing period. Thiosulfate ion is formed in a side reaction involving sulfite ion and elemental sulfur. Sulfur is formed by the oxidation of sulfide ion. With concentrations exceeding 20,000 ppm, the calcium ion concentration was at 2,000 ppm. At this calcium ion

concentration, a high scaling potential exists where the scale would be a combination of calcium sulfite/calcium sulfate.

The final week of process testing utilized sodium dithionate/ascorbic acid for one day as the chemical regeneration agent. Dry sodium sulfide and sodium sulfide in solution form were also introduced directly to the recycle tank and tested for their effectiveness at regenerating ferrous ion and NO_x removal. A mixture of sodium dithionate/ascorbic acid was added at 70 g-moles/hr at a cost of \$42.80/hr whereas both forms of sodium sulfide were added at 102 g-moles/hr at a cost of \$5.60/hr. In each case, the ferrous ion concentrations and NO_x removals were the same. Sodium sulfide has a much lower cost associated with it than the combination sodium dithionate/ascorbic acid but its regeneration activity for 16 mM ferrous ion is only 70% of the sodium dithionate/ascorbic acid mixture. Even so, based on the testing at Miami Fort, sodium sulfide is a more effective regeneration agent than a combination sodium dithionate/ascorbic acid. It is interesting that at 16 mM ferrous ion concentration, the NO_x removals were the same for both regeneration agents. The data also shows that NO_x removal did not depend on the method employed for sodium sulfide addition to the recycle tank. This finding will simplify the introduction of this regeneration agent into the Thio NO_x process.

b) Test Results

The SO_2 removal trend for the first week of testing is shown in Figure 162. From the graph it is evident that SO_2 capture is higher than 99% throughout most of the week. On the last day of operation, the alkalinity rose to 4,000 ppm, the sulfite ion concentration increased to 4,000 ppm, and the magnesium ion concentration rose to 7,500 ppm. This is shown in Figure 163.

With the addition of ferrous sulfate and EDTA on the fourth day of operation, the NO_x removal and total iron concentration increased to 25% and 45 mM,

respectively. However, the NO_x removal dropped to nearly 0% as ferrous ion in the system oxidized. This is shown in Figure 164. No regeneration agent was added during this week.

The SO_2 removal was greater than 99% for the second week of testing as shown in Figure 165. This high removal can be partially attributed to the alkalinity level exceeding 3,000 ppm. In the middle of the week sodium sulfide solution was added to the recycle tank in quantities of 10 to 20 lbs/hr as depicted in Figure 166. This resulted in an increase in ferrous ion concentration and in the corresponding NO_x removal. The effect of adding sodium sulfide solution on ferrous ion concentration is evident in Figure 166. As soon as sodium sulfide solution is added ferrous ion concentration shows a corresponding increase of 10 to 20 mM.

The SO_2 removal was above 99% throughout the third week of testing. This is partly made possible by the alkalinity ranging from 2,000 to 3,000 ppm. The SO_2 removal trend is shown in Figure 167. The thiosulfate ion concentration increased from 10,000 ppm at the beginning of the week to 27,500 ppm at the end of the week. The thiosulfate ion curve is shown in Figure 168. The addition rate of sodium sulfide varied from 20 lbs/hr to 63 lbs/hr during the week as shown in Figure 168. The ferrous ion concentration was observed to increase with higher sodium sulfide addition rates. For this week, the ferrous ion concentration varied from 15 mM to 65 mM. With ferrous ion concentrations above 60 mM, the NO_x removal reached 46%. This is shown in Figure 169.

SO_2 removal was greater than 99% the last week of testing as shown in Figure 170. Throughout Thio NO_x testing at the Miami Fort pilot plant, SO_2 removal was observed to be above 99%. This represents excellent removal. The first chemical regeneration agent to be added to the liquor the last week of operation was a 24 lb/hr mixture of sodium dithionate/ascorbic acid (5:1 weigh ratio). The second chemical regeneration agent to be added was 15 to 20 lbs/hr of dry sodium sulfide.

The third test involved 17 lbs/hr of sodium sulfide solution added. In each case the ferrous ion concentration ranged from 10 to 20 mM as shown in Figure 171. The NO_x removal for each chemical regeneration agent remained the same ranging from 20 to 30%.

c) Attainment of Objectives

For the first week, process testing was successful in developing a typical Thiosorbic scrubbing chemistry. From this perspective, the goals for this week were accomplished since the final alkalinity was above 3,750 ppm. In addition, the total iron chelate concentration was brought to 45 mM. This helped prepare the system for the Thio NO_x process in the following weeks.

In the second week of process testing, it was clearly shown that adding sodium sulfide regeneration agent can build up and maintain a ferrous ion concentration of 15 mM enabling comparisons to be drawn in terms of regeneration activity with testing conducted in 1991 using a combination sodium dithionate/ascorbic acid in which 15 mM ferrous ion concentration was maintained.

For the third week, 60% NO_x removal could not be achieved despite the addition rate of 63 lbs/hr of sodium sulfide. The ferrous ion concentration of 75 mM could also not be met with 65 mM being the highest ferrous ion concentration that could be reached.

For the final week, it was demonstrated that 17.5 lbs/hr of sodium sulfide and 24 lbs/hr of the combination sodium dithionate/ascorbic acid have the same NO_x removal at 16 mM ferrous ion concentration. It was also shown that the mode of sodium sulfide addition does not affect the NO_x removal at 16 mM ferrous ion concentration.

3. Significant Problems Encountered

There were no significant problems which developed during the first week of testing from 3/13/95 to 3/17/95. For the second week, the liquor in the thickener overflow tank had a pH of 7.0 for most of the week. At this pH, a fraction of the total iron will be unchelated to EDTA which will possess an affinity to calcium and magnesium ion. The thickener overflow tank pH was lowered to 6.5 by decreasing the recycle tank pH to 6.0. At a pH of 6.5, virtually all of the iron would remain chelated to EDTA. From 3/27/95 to 3/31/95 the thiosulfate ion concentration rose from 10,000 ppm to 27,500 ppm. This high concentration of thiosulfate ion significantly changes the ThioNO_x liquor. The increase in anion concentration will result in higher concentrations of both calcium and magnesium ion to maintain charge balance. The higher calcium ion concentration will lead to calcium sulfite/calcium sulfate scaling in the recycle tank as the thiosulfate ion concentration continues to increase. It also introduces an additional impurity in the filtercake as well as a possible interference with spectrophotometric methods. The concentration at which thiosulfate ion precipitates as calcium or magnesium thiosulfate was not determined. The last week of process testing was met with several problems as a result of excessive scaling. The scale resulted in temporary shut down of the pilot plant as the mist eliminator nozzles and recycle tank level control sensor were cleaned of scale deposits. The scaling resulted from high calcium ion concentrations brought into solution by elevated concentrations of thiosulfate ion.

4. Summary

Thiosorbic chemistry was established the first week of pilot plant operation where an alkalinity greater than 1500 ppm (as calcium carbonate) and magnesium ion concentration of 5,000 ppm were achieved. The high alkalinity and absorber packing enabled SO₂ removals greater than 99%. Later in the week, ferrous sulfate and EDTA were added to the system to reach a total iron concentration of 45 mM. With no regeneration agent,

oxidation quickly yielded low ferrous ion concentrations. Even so, the system was prepared for regeneration agent addition.

For the week of 3/20/95 to 3/24/95, the target total iron concentration of 35 mM and EDTA concentration of 43 mM were achieved. Sodium sulfide regeneration agent was found effective at maintaining a target ferrous ion concentration of 15 mM when added at 20 lbs/hr. This led to a NO_x removal of over 30%. When compared with similar testing performed in 1991 using the combination sodium dithionate/ascorbic acid at 15 mM ferrous ion concentration, the regeneration activity of sodium sulfide was found to be less than sodium dithionate/ascorbic acid.

In the third week of process testing it was demonstrated that increasing sodium sulfide additions to 63.5 lbs/hr could regenerate sufficient ferrous ion to achieve NO_x removals of 46%. As expected, the ferrous ion concentration and subsequently the NO_x removal declined when the sodium sulfide addition rate was reduced. The maximum NO_x removal of 46% and ferrous ion concentration of 65 mM were lower than the targets set for this week. The thiosulfate ion concentration increased from 10,000 ppm to 27,500 ppm which indicated the side reaction involving sodium sulfide was occurring extensively.

An economic evaluation of sodium sulfide addition was performed during the final week of testing. It was found that sodium sulfide had a lower cost at a ferrous ion concentration of 16 mM than a mixture of sodium dithionate/ascorbic acid although it has less regeneration activity. The NO_x removals at 16 mM ferrous ion concentration were the same for both regeneration agents. In addition, NO_x removal was found to be independent of the method of sodium sulfide addition. This means sodium sulfide can be introduced in solution form without any loss in regeneration activity.

This four weeks of effort demonstrated the ability of sodium sulfide to regenerate the ferrous ion in a more economical manner than the sodium dithionate / ascorbic acid mixture. However the side reactions of the sulfide with the sulfite ion within the scrubbing

liquor reduced the utilization of this additive and generated thiosulfate which began to interfere with the operation of the process. As a result of the significant increase in the Thiosulfate ion and the resulting scaling of the process equipment, testing at the pilot plant was suspended so that additional long term studies on the 5 kW bench scale scrubber could be pursue to remedy these problems.

Figure 162. SO₂ Removal Versus Time

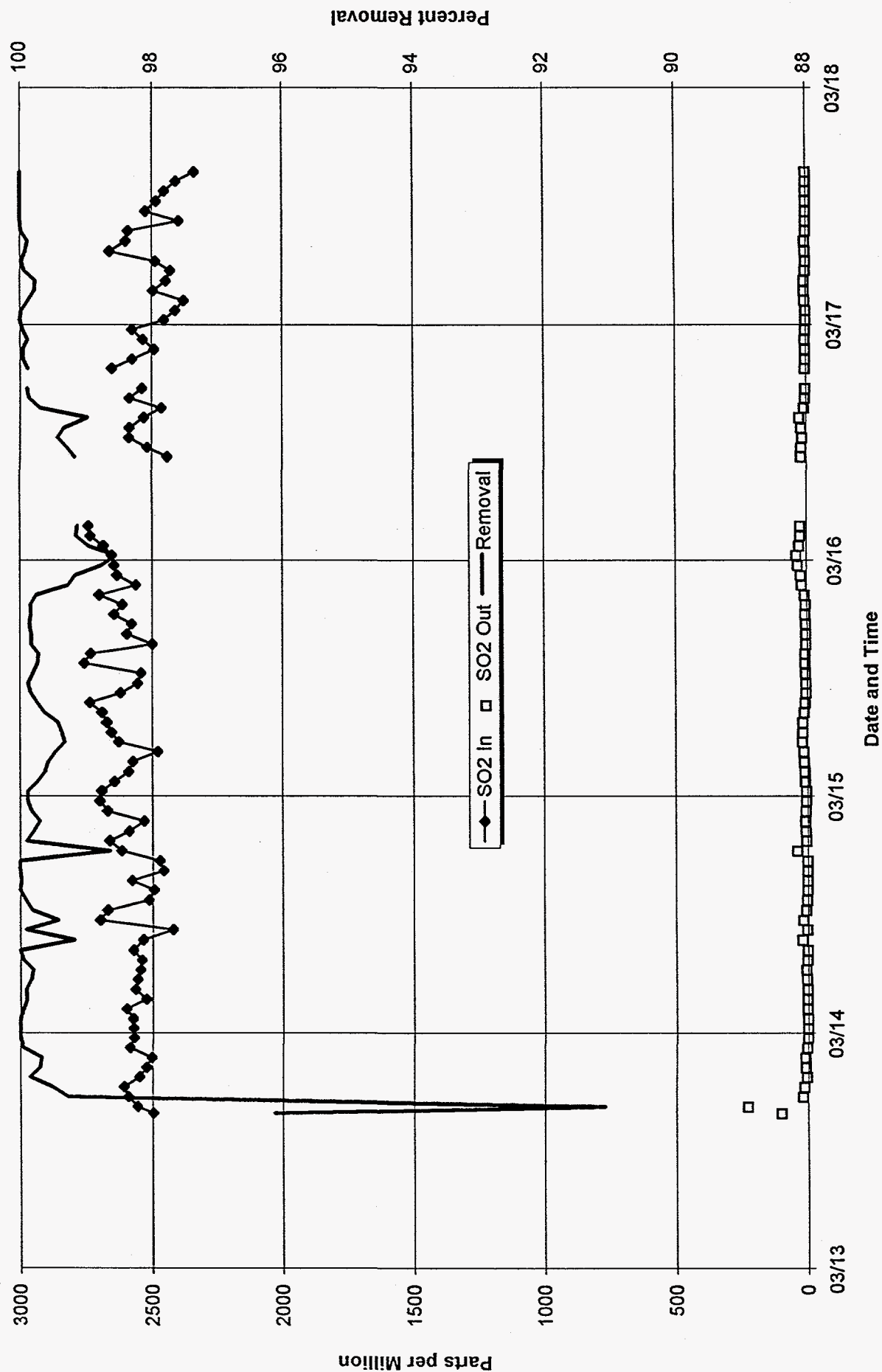


Figure 163. Recycle Tank Liquor Chemistry with Date

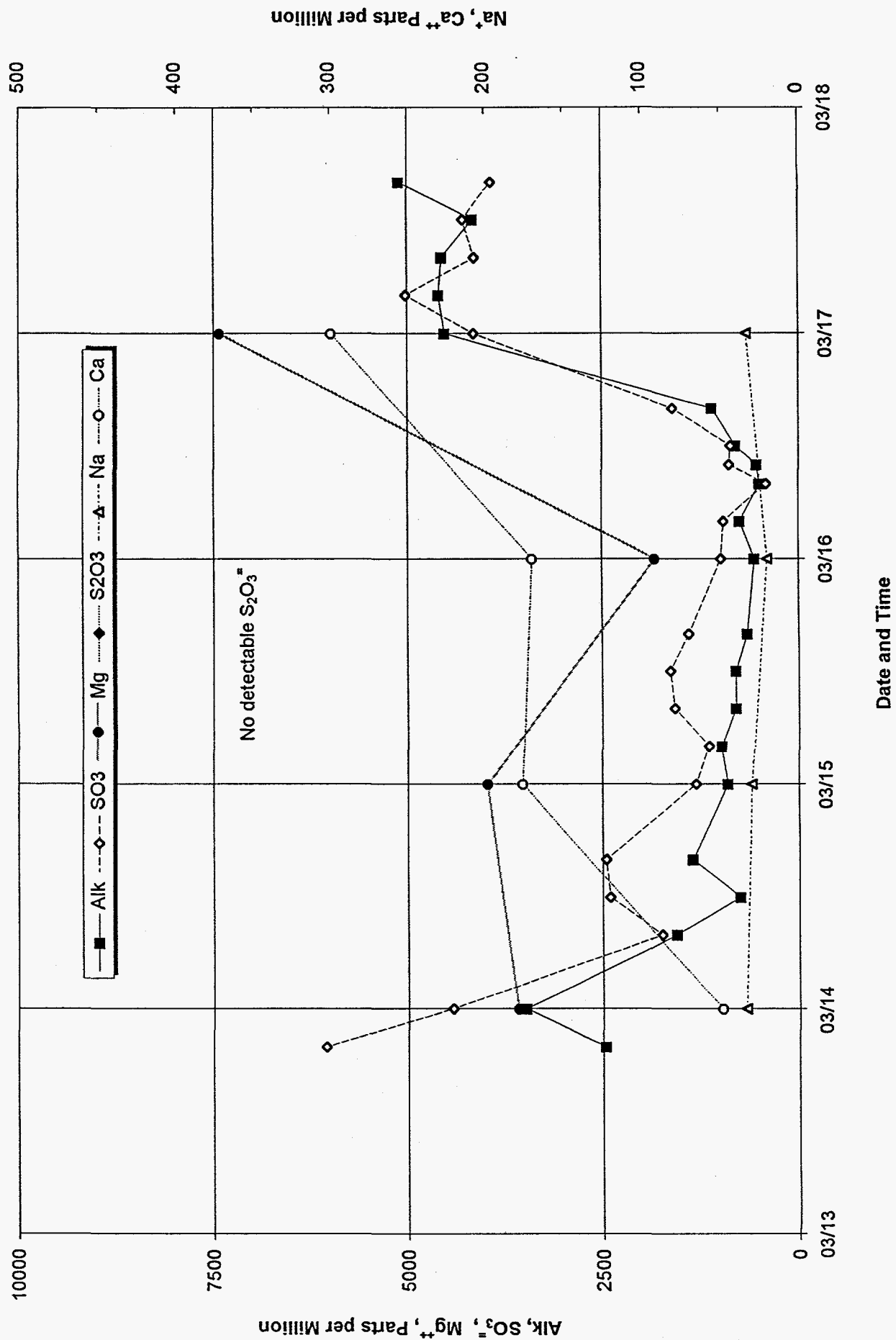


Figure 164. NO Removal Versus Time

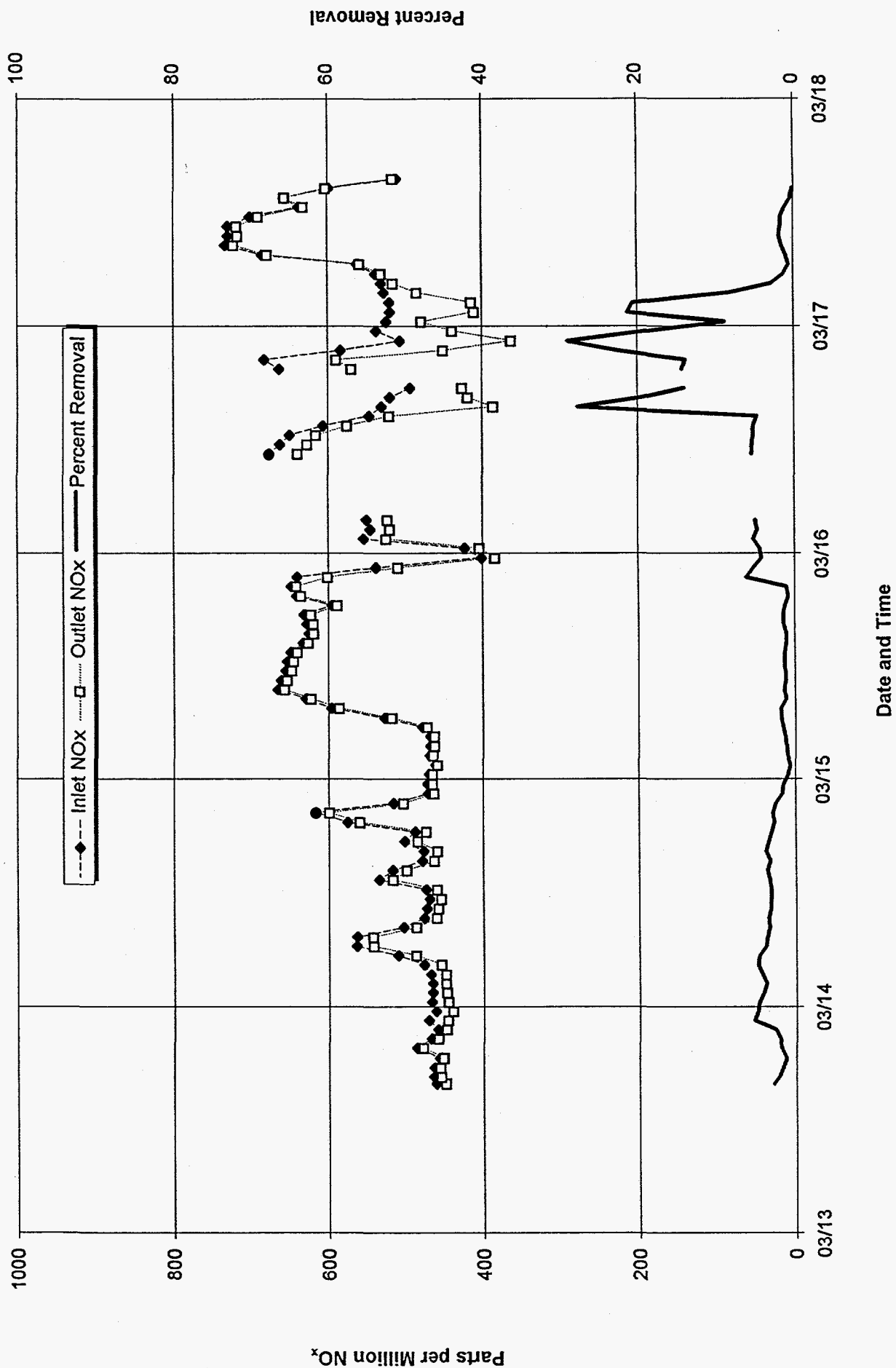


Figure 165. SO₂ Removal

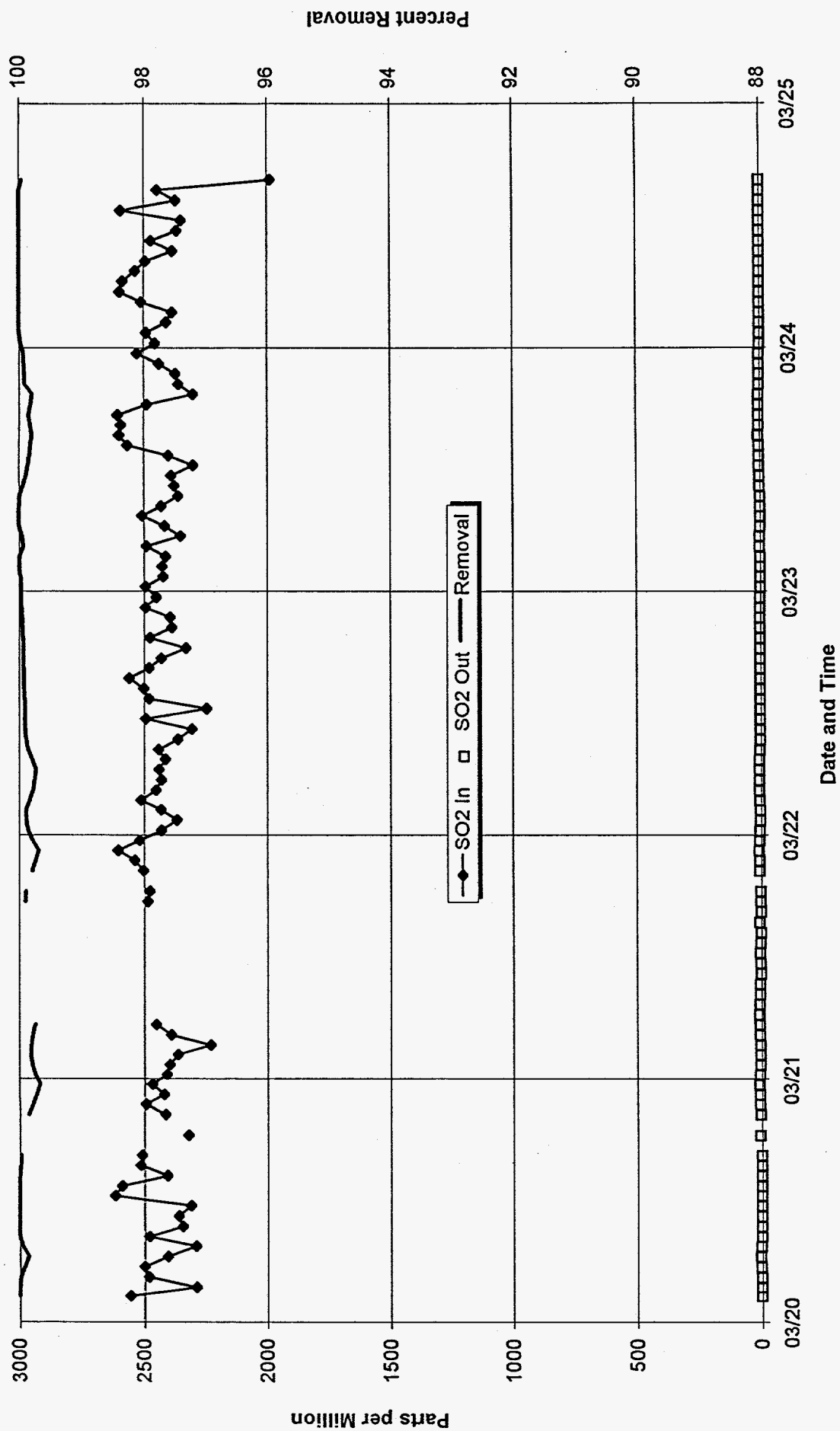


Figure 166. Regeneration Reagent, Ferrous Concentration, NO_x Removal, Inlet O₂

Date and Time

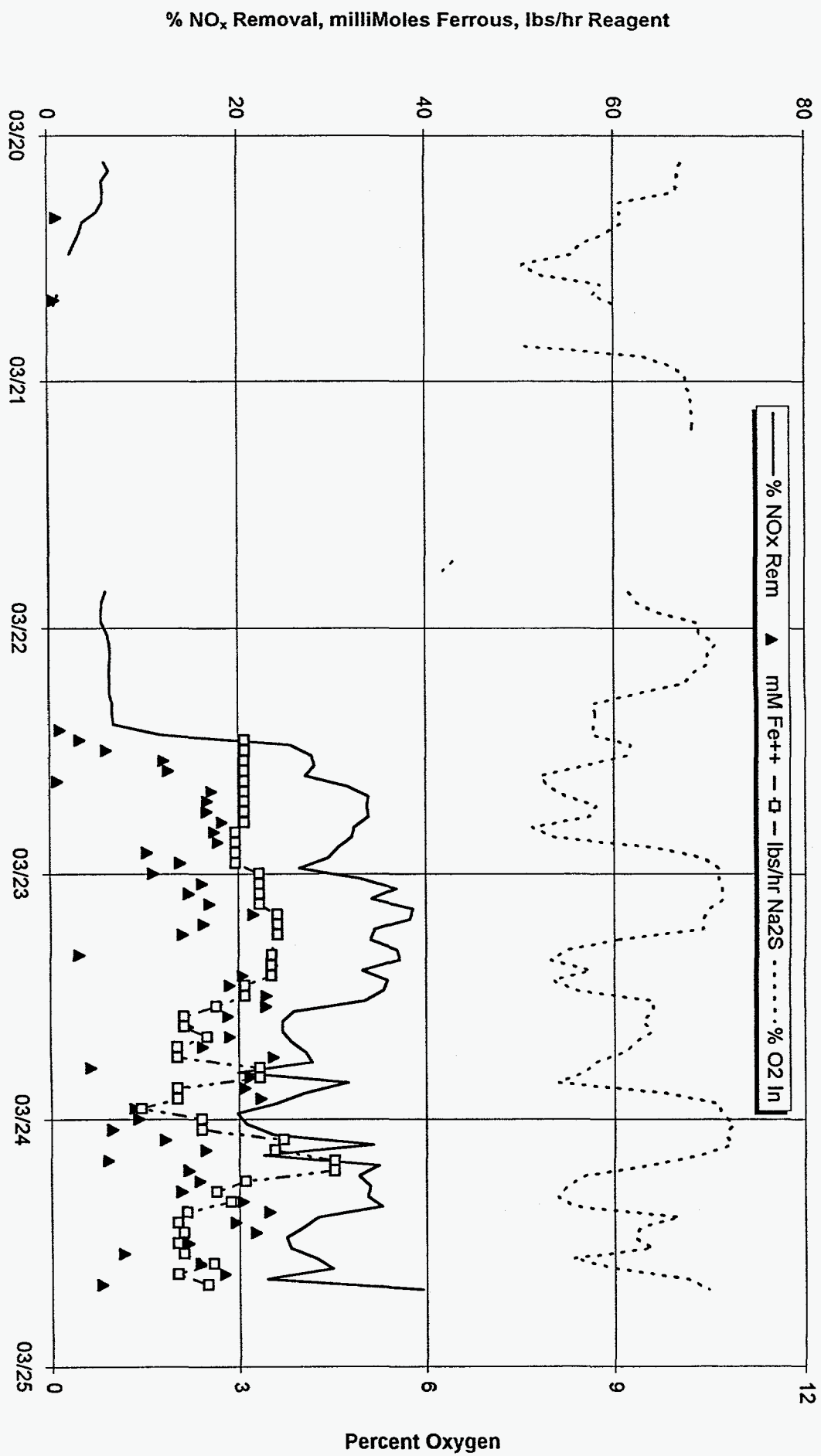


Figure 167. SO₂ Removal

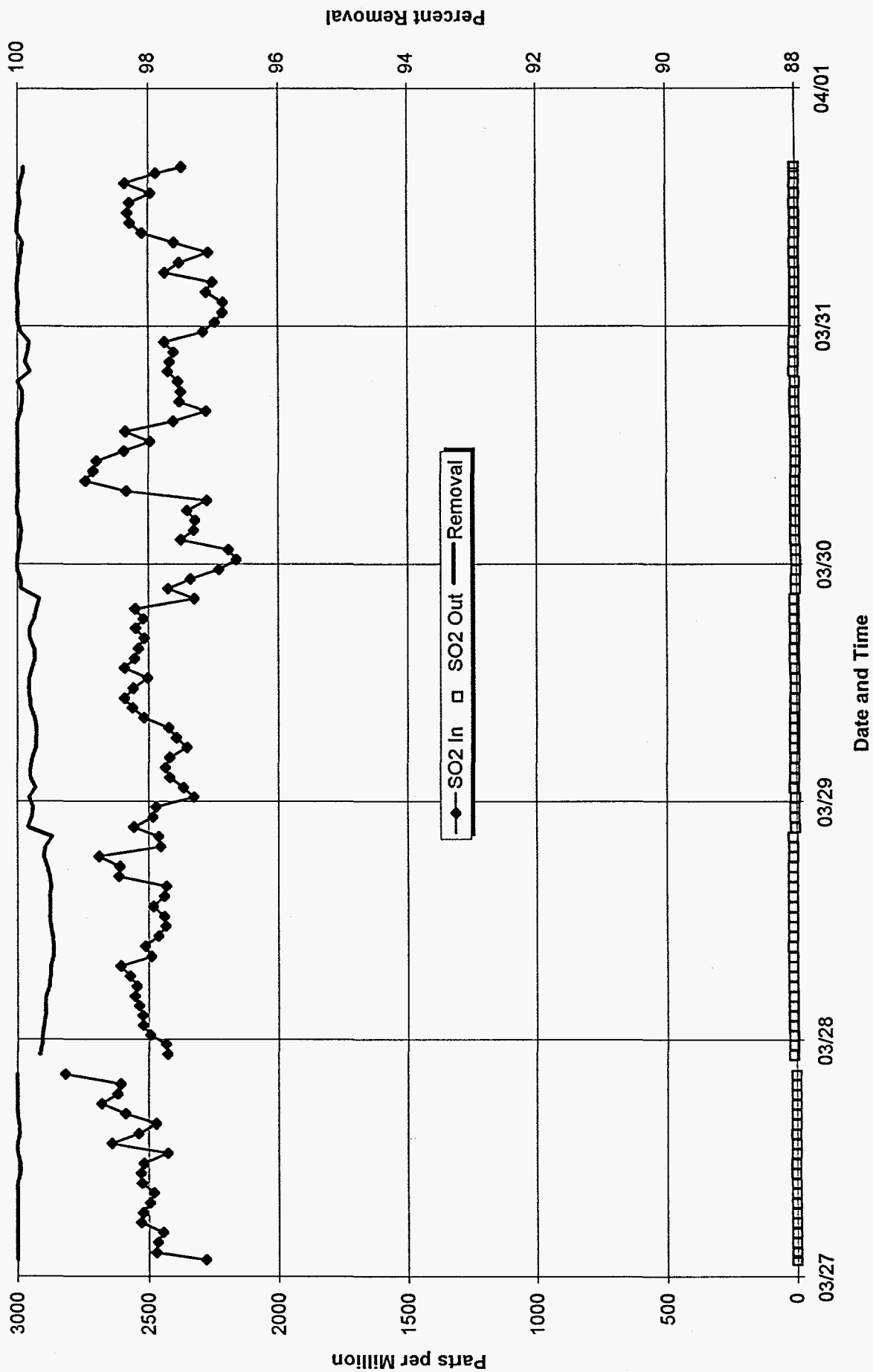


Figure 168. Sulfite and Thiosulfate Concentrations and Regeneration Reagent Rate

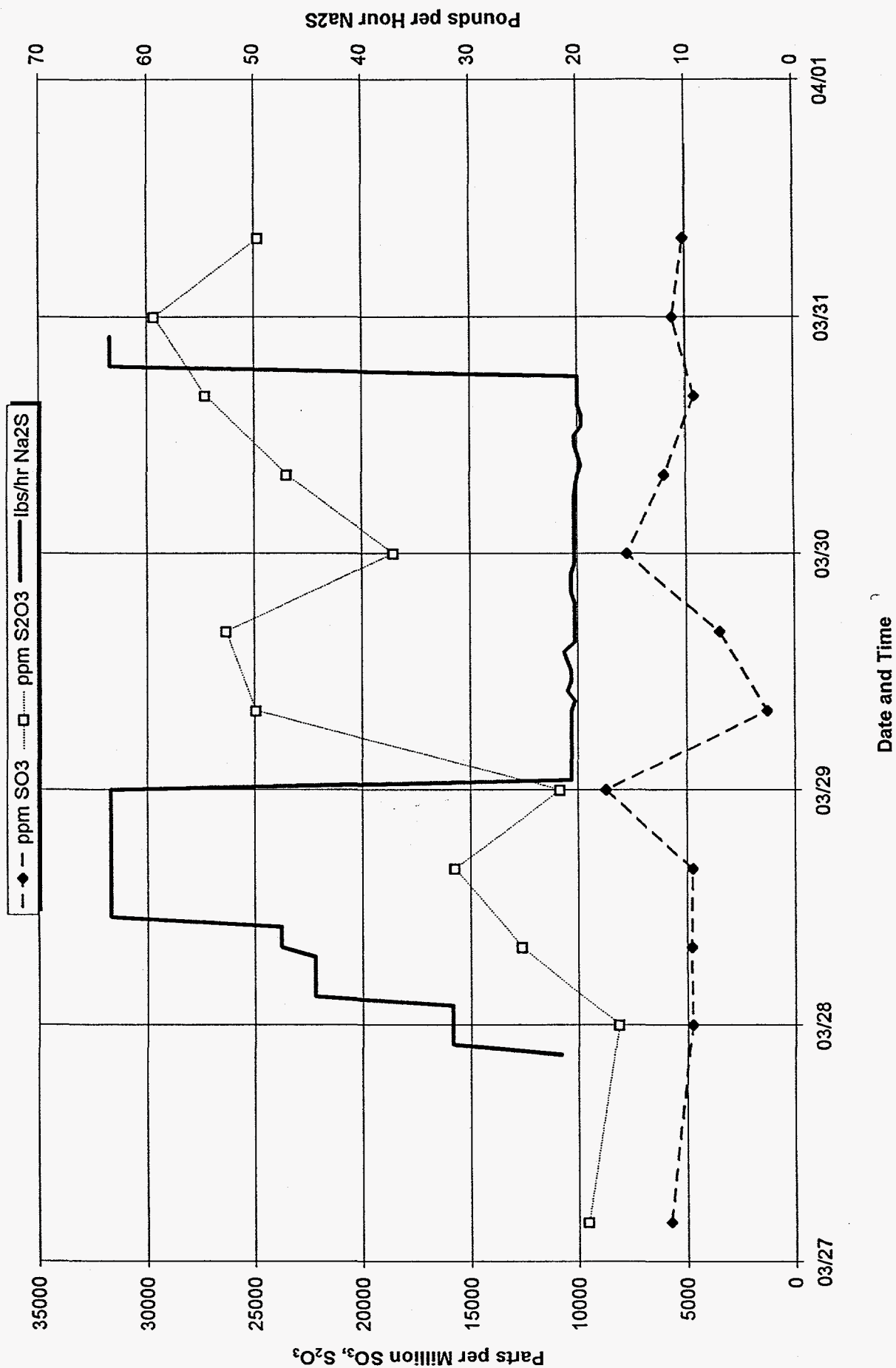


Figure 169. Regeneration Reagent, Ferrous Concentration, NO_x Removal, Inlet O₂

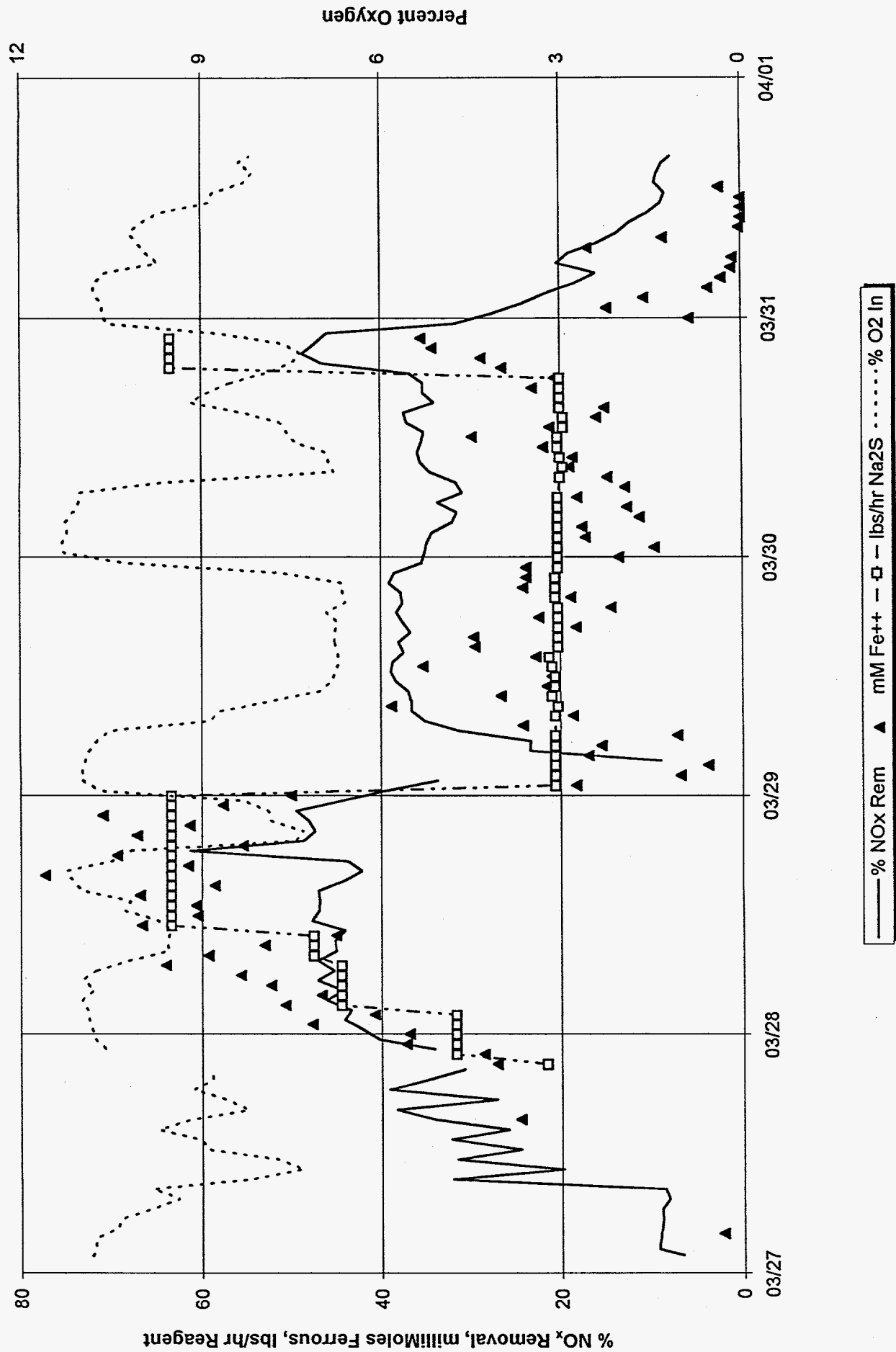


Figure 170. SO₂ Removal

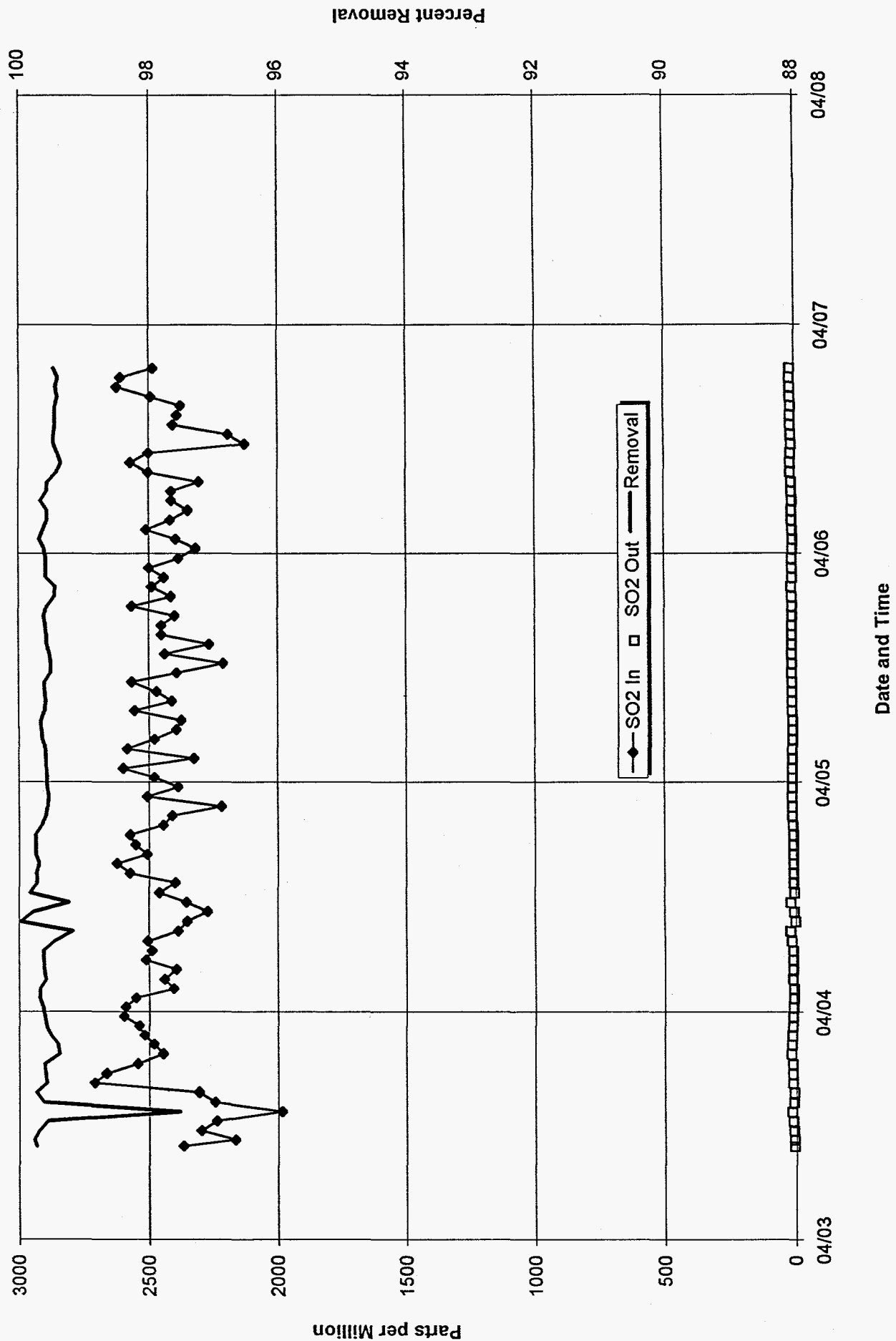
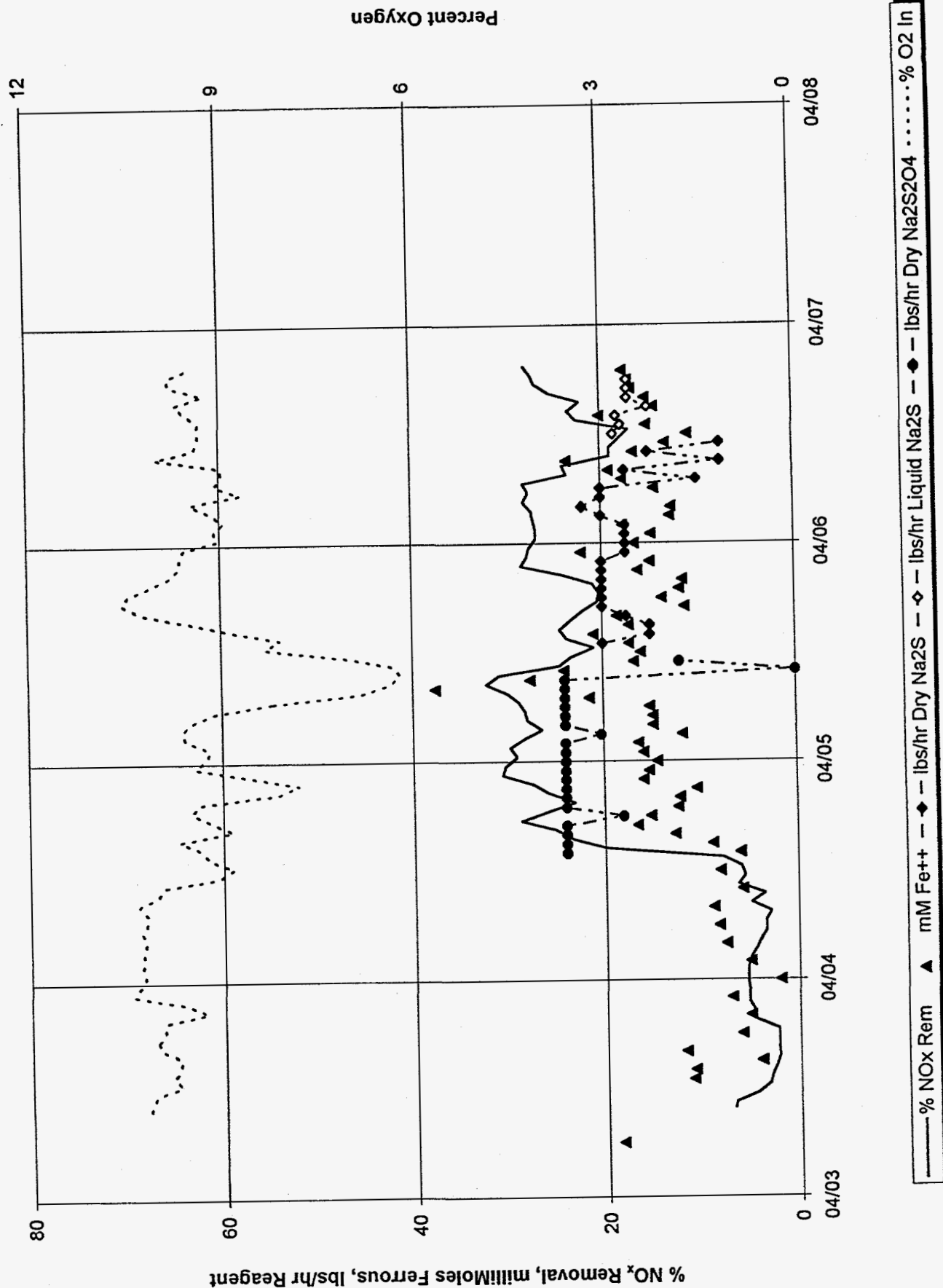


Figure 171. Regeneration Reagent, Ferrous Concentration, NO_x Removal, Inlet O₂



B. Project Budget

TABLE 39
OCDO Expenditures - Phase 1 *

<u>Budget Categories</u>	<u>Amount Budgeted</u>	<u>Funds Expended</u>
Personnel	\$27,422.00	\$27,505.60
Travel	\$1,403.00	\$1,092.41
Equipment	\$21,000.00	\$18,551.97
Supplies	\$10,300.00	\$9,442.48
Contractual	\$0.00	\$0.00
Indirect Charges	\$82,367.00	\$80,870.01
Total	\$142,491.00	\$137,462.48

Table 40
OCDO Expenditures - Phase 2 *

<u>Budget Categories</u>	<u>Amount Budgeted</u>	<u>Funds Expended</u>
Personnel	\$312,760.00	\$54,968.53
Travel	\$11,973.00	\$9,861.98
Equipment	\$136,000.00	\$25,780.21
Supplies	\$362,690.00	\$38,626.09
Contractual	\$7,500.00	\$6,061.04
Indirect Charges	\$214,458.00	\$46,602.22
Total	\$1,045,380.00	\$181,900.07

* Amount budgeted reflects agreement modification request dated August 21, 1996.

Table 41
Total Project Budget

<u>Budget Categories</u>	<u>Participants</u>	<u>Amount Budgeted</u>	<u>Funds Expended</u>
Personnel	OCDO	\$340,182.00	\$82,474.14
	CG&E	\$0.00	*
	DLC	\$208,899.00	\$123,804.29
Travel	OCDO	\$13,376.00	\$10,954.39
	CG&E	\$0.00	*
	DLC	\$13,376.00	\$10,954.39
Equipment	OCDO	\$157,000.00	\$44,332.18
	CG&E	\$60,000.00	*
	DLC	\$157,000.00	\$44,332.18
Supplies	OCDO	\$372,990.00	\$48,068.57
	CG&E	\$0.00	*
	DLC	\$372,990.00	\$48,068.57
Contractual	OCDO	\$7,500.00	\$6,061.04
	CG&E	\$40,000.00	*
	DLC	\$7,500.00	\$6,061.04
Indirect Charges	OCDO	\$296,825.00	\$98,650.24
	CG&E	\$0.00	*
	DLC	\$551,245.00	\$183,207.60
Total	OCDO	\$1,187,871.00	\$319,362.55
	CG&E	\$100,000.00	\$4,950.00
	DLC	\$1,311,011.00	\$469,954.63

* CG&E's budget category expenditures were not available at report time.