

**INTEGRATED DRY NO<sub>x</sub>/SO<sub>2</sub> EMISSIONS CONTROL SYSTEM**

**FINAL REPORT, VOLUME 2: PROJECT PERFORMANCE AND ECONOMICS**

**Appendix F**

**BENCH SCALE TEST REPORT  
BY  
COLORADO SCHOOL OF MINES**

**SIMULTANEOUS REMOVAL OF SO<sub>2</sub> AND NO<sub>x</sub>  
BY SELECTED SODIUM BASED DRY SORBENTS**

## TABLE OF CONTENT

	Page
ABSTRACT .....	i
LIST OF TABLE .....	vii
LIST OF FIGURE .....	x
ACKNOWLEDGEMENTS .....	xv
CHAPTER	
I INTRODUCTION .....	1
1.1 Background and Objectives .....	1
1.2 Reaction Mechanisms .....	3
1.2.1 Decomposition of sodium based dry sorbents to sodium bicarbonate	4
1.2.2 Removal of SO <sub>2</sub> by selected dry sorbents .....	5
1.2.3 Removal of NO by selected dry sorbents .....	6
1.2.4 Formation and Reduction of NO <sub>2</sub> .....	7
1.2.5 Summary of mechanisms .....	8
II EXPERIMENTAL PROCEDURE .....	10
2.1 Reactor Configuration .....	10
2.2 Analytical Techniques .....	12
2.2.1 Analysis of SO <sub>2</sub> .....	13
2.2.2 Analysis of NO and NO <sub>x</sub> .....	18

2.3 Preparation of Dry Sorbents .....	25
2.4 Routine Operating Procedure .....	30
<b>III DISCUSSION OF MODELS .....</b>	<b>35</b>
3.1 Model from EPRI's work .....	35
3.1.1 Simultaneous reduction of SO <sub>2</sub> and NO <sub>x</sub> by sodium bicarbonate ..	35
3.1.2 Simultaneous reduction of SO <sub>2</sub> and NO <sub>x</sub> by sodium sesquicarbonate	42
3.2 Model from Sovay's work .....	44
3.2.1 Simultaneous reduction of SO <sub>2</sub> and NO <sub>x</sub> by sodium bicarbonate ...	44
3.3 Numerical solution for the reaction system .....	52
<b>IV EXPERIMENTAL RESULTS .....</b>	<b>54</b>
4.1 Initial Studies .....	59
4.1.1 NO <sub>x</sub> Removal by Sodium Bicarbonate Enhanced by SO <sub>2</sub> .....	59
4.1.2 NO <sub>2</sub> Formation Enhanced by SO <sub>2</sub> in NO <sub>2</sub> -NO-O <sub>2</sub> -SO <sub>2</sub> Gas Mixture	64
4.2 Sodium Bicarbonate Injection .....	64
4.2.1 Sorbent Dose Effect .....	66
4.2.2 Stirring Speed Effect .....	66
4.2.3 Temperature Effect .....	66
4.2.4 Water Effect .....	70
4.3 Sodium Sesquicarbonate Injection .....	70
4.3.1 Sorbent Dose Effect .....	70

4.3.2 Sorbent Particle Size Effect .....	73
4.3.3 Water Effect .....	75
4.3.4 Temperature Effect .....	75
4.3.5 Low Concentrations of SO <sub>2</sub> and NO <sub>x</sub> .....	75
4.4 Byproduct Identification .....	84
4.5 Chemical Effect on the NO <sub>x</sub> Removal and NO <sub>2</sub> Formation .....	85
4.5.1 The Fate of NO <sub>x</sub> in the Existence of Sodium Sulfite .....	85
4.5.2 Comparison of Three Dry Sorbent Injection .....	89
4.6 Difficulties of High Concentration SO <sub>2</sub> Analysis .....	81
4.7 Real Time Analysis for the Reaction of the Flue Gas and Dry Sorbents	97
4.7.1 Real Time Analysis for the Reaction of the Flue Gas and Sodium Bicarbonate .....	98
4.7.2 Real Time Analysis for the Reaction of the Flue Gas and Sodium Sesquicarbonate .....	104
V MODEL RESULTS .....	116
5.1 Experimental data correction for the bleeding rate of the system .....	116
5.1.1 Correction for the case of NSR equal to 13.5 .....	117
5.1.2 Correction for the remaining cases .....	123
5.2 Experimental curve fitting by EPRI's model .....	123
5.2.1 Simplified rate expression for EPRI's model .....	128



5.2.2 Evaluation of rate constants for EPRI's model .....	129
5.2.3 Kinetics modeling by computer programming .....	131
5.3 Experimental curve fitting by Solvay's model .....	139
5.3.1 Simplified rate expression for Solvay's model in the SO <sub>2</sub> -NO <sub>x</sub> -[NaHCO <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> -2H <sub>2</sub> O] reaction system .....	139
5.3.2 Evaluations of kinetics parameters k <sub>A</sub> , k <sub>B</sub> , and x for the gas-sodium sesquicarbonate reaction system .....	140
5.3.3 Computer simulation using Solvay's model in the SO <sub>2</sub> -NO <sub>x</sub> -[NaHCO <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> -2H <sub>2</sub> O] reaction system .....	144
5.3.4 Computer simulation for the SO <sub>2</sub> -NO <sub>x</sub> -NaHCO <sub>3</sub> reaction system .....	144
VI CONCLUSION AND RECOMMENDATION .....	169
REFERENCES .....	171
APPENDIX A - THE PRIMARY EXPERIMENTAL RESULTS .....	173
APPENDIX B - COMPUTER MODELING RESULTS .....	255
APPENDIX C - EXAMPLE COMPUTER PROGRAM .....	289

## LIST OF TABLES

Table	Page
Table 1. Operation Conditions of Gas Chromatograph .....	14
Table 2. Calibration for a Constant Input Syringe .....	16
Table 3. Calibration of a Sample Size for Gas Chromatograph .....	17
Table 4. Calibration for a 2.8 ml Constant Input Syringe .....	24
Table 5. List of Chemicals .....	28
Table 6. Typical Sampling Schedule .....	33
Table 7. Typical Results of SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Bicarbonate .....	56
Table 8. NSR Effect on SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Bicarbonate .....	67
Table 9. Stirring Effect on SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Bicarbonate .....	68
Table 10. Temperature Effect on SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Bicarbonate .....	69
Table 11. Water Effect on SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Bicarbonate .....	71
Table 12. Dose Effect on SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Sesquicarbonate .....	72

Table 13. Sorbent Particle Size Effect on SO <sub>2</sub> and NO <sub>x</sub> Removal	
by Sodium Sesquicarbonate .....	74
Table 14. Water Effect on SO <sub>2</sub> and NO <sub>x</sub> Removal	
by Sodium Sesquicarbonate .....	76
Table 15. Temperature Effect on SO <sub>2</sub> and NO <sub>x</sub> Removal	
by Sodium Sesquicarbonate .....	77
Table 16. SO <sub>2</sub> and NO <sub>x</sub> Removal at Low Concentration	
by Sodium Sesquicarbonate .....	83
Table 17. SO <sub>2</sub> and NO <sub>x</sub> Removal by Three Chemicals .....	87
Table 18. Raw Data for SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Bicarbonate	
with NSR=0.85 .....	98
Table 19. Raw Data for SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Bicarbonate	
with NSR=3.4. ....	100
Table 20. Raw Data for SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Bicarbonate	
with NSR=13.5. ....	102
Table 21. Raw Data for SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Sesquicarbonate	
with NSR=0.85 .....	107
Table 22. Raw Data for SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Sesquicarbonate	
with NSR=3.4 .....	108
Table 23. Bleeding Rate Study at rpm=300 .....	118

Table 24. Regression on the Results of Bleeding Rate Study .....	120
Table 25. Corrected Concentrations for Three Gases .....	121
Table 26. Bleeding Rate Study at rpm = 700 .....	124
Table 27. Results of Bleeding Rate Study .....	125
Table 28. Bleeding Rate Study on the $\text{SO}_2\text{-NO}_x\text{-[NaHCO}_3\text{-Na}_2\text{CO}_3\text{-2H}_2\text{O]}$	
Reaction System .....	126
Table 29. Simulation Results for EPRI's Reaction Scheme .....	134
Table 30. Rate Constant Effect on the Concentrations of Three Gases .....	137
Table 31. $k_A$ , $k_B$ , and $x$ Obtained from Initial Rate Approach	
(for Sodium Sesquicarbonate) .....	143
Table 32. $k_A$ , $k_B$ , and $x$ Obtained from Initial Rate Approach	
(for Sodium Bicarbonate) .....	167
Table 33. Average $k_A$ , $k_B$ , and $x$ Obtained from Initial Rate Approach	
(for Both Sodium Bicarbonate and Sodium Sesquicarbonate) .....	168

## LIST OF FIGURES

Figure	Page
Figure 1. Dry Sorbent Scrubber System .....	11
Figure 2. SO <sub>2</sub> Calibration Curve Using GC Equipped with TCD .....	15
Figure 3. Chemiluminescent NO-NO <sub>x</sub> Analyzer .....	20
Figure 4. Flow Diagram for NO and NO <sub>x</sub> Analysis .....	21
Figure 5. Calibration for NO <sub>x</sub> Concentration Using NO <sub>x</sub> Analyzer .....	26
Figure 6. Calibration for NO Concentration Using NO <sub>x</sub> Analyzer .....	27
Figure 7. Typical Result of SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Bicarbonate ..	57
Figure 8. SO <sub>2</sub> and NO <sub>x</sub> Simultaneous Removal by Sodium Bicarbonate .....	61
Figure 9. NO <sub>x</sub> Removal by Sodium Bicarbonate .....	62
Figure 10. NO <sub>x</sub> Removal by Sodium Bicarbonate after SO <sub>2</sub> Completely Removed .....	63
Figure 11. Comparison between the NO <sub>x</sub> System with SO <sub>2</sub> and the NO <sub>x</sub> System without SO <sub>2</sub> .....	65
Figure 12. Calibration for Low Concentration SO <sub>2</sub> Using GC Equipped with TCD .....	79
Figure 13. Calibration Curve for Low Concentration NO .....	80
Figure 14. Calibration Curve for Low Concentration NO <sub>x</sub> .....	81
Figure 15. Blank Test for Low Concentration NO, NO <sub>x</sub> and SO <sub>2</sub> .....	82

Figure 16. NO <sub>x</sub> Removal by Sodium Pyrosulfite .....	86
Figure 17. NO <sub>x</sub> Removal by Sodium Sulfite .....	88
Figure 18. SO <sub>2</sub> and NO <sub>x</sub> Degradation without Dry Sorbent .....	90
Figure 19. Blank Test without NO <sub>x</sub> .....	92
Figure 20. Blank Test without SO <sub>2</sub> .....	93
Figure 21. Calibration for High Concentration SO <sub>2</sub> Using GC Equipped with TCD .....	95
Figure 22. Blank Test with and without Sample Storage .....	96
Figure 23. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Bicarbonate (NSR=0.85) .....	99
Figure 24. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Bicarbonate (NSR=3.4) .....	101
Figure 25. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Bicarbonate (NSR=13.5) .....	105
Figure 26. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Bicarbonate (Duplicated : NSR=3.4) .....	104
Figure 27. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Sesquicarbonate (NSR=0.85) ...	109
Figure 28. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Sesquicarbonate (NSR=3.4) .....	110
Figure 29. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Sesquicarbonate (Duplicated Run : NSR=3.4) .....	111
Figure 30. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Sesquicarbonate (Duplicated Run : NSR=3.4) .....	112
Figure 31. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Sesquicarbonate	

(Duplicated Run : NSR=3.4) .....	113
Figure 32. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Sesquicarbonate	
(Duplicated Run : NSR=0.85) .....	114
Figure 33. SO <sub>2</sub> and NO <sub>x</sub> Decrease Adding no Dry Sorbent .....	122
Figure 34. SO <sub>2</sub> and NO <sub>x</sub> Simultaneous Reaction by Sodium Bicarbonate .....	127
Figure 35. Correction of SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Sesquicarbonate .....	133
Figure 36. Flow Diagram of Computer Programming for EPRI's Model .....	133
Figure 37. SO <sub>2</sub> and NO <sub>x</sub> Simultaneous Reaction by Sodium Bicarbonate .....	135
Figure 38. Prediction for the Shrinking Radius of Sodium Bicarbonate Particle	136
Figure 39. SO <sub>2</sub> and NO <sub>x</sub> Simultaneous Reaction by Sodium Bicarbonate .....	138
Figure 40. Evaluation of Kinetics Parameters .....	142
Figure 41. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Sesquicarbonate	
(from Figure 28) .....	145
Figure 42. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Sesquicarbonate	
(from Figure 28) .....	146
Figure 43. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Sesquicarbonate	
(from Figure 29) .....	147
Figure 44. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Sesquicarbonate	
(from Figure 29) .....	148
Figure 45. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Sesquicarbonate	

(from Figure 30) .....	149
Figure 46. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Sesquicarbonate	
(from Figure 30) .....	150
Figure 47. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Sesquicarbonate	
(from Figure 31) .....	151
Figure 48. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Sesquicarbonate	
(from Figure 31) .....	152
Figure 49. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Sesquicarbonate	
(from Figure 27) .....	153
Figure 40. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Sesquicarbonate	
(from Figure 27) .....	154
Figure 51. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Sesquicarbonate	
(from Figure 32) .....	155
Figure 52. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Sesquicarbonate	
(from Figure 32) .....	156
Figure 53. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Bicarbonate	
(from Figure 24) .....	159
Figure 54. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Bicarbonate	
(from Figure 24) .....	160
Figure 55. SO <sub>2</sub> and NO <sub>x</sub> Removal by Sodium Bicarbonate	



	(from Figure 25) .....	161
<b>Figure 56. SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Bicarbonate</b>		
	(from Figure 25) .....	162
<b>Figure 57. SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Bicarbonate</b>		
	(from Figure 23) .....	163
<b>Figure 58. SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Bicarbonate</b>		
	(from Figure 23) .....	164
<b>Figure 59. SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Bicarbonate</b>		
	(from Figure 26) .....	165
<b>Figure 60. SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Bicarbonate</b>		
	(from Figure 26) .....	166

# CHAPTER I

## INTRODUCTION

### 1.1 Background and Objectives

In recent years, international pressures to decrease NO<sub>x</sub> emissions are becoming as strong as those regarding SO<sub>2</sub>. Until now the technology of choice to achieve this requirement is selective catalytic reduction, SCR. Due to the high investment and operation costs of the SCR process, the interest in the development of lower-cost NO<sub>x</sub>/SO<sub>2</sub> abatement process has been renewed<sup>(1), (2)</sup>.

Now it is well established that Sodium Bicarbonate is a very effective reagent for SO<sub>2</sub> removal in flue gas by a low investment cost dry injection process<sup>(3), (4), (5)</sup>. Researchers working for the Electric Power Research Institute, EPRI, have investigated the use of sodium compounds as dry desulfurization agents since 1965. In their final report, EPRI GS-6850, published in 1990<sup>(6)</sup>, they found that, of the five sodium sorbents evaluated, sodium bicarbonate and sodium sesquicarbonate exhibited the best performance, with 70-90% sulfur dioxide removal for subbituminous coals. The most important parameters for achieving high sulfur dioxide removals were flue gas temperature and sorbent particle size. Laboratory investigations into the reaction mechanism showed a complex system chemistry. A sodium sorbent, sulfur dioxide, nitric oxide, and oxygen are all required for nitrogen dioxide generation. Of several additive materials evaluated for effectiveness in mitigating nitrogen dioxide production,

the two most promising were urea and anhydrous ammonia. However, the study on additive effects on nitrogen dioxide removal is not included in this report. EPRI's work also revealed that the amount of nitrogen oxide removal that was possible was a direct function of the amount of sulfur dioxide captured. In the sorbent-NO<sub>x</sub>-SO<sub>2</sub> reaction system, they found that the higher the SO<sub>2</sub> concentration entering the system, the higher the NO<sub>x</sub> removal potential. The optimum temperature for NO<sub>x</sub> removal appears to be 350°±75°F. Furthermore, it appears as if oxidation of NO to NO<sub>2</sub> only occurs on the surface of the sodium and when SO<sub>2</sub> is actively being reacted with the sorbent.

Public Service Company of Colorado has received a contract from the Department of Energy Clean Coal Program to develop a commercial scale demonstration project which includes utilization of a sodium based dry scrubbing retrofit process for SO<sub>2</sub> and NO<sub>x</sub> removal from power plant flue gases. Sodium based scrubbing agents, such as sodium bicarbonate have the advantage over calcium based agents in that they are much more reactive. For example, direct injection of solid sodium bicarbonate into a flue gas stream prior to a fabric filter particulate removal system in an actual power plant can result in an 80% SO<sub>2</sub> removal efficiency. Such a system can be added to an existing power plant much easier than a calcium based wet scrubbing system, and operating costs are much less. Sodium bicarbonates can also significantly reduce NO<sub>x</sub> emissions. However, NO that is formed in the furnace is converted in the process to NO<sub>2</sub>, which is a brown colored gas. The net effect is a flue gas with significantly lower levels of

NO<sub>x</sub> pollutants, unfortunately with the characteristic brown plume of NO<sub>2</sub>, which is visually offensive.

As part of their contract, we have performed bench scale studies to develop a kinetic model from experimental measurements of this reaction system, with the objective of gaining an understanding of the kinetics of NO<sub>2</sub> formation, with ultimate goals of minimizing its formation. Among the variables to be investigated include: water vapor concentration in the feed, reaction temperature, concentrations of SO<sub>2</sub> and NO<sub>x</sub> in the flue gas, and choice of solid (sodium bicarbonate versus sodium sesquicarbonate). Although the ultimate objective of the program is to develop a kinetic model, the experimental results can also be used to determine, qualitatively, how each of the variables affects the removal of SO<sub>2</sub> and NO<sub>x</sub> and the generation rate of NO<sub>2</sub> in the product gas. Thus, one purpose of this report is to present the qualitative conclusions that can be drawn from the data.

## 1.2 Reaction Mechanisms:

To study the kinetics of this gas-solid reaction, we must know the reaction chemistry first. Two different reaction chemistries which have been proposed were included in the kinetic studies of this report. The one was developed by work supported by EPRI<sup>(6)</sup> and the other is work done by Solvay<sup>(12)</sup>. These are described below.

### 1.2.1 Decomposition of sodium based dry sorbents to sodium carbonate.

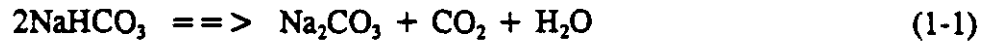
In EPRI's work, the sodium carbonate must be made available to  $\text{SO}_2$  in the flue gas stream by the injection of a sodium bearing compound which thermally decomposes to form sodium carbonate. To verify the decomposition of these sodium based dry sorbents which depends highly on temperature, a brief series of flow reactor tests were conducted to investigate the extent of decomposition of nahcolite, trona, and processed sodium sesquicarbonate in the dispersed phase without any flue gas being present.

At a temperature of  $275^\circ\text{F}$ , nahcolite exhibited very little decomposition at residence times up to 1.2 seconds; but at a temperature of  $550^\circ\text{F}$ , over 70 percent of the bicarbonate component of the nahcolite decomposed at residence times as low as 0.5 seconds. The trona materials exhibited a higher degree of decomposition at the lower temperature ( $275^\circ\text{F}$ ). Reviewing these resulting data suggests that the initial availability of carbonate in the trona coupled with the decomposition of the material at low temperature may explain the more rapid reaction with  $\text{SO}_2$  compared to nahcolite.

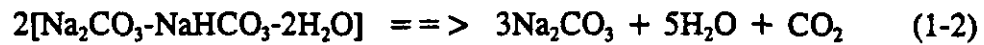
Also, the decomposition of the sorbents resulting in the evolution of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  can lead to an increase in the specific surface area of the reactive sorbent. Since the dry  $\text{SO}_2$  removal process involves a gas solid reaction, the reaction rate and ultimate sorbent utilization are normally considered to be a function of the surface area which also explains why  $\text{SO}_2$  is removed more rapidly in the presence of trona than in the presence of nahcolite. The postulated initial reactions for the dry sodium scrubbing process

proposed by EPRI were:

Bicarbonate

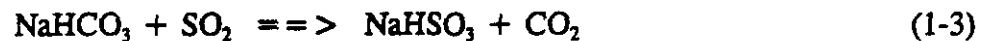


Sesquicarbonate



1.2.2 Removal of SO<sub>2</sub> by dry sorbents

In Solvay's work, the IFP (Institute Francais du P'etrole) laboratory gives confirmation of the ability of sodium bicarbonate to remove simultaneously SO<sub>2</sub> and NO<sub>x</sub> in flue gas. They ascribed the abatement of SO<sub>2</sub> to the reaction between undecomposed dry sorbents and SO<sub>2</sub>. The reaction describing sodium bicarbonate sulfation is as follows :



and sodium bisulfite later will dehydrate to the sodium pyrosulfite :



EPRI proposed that  $\text{Na}_2\text{CO}_3$  is the reactant which causes  $\text{SO}_2$  reduction. The typical reaction between sodium carbonate and sulfur dioxide is as follows :



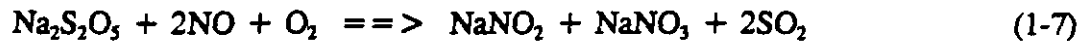
The formation of sodium sulfate,  $\text{Na}_2\text{SO}_4$ , or sulfite,  $\text{Na}_2\text{SO}_3$  as the reaction product is strongly dependent on flue gas temperature if nitric oxide is not present in the test gas. Nitric oxide in the test gas, however, appears to not only change the  $\text{SO}_2$  removal chemistry but also takes part itself in a complicated set of reactions which result in sodium nitrate formation and  $\text{NO}_2$  production. The EPRI study proposed the following reaction for NO reduction in the presence of  $\text{SO}_2$  and sodium with some undetermined intermediate steps:



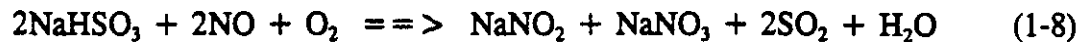
### 1.2.3 Removal of NO by dry sorbents

With the intermediate sodium pyrosulfite formation, Solvay has an alternate interpretation for nitric oxide reduction and sodium nitrate formation. They believe the NO reduction results from the sodium pyrosulfite nitration and sodium bisulfite nitration are described as follows:

### Sodium pyrosulfite nitration



### Sodium bisulfite nitration

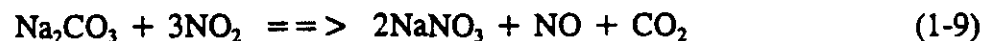


The stoichiometric ratio of NO to SO<sub>2</sub> in equation (1-7) has later been demonstrated in my experimental program which suggests that Equation (1-7) is in fact the reaction step and sodium pyrosulfite is the intermediate sulfur compound required for the removal of NO.

#### 1.2.4 Formation and reduction of NO<sub>2</sub>

Solvay did not discuss the formation and reduction of NO<sub>2</sub> in their work<sup>(12)</sup>. However, from Equation (7) and Equation (8), NO<sub>2</sub> might be produced by decomposition of the relatively unstable sodium nitrite. This behavior has been observed in our laboratory.

In EPRI's work<sup>(6)</sup>, it is believed that NO<sub>2</sub> formation occurs directly from NO and that NO<sub>x</sub> removal only occurs by the reaction of NO<sub>2</sub> with the sodium based dry sorbent. This reaction is described as follows:



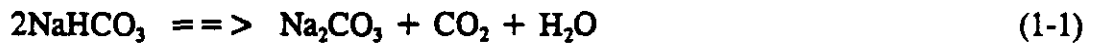


### 1.2.5 Summary of mechanisms

For the simultaneous removal of SO<sub>2</sub> and NO<sub>x</sub> by sodium bicarbonate, the following are the possible mechanisms proposed by EPRI and by Solvay:

#### EPRI's mechanism

##### Decomposition of sodium bicarbonate



##### Sulfation of sodium carbonate



##### Oxidation of nitric oxide



##### Nitration of sodium carbonate and removal of NO<sub>2</sub>



#### Solvay's mechanism

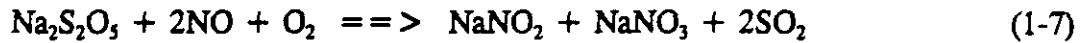
##### Sulfation of sodium bicarbonate



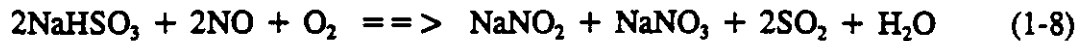
##### Dehydration of sodium bisulfite



Nitration of sodium pyrosulfite



Nitration of sodium bisulfite



The major difference between the two schemes is the manner in which NO reacts with the solid. In the EPRI scheme NO is first oxidized to NO<sub>2</sub> and the NO<sub>2</sub> reacts with the solid. In the Solvay scheme NO reacts directly with a reaction intermediate formed from the removal of SO<sub>2</sub>. The significant difference using these different schemes will be discussed in Chapter V. Another difference is the reaction for the removal of SO<sub>2</sub>, which reacts directly with the solid by the Solvay scheme and reacts with Na<sub>2</sub>CO<sub>3</sub> formed after removal of H<sub>2</sub>O and CO<sub>2</sub> from NaHCO<sub>3</sub>. This difference is of less significance since dehydration of the solid can occur either before or after the sulfation without there being a significant effect on the kinetics.

## CHAPTER II

### EXPERIMENTAL PROCEDURE

#### 2.1 Reactor Configuration

A dry sorbent, bench scale, batch reactor was erected to conduct the experimental study. The objective of the experimental study was to obtain the intrinsic rate of the acid gas removal reactions by either sodium bicarbonate or sodium sesquicarbonate. The apparatus used in this investigation consists of SO<sub>2</sub> and NO feed units, a neutralization bottle containing 1M NaOH solution designed for trapping SO<sub>2</sub> and NO<sub>x</sub> acid gases, a background gas feed unit containing 3% oxygen and 97% nitrogen, a batch reactor with heating control unit, and a gas analysis system.

A batch reactor, designed and constructed for this study is shown in Figure 1. The basic components of the batch reactor system are a 12864 ml batch reactor to contain the reaction mixtures, a dry sorbent, a heating control unit to keep reaction temperature constant between 100 to 300°C, and a propeller type mixing unit to eliminate temperature and mass transfer gradients surrounding the dry sorbent particles.

The batch reactor is made of stainless steel with four fittings on the top cover. The first fitting, V2, a control valve with 1/2" opening, is designed for either gas or sorbent powder injection. The second fitting, V3, also a control valve with 1/4" opening, is designed for draining the unreacted acid gases to a neutralization bottle containing 1M

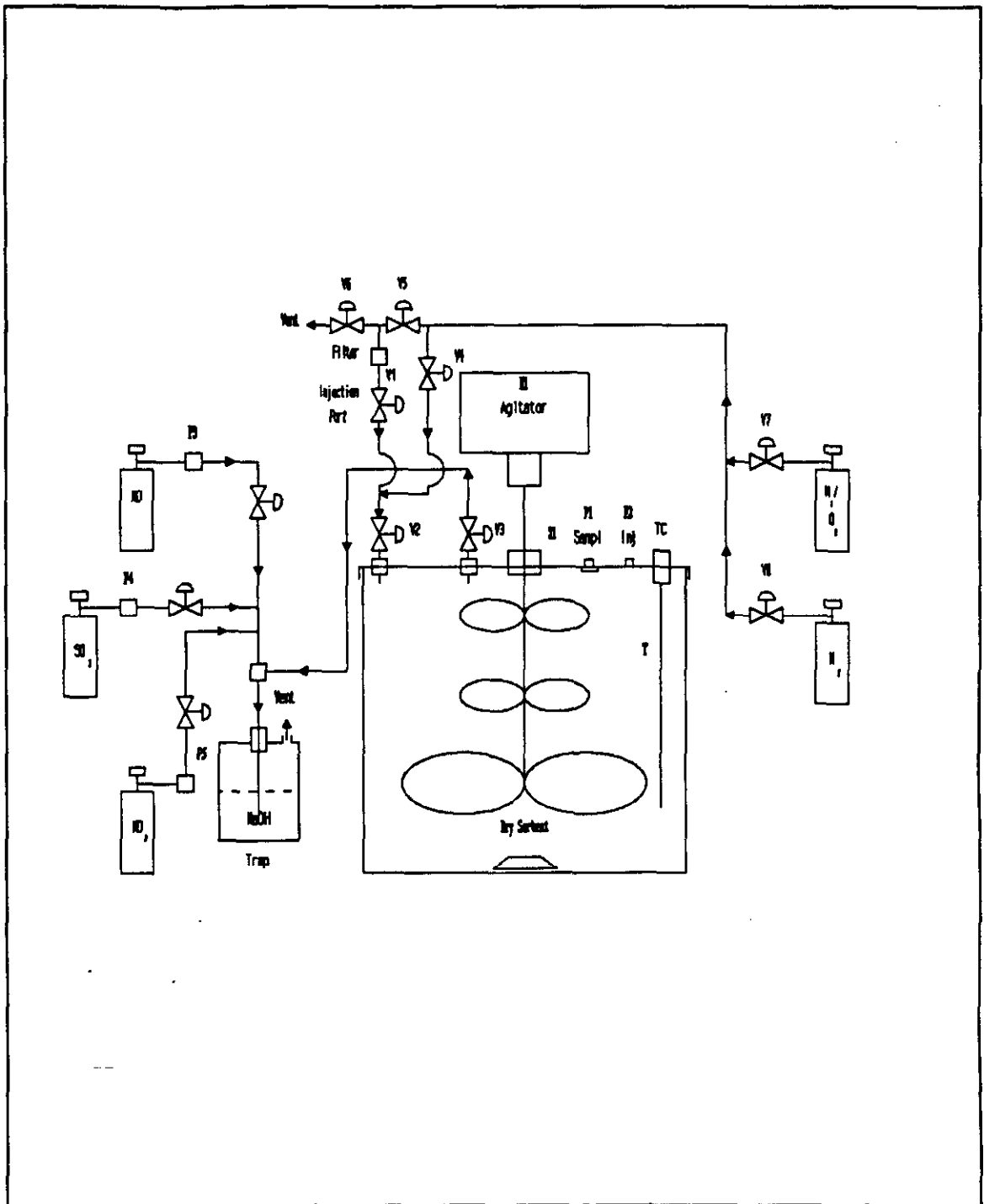


Figure 1. DRY SORBENT SCRUBBER SYSTEM

NaOH solution. The third fitting, P1, a sampling port with 1/2" opening, is a swagelock fitting equipped with a 9 millimeter diameter septum. The fourth fitting, P2, an injection port with 1/2" opening, is the same as the sampling port. Both sampling and injection ports are used for withdrawing the reacting gas mixtures and for injecting acid gases, SO<sub>2</sub> and NO.

A Haake Buchler stirring motor, M1, with a torque range from 55 to 60 in-lb is used to actuate a propeller type mixing device with the speed ranging from 0 to 700 rpm. The mixing device is composed of a 10" length x 1/4" diameter stainless steel stirring rod, two pairs of 3" long blades, and one pair of MixMor 7-1/2" propellers. The blades are tightened with screws on the stirring rod in different positions as shown in Figure 1. A teflon type Conax sealant is used to seal the rotating rod at ambient pressure in the reactor.

The major components in the heating control unit are a Watlow mica band heater with a size of 9" ID x 2" width and output power 1800 Watt, an Omega Series 920 temperature controller TC with an accuracy of 1% full scale, and an Omega type K thermocouple, T.

## 2.2 Analytical Techniques

Analytical techniques include analysis of SO<sub>2</sub> and analysis of NO<sub>x</sub> and NO. Conventionally, the extent of conversion in a gas-solid reaction is measured by recording the weight gain of the pellet with a thermal balance during the reaction. However, in

the  $\text{SO}_2$ - $\text{NaHCO}_3$  or  $\text{NO}_x$ - $\text{NaHCO}_3$  system, the molecular weight difference between solid reactant  $\text{NaHCO}_3$  and solid product either  $\text{Na}_2\text{SO}_3$ , or  $\text{NaNO}_3$ , is small and since formation of  $\text{Na}_2\text{SO}_4$  and  $\text{NaNO}_2$  can also occur, the weight change is not a measure of the extent of gaseous reaction. Use of a gas chromatograph makes it relatively easy to follow the reaction by observing the varying concentrations of gas reactants  $\text{SO}_2$  and  $\text{NO}$  or  $\text{NO}_x$ .

### 2.2.1 Analysis of $\text{SO}_2$

The internal standard method was used to determine the concentrations of  $\text{SO}_2$  accomplished by an Hewlett Packard model 5890 gas chromatograph equipped with a thermal conductivity detector. Initially, a 8' x 1/4" Supelco porapak Q glass column with particle size 80/100 at a temperature of 70°C separated air first, then carbon dioxide, water, and sulfur dioxide in order of retention times of about 0.31, 0.83, 3.97, and 8 minutes, respectively. Helium was used as a carrier gas. The operating conditions for the  $\text{SO}_2$  analysis are stated in Table 1. The calibration curve is shown in Figure 2. The concentrations of  $\text{SO}_2$  used for the calibration were determined by injecting a known amount of  $\text{SO}_2$  into the reactor of known volume. The calibrated input volume of  $\text{SO}_2$  was determined by a syringe and a stainless steel rod that was calibrated using measured water volumes. The calibration data are shown in Table 2. The sample size used in the gas chromatograph was also calibrated and the raw data are shown in Table 3. Later,

Table 1. Operation Conditions of Gas Chromatograph

---

Parameters	Conditions
Column Temperature :	70°C
Injector Temperature :	70°C
Detector Temperature :	100°C
Column Pressure :	30 psig
Column Flow Rate :	15 ml/min
Attenuation :	0
Zero :	0 ± 0.01 mV

---

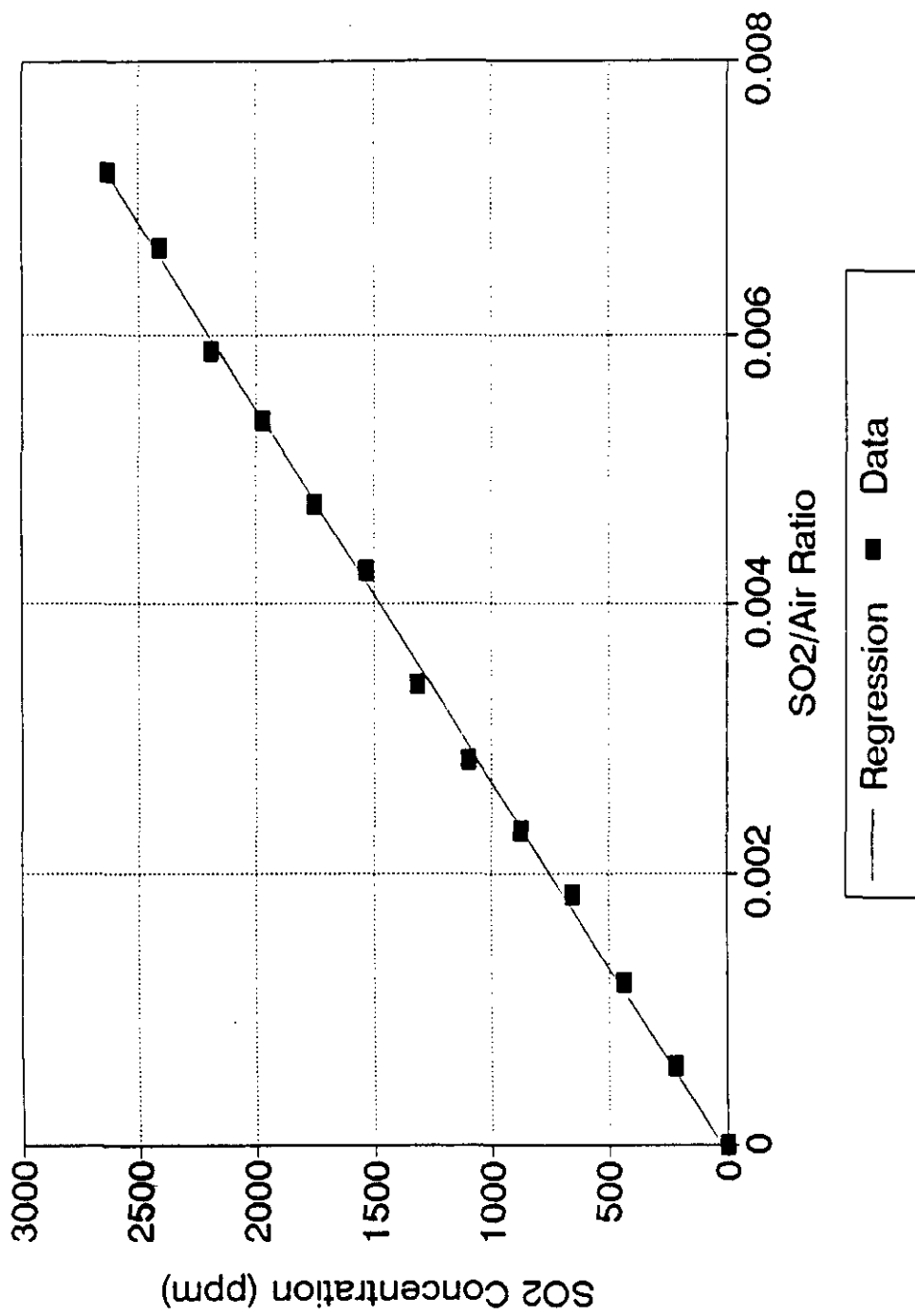


Figure 2. SO2 Calibration Curve Using GC Equipped with TCD



Table 2. Calibration for a constant input syringe

No.	W1 (g)	W2 (g)	DW (g)	V (ml)
1	13	15.8	2.8	2.804965
2	12.96	15.76	2.8	2.804965
3	12.76	15.58	2.82	2.825
4	12.92	15.72	2.8	2.804965
5	12.82	15.59	2.77	2.774912

\* No : order of sampling bottle which is used to contain distilled water

W1: weight of bottle without water

W2: weight of bottle plus constant input of water

DW: net weight of a constant water input

V : volume of water estimated from DW with water density 0.99823 g/cc at 20°C

\* The constant input volume is 2.80 ml

Standard Error = 4.86E-6 ml

Table 3. Calibration of a sample size for gas chromatograph

No.	Bottle	+ Water	Water	Inj. Vol.
	(g)	(g)	(g)	(ml)
1	12.72	17.59	4.87	4.86138
2	12.9	17.77	4.87	4.86138
3	12.67	17.54	4.87	4.86138
4	12.86	17.74	4.88	4.871362
5	12.81	17.66	4.85	4.841416

\* The standard error is 0.003599 ml

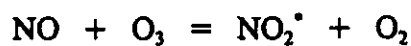
it is shown that this gas chromatographic procedure leads to errors in the SO<sub>2</sub> concentration due to the presence of NO<sub>x</sub> in the reaction mixture. The evidence of this phenomena obtained from blank tests will be discussed later.

### 2.2.2 Analysis of NO and NO<sub>x</sub>

The Porapak Q glass collum used to determine SO<sub>2</sub> concentration with sample size greater than 50 ul was not able to separate NO from air due to the large amount of background gas, 97% nitrogen and 3% oxygen. The gas chromatographic (GC) determination of sulphur and nitrogen gases (H<sub>2</sub>S, COS, SO<sub>2</sub>, NH<sub>3</sub>, N<sub>2</sub>O, NO, NO<sub>2</sub>) has previously been reported by many workers<sup>(7)</sup> with different detectors and stationary phases. From the early commercial availability of porous polymer beads (PPBs), these polymeric phases were considered a good choice for the determination of reactive gases, owing to their low polarity<sup>(8),(9)</sup> and good stability<sup>(10)</sup>. Gianrico Castello and his coworker<sup>(7)</sup> performed a series of investigation on various Chromosorb Century Series porous polymer bead stationary phases for the simultaneous determination of sulphur and nitrogen gaseous compounds. According to their results, it seemed that we would be able to use Chromosorb 103 to separate our chemicals at low temperature, less than 30°C. A 10 feet long glass column with 2 millimeter inside diameter packed with 80/100 Chromosorb 103 polymer beads and a 30 feet stainless steel column with 0.085 inch inside diameter packed with Gas Chrom MP-1 suggested by Alltech Company were therefore used. Unfortunately, the adsorption and decomposition phenomena often

indicated as the cause of the anomalous response of reactive gases on porous polymer columns were found to be a real problem for polar compounds. Reaction of nitrogen oxides with the polymer, resulting in sample disappearance, formation of decomposition products, yellowing of the polymer beads and changes in retention times of non-reactive compounds, after the injection of large reactive samples, was also observed in our testing. Reproducible data could not even be obtained at very low temperatures of 18°C where reactivity of nitrogen gases might be minimized.

After a significant unsuccessful effort in trying the simultaneous determination of SO<sub>2</sub> and NO<sub>x</sub> by gas chromatography, a chemiluminescent NO-NO<sub>x</sub> analyzer, model 44, developed by Thermo Electron Corporation was ultimately used to detect concentrations of NO and NO<sub>x</sub>, while SO<sub>2</sub> were determined by the separate instrument, GC. The configuration of this analytical device and its flow diagram are shown on Figure 3, and Figure 4 respectively. A dry air gas is used to create ozone which later reacts with nitric oxide (NO) molecules in the gas phase. In the reaction a chemiluminescent decay of the resulting excited nitrogen dioxide (NO<sub>2</sub><sup>\*</sup>) molecules would produce characteristic light by which the concentration of NO is detected. The typical reactions are described as follows:



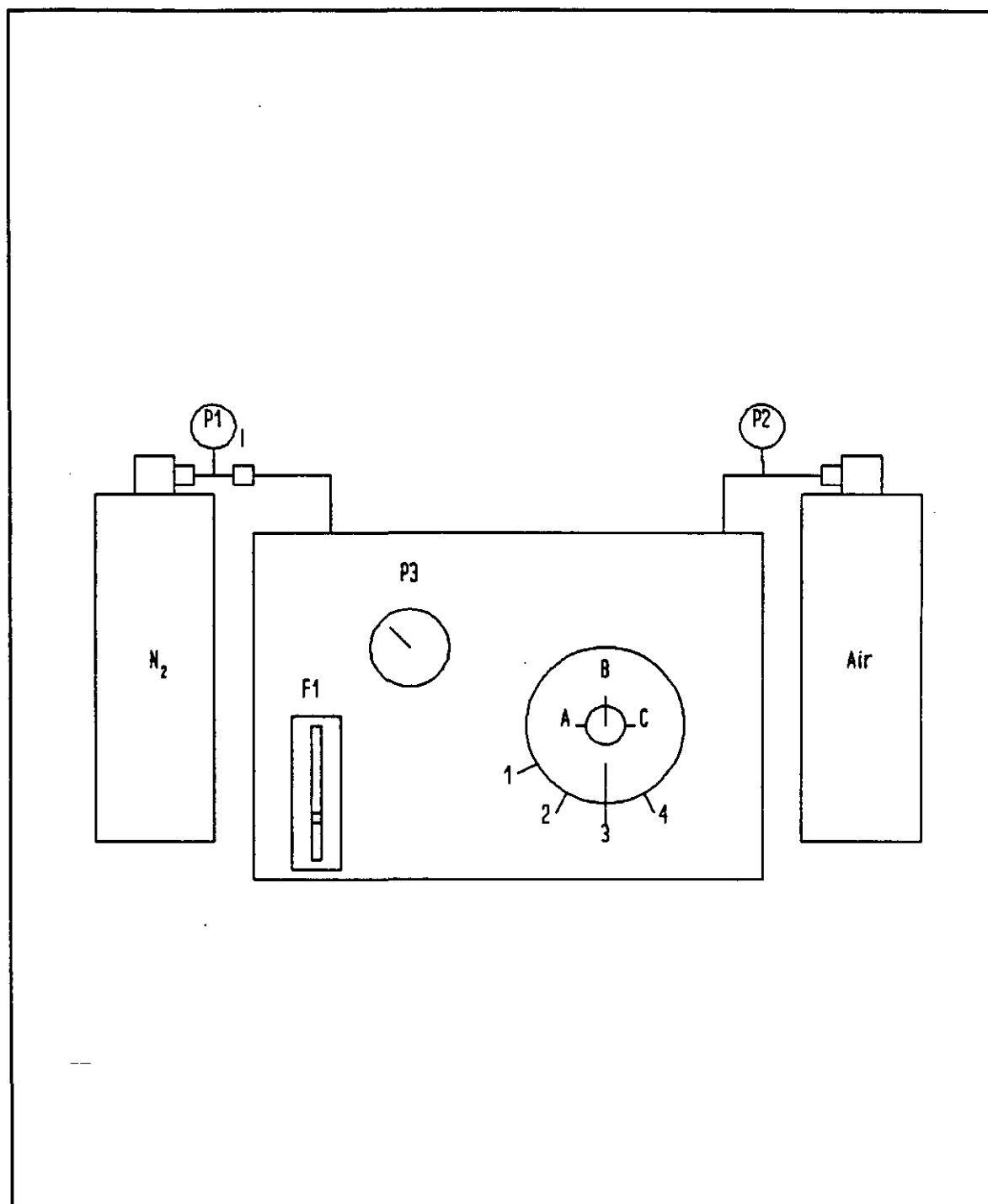


Figure 3. Chemiluminescent NO-NOx Analyzer

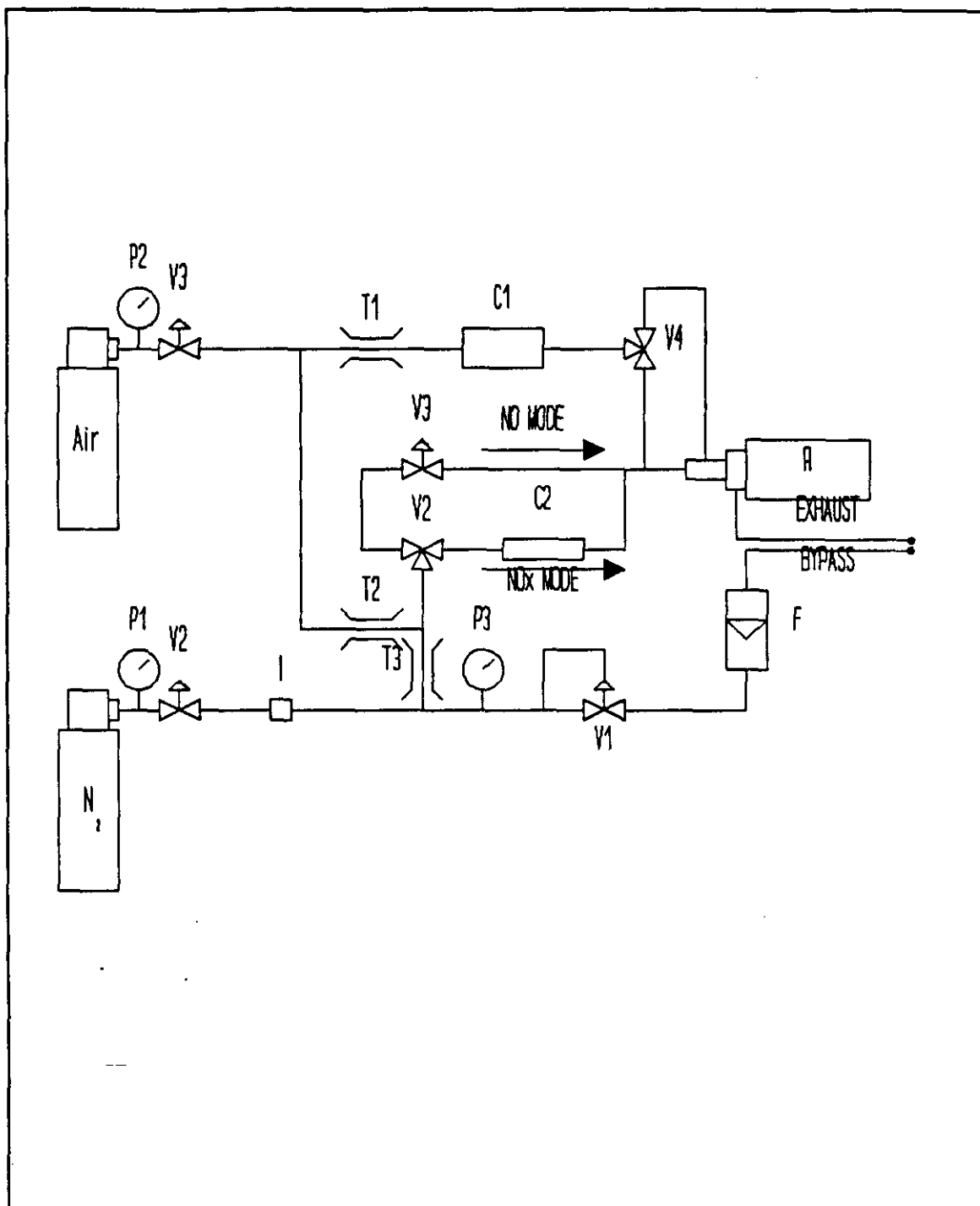


Figure 4. Flow Diagram for NO and NO<sub>x</sub> Analysis.

As we can see in Figure 4, a sample which includes a gas mixture of NO and NO<sub>x</sub> is introduced from injection port I. Industrial grade nitrogen is used as a carrier gas to carry the NO-NO<sub>x</sub> mixture to a reaction chamber, R, in which NO reacts with ozone gas from the top transport line as shown on the diagram. If we turn on the analyzer to NO<sub>x</sub> mode, then all NO<sub>2</sub> molecule would be converted to NO first in a NO converter, C2, then go to the reaction chamber; otherwise the gas goes directly to the reactor and only NO molecules are detected using the NO mode.

This instrument is normally used to analyze in situ dynamic sampling. If this is not the case, an alternative method is to inject the sample to a sampling bag and then pump it to the NO<sub>x</sub> analyzer. The reading obtained from the analyzer is exactly the value of the sample concentration. Neither of the above methods could be applied in our experiment due to the small total sample size, 12864 ml, and the likely loss or decomposition of samples while transferring from the reactor to the sampling bag. Another method, which later was proven to be reproducible for low concentrations of NO and NO<sub>x</sub>, was used to analyze NO and NO<sub>x</sub> concentration in the samples.

A set of high concentration calibration curves ranging from 0 to 2500 ppm were obtained by the following procedure:

Step1. Calibrate a displaced volume I, which was later used to determine the concentrations of NO and NO<sub>x</sub> in the reactor, by drawing a constant volume of water using a 5 ml syringe and a stainless steel rod.

- Step2. Calibrate another displaced volume II, which was later used to obtain a constant injection volume into the NO-NO<sub>x</sub> analyzer by drawing a constant volume of water using another stainless steel rod and a 5 ml syringe.
- Step3. Heat the reactor to 260°F, open the valves V8, V4, V2, and V3; then flush it for twenty minutes with industrial grade compressed nitrogen gas. Keep the outlet flowing to the neutralization bottle just beneath the water level so that the pressure inside the reactor is about ambient.
- Step4. Close all valves in the reactor system. Open the valve of another compressed industrial grade nitrogen at 10 psig to the NO-NO<sub>x</sub> analyzer, adjust the bypass stream pressure to 3 psig, and adjust the concentration range to a desired mode, B3.
- Step5. Pull out a constant amount of NO gas at ambient temperature with the calibrated syringe, and inject it into the reactor. The calibration data for this syringe are shown in Table 4.
- Step6. Pull out a constant amount of gas mixture at 260°F with the same calibrated syringe as described in step 5, then inject it into the NO-NO<sub>x</sub> analyzer.
- Step7. Observe the highest reading, the index value of either NO or NO<sub>x</sub> from the analyzer, and record it.
- Step8. Repeat the procedure from steps 5 to step 7 until reaching the high concentration limit.



Table 4. Calibration for a 2.8 ml constant input syringe.

No.	W1 (g)	W2 (g)	DW (g)	V (ml)
1	13	15.8	2.8	2.804965
2	12.96	15.76	2.8	2.804965
3	12.76	15.58	2.82	2.825
4	12.92	15.72	2.8	2.804965
5	12.82	15.59	2.77	2.774912

Step9. Plot concentration determined from step 5 versus the reading index. The resultant plots are shown in Figure 5 and Figure 6.

Step10. Use the data with a linear relationship obtained from the results by regression using QPro computer software. The relation between the actual concentration and the index later was used to determine the concentration of reacting gas, NO or NO<sub>x</sub>, in the reactor. The concentration of NO<sub>2</sub> can be determined by the difference in concentration between that of NO, and that of NO<sub>x</sub>.

### 2.3 Preparation of dry sorbents

Sodium bicarbonate, sodium sesquicarbonate, and sodium sulfite are used to investigate the capability of removing acid gases from the mixture in the reactor. Sodium pyrosulfite, or sodium metabisulfite, is used to see if it is a intermediate in the reaction of sodium bicarbonate and the acid gases in the mixture. Acid gases and sorbents used in the experiments are listed in Table 5. The sorbent is first ground by a mortar, then separated using different sizes of sieves. The separated sorbents are then stored in the same desiccant jar, except the sodium pyrosulfite, which is active and might produce SO<sub>2</sub>, and was stored in a separate desiccant.

For the sake of convenience to compare the results with each other, the doses of dry sorbents have been converted in terms of NSR (Normal Stoichiometric Ratio) which corresponds to the amount of SO<sub>2</sub> used in the reactions. SO<sub>2</sub> concentration of 1800 ppm has been chosen to be the reference with NSR equal to one for both sodium bicarbonate

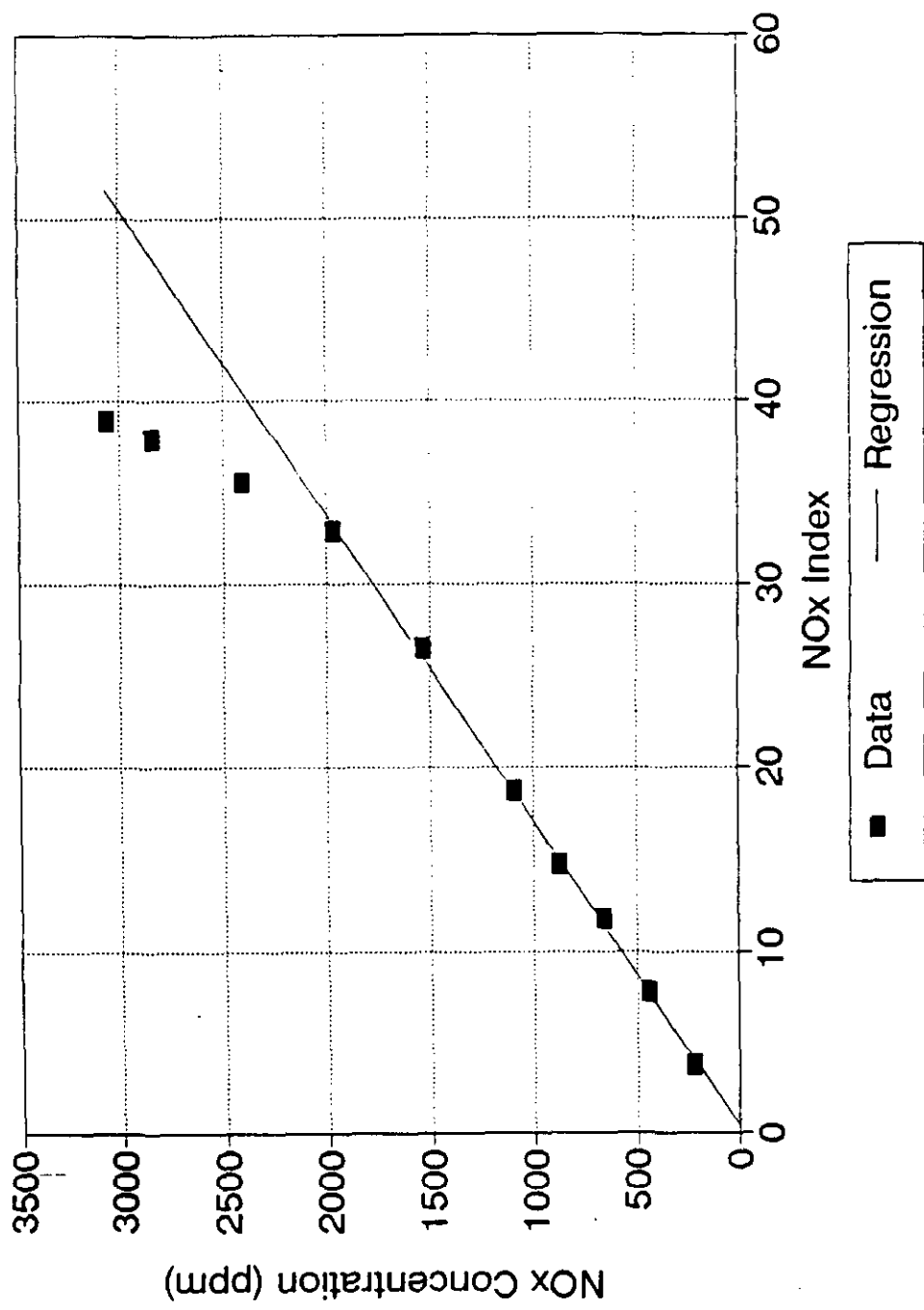


Figure 5. Calibration for NOx Concentration Using NOx Analyzer

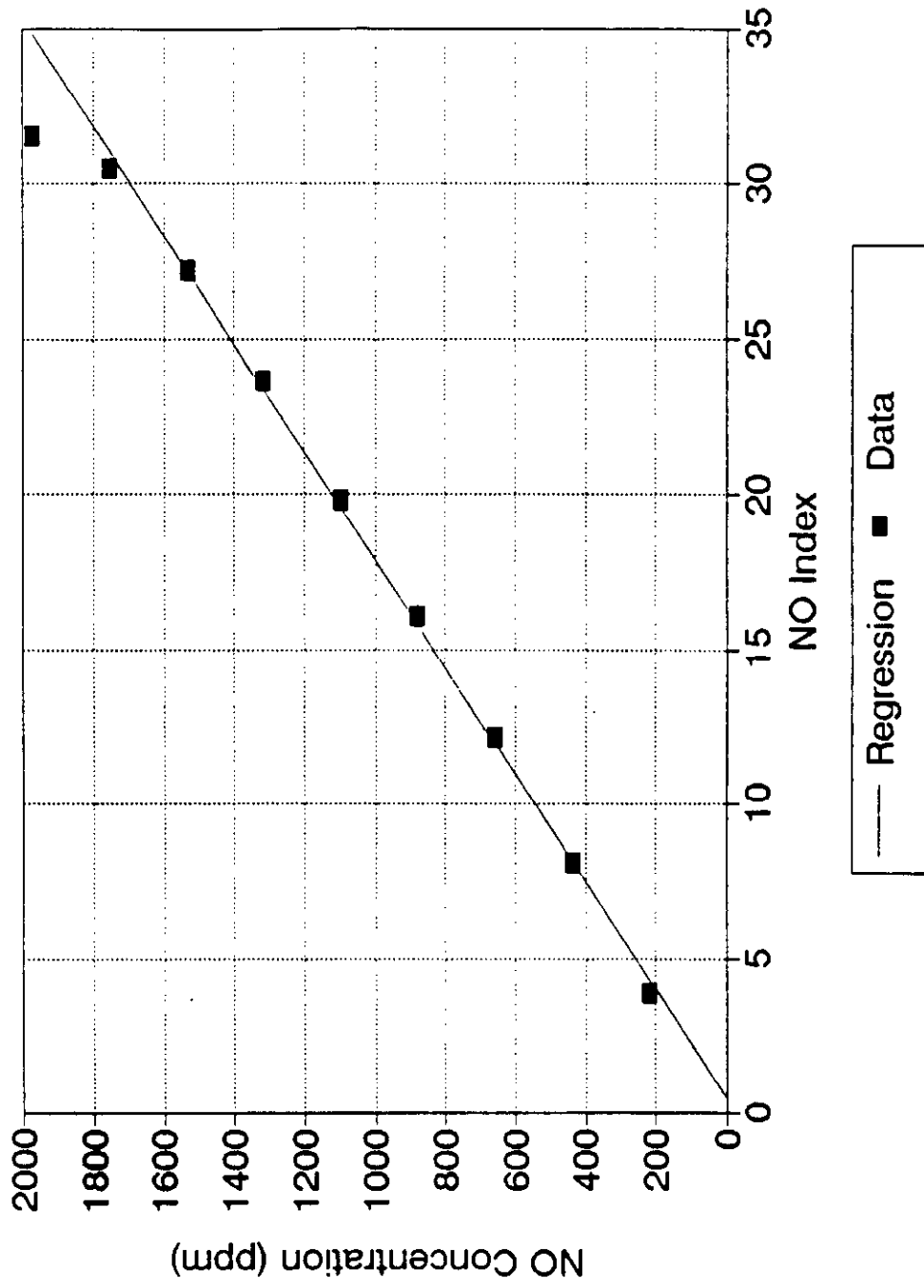


Figure 6. Calibration for NO Concentration Using NOx Analyzer

Table 5. List of chemicals

Chemical	Formula	Company	Purity
Sodium Bicarbonate	NaHCO <sub>3</sub>	CMS	99.7+ %
Sodium Sesquicarbonate	Na <sub>2</sub> CO <sub>3</sub> -NaHCO <sub>3</sub> -2H <sub>2</sub> O	B&D Chemical.	99.0+ %
Sodium Pyrosulfite	Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub>	CMS	97+ %
Sodium Sulfite	Na <sub>2</sub> SO <sub>3</sub>	CMS	99%
Sulfur Dioxide	SO <sub>2</sub>	Aldrich Chemical.	99.9+ %
Nitric Oxide	NO	Matheson	99+ %
Nitrogen Dioxide	NO <sub>2</sub>	Aldrich Chemical	99.5+ %
Helium	He	Denver General Gas	99.999%
Nitrogen	N <sub>2</sub>	Denver General Gas	99.99%
Gas Mixture	3% O <sub>2</sub> & 97% N <sub>2</sub>	Denver General Gas	Certified

and sodium sesquicarbonate injection according to the Equation (1-1), Equation (1-2) and Equation (1-5). The typical doses of dry sorbents are calculated as follows :

Reactor operating condition

(1)  $V$  (Reactor volume) = 12864 ml = 12.864 L

(2)  $P$  (Pressure) = 1 atm.

(3)  $T$  (Temperature) = 260°F = 400°K

(4)  $N_t$  (Total mol of gas mixture in reactor)

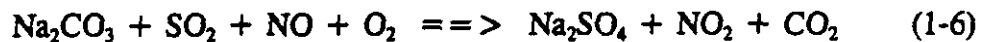
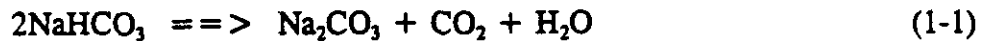
$$N_t = P V / R T = 0.392 \text{ mol}$$

where  $R$  is ideal gas law constant = 0.082 atm L/mol °K

(5)  $N_A$  (Mol of  $SO_2$  with concentration of 1800 ppm in the reactor)

$$N_A = 1800E-6 * N_t = 0.706E-3 \text{ mol}$$

For  $NaHCO_3$  ( $M_{NaHCO_3} = 84.01 \text{ g/mol}$ )



(1)  $NSR=3.37$  (base case):

$$N_{NaHCO_3} \text{ (Mol required for } NSR=3.37)$$

$$= 2N_A * NSR = 4.76E-3 \text{ mol}$$

$$W_{NaHCO_3} \text{ (mass required for } NSR=3.37)$$

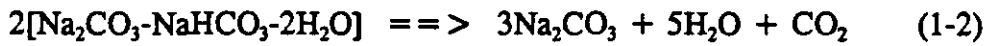
$$= N_{\text{NaHCO}_3} * M_{\text{NaHCO}_3} = 0.4 \text{ g}$$

(2) NSR=0.79 :

$$W_{\text{NaHCO}_3} \text{ (mass required for NSR=0.79)}$$

$$= 0.79/3.37 * [W_{\text{NaHCO}_3}]_{\text{NSR}=3.37} * M_{\text{NaHCO}_3} = 0.093 \text{ g}$$

For  $2[\text{Na}_2\text{CO}_3\text{-NaHCO}_3\text{-}2\text{H}_2\text{O}]$  ( $M_{\text{Na}_2\text{CO}_3\text{-NaHCO}_3\text{-}2\text{H}_2\text{O}} = 226.04 \text{ g/mol}$ )



(1) NSR=3.38 (base case):

$$N_{\text{Na}_2\text{CO}_3\text{-NaHCO}_3\text{-}2\text{H}_2\text{O}} \text{ (Mol required for NSR=3.38)}$$

$$= 2/3 N_A * \text{NSR} = 4.76\text{E-}3 \text{ mol}$$

$$W_{\text{Na}_2\text{CO}_3\text{-NaHCO}_3\text{-}2\text{H}_2\text{O}} \text{ (mass required for NSR=3.37)}$$

$$= N_{\text{Na}_2\text{CO}_3\text{-NaHCO}_3\text{-}2\text{H}_2\text{O}} * M_{\text{Na}_2\text{CO}_3\text{-NaHCO}_3\text{-}2\text{H}_2\text{O}} = 0.36 \text{ g}$$

(2) NSR=0.79 :

$$W_{\text{Na}_2\text{CO}_3\text{-NaHCO}_3\text{-}2\text{H}_2\text{O}} \text{ (mass required for NSR=0.79)}$$

$$= 0.79/3.37 * [W_{\text{Na}_2\text{CO}_3\text{-NaHCO}_3\text{-}2\text{H}_2\text{O}}]_{\text{NSR}=3.38} * M_{\text{NaHCO}_3} = 0.084 \text{ g}$$

## 2.4 Routine Operating Procedure

Before normal operation, the gas chromatograph, the NO-NO<sub>x</sub> analyzer, and the reactor system are set at the desired operating conditions, the motor is rotating, all valves

are closed, and all fittings are tightened except V1. The procedure for routine operation is described as follows:

Step1. Remove about 5 ml of gas from the reactor and inject it to gas chromatograph to make sure the concentration of water is under 0.01%. If this is not the case then we need additional flushing by opening valves V7, V4, V2 and V3 using the background gas which is 3% oxygen and balance nitrogen.

Step2. Once the water level in the reactor is under 0.01%, close valves V7, V4, V2 and V3. Weigh a desired amount of sorbent powder, pour it into the 1/2" opening port V1, and securely tighten the fitting.

Step3. Open valve V7, V5, V6 and V1 and flush the solid powder at 5 psig to avoid water vapor, extra oxygen or carbon dioxide from being trapped in the sorbent.

Step4. Pour some distilled water into a beaker, strip it using industrial grade nitrogen gas for two minutes to reduce the carbon dioxide in the water, draw the desired amount of water using a 1 ml syringe, and then inject it into the reactor.

Step5. Use a 50 ml syringe to pull out 50 ml of SO<sub>2</sub> gas from sampling port P4, which is actually a swagelock fitting sealed with a septum. Vent the gas completely from the syringe and then draw another 50 ml SO<sub>2</sub> again. Push the gas out of the syringe slowly until the end of piston reaches the 20 ml mark. Inject this 20 ml SO<sub>2</sub> immediately into the reactor.

Step6. Pull out about a 5 ml gas sample from the reactor, inject it immediately into the



gas chromatograph.

- Step7. Wait for all peaks to elute from the GC, then check if the SO<sub>2</sub> peak is about the desired ratio. If not, then we need to repeat step 6 again; or else, follow step 5 to inject the NO gas into the reactor.
- Step8. Pull out about a 5 ml gas sample from the reactor, inject it immediately into the gas chromatograph. Then pull out another two sample gases, one for NO analysis and the other for NO<sub>x</sub> analysis, and inject constant amounts of gases into the NO-NO<sub>x</sub> analyzer to obtain the NO and NO<sub>x</sub> index from the analyzer reading.
- Step9. Duplicate NO and NO<sub>x</sub> sampling, then close the valves in the order of V6, V1, and V5.
- Step10. Open the valve V2 and simultaneously close the same valve V2 and start the stop watch.
- Step11. Start taking gas samples according to the arranged sampling schedule. A typical sampling schedule is listed in Table 6. In order to get as many samples as possible, SO<sub>2</sub> gas samples are stored and later injected into the GC when previous runs are completed. NO and NO<sub>x</sub> samples are injected into the NO-NO<sub>x</sub> analyzer immediately after they are removed from the reactor in increments of thirty second.
- Step12. Use Qpro to convert the SO<sub>2</sub> to air ratio to SO<sub>2</sub> concentration, ppm, and NO and NO<sub>x</sub> index to NO and NO<sub>x</sub> concentration, ppm. Plot gas concentration, ppm,

Table 6. Typical sampling schedule

---

Time (min)	SO <sub>2</sub>	NO	NO <sub>x</sub>
0	X	X	X
0.0833	X		
0.25	X		
0.4166	X		
0.5			X
0.9166	X		
1.0		X	
1.5			X
1.9166	X		
2.0		X	
2.5			X
2.9166	X		
3.0		X	
3.5			X
3.9166	X		
4.0		X	
4.5			X
4.9166	X		
5.0		X	
5.5			X
6.0	X		
6.5			X
7.0	X		

versus reaction time, min.

## CHAPTER III

### DISCUSSION OF MODELS

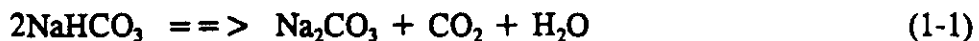
Postulated equations for simultaneous reaction of  $\text{SO}_2$  and  $\text{NO}_x$  from chapter one are used in this chapter to set up the kinetics models. There are two different schematic models; the one is from EPRI and the other is from Solvay. A good model needs to be able to represent the experimental data. The purpose of this chapter is to construct the rate laws for the four main compounds  $\text{SO}_2$ ,  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{Na}_2\text{CO}_3$ . The rate laws for the removal of the three gases are based on their concentrations in the continuous stirred batch reactor. The rate law for the removal of sodium carbonate is based on the changing radius of unreacted solid, which is based on the shrinking core model.

#### 3.1 Model from EPRI's work

##### 3.1.1 Simultaneous reduction of $\text{SO}_2$ and $\text{NO}_x$ by sodium bicarbonate

EPRI's mechanism for the simultaneous reduction of  $\text{SO}_2$  and  $\text{NO}_x$  is composed of four steps and described by Equation (1-1), Equation (1-5), Equation (1-6), and Equation (1-9) which have been discussed in Chapter one:

##### Decomposition of sodium bicarbonate



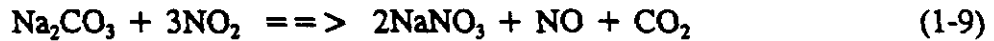
##### Sulfation of sodium carbonate



##### Oxidation of nitric oxide



Nitration of sodium carbonate and removal of NO<sub>2</sub>



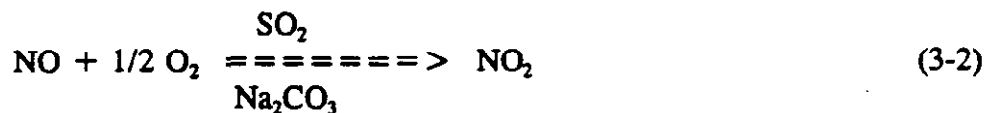
The decomposition rate of sodium bicarbonate has been proven to be very fast<sup>(12)</sup> (about 20% decomposed at 275°F in 0.5 second and about 100% decomposed based on the carbon analysis at 350°F in 0.8 second in the absence of NO or SO<sub>2</sub>). It seems that we can neglect the sodium bicarbonate decomposition step due to its fast rate compared with the other slower reactions.

EPRI's study suggests that the dependence of SO<sub>2</sub> removal on the concentration of NO is not significant while NO removal highly depends on the concentration of SO<sub>2</sub>. So, Equations (1-5) and (1-6) might be rewritten as:

Removal of SO<sub>2</sub> by Na<sub>2</sub>CO<sub>3</sub>

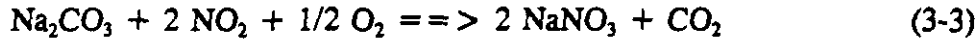


Formation of NO<sub>2</sub>



Furthermore, to simplify the kinetic analysis we can write a simplified version of (1-9) as:

### Reaction of NO<sub>2</sub>



In the EPRI work the removal of SO<sub>2</sub> depends on the concentration of SO<sub>2</sub> and the normal stoichiometric ratio, NSR, used in the reaction which is equivalent to the amount of Na<sub>2</sub>CO<sub>3</sub> injected. Either the SO<sub>2</sub> or the NO removal or the NO<sub>2</sub> formation does not highly depend on the concentration of oxygen due to the large excess amount of O<sub>2</sub> used, which was about 10%. In this report, the amount of O<sub>2</sub> used in each set of experiments is a constant of 3% which is still much greater than 1800 ppm or 0.18% of SO<sub>2</sub>. So, when we construct the rate law the concentration of O<sub>2</sub> might be ascribed to the pseudo rate constant.

From Equation (3-1) and the above discussion, we can write the rate law for an intrinsic rate reaction of SO<sub>2</sub> as

$$R_A = -dC_A/dt = k_A C_A s \quad (3-4)$$

where A : SO<sub>2</sub>

R<sub>A</sub>: removal rate of A, mol/cm<sup>3</sup> min

C<sub>A</sub>: concentration of A, mol/cm<sup>3</sup>

t : reaction time, minute

k<sub>A</sub>: rate constant of removing A, cm/min

s : total surface area per volume, mol/cm<sup>3</sup>

From the definition, s could be expressed as

$$s = S/V = (4 \text{ Pi } R^2) N / V \quad (3-5)$$

where

S : total surface area, cm<sup>2</sup>

V : reactor volume, cm<sup>3</sup>

Pi: constant, 3.14159

R : radius of solid particle, cm

N : total number of particles, ea

N could be estimated outside the reactor by assuming that the number of solid particles remained constant before and during the reaction:

$$N = W / (4/3 \text{ Pi } R_o^3) D \quad (3-6)$$

where

W : weight of NaHCO<sub>3</sub> measured outside the reactor, g

R<sub>o</sub>: mean radius of NaHCO<sub>3</sub> obtained outside the reactor, 0.0029 cm

D : density of NaHCO<sub>3</sub>, 2.2 g/cm<sup>3</sup>

Also, we can write the consumption rate of Na<sub>2</sub>CO<sub>3</sub> from Equation (3-1)

$$R_{E0} = - dC_{E0}/dt = k_A C_A s \quad (3-7)$$

where E : Na<sub>2</sub>CO<sub>3</sub>

0 : reaction contributed by Equation (3-1)

R<sub>E0</sub>: removal rate of A due to reaction (3-1), mol/cm<sup>3</sup> min

$\text{Na}_2\text{CO}_3$ , the concentrations of  $\text{SO}_2$  and  $\text{O}_2$ . Since the concentration of  $\text{O}_2$  is in large excess, we can again incorporate this term into the rate constant.

From Equation (3-1) and the above discussion, we can write the rate law for an intrinsic rate of reaction of  $\text{SO}_2$  as

$$R_A = - dC_A/dt = k_A C_A s \quad (3-3)$$

where A :  $\text{SO}_2$

$R_A$ : removal rate of A, mol/cm<sup>3</sup> min

$C_A$ : concentration of A, mol/cm<sup>3</sup>

t : reacting time, minute

$k_A$ : rate constant of removing A, cm/min

s : total surface area of  $\text{Na}_2\text{CO}_3$  per volume, mol/cm<sup>3</sup>

As for the evaluation of s, we can still use Equation (3-5) and Equation (3-6).

To evaluate the consumption rate of sodium carbonate, we can use Equation (3-7),

$$R_{E0} = - dC_{E0}/dt = k_A C_A s \quad (3-7)$$

where E :  $\text{Na}_2\text{CO}_3$

0 : reaction contributed by Equation (3-1)

$R_{E0}$ : removal rate of A due to reaction (3-1), mol/cm<sup>3</sup> min

$C_E$ : mol of E per volum, mol/cm<sub>3</sub>

To evaluate the derivative of  $C_E$  with respect to reaction time t, we can just plug in



Equation (3-8) into Equation (3-7).

$$\begin{aligned} dC_B/dt &= 1/V (dn_B/dt) \\ &= 1/V (4 \pi N R^2 dR D/M) \end{aligned} \quad (3-8)$$

where M is the molecular weight of sodium bicarbonate.

For the NO removal step Equation (3-17) indicates that the removal of NO depends on the concentration of NO, the concentration of O<sub>2</sub>, the concentration of SO<sub>2</sub>, and the amount of Na<sub>2</sub>CO<sub>3</sub> used in this reaction. Since the O<sub>2</sub> is in large excess; consequently, the rate expression can be written the same as Equation (3-9) as described in section 3.1.1 :

$$R_B = - dC_B/dt = k_B C_A C_B s \quad (3-9)$$

where B : NO

R<sub>B</sub>: removal rate of B, mol/cm<sup>3</sup> min

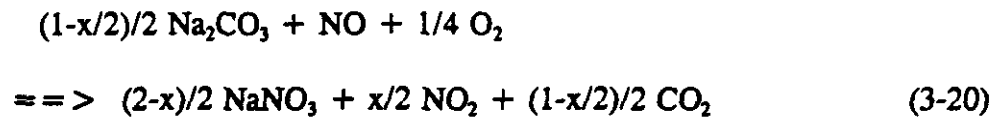
C<sub>B</sub>: concentration of B, mol/cm<sup>3</sup>

k<sub>B</sub>: rate constant of removing B, cm/min

The definitions of t and s are the same as that for SO<sub>2</sub>.

The reaction of NaNO<sub>2</sub> can significantly complicate the reaction kinetics, since it would be present in the reacted core of the solid and its disappearance would make the shrinking core model invalid. In order to simplify our kinetics and keep the shrinking core model in use, we can assume that the NaNO<sub>2</sub> is very reactive which implies that the

reaction rates in Equation (3-18) and Equation (3-19) are very fast. Thus all of the solid reaction will still occur at the surface of the shrinking core. However, since the  $\text{NaNO}_2$  can react to form either  $\text{NaNO}_3$  or can generate  $\text{NO}_2$ , an additional stoichiometric constant  $x$  must be incorporated into the model to define the selectivity of the two reactions. To achieve this, Equation (3-18) with ratio  $x$  and Equation (3-19) with ratio  $1-x$  are added to Equation (3-17) to account for the immediate disappearance of  $\text{NaNO}_2$ . The final form of these combined equations is:



From this final expression Equation (3-20), we can setup the  $\text{NO}_2$  formation rate expression in terms of the removal rate of  $\text{NO}$ :

$$R_C = dC_C/dt = -x/2 dC_B/dt = x/2 k_B C_A C_B \quad (3-21)$$

where  $C$  :  $\text{NO}_2$

$x$  : undefined stoichiometric constant, which is between 0 and 1.

$R_C$  : formation rate of  $C$ ,  $\text{mol/cm}^3 \text{ min}$

$C_C$ : concentration of  $C$ ,  $\text{mol/cm}^3$

$k_B$ : rate constant of removal of  $B$ ,  $\text{cm/min}$

Also, we can write the consumption rate of  $\text{Na}_2\text{CO}_3$  by this reaction, which is equivalent to the NO removal rate with a stoichiometric constant  $(1-x/2)/2$ , according to the Equation (3-9)

$$\begin{aligned} R_{E1} &= -dC_{E1}/dt = (1-x/2)/2 R_B \\ &= (1-x/2)/2 k_B C_A C_B s \end{aligned} \quad (3-22)$$

where E :  $\text{Na}_2\text{CO}_3$

1 : reaction due to Equation (3-20)

$R_{E1}$ : removal rate of E due to reaction (3-20), mol/cm<sup>3</sup> min

The overall consumption of the dry sorbent  $\text{Na}_2\text{CO}_3$  is the contribution from the two reaction steps, Equation (3-1) and Equation (3-20). According to the stoichiometric ratio from these two equations, the overall consumption rate of sodium carbonate could be expressed as the summation of Equation (3-7) and Equation (3-22):

$$\begin{aligned} R_E &= R_{E0} + R_{E1} = -dC_{E0}/dt - dC_{E1}/dt \\ &= k_A C_A s + (1-x/2)/2 k_B C_A C_B s \end{aligned} \quad (3-23)$$

Equation (3-23) can be expressed in term of the solid shrinking core radius by combining Equation (3-4) and Equation (3-7). The final form of (3-23) could be written as:

$$R_R = dR/dt = -0.5 M/D * [k_A C_A + (1-x/2)/2 k_B C_A C_B] \quad (3-24)$$

The value 0.5 in Equation (3-24) is a stoichiometric conversion factor from sodium bicarbonate to sodium carbonate which can be obtained from Equation (1-1).

The kinetic variables of main interest in this study are the concentrations of SO<sub>2</sub>, NO, and NO<sub>2</sub>; and the radius of shrinking core of the dry sorbent R. Therefore, the following summary is made for these four variables.

Summary of rate expressions for the reaction using NaHCO<sub>3</sub>

Removal rate of SO<sub>2</sub>

$$R_A = -dC_A/dt = k_A C_A s \quad (3-3)$$

Removal rate of NO

$$R_B = -dC_B/dt = k_B C_A C_B s \quad (3-8)$$

Formation rate of NO<sub>2</sub>

$$R_C = dC_C/dt = -x/2 dC_B/dt = x/2 k_B C_A C_B s \quad (3-21)$$

Shrinking rate of radius R

$$R_R = dR/dt = -0.5 M/D * [k_A C_A + (1-x/2)/2 k_B C_A C_B] \quad (3-24)$$

Evaluation of s and N

$$s = S/V = (4 \text{ Pi } R^2) N / V \quad (3-4)$$

$$N = W / (4/3 \text{ Pi } R_0^3) D \quad (3-5)$$

A similar analysis can be performed for sodium sesquicarbonate and as in the case of the EPRI model all of the equations remain the same with the exception of the

equation for the radius of the shrinking core, where the stoichiometric coefficient of 0.5 must be replaced with 1.5 in switching from Equation (1-1) to Equation (1-2). The resulting equation is:

Shrinking rate of radius R

$$R_r = dR/dt = -1.5 M/D * [k_A C_A + (1-x/2)/2 k_B C_A C_B] \quad (3-25)$$

where M and D now refer to the molecular weight and particle density for sodium sesquicarbonate.

### 3.3 Numerical solution for the reaction system

The above governing equations (Equations (3-3), (3-8), (3-11) and (3-15) for sodium bicarbonate and Equations (3-3), (3-8), (3-11), and (3-16) for sodium sesquicarbonate) represent a complete statement of the reaction system for the EPRI scheme. Similarly Equations (3-3), (3-8), (3-21) and (3-24) for sodium bicarbonate and Equations (3-3), (3-8), (3-21) and (3-25) represent a complete statement of the reaction system for the Solvay scheme. It is still impossible to solve any of the above simultaneous sets of equations analytically. There are several finite difference methods for solving these simultaneous first order initial value ordinary differential equations.<sup>(14)</sup> The first order Euler method and the second order modified Euler method are clearly inferior to the fourth order methods. The Runge-Kutta method is an excellent method; however, it requires four derivative function evaluation per step, compared to one for the Adams-Bashforth method

and two for the Adams-Bashforth-Moulton method. The Runge-Kutta method and the Adams-Bashforth method both suffer from the lack of an efficient error control procedure. The Adams-Bashforth-Moulton method, which has a simple error control procedure, is the best compromise between accuracy and error control efficiency. Consequently, the Adams-Bashforth-Moulton method with a Runge-Kutta starting procedure is recommended for solving most first-order initial-value ordinary differential equations. This project therefore use this combined methods to solve the sets of simultaneous ordinary differential equations.

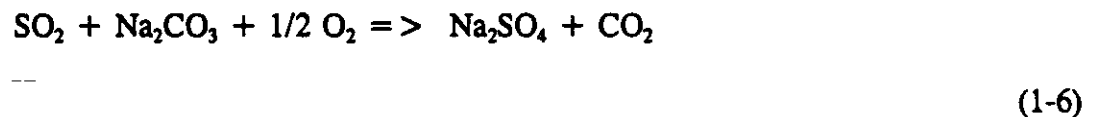
CHAPTER IV  
EXPERIMENTAL RESULTS

From previous studies of SO<sub>2</sub> removal by Sodium Bicarbonate, NaHCO<sub>3</sub>, conducted by Chang<sup>11</sup>, we know that humidity plays an important role in this reaction system. Water content in the system SO<sub>2</sub>-NO<sub>x</sub>-dry sorbent is therefore likely to be an important parameter. Obviously, normalized stoichiometric ratio, NSR, which is the ratio of the amount of sorbent equivalent to the concentration of SO<sub>2</sub> to the concentration of SO<sub>2</sub> in the reaction system is also an important parameter. NSR is defined according to the following reactions described in the literature<sup>6</sup> in which the reaction stoichiometry is presented below:

Sorbent decomposition :



Removal of sulfur dioxide :



Although both SO<sub>2</sub> and NO can react with either sodium bicarbonate or sodium

sesquicarbonate, the established convention for defining NSR is to consider only the reactions involving  $\text{SO}_2$ .

Besides water content and NSR, the stirring speed of the motor, the size of the sorbent particle, and reaction temperature were also considered as parameters in the  $\text{SO}_2$ - $\text{NO}_x$ -sorbent reaction system. Furthermore, the initial ratio of  $\text{SO}_2/\text{NO}$  which has been considered to be a very important parameter in the literature<sup>7,12</sup> was also varied by considering lower concentrations of  $\text{SO}_2$  and  $\text{NO}$  reacting with sodium sesquicarbonate to test this effect on  $\text{SO}_2$  and  $\text{NO}_x$  removal. The base case initial gas concentration of  $\text{SO}_2$  and  $\text{NO}_x$  for each run were set approximately to:  $\text{SO}_2 = 1800$  ppm,  $\text{NO} = 1800$  ppm. At these relatively high concentrations we would expect to see greater changes in component concentrations as the operating variables were varied. That is, the effects would be enhanced and more readily measured. In addition we generally set  $\text{O}_2 = 3\%$  and  $\text{H}_2\text{O} = 5\%$  with the balance nitrogen. The typical particle size of sorbents used in these tests was 58  $\mu\text{m}$  which is the mean value of the particle size range from 53 to 63  $\mu\text{m}$ .

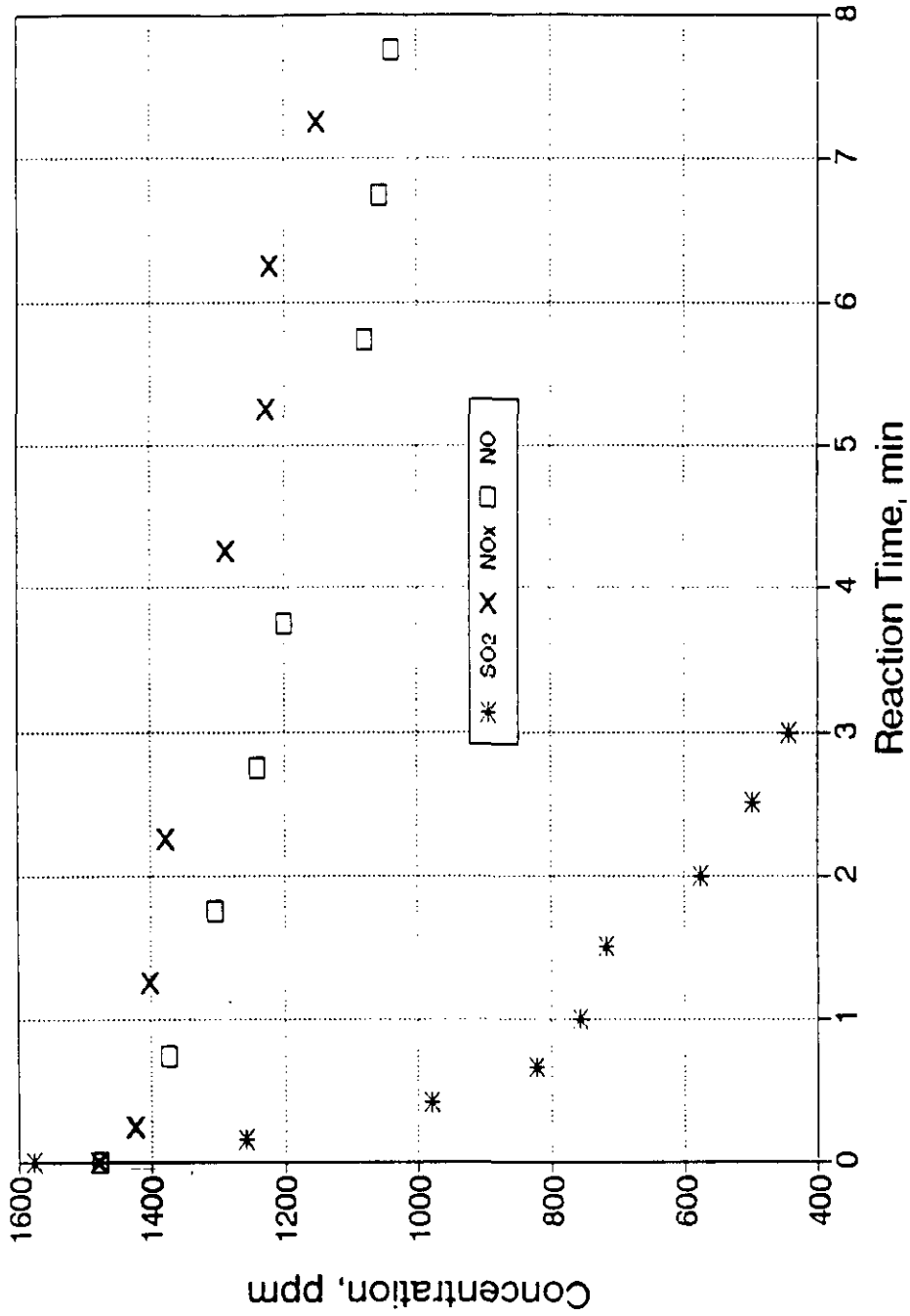
Typical results for an experimental run are presented in Table 7, and are illustrated graphically in Figure 7. This run was for a sodium bicarbonate sample at the typical operating conditions,  $\text{NSR} = 3.4$ , and reactor temperature at  $260^\circ\text{F}$ , the approximate operating temperature of the Arapahoe 4 scrubbing system. As can be seen from the Figure, the  $\text{NO}_2$  concentration must be determined as the difference between the



Table 7. Typical Results of SO<sub>2</sub> and NO<sub>x</sub> Removal by NaHCO<sub>3</sub> :

Date : 05-25-93 Temp.(F) : 260  
 Sorbent : Sodium Bicarbonate rpm : 700  
 Water(%) : 5 NSR : 3  
 Size(um) : (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.004274	1576.537	25.11	26.2	1480.523	1476.388
0.1667	0.003402	1259.431				
0.25			24.2		1425.894	
0.4167	0.002633	980.0017				
0.6667	0.0022	822.4727				
0.75				24.4		1372.868
1	0.002022	757.7006				
1.25			23.8		1401.882	
1.5	0.001912	717.6988				
1.75				23.2		1303.855
2	0.001521	575.3917				
2.25			23.4		1377.869	
2.5	0.001304	496.5845				
2.75				22.1		1240.593
3	0.001151	440.9603				
3.75				21.4		1200.335
4.25			21.9		1287.822	
5.25			20.9		1227.791	
5.75				19.3		1079.562
6.25			20.8		1221.788	
6.75				18.9		1056.558
7.25			19.6		1149.751	
7.75				18.6		1039.305



NSR=3.4, Water=5%, 260F, 700 rpm, 53um < d < 63um

Figure 7. Typical Result of SO2 and NOx Removal by Sodium Bicarbonate

interpolated concentrations of  $\text{NO}_x$  and  $\text{NO}$ . From these results it appeared as though the  $\text{SO}_2$  concentration decayed rapidly to zero. However, as will be discussed below, the  $\text{SO}_2$  results are believed to be erroneously low. The remaining experimental results are presented as tables and graphs in the appendix.

In order to determine qualitatively the effects that the operating variables have on  $\text{NO}_x$  reduction and, especially,  $\text{NO}_2$  formation, the resultant data of the observed values of  $\text{SO}_2$ ,  $\text{NO}$ ,  $\text{NO}_x$ , and  $\text{NO}_2$  at time zero, at 3 minutes for  $\text{SO}_2$  and at 5 minutes for  $\text{NO}$ ,  $\text{NO}_x$ , and  $\text{NO}_2$  are tabulated from Table 8 through Table 17. These results were obtained by interpolating the graphs of the experimental results, presented in the appendix. A time of 5 minutes was selected for the nitrogen oxides, since by that time significant reaction had occurred. However, by that time the experimentally determined concentrations for  $\text{SO}_2$  were essentially zero. Therefore, a shorter time, 3 minutes was selected for  $\text{SO}_2$ .

Symbols used in these tables are defined as follows:

- \*  $(A)_0$ ,  $(A)_3$ ,  $(A)_5$ : concentration of chemical A at reaction time 0, 3 minute and 5 minute
- \* Chemical A could be  $\text{SO}_2$ ,  $\text{NO}$ ,  $\text{NO}_2$  or  $\text{NO}_x$
- \*  $d(A)_5$ : the concentration difference of chemical A between reaction time 0 and 5 minutes.
- \*  $R\%(A)_3$ : removal % of chemical A at reaction time at 3 minute; i.e.,  $[(A)_0 - (A)_3] / (A)_0 * 100\%$

\*  $R\%(A)5$ : removal % of chemical A at reaction time at 5 minute; i.e.,  $[(A)o - (A)5] / (A)o * 100\%$

The concentration of nitrogen dioxide is determined by the following relationship:

$$[NO_2] = [NO_x] - [NO]$$

#### 4.1 Initial Studies

According to EPRI's Final Report<sup>6</sup> published on May 1990,  $NO_x$  reduction potential depends on temperature and the amount of  $SO_2$  presents in the system. The higher the  $SO_2$  concentration presents in the system, the higher the  $NO_x$  removal potential. They found that the optimum temperature for  $NO_x$  removal appears to be approximately  $350^\circ F \pm 75^\circ F$ . Above this temperature region, NO oxidation to  $NO_x$  and nitrate formation are impeded. Below the temperature band very little sorbent decomposition is possible, limiting  $SO_2$  capture and subsequently the dependent  $NO_x$  reaction. As for the  $NO_x$  reduction mechanism, in their opinion, the NO and  $NO_2$  oxidation process is heavily surface dependent which means oxidation of NO to  $NO_2$  only occurs on the surface of the sodium sorbent and when  $SO_2$  is actively being reacted with the sorbent. Five experimental runs therefore designed for investigating the effect of  $SO_2$  on  $NO_x$  reduction.

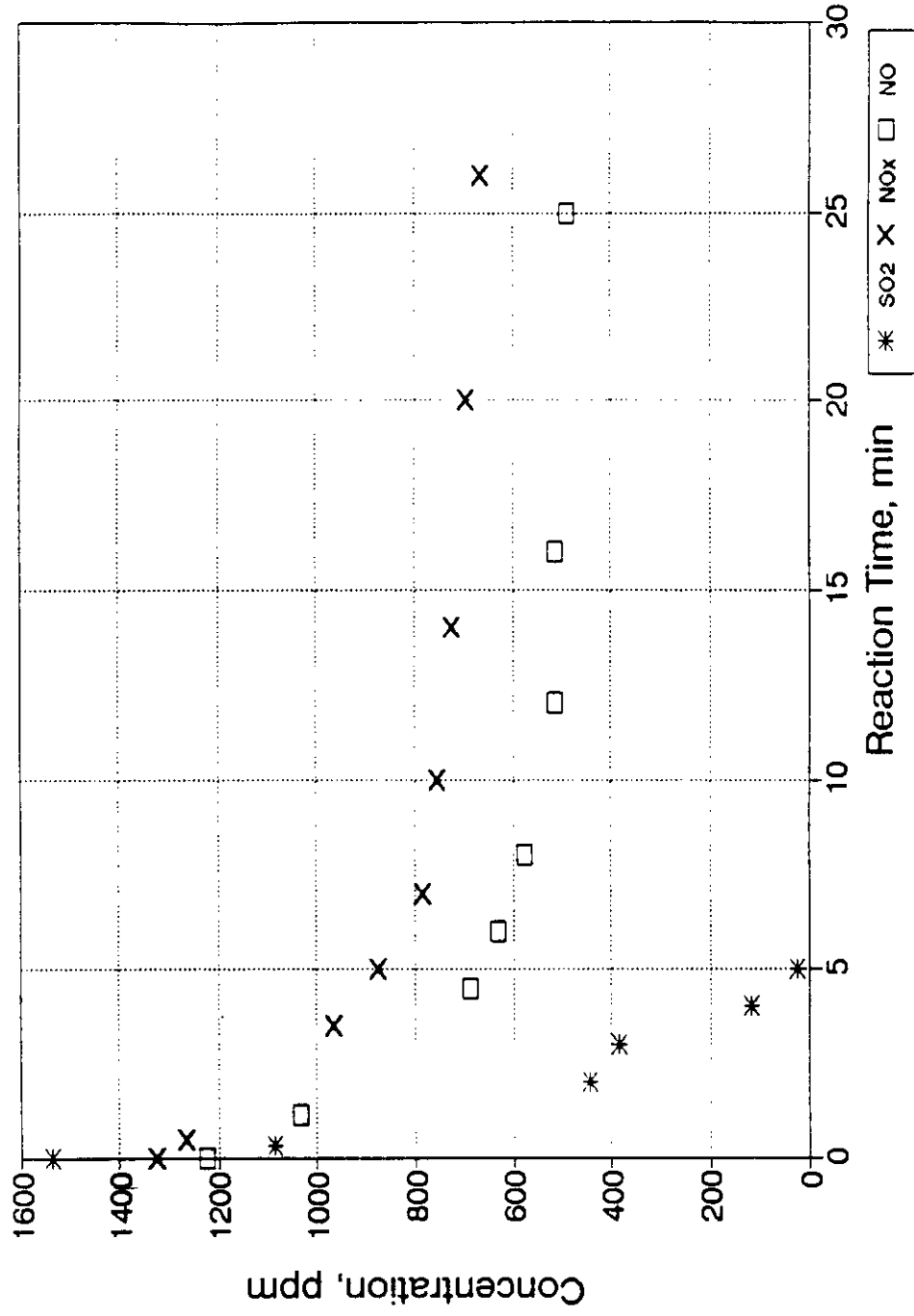
##### 4.1.1 $NO_x$ Removal by Sodium Bicarbonate Enhanced by $SO_2$ .

Three experimental runs were designed to see the effect of  $SO_2$  on  $NO_x$  removal by sodium bicarbonate. The first was  $NO_x$  and  $SO_2$  simultaneous removal by sodium

bicarbonate with  $NSR=13.5$ , 3% water, mean particle size 58  $\mu\text{m}$ , at  $300^\circ\text{F}$  and 300 rpm. Result of this run has been plotted on Figure 8. It shows that in twenty minutes,  $\text{NO}_x$  was reduced from 1324 ppm to 694 ppm which was about 630 ppm or 48% removal and  $\text{NO}_2$  formed was increased from 100 ppm to 200 ppm.

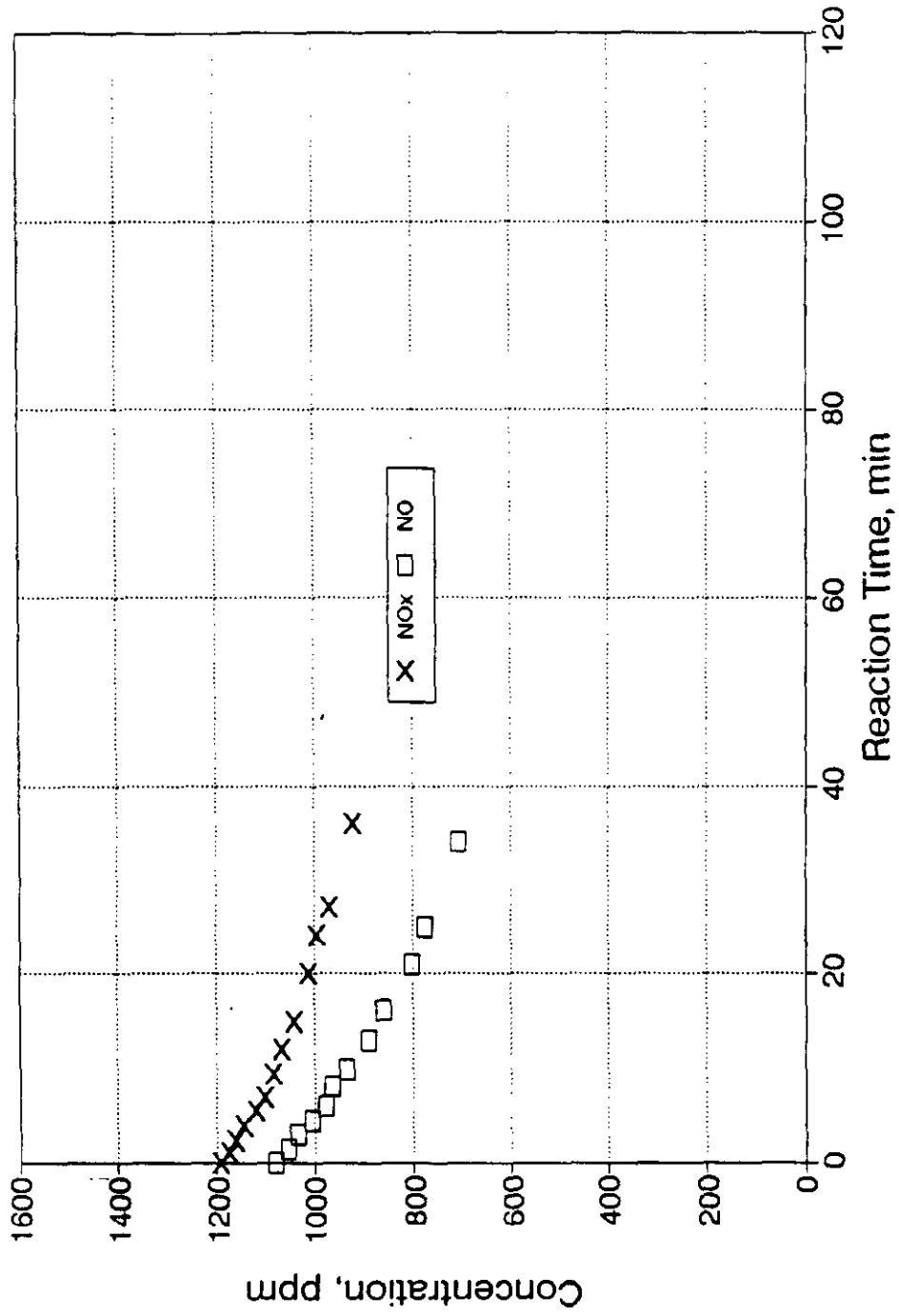
With the same operation condition, in the second run, we introduce  $\text{NO}_x$  only with corresponding  $NSR$  value of 13.5. Results from this experimental run is shown in Figure 9. From the figure, we can see the  $\text{NO}_x$  was removed less than that of the first run. The  $\text{NO}_x$  was removed from about 1200 ppm to 1000 ppm with 200 ppm or 17% removal within twenty minutes.  $\text{NO}_2$  concentration which is the difference between  $\text{NO}_x$  and  $\text{NO}$ , was found to increase from 110 ppm to about 200 ppm at the end of twenty minutes.

The third run was operated as the same condition as the first run except that  $\text{NO}_x$  was injected at twelve minutes at which the reaction of  $\text{SO}_2$  was complete. Later we will show that the  $\text{SO}_2$  concentrations measured in Figure 8 were too low due to their long sample storage time. At the end of this chapter we will also show that the twelve minute complete reaction time for  $\text{SO}_2$  is approximately correct. Results from this experimental run are shown in Figure 10. As we can see in Figure 10,  $\text{NO}_x$  was removed from about 1520 ppm to about 1200 ppm with about 320 ppm or 21% removal which was less than that of the first run, but slightly more than that in run two. At the end of twelve minute, only a little  $\text{SO}_2$  was present in the reactor.  $\text{NO}_x$  removal rate in this run is larger than



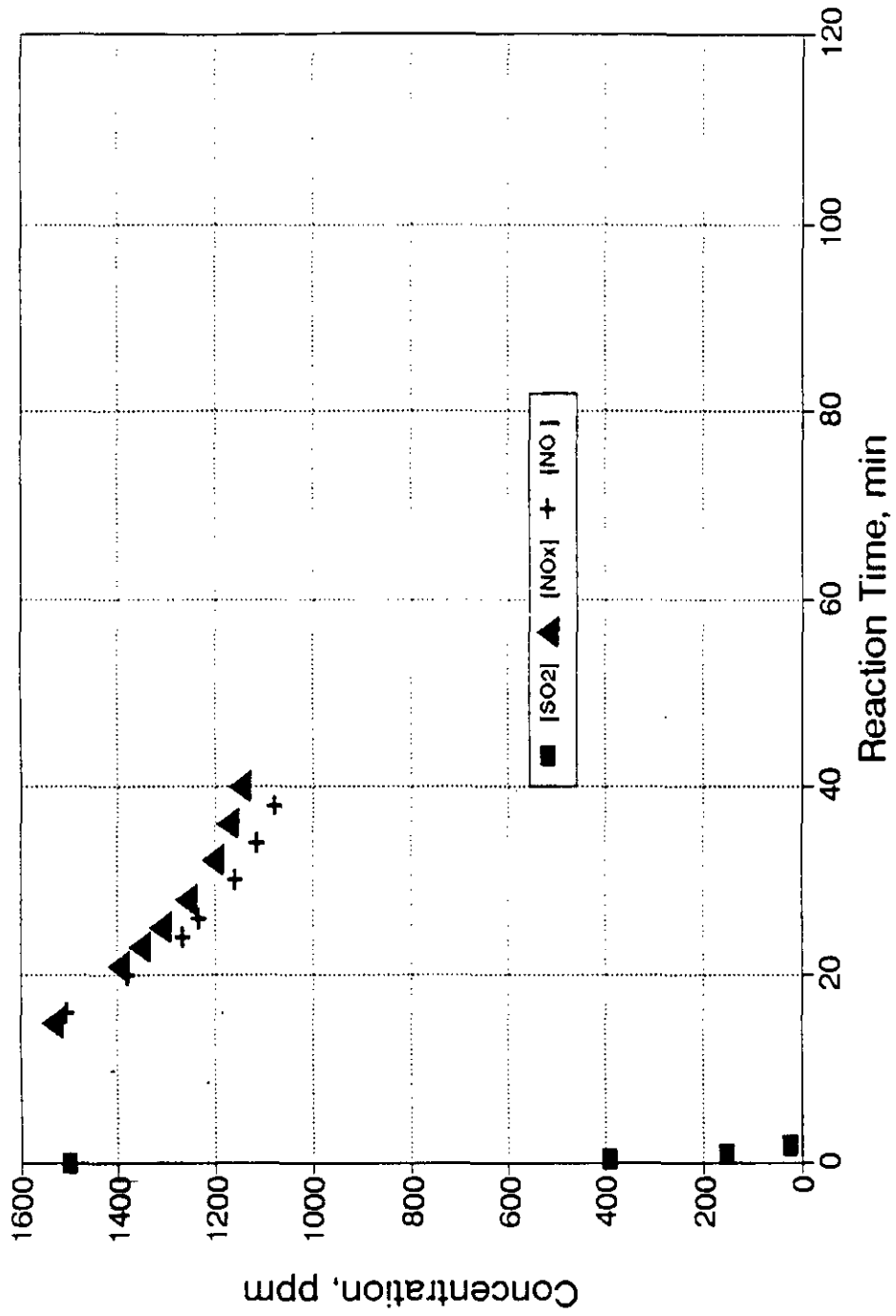
NSR=13.5, Water=3.5%, 300F, 300 rpm, 53um < d < 63um

Figure 8. SO2 and NOx Simultaneous Removal by Sodium Bicarbonate



NSR=13.5, Water=3%, 300F, 300 rpm, 53um < d < 63um

Figure 9. NOx Removal by Sodium Bicarbonate



NSR=13.5, Water=3%, 300 F, 300 rpm, 53um < d < 63um

Figure 10. NOx Removal by Sodium Bicarbonate After SO2 Completely Removed



that in run two because of the trace  $\text{SO}_2$  present in the system.  $\text{NO}_2$  formed increased from about 10 ppm to 20 ppm from the twelve minute to thirty two minutes. The  $\text{NO}_2$  formation at the end of twenty minutes was found to be the least amount among these three runs.

#### 4.1.2 $\text{NO}_2$ Formation enhanced by $\text{SO}_2$ in $\text{NO}_2$ - $\text{NO}$ - $\text{O}_2$ Gas Mixture.

Two experimental runs were conducted at  $300^\circ\text{F}$  and 300 rpm without any sorbent injection. Result from this set of runs was illustrated in Figure 11.  $\text{NO}_x$  removed without  $\text{SO}_2$  was from 1378 ppm to about 1250 ppm with about 128 ppm or 9%  $\text{NO}_x$  removal at the end of forty minutes due to the system bleeding.  $\text{NO}_2$  formation in this experimental run was from 5 ppm to 150 ppm within forty minutes.  $\text{NO}_x$  removal with the presence of  $\text{SO}_2$  was from 1342 ppm to 1080 ppm with about 157 ppm or 12 % removal.  $\text{NO}_2$  formation in this experimental run was from 9 ppm to about 202 ppm which was slightly higher than that of the system without  $\text{SO}_2$ . It appears the  $\text{NO}_2$  formation in this system is due to the oxidation of  $\text{NO}$  and  $\text{O}_2$  in the gas phase.

#### 4.2 Sodium Bicarbonate Injection

The typical operating conditions used in these tests were 300 rpm stirring speed,  $300^\circ\text{F}$  and  $\text{NSR}=13.5$  for the earlier experiments, and 700 rpm,  $260^\circ\text{F}$  and  $\text{NSR}=3.4$  for the rest of the tests. Sorbent dose, motor stirring speed, reaction temperature, and water content were used to test their effects on the removal of  $\text{NO}$  and  $\text{NO}_x$ , and the

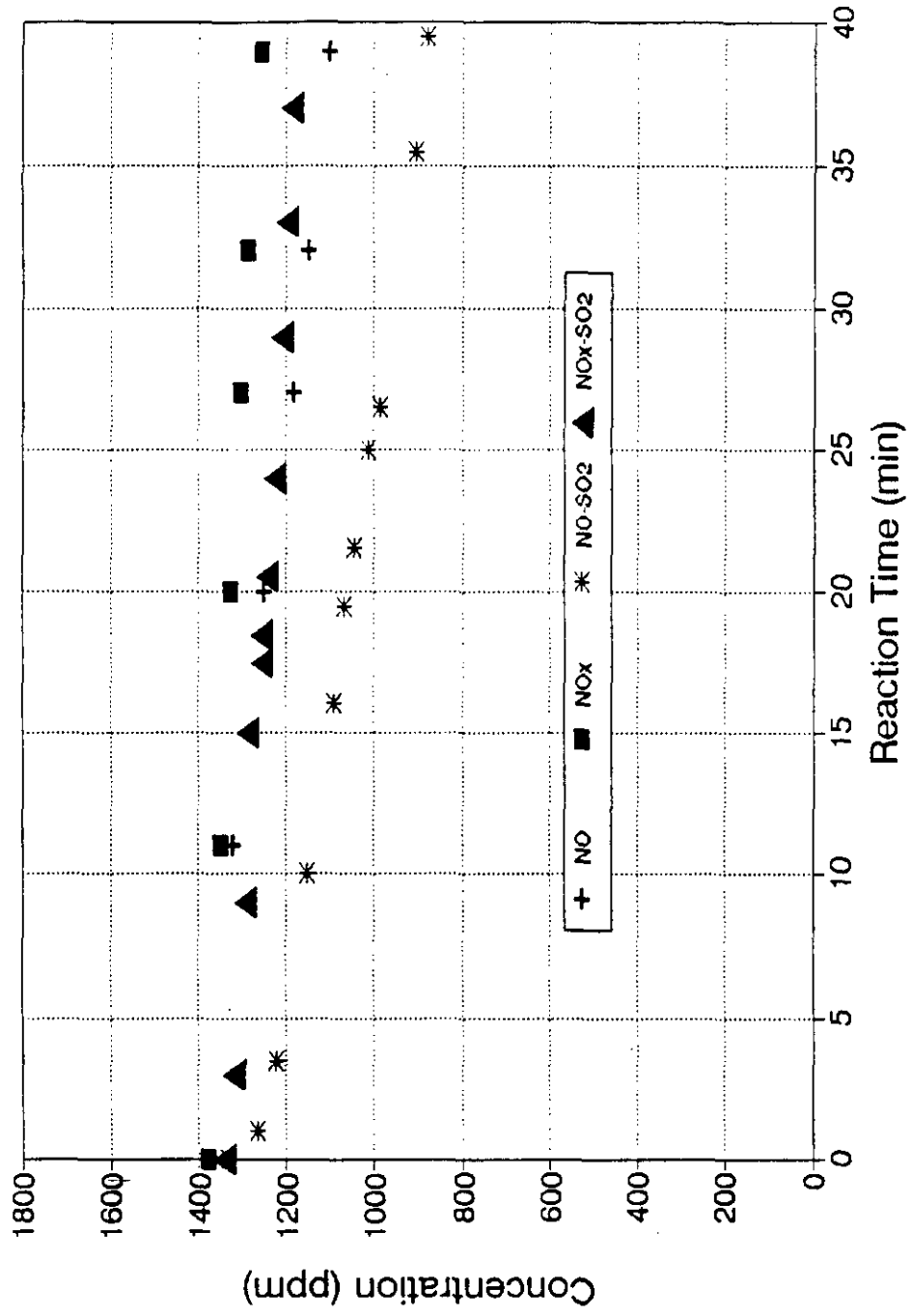


Figure 11. Comparison between the NOx System with SO2 and the NOx System without SO2

yield of  $\text{NO}_2$  at the end of reaction.

#### 4.2.1 Sorbent Dose Effect

Sorbent dose effect, or NSR effect, using sodium bicarbonate was investigated from four experimental runs, three base runs with  $\text{NSR}=3.4$  and one run with  $\text{NSR}=0.6$ , under the typical operation conditions. As we can see from the resultant data tabulated in Table 8, the tests with  $\text{NSR}=3.4$  have values of  $\text{NO}_x$  removal around 13% which is greater than the 5% removal in the test with  $\text{NSR}=0.6$  at 5 minutes.  $\text{NO}_2$  formation is about 150 ppm for  $\text{NSR}=3.4$  and for  $\text{NSR}=0.6$ ,  $\text{NO}_2$  formation is about 45 ppm. This is obviously what is expected, since a greater solids presence should result in a greater conversion.

#### 4.2.2 Stirring Speed Effect

Resultant data from three base runs and one run with stirring speed 300 rpm were used to investigate the contribution of fluid velocity to the  $\text{SO}_2$  and  $\text{NO}_x$  removal. It seems higher  $\text{NO}_x$  removal was obtained at lower stirring speed as we can see in Table 9. At the same time somewhat less  $\text{NO}_2$  was formed. If mass transfer effects were important one would expect at least a lower conversion of  $\text{NO}_x$ . Thus, mass transfer effects are probably not important.

#### 4.2.3 Temperature Effect

Three experimental runs, two at 300°F and the other at 240°F, illustrate the effect of temperature alone on  $\text{NO}_x$  removal by sodium bicarbonate with the conditions of 7%

Table 8. NSR Effect on SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Bicarbonate:

Parameter	08-08-93	05-25-93	05-31-93	08-07-93
Sorbent	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>
Water(%)	5	5	5	5
Temp.(F)	260	260	260	260
rpm	700	700	700	700
NSR	3.4	3.4	3.4	0.6
Size(um)	53 < d < 63	53 < d < 63	53 < d < 63	53 < d < 63
(SO <sub>2</sub> ) <sub>0</sub>	1617	1577	1478	1543
(NO <sub>x</sub> ) <sub>0</sub>	1468	1480	1450	1432
(NO ) <sub>0</sub>	1453	1476	1448	1430
(NO <sub>2</sub> ) <sub>0</sub>	15	4	2	2
(SO <sub>2</sub> ) <sub>3</sub>	176	440	230	350
(NO <sub>x</sub> ) <sub>5</sub>	1284	1300	1255	1356
(NO ) <sub>5</sub>	1160	1120	1100	1309
(NO <sub>2</sub> ) <sub>5</sub>	124	180	155	47
d(NO <sub>2</sub> ) <sub>5</sub>	109	176	153	45
R%(SO <sub>2</sub> ) <sub>3</sub>	89	72	84	77
R%(NO <sub>x</sub> ) <sub>5</sub>	13	12	13	5

Table 9. Stirring Effect on SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Bicarbonate:

Parameter	08-08-93	05-25-93	05-31-93	05-20-93
Sorbent	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>
Water(%)	5	5	5	5
Temp.(F)	260	260	260	260
rpm	700	700	700	300
NSR	3.4	3.4	3.4	3.4
Size(um)	53 < d < 63	53 < d < 63	53 < d < 63	53 < d < 63
(SO <sub>2</sub> ) <sub>o</sub>	1617	1577	1478	1610
(NO <sub>x</sub> ) <sub>o</sub>	1468	1480	1450	1471
(NO) <sub>o</sub>	1453	1476	1448	1454
(NO <sub>2</sub> ) <sub>o</sub>	15	4	2	15
(SO <sub>2</sub> ) <sub>3</sub>	176	440	230	189
(NO <sub>x</sub> ) <sub>5</sub>	1284	1300	1255	1215
(NO) <sub>5</sub>	1160	1120	1100	1080
(NO <sub>2</sub> ) <sub>5</sub>	124	180	155	135
d(NO <sub>2</sub> ) <sub>5</sub>	109	176	153	120
R%(SO <sub>2</sub> ) <sub>3</sub>	89	72	84	88
R%(NO <sub>x</sub> ) <sub>5</sub>	13	12	13	17

water, 300 rpm stirring speed, and NSR=13.5. It is shown in Table 10 that there is not much difference in either reduction of NO<sub>x</sub> or formation of NO<sub>2</sub>. Although one would expect a greater rate of reaction of NO<sub>x</sub> at higher temperature, SO<sub>2</sub>, which is believed to be necessary for reaction of NO<sub>2</sub>, is also more rapidly depleted.

#### 4.2.4 Water Effect

The effects of water vapor concentration on NO<sub>x</sub> removal and NO<sub>2</sub> formation in the system of NaHCO<sub>3</sub>-SO<sub>2</sub>-NO can be determined by comparing the results of seven experimental runs ranging from 0% to 10% water. Results from these experiments are shown in Table 11. The most significant affect appears to be the very low conversion of SO<sub>2</sub> that occurs in the absence of moisture. It seems that systems with lower water contents yielded slightly higher NO<sub>x</sub> removal. As for the NO<sub>2</sub> formation, the NO<sub>2</sub> level is higher at water content about 3%. However, these latter effects were minor.

### 4.3 Sodium Sesquicarbonate Injection

The typical operating conditions used in these tests were 300 rpm stirring speed, 300°F and NSR=13.5 for the beginning of this phase, and 700 rpm, 260°F and NSR=3.4 for the rest of the tests. Sorbent doses, motor stirring speeds, reaction temperatures, and particle size were used to test their effects on the removal of NO and NO<sub>x</sub>, and the yield of NO<sub>2</sub> at five minutes after reaction.

#### 4.3.1 Sorbent Dose Effect

Sorbent dose effect, or NSR effect, using sodium sesquicarbonate was investigated

Table 10. Temperature Effect on SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Bicarbonate:

Parameter	04-20-93	04-23-93	05-07-93
Sorbent	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>
Water(%)	7	7	6.7
Temp.(F)	300	300	240
rpm	300	300	300
NSR	13.5	13.5	13.5
Size(um)	53 < d < 63	53 < d < 63	53 < d < 63
(SO <sub>2</sub> ) <sub>0</sub>	1380	1504	1640
(NO <sub>x</sub> ) <sub>0</sub>	1564	1564	1480
(NO ) <sub>0</sub>	1522	1522	1480
(NO <sub>2</sub> ) <sub>0</sub>	42	42	0
(SO <sub>2</sub> ) <sub>3</sub>	140	270	180
(NO <sub>x</sub> ) <sub>5</sub>	1120	1180	1120
(NO ) <sub>5</sub>	995	1035	1000
(NO <sub>2</sub> ) <sub>5</sub>	125	145	120
d(NO <sub>2</sub> ) <sub>5</sub>	83	103	120
R%(SO <sub>2</sub> ) <sub>3</sub>	90	82	89
R%(NO <sub>x</sub> ) <sub>5</sub>	28	25	24

Table 11. Water Effect on SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Bicarbonate:

Parameter	04-21-93	04-27-93	04-16-93	04-27-93	04-20-93	04-23-93	04-30-93
Sorbent	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>	NaHCO <sub>3</sub>
Water(%)	0	2.9	3.5	3.5	7	7	10
Temp.(F)	300	300	300	300	300	300	300
rpm	300	300	300	300	300	300	300
NSR	13.5	13.5	13.5	13.5	13.5	13.5	13.5
Size(um)	53 < d < 63	53 < d < 63	53 < d < 63	53 < d < 63	53 < d < 63	53 < d < 63	53 < d < 63
(SO <sub>2</sub> ) <sub>o</sub>	1381	1470	1384	1405	1380	1504	1547
(NO <sub>x</sub> ) <sub>o</sub>	1504	1402	1383	1450	1564	1564	1474
(NO) <sub>o</sub>	1464	1387	1252	1440	1522	1522	1465
(NO <sub>2</sub> ) <sub>o</sub>	40	15	131	10	42	42	9
(SO <sub>2</sub> ) <sub>5</sub>	724	313	270	200	140	270	111
(NO <sub>x</sub> ) <sub>5</sub>	1045	965	996	1020	1120	1180	1090
(NO) <sub>5</sub>	900	792	804	850	995	1035	950
(NO <sub>2</sub> ) <sub>5</sub>	145	173	192	170	125	145	140
d(NO <sub>2</sub> ) <sub>5</sub>	105	158	61	160	83	103	131
R%(SO <sub>2</sub> ) <sub>3</sub>	48	79	80	86	90	82	93
R%(NO <sub>x</sub> ) <sub>5</sub>	31	31	28	30	28	25	26



by five experimental runs, one base runs with  $NSR=3.4$ , two runs with  $NSR=1.7$ , and two runs with  $NSR=0.85$ , under the typical operation conditions. As we can see from resultant data tabulated in Table 12, the tests with  $NSR=3.4$  result in a value of  $NO_x$  removal of 19% which is greater than the 13% removal in the test of sodium bicarbonate with the same operating and sorbent dose conditions. The  $NO_2$  formation at 5 minute is about 120 ppm which is less than that of 150 ppm in the tests of sodium bicarbonate. As for sodium sesquicarbonate itself, the removal of  $NO_x$  with  $NSR=1.7$  and with  $NSR=0.85$  at 5 minute are about 16% and 13% respectively. The  $NO_2$  formation with  $NSR=1.7$  and with  $NSR=0.85$  at 5 minute are about 54 and 48 ppm respectively. The lower  $NO_x$  removal results compared with those from EPRI<sup>6</sup> might be due to insufficient stirring speeds used in our experiments at which mass transfer effects can be important.

#### 4.3.2 Sorbent Particle Size Effect

Three sizes of sorbent particles have been selected to study the effect on  $NO_x$  removal and  $NO_2$  formation. Experimental results were tabulated in Table 13. As we can see in Table 12, the  $NO_x$  removal rate increases while we decrease the particle size. The  $NO_x$  removal at 5 minutes after reaction for particle size 58, 29 and 24  $\mu m$  are 19%, 24% and 25% respectively, which implies that the  $NO_x$  removal by sodium sesquicarbonate is proportional to the surface area. In this set of data,  $NO_2$  formation seems lower for the result of particle size 24  $\mu m$  than for the other two sizes.

Table 12. Dose Effect on SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Sesquicarbonate:

Parameter	06-18-93	06-22-93	06-21-93	06-17-93	05-27-93
Sorbent	Sesq-	Sesq-	Sesq-	Sesq-	Sesq-
Water(%)	5	5	5	5	5
Temp.(F)	260	260	260	260	260
rpm	700	700	700	700	700
NSR	0.85	0.85	1.7	1.7	3.4
Size(um)	53 < d < 63	53 < d < 63	53 < d < 63	53 < d < 63	53 < d < 63
(SO <sub>2</sub> ) <sub>o</sub>	1627	1795	1546	1620	1540
(NO <sub>x</sub> ) <sub>o</sub>	1384	1498	1468	1384	1230
(NO ) <sub>o</sub>	1338	1482	1465	1349	1206
(NO <sub>2</sub> ) <sub>o</sub>	46	16	3	35	24
(SO <sub>2</sub> ) <sub>3</sub>	137	176	150	224	188
(NO <sub>x</sub> ) <sub>5</sub>	1210	1300	1230	1220	1000
(NO ) <sub>5</sub>	1131	1220	1154	1150	880
(NO <sub>2</sub> ) <sub>5</sub>	79	80	76	70	120
d(NO <sub>2</sub> ) <sub>5</sub>	33	64	73	35	96
R%(SO <sub>2</sub> ) <sub>3</sub>	92	90	90	86	88
R%(NO <sub>x</sub> ) <sub>5</sub>	13	13	16	12	19

Table 13. Sorbent Particle Size Effect on SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Sesquicarbonate :

Parameter	05-27-93	06-23-93	06-23-93
Sorbent	Sesq-	Sesq-	Sesq-
Water(%)	5	5	5
Temp.(F)	260	260	260
rpm	700	700	700
NSR	3.4	3.4	3.4
Size(um)	53 < d < 63	45 < d < 53	15 < d < 32
(SO <sub>2</sub> ) <sub>o</sub>	1540	1752	1744
(NO <sub>x</sub> ) <sub>o</sub>	1230	1424	1474
(NO ) <sub>o</sub>	1206	1424	1465
(NO <sub>2</sub> ) <sub>o</sub>	24	0	9
(SO <sub>2</sub> ) <sub>3</sub>	188	22.4	180
(NO <sub>x</sub> ) <sub>5</sub>	1000	1080	1100
(NO ) <sub>5</sub>	880	953	1010
(NO <sub>2</sub> ) <sub>5</sub>	120	127	90
d(NO <sub>2</sub> ) <sub>5</sub>	96	127	81
R%(SO <sub>2</sub> ) <sub>3</sub>	88	99	90
R%(NO <sub>x</sub> ) <sub>5</sub>	19	24	25

#### 4.3.3 Water Effect

The effect of humidity on  $\text{NO}_x$  removal and  $\text{NO}_2$  formation in the system of Sodium sesquicarbonate- $\text{SO}_2$ - $\text{NO}$  is also investigated by comparing three experimental runs ranging from 0% to 10% water. Experiments for 0% and 10% water lack  $\text{SO}_2$  data. Results for these experiments are shown in Table 14. Water seemed to have very little effect on  $\text{NO}_x$  removal. As for  $\text{NO}_2$  formation, the  $\text{NO}_2$  level is slightly higher at lower water content.  $\text{NO}_2$  values were 145, 120 and 110 ppm for water content of 0%, 5% and 10% respectively.

#### 4.3.4 Temperature Effects

Only two experimental runs with sorbent dose  $\text{NSR}=13.5$  could be directly compared in this investigation, at 240°F and 300°F. The experiment at 300°F lacked  $\text{SO}_2$  data. From Table 15, it is shown that lower reaction temperature results in lower  $\text{NO}_x$  removal, 38% versus 45%, and lower  $\text{NO}_2$  formation, 60 versus 120 ppm.

#### 4.3.5 Low Concentrations $\text{SO}_2$ and $\text{NO}_x$

To investigate the removal of  $\text{SO}_2$  and  $\text{NO}_x$  at low initial concentrations ranging from 200 to 1100 ppm, the calibration data for both  $\text{SO}_2$  and  $\text{NO}_x$  had to be redone because a more sensitive method is required to observe the concentration differences from each other. The calibration procedure for  $\text{SO}_2$  is the same as the one described in chapter 2 except that the  $\text{CO}_2$  peak was combined with the air peak since trace amounts of  $\text{CO}_2$  are negligible while compared with the huge amount of air. The retention time

Table 14. Water Effect on SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Sesquicarbonate:

Parameter	07-22-93	05-27-93	07-22-93
Sorbent	Sesq-	Sesq-	Sesq-
Water(%)	0	5	10
Temp.(F)	260	260	260
rpm	700	700	700
NSR	3.4	3.4	3.4
Size(um)	53 < d < 63	53 < d < 63	53 < d < 63
(SO <sub>2</sub> ) <sub>o</sub>	-	1540	-
(NO <sub>x</sub> ) <sub>o</sub>	1474	1230	1461
(NO ) <sub>o</sub>	1436	1206	1430
(NO <sub>2</sub> ) <sub>o</sub>	38	24	31
(SO <sub>2</sub> ) <sub>3</sub>	-	188	-
(NO <sub>x</sub> ) <sub>5</sub>	1200	1000	1160
(NO ) <sub>5</sub>	1055	880	1050
(NO <sub>2</sub> ) <sub>5</sub>	45	120	110
d(NO <sub>2</sub> ) <sub>5</sub>	107	96	79
R%(SO <sub>2</sub> ) <sub>3</sub>	-	88	-
R%(NO <sub>x</sub> ) <sub>5</sub>	19	19	21

Table 15. Temperature Effect on SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Sesquicarbonate:

Parameter	05-10-93	05-03-93
Sorbent	Sesq-	Sesq-
Water(%)	6.7	3.5
Temp.(F)	240	300
rpm	300	300
NSR	13.5	13.5
Size(um)	53 < d < 63	53 < d < 63
(SO <sub>2</sub> ) <sub>o</sub>	1530	
(NO <sub>x</sub> ) <sub>o</sub>	1550	1550
(NO ) <sub>o</sub>	1525	1540
(NO <sub>2</sub> ) <sub>o</sub>	25	10
(SO <sub>2</sub> ) <sub>3</sub>	110	
(NO <sub>x</sub> ) <sub>5</sub>	960	860
(NO ) <sub>5</sub>	900	740
(NO <sub>2</sub> ) <sub>5</sub>	60	120
d(NO <sub>2</sub> ) <sub>5</sub>	35	110
R%(SO <sub>2</sub> ) <sub>3</sub>	93	
R%(NO <sub>x</sub> ) <sub>5</sub>	38	45

for air, water and SO<sub>2</sub> were about 0.3, 1.4, and 2.5 minute respectively on which the internal standard method can still be applied. The calibration curves for SO<sub>2</sub>, NO and NO<sub>x</sub> are shown in Figure 12, Figure 13, and Figure 14 respectively. The reliabilities of these calibration methods were investigated by conducting a blank test at low concentrations of SO<sub>2</sub>, NO and NO<sub>x</sub>.

The initial concentrations used in this investigation were 600 ppm for SO<sub>2</sub> and 550 ppm for NO. The sampling schedule for this blank test was identical to the typical one. The operation conditions also follow the normal operation condition, 260°F and 700 rpm, except the sorbent content was zero. The result of this investigation were plotted into Figure 15. It showed that there is no significant change for both NO and NO<sub>x</sub> concentration and only about a 50 ppm difference was detected for a reaction time of three minute.

Six experimental runs with different initial ratio of SO<sub>2</sub> to NO<sub>x</sub> were conducted at normal operating conditions with identical amount of sorbent injection (about 0.12 gram). This dose of sorbent is about an NSR=2 defined as initial amount of NO plus initial amount of SO<sub>2</sub>. Data from these experiments is tabulated in Table 16 arranged from low initial concentration to high initial concentration for SO<sub>2</sub>, and from high initial concentration to low initial concentration for NO. It is found in Table 16 that higher SO<sub>2</sub> to NO<sub>x</sub> ratio, or higher SO<sub>2</sub> and lower NO<sub>x</sub> concentration, results in lower SO<sub>2</sub> and higher NO<sub>x</sub> removal and also yields higher NO<sub>2</sub> formation. As we can see SO<sub>2</sub> removal

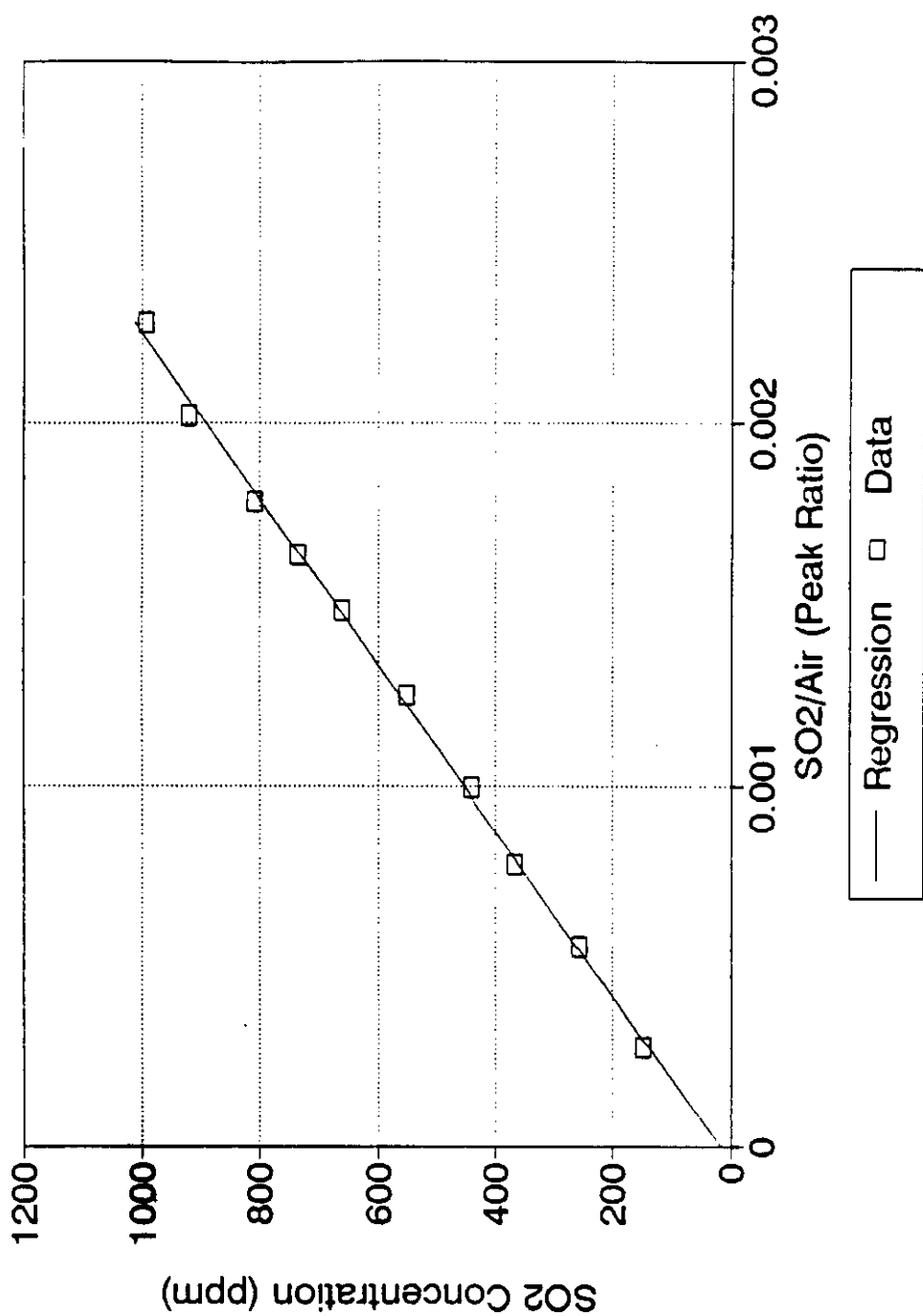


Figure 12. Calibration for Low Concentration SO2 Using GC Equipped with TCD



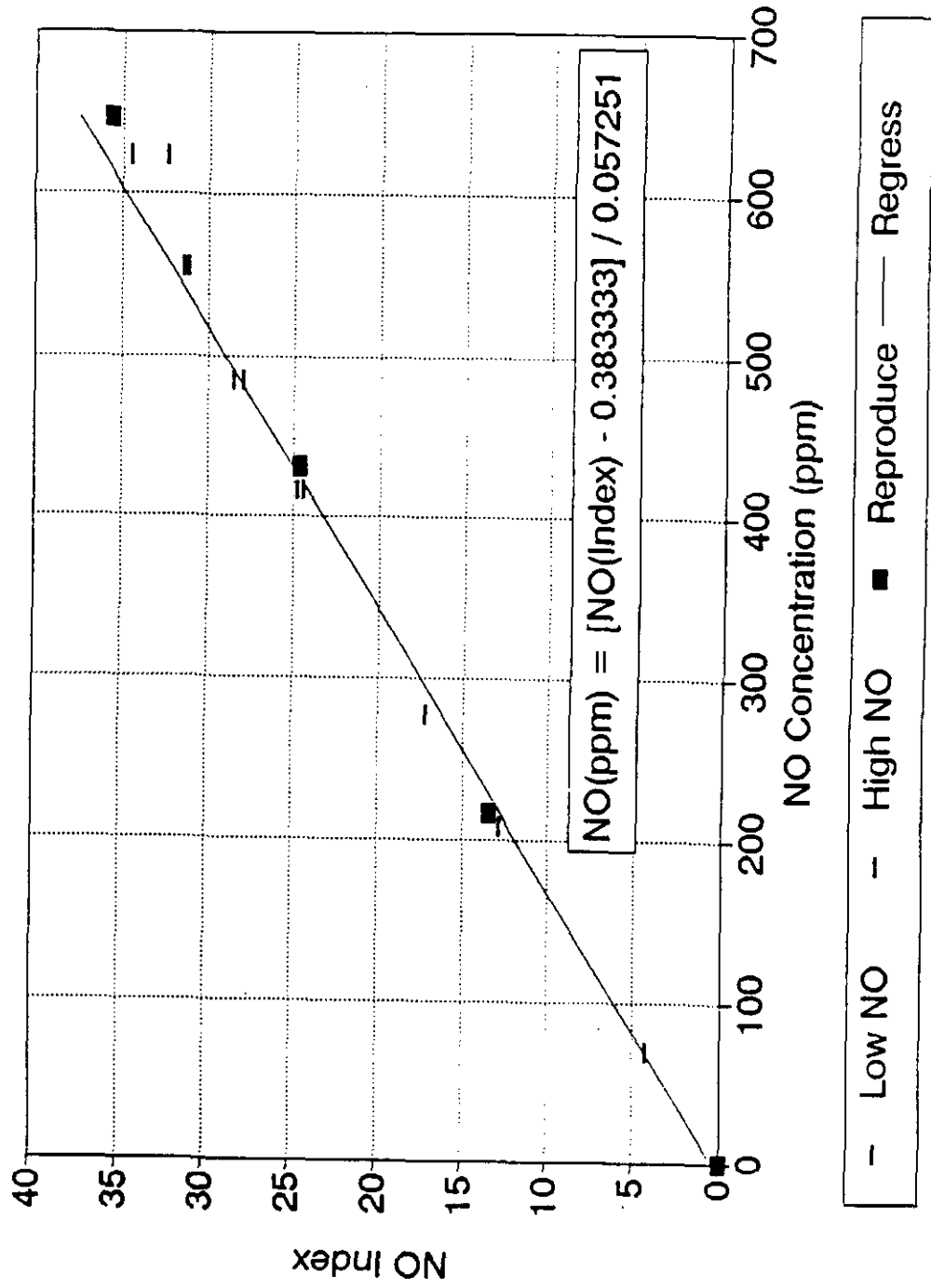


Figure 13. Calibration curve for low concentration NO

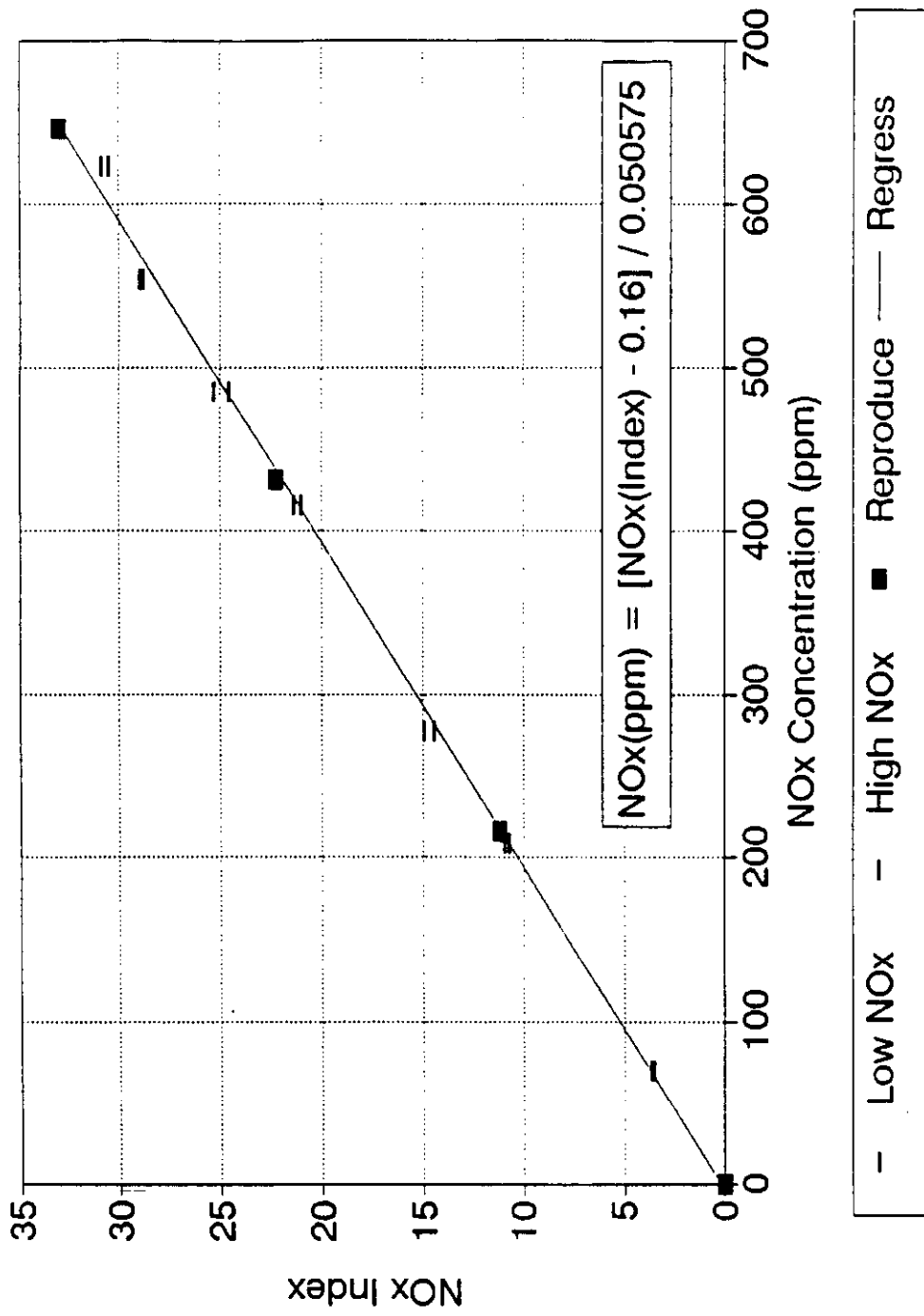
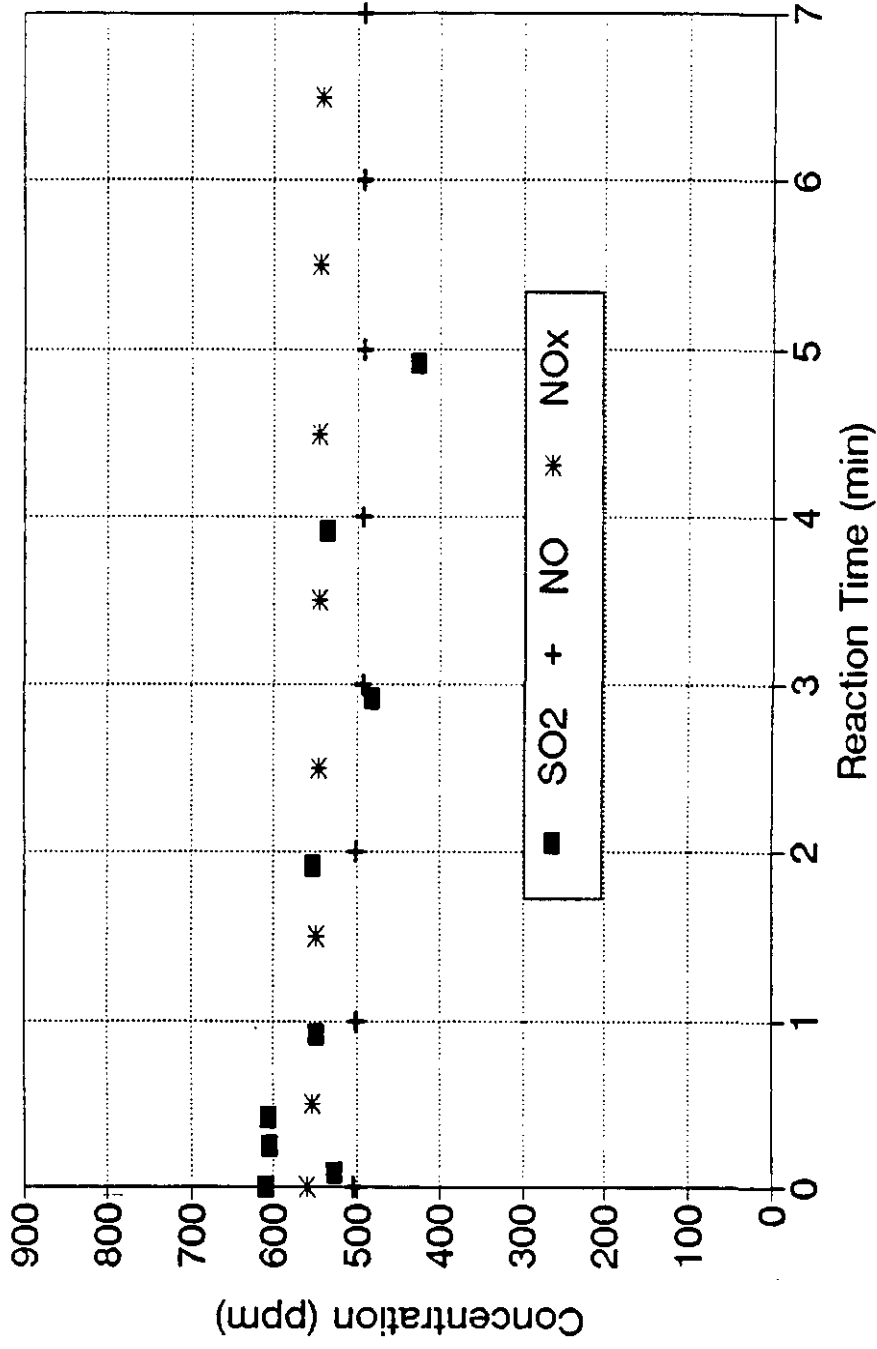


Figure 14. Calibration curve for low concentration NOx



700 rpm, 300 F without sorbent

Figure 15. Blank Test for Low Concentration NO, NOx, and SO2

Table 16. SO<sub>2</sub> and NO<sub>x</sub> Removal at Low Concentration by Sodium Sesquicarbonate:

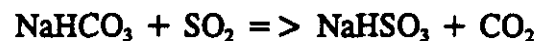
Parameter	06-27-93	06-09-93	06-22-93	06-22-93	06-27-93	06-27-93
Sorbent	Sesq-	Sesq-	Sesq-	Sesq-	Sesq-	Sesq-
Water(%)	5	5	5	5	5	5
Temp.(F)	260	260	260	260	260	260
rpm	700	700	300	700	700	700
NSR	3.4	3.4	3.4	3.4	3.4	3.4
Size(um)	53 < d < 63	53 < d < 63	53 < d < 63	53 < d < 63	53 < d < 63	53 < d < 63
(SO <sub>2</sub> ) <sub>0</sub>	220	295	379	464	785	871
(NO <sub>x</sub> ) <sub>0</sub>	1084	850	785	585	289	252
(NO) <sub>0</sub>	1080	850	779	579	264	238
(NO <sub>2</sub> ) <sub>0</sub>	4	0	6	6	25	14
(SO <sub>2</sub> ) <sub>3</sub>	88	75	140	145	450	530
(NO <sub>x</sub> ) <sub>5</sub>	975	720	667	492	200	182
(NO) <sub>5</sub>	953	714	645	481	142	129
(NO <sub>2</sub> ) <sub>5</sub>	22	6	22	11	58	53
d(NO <sub>2</sub> ) <sub>5</sub>	18	6	16	5	33	39
R%(SO <sub>2</sub> ) <sub>3</sub>	80	75	63	69	43	39
R%(NO <sub>x</sub> ) <sub>5</sub>	10	15	15	16	31	28

decreases from 80% to about 39%, NO<sub>x</sub> removal increases from 10% to about 30%, and NO<sub>2</sub> formation increases from about 20 to 55 ppm when the SO<sub>2</sub> to NO<sub>x</sub> ratio increased from about 0.2 to 3.5. This phenomena also was observed in EPRI's<sup>6</sup> study as described in section seven. It should also be noted that NO<sub>2</sub> formation is considerably lower at these lower concentrations than for the high concentration runs.

#### 4.4 Byproduct Identification

According to the work from J. Verlaeten<sup>12</sup> and his coworker in France, simultaneous reduction of SO<sub>2</sub> and NO<sub>x</sub> by sodium bicarbonate occurs by the following four steps:

Step 1. Sodium bicarbonate sulfation:



Step 2. Sodium bisulfite dehydration:



Step 3. Sodium pyrosulfite nitration:



Step 4. Sodium bisulfite nitration:



If the above reaction mechanism is right, then one mole of sodium pyrosulfite reacted with excess NO and oxygen should yield one mole of NaNO<sub>2</sub>, one mole of NaNO<sub>3</sub>, and

2 moles of  $\text{SO}_2$ . An experiment was therefore designed to determine if sodium pyrosulfite would in fact react with NO and, if it did, the stoichiometry for these chemicals. The quantities of material used for this experiment were 3000 ppm, 1500 ppm and 3 percent for sodium pyrosulfite, nitrogen oxide and oxygen respectively. Operating conditions in this experiment were 260°F, 700 rpm with water content 5%. As shown in Figure 16,  $\text{NO}_x$  removal is approximately equal to the amount of  $\text{SO}_2$  formation. Thus, it appears that sodium pyrosulfite may indeed be an intermediate in the removal of  $\text{NO}_x$  by sodium based solids.

Qualitative and quantitative identification for both  $\text{NaNO}_2$  and  $\text{NaNO}_3$  were performed by the method of X-ray diffraction. Calibration curves made for  $\text{NaNO}_2$  and  $\text{NaNO}_3$  were not reproducible due to high reactivity and high water sensitivity of these two chemicals; so, no conclusion could be made at this point regarding the solids that are produced.

#### 4.5 Chemical effect on the $\text{NO}_x$ removal and $\text{NO}_2$ formation

##### 4.5.1 The fate of $\text{NO}_x$ in the existence of sodium sulfite

According to the work from J. Verlaeten<sup>12</sup> sodium bisulfite would react with  $\text{NO}_x$ . An experiment therefore was designed to test if the  $\text{NO}_x$  could also be removed by sodium sulfite. The NSR for this dry sorbent of 2, was based on the initial NO concentration. Resultant data have been tabulated and plotted in Table 17 and Figure 17.

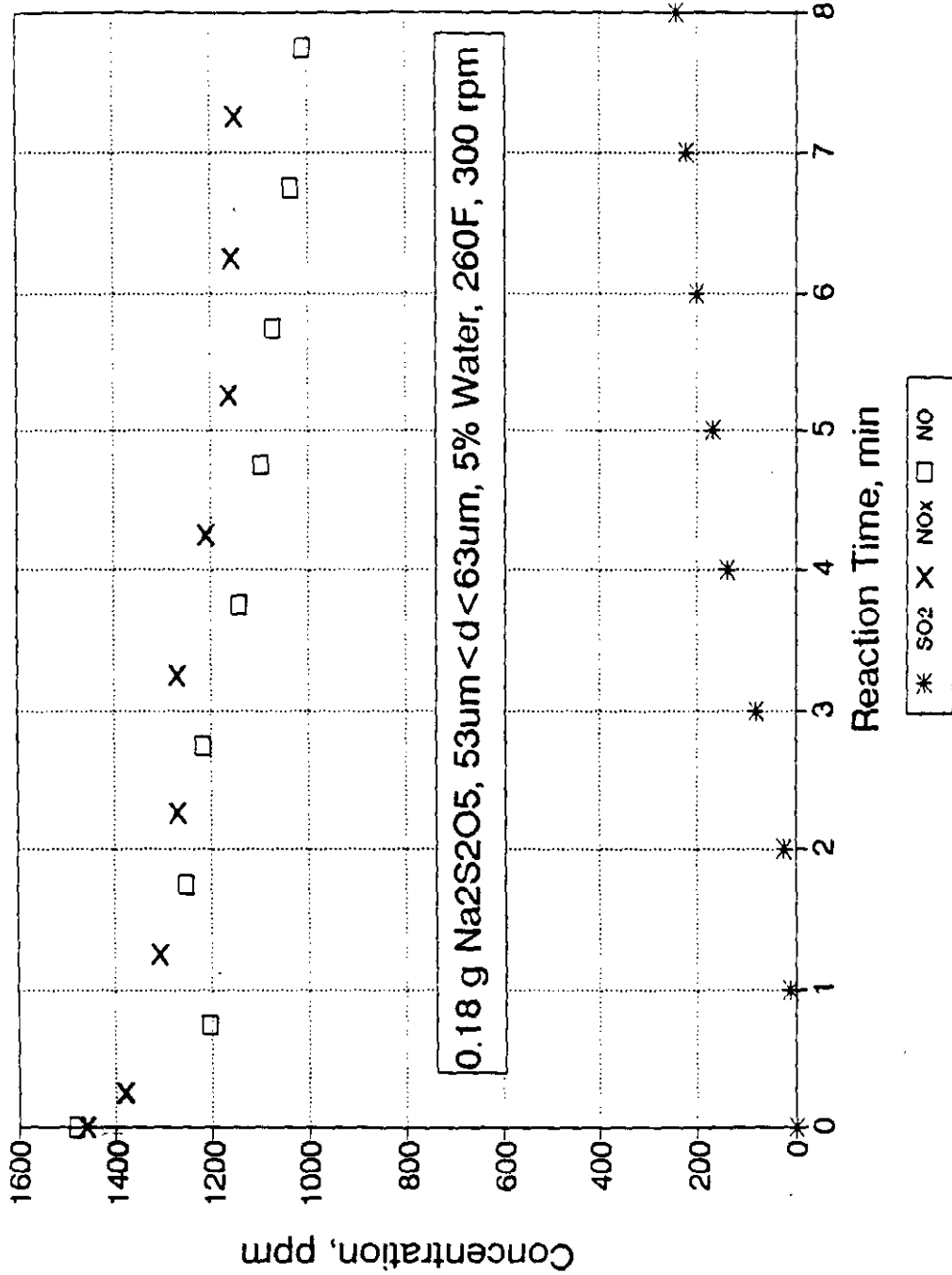


Figure 16. NO<sub>x</sub> Removal by Sodium Pyrosulfite

Table 17. SO<sub>2</sub> and NO<sub>x</sub> Removal by Three Chemicals :

Parameter	05-27-93	08-08-93	05-25-93	05-31-93	06-25-93	07-24-93	08-08-93
Sorbent	Sesq-	Bic-	Bic-	Bic-	Na <sub>2</sub> SO <sub>3</sub>	Na <sub>2</sub> SO <sub>3</sub>	Blank
Water(%)	5	5	5	5	5	5	5
Temp.(F)	260	260	260	260	260	260	260
rpm	700	700	700	700	700	700	700
NSR	3.4	3.4	3.4	3.4	2	2	0
Size(um)	53 < d < 63	53 < d < 63	53 < d < 63	53 < d < 63	53 < d < 63	53 < d < 63	0
(SO <sub>2</sub> ) <sub>o</sub>	1540	1617	1577	1478	0	0	1538
(NO <sub>x</sub> ) <sub>o</sub>	1230	1468	1480	1450	1439	1426	1424
(NO ) <sub>o</sub>	1206	1453	1476	1448	1435	1425	1419
(NO <sub>2</sub> ) <sub>o</sub>	24	15	4	2	4	1	5
(SO <sub>2</sub> ) <sub>5</sub>	188	176	440	230	0	0	280
(NO <sub>x</sub> ) <sub>5</sub>	1000	1284	1300	1255	1300	1296	1405
(NO ) <sub>5</sub>	880	1160	1120	1100	1281	1257	1384
(NO <sub>2</sub> ) <sub>5</sub>	120	124	180	155	19	39	21
d(NO <sub>2</sub> ) <sub>5</sub>	96	109	176	153	15	38	16
R%(SO <sub>2</sub> ) <sub>3</sub>	88	89	72	84	0	0	82
R%(NO <sub>x</sub> ) <sub>5</sub>	19	13	12	13	10	9	1



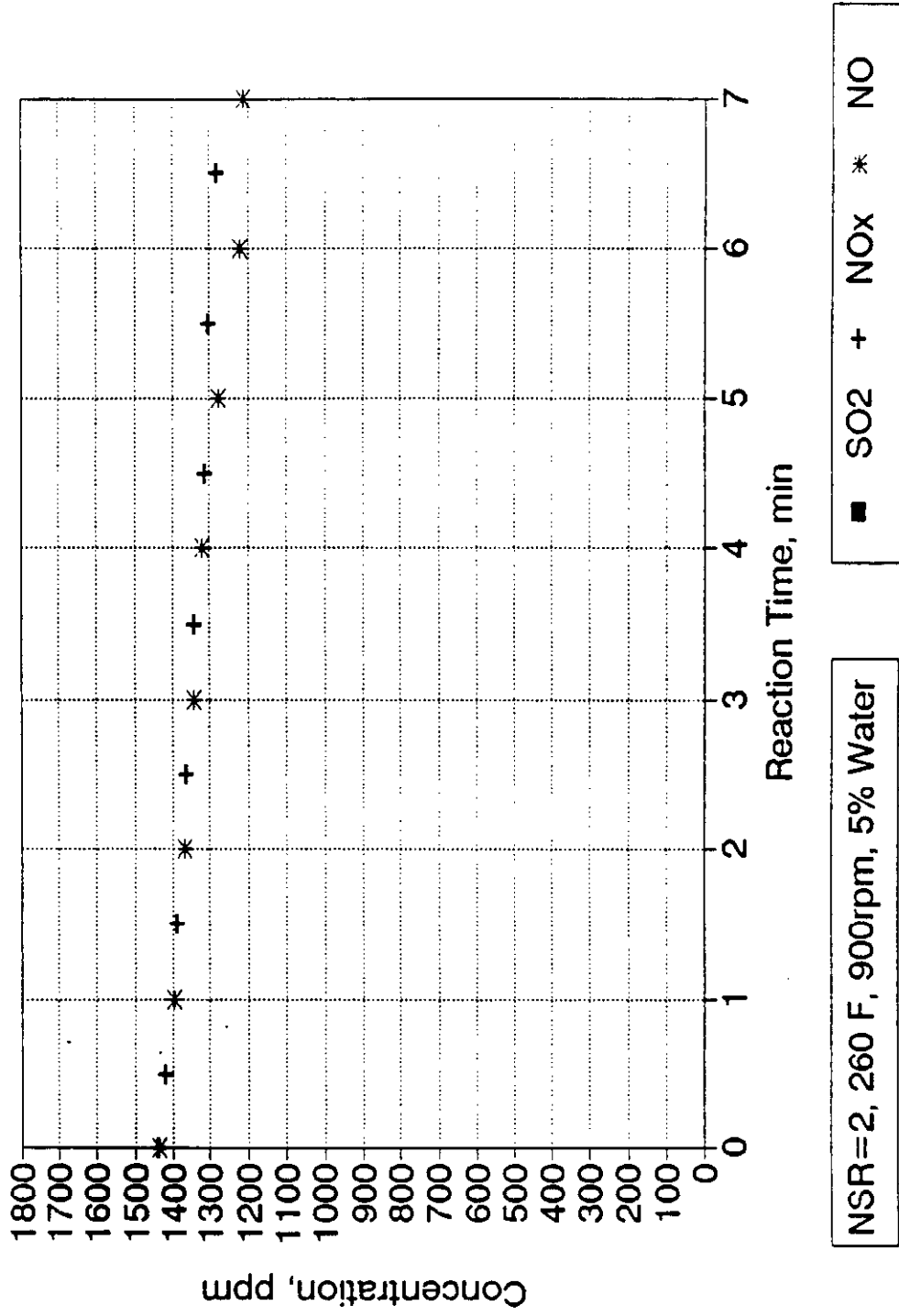
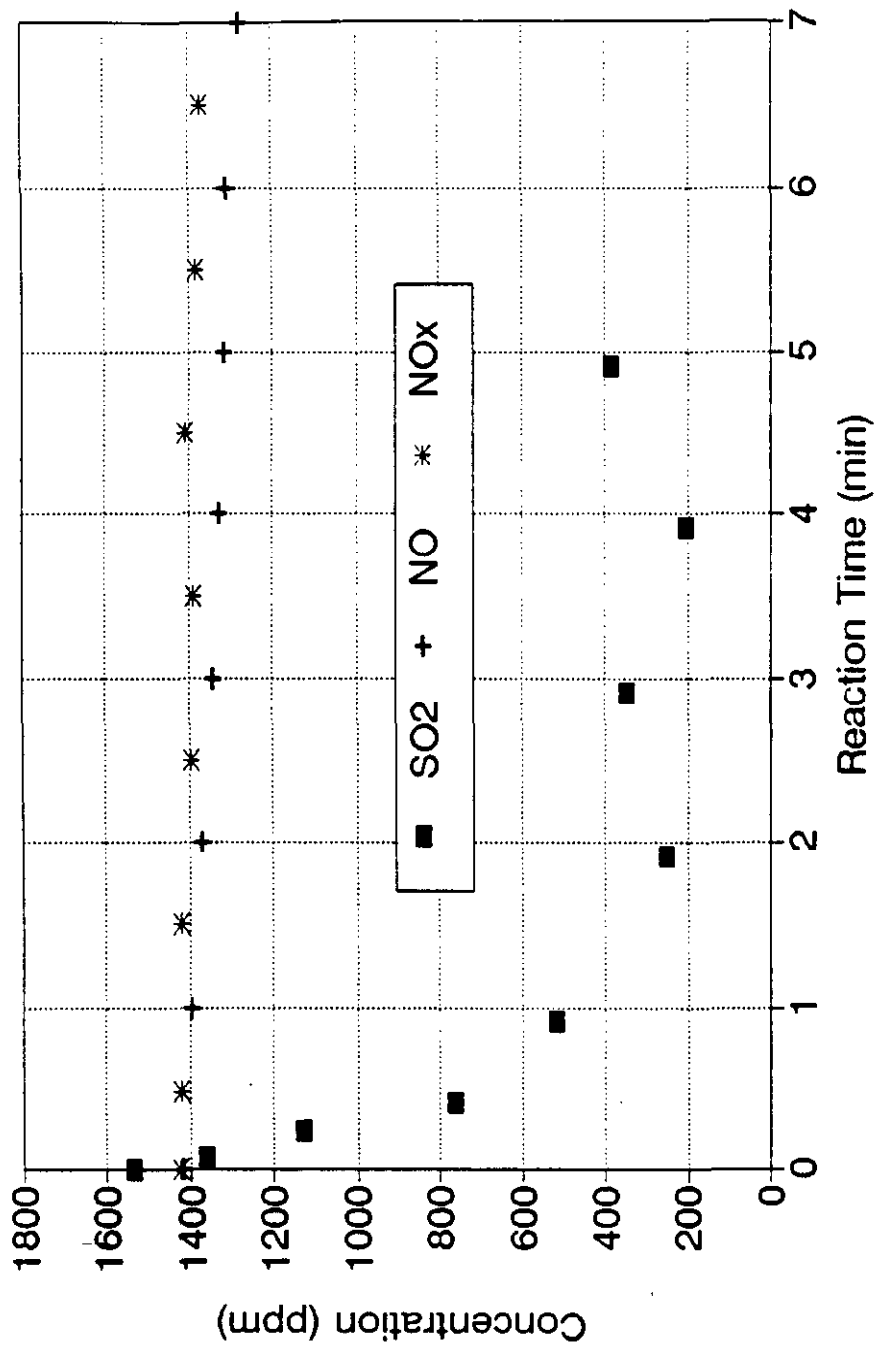


Figure 17. NOx Removed by Sodium Sulfite

No SO<sub>2</sub> was detected accompanying with the NO<sub>x</sub> removal. It shows that about 180 ppm NO<sub>x</sub>, which was somewhat greater than the value from a blank test, has been removed. The blank test like the one that we have already discussed for low concentration was conducted at the same operation condition. Results from this test are shown in Figure 18 which indicates that only 20 ppm NO<sub>x</sub> was removed from the system during the reaction. According to the book, "Handbook of Fluid Sealing<sup>(19)</sup>", the loss of NO and NO<sub>x</sub> might be due to the rotation process. Direct contact of teflon sealant with the rotating shaft will create friction which would wear out the surface of teflon and finally form a gap between teflon and the rotating shaft. However, the reduction in SO<sub>2</sub> is very significant and will be discussed below. We believe this reduction is due to our sampling procedure.

#### 4.5.2 Comparison of three dry sorbents

Six experimental runs including three runs from sodium bicarbonate, one sodium sesquicarbonate and two for sodium sulfite can be compared to investigate the difference in the NO<sub>x</sub> removal efficiency between these three chemicals. The results from these data plus a blank at high concentration were tabulated in Table 17 which showed that sodium sesquicarbonate had the highest NO<sub>x</sub> removal efficiency among these three chemicals. The removal of NO<sub>x</sub> for sodium sesquicarbonate, sodium carbonate and sodium sulfite were 19%, 13% and 10% respectively. The removal of NO<sub>x</sub> by sodium sulfite was somewhat surprising. While compared with the result from the blank which



NSR=0, Water=5%, 260F, 700 rpm

Figure 18 . SO2 and NOx Reduction without Dry Sorbent

was 1% removal, the loss of  $\text{NO}_x$  from the system should be negligible.

#### 4.6 Difficulties of high concentration $\text{SO}_2$ analysis

As we can see from the blank run of Figure 18, there is quite a reduction in the  $\text{SO}_2$  concentration which indicates that the  $\text{SO}_2$  analytical method might be in error for these runs as discussed above. A more thorough study on this phenomena was therefore done by conducting a series of runs with stirring speed 700 rpm, water content 5%, and system temperature 260°F without adding any sorbent. Runs conducted were as follows:

##### Run 1. Blank test without $\text{NO}_x$

An experiment was designed to determine if there is a difference between the blank test with  $\text{SO}_2$  and  $\text{NO}$ , and the blank test with  $\text{SO}_2$  alone. This test demonstrated that without  $\text{NO}_x$  there is not a large decrease in the  $\text{SO}_2$  concentration, and the analytical method for  $\text{SO}_2$  is still valid. The  $\text{SO}_2$  decrease may be due to  $\text{SO}_2$  diffusion from the syringe to the environment through the needle. The result has been plotted in Figure 19.

##### Run 2. Blank test without $\text{SO}_2$

An experiment was designed to find out if there is a difference between the blank test with  $\text{SO}_2$  and  $\text{NO}$ , and the blank test with  $\text{NO}$  alone. This test demonstrated that without  $\text{SO}_2$ , the result for both  $\text{NO}$  and  $\text{NO}_x$  is close to the one with  $\text{SO}_2$ . The  $\text{NO}_x$  decrease is mainly due to the bleeding from the reactor to the environment

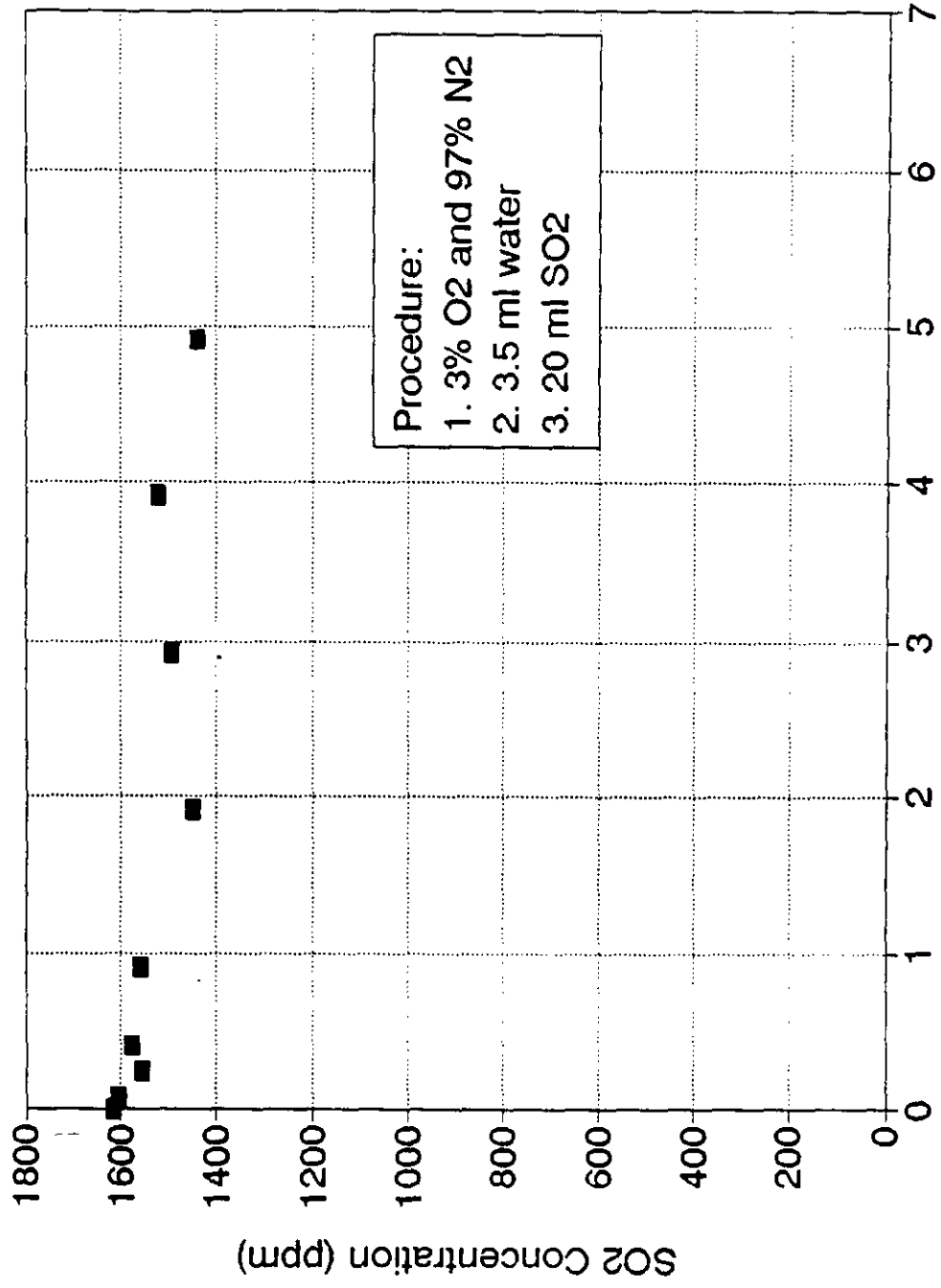


Figure 19. Blank Test without NOx

through the stirring process. The result has been plotted in Figure 20.

### Run 3. Blank test with SO<sub>2</sub> and NO<sub>x</sub> using direct injection

Another blank test was designed to determine if there is a difference if we shorten the sample waiting time. To speed up the SO<sub>2</sub> analysis procedure, a new calibration curve based on the method used for low SO<sub>2</sub> concentration was obtained and presented in Figure 21 for this blank test. This test demonstrated that by directly injecting the SO<sub>2</sub> sample into the gas chromatograph immediately after removal from the reactor (as was done at zero two and five minutes), the resultant values for SO<sub>2</sub> concentrations detected by GC are close to the initial values. While those concentrations determined from other SO<sub>2</sub> samples which were put aside while waiting for the GC to finish other analyses were significantly lower in concentration. Results for NO and NO<sub>x</sub> are similar to the one with SO<sub>2</sub> which was shown in Figure 19 and the one without SO<sub>2</sub> which was shown in Figure 20. The results from this test have been plotted in Figure 22.

The analytical procedure which was used in our high concentration analysis for SO<sub>2</sub> required about 8.5 minutes for the GC to finish a run. Normally, we determined eight samples for each experiment which took about sixty eight minutes to finish the GC SO<sub>2</sub> analysis. During the waiting time for GC analysis, something was happening to the SO<sub>2</sub> in the presence of NO<sub>x</sub> at room temperature as we can see from Figure 18, 19, 20 and 22. Thus, we believe that the low SO<sub>2</sub> concentrations obtained during the earlier runs

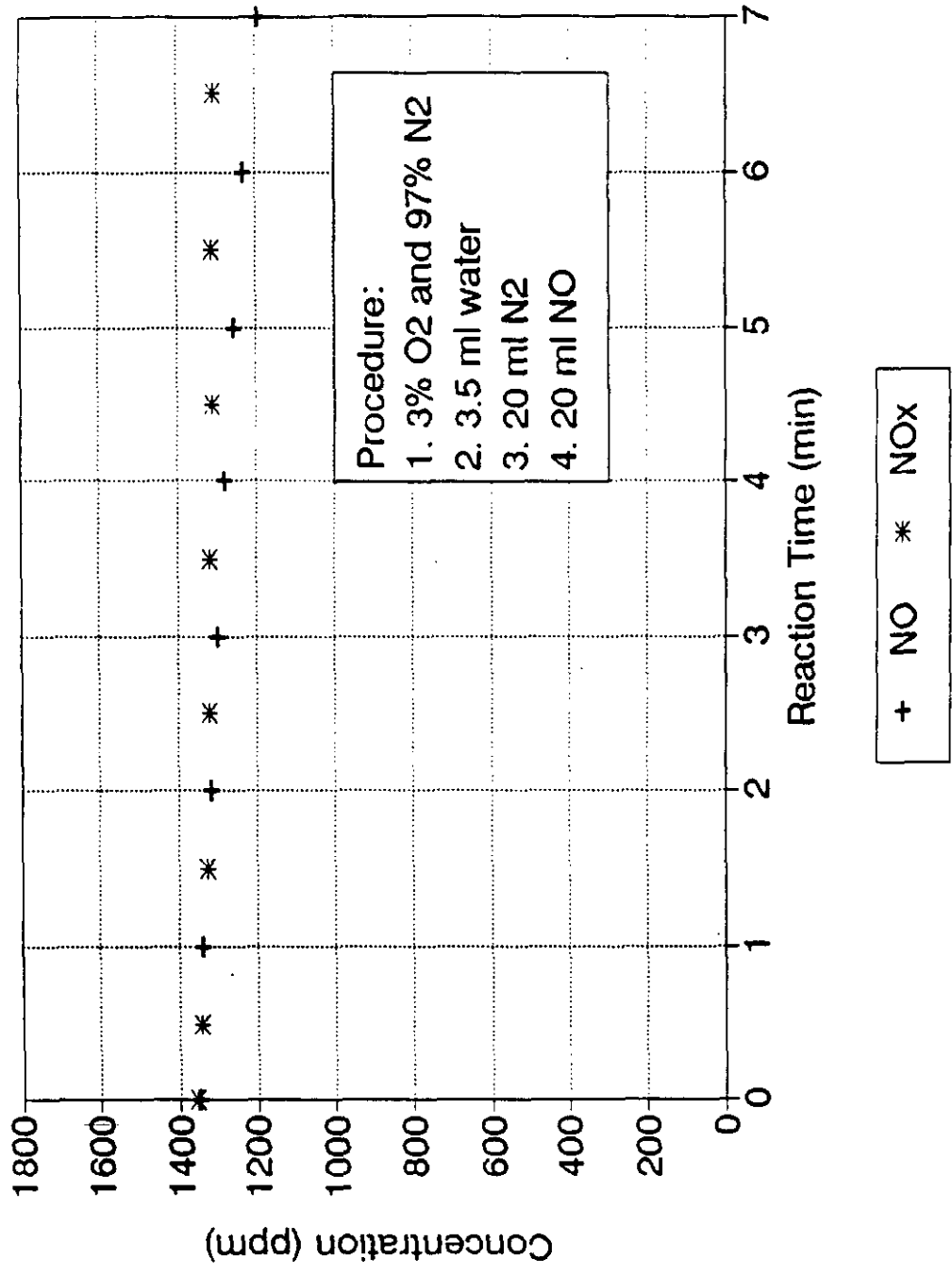


Figure 20. Blank Test without SO2

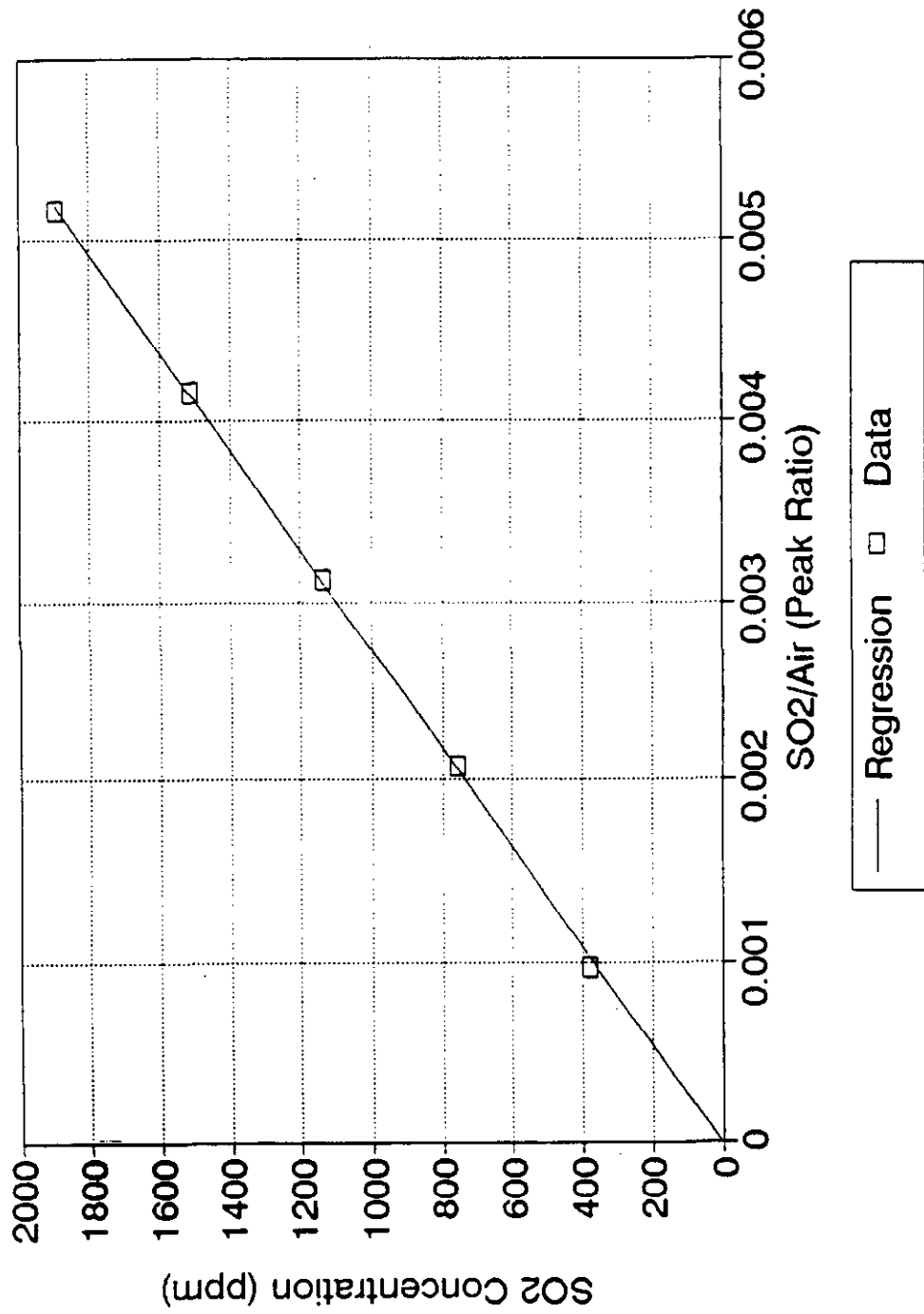


Figure 21. Calibration for High Concentration SO<sub>2</sub> Using GC Equipped with TCD



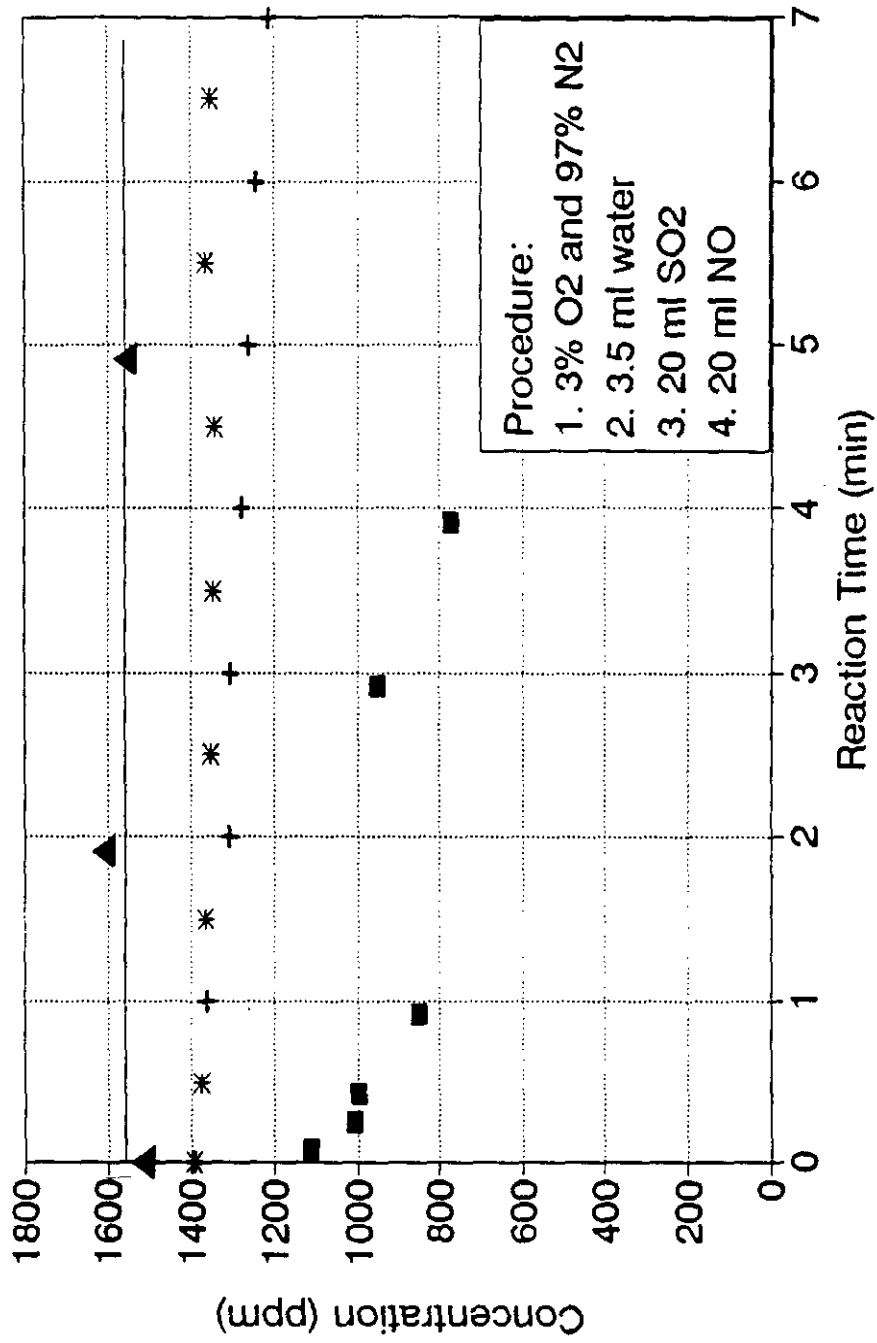


Figure 22. Blank Test with / without Sample Storage

were in error.

#### 4.7 Real time analysis for the reaction of flue gas and dry sorbents

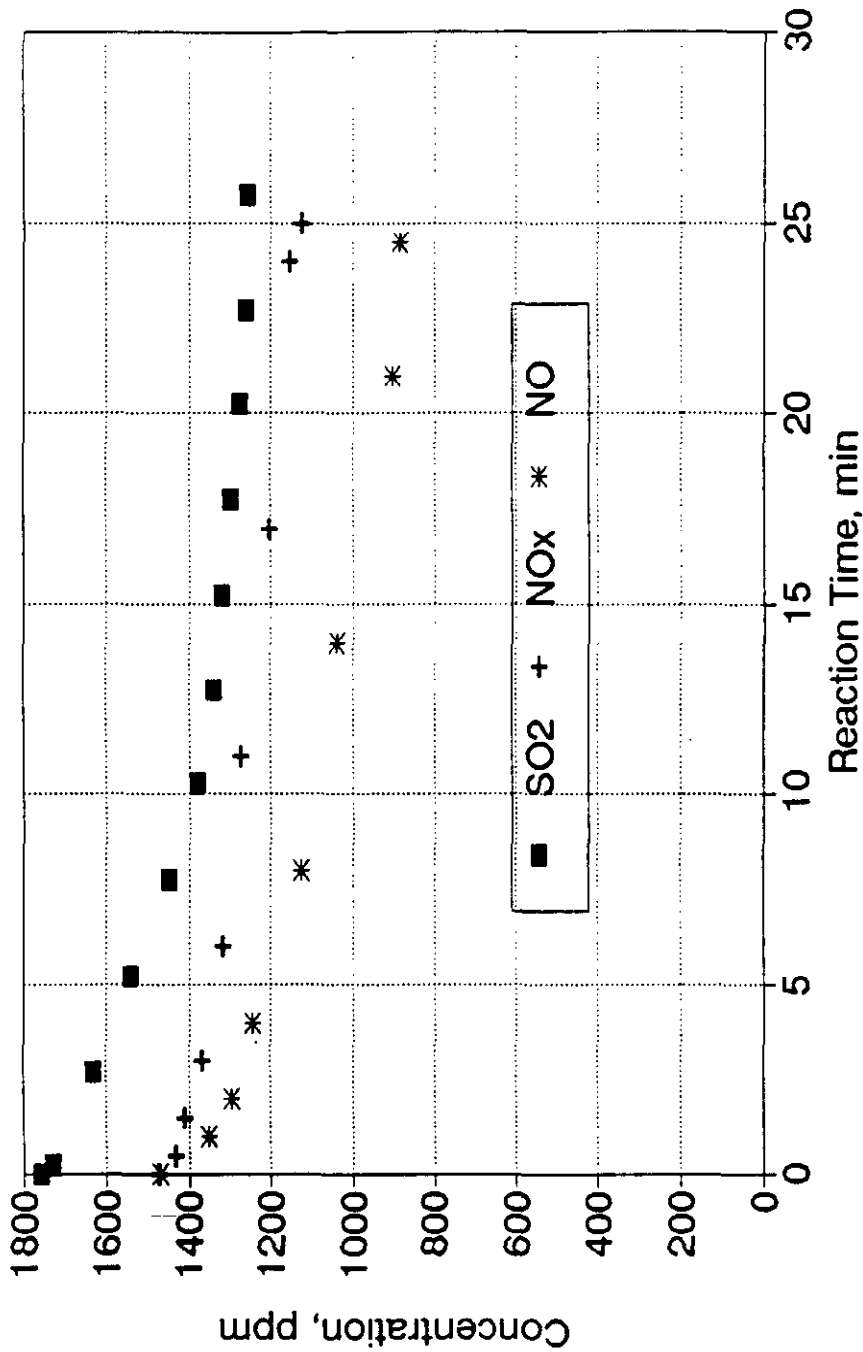
With the new calibration method for  $\text{SO}_2$  based on the calibration curve, Figure 21, the determination of  $\text{SO}_2$  concentration by GC was speeded up. Three reaction runs of flue gas with sodium bicarbonate and two experimental runs for sodium sesquicarbonate were obtained to set up the basic reaction runs for each dry sorbent without any sample storage. Two additional blank runs based on this analytical method were also presented at the end of this chapter.

##### 4.7.1 Real time analysis for the reaction of flue gas and sodium bicarbonate

With the new calibration method for  $\text{SO}_2$  based on the calibration curve, three reaction runs of flue gas in the dry scrubber system using sodium bicarbonate, one with  $\text{NSR}=0.85$ , another with  $\text{NSR}=3.4$  and the other with  $\text{NSR}=13.5$ , were obtained to set up the basic runs for the sodium sesquicarbonate under the normal operation condition with 700 rpm stirring speed, 58  $\mu\text{m}$  mean particle size, 5% water content at temperature of 300°F for  $\text{NSR}=13.5$  and 260°F for the rest. Raw data for this study were tabulated and plotted in Table 18 and Figure 23 for the case of  $\text{NSR}=0.85$ ; Table 19 and Figure 24 for the case of  $\text{NSR}=3.4$ ; and Table 20 and Figure 25 for the case of  $\text{NSR}=13.5$  respectively. The dry scrubber system with sodium bicarbonate injection with  $\text{NSR}=0.85$  was found to be capable of removing  $\text{SO}_2$  from 1758 ppm to 1270 ppm and

Table 18. Raw Data for SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Bicarbonate with NSR=0.85 :

Time (min)	SO <sub>2</sub> /Air (Ratio)	SO <sub>2</sub> (ppm)	NO <sub>x</sub> (Index)	NO (Index)	NO <sub>x</sub> (ppm)	NO (ppm)
0	0.004819	1758.467	25	26.1	1473.919	1470.637
0.25	0.004744	1731.227				
0.5			24.3		1431.897	
1				24		1349.864
1.5			23.9		1407.885	
2				23		1292.353
2.75	0.004461	1628.402				
3			23.2		1365.863	
4				22.2		1246.344
5.25	0.00422	1540.655				
6			22.4		1317.838	
7.75	0.00396	1446.109				
8				20.1		1125.571
10.25	0.003775	1378.948				
11			21.6		1269.813	
12.75	0.00367	1340.655				
14				18.6		1039.305
15.25	0.00361	1318.836				
17			20.5		1203.779	
17.75	0.00355	1297.018				
20.25	0.00349	1275.2				
21				16.2		901.2784
22.75	0.003445	1258.711				
24			19.7		1155.754	
24.5				15.9		884.0251
25			19.2		1125.738	
25.75	0.00344	1257.018				

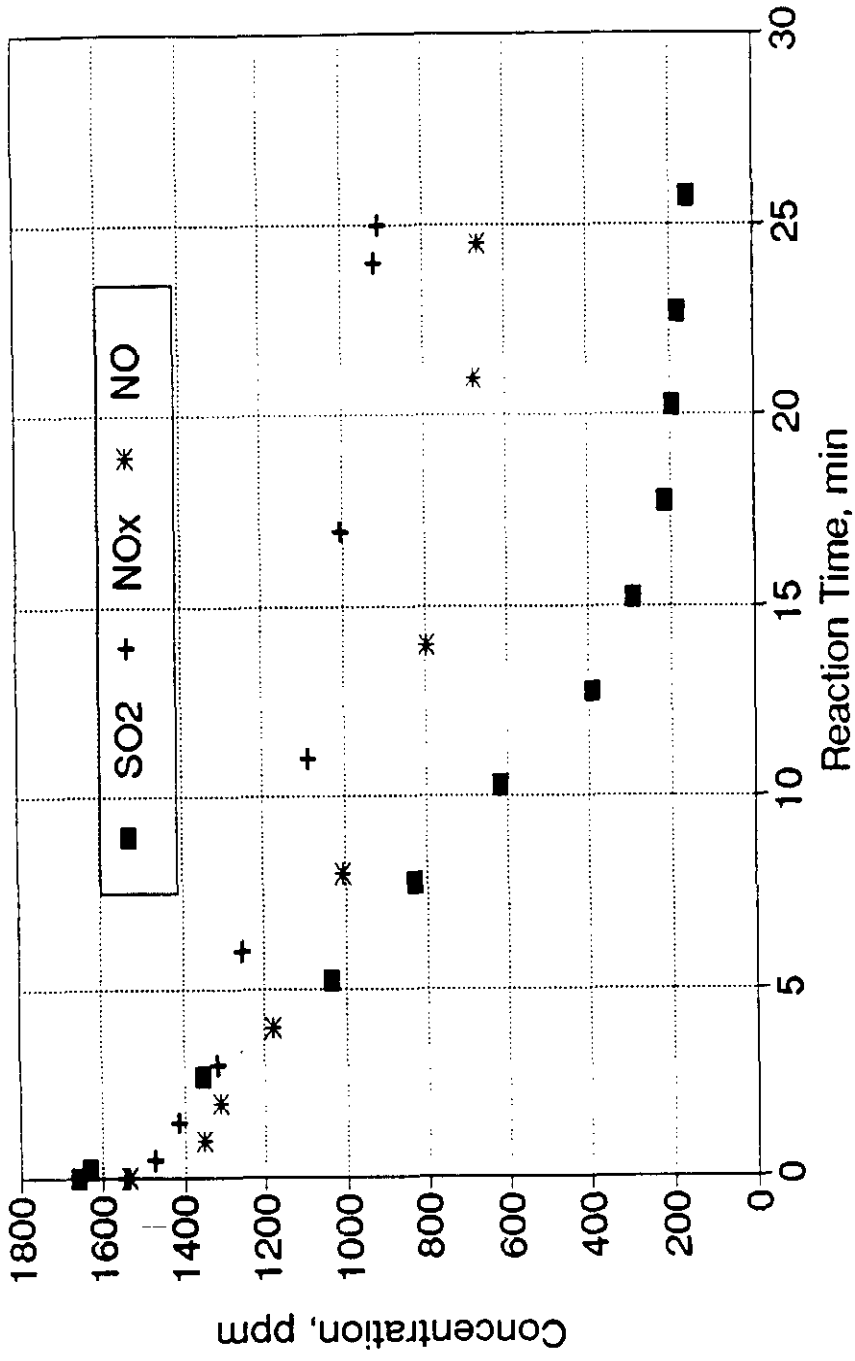


NSR=0.85, 260 F, 700rpm, 5% Water, 53um < d < 63um

Figure 23. SO2 and NOx Removed by Sodium Bicarbonate

Table 19. Raw Data for SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Bicarbonate with NSR=3.4 :

Time (min)	SO <sub>2</sub> /Air (Ratio)	SO <sub>2</sub> (ppm)	NO <sub>x</sub> (Index)	NO (Index)	NO <sub>x</sub> (ppm)	NO (ppm)
0	0.004526	1652.04	24.9	26.2	1467.916	1476.388
0.25	0.004526	1652.04				
0.5			24.5		1443.904	
1				24.6		1384.37
1.5			23.8		1401.882	
2				24		1349.864
2.75	0.003467	1266.887				
3			23.1		1359.86	
4				21.4		1200.335
5.25	0.002785	1018.684				
6			21.3		1251.804	
7.75	0.002115	775.0761				
8				17.5		976.0426
10.25	0.001505	553.2198				
11			17.4		1017.682	
12.75	0.001233	454.2929				
14				14		774.7544
15.25	0.000834	309.4106				
17			15.4		897.6195	
17.75	0.000569	212.9872				
20.25	0.000478	179.7919				
21				12		659.7325
22.75	0.000335	128.0145				
24			14.8		861.6007	
24.5				11		602.2216
25			14.5		843.5914	
25.75	0.000254	98.53301				

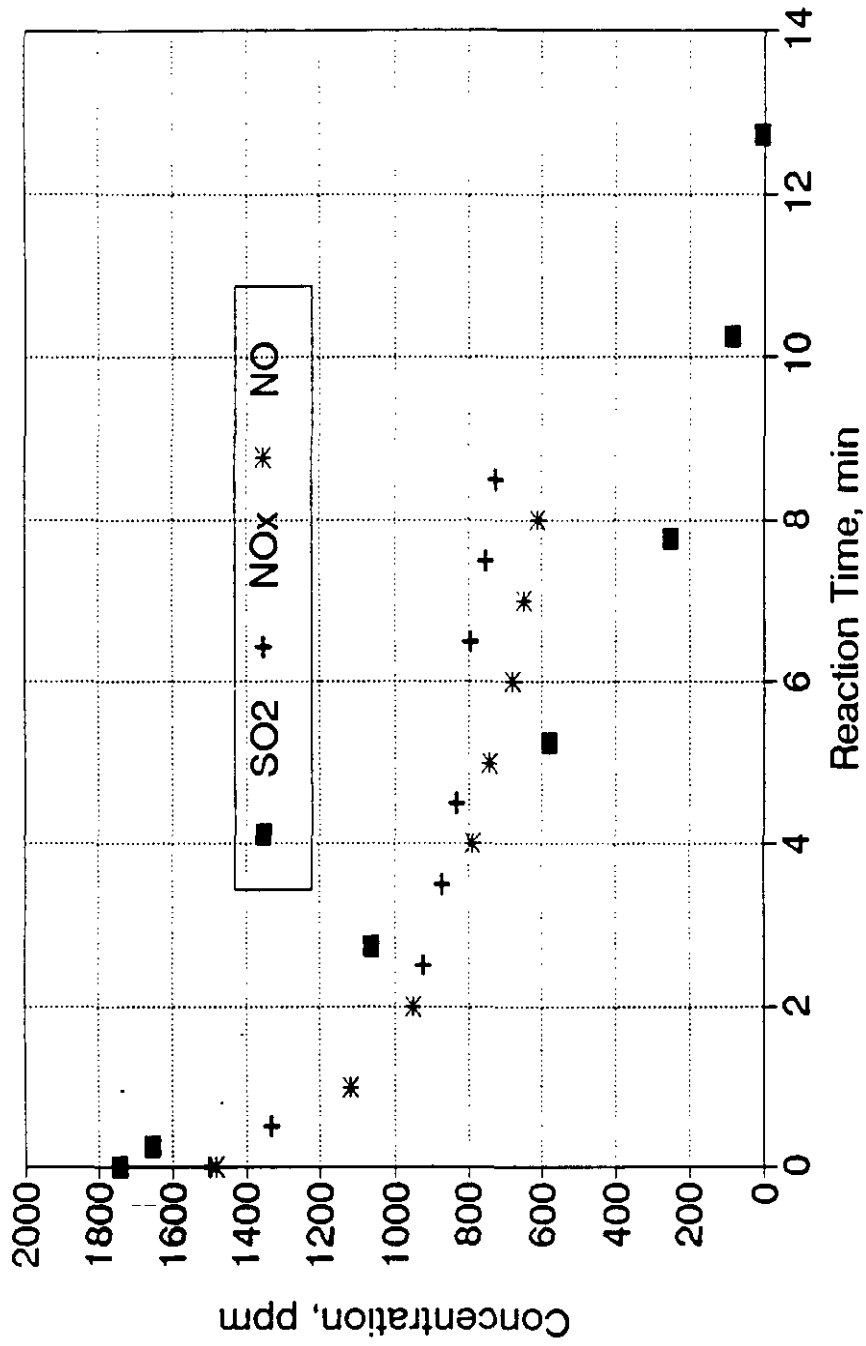


NSR=3.4, 260 F, 700rpm, 5% Water, 53um < d < 63um

Figure 24. SO2 and NOx Removed by Sodium Bicarbonate

Table 20. Raw Data for SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Bicarbonate with NSR=13.5 :

Time (min)	SO <sub>2</sub> /Air (Ratio)	SO <sub>2</sub> (ppm)	NO <sub>x</sub> (Index)	NO (Index)	NO <sub>x</sub> (ppm)	NO (ppm)
0	0.004783	1745.432	25.4	26.3	1497.932	1482.139
0.25	0.004526	1652.04				
0.5			22.7		1335.847	
1				20		1119.82
2				17		947.2872
2.5			15.8		921.6319	
2.75	0.002912	1065.018				
3.5			14.9		867.6039	
4				14.2		786.2566
4.5			14.3		831.5851	
5				13.4		740.2478
5.25	0.001575	578.8172				
6				12.3		676.9858
6.5			13.7		795.5664	
7				11.8		648.2303
7.5			13		753.5445	
7.75	0.000671	250.0586				
8				11.2		613.7238
8.5			12.5		723.5289	
10.25	0.000212	83.29007				
12.75	0	6.109091				



NSR=13.5, 300 F, 300rpm, 5% Water, 53um < d < 63um

Figure 25. SO2 and NOx Simultaneous Removed by Sodium Bicarbonate

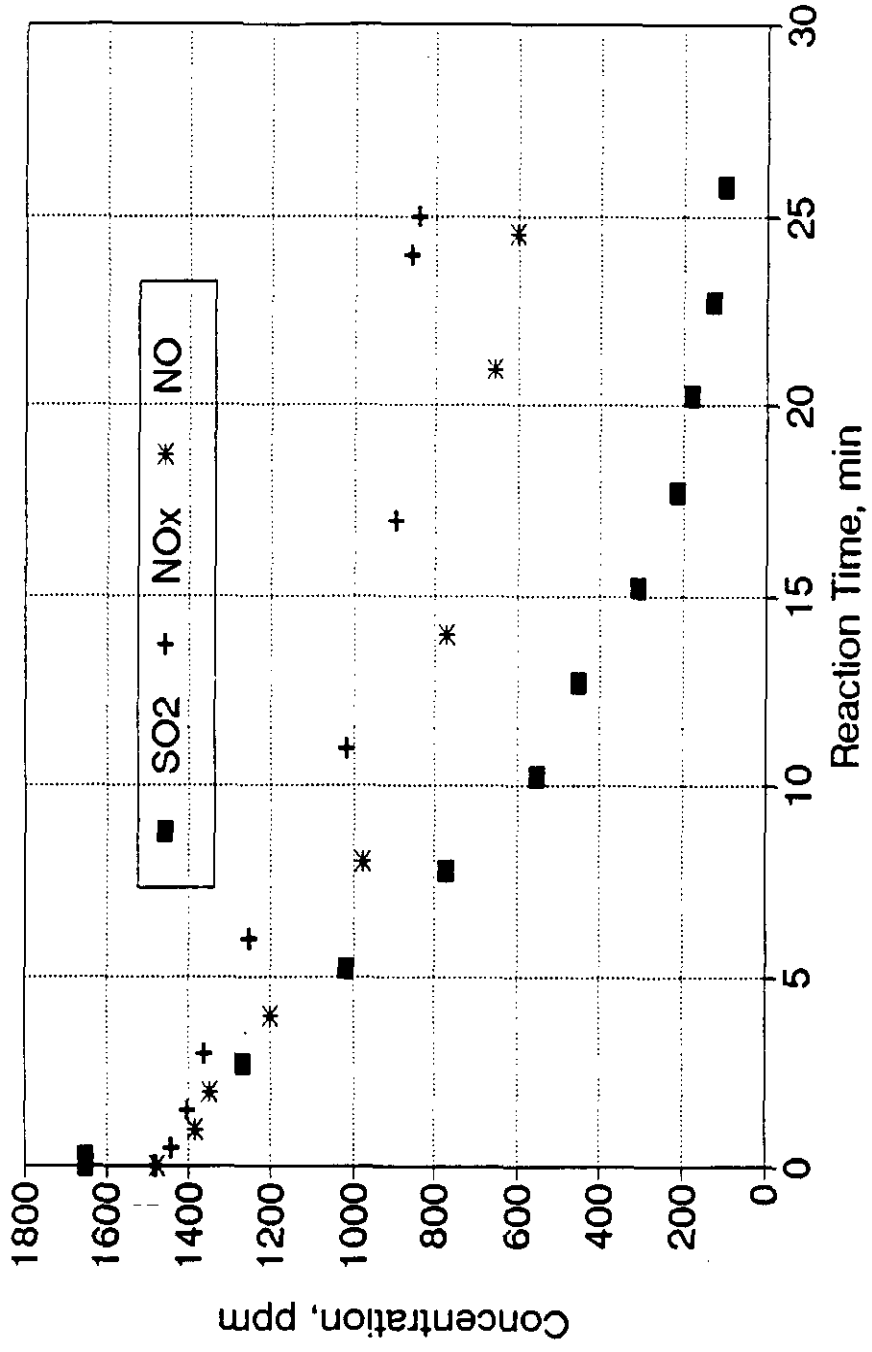


NO<sub>x</sub> from 1474 ppm to 1180 ppm within twenty minutes, or about 488 ppm or 28% SO<sub>2</sub> removal, 290 ppm or 20% NO<sub>x</sub> removal, and there was about 260 ppm NO<sub>2</sub> formed at the end of twenty minutes. As for NSR=3.4, after 25 minutes from concentration of SO<sub>2</sub> and NO<sub>x</sub> initial concentrations of about 1650 ppm, over 94% removal for SO<sub>2</sub> occurred, and 50% removal for NO<sub>x</sub>, and with the formation of 200 ppm NO<sub>2</sub>. In the case of NSR=13.5 at 300°F, this dry scrubber system was found to require 15 minutes to remove SO<sub>2</sub> from 1750 ppm to under detectable limits and to remove NO<sub>x</sub> from about 1500 to 750 ppm at 8 minutes and produce an NO<sub>2</sub> yield at 8 minutes of about 140 ppm. An additional run was also done to duplicate the run with NSR=3.4. It showed that we can duplicate the run with NSR=3.4 very well. The results of this experimental run are shown in Figure 26.

It is very important to look at how the SO<sub>2</sub> and the NO<sub>x</sub> removal occurred in Figure 23 through Figure 25. It seems that the reaction of SO<sub>2</sub> and the reaction of NO<sub>x</sub> all followed first order reaction kinetics. It also implies that for sodium bicarbonate, the removal of the flue gases highly depends on the solid present. If we fixed the particle size, then the reaction rate depends on the amount of sodium bicarbonate we used.

#### 4.7.2 Real time analysis for the reaction of flue gas and sodium sesquicarbonate

With the new calibration method for SO<sub>2</sub> based on the calibration curve, Figure 21, two complete reaction runs of flue gases in the dry scrubber system using sodium sesquicarbonate, one with NSR=0.85 and the other with NSR=3.4, were conducted to



NSR=3.4, 260 F, 700rpm, 5% Water

Figure 26. SO2 and NOx Removed by Sodium Bicarbonate

set up the basic runs for the sodium sesquicarbonate under the typical operation condition with 700 rpm stirring speed, 58 um mean particle size, 5% water content at 260°F. Raw data for this study were tabulated and plotted in Table 21 and Figure 27 for the case of  $NSR=0.85$ ; Table 22 and Figure 28 for the case of  $NSR=3.4$  respectively. The dry scrubber system with sodium bicarbonate injection with  $NSR=0.85$  was found to be capable of removing  $SO_2$  from 1726 ppm to 1285 ppm and  $NO_x$  from 1492 ppm to 1185 ppm within twenty minutes. This is about 441 ppm or 26%  $SO_2$  removal, 307 ppm or 21%  $NO_x$  removal, and there was about 230 ppm  $NO_2$  formed at the end of twenty minute. As for  $NSR=3.4$ , it was found to require 20 minutes to remove  $SO_2$  and  $NO_x$  from initial concentrations of 1508 ppm and 1534 ppm to the concentration of 150 ppm and 930 ppm at the end of twenty minute. The removal of  $SO_2$  is about 1358 ppm or 90%, and about 604 ppm or 39% removal for  $NO_x$ . The  $NO_2$  yield at the end of twenty minutes was about 230 ppm. The reduction of flue gases by sodium sesquicarbonate is similar to that of sodium bicarbonate. It seems that the initial rate of the flue gases reduction by sodium sesquicarbonate is faster than that by sodium bicarbonate. It might be due to the different chemical structure of sodium sesquicarbonate.

In order to duplicate the above results, three additional runs at  $NSR=3.4$  and one additional run at  $NSR=0.85$  were also done under the same operational conditions. Results for these four runs, shown in Figure 29 through Figure 32, were consistent with the previous two runs. The reduction rates of  $SO_2$ ,  $NO$  and  $NO_x$  at  $NSR=0.85$  slows

Table 21. Raw Data for SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Sesquicarbonate with NSR=0.85:

Time (min)	SO <sub>2</sub> /Air (Ratio)	SO <sub>2</sub> (ppm)	NO <sub>x</sub> (Index)	NO (Index)	NO <sub>x</sub> (ppm)	NO (ppm)
0	0.004728	1725.517	25.3	26.4	1491.929	1487.89
0.25	0.004439	1620.329				
0.5			24.8		1461.913	
1				24		1349.864
1.5			23.5		1383.872	
2				22.9		1286.602
2.75	0.004186	1528.297				
3			23.2		1365.863	
4				22.2		1246.344
5.25	0.003924	1433.181				
6			21.3		1251.804	
7.75						
8				20.1		1125.571
10.25	0.003678	1343.537				
11			20.9		1227.791	
12.75	0.00363	1326.151				
14				18.9		1056.558
15.25	0.003616	1320.908				
17			20.4		1197.776	
17.75	0.00354	1293.54				
20.25	0.003524	1287.445				
21				17		947.2872
22.75	0.003492	1275.983				
24			19.8		1161.757	
24.5				16.2		901.2784
25			19.3		1131.741	

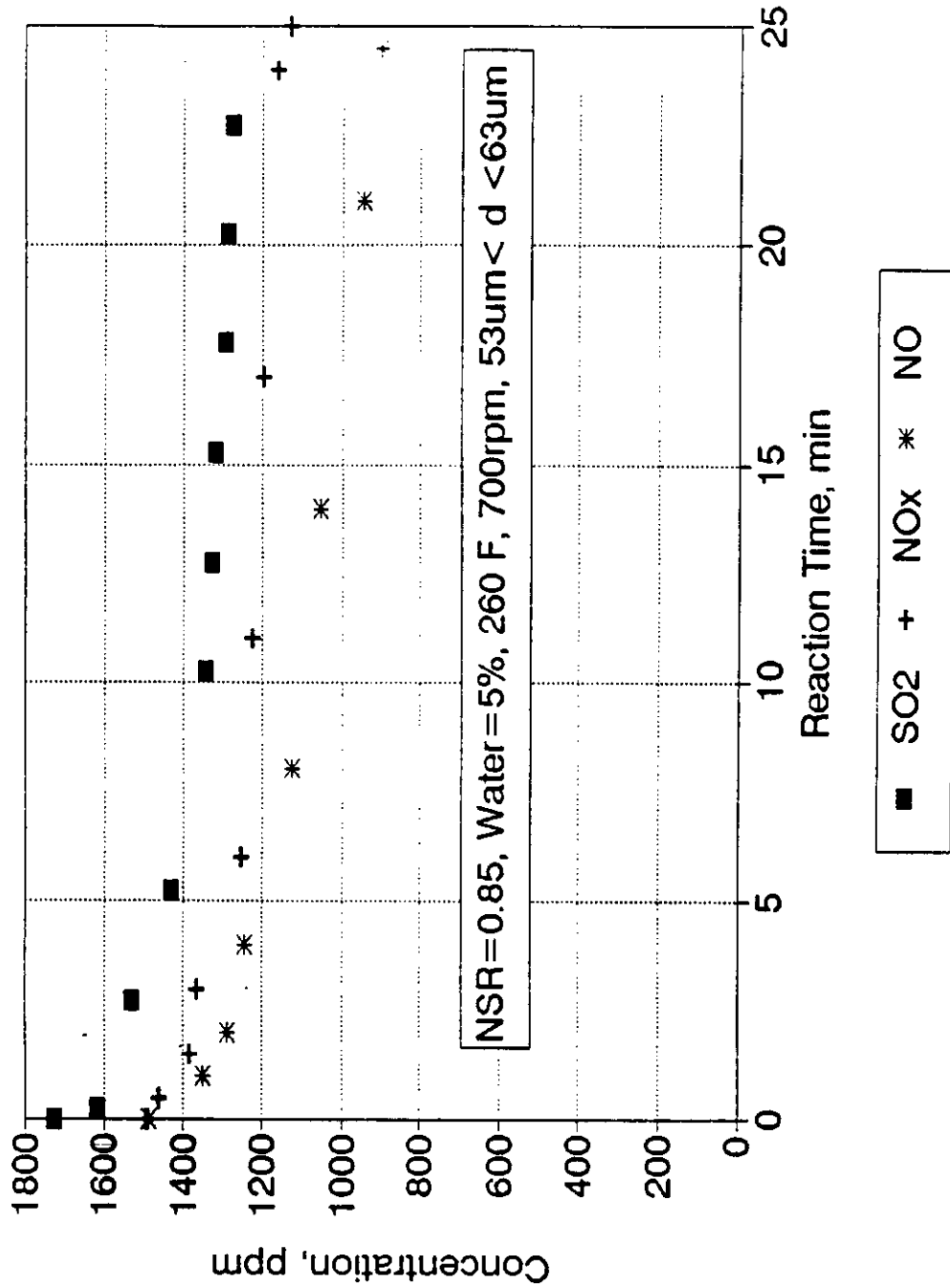


Figure 27. SO2 and NOx Removal by Sodium Sesquicarbonate

Table 22. Raw Data for SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Sesquicarbonate with NSR=3.4 :

Time (min)	SO <sub>2</sub> /Air (Ratio)	SO <sub>2</sub> (ppm)	NO <sub>x</sub> (Index)	NO (Index)	NO <sub>x</sub> (ppm)	NO (ppm)
0	0.004129	1507.547	26	26.4	1533.95	1487.89
1			24.6		1449.907	
2				22.2		1246.344
3	0.002325	851.4231				
4			20.9		1227.791	
5				18.3		1022.051
6	0.001724	633.1955				
7			19.9		1167.76	
8				16.8		935.785
9	0.001401	515.4968				
10			18.9		1107.729	
11				15.8		878.274
12	0.001143	421.9122				
15	0.000967	357.7891				
16			17.1		999.6725	
17				14.6		809.2609
18	0.000784	291.1866				
21	0.00066	245.9431				
22			16.5		963.6538	
23				13.1		722.9945
24	0.000375	142.529				
27	0.000435	164.3607				
28			15.5		903.6226	
29				12		659.7325
30	0.000324	124.0352				

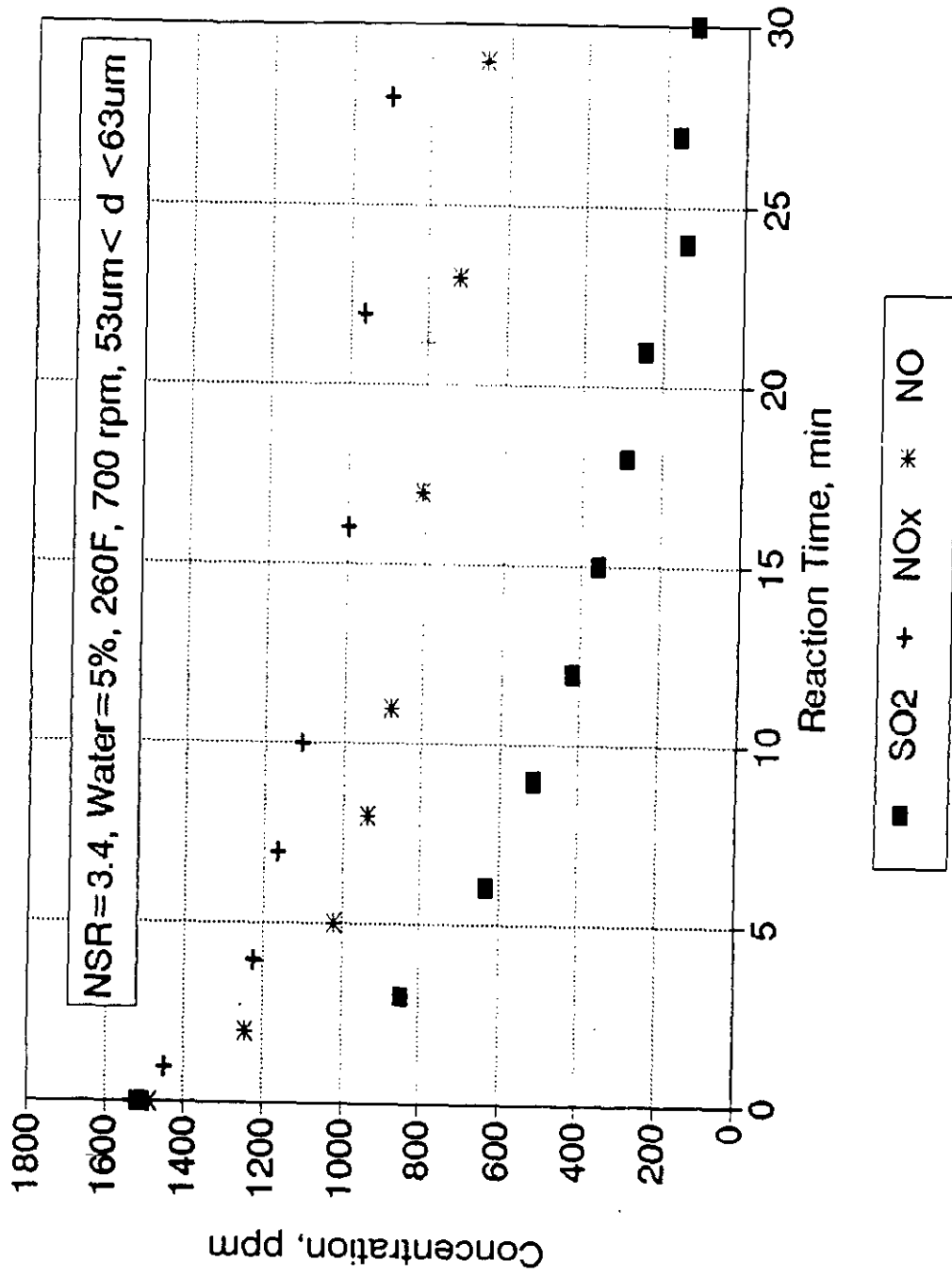


Figure 28. SO2 and NOx Removal by Sodium Sesquicarbonate

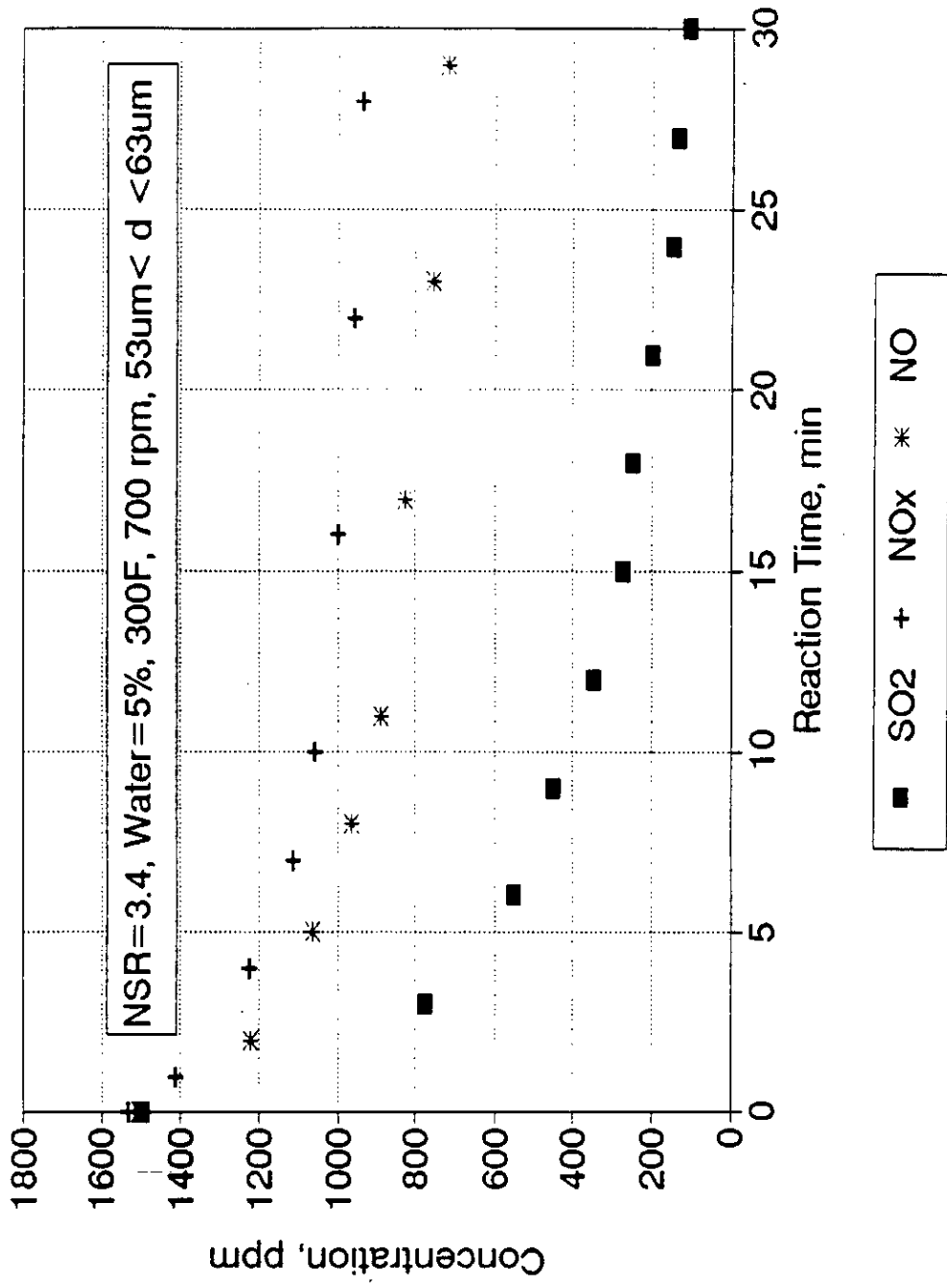


Figure 29. SO2 and NOx Removal by Sodium Sesquicarbonate



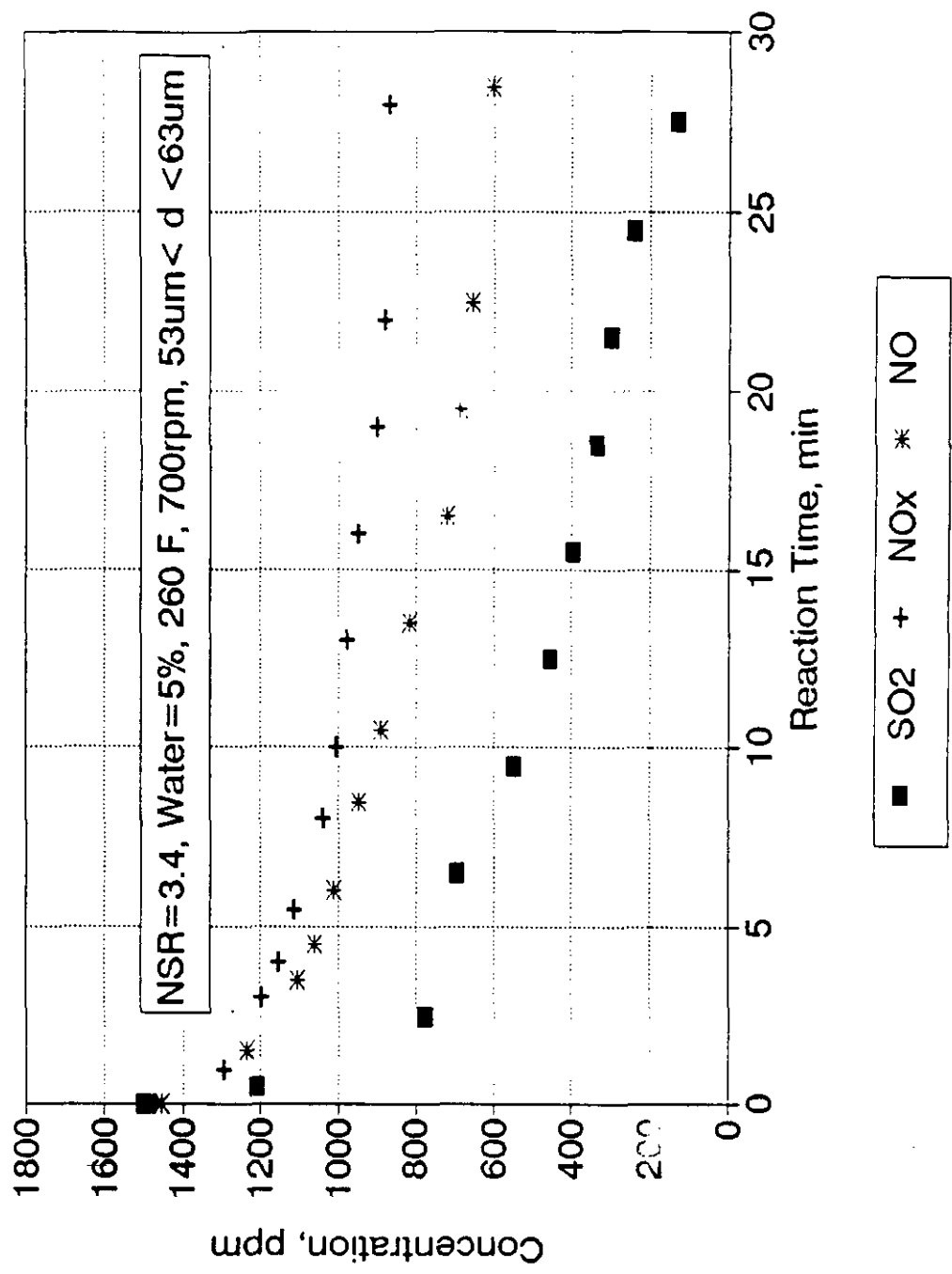


Figure 30. SO2 and NOx Removal by Sodium Sesquicarbonate

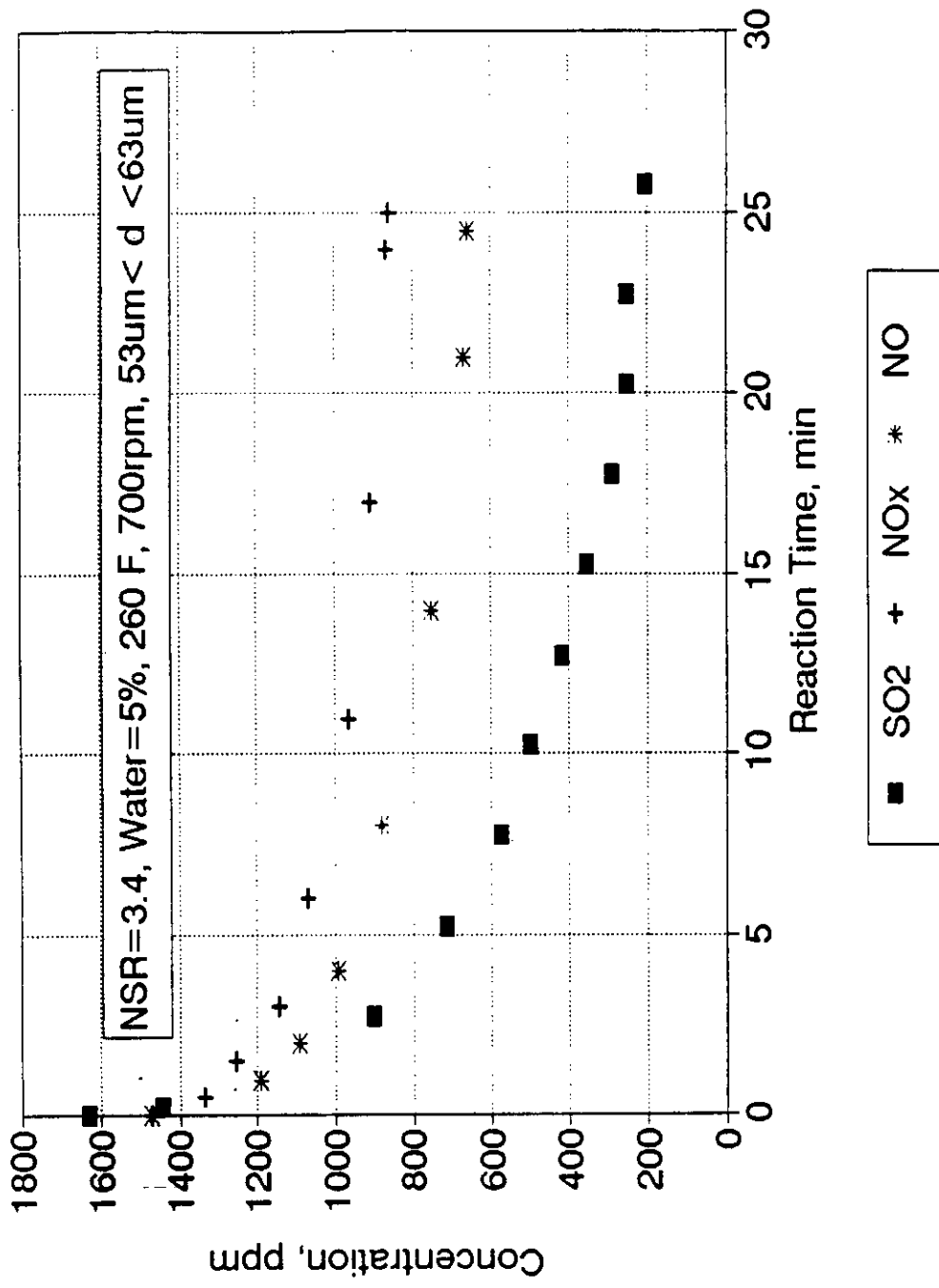


Figure 31. SO2 and NOx Removal by Sodium Sesquicarbonate

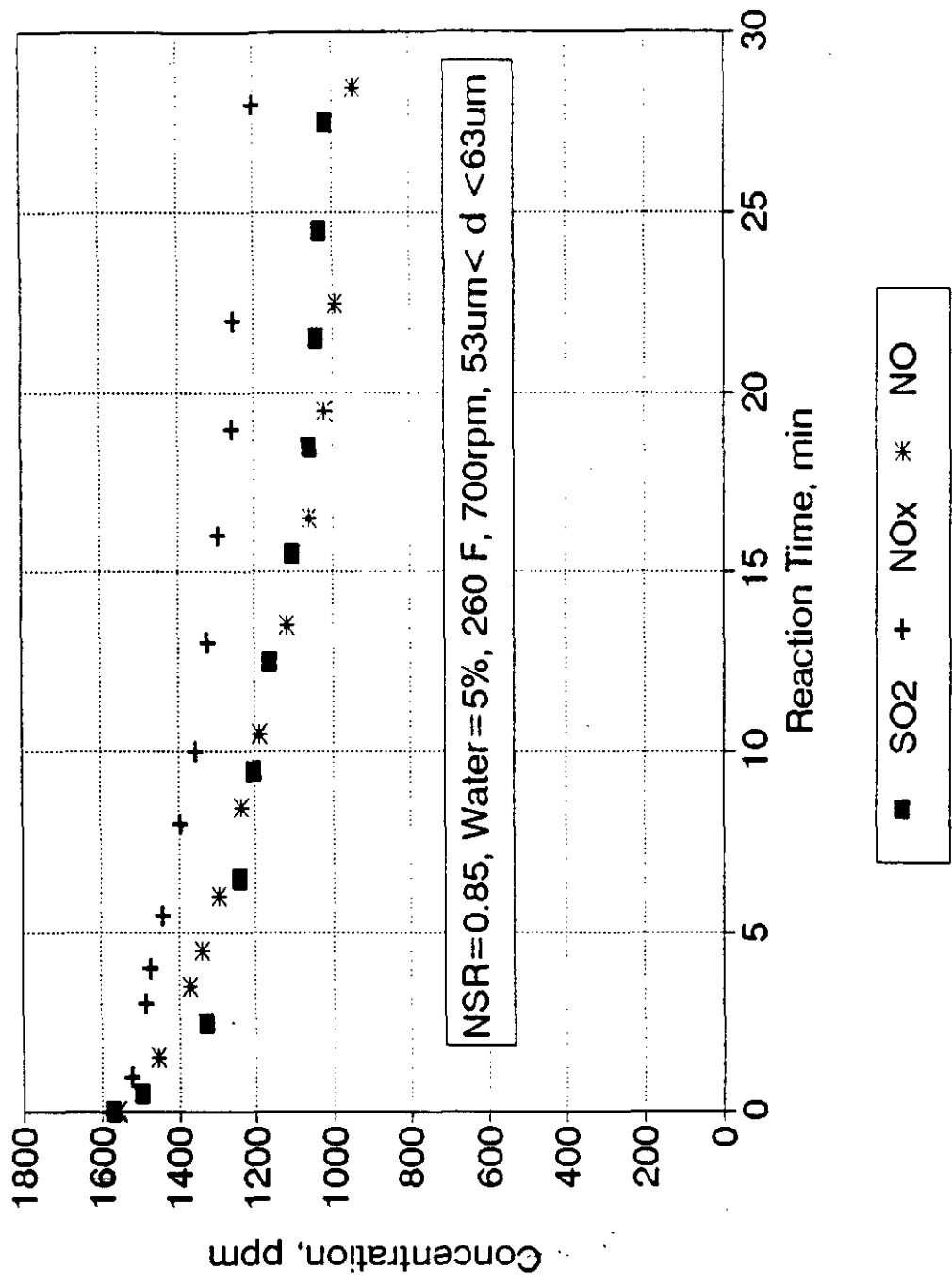


Figure 32. SO2 and NOx Removal by Sodium Sesquicarbonate

down after fifteen minutes. On the other hand, the reduction rates of SO<sub>2</sub>, NO and NO<sub>x</sub> at NSR=3.4 slows down after twenty five minutes.

## CHAPTER V

### MODEL RESULTS

The Adams-Bashforth-Moulton method with a Runge-Kutta starting procedure is recommended for solving most first-order initial-value ordinary differential equations<sup>(14)</sup>. This project therefore uses this combined method to solve sets of ordinary differential equations. An experimental data set for simultaneous removal of NO<sub>x</sub> and SO<sub>2</sub> by NaHCO<sub>3</sub> with an NSR equal to 13.5 was initially used to verify the two models described in Chapter three. The experimental data were first corrected for the bleeding rate of the system. The corrected data were then used to evaluate rate constants and the selectivity constant by the initial rate approach. The gas concentration results of the computer simulation are then compared with the experimental results and the radius of the unreacted Na<sub>2</sub>CO<sub>3</sub> is predicted from the model.

#### 5.1 Experimental data correction for the bleeding rate of the system

In some cases, chemical bleeding from a shaft rotating system is not unusual. Corrections are often made for this system bleeding by assuming a constant bleeding rate which is described in the book "Fluid Sealant Handbook" published by McGraw Hill Book Company<sup>(13)</sup>. Two experiments were therefore conducted to investigate the bleeding rates at two sets of operating conditions; one was at 300°F with a stirring speed

of 300 rpm and the other was for the remaining runs at 260°F with a stirring speed of 700 rpm.

#### 5.1.1 Correction for the case of NSR equal to 13.5 at 300°F

An experiment was conducted with initial concentrations of about 1600 ppm SO<sub>2</sub> and NO, 3% O<sub>2</sub>, and 5% water without any dry sorbent injected under the operating conditions of 300°F and a stirring speed of 300 rpm. The results of this experimental run are shown in Table 23. From the blank test presented in chapter four, which was shown in Figure 22, we know that the concentration change of SO<sub>2</sub> is not significant and could be ignored compare to the total change in SO<sub>2</sub> concentration. Such is not the case for NO and NO<sub>2</sub> which are the constituents of NO<sub>x</sub>, since the change in concentration of these components is not very large. Consequently, we used the reduction in the NO<sub>x</sub> copncentration during the blank run to correct the experimental data. The resulting data from Table 23 are illustrated in Figure 33. From this figure, it seems we can use a linear relationship to represent concentration change versus reaction time. A regression technique was therefore used to obtain the constant bleeding rate which is the X coefficient shown in Table 24. The value of the bleeding rate is 4.79 ppm per minute which was then used to obtain the corrected concentration of NO<sub>x</sub> and the concentration of NO by simply adding 4.79 ppm per minute to the experimental data. Data from Table 20 were therefore corrected by this bleeding rate and are shown in Table 25 and Figure 34.

Table 23. Bleeding Rate Study at rpm=300

Date : 11-09-93                      Temp.(F) : 300  
 Sorbent : None                              rpm : 300  
 Water(%) : 5                              NSR : 0  
    Size(um) : 0

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.004338	1599.887	27.2	28	1605.988	1579.907
0.5	0.004703	1732.512				
1			27.2		1605.988	
1.5				27.4		1545.401
2.5			27.2		1605.988	
3				27.2		1533.899
3.5	0.004739	1745.78				
4			27		1593.982	
4.5				27		1522.396
5.5			26.9		1587.978	
6				26.3		1482.139
7			26.9		1587.978	
8				25.8		1453.383
9.5			26.6		1569.969	
10				25		1407.375
11	0.004802	1768.532				
12			26.4		1557.963	
13				24.5		1378.619
15			26		1533.95	
16				23.6		1326.859
18	0.00425	1567.998				
20			25		1473.919	
21				22.5		1263.597
27			24		1413.888	
29				20		1119.82
30	0.004632	1706.78				

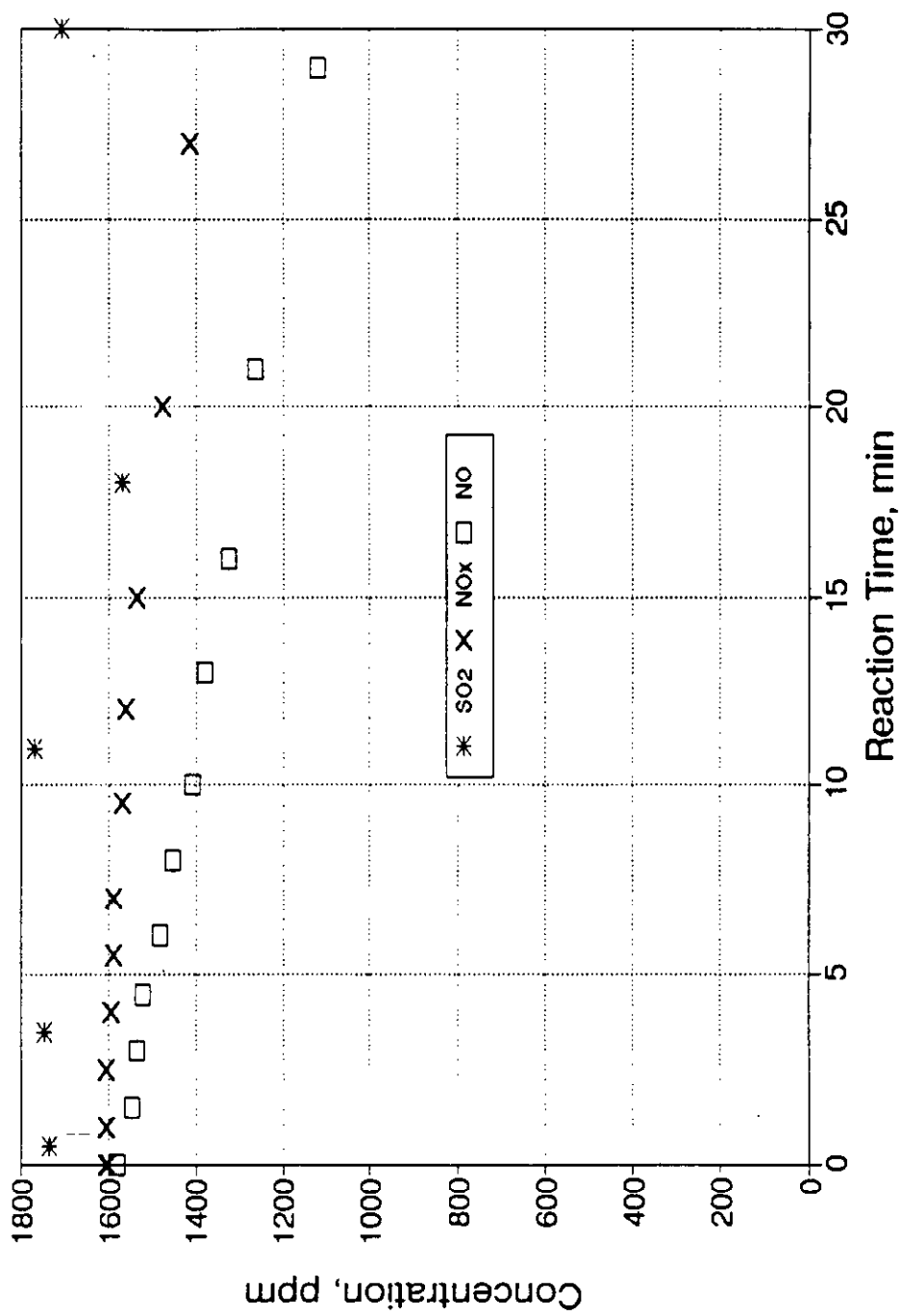


Figure 33. SO2 and NOx Decrease Adding no Dry Sorbents



Table 24. Regression on the Results of Bleeding Rate Study (300 rpm)

Time (min)	SO2 (ppm)	Time (min)	NOx (ppm)	Time (min)	NO (ppm)
0	1599.887	0	1605.988	0	1579.907
0.5	1732.512	1	1605.988	1.5	1545.401
3.5	1745.78	2.5	1605.988	3	1533.899
11	1768.532	4	1593.982	4.5	1522.396
18	1567.998	5.5	1587.978	6	1482.139
30	1706.78	7	1587.978	8	1453.383
		9.5	1569.969		
		12	1557.963		
		15	1533.95		

NOx Regression Output:

Constant 1613.351  
 Std Err of Y Est 5.548794  
 R Squared 0.956523  
 No. of Observations 9  
 Degrees of Freedom 7

X Coefficient(s) -4.78542  
 Std Err of Coef. 0.385616

$$(\text{NOx}) = 1613.351 - 4.785424 * t$$

Tabel 25. Corrected Concentrations for Three Gases (300 rpm) :

Corrected Data				
Time (min)	(SO <sub>2</sub> ) (ppm)	(NO <sub>x</sub> ) (ppm)	(NO) (ppm)	(NO <sub>2</sub> ) (ppm)
0	1745.432	1497.932	1482.139	15.79285
0.25	1652.04			
0.5		1338.24		
1			1124.605	27
2			956.858	43.142
2.5		933.5955		
2.75	1065.018			
3.5		884.3528		
4			805.3983	67
4.5		853.1195		
5			764.1749	82
5.25	578.8172			
6			705.6983	102.3551
6.5		826.6717		
7			681.7283	107.7069
7.5		789.4352		
7.75	250.0586			
8			652.0072	137.4281
8.5		764.205		
10.25	83.29007			
12.75	6.109091			

Initial Rate of SO<sub>2</sub> = -373.566 ppm/min = -1.1E-08 mol/(min)(ml)  
 Initial Rate of NO<sub>x</sub> = -319.383 ppm/min = -9.2E-09 mol/(min)(ml)  
 Initial Rate of NO = -357.533 ppm/min = -1E-08 mol/(min)(ml)  
 Initial Rate of NO<sub>2</sub> = 38.15027 ppm/min = 1.1E-09 mol/(min)(ml)

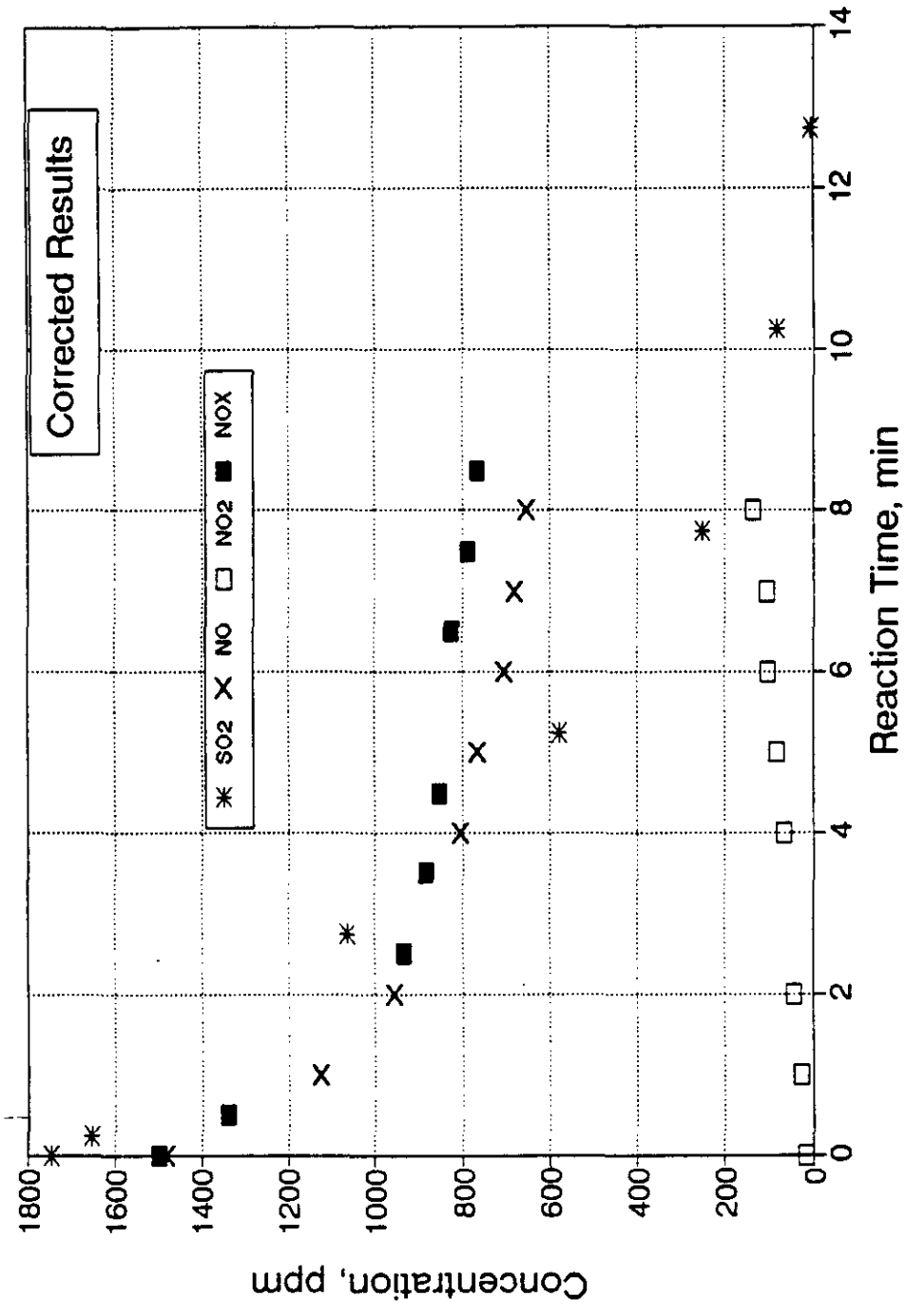


Figure 34. SO2 and NOx Simultaneous Reaction by Sodium Bicarbonate

### 5.1.2 Correction for the remaining cases

Another experiment was conducted with initial concentration of about 1600 ppm SO<sub>2</sub> and 1400 ppm NO<sub>x</sub>, 3% O<sub>2</sub>, and 5% water without no dry sorbent injected under the operating conditions of 260°F and stirring speed of 700 rpm. The result of this experimental run is the blank test already reported in chapter four and shown in Figure 22. Again, the concentration change of SO<sub>2</sub> is not significant and could be ignored and consequently, we only use the bleeding rate of the NO<sub>x</sub> to correct the experimental data for these cases. Raw data from Figure 22 are shown in Table 26. After performing the regression on the data taken from Table 26, we obtain the constant bleeding rate at 7.4 ppm per minute which is the X coefficient shown in Table 27. To demonstrate the effect of the system bleeding at 700 rpm and 260°F on the experimental results, the results taken from Figure 28 was used as an example. The corrected results were shown in Table 28 and Figure 35.

### 5.2 Experimental curve fitting by EPRI's model

Rate laws proposed by EPRI, which are given in Chapter 3.1 were applied to simulate the resulting data. The experimental results is for the SO<sub>2</sub>-NO<sub>x</sub>-NaHCO<sub>3</sub> reaction system with normal stoichiometric ratio equal to 13.5 at 300°F stirred at 300 rpm. Results of this experiment have been shown in Table 20 and Figure 25.

Table 26. Bleeding Rate Study at rpm=700

Date 08-08-93 Temp.(F) 260  
 Sorbent Nil rpm 700  
 Water(%) 0 NSR 0  
 Size(um) 0

Time (min)	SO2/N2 (Ratio)	SO2/N2 (ppm)	NO (Index)	NOx (Index)	NO (ppm)	NOx (ppm)
0	0.004166	1537.532	25.2	24.2	1418.877	1425.894
0.083333	0.003676	1359.344				
0.25	0.003042	1128.767				
0.416667	0.002038	763.5321				
0.5				24.1		1419.891
0.916667	0.001363	518.0101				
1			24.8		1395.872	
1.5				24.1		1419.891
1.916667	0.000628	250.7347				
2			24.4		1372.868	
2.5				23.7		1395.879
2.916667	0.000897	348.5613				
3			23.9		1344.113	
3.5				23.6		1389.875
3.916667	0.000499	204.0983				
4			23.6		1326.859	
4.5				23.9		1407.885
4.916667	0.000999	385.7238				
5			23.4		1315.357	
5.5				23.5		1383.872
6			23.3		1309.606	
6.5				23.3		1371.866
7			22.8		1280.851	

Table 27. Results of Bleeding Rate (rpm = 700) :

Time (min)	NOx (ppm)	(NOx)sim (ppm)
0	1425.894	1424.673
0.5	1419.891	1420.952
1.5	1419.891	1413.51
2.5	1395.879	1406.068
3.5	1389.875	1398.626
4.5	1407.885	1391.183
5.5	1383.872	1383.741
6.5	1371.866	1376.299

Regression Output:

Constant	1424.673
Std Err of Y Est	9.330284
R Squared	0.804136
No. of Observations	8
Degrees of Freedom	6

X Coefficient(s) -7.44213  
 Std Err of Coef. 1.499458

BLEEDING RATE = 7.44 ppm/min

Table 28. Bleeding Rate Study on the SO<sub>2</sub>-NO<sub>x</sub>-  
[NaHCO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub>-2H<sub>2</sub>O] Reaction System

RAW DATA			CORRECTED DATA		
Time (min)	SO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)	NO (ppm)	NO <sub>x</sub> (ppm)	NO (ppm)
0	1507.547	1533.95	1487.89	1533.95	1487.89
1		1449.907		1457.307	
2			1246.344		1261.144
3	851.4231				
4		1227.791		1257.391	
5			1022.051		1059.051
6	633.1955				
7		1167.76		1219.56	
8			935.785		994.985
9	515.4968				
10		1107.729		1181.729	
11			878.274		959.674
12	421.9122				
15	357.7891				
16		999.6725		1118.073	
17			809.2609		935.0609
18	291.1866				
21	245.9431				
22		963.6538		1126.454	
23			722.9945		893.1945
24	142.529				
27	164.3607				
28		903.6226		1110.823	
29			659.7325		874.3325
30	124.0352				

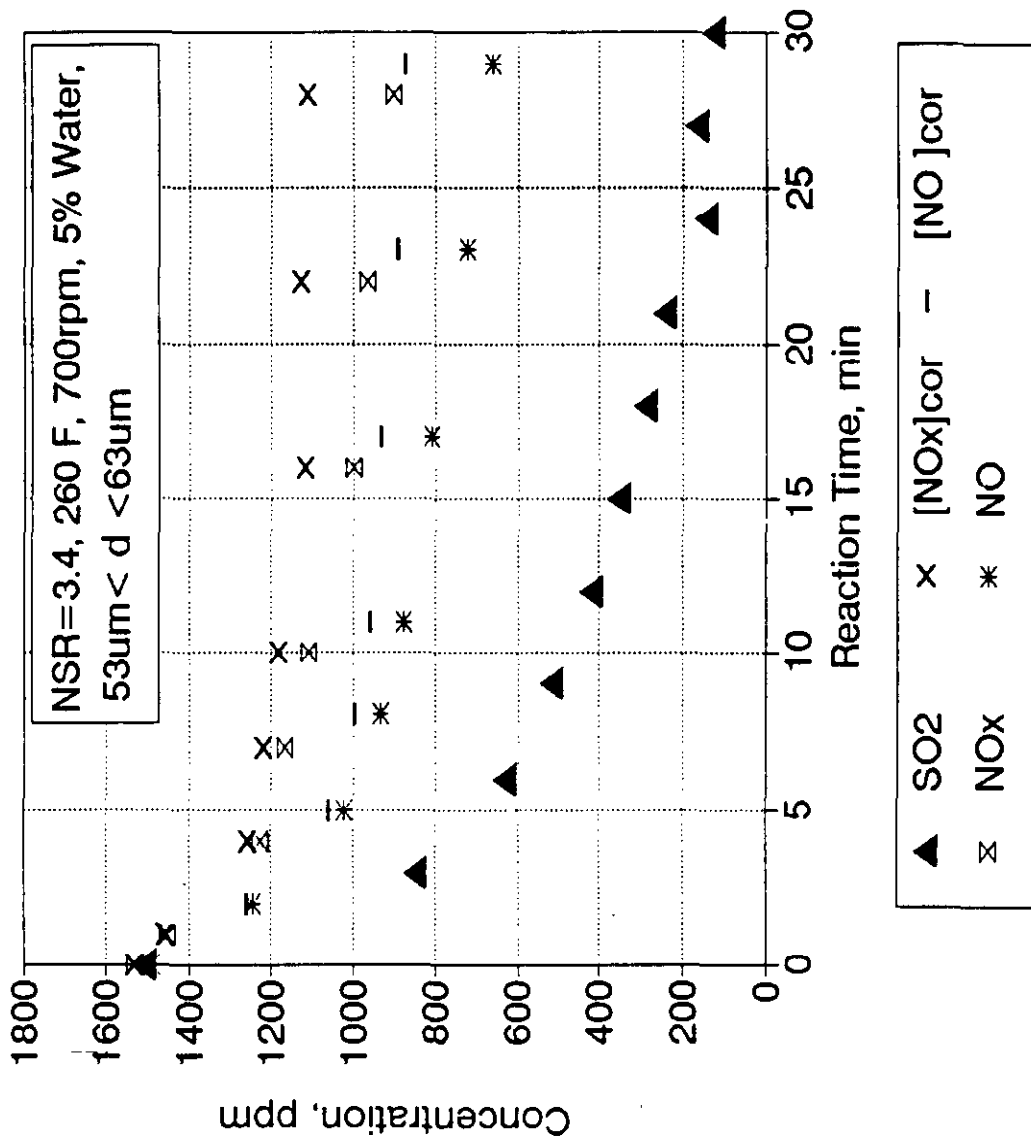


Figure 35. Correction of SO2 and NOx Removal by Sodium Sesquicarbonate



This model was found to be poor in describing the NO<sub>2</sub> formation as will be shown below. The complete set of simultaneous ordinary differential equations describing the model were presented in chapter 3.

### 5.2.1 Simplified rate expressions for EPRI's model

Since the total surface area per volume of Na<sub>2</sub>CO<sub>3</sub> is proportional to the square of the shrinking core radius which is described in Equation (3-5), Equation (3-4), Equation (3-9) and Equation (3-12) can be expressed in terms of radius. In the reaction system, system temperature and pressure are assumed to be constant; so, the only variables needed to describe the complete reaction system are the concentrations of SO<sub>2</sub>, NO and NO<sub>2</sub>, and the radius of unreacted Na<sub>2</sub>CO<sub>3</sub>.

For the case of NSR=13.5, the amount of NaHCO<sub>3</sub> with a density of 2.2 g/cm<sup>3</sup> injected was 1.6 grams and the mean radius of particles is 0.0029 cm. From Equation (3-6), we can obtain the total number of NaHCO<sub>3</sub> particles used in this experiment: N=7.12E6 ea. So, the group parameter 4 Pi N/V in Equation (3-5) is 6954.22 ea/cm<sup>3</sup>. Consequently, equations (3-4), (3-9), and (3-12) can be rewritten as follows:

Removal rate of SO<sub>2</sub>

$$R_A = R_A(C_A, R) = dC_A/dt = - 6954.22 k_A C_A R^2 \quad (5-1)$$

Removal rate of NO

$$R_B = R_B(C_A, C_B, R) = dC_B/dt = - 6954.22 k_B C_A C_B R^2 \quad (5-2)$$

Formation rate of NO<sub>2</sub>

$$\begin{aligned} R_C &= R_C(C_A, C_B, C_C, R) = dC_C/dt = R_{C1} - R_{C2} \\ &= 6954.22 (k_B C_A C_B - k_C C_C) R^2 \end{aligned} \quad (5-3)$$

For the consumption rate of Na<sub>2</sub>CO<sub>3</sub>, the value of the group constant 0.5 M/D in Equation (3-15) is 20.92; therefore, Equation (3-15) can be written as:

Shrinking rate of radius R

$$\begin{aligned} R_R &= R_R(C_A, C_C) = dR/dt \\ &= -41.84 [k_A C_A + 1/2 k_C C_C] \end{aligned} \quad (5-4)$$

### 5.2.2 Evaluations of rate constants for EPRI's model

The use of the differential method of data analysis to determine reaction orders and specific reaction rates is clearly one of the easiest, since it requires only one experiment<sup>(15)</sup>. Inspecting our model, the determination of reaction order is not required because we assumed first order for all chemicals. However, we can not use the differential method to estimate the rate constants due to the difficulties in determining the changing core radius vs reaction time. The same problem occurs for the integral method and the method of half life time. So, the method of initial rates, which only requires information at the initial condition, seems to be the best way to determine the reaction

rate constants. Information required to determine the rate constants using the initial rate approach are initial concentrations of  $\text{SO}_2$ ,  $\text{NO}$ , and  $\text{NO}_2$ ; the initial radius of  $\text{NaHCO}_3$ ; and the initial rates of  $\text{SO}_2$ ,  $\text{NO}$ , and  $\text{NO}_2$ . The concentration of  $\text{NO}_2$  can be obtained from the concentration difference of  $\text{NO}_x$  and  $\text{NO}$ . The initial radius can be obtained from the mean radius of unreacted  $\text{NaHCO}_3$  particles which is about 0.0028 cm; i.e.,  $R=0.0028$  cm. The initial rates for gases can be roughly estimated by the two point method. With the initial concentrations of gases, the initial radius of  $\text{NaHCO}_3$ , and the initial estimated reaction rate for each gas chemical, the specific reaction rates could then be calculated from Equation (5-1) through Equation (5-4). The best curves of concentration versus time for determining the initial rates are obtained by naked eyeball such that the modeled points do not deviate significantly from the average of the data points. After the best curves are located, the values of rate constant used in the model are determined.

The units of gas concentration, ppm, can be converted to units of  $\text{mol}/\text{cm}^3$  by simply applying the ideal gas law. From Table 20, the concentration of  $\text{SO}_2$ , or  $C_A$ , is 1745.43 ppm, or  $5.04\text{E-}8$   $\text{mol}/\text{cm}^3$ ; the concentration of  $\text{NO}$ , or  $C_B$ , is 1482.14 ppm, or  $4.28\text{E-}8$   $\text{mol}/\text{cm}^3$ ; and the concentration of  $\text{NO}_2$ , or  $C_C$ , which is the concentration difference between  $\text{NO}$  and  $\text{NO}_x$  ( $1497.93 - 1482.14$ ) ppm is 15.79 ppm, or  $4.56\text{E-}10$   $\text{mol}/\text{cm}^3$ .

Also, the units of initial rates, ppm/min, which is directly obtained from the

resulting data can be converted to the units of mol/cm<sup>3</sup> min using the ideal gas law. The final initial rates are listed below:

$$R_A = -373.57 \text{ ppm/min} = -1.08\text{E-}8 \text{ mol/cm}^3 \text{ min}$$

$$R_B = -357.53 \text{ ppm/min} = -1.03\text{E-}8 \text{ mol/cm}^3 \text{ min}$$

$$R_C = 38.15 \text{ ppm/min} = 1.10\text{E-}9 \text{ mol/cm}^3 \text{ min}$$

Plugging these initial values,  $C_A$ ,  $C_B$ ,  $C_C$ ,  $R$ ,  $R_A$ ,  $R_B$ , and  $R_C$  into Equation (5-1), Equation (5-2) and Equation (5-3), rate constants  $k_A$ ,  $k_B$  and  $k_C$  can be obtained. The values of rate constants  $k_A$ ,  $k_B$  and  $k_C$  are 3.66 cm/min,  $8.18\text{E}7 \text{ cm}^4/\text{min mol}$  and 345.78 cm/min respectively.

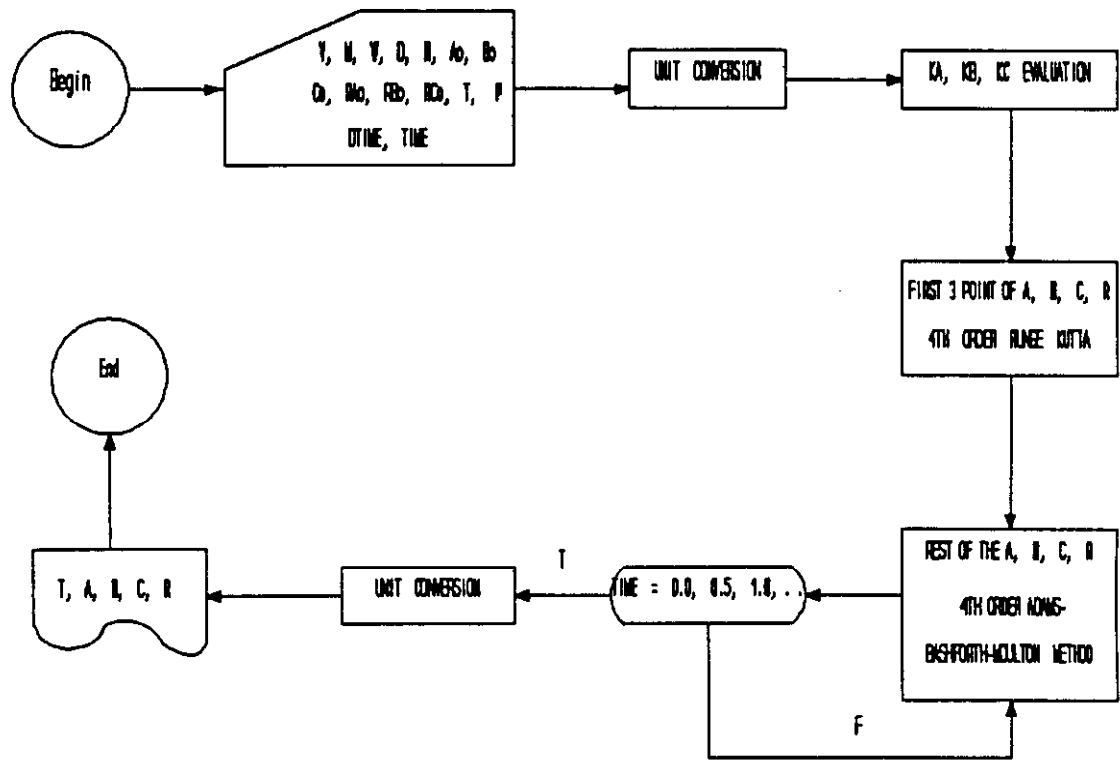
### 5.2.3 Kinetics modeling by computer programming

Once the rate constants have been obtained, the one point fourth order Runge-Kutta method is applied on the simultaneous ordinary equations from Equation (5-1) through Equation (5-4) to evaluate the first three points with time difference 0.0005 minute; and then, these three points together with initial values of  $C_A$ ,  $C_B$ ,  $C_C$ , and  $R$  are used to solve for variables  $C_A$ ,  $C_B$ ,  $C_C$ , and  $R$  as function of time by the four point Adams-Bashworth-Moulton method. The program using this approach was found to converge when the time difference  $dt$  was less than 0.001 minutes. The differences in concentration for the three gases and the changing radius between 1000 time divisions and 2000 time divisions were found to be less than 0.1 ppm. The FORTRAN 77

computer program using this approach is listed in Appendix C. The flow diagram is illustrated in Figure 36. Results from this computer program were imported into QPRO software and were arranged with the corrected data, which were taken from Table 25, and are presented in Table 29 and Figure 37 and Figure 38. Results from the computer simulation for the gas concentrations vs reaction time were compared with the experimental results. Since the radius of shrinking core of the solid could not be obtained experimentally, the computer simulation was used to predict how fast the dry sorbent will be used.

From Figure 37, we can see that there is almost no difference between NO and NO<sub>x</sub> and no NO<sub>2</sub> production. After studying the effects of the three rate constants on the three gas species, which is illustrated in Table 30, it is possible to increase the concentration of NO<sub>2</sub> when the value of  $k_c$  is decreased. A second set of rate constants was therefore used by changing the value of  $k_c$  from 345.78 to 17. The simulated results shown in Figure 39 indicated that a large amount of NO<sub>2</sub> formed at the beginning of the reaction and finally disappeared at the end of the reaction. Obviously, this model cannot describe the kinetic phenomena very well over the entire concentration region.

The EPRI model assumes that the removal of NO<sub>x</sub> occurs as a series reaction sequence. Initially, NO reacts to form NO<sub>2</sub>, which reacts with the solid to result in the removal of NO<sub>x</sub>. Thus, no NO<sub>x</sub> is removed until a buildup of NO<sub>2</sub> occurs in the reaction system. This means that initially the curve of NO<sub>x</sub> concentration versus time must be



FLOW DIAGRAM

Figure 36. Flow diagram of computer programming for EPRI's model.

Table 29. Simulation Results for EPRI's reaction scheme :

Time (min)	Corrected Data			Simulated Data				
	(SO <sub>2</sub> ) (ppm)	(NO <sub>x</sub> ) (ppm)	(NO) (ppm)	(SO <sub>2</sub> ) (ppm)	(NO <sub>x</sub> ) (ppm)	(NO) (ppm)	R (um)	R X 100
0	1745.432	1497.932	1482.139	1745.43	1482.14	1497.93	29	2900
0.25	1652.04			1654.55	1397.65	1413.8	28.9816	2898.16
0.5		1338.24		1568.5	1322.1	1336.58	28.9637	2896.37
1			1124.605	1409.87	1193.37	1205.11	28.9285	2892.85
1.5				1267.6	1088.62	1098.24	28.8949	2889.49
2			956.858	1139.97	1002.49	1010.45	28.863	2886.3
2.5		933.5955		1025.42	931.01	937.65	28.8333	2883.33
2.75	1065.018			972.61	899.8	905.88	28.8192	2881.92
3				922.57	871.19	876.77	28.8056	2880.56
3.5		884.3528		830.2	820.74	825.47	28.7801	2878.01
4			805.3983	747.22	777.91	781.95	28.7567	2875.67
4.5		853.1195		672.63	741.34	744.8	28.7352	2873.52
5			764.1749	605.59	709.92	712.91	28.7155	2871.55
5.25	578.8172			574.65	695.88	698.65	28.7064	2870.64
5.5				545.3	682.82	685.4	28.6976	2869.76
6			705.6983	491.08	659.32	661.57	28.6813	2868.13
6.5		826.6717		442.29	638.88	640.83	28.6665	2866.65
7			681.7283	398.4	621.02	622.73	28.6531	2865.31
7.5		789.4352		358.89	605.38	606.88	28.6409	2864.09
7.75	250.0586			340.64	598.29	599.7	28.6352	2863.52
8			652.0072	323.33	591.63	592.96	28.6298	2862.98
8.5		764.205		291.32	579.53	580.7	28.6198	2861.98
9				262.49	568.84	569.87	28.6107	2861.07
9.5				236.53	559.38	560.3	28.6025	2860.25
10				213.15	551	551.82	28.5951	2859.51
10.25	83.29007			202.35	547.17	547.94	28.5916	2859.16
10.5				192.09	543.56	544.28	28.5884	2858.84
11				173.12	536.94	537.59	28.5823	2858.23
12				140.63	525.8	526.31	28.5719	2857.19
12.75	6.109091			120.34	518.95	519.38	28.5653	2856.53
13				114.26	516.92	517.32	28.5634	2856.34

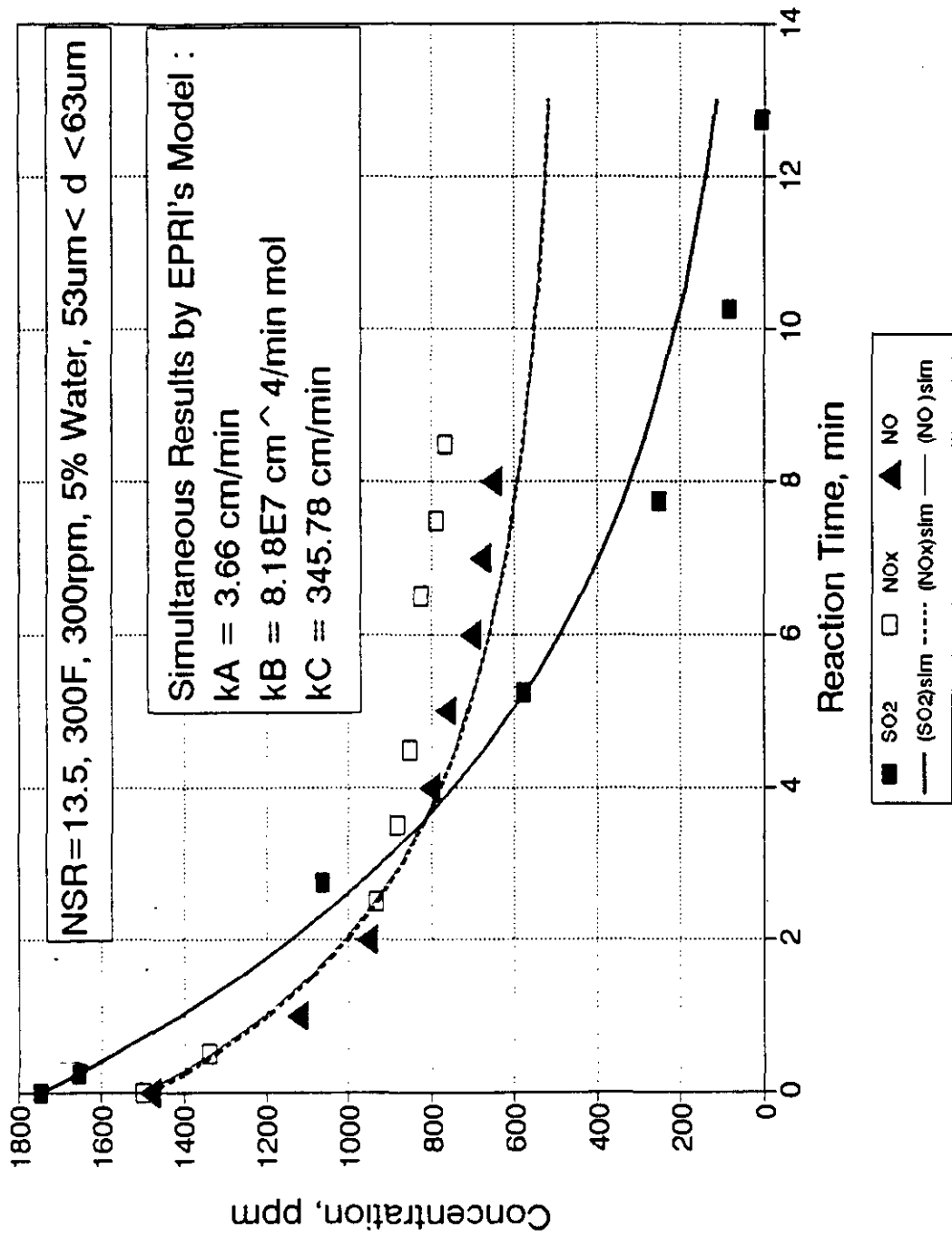


Figure 37. SO2 and NOx Simultaneous Reaction by Sodium Bicarbonate



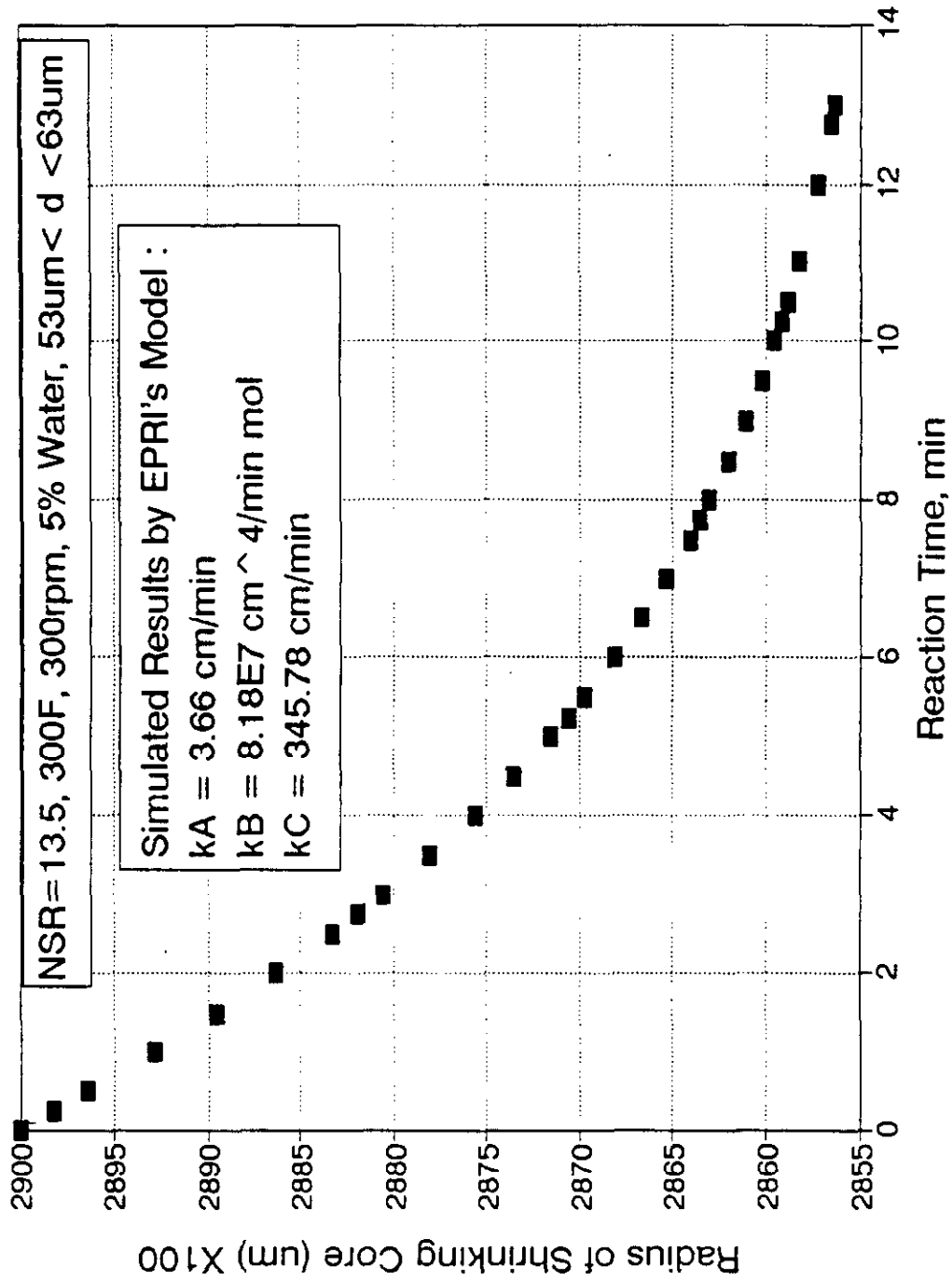


Figure 38. Prediction for the Shrinking Radius of Sodium Bicarbonate Particle

Table 30. Rate constant effect on the concentrations of three gases

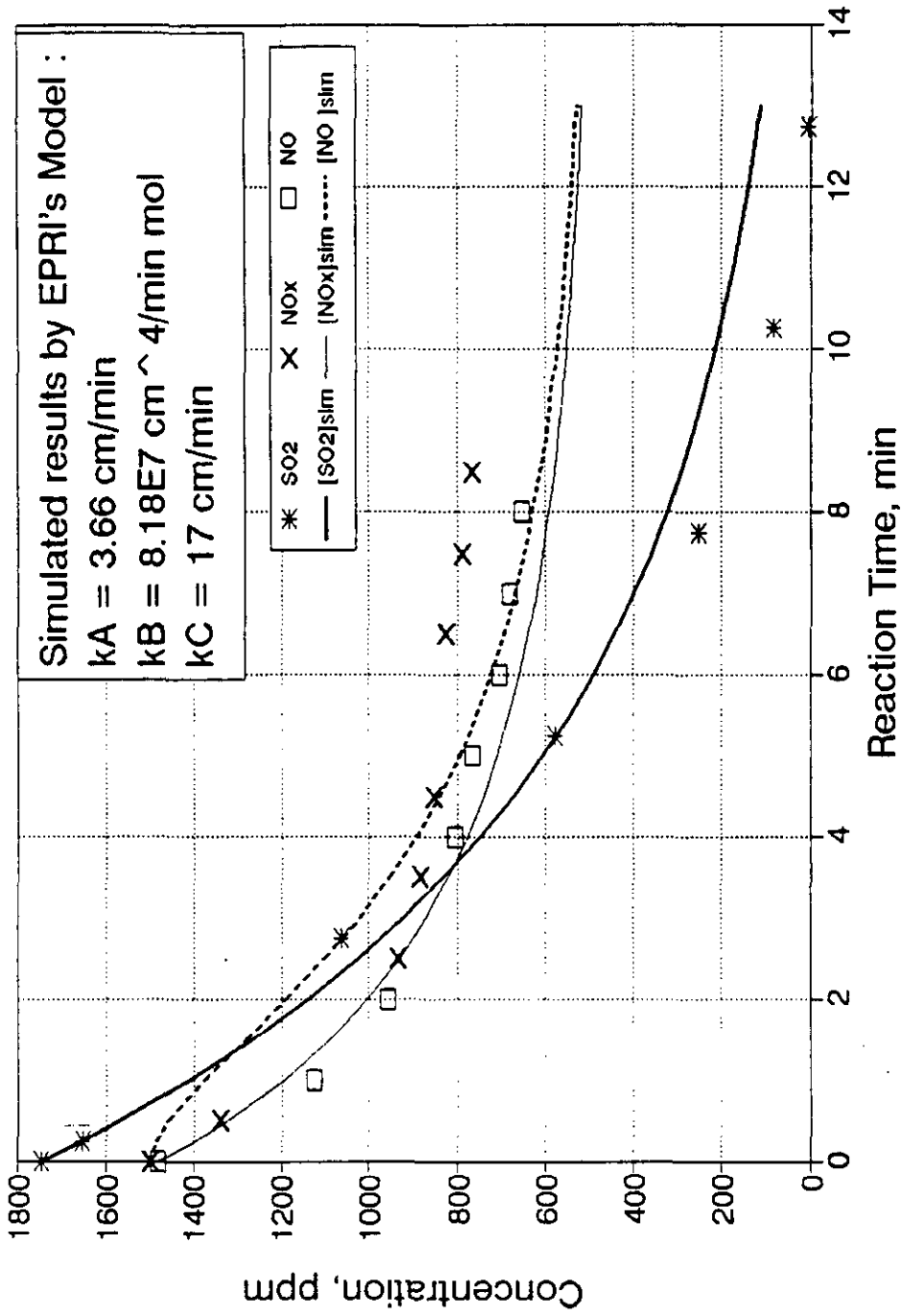
$k_A$	$k_B$	$k_C$	A	B	C
IN	--	--	DE	IN	IN
--	IN	--	--	DE	DE
--	--	IN	--	--	DE

\*  $k_A$ ,  $k_B$ , and  $k_C$  : rate constants in EPRI's mechanism

\* A : SO<sub>2</sub>, B : NO, C : NO<sub>x</sub>

\* IN : increase, DE : decrease

\* -- : remain constant



NSR=13.5, 300F, 300rpm, 5% Water, 53um < d < 63um

Figure 39. SO2 and NOx Simultaneous Reaction by Sodium Bicarbonate

horizontal. However, by observing any of our experimental results, it is quite clear that the concentration of  $\text{NO}_x$  immediately begins to decrease. This can occur only if the  $\text{NO}_x$  which is initially present actually reacts with the solid. For this reason we believe that the Solvay model is more realistic.

### 5.3 Experimental curve fitting for Solvay's model

Solvay's mechanism was used to simulate the experimental data, which eventually was shown to be capable of describing the simultaneous removal of  $\text{SO}_2$  and  $\text{NO}_x$  using the two dry sorbents. Six experimental results with sodium sesquicarbonate, four experiments with  $\text{NSR}=3.38$  and two experiments with  $\text{NSR}=0.8$ , were used to demonstrate the validity of this model. These results are presented in Figures 27 through 32. Using the same procedure, rate constants,  $k$ 's, and the selectivity constant  $x$  for the six experiments were obtained.

#### 5.3.1 Simplified rate expressions for Solvay's model in the

$\text{SO}_2\text{-NO}_x\text{-}[\text{NaHCO}_3\text{-Na}_2\text{CO}_3\text{-}2\text{H}_2\text{O}]$  reaction system

As in Section 5.2.1 the total surface area per volume of  $\text{Na}_2\text{CO}_3$  could be expressed as a function of core radius. For the cases of  $\text{NSR}=3.38$ , when 0.36 g sodium sesquicarbonate was injected, the initial density is  $2.112 \text{ g/cm}^3$  and the initial molecular weight is  $226.04 \text{ g/mol}$ ; so, the value of  $1.5 \text{ M/D}$  in Equation (3-25) is 160.54. The

number of particles per volume  $N$  estimated by Equation (3-5) is  $1.67E6$  ea/cm<sup>3</sup> and the constant group  $4 \text{ Pi } N/V$  in Equation (3-4) is 1631.44. With the same treatment as that in Chapter 5.2.1 Equation (3-3), Equation (3-8) Equation (3-21) and Equation (3-25) can be rewritten as:

Removal rate of SO<sub>2</sub>

$$R_A = dC_A/dt = R_A(C_A, R) = -1631.44 k_A C_A R^2 \quad (5-5)$$

Removal rate of NO

$$R_B = dC_B/dt = R_B(C_A, C_B, R) = -1631.44 k_B C_A C_B R^2 \quad (5-6)$$

Formation rate of NO<sub>2</sub>

$$R_C = dC_C/dt = R_C(C_A, C_B, R) = -x/2 dC_B/dt = 815.72xk_B C_A C_B R^2 \quad (5-7)$$

Shrinking rate of radius  $R$

$$R_R = dR/dt = R_R(C_A, C_B) = -160.54 [k_A C_A + (1-x/2)/2 k_B C_A C_B] \quad (5-8)$$

With the above equations, simulation of the SO<sub>2</sub> and NO<sub>x</sub> simultaneous removal by sodium sesquicarbonate with NSR equal to 3.38 could be programmed.

### 5.3.2 Evaluations of kinetics parameters $k_A$ , $k_B$ , and $x$ for the gas-sodium sesquicarbonate reaction system

Evaluation of rate constants  $k_A$  and  $k_B$  and the selectivity constant  $x$  for the SO<sub>2</sub>-

$\text{NO}_x$ - $[\text{NaHCO}_3\text{-Na}_2\text{CO}_3\text{-2H}_2\text{O}]$  reaction system is similar to the procedure described in Chapter 5.3.2. The resultant data taken from Figure 27 through Figure 32 were also corrected by the system bleeding rate and were used to obtain the rate constants and the selectivity constant and then compared with the simulated results. Information required to determine the rate constants using the initial rate approach are initial concentrations of  $\text{SO}_2$ ,  $\text{NO}$ , and  $\text{NO}_2$ ; the initial radius of  $[\text{NaHCO}_3\text{-Na}_2\text{CO}_3\text{-2H}_2\text{O}]$ ; and the initial rates of  $\text{SO}_2$ ,  $\text{NO}$ , and  $\text{NO}_2$ . The initial radius of  $[\text{NaHCO}_3\text{-Na}_2\text{CO}_3\text{-2H}_2\text{O}]$   $R$  is identical to that used in  $\text{NaHCO}_3$  and is equal to 0.0028 cm. The selectivity constant  $x$  can be evaluated from equation (5-8) from the initial formation rate of  $\text{NO}_2$ , which is the initial rate difference between  $\text{NO}_x$  and  $\text{NO}$ , and the initial values of  $\text{SO}_2$ ,  $\text{NO}$  and radius  $R$ . The best curve fitting was accomplished as described above. Experimental results taken from Figure 28, or Table 22, is used to demonstrate the procedure for obtaining rate constants. Correction of the system bleeding for this experiment has been shown in Table 28 and Figure 35; and the demonstration of the kinetics parameter evaluation is shown in Figure 40. This same procedure was used for the parameters obtained for runs taken from Figure 27 and Figure 29 through Figure 32. The bleeding rate corrections are shown in Appendix B. The kinetic parameters obtained for all runs are shown in Table 31. It should be noted that the range of values for the parameters obtained is quite satisfactory. Average values for the parameters at NSR of 3.38 are as follows:

$$k_A = 8.77 \text{ cm/min}$$

Figure 40. Evaluation of kinetics parameters :

Step 1. Initial rate study.

INITIAL CONCENTRATION (mol/cc)			
SO2	NOx	NO	NO2
2.48E-08	3.44E-08	3.26E-08	1.73E-09
=====			
INITIAL RATE (mol/cc min)			
SO2	NOx	NO	NO2
-2.9E-09	-9.6E-10	-1.4E-09	3.87E-10
=====			

Step 2. Constant evaluation :

$$N = \frac{W}{(4/3 \pi R_o^3 \text{Den})} = 1668501$$

$$4 \pi N/V = 1629.896$$

$$-dCA/dt = K_1 CA^2 \pi R^2 N / 1629.896 = K_1 CA R^2$$

$$-dCB/dt = 4 K_2 CA CB \pi R^2 N / V$$

$$= 16K_2 CA CB R^2$$

$$dCC/dt = -X/2 * dCB/dt = -814.948 K_2 CA CB X R^2$$

$$M'/D' = 107.0265$$

$$dR/dt = -M'/D' * [K_1 CA + (1-X/2)/2 * K_2 CA CB]$$

$$= -107.027 * [K_1 CA + (1-X/2)/2 * K_2 CA CB]$$

$$R_o = 0.0029 \text{ cm}$$

(1)  $-dCA_o/dt = 1629.896 K_1 CA_o R_o^2$   
 $K_1 = 8.546949$

(2)  $-dCB_o/dt = 1629.896 K_2 CA_o CB_o R_o^2$   
 $K_2 = 1.22E+08$

(3)  $dCC_c/dt = -X/2 * dCB_o/dt = 3.87E-10$   
 $X = 0.572526$

Table 31.  $k_A$ ,  $k_B$ , and  $x$  obtained from initial rate approach :

Source	Sorbent	NSR	$k_A$ (cm/min)	$k_B$ (cm <sup>4</sup> /cm mol)	$x$
Figure 27	Sesq-	0.85	7.42	1.24E8	0.61
Figure 32	Sesq-	0.85	9.59	1.47E8	0.54
Figure 28	Sesq-	3.38	8.55	1.22E8	0.57
Figure 29	Sesq-	3.38	9.37	1.17E8	0.54
Figure 30	Sesq-	3.38	7.94	1.21E8	0.54
Figure 31	Sesq-	3.38	9.20	1.34E8	0.55

\* Sesq- : Sodium Sesquicarbonate



$$k_B = 1.24E8 \text{ cm}^4/\text{min mol}$$

$$x = 0.55$$

These average values are the values used in the computer simulation.

### 5.3.3 Computer simulation using Solvay's model in the $\text{SO}_2\text{-NO}_x\text{-[NaHCO}_3\text{-Na}_2\text{CO}_3\text{-2H}_2\text{O]}$ reaction system

Once the rate constants  $k_A$  and  $k_B$ , and the stoichiometric constant  $x$  were obtained, the Adams-Bashforth-Moulton, as discussed above, was employed. The results using the average parameters are shown in Appendix B and were plotted on Figures 41 through Figure 52. The model does a reasonably good job in fitting the data at  $\text{NSR} = 3.38$ . However, for  $\text{NSR} = 0.85$ , the curves deviate from the data at longer times. We believe that this is due to a portion of the solid not entering the reaction system at the start of the run. This would result in a flattening out of the concentrations at higher values than expected. This is what is observed in the experimental results.

### 5.3.4 Computer simulation for the $\text{SO}_2\text{-NO}_x\text{-NaHCO}_3$ reaction system

Equations used for the  $\text{SO}_2\text{-NO}_x\text{-NaHCO}_3$  reaction system are the Equation (3-3), Equation (3-8), Equation (3-21) and Equation (3-24). The simplified equations are shown below:

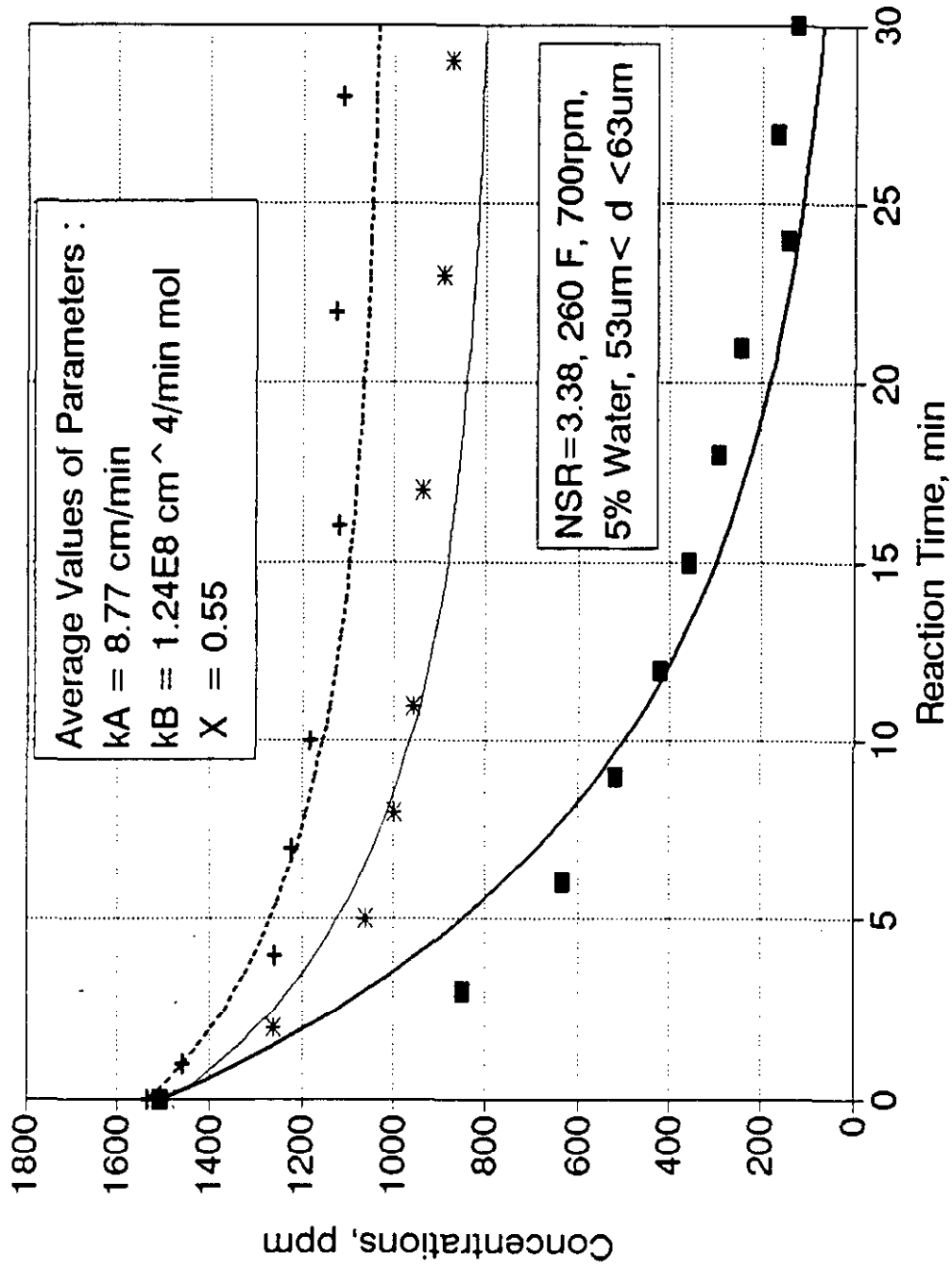


Figure 41. SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Sesquicarbonate

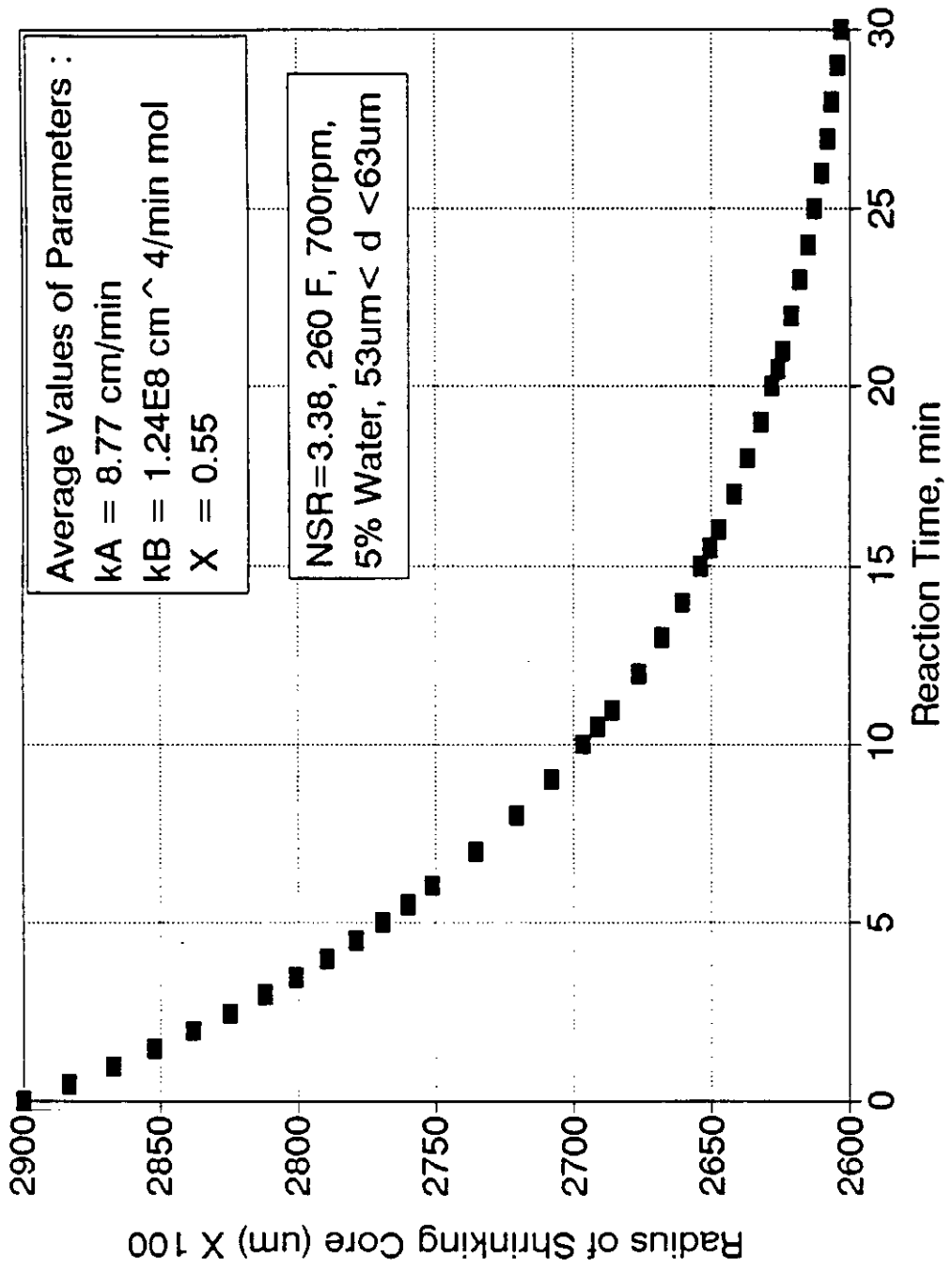


Figure 42. SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Sesquicarbonate

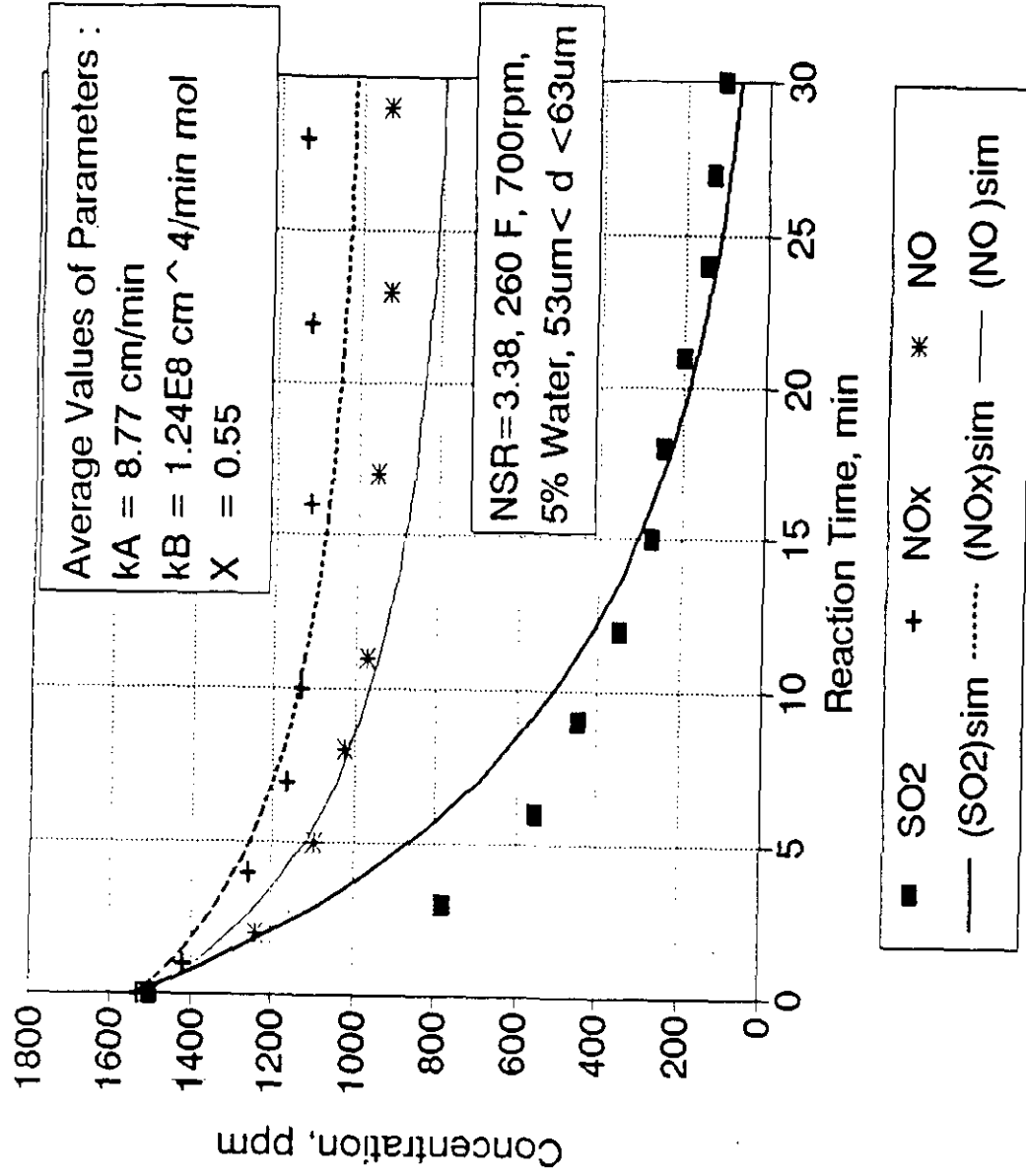


Figure 43.. SO2 and NOx Removal by Sodium Sesquicarbonate

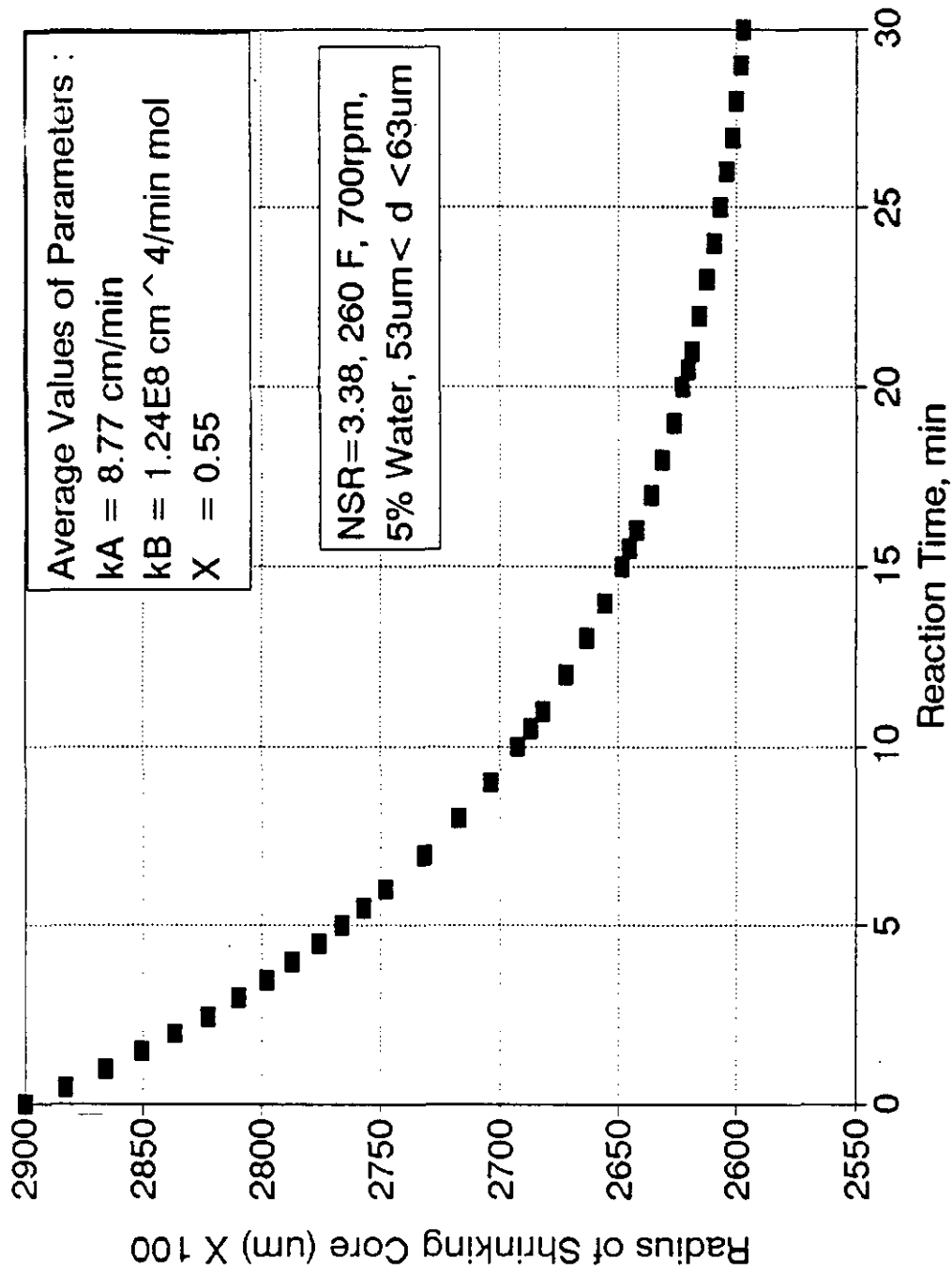


Figure 44. SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Sesquicarbonate

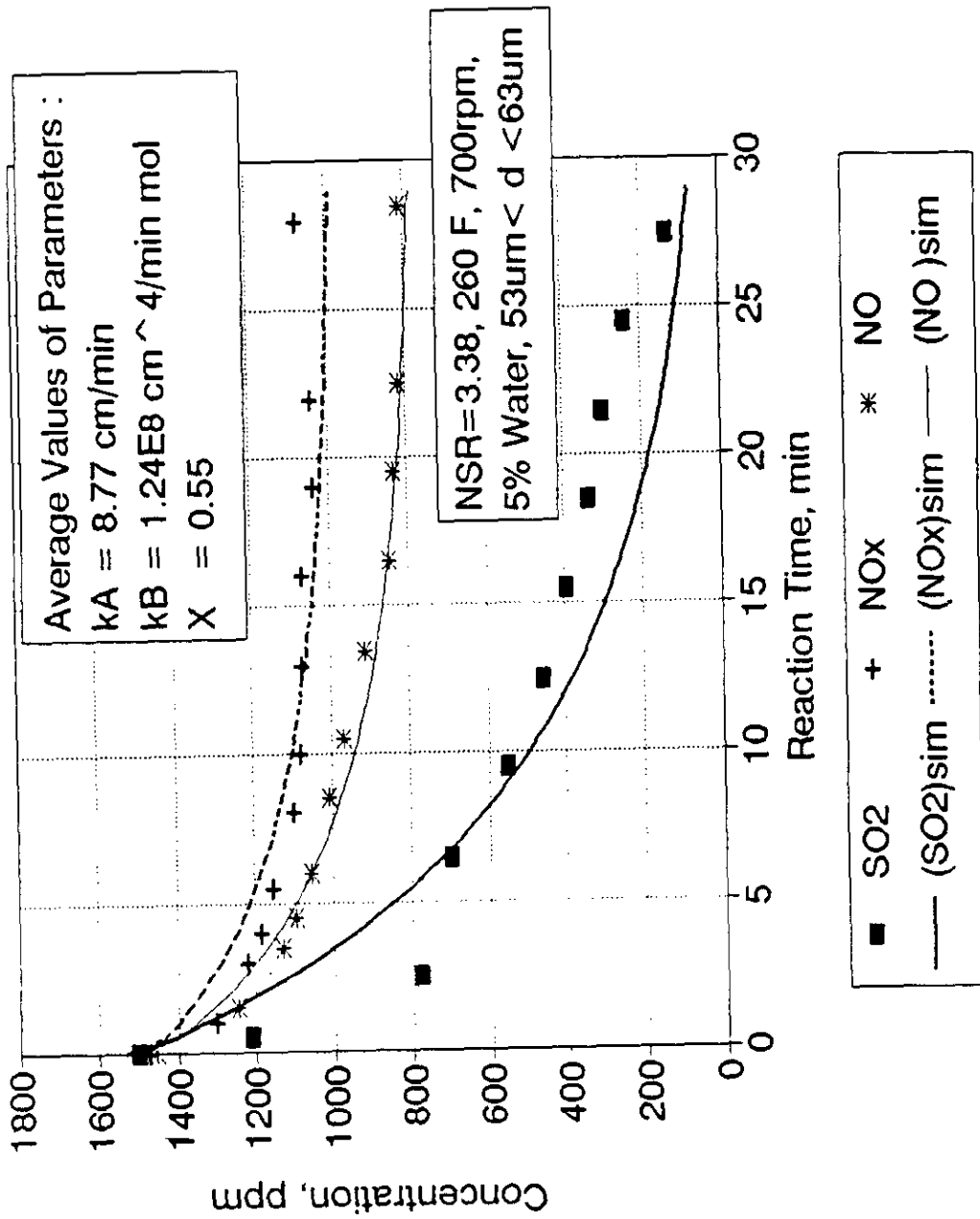


Figure 45. SO2 and NOx Removal by Sodium Sesquicarbonate

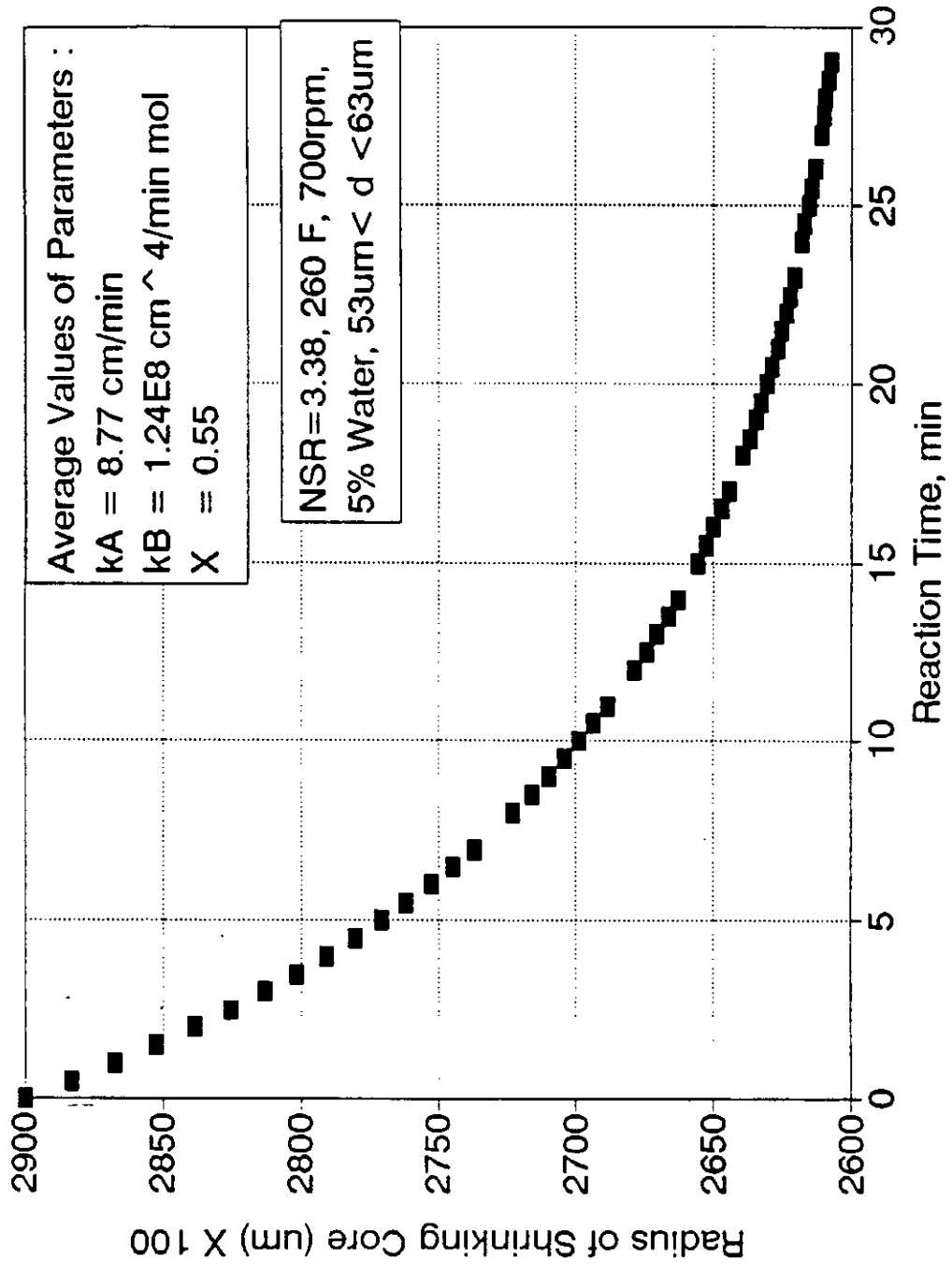


Figure 46. SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Sesquicarbonate

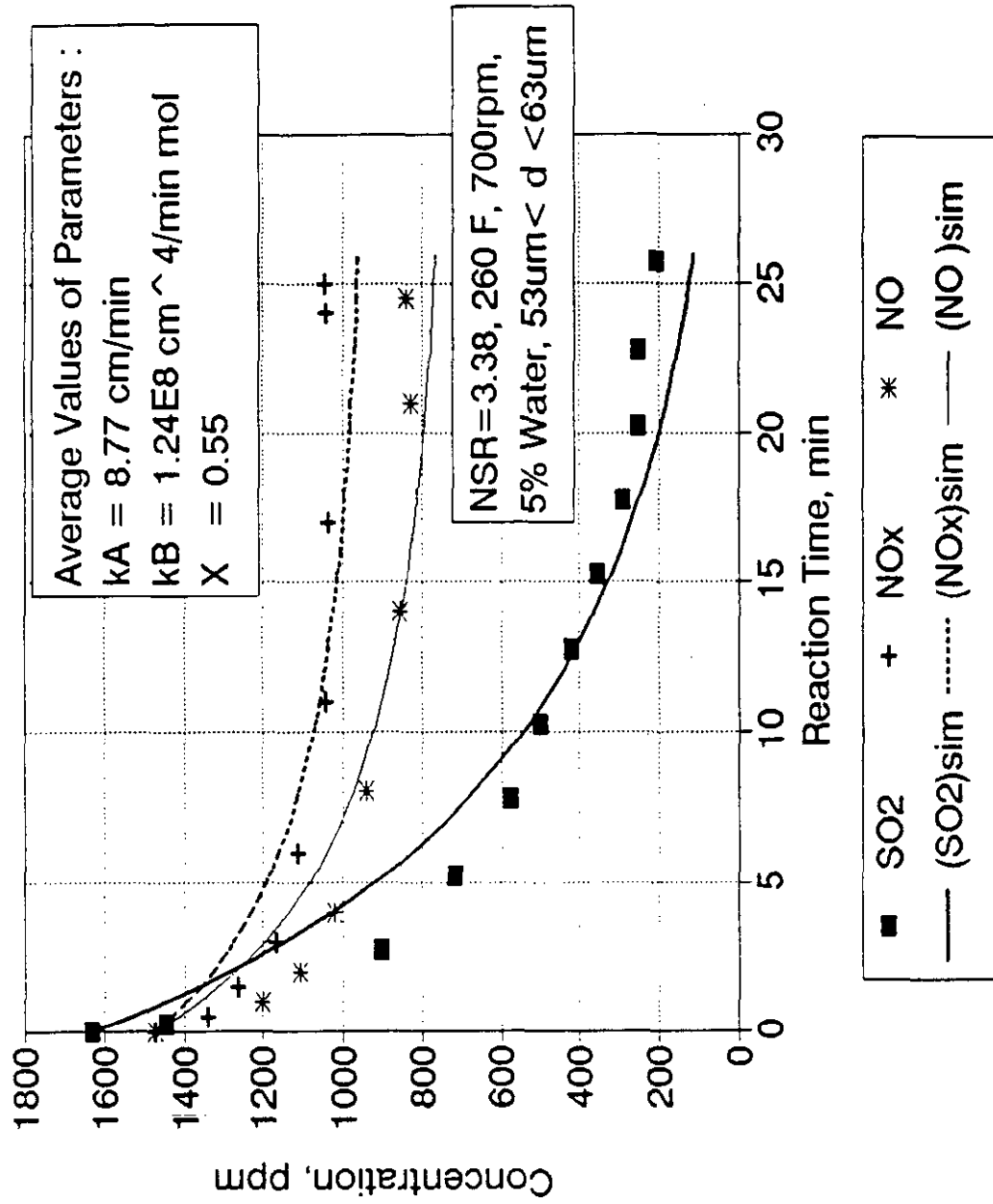


Figure 47. SO2 and NOx Removal by Sodium Sesquicarbonate



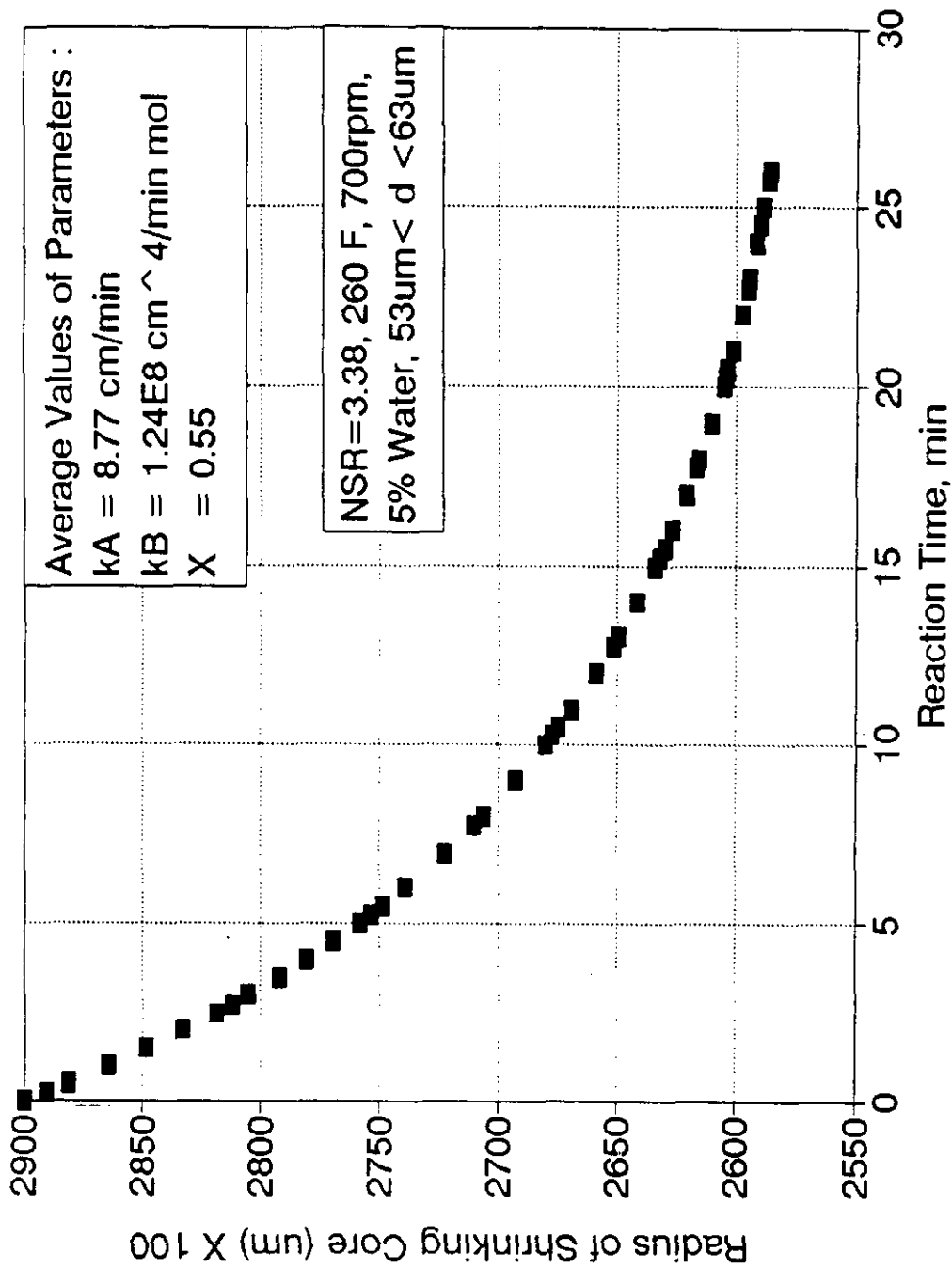


Figure 48. SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Sesquicarbonate

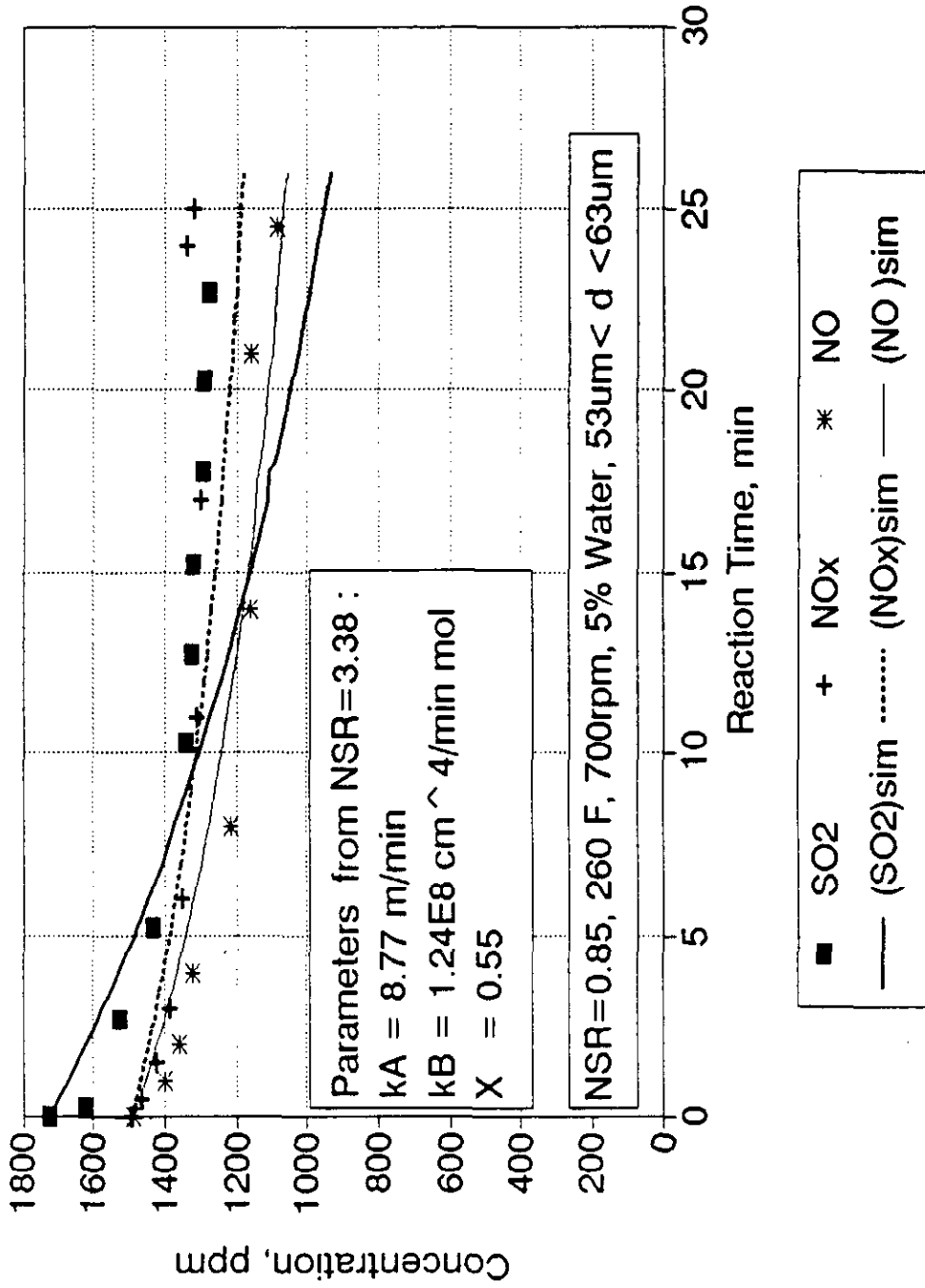


Figure 49. SO2 and NOx Removal by Sodium Sesquicarbonate

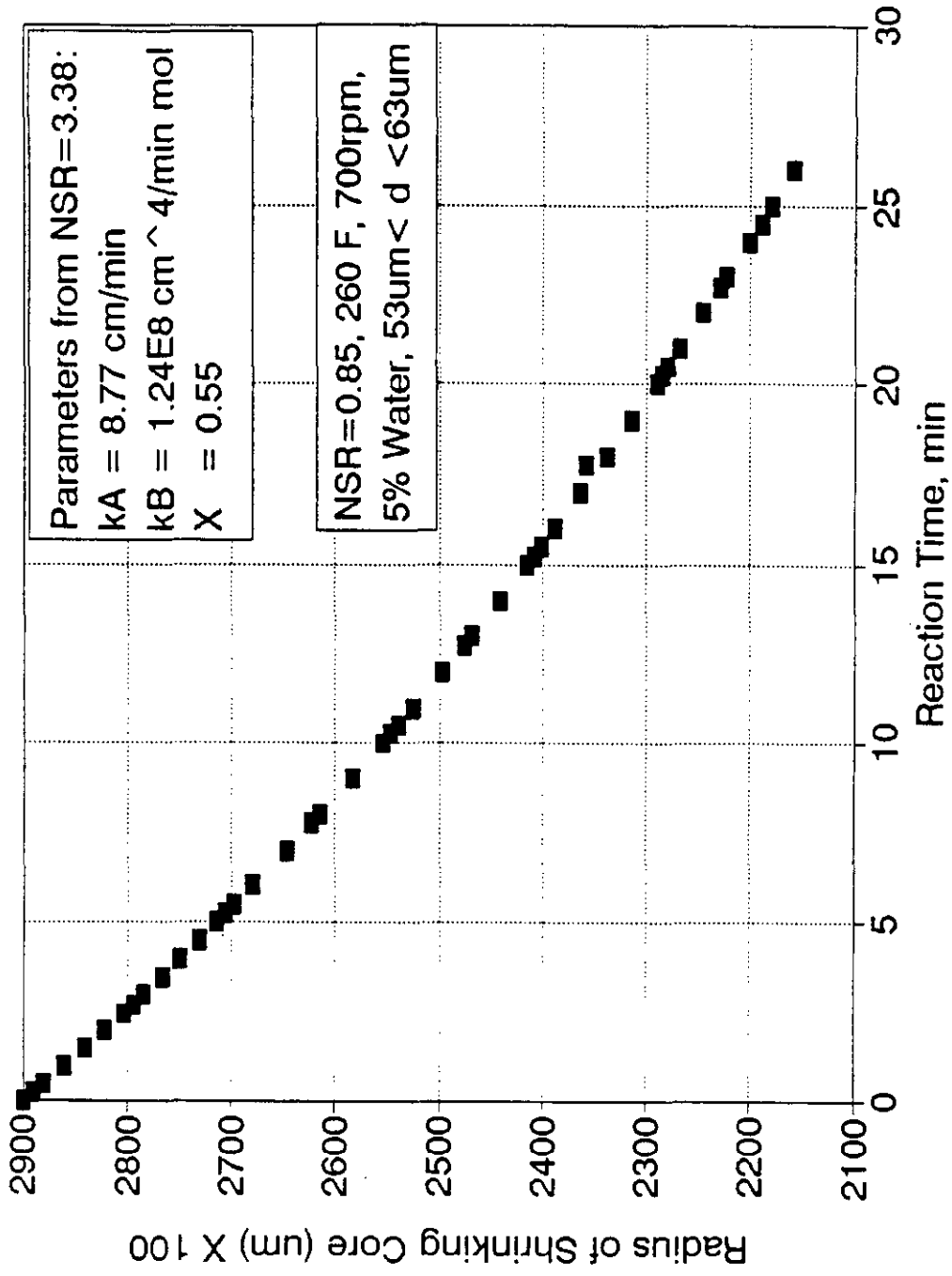


Figure 50. SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Sesquicarbonate

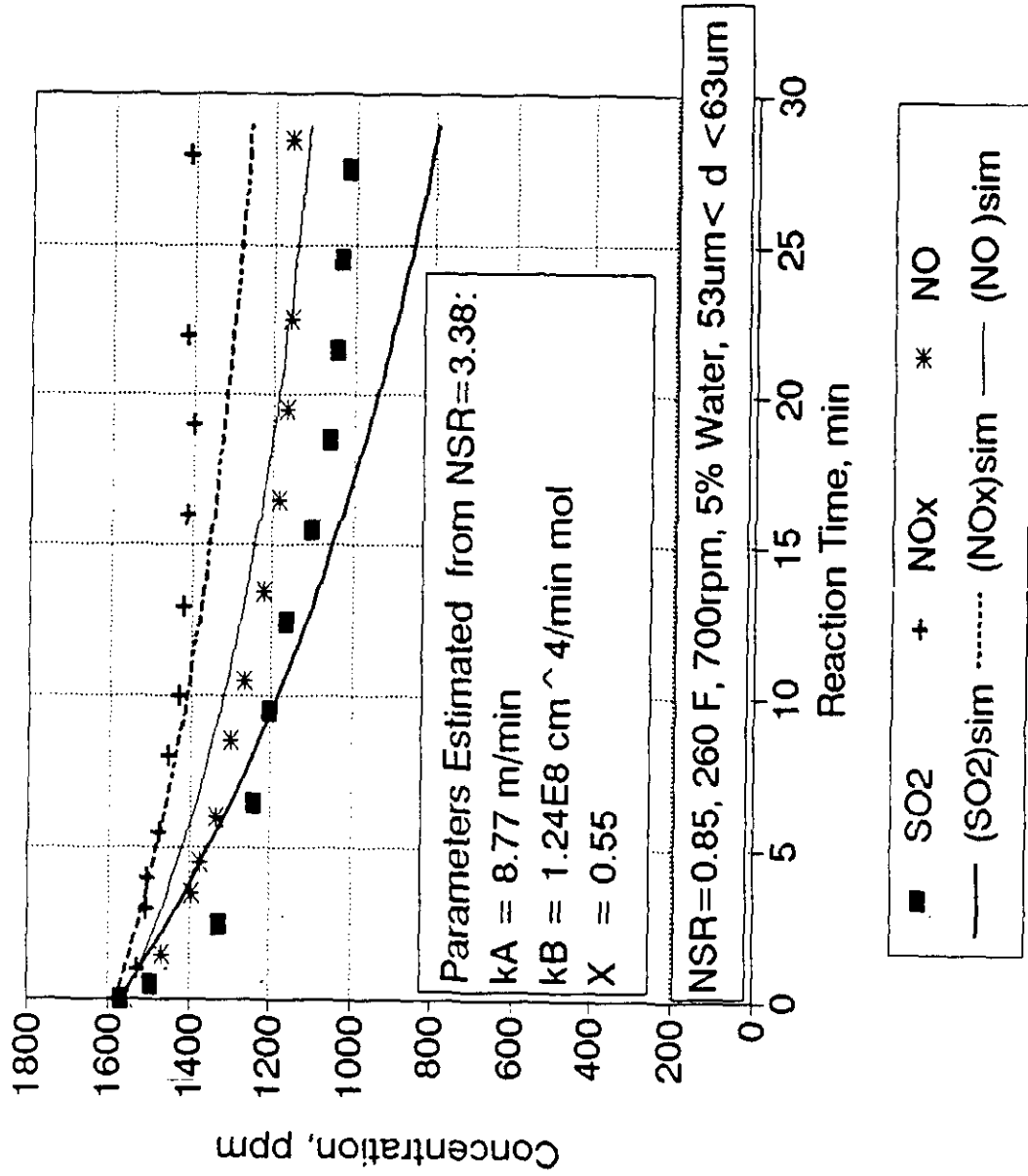


Figure 51. SO2 and NOx Removal by Sodium Sesquicarbonate

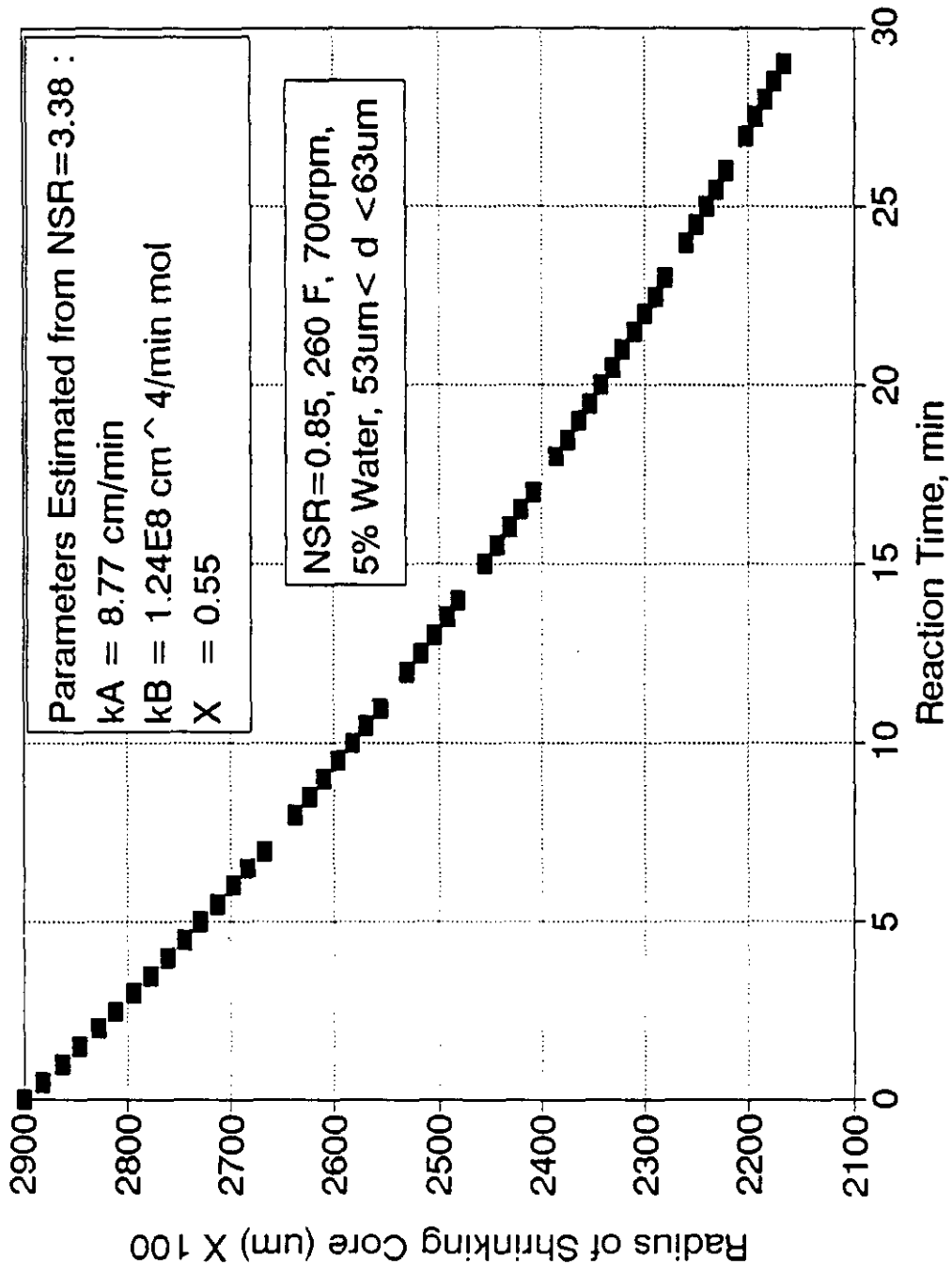


Figure 52. SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Sesquicarbonate

Removal rate of SO<sub>2</sub>

$$R_A = dC_A/dt = -6954.22 k_A C_A R^2 \quad (5-9)$$

Removal rate of NO

$$R_B = dC_B/dt = -6954.22 k_B C_A C_B R^2 \quad (5-10)$$

Formation rate of NO<sub>2</sub>

$$R_C = dC_C/dt = 3477.11 x k_B C_A C_B R^2 \quad (5-11)$$

Shrinking rate of radius R

$$R_R = dR/dt = -20.92 [k_A C_A + (1-x)/2 k_B C_A C_B] \quad (5-12)$$

As in the previous section, average kinetics parameter are obtained from the case of NSR=3.37 first, with these values of  $k_A$ ,  $k_B$ , and  $x$ , then used to predict results for the case of NSR=13 and the case of NSR=0.8. Kinetics parameters of these runs are shown in Table 32. Except for the case of the large NSR = 13.49. The average values for  $k_A$ ,  $k_B$  and  $x$  for the case of NSR=3.37 are as follow :

$$k_A = 7.65 \text{ cm/min}$$

$$k_B = 1.06E7 \text{ cm}^4/\text{min mol}$$

$$x = 0.7$$

Table 32.  $k_A$ ,  $k_B$ , and  $x$  Obtained from Initial Rate Approach :

Source	Sorbent	NSR	$k_A$ (cm/min)	$k_B$ (cm <sup>4</sup> /cm mol)	$x$
Figure 23	Bic-	0.85	6.56	1.47E8	0.97
Figure 24	Bic-	3.37	7.42	1.07E8	0.70
Figure 25	Bic-	3.37	7.88	1.04E8	0.70
Figure 26	Bic-	13.5	4.16	8.27E7	0.26

\* Bic- : Sodium bicarbonate

With these values, simulation have been done and are plotted on Figures 53 through 60. The results are similar to those for sodium sesquicarbonate. Again it appears that some solid is remaining in the injection system resulting in less removal of gases at low NSR. For the high NSR run is appears that the actual reaction rate for the removal of  $\text{SO}_2$  is somewhat less than that predicted by the model. The average kinetic parameters for the two solids are listed in table 33. From Table 33, it appears that sodium sesquicarbonate has the higher reaction rate constant for removing both  $\text{SO}_2$  and  $\text{NO}$  and lower potential in forming  $\text{NO}_2$  which is characterized by the parameter  $x$ .



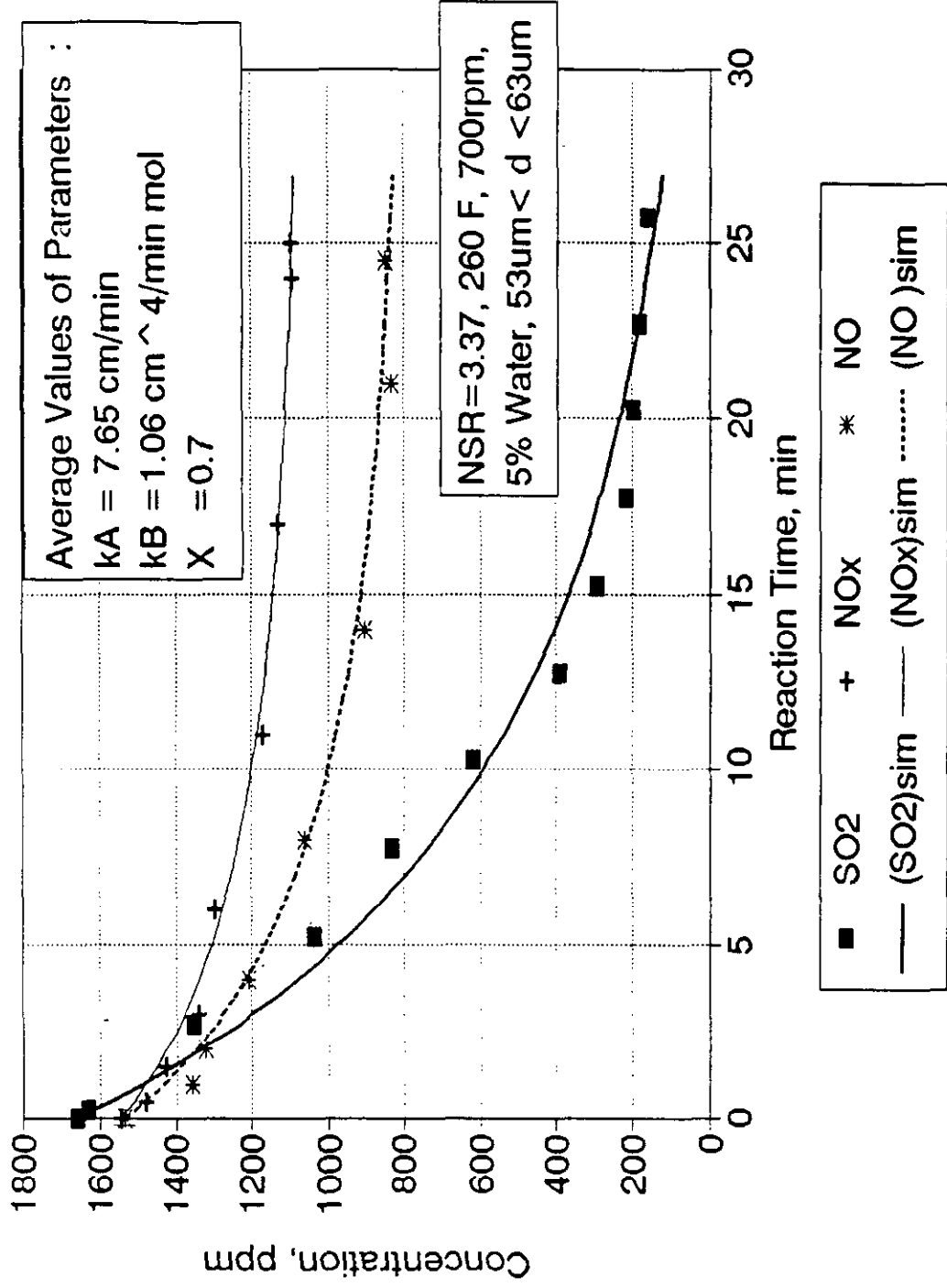


Figure 53. SO2 and NOx Removal by Sodium Bicarbonate

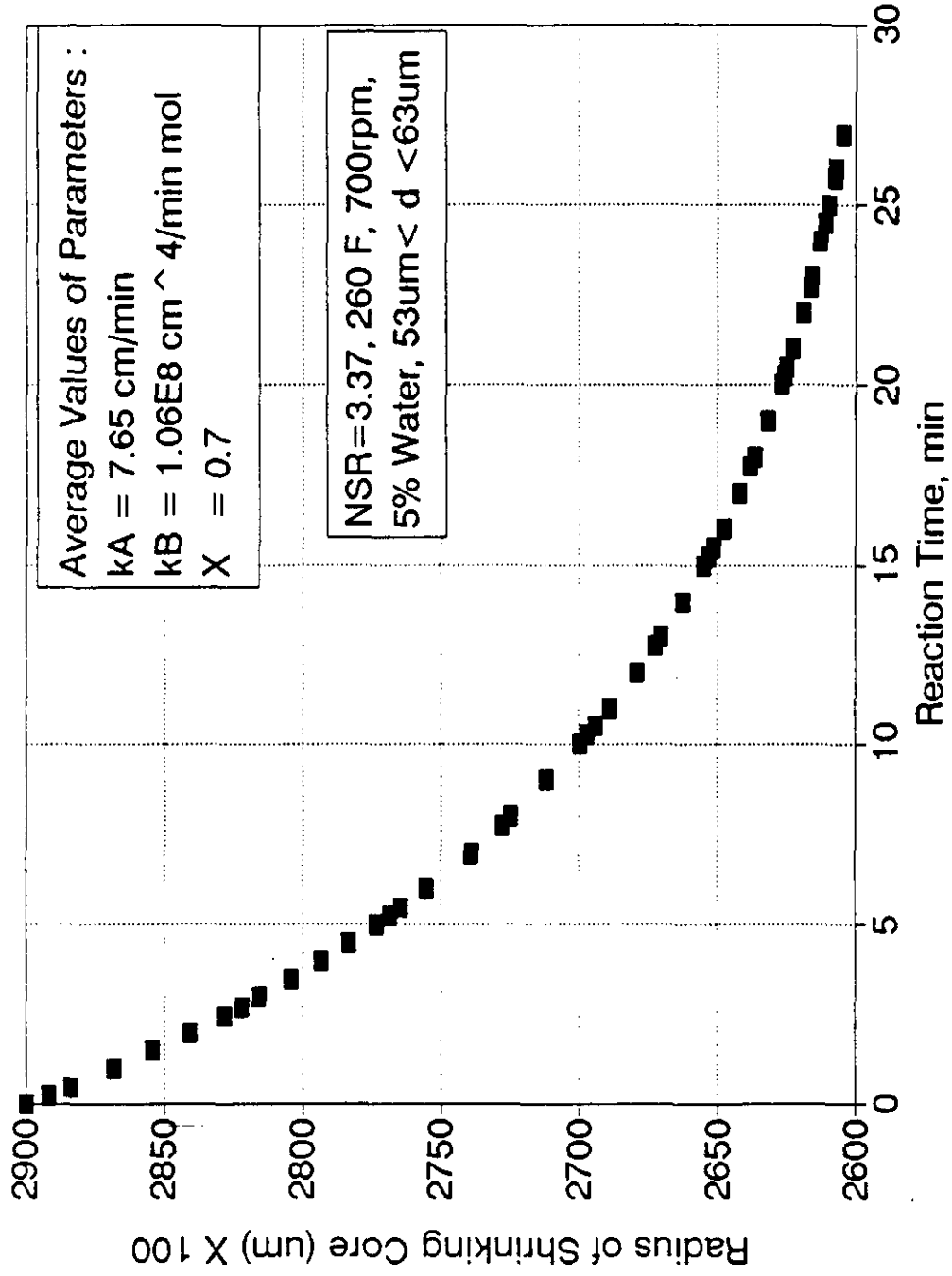


Figure 54. SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Bicarbonate

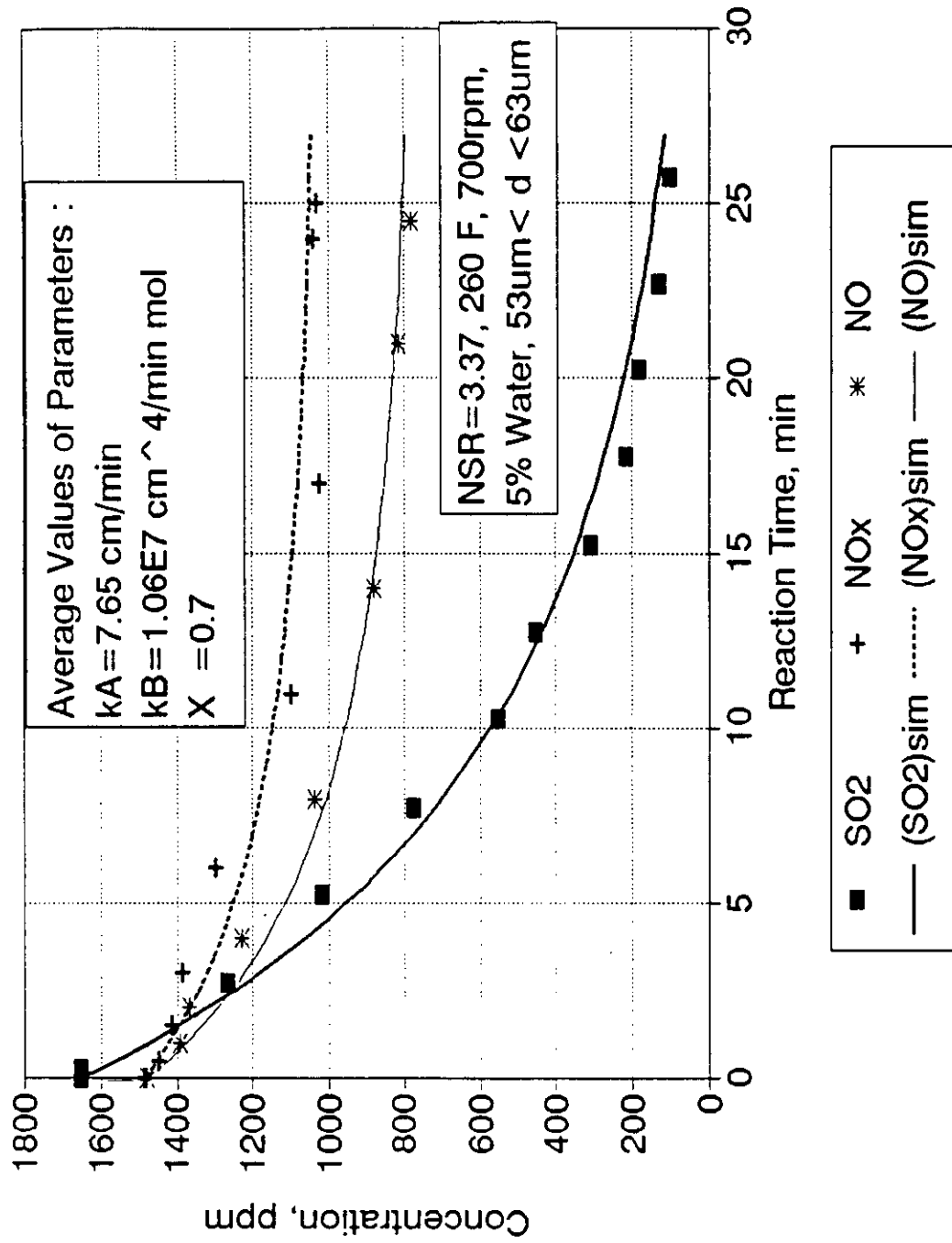


Figure 55. SO2 and NOx Removal by Sodium Bicarbonate

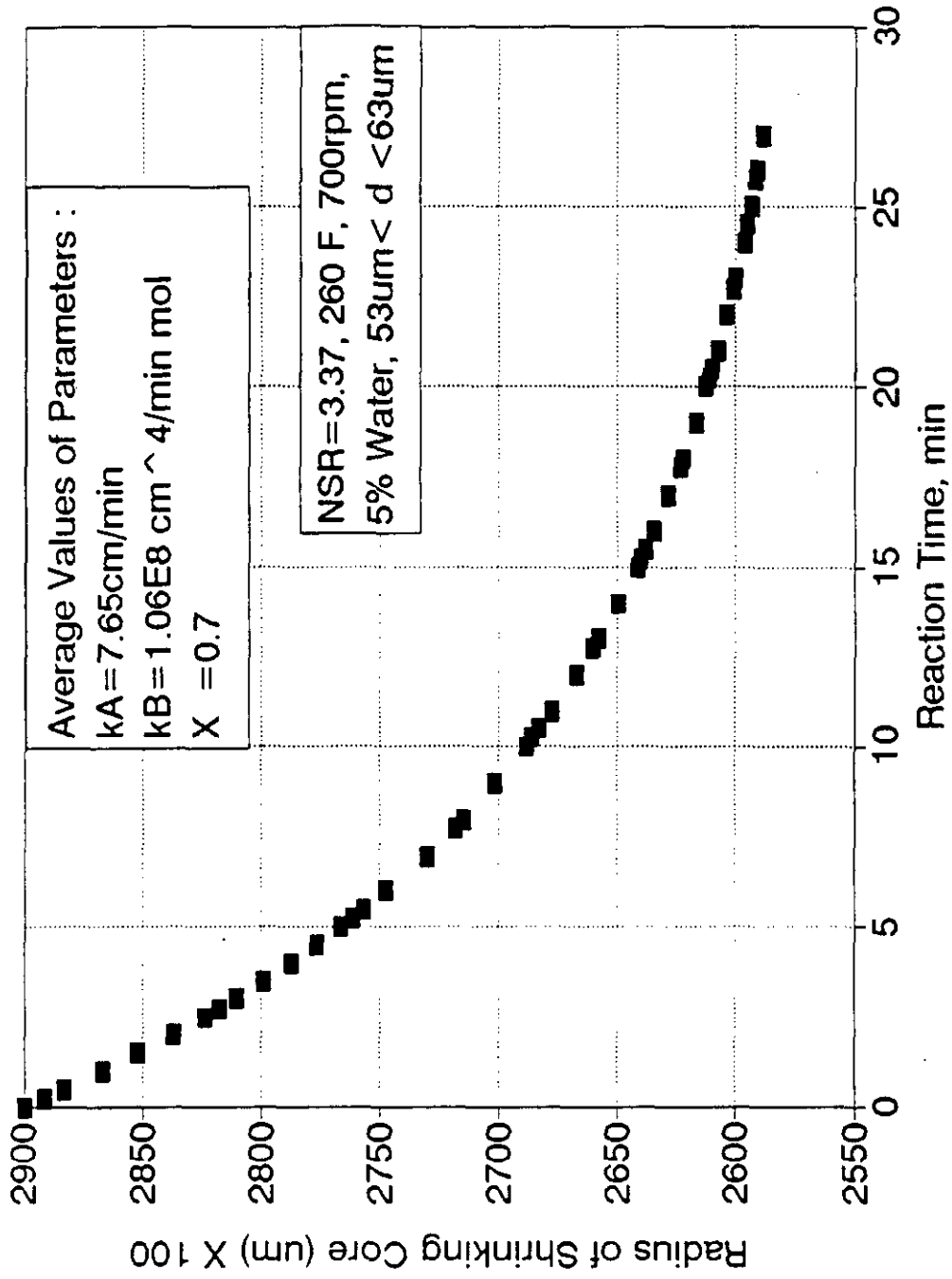


Figure 56. SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Bicarbonate

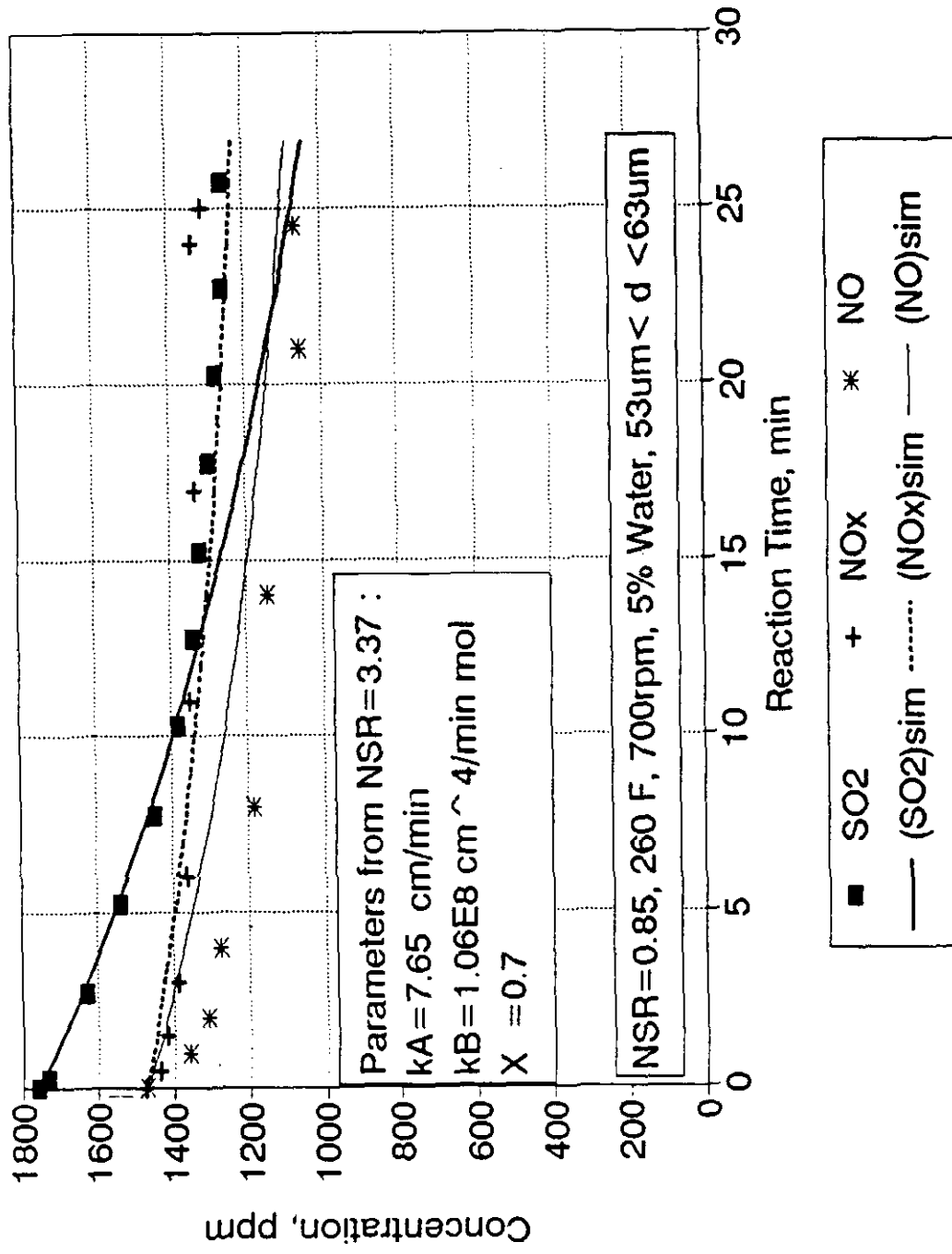


Figure 57. SO2 and NOx Removal by Sodium Bicarbonate

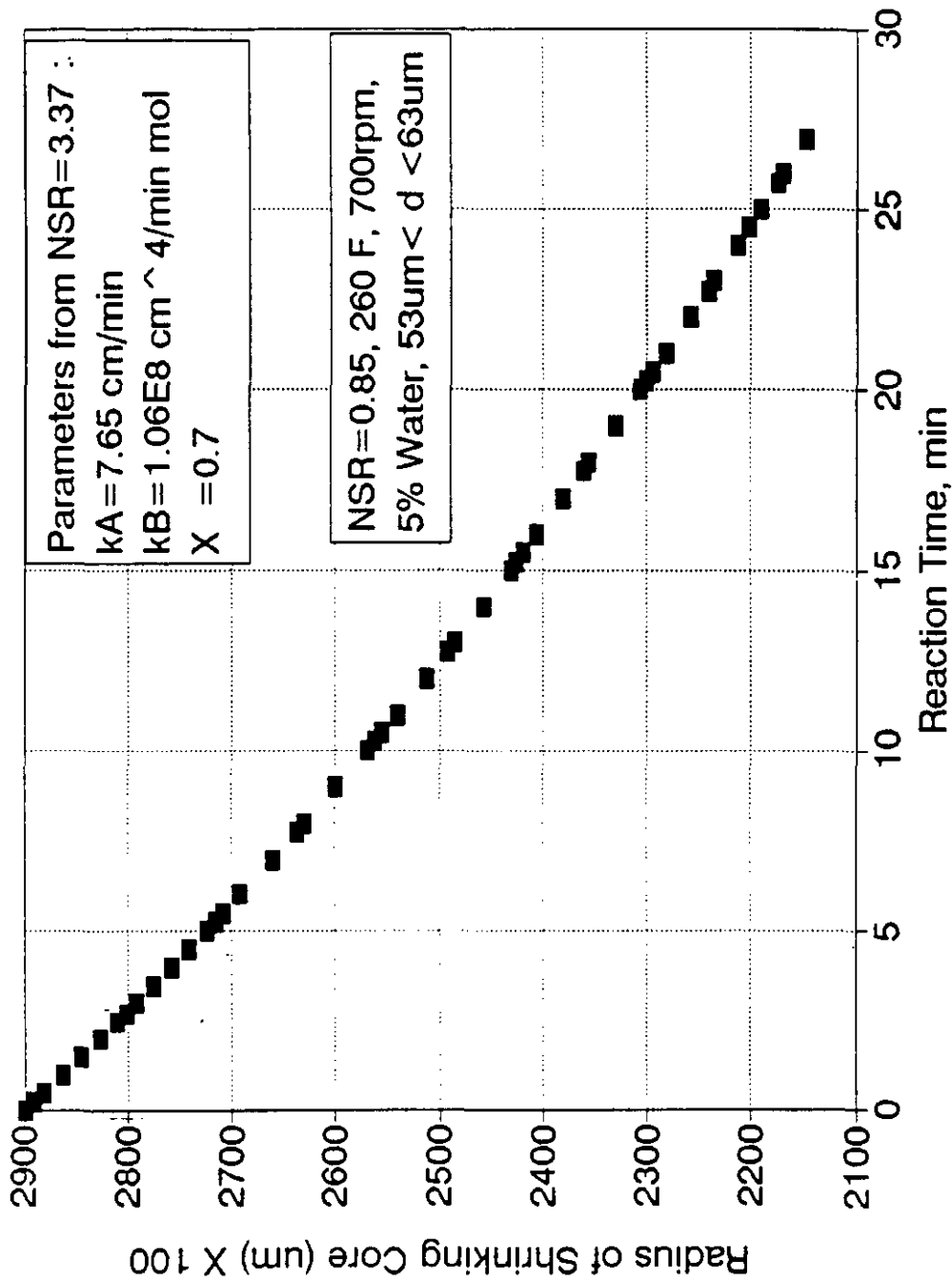


Figure 58. SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Bicarbonate

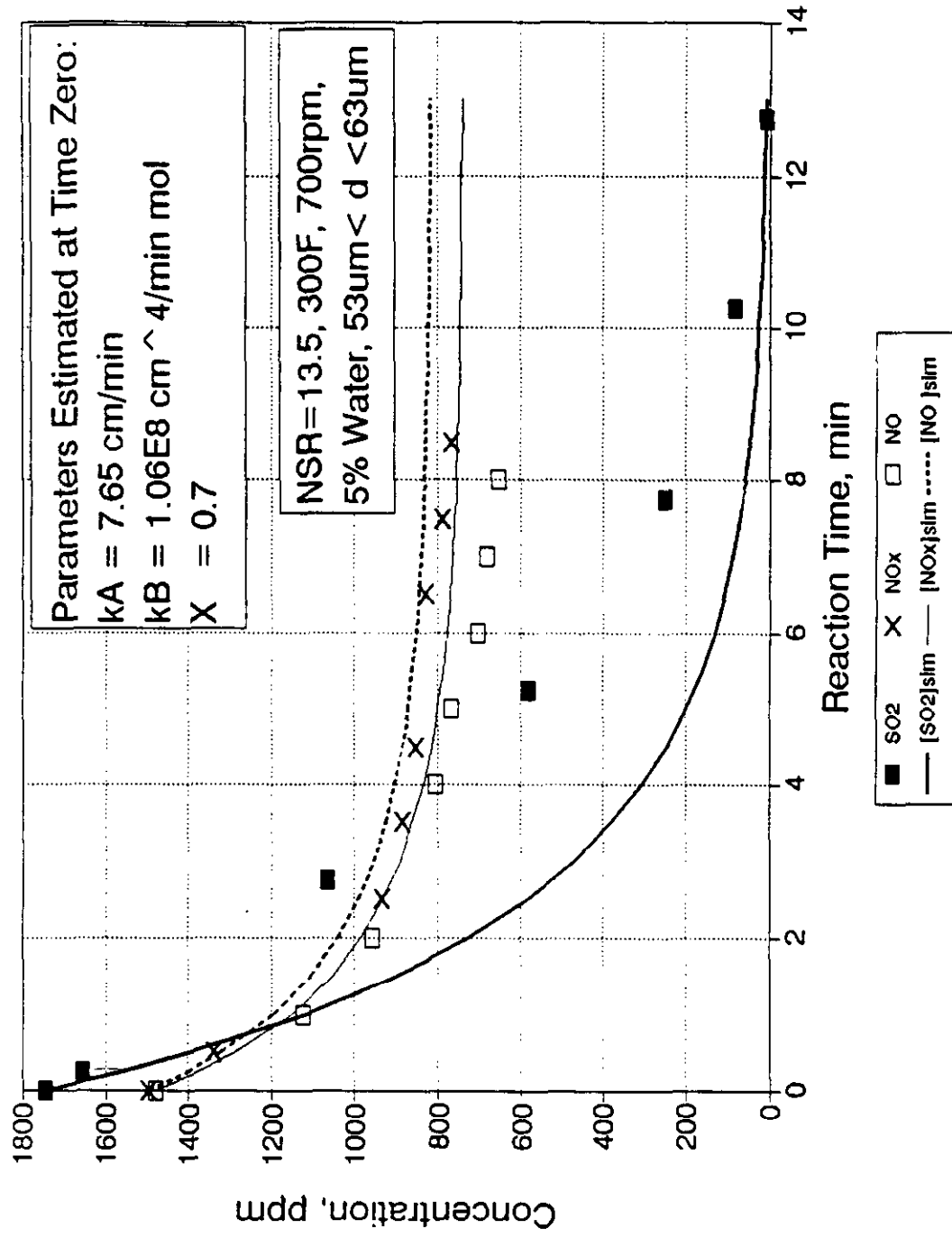


Figure 59. SO2 and NOx Simultaneous Reaction by Sodium Bicarbonate

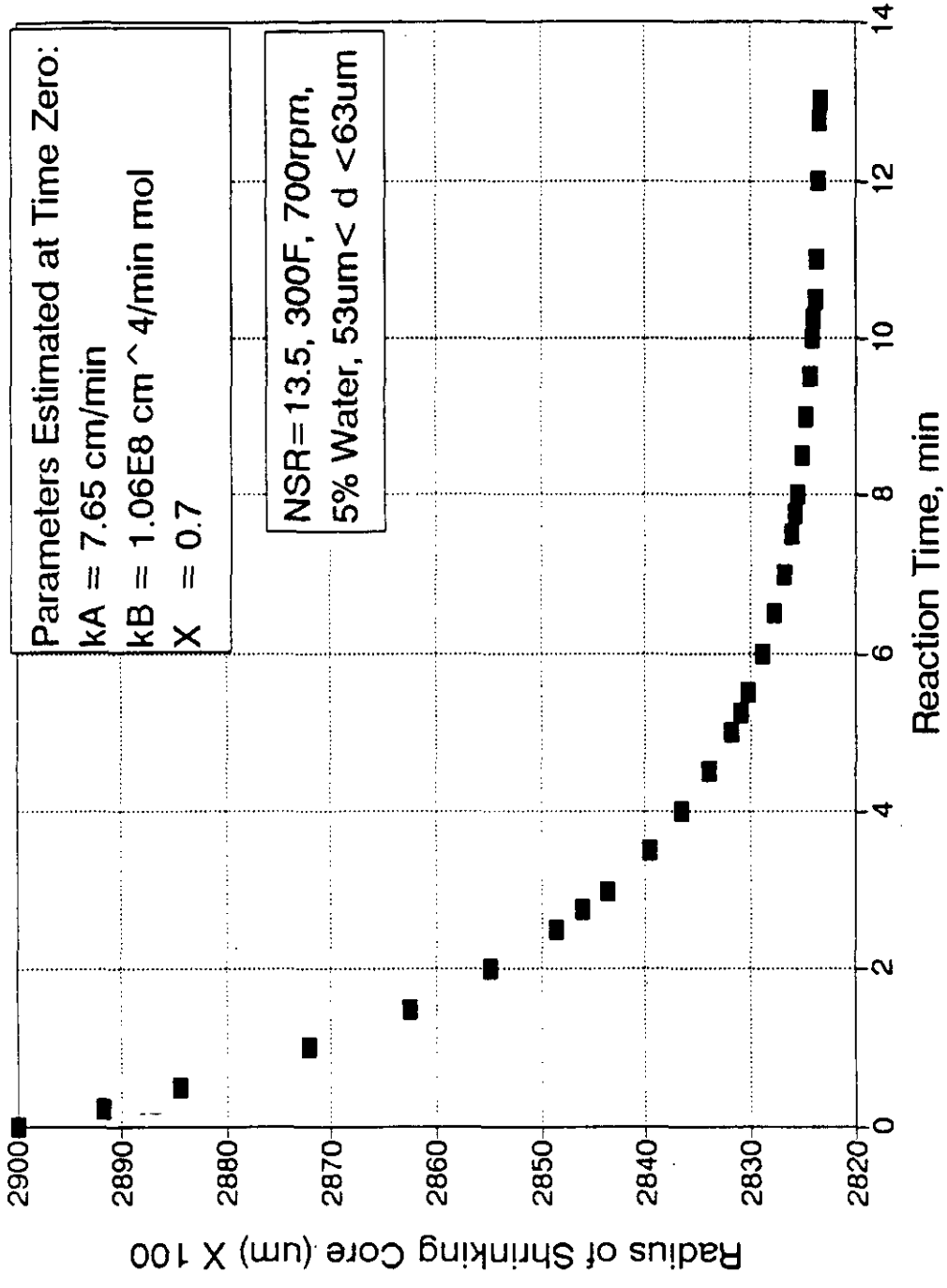


Figure 60. SO<sub>2</sub> and NO<sub>x</sub> Simultaneous Reaction by Sodium Bicarbonate



Table 33.  $k_A$ ,  $k_B$ , and  $x$  Obtained from Initial Rate Approach :

Sorbent	$k_A$ (cm/min)	$k_B$ (cm <sup>4</sup> /cm mol)	$x$
Sesquicarbonate	8.77	1.24E8	0.55
Bicarbonate	7.65	1.06E8	0.70

## CHAPTER VI

### CONCLUSION AND RECOMMENDATION

The following conclusions and recommendations may be drawn from the above results:

1. Sodium sesquicarbonate shows higher promise over sodium bicarbonate due to higher  $\text{NO}_x$  removal rate and lower  $\text{NO}_2$  formation rate.
2. The preferred reaction sequence for the removal of  $\text{NO}_x$  and the formation of  $\text{NO}_2$  appears to be that proposed by the Solvay group.  $\text{NO}$  reacts directly with the solid in the presence of intermediate sulfur compounds to form sodium nitrite and sodium nitrate.  $\text{NO}_2$  appears to be formed by decomposition of sodium nitrite.
3. Sodium pyrosulfite appears to be an intermediate in the reaction of sodium based solids with  $\text{NO}$ .
4. Sodium sesquicarbonate with a high percent of water at low temperature resulted in the lowest  $\text{NO}_2$  formation.
5. Higher NSR values resulted in higher  $\text{NO}_x$  removal rate for both sodium bicarbonate and sodium sesquicarbonate and resulted in higher  $\text{NO}_2$  formation rate.
6. The particle size effect study for sodium sesquicarbonate showed higher  $\text{NO}_x$  removal rate and lower  $\text{NO}_2$  formation rate with smaller particles.
7. Increasing reaction temperature for sodium bicarbonate or sodium sesquicarbonate and the flue gas system will increase  $\text{NO}_x$  removal rate but will result in higher  $\text{NO}_2$

formation.

8. Lower stirrer speed seemed to have little effect.
9. The previously used  $\text{SO}_2$  analytical procedure resulted in erroneous  $\text{SO}_2$  concentrations.
10. From Solvay's model, sodium sesquicarbonate was found to have a higher rate constant for removing both  $\text{SO}_2$  and  $\text{NO}$  and lower potential in forming  $\text{NO}_2$  while compared with the simulation results from sodium bicarbonate.

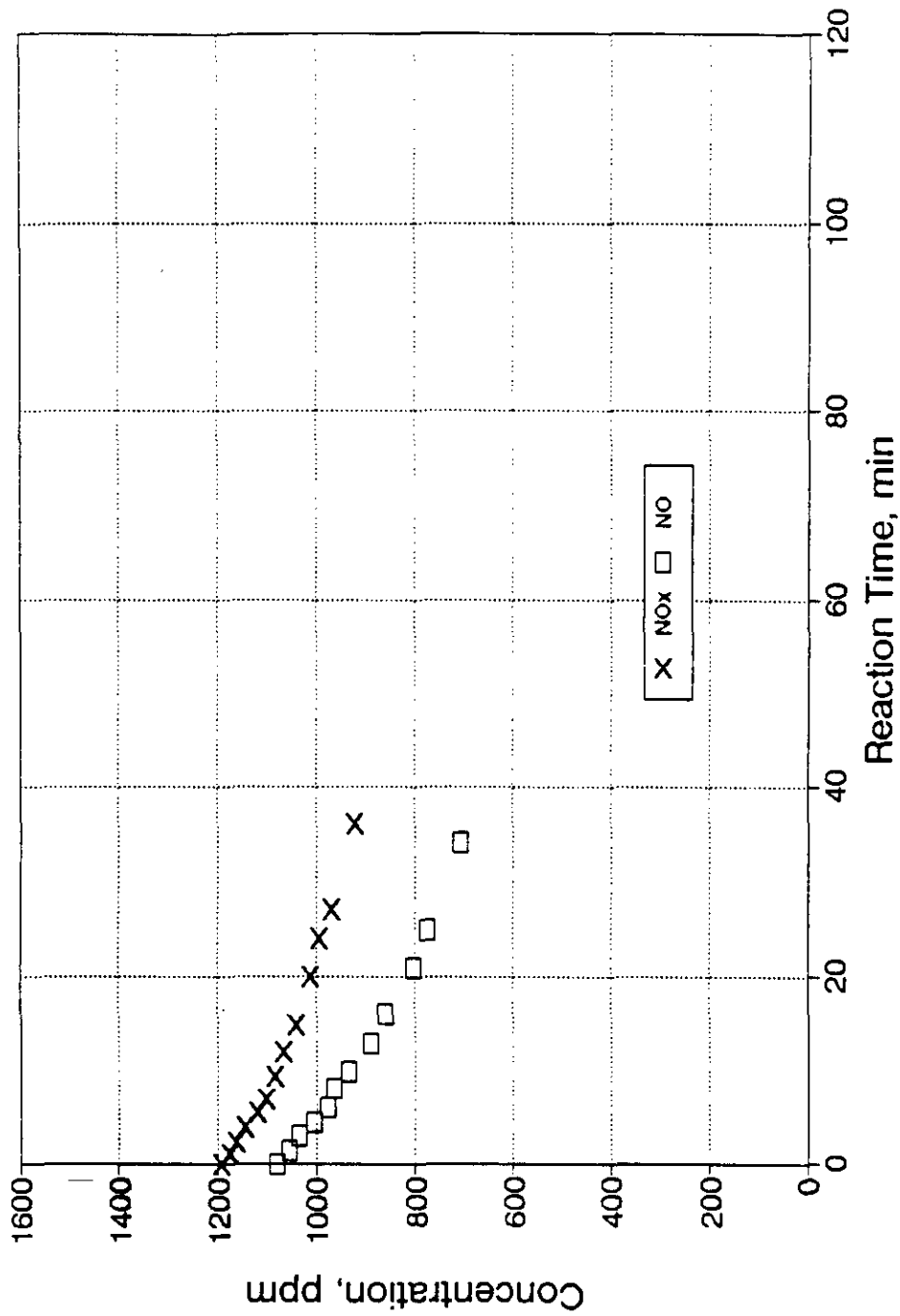
## REFERENCES

1. "Proceedings : 1990 SO<sub>2</sub> Control Symposium - Session 6 B combined SO<sub>x</sub>/NO<sub>x</sub> Technologies." New Orleans, Louisiana, Electric Power Research Institute, May 1990.
2. Earl D. Oliver, "NO<sub>x</sub> Removal, SRI International Report No 200", Menlo Park, California, May 1989.
3. "Sodium Bicarbonate - Purification of Flue Gases - Results of the Purification of Flue Gases from the Edegem (Antwerp) Refuse Incineration Plant - Test Period : May 30 to June 3, 1988", Solvay Leaflet Tr 895/2c-B-1-0989, Brussels, Belgium.
4. "Sodium Bicarbonate - Purification of Flue Gases - Results of Trials on the Purification of Flue Gases at the Solvay Factory Power Station at Heilbronn (West Germany) - Test Period : September 6 to October 27, 1988", Solvay Leaflet Tr. 895/3c-B-1-0989, Brussels, Belgium.
5. "Sodium Bicarbonate - Purification of Flue Gases - Results of Trials on the Purification of Flue gases from the City of Gardanne Power Station (Bouches du Rhone - France) carried out in collaboration with the Firm Syprim Air Industries Environment - Test Period : February 27 to March 3, 1989", Solvay Leaflet Tr. 895/4c-B-1-0989, Brussels, Belgium.
6. "Evaluation of Dry sodium Sorbent Utilization in Combustion Gas SO<sub>x</sub>/NO<sub>x</sub> Reduction", EPRI GS-6850, Project 1682-2, Final Report, Irvine, California, May

1990.

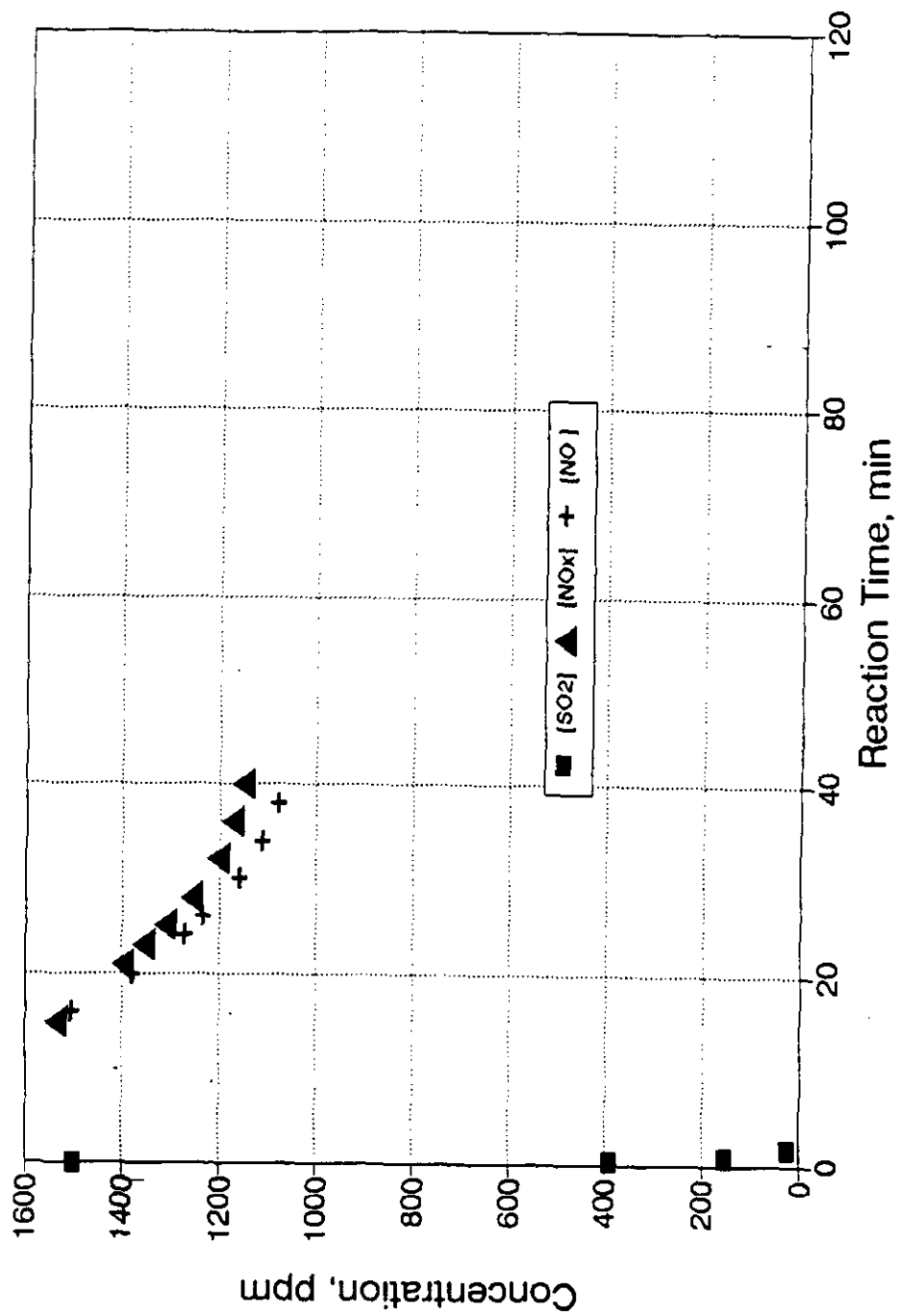
7. Gianrico Castello\* and Giuseppina D'Amato, "Determination of sulphur and nitrogen gases by gas chromatography on polystyrene porous polymer columns", *Journal of Chromatography*, 585, (1991), 93-100.
8. G. Castello and G. D'Amato, *Journal of Chromatography*, 254, (1983), 69.
9. G. Castello and G. D'Amato, *Journal of Chromatography*, 269, (1983), 153.
10. G. Castello, G. D'Amato and M. Nicchia, , *Journal of Chromatography*, 521, (1990), 153.
11. Chang, Oliver K., "Experimental study of the grain model using the sulfur dioxide-sodium carbonate reaction." Ph. D. Degree Thesis, 1978
12. Solvay, J. Verlaeten, G. C. De Soete, and L. Ninane & J. M. Blondel Solvay, "Combined SO<sub>2</sub>/NO<sub>x</sub> abatement by sodium bicarbonate dry injection.", 1050 Brussels, Belgium, 1993.
13. Brink, Robert V., Daniel E. Czernik, and Leslie A. Horve, "Handbook of Fluid Sealing", McGraw-Hill, Inc., New York, New York, 1993
14. Hoffman, Joe D., "Numerical Methods for Engineers and Scientists" McGraw-Hill, Inc., New York, New York, 1992.
15. Fogler, H. Scott, "Elements of Chemical Reaction Engineering", Prentice-Hall, Inc., 1992.

**APPENDIX A**



NSR=13.5, Water=3%, 300F, 300 rpm, 53um < d < 63um

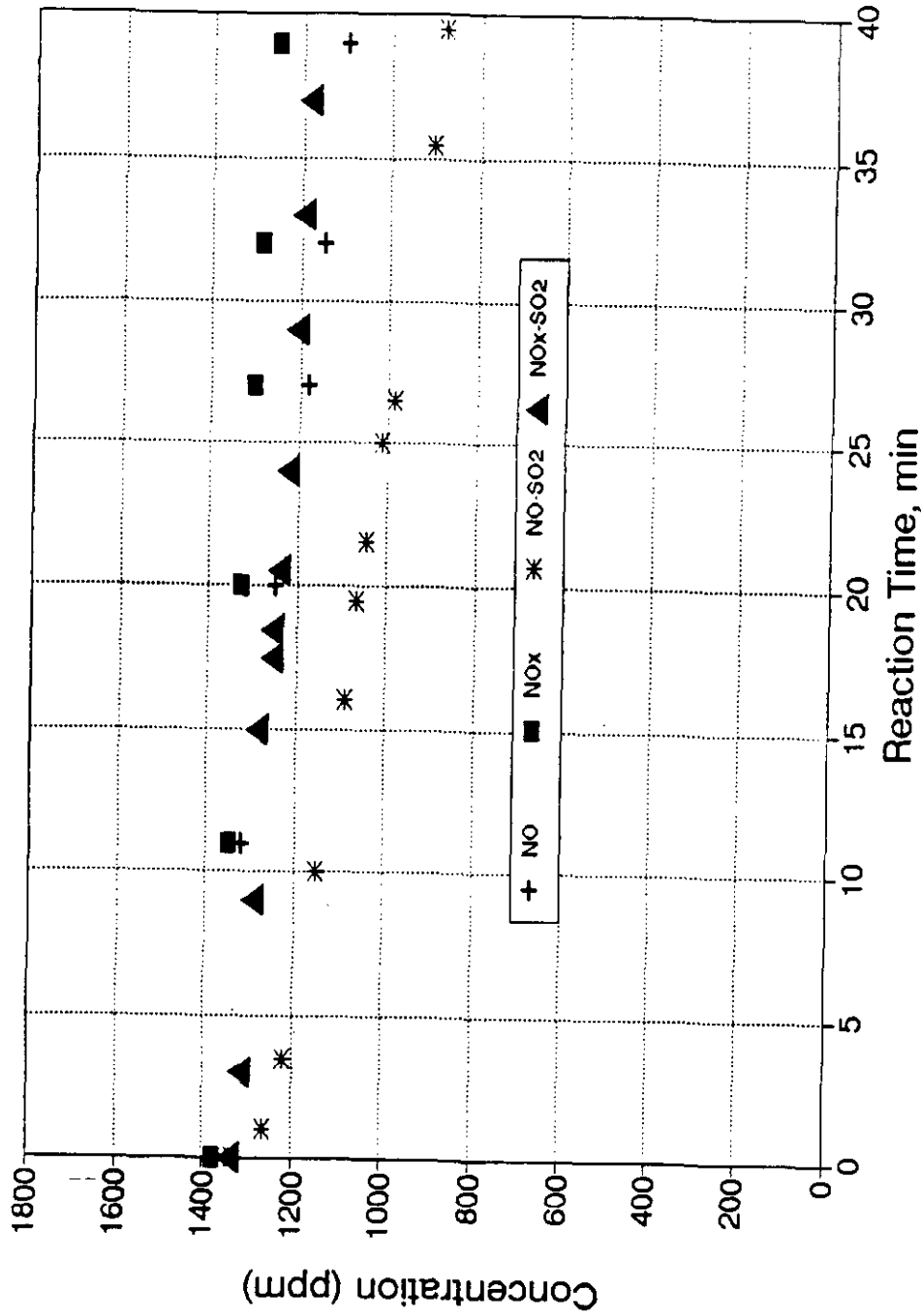
Figure A1. 02-26-93 : NOx Removal by Sodium Bicarbonate



NSR=13.5, Water=3%, 300 F, 300 rpm, 53um < d < 63um

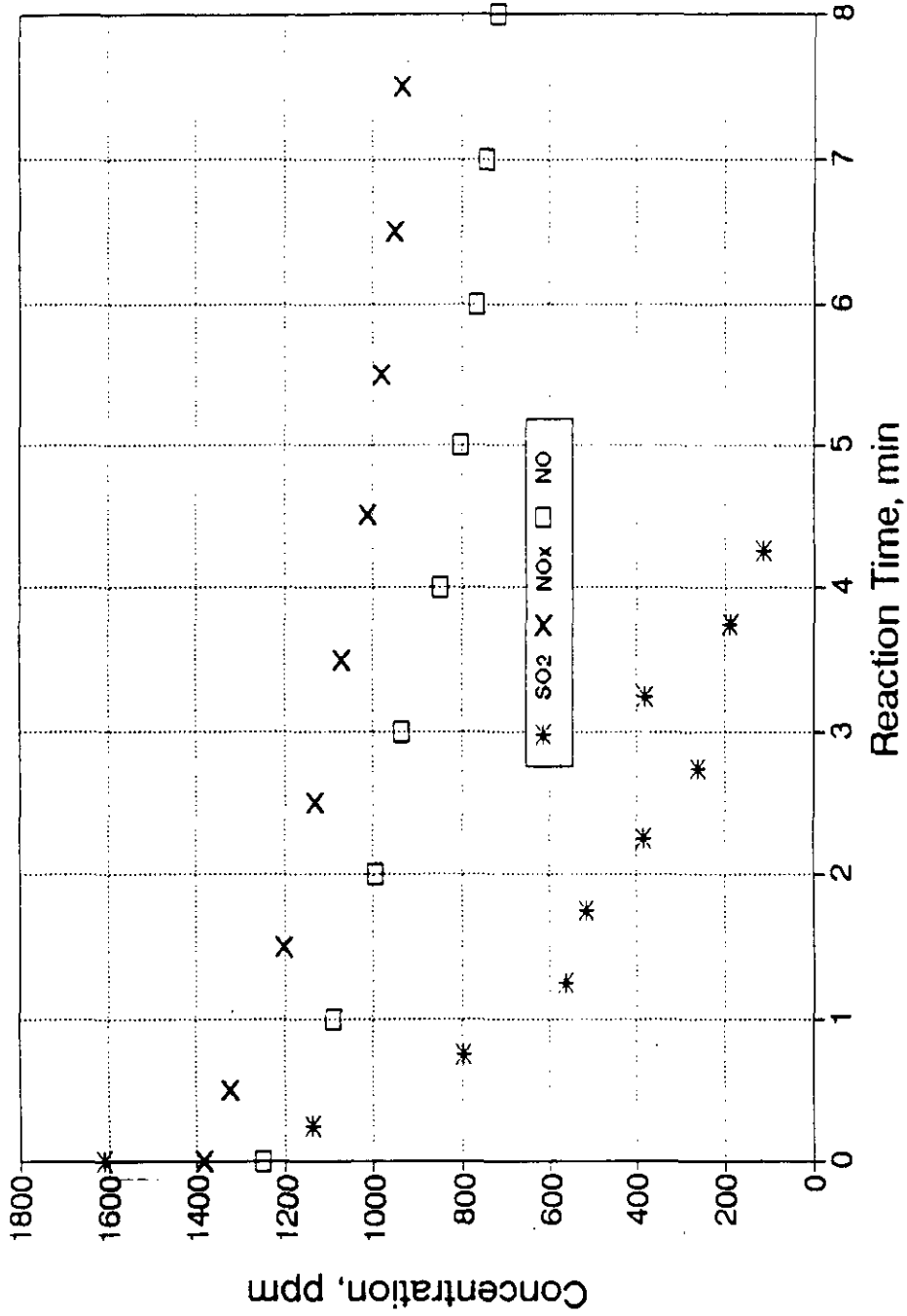
Figure A2. 03-13-93 : SO2 and NOx Removal by Sodium Bicarbonate





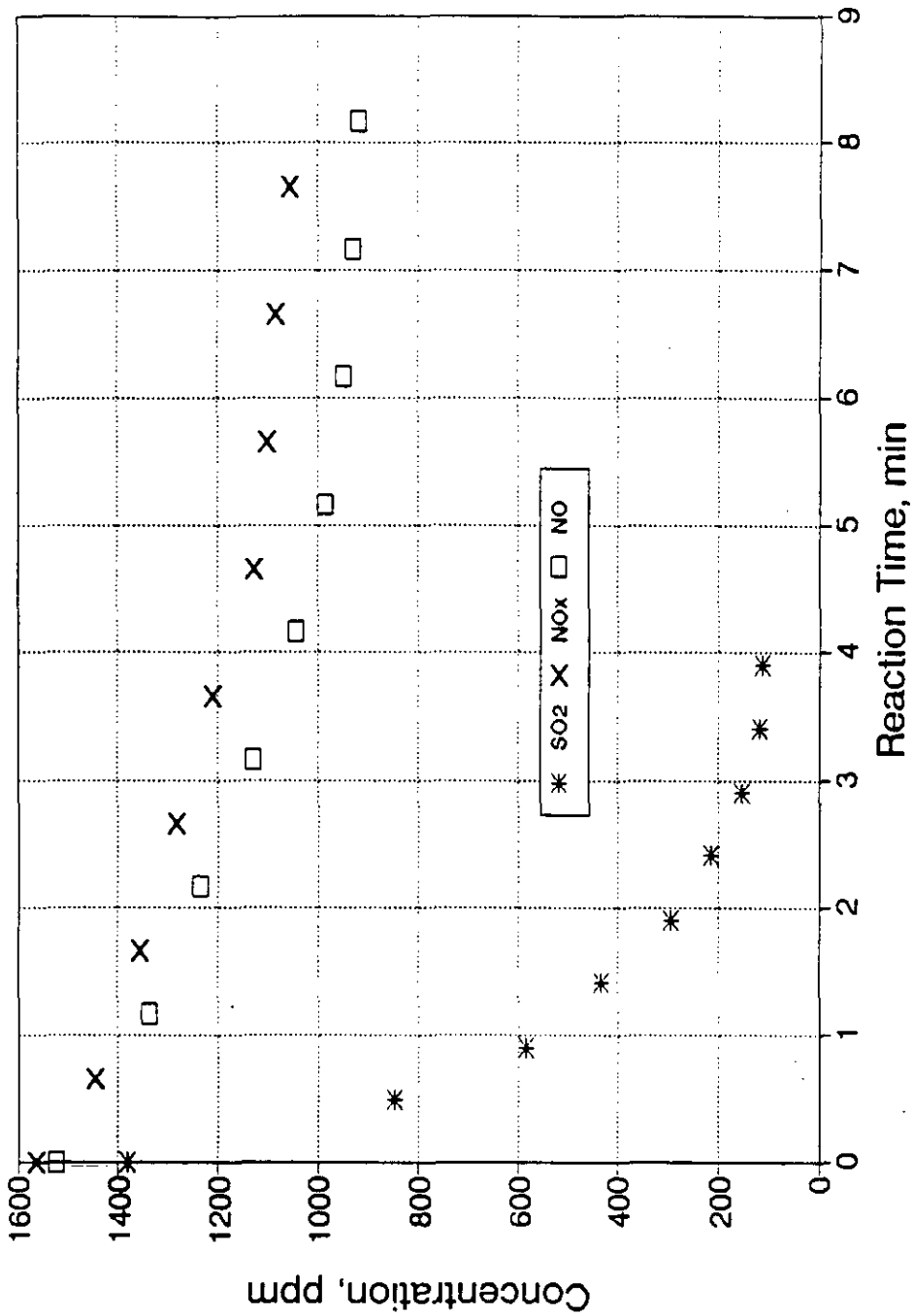
Water 300 F, 300 rpm, Blank

Figure A3. 03-02-93 : Comparison between the NOx System with SO2 and the NOx System without SO2



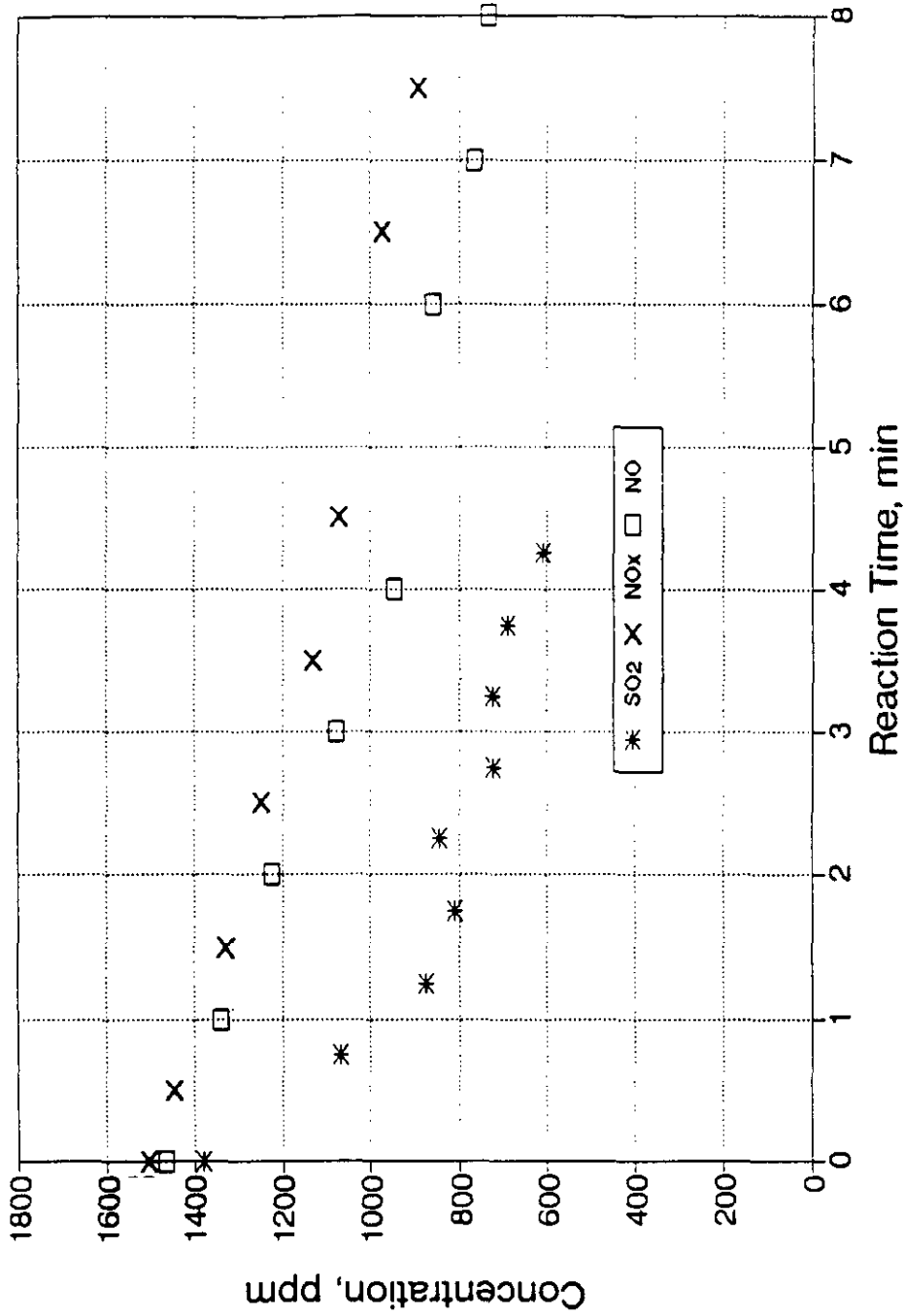
NSR=13.5, Water=3.5%, 300F, 300 rpm, 53um < d < 63um

Figure A4. 04-16-93 : SO2 and NOx Removal by Sodium Bicarbonate



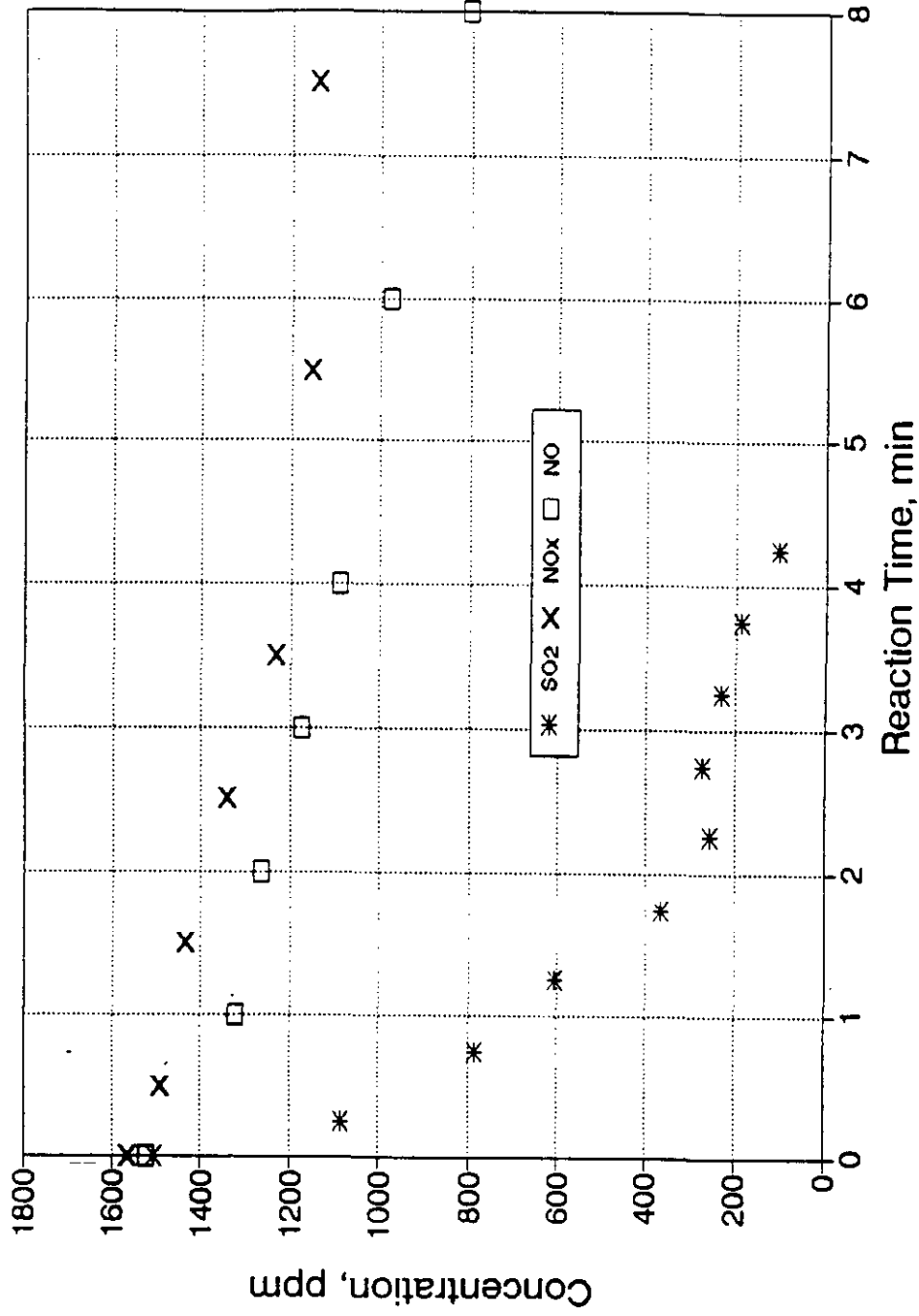
NSR=13.5, Water=7%, 300F, 300 rpm, 53um < d < 63um

Figure A5. 04-20-93 : SO2 and NOx removal by Sodium Bicarbonate



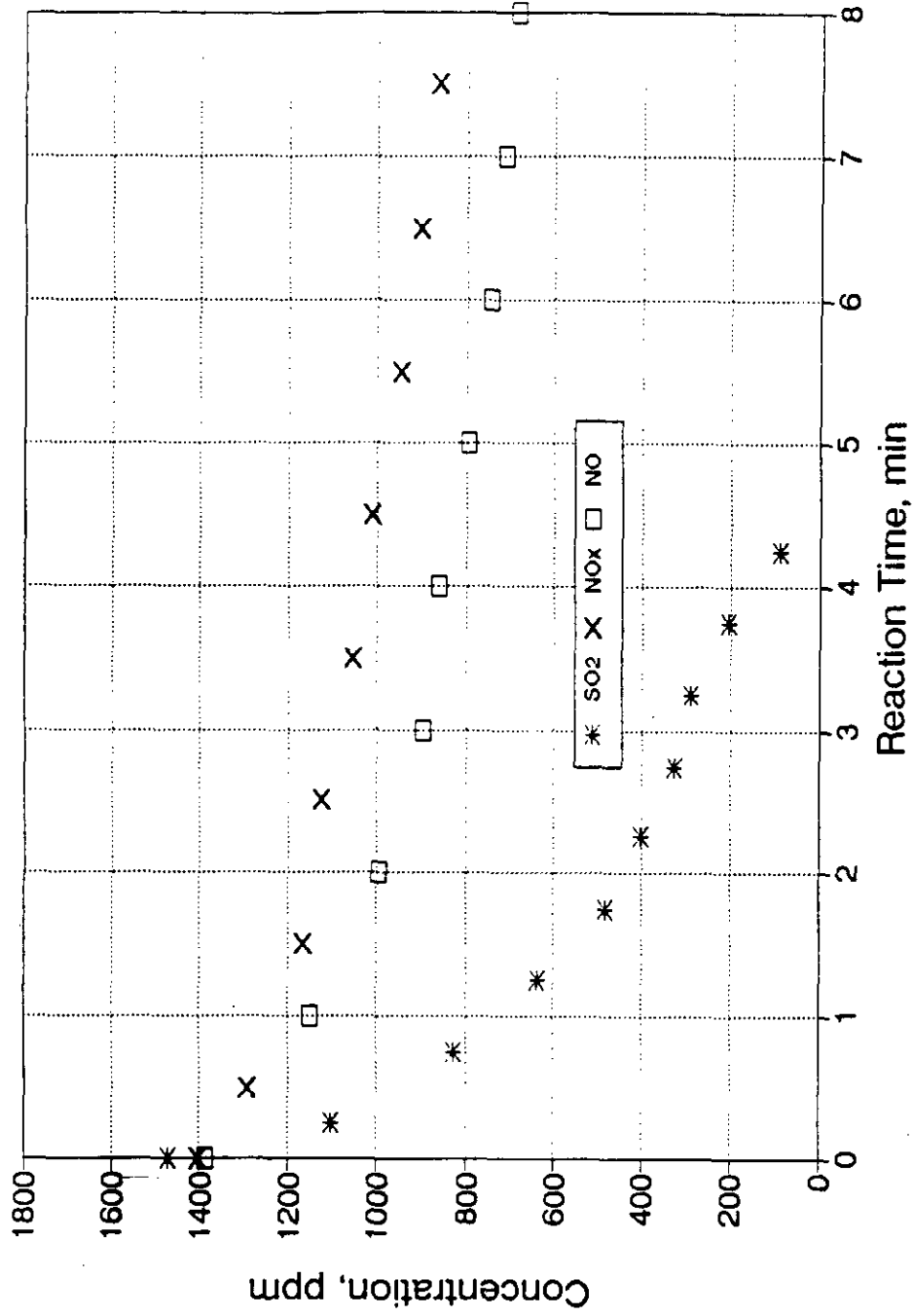
NSR=13.5, Water=0%, 300F, 300rpm, 53um < d < 65um

Figure A6. 04-21-93 : SO2 and NOx Removal by Sodium Bicarbonate



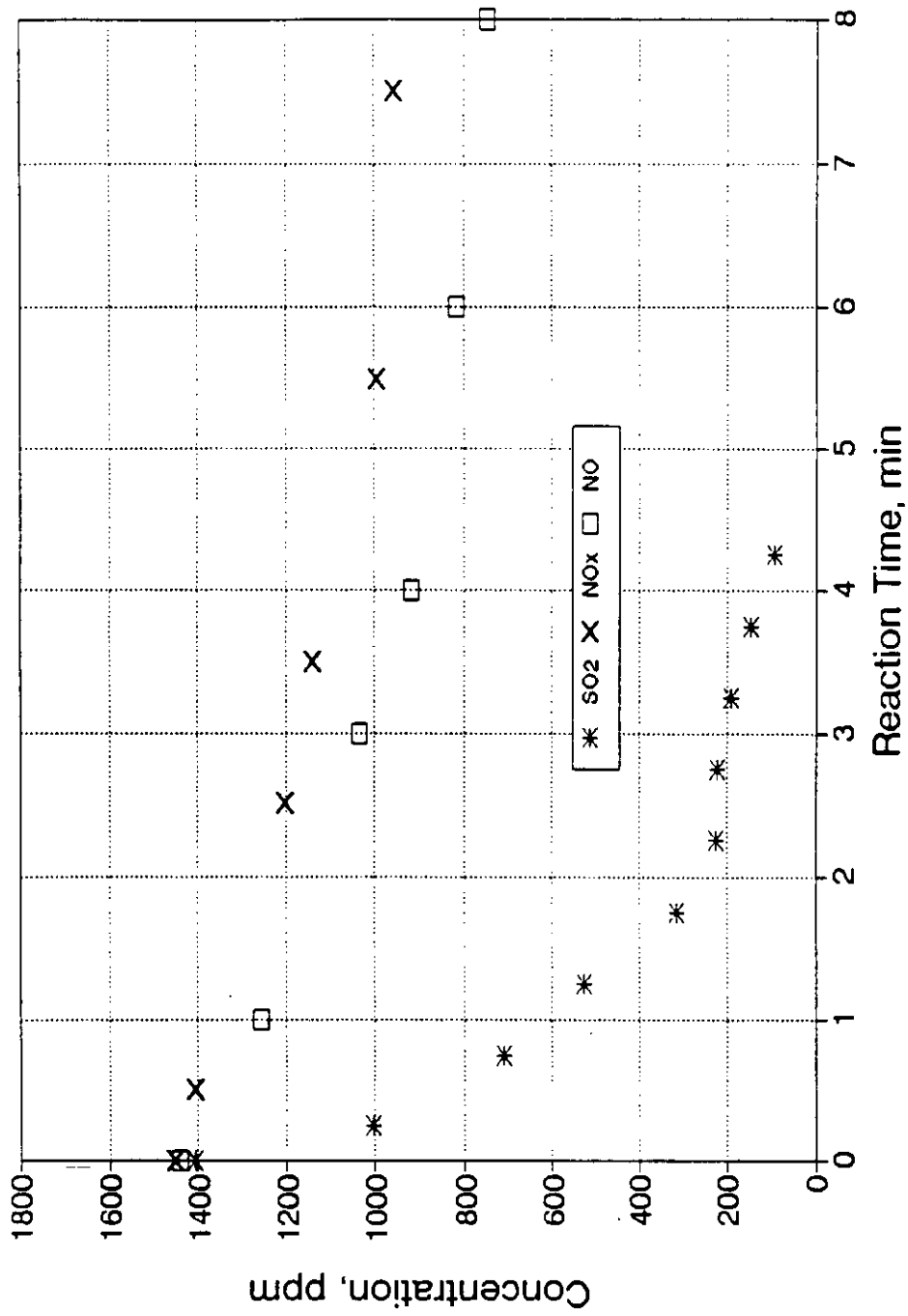
NSR=13.5, Water=7%, 300F, 300 rpm, 53um < d < 63um

Figure A7. 04-23-93 : SO2 and NOx Removal by Sodium Bicarbonate



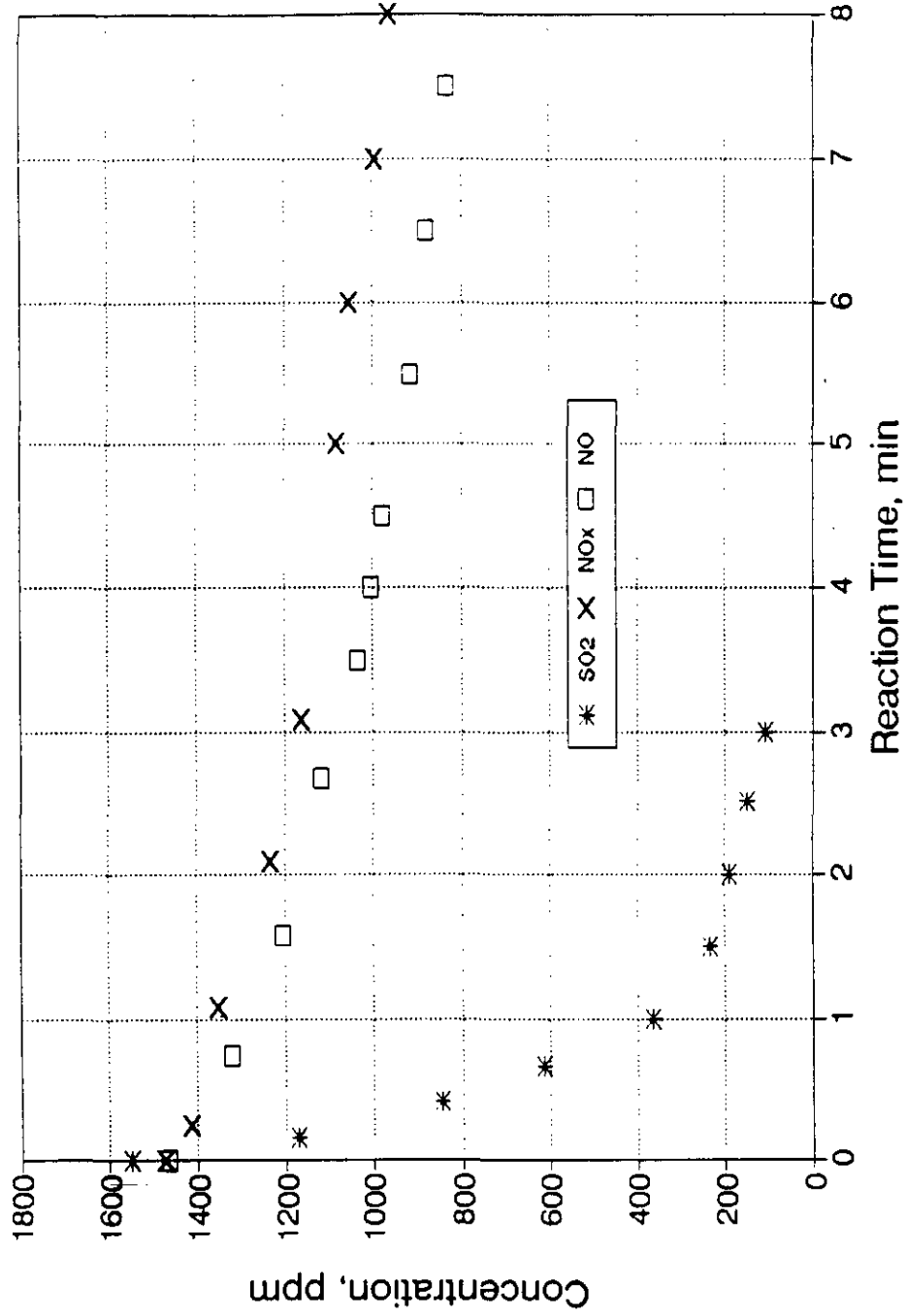
NSR=13.5, Water=2.9, 300F, 300 rpm, 53um < d < 63um

Figure A8. 04-27-93 : SO2 and NOx Removal by Sodium Bicarbonate



NSR=13.5, Water=3.5%, 300F, 300 rpm, 53um < d < 63um

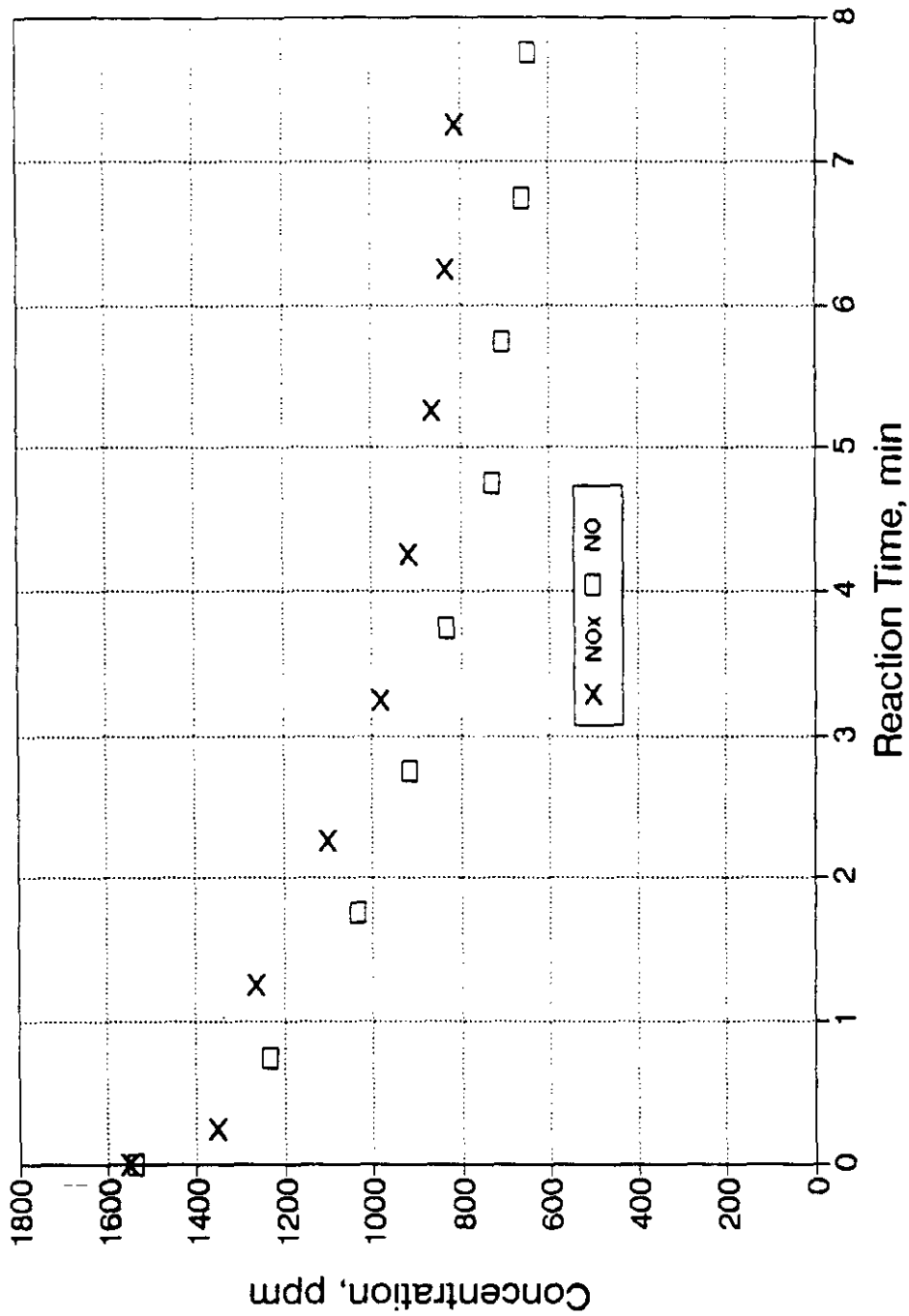
Figure A9. 04-27-93 : SO2 and NOx Removal by Sodium Bicarbonate



NSR=13.5, Water=10%, 300F, 300 rpm, 53um < d < 63um

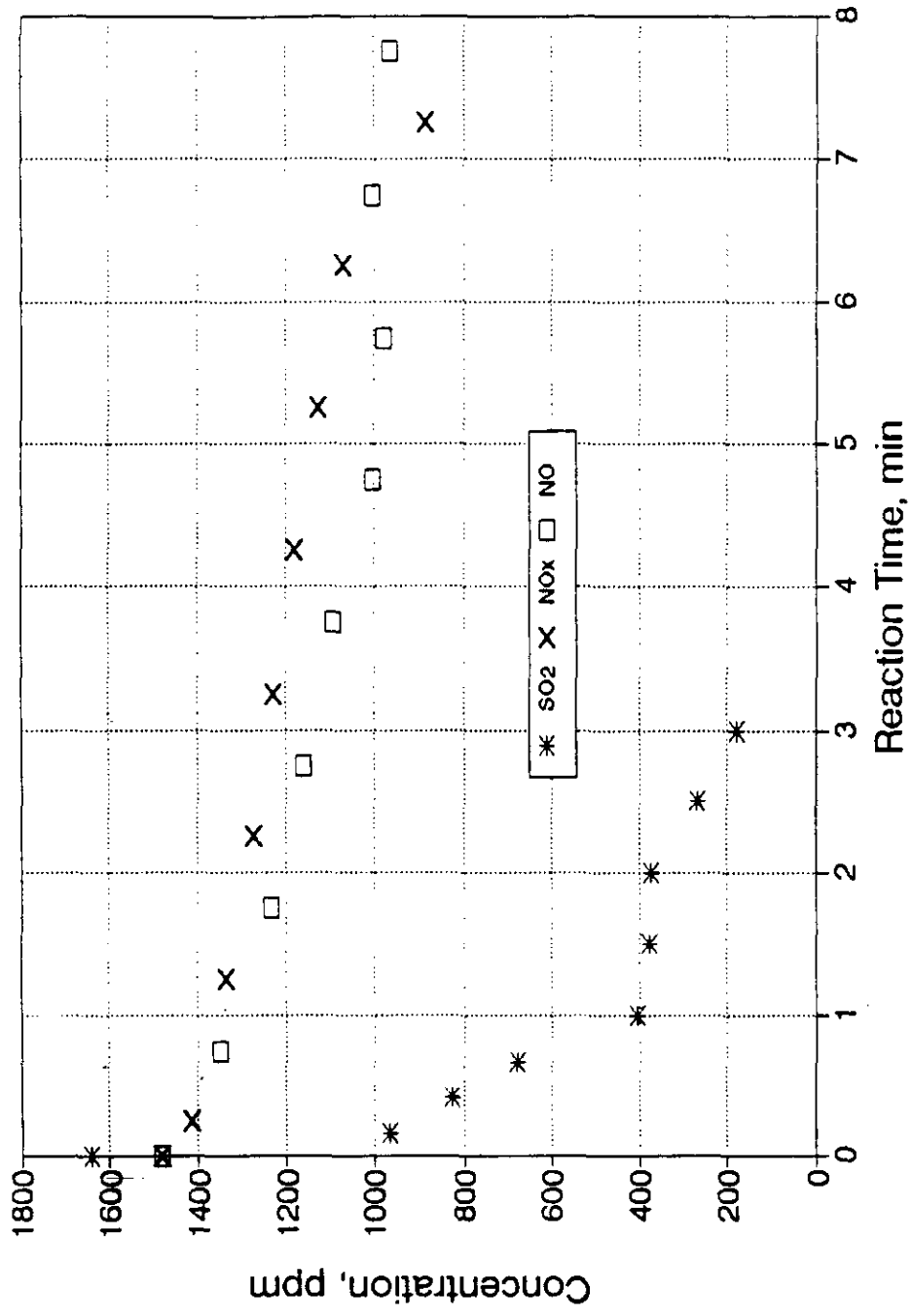
Figure A10. 04-30-93 : SO2 and NOx Removal by Sodium Bicarbonate





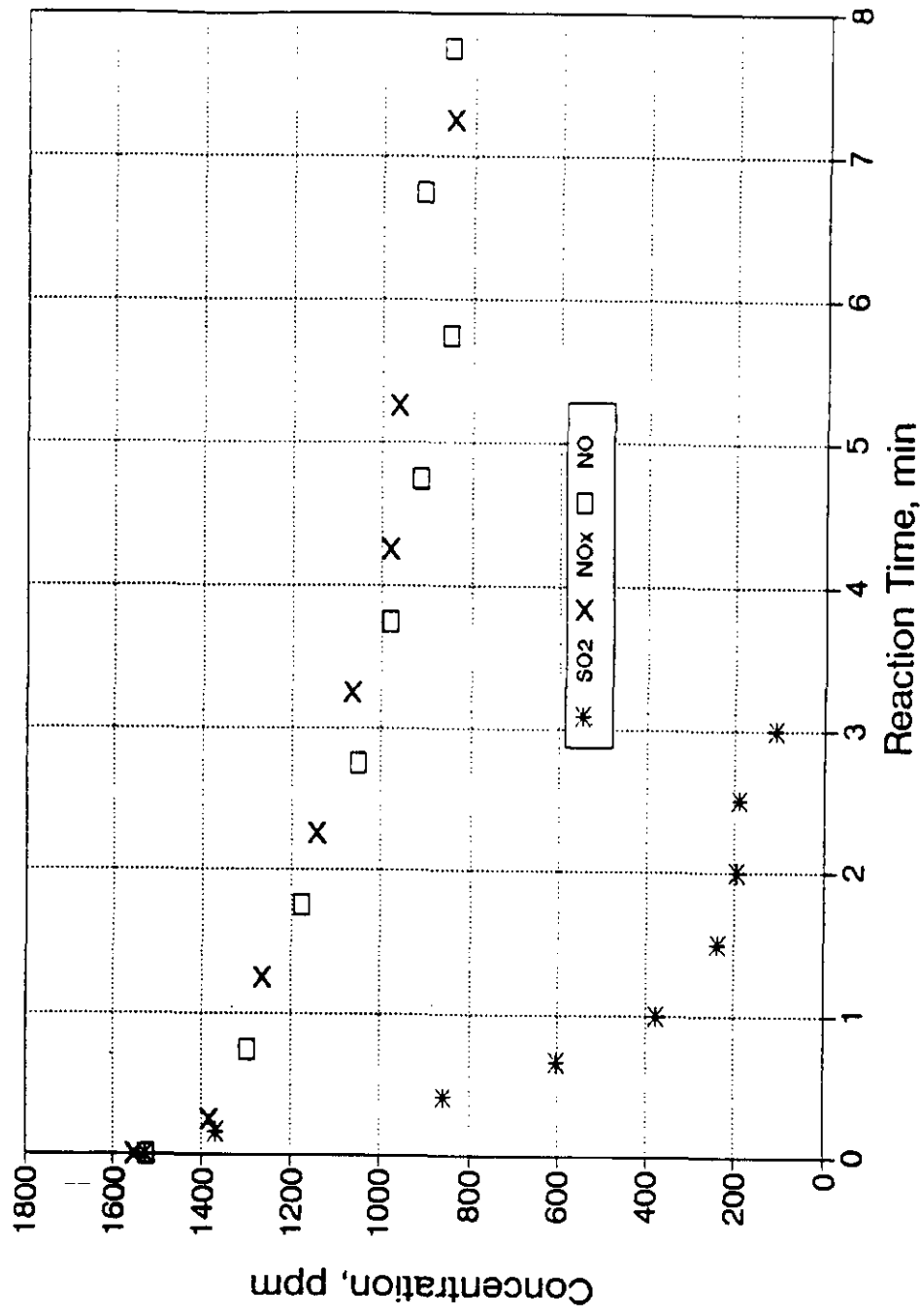
NSR=13.5, Water=3.5%, 300F, 300 rpm, 53um < d < 63um

Figure A11. 05-03-93 : SO<sub>2</sub> and NO<sub>x</sub> Removal by Sodium Sesquicarbonate



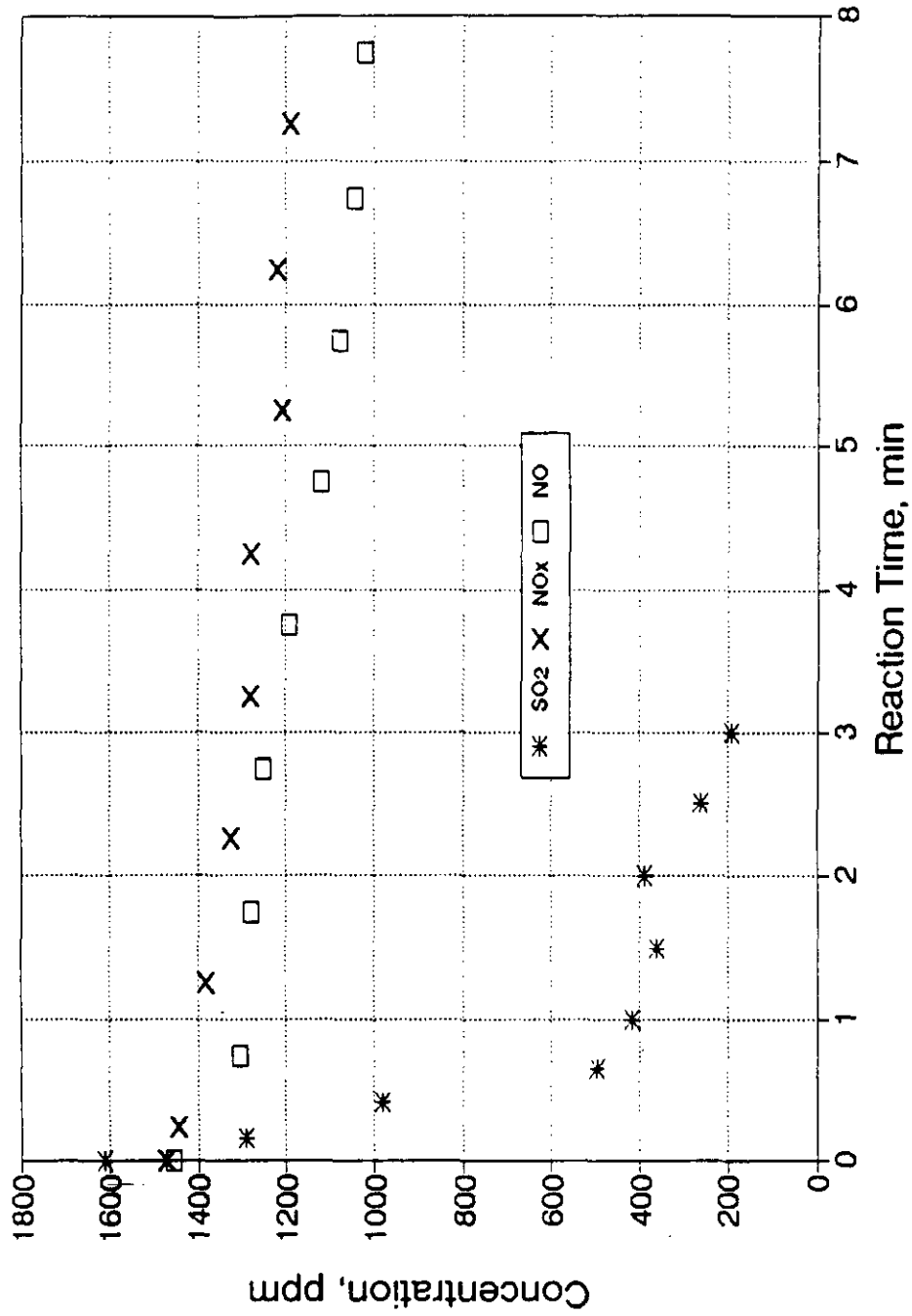
NSR=13.5, Water=6.7%, 240F, 300 rpm, 53um < d < 63um

Figure A12: 05-07-93 : SO2 and NOx Removal by Sodium Bicarbonate



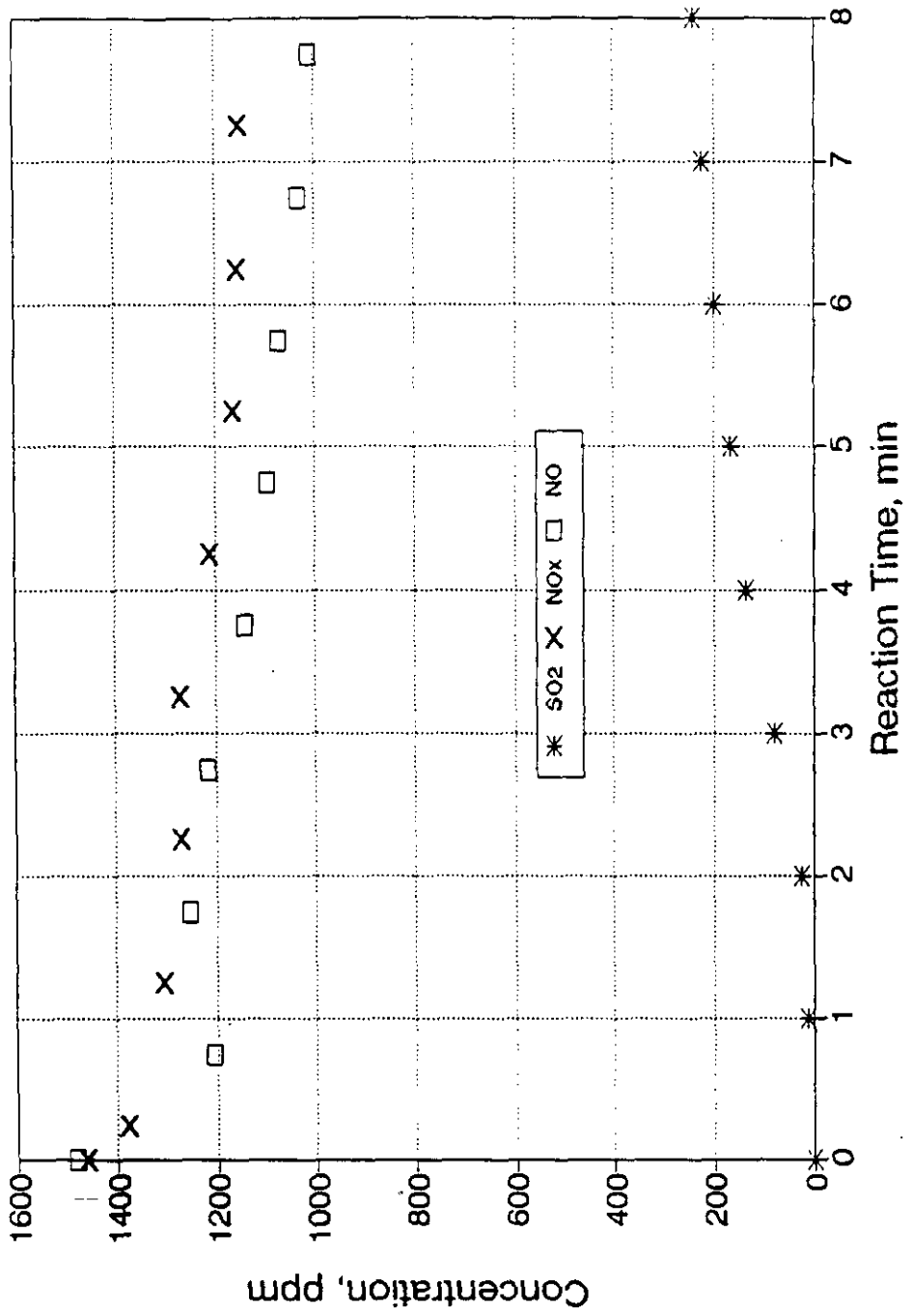
NSR=13.5, Water=6.7%, 240F, 300rpm, 53um < d < 63um

Figure A13. 05-10-93 : SO2 and NOx Removal by Sodium Sesquicarbonate



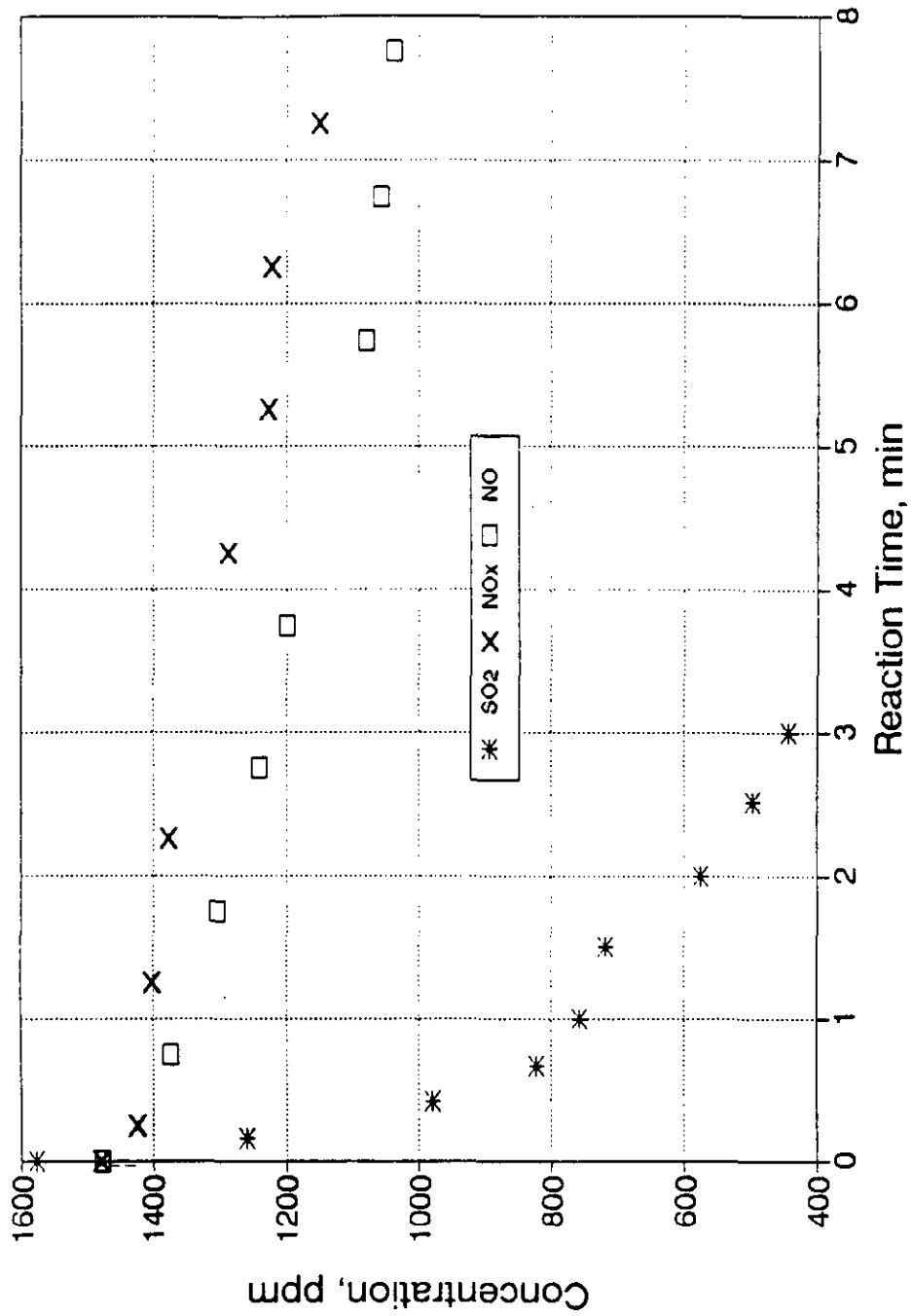
NSR=3.4, Water=5%, 260F, 300 rpm, 53um < d < 63um

Figure A14. 05-20-93 : SO2 and NOx Removal by Sodium Bicarbonate



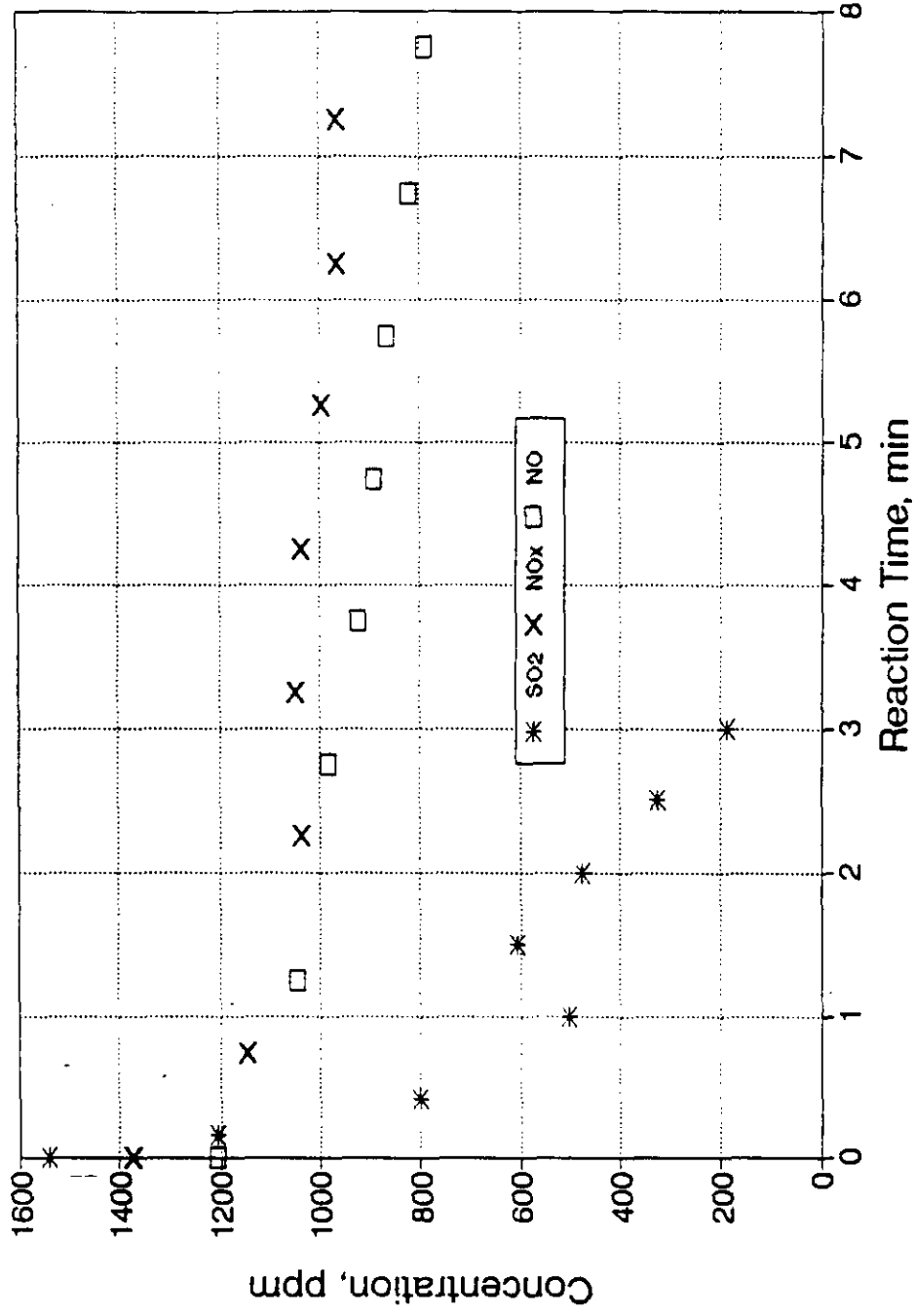
NSR=13.5, Water=5%, 260F, 300 rpm, 53um < d < 63um

Figure A15. 05-24-93 : SO2 and NOx Removal by Sodium Pyrosulfite



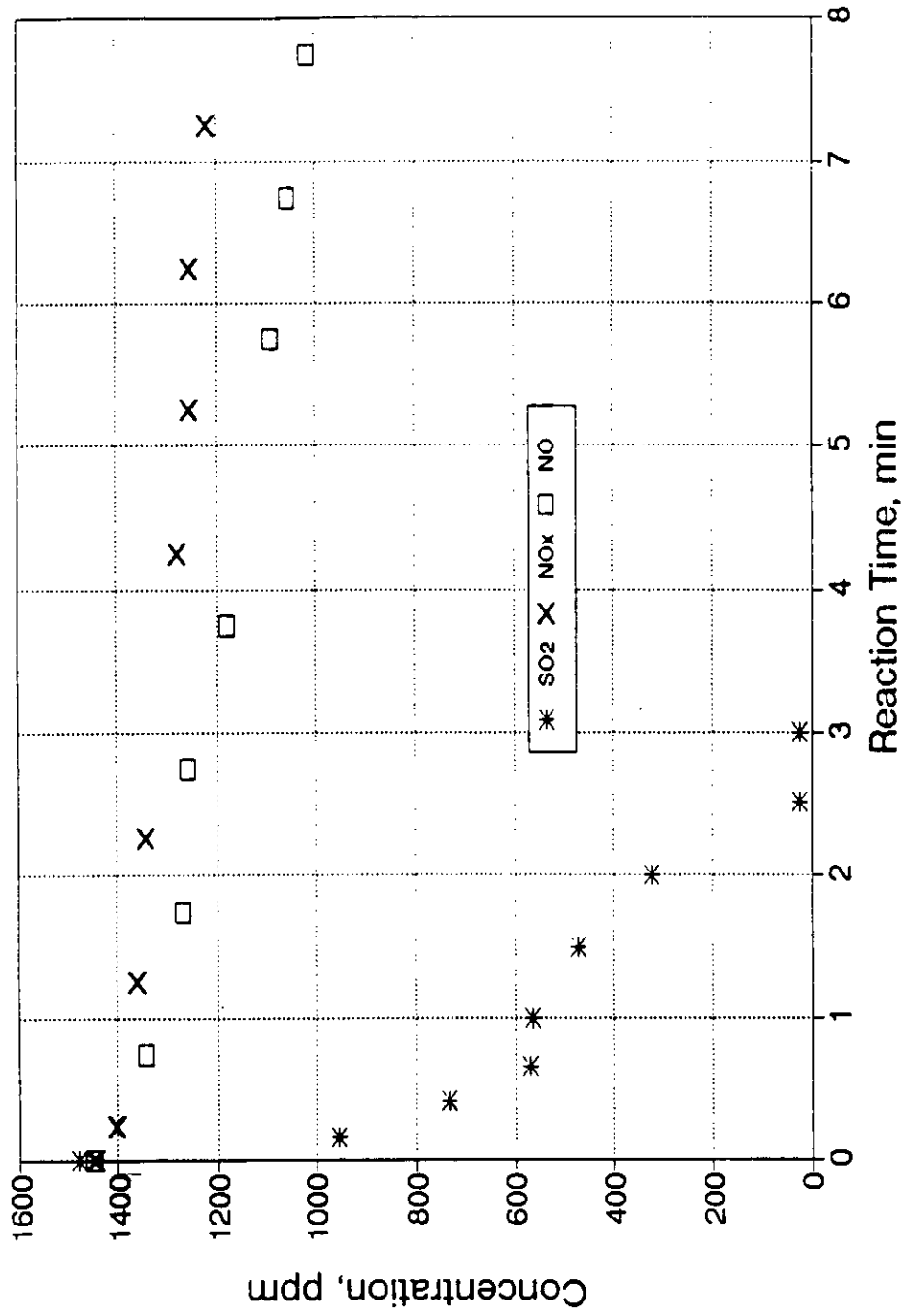
NSR=3.4, Water=5%, 260F, 700 rpm, 53um < d < 63um

Figure A16. 05-25-93 : SO2 and NOx Removal by Sodium Bicarbonate



NSR=3.4, Water=5%, 260F, 700 rpm, 53um < d < 63um

Figure A17. 05-27-93 : SO2 and NOx Removal by Sodium Sesquicarbonate



NSR=3.4, Water=5%, 260F, 700 rpm, 53um < d < 63um

Figure A18. 05-31-93 : SO2 and NOx Removal by Sodium Bicarbonate



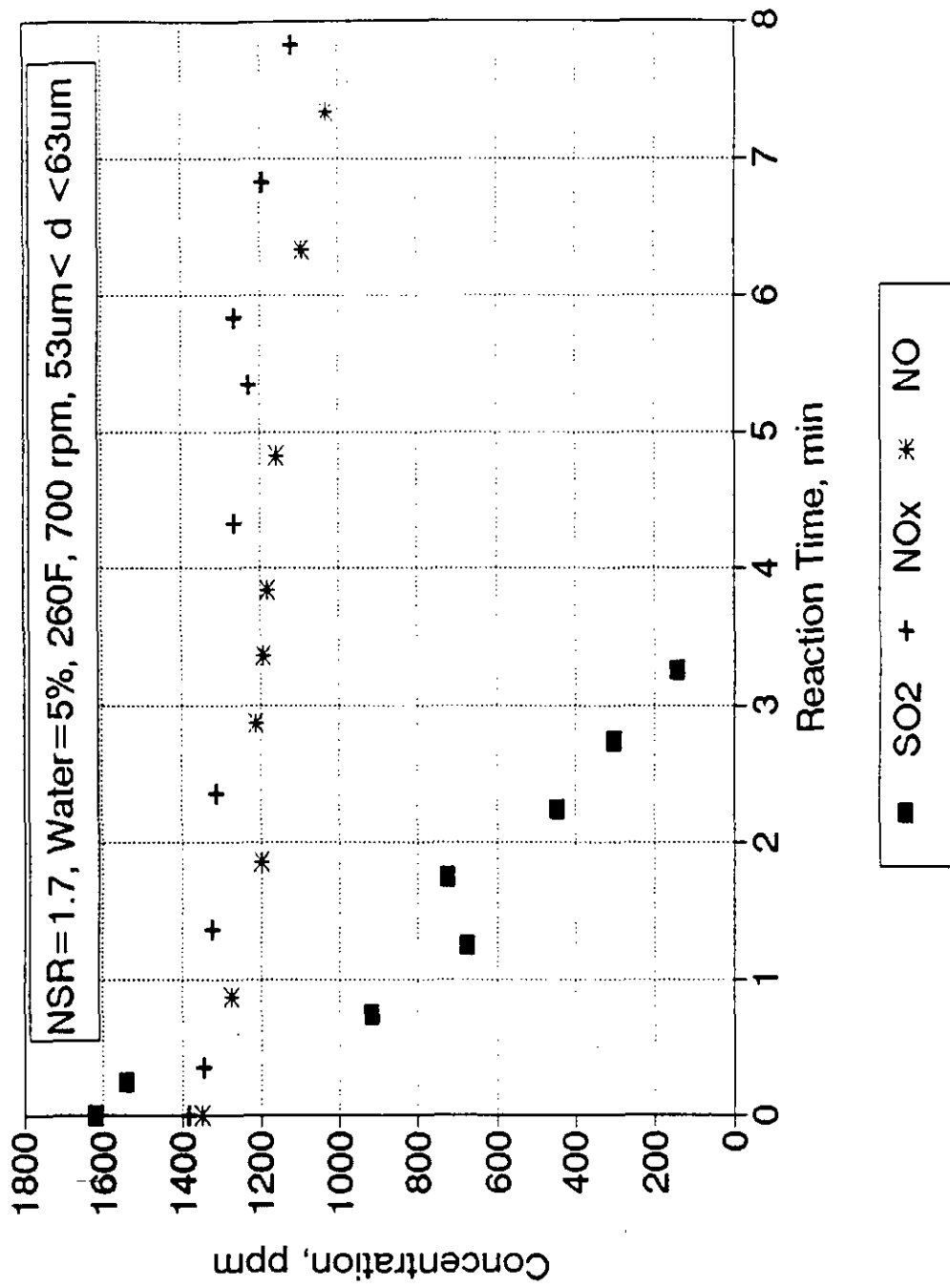


Figure A19. 06-17-93 : SO2 and NOx Removal by Sodium Sesquicarbonate

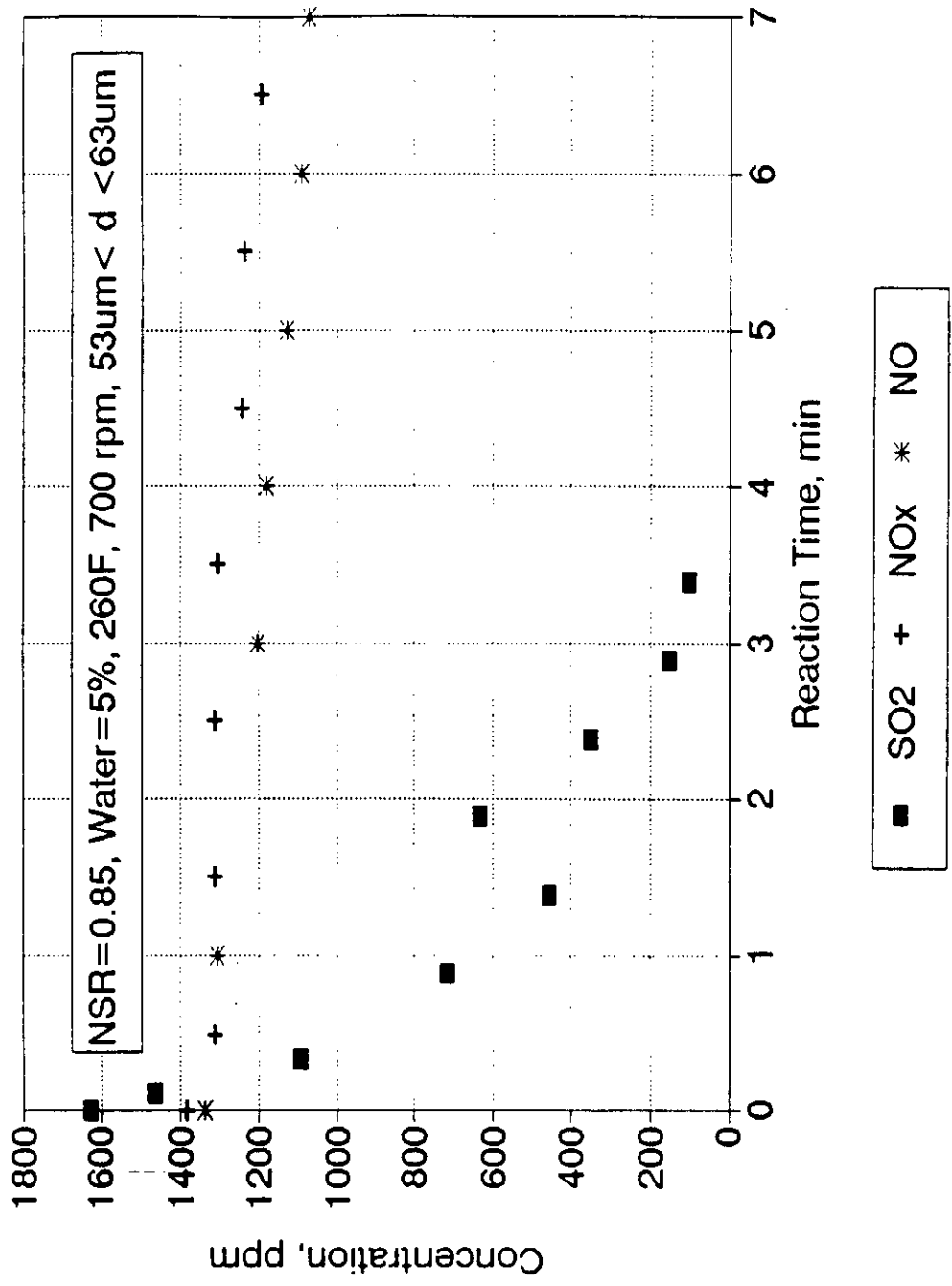


Figure A20. 06-18-93 : SO2 and NOx Removal by Sodium Sesquicarbonate

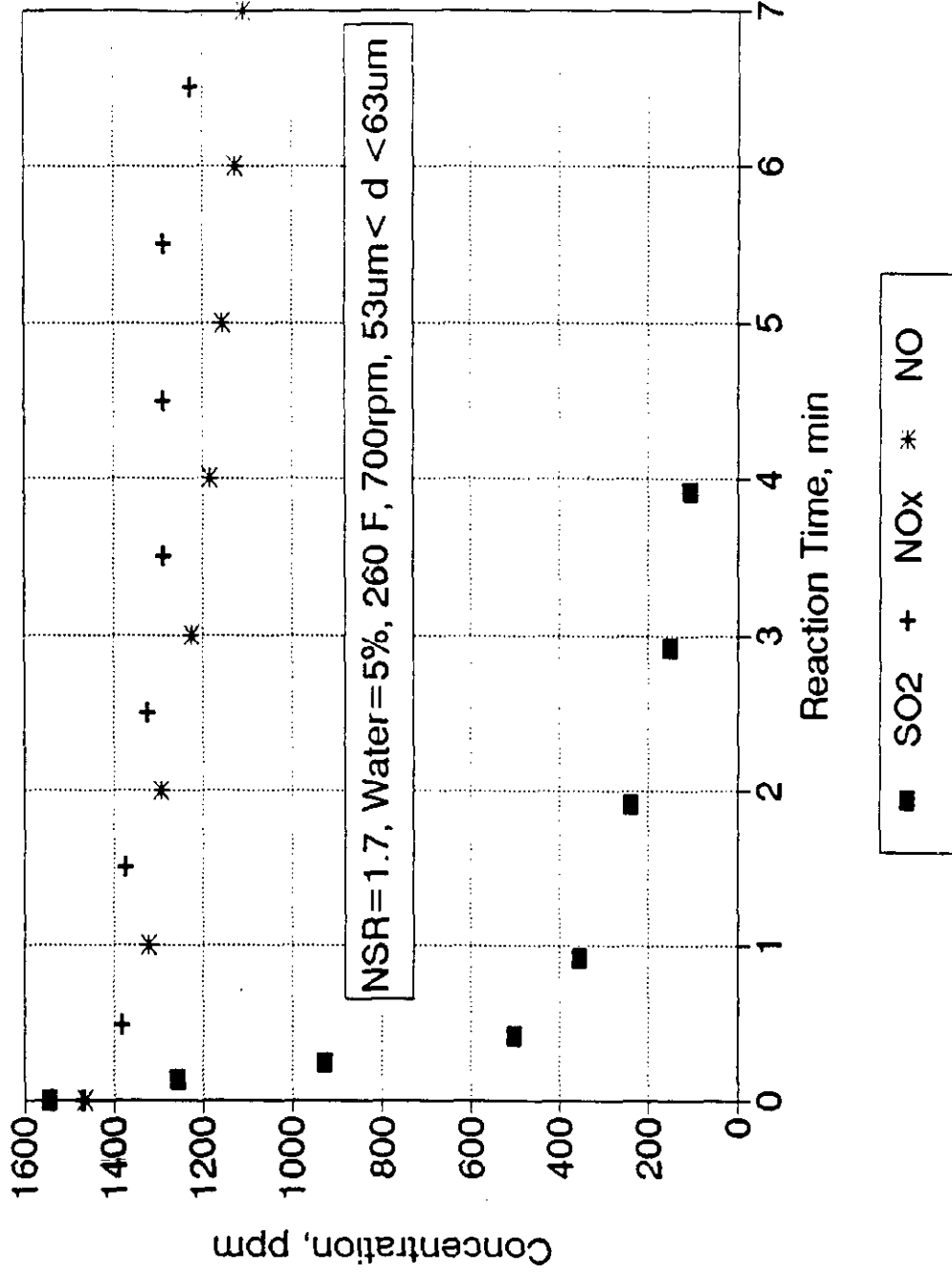


Figure A21. 06-21-93 : SO2 and NOx Removal by Sodium Sesquicarbonate

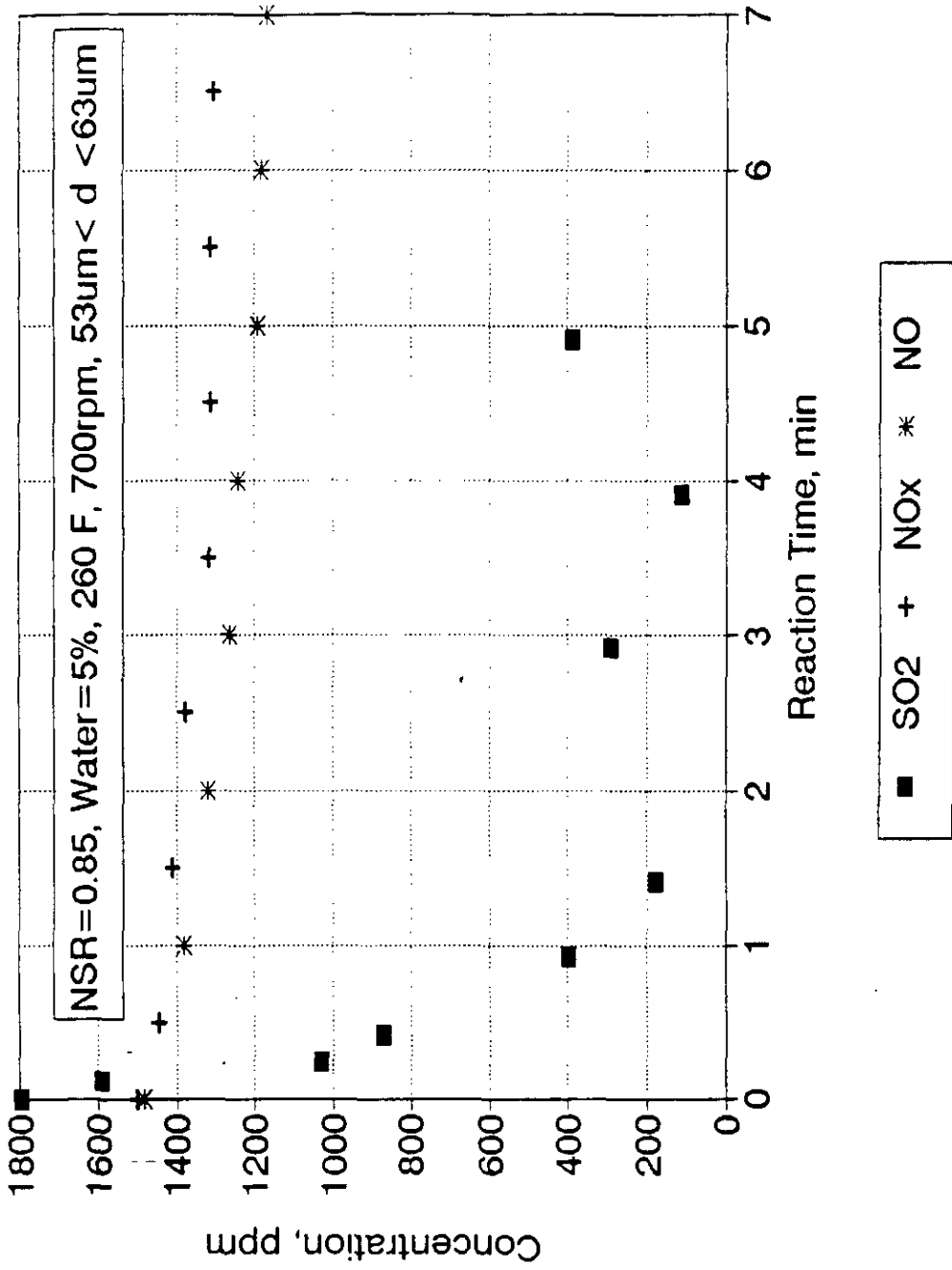


Figure A22. 06-22-93 : SO2 and NOx Removal by Sodium Sesquicarbonate

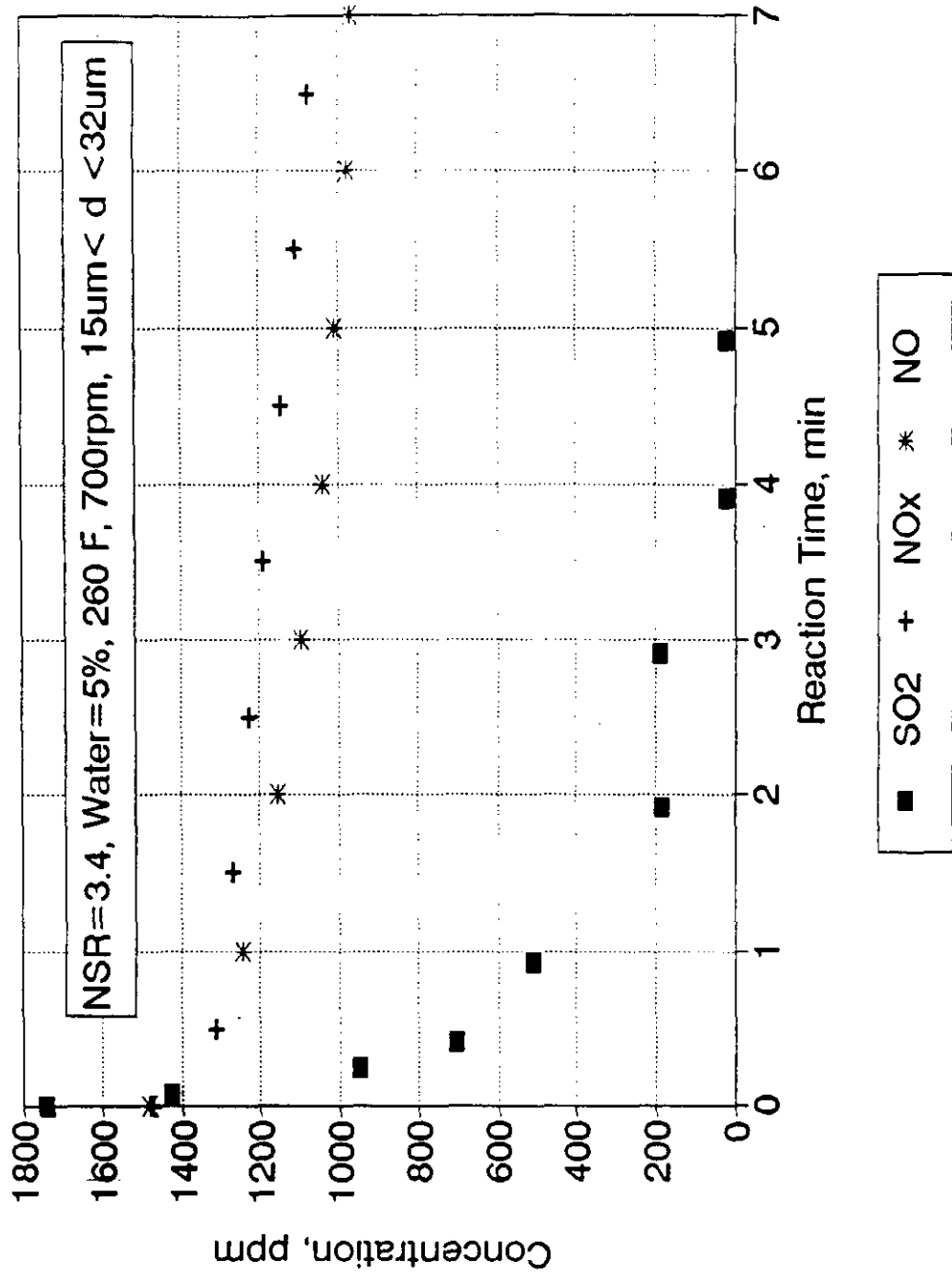


Figure A23. 06-23-93 : SO2 and NOx Removal by Sodium Sesquicarbonate

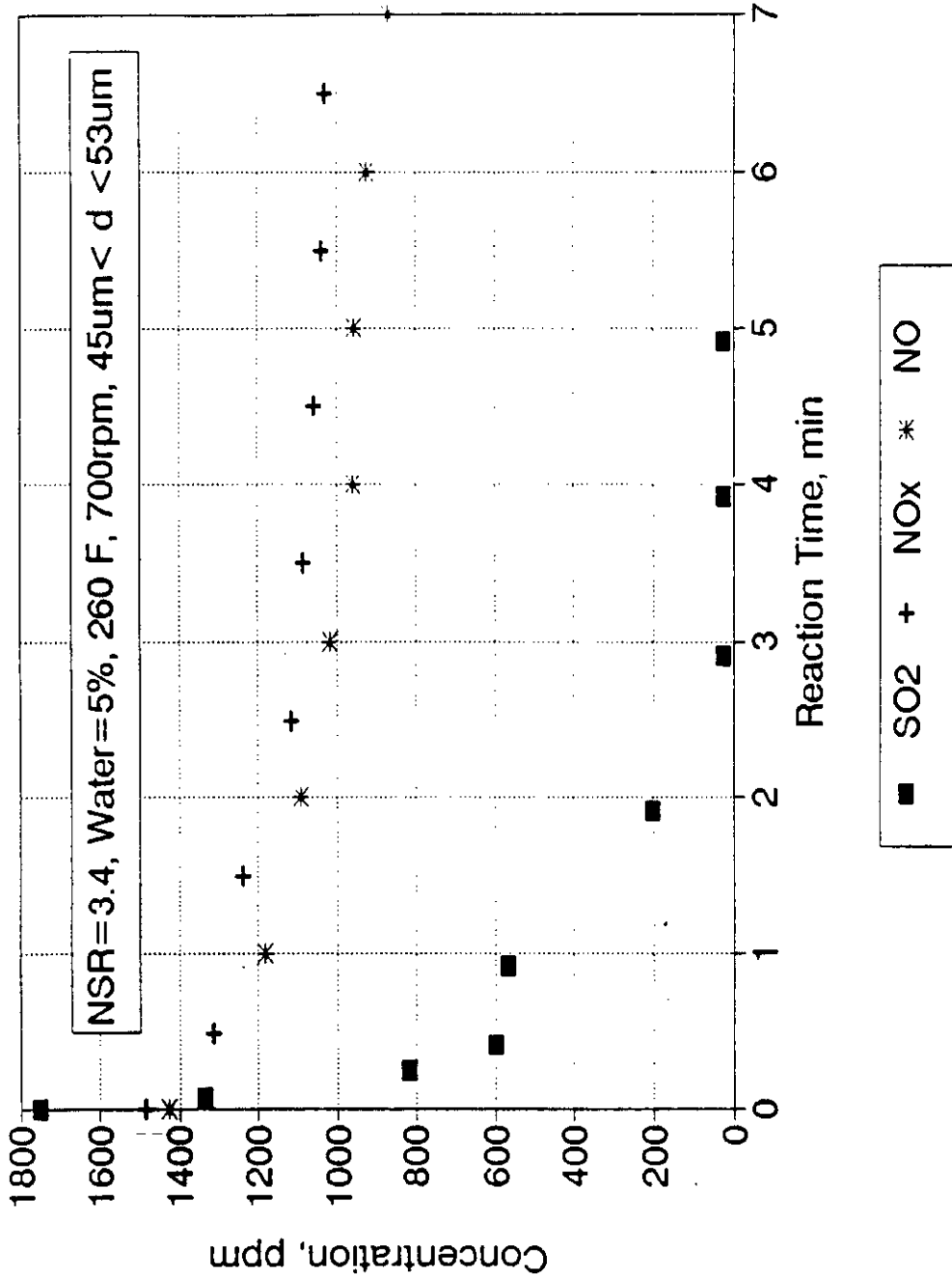
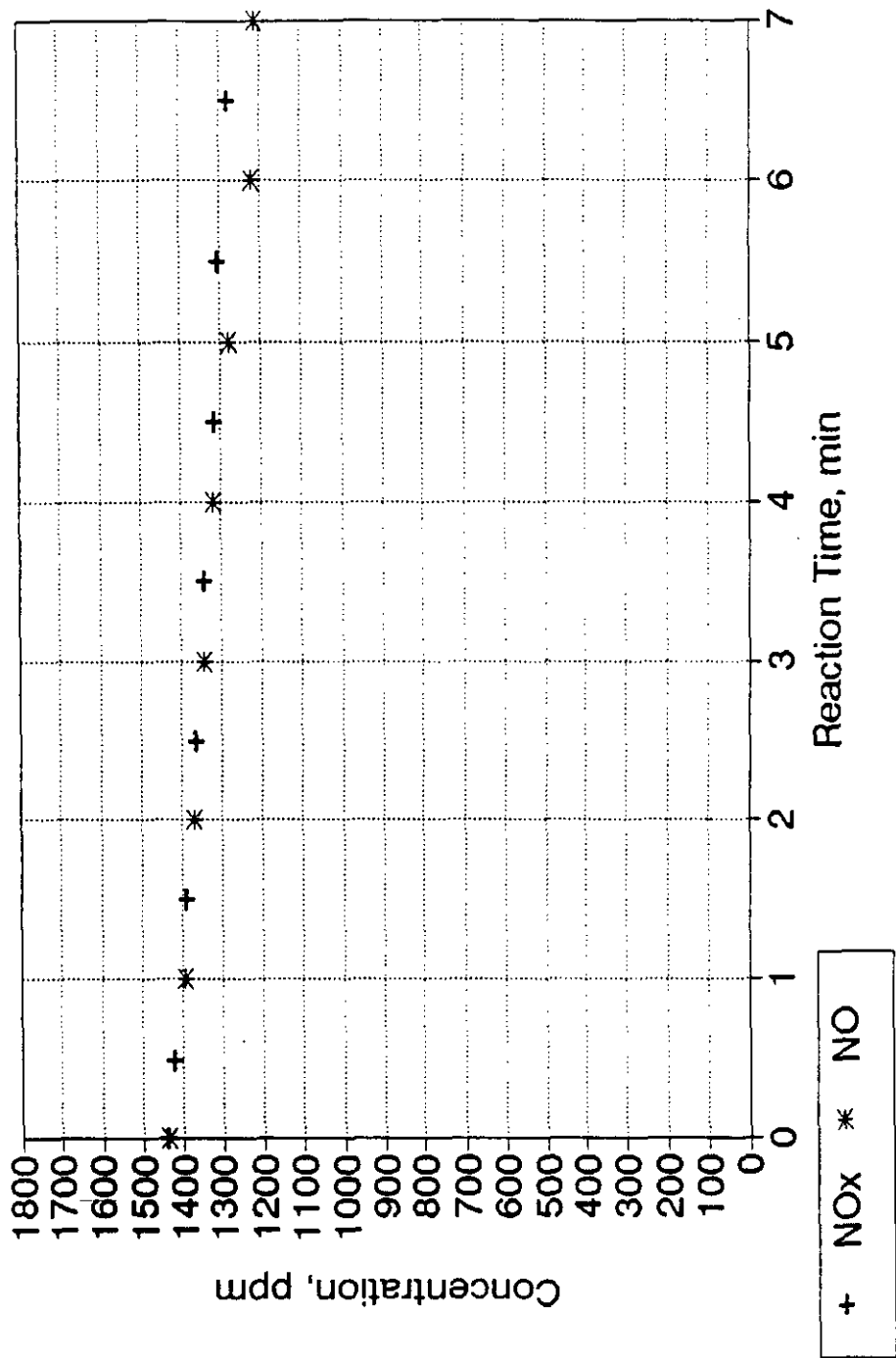


Figure A24. 06-23-93 : SO2 and NOx Removal by Sodium Sesquicarbonate



NSR=2, Water=5%, 260 F, 700rpm, 53um < d < 63um

Figure A25. 06-25-93 : NO and NOx Removed by Sodium Sulfite

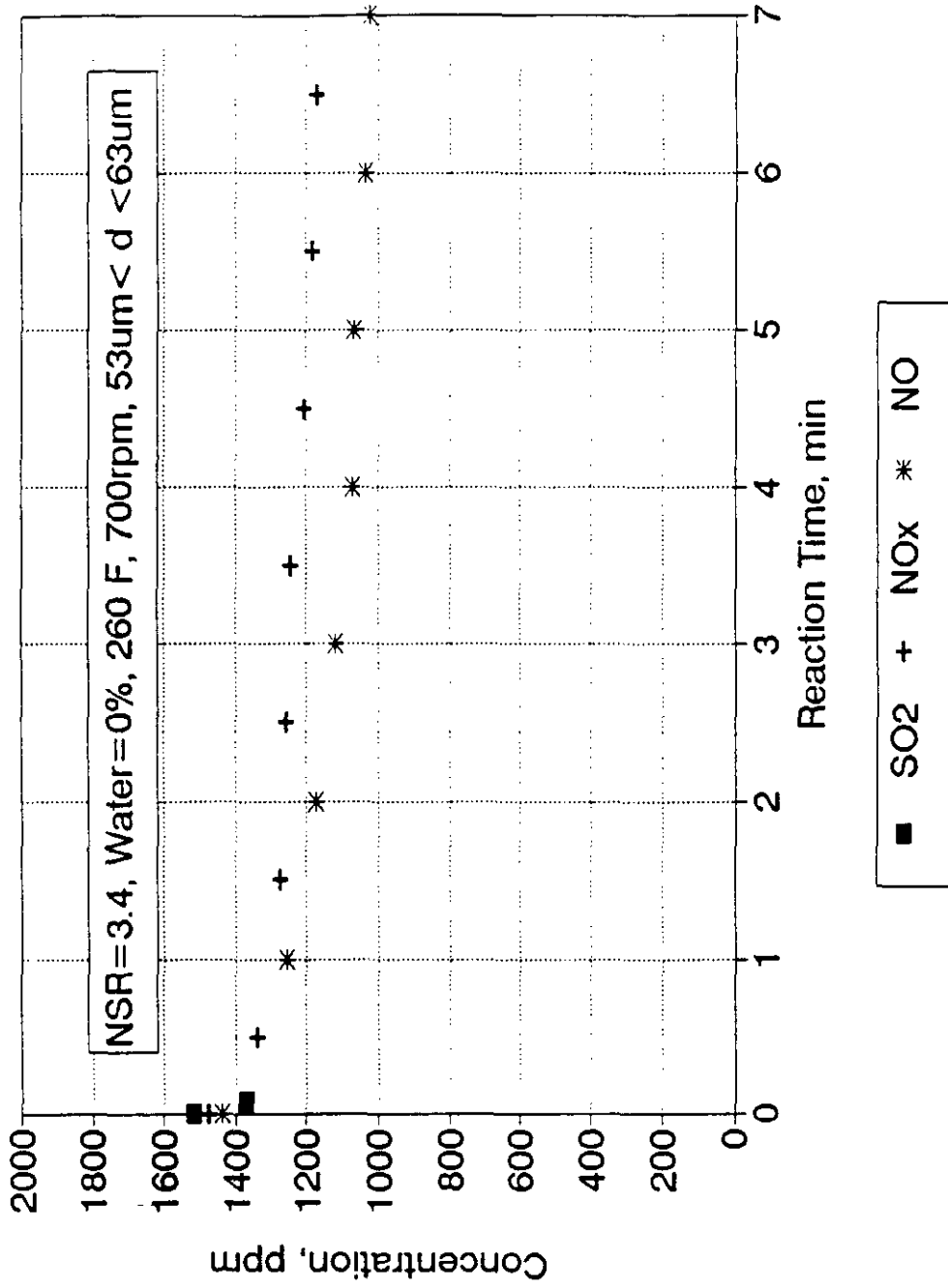


Figure A26. 07-22-93 : SO2 and NOx Removal by Sodium Sesquicarbonate



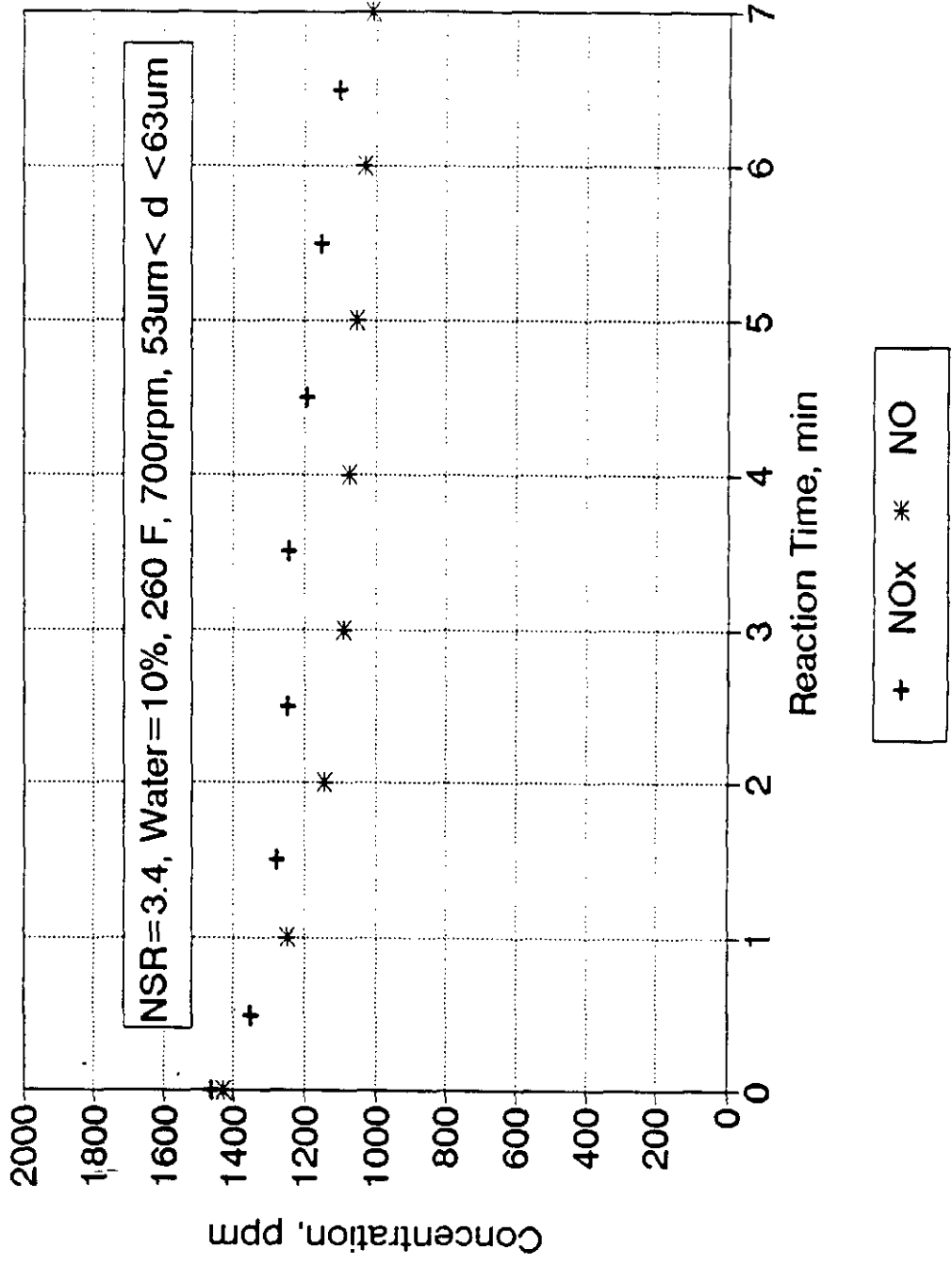
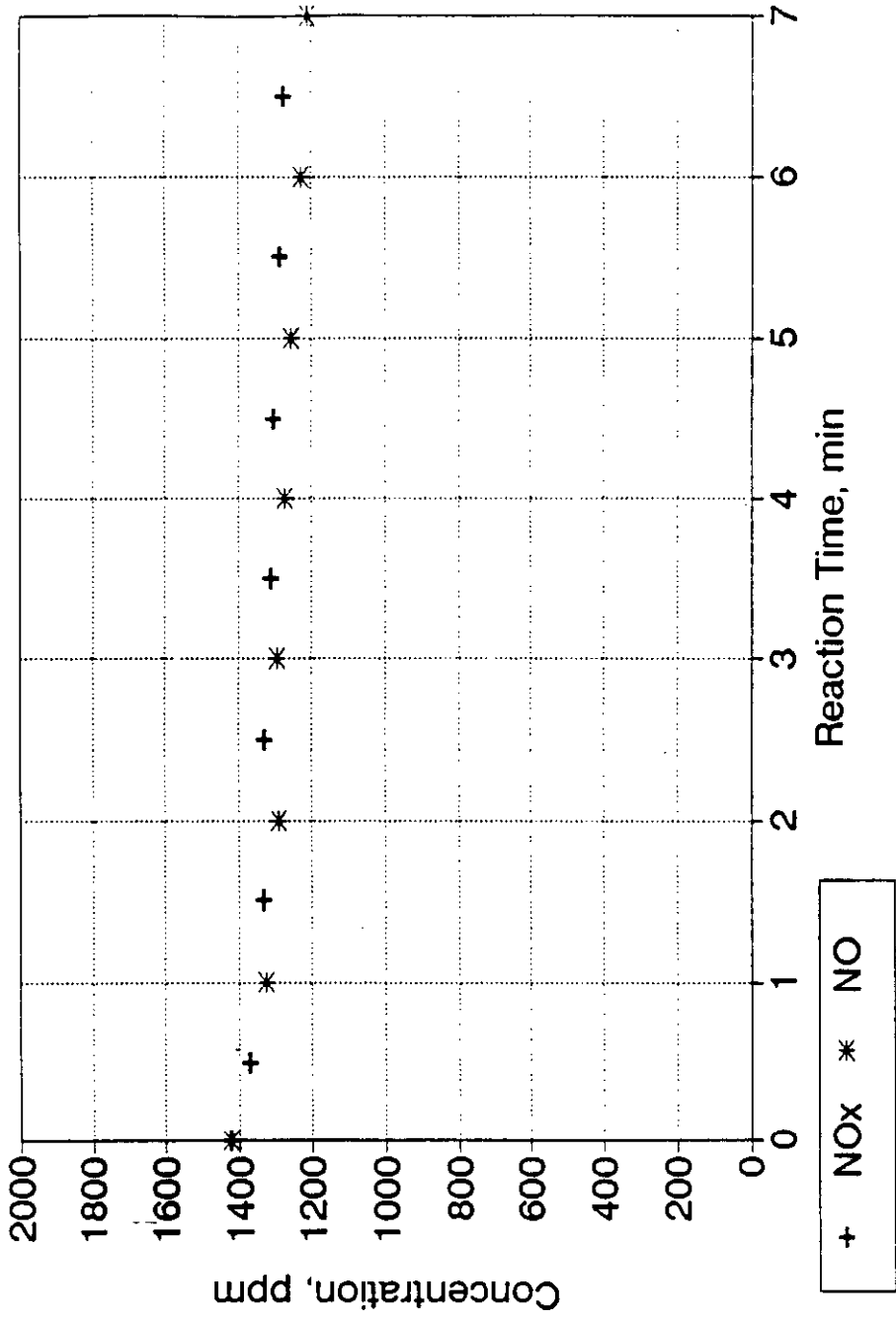


Figure A27. 07-22-93 : SO2 and NOx Removal by Sodium Sesquicarbonate



NSR=2, Water=5%, 260 F, 700rpm, 53um < d < 63um

Figure A28. 07-24-93 : NO and NOx Removed by Sodium Sulfite

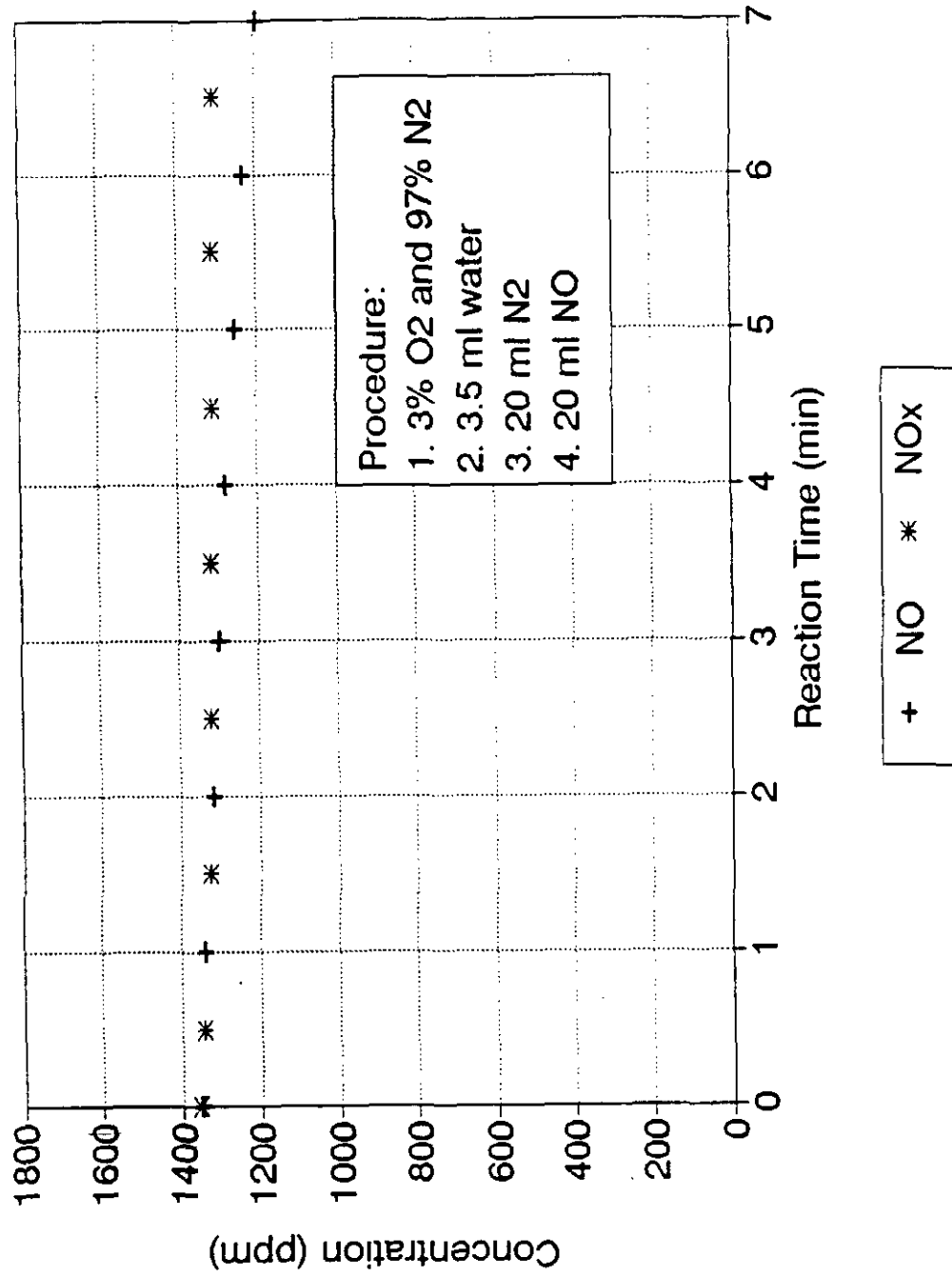


Figure A29. 08-01-93 : Blank test without SO<sub>2</sub>

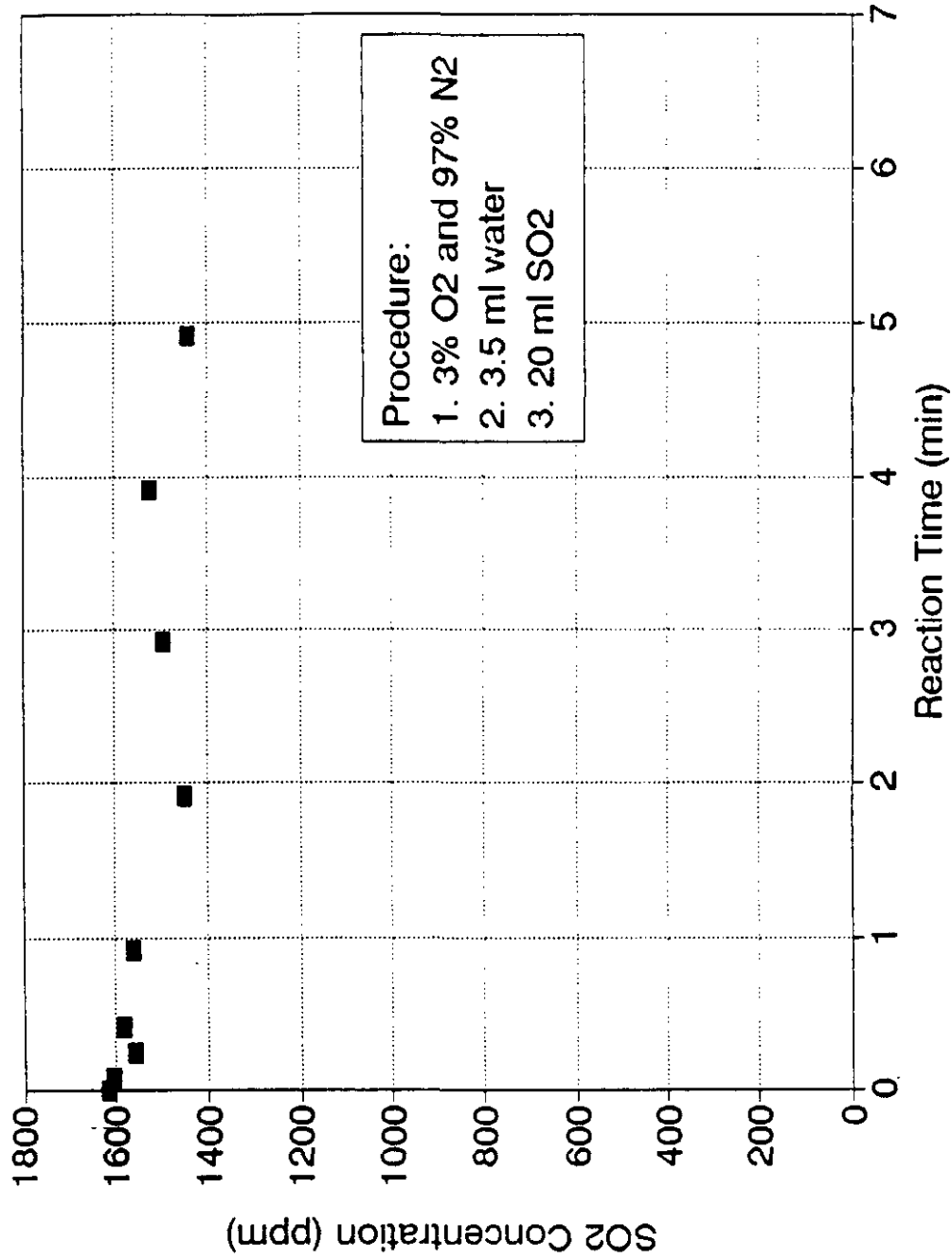


Figure A30. 08-07-93 : Blank test without NOx

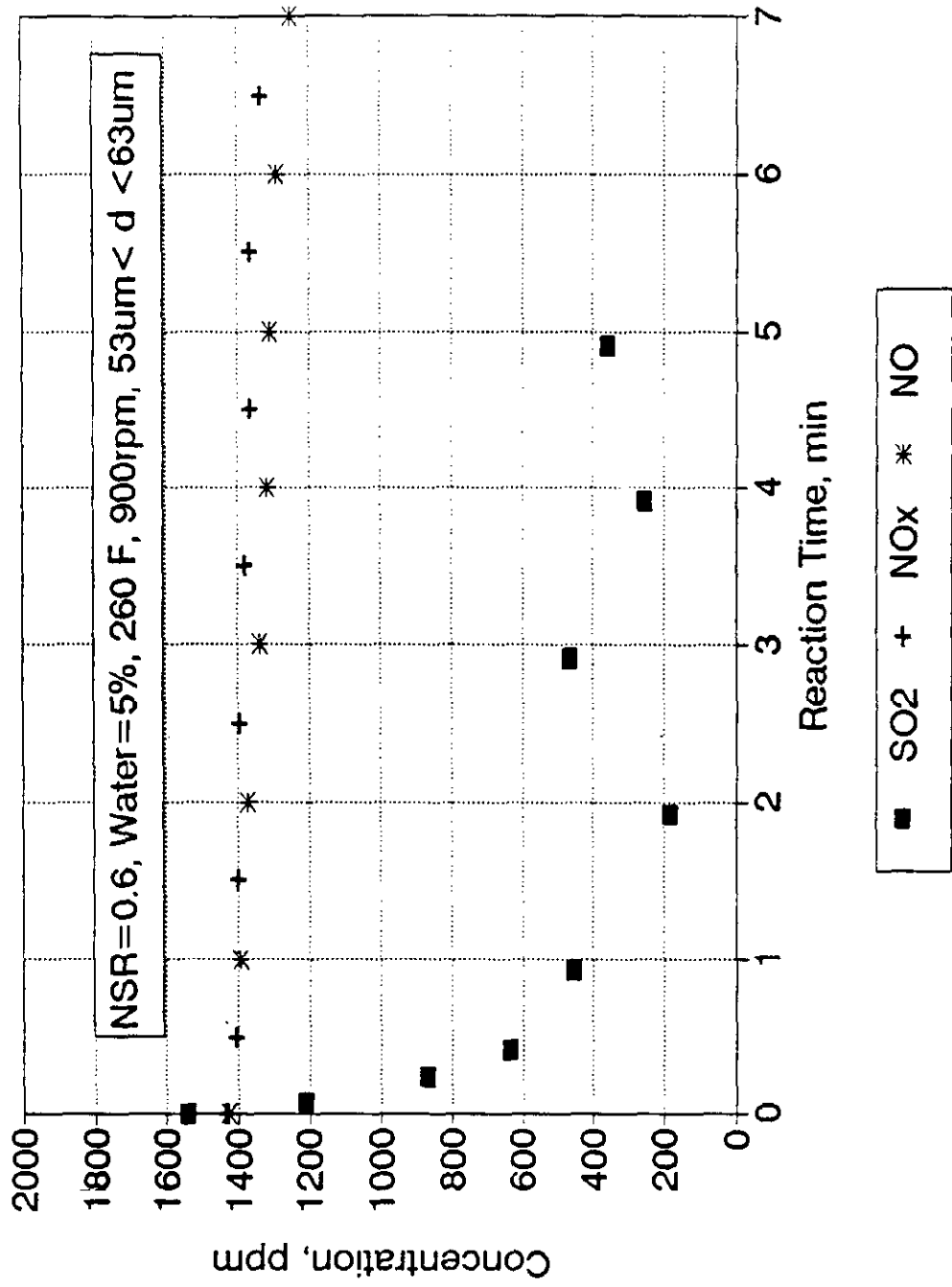


Figure A31. 08-07-93 : SO2 and NOx Removal by Sodium Bicarbonate

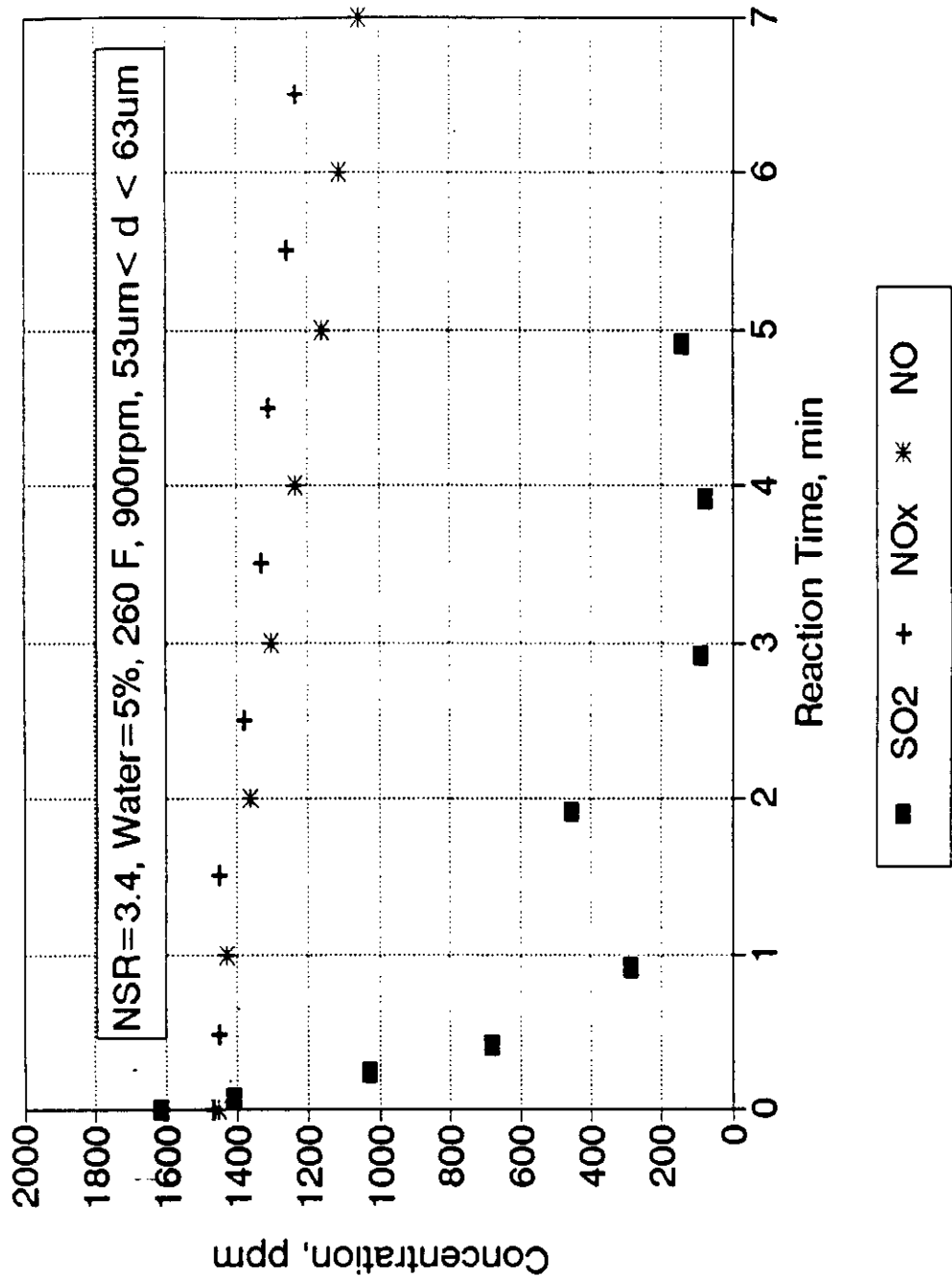
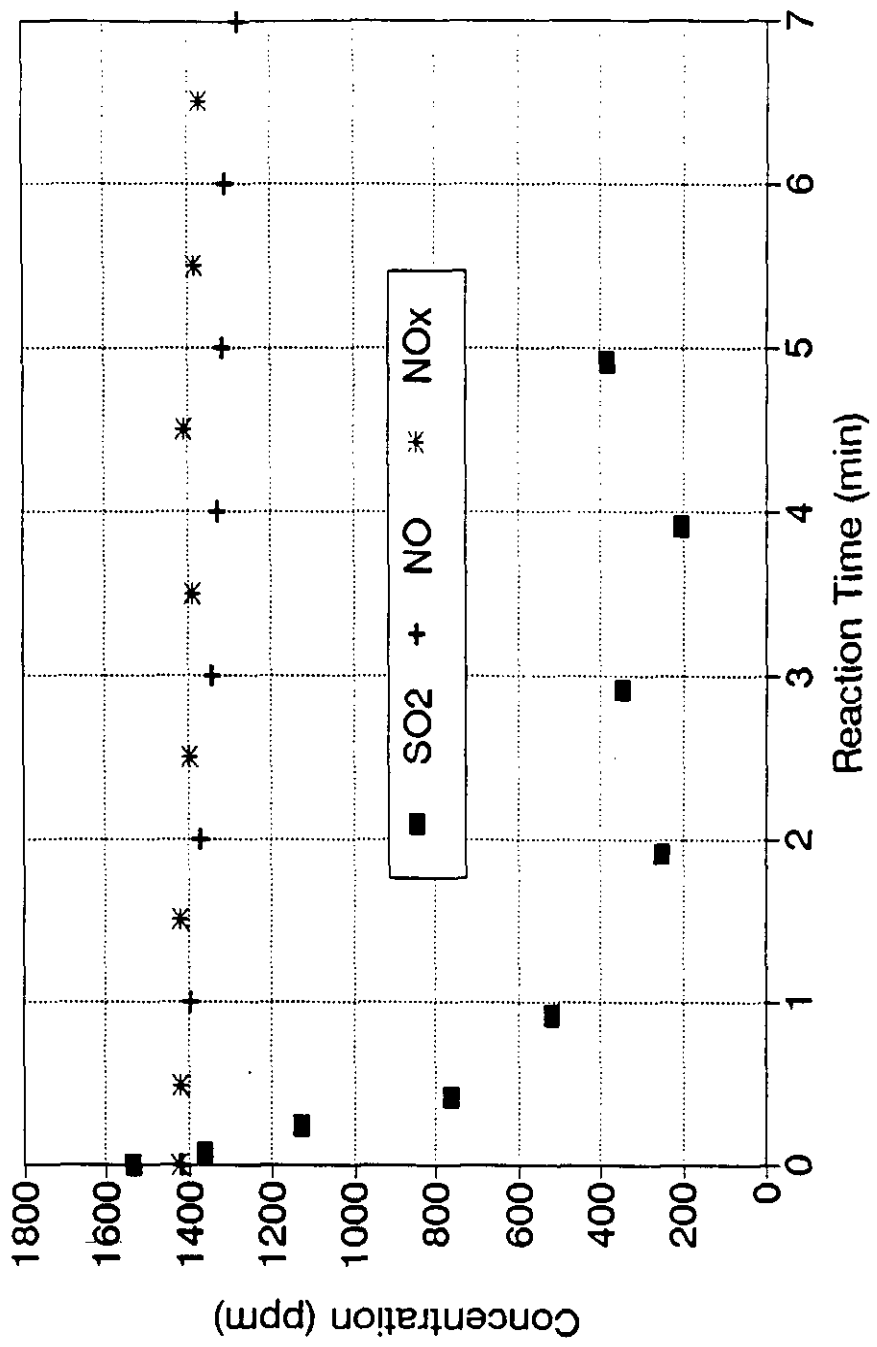


Figure A32. 08-08-93 : SO2 and NOx Removal by Sodium Bicarbonate



NSR=0, Water=5%, 260F, 700 rpm

Figure A33. 08-08-93 : SO2 and NOx Reduction without Dry Sorbent

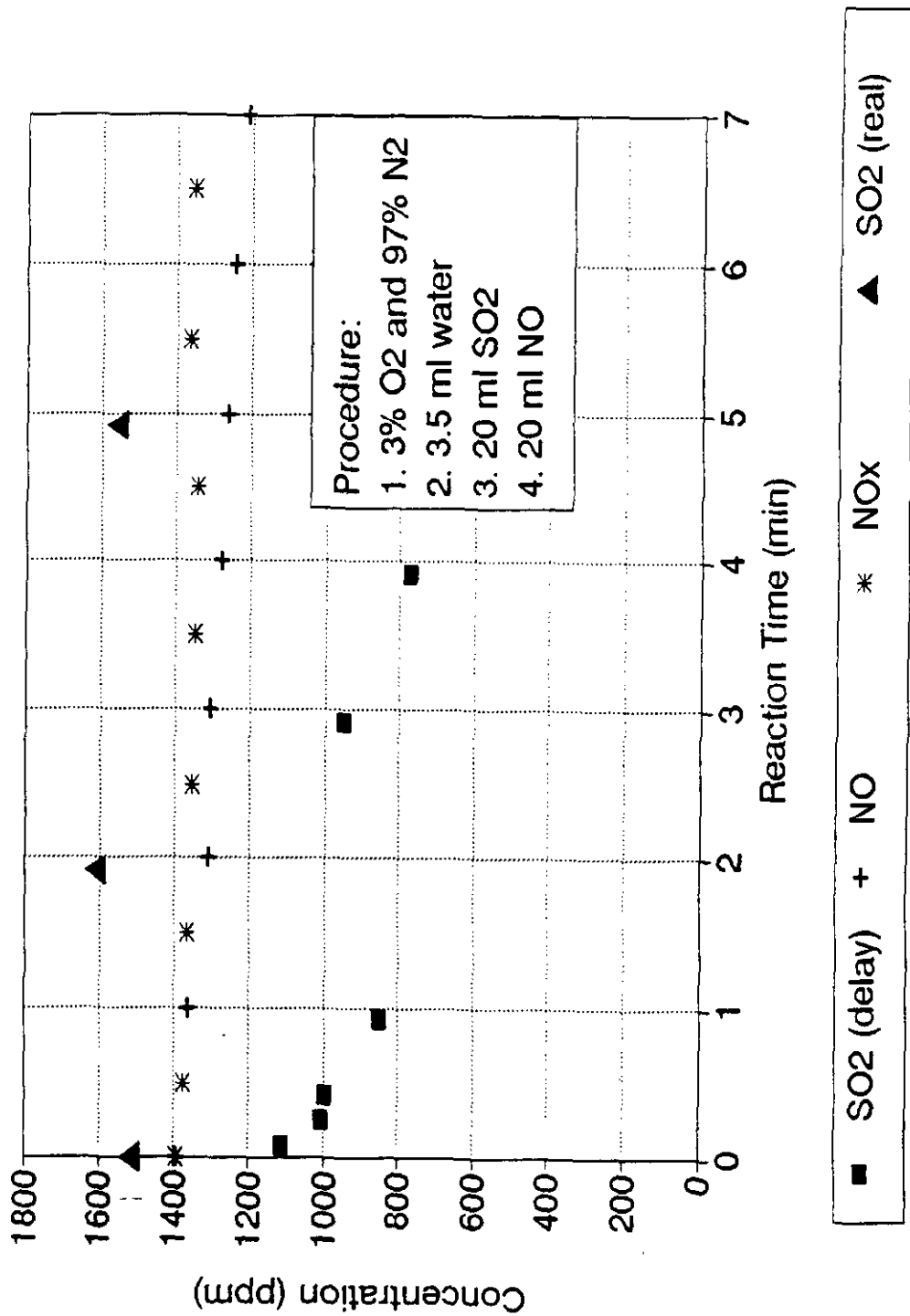
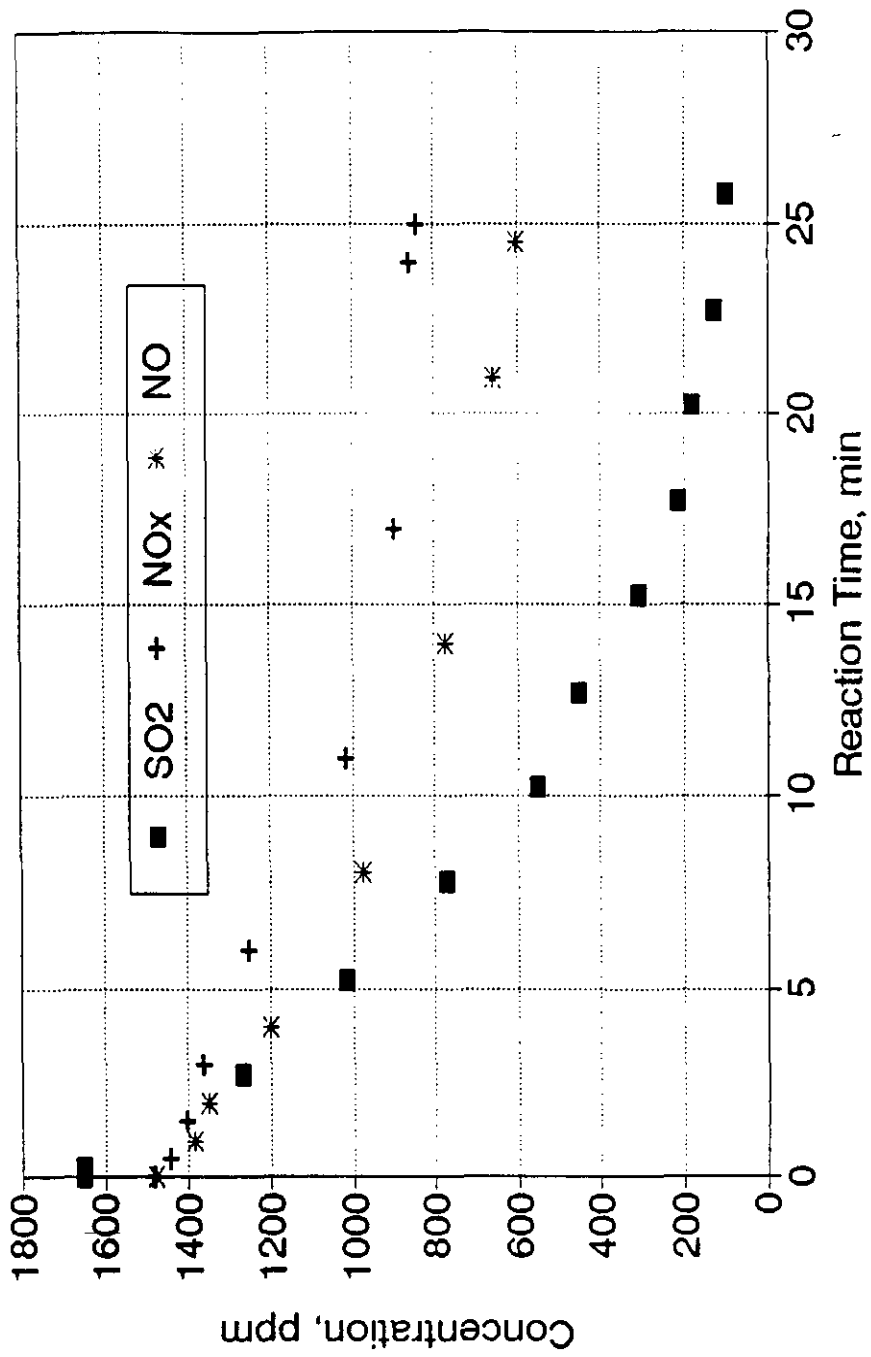


Figure A34. 08-10-93 : SO<sub>2</sub> and NO<sub>x</sub> Reduction without Dry Sorbent





NSR=3.4, 260 F, 700rpm, 5% Water

Figure A35. 08-10-93 : SO2 and NOx Removed by Sodium Bicarbonate

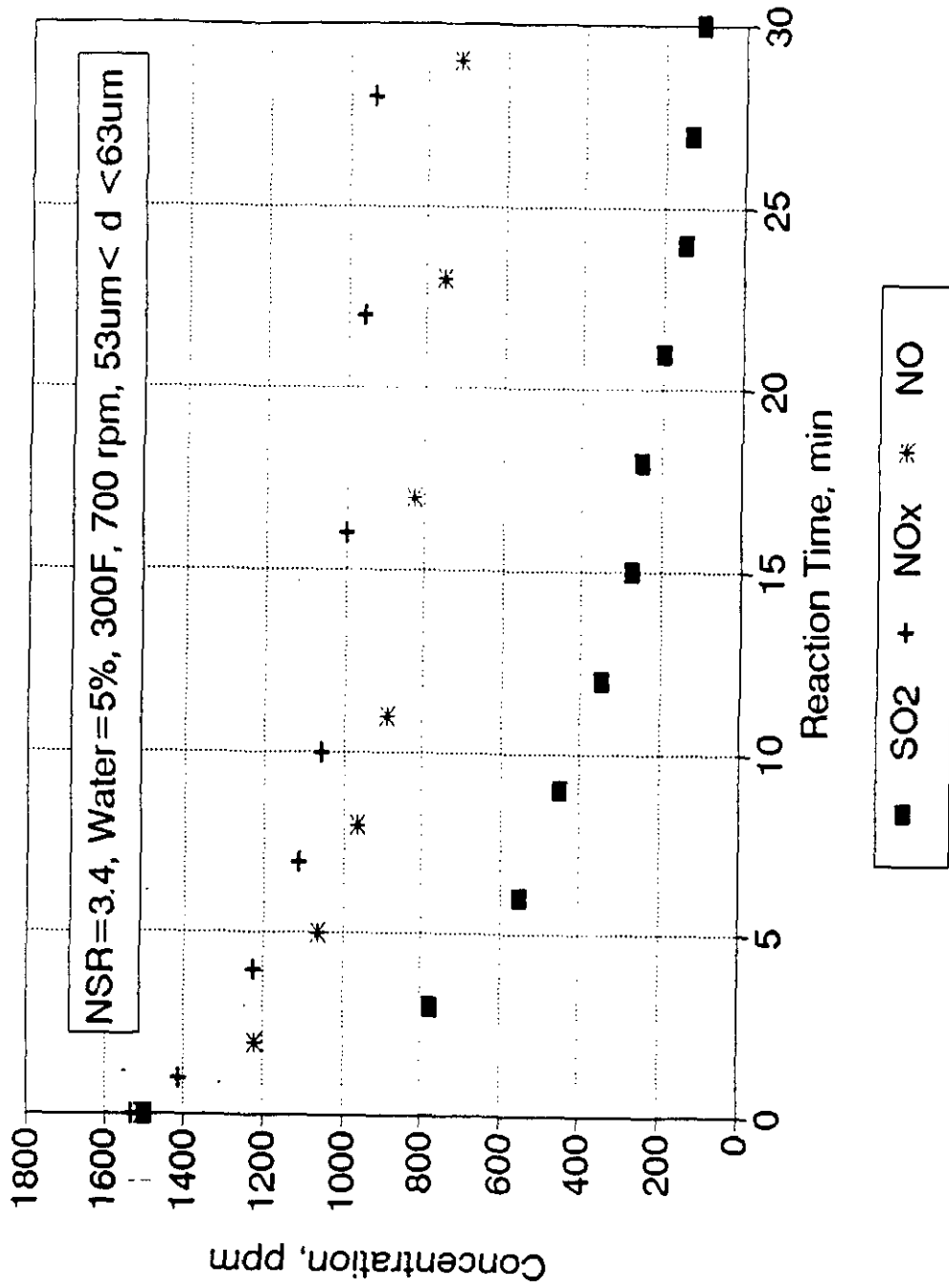


Figure A36. 09-20-93: SO2 and NOx Removal by Sodium Sesquicarbonate

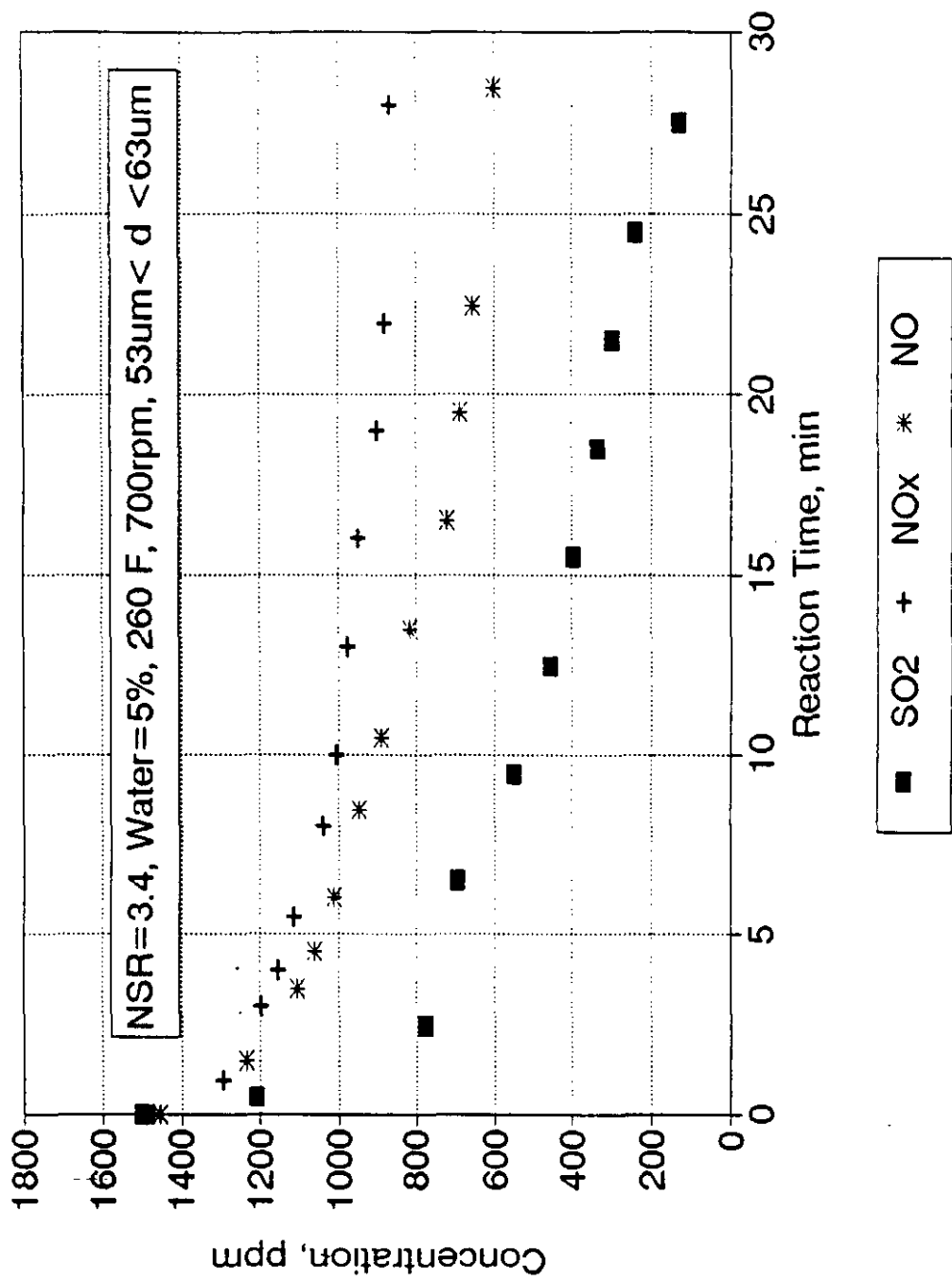


Figure A37. 10-21-93 : SO2 and NOx Removal by Sodium Sesquicarbonate

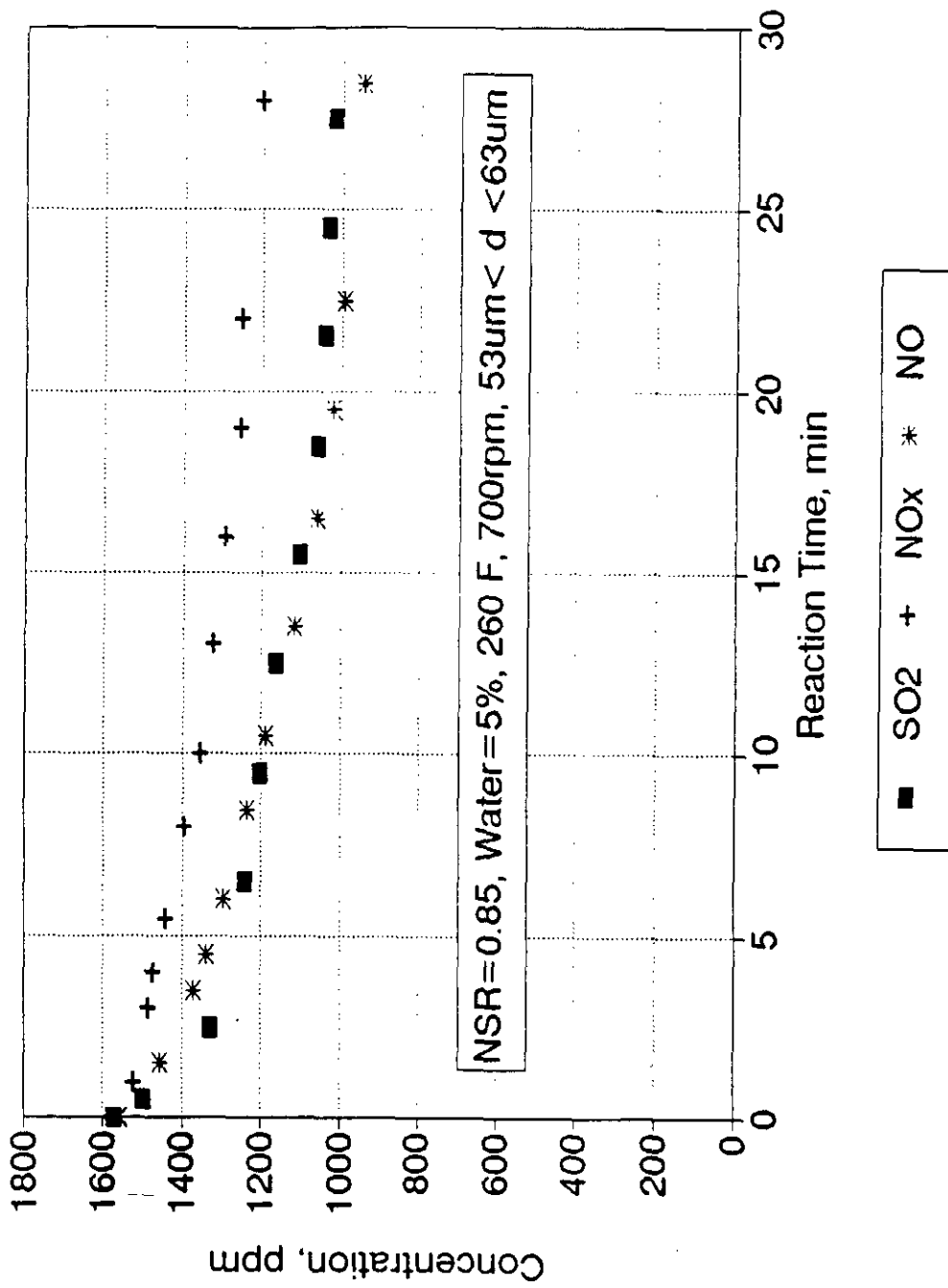


Figure A38. 10-22-93 : SO2 and NOx Removal by Sodium Sesquicarbonate

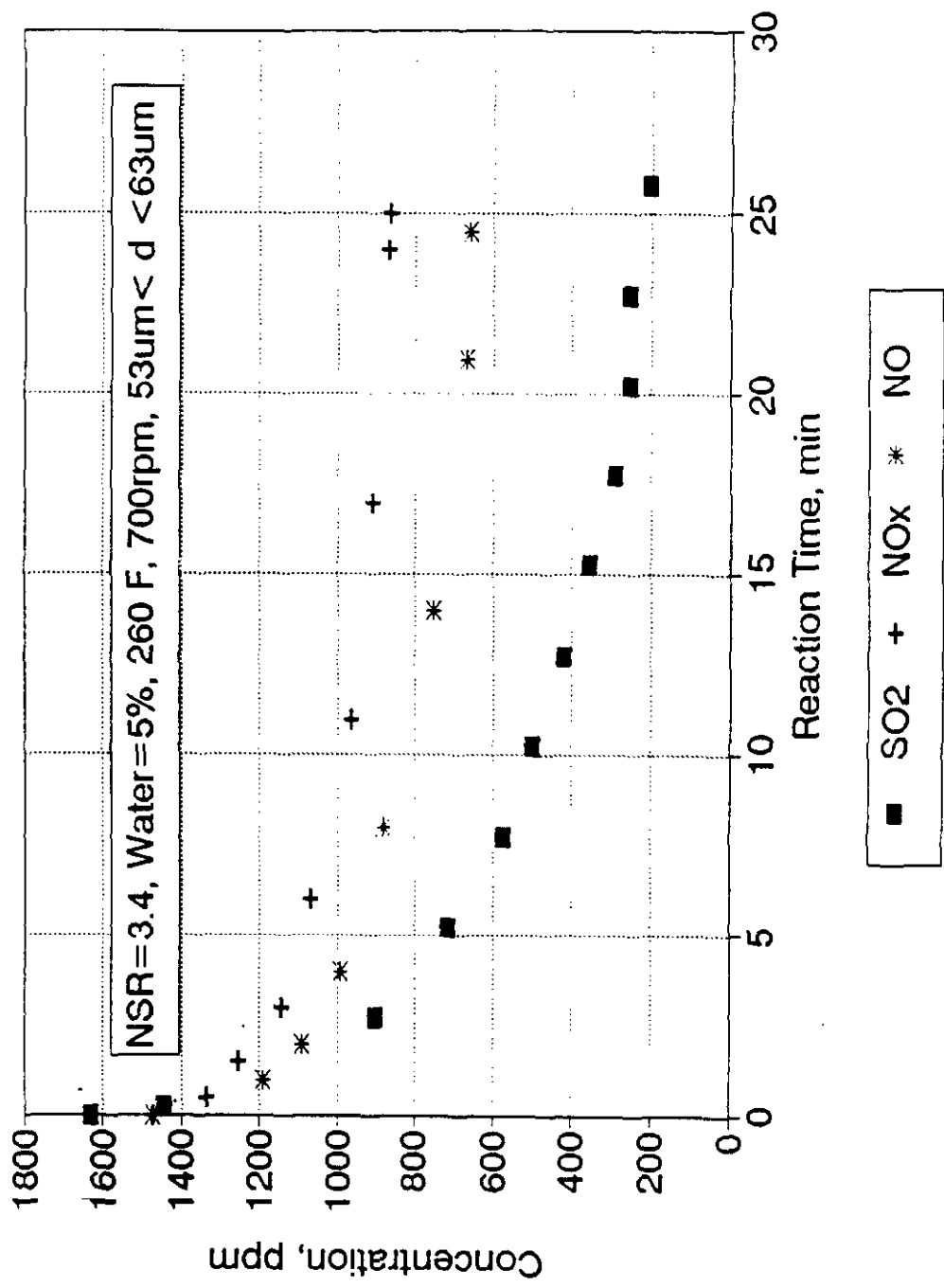


Figure A39. 10-24-93 : SO2 and NOx Removal by Sodium Sesquicarbonate

Table A1: SO2 and NOx Removal by Sodium Bicarbonate

Date : 02-19-93 Temp.(F) 300  
 Sorbent: NaHCO3 rpm : 300  
 Water(%) 3.5 NSR : 13.5  
 Size(um) (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.00395	1458.996	22.3	17.5	1311.835	976.0427
0.5	0.001731	652.0435				
1			19		1113.732	
1.5				13.5		745.999
2	0.001175	449.6815				
2.5			17.5		1023.685	
3				12.5		688.488
3.5	0.000113	63.39763				
4				11.8		648.2304
4.5				11.7		642.4793
5	0.000226	104.5114				
5.5			15.5		903.6226	
6				10		544.7107
6.5	3.08E-05	33.67326				
7			14.5		843.5914	
8				9.5		515.9553
8.5	0	22.47273				
9.5			14		813.5758	
10				8.7		495.4103
12			13.5		783.5602	
13				8.5		483.4041
15			13.5		783.5602	
16				8		453.3885
24			12.8		741.5383	
25				7.5		423.3729
36			12.5			

43

7.5

423.3729

54

12

693.5133

=====

Table A2. SO2 and NOx Removal by Sodium Bicarbonate

Date : 03-13-93 Temp.(F) 300  
 Sorbent: NaHCO3 rpm : 300  
 Water(%) 3 NSR : 13.5  
 Size(um) (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.004064	1500.323				
0.5	0.001014	391.227				
1	0.000359	153.0678				
2	0	22.47273				
15			26		1533.95	
16				26.7		1505.143
20				24.5		1378.619
21			23.7		1395.879	
23			23		1353.857	
24				22.6		1269.348
25			22.3		1311.835	
26				22		1234.842
28			21.4		1257.807	
30				20.7		1160.078
32			20.5		1203.779	
34				19.9		1114.069
36			20		1173.763	
38				19.3		1079.562
40			19.6		1149.751	



Table A3-1. Comparison between the NOx System with SO2 and the NOx System without SO2.

Date : 03-21-93	Water(%):	3.5
Sorbent : Blank	Temp(F) :	300
	rpm :	300

(1) RUN #1 (without SO2) :

Time (min)	NO Index	NOx Index	NO ppm	NOx ppm	NO2 ppm
0	24.5	23.4	1378.619	1377.869	
11	23.5	22.9	1321.108	1347.854	
20	22.3	22.6	1252.095	1329.844	
27	21.1	22.2	1183.082	1305.832	
32	20.5	21.9	1148.575	1287.822	
39	19.7	21.4	1102.567	1257.807	

Table A3-2. Comparison between the NOx System with SO2 and the NOx System without SO2.

(2) RUN #2 (with SO2) :

Time (min)	NO Index	NOx Index	NO ppm	NOx ppm
0	23.7	22.8	1332.61	1341.85
1	22.5		1263.597	
3		22.4		1317.838
3.5	21.8		1223.34	
9		22		1293.825
10	20.6		1154.326	
15		21.9		1287.822
16	19.5		1091.064	
17.5		21.4		1257.807
18.5		21.4		1257.807
19.5	19.1		1068.06	
20.5		21.2		1245.801
21.5	18.7		1045.056	
24		20.9		1227.791
25	18.1		1010.549	
26.5	17.7		987.5448	
29		20.6		1209.782
33		20.4		1197.776
35.5	16.3		907.0295	
37		20.2		1185.769
39.5	15.8		878.274	

Table A4. SO2 and NOx Removal by Sodium Bicarbonate

Date : 04-16-93 Temp.(F) 300  
 Sorbent: NaHCO3 rpm : 300  
 Water(%) 3.5 NSR : 13.5  
 Size(um) (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.00416	1535.272	22.5	21.8	1323.841	1223.34
0.33	0.002923	1085.521				
0.5			21.5		1263.81	
1	0.002186					
1.17				18.5		1033.554
2	0.001155	442.3976				
3	0.000994	383.8403				
3.5			16.5		963.6538	
4	0.000257	115.9958				
4.5				12.5		688.488
5	0	22.47273	15		873.607	
6				11.5		630.9771
7			13.5		783.5602	
8				10.5		573.4662
10			13		753.5445	
12				9.5		515.9553
14			12.5		723.5289	
16				9.5		515.9553
20			12		693.5133	
25				9		487.1998
26			11.5		663.4977	

Table A5. SO2 and NOx Removal by Sodium Bicarbonate

Date : 04-20-93 Temp.(F) 300  
 Sorbent: NaHCO3 rpm : 300  
 Water(%) 7 NSR : 13.5  
 Size(um) (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.003733	1379.881	26.5	27	1563.966	1522.396
0.50	0.002273	849.1706				
0.67			24.5		1443.904	
0.92	0.001545	584.1589				
1.17				23.8		1338.362
1.42	0.001129	432.9685				
1.67			23		1353.857	
1.92	0.000753	296.1366				
2.17				22		1234.842
2.42	0.000531	215.6276				
2.67			21.8		1281.819	
2.92	0.000354	151.2427				
3.17				20.2		1131.322
3.42	0.000266	119.3193				
3.67			20.6		1209.782	
3.92	0.00025	113.3818				
4.17				18.7		1045.056
4.67			19.2		1125.738	
5.17				17.7		987.5449
5.67			18.8		1101.726	
6.17				17		947.2872
6.67			18.5		1083.716	
7.17				16.7		930.0339
7.67			18		1053.701	
8.17				16.5		918.5317

Table A6. SO2 and NOx Removal by Sodium Bicarbonate

Date : 04-21-93 Temp.(F) 300  
 Sorbent: NaHCO3 rpm : 300  
 Water(%) 7 NSR : 13.5  
 Size(um) (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.003735	1380.581	25.5	26	1503.935	1463.886
0.5			24.5		1443.904	
0.75	0.002881	1070.065				
1				23.8		1338.362
1.25	0.002346	875.6994				
1.5			22.6		1329.844	
1.75	0.002174	813.0347				
2				21.8		1223.34
2.25	0.002264	845.624				
2.5			21.3		1251.804	
2.75	0.001929	723.8072				
3				19.3		1079.562
3.25	0.001929	724.0124				
3.5			19.3		1131.741	
3.75	0.001833	688.9672				
4				17		947.2872
4.25	0.001617	610.4084				
4.5			18.3		1071.71	
6				15.5		861.0208
6.5			16.7		975.66	
7				13.8		763.2522
7.5			15.3		891.6163	
8				13.3		734.4968

Table A7. SO2 and NOx Removal by Sodium Bicarbonate

Date : 04-23-93 Temp.(F) 300  
 Sorbent: NaHCO3 rpm : 300  
 Water(%) 7 NSR : 13.5  
 Size(um) (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.004075	1504.223	26.5	27	1563.966	1522.396
0.25	0.002924	1085.661				
0.5			25.3		1491.929	
0.75	0.002102	786.8491				
1				23.5		1321.108
1.25	0.001606	606.4316				
1.5			24.3		1431.897	
1.75	0.000947	366.6641				
2				22.5		1263.597
2.25	0.000642	255.8223				
2.5			22.8		1341.85	
2.75	0.000683	270.8684				
3				21		1177.331
3.25	0.000572	230.5899				
3.5			21		1233.794	
3.75	0.00045	186.1874				
4				19.5		1091.065
4.25	0.000225	104.3301				
5.5			19.7		1155.754	
6				17.5		976.0427
7.5			19.5		1143.747	
8				14.5		803.5099

Table A8. SO2 and NOx Removal by Sodium Bicarbonate

Date : 04-27-93 Temp.(F) 300  
 Sorbent: NaHCO3 rpm : 300  
 Water(%) 2.9 NSR : 13.5  
 Size(um) (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.003981	1470.24	23.8	24.65	1401.882	1387.246
0.25	0.002966	1101.185				
0.5			22		1293.825	
0.75	0.002208	825.3321				
1				20.5		1148.575
1.25	0.001684	635.0155				
1.5			19.9		1167.76	
1.75	0.00126	480.723				
2				17.8		993.296
2.25	0.001047	403.3057				
2.5			19.2		1125.738	
2.75	0.000836	326.4855				
3				16.1		895.5274
3.25	0.000735	289.6696				
3.5			18		1053.701	
3.75	0.000501	204.4952				
4				15.5		861.0208
4.25	0.000174	85.6912				
4.5			17.3		1011.679	
5				14.3		792.0077
5.5			16.2		945.6444	
6				13.5		745.999
6.5			15.5		903.6226	
7				12.9		711.4924
7.5			14.8		861.6007	
8				12.4		682.7369

Table A9. SO2 and NOx Removal by Sodium Bicarbonate

Date : 04-27-93 Temp.(F) 300  
 Sorbent: NaHCO3 rpm : 300  
 Water(%) 3.5 NSR : 13.5  
 Size(um) (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.003803	1405.382		25.57	1449.907	1440.156
0.25	0.002704	1005.821				
0.5			23.9		1407.885	
0.75	0.002102	706.8491				
1				22.4		1257.846
1.25	0.001606	526.4316				
1.75	0.000947	316.6641				
2.25	0.000642	225.8223				
2.5			20.5		1203.779	
2.75	0.000683	220.8684				
3				18.5		1033.554
3.25	0.000572	190.5899				
3.5			19.5		1143.747	
3.75	0.00045	146.1874				
4				16.5		918.5317
4.25	0.000225	94.33007				
4.5			18			
5				15.5		
5.5			17		993.6694	
6				14.7		815.0121
6.5			16.8			
7				14		
7.5			16.4		957.6507	
8				13.5		745.999



Table A10. SO2 and NOx Removal by Sodium Bicarbonate

Date : 04-30-93 Temp.(F) 300  
 Sorbent: NaHCO3 rpm : 300  
 Water(%) 10 NSR : 13.5  
 Size(um) (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.004193	1547.247	25	26	1473.919	1464.886
0.166667	0.003168	1174.342				
0.25			24		1413.888	
0.416667	0.002262	844.9041				
0.666667	0.001625	613.5531				
0.75				23.5		1321.108
1	0.000945	365.9998				
1.083333			23		1353.857	
1.5	0.00058	233.4631				
1.583333				21.5		1206.086
2	0.000464	191.265				
2.083333			21		1233.794	
2.5	0.000348	149.067				
2.666667				20		1119.82
3	0.000244	111.0887				
3.083333			19.8		1161.757	
3.5				18.5		1033.554
4				18		1004.798
4.5				17.5		976.0427
5			18.5		1083.716	
5.5				16.5		918.5317
6			18		1053.701	
6.5				15.8		878.2741
7			17		993.6694	
7.5				15		832.2654
8			16.5		963.6538	



Table A12. SO2 and NOx Removal by Sodium Bicarbonate

Date : 05-07-93 Temp.(F) 240  
 Sorbent: NaHCO3 rpm : 300  
 Water(%) 6.7 NSR : 13.5  
 Size(um) (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.00445	1640.655	25.1	26.26	1479.922	1479.838
0.166667	0.0026	967.9273				
0.25			24		1413.888	
0.416667	0.00221	826.1091				
0.666667	0.0018	677.0182				
0.75				24		1349.864
1	0.00105	404.2909				
1.25			22.7		1335.847	
1.5	0.00097	375.2				
1.75				22		1234.842
2	0.00096	371.5636				
2.25			21.7		1275.816	
2.5	0.00068	269.7455				
2.75				20.7		1160.078
3	0.000433	179.9273				
3.25			20.9		1227.791	
3.75				19.5		1091.065
4.25			20.1		1179.766	
4.75				18		1004.798
5.25			19.2		1125.738	
5.75				17.5		976.0427
6.25			18.3		1071.71	
6.75				18		1004.798
7.25			15.2		885.6132	
7.75				17.3		964.5405

Table A13. SO2 and NOx Removal by Sodium Sesquicarbonate

Date : 05-10-93 Temp.(F) 240  
 Sorbent: Sodium Sesquicarbonate rpm : 300  
 Water(%) 6.7 NSR : 13.5  
 Size(um) (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.004145	1529.745	26.27	27.05	1550.159	1525.272
0.166667	0.0037	1367.927				
0.25			23.5		1383.872	
0.416667	0.00229	855.2				
0.666667	0.0016	604.2909				
0.75				23.1		1298.104
1	0.00097	375.2				
1.25			21.5		1263.81	
1.5	0.00059	237.0182				
1.75				21		1177.331
2	0.000481	197.3818				
2.25			19.5		1143.747	
2.5	0.000463	190.8364				
2.75				18.8		1050.807
3	0.000241	110.1091				
3.25			18.2		1065.707	
3.75				17.6		981.7938
4.25			16.8		981.6632	
4.75				16.4		912.7807
5.25			16.5		963.6538	
5.75				15.3		849.5186
6.75				16.3		907.0296
7.25			14.5		843.5914	
7.75				15.3		849.5186

Table A14. SO2 and NOx Removal by Sodium Bicarbonate

Date : 05-20-93 Temp.(F) 260  
 Sorbent: Sodium Bicarbonate rpm : 300  
 Water(%) 5 NSR : 3.4  
 Size(um) (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.004366	1610.263	24.95	25.8	1470.918	1453.383
0.166667	0.003493	1292.676				
0.25			24.5		1443.904	
0.416667	0.002641	982.7314				
0.666667	0.001295	493.5472				
0.75				23.2		1303.855
1	0.001083	416.3293				
1.25			23.5		1383.872	
1.5	0.00093	360.7973				
1.75				22.8		1280.851
2	0.001012	390.3396				
2.25			22.5		1323.841	
2.5	0.000657	261.3252				
2.75				22.3		1252.095
3	0.00046	189.6695				
3.25			21.8		1281.819	
3.75				21.3		1194.584
4.25			21.8		1281.819	
4.75				20		1119.82
5.25			20.6		1209.782	
5.75				19.3		1079.562
6.25			20.8		1221.788	
6.75				18.7		1045.056
7.25			20.3		1191.772	
7.75				18.3		1022.051

Table A15. SO2 and NOx Removal by Sodium Pyrosulfite

Date : 05-24-93 Temp.(F) 260  
 Sorbent: Sodium Pyrosulfite rpm : 300  
 Water(%) 5 NSR : 2  
 Size(um) (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0	0	24.8	26.3	1461.913	1482.139
0.25			23.4		1377.869	
0.75				21.5		1206.086
1	0	11.23636		23.6		
1.25			22.2		1305.832	
1.75				22.3		1252.095
2	0	22.47273				
2.25			21.6		1269.813	
2.75				21.7		1217.589
3	0.000157	79.44483				
3.25			21.6		1269.813	
3.75				20.4		1142.824
4	0.000313	136.4169				
4.25			20.6		1209.782	
4.75				19.6		1096.816
5	0.000399	167.7025				
5.25			19.8		1161.757	
5.75				19.2		1073.811
6	0.000485	198.9881				
6.25			19.7		1155.754	
6.75				18.5		1033.554
7	0.000498	225				
7.25			19.6		1149.751	
7.75				18.1		1010.549
8	0.000285	243				



Table A17. SO2 and NOx Removal by Sodium Sesquicarbonate

Date : 05-27-93 Temp.(F) 260  
 Sorbent: Sodium Sesquicarbonate rpm : 700  
 Water(%) 5 NSR : 3.4  
 Size(um) (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.004174	1540.471	23.3	21.5	1371.866	1206.086
0.166667	0.003249	1204.021				
0.25						
0.416667	0.002137	799.5758				
0.75			19.5		1143.747	
1	0.001317	501.4798				
1.25				18.7		1045.056
1.5	0.001603	605.3356				
2	0.001247	475.8105				
2.25			17.7		1035.691	
2.5	0.000831	324.7872				
2.75				17.6		981.7938
3	0.000456	188.1536				
3.25			17.9		1047.698	
3.75				16.6		924.2828
4.25			17.7		1035.691	
4.75				16		889.7763
5.25			17		993.6694	
5.75				15.6		866.7719
6.25			16.5		963.6538	
6.75				14.8		820.7632
7.25			16.5		963.6538	
7.75				14.3		792.0077



Table A18. SO2 and NOx Removal by Sodium Bicarbonate

Date : 05-30-93 Temp.(F) 260  
 Sorbent: Sodium Bicarbonate rpm : 700  
 Water(%) 5 NSR : 3.4  
 Size(um) (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.004003	1478.112	24.5	25.7	1443.904	1447.632
0.16667	0.002571	957.4882				
0.25			23.8		1401.882	
0.41667	0.001959	734.8266				
0.66667	0.001502	568.6783				
0.75				23.9		1344.113
1	0.001488	563.4668				
1.25			23.1		1359.86	
1.5	0.001234	471.1341				
1.75				22.6		1269.348
2	0.000828	323.7213				
2.25			22.8		1341.85	
2.5	0	22.47273				
2.75				22.4		1257.846
3	0	22.47273				
3.75				21		1177.331
4.25			21.7		1275.816	
5.25			21.3		1251.804	
5.75				19.5		1091.065
6.25			21.3		1251.804	
6.75				18.9		1056.558
7.25			20.7		1215.785	
7.75				18.2		1016.3

Table A19. SO2 and NOx Removal by Sodium Sesquicarbonate.

Date : 06-17-93 Temp.(F) 260  
 Sorbent Sodium Sesquicarbonate rpm : 700  
 Water(%) 5 NSR : 1.7  
 Size(um) : (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.004392	1619.731	23.5	24	1383.872	1349.864
0.25	0.004169	1538.593				
0.366667			22.9		1347.854	
0.75	0.002468	920.0678				
0.866667				22.7		1275.099
1.25	0.0018	677.0572				
1.366667			22.5		1323.841	
1.75	0.00194	727.8779				
1.866667				21.4		1200.335
2.25	0.001164	445.7158				
2.366667			22.3		1311.835	
2.75	0.000776	304.6348				
2.866667				21.6		1211.837
3.25	0.000333	143.5686				
3.366667				21.3		1194.584
3.833333				21.1		1183.082
4.333333			21.5		1263.81	
4.833333				20.7		1160.078
5.333333			20.9		1227.791	
5.833333			21.5		1263.81	
6.333333				19.5		1091.064
6.833333			20.3		1191.772	
7.333333				18.5		1033.554
7.833333			19.1		1119.735	

Table A20. SO2 and NOx Removal by Sodium Sesquicarbonate.

Date : 06-18-93 Temp.(F) 260  
 Sorbent Sodium Sesquicarbonate rpm : 700  
 Water(%) 5 NSR : 0.85  
 Size(um) : (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.004411	1626.588	23.5	23.8	1383.872	1338.361
0.116667	0.003974	1467.522				
0.333333	0.002947	1094.212				
0.5			22.3		1311.835	
0.883333	0.001918	720.107				
1				23.2		1303.855
1.383333	0.001201	459.0374				
1.5			22.3		1311.835	
1.883333	0.001678	632.5084				
2						
2.383333	0.000907	352.4679				
2.5			22.3		1311.835	
2.883333	0.000353	150.7693				
3				21.5		1206.086
3.383333	0.000222	103.1797				
3.5			22.2		1305.832	
4				21.1		1183.082
4.5			21.2		1245.801	
5				20.2		1131.322
5.5			21.1		1239.797	
6				19.5		1091.064
6.5			20.3		1191.772	
7				19.2		1073.811

Table A21. SO2 and NOx Removal by Sodium Sesquicarbonate.

Date : 06-21-93 Temp.(F) 260  
 Sorbent Sodium Sesquicarbonate rpm : 700  
 Water(%) 5 NSR : 1.7  
 Size(um) : (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.004189	1545.661	24.9	26	1467.916	1464.885
0.133333	0.003392	1255.987				
0.25	0.002489	927.4801				
0.416667	0.001324	504.0373				
0.5			23.5		1383.872	
0.916667	0.000918	356.2894				
1				23.5		1321.108
1.5			23.3		1371.866	
1.916667	0.000596	239.135				
2				23		1292.353
2.5			22.5		1323.841	
2.916667	0.000357	152.4701				
3				21.8		1223.34
3.5			21.9		1287.822	
3.916667	0.000238	109.1376				
4				21.1		1183.082
4.5			21.9		1287.822	
5				20.6		1154.326
5.5			21.9		1287.822	
6				20.1		1125.571
6.5			20.9		1227.791	
7				19.8		1108.318

Table A22. SO2 and NOx Removal by Sodium Sesquicarbonate.

Date : 06-22-93 Temp.(F) 260  
 Sorbent Sodium Sesquicarbonate rpm : 700  
 Water(%) 5 NSR : 0.85  
 Size(um) : (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.004875	1795.104	25.4	26.3	1497.932	1482.139
0.116667	0.004308	1588.87				
0.25	0.002771	1030.255				
0.416667	0.002334	871.2405				
0.5			24.5		1443.904	
0.916667	0.001029	396.5503				
1				24.5		1378.619
1.416667	0.000423	176.4006				
1.5			23.9		1407.885	
2				23.5		1321.108
2.5			23.4		1377.869	
2.916667	0.000746	293.8349				
3				22.5		1263.597
3.5			22.4		1317.838	
3.916667	0.000249	112.9268				
4				22.1		1240.593
4.5			22.3		1311.835	
4.916667	0.00101	389.8713				
5				21.3		1194.584
5.5			22.3		1311.835	
6				21.1		1183.082
6.5			22.2		1305.832	
7				20.9		1171.58

Table A23. SO2 and NOx Removal by Sodium Sesquicarbonate

Date : 06-23-93 Temp.(F) 260  
 Sorbent : Sodium Sesquicarbonate rpm : 700  
 Water(%) 5 NSR : 3.4  
 Size(um) : (15, 32)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.004734	1743.767	25	26.3	1473.919	182.139
0.083333	0.003856	1424.75				
0.25	0.002548	948.8925				
0.416667	0.001886	708.4329				
0.5			22.3		1311.835	
0.916667	0.00134	509.5697				
1				22.2		1246.344
1.5			21.6		1269.813	
1.916667	0.000447	184.8384				
2				20.6		1154.326
2.5			20.9		1227.791	
2.916667	0.000466	191.7788				
3				19.6		1096.816
3.5			20.3		1191.772	
3.916667	0	22.47273				
4				18.6		1039.305
4.5			19.5		1143.747	
4.916667	0	22.47273				
5				18.1		1010.549
5.5			18.9		1107.729	
6				17.5		976.0426
6.5			18.4		1077.713	
7				17.4		970.2915

Table A24. SO2 and NOx Removal by Sodium Sesquicarbonate

Date : 06-23-93 Temp.(F) 260  
 Sorbent : Sodium Sesquicarbonate rpm : 700  
 Water(%) 5 NSR : 3.4  
 Size(um) : (45, 53)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.004757	1752.279	25.2	25.3	1485.925	1424.628
0.083333	0.003612	1335.812				
0.25	0.00219	818.7002				
0.416667	0.001591	601.0655				
0.5			22.3		1311.835	
0.916667	0.001501	568.3182				
1				21.1		1183.082
1.5			21.1		1239.797	
1.916667	0.0005	204.4212				
2				19.5		1091.064
2.5			19.1		1119.735	
2.916667	0	22.47273				
3				18.2		1016.3
3.5			18.5		1083.716	
3.916667	0	22.47273				
4				17.2		958.7893
4.5			18.1		1059.704	
4.916667	0	22.47273				
5				17.1		953.0382
5.5			17.8		1041.694	
6				16.6		924.2828
6.5			17.6		1029.688	
7				15.6		866.7719

Table A25. SO2 and NOx Removed by Sodium Sulfite

Date : 06-25-93 Temp.(F) 260  
 Sorbent : Sodium Sulfite rpm : 700  
 Water(%) 5 NSR : 2  
 Size(um) : (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0			24.43	25.48	1439.701	1434.98
0.116667						
0.25						
0.416667						
0.5			24.1		1419.891	
0.916667						
1				24.8		1395.872
1.416667						
1.5			23.6		1389.875	
2				24.3		1367.117
2.5			23.2		1365.863	
2.916667						
3				23.9		1344.113
3.5			22.8		1341.85	
3.916667						
4				23.5		1321.108
4.5			22.4		1317.838	
4.916667						
5				22.8		1280.851
5.5			22.2		1305.832	
6				21.8		1223.34
6.5			21.8		1281.819	
7				21.6		1211.837



Table A26: SO2 and NOx Removal by Sodium Sesquicarbonate

Date : 07-22-93 Temp.(F) : 300  
 Sorbent: Sesqui- rpm : 300  
 Water(%) : 0 NSR : 3.4  
 Size(um) : (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.004152	1515.869	25	25.5	1473.919	1436.13
0.083333	0.00375	1369.745				
0.25	0.00346	1264.291				
0.416667	0.003244	1185.795				
0.5			22.8		1341.85	
0.916667	0.00275	1006.109				
1				22.4		1257.846
1.5			21.7		1275.816	
1.916667	0.002093	767.2527				
2				21		1177.331
2.5			21.4		1257.807	
2.916667	0.001226	452.0241				
3				20		1119.82
3.5			21.2		1245.801	
3.916667	0.001943	712.6754				
4				19.2		1073.811
4.5			20.6		1209.782	
4.916667	0.000945	349.7347				
5				19.1		1068.06
5.5			20.2		1185.769	
6				18.5		1033.554
6.5			20		1173.763	
7				18.3		1022.051

Table A27: SO2 and NOx Removal by Sodium Sesquicarbonate

Date : 07-22-93 Temp.(F) : 300  
 Sorbent: Sesqui- rpm : 300  
 Water(%) : 10 NSR : 3.4  
 Size(um) : (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.004014	1465.837	24.8	25.4	1461.913	1430.379
0.083333	0.003259	1191.3				
0.25	0.002604	953.1268				
0.416667	0.0021	769.7455				
0.5			23		1353.857	
0.916667	0.001863	683.402				
1				22.3		1252.095
1.5			21.8		1281.819	
1.916667	0.001567	575.9798				
2				20.5		1148.575
2.5			21.3		1251.804	
2.916667	0.00109	402.327				
3				19.5		1091.064
3.5			21.2		1245.801	
3.916667	0.00103	380.655				
4				19.2		1073.811
4.5			20.3		1191.772	
4.916667	0.000535	200.5435				
5				18.8		1050.807
5.5			19.6		1149.751	
6				18.4		1027.802
6.5			18.8		1101.726	
7				18		1004.798

Table A28. SO2 and NOx Removal by Sodium Sulfite

Date : 07-24-93 Temp.(F) 260  
 Sorbent : Sodium Sulfite rpm : 700  
 Water(%) 5 NSR : 2  
 Size(um) : (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0			24.2	25.3	1425.894	1424.628
0.116667						
0.25						
0.416667						
0.5			23.3		1371.866	
0.916667						
1				23.6		1326.859
1.416667						
1.5			22.7		1335.847	
2				23		1292.353
2.5			22.6		1329.844	
2.916667						
3				23.1		1298.104
3.5			22.3		1311.835	
3.916667						
4				22.7		1275.099
4.5			22.2		1305.832	
4.916667						
5				22.4		1257.846
5.5			21.9		1287.822	
6				21.9		1229.091
6.5			21.8		1281.819	
7				21.6		1211.837

Table A29. Blank Test at 300 F, 500 rpm, 5% Water  
 High Concentration (1500 ppm-Method II)  
 N2-Air-Water-NO System :

Time (min)	SO2/N2 Ratio)	SO2/N2 (ppm)	NO (Index)	NOx (Index)	NO (ppm)	NOx (ppm)
0			24.3	23	1350	1353.857
0.5				22.8		1341.85
1			24.3		1339	
1.5				22		1327
2			23.4		1315.357	
2.5				22		1320
3			23.1		1298.104	
3.5				22.4		1317.838
4			22.8		1280.851	
4.5				21.5		1314
5			22.4		1257.846	
5.5				22.3		1311.835
6			21.9		1229.091	
6.5				21.4		1307
7			21.3		1194.584	

Table A30. Blank Test at 300 F, 500 rpm, 5% Water  
(Water-SO2-Air)

Time (min)	SO2/N2 (Ratio)	SO2/N2 (ppm)	NO (Index)	NOx (Index)	NO (ppm)	NOx (ppm)
0	0.00438	1615.159				
0.083333	0.004357	1606.937				
0.25	0.004221	1557.3				
0.416667	0.004281	1579.069				
0.5						
0.916667	0.00423	1560.545				
1						
1.5						
1.916667	0.003927	1450.446				
2						
2.5						
2.916667	0.00405	1495.192				
3						
3.5						
3.916667	0.004127	1523.051				
4						
4.5						
4.916667	0.0039	1440.697				
5						
5.5						
6						
6.5						
7						

Table A31. SO2 and NOx Removal by Sodium Bicarbonate.

Date : 08-07-93 Temp.(F) 260  
 Sorbent : Sodium Bicarbonate rpm : 700  
 Water(%) 5 NSR : 0.6  
 Size(um) : (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.004182	1543.255	24.3	25.4	1431.897	1430.379
0.083333	0.003274	1212.844				
0.25	0.002331	870.0159				
0.416667	0.001694	638.6191				
0.5			23.9		1407.885	
0.916667	0.0012	458.7337				
1				24.7		1390.121
1.5			23.8		1401.882	
1.916667	0.000441	182.6561				
2				24.4		1372.868
2.5			23.7		1395.879	
2.916667	0.00122	466.0569				
3				23.8		1338.361
3.5			23.4		1377.869	
3.916667	0.000645	257.0106				
4				23.4		1315.357
4.5			23.2		1365.863	
4.916667	0.000928	359.8556				
5				23.3		1309.606
5.5			23.2		1365.863	
6				22.9		1286.602
6.5			22.7		1335.847	
7				22.3		1252.095



19.5				18.3	1022.051
21.5	0.00285	1042.473			
22			21.3	1251.804	
22.5				17.8	993.2959
24.5	0.002823	1032.621			
25			21.2		
25.5				17.7	
27.5	0.002777	1015.881			
28			20.5	1203.779	
28.5				17	947.2872

=====



Table A39. SO2 and NOx Removal by Sodium Sesquicarbonate

Date : 10-24-93 Temp.(F) 260  
 Sorbent Sodium Sesquicarbonate rpm : 700  
 Water(%) 5 NSR : 3.4  
 Size(um) : (53, 63)

Time (min)	SO2/Air (Ratio)	SO2 (ppm)	NOx (Index)	NO (Index)	NOx (ppm)	NO (ppm)
0	0.004462	1628.628	25	26.15	1473.919	1473.512
0.25	0.003957	1444.873				
0.5			22.7		1335.847	
1				21.3		1194.584
1.5			21.3		1251.804	
2				19.5		1091.064
2.75	0.002467	903.0249				
3			19.5		1143.747	
4				17.8		993.2959
5.25	0.001947	713.9838				
6			18.3		1071.71	
7.75	0.001569	576.7865				
8				15.8		878.274
10.25	0.001365	502.3186				
11			16.5		963.6538	
12.75	0.00114	420.6867				
14				13.6		751.75
15.25	0.000966	357.2379				
17			15.6		909.6257	
17.75	0.000784	291.2502				
20.25	0.000672	250.4137				
21				12.2		671.2347
22.75	0.000672	250.3218				
24			14.9		867.6039	
24.5				12		659.7325

25 14.8 861.6007  
25.75 0.000549 205.7772

=====

**APPENDIX B**

Table B1-1. Corrected Results from the case of Sodium Bicarbonate  
with NSR = 0.85 (Figure 23)

=====

CORRECTED DATA

=====

Time (min)	SO2 (ppm)	NOx (ppm)	NO (ppm)
0	1758.467	1473.919	1470.637
0.25	1731.227		
0.5		1435.597	
1			1357.264
1.5		1418.985	
2			1307.153
2.5			
2.75	1628.402		
3		1388.063	
3.5			
4			1275.944
4.5			
5			
5.25	1540.655		
5.5			
6		1362.238	
7			
7.75	1446.109		
8			1184.771
9			
10			
10.25	1378.948		
10.5			
11		1351.213	
12			

12.75	1340.655		
13			
14			1142.905
15			
15.25	1318.836		
15.5			
16			
17		1329.579	
17.75	1297.018		
18			
19			
20			
20.25	1275.2		
20.5			
21			1056.678
22			
22.75	1258.711		
23			
24		1333.354	
24.5			1065.325
25		1310.738	
25.75	1257.018		
26			
27			

=====

Table B1-2. Simulation Results from the Case of Sodium Bicarbonate with NSR = 0.85 (Figure 23)

SIMULATION (with  $k_A=7.65$ ,  $k_B=1.06E8$ , and  $x=0.70$ )

=====

SO2 (ppm)	NO (ppm)	NOx (ppm)	R (um)	R(um) X 100
1758.47	1470.64	1473.92	29	2900
1747.11	1463.6	1469.34	28.9062	2890.62
1735.9	1456.68	1464.85	28.8131	2881.31
1713.9	1443.21	1456.09	28.6289	2862.89
1692.45	1430.19	1447.63	28.4473	2844.73
1671.54	1417.61	1439.45	28.2682	2826.82
1651.14	1405.45	1431.55	28.0916	2809.16
1641.13	1399.52	1427.69	28.0042	2800.42
1631.24	1393.68	1423.9	27.9173	2791.73
1611.82	1382.3	1416.5	27.7454	2774.54
1592.87	1371.27	1409.33	27.5757	2757.57
1574.36	1360.6	1402.39	27.4082	2740.82
1556.29	1350.25	1395.67	27.2429	2724.29
1547.41	1345.19	1392.38	27.161	2716.1
1538.64	1340.22	1389.15	27.0796	2707.96
1521.4	1330.49	1382.82	26.9184	2691.84
1488.08	1311.89	1370.74	26.6017	2660.17
1464.07	1298.65	1362.13	26.3692	2636.92
1456.24	1294.37	1359.34	26.2926	2629.26
1425.79	1277.82	1348.59	25.9906	2599.06
1396.65	1262.19	1338.43	25.6955	2569.55
1389.56	1258.41	1335.97	25.6227	2562.27
1382.54	1254.69	1333.55	25.5503	2555.03
1368.74	1247.39	1328.81	25.4067	2540.67

=====

1341.98	1233.37	1319.7	25.1242	2512.42
1322.64	1223.34	1313.17	24.9162	2491.62
1316.33	1220.08	1311.05	24.8476	2484.76
1291.7	1207.45	1302.85	24.5766	2457.66
1268.06	1195.45	1295.05	24.3111	2431.11
1262.29	1192.54	1293.16	24.2455	2424.55
1256.58	1189.67	1291.29	24.1802	2418.02
1245.33	1184.03	1287.62	24.0507	2405.07
1223.49	1173.15	1280.55	23.7952	2379.52
1207.65	1165.33	1275.47	23.6068	2360.68
1202.48	1162.79	1273.82	23.5445	2354.45
1182.25	1152.89	1267.39	23.2984	2329.84
1162.77	1143.45	1261.24	23.0566	2305.66
1158.02	1141.15	1259.75	22.9969	2299.69
1153.3	1138.88	1258.28	22.9373	2293.73
1144.01	1134.42	1255.38	22.8191	2281.91
1125.92	1125.78	1249.76	22.5855	2258.55
1112.78	1119.55	1245.71	22.413	2241.3
1108.48	1117.52	1244.39	22.3559	2235.59
1091.65	1109.6	1239.25	22.13	2213
1083.46	1105.77	1236.75	22.0184	2201.84
1075.41	1102.01	1234.31	21.9077	2190.77
1063.59	1096.53	1230.75	21.7433	2174.33
1059.72	1094.74	1229.58	21.6889	2168.89
1044.57	1087.75	1225.04	21.4734	2147.34

=====

Table B2-1. Corrected Results from the Case of Sodium Bicarbonate  
with NSR = 3.37 (Figure 24) :

```

=====
CORRECTED DATA
=====

```

Time (min)	SO2 (ppm)	NOx (ppm)	NO (ppm)
0	1660.945	1545.957	1533.899
0.25	1629.602		
0.5		1477.619	
1			1357.264
1.5		1424.988	
2			1324.406
2.5			
2.75	1354.878		
3		1340.038	
3.5			
4			1206.931
4.5			
5			
5.25	1037.27		
5.5			
6		1296.204	
7			
7.75	829.3276		
8			1063.998
9			
10			
10.25	616.3675		
10.5			



11		1171.119	
12			
12.75	394.5502		
13			
14			901.3587
15			
15.25	292.2909		
15.5			
16			
17		1131.476	
17.75	212.9872		
18			
19			
20			
20.25	197.7455		
20.5			
21			832.3858
22			
22.75	182.3518		
23			
24		1093.229	
24.5			846.7836
25		1094.626	
25.75	159.5636		
26			
27			

=====

Table B2-2. Simulation Results from the Case of Sodium Bicarbonate  
with NSR = 3.37 (Figure 24) :

SIMULATION (with  $k_A=7.65$ ,  $k_B=1.06E8$ , and  $x=0.70$ )

SO2 (ppm)	NO (ppm)	NOx (ppm)	R(um)	R(um) X 100
1661	1534	1546	29	2900
1615.32	1506.21	1527.94	28.9172	2891.72
1571.15	1479.82	1510.78	28.837	2883.7
1487.06	1430.85	1478.95	28.6836	2868.36
1408.28	1386.43	1450.08	28.5391	2853.91
1334.37	1346.03	1423.82	28.4028	2840.28
1264.98	1309.16	1399.85	28.2743	2827.43
1231.87	1291.92	1388.65	28.2127	2821.27
1199.76	1275.43	1377.93	28.1529	2815.29
1138.41	1244.49	1357.82	28.0381	2803.81
1080.64	1216.05	1339.33	27.9295	2792.95
1026.21	1189.85	1322.3	27.8267	2782.67
974.88	1165.65	1306.57	27.7294	2772.94
950.31	1154.25	1299.16	27.6827	2768.27
926.44	1143.27	1292.03	27.6372	2763.72
880.7	1122.53	1278.55	27.5497	2754.97
796.62	1085.39	1254.4	27.388	2738.8
739.41	1060.82	1238.43	27.2773	2727.73
721.36	1053.19	1233.47	27.2423	2724.23
653.88	1025.12	1215.23	27.1106	2711.06
593.24	1000.54	1199.25	26.9917	2699.17
579.06	994.88	1195.57	26.9637	2696.37
565.24	989.39	1192.01	26.9365	2693.65

538.66	978.93	1185.2	26.8839	2688.39
489.47	959.84	1172.8	26.7863	2678.63
455.74	946.97	1164.43	26.7191	2671.91
445.06	942.93	1161.81	26.6978	2669.78
404.92	927.91	1152.04	26.6174	2661.74
368.61	914.52	1143.34	26.5444	2654.44
360.08	911.4	1141.31	26.5272	2652.72
351.75	908.37	1139.34	26.5104	2651.04
335.71	902.56	1135.56	26.478	2647.8
305.89	891.85	1128.6	26.4176	2641.76
285.35	884.55	1123.86	26.3759	2637.59
278.83	882.24	1122.36	26.3626	2636.26
254.25	873.61	1116.75	26.3125	2631.25
231.93	865.84	1111.69	26.2669	2626.69
226.67	864.02	1110.51	26.2561	2625.61
221.53	862.24	1109.36	26.2456	2624.56
211.62	858.83	1107.14	26.2253	2622.53
193.15	852.5	1103.03	26.1874	2618.74
180.39	848.16	1100.2	26.1611	2616.11
176.33	846.78	1099.31	26.1528	2615.28
161.02	841.61	1095.95	26.1212	2612.12
153.88	839.21	1094.39	26.1065	2610.65
147.06	836.92	1092.9	26.0924	2609.24
137.41	833.7	1090.8	26.0724	2607.24
134.34	832.67	1090.14	26.0661	2606.61
122.75	828.82	1087.63	26.0421	2604.21

=====

Table B3-1. Corrected Results from the Case of Sodium Bicarbonate  
with NSR = 3.37 (Figure 25) :

=====			
CORRECTED DATA			
=====			
Time (min)	SO2 (ppm)	NOx (ppm)	NO (ppm)
0	1652.04	1485.925	1476.388
0.25	1652.04		
0.5		1447.604	
1			1391.77
1.5		1412.982	
2			1364.664
2.5			
2.75	1266.887		
3		1382.06	
3.5			
4			1229.935
4.5			
5			
5.25	1018.684		
5.5			
6		1296.204	
7			
7.75	775.0761		
8			1035.243
9			
10			
10.25	553.2198		
10.5			
11		1099.082	

12			
12.75	454.2929		
13			
14			878.3544
15			
15.25	309.4106		
15.5			
16			
17		1023.419	
17.75	212.9872		
18			
19			
20			
20.25	179.7919		
20.5			
21			815.1325
22			
22.75	128.0145		
23			
24		1039.201	
24.5			783.5216
25		1028.591	
25.75	98.53301		
26			
27			

=====

Table B3-2. Simulated Results from the Case of Sodium  
with NSR = 3.37 (Figure 25) :

SIMULATION (with  $k_A=7.65$ ,  $k_B=1.06E8$ ,  $x=0.70$ )

SO2 (ppm)	NO (ppm)	NOx (ppm)	R (um)	R X100
1652.04	1476.39	1485.93	29	2900
1606.62	1448.33	1467.69	28.9129	2891.29
1562.7	1421.71	1450.39	28.8284	2882.84
1479.14	1372.39	1418.33	28.667	2866.7
1400.88	1327.76	1389.32	28.515	2851.5
1327.5	1287.24	1362.98	28.3718	2837.18
1258.63	1250.32	1338.99	28.2366	2823.66
1225.78	1233.09	1327.79	28.1718	2817.18
1193.92	1216.61	1317.07	28.1089	2810.89
1133.07	1185.73	1297	27.9882	2798.82
1075.78	1157.38	1278.57	27.8741	2787.41
1021.81	1131.29	1261.62	27.766	2776.6
970.93	1107.23	1245.98	27.6636	2766.36
946.58	1095.9	1238.61	27.6145	2761.45
922.92	1085	1231.53	27.5666	2756.66
877.59	1064.42	1218.15	27.4746	2747.46
794.26	1027.6	1194.22	27.3045	2730.45
737.57	1003.29	1178.41	27.188	2718.8
719.69	995.73	1173.5	27.1511	2715.11
652.8	967.99	1155.47	27.0125	2701.25
592.7	943.72	1139.7	26.8871	2688.71
578.63	938.13	1136.06	26.8577	2685.77
564.94	932.72	1132.55	26.8289	2682.89

538.58	922.4	1125.83	26.7735	2677.35
489.79	903.58	1113.6	26.6706	2667.06
456.33	890.89	1105.36	26.5996	2659.96
445.73	886.91	1102.77	26.5771	2657.71
405.88	872.11	1093.15	26.4921	2649.21
369.81	858.92	1084.57	26.4149	2641.49
361.34	855.85	1082.58	26.3967	2639.67
353.07	852.87	1080.64	26.3789	2637.89
337.12	847.14	1076.92	26.3446	2634.46
307.46	836.59	1070.06	26.2806	2628.06
287.03	829.4	1065.39	26.2364	2623.64
280.54	827.13	1063.91	26.2223	2622.23
256.07	818.62	1058.38	26.1691	2616.91
233.81	810.96	1053.4	26.1207	2612.07
228.57	809.17	1052.24	26.1092	2610.92
223.45	807.42	1051.1	26.098	2609.8
213.56	804.06	1048.91	26.0764	2607.64
195.12	797.82	1044.86	26.0361	2603.61
182.38	793.53	1042.07	26.0081	2600.81
178.32	792.18	1041.19	25.9992	2599.92
163.01	787.07	1037.87	25.9655	2596.55
155.87	784.7	1036.33	25.9498	2594.98
149.05	782.44	1034.86	25.9348	2593.48
139.38	779.25	1032.79	25.9134	2591.34
136.31	778.24	1032.13	25.9066	2590.66
124.68	774.42	1029.65	25.8809	2588.09

=====

Table B4-1. Corrected Results from the Case of Sodium Bicarbonate with NSR = 13.5 (Figure 26)

Corrected Data			
Time (min)	(SO <sub>2</sub> ) (ppm)	(NO <sub>x</sub> ) (ppm)	(NO) (ppm)
0	1745.43	1497.93	1482.14
0.25	1652.04		
0.5		1338.24	
1			1124.61
1.5			
2			956.858
2.5		933.596	
2.75	1065.02		
3			
3.5		884.353	
4			805.398
4.5		853.12	
5			764.175
5.25	578.817		
5.5			
6			705.698
6.5		826.672	
7			681.728
7.5		789.435	
7.75	250.059		
8			652.007
8.5		764.205	
9			
9.5			
10			
10.25	83.2901		
10.5			



11  
12  
12.75 6.10909  
13

=====

Table B4-2. Simulation Results from the Case of Sodium Bicarbonate  
with NSR = 13.5 (Figure 26)

Simulated Data (with  $k_A=7.65$ ,  $k_B=1.06E8$ , and  $x=0.70$ )

(SO <sub>2</sub> ) (ppm)	(NO <sub>x</sub> ) (ppm)	(NO) (ppm)	R ( $\mu$ m)	R*100 ( $\mu$ m)
1745.43	1482.14	1497.93	29	2900
1561.21	1376.78	1401.25	28.9174	2891.74
1397.26	1289.34	1321.01	28.8442	2884.42
1120.92	1154.34	1197.13	28.7216	2872.16
900.74	1056.97	1107.78	28.6244	2862.44
724.76	985.09	1041.82	28.5471	2854.71
583.78	931.04	992.22	28.4852	2848.52
524.11	909.07	972.06	28.4591	2845.91
470.62	889.82	954.39	28.4357	2843.57
379.65	858	925.2	28.3959	2839.59
306.43	833.23	902.46	28.3639	2836.39
247.44	813.78	884.62	28.3381	2833.81
199.88	798.44	870.54	28.3173	2831.73
179.66	792.01	864.64	28.3085	2830.85
161.5	786.27	859.37	28.3006	2830.06
130.52	776.58	850.48	28.287	2828.7
105.5	768.85	843.38	28.2761	2827.61
85.29	762.65	837.7	28.2673	2826.73
68.96	757.68	833.14	28.2602	2826.02
62.01	755.58	831.21	28.2571	2825.71
55.77	753.69	829.48	28.2544	2825.44
45.1	750.48	826.53	28.2498	2824.98
36.47	747.9	824.16	28.246	2824.6
29.5	745.81	822.25	28.243	2824.3
23.86	744.13	820.7	28.2405	2824.05
21.46	743.41	820.05	28.2394	2823.94
19.3	742.77	819.46	28.2385	2823.85

15.61	741.68	818.45	28.2369	2823.69
10.21	740.08	816.98	28.2345	2823.45
7.43	739.25	816.23	28.2333	2823.33
6.68	739.03	816.03	28.233	2823.3

=====

Table B5-1. Corrected Results from the Case of Sodium Sesquicarbonate with NSR = 0.85 (Figure 27)

=====			
CORRECTED DATA			
=====			
Time (min)	SO2 (ppm)	NOx (ppm)	NO (ppm)
0	1725.517	1491.929	1487.89
0.25	1620.329		
0.5		1465.613	
1			1397.521
1.5		1424.988	
2			1358.913
2.5			
2.75	1528.297		
3		1388.063	
3.5			
4			1321.953
4.5			
5			
5.25	1433.181		
5.5			
6		1350.232	
7			
7.75			
8			1213.526
9			
10			
10.25	1343.537		
10.5			

11		1309.191	
12			
12.75	1326.151		
13			
14			1160.158
15			
15.25	1320.908		
15.5			
16			
17		1299.563	
17.75	1293.54		
18			
19			
20			
20.25	1287.445		
20.5			
21			1160.198
22			
22.75	1275.983		
23			
24		1339.357	
24.5			1082.578
25		1316.741	
26			

=====

Table B5-2. Simulation Results from the Case of Sodium Sesquicarbonate with NSR = 0.85 (Figure 27)

SIMULATION (with  $k_A=8.77$ ,  $k_B=1.24E8$ , and  $x=0.55$ )

=====

SO2 (ppm)	NO (ppm)	NOx (ppm)	R(um)	R(um) X 100
1725.52	1487.89	1491.93	29	2900
1711.94	1479.2	1485.63	28.899	2889.9
1698.55	1470.69	1479.46	28.7989	2879.89
1672.37	1454.19	1467.5	28.6014	2860.14
1646.94	1438.33	1456	28.4074	2840.74
1622.23	1423.09	1444.95	28.2166	2821.66
1598.21	1408.43	1434.32	28.029	2802.9
1586.45	1401.31	1429.16	27.9364	2793.64
1574.85	1394.33	1424.1	27.8445	2784.45
1552.14	1380.74	1414.25	27.6631	2766.31
1530.04	1367.65	1404.76	27.4845	2748.45
1508.54	1355.03	1395.61	27.3088	2730.88
1487.6	1342.85	1386.78	27.1357	2713.57
1477.34	1336.93	1382.48	27.0502	2705.02
1467.21	1331.1	1378.26	26.9654	2696.54
1447.35	1319.76	1370.03	26.7976	2679.76
1409.14	1298.19	1354.4	26.4694	2646.94
1381.73	1282.95	1343.35	26.2295	2622.95
1372.82	1278.03	1339.78	26.1507	2615.07
1338.27	1259.14	1326.08	25.8408	2584.08
1305.36	1241.4	1313.23	25.5394	2553.94
1297.38	1237.14	1310.13	25.4653	2546.53
1289.5	1232.94	1307.09	25.3917	2539.17

=====

1274	1224.73	1301.14	25.246	2524.6
1244.07	1209.03	1289.76	24.9502	2496.02
1222.52	1197.85	1281.65	24.7505	2475.05
1215.5	1194.23	1279.03	24.6815	2468.15
1188.18	1180.25	1268.89	24.4097	2440.97
1162.06	1167.04	1259.31	24.1444	2414.44
1155.71	1163.84	1257	24.0791	2407.91
1149.42	1160.7	1254.71	24.0141	2401.41
1137.06	1154.52	1250.24	23.8854	2388.54
1113.1	1142.66	1241.64	23.6322	2363.22
1107.27	1139.79	1239.56	23.5698	2356.98
1090.14	1131.41	1233.48	23.3847	2338.47
1068.11	1120.72	1225.73	23.1426	2314.26
1046.96	1110.55	1218.36	22.9057	2290.57
1041.81	1108.08	1216.57	22.8473	2284.73
1036.71	1105.65	1214.8	22.7891	2278.91
1026.65	1100.86	1211.34	22.6738	2267.38
1007.13	1091.64	1204.65	22.4466	2244.66
992.98	1085	1199.84	22.2791	2227.91
988.36	1082.84	1198.27	22.2239	2222.39
970.29	1074.44	1192.18	22.0056	2200.56
961.51	1070.38	1189.24	21.898	2189.8
952.9	1066.41	1186.36	21.7914	2179.14
936.14	1058.74	1180.8	21.5813	2158.13

=====

Table B6-1. Corrected Results from the Case of Sodium Sesquicarbonate with NSR = 0.85 (Figure 32)

CORRECTED DATA			
Time (min)	SO2 (ppm)	NOx (ppm)	NO (ppm)
0	1569.756	1581.975	1556.903
0.5	1497.018		
1		1529.344	
1.5			1464.483
2			
2.5	1326.406		
3		1508.125	
3.5			1393.017
4		1503.519	
4.5			1371.661
5			
5.5		1478.6	
6			1336.753
6.5	1242.473		
7			
8		1455.079	
8.5			1297.742
9			
9.5	1206.109		
10		1427.857	
10.5			1266.533
11			
12			



12.5	1163.304		
13		1420.041	
13.5			1219.72
14			
15			
15.5	1103.927		
16		1412.225	
16.5			1184.409
17			
18			
18.5	1060.655		
19		1398.407	
19.5			1166.351
20			
20.5			
21			
21.5	1042.473		
22		1414.604	
22.5			1159.796
23			
24			
24.5	1032.621		
25			
25.5			
26			
27			
27.5	1015.881		
28		1410.979	
28.5			1158.187
29			

=====

Table B6-2. Simulation Results from the Case of Sodium Sesquicarbonate with NSR = 0.85 (Figure 32)

SIMULATION (with  $k_A=8.77$ ,  $k_B=1.24E8$ ,  $x=0.55$ )

SO2 (ppm)	NO (ppm)	NOx (ppm)	R(um)	R(um) X 100
1569.76	1556.9	1581.98	29	2900
1545.21	1540.51	1570.1	28.8155	2881.55
1521.35	1524.75	1558.67	28.6342	2863.42
1498.15	1509.57	1547.67	28.4561	2845.61
1475.58	1494.96	1537.07	28.2809	2828.09
1453.63	1480.88	1526.86	28.1088	2810.88
1432.25	1467.3	1517.02	27.9394	2793.94
1411.44	1454.19	1507.52	27.7728	2777.28
1391.18	1441.54	1498.35	27.6089	2760.89
1371.44	1429.33	1489.49	27.4476	2744.76
1352.2	1417.52	1480.93	27.2888	2728.88
1333.45	1406.11	1472.66	27.1325	2713.25
1315.16	1395.07	1464.66	26.9785	2697.85
1297.33	1384.39	1456.91	26.8268	2682.68
1279.94	1374.05	1449.41	26.6774	2667.74
1246.4	1354.33	1435.12	26.3851	2638.51
1230.23	1344.92	1428.3	26.2421	2624.21
1214.44	1335.8	1421.68	26.1011	2610.11
1199.02	1326.95	1415.26	25.962	2596.2
1183.95	1318.36	1409.04	25.8249	2582.49
1169.23	1310.02	1402.99	25.6896	2568.96
1154.84	1301.92	1397.12	25.5561	2555.61
1127.02	1286.4	1385.86	25.2945	2529.45

1113.57	1278.96	1380.47	25.1662	2516.62
1100.42	1271.73	1375.23	25.0396	2503.96
1087.54	1264.69	1370.13	24.9145	2491.45
1074.95	1257.84	1365.16	24.7911	2479.11
1050.55	1244.68	1355.62	24.5487	2454.87
1038.74	1238.36	1351.04	24.4297	2442.97
1027.17	1232.2	1346.57	24.3122	2431.22
1015.83	1226.19	1342.22	24.196	2419.6
1004.73	1220.34	1337.97	24.0812	2408.12
983.19	1209.06	1329.8	23.8556	2385.56
972.74	1203.63	1325.86	23.7447	2374.47
962.5	1198.32	1322.01	23.6351	2363.51
952.46	1193.15	1318.26	23.5267	2352.67
942.61	1188.1	1314.6	23.4195	2341.95
932.96	1183.16	1311.02	23.3135	2331.35
923.48	1178.34	1307.52	23.2086	2320.86
914.19	1173.63	1304.11	23.1049	2310.49
905.07	1169.02	1300.77	23.0022	2300.22
896.13	1164.52	1297.51	22.9007	2290.07
887.34	1160.12	1294.32	22.8001	2280.01
870.26	1151.61	1288.15	22.6022	2260.22
861.95	1147.49	1285.16	22.5048	2250.48
853.79	1143.47	1282.24	22.4083	2240.83
845.78	1139.52	1279.38	22.3128	2231.28
837.91	1135.66	1276.58	22.2182	2221.82
822.58	1128.18	1271.16	22.0318	2203.18
815.11	1124.56	1268.53	21.9399	2193.99
807.78	1121.01	1265.96	21.849	2184.9
800.57	1117.53	1263.44	21.7588	2175.88
793.48	1114.12	1260.96	21.6696	2166.96

=====

Table B7-1. Corrected Results from the Case of Sodium Sesquicarbonate with NSR = 3.38 (Figure 28)

=====			
CORRECTED DATA			
=====			
Time (min)	SO2 (ppm)	NOx (ppm)	NO (ppm)
0	1507.547	1533.95	1487.89
0.5			
1		1457.307	
1.5			
2			1261.144
2.5			
3	851.4231		
3.5			
4		1257.391	
4.5			
5			1059.051
5.5			
6	633.1955		
7		1219.56	
8			994.985
9	515.4968		
10		1181.729	
10.5			
11			959.674
12	421.9122		
13			
14			
15	357.7891		
15.5			

16		1118.073	
17			935.0609
18	291.1866		
19			
20			
20.5			
21	245.9431		
22		1126.454	
23			893.1945
24	142.529		
25			
26			
27	164.3607		
28		1110.823	
29			874.3325
30	124.0352		

=====

Table B7-2. Simulation Results from the Case of Sodium Sesquicarbonate with NSR = 3.38 (Figure 28)

SIMULATION (with  $k_A=8.77$ ,  $k_B=1.24$ , and  $x=0.55$ )

SO2 (ppm)	NO (ppm)	NOx (ppm)	R (um)	R(um) X100
1507.55	1487.89	1533.95	29	2900
1420.11	1432.85	1494.05	28.8286	2882.86
1338.66	1383.41	1458.2	28.6681	2866.81
1262.68	1338.84	1425.89	28.5177	2851.77
1191.72	1298.5	1396.64	28.3765	2837.65
1125.38	1261.89	1370.1	28.244	2824.4
1063.28	1228.56	1345.94	28.1193	2811.93
1005.09	1198.13	1323.87	28.002	2800.2
950.53	1170.27	1303.68	27.8915	2789.15
899.31	1144.72	1285.15	27.7873	2778.73
851.19	1121.22	1268.11	27.6891	2768.91
805.95	1099.56	1252.41	27.5963	2759.63
763.38	1079.57	1237.92	27.5088	2750.88
685.56	1043.96	1212.1	27.3478	2734.78
616.4	1013.29	1189.87	27.2038	2720.38
554.81	986.74	1170.62	27.0747	2707.47
499.84	963.64	1153.87	26.9589	2695.89
474.59	953.2	1146.3	26.9055	2690.55
450.7	943.44	1139.22	26.8548	2685.48
406.7	925.71	1126.37	26.7612	2676.12
367.25	910.1	1115.05	26.6768	2667.68
331.82	896.31	1105.05	26.6008	2660.08
299.98	884.09	1096.2	26.5322	2653.22
285.28	878.5	1092.15	26.5005	2650.05

271.33	873.24	1088.33	26.4703	2647.03
245.52	863.58	1081.32	26.4144	2641.44
222.26	854.96	1075.08	26.3638	2636.38
201.27	847.26	1069.49	26.3181	2631.81
182.33	840.37	1064.5	26.2767	2627.67
173.55	837.2	1062.2	26.2575	2625.75
165.22	834.19	1060.02	26.2392	2623.92
149.75	828.65	1056	26.2053	2620.53
135.76	823.67	1052.39	26.1746	2617.46
123.11	819.19	1049.14	26.1467	2614.67
111.66	815.16	1046.22	26.1215	2612.15
101.29	811.52	1043.58	26.0986	2609.86
91.9	808.24	1041.21	26.0779	2607.79
83.39	805.28	1039.06	26.0591	2605.91
75.68	802.61	1037.12	26.042	2604.2
68.7	800.2	1035.37	26.0265	2602.65

=====

Table B8-1. Corrected Results from the Case of Sodium Sesquicarbonate with NSR = 3.38 (Figure 29)

```

=====
CORRECTED DATA
=====

```

Time (min)	SO2 (ppm)	NOx (ppm)	NO (ppm)
0	1498.712	1533.95	1505.143
0.5			
1		1421.288	
1.5			
2			1238.14
2.5			
3	779.2395		
3.5			
4		1257.391	
4.5			
5			1099.309
5.5			
6	554.2251		
7		1165.532	
8			1023.74
9	451.2955		
10		1133.704	
10.5			
11			971.1762
12	349.0822		
13			
14			
15	275.2263		



15.5			
16		1118.073	
17			952.3142
18	249.0683		
19			
20			
20.5			
21	201.1042		
22		1120.451	
23			927.7011
24	146.1053		
25			
26			
27	131.2129		
28		1140.838	
29			931.8434
30	105.6567		

=====

Table B8-2. Simulation Results from the Case of Sodium Sesquicarbonate with NSR = 3.38 (Figure 29)

SIMULATION (with  $k_A=8.77$ ,  $k_B=1.24E8$ , and  $x=0.55$ )

=====

SO2 (ppm)	NO (ppm)	NOx (ppm)	R(um)	R(um) X 100
1533.95	1505.14	1533.95	29	2900
1444.99	1442.32	1486.64	28.8253	2882.53
1362.14	1391.72	1449.95	28.6619	2866.19
1284.87	1346.12	1416.9	28.5087	2850.87
1212.71	1304.9	1387.01	28.3649	2836.49
1145.26	1267.5	1359.89	28.2299	2822.99
1082.13	1233.47	1335.22	28.1029	2810.29
1022.98	1202.42	1312.71	27.9834	2798.34
967.52	1174.01	1292.12	27.8709	2787.09
915.46	1147.96	1273.23	27.7648	2776.48
866.56	1124.02	1255.87	27.6648	2766.48
820.59	1101.96	1239.87	27.5704	2757.04
777.33	1081.6	1225.12	27.4812	2748.12
698.24	1045.35	1198.83	27.3172	2731.72
627.96	1014.15	1176.22	27.1705	2717.05
565.36	987.15	1156.64	27.039	2703.9
509.5	963.66	1139.61	26.9209	2692.09
483.83	953.06	1131.92	26.8665	2686.65
459.55	943.13	1124.73	26.8148	2681.48
414.81	925.12	1111.67	26.7193	2671.93
374.69	909.26	1100.17	26.6333	2663.33
338.66	895.25	1090.01	26.5557	2655.57

=====

306.27	882.83	1081.01	26.4857	2648.57
291.31	877.16	1076.9	26.4533	2645.33
277.12	871.81	1073.02	26.4225	2642.25
250.85	861.99	1065.9	26.3654	2636.54
227.17	853.24	1059.55	26.3137	2631.37
205.8	845.41	1053.88	26.267	2626.7
186.5	838.41	1048.8	26.2246	2622.46
177.56	835.18	1046.46	26.205	2620.5
169.06	832.13	1044.25	26.1863	2618.63
153.3	826.49	1040.16	26.1516	2615.16
139.04	821.43	1036.49	26.1202	2612.02
126.13	816.87	1033.19	26.0917	2609.17
114.45	812.77	1030.21	26.0658	2606.58
103.86	809.07	1027.53	26.0424	2604.24
94.27	805.73	1025.11	26.0211	2602.11
85.58	802.72	1022.93	26.0018	2600.18
77.7	800	1020.95	25.9843	2598.43
70.56	797.54	1019.17	25.9684	2596.84

=====

Table B9-1. Corrected Results from the Case of Sodium Sesquicarbonate with NSR = 3.38 (Figure 30)

=====			
CORRECTED DATA			
=====			
Time (min)	SO2 (ppm)	NOx (ppm)	NO (ppm)
0	1497.735	1473.919	1453.383
0.5	1210.789		
1		1301.225	
1.5			1245.942
2			
2.5	779.2395		
3		1219.976	
3.5			1128.467
4		1185.354	
4.5			1095.609
5			
5.5		1154.432	
6			1054.949
6.5	697.5384		
7			
8		1100.894	
8.5			1010.187
9			
9.5	551.3629		
10		1079.676	
10.5			967.4762
11			
12			
12.5	458.3382		

13		1071.86	
13.5			914.912
14			
15			
15.5	397.4017		
16		1070.048	
16.5			845.0945
17			
18			
18.5	338.9096		
19		1038.219	
19.5			832.788
20			
20.5			
21			
21.5	302.3264		
22		1042.41	
22.5			820.4814
23			
24			
24.5	242.6758		
25			
25.5			
26			
27			
27.5	131.2129		
28		1074.804	
28.5			813.1216
29			

=====

Table B9-2. Simulation Results from the Case of Sodium Sesquicarbonate with NSR = 3.38 (Figure 30)

SIMULATION (with  $k_A=8.77$ ,  $k_B=1.24E8$ , and  $x=0.55$ )

SO2 (ppm)	NO (ppm)	NOx (ppm)	R(um)	R(um) X 100
1533.95	1505.14	1533.95	29	2900
1410.86	1399.96	1435.19	28.8304	2883.04
1329.93	1351.95	1400.39	28.6716	2867.16
1254.42	1308.66	1369	28.5228	2852.28
1183.9	1269.47	1340.59	28.3831	2838.31
1117.96	1233.89	1314.79	28.2519	2825.19
1056.23	1201.5	1291.3	28.1285	2812.85
998.39	1171.91	1269.85	28.0124	2801.24
944.15	1144.82	1250.22	27.903	2790.3
893.23	1119.97	1232.2	27.7999	2779.99
845.39	1097.11	1215.62	27.7026	2770.26
800.42	1076.04	1200.35	27.6108	2761.08
758.1	1056.59	1186.25	27.5241	2752.41
718.26	1038.6	1173.21	27.4422	2744.22
680.73	1021.93	1161.12	27.3647	2736.47
611.97	992.09	1139.48	27.2222	2722.22
580.48	978.71	1129.78	27.1566	2715.66
550.74	966.24	1120.75	27.0944	2709.44
522.65	954.61	1112.31	27.0356	2703.56
496.1	943.75	1104.44	26.9798	2697.98
471	933.59	1097.07	26.9269	2692.69
447.25	924.09	1090.18	26.8768	2687.68
403.52	906.83	1077.67	26.7841	2678.41

383.38	898.99	1071.99	26.7413	2674.13
364.31	891.63	1066.65	26.7006	2670.06
346.24	884.71	1061.64	26.662	2666.2
329.11	878.2	1056.92	26.6254	2662.54
297.47	866.31	1048.29	26.5575	2655.75
282.86	860.87	1044.35	26.5261	2652.61
269	855.74	1040.63	26.4963	2649.63
255.85	850.9	1037.12	26.4679	2646.79
243.37	846.34	1033.81	26.441	2644.1
220.27	837.95	1027.73	26.391	2639.1
209.58	834.1	1024.94	26.3678	2636.78
199.43	830.46	1022.3	26.3457	2634.57
189.78	827.01	1019.8	26.3248	2632.48
180.62	823.75	1017.44	26.3048	2630.48
171.91	820.66	1015.2	26.2859	2628.59
163.63	817.74	1013.08	26.2678	2626.78
155.76	814.97	1011.07	26.2506	2625.06
148.28	812.35	1009.17	26.2343	2623.43
141.17	809.86	1007.37	26.2188	2621.88
134.4	807.5	1005.66	26.2039	2620.39
121.85	803.14	1002.5	26.1765	2617.65
116.03	801.13	1001.04	26.1637	2616.37
110.49	799.22	999.66	26.1515	2615.15
105.22	797.41	998.34	26.14	2614
100.21	795.69	997.09	26.1289	2612.89
90.9	792.5	994.78	26.1085	2610.85
86.58	791.03	993.71	26.099	2609.9
82.47	789.62	992.7	26.0899	2608.99
78.55	788.29	991.73	26.0813	2608.13
74.82	787.03	990.81	26.0731	2607.31

=====

Table B10-1. Corrected Results from the Case of Sodium Sesquicarbonate with NSR = 3.38 (Figure 31)

CORRECTED DATA			
Time (min)	SO2 (ppm)	NOx (ppm)	NO (ppm)
0	1628.628	1473.919	1473.512
0.25	1444.873		
0.5		1339.547	
1			1201.984
1.5		1262.904	
2			1105.864
2.5			
2.75	903.0249		
3		1165.947	
3.5			
4			1022.896
4.5			
5			
5.25	713.9838		
5.5			
6		1116.11	
7			
7.75	576.7865		
8			937.474
9			
10			
10.25	502.3186		
10.5			



11		1045.054	
12			
12.75	420.6867		
13			
14			855.35
15			
15.25	357.2379		
15.5			
16			
17		1035.426	
17.75	291.2502		
18			
19			
20			
20.25	250.4137		
20.5			
21			826.6347
22			
22.75	250.3218		
23			
24		1045.204	
24.5			841.0325
25		1046.601	
25.75	205.7772		
26			

=====

Table B10-2. Simulation Results from the Case of Sodium Sesquicarbonate with NSR = 3.38 (Figure 31)

SIMULATION (with  $k_A=8.77$ ,  $k_B=1.24E8$ ,  $x=0.55$ )

=====

SO2 (ppm)	NO (ppm)	NOx (ppm)	R(um)	R(um) X 100
1628.63	1473.51	1473.92	29	2900
1580.56	1443.29	1452.01	28.906	2890.6
1534.21	1414.74	1431.31	28.8152	2881.52
1446.33	1362.15	1393.18	28.6422	2864.22
1364.42	1314.89	1358.92	28.4802	2848.02
1287.97	1272.26	1328.01	28.3282	2832.82
1216.53	1233.68	1300.04	28.1854	2818.54
1182.56	1215.74	1287.04	28.1172	2811.72
1149.69	1198.64	1274.64	28.0511	2805.11
1087.1	1166.73	1251.5	27.9247	2792.47
1028.41	1137.58	1230.37	27.8057	2780.57
973.34	1110.89	1211.02	27.6935	2769.35
921.62	1086.4	1193.26	27.5876	2758.76
896.93	1074.9	1184.93	27.5369	2753.69
873	1063.87	1176.93	27.4877	2748.77
827.26	1043.1	1161.87	27.3933	2739.33
743.63	1006.16	1135.09	27.2196	2721.96
687.08	981.93	1117.53	27.1014	2710.14
669.31	974.44	1112.09	27.0641	2706.41
603.1	947.02	1092.22	26.9247	2692.47
544	923.2	1074.94	26.7994	2679.94
530.23	917.73	1070.98	26.7701	2677.01

=====

516.84	912.45	1067.15	26.7415	2674.15
491.14	902.4	1059.86	26.6867	2668.67
443.77	884.16	1046.64	26.5851	2658.51
411.47	871.93	1037.78	26.5156	2651.56
401.27	868.11	1035	26.4936	2649.36
363.08	853.93	1024.73	26.4109	2641.09
328.72	841.38	1015.62	26.3362	2633.62
320.67	838.47	1013.51	26.3187	2631.87
312.84	835.64	1011.46	26.3016	2630.16
297.77	830.23	1007.54	26.2687	2626.87
269.86	820.3	1000.34	26.2077	2620.77
250.73	813.56	995.46	26.1657	2616.57
244.67	811.44	993.92	26.1524	2615.24
221.93	803.52	988.18	26.1023	2610.23
201.37	796.43	983.04	26.0569	2605.69
196.54	794.78	981.84	26.0462	2604.62
191.84	793.17	980.67	26.0358	2603.58
182.77	790.07	978.43	26.0157	2601.57
165.94	784.36	974.29	25.9784	2597.84
154.37	780.46	971.46	25.9527	2595.27
150.7	779.23	970.56	25.9445	2594.45
136.89	774.6	967.21	25.9138	2591.38
130.48	772.46	965.66	25.8995	2589.95
124.37	770.43	964.19	25.8859	2588.59
115.76	767.58	962.12	25.8667	2586.67
113.02	766.67	961.46	25.8606	2586.06

=====

## APPENDIX C

C===== PURPOSE OF THE PROGRAM =====

C  
C THE FOLLOWING PROGRAM IS AN EXAMPLE PROGRAM TO  
C DEMONSTRATE THE SIMULATION PROCESS USING SOLVAY'S  
C MODEL. DATA ARE TAKEN FROM TABLE 22, OR FIGURE 28,  
C FOR THE CASE OF SODIUM SESQUICARBONATE WITH NSR=3.4.  
C KINETIC PARAMETERS KA, KB, AND X WERE OBTAINED FROM  
C QPRO SOFTWARE FIRST, WITH WHICH THE CONCENTRATIONS  
C OF SO2, NO, AND NOX AND THE SHRINKING CORE RADIUS VS  
C REACTION TIME COULD BE PREDICTED.

C  
C=====

C\*\*\*\*\* DEFINITION OF VARIABLES & EXPERIMENTAL DATA \*\*\*\*\*

C  
C V: REACTOR VOLUME = 12864 ml = 12864 cm<sup>3</sup>  
C M: MOLECULAR WEIGHT OF SODIUM SESQUICARBONATE :  
C 226.04 g/mol  
C D: DENSITY OF SODIUM SESQUICARBONATE :  
C 2.112 g/ml ( g/cm<sup>3</sup> )  
C W: WEIGHT OF SODIUM SESQUICARBONATE INJECTED :  
C W = 0.36 g  
C R: MEAN RADIUS OF SHRINKING PARTICLES.  
C RO: INITIAL MEAN RADIUS OF PARTICLES  
C Ro = 58/2 um = 0.0029 cm  
C N: TOTAL NUMBER OF NaHCO3 PARTICLES INJECTED  
C N = W/(4/3\*3.14159\*Ro<sup>3</sup>\*D)  
C X: CONSTANT USED TO SIMPLIFY THE RATE EXPRESSION  
C X = 4\*PI\*N/V  
C A: CONCENTRATION OF SO2  
C AO: INITIAL CONCENTRALTION OF SO2  
C Ao = 1507.55 ppm  
C B: CONCENTRATION OF NO  
C --BO: INITIAL CONCENTRATION OF NO  
C Bo = 1487.89 ppm  
C C: CONCENTRATION OF NO2  
C CO: INITIAL CONCENTRATION OF NO2  
C Co = (NO2)o =46.06 ppm  
C NOX: INITIAL CONCENTRATION OF NOX

```

C      NOX = 1533.95 ppm
C XXX: CONCENTRATION OF NOX AT TIME TIME
C      XXX = A + B
C      KA: RATE CONSTANT FOR SO2 REMOVAL = 8.77 cm/min
C      KB: RATE CONSTANT FOR NO REMOVAL = 1.24E8 cm^4/(min)(mol)
C      XX: SELECTIVITY COEFFICIENT DEFINED IN EQUATION (3-20)
C      XX = 0.55
C      RA: DISAPPEARANCE RATE OF SO2
C      RA = dA/dt = -N*(4*3.14159*R^2)*KA*A / V
C      RB: DISAPPEARANCE RATE OF NO
C      RB = dB/dt = -N*(4*3.14159*R^2)*KB*A*B / V
C      RC: GENERATION RATE OF NO2
C      RC = dC/dt = - XX/2 RB
C      RR: RADIUS SHRINKING RATE OF PARTICLES
C      RR = -Y*(KA*A+KB*(1-XX/2)/2*A*B)
C      Y: CONSTANT USED TO SIMPLIFY THE RR EQUATION
C      Y = 0.666667*M/D
C      RG: IDEAL GAS LAW CONSTANT
C      RG = 0.082 atm L/mol K
C      T: REACTION TEMPERATURE
C      T = 260 F
C      P: REACTOR PRESSURE
C      P = 1 atm
C      TIME: REACTION TIME, min
C      DTIME: TIME DIVISION USED IN THE NUMERICAL METHOD FOR
C      SOLVING SIMULTANEOUS ORDINARY DIFFERENTIAL EQUATIONS
C      DTIME = 0.0005 min
C      KRA: A CONSTANT ( KRA=KA*X )
C      KRB: A CONSTANT ( KRB=KB*X )
C      FLAG: ACCUMULATED RUNNING TIME CORRESPONDING TO THE
C      TIME DIVISION, DTIME
C-----
C      DA, DB, DC, DR : PARAMETERS USED IN RUNGE-KUTTA METHOD
C-----
C      FA, FB, FC, FR, ADA, ADB, ADC, ADR, FPA, FPB, FPC, FPR,
C      PA, PB, PC, PR : PARAMETERS USED IN ADAMS-BASHFORTH-MOULTON
C      METHOD
C
C*****

```

```

REAL*8 A, B, C, R, AO, BO, CO, RO, KA, KB, V, M, D
REAL*8 W, N, VG, MOL, PI, RAO, RBO, RCO,X,Y, XX, NOX
REAL*8 KRA, KRB, TIME, DTIME, DA(4), DB(4), DC(4), DR(4)
REAL*8 FA(4),FB(4),FC(4),FR(4),ADA(4),ADB(4),ADC(4),ADR(4)
REAL*8 FPA, FPB, FPC, FPR, PA, PB, PC, PR, CCC
INTEGER FLAG
RA(A, R)=-KRA*A*R**2
RB(A, B, R)=-KRB*A*B*R**2
RC(A, B, R)=KRB/2*XX*A*B*R**2
RR(A, B) = -Y*(KA*A+KB*(1-XX/2)/2*A*B)
DATA V,M,D,W,RO,XX/12864, 226.04, 2.112, 0.36, 0.0029, 0.55/
DATA AO,BO,CO,PI/ 1507.55, 1487.89, 46.06, 3.14159/
DATA RG, T, P, DTIME/ 0.082, 260, 1., 0.0005/

```

```

C***** CALCULATION FOR THE NUMBER OF PARTICLES *****
C*****
N=W/4*3/PI/RO**3/D

```

```

C***** UNIT CONVERSION FROM ppm TO mol/cc FOR AO, BO AND CO *****
C*****
VG=AO*1.0E-9
T=(T+460)/1.8
MOL=P*VG/RG/T
AO=MOL
VG=BO*1.0E-9
MOL=P*VG/RG/T
BO=MOL
VG=CO*1.0E-9
MOL=P*VG/RG/T
CO=MOL

```

```

C***** CACULATION OF X, Y, KRA AND KRB *****
C*****
X=4*PI*N/V
Y=0.666667*M/D

```

```

KA=8.77
KB=1.24E8
KRA=KA*X
KRB=KB*X

```

```

C***** INITIALIZE A, B, C, R, AND TIME *****
C*****

```

```

A=AO
B=BO
C=CO
R=RO
TIME=0

```

```

C***** OUTPUT FILE SETUP FOR A PROGRAMMED RESULTS *****
C*****

```

```

OPEN(4, FILE='S31',STATUS='NEW',FORM='FORMATTED',ERR=902)
WRITE(4,*) '-----'
WRITE(4,*) ' TIME (SO2) (NO) (NOx) R'
WRITE(4,*) ' (min) (ppm) (ppm) (ppm) (um)'
WRITE(4,*) '-----'
WRITE(4,*) ' 0.0 1507.55 1487.89 1533.95 29.0000'

```

```

C***** RUNGE KUTTA METHOD APPLIED IN 1ST 4 POINTS *****
C*****

```

```

DO 10 I=1, 4
FA(I)=A
FB(I)=B
FC(I)=C
FR(I)=R
TIME=TIME+DTIME
DA(1)=DTIME*RA(A,R)
DB(1)=DTIME*RB(A,B,R)
DC(1)=DTIME*RC(A,B,R)
DR(1)=DTIME*RR(A,B)
DA(2)=DTIME*RA(A+DA(1)/2,R+DR(1)/2)
DB(2)=DTIME*RB(A+DA(1)/2,B+DB(1)/2,R+DR(1)/2)

```



```

DC(2)=DTIME*RC(A+DA(1)/2,B+DB(1)/2,R+DR(1)/2)
DR(2)=DTIME*RR(A+DA(1)/2,B+DB(1)/2)
DA(3)=DTIME*RA(A+DA(2)/2,R+DR(2)/2)
DB(3)=DTIME*RB(A+DA(2)/2,B+DB(2)/2,R+DR(2)/2)
DC(3)=DTIME*RC(A+DA(2)/2,B+DB(2)/2,R+DR(2)/2)
DR(3)=DTIME*RR(A+DA(2)/2,B+DB(2)/2)
DA(4)=DTIME*RA(A+DA(3),R+DR(3))
DB(4)=DTIME*RB(A+DA(3),B+DB(3),R+DR(3))
DC(4)=DTIME*RC(A+DA(3),B+DB(3),R+DR(3))
DR(4)=DTIME*RR(A+DA(3),B+DB(3))
A=A+(DA(1)+2*DA(2)+2*DA(3)+DA(4))/6
B=B+(DB(1)+2*DB(2)+2*DB(3)+DB(4))/6
C=C+(DC(1)+2*DC(2)+2*DC(3)+DC(4))/6
R=R+(DR(1)+2*DR(2)+2*DR(3)+DR(4))/6

```

10 CONTINUE

FLAG=3

C\*\*\*\*\* MARK FOR THE NEXT TIME DIVISION CALCULATION \*\*\*\*\*  
C\*\*\*\*\*

5 FLAG=FLAG+1  
TIME=FLAG\*DTIME

C\*\*\*\*\* ADAMS-BASHFORTH-MOULTON METHOD APPLIED FOR THE REST  
C\*\*\*\*\*

```

ADA(1)=RA(FA(1), FR(1))
ADB(1)=RB(FA(1), FB(1), FR(1))
ADC(1)=RC(FA(1), FB(1), FR(1))
ADR(1)=RR(FA(1), FB(1))
ADA(2)=RA(FA(2), FR(2))
ADB(2)=RB(FA(2), FB(2), FR(2))
ADC(2)=RC(FA(2), FB(2), FR(2))
ADR(2)=RR(FA(2), FB(2))
ADA(3)=RA(FA(3), FR(3))
ADB(3)=RB(FA(3), FB(3), FR(3))
ADC(3)=RC(FA(3), FB(3), FR(3))
ADR(3)=RR(FA(3), FB(3))

```



