

**IPST Technical Paper Series Number 548**

The Rate of Depletion of NO by Reaction with Molten Sodium Salts

L.M. Thompson and H.J. Empie

January 1995

Submitted to  
Journal of Pulp and Paper Science

*Copyright© 1995 by the Institute of Paper Science and Technology*

*For Members Only*

## The Rate of Depletion of NO by Reaction with Molten Sodium Salts

Laura M. Thompson and H. Jeff Empie

Institute of Paper Science and Technology

Atlanta, Georgia

### Abstract

Reactions of NO with molten sodium species have been identified as a possible depletion mechanism in a kraft recovery furnace. Experiments have been conducted in which nitric oxide in helium was bubbled through molten sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and mixtures of  $\text{Na}_2\text{CO}_3$  and sodium sulfide ( $\text{Na}_2\text{S}$ ). Results show that the depletion of NO follows a pseudo first order rate expression. The rate of reaction is enhanced by the presence of sodium sulfide. Calculated activation energies are 89.0 and 41.2 kcal/mol for reaction with  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3/\text{Na}_2\text{S}$  mixtures, respectively. Analysis of gaseous products indicate that NO is being reduced to nitrogen and oxygen according to the overall stoichiometry:  $\text{NO} \rightarrow \frac{1}{2}\text{N}_2 + \frac{1}{2}\text{O}_2$ .

### Introduction

The formation of  $\text{NO}_x$  in a kraft recovery furnace is believed to occur by way of the fuel  $\text{NO}_x$  formation mechanism. However, it has been estimated that only ~ 25 % of the nitrogen in black liquor is emitted as  $\text{NO}_x$  from a typical recovery furnace.<sup>1</sup> Thus, the question remains as to the fate of the remaining nitrogen. It is feasible that a portion of the nitrogen does not get oxidized and either remains in the char or is released as a reduced nitrogen species in the flue gas. It is also possible that once  $\text{NO}_x$  is formed it reacts with other species present in the furnace and is reduced.

In previous papers we presented the concept that the concentration of nitric oxide could potentially be reduced in a recovery furnace by reacting with molten sodium species.<sup>2,3</sup> Experiments were conducted in which nitric oxide in helium was bubbled through molten sodium carbonate ( $\text{Na}_2\text{CO}_3$ ). Results showed that NO was reduced by 10 to 75% over the temperature range of 860 to 973°C.<sup>3</sup> The rate of depletion was shown to follow a pseudo first order rate expression as follows:

$$-r_{\text{NO}} = -\frac{1}{V_L} \frac{\delta N_{\text{NO}}}{\delta t} = \frac{aP_{\text{NO}}}{\frac{1}{k_g} + \frac{H_{\text{NO}}}{\sqrt{D_{\text{NO}}/Na}k_1}} \quad (\text{Eq. 1})$$

Upon integration and rearranging terms, equation (1) can be written as:

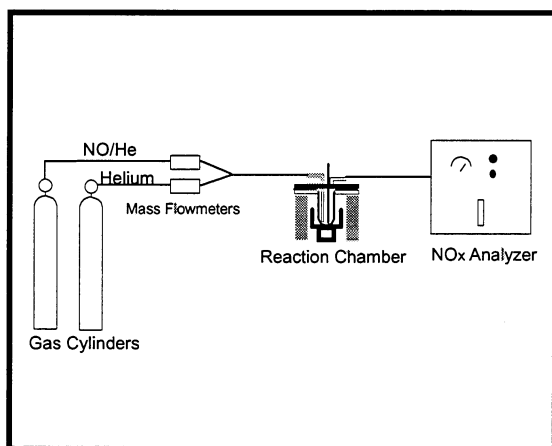
$$k_1 = \left( \frac{1}{\frac{a}{-\ln \Psi} - \frac{1}{H_{\text{NO}}k_g}} \right)^2 \frac{1}{(D_{\text{NO}}/Na)} \quad (\text{sec}^{-1}) \quad \text{where, } \Psi = P_{\text{NO},f}/P_{\text{NO},i} \quad (\text{Eq. 2})$$

Constants in equation (2) are calculated from correlations found in the literature. In short,  $a$  and  $t$  are functions of the gas flow rate.  $H_{\text{NO}}$ ,  $k_g$ , and  $D_{\text{NO/Na}}$  are dependent on temperature. Thus, the pseudo first order rate constant can be found as a function of concentration, flow rate, and temperature. A complete list of equations and notation is included at the end of the paper.

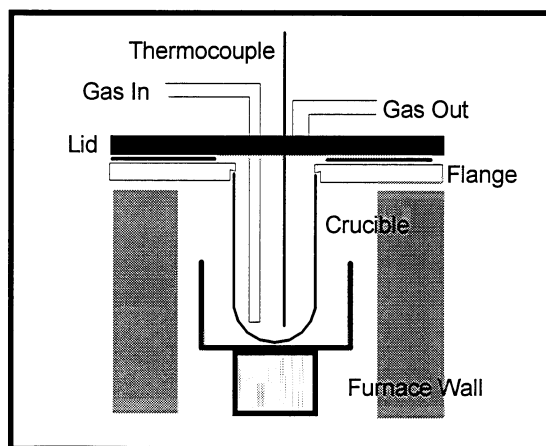
The derivation of equation (1) assumes the reaction to be first order with respect to  $\text{NO}$ .<sup>4</sup> Data verifying this assumption will be presented here. This paper also presents results of experiments investigating the reaction of  $\text{NO}$  with mixtures of  $\text{Na}_2\text{CO}_3$  and sodium sulfide ( $\text{Na}_2\text{S}$ ). In addition to the rate data, analysis of the gaseous products has been conducted by on-line gas chromatography to determine the products of the reaction.

### Experimental Apparatus

A schematic of the experimental apparatus is shown below in Figure 1. Helium and a mixed gas of nitric oxide in helium are fed from pressurized gas cylinders. Flow is measured by Hastings-Teledyne™ digital mass flowmeters and is controlled manually by needle valves. The gas is fed to the reaction chamber (Figure 2) which is described in detail below. Exit gas from the system is analyzed by a chemiluminescent  $\text{NO}_x$  analyzer (Thermo Environmental™ Model 10AR). A Carle™ Model 8000 Basic Gas Chromatograph equipped with a six port sampling valve was used for detection of oxygen ( $\text{O}_2$ ) and nitrogen ( $\text{N}_2$ ) in the exit gas. The GC was fitted with a 15 foot x 1/8 inch stainless steel column packed with Carboxen™ 1000. The column and inlet temperatures were held constant at approximately  $40^\circ\text{C}$ . Chromatographic grade helium was used as the carrier gas at a flow rate of 28 ml/min. The sample loop on the sampling valve had a volume of 1.0 ml.



**Figure 1:** Experimental Apparatus



**Figure 2:** Reaction Chamber

Molten salt is contained in a 4 cm x 10 cm alumina crucible which is cemented to a stainless steel flange. A graphite gasket is placed between the flange and the lid which is held in place by eight bolts to form a gas-tight seal. The reaction vessel is heated by a tube furnace. Gases are bubbled through the salt using a 0.4 cm ID alumina tube. A type-K thermocouple, protected by an alumina well, is used to measure the temperature of the molten salt. The mass flowmeters, thermocouple, and NO<sub>x</sub> analyzer are connected to a personal computer for data acquisition. Data are acquired at a rate of 0.5 Hz.

### Experimental Conditions

The independent variables for each experiment include: gas flow rate, NO concentration, temperature, and the mass of each salt. The experimental conditions for each run are listed below in Tables 1, 2, and 3. The first set of experiments was conducted to verify the assumption of the first order behavior with respect to the concentration of NO. For the second set of experiments, the exit gases were analyzed by on-line GC. The third set of experiments was conducted to compare the rate of reaction for mixtures of Na<sub>2</sub>CO<sub>3</sub>/Na<sub>2</sub>S with the results for Na<sub>2</sub>CO<sub>3</sub> only. On-line GC analysis was conducted for all of the experiments with the mixed salts. For experiments where samples were analyzed by GC, three to five replicate samples were analyzed at each set of conditions.

**Table 1:** Experimental Conditions For Determining Order of Reaction With Respect to [NO].

Experiment	Total Flow Rate (L/min)	[NO] <sub>in</sub> (ppm in helium)	Temperature (°C)	Mass of Na <sub>2</sub> CO <sub>3</sub> (g)	Mass of Na <sub>2</sub> S (g)
1	1.3	2700-8400	864-946	35.0	---
2	1.3	2700-8400	868-954	35.0	---
3	1.3	2000-9400	883-890	38.0	2.0
4	1.3	2000-9400	895-912	38.0	2.0

**Table 2:** Experimental Conditions For Depletion of NO by Na<sub>2</sub>CO<sub>3</sub> With Gas Analysis by GC.

Experiment	Total Flow Rate (L/min)	[NO] <sub>in</sub> (ppm in helium)	Temperature (°C)	Mass of Na <sub>2</sub> CO <sub>3</sub> (g)	Mass of Na <sub>2</sub> S (g)
5	1.1	8400	887-961	30.0	---
6	1.1	8400	897-962	30.0	---
7	1.0	8400	894-966	40.0	---
8	1.0	8400	905-962	40.0	---
9	1.2	8400	910-946	25.0	---
10	1.3	9600	889-951	40.0	---

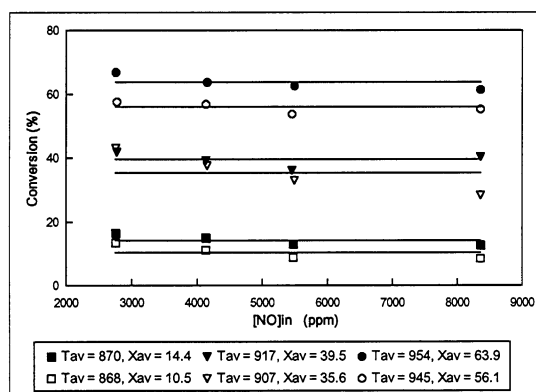
**Table 3:** Experimental Conditions For Depletion of NO by Mixtures of Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>S With Gas Analysis by GC.

Experiment	Total Flow Rate (L/min)	[NO] <sub>in</sub> (ppm in helium)	Temperature (°C)	Mass of Na <sub>2</sub> CO <sub>3</sub> (g)	Mass of Na <sub>2</sub> S (g)
11	1.3	9600	887-934	40.0	1.5
12	1.3	9600	860-914	40.0	1.5
13	1.3	9600	878-920	40.0	1.5
14	1.0	9600	878-917	35.0	1.3
15	1.0	9600	879-914	35.0	1.3
16	1.1	9600	882-915	30.0	2.0
17	1.1	9600	864-928	30.0	2.0
18	0.92-1.3	9600	870-916	37.0	3.0

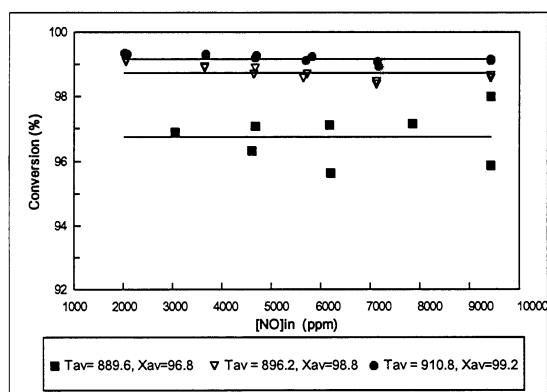
## Results

To verify that the depletion of NO is first order with respect to [NO], experiments were conducted in which the inlet concentration was varied between 2000 to 9400 ppm at a constant temperature. This was repeated at several temperatures between 860 to 955°C for reactions with Na<sub>2</sub>CO<sub>3</sub> and a mixture of Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>S. The results of these experiments were plotted as conversion vs. inlet concentration. The data are shown below in Figures 3 and 4. The percent conversion is defined as:

$$X = 100 \left( 1 - \frac{[NO]_f}{[NO]_i} \right). \quad (\text{Eq. 3})$$



**Figure 3:** Conversion of NO is Independent of Inlet Concentration. Data From Experiments 1 and 2. Reactant: Na<sub>2</sub>CO<sub>3</sub>.



**Figure 4:** Conversion of NO is Independent of Inlet Concentration. Data From Experiments 3 and 4. Reactant: Na<sub>2</sub>CO<sub>3</sub>/Na<sub>2</sub>S Mixture.

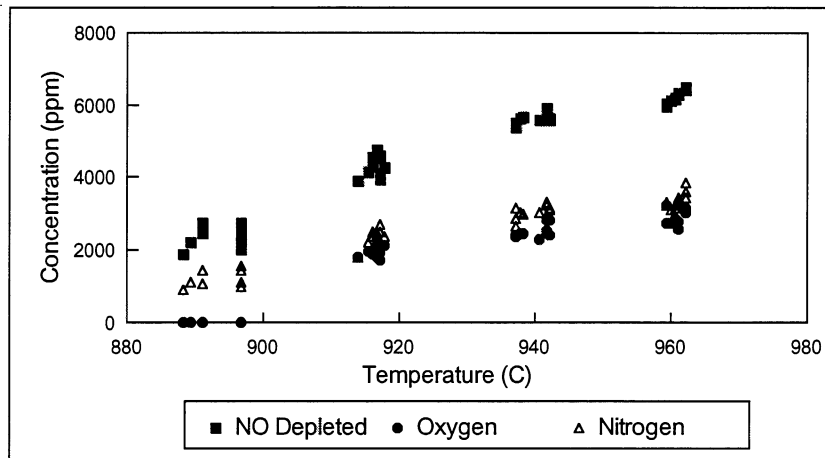
Inspection of Figures 3 and 4 shows constant conversion over the range of inlet concentrations at each temperature. This behavior is indicative of a first order reaction. It should also be noted that much higher conversions are observed for the reactions with the mixed salt.

The gas chromatograph was calibrated using a certified gas mix standard of 5100 ppm O<sub>2</sub> and 5040 ppm N<sub>2</sub> in UHP helium. By mixing the standard with NO in helium, the GC was calibrated at five concentrations between 0 to 5100 ppm O<sub>2</sub>, 0 to 5040 ppm N<sub>2</sub>, and 0 to 4600 ppm NO. The peak areas for nitrogen were linear with respect to concentration. It was found that the presence of nitric oxide reduces the peak area for oxygen. Therefore, a multiple linear regression for peak area as a function of NO and O<sub>2</sub> concentration was used. Typical results from the regression analyses are as follows:

$$\text{For Nitrogen: Peak Area} = 9.40 \times [\text{N}_2] \quad (\text{R-squared} = 0.975) \quad (\text{Eq. 4})$$

$$\text{For Oxygen: Peak Area} = 7.05 \times [\text{O}_2] - 2.13 \times [\text{NO}] \quad (\text{R-squared} = 0.953) \quad (\text{Eq. 5})$$

It should be noted that at low peak areas for O<sub>2</sub> and/or high concentrations of NO, the multiple regression model will over predict the O<sub>2</sub> concentration.

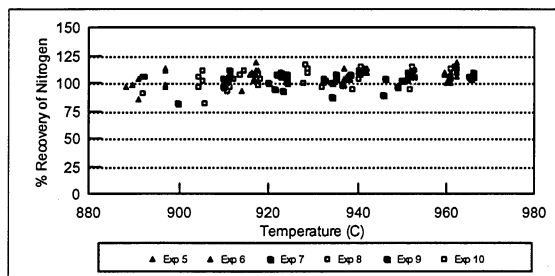


**Figure 5:** GC Analysis of Exit Gas For Experiments 5 and 6.

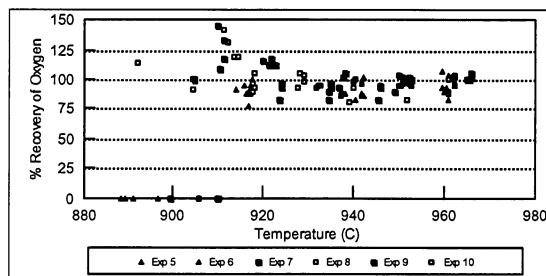
Figure 5 shows the amount of NO depleted ( $\text{NO}_{\text{in}} - \text{NO}_{\text{out}}$ ) and the exit gas concentrations for oxygen and nitrogen for experiments 5 and 6. These data show that over the temperature range 890 to 965°C, the O<sub>2</sub> and N<sub>2</sub> concentrations are approximately equal to each other and approximately half of the NO concentration that was depleted. This indicates that the NO is being reduced completely to N<sub>2</sub> and O<sub>2</sub> which can be represented by the stoichiometric equation :  $\text{NO} = \frac{1}{2} \text{N}_2 + \frac{1}{2} \text{O}_2$ . By assuming this stoichiometry, the percent recovery for each species can be calculated as follows:

$$\% \text{ Recovery} = 100 * 2 * [\text{O}_2 \text{ or } \text{N}_2] / [\text{NO}]_{\text{depleted}} \quad (\text{Eq. 6})$$

Figures 6 and 7 show the percent recovery of each species for experiments 5 through 10. The data shown in Figures 6 and 7 are summarized in Table 4. The percent recovery is reported as the average for each experiment plus or minus one standard deviation.



**Figure 6:** Recovery of NO as Nitrogen ( $N_2$ ).



**Figure 7:** Recovery of NO as Oxygen ( $O_2$ ).

**Table 4:** Recovery of NO as Nitrogen and Oxygen For Experiments 5 - 10.

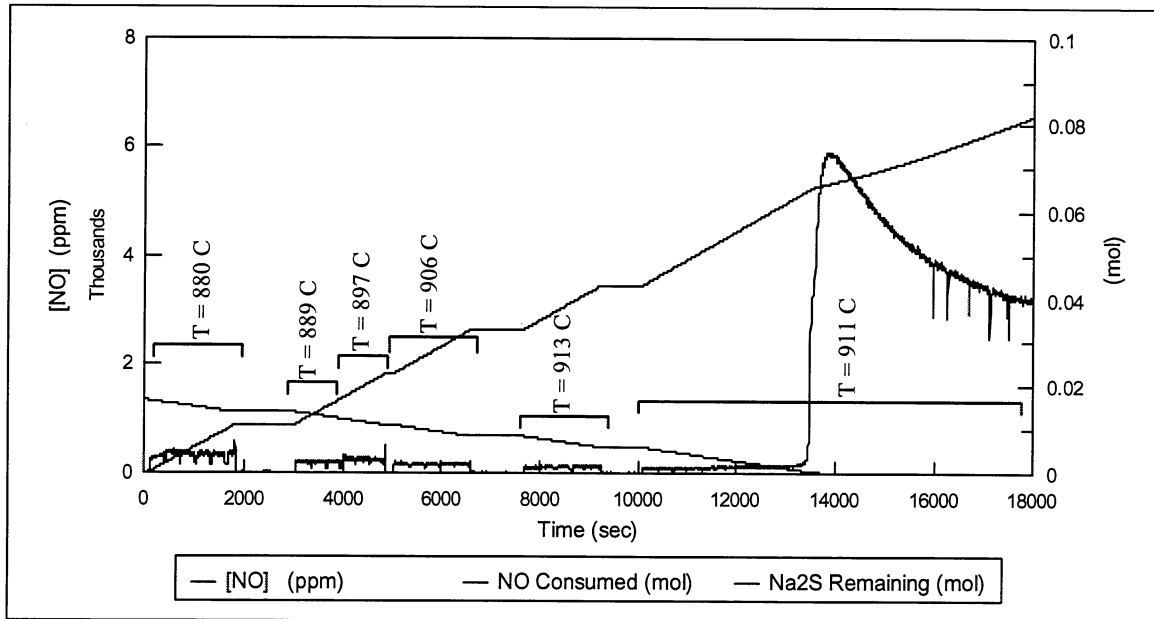
Experiment	5	6	7	8	9	10
% Recovery as $N_2$	$103.5 \pm 6.3$	$109.8 \pm 5.3$	$103.9 \pm 6.4$	$107.2 \pm 8.5$	$102.2 \pm 6.3$	$102.7 \pm 4.4$
% Recovery as $O_2$	$89.8 \pm 5.8$	$92.6 \pm 6.4$	$103.8 \pm 7.1$	$102.0 \pm 13.7$	$99.2 \pm 17.0$	$97.2 \pm 5.8$

The third set of experiments (11-18) was conducted to determine the rate of depletion of NO by reaction with mixtures of  $Na_2CO_3$  and  $Na_2S$ . During these experiments the exit gas was also analyzed by on-line GC. In the presence of sodium sulfide it was not possible to detect any oxygen in the exit gas. It was therefore assumed that the oxygen was reacting with sulfide to form sodium sulfate. Results of analysis of the salts from experiments 16 and 17 is shown below in Table 5. These results verify the assumption of complete conversion of all sulfide to sulfate with minor amounts of thiosulfate indicated.

**Table 5:** Analysis of  $Na_2CO_3/Na_2S$  Mixtures After Exposure To Nitric Oxide. All Concentrations are Reported as Percent by Weight. Results Indicate Complete Conversion of Sodium Sulfide to Sodium Sulfate. ND Indicates Not Detectable.

Ion	Experiment 16	Experiment 17
Sulfite, $SO_3^-$	-ND-	-ND-
Thiosulfate, $S_2O_3^-$	0.04 %	0.02 %
Sulfate, $SO_4^-$	6.38 %	6.26 %
Carbonate, $CO_3^-$	54.25 %	51.34 %
Sodium, $Na^+$	40.4 %	44.6 %
Total	101.07 %	102.22 %

By assuming the overall reaction:  $4NO + Na_2S \rightarrow Na_2SO_4 + 2N_2$ , it is possible to calculate the rate of depletion of  $Na_2S$  as a function of the amount of  $NO$  depleted. Figure 8 shows the measured values of the  $NO$  concentration along with the calculated values for total  $NO$  consumed and total  $Na_2S$  remaining as a function of time for experiment 15.

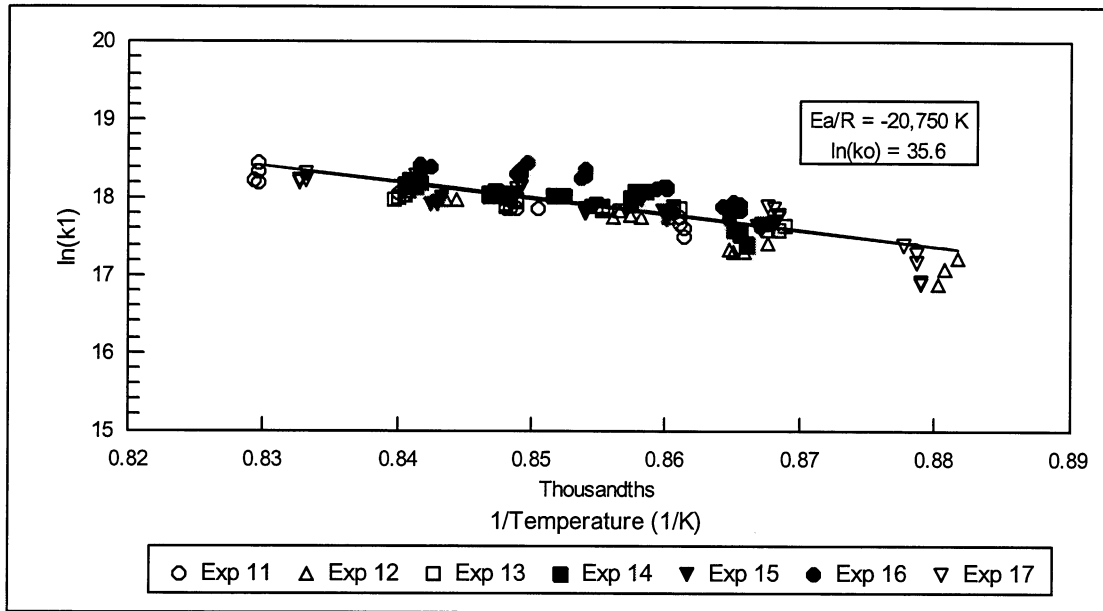


**Figure 8:** Depletion of  $NO$  by Reaction with Molten  $Na_2CO_3/Na_2S$ ; Experiment 15.

Inspection of Figure 8 reveals several interesting points:

- ♦ When all of the sodium sulfide has reacted ( $Na_2S$  remaining = 0) there is a sudden rise in the concentration of  $NO$ . This indicates a shift in the reaction mechanism upon total consumption of  $Na_2S$ .
- ♦ GC analysis of gas samples analyzed after this point show the presence of oxygen ( $O_2$ ) in equal proportion to  $N_2$ . This also supports the concept that the sulfide has been completely oxidized.
- ♦ As long as  $Na_2S$  is present, the concentration of  $NO$  is constant at any given temperature independent of the concentration of  $Na_2S$ . Just before the sulfide is completely consumed, the  $NO$  concentration starts to change. This supports the concept that the reaction is pseudo first order as long as there is at least approximately 0.002 mol of  $Na_2S$  in the melt.

Equation 2 was used to calculate values for  $k_1$  over the temperature range,  $T = 860$  to  $934^\circ\text{C}$ , for experiments 11 through 17. These results were then used to calculate the activation energy ( $E_a$ ) and the pre-exponential factor ( $k_0$ ) by plotting  $\ln(k_1)$  vs.  $1/T$  as shown in Figure 9.



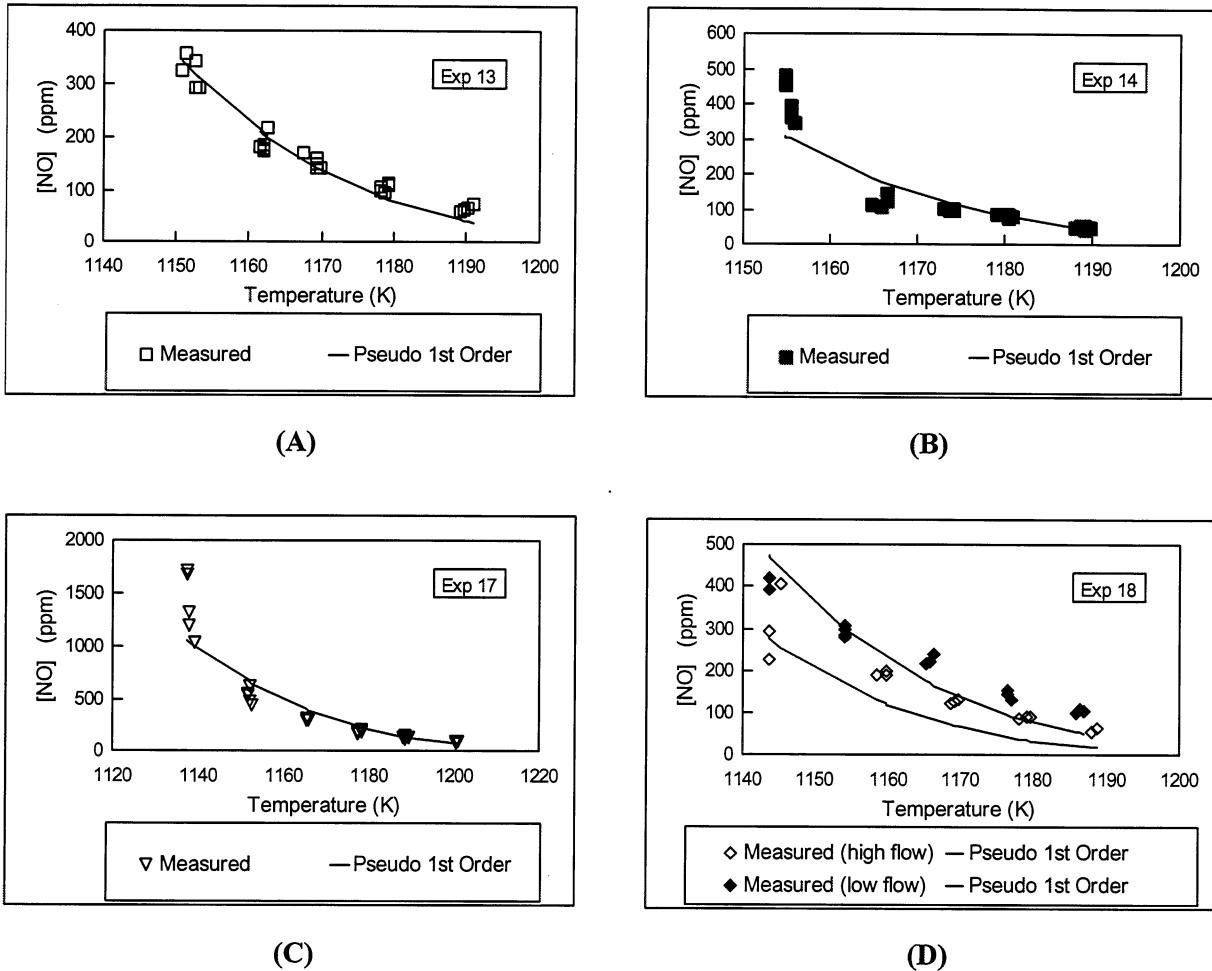
**Figure 9:** Determination of Activation Energy for Depletion of NO by  $\text{Na}_2\text{CO}_3/\text{Na}_2\text{S}$  Mixtures. Experiments 11-17.

Based on the results in Figure 9, the slope,  $-E_a/R$ , and intercept,  $\ln(k_0)$ , were found to be  $-20,750 \pm 2457$  K and  $35.63 \pm 0.37$ , respectively. These results are reported at a confidence level of 95%. Thus, the pseudo first order rate constant,  $k_1$ , may be written as:  $k_1 = 2.98 \times 10^{15} e^{-20,750/T} (\text{s}^{-1})$ .

With values for the rate constant it becomes possible to predict the exit gas concentration as:

$$[NO]_f = [NO]_i \times \exp\left(-\frac{at}{\frac{1}{H_{NO}k_g} + \frac{1}{\sqrt{D_{NO}/N_d k_1}}}\right). \quad (\text{Eq. 7})$$

This expression was used to compare predicted values for NO concentration with the measured values. Results of this comparison are shown in Figures 10A-D for experiments 13, 14, 17, and 18. Inspection of Figures 10A-D shows excellent agreement between the experimental and predicted values for the concentration of NO in the exit gas over a wide range of experimental conditions.



**Figure 10:** Comparison of Predicted and Measured Values for Concentration of Nitric Oxide in Exit Gas; Experiments 13,14,17 and 18.  $[\text{NO}]_{\text{in}} = 9600$  ppm for Each Experiment.

### Discussion/Conclusions

The rate of depletion of nitric oxide by reaction with molten  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3/\text{Na}_2\text{S}$  has been shown to follow a pseudo-first order rate expression. A comparison of the two systems is summarized in Table 6 below. The results show the depletion of NO to be greatly enhanced by the presence of  $\text{Na}_2\text{S}$ .

**Table 6:** A Comparison of Kinetic Parameters for the Depletion of NO by Reaction with  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3/\text{Na}_2\text{S}$  Mixtures.

Reactant	Temperature Range (°C)	% Conversion of NO	$E_a/R$ (°K)	$k_1$ at $T = 900$ °C ( $\text{s}^{-1}$ )
$\text{Na}_2\text{CO}_3$	860-973	10-75	44,780	$8.14 \times 10^5$
$\text{Na}_2\text{CO}_3/\text{Na}_2\text{S}$	860-934	90-99.9	20,750	$6.19 \times 10^7$

It is not clear at this point what the mechanism for the reaction is; however, analysis of the exit gas shows that all of the NO that is depleted can be detected as O<sub>2</sub> and N<sub>2</sub>. It is feasible that a nitrite or nitrate intermediate is formed which then thermally decomposes to nitrogen and oxygen. In the presence of sulfide, the oxygen is consumed forming sodium sulfate. Because the rate is independent of the concentration of Na<sub>2</sub>S, the consumption of Na<sub>2</sub>S does not affect the rate of reaction until nearly all of the sulfide has been oxidized.

These reaction data coupled with an aerosol (fume) formation model should be able to predict the amount of depletion that occurs in the upper region of a recovery furnace. However, it should be noted that it is not known what affect other gases (e.g. H<sub>2</sub>O, O<sub>2</sub>, CO, CO<sub>2</sub>, SO<sub>x</sub>) may have on the rate of depletion of NO.

### **Acknowledgments**

Portions of this work were used by L.M.T. as partial fulfillment of the requirements for the Ph.D. degree at the Institute of Paper Science and Technology. Daniel Wilberforce is gratefully acknowledged for his analysis of the salts. The authors would also like to acknowledge the Environmental Protection Agency for the loan of a chemiluminescent NO<sub>x</sub> analyzer.

## Equations

$$(Eq. 8)^5 \quad a = \frac{6\varepsilon}{d_b}$$

$$(Eq. 9)^6 \quad \varepsilon = 0.5 \left( \frac{U_{br}}{\sqrt{gR_c}} \right)^{0.4} \left( \frac{U_{gs}}{U_{br}} \right)^{0.8}$$

$$(Eq. 10)^7 \quad d_b = \left[ \left( \frac{\alpha \gamma D_t}{\Delta \rho g} \right)^2 + 9.5 \left( \frac{V_g^2 D_t}{g} \right)^{0.867} \right]^{\frac{1}{6}}$$

$$(Eq. 11)^8 \quad D_{NO/He} = \frac{10^{-4} (1.084 - 0.249 \sqrt{1/M_{NO} + 1/M_{He}}) T^{1.5} \sqrt{1/M_{NO} + 1/M_{He}}}{P_t (r_{NO/He})^2 f \left( \frac{kT}{\varepsilon_{AB}} \right)}$$

$$(Eq. 12)^9 \quad D_{NO/Na} = \frac{(117.3 \times 10^{-18}) (\varphi M_{Na})^{0.5} T}{\mu^{0.6}}$$

$$(Eq. 13)^{10} \quad k_g = \frac{D_{NO/He} P_t}{RT z P_{He,m}}$$

$$(Eq. 14)^{11} \quad k_L = 0.42 \left( \frac{D_{NO/Na}}{d_b} \right) \left( \frac{d_b^3 g \rho^2}{\mu^2} \right)^{\frac{1}{3}} \left( \frac{\mu}{\rho D_{NO/Na}} \right)^{0.5}$$

$$(Eq. 15)^{12} \quad K_H = \frac{\exp \left( \frac{-4119 - 2\gamma}{8.314T} \right)}{82.06T}$$

Physical properties of molten sodium carbonate can be calculated as a function of temperature according to the following:

$$(Eq. 16)^{13} \quad \rho = 2.4797 - 0.4487 * 10^{-3} T \text{ (g/cm}^3\text{)}$$

$$(Eq. 17)^{13} \quad \mu = 3.832 * 10^{-5} \exp(13215/T) \text{ (cp)}$$

$$(Eq. 18)^{14} \quad \gamma = (254.8 - 0.0502 t)/1000 \text{ (N/m), } t = \text{temperature (}^\circ\text{C)}$$

## Notation

a = interfacial area per unit volume (cm<sup>2</sup>/cm<sup>3</sup>)

A = solute gas

[A\*] = interfacial concentration of A (mol/cm<sup>3</sup>)

B = non-volatile reactant

[B<sub>o</sub>] = concentration of B in the bulk (mol/cm<sup>3</sup>)

C<sub>Na<sub>2</sub>CO<sub>3</sub></sub> = concentration of molten Na<sub>2</sub>CO<sub>3</sub> (mol/cm<sup>3</sup>)

C<sub>NO</sub> = concentration of NO in liquid film (mol/cm<sup>3</sup>)

d<sub>b</sub> = bubble diameter (cm)

D<sub>NO/He</sub> = diffusivity of NO in Helium (m<sup>2</sup>/s)

D<sub>NO/Na</sub> = diffusivity of NO in Na<sub>2</sub>CO<sub>3</sub> (m<sup>2</sup>/s)

D<sub>t</sub> = outside diameter of purge tube (m)

E<sub>a</sub> = activation energy (J/mol)

f(kT/ε<sub>AB</sub>) = collision function (= 0.31) (Treybal<sup>10</sup>, p. 32)

g = gravitational constant = (9.81 m/s)

H<sub>NO</sub> = phase distribution coefficient (atm cm<sup>3</sup>/mol)

$k$  = second order rate constant ( $\text{mol}/\text{cm}^3 \text{ s}$ )  
 $k_0$  = pre-exponential factor ( $1/\text{s}$ )  
 $k_1$  = pseudo first order rate constant ( $1/\text{s}$ )  
 $K_{\text{H}}$  = Henry's Law constant ( $\text{mol}/\text{cm}^3 \text{ atm}$ )  
 $m$  = order of reaction with respect to A  
 $m_{\text{Na}}$  = mass of  $\text{Na}_2\text{CO}_3$  (g)  
 $M_i$  = molecular weight of species,  $i$   
 $n$  = order of reaction with respect to B  
 $N$  = Avogadro's number = ( $6.022 \times 10^{23}$ )  
 $N_{\text{NO}}$  = moles of NO (mol)  
 $[\text{NO}]_f$  = exit concentration of NO (ppm)  
 $[\text{NO}]_i$  = inlet concentration of NO (ppm)  
 $P_{\text{He,m}}$  = log mean pressure of helium (atm)  
 $P_{\text{NO}}$  = partial pressure of NO (atm)  
 $P_t$  = total pressure (atm)  
 $r$  = molecular radius (m)  
 $-r_{\text{NO}}$  = rate of depletion of NO based on volume of liquid ( $\text{mol}/\text{cm}^3 \text{ s}$ )  
 $r_{\text{NO/He}}$  = molecular separation at collision (nm)  
 $R$  = universal gas constant = ( $8.314 \text{ m}^3 \text{ J/mol K}$ )  
 $R_c$  = radius of column = (0.02 m)  
 $t$  = time (s)  
 $T$  = absolute temperature (K)  
 $U_{\text{br}}$  = bubble rise velocity (m/s)  
 $U_{\text{gs}}$  = superficial gas velocity (m/s)  
 $V$  = flow rate of gas ( $\text{cm}^3/\text{s}$ )  
 $V_g$  = flow rate of gas ( $\text{m}^3/\text{s}$ )  
 $V_l$  = volume of molten salt ( $\text{cm}^3$ )  
 $X$  = percent conversion of NO  
 $z$  = film thickness = ( $10^{-4} \text{ m}$ ) (estimated)  
 $\alpha$  = correlation factor (assumed 30)  
 $\varepsilon$  = gas hold up  
 $\phi$  = association factor for solvent = 1  
 $v_{\text{NO}}$  = solute molal volume at boiling point (=  $0.0236 \text{ m}^3/\text{kmol}$ )

## References

1. Nichols, K.M., and Lien, S.J. Formation of Fuel  $\text{NO}_x$  During Black Liquor Combustion, Tappi Journal, 76(3):185(1993).
2. Thompson, L.M., and Empie, H.J. A Proposed Mechanism for the Depletion of  $\text{NO}_x$  in a Kraft Recovery Furnace, Proceedings of the 1993 TAPPI Environmental Conference, Boston, MA, 643-647(1993).
3. Thompson, L.M., and Empie, H.J. Kinetics of NO Depletion by Reaction with Molten Sodium Carbonate, AIChE Symposium Series, Volume 90:33-38(1994).
4. Levenspiel, O. Chemical Reaction Engineering, 2nd Edition, Chapter 13: Fluid-Fluid Reactions, John Wiley & Sons, New York, 1972.

5. Treybal, R.E. Mass-Transfer Operations, 3rd Edition, McGraw-Hill Book Company, New York, 1980, p.144.
6. Cheremisinoff, N.P. Encyclopedia of Fluid Mechanics, Volume 3: Gas-Liquid Flows, Gulf Publishing Company, Houston, 1986, p.1199.
7. Cheremisinoff, N.P. Encyclopedia of Fluid Mechanics, Volume 3: Gas-Liquid Flows, Gulf Publishing Company, Houston, 1986, p.228.
8. Treybal, R.E. Mass-Transfer Operations, 3rd Edition, McGraw-Hill Book Company, New York, 1980, p.31.
9. Treybal, R.E. Mass-Transfer Operations, 3rd Edition, McGraw-Hill Book Company, New York, 1980, p.35.
10. Treybal, R.E. Mass-Transfer Operations, 3rd Edition, McGraw-Hill Book Company, New York, 1980, p. 45.
11. Cussler, E.L. Diffusion: Mass Transfer in Fluid Systems, Cambridge University Press, New York, 1984, p.230.
12. Andresen, R.E. Journal of the Electrochemical Society, 328-334(1979).
13. Janz, G.J., Dampier, F.W., Lakshminarayanan, G.R., Lorenz, P.K., and Tomkins, R.P.T. Molten Salts: Volume 1, Electrical Conductance, Density, and Viscosity Data, National Standard Reference Data Series-National Bureau of Standards 15, October, 1968.
14. Janz, G.J., Lakshminarayanan, G.R., Tomkins, R.P.T., and Wong, J. Molten Salts: Volume 2, Section 2: Surface Tension Data, National Standard Reference Data Series-National Bureau of Standards 28, August, 1969.



