Absorption of Nitric Oxide from Flue Gas using Ammoniacal Cobalt(II) Solutions

by Hesheng Yu
Supervisor: Dr. Zhongchao Tan
Outline

1. Background
2. Selection of Absorbent
3. Determination of Equilibrium Constants
4. Kinetic Study
5. Effect of Oxygen and Absorbent Regeneration
6. Mass Transfer in Industrial Gas-Liquid Contactors
7. Conclusions
1. Background
NOx Emissions from Conventional Power Plants in U.S., 1999-2010
## Nitrogen Oxides Facts

<table>
<thead>
<tr>
<th>Formula</th>
<th>Name</th>
<th>Nitrogen Valence</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{2}O\textsubscript{2}</td>
<td>nitrous oxide</td>
<td>1</td>
<td>colorless gas</td>
</tr>
<tr>
<td>NO</td>
<td>nitric oxide</td>
<td>2</td>
<td>colorless gas</td>
</tr>
<tr>
<td></td>
<td>dinitrogen dioxide</td>
<td></td>
<td>slightly water soluble</td>
</tr>
<tr>
<td>N\textsubscript{2}O\textsubscript{3}</td>
<td>dinitrogen trioxide</td>
<td>3</td>
<td>black solid</td>
</tr>
<tr>
<td>NO\textsubscript{2}</td>
<td>nitrogen dioxide</td>
<td>4</td>
<td>red-brown gas</td>
</tr>
<tr>
<td></td>
<td>dinitrogen tetroixe</td>
<td></td>
<td>very water soluble, decomposes in water</td>
</tr>
<tr>
<td>N\textsubscript{2}O\textsubscript{5}</td>
<td>dinitrogen pentoxide</td>
<td>5</td>
<td>white solid</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>very water soluble, decomposes in water</td>
</tr>
</tbody>
</table>
NOx Hazards & Threats:

Tropospheric Ozone

Acid Rain

WATERLOO ENGINEERING

APRIL Group
2013-03-16
NOx Control Technologies

Fuel Switching

- Reduce nitrogen content
  - Less Excess Air
  - Staged combustion
  - Flue gas recirculation
  - Low-NOx burners
  - Water/steam injection

Combustion Modification

- Flue Gas Treatment (FGT)
  - Selective catalytic reduction
  - Selective non-catalytic reduction
  - Combined plasma photolysis
  - Adsorption
  - Wet scrubbing

*(not very realistic)*

*(20-70%)*

Required to meet increasingly stringent (<15ppm) emission regulation

*(cost-effective)*
Absorbent for Wet Scrubbing

**Absorbent**

- Strong Oxidant for conversion NO into NO₂
  
  \[3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + (\text{NO})\uparrow\]

- Reagent for formation of a nitrosyl complex

**Advantages of Ammoniacal Cobalt(II) Complexes:**

- Fast reaction
- Positive effect of oxygen on NO absorption
- Easy regeneration
- Potential to simultaneously remove NO and SO₂
- Environmentally friendly by-products – Nitrate and nitrite
# Ammonia – Cobalt(II) System (with concentrated ammonium)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Co(H}_2\text{O)}_6^{2+} + \text{NH}_3 \rightleftharpoons \text{Co(NH}_3)(\text{H}_2\text{O})_5^{2+} + \text{H}_2\text{O}$</td>
<td>(1-1)</td>
</tr>
<tr>
<td>$\text{Co(NH}_3)(\text{H}_2\text{O})_5^{2+} + \text{NH}_3 \rightleftharpoons \text{Co(NH}_3)_2(\text{H}_2\text{O})_4^{2+} + \text{H}_2\text{O}$</td>
<td>(1-2)</td>
</tr>
<tr>
<td>$\text{Co(NH}_3)_2(\text{H}_2\text{O})_4^{2+} + \text{NH}_3 \rightleftharpoons \text{Co(NH}_3)_3(\text{H}_2\text{O})_3^{2+} + \text{H}_2\text{O}$</td>
<td>(1-3)</td>
</tr>
<tr>
<td>$\text{Co(NH}_3)_3(\text{H}_2\text{O})_3^{2+} + \text{NH}_3 \rightleftharpoons \text{Co(NH}_3)_4(\text{H}_2\text{O})_2^{2+} + \text{H}_2\text{O}$</td>
<td>(1-4)</td>
</tr>
<tr>
<td>$\text{Co(NH}_3)_4(\text{H}_2\text{O})_2^{2+} + \text{NH}_3 \rightleftharpoons \text{Co(NH}_3)_5(\text{H}_2\text{O})^{2+} + \text{H}_2\text{O}$</td>
<td>(1-5)</td>
</tr>
<tr>
<td>$\text{Co(NH}_3)_5(\text{H}_2\text{O})^{2+} + \text{NH}_3 \rightleftharpoons \text{Co(NH}_3)_6^{2+} + \text{H}_2\text{O}$</td>
<td>(1-6)</td>
</tr>
<tr>
<td>$\text{NH}_4^{+} \rightleftharpoons \text{NH}_3 + \text{H}^{+}$</td>
<td>(1-7)</td>
</tr>
</tbody>
</table>
Ammonia - Cobalt (II) System for different pH values at T=30 °C

\[
A=\text{NH}_3
\]
\[
[\text{NH}_4^+] = 2\text{mol} \cdot \text{L}^{-1}
\]

\[
\text{pH} = 7.5
\]
Reactions of NO Absorption into Penta- and Hexa-amminecobalt(II) solutions

\[ 2NO + 2[Co(NH_3)_6]^{2+} \rightleftharpoons [Co(NH_3)_5N_2O_2(NH_3)_5Co]^{4+} + 2NH_3 \]  
\[ (1-8) \]

\[ 2NO + 2[Co(NH_3)_5]^{2+} \rightleftharpoons [Co(NH_3)_5N_2O_2(NH_3)_5Co]^{4+} \]  
\[ (1-9) \]

Light Yellow

Pink or Red
2. Selection of Absorbent
Experimental Setup for Absorbent Selection

Testo 350 XL

Valve 2

Valve 3

Valve 4

Valve 5

Column Reactor

Water Jacket

Mixer

Mass flow meters

N₂

O₂

NO

Connectors

Beaker

Thermostatic Bath

Scrubbing bottle

N₂

O₂

NO
Comparison of NO Reduction between Different Absorbents

Time (min)

NO Removal (%)

Hydrogen Peroxide

Fe(II)-EDTA
Effect of Temperature on NO Removal Efficiency

Inlet flow rate = 500ml/min, NO = 500 ppm, O2 = 5.0%, pH = 10.5, Cobalt (II) = 0.06 mol·L⁻¹
3. Determination of Equilibrium Constants
Laboratory Setup for Equilibrium Study
Picture of Main Section of Testing Rig

- Ammonia scrubber
- Bubble column reactor
- Pressure dumping flow meter
- Water bath
- Data logger
- CAI gas analyzer
- Sampling conditioner
Validation of Complex Reactivity – NO Absorption Curve

Cobalt (II) – ammonia system at pH = 7.63, T = 31 °C, [NH₄⁺] = 2 mol/L

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co²⁺</td>
<td>4.30%</td>
</tr>
<tr>
<td>Co(NH₃)²⁺</td>
<td>24.01%</td>
</tr>
<tr>
<td>Co(NH₃)₂⁺</td>
<td>44.38%</td>
</tr>
<tr>
<td>Co(NH₃)₃⁺</td>
<td>21.58%</td>
</tr>
<tr>
<td>Co(NH₃)₄⁺</td>
<td>5.38%</td>
</tr>
<tr>
<td>Co(NH₃)₅⁺</td>
<td>0.35%</td>
</tr>
<tr>
<td>Co(NH₃)₆⁺</td>
<td>0</td>
</tr>
</tbody>
</table>

99.65%

pH = 7.63, T = 31 °C;
NO concentration = 605 ppm
Validation of Complex Reactivity – Colour Change

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>[2\text{NO} + 2[Co(NH}_3)_6^{2+} \rightleftharpoons [Co(NH}_3)_5N_2O_2(NH}_3)_5Co]^{4+} + 2\text{NH}_3]</td>
<td>(3-1) Light Yellow</td>
</tr>
<tr>
<td>[2\text{NO} + 2[Co(NH}_3)_5^{2+} \rightleftharpoons [Co(NH}_3)_5N_2O_2(NH}_3)_5Co]^{4+}]</td>
<td>(3-2) Pink or Red</td>
</tr>
</tbody>
</table>
**Brief Calculation of Equilibrium Constants**

\[
2NO + 2[Co(NH_3)_6]^{2+} \rightleftharpoons [Co(NH_3)_5N_2O_2(NH_3)_5Co]^{4+} + 2NH_3 \tag{3-1}
\]

\[
2NO + 2[Co(NH_3)_5]^{2+} \rightleftharpoons [Co(NH_3)_5N_2O_2(NH_3)_5Co]^{4+} \tag{3-2}
\]

\[
K_{NO}^5 = \frac{[(NH_3)_5Co(N_2O_2)Co(NH_3)_5]^{4+} e a_w^2}{[Co(NH_3)_5(H_2O)^{2+}]_e^2 [NO]_e^2}
\]

\[
[NO]_e = \frac{P_T y_{in}}{H}
\]

\[
[(NH_3)_5Co(N_2O_2)Co(NH_3)_5]^{4+} e = \frac{1}{2} \left( \frac{G_m y_{in}}{V_L} \int_0^\infty \eta dt - [NO]_e \right)
\]

\[
[Co(NH_3)_{5-6}]^{2+}_e \text{ is given by mass balance of cobalt(II)}
\]

where \(a_w = \text{water activity}\); \(f_{NH3} = \text{the activity coefficient of the ammonia}\);

\(G_m = \text{molar flow rate, mol} \cdot \text{s}^{-1}\)

\(K_{NO}^5 = \text{the equilibrium constant of Reaction 3-1, L}^3\cdot\text{mol}^{-3}\);

\(K_{NO}^6 = \text{the equilibrium constant of Reaction 3-2, L}^3\cdot\text{mol}^{-3}\);

\(P_T = \text{total pressure, atm}\);

\(y_{in}, y_{out} = \text{NO concentration at inlet and out, ppm}\);

\(\eta = \text{NO removal efficiency}\).
Equilibrium Constants of Reactions (3-1) and (3-2)

\[ \ln K_{NO}^5 = 3598.5 \cdot \frac{1}{T} + 16.759 \]  \hspace{1cm} (R^2=0.994) \hspace{1cm} (3-3)

\[ \ln K_{NO}^6 = 1476.4 \cdot \frac{1}{T} + 26.597 \]  \hspace{1cm} (R^2=0.970) \hspace{1cm} (3-4)

Rewritten as,

\[ K_{NO}^5 = 1.90 \times 10^7 \exp\left(\frac{3598.5}{T}\right) \]  \hspace{1cm} (3-5)

\[ K_{NO}^6 = 3.56 \times 10^{11} \exp\left(\frac{1476.4}{T}\right) \]  \hspace{1cm} (3-6)

where \( K_{NO}^5 \) --- the equilibrium constant of Reaction 3-1, \( L^3 \cdot \text{mol}^{-3} \);
\( K_{NO}^6 \) --- the equilibrium constant of Reaction 3-2, \( L^3 \cdot \text{mol}^{-3} \);
\( T \) --- temperature, K
4. Kinetic Study
Double-Stirred Tank Reactor
Laboratorial Setup for Kinetic Study
Picture of actual laboratorial setup for kinetic study

(a) flue gas simulation system
(b) double stirred tank section
## Calculation Scheme

<table>
<thead>
<tr>
<th>2NO + 2[Co(NH₃)₆]²⁺ ⇌ [Co(NH₃)₅N₂O₂(NH₃)₅Co]⁴⁺ + 2NH₃</th>
<th>(4-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2NO + 2[Co(NH₃)₅]²⁺ ⇌ [Co(NH₃)₅N₂O₂(NH₃)₅Co]⁴⁺</td>
<td>(4-2)</td>
</tr>
</tbody>
</table>

According to film theory and enhancement factor for parallel reactions, the rate of NO absorption into ammoniacal cobalt(II) solutions, presented in Reactions 4-1 and 4-2, can be described as follows:

\[ N_{NO} = \left( \frac{1}{Hk_G} + \frac{1}{\sqrt{D_{NO}} \sqrt{\frac{2}{m+1}k_m^5k_p^6c_{NOi}^{m-1} + \frac{2}{p+1}k_p^6B_6^q c_{NOi}^{p-1}}} \right)^{-1}c_{NOi} \]  

(4-3)

where \( N_{NO} \) --- NO absorption rate, \( \text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \);

\( H \) --- Henry Law constant, \( \text{L} \cdot \text{atm} \cdot \text{mol}^{-1} \);

\( k_G \) --- gas-phase mass transfer coefficient, \( \text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-2} \cdot \text{atm}^{-1} \);

\( D_{NO} \) --- molecular diffusivity of NO in liquid phase, \( \text{m}^2 \cdot \text{s}^{-1} \);

\( m, n, p, q \) --- reaction orders with respect to reactant;

\( k \) --- reaction rate, unit is dependent upon reaction orders
Determination of Reaction Order with regard to NO

\[ N_{NO} = \left( \frac{1}{Hk_G} + \frac{1}{\sqrt{D_{NO}}} \frac{2}{m+1} k_{mn}^5 B_5^n c_{NOi}^{m-1} + \frac{2}{p+1} k_{pq}^6 B_6^q c_{NOi}^{p-1} \right)^{-1} c_{NOi} \]  (4-3)

\( m=p=1 \) can be given by the obvious linear relationship between \( N_{NO} \) and \( c_{NOi} \) as shown in the figure. Therefore, substituting of \( m=p=1 \) into Eq. 4-3 gives

\[ k_{1n}^5 B_5^n + k_{1q}^6 B_6^q = \left( \frac{c_{NOi}}{N_{NO} - \frac{1}{Hk_G}} \right)^{-2} \]  (4-4)
## Determination of Reaction Orders with regard to Penta- and Hexa-amminecobalt(II) Solutions

The value of reaction rate decreases with temperature.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>n=q=0.5 (L^{0.5} \cdot mol^{0.5} \cdot s^{-1})</th>
<th>n=q=1 (L \cdot mol^{-1} \cdot s^{-1})</th>
<th>n=q=2 (L^{2} \cdot mol^{2} \cdot s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_{1.5}^5$</td>
<td>$k_{1.5}^6$</td>
<td>$k_2^5$</td>
</tr>
<tr>
<td>298.15</td>
<td>8.41E+05</td>
<td>1.04E+06</td>
<td>6.43E+06</td>
</tr>
<tr>
<td>303.15</td>
<td>7.22E+05</td>
<td>1.43E+06</td>
<td>7.57E+06</td>
</tr>
</tbody>
</table>
Analysis of Reaction Orders with respect to Penta- and Hexa-amminecobalt(II) Solutions

\[
\left( \frac{c_{NOi}}{N_{NO}} - \frac{1}{Hk_G} \right)^{-2} \frac{D_{NO}}{k_2 B_6} = k_2^5 B_5 \quad (4-5)
\]

\[
\left( \frac{c_{NOi}}{N_{NO}} - \frac{1}{Hk_G} \right)^{-2} \frac{D_{NO}}{k_2 B_5} = k_2^6 B_6 \quad (4-6)
\]
5. Effect of Oxygen and Regeneration
Laboratory Setup
Effect of Oxygen on NO Absorption into Ammonical Cobaltous Solutions
Proposed Scheme for NO Absorption with Presence of Oxygen

Hentaaminecobalt(II) → Pexaaminecobalt(II) → μ-peroxo-bis[pentaamminecobalt(III)] (2b) → Nitrosylpentaamminecobalt(III) (1b) → Cobalt peroxynitrito → Cobalt peroxynitrite intermediate → Nitrate and/or Nitrite

Oxygen (O₂) and NO involvement in the scheme.
Proposed Scheme for NO Absorption with Presence of Oxygen

\[
2NO + 2[Co(NH_3)_6]^{2+} \rightleftharpoons [Co(NH_3)_5N_2O_2(NH_3)_5Co]^{4+} + 2NH_3 \quad (5-1)
\]

\[
2NO + 2[Co(NH_3)_5]^{2+} \rightleftharpoons [Co(NH_3)_5N_2O_2(NH_3)_5Co]^{4+} \quad (5-2)
\]

**Conclusion:**

For continuous feed of flue gas into ammoniacal cobalt(II) system, Reactions 5-1 and 5-2 are in fact irreversible with the existence of oxygen. The presence of oxygen significantly improves the NO absorption into ammoniacal cobaltous complexes. The final NO absorption amount into the ammoniacal absorbent is entirely dependent upon the original absorbent concentration regardless of nitric oxide and oxygen concentration. This finding corresponds with our experimental results.
Regeneration Tests of Different Additives at Various Temperatures
Regeneration Tests of Different Additives at Various Temperatures

- Without KI at 52 °C
- With KI at 52 °C
- With Na2S5O8 at room temp.
Performance of Combination of AC and Na$_2$S$_5$O$_8$
Performance of Combination of AC and KI

This period represents the stirring period of around 75 minutes. The absolute time of abscissa does not represent real time after this interruption.

NO outlet concentration (ppm)

Time (s)

With KI

Add AC after equilibrium
6. Mass Transfer in Industrial Gas-Liquid Contactors
Experimental Setup of the Gas-Liquid Contactor System
Effect of Impeller Speed on Degassing Efficiency in GIAT and CSTR

CSTR: conventional stirred tank reactor

GIAT: gas-inducing agitated tank

\[ k_L a_G = 1.212 \left( \frac{P_c}{V_L} \right)^{0.0816} \left( \frac{Q_I}{d_T^2} \right)^{0.692} \left( \frac{s}{d_T} \right)^{-0.390} \]

\[ k_L a_C = 1.59 \left( \frac{N_i}{N_{cd}} \right)^{1.342} U_G^{0.93} \left( \frac{d_T}{d_i} \right)^{0.415} \]
Effect of Purge Nitrogen Flow Rate on Degassing Efficiency in CSTR and BC

CSTR: conventional stirred tank reactor

BC: bubble column

\[ k_L a_C = 1.59 \left( \frac{N_I}{N_{cd}} \right)^{1.342} U_G^{0.93} \left( \frac{d_T}{d_I} \right)^{0.415} \]

\[ k_L a_B = 1.091 U_G^{0.8} \] (Porous media)

\[ \frac{k_L a_B d_T^2}{D_L} = 0.6 \left( \frac{v_L}{D_L} \right)^{0.5} \left( \frac{g d_T^2 \rho_L}{\sigma_L} \right)^{0.62} \left( \frac{g d_T^2}{v_L^2} \right)^{0.31} \varepsilon_G^{1.1} \] (Multiorifice)
Degassing Efficiency of the Semi-batch Degasser at Different Conditions

- Experimental NI=10.3 Hz, QG=0.000393 m3/s
- Modeling NI=10.3 Hz, QG=0.000393 m3/s
- Experimental NI=16.65 Hz, QG=0.000590 m3/s
- Modeling NI=16.65 Hz, QG=0.000590 m3/s
7. Conclusions
Conclusions:

\[
2NO + 2[Co(NH_3)_6]^{2+} \rightleftharpoons [Co(NH_3)_5N_2O_2(NH_3)_5Co]^{4+} + 2NH_3
\]  
(3-1)

\[
2NO + 2[Co(NH_3)_5]^{2+} \rightleftharpoons [Co(NH_3)_5N_2O_2(NH_3)_5Co]^{4+}
\]  
(3-2)

\[
\ln K_{NO}^5 = 3598.5 \cdot \frac{1}{T} + 16.759 \quad (R^2=0.994)
\]  
(3-3)

\[
\ln K_{NO}^6 = 1476.4 \cdot \frac{1}{T} + 26.597 \quad (R^2=0.970)
\]  
(3-4)

The reaction rate constants of Reactions 3-1 and 3-2 are calculated based on the enhancement factor derived for gas absorption accompanied by parallel chemical reactions. Both reactions are first order with respect to NO and first order with respect to liquid absorbent. The forward reaction rate constants of Reactions 3-1 and 3-2 are \(6.43 \times 10^6\) and \(1.00 \times 10^7\) L·mol\(^{-1}\)·s\(^{-1}\), respectively at 298.15 K, and increase to \(7.57 \times 10^6\) and \(1.12 \times 10^7\) L·mol\(^{-1}\)·s\(^{-1}\), respectively at 303.15 K.
Conclusions:

Proposed Scheme for NO Absorption with Presence of Oxygen

Hentaaminecobalt(II) → NO → Cobalt peroxynitrito

O₂ → μ-peroxo-bis[pentaamminecobalt(III)] (2b) → NO → Nitrosylpentaamminecobalt(III) (1b)

O₂ → Pexaaminecobalt(II) → NO → Nitrosylpentaamminecobalt(III) (1b)

Nitrate and/or Nitrite

Cobalt peroxynitrito intermediate
Conclusions:

Liquid-phase mass transfer coefficient for different reactors

<table>
<thead>
<tr>
<th>Reactor Type</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional stirred tank reactor</td>
<td>$k_L a_C = 1.59 \left( \frac{N_I}{N_{cd}} \right)^{1.342} U_G^{0.93} \left( \frac{d_T}{d_I} \right)^{0.415}$</td>
</tr>
<tr>
<td>Gas-inducing agitated tank</td>
<td>$k_L a_{GI} = 1.212 \left( \frac{P_c}{V_L} \right)^{0.0816} \frac{Q_I}{d_T^2}^{0.692} \left( \frac{s}{d_T} \right)^{-0.390}$</td>
</tr>
<tr>
<td>Bubble column with efficient gas sparger</td>
<td>$k_L a_B = 1.091 U_G^{0.8}$</td>
</tr>
<tr>
<td>Bubble column with simple gas sparger</td>
<td>$\frac{k_L a_B d_T^2}{D_L} = 0.6 \left( \frac{V_L}{D_L} \right)^{0.5} \left( \frac{g d_T^2 \rho_L}{\sigma_L} \right)^{0.62} \left( \frac{g d_T^3}{V_L^2} \right)^{0.31} \epsilon_G^{1.1}$</td>
</tr>
</tbody>
</table>
Acknowledgement

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Questions?