NO and O₂ absorption in FeII(EDTA) solutions
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Chapter 5

Experimental and Modeling Studies on the Simultaneous Absorption of NO and O\(_2\) in Aqueous Ferrous EDTA Solutions

Abstract
The simultaneous absorption of NO and O\(_2\) in aqueous Fe\(^{II}\)(EDTA) solutions was studied experimentally in a stirred cell contactor in the range \(T = 298 - 323\) K, \(C_{\text{Fe}^{II}(EDTA)} = 10 - 50\) mol/m\(^3\), \(C_{\text{NO}in} = 100 - 500\) vppm and \(C_{\text{O2}in} = 5 - 10\) vol\%. The process is an interesting example of the simultaneous absorption of two gases followed by dependent parallel reactions with a third reactant. Explicit expressions for the enhancement factors for this system have not been reported to date. A volume-element model based on the film theory for reactive gas absorption was developed and novel, explicit analytical relations for the enhancement factors for both gases will be provided. The experimental results were modeled successfully using these relations. To promote NO and to suppress oxygen absorption, it is advantageous to perform the absorption process at low temperatures and low oxygen concentrations.
5.1 Introduction

In the first step of the BiodeNOx process, NO from a flue gas stream is absorbed in an Fe\textsuperscript{II}(EDTA) solution according to:

$$Fe^{\text{II}}(EDTA) + NO \rightleftharpoons Fe^{\text{II}}(EDTA)(NO) \quad (1)$$

However, various other gas phase components like oxygen and acids like SOx, HF and HCl may be present in the flue gas. Especially the reaction with oxygen (eq. (2)) may interfere with the desired reaction of the iron chelate with NO, since the oxidation product, Fe\textsuperscript{III}(EDTA), is not capable of binding NO.

$$O_2 + 4Fe^{\text{II}}(EDTA) + 2H_2O \rightarrow 4Fe^{\text{III}}(EDTA) + 4OH^- \quad (2)$$

To achieve high NO removal efficiencies in the process, the oxidation reaction should be suppressed as much as possible. To quantify the effects of the various process conditions on the absorption rates of both NO and oxygen and to maximize the NO absorption rate, the intrinsic kinetics of the reactions have to be known.

The kinetics of the reaction of NO with Fe\textsuperscript{II}(EDTA) have been investigated thoroughly in the last two decades. Several authors reported the reaction to be first order in both NO and Fe\textsuperscript{II}(EDTA) [44, 46, 65, 68, 69, 70]. Recent studies have unequivocally proven that the reaction is reversible and that it is of utmost importance to take this aspect into account [46, 106]. The reaction is intrinsically very fast and mass transfer limitation of NO as well as of the Fe\textsuperscript{II}(EDTA) complex plays an important role [44]. As a consequence, the reaction often takes place in the instantaneous regime of reactive gas absorption.

The reaction of Fe\textsuperscript{II}(EDTA) with oxygen has also been the subject of various studies and is known to be an irreversible reaction [45, 57, 94, 96, 97]. All kinetic studies indicate that the reaction is first order in oxygen. However, the order in iron chelate appears to be more complex and values between 1 and 2 have been reported [94, 96, 97]. Recent studies have indicated that the order in iron is a function of the iron chelate concentration [45, 57]. At low concentrations (< 10 mol/m\textsuperscript{3}), the reaction is first order in iron whereas it becomes second order at higher concentrations. At typical BiodeNOx absorption conditions ($T = 50 - 55 \, ^\circ C$, $C_{Fe^{\text{II}}(EDTA)} = 10 - 50 \, \text{mol/m}^3$, $C_{O_2\text{in}} = 10 - 20 \, \%$, pH = 7), the reaction was proven to be first order in oxygen and second order in iron chelate [107]. Under these conditions and using a typical laboratory gas-liquid stirred cell contactor, the oxidation reaction takes place in the intermediate regime between fast and instantaneous [57, 107]. Studies on the simultaneous absorption of NO and oxygen in aqueous iron chelate solutions have, to the best of our knowledge, not been performed yet. Here, we report on experimental investigations into the simultaneous absorption of NO and oxygen in iron-chelate solutions and on volume-element modelling of the experimental findings. The overall objective of this study is to gain insights into the effects of process conditions on the gas absorption rates and to determine those process conditions which allow for the highest rate and selectivity of NO absorption. This information is of pivotal importance in the design of BiodeNOx absorber units.
5.2 Experimental section

5.2.1 Chemicals

Na₄-EDTA (39% in water) was obtained from Caldic Nederland; FeSO₄·7H₂O and CeSO₄·4H₂O (> 99%) from Acros; Na₂CO₃ and H₂SO₄ (99%) from Merck; NaOH (33% in water) from Boom; NO (1008 vppm in N₂ and 10000 vppm in N₂), N₂O (> 99%), O₂ (>99.9%) and N₂ (> 99.99 %) from Hoek Loos. Reverse osmosis water was applied to prepare the iron solutions.

5.2.2 Experimental set-up

All the kinetic experiments were carried out in a stirred cell reactor, equipped with four glass baffles. The reactor may be operated in batch as well as continuous mode with respect to the gas phase. A stainless steel turbine impeller was used to stir the gas phase, while a magnetic stirrer bar (2 cm) in combination with an external magnetic drive was used for the liquid phase. The double wall of the reactor allowed the use of a water bath (Julabo, MV basis) to regulate the temperature of the liquid and gas phase during the experiments. Typical dimensions of the reactor are given in Table 1.

Table 1. Dimensions and characteristics of the stirred cell contactor.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total reactor volume (m³)</td>
<td>1.245 · 10⁻³</td>
</tr>
<tr>
<td>Gas phase volume (m³)</td>
<td>1.0 · 10⁻³</td>
</tr>
<tr>
<td>Interfacial area (m²)</td>
<td>7.79 · 10⁻³</td>
</tr>
<tr>
<td>Φ₀ (m³/s)</td>
<td>8.33 · 10⁻⁶</td>
</tr>
<tr>
<td>Gas impeller (m)</td>
<td>Six bladed turbine</td>
</tr>
<tr>
<td>d₀ (m)</td>
<td>6 · 10⁻²</td>
</tr>
<tr>
<td>Nₐ, liquid stirrer (rpm)ᵃ</td>
<td>100</td>
</tr>
<tr>
<td>Nₐ, gas impeller (rpm)</td>
<td>2000</td>
</tr>
</tbody>
</table>

ᵃ. measured using a Philips PR 9107 stroboscope.

A temperature indicator (PT-100) and pressure transducer (Trafag, ECO 2.5 A) were used to determine the temperature and pressure during an experiment. The state of oxidation of the solution was monitored using a Pt/Ag redox potential electrode (WTW- ORP). The NO concentration in the outlet was measured using a NO analyser (Thermo Electron-Model 10). The NO analyser was calibrated before and after every experiment using an NO gas mixture at known concentration. The oxygen concentration was measured with an oxygen analyser (M&C, PMA 20). The NO analyser, the oxygen analyser, the redox potential electrode, the temperature and pressure transducer were connected to a computer equipped with a NI-4351 PCI (National Instrument) data acquisition card. The reactor set-up is schematically represented in Fig. 1.
**5.2.3 Preparation of the Fe\(\text{II}(\text{EDTA})\) solutions**

Aqueous solutions of Fe\(\text{II}(\text{EDTA})\) are extremely air-sensitive and should be handled under a protective nitrogen atmosphere. The Fe\(\text{II}(\text{EDTA})\) solution was prepared by diluting a predetermined amount of EDTA solution (Na\(_4\text{EDTA}\)) in degassed water (1.5·10\(^{-4}\) m\(^3\)). The pH was decreased from 11 to 9 by carefully addition of some drops of a 1 M H\(_2\text{SO}_4\) solution. The appropriate amount of FeSO\(_4\)-7H\(_2\text{O}\) (Fe : EDTA ratio = 1 : 1.1 mol/mol) was added to the EDTA solution, giving a slightly green, clear solution with a pH of about 5. Next, the solution was diluted with degassed water to 9·10\(^{-4}\) m\(^3\). At this stage, the pH was adjusted to the desired value by the addition of a 4 M NaOH solution. Finally, degassed water was added to adjust the total volume to 10\(^{-3}\) m\(^3\).

**5.2.4 Description of a typical reactive absorption experiment**

Reactive absorption experiments were carried out batch-wise with respect to the liquid phase and continuously with respect to the gas phase. The reactor was filled with the appropriate amount of solution and degassed under vacuum for about 15 minutes. After degassing, the reactor was filled with nitrogen gas until atmospheric pressure was reached. The gas mixture was prepared using mass flow controllers in order to regulate the concentration of NO, N\(_2\), and dry air and bypassing around the reactor to the analysis unit. The reaction was started by closing the bypass valves and admitting the mixture gas to the reactor. The NO concentration and the concentration of oxygen in the outlet of the reactor were measured as a function of time.
5.2.5 Determination of the $\text{Fe}^{2+}$ content in the solution

The concentration of $\text{Fe}^{\text{II}}$ in the solution was determined before and after every absorption experiment by titration with a 0.1 M Ce(SO$_4$)$_2$ solution, using a 0.025 M ferroine as indicator [72]. To obtain reproducible results, the iron-chelate sample was diluted with an approximate 10-fold volume of sulphuric acid (2 - 4 kmol/m$^3$) and subsequently degassed by adding approximately 1 g of NaHCO$_3$ prior to the titration.

5.3 Theory: simultaneous absorption of two gases followed by dependent parallel reactions with a third reactant

Simultaneous absorption of two gases in a liquid with a third reactant has been the topic of various studies and is of prime industrial importance (e.g. gas cleaning and various multi-phase chemical processes). The simultaneous absorption of $\text{NO}$ (A) and oxygen (O) in a liquid containing an iron chelate (B) may be represented by the following scheme:

$$
A_G \rightarrow A_L \quad (3)
$$

$$
O_G \rightarrow O_L \quad (4)
$$

$$
A + B \leftrightarrow P \quad (5)
$$

$$
O + v_B B \rightarrow v_B Q \quad (6)
$$

Various theoretical studies have been published on the simultaneous absorption of two gases followed by dependent parallel reactions with a third reactant [73][108]. However, the isothermal case where one of the reactions is reversible and the other irreversible has not been considered so far and analytical expressions for the enhancement factor are lacking. A general equation for the absorption of a gas in a solution followed by reaction is given by [73]:

$$
J_A = \frac{C_{A,G}^b}{1 + \frac{1}{m_A} \frac{C_{A,L}^b}{k_{gA} + m_A E_A k_{L,A}}} \quad (7)
$$

The theoretical value for the enhancement factor ($E_A$) may be obtained from the various theories of mass transfer with simultaneous reaction. We have applied the film theory of mass transfer and reaction in parallel to obtain explicit expressions for the enhancement factors of $\text{O}_2$ and $\text{NO}$. This allows the calculation of the selectivity of the absorption process and the optimization of the absorption rate of $\text{NO}$. The derivation of these equations will be reported separately. In this study, a brief summary of the results will be presented and the implications for the simultaneous absorption of $\text{NO}$ and $\text{O}_2$ will be discussed.

Reaction (5) is an equilibrium reaction and the following equilibrium relation holds:

$$
K = \frac{C_{P,eq}}{C_{A,eq} C_{B,eq}} \quad (8)
$$
Reaction (6) is an irreversible reaction of an order \((1, n)\) with the reaction rate defined as:

\[
r_2 = k_{1a}C_oC_B^n
\]  

(9)

The reaction order is a function of the iron concentration (\textit{vide supra}). For \(C_{Fe^{II}(EDTA)}\) exceeding 10 mol/m\(^3\), the reaction is considered to be second order in iron and first order in oxygen. In this case, the reaction modulus, \(\phi\), is given by:

\[
\phi = \frac{C_{B,L}^b}{k_{LO}} \sqrt{\frac{k_{12}}{D_o}}
\]  

(10)

When assuming that the reaction between NO and Fe\(^{II}\)(EDTA) is instantaneous, the influence of the oxidation reaction (6) on the rate of mass transfer of A (NO) varies, in general, between two limiting situations. In case reaction (6) occurs in the slow regime \((\phi < 0.2)\), the absorption of oxygen is not enhanced by the oxidation reaction. In this situation, the absorption of A has the maximum enhancement [109]:

\[
E_A = E_{A_{\infty}} = 1 + \frac{D_p}{D_A} \left(1 + \frac{D_p}{D_B}KC_{B,L}^{b}\right)
\]  

(11)

In case reaction (6) is also instantaneous, i.e. when \(\phi \gg \frac{D_BC_{B,L}^{b}}{\nu_B D_o C_{O,L}^i}\), the enhancement factor for O is maximum and that of A approaches 1 [109]:

\[
E_A = 1
\]  

(12)

\[
E_{O_{\infty}} = 1 + \frac{D_BC_{B,L}^{b}}{\nu_B D_o C_{O,L}^i}
\]  

(13)

Therefore, depending on the rate of reaction (6), the enhancement factor for the absorption of A can vary between 1 and \(E_{A_{\infty}}\), even though reaction (5) is instantaneous.

For a number of special cases, explicit analytic expressions for the enhancement factor of NO and oxygen as a function of \(\phi\) may be obtained. For the case that \(C_{O,L}^{b} = 0, C_{A,L}^i \gg C_{A,L}^{b}, n = 2, \) and \(\phi = \phi_i\frac{C_{B,L}^{b}}{C_{B,L}^{i}}\), the following relations may be derived:
\[ E_O = \frac{E_{O\infty}}{1 + \left(1 + \frac{D_P}{D_B} KC_{A,L} \right) \frac{E_{O\infty} - 1}{\phi} \frac{E_{O\infty}}{E_{O\infty} - 1}} \]  

\[ E_A = 1 + \frac{E_{A\infty} - 1}{E_{O\infty} - 1} (E_{O\infty} - E_O) \]  

where \( E_{A\infty} \) and \( E_{O\infty} \) are given by eq (11) and (14).

A typical example of interaction between the enhancement factors of the two reactions as a function of \( \phi \) is given in Fig. 2.

Figure 2. Enhancement factors of oxygen (\( E_O = \) solid line) and NO (\( E_A = \) dashed line) as a function of the reaction modulus, \( \phi \). Conditions: \( K = 500 \, \text{m}^3/\text{mol} \), \( C_{A,L} = 10^{-3} \, \text{mol/m}^3 \), \( C_{O,L} = 10^{-2} \, \text{mol/m}^3 \), \( C_B = 10 \, \text{mol/m}^3 \), \( D_B / D_A = D_P / D_A = 0.1 \), \( D_O / D_A = 0.5 \) (\( E_{A\infty} = 334 \), \( E_{O\infty} = 51 \)).

5.4. Relevant kinetic, thermodynamic and hydrodynamic data

To analyze the experimental data, the values for the mass transfer coefficients of oxygen and NO as well as physical properties like the solubility and diffusion coefficients of the gases in iron chelate solutions at different temperatures are required. In addition, kinetic and thermodynamic data for both reactions need to be known.

The mass transfer coefficients for the stirred cell reactor system were measured at various conditions, see [106] for details. An overview of the experimental data is reported in Table 2. The \( k_G \) for oxygen is taken equal to the \( k_G \) for NO.
Table 2: Mass transfer coefficients of NO and oxygen for the stirred cell reactor.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>298</th>
<th>303</th>
<th>313</th>
<th>328</th>
</tr>
</thead>
<tbody>
<tr>
<td>k_{LO} (m/s)</td>
<td>(1.73 \cdot 10^{-5})</td>
<td>(1.76 \cdot 10^{-5})</td>
<td>(2.08 \cdot 10^{-5})</td>
<td>(2.15 \cdot 10^{-5})</td>
</tr>
<tr>
<td>k_{LA} (m/s)</td>
<td>(1.79 \cdot 10^{-5})</td>
<td>(2.01 \cdot 10^{-5})</td>
<td>(2.50 \cdot 10^{-5})</td>
<td>(3.15 \cdot 10^{-5})</td>
</tr>
<tr>
<td>k_{GA} (m/s)</td>
<td>0.014</td>
<td>0.018</td>
<td>0.028</td>
<td>0.054</td>
</tr>
<tr>
<td>k_{GO} (m/s)</td>
<td>0.014</td>
<td>0.018</td>
<td>0.028</td>
<td>0.054</td>
</tr>
</tbody>
</table>

The solubility of NO in Fe^{II}(EDTA) solution was measured earlier [106] and may be expressed as:

\[ \text{He}_A = 697.11 \cdot T - 155.62 \cdot 10^3 + C_{Fe^{II}(EDTA)} \cdot (4.70 \cdot T - 1281.8) \]  \hspace{1cm} (17)

The Henry coefficient for oxygen in Fe^{II}(EDTA) solution was reported by Wubs [57]. The ratio of the diffusion coefficients, \(D_P/D_A\), was taken from a previous study [106]:

\[ \frac{D_P}{D_A} = -1.778 \cdot T^2 + 0.11 \cdot T - 16.93 \]  \hspace{1cm} (18)

The value of the diffusion coefficient of oxygen in Fe^{II}(EDTA) was calculated using the diffusivity of oxygen in water [82] and applying a correction for the influence of viscosity in aqueous electrolyte solutions [80]. The diffusion coefficients of the iron chelate, \(D_B\), was taken from O’ Connor at al.[103].

The equilibrium constant for the NO absorption in Fe^{II}(EDTA) solution as a function of the temperature was measured earlier [106]:

\[ K = \exp\left(\frac{4702}{T} - 8.53\right) \text{ (m}^3/\text{mol}) \]  \hspace{1cm} (19)

The kinetic constants of the reaction between Fe^{II}(EDTA) and oxygen as a function of the temperature were measured earlier in our group and may be expressed as [107]:

\[ k_{12} = 5.3 \cdot 10^3 \cdot e^{-\frac{4698}{T}} \text{ (m}^6/\text{mol}^2 \text{ s}) \]  \hspace{1cm} (20)

5.5 Results
5.5.1 The experiments
The effects of various process conditions (temperature, iron chelate concentration, NO and O_2 concentration in the gas phase) on the rate and selectivity of NO absorption in the presence of oxygen were investigated with simultaneous gas absorption experiments. An overview of the experiments is provided in Table 3.

Typical NO absorption profiles for two experiments are provided in Fig. 3. A first stage of about 200 s with rapid concentrations changes due to start-up of the reactor was observed. Subsequently, a second phase characterised by a slow increase of the NO concentration in the reactor outlet was observed. In this pseudo steady state, the concentration of Fe^{II}(EDTA) in solution slowly decreases due to reaction, resulting in
a slow increase in the concentration of NO in the reactor outlet. The reaction time for every experiment was about two hours.

Table 3. Overview of the experiments.

<table>
<thead>
<tr>
<th>#</th>
<th>(C^0_{\text{Fe(EDTA)}}) (mol/m³)</th>
<th>T (K)</th>
<th>(C_{\text{NOin}}) (vppm)</th>
<th>(C_{\text{NOout}}) (vppm)</th>
<th>(C_{O2in}) (vol %)</th>
<th>(J_{\text{NO exp}}) (mol/m² s)</th>
<th>(J_{O \text{ exp}}) (mol/m² s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>323</td>
<td>246</td>
<td>205</td>
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<td>1.83 \times 10^6</td>
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</tr>
<tr>
<td>2</td>
<td>10</td>
<td>298</td>
<td>254</td>
<td>156</td>
<td>10</td>
<td>4.37 \times 10^6</td>
<td>7.37 \times 10^6</td>
</tr>
<tr>
<td>3</td>
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<td>303</td>
<td>248</td>
<td>161</td>
<td>10</td>
<td>3.94 \times 10^6</td>
<td>8.63 \times 10^6</td>
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<tr>
<td>4</td>
<td>10</td>
<td>313</td>
<td>240</td>
<td>165</td>
<td>10</td>
<td>2.97 \times 10^6</td>
<td>9.69 \times 10^6</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>298</td>
<td>250</td>
<td>99</td>
<td>10</td>
<td>6.72 \times 10^6</td>
<td>9.95 \times 10^6</td>
</tr>
<tr>
<td>6</td>
<td>25</td>
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<td>244</td>
<td>109</td>
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<td>130</td>
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<tr>
<td>8</td>
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<td>323</td>
<td>252</td>
<td>167</td>
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<td>3.84 \times 10^6</td>
<td>1.79 \times 10^3</td>
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<tr>
<td>9</td>
<td>50</td>
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<td>257</td>
<td>84</td>
<td>10</td>
<td>7.93 \times 10^6</td>
<td>1.56 \times 10^3</td>
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<tr>
<td>10</td>
<td>50</td>
<td>303</td>
<td>259</td>
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<td>10</td>
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<td>1.89 \times 10^3</td>
</tr>
<tr>
<td>11</td>
<td>50</td>
<td>313</td>
<td>257</td>
<td>97</td>
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<td>2.16 \times 10^3</td>
</tr>
<tr>
<td>12</td>
<td>50</td>
<td>323</td>
<td>262</td>
<td>124</td>
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<td>5.42 \times 10^6</td>
<td>2.51 \times 10^3</td>
</tr>
<tr>
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<td>50</td>
<td>298</td>
<td>261</td>
<td>84</td>
<td>5</td>
<td>7.86 \times 10^6</td>
<td>1.09 \times 10^3</td>
</tr>
<tr>
<td>14</td>
<td>10</td>
<td>298</td>
<td>257</td>
<td>140</td>
<td>5</td>
<td>5.28 \times 10^6</td>
<td>6.54 \times 10^6</td>
</tr>
<tr>
<td>15</td>
<td>10</td>
<td>303</td>
<td>255</td>
<td>153</td>
<td>5</td>
<td>4.52 \times 10^6</td>
<td>6.82 \times 10^6</td>
</tr>
<tr>
<td>16</td>
<td>10</td>
<td>313</td>
<td>254</td>
<td>180</td>
<td>5</td>
<td>3.22 \times 10^6</td>
<td>7.32 \times 10^6</td>
</tr>
<tr>
<td>17</td>
<td>10</td>
<td>323</td>
<td>264</td>
<td>209</td>
<td>5</td>
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<td>9.41 \times 10^6</td>
</tr>
<tr>
<td>18</td>
<td>25</td>
<td>313</td>
<td>252</td>
<td>73</td>
<td>0</td>
<td>7.45 \times 10^6</td>
<td>-</td>
</tr>
<tr>
<td>19</td>
<td>10</td>
<td>323</td>
<td>466</td>
<td>387</td>
<td>10</td>
<td>3.7 \times 10^6</td>
<td>1.02 \times 10^3</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>323</td>
<td>113</td>
<td>91</td>
<td>10</td>
<td>9.1 \times 10^7</td>
<td>1.02 \times 10^5</td>
</tr>
</tbody>
</table>

Figure 3. Typical NO absorption profiles in Fe^{II}(EDTA) solutions. \(C^0_{\text{Fe(EDTA)}} = 25\) mol/m³, \(C_{\text{NOin}} = 250\) vppm, \(T = 313\) K. Solid line: \(C_{O2in} = 10\) vol%. Dotted line: no oxygen present.
The selectivity ratio of the absorption process is defined as:

$$\sigma = \frac{J_A}{J_O}$$  \hspace{1cm} (21)

Here, $J_A$ and $J_O$ are the average flux of NO and O$_2$ respectively, for the total reaction time. The selectivity is defined on the basis of the average fluxes and not on the instantaneous fluxes of both gases as the oxygen flux at a certain reaction time cannot be determined experimentally. This is due to the fact that the uptake of oxygen is very low compared to the absolute oxygen concentration in the reactor (5 – 10 vol%), leading to very small oxygen concentration differences between in- and outlet. $J_A$ in the pseudo steady state regime may be calculated from the total uptake of NO during an experiment:

$$J_A = \frac{C_{A, \text{in}} \cdot t_{\text{exp}} - \int_0^{t_{\text{exp}}} C_{A,G} \cdot \frac{V_G}{V_L} \cdot \exp(t/a \cdot \tau \cdot t_{\text{exp}})}{a \cdot \tau \cdot t_{\text{exp}}}$$  \hspace{1cm} (22)

The average flux of oxygen was calculated using the following expression:

$$J_O = \frac{C_B^0 - C_B - C_p}{V_B \cdot a \cdot t_{\text{exp}}}$$  \hspace{1cm} (23)

The values of $C_B$ were obtained by titration. The stoichiometric coefficient, $v_B$, of the reaction between Fe$^{II}$(EDTA) and O$_2$ was assumed to be equal to 4.

For all experiments, the $J_{NO}$ in the presence of oxygen is always lower than the $J_{NO}$ in the absence of oxygen (Table 3, Fig. 3). Furthermore, for all experiments, $J_{NO}$ is smaller than $J_O$, and consequently, the selectivity ratio is always less than 1. In the following, the effects of the process parameters ($T, CO_2, C_{Fe^{II}(EDTA)}, C_{NO}$) on the rate and selectivity ratio of the absorption process will be discussed.

5.5.2 Effect of the inlet NO concentration
The effect of the NO concentration in the inlet of the reactor (100 - 500 vppm) on the absorption process was investigated at a constant initial Fe$^{II}$(EDTA) concentration of 10 mol/m$^3$, an inlet oxygen concentration of 10 vol% and a temperature of 323 K. The results are provided in Fig. 4. The $J_{NO}$ increases upon applying a higher $C_{NO}$ whereas the $J_O$ is hardly affected. As a consequence, $\sigma$ increases when increasing the $C_{NO}$ and an almost linear dependency was observed.

5.5.3 Effect of the oxygen inlet concentration
The effect of different concentration of oxygen in the reactor inlet was tested at two concentration levels, 5 and 10 vol% ($T = 298 – 323 \text{ K}, C_{NO, \text{in}} \approx 250 \text{ vppm}, C_{Fe^{II}(EDTA)} = 10 - 50 \text{ mol/m}^3$). The $J_O$ increases upon higher oxygen levels whereas the $J_{NO}$ is
slightly reduced. As a result, $\sigma$ decreases at higher oxygen levels in the reactor (Fig. 5).

Figure 4. Effect of $C_{\text{NOin}}$ on $\sigma$ and $J_{\text{NO}} \cdot C_{\text{FeII(EDTA)}}^0 = 10 \text{ mol/m}^3$, $C_{O2in} = 10 \text{ vol}\%$, $T = 323 \text{ K}$. ■: $\sigma$; ○: $J_{\text{NO}}$. Solid line: for illustrative purposes only.

![Figure 4](image)

Figure 5. Effect of $C_{O2in}$ on $\sigma$ and $J_{\text{NO}} \cdot C_{\text{FeII(EDTA)}}^0 = 10 \text{ mol/m}^3$, $C_{\text{NOin}} \approx 250 \text{ vppm}$, $T = 323 \text{ K}$. ■: $\sigma$; ○: $J_{\text{NO}}$. Solid lines: for illustrative purposes only.

![Figure 5](image)

5.5.4 Temperature effects
A group of experiments (1 - 4 in Table 2) was performed to investigate the effect of temperature (298 – 323 K) on the absorption rates of NO and oxygen ($C_{\text{FeII(EDTA)}}^0 = 10$...
mol/m³, \( C_{\text{NO in}} \approx 250 \text{ vppm} \), \( C_{\text{O2}} = 10 \text{ vol\%} \). The results are given in Fig. 6. \( \bar{J}_{\text{NO}} \) is considerably reduced when increasing the temperature whereas the \( \bar{J}_{\text{O}} \) slightly increases. As a result, \( \sigma \) is highly temperature dependent and for instance, at \( T = 298 \text{ K} \), \( \sigma \) is about three times higher than at \( T = 323 \text{ K} \). These findings imply that operation at low temperature is favoured as both the rate of NO absorption and the selectivity ratio are considerably higher than at elevated temperatures.

![Figure 6: Temperature effect on \( \sigma \) and \( \bar{J}_{\text{NO}} \).](image)

\( C_{\text{FeII(EDTA)}} = 10 \text{ mol/m}^3, C_{\text{O2 in}} = 10 \text{ vol\%}, C_{\text{NO in}} \approx 250 \text{ vppm}. \)

\( \blacklozenge: \sigma; \circ: \bar{J}_{\text{NO}}. \) Solid lines: for illustrative purposes only.

### 5.5.5 Effect of the initial Fe⁹⁺(EDTA) concentration

The effects of the initial Fe²⁺(EDTA) concentration on \( \sigma \) and \( \bar{J}_{\text{NO}} \) are reported in Fig. 7 (\( C_{\text{O2 in}} = 10 \text{ vol\%}, C_{\text{NO in}} \approx 250 \text{ vppm}, T = 323 \text{ K} \)). Both \( \bar{J}_{\text{NO}} \) and \( \bar{J}_{\text{O}} \) increase at higher Fe loading (Table 2). As a result, the initial Fe²⁺(EDTA) concentration does not have a dramatic effect on \( \sigma \) and variations between 0.18 and 0.22 were observed.

### 5.6 Modeling the experimental results

The \( J_{\text{NO}} \) measured at \( t = 500 \text{ s} \) were modeled using the general flux expression (eq. (7)). The NO flux after 500 s reaction time was considered as at this stage, the \( C_{\text{FeII(EDTA)}} \) is about equal to the known initial value and this significantly simplifies the calculations. The enhancement factors were calculated using the approximate analytical solutions provided in the theory part (eq. (15) and (16)). The values for the gas side mass transfer coefficients and gas solubilities were either measured or taken from literature (see section 5.4). The ratio of the diffusion coefficients, \( \frac{D_B}{D_A} \), was used as the fitting parameter. Optimisation of this parameter was performed using a standard Newton-Raphson optimization routine and resulted in a value of 0.134 +/- 0.03. This value is in good agreement with the value obtained in a previous study on
the kinetics of the reaction between NO and Fe\textsuperscript{II}(EDTA) in a stirred cell contactor [106]. As shown in Fig. 8, agreement between experiment and model is good.

Figure 7. Effect of initial concentration of iron chelate on $\sigma$ and $J_{NO}$. $C_{Fe^{II}(EDTA)} = 50$ mol/m$^3$; $C_{Fe^{II}(EDTA)} = 25$ mol/m$^3$; $C_{Fe^{II}(EDTA)} = 10$ mol/m$^3$.

Figure 8. Comparison between the experimental values of $J_{NO}$ in presence of oxygen and the expected trends according to the film theory, $J_{NO,mod.}$. $C_{NOin} \approx 250$ vppm, $C_{O2in} = 10$ vol%, $T = 323$ K. $\sigma$: $J_{NO}$.

5.7 Discussion
In the following, the observed effects of the process conditions on the rate of gas absorption and on $\sigma$ will be discussed using the general flux model for gas absorption (eq (7)) in combination with the explicit relations for the enhancement factors (eq (15)).
and (16)). At first instance, the effect of gas phase resistance on the results was assessed. Calculations indicate that all the experiments were carried in the near absence of gas phase resistance (<7% of the total resistance) and that fluxes of the gases and the $\sigma$ of the process are governed by the processes taking place in the liquid film layer.

### 5.7.1 Effect of NO concentration

Experimentally it was observed that $J_{NO}$ and $\sigma$ are a strong function of the NO concentration. When considering the general flux equation (7), most of the observed trends are associated with a higher driving force for NO mass transfer at higher NO levels. In addition, $E_A$ is slightly affected by the $C_{NO}$. To gain some insights of the magnitude of this effect, the $E_A$ was calculated using eqs (11) - (16) for different concentrations of NO as a function of $\phi$ (Fig. 9). All the experiments were carried out in the regime $2 < \phi < 11$. Hence, the predicted effect of $C_{NO}$ on $E_A$ is relatively small in the range 100 - 250 vppm and the main effect is the driving force ($C_{NO,G} - C_{NO,L}$) for mass transfer.

![Figure 9. $E_A$ as a function of $\phi$ for different $C_{NO}$. $C_{\text{Fe(EDTA)}}^\theta = 10$ mol/m$^3$, $T = 328$ K, $C_{O2in} = 10$ vol%. Solid line: $C_{NOin} = 250$ vppm; dotted line: $C_{NOin} = 100$ vppm; dashed line: $C_{NOin} = 500$ vppm.](image)

### 5.6.2. Effect of oxygen concentration

Both the $\tilde{J}_{NO}$ and $\sigma$ are negatively affected when increasing the oxygen concentration in the reactor. The decrease in the $\tilde{J}_{NO}$ is mainly due to a decrease in $E_A$ (187 to 171) when increasing $C_{O2in}$ from 5 to 10 vol%. This result clearly illustrates the mutual interaction between the NO and oxygen absorption rates in this reactive absorption gas-liquid system. $\tilde{J}_O$ is increased when operating at higher oxygen levels and as a result, the $\sigma$ is lowered at higher oxygen levels.
5.6.3 Temperature effects
The temperature is a critical parameter that has a profound effect on both the $J_{NO}$ and the $\sigma$ (Fig. 10). $J_{NO}$ is considerably reduced at high temperatures. This effect has already been observed for reactive NO absorption studies in Fe$^{II}$(EDTA) solutions [106] and is due to the fact that the reaction between NO and Fe$^{II}$(EDTA) is an exothermic equilibrium reaction.

In combination with the general flux equation (7), it is possible to evaluate the main factors responsible for the reduction in $J_{NO}$ when performing the simultaneous absorption of oxygen and NO. Evidently, the mass transfer coefficients and the solubility of the gases are also affected by temperature. However, the most important factor is the enhancement factor for NO. Upon increasing the temperature from 298 to 323 K, $E_A$ reduces from 746 to 170, caused by a 4-fold decrease in the equilibrium constant of the reaction between NO and Fe$^{II}$(EDTA). To visualize these effects, the $E_A$ values as a function of $\phi$ were modeled for different temperatures using eq. (15) and (16). The results are presented in Fig. 10. It is evident that $E_A$ is considerably reduced when operating at higher temperatures.

![Figure 10. $E_A$ as a function of $\phi$ calculated for different temperatures. $C_{Fe^{II}(EDTA)} = 10 \text{ mol/m}^3$, $C_{NO,in} = 250 \text{ vppm}, C_{O_2,in} = 10 \text{ vol}\%$. Solid line: $T = 328 \text{ K};$ dotted line: $T = 313 \text{ K};$ dashed line: $T = 298 \text{ K}$.](image)

5.6.4 Effect of the initial Fe$^{II}$(EDTA) concentration
The $J_{NO,exp}$ considerably increased at higher Fe$^{II}$(EDTA) concentrations. However, the selectivity remained about constant as the $J_O$ increased to the same extent (Fig. 7). Our model implies that the $J_{NO}$ increases due to a significant increase in the $E_A$ at higher iron concentrations, see Fig. 11 for details. These results suggest that a high metal chelate concentration in the BiodeNOx process could be advantageous with respect to the rate of NO absorption without affecting the selectivity. However, the hydrodynamics in a real absorber unit, and particularly the mass transfer coefficients will deviate considerably from that in a stirred cell contactor and this may have a
dramatic effect on the absorption rates and selectivity. This aspect will be discussed in more detail in the following section.

![Graph showing the effect of \( \phi \) on \( E_A \) for different \( C_{Fe(II)(EDTA)} \).](image)

Figure 11. \( E_A \) as a function of \( \phi \) for different \( C_{Fe(II)(EDTA)} \). \( T = 328 \) K, \( C_{NO} = 250 \) vppm, \( C_{O2(a)} = 10 \) vol\%. Solid line: \( C_{Fe(II)(EDTA)} = 10 \) mol/m\(^3\); dotted line: \( C_{Fe(II)(EDTA)} = 25 \) mol/m\(^3\); dashed line: \( C_{Fe(II)(EDTA)} = 50 \) mol/m\(^3\).

### 5.6.5 Implications for BiodeNOx reactor design

In the previous part, a volume element model was presented to predict the fluxes of NO and oxygen in aqueous Fe\(^{II}\)(EDTA) solutions in case of simultaneous absorption. This model may also be applied to gain insights in the absorption rates and the selectivity as a function of commonly applied absorber units, e.g. spray towers and packed column absorbers. To predict the fluxes, typical ranges of the mass transfer coefficients (\( k_L \) and \( k_G \)) for both contactors are required, and these are reported in Table 4, together with the typical BiodeNOx process conditions considered. For simplicity, the concentration of Fe\(^{II}\)(EDTA)(NO) in the liquid phase is neglected, i.e. backpressure due to the reversibility of reaction (1) is ignored. Average concentration levels of reactants in the absorber units were taken, see Table 4 for details.

\( \bar{J}_{NO}, \bar{J}_{O}, \) and \( \sigma \) were calculated using eq. (7), (11) - (16) and (20). The predicted \( \sigma \) values for both absorbers as a function of the ranges of \( k_L \) and \( k_G \) values are given in Fig. 12.

The predicted selectivity exceeds 1 only in case of a spray tower operated at high \( k_L \) and \( k_G \) values. It seems that oxygen absorption is always favored compared to NO absorption when using a packed tower reactor. For both absorbers, the selectivity reduces considerably at low \( k_G \) and \( k_L \) values and is about 0.2 for both types of absorbers. Hence, these volume-element models suggest that to suppress the undesired oxidation reaction and to obtain high \( \sigma \) values, a spray tower operating at high \( k_L \) and \( k_G \) values is the optimum absorber configuration.
Table 4: Input data for the prediction of the NO and O\textsubscript{2} absorption rates and the $\sigma$ in two absorber configurations.

<table>
<thead>
<tr>
<th>Reactor type</th>
<th>Spray Tower</th>
<th>Packed tower</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Countercurrent</td>
<td>Countercurrent</td>
</tr>
<tr>
<td>$k_G$ (m/s)</td>
<td>0.05 – 0.2 [110]</td>
<td>0.03 – 0.06 [111]</td>
</tr>
<tr>
<td>$k_L$ (m/s)</td>
<td>(1 – 3) · 10\textsuperscript{-4} [110]</td>
<td>(0.5 – 2) · 10\textsuperscript{-4} [73]</td>
</tr>
<tr>
<td>$T$ (K)</td>
<td>323</td>
<td>323</td>
</tr>
<tr>
<td>$C_O$ (vol%)</td>
<td>10 %</td>
<td>10 %</td>
</tr>
<tr>
<td>$C_{\text{Fe(EDTA)}}$ (vppm)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>$C_{\text{Fe(EDTA)}}$ (mol/m\textsuperscript{3})</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

(a): It is assumed that the mass transfer coefficients for NO and O\textsubscript{2} are equal.
(b): Average concentrations in the absorber.

Figure 12. $\sigma$ as a function of the mass transfer coefficients for both absorber configurations. Solid line: spray tower, $k_G = 0.05$ m/s. Dashed line: spray tower, $k_G = 0.2$ m/s. Dotted line: packed tower, $k_G = 0.03$ m/s. Dotted-dashed line: packed tower, $k_G = 0.06$ m/s.
5.7 Conclusions

In the present work, the simultaneous absorption of NO and O$_2$ in Fe$^{II}$(EDTA) solution in a gas-liquid stirred cell reactor was investigated in a range of process conditions of relevance for the BiodeNOx process. The NO absorption rates and the selectivity of the absorption process are strongly affected by the presence of oxygen. Particularly, the temperature has a profound effect on both the absorption rates and the selectivity. To enhance the rate of NO absorption and to obtain high $\sigma$ values, it is advantageous to work at low temperatures.

The experimental NO fluxes were modeled using the film theory for reactive gas absorption. Explicit, analytical expressions for the NO enhancement factor in the presence of oxygen were derived. Agreement between the experimental and modeled NO fluxes at various process conditions was good.

The volume element flux model has been applied to gain some insights in the optimum reactor configuration for the absorption process. The model implies that NO absorption using typical BiodeNOx conditions is favoured when operating at high $k_L$ and $k_G$ values and in this respect, a spray tower appears to be a better choice than a packed column.