Research and Development of an Air Pollution Technology for Simultaneous Desulfurization and Denitrification

ANNUAL REPORT

Prepared for the
Natural Sciences and Engineering Research Council of Canada
Lakes Environmental Research Inc.
University of Waterloo

Submitted By

Dr. Hesheng Yu

Pollution Equipment Researcher
Lakes Environmental Research Inc.
Waterloo, Ontario, CANADA, N2L 3L3
Postdoctoral Fellow
University of Waterloo
Waterloo, Ontario, CANADA, N2L 3G1
Tel.: (519) 9989619
Email: yuhesheng@gmail.com
Executive Summary

This proposed project was funded by NSERC Industrial R&D Fellowships (IRDF) program and Ontario-China Research and Innovation Fund (OCRIF) to develop and commercialize a technology that could control multiple air pollutants and emissions in flue gas. It was also supported by in-kind contributions from Lakes Environmental Research Inc. Its research areas include: screening and validation of the continuous process for simultaneous desulfurization and denitrification, gas absorption in a cross-flow hollow fiber membrane contactor (HFMC), mass transfer coefficient of the HFMC, modeling of gas absorption in the cross-flow HFMC, optimization of the selected process based on experimental data and reactor modeling, fundamental study of CO$_2$ absorption into ammonia solutions, and field testing of the validated processes. Drs. Zhongchao Tan and Jesse Thé are the Principle Investigators, and Dr. Hesheng Yu is responsible for the development of research idea, the preparation of proposal, experimental validation, preparation of research plan, instrumentation, methodologies, data collection and analysis, and result delivery. This report covers the work completed during the period between October 1, 2014 and September 30, 2015.

Fossil fuel, especially coal, will continue to supply most electricity generation worldwide. Severe air pollution stemming from fuel combustion poses threat to human health and the environment. Effective air pollution control technologies allow us to utilize fossil fuel without causing negative impacts. However, existing flue gas treatment systems are expensive and complicated. Cost-effective air pollution control technology is greatly desired. The combined absorption of SO$_2$ and NO$_x$ using wet scrubbing is deemed as a promising alternative to available technologies.

Three air pollution control processes including wet scrubbing and liquid treatment have been proposed to effectively address post-combustion flue gas in industrial practices. They are sequential absorption of SO$_2$ and NO$_x$, simultaneous removal of SO$_2$ and NO$_x$, and gas phase pre-oxidation of nitric oxide. Hollow fiber membrane contactor (HFMC) is expected to replace traditional wet scrubber. A continuous wet scrubbing system using simulated flue gas has been established to validate the proposed processes in laboratory.
In order to verify the use of HFMC in air pollution control, the absorption of SO\textsubscript{2} in a cross flow HFMC using water at 27 °C was performed. Experimental results show that the efficiency of SO\textsubscript{2} removal using water in the HFMC remains greater than 99% at Q\textsubscript{G} = 8276 mL/min with liquid-to-gas (L/G) ratio ranging from 0.02 to 0.06. The gas and liquid flow rates can be regulated independently without causing operational failures. The SO\textsubscript{2} removal efficiency increases with increasing liquid flow rate and decreasing gas flow rate and SO\textsubscript{2} inlet concentration, respectively. The overall volumetric gas phase mass transfer coefficient (\(K_{G\alpha}\)) of the HFMC is in the range of 10\(^{-3}\) \(mol \cdot s^{-1} \cdot m^{-3} \cdot Pa^{-1}\), which is higher than those of conventional wet SO\textsubscript{2} scrubbers although water is used in HFMC while effective alkaline absorbents are used in the compared reactors. It indicates that the HFMC has advantage in SO\textsubscript{2} absorption over conventional absorbers.

Furthermore, the liquid side mass transfer coefficient of the HFMC was determined by the absorption of CO\textsubscript{2} into pure water. A correlation, \(Sh = 0.28Re^{0.97}Sc^{0.33}\), was proposed to estimate the liquid-side mass transfer coefficient in the Liqui-Cel HFMC. This correlation will be used in reactor modeling.

The regeneration of ammoniacal cobalt(II) solutions is the key to simultaneous absorption of SO\textsubscript{2} and NO\textsubscript{x} using such absorbent. The UVC irradiation was used for the absorbent regeneration because of the well-known photochemistry of cobalt complexes. More importantly, this method will not bring in new contaminants compared with chemical regeneration. Several UVC reactors were tested; however, the regeneration of absorbent was not obvious. Therefore, we moved forward to another proposed process – pre-oxidation of NO.

Effective oxidation of inactive NO into soluble NO\textsubscript{2} enables us to utilize wet scrubbing for multiple air pollutant control. TiO\textsubscript{2}-assisted photocatalytic oxidation of NO into NO\textsubscript{2} was performed in a simple customized column. Experimental results indicate that TiO\textsubscript{2}-assisted photocatalytic NO oxidation is effective. The NO conversion efficiency is 53% when the inlet NO concentration is 400 ppm, and O\textsubscript{2} is 6%. The temperature for TiO\textsubscript{2} thin film preparation and regeneration is critical to the NO conversion efficiency. A calcination temperature of 500-550 °C is deemed suitable.
The feasibility of using photocatalytic technology for flue gas treatment on an industrial scale was then analyzed taking account of reaction nature, available UV lamp, equipment materials, scale-up, installation and fouling, and economics. The TiO$_2$-assisted UV technology can effectively remove SO$_2$ and NO$_x$ simultaneously based on our experimental results and literature. Mature UV lamp technology and high quality fused quartz materials ensure the application of UV technology in flue gas treatment. The UV technology can be scaled up to large installations, and the quartz material can withstand fine particles and fouling. It would probably possess huge economic advantages over other available methods such as EBFGT. Therefore, it is feasible to use UV technology for de-SOxNOx purpose. A UVC reactor prototype using aluminum materials was then designed.

In addition to SO$_2$ and NO$_x$, CO$_2$ is another subject we are interested in. The extension to CO$_2$ absorption enables us to cover the control of all major emissions present in real flue gas, which maximizes the advantages of our proposed technology. The understanding of the kinetics of CO$_2$ absorption into ammonia solutions will well prepare us to be a player in carbon capture and storage (CCS) area. The kinetic information will greatly benefit future reactor design and modeling; therefore, can allow us to include CO$_2$ capture in our proposed technology once funds are available. The kinetics of CO$_2$ absorption into aqueous ammonia solutions were investigated using a DSTR system. It is explicitly determined that the reactive absorption is first order with respect to CO$_2$ but fractional orders between 1.6 – 1.8 with respect to ammonia. The kinetics data can be satisfactorily interpreted by the termolecular mechanism using $k_{\text{NH}_3}^T = 7.6089 \times 10^8 e^{-\frac{4018.4}{T}}$ and $k_{\text{H}_2\text{O}}^T = 7.9161 \times 10^7 e^{-\frac{4356.4}{T}}$.

In summary, the proposed technologies can effectively control multiple air pollutants and/or emissions in industrial flue gas. The use of novel HFMC reactor is expected to further enhance the competitiveness of the proposed wet scrubbing technology. The inclusion of CO$_2$ capture will maximize the advantage of our proposed technology. Fundamental studies in mass transfer and kinetics are beneficial to reactor design and process optimization.
Table of Contents

Executive Summary .................................................................................................................. ii
Table of Contents ...................................................................................................................... v
List of Figures ........................................................................................................................ viii
List of Tables ........................................................................................................................... xi
1. Introduction ....................................................................................................................... 1
2. Screening Overall Process for Simultaneous Absorption of Sulphur Dioxide and Nitric Oxide ......................................................................................................................... 4
   2.1 Different processes to treat post-combustion flue gas .................................................... 4
   2.2 Summary ....................................................................................................................... 10
3. Establishment of a continuous wet scrubbing system ..................................................... 11
   3.1 De-SOxNOx System with a Coal Stove ...................................................................... 11
      3.1.1 Coal ......................................................................................................................... 12
      3.1.2 Coal/Wood Stove .................................................................................................. 13
      3.1.3 Gas Filter ............................................................................................................... 14
      3.1.4 HFMC/Spray Tower ............................................................................................. 14
      3.1.5 Circulation tank and pump .................................................................................... 16
      3.1.6 Portable oxygen analyzer ....................................................................................... 16
   3.2 Continuous De-SOxNOx System with Simulated Flue Gas ......................................... 17
      3.2.1 Different Cylinders ............................................................................................... 18
      3.2.2 Mass Flow Controllers ......................................................................................... 18
      3.2.3 Electric Inline Heater ............................................................................................ 20
   3.3 Summary ....................................................................................................................... 20
4. Absorption of SO2 in a Cross-Flow Hollow Fiber Membrane Contactor using Water ... 21
   4.1 Experimental Setup .................................................................................................... 21
   4.2 Calculations ................................................................................................................ 23
   4.3 Results of the Absorption of SO2 into Water .............................................................. 25
   4.4 Summary ....................................................................................................................... 27
5. Liquid-Side Mass Transfer Coefficient in the Cross-Flow Hollow Fiber Membrane Contactor ..................................................................................................................... 28
List of Figures

Figure 1. Flow sheet of a typical post-combustion flue gas treatment system ......................... 2
Figure 2. a) a train of three absorbers; b) simultaneous removal of SO₂ and NOx; c) simultaneous removal of SO₂, NOₓ and CO₂; and d) peroxidation of NO. ................................. 6
Figure 3. Three wet scrubbing options to treat SO₂ and NOₓ in the post-combustion flue gas without CO₂ capture including a) sequential control of SO₂ and NOₓ; b) simultaneous removal of SO₂ and NOₓ, and c) preoxidation ........................................................................... 7
Figure 4. A continuous flue gas treatment system with coal stove ....................................... 12
Figure 5. Assemble of a spray tower using sanitary tubings and fittings ......................... 15
Figure 6. Continuous flue gas treatment system with simulated gas source ................. 18
Figure 7. Experimental setup for gas absorption in a HFMC ................................................. 23
Figure 8. The SO₂ absorption efficiency at different liquid flow rate in an HFMC .............. 25
Figure 9. SO₂ absorption efficiency in the HFMC under different liquid flow rates and inlet concentrations at $Q_G = 11425 \text{ mL/min}$ .............................................................................. 27
Figure 10. An illustration of the HFMC ............................................................................. 29
Figure 11. Experimental setup for simultaneous removal of SO₂ and NO with photochemical regeneration of CoⅡion ........................................................................................................ 32
Figure 12. NO concentration at outlet of column with different methods (Inlet concentration = 480 ppm) .................................................................................................................. 34
Figure 13. The NO concentration at column outlet for inlet NO = 425 ppm, SO₂ = 1500 ppm, and O₂ = 5% ........................................................................................................... 35
Figure 14. Comparison of two continuous UVC reactors (a) Absolute H₂O (b) NanoZapp .. 36
Figure 15. UV regeneration of used cobalt(II) absorbent ..................................................... 37
Figure 16. Proposed experimental rig for the option using peroxidation ............................ 39
Figure 17. Experimental setup for a simplified UV reactor system ................................ 42
Figure 18. Diagrams of a) blank test, b) column with two fillets of TiO₂ filter, and c) commercial TiO₂ filter ........................................................................................................... 43
Figure 19. Pictures of TiO₂ thin film coated on quartz sleeve ............................................. 44
Figure 20. The change in NO and NO$_2$ concentrations before and after UVC irradiation at experimental conditions of NO = 400 ppm, O$_2$ = 6%, and QG = 300 mL/min ..................... 44

Figure 21. NO and NO$_2$ change before and after UVC irradiation with the assistant of TiO$_2$ under experimental conditions of NO = 400 ppm, O$_2$ = 6%, and QG = 300 mL/min ........... 45

Figure 22. The distribution of NO$_x$ species under photocatalytic oxidation (TiO$_2$ catalyst was baked at 280 oC) ..................................................................................................................... 46

Figure 23. Results of (upper) 1st regeneration, and (lower) 2nd regeneration at 280 °C ...... 48

Figure 24. Performance comparison between new catalyst and catalyst regenerated at 500 °C for 2hr...................................................................................................................................... 49

Figure 25. Typical results of long-term behavior of the TiO$_2$ catalyst (all concentrations are measured in the effluent, space time: 12 s, inlet NO concentration: 40 ppm, light source:2 × 8W BL, relative humidity: 50%, catalyst weight: 1.11 mg/cm$^2$. Adapted from Devahasdin 32)............................................................................................................................................. 52

Figure 26. (A) Relation between catalytic efficiency and irradiation time. (B) SO$_2$ and NO removal efficiencies at 7 h with respect to first test (from panel A) and that of second test (after catalyst regeneration). (Adapted from Su 36). ............................................................... 54

Figure 27. Photoreactor for the treatment of odorous waste air streams (adapted from Oppenländer$^{37}$) ........................................................................................................................ 56

Figure 28. A proposed method for the contact free installation of UV lamps.......................... 57

Figure 29. The double window construction applied in Polish Pilot Plant facility: (1) accelerator output device. (2) air cooling inlet (accelerator). (3) air cooling inlet (process vessel). (4) process vessel. (5) accelerator window. (6) process vessel window (Adapted from Chmielewski$^{38}$). ...................................................................................................................... 58

Figure 30. Picture of a wastewater influent (source: http://www.astwater.com/?page=TECHNOLOGIES) ............................................................................................................................................. 59

Figure 31. Picture of a UV reactor for wastewater treatment ................................................. 60

Figure 32. The design of an aluminum UVC reactor .............................................................. 63

Figure 33. Experimental system for the kinetics study of CO$_2$ absorption into aqueous ammonia solution.................................................................................................................... 68
Figure 34. The gas phase mass transfer coefficients of SO$_2$ and CO$_2$ at different temperatures ...................................................................................................................................................................................... 74

Figure 35. The relationship between NCO$_2$ and PCO$_2$ at 273.15 K. .................................................. 75

Figure 36. Plot of $k_{app}$ versus $[NH3]$ at temperatures from 273.15 – 293.15 K. ..................... 76

Figure 37. Parity plot of apparent pseudo-first order rate constant of Reaction 2 using the termolecular mechanism .................................................................................................................................................................................. 78

Figure 38. Comparison between available models (and data) at different concentrations and temperatures .................................................................................................................................................................................. 80
List of Tables

Table 1. Summary of air pollutants emitted from power plants in China and the U.S. in 2012 (Thousand Metric Tons) ........................................................................................................................................ 1
Table 2. Summary of assemble parts in Figure 5 ........................................................................ 17
Table 3. Flue gas calculation at $Q_G = 16.7 \text{ L/min} (= 1 \text{ m}^3/\text{hr})$ ............................................................... 19
Table 4. Summary of $K_G$ at different gas and liquid flow rates ($P_{SO_2, in} = 216.44 \text{ Pa}$, $a = 5328 \text{ m}^{-1}$) ........................................................................................................................................ 26
Table 5. The values of liquid-side mass transfer coefficients at different conditions .......... 30
Table 6. Materials and equipment for different NO oxidation ................................................. 40
Table 7. Lennard-Jones potentials as determined from viscosity data65 ........................................ 73
Table 8. Summary of optimal fitting parameters of zwitterion mechanism ......................... 77
Table 9. Summary of fitting parameters in termolecular mechanism ................................... 77
1. Introduction

Coal will continue to supply most electricity generation worldwide. In 2010, coal-fired power plants contributed to 40% of total worldwide electricity generation.\(^1\) In China, around 66% of electricity was generated by burning coal in 2012.\(^2,3\) In the U.S., coal provided approximately 39% of electric power in 2013.\(^4\) Although international governments plan to rely on cleaner energy such as nuclear and natural gas, the heavy reliance on coal will not significantly changed. According to latest annual energy outlook from U.S. Energy Information Administration (EIA), the coal share of total electricity generation is expected to drop to 34% in 2040 in the U.S.,\(^5\) and 52% in China.\(^1\)

As we enjoy economic development given by the consumption of coal, environmental issues it has caused cannot be evaded. For example, the reports on air pollution in metropolis had been repeatedly hit international media.\(^6\) The major causes of such smog are nitrogen oxides, sulfur dioxide, and particulate matters (PM), and coal-fired power plants are one of the primary contributors to those air pollutants.\(^7,8\) Table 1 summarizes the statistics of the major air pollutants from electricity generation sector in China and the U.S. in 2012.

Table 1. Summary of air pollutants emitted from power plants in China and the U.S. in 2012 (Thousand Metric Tons)

<table>
<thead>
<tr>
<th>Country</th>
<th>NO(_x)</th>
<th>SO(_2)</th>
<th>PM 2.5</th>
<th>PM 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>China(^9)</td>
<td>10187</td>
<td>7970</td>
<td>2228*</td>
<td></td>
</tr>
<tr>
<td>U.S.(^{10,11})</td>
<td>2148</td>
<td>3704</td>
<td>205</td>
<td>280</td>
</tr>
</tbody>
</table>

* China’s statistics only include total PM, which is the summation of PM 2.5 and PM 10.

Given the disastrous consequences associated with severe air pollution, numerous stringent regulations and laws have been issued to protect public health and environment. For example, China’s latest national air emission standards, even stricter than those in European Union (EU) and the U.S., was enforced in January 2012.\(^12\) In the U.S., EPA has issued sequentially the Clean Air Interstate Rule (CAIR), Cross State Air Pollution Rule (CSAPR) and Mercury and Air Toxic Standards (MATS) rule since 2005 to significantly cut major air pollutants from various...
In response to those regulations, air pollution control measures are required in industrial sectors. Existing post-combustion air pollution control system is usually very complicated and expensive. Figure 1 is a flow sheet diagram of a typical air pollution control system in conventional power plant. The nitric oxide and nitrogen dioxide in the high temperature flue gas are firstly removed through a selective catalytic reduction (SCR) unit, followed by an electrostatic precipitator to capture at least 99% of particles. The pretreated flue gas stream is then passing through a gas-gas heat exchanger by an induced draft fan to recover waste heat before entering a flue gas desulphurization scrubber for the absorption SO$_2$ emissions. Finally, the cleaned gas without acid gases and particulate matters are pumped to stack for release to atmosphere by a boost up fan.

Figure 1. Flow sheet of a typical post-combustion flue gas treatment system

Due to the high cost and complexity of prevalent flue gas treatment system, cost-effective air pollution control technology to meet more and more stringent standards and rules is greatly desired. The combined absorption of SO$_2$ and NO$_x$ using scrubbing is deemed as a promising alternative to current technology. The research and development of such an air pollution control technology is the core of this project.

Specifically, our objectives include the following areas:

i) to screen candidate processes for simultaneous control of multiple air pollutants and emissions;

ii) to prove the effectiveness of selected processes;
iii) to develop a novel technology for multiple gases removal based on proven technology;
iv) to experimentally investigate the performance of the reactor used in proven process under different experimental conditions;
v) to provide a fundamental understanding of gas absorption by ammonia-based solvents;
vii) to evaluate the reactor performance and optimize the proven technology for multiple air pollutants control by a mathematical model based on mass transfer and chemical kinetics.
2. Screening Overall Process for Simultaneous Absorption of Sulphur Dioxide and Nitric Oxide

The objective of this project is to develop a novel technology for the control of multiple air pollutants. Considerable progress has been made towards the proposed objectives by now, summarized as follows.

At the beginning, four schemes for the treatment of post-combustion flue gas have been proposed based on our developed absorbents. The feasible technologies are selected after repeated discussion, analysis and justification. The CO₂ capture was firstly considered, but excluded later due to research priority and funding availability.

2.1 Different processes to treat post-combustion flue gas

At first, four strategies were proposed taking CO₂ into account as presented in Figure 2. They are a) three absorbers in series; b) simultaneous removal of SO₂ and NOx; c) simultaneous removal of SO₂, NOx and CO₂; and d) peroxidation of NO. Later on, we decided to focus our attention and resources on SO₂ and NOx at this stage. Accordingly, those four options were reconsidered. As Option 3 was supposed to treat three gases simultaneously and CO₂ would not present in the following plan, it would not be applicable. Ultimately, three modules were drafted for consideration and selection, and are shown in Figure 3.
Figure 2. a) a train of three absorbers; b) simultaneous removal of SO₂ and NOx; c) simultaneous removal of SO₂, NOx and CO₂; and d) peroxidation of NO.

Figure 3(a) shows an air pollution control system that sequentially treat SO₂ in a spray tower (or packed bed tower) and NOx in a hollow fiber membrane contactor. The heat of flue gas is first recovered by an air preheater downstream economizer. The temperature of flue gas is usually reduced to around 160 °C. Further reduction in temperature is not favorable due to the condensation of sulfuric acid that will corrode the material of air preheater. The flue gas is then pretreated by an electrostatic precipitator (ESP) to capture at least 99% of particles before entering the spray tower from at bottom inlet. Aqueous ammonia solution is sprayed into the scrubber from the top entrance and flows downwards. It counter-currently contacts with the flue gas and reacts with SO₂ in the gas phase to form ammonium sulfite.

Liquid solution is collected in the bottom section of the scrubber. Air is pumped into this bottom liquid zone to oxidize sulfite into sulfate. A portion of the absorber slurry containing ammonium sulfate crystals is automatically withdrawn for dewatering and the separation of ammonium sulfate. This slurry bleed is first dewatered in a hydroclone and then in a centrifuge to produce ammonium sulfate cake with low moisture. All liquor recovered from the dewatering process is
returned to the absorber. The centrifuge cake is dried and cooled to produce a sugar-like crystal ammonium sulfate product that can be applied directly as a fertilizer.

Figure 3. Three wet scrubbing options to treat SO$_2$ and NO$_x$ in the post-combustion flue gas without CO$_2$ capture including a) sequential control of SO$_2$ and NO$_x$; b) simultaneous removal of SO$_2$ and NO$_x$, and c) preoxidation

The treated gas free of SO$_2$ passes through an ESP before entering the lumen side of a hollow fiber membrane contactor (HFMC). Ammoniacal cobalt(II) complexes counter-currently flow
into the shell side of the HFMC and contact with nitric oxide (NO) at the pore mouth located at
the liquid (shell) side. Afterwards, the cleaned flue gas without SO2 and NOx is delivered to
stack by a boost up fan (BUF) for release to atmosphere. The nitrosyl product is pumped into a
photochemical reactor (PCR) for the regeneration of cobalt(II) absorbent. The liquor emitted
from the PCR then primarily contains ammonical cobalt(II) complexes, ammonia, ammonium
nitrite and ammonium nitrate. This liquid mixture is recycled to absorb NOx until the
concentrations of nitrite and nitrate reach a specific level, say crystallization occurs. Afterwards,
a portion of this liquid mixture is bled out of the system for the separation of cobalt(II)
complexes from ammonia, nitrite and nitrate. Then the nitrite is oxidized into nitrate by air.
Ammonia can be recovered by heating and water scrubbing for reuse. The remaining ammonium
nitrate is an excellent source of fertilizer for certain crops. It can also be mixed with another
coproduct ammonium sulfate to produce compound fertilizer.

Figure 3(b) presents a flue gas treatment system that remove SO2 and NOx simultaneously in a
wet scrubber. The pretreatment of flue gas upstream the scrubber is the same as that in Figure
3(a). The difference lies in the absorbent system. Cobalt(II) salt such as cobalt(II) nitrate is added
to the absorbent preparation tank besides aqueous ammonia. Ammoniacal cobalt (II) complexes
formed will absorb NOx in the flue gas, and SO2 is removed by liquid ammonia solution.
Pretreated flue gas enters into the wet scrubber at bottom inlet and flows upwards. The ammonia-
based absorbent is sprayed into the tower from the top entrance and counter-currently contacts
with flue gas to produce ammonium sulfite and a cobalt(III) nitrosyl.

In order to regenerate the cobalt(II) complex for NO absorption, the produced liquid solution will
be passing through a PCR for UV irradiation to decompose nitrosyl to cobalt(II) ion, nitrite and
nitrate. Therefore, The liquor emitted from the PCR then primarily contains ammonical cobalt(II)
complexes, ammonia, ammonium sulfite, ammonium nitrite and ammonium nitrate.

This liquid mixture is recycled to absorb SO2 and NOx until the concentrations of sulfite, nitrite
and nitrate reach a specific level, say crystallization occurs. Afterwards, a portion of this liquid
mixture is bled out of the system for the separation of cobalt(II) complexes from ammonia,
sulfite, nitrite and nitrate. Then the sulfite and nitrite are oxidized into sulfate and nitrate by air.
Ammonia can be recovered by heating and water scrubbing for reuse. The remaining ammonium sulfate and ammonium nitrate are excellent compound fertilizer.

Figure 3(c) shows a different concept for the control of SO$_2$ and NO$_x$. This method pre-oxidize the NO and SO$_2$ into NO$_2$ and SO$_3$. Then the NO$_2$ and SO$_3$ are easily absorbed by liquid ammonia to produce ammonium nitrate and ammonium sulfate as compound fertilizer. The dewatering and separation of this liquid mixture is very similar to that described in Figure 3(a).

Each module mentioned in Figure 3 has its advantages and disadvantages. An economic analysis for industrial processes developed based on these three modules is highly desired in the future. In this project, we will first prove each module in a small-scale reactor before moving further. Module b) will be investigated, followed by modules c) and a). A continuous wet scrubbing system will be required for all of the three modes. Advanced HFMC will be used to replace traditional spray tower if possible because the use of HFMC will greatly highlight our technical strength. The CO$_2$ capture is expected to be included on a later stage of the project.

Therefore, research tasks can be identified upon the determination of the process for simultaneous desulfurization and denitrification. They are summarized as follows. Please note these tasks probably will not be completed in the presented order, but be conducted taking account of available materials and instruments, and research priority.

1) to establish a continuous wet scrubbing system using spray tower and HFMC;
2) to study the gas absorption performance of novel HFMC;
3) to prove the effectiveness of proposed air pollution control processes including gas absorption and absorbent regeneration;
4) to systematically investigate the performance of proven schemes using the continuous wet scrubbing system from individual gas removal to multiple gaseous pollutants control under different experimental conditions;
5) to study the mass transfer of wet scrubbers used in the gas absorption system;
6) to study the kinetics of the absorption of individual gas into ammonia-based solvents;
7) to evaluate the performance of the proposed process using mathematic models developed based on the information of mass transfer and kinetics.

2.2 Summary

In this section, three post-combustion flue gas treatment systems have been proposed, and detailed tasked have been identified to prove the proposed air pollution technologies.
3. Establishment of a continuous wet scrubbing system

As mentioned in Section 2, a continuous wet scrubbing system is required by all three proposed schemes for simultaneous desulfurization and denitrification. This section is prepared for the establishment of a continuous de-SOxNOx system. It covers two candidates for the continuous flue gas treatment system. The first option is using a coal stove to generate real flue gas, followed by particle filtration. The second will simulate flue gas by mixing various cylinder gases (and stream from particle generator, optional), followed by heating the gas to 120 °C. The flue gas flow rate will be set at 1 m³/hr (=16.7 L/min), and the L/G ratio equals to 10 mL/L. The memo primarily contains information of equipment, instruments, and materials and supplies for each option. Both systems have advantages and disadvantages. A final option is expected to be settled after discussion.

3.1 De-SOxNOx System with a Coal Stove

Figure 4 shows a continuous testing rig to treat the flue gas treatment from a coal stove. In this section, flue gas is generated by a coal stove burning blacksmithing coal from the U.S. This is the only distributor I found for bituminous coal in Canada. Other sources usually ask you to buy a minimum of several tons. The size is considered as $P_{90} = 1.91$ cm. The temperature of flue gas is first reduced by built-in heat exchanger. An air blower is optional. The flue gas temperature at outlet is monitored by a thermocouple which is connected with a data logger for data display. A heat exchanger (or even a heater) may be needed to obtain desired gas temperature. Another thermocouple will be used to check if the set temperature is reached. A gas filter is used to capture fine particulates from cooled flue gas. Afterwards, the pre-cleaned gas is directed to the bottom of a stainless steel tower with upper and lower glass indicators. Aqueous absorbent is sprayed into the column in the form of fine droplets by (atomizing) nozzles. The liquid absorbent counter-currently contacts with rising gas and flows downwards to a collection tank into which air is purged to oxidize sulfite products. The liquid is then recirculated to the spray tower by a peristaltic pump. The spray tower will have an inside diameter of 100 mm, and height of 1000 mm. The flue gas flow rate will be set at 1 m³/hr (16.7 L/min), and the L/G ratio equals to 10 mL/L. The concentrations of NOₓ and SO₂ are measured by an F.T.I.R, while oxygen is monitored by a portable analyzer. The required equipment, materials and supplies for such system are summarized as follows.
3.1.1 Coal

In this project, coal will be chosen as the burning fuel. Other fuels including gas, oil and biomass are much cleaner than coal. The emissions of those fuels contain very small amount of SO₂. High-sulfur diesel may effectively generate SO₂, but it is for special use and not available in market. Although bituminous coal may not produce enough SO₂ either, its flue gas is closest to real industrial emissions. Therefore, we may still have to add SO₂ and NOₓ to stove chimney to increase their concentrations even we burn coal in our lab.

Coal will be supplied by a local ironworks shop (Thak). The size is around ¾" with most chunks being about the size of the last joint of our thumb. The sulfur content of the coal is unknown. Coal supply in Canada is rather limited as it is not a heating source for Canadian homes. A minimum of several tons are required if we buy from a company. There are few distributors in the marketplace. According to my knowledge, Thak is the only bituminous coal retailer in Canada. Some others may provide anthracite coal. In conclusion, we can buy coal of ¾" chunks. This needs to be considered in choosing coal stove.
3.1.2 Coal/Wood Stove

Coal stove suppliers are really rare in Canada because coal is not used for residential heating. A retailer on Amazon is selling a coal stove from Poland. It is KSW Alfa Coal Multifuel Solid Fuel Heating Boiler made by Per-Eko. The following link will direct you to the product. The price is CDN$ 1,776.72. If we buy this combustor, we have to purchase an air blower to adjust primary air for combustion.

http://www.amazon.ca/gp/product/B00OMZHIRC?colid=29ZGRLH0E4PC1&coliid=I2L4CGG1YPACK6&ref_=wl_it_dp_o_pC_S_ttl

For this coal burner, we have to connect it to tap water system, and even have to equip a large water container for temperature adjustment. The space is a problem in our lab. It has built-in heat exchanger. The outlet flue gas temperature could be regulated by adjusting water flow. The gas temperature at the outlet will be measured by a thermocouple (TC). If an additional external heat exchanger is required to reach desired temperature, gas temperature downstream the heat exchanger will be monitored by a second TC. A data logger will be connected with the TCs to record temperatures.

One concern is the amount of SO$_2$ and NO$_x$ in flue gas of the coal stove. The produced flue gas may not contain high concentrations of SO$_2$ and NO$_x$. According to an EPA report, flue gas of residential coal stoves burning bituminous coals had SO$_2$ of 300 ppm or so, and non-detected NO$_x$ in 1983. Interestingly, wood/pellet stoves produced more pollutants, but still in low concentrations. With technology advancement coal stoves possess a high fuel efficiency now, and available coals are clean (low sulfur and ash). The gaseous pollutant level should be even lower than that of 1983. Thus, we may still have to add SO$_2$ and NO$_x$ from cylinders to make their concentration closer to the concentrations of industrial flue gas.

They are also various models available in China. For example, the following burners are sold on AliExpress, and can be exported to Canada. The first one is an advanced boiler, and the second one is a residential stove. Numerous great stoves can be found on Taobao in China.
Item 1: Boilers fired stove to warm the boiler environmental protection boiler coal storage rejuvenation series

Item 2: Cheap 40 coal-fired heating stove coal home heating stove heating stove coal stove to warm the boiler

3.1.3 Gas Filter
As the gas temperature at the outlet of coal stove is not high, common gas filter can be used. Our current filter capsule may be applicable. Or otherwise, we can buy it from Fisher. Most laboratory filters can handle a temperature up to 82 °C.

3.1.4 HFMC/Spray Tower
For the HFMC, we first would like to prove the effectiveness in gas absorption. A commercial product would be preferred; therefore, the Extra-Flow 2.5 X 8 model from Liqui-Cel was purchased. As for spray tower, we will build one using high-quality stainless steel tubing.

Figure 5 shows a spray tower assembled by stainless steel sanitary tubes. All pieces are largely available and can be purchased from AliExpress (the Chinese Amazon). The sellers will ship their goods to international customers. The design and mounting of such a tower will be very flexible. We can adjust diameter and height easily. Also, the stainless steel materials allow us to mount gauges and meters on the wall. Most importantly, they are much cheaper than those from Amazon.
Two sight glass indicators are used to observe the spray pattern on the top and liquid level at the bottom. The tower has I.D. of 100 mm. The diameter can be as large as 12” (300mm). However, the largest sight glass indicator is of 4” I.D. We may ask suppliers to customize it for us. Every
two pieces are connected by a tri-clamp. Gas enters the tower from the lower Tee, and exits at the upper tee. All open ends are covered by end cap. The thickness of the end cap is around 6 mm. We can then drill holes on it to connect tubes and pipes. The upper tee is also used to install mist eliminator, which can be stainless stain wire mesh or pad, or even sponges. The entire column will be mounted to the wall by three brackets.

Spray nozzles are selected according to liquid flow rate. In our project, the flue gas flow rate will be set at 1 m3/hr (16.7 L/min), and the L/G ratio equals to 10 mL/L. Hence, the liquid flow rate will be 167 mL/min. This may be high enough to use hydraulic full cone nozzle to produce fine droplets. Otherwise, we can consider twin fluid atomizing nozzles. The other flow could be compressed air. We just need to know the flow rate of compressed air. Then we can correct the diluted gas concentrations. Nozzles can be purchased from Spraying System Company. I would also appreciate it if Dr. Tan and Li could recommend some nozzles for this range of liquid flow rate. All the assembling parts is tabulated in Table 2. The estimated price is around US$ 413 (shipping fee is excluded). It is much quicker than machine shop and also way cheaper.

3.1.5 Circulation tank and pump

It can be bought from local supermarket and modified in the lab. 4L volume should be enough. We already have a small peristaltic pump in our lab.

3.1.6 Portable oxygen analyzer

This could be a large expense. FTIR cannot measure the concentration of oxygen in gas. In this system, we cannot roughly calculate the O2 concentration like what we will do in Section 2. Therefore, we have to buy a portable oxygen (flue gas) analyzer at around 2000 CAD.
### Table 2. Summary of assemble parts in Figure 5

<table>
<thead>
<tr>
<th>Part Name</th>
<th>Size</th>
<th>Qty.</th>
<th>Unit Price (US $)</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>4” O.D. Sanitary Tube</td>
<td>36” L x 2.8 mm T</td>
<td>2</td>
<td>46</td>
<td>NEW TEK MACHINERY FACTORY</td>
</tr>
<tr>
<td>Tee</td>
<td>4”</td>
<td>1</td>
<td>40</td>
<td>Wenzhou Kuwata Fluid Automation Equipment Co., Ltd</td>
</tr>
<tr>
<td>Tee</td>
<td>2”</td>
<td>1</td>
<td>18</td>
<td>Wenzhou Kuwata Fluid Automation Equipment Co., Ltd</td>
</tr>
<tr>
<td>Sight Glass</td>
<td>4”</td>
<td>1</td>
<td>69.29</td>
<td>Wenzhou Shifeng Metals Co., Ltd.</td>
</tr>
<tr>
<td>Sight Glass</td>
<td>2”</td>
<td>1</td>
<td>46.04</td>
<td>Wenzhou Shifeng Metals Co., Ltd.</td>
</tr>
<tr>
<td>Reducer</td>
<td>4” x 2”</td>
<td>1</td>
<td>16.20</td>
<td>D&amp;S 2012</td>
</tr>
<tr>
<td>Supporting Brackets</td>
<td>0-200mm Diameter Flex.</td>
<td>3</td>
<td>24.29</td>
<td>CCTVSHOP</td>
</tr>
<tr>
<td>End cap</td>
<td>4”</td>
<td>2</td>
<td>6</td>
<td>NEW TEK MACHINERY FACTORY</td>
</tr>
<tr>
<td>Tri-clamp</td>
<td>4”</td>
<td>5</td>
<td>5</td>
<td>NEW TEK MACHINERY FACTORY</td>
</tr>
<tr>
<td>EPDM gasket</td>
<td>4”</td>
<td>5</td>
<td>0.6</td>
<td>NEW TEK MACHINERY FACTORY</td>
</tr>
<tr>
<td>End cap</td>
<td>2”</td>
<td>2</td>
<td>2.2</td>
<td>NEW TEK MACHINERY FACTORY</td>
</tr>
<tr>
<td>Tri-clamp</td>
<td>2”</td>
<td>4</td>
<td>3.2</td>
<td>NEW TEK MACHINERY FACTORY</td>
</tr>
<tr>
<td>EPDM gasket</td>
<td>2”</td>
<td>4</td>
<td>0.4</td>
<td>NEW TEK MACHINERY FACTORY</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td><strong>413.2</strong></td>
<td></td>
</tr>
</tbody>
</table>

### 3.2 Continuous De-SOxNOx System with Simulated Flue Gas

The second option for the continuous De-SOxNOx system is shown in Figure 6. It is to simulate flue gas in the lab by mixing different gases from compressed cylinders. In order to ensure
experimental conditions close to industrial environment, a particle generator is used to add particulate matters into the simulated flue gas. The simulated gas stream is mixed by an inline static mixer before passing a gas filter. It is then heated up to around 120 °C by an inline electrical heater. Temperatures upstream and downstream of the heater are monitored by two thermocouples, and recorded in a two-channel data logger. In order to adjust the heater efficiency for different gas rate, a variable voltage transformer will be used. The pre-treated flue gas will then directed to the following gas absorption section, which is the same as that in Figure 4. The required equipment, materials and supplies for this system are summarized as follows. Those already mentioned in Section 3.1 will not be repeated herein.

![Figure 6. Continuous flue gas treatment system with simulated gas source](image)

**3.2.1 Different Cylinders**

All cylinders except 50% CO₂ and specialty pressure regulators are available in our lab. CO₂ cylinder with purity higher than 50% will require a pressure regulator unavailable in our group.

**3.2.2 Mass Flow Controllers**

The mass flow controllers (MFCs) will require a large investment. Currently we have four mass flow meters rather than controllers in our lab. They are 5 L/min N₂ meter, 500 mL/min O₂ meter, 200 mL/min SO₂ meter, and 200 mL/min NO meter. The flow rate of each gas is controlled by four metering (needle) valve. In addition, we have 2 rotameters with ranges of 16 and 23 L/min, respectively. As we will choose a flue gas rate of 33 L/min or higher, the mass flow meters may
be out of range except the 5L/min N₂ meter. In addition, the reading of mass flow meters fluctuate greatly at high gas flow, and will always decrease or increase with time. They are very inconvenient for long-term operation. Mass flow controllers with built-in control valves are more suitable for our experiments, and much easier for the researchers to run tests. The MFCs allow us to adjust set points for flow rate, and we do not have to monitor the reading all the time.

I will use \( Q_G = 16.7 \text{ L/min} (1 \text{ m}^3/\text{hr}) \) to choose the range of each MFC, and summarize the results in Table 3. All cylinders will be from Praxair, and the purity of each cylinders are in the fourth column of Table 3. The flow rate from each cylinder to simulate a gas stream containing 15% CO₂, 5% O₂, 1500 ppm SO₂, and 500 ppm NO is tabulated in the fifth column highlighted in red. Assuming the flow rate for each cylinder is around the middle of the range of a MFC, and checking the availability of MFCs on ColeParmer website, the preferred ranges of each MFC can be found in the second last column with the price in the last column. Those ranges will also allow us to choose higher flue gas rates. The price does not represent discount. We can get a minimum discount of 10% off.

(Optional: We may also require a MFC for particle delivery. The range of 5L/min will be recommended.)

<table>
<thead>
<tr>
<th>Gas</th>
<th>Desired Concentration</th>
<th>Required Flow Rate (mL/min)</th>
<th>Cylinder Purity</th>
<th>Cylinder Flow Rate (mL/min)</th>
<th>MFC Range (mL/min)</th>
<th>Price (CAD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>79.8 %</td>
<td>26599.73</td>
<td>1</td>
<td>4781.75</td>
<td>10000</td>
<td>1995.30</td>
</tr>
<tr>
<td>CO₂</td>
<td>15 %</td>
<td>4999.95</td>
<td>0.5</td>
<td>5000.00</td>
<td>10000</td>
<td>1995.30</td>
</tr>
<tr>
<td>O₂</td>
<td>5 %</td>
<td>1666.65</td>
<td>0.21</td>
<td>3968.25</td>
<td>5000</td>
<td>1995.30</td>
</tr>
<tr>
<td>SO₂</td>
<td>1500 ppm</td>
<td>50</td>
<td>0.01</td>
<td>2500.00</td>
<td>5000</td>
<td>1995.30</td>
</tr>
<tr>
<td>NO</td>
<td>500 ppm</td>
<td>16.67</td>
<td>0.02</td>
<td>416.67</td>
<td>1000</td>
<td>2011.14</td>
</tr>
</tbody>
</table>

Total 9992.34
3.2.3 Electric Inline Heater

A T-type air process heater (Model AHP-3741) can be bought from Omega. The temperature will depend on the input power. Therefore, a voltage transformer is needed for gas heating. A transformer that can supply 0 – 140 V voltage is available in our lab. Testing results given by a multimeter show that it is working properly.

Ultimately, the second proposed system was chosen after group discussion according to lab conditions and ease of control.

3.3 Summary

Two continuous wet scrubbing systems have been proposed. After several runs of group discussion, the system described in Section 3.2 has been selected in the laboratory-scale testing based on lab space, university safety guideline and ease of control. The continuous gas absorption using HFMC has been established, and that using spray tower is in progress. Orders for major components have been placed, and we expect to have them by the end of November 2015.
4. Absorption of SO$_2$ in a Cross-Flow Hollow Fiber Membrane Contactor using Water

This part of work is to verify that the cross-flow hollow fiber membrane contactor (HFMC), which was commonly used in liquid extraction and degassing, can be employed in flue gas clean up as shown in Option 1 (see Figure 3a). The HFMC is deemed as a superior reactor to conventional reactor such as spray tower primarily due to the following reasons. First, it has a much higher interfacial area. Secondly, the gas and liquid phases can be regulated independently; therefore, it eliminates the operational problems like flooding and unloading. Least but not last, its compactness and linear scale-up ensure economic advantages. The use of HFMC has attracted numerous attention in CO$_2$ capture, but the information on toxic gases including SO$_2$ and NO$_x$ is very limited. This subproject is to investigate the applicability of HFMC in SO$_2$ absorption, and to justify its use in our future plan.

4.1 Experimental Setup

Figure 7 shows the experimental system for the absorption of SO$_2$ into deionized (DI) water in a HFMC. Flue gas streams with 2000 ppm SO$_2$ were prepared by diluting the gas flow from a concentrated SO$_2$ cylinder using pure N$_2$. The flow rates of SO$_2$ and N$_2$ were regulated by a mass flow controller (Model 32649-58 with accuracy of ± 1% full scale) and a high-resolution correlated flowmeter (Model 03229-33 with accuracy of ± 2% full-scale). The flow controller and flowmeter were from Cole-Parmer Canada Inc. The overall gas flow rate was between 8276 and 18073 mL·min$^{-1}$. All gas cylinders were from Praxair Inc. (Waterloo, Ontario, Canada). Pure N$_2$ cylinder was of grade 4.8, and the SO$_2$ cylinder contained 15% SO$_2$ balanced in N$_2$.

Simulated flue gas passed through an in-line mixer before being filtered by a 0.2 µm filter capsule. The gas then entered the lumen side of a cross-flow hollow fiber membrane contactor (HFMC, Liqui-Cel Extra-Flow 2.5 x 8) via its top gas connection. Gas pressures at inlet and outlet were monitored by pressure gauges. The pressure drop of gas phase was negligible. The SO$_2$ concentration of treated gas was continuously measured by a gas analyzer with repeatability of ≤ 0.5% of span (Model EL3020 from ABB). The flow rate of sampling gas was maintained at 1.5 L·min$^{-1}$. An ice bath was required prior to the analyzer to remove moisture from sampling gas.
Fresh DI water at 27 °C was introduced to the shell side of HFMC through liquid bottom connection by a peristaltic pump. It was filtered by a 5.0 µm filter capsule upstream of the HFMC. The water flow rate varied from 194 to 463 mL·min⁻¹. The liquid pressures at both inlet and outlet were manipulated by a pressure regulator valve and measured by pressure gauges. The liquid pressure should always be higher than gas pressure to ensure that bubbles were not generated in the liquid phase. Gas and liquid then counter-currently contacted at the pore mouth located on the liquid side. The used absorbent was collected in a storage tank.

The system reached a steady state quickly. The stable reading given by the gas analyzer was then collected as the SO₂ concentration at outlet for a specific experimental condition. The SO₂ removal efficiency is described as follows. At least 5 replicates were taken at each fixed condition. The average value will then be presented.

\[
\eta = 1 - \frac{y_{\text{out}}}{y_{\text{in}}}
\]  

(1)

where \(y_{\text{in}}\) and \(y_{\text{out}}\) are the SO₂ concentration at the inlet and outlet, respectively, and \(\eta\) is the removal efficiency.
Figure 7. Experimental setup for gas absorption in a HFMC

Fresh DI water is introduced to the shell side of HFMC through liquid bottom connection by a peristaltic pump. The aqueous absorbent is filtered by a 5.0 µm filter capsule upstream of the HFMC. The liquid pressures at both inlet and outlet are manipulated by a pressure regulator valve and measured by pressure gauges. The liquid pressure should always be higher than gas pressure to ensure that bubbles are not generated in liquid phase. Gas and liquid then counter-currently contact at the pore mouth located on the liquid side. The used absorbent with by-products are collected in a storage tank.

4.2 Calculations

Mass balance on the gas phase using logarithmic mean driving force results in the following equation.\(^7\) According to manufacturer’s data, the constant interfacial area for gas-liquid contact is 1.674 m\(^2\). Therefore, the specific interfacial area, \(a = \frac{A_r}{V} = 5328 \text{ m}^{-1}\).

\[ Q_G \cdot C_{G,in} = Q_G \cdot C_{G,out} + K_G A_r \cdot \Delta P_{im} \tag{2} \]

where

\[ \Delta P_{im} = \frac{\Delta P_{in} - \Delta P_{out}}{\ln \left( \frac{\Delta P_{in}}{\Delta P_{out}} \right)} \tag{3} \]

Henry’s Law leads to

\[ \Delta P_{in} = P_{G,in} - H[SO_2]_L \tag{4} \]
\[ \Delta P_{out} = P_{G,out} \tag{5} \]

Substituting Eqs. 3-5 into Eq. 2 leads to the expression of overall gas phase mass transfer coefficient.

\[ K_G = \frac{Q_G (C_{G,in} - C_{G,out})}{A_r (P_{G,in} - H[SO_2]_L - P_{G,out})} \ln \left( \frac{P_{G,in} - H[SO_2]_L}{P_{G,out}} \right) \tag{6} \]

The absorption of SO\(_2\) in water is a fast reversible reaction describe as follows.

\[ SO_2 + H_2O \rightleftharpoons H^+ + HSO_3^- \tag{7} \]
The rate constant \( k_1 \) and equilibrium constant \( K \) of Reaction 7 are \( 3.4 \times 10^6 \, s^{-1} \) at 25 °C and 13.2 mol·m\(^{-3} \) at 27 °C. Therefore, it is justifiable to assume the dissolved \( \text{SO}_2 \) in water and \( \text{HSO}_3^- \) ion are in equilibrium at liquid outlet. Then the equilibrium constant is,

\[
K = \frac{[H^+][\text{HSO}_3^-]}{[\text{SO}_2]_{\text{Lo}}}
\]  

(8)

In addition, due to the electroneutrality of the solution,

\[
[H^+] = [\text{HSO}_3^-]
\]

(9)

Combination of Eqs. 8 and 9 gives,

\[
[\text{HSO}_3^-] = \sqrt{K[\text{SO}_2]_{\text{Lo}}}
\]

(10)

Then the total concentration of S(IV) in the liquid at outlet is described as

\[
[S(IV)]_{\text{out}} = [\text{SO}_2]_{\text{Lo}} + \sqrt{K[\text{SO}_2]_{\text{Lo}}}
\]

(11)

The expression of \([\text{SO}_2]_{\text{Lo}}\) is presented as follows by solving Eq. 11.

\[
[\text{SO}_2]_{\text{Lo}} = \frac{K + 2[S(IV)]_{\text{out}} - \sqrt{K^2 + 4K[S(IV)]_{\text{out}}}}{2}
\]

(12)

Overall mass balance on the entire membrane contactor gives,

\[
Q_G \cdot C_{G,in} = Q_G \cdot C_{G,out} + Q_L [S(IV)]_{\text{out}}
\]

(13)

Rewriting Eq. 13 and applying the Ideal Gas Law result in,

\[
[S(IV)]_{\text{out}} = \frac{Q_G}{RTQ_L} (P_{G,in} - P_{G,out})
\]

(14)

The combination of Eqs. 6, 13 and 14 finally leads to,

\[
K_G = \frac{Q_G (P_{G,in} - P_{G,out})}{A_T RT (P_{G,in} - P_{G,out} - H[\text{SO}_2]_{\text{Lo}})} \ln \left( \frac{P_{G,in} - H[\text{SO}_2]_{\text{Lo}}}{P_{G,out}} \right)
\]

(15)

where

\[
[\text{SO}_2]_{\text{Lo}} = \frac{K}{2} + \frac{Q_G}{RTQ_L} (P_{G,in} - P_{G,out}) - \frac{\sqrt{K^2 + 4KQ_G}}{2} \frac{Q_G}{RTQ_L} (P_{G,in} - P_{G,out})
\]

(16)
4.3 Results of the Absorption of SO₂ into Water

The performance of the HFMC is shown in Figure 8. The gas flow rate varies from 8276 to 18073 mL/min, and the liquid rate is between 194 and 463 mL/min. Thus, the gas to liquid ratio (G/L) is 18 – 83, excessively greater than that of conventional reactor which is 6-10. It shows that both gas and liquid phases can be manipulated independently. Therefore, with the same gas processing capacity, it can achieve a comparable performance to conventional reactor at a much smaller size and a much lower liquid consumption and relevant operational costs like pumping expense. For example, at the gas flow rate of 8276 mL/min, an absorption efficiency higher than 99.5% can be achieved at a liquid flow rate as low as 261 mL/min.

![Figure 8. The SO₂ absorption efficiency at different liquid flow rate in an HFMC](image)

Table 4 summarizes the value of $\dot{K}_G$ calculated according to Eqs. 15 and 16 under different experimental conditions at the inlet SO₂ concentration of 2000 ppm. As expected, the $\dot{K}_G$ increases with increasing liquid flow rate and decreasing gas flow rate, respectively. Because the interfacial area as well as specific area remains unchanged regardless of gas and liquid flow rates, the change in overall volumetric mass transfer coefficient, $K_Ga$, shares the same trend as that in $\dot{K}_G$. This merit allows us to manipulate gas and liquid flow rate independently, which is
another advantage of HFMC. The value of $K_G \alpha$ of the HFMC is in the order of $10^{-3}$ mol/(s·m³·Pa), which is higher than those of conventional wet SO₂ scrubbers although water is used in HFMC while effective alkaline absorbents are used in the compared reactors.\textsuperscript{18-20} It indicates that the HFMC has advantage in SO₂ absorption over conventional absorbers.

Table 4. Summary of $K_G$ at different gas and liquid flow rates ($P_{SO_2,in} = 216.44$ Pa, $a = 5328$ m\(^{-1}\))

<table>
<thead>
<tr>
<th>$Q_G$ mL/min</th>
<th>$Q_L$ mL/min</th>
<th>$P_{SO_2,out}$ Pa</th>
<th>$[SO_2]_{L,o}$ mol/m(^3)</th>
<th>$K_G$ (10^7) mol/(s·m(^2)·Pa)</th>
<th>$K_G \alpha$ (10^3) mol/(s·m(^3)·Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>194</td>
<td>1.92</td>
<td>0.68</td>
<td>1.97</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>261</td>
<td>1.13</td>
<td>0.41</td>
<td>1.99</td>
<td>1.06</td>
<td></td>
</tr>
<tr>
<td>8276</td>
<td>330</td>
<td>0.83</td>
<td>0.27</td>
<td>2.01</td>
<td>1.07</td>
</tr>
<tr>
<td>397</td>
<td>0.47</td>
<td>0.20</td>
<td>2.16</td>
<td>1.15</td>
<td></td>
</tr>
<tr>
<td>463</td>
<td>0.28</td>
<td>0.15</td>
<td>2.31</td>
<td>1.23</td>
<td></td>
</tr>
<tr>
<td>194</td>
<td>12.53</td>
<td>1.06</td>
<td>1.86</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>261</td>
<td>7.36</td>
<td>0.68</td>
<td>1.92</td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>11425</td>
<td>330</td>
<td>5.59</td>
<td>0.46</td>
<td>1.92</td>
<td>1.03</td>
</tr>
<tr>
<td>397</td>
<td>5.04</td>
<td>0.33</td>
<td>1.90</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>463</td>
<td>4.17</td>
<td>0.26</td>
<td>1.95</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>194</td>
<td>31.64</td>
<td>1.37</td>
<td>1.79</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>261</td>
<td>23.16</td>
<td>0.91</td>
<td>1.74</td>
<td>0.93</td>
<td></td>
</tr>
<tr>
<td>14751</td>
<td>330</td>
<td>16.94</td>
<td>0.65</td>
<td>1.82</td>
<td>0.97</td>
</tr>
<tr>
<td>397</td>
<td>13.44</td>
<td>0.49</td>
<td>1.89</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>463</td>
<td>10.63</td>
<td>0.38</td>
<td>1.98</td>
<td>1.06</td>
<td></td>
</tr>
<tr>
<td>194</td>
<td>49.08</td>
<td>1.62</td>
<td>1.86</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>261</td>
<td>34.56</td>
<td>1.15</td>
<td>1.89</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>18073</td>
<td>330</td>
<td>27.42</td>
<td>0.83</td>
<td>1.91</td>
<td>1.02</td>
</tr>
<tr>
<td>397</td>
<td>23.57</td>
<td>0.63</td>
<td>1.92</td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>463</td>
<td>20.85</td>
<td>0.50</td>
<td>1.94</td>
<td>1.03</td>
<td></td>
</tr>
</tbody>
</table>

Figure 9 shows the removal efficiency of SO₂ absorption into water in the HFMC at different liquid flow rates and inlet concentrations. The gas flow rate was set at 11425 mL/min. The efficiency steadily decreases with increasing inlet SO₂ concentrations and decreasing liquid flow rates, respectively. At $Q_L = 330$ mL/min, at which G/L is 34.6, the efficiency drops from 98.45% to 96.64% as inlet SO₂ concentration increases from 1000 to 3000 ppm.
Figure 9. SO2 absorption efficiency in the HFMC under different liquid flow rates and inlet concentrations at $Q_G = 11425 \text{ mL/min}$

### 4.4 Summary

The efficiency of SO2 removal using water in the HFMC remains greater than 99% at $Q_G = 8276 \text{ mL/min}$ with liquid-to-gas (L/G) ratio ranging from 0.02 to 0.06. The gas and liquid flow rates can be regulated independently without causing operational failures. The SO2 removal efficiency increases with increasing liquid flow rate and decreasing gas flow rate and SO2 inlet concentration, respectively. The overall volumetric gas phase mass transfer coefficient ($K_G\alpha$) of the HFMC is in the range of $10^{-3} \text{ mol} \cdot \text{s}^{-1} \text{m}^{-3} \text{Pa}^{-1}$, which is higher than those of conventional wet SO2 scrubbers although water is used in HFMC while effective alkaline absorbents are used in the compared reactors. It indicates that the HFMC has advantage in SO2 absorption over conventional absorbers.
5. Liquid-Side Mass Transfer Coefficient in the Cross-Flow Hollow Fiber Membrane Contactor

This part of work is to measure the liquid-side mass transfer coefficient ($k_L$) in the HFMC used in our project. Reactor modelling is a strong tool towards the commercialization of the proposed technology. It can provide information on performance at specific industrial condition. Therefore, it is desired to establish a reactor model of the HFMC, and use the experimental data to verify this model. An important parameter required in the development of reactor model is the information on $k_L$. Because this type of HFMC is usually used in liquid extraction and degassing, the available empirical correlations for the determination of $k_L$ value may not applicable. This subproject is to propose an empirical correlation for $k_L$ estimation.

5.1 Experimental Section

The experimental setup is shown in Figure 7 as mentioned above. However, the gas-liquid subject is now the CO$_2$-H$_2$O system because the physical absorption of CO$_2$ into water is known as a process controlled by liquid side resistance. This testing system has also been used by previous researchers. The absorption of 15% carbon dioxide into water is conducted to measure the value of $k_L$ at gas flow rate from 797 to 13094 mL·min$^{-1}$, and liquid rate between 121-463 mL·min$^{-1}$. The CO$_2$ concentration is determined by titration with NaOH according to a standardized method. Results of CO$_2$ absorption into water at different gas and liquid flow rates are collected to develop the empirical correlation, which ultimately will be in the following form.

$$Sh = aRe^bSc^c$$

(17)

The expression of each dimensionless group and involved parameters are presented as below. The meaning of important sizes are shown in Figure 10.

$$Sh = \frac{k_L \cdot d_h}{D_{CO_2,L}}$$

(18)

$$Re = \frac{\bar{u}_L \cdot d_h}{v}$$

(19)

$$Sc = \frac{v}{D_{CO_2,L}}$$

(20)

$$d_h = \frac{d_a^2 - d_T^2 - nd_o^2}{nd_o}$$

(21)
\[
\bar{u}_L = \frac{2Q_L}{\pi L} \cdot \frac{\ln(d_a/d_T)}{d_a - d_T}
\]  

(22)

5.2 Results

The calculation of \(k_L\) values is similar to that described in Section 4.2, and will not be described herein. The \(k_L\) was in the order of magnitude of \(10^{-6}\) m·s\(^{-1}\). Experimental results for different conditions are summarized in Table 5. The proposed correlation for the estimate of \(k_L\) value is as follows.

\[
Sh = 0.28Re^{0.97}Sc^{0.33}
\]

(23)

with \(R^2 = 0.9963\) was then proposed for different Reynolds numbers ranging from 0.084 to 0.322.
Table 5. The values of liquid-side mass transfer coefficients at different conditions

<table>
<thead>
<tr>
<th>$Q_L$ ($m^3/s$)</th>
<th>$Q_G$ ($m^3/s$)</th>
<th>$P_{G,in}$ (psi)</th>
<th>$k_L$ ($m/s$)</th>
<th>Std. Dev. of $k_L$ ($m/s$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.02E-06</td>
<td>1.33E-05</td>
<td>0.2</td>
<td>1.26E-06</td>
<td>5.56E-08</td>
</tr>
<tr>
<td></td>
<td>6.23E-05</td>
<td>1.0</td>
<td>1.10E-06</td>
<td>7.91E-08</td>
</tr>
<tr>
<td></td>
<td>1.38E-04</td>
<td>2.0</td>
<td>1.20E-06</td>
<td>6.26E-08</td>
</tr>
<tr>
<td>3.23E-06</td>
<td>1.33E-05</td>
<td>0.2</td>
<td>2.07E-06</td>
<td>8.88E-08</td>
</tr>
<tr>
<td></td>
<td>6.23E-05</td>
<td>1.0</td>
<td>2.1E-06</td>
<td>1.45E-07</td>
</tr>
<tr>
<td></td>
<td>1.38E-04</td>
<td>2.0</td>
<td>1.97E-06</td>
<td>1.48E-07</td>
</tr>
<tr>
<td>4.35E-06</td>
<td>1.33E-05</td>
<td>0.2</td>
<td>2.77E-06</td>
<td>3.35E-08</td>
</tr>
<tr>
<td></td>
<td>6.23E-05</td>
<td>0.2</td>
<td>2.64E-06</td>
<td>4.33E-08</td>
</tr>
<tr>
<td></td>
<td>1.38E-04</td>
<td>2.0</td>
<td>2.37E-06</td>
<td>2.14E-07</td>
</tr>
<tr>
<td>5.5E-06</td>
<td>1.33E-05</td>
<td>0.9</td>
<td>3.45E-06</td>
<td>2.43E-07</td>
</tr>
<tr>
<td></td>
<td>2.08E-05</td>
<td>0.5</td>
<td>3.47E-06</td>
<td>3.34E-07</td>
</tr>
<tr>
<td></td>
<td>3.75E-05</td>
<td>1.0</td>
<td>3.14E-06</td>
<td>1.91E-07</td>
</tr>
<tr>
<td></td>
<td>6.23E-05</td>
<td>1.0</td>
<td>3.17E-06</td>
<td>2.57E-07</td>
</tr>
<tr>
<td></td>
<td>1.01E-04</td>
<td>1.5</td>
<td>2.93E-06</td>
<td>9.07E-08</td>
</tr>
<tr>
<td></td>
<td>1.38E-04</td>
<td>2.0</td>
<td>3.11E-06</td>
<td>2.20E-07</td>
</tr>
<tr>
<td>6.62E-06</td>
<td>1.33E-05</td>
<td>0.2</td>
<td>4.37E-06</td>
<td>1.11E-07</td>
</tr>
<tr>
<td></td>
<td>6.23E-05</td>
<td>1.0</td>
<td>3.76E-06</td>
<td>2.39E-07</td>
</tr>
<tr>
<td></td>
<td>1.38E-04</td>
<td>2.0</td>
<td>3.64E-06</td>
<td>1.95E-07</td>
</tr>
<tr>
<td>7.72E-06</td>
<td>1.33E-05</td>
<td>0.2</td>
<td>5.23E-06</td>
<td>2.85E-07</td>
</tr>
<tr>
<td></td>
<td>6.23E-05</td>
<td>1.0</td>
<td>4.16E-06</td>
<td>3.26E-07</td>
</tr>
<tr>
<td></td>
<td>1.38E-04</td>
<td>2.0</td>
<td>4.24E-06</td>
<td>3.32E-07</td>
</tr>
</tbody>
</table>

5.3 Summary

A correlation, $Sh = 0.28Re^{0.97}Sc^{0.33}$ is proposed to estimate liquid-side mass transfer coefficient in the Liqui-Cel HFMC. This correlation will be used in reactor modeling.
6. Simultaneous Absorption of SO2 and NOx and Regeneration of Cobalt(II) Complexes (Module b)

The objective of this section is to show that the developed idea in Figure 3b can work; the efficiency of absorption is not a concern herein. As the absorption of SO2 and NO by ammonical cobalt(II) has already verified by in previous research,7 this section focuses more on the regeneration of used absorbent. An effective regeneration can ensure the success of Module b shown in Figure 3.

This section briefly summarizes the experimental results of the UV regeneration of cobalt(II) ions. The used absorbent was circulated with and without UV reactor, respectively. The regeneration was shown by comparing the performance between cases with and without UV reactor. The absorption efficiency is not the concern in the current proof of UV regeneration, and it will be the focus in the following process optimization after present concept validation.

6.1 Experimental Section

Figure 11 shows the laboratory system for the absorption of NOx and SO2 into ammoniacal cobalt(II) solutions. The wet scrubber used is a packed bed column with inner diameter of 3/4”. The height of the column is 36”. Simulated flue gas stream with 5% oxygen, 1500 ppm SO2 and 500 ppm NO is fed into the packed bed at a flow rate of 500 mL/min. Ammoniacal cobalt(II) absorbent is sprayed into the scrubber from top entrance at a rate of 50 mL/min, and countercurrently contacts with gas phase on packing surface. The concentrations of SO2 and NO in cleaned gas are continuously measured by an FTIR analyzer and recorded by a computer. As SO2 will be adsorbed by most driers, an ice bath is placed upstream the analyzer to remove moisture.

The product liquid that primarily contains aqueous ammonia, ammonium sulfite, cobalt(III) nitrosyl enters a photochemical reactor (PCR) emitting 254 nm UV rays by gravity. The cobalt(III) nitrosyl complex is decomposed into cobalt(II) ion, nitrite and nitrate in the PCR. Therefore, liquid solution after irradiation in the PCR is regenerated and recycled to the packed bed column.
The initial cobalt(II) concentration is set at 0.01 mol/L. This system is working at room temperature and atmospheric pressure at this stage. If this system can continuously remove SO₂ and NO regardless of removal efficiency, this concept of gas absorption integrated with absorbent regeneration is deemed successful. The following task is then the optimization of this process to achieve high efficiency.

In order to compare the regeneration efficiency, performance comparison will be conducted between the cases with and without UV reactor. As a benchmark, the absorbent solution is circulated without entering the UV reactor through the by-pass line. The concentration of NO at the outlet is recorded at every 4 seconds. As a comparison, the used absorbent is directed to the UV reactor before flowing into the absorbent tank. The concentration of NO at the outlet is also recorded at every 4 seconds. Comparing continuous measurement curves of with and without UV reactor will show the regeneration performance. If the difference between two curves is large, it can be concluded that UV regeneration works.

![Figure 11. Experimental setup for simultaneous removal of SO₂ and NO with photochemical regeneration of Co²⁺ ion](image)

Figure 11. Experimental setup for simultaneous removal of SO₂ and NO with photochemical regeneration of Co²⁺ ion
6.2 Preliminary Results

Figure 12 shows the results of UV regeneration. The blue line is the results for Test 1: using UV radiation after a long period of run. The orange one shows data for Test 2: using UV radiation in the beginning. The y-axis represents the NO concentration at the column outlet. The lower this concentration, the better the performance of NO regeneration.

It seems that UV radiation is not useful in Test 1 – using UV radiation after a long period (around 7.2 hours) of run. This is mainly because the product in the solution after a long time of operation is \([\text{Co(NH}_3\text{)}_6]^3+\). This ion may need a co-catalyst like \(\Gamma\) for UV regeneration.

In Test 2 – using UV in the very beginning, UV has impact on regeneration compared to Test 1 (please see comparison between the results of Test1 and Test 2 before 15000 s) although it is weak. This might be because the oxidized product is \([[\text{NH}_3]_5\text{-Co-o-o-Co(NH}_3\text{)}_3]^4+\), which has a similar property to hydrogen peroxide. As we know, \(\text{H}_2\text{O}_2\) can be photo-decomposed by UV directly. Likewise this complex may also be decomposed by UV. After 15000s, the two results overlapped. It means that after a long period of run, \([\text{Co(NH}_3\text{)}_6]^3+\) again dominated the solution.

The reasons for such a weak effect could be due to the UV reactor. It was too huge to effectively work for our laboratory scale. Horizontal installation was used according to manual. 4L solution was needed to fill the reactor (10cm ID * 50cm long). The circulated liquid flow rate was 287 mL/min. The flow inside the UV reactor is laminar, and probably only the layer close to the center quartz tube be regenerated. The outer layers cannot be effectively radiated. There is barely radial mixing inside the reactor at such a low liquid flow (287 mL/min).

This weak regeneration needs to be verified by repeated experiments. I will also change the setup this week to make the repetition easier. I will install the UV vertically, which allows us to use low flow rate. A thin layer would flow downwards along the wall of UV reactor, and can be radiated by UV lamp. It then will be working as a falling film UV reactor.
Figure 12. NO concentration at outlet of column with different methods (Inlet concentration = 480 ppm)

Figure 13 shows the performance of the falling film UV reactor. The figure itself can show that the concentration of NO at outlet for the case of using UV reactor is lower than that for none UV reactor. The concentration difference is obvious.

However, after observation of several runs, I found that the NO readings are affected greatly by the reading of ammonia. The ammonia readings for the two cases were different. In the case of without UV, ammonia had readings, even at high values. But in the case of with UV, the readings of ammonia was “NaN”. I checked all the data, and found that NO readings were higher with a valid ammonia value, and lower if the “NaN” appeared. Therefore, the difference in NO
concentration could be from FTIR instrumental errors. We also found that the laser voltage and single beam peak kept reducing with time, which further makes FTIR readings suspicious.

The good sign from Figure 13 is that, after 2000 seconds of operation, the increase in NO concentration is much slower when using UV reactor in comparison with the case without UV reactor. This trend can somewhat reflect the regeneration of cobalt(II) ion.

![Figure 13](image-url)

Figure 13. The NO concentration at column outlet for inlet NO = 425 ppm, SO2 = 1500 ppm, and O2 = 5%.

Later, we confirmed that the FTIR had malfunction and needed a repair. Therefore, it was very difficult to conclude if the UV regeneration worked or not by results in Figure 13. Solid experimental results are needed to make final conclusion. I would re-check UV regeneration when the instrument was fixed. At the same time, the improvement of the efficiency of UV
reactor will be taken. The inline micro UV reactor may be more suitable for our laboratory scale. The inline UVC reactor has been purchased and is on its way to the lab.

6.3 Improvements according to Previous Experiments

Plan 1: The use of continuous flow UVC reactor of suitable size

![Figure 14 Comparison of two continuous UVC reactors (a) Absolute H2O (b) NanoZapp](image)

After the repair of FTIR, I would use the new UVC reactor (as shown in Figure 14b) to regenerate cobalt(II) ions. This is the core part of this concept proof. The small reactor will allow used absorbent to have a residence time of 51 sec, which is long enough for the exposure of used absorbent to UVC irradiation. Also, the small diameter will enable UVC light to penetrate to most layers surrounding the quartz tube.

Plan 2: Coating of a thin film of nano TiO2 as photocatalyst on quartz tube

In order to further improve the efficiency of the UVC reactor, the use of photocatalyst, TiO2 will be used. A thin film of nano TiO2 will be coated on the quartz tube. Our lab can do the coating now. Sigma and a local company have confirmed the supply of nano TiO2 suspensions. The
comparison between the performance with and without TiO2 catalyst can indicate the effectiveness of nano TiO2 film.

Note: The other option for the use of TiO2 is to directly add nano-sized TiO2 (P25) particle in the solution. This case is expected to have inferior performance to the coated film. The slurry can only be used in traditional reactors rather than membrane contactor as the nano particles may block the pores.

6.4 New Data with Bubble Column and Fixed FTIR

The scrubber used was a bubble column rather than a packed tower. Therefore, some specifications are described herein. The bubble column containing 400 mL ammoniacal cobalt(II) absorbent with pH of 11 and 1 mol/L NH4NO3. When the absorption reached equilibrium, the used absorbent would be subjected to UV irradiation with wavelength of 254nm for 30 min. The inlet gas contained 610 ppm NO and 6% O2, and was delivered at 500 mL/min. In order to verify the complete consumption and efficient regeneration of absorbent, a span gas of 978 ppm NO from Praxair was used before and after UV irradiation. The corresponding results are demonstrated in Figure 15.

![Figure 15. UV regeneration of used cobalt(II) absorbent](image-url)
It can be seen from Figure 15 that UV irradiation has negligible effect on cobalt(II) absorbent regeneration. The reading of span gas remained almost unchanged before and after 30 min of UV irradiation.

It is concluded that UV irradiation did not work. At this stage, we will move to next option: preoxidation of NO into NO₂.

### 6.5 Summary

In this section, we tried to verify the regeneration of used ammoniacal cobalt(II) solutions using UV irradiation. Several UV reactors were tested; however, the regeneration of absorbent was not obvious regardless of UVC reactor and regeneration sequence. In order to put forward the development progress, we will place our priority onto another module: gas phase pre-oxidation of nitric oxide as shown in Figure 3c.
7. Gas Phase Pre-oxidation of NO into NO\textsubscript{2} followed by wet scrubbing (Module c)

This option is very promising as it avoids complicated treatment of liquid waste. The economic advantages of peroxidation of NO into NO\textsubscript{2} have been acknowledged by many researchers. The oxidation of NO into NO\textsubscript{2} is desired in both wet scrubbing and SCR process. In wet technology, the NO\textsubscript{2} is much easier to be addressed by common WFGD absorbents. In the SCR process, the optimum ratio of NO : NO\textsubscript{2} is 1:1. As we know, NO accounts for 90% of NO\textsubscript{x} in flue gas and mobile exhaust. Therefore, oxidation technology is attractive to us, and it will enable us to expand to the dry flue gas treatment method.

Figure 16 shows the proposed experimental setup for the integrated simultaneous removal of NO\textsubscript{x} and SO\textsubscript{2}. This will be used to demonstrate the feasibility of peroxidation of gas phases. However, we will study this technology piece by piece. The first part will be the oxidation of NO into NO\textsubscript{2} in gas phase, followed by the simultaneous absorption of NO\textsubscript{2} and SO\textsubscript{2}.

Figure 16. Proposed experimental rig for the option using peroxidation
Currently, the reported gas phase oxidation methods primarily include ozonation, electron beam, dielectric barrier discharge, photocatalysis and catalytic oxidation using platinum, metal oxides, and activated carbon (fiber). Among them, only platinum based catalyst is commercially available for diesel engine exhaust. However, the treatment and disposal of deactivated precious metal catalyst is expensive.

Based on current facilities in our lab, photocatalytic oxide was selected due to the following considerations. The costly ozone generation limits the use of ozone. If we would like to proceed with this method, an air- or oxygen-based ozone generator is required. Platinum catalyst is much more expensive than metal oxides. If needed, we can compare the performance of metal oxide with that of commercially available Pt catalyst. The required materials or equipment for the other options are summarized in Table 6. The most important factors for NO oxidation are temperature and humidity. In addition, other parameters like flue gas components, flow rate, fix-bed depth, etc. also have significant impacts on performance.

<table>
<thead>
<tr>
<th>Oxidation Method</th>
<th>Materials and Equipment</th>
</tr>
</thead>
</table>
| Photocatalytic Oxidation  | 1. Nano TiO₂ suspension  
                           2. Quartz tubes  
                           3. UV lamps with different intensity and wavelength  
                           4. UV intensity meter |
| Metal oxides catalyst    | 1. Precursor metal salts (Sigma has most of required chemicals)  
                           2. Tube furnace for calcination and reaction (Cole-Parmer)  
                           3. Temperature Programmed Desorption can be customized using a temperature controller and FTIR or substituted by a TGA |
The simultaneous absorption of SO$_2$ and NO$_2$ can be achieved by both wet and dry FGD sorbents. Although this is a common sense, not too many researchers are working in this field due to the fact that 90% of NOx is inactive NO. We then need to compare the performance of different FGD sorbents including limestone (CaO/Ca(OH)$_2$), MgO slurry, aqueous ammonia and MnO$_2$. The reactor could be traditional scrubbers or membrane contactor. Then the integration of peroxidation and simultaneous absorption is the concept for final patent.

**7.1 Mechanisms of Photocatalytic Oxidation**

In a flue gas containing nitric oxide, oxygen, moisture, the gas phase oxidation of nitric oxide into nitrogen dioxide using UV irradiation with the assistance of TiO$_2$ catalyst can be described by the following mechanism.

Upon UV irradiation, electron-hole pairs are generated in TiO$_2$ when UV light photons are absorbed by TiO$_2$. The photo-generated holes have strong oxidizing power ($\sim 3.0$ V vs SHE) with which most pollutants in air and water can be completely decomposed and mineralized.$^{21}$

\begin{align*}
TiO_2 \rightarrow h^+ + e^- & \quad (24) \\
H_2O + h^+ & \rightarrow OH + H^+ \quad (25) \\
OH^- + h^+ & \rightarrow \cdot OH \quad (26) \\
O_2 + e^- & \rightarrow O_2^- \quad (27) \\
\cdot O_2^- + H_2O & \rightarrow OOH + OH^- \quad (28) \\
2 \cdot OOH + H_2O + e^- & \rightarrow H_2O_2 + OH^- \quad (29) \\
H_2O_2 + e^- & \rightarrow OH^- + OH^- \quad (30) \\
NO + \cdot OOH & \rightarrow NO_2 + \cdot OH \quad (31) \\
NO + 2 \cdot OH & \rightarrow NO_2 + H_2O \quad (32) \\
NO_2 + \cdot OH & \rightarrow HNO_3 \quad (33)
\end{align*}

**7.2 Experimental Section**

Figure 17 shows the testing system of a UV reactor with peroxidation section only. The UV reactor is a customized column with a quartz tube installed in the center from the top. A UVC lamp (12W, 254nm from UV Max) is then mounted inside the transparent quartz tube. The inside
diameter of the column is 1.5” and the outside diameter of the quartz tube is 7/8". The length of the column and quartz tube are 16” and 14”, respectively. The flue gas simulation section and the measurement part are the same as those in Section 5.1. The flue gas stream consisting of 400 ppmv NO, 6% of O₂, and 2% H₂O flew into the reactor at 300 mL/min.

In order to test effect of TiO₂ catalyst, three cases are investigated. They are 1) blank test without TiO₂, 2) with two fillets of commercial honeycomb TiO₂ filter from Sunpentown, and 3) TiO₂ thin film coated on the outside of a quartz sleeve. The fillet of 2”(w) X 12” (L) is directly cut from the commercial TiO₂ filter. The UVC reactor can only hold two pieces of TiO₂ fillet. The TiO₂ thin film is coated onto the cylindrical quartz tube by spraying TiO₂ nanoparticle suspension followed by 8 min heating in an oven at 280 °C. This process is repeated 5-6 times until a desired weight of TiO₂ is reached. Then the thin film of TiO₂ coating is regenerated by 30min immersion in DI water combined with 2 hours of 280 °C baking in oven or with 2 hours of 500 °C calcination in furnace. Figure 18 and Figure 19 show diagrams or pictures of different experimental scenarios.
Figure 18. Diagrams of a) blank test, b) column with two fillets of TiO$_2$ filter, and c) commercial TiO$_2$ filter.
7.3 Results and Discussion

7.3.1 Blank test without TiO$_2$ catalyst

Figure 20 illustrates the de-NOx performance under 254 nm UV irradiation only. The NO and NO$_2$ concentration are described by left and right y-axis, respectively. It can be seen that the concentration of nitric oxide remains almost unchanged with UVC beam. As for NO$_2$, it slightly decreases from 10-12 ppm to 6-8 ppm. The nitric oxide is more stubborn than NO$_2$. Without a catalyst, homogeneous photochemical reaction between NO and other matters cannot occur. However, NO$_2$ can be readily broken off to NO and ·O by UV light, and the ·O can further react with oxygen to generation O$_3$. Therefore, in our experiments, the decrease in NO$_2$ concentration upon UV light is accompanied by a slight increase in NO concentration. Due to the ineffectiveness of NO reduction and the fact that 90-95% of NO$_x$ exists in the form of NO, the use of UV without a catalyst for denitrification is not feasible.

Figure 20. The change in NO and NO$_2$ concentrations before and after UVC irradiation at experimental conditions of NO = 400 ppm, O$_2$ = 6%, and QG = 300 mL/min
7.3.2 UV with fillets of TiO\textsubscript{2} filter

Figure 21 shows the effect of TiO\textsubscript{2} on the NO\textsubscript{x} removal using UVC irradiation. The NO and NO\textsubscript{2} concentration are described by left and right y-axis, respectively. Once the UVC light is on, the NO concentration firstly decreases from 390 ppm to 320 ppm and then gradually goes up to 370 ppm in 1120 seconds. When the light is off, the reading of NO bounces up to 390 ppm again. As for NO\textsubscript{2}, it decreases from 5.5 ppm to 2.8 ppm very quickly, and maintains at 2.8 ppm until the end of the test of this case. It is concluded that TiO\textsubscript{2} filter can assist the UVC denitrification but at a very limited degree. This derives us to find a new way to immobilize the TiO\textsubscript{2} catalyst. Accordingly, the coating of TiO\textsubscript{2} thin film on the quartz sleeve is developed.

![Figure 21. NO and NO\textsubscript{2} change before and after UVC irradiation with the assistant of TiO\textsubscript{2} under experimental conditions of NO = 400 ppm, O\textsubscript{2} = 6\%, and QG = 300 mL/min](image)

7.3.3 TiO\textsubscript{2} thin film coated on quartz sleeve

Figure 22 shows the conversion of NO into NO\textsubscript{2} under TiO\textsubscript{2}-assisted UVC irradiation. The reduction of NO by photocatalytic is quite obvious. The inlet flue gas contains 402 ppm NO\textsubscript{x} (= 386 ppm NO + 16 ppm NO\textsubscript{2}). Although there is some fluctuation in NO concentration, it steadily reduces from 386 ppm to 188 ppm in the first 1500 seconds after UVC initiates. The NO removal efficiency is around 53\%. Then it gradually increases and reaches its initial reading at 5000 seconds. As far as NO\textsubscript{2} is concerned, its concentration rapidly increased from 16 ppm to 170 ppm in the first 1500 seconds during which NO concentration decreases. It means most NO...
is converted into NO\textsubscript{2}. But some NO is transformed to other nitrogen species like HNO\textsubscript{3} and HNO\textsubscript{2}.\textsuperscript{23} The generation of other nitrogen species can be more easily depicted by the NO\textsubscript{x} curve (in red dash line). The NO\textsubscript{x} concentration, which is the summation of NO and NO\textsubscript{2} concentration, is always lower than initial one upon UVC irradiation. It will be back to initial value after UV light is shut off. The generated HNO\textsubscript{3} and/or HNO\textsubscript{2} is the main cause for the deactivation of TiO\textsubscript{2} catalyst with time. Therefore, we tried to regenerate the TiO\textsubscript{2} catalyst by DI rinse and heat. HNO\textsubscript{3} can be readily decomposed at a temperature higher than 475 °C.\textsuperscript{24} However, we could only access to a 280 °C oven at first. That is why we had regeneration at 280 °C first, followed by 500 °C.

![Figure 22. The distribution of NO\textsubscript{x} species under photocatalytic oxidation (TiO\textsubscript{2} catalyst was baked at 280 oC)](image)

Figure 23 show the effectiveness of TiO\textsubscript{2} regeneration at 280 oC for 2 hours. Two cycles of regeneration are conducted. The regenerated TiO\textsubscript{2} catalyst lost much efficiency compared to the fresh one. The NO concentration drops from 390 ppm to 317 in the first 1200 seconds. It rebounds back to 390 ppm in 3400s. The greatest NO removal efficiency is lower than that of fresh catalyst, and the duration is much shorter in comparison with the fresh one. According to the lower chart of Figure 23, the performance of 2nd regeneration at 280 oC for 2hr is poorer than that of the 1st regeneration. It is concluded that regeneration of TiO\textsubscript{2} catalyst at 280 oC can...
only offer limited performance. Therefore, we conducted the regeneration of catalyst at 500 oC. In order to truly reflect the effect of temperature on TiO2 regeneration, we recoat a new thin film on the quartz tube and compare the performance of new and regenerated TiO2 catalyst. The comparison is illustrated in Figure 24.

It can be found from Figure 24 that the temperature plays a significant role in the regeneration of TiO2 catalyst. Interestingly, the regenerated catalyst even has a better performance than the fresh one. Although the fresh catalyst can readily reduce NO from 380ppm to 250 ppm in 1400 seconds, it can only last at 250 ppm for 400 seconds. As for the regenerated catalyst, it is able to reduce NO from 380 to 308 ppm in 1400 seconds; however, it can remain this efficiency for greater than 6600 seconds (not shown in Figure 24). Therefore, the overall deNOx efficiency of regenerated TiO2 catalyst is much higher than the new one. A temperature of 500 oC not only decomposes the deposited HNO3, but also changes the crystallization phase of TiO2.25 TiO2 catalyst without high temperature (at least 450 °C) is amorphous. When coated TiO2 catalyst is subjected to 500 oC annealing, the anatase phase of TiO2 crystalline occurs and dominates the thin film on the quartz sleeve. The anatase phase is more effective for photocatalytic oxidation.26 Therefore, a temperature between 500-550 oC is preferred for TiO2 thin film preparation.
Figure 23. Results of (upper) 1st regeneration, and (lower) 2nd regeneration at 280 °C
Figure 24. Performance comparison between new catalyst and catalyst regenerated at 500 °C for 2hr

7.4 Summary

In summary, experimental results indicate that TiO$_2$-assisted photocatalytic de-NOx is effective. The NO conversion efficiency is 53% when the inlet NO concentration is 400 ppm, and O$_2$ is 6%. The temperature for TiO$_2$ thin film preparation and regeneration is critical to the NO conversion efficiency. A temperature of 500-550 °C is deemed as a suitable range. It is concluded that the concept of peroxidation of NO into NO$_2$ by photocatalytic oxidation is feasible. The following tasks will include 1) study the feasibility of using TiO$_2$-assisted UV
technology in an industrial environment, 2) optimize UVC reactor design, 3) compare with other peroxidation options and 4) integrate peroxidation with gas absorption.
8. Feasibility of Multiple Pollutant Control using TiO₂-Assisted UV Irradiation

This section is to analyze the feasibility of using photocatalytic technology for flue gas treatment. The UV-based advanced oxidation technology is a mature option commercially available for organics abatement. TiO₂-assisted illumination has also found numerous applications in indoor air quality and building engineering. However, few studies have been conducted on flue gas treatment. Literature information and our preliminary results show that photocatalytic irradiation can effectively remove air pollutant such as inactive nitric oxide. It would be a very promising technology if it could be scaled up for industrial flue gas treatment. Therefore, this part is to probe the possibility of the utilization of UV technology for flue gas treatment in a power plant circumstance. Such investigation is conducted based on reaction nature, UV lamp technology, and chemical reactor design. Also, a very brief economic comparison was conducted with its potential competitors. It is finally concluded that UV technology is feasible for the de-NOx purpose.

8.1 Reaction Nature

The photocatalytic oxidation of nitric oxide has been widely used in buildings and pavement. Numerous companies that produce TiO₂ paint have been established. Well-known companies include Evonik, Kemira, Kronos, Millennium, Sachtleben and Tayca. An emerging company named Green Earth Nano Science Inc. is also located in Toronto (http://gensnano.com/). Maggos et al covered the ceiling surface of a real-size car park with TiO₂ containing paint from Millennium Chemicals to study the deNOx performance of such catalyst. The illumination was provided by 20 UV lamps. The total UV irradiance near the active surface (ceiling) was 1 W·m⁻². The results indicated a significant photocatalytic oxidation of NOx gases. The photocatalytic removal of NO and NO₂ was 19% and 20%, respectively. Águia et al compared the performances of different commercial TiO₂ catalyst as an exterior paint following the ISO 22197-1:2007(E) standard. Those TiO₂ products have been prove effectively for the oxidation of 1 ppm of NO under UV light of 365 nm wavelength. The city of Copenhagen (Denmark) investigated the De-NOx photocatalytic paving TiO₂ in a field test under solar UV exposure. A monthly abatement of NO around 22% was measured in the summer months.
Therefore, it is concluded that TiO₂ photocatalysts could successfully dealing with low concentrations of NOₓ (1 - 2.5 ppm) to improve air quality.

Researches have attempted to extend the TiO₂-assisted UV irradiation from building engineering to industrial flue gas treatment. The main idea is the conversion of inactive NO into NO₂ followed by adsorption or absorption of NO₂. Devahasdin et al.\textsuperscript{32} studied the oxidation of nitric oxide up to 60 ppm using a thin film of P-25 TiO₂ powder in a Pyrex reactor. The light source was UVA with wavelength between 320-390 nm. Results showed that NO was converted in NO₂ and HNO₃. A pronounced transient period, typically lasting several hours, was reported. The conversion of increases with space time and decreases with inlet concentration. The reactions, however, are limited by thermodynamic equilibrium after 12 s space time. Figure 25 shows the performance of TiO₂ catalyst for inlet NO concentration of 40 ppm. The steady state was reached after 6 h of operation, and the conversion of NO was approximately 35%.

![Figure 25. Typical results of long-term behavior of the TiO₂ catalyst (all concentrations are measured in the effluent, space time: 12 s, inlet NO concentration: 40 ppm, light source: 2 × 8W BL, relative humidity: 50%, catalyst weight: 1.11 mg/cm². Adapted from Devahasdin\textsuperscript{32}).](image)

Wang et al.\textsuperscript{33} immobilized P-25 TiO₂ catalyst on woven glass fabric instead of glass plate to address high concentration of NOx which was between 20 – 168 ppm in a Pyrex reactor. The UV
source was a Hg-arc lamp from Philips (the wavelength was unknown). They argued that the deactivation of TiO2 catalyst was due to the accumulation of HNO3. A water rinse combined with hot treatment was recommended to regenerate the deactivated catalyst; however, corresponding data with regard to regeneration were not shown. At high concentrations of inlet NO (147 ppm), the PCO efficiency reached 27%. The hydroxyl radical and active oxide play an important role in the oxidation of NO.

Later on, Zhao et al.34 and Yuan et al.35 studied simultaneous removal of SO2 and NO using TiO2-based photo-oxidation in a fixed bed reactor. Zhao used quartz sand as catalyst carrier, and Yuan utilized aluminum silicate fiber as support. The light source were 254 nm UVC for both studies. Zhao stated that under the optimal experimental conditions, a removal efficiency of 98% for SO2 and 50% for NO were achieved at inlet SO2 = 1500 mg/m3 and NO = 600 mg/m3. The presence of SO2 enhances the removal of NO, and vice versa. Yuan’s work showed the reduction efficiency of NO and SO2 were 37 % and 35%, respectively for flue gas containing 4% O2, 2% H2O, 12% CO2, 400 ppm SO2, and 50 ppm NO. In contradistinction to Zhao’s statement, Yuan argued that SO2 and NO were inhibitors to each other due to competition of active radicals. Yuan also claimed that the developed TiO2 catalyst could be used to capture mercury.

Recently Su et al. reported simultaneous desulfurization and denitrification using TiO2–PAN photocatalyst under 250 nm illumination.36 The results demonstrated that removal efficiencies of 99.3% for SO2 and 71.2% for NO were attained under the following optimal experiment conditions: titanium loading content, 6.78 wt %; gas flow rate, 200 mL/ min; SO2, 1700 mg/m3; NO, 650 mg/m3; flue gas humidity, 5%; inlet flue gas temperature, 40 oC. The catalyst was effectively regenerated by leaching with deionized water followed by exposure to infrared lamp irradiation for 2 h. Figure 26 shows the regeneration of TiO2-PAN catalyst. The loss of photocatalytic activity after regeneration is minor.
Also, our preliminary results in Section 4.1.2 show photocatalytic oxidation of NO into NO2 is feasible. Our photocatalytic reactor (PCR) was a cylindrical column equipped with a 12W UV lamp that emitted light of 254nm. The inside diameter of the PCR is 1.5” and the outside diameter of the quartz tube is 7/8”. The length of the column and quartz tube are 16” and 14”, respectively. A thin film of TiO2 nanoparticles was coated on a quartz sleeve as photocatalyst. The TiO2 thin film is coated onto the cylindrical quartz tube by spraying TiO2 nanoparticle suspension followed by 8 min heating in an oven at 280 °C. This process is repeated 5-6 times until a desired weight of TiO2 is reached. Then the TiO2 thin film coating is regenerated by 30min immersion in DI water combined with 2 hours of 500 °C calcination in furnace. The flue gas stream consisting of 400 ppmv NO, 6% of O2, and 2% H2O flew into the reactor at 300 mL/min.

In conclusion, both literature information and our preliminary results show that TiO2-assisted UV oxidation can be used for industrial flue gas deNOx. As this technology is still under development on laboratory scale, next comes the proof of potential industrial application and manufacturing. It is important to ensure that this technology can be scaled up and has economic advantages. UV lamp technology, mechanical properties of reactor body and economics of UV process will be elaborated.
8.2 Possibility of Application of UV Technology on Industrial Scale

8.2.1 UV Lamp Technology

Owing to the substantial advancement of advanced oxidation process (AOP) in past years, UV lamp technology has also made great stride. Commercial low pressure Hg lamp emits monochromatic source of 254 nm and can have power up to 300 W. Medium pressure Hg lamp irradiates 200 – 280nm broad band, and can possess as high as 30 kW. Average life of a low pressure UVC lamp is 9000 h (= 375 days), while that of a medium pressure lamp is slightly shorter. In addition, advanced incoherent excimer lamps that illuminate high intensity short wave vacuum UV lights are being under development. Such progress in UV lamp technology ensures the utilization of UV technology in a large industrial scale. For example, HDN-Technik GmbH, Rednitzhembach, Germany developed a photoreactor technology for odor abatement. It can be applied for the irradiation of volume flow rates of waste gas over 100000 m$^3\cdot$h$^{-1}$. Large installations contain up to 72 LP Hg lamps with a total electric input power $P_{el}^{in}$ of 5.4 kW. The dimensions of the reactor was 2.0 m × 2.0 m × 5.6 m. Figure 27 shows a picture of the photoreactor. If we would like to greatly enhance the input power, we can use medium pressure lamp. As mentioned above, a single medium pressure lamp can have an input power of 30 kW.

The reactor shown in Figure 27 can treat gas flow rate up to 100000 m$^3$/h. In large thermal power plant, typical flue gas rate is around 1000000 m$^3$/h. It is 10 times higher than the capacity of the reactor. It is very possible to scale up the illustrated technology to treat flue gas emitted from power plant.
8.2.2 Installation of UV Lamps

Two ways can be used to install UV lamps in the reactor. One is illustrated in Figure 27. A UV-transmission material is utilized as a sleeve to protect the UV lamp. The commercially ready as well as cheap option for the material is fused quartz. It has a transmission of 90% for UVC light. The other is a contact free manner that uses a UV transmission window and a reflector as demonstrated in Figure 28. The window can be made of fused quartz, and aluminum is a perfect material for reflector. This idea is borrowed from the electron beam flue gas technology (EBFGT). But the UV system is much simpler and cheaper than the electron accelerator of EBFGT.
EBFGT is a commercially ready process for the simultaneous removal of SO$_2$ and NO$_x$. In its process, it uses two windows for the introduction of electron beams as shown in Figure 29.\textsuperscript{38} The window material was a 50 um thick titanium foil.
Figure 29. The double window construction applied in Polish Pilot Plant facility: (1) accelerator output device. (2) air cooling inlet (accelerator). (3) air cooling inlet (process vessel), (4) process vessel, (5) accelerator window. (6) process vessel window (Adapted from Chmielewski38).

8.2.3 Materials of UV Sleeve and/or Window

The best option for UV sleeve or window is fused quartz. The major concern of quartz tube lies on its hardness – would it be easily broken during operation. I would like to say no as I believe the hardness of commercial fused quartz is high enough for industrial use.

Although there is some particles in the treated flue gas after ESP, most of them are very fine. Their kinetic energy is low. I do not think such kinetic energy can break a 10 mm quartz tube easily. I would like to compare the quartz material with car windshield to support my point. We assume the flow rate of flue gas is $10^6 m^3/h$, and the length and diameter of reactor is 10m and 3 m, respectively. Therefore, the velocity of gas (and particle) is 39 m/s. This velocity can be significantly lowered if the diameter is larger. Then we consider a car travelling at 140 kph (which is around 39 m/s) on highway. Although there are lots of fine particles or dust in the air above the ground, the windshield will not be broken unless it is unluckily hit by sand or stone of several millimeters.

Fused quartz has a hardness: 5.5–7 Mohs’ Scale, and most windshields manufactured for cars has around 5.5 on the Mohs scales. If a windshield can stand the hit of particle of several millimeters, the quartz that has even or higher hardness should be able to withstand the same level of hit. As the fine particles in pretreated flue gas usually has diameter in the micron range, the use of quartz materials will not be a problem.

(Sources for hardness: http://www.technicalglass.com/technical_properties.html
http://www.mt-berlin.com/frames_cryst/descriptions/quartz%20.htm, and
8.2.4 Fouling on Quartz Sleeve or Window

Fouling on quartz sleeve or window and on reactor body will occur with time, but it will not impede the application of UV technology. Again, we would like to use commercial available UV technology to support my point.

UV degradation is a very mature technology for the treatment of wastewater from different sources. It can work for wastewater from pulp mill that contains large amount of suspended solid.\textsuperscript{39,40} TiO\textsubscript{2} based advanced oxidation process (AOP) is commercially applied to treat urban wastewater treatment plant (UWWTPs) effluents with total suspended solid of 11 mg/L (= 11000 mg/m\textsuperscript{3}, which is much higher than 30 mg/m\textsuperscript{3} requirement in air)\textsuperscript{41}. It shows that UV reactor can handle solids in wastewater, and the capacity of wastewater treatment can be as high as 1000000 m\textsuperscript{3}/day.\textsuperscript{42,43} Figure 30 shows a picture of wastewater influent with high loading of suspended solids, and Figure 31 is a commercial UV reactor for wastewater treatment.

Figure 30. Picture of a wastewater influent (source: http://www.ast-water.com/?page=TECHNOLOGIES)
The concentration of particulate matters (PM) in pretreated flue gas is much lower than that of suspended solid (SS) in wastewater. If UV technology can handle the high SS in water, it should be able to handle the low PM concentration in air. In conclusion, fouling will not be a barrier to the utilization of UV technology in flue gas treatment.

8.2.5 Economics

As there is no economic data for UV deNOx, the economic comparison will be hypothetical and very brief. The comparison is conducted based on the power requirement for the capacity of 100,000 m³/h. I use the power input of UV technology for odor control as an example and assume the energy requirement for deNOx is the same as that for deodorization. For flow rate of 100,000 m³/h, the total input power of low pressure UV lamp is 5.4 kW. As for EBFGT, the
power of source is 260 kW at flow rate = 270000 m³/h. Therefore, the power consumption of EBFGT for the capacity of 100000 m³/h is 96.3 kW, much higher than that of UV technology. In addition, the price of electron accelerator is much more expensive than UV lamps. As competitors in the area of simultaneous removal of SO₂ and NOₓ, UV technology probably has huge economic strength over EBFGT.

8.3 Summary

The TiO₂-assisted UV technology can effectively remove SO₂ and NOₓ simultaneously. Mature UV lamp technology and high quality fused quartz materials ensure the application of UV technology in flue gas treatment. The UV technology can be scaled up to large installations, and the quartz material can withstand fine particles and fouling. It would probably possess huge economic advantages over other available methods such as EBFGT. Therefore, it is feasible to use UV technology for de-NOₓ purpose.
9. Design of A UVC Reactor

The prototype of a metal UVC reactor includes primarily 1) main body, 2) UVC lamp, 3) 2 stainless steel sheets coated with TiO2 thin film, and 4) gas inlet and outlet ports. As the material is metal, we can drill holes for thermalcouple and pressure transducer if needed.

9.1 Selection of Main Body

The selection of main body includes material, size, openings for installation and ports.

Aluminum is selected based on chemical and thermal stability, ease to modify, and cost. Aluminum is an excellent option for the main body. It is light and compatible to SO2, SO3 and dilute HNO3. It can withstand high temperature and can be modified easily. Also, it is a cheap material. Steel cannot handle acid gases. The option for stainless steel rectangular tube is rare. We can cut and drill holes on thick wall aluminum in lab, but sometimes it is difficult to do so on stainless steel.

Commercial rectangular tube is chose for the reactor body. As we are dealing with toxic and corrosive gases, excellent seal is critical to the design of reactor although we place the reactor in fume hood. Electric aluminum project box is very nice but the size cannot meet our requirement. The largest commercial project box is around 9”; however, the UV lamp length is about 10”. If we ask machine shop to weld four piece of plate to make a box, it is not only time consuming, but also expensive. Therefore, commercial rectangular tube is a good option as long as the size is fine. I searched online and found a product with (5” X 3” X ¼”). Here is the link. http://www.metalsdepot.com/products/alum2.phtml?page=aluminum%20rectangle%20tube&ImAcc=%20&aident=

We can buy 2 feet of such a tube and cut it into the length we want. The ¼” wall allows us to drill holes for the installation of top and bottom covers. A customized gasket will be used to ensure seal. Figure 32 shows difference views of the design of a rectangular UVC Reactor with the aluminum tube. The outside dimensions of the reactor body are 12 (H) × 5” (L) × 3” (W).
The wall thickness is 1/4″. Two aluminum plates with thickness of 1/2″ are used as top and bottom cover, respectively. They are installed by 6 bolts (or screws).

The gas inlet port (1/4 ″) is drilled on the bottom cover, and outlet port on one of the side wall as shown in Figure 32. On the top cover, an opening is cut for the installing of UVC lamps.

Figure 32. The design of an aluminum UVC reactor

9.2 UVC Lamps

Philips 210641 18-watt PL-L TUV Germicidal with 4-Pin Base Light Bulb is selected. This series also has 36 W UVC. It has a size of 9” X 1.5” X 1.5”

http://www.amazon.com/gp/product/B0018C6ZYY/ref=ox_sc_act_title_1?ie=UTF8&psc=1&smid=API63TIB17EDF
The lamp holder and ballast can also be bought from Amazon.

Note: Active cooling (by air flow) at the top end needs to be imposed when the lamp is in a vertical orientation or in the case of CFBRs.

9.3 Stainless Steel Sheet for Coating

Machine shop has a selection of SS plate in stock. Will cut the right size to fit in the reactor later.

9.4 TiO₂ Gel

A Toronto company can supply at $450/L. It is a commercial TiO₂ paint.

http://gensnano.com/

It is more expensive than the TiO₂ solution of Sigma. We already bought TiO₂ nanoparticle suspensions and paste from Sigma. We have to characterize the thin film on our own later.

In the future, we will manufacture TiO₂ nanoparticles using titanium precursors. The facilities are available in the APRIL lab.
10. Kinetic Investigation into the Absorption of CO₂ into Aqueous Ammonia Solutions

In addition to SO₂ and NOₓ, CO₂ is another subject we are interested in. The extension to CO₂ absorption enables us to cover the control of all major emissions present in real flue gas, which maximizes the advantages of our proposed technology. Although we may not be able to include CO₂ capture in the continuous absorption system in this stage, we can conduct fundamental study on CO₂ absorption. The understanding of the kinetics of CO₂ absorption into ammonia solutions will well prepare us to be a player in carbon capture and storage (CCS) area. The kinetic information will greatly benefit future reactor design and modeling; therefore, can allow us to include CO₂ capture in our proposed technology once funds are available.

10.1 Reaction Mechanism

The absorption of CO₂ into an ammonia solution is a complex process that generates different products at various CO₂ loadings and temperatures. When CO₂ is absorbed in an unloaded NH₃ solution, two reactions will contribute to the overall absorption rate at high pH values. The reaction with OH⁻ ions leads to the formation of bicarbonate and that with free ammonia molecules generates carbamate. The production of carbonic acid by CO₂ and H₂O is very slow compared with Reactions 34 and 35, and therefore, is negligible.

\[
CO₂ + OH⁻ \rightarrow HCO₃⁻ \quad (34)
\]
\[
CO₂ + 2NH₃ ⇌ NH₂COO⁻ + NH₄⁺ \quad (35)
\]

Reaction 34 is a second order reaction, and has first order with respect to CO₂ and OH⁻ ions, respectively. Its rate constant between 273 – 313 K is described as

\[
k_{OH⁻} = 4.2 \times 10^{13} e^{(-\frac{6666}{T})} \quad (36)
\]

Reaction 35 is an overall equation for the reaction between CO₂ and NH₃. It is not as simple as it is presented; otherwise, the reaction order with respect to CO₂ and NH₃ should be 1 and 2, respectively. Instead, it may include several stepwise reactions. The reaction order with respect to a reactant could be fractional, especially with respect to ammonia, and this will be confirmed in the following section. The nature behind Reaction 35 might be represented by either a two-step mechanism or an advanced mechanism like the zwitterion or termolecular mechanisms by analogy with CO₂ absorption into alkanolamine.
10.1.1 Simple Two-Step Mechanism

Pinsent\textsuperscript{49} assumed that Reaction 35 included two simple reactions as follows. The first step was the formation of carbamic acid, followed by the deprotonation to form ammonium carbamate.

\[ CO_2 + NH_3 \rightarrow NH_2COO^- + H^+ \tag{37} \]
\[ H^+ + NH_3 \rightarrow NH_4^+ \tag{38} \]

As Reaction 38 was a proton transferring process, it was considered instantaneous. That is to say, all the hydrogen ions generated in Reaction 37 would be instantaneously transferred to ammonium ions. Therefore, Reaction 37 was the rate-determining step. The overall reaction (Reaction 35) was 1\textsuperscript{st} order with respect to CO\textsubscript{2} and NH\textsubscript{3}, respectively. This mechanism could not explain the occurrence of fractional order with respect to ammonia in CO\textsubscript{2} absorption. If a non-integral order for Reaction 35 is experimentally determined, advanced mechanisms like the zwitterion and termolecular mechanisms would be more suitable.

10.1.2 Zwitterion Mechanism

The zwitterion mechanism for CO\textsubscript{2} absorption into primary and secondary alkanolamines is expected to describe Reaction 35.\textsuperscript{46,50} In the first step, CO\textsubscript{2} and NH\textsubscript{3} combine together to form a zwitterion intermediate, which will be deprotonated by all bases including OH\textsuperscript{-} ions, NH\textsubscript{3} and H\textsubscript{2}O in the solution. In an aqueous ammonia solution, the hydroxide ions contribute little to the deprotonation of zwitterion. Ammonia and water will be the predominant bases for Reaction 40.\textsuperscript{47}

\[
CO_2 + NH_3 \xrightleftharpoons[k_2]{k_1} NH_3^+COO^- \tag{39}
\]
\[
NH_3^+COO^- + B \xrightarrow[k_B]{k_B} NH_2COO^- + BH^+ \tag{40}
\]

The overall rate of Reaction 35 is then expressed in Eq. 41.\textsuperscript{51} Therefore, this mechanism suggests a 1\textsuperscript{st} order with respect to CO\textsubscript{2}, and can result in a fractional order in ammonia.

\[
r_{CO_2-NH_3}^z = \frac{[CO_2][NH_3]}{(1/k_2) + \frac{k_{-1}/k_2}{k_{NH_3}^z[NH_3] + k_{H_2O}^z[H_2O]}} \tag{41}
\]
10.1.3 Termolecular Mechanism

The termolecular mechanism is another well-known model for the absorption of CO₂ into alkanolamine solutions. It is a single step mechanism that assumes one ammonia molecule reacts simultaneously with one CO₂ molecule and one base molecule as shown in Reaction 42.

\[
\begin{align*}
\text{H}_2\text{N} & \text{C} \text{H}_3 & \xrightleftharpoons{\text{K}_B} & \frac{k_B}{k_{B^*}} \text{NH}_2\text{COO}^- + \text{BH}^+ \\
\text{B}_2 & \text{H}_2 &
\end{align*}
\] (42)

As ammonia and water are the predominant bases in CO₂ absorption, the reaction rate of termolecular mechanism is represented by Eq. 43. This mechanism also appears to be 1st order with respect to CO₂, and can show a fractional order with respect to ammonia.

\[
r_{\text{CO}_2-N\text{H}_3}^T = (k_{\text{N}_3}[\text{NH}_3] + k_{\text{H}_2\text{O}}[\text{H}_2\text{O}])[\text{CO}_2][\text{NH}_3]
\] (43)

10.2 Experimental Section

Figure 33 shows the experimental setup for the kinetic study of CO₂ absorption into aqueous ammonia. CO₂ absorption took place in a double stirred tank reactor filled with 500 mL of ammonia at a concentration between 0.42 and 7.67 mol·L⁻¹. The details of the absorber can be found elsewhere. Briefly, the reactor was operated continuously with respect to the gas phase and batch-wise with respect to the liquid phase. The rotational speeds of the gas and liquid phases were 710 and 230 rpm, respectively. The reaction temperature was between 273 and 293 K with a fluctuation of ±0.5 K, which was regulated by a circulating thermostatic bath.

Gas cylinders and chemicals were from Praxair and Sigma-Aldrich, respectively, unless otherwise specified. The feed gas stream was produced by diluting the flow from a compressed CO₂ cylinder (15 vol% with N₂ balance) using N₂ (Grade 4.5). The gas stream with CO₂ concentrations ranging from 1 to 5 vol% was controlled at 1.5 L·min⁻¹. The flow rate of CO₂ and N₂ were regulated by two mass flow controllers (MFCs) from Cole-Parmer. Complete mixing of the gases was achieved after passing through an in-line static mixer (Model RK-04669-05 from Koflo Corporation). Before each test, the flow was directed to a Fourier transform infrared (FTIR) continuous gas analyzer (MultiGas 2030 from MKS Instruments Inc.) via a by-pass route to determine the CO₂ concentration at the reactor inlet, with FTIR data collection every 2 seconds. The inlet CO₂ concentration was the average of stable readings in a 3-minute duration.
prior to the onset of the test. Afterwards, the gas stream was directed to the reactor by a three-way valve, and the CO₂ concentration at the outlet was continuously recorded by the FTIR. The outlet reading stabilized in 3-5 min, and the outlet concentration was the average of the stable readings. The tank pressure was monitored by a pressure gauge. The total pressure ranged from $1.034 \times 10^5$ to $1.068 \times 10^5$ Pa. Due to the vaporization of ammonia, a gas scrubbing bottle filled with 100 mL of concentrated sulfuric acid (95-98%) was placed upstream of the FTIR to eliminate the inference of ammonia vapor. The addition of acid wash was expected to have little influence on the CO₂ reading,⁵⁴ which was also proven during the current study. We compared the CO₂ readings of 1, 5 and 15 vol% given by FTIR with and without acid wash, and the difference was negligible.

Figure 33. Experimental system for the kinetics study of CO₂ absorption into aqueous ammonia solution

The absorbent solution with a specific ammonia concentration was prepared by diluting concentrated aqueous ammonia solution (28–30 wt%). The concentration of ammonia was then determined by titration using a standard sulfuric acid solution with methyl orange as the indicator
(certified 0.1% w/v from Fisher Scientific). Three replicates were taken for each titration, and the average was used. The rate of CO₂ absorption into ammonia can be expressed by Eq. 44 based on mass balance and the ideal gas law.

\[
N_{CO_2} = \frac{Q_{CO_2} P_T}{RTS} (y_{in} - y_{out})
\]  

(44)

The gas phase mass transfer coefficient, \(k_G\), was measured using the same testing rig by the absorption of dilute SO₂ into 1 mol·L⁻¹ NaOH assuming an instantaneous reaction between SO₂ and OH⁻ ion even at a low concentrations around 0.01 mol·L⁻¹.⁵⁵,⁵⁶ A standard cylinder containing 1280 ppmv of SO₂ balanced in N₂ was utilized, and 1 mol·L⁻¹ NaOH solution was prepared by diluting 10 mol·L⁻¹ standard NaOH solution from Fisher Scientific. The SO₂-NaOH system was operated under the same conditions as the CO₂-NH₃ system. The value of \(k_G\) is then described as

\[
k_{G,SO_2-N_2} = \frac{Q_{SO_2}}{RTS} \left( \frac{y_{in} - y_{out}}{y_{out}} \right)_{SO_2}
\]  

(45)

10.3 Theoretical Calculation

Data from the DSTR provides a measure of the overall reaction rate of CO₂ absorption into the ammonia solution. According to the two-film theory, the absorption rate of CO₂ is described as follows.

\[
N_{CO_2} = \left( \frac{H}{Ek_L} + \frac{1}{k_G} \right)^{-1} \left( P_{CO_2} - P_{CO_2}^{*} \right)
\]  

(46)

The saturated CO₂ partial pressure at the gas-liquid interface in equilibrium with the bulk liquid concentration can be described by the Henry’s Law.

\[
P_{CO_2}^{*} = H_{CO_2,bl}^{*}
\]  

(47)

In this study, we focus on the reaction between CO₂ and unloaded ammonia solutions, and the CO₂ concentration in the bulk liquid is thus zero. Then Eq. 46 is simplified to

\[
N_{CO_2} = \left( \frac{H}{Ek_L} + \frac{1}{k_G} \right)^{-1} P_{CO_2}
\]  

(48)

As mentioned above, parallel reactions 34 and 35 contribute primarily to the absorption of CO₂. Because the aqueous ammonia is in great excess of CO₂, these two reactions are considered irreversible. The general asymptotic solution to the enhancement factor for gas absorption
accompanied by two irreversible parallel reactions was studied by Onda et al.\textsuperscript{57} For parallel reactions with apparent m-th order and p-th order with respect to gaseous species A, and n-th and q-th orders with respect to liquid reactants B and C, respectively, the enhancement factor, \( E \), is

\[
E = \frac{1}{k_L} \sqrt{\frac{2}{m + 1} \cdot k_{mn} D_A B^n c_{A,l}^{m-1} \left( 1 + \frac{m + 1}{p + 1} \cdot \frac{k_{pq} C_A c_{A,l}^{p-m}}{k_{mn} B^n} \right)} \tag{49}
\]

The reaction between \( CO_2 \) and \( OH^- \) is first order with respect to \( CO_2 \) and \( OH^- \), respectively.\textsuperscript{48} Therefore, \( p = q = 1 \). Then Eq. 49 becomes

\[
E = \frac{1}{k_L} \sqrt{\frac{2}{m + 1} \cdot k_{ow} D_{CO_2} [NH_3]^n c_{CO_2,l}^{m-1} + k_{OH^-} D_{CO_2} [OH^-]} \tag{50}
\]

The interfacial \( CO_2 \) concentration is assumed to be at equilibrium with the bulk gas partial pressure, and then can be determined by Henry’s law.

\[
c_{CO_2,l} = \frac{P_{CO_2}}{H} \tag{51}
\]

Substituting Eqs. 50 and 51 into Eq. 48 leads to

\[
N_{CO_2} = \left( \frac{H}{\sqrt{\frac{2}{m + 1} \cdot k_{ow} D_{CO_2} [NH_3]^n \left( \frac{P_{CO_2}}{H} \right)^{m-1} + k_{OH^-} D_{CO_2} [OH^-]} + \frac{1}{k_G}} \right)^{-1} P_{CO_2} \tag{52}
\]

The value of reaction orders, \( m \) and \( n \), will be graphically determined. The apparent kinetic rate constant of Reaction 35 is then calculated with the knowledge of \( H, D_{CO_2}, \) and \( k_G \). In this study, the values of \( H \) and \( D_{CO_2} \) will be estimated by correlation, and \( k_G \) is experimentally measured using the procedure described in the experimental section. If \( n = 1 \), then all three mechanisms described previously are applicable. If \( n \) is a fractional number, zwitterion and termolecular mechanism will be used to describe the nature of Reaction 35.

Sander compiled the Henry’s Law constant of different gas-water systems,\textsuperscript{58} where the temperature dependence of \( H_{CO_2-H_2O} \) is represented by the following equation.
Besides temperature, ionic strength also plays an important role in the Henry’s Law constant. In the current study, the aqueous ammonia solution has a concentration of 0.42 – 7.67 \text{ mol} \cdot \text{L}^{-1}. The major ions in the solution include \( NH_4^+ \) and \( OH^- \). The dissociation equilibrium of ammonium ion is presented as

\[
NH_4^+ \rightleftharpoons NH_3 + H^+
\]  

(54)

The acid dissociation constants, \( K_a \), of ammonium ions at different temperatures ranging from 273 to 323 K are available in literature. \( K_a \) at a specific temperature within this range. The concentration of \( NH_4^+ \) is then calculated by

\[
[NH_4^+] = \frac{[NH_3][H^+]}{K_a}
\]  

(55)

Due to neutrality of the aqueous solution, \([NH_4^+] = [OH^-]\). The contribution of hydrogen ion to cations has been neglected because the aqueous solution is alkaline and \([H^+]\) is significantly less than \([NH_4^+]\). The ionization constant of water, \( K_w \), can be accurately estimated using the formula developed by Bandura. \( K_w \) for different temperatures and pressures. Then Eq. 55 turns into

\[
[OH^-] = [NH_4^+] = \sqrt{[NH_3] \cdot K_w/K_a}
\]  

(56)

Therefore, the ionic strength of an aqueous ammonia solution is expressed in Eq. 57.

\[
I = \frac{1}{2}([NH_4^+] + [OH^-]) = \sqrt{[NH_3] \cdot K_w/K_a}
\]  

(57)

The value of \( K_w/K_a \) is always lower than \( 2 \times 10^{-5} \) over temperatures from 273 to 323 K. Hence, the ionic strength of the aqueous ammonia in the current study is very low, and its effect on Henry’s Law constant is negligible. This conclusion well corresponds to the experimental data of Derks et al. and Qin et al. who both stated that the presence of ammonia had a negligible impact on CO2 solubility.

The diffusivity of CO2 in aqueous ammonia solutions is correlated with its viscosity by the modified Stokes-Einstein equation as follows.
\[ D_{\text{CO}_2-N\text{H}_3} = D_{\text{CO}_2-\text{H}_2\text{O}} \left( \frac{\mu_{\text{H}_2\text{O}}}{\mu_{\text{N}\text{H}_3}} \right)^{0.8} \]  

(58)

The diffusivity of CO\(_2\) in water can be well predicted by the Wilke-Chang equation.\(^{64,65}\)

\[ D_{\text{CO}_2-\text{H}_2\text{O}} = 7.4 \times 10^{-12} \left( \phi M_{\text{H}_2\text{O}} \right)^{0.5} \frac{T}{\mu_{\text{H}_2\text{O}} V_{bA}^{0.6}} \]  

(59)

The association factor for water is 2.26, and the molar volume of CO\(_2\) at the normal boiling temperature is 34 cm\(^3\)·mol\(^{-1}\). Water viscosities at various temperatures are readily available in the literature.\(^{66}\)

The viscosity of an aqueous ammonia solution depends on the concentration of NH\(_3\) and temperature, and can be described by the following correlation.\(^{67}\)

\[ \mu_{\text{N}\text{H}_3} = \left( 0.67 + 0.78 x_{\text{N}\text{H}_3} \right) \times 10^{-6} e^{\left( \frac{17900}{RT} \right)} \]  

(60)

The mole fraction of NH\(_3\) in water, \(x_{\text{N}\text{H}_3}\), can be calculated with the information of ammonia density at different weight percentage and temperature given by Jennings.\(^{68}\) The information is very close to the measured data by Qin et al.\(^{63}\)

In general, the Chapman-Enskog correlation in Eq. 61 is used to estimate the gas diffusivity of a binary gas system containing gases A and B at low pressures.\(^{65}\)

\[ D_{AB} = \frac{2.66 \times 10^{-7} T^{3/2}}{PM_{AB}^{1/2} \sigma_{AB}^{2} \Omega_{D}} \]  

(61)

where

\[ M_{AB} = \frac{2}{1/M_A + 1/M_B} \]  

(62)

\[ \sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \]  

(63)

\[ \Omega_{D} = \frac{1.06036}{(T^{*})^{0.15610}} + \frac{0.19300}{\exp(0.47635T^{*})} + \frac{1.03587}{\exp(1.52996T^{*})} + \frac{1.76474}{\exp(3.89417T^{*})} \]  

(64)
\[ T^* = \frac{kT}{(\epsilon_A \epsilon_B)^{1/2}} \quad (65) \]

The values of \( \sigma \) and \( \epsilon/k \) for various gases are summarized in Table 7.

<table>
<thead>
<tr>
<th>Gas species</th>
<th>( \sigma, \text{Å} )</th>
<th>( \epsilon/k, \text{K} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>3.941</td>
<td>195.2</td>
</tr>
<tr>
<td>N(_2)</td>
<td>3.798</td>
<td>71.4</td>
</tr>
<tr>
<td>SO(_2)</td>
<td>4.112</td>
<td>335.4</td>
</tr>
</tbody>
</table>

**10.4 Results and Discussion**

**10.4.1 Determination of gas-phase mass transfer coefficient**

Figure 34 shows the temperature dependence of \( k_G \) with standard deviations shown as error bars. The value of \( k_G \) slightly decreases from \( 7.71 \times 10^{-6} \) to \( 7.02 \times 10^{-6} \text{ mol \cdot m}^{-2} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1} \) with increasing temperature from 273.15 to 293.15 K. This is likely because the solubility of SO\(_2\) in solution decreases with temperature. The gas phase mass transfer coefficient of CO\(_2\) is then correlated with gas diffusivity through the following equation, and is shown by the right vertical axis.

\[ k_{G,CO_2-N_2} = k_{G,SO_2-N_2} \left( \frac{D_{CO_2-N_2}}{D_{SO_2-N_2}} \right)^{2/3} \quad (66) \]


10.4.2 Determination of Reaction Rate Constant for CO₂ Absorption into Aqueous Ammonia Solutions

10.4.2.1 Determination of reaction order with respect to CO₂

Eq. 52 indicates that \( N_{CO₂} \) is a function of \( P_{CO₂} \). At a specific ammonia concentration and temperature, variables including \( H, k_G, m, k_{app}, D_{CO₂}, k_{OH^-}, K_w, K_d \) are constants. Therefore, the concentration of hydroxide ion \([OH^-]\) is also a constant according to Eq. 56. As a result, a linear relationship will exist only if \( m = 1 \) at a fixed \([NH₃]\) and \( T \). Figure 35 illustrates the change in CO₂ absorption rate with CO₂ partial pressure at 273.15 K. Due to the volatile nature of the ammonia solution, it was very difficult to have exactly the same \([NH₃]\) in every two tests. Hence, \([NH₃]\) fell in a very small range for a set ammonia concentration. For example, we planned to have \([NH₃]\) equal to \( 5.189 \text{ mol} \cdot \text{L}^{-1} \); the actual \([NH₃]\) was within \( 4.978 – 5.400 \text{ mol} \cdot \text{L}^{-1} \). Because the range was rather small (\(< \pm 4\%\)), we considered \([NH₃]\) unchanged for various CO₂ partial pressures. It is evident that \( N_{CO₂} \) is linearly correlated with \( P_{CO₂} \) for all three ammonia concentrations, which indicates that the reaction order with respect to CO₂ is \( m = 1 \). This finding corresponds to all three possible mechanisms described above. Eq. 52 then turns into

\[
N_{CO₂} = k_{CO₂} \cdot P_{CO₂}^m \cdot \text{constant}
\]
\[ N_{CO_2} = \left( \frac{H}{\sqrt{k_{NH_3}^{OV} D_{CO_2}[NH_3]^n + k_{OH^-}D_{CO_2}[OH^-]} + \frac{1}{k_G}} \right)^{-1} P_{CO_2} \]  

(67)

Figure 35. The relationship between \( N_{CO_2} \) and \( P_{CO_2} \) at 273.15 K.

10.4.2.2 Determination of overall reaction order with respect to NH\(_3\)

Further transformation of Eq. 67 leads to

\[ k_{app} = k_{NH_3}^{OV} [NH_3]^n \]  

(68)

where

\[ k_{app} = \frac{H^2}{D_{CO_2}} \left( \frac{P_{CO_2}}{N_{CO_2}} - \frac{1}{k_G} \right)^{-2} - k_{OH^-}[OH^-] \]  

(69)

The parameter \( k_{app} \) is called the apparent pseudo first order reaction rate constant with respect to CO\(_2\) for Reaction 35. Figure 36 shows the variation of \( k_{app} \) with \([NH_3]\) at different temperatures. The overall reaction order with respect to NH\(_3\) is within the range of 1.6 – 1.8. This fractional order cannot be properly explained by the simple two-step mechanism, which indicates that the order with respect to NH\(_3\) is 1. Therefore, a more complicated model like the
zwitterion or termolecular mechanism is needed to better understand the absorption of CO₂ into the ammonia solution. The experimental apparent kinetics data in the current study are then fitted against Eqs. 41 and 43.

10.4.2.3 Kinetics of CO₂ absorption according to the zwitterion mechanism

According to Eq. 41, the apparent pseudo first order reaction rate constant based on the zwitterion mechanism can be described as follows.

$$
k^z_{app} = \frac{[NH_3]}{(1/k_2) + \frac{k_{-1}/k_2}{k_{NH3}^2[NH_3] + k_{H_2O}^2[H_2O]}}
$$  (70)

A nonlinear regression was completed using the Trust-Region algorithm along with robust least absolute residuals (LAR) in Matlab. The adjusted R² is used as an indicator for the goodness of fit. The optimum results for the fitting parameters are tabulated in Table 8. Although the fitting results for each temperature seem satisfactory, they are unreasonable when the experimental temperatures are in the range of 273.15 – 293.15 K. For example, the parameters $k_{NH3}^2 \cdot k_2/k_{-1}$ and $k_{H_2O}^2 \cdot k_2/k_{-1}$ do not monotonically increase with increasing temperature. The value of $1/k_2$ drops dramatically from $1.36 \times 10^{-4}$ to $1.51 \times 10^{-13}$ when temperature grows from
283.15 to 293.15 K. The data fitting of temperature dependence of rate constants is rather poor. We attempted to fit the experimental data with temperature dependence taken into account but failed; the adjusted $R^2$ even could be a negative value. Therefore, the experimental apparent kinetic data in the present work cannot be successfully interpreted by the zwitterion mechanism. This conclusion agrees with Qin’s.63

Table 8. Summary of optimal fitting parameters of zwitterion mechanism

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$1/k_2$ ($mol \cdot s \cdot L^{-1}$)</th>
<th>$k_{NH_3}^z \cdot k_2 / k_{-1}$ ($L^2 \cdot mol^{-2} \cdot s^{-1}$)</th>
<th>$k_{H_2O}^z \cdot k_2 / k_{-1}$ ($L^2 \cdot mol^{-2} \cdot s^{-1}$)</th>
<th>Adjusted $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.15</td>
<td>3.17E-04</td>
<td>1279</td>
<td>1.54E-09</td>
<td>0.9647</td>
</tr>
<tr>
<td>283.15</td>
<td>1.36E-04</td>
<td>1691</td>
<td>1.79E-12</td>
<td>0.9709</td>
</tr>
<tr>
<td>293.15</td>
<td>1.51E-13</td>
<td>1317</td>
<td>2.17E-11</td>
<td>0.9900</td>
</tr>
</tbody>
</table>

10.4.2.4 Kinetics of CO$_2$ absorption according to termolecular mechanism

The apparent rate constant of the termolecular mechanism is derived from Eq. 43 and is presented in Eq. 71.

$$
 k_{app}^T = k_{NH_3}^T [NH_3]^2 + k_{H_2O}^T [NH_3][H_2O] 
$$

(71)

Such parameters as $k_{NH_3}^T$ and $k_{H_2O}^T$ can commonly be obtained using a multiple linear regression (MLR) with the least squares method. However, the obvious relationship between [NH$_3$] and [H$_2$O] will bring in multicollinearity, voiding the MLR in this work. Instead, the Trust-Region algorithm along with robust LAR were used to fit the experimental data. Also, the fitting results are subject to temperature dependence. The value of adjusted $R^2$ is then used as an indicator for the goodness of fit. Table 9 summarizes the fitting parameters of the termolecular mechanism at different temperatures. Figure 37 shows the comparison between experimental results and predicted values using the parameters listed in Table 9 for temperatures from 273.15 to 293.15 K. Approximately 80% of predicted values fall within $\pm 20\%$ of experimental data, indicating that the termolecular mechanism is preferred for modelling CO$_2$ absorption into ammonia solutions.

Table 9. Summary of fitting parameters in termolecular mechanism

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$k_{NH_3}^T (L^2 \cdot mol^{-2} \cdot s^{-1})$</th>
<th>$k_{H_2O}^T (L^2 \cdot mol^{-2} \cdot s^{-1})$</th>
<th>Adjusted $R^2$</th>
</tr>
</thead>
</table>
The temperature dependence of rate constant is generally represented by the Arrhenius equation as follows.\(^7^0,\)\(^7^1\)

\[
k = A \cdot e\left(\frac{-E_a}{RT}\right)
\]  
(72)

The rate constants in Table 9 can then be represented by the following equations using linear regression.

\[
k^T_{\text{NH}_3} = 7.6089 \times 10^8 e^{(-\frac{4018.4}{T})}
\]  
(73)

\[
k^T_{\text{H}_2\text{O}} = 7.9161 \times 10^7 e^{(-\frac{4356.4}{T})}
\]  
(74)

10.4.2.5 Comparison with available data for \(\text{NH}_3\) and \(\text{MEA}\)

Existing kinetics models and/or data of \(\text{CO}_2\) absorption into ammonia were compared to identify the differences between various studies. Experimental data in the literature were considered first whenever available, otherwise models proposed by other researchers were compared. In addition,
ammonia appears as an alternative to MEA solution in CO₂ capture. Several researchers directly compared their performances in a specific reactor geometry. The kinetic information for MEA has been extensively investigated. With the available knowledge of MEA-CO₂ kinetics, the first-hand comparison data allows us to predict the kinetics of ammonia-CO₂ system. In order to compare the results of different mechanisms, the apparent pseudo first-order kinetic rate constant was used. The definition of \( k_{\text{app}} \) for the zwitterion and termolecular mechanisms is described in Eqs. 70 and 71, respectively, while for the simple two-step mechanism, \( k_{\text{app}} = k_2[NH_3] \).

Figure 38 shows the comparison between different kinetic models and/or data over temperatures between 273.15 and 303.15 K. It also includes the kinetic information for MEA in the solid red line which is produced according to Aboudheir. The dashed red curve, which represents half of the apparent rate constant of MEA at a specific temperature, is introduced as a reference line because a quantitative analysis indicates that \( \frac{k_{2-\text{MEA}}}{k_{2-NH_3}} = 1.50 - 2.41 \). The top half of Figure 38 shows the comparison at an absorbent concentration of 4.5 mol ⋅ L⁻¹, while the lower shows 1 mol ⋅ L⁻¹.
Figure 38. Comparison between available models (and data) at different concentrations and temperatures

It can be seen from Figure 6 that the results depend strongly on the assumed model. Unlike others, Qin’s model predicts little temperature dependence on the apparent kinetic rate at both concentrations. Darde’s model constantly predicts lower values than Puxty’s model, our model, and Derks’ experimental data. At an ammonia concentration of $1 \text{ mol} \cdot \text{L}^{-1}$, our model gives the highest rate constant at temperatures lower than 293 K, while the Puxty model delivers the highest estimates at temperatures above 293 K. Derks’ experimental data falls between our model and Darde’s model. At $[\text{NH}_3] = 4.5 \text{ mol} \cdot \text{L}^{-1}$, Derks data appears rather close to our modelling results, while the Puxty and Darde models lead to similar results. Derks and our work showed larger apparent higher rate constants than the others. In summary, our current work compares favourably with results obtained in different reactors at both high and low NH$_3$ concentrations. The results supported by multiple experimental methods are usually more reliable as any intrinsic system error is expected to be substantially reduced.

Furthermore, all models and data unanimously agree that MEA has a higher rate constant than NH$_3$. The difference is the degree of departure of the NH$_3$ models from the MEA line. As Yeh’s data indicated the kinetic rate constant of MEA is 1.50 – 2.41 times greater than that of NH$_3$, a line which represents the half of $k_{\text{app-MEA}}$ is employed as a reference. Our model agrees satisfactorily with this reference line at either concentration, especially at the lower one. Derks’ data fall close to the reference line at higher concentrations, but it is not the case at 1 mol·L$^{-1}$.

In summary, this work agrees well with models and data that are obtained in different reactors at both high and low NH$_3$ concentrations. In addition, our model supports Yeh’s experimental data regarding the comparison between NH$_3$ and MEA in terms of CO$_2$ capture.

10.5 Summary
The kinetics of CO$_2$ absorption into ammonia aqueous solution was investigated using a DSTR system. It is explicitly determined that the reactive absorption is first order with respect to CO$_2$
but fractional orders between 1.6 – 1.8 with respect to ammonia. The kinetics data can be satisfactorily interpreted by the termolecular mechanism using $k_{NH_3}^T = 7.6089 \times 10^8 e^{(-\frac{4018.4}{T})}$ and $k_{H_2O}^T = 7.9161 \times 10^7 e^{(-\frac{4356.4}{T})}$.

The model in this work was compared with similar models and experimental data obtained in batch thermostatic stirred cells and wetted wall columns at both high and low NH$_3$ concentrations, showing good agreement and general applicability. Furthermore, the present work agrees well with first-hand literature data that compared CO$_2$ absorption into NH$_3$ with that into MEA.
11. Conclusions

The proposed research aims to develop a cost-effective technology that can control multiple air pollutants from industrial flue gas. The overall objective is to commercialize such a technology. Substantial progress has been made towards the overall objective over the period between October 1, 2014 and September 30, 2015. The main results/achievements for the current stage are summarized as follows:

1) Three air pollution control processes including wet scrubbing and liquid treatment have been proposed to effectively address post-combustion flue gas in industrial practices.
2) A continuous wet scrubbing system using simulated flue gas has been established to validate the proposed processes in laboratory.
3) The utilization of a cross-flow HFMC in air pollution control is verified by the absorption of SO$_2$ into water at 27 °C. It has better performance than traditional wet scrubbers.
4) The liquid-side mass transfer coefficient of the HFMC is correlated by $Sh = 0.28Re^{0.97}Sc^{0.33}$.
5) The pre-oxidation of NO into NO$_2$ is validated by preliminary experiments. The NO conversion efficiency is 53% when the inlet NO concentration is 400 ppm, and O$_2$ is 6%. The temperature for TiO$_2$ thin film preparation and regeneration is critical to the NO conversion efficiency. A calcination temperature of 500-550 °C is deemed suitable.
6) The feasibility of using TiO$_2$-assisted UVC technology for flue gas treatment on an industrial scale is confirmed by taking account of reaction nature, available UV lamp, equipment scale-up and installation, materials, fouling and economics.
7) A prototype of UVC reactor has been designed.
8) The kinetics of CO$_2$ absorption into ammonia solution has been investigated.
References


