

FIELD MEASUREMENTS AND MODELING OF GASEOUS NO_x, SO₂, HNO₃ AND H₂SO₄
FORMATION FROM A NOVEL ELECTROSTATIC PRECIPITATOR

BY

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THESIS

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ABSTRACT

Post-combustion CO₂ capture (PCC) is a leading technology to reduce CO₂ emissions from coal-fired power plants. Amine-based solvent PCC is a method for capturing CO₂ however, sub-micrometer diameter particles in flue gas can have a detrimental effect on the efficiency and cost-effectiveness of solvent-based PCC. A novel electrostatic precipitator (ESP), utilizing soft X-ray photoionization, was developed and tested at Abbott Power Plant at the University of Illinois at Urbana-Champaign, USA to determine its effectiveness at capturing sub-micrometer diameter particles. This research investigated whether a novel ESP, utilizing soft X-ray photoionization, causes unintentional formation of gaseous species, including nitric oxide (NO), nitrogen dioxide (NO₂), sulfur dioxide (SO₂), nitric acid (HNO₃) and sulfuric acid (H₂SO₄). Experimental and modeled results showed the emission rate of NO₂ changed the most after passing through the novel ESP. For NO, NO₂ and SO₂, the best agreement between modeled and experimental data was observed on March 13th, 2020 with the average difference between emission at 2.7, 2.5, and 0.7 %, respectively. Furthermore, the model showed both flue gas temperature and volumetric flow rate would affect emission rate independently. It was shown the modeled NO₂ emission rate increased a maximum of 44 % and 215 % at 400 K without and with the application of soft X-ray photoionization in the ESP, respectively. The modeled emission rate of NO decreased a maximum of 8 % and 41 % at 400 K without and with the application of soft X-ray photoionization, respectively. The modeled SO₂ emission rate decreased by a maximum of 2 % overall while H₂SO₄ increased by a maximum of 7 %. Modeled HNO₃ was shown to be generated in the ESP, however the emission rate was at a maximum of 2.6 mg/MJ. These results show that an ESP with or without the application of soft X-ray photoionization, can significantly alter emission rates of NO and NO₂. However, the

influence of soft X-ray photoionization in the ESP on gaseous NO and NO₂ emission rates could not be verified during operation due to equipment issues. Gaseous H₂SO₄ and HNO₃ were produced as well but to a lesser extent. The formation of gaseous NO₂, in particular, is important for an amine solvent-based PCC process as degradation of solvent can occur posing economic and environmental costs. This research presents a model, based off flue gas temperature, pressure, volumetric flow rate, and flue gas composition that determines how the emission rates of gaseous NO, NO₂, SO₂, H₂SO₄ and HNO₃ will be affected after passing through an ESP that utilizes soft X-ray photoionization. This is important because model parameters can be set to optimize the upstream conditions (temperature, pressure, flow rate, flue gas composition) so that formation of gaseous NO₂ is minimized to reduce its effect in a solvent-based PCC process.

To my parents, Tom and Katy; my sisters, Lucy and Kathleen
and
Danielle, my fiancé and best friend

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Chapter 1: Introduction

Electrostatic precipitators (ESPs) are commonly used in industrial and residential settings to remove suspended particles from air or a process gas. Research presented in this thesis builds upon the United States Department of Energy (DOE) project *Flue Gas Aerosol Pretreatment Technologies to Minimize PCC Solvent Losses* (project) (Bostick 2017). The project goal was to evaluate different methods for removing sub-micrometer diameter particles from the flue gas at Abbott Power Plant (APP), located at the University of Illinois at Urbana-Champaign, USA (Bostick 2017). This was done to determine which method, or combination of methods, would work best to reduce the particle number concentrations in flue gas to be treated by an amine-based CO₂ capture plant. While the project goal was to determine the best method(s) for achieving this, the research presented here evaluates the potential effects an ESP has on secondary gaseous pollutant formation and the resulting consequences this may have for an amine-based CO₂ capture process.

Fossil fuel-fired power plants provided 63.6 % of the United States electricity needs in 2018 (*Table 7.2a Electricity Net Generation: Total (All Sectors) 2021*). Furthermore, the electric power sector accounted for 34.8 % of CO₂ emissions through fossil fuel combustion in the United States that year (*Fast Facts 1990-2018 National-Level U.S. Greenhouse Gas Inventory 2020*). CO₂ emissions from the electric power sector produced 1,752.8 million metric tons of CO₂-equivalent from fossil fuel combustion in 2018 (*Fast Facts 1990-2018 National-Level U.S. Greenhouse Gas Inventory 2020*). A method to reduce CO₂ emissions, while maintaining fossil-fuel use, is through CO₂ capture and storage. Amine-based CO₂ absorption is widely considered a mature technology for post-combustion CO₂ capture (Dai and Mitch 2014). In this process, flue gas containing CO₂ is passed through a countercurrent stream of an amine-based solvent in

an absorber column (Dai and Mitch 2014). Through this process, CO₂ is absorbed into the liquid phase by reacting with the solvent (Dai and Mitch 2014). CO₂-lean flue gas is emitted to the atmosphere after being treated in a washwater unit (Dai and Mitch 2014). Captured CO₂ is later desorbed from the solvent where it can then be compressed and utilized for industrial applications or pumped into underground storage sites. However, the efficiency of a PCC facility can be hindered by aerosol-driven amine-based solvent loss causing high operational cost and logistical challenges (Bostick 2017). As noted by Bostick; Sherlock, Dhanraj, and Bostick (2017; 2018), aerosol-driven solvent loss can occur through several thermodynamic mechanisms⁶. Furthermore, Bostick (2017) states that aerosol-driven solvent losses are largely influenced by the number concentration and size distribution of particles in the flue gas upstream of a PCC facility in addition to aerosol growth rates due to water condensation and absorption⁷. Bostick (2017) states that particles less than 200 nanometers (nm) in diameter and greater than 10⁵ particles/cm³ produce the most severe solvent losses in a PCC facility. This provided the impetus for the DOE project where research was conducted on novel methods to reduce the number concentration of sub-micrometer diameter particles in flue gas.

ESPs remove suspended particles in a gaseous medium, or aerosols, through the application of a high-strength electric field. Particles become charged and a net force is exerted on them perpendicular to the gas flow (Flagan and Seinfeld 1988). These particles then migrate towards the collection electrode(s) of the ESP (Flagan and Seinfeld 1988). Electrostatic precipitators vary in their design and application; however, all ESPs operate by a direct current

⁶ These mechanisms are dependent upon the Kelvin Equation, which describes the relationship between saturation ratio (relative humidity) and particle diameter at equilibrium, i.e., no condensation or evaporation occurs at the particle surface.

⁷ Solvent losses can also occur due to temperature gradients and supersaturated conditions in a PCC facility regardless of upstream particle number concentrations (Bostick 2017).

(DC) voltage, that is, ~10s of kV, applied between at least one discharge and one collection electrode. Under this applied voltage, a corona, or region of ionized gas, forms around the discharge electrode(s). Additionally, when the discharge electrode is at a positive voltage, free electrons migrate from the surface of the collection electrode(s) towards the discharge electrode(s) (Flagan and Seinfeld 1988). These electrons ionize gas molecules and form positive ions, which in turn, attach to particles and draw them towards the collection electrode(s) (Flagan and Seinfeld 1988).

The novel ESP (WASHU-ESP) evaluated at Abbott Power Plant used an electric field to charge suspended particles in the flue gas. However, to capture sub-micrometer diameter particles with > 98% efficiency, it was designed with a soft X-ray (wavelengths in the range of 0.2 – 10 nm) photoionization stage to increase particle charging (Bostick 2017). It is known that ESPs can have an effect on gas composition through the formation of ozone and other gas-phase radicals (Katatani, Yahata, and Mizuno 2010; Chang et al. 1991). For example, Katatani, Yahata and Mizuno (2010) state that corona discharges in ESPs generate ozone and NO_x, where NO_x is nitric oxide (NO) and nitrogen dioxide (NO₂). However, nearly all of the NO_x produced by a DC positive corona is NO₂ and NO_x generation is positively correlated with gas humidity (Katatani, Yahata, and Mizuno 2010). Furthermore, they also state that O₃ produced in a corona discharge is consumed through the oxidation of NO to NO₂ (Katatani, Yahata, and Mizuno 2010). In a related study, the gas-phase oxidation of SO₂ in pulsed corona discharges and dielectric barrier discharges is discussed and it is shown that SO₂ can be converted into SO₃ and HSO₃ before conversion into H₂SO₄ (Chang et al. 1991). This process relies upon the production of gas-phase radicals and molecules including O, OH, HO₂ and H₂O (Chang et al. 1991).

The formation of NO_x , in particular, is of concern for amine-based CO_2 capture systems. Dai and Mitch (2014) state that nitramines and nitrosamines are potentially carcinogenic compounds that may result in air and water contamination if emitted to the atmosphere. These compounds may form through the reaction of NO and NO_2 with amines found in the absorber section of a PCC plant (Dai and Mitch 2014). Furthermore, Dai and Mitch (2014) show that NO and NO_2 concentrations were linearly correlated with the accumulation rate of nitrosamines in PCC amine-based solvent and washwater. It is also shown that NO_2 concentrations increase the accumulation rate of nitramines in PCC amine-based solvent and washwater (Dai and Mitch 2014). Additionally, in a study by Jing et al. (2015), it was shown that through the application of soft X-ray photoionization, the electron number concentration – which is needed for the formation of gas-phase radicals, increased by about 5 times. For this reason, it is important to understand the effect soft X-ray photoionization has on gas composition, given that NO_x can form in an ESP.

The formation of H_2SO_4 particles in ESPs has been noted by Bostick (2017) in which SO_2 can become oxidized. While not in the scope of this thesis to evaluate secondary particle formation due to the ESP, gaseous SO_2 , H_2SO_4 and HNO_3 were included in this analysis as a comparison to other published work. Furthermore, the results of gaseous H_2SO_4 and HNO_3 formation in this analysis can be used as a benchmark to evaluate secondary particle formation in future research.

In conclusion, the research objective in this thesis is to determine any effect the WASHU-ESP, utilizing soft X-ray photoionization, had on the emission rate of gaseous NO_x , SO_2 , H_2SO_4 and HNO_3 and the possible consequences for an amine-based CO_2 capture system given its susceptibility to NO_x . Dai and Mitch (2014), show that nitrosamine accumulation in

PCC amine-based solvent and washwater increased linearly with both NO and NO₂ concentrations. Dai and Mitch (2014), also show that nitramine accumulation increased with NO₂ concentration. This can cause solvent degradation, contributing to higher operating costs of a PCC plant and the possible release of nitrosamines and nitramines in the atmosphere, which are potential carcinogens (Dai and Mitch 2014). The following chapters present an overview of the measurement apparatus used at APP and an overview of the modeling and measurements methods. Finally, a detailed analysis is given of both the experimental and modeled results.

Chapter 2: Apparatus Set-up

This chapter provides the description of the apparatus used to detect secondary gaseous pollutant formation from the WASHU-ESP used during the project at APP which was conducted from January 15th through March 17th, 2020. As stated in Chapter 1, the research objective was to determine the effect the ESP, utilizing soft X-ray photoionization, had on the emission rate of gaseous NO_x, SO₂, H₂SO₄ and HNO₃ and the possible consequences for an amine-based CO₂ capture system. Here, a detailed explanation of the equipment used in the project, along with all relevant operating parameters, will be discussed.

2.1 Test Skid Design and Setup

The test facility for the project was APP, the main supplier of electricity and steam for the University of Illinois at Urbana-Champaign – <https://fs.illinois.edu/services/utilities-energy/production/abbott-power-plant>. APP is a co-generation plant, and utilizes both coal and natural gas combustion to provide electricity and steam. APP's coal boilers were used for the project, as they produced up to 1.40×10^7 particles/cm³ in the range of 10 – 400 nm (Dhanraj et al. 2018). An experimental platform (pilot skid) was installed to evaluate different, novel technologies, including the WASHU-ESP, for reducing the number concentration of sub-micrometer diameter particles. To evaluate the WASHU-ESP, a slipstream was installed so flue gas could be delivered to the pilot skid prior to exiting the stack – this is shown in Figure 2.1.

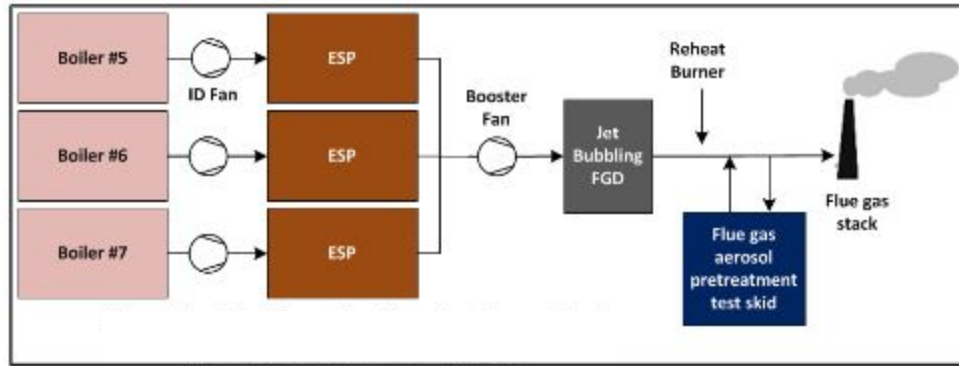


Figure 2.1. Schematic showing flue gas flow path at APP. This includes the placement of the pilot skid used during the project. APP's own emission measurements for environmental compliance were made before the pilot skid, labeled as "Flue gas aerosol pretreatment test skid" and after the Jet Bubbling FGD. Figure adapted from Bostick (2017).

This was done to, 1) mimic the design of a post-combustion CO₂ capture plant where flue gas would need to be treated for particles and 2) not interfere with the emission measurements of the coal boilers for environmental compliance. The flow rate of the slipstream was adjusted through a variable frequency drive induced-draft blower and could be set up to 0.47 sm³/s (1000 scfm), where sm³/s and scfm denote standard meters cubed per second and standard cubic feet per minute respectively. In this thesis, standard temperature and pressure are defined as 20 °C and 1 atm and all gas volumes are reported at these conditions unless otherwise noted. Flue gas was not conditioned or altered in any way before entering the test skid except being treated by APP's ESPs, jet bubbling flue gas desulfurization unit and reheat burner as shown in Figure 2.1. After flowing through the pilot skid, treated flue gas would be reintroduced to the main flue gas flow and exit the stack. The WASHU-ESP and the induced-draft blower could be operated by the engineer(s) conducting the project.

Figure 2.2 provides a detailed schematic of the equipment used in the project at APP. In the figure, the aerosol pretreatment pilot skid is shown along with equipment internal to it (within the ISBL) and the required process inputs and outputs.

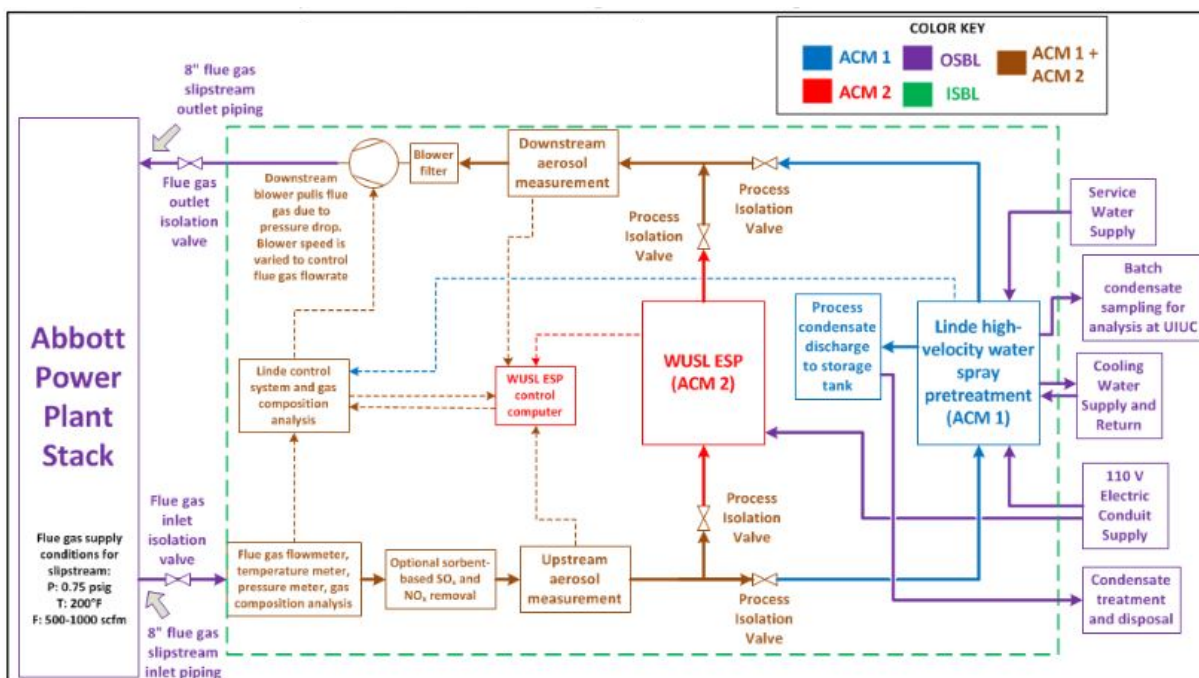


Figure 2.2. Detailed schematic showing flue gas flow path at APP. Figure adapted from Bostick (2017).

To assess the performance of each technology and meet project deliverables, particle number and mass concentration measurements were carried out by members of the Aerosol and Air Quality Research Laboratory. Gas composition measurements were carried out by myself (Wyatt Sherlock) and Devin Bostick. The gas composition measurements were done at the supply and return ports of the pilot skid and two systems were used for the analysis. Primary measurements were with a Fourier Transform Infrared Spectroscopy (FTIR) analyzer, described in Chapter 2.3.1.1. Additional analyzers, described in Chapter 2.3.1.2, capable of measuring specific species were used as a back-up system.

2.2 Electrostatic Precipitator Description

As described in 2.1, the main scope of the DOE project was to evaluate the effectiveness of a novel ESP and HVST in reducing the flue gas sub-micrometer diameter particle concentration. Research in this thesis, however only focuses on the WASHU-ESP and any secondary gaseous pollutant formation. The WASHU-ESP was designed and operated by

members at the Aerosol and Air Quality Research Laboratory at Washington University in St. Louis (Bostick 2017). Figure 2.3 gives a Computer-Aided Design drawing of the ESP complete with location of the inlet, photoionization stage, charging stage and collection stage.

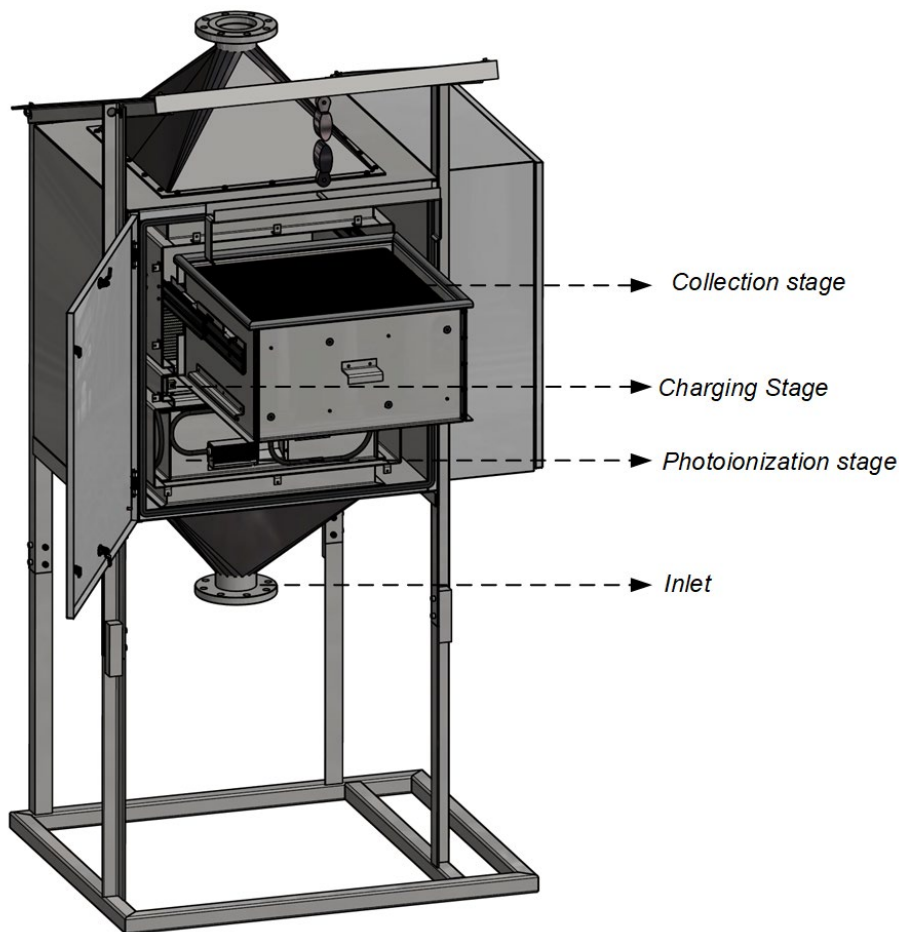


Figure 2.3. Computer-Aided Design drawing of the ESP used in the project at Abbott Power Plant. The three portions of the ESP are shown 1) the photoionization stage, 2) the charging stage and 3) the collection stage. Flue gas flowed from bottom to top. Image provided courtesy of the Aerosol and Air Quality Research Laboratory at Washington University in St. Louis.

The WASHU-ESP was rectangular in design and consisted of three sections; the soft X-ray photoionizers, 1st (charging) stage and then 2nd (collection) stage. This design was used to enhance the charging of sub-micrometer particles in the flue gas. Flue gas entered from the bottom of the unit, passed through the photoionizers, charging and collection stage before exiting

from the top. The photoionizers and each stage were independently powered. During operation, the voltage and current of each stage along with the photoionizer power level could be recorded. Furthermore, the specific voltage or current could be set, as a variable, by the operator. Feedback values, i.e., the actual voltage and current were recorded as well and could be viewed by the operator.

2.2.1 WASHU-ESP Operational Parameters

Applied voltage, current, collection electrode area and residence time (flow rate) are the governing parameters that determine the collection efficiency of an ESP. Voltage and current were set on the charging stage of the WASHU-ESP. During the project, the voltage and slip stream flow rate were set by the operator. Current could be set also, in lieu of voltage, if current was the controlled variable. For the results shown in Chapter 4, voltage was the controlled variable. Inside the photoionization stage, the soft X-ray photoionizers could be operated at a set power level. However, due to equipment issues the photoionizers were not used during the project. Voltage and current values were controlled by a laptop which interfaced directly with the ESP. Operational data from the WASHU-ESP was collected in an on-site acquisition system and was on a per-minute basis. Residence time could be set by adjusting the flow rate of flue gas through the ESP.

2.3 Analytical Trailer and Experimental System Setup

Next to the pilot skid, a container (analytical container) was used to support the measurement systems in addition to the WASHU-ESP and other control technologies evaluated during the project. Power feeds for all the instrumentation used in the project was provided through the container as shown in Figure 2.2. Also, the particle size distribution and number count measurements in addition to a portion of the gas composition analysis were done in the analytical container.

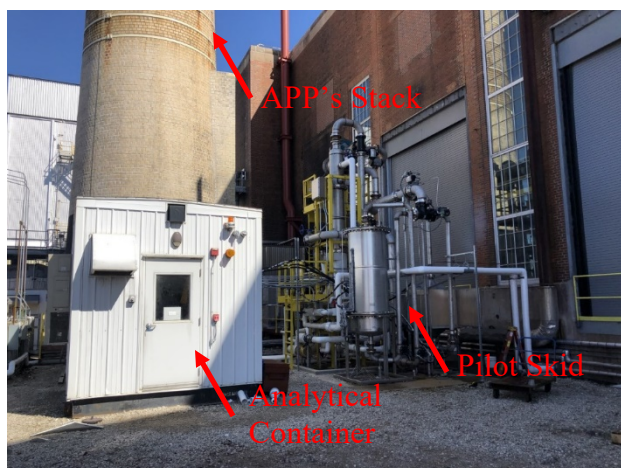


Figure 2.4. North facing view of the pilot skid, analytical container and coal boiler stack at Abbott Power Plant.



Figure 2.5. South facing view of the pilot skid and Fourier Transform Infrared Spectroscopy (FTIR) cabinet at Abbott Power Plant.

2.3.1 Gas Composition Analysis

Two systems were used to measure the concentration of stack gas species entering and leaving the pilot skid. The primary system used Fourier Transform Infrared Spectroscopy (FTIR) as the measurement technique. The secondary analysis system (SAS) consisted of a set of analyzers that provided redundancy to the FTIR system. Both systems measured O_2 , CO_2 , NO , NO_2 and SO_2 however the FTIR provided concentration measurements of several other gas species including but not limited to nitric acid (HNO_3), nitrous oxide (N_2O), water vapor (H_2O), methane (CH_4) and carbon monoxide (CO). Gas was sampled upstream and downstream of the pilot skid. The upstream measurements provided an analysis of species in supply flue gas. The downstream measurements provided an analysis of species in the treated flue gas, i.e., gas that passed through the ESP.

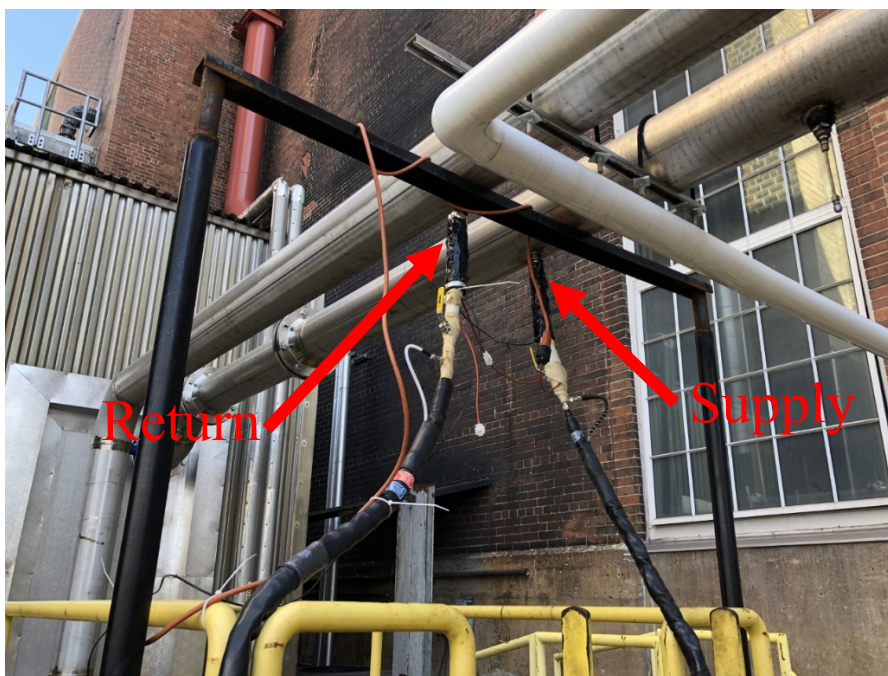


Figure 2.6. Sample probes used to deliver flue gas to the FTIR and SAS.

Due to project limitations and constraints, flue gas could only be sampled from either the supply or return port at a given time. Flue gas was measured by the FTIR and SAS, as shown in Figure A.1. The measurement stream (either pilot skid supply or return) could be selected by the operator. Regardless of the stream, both the FTIR and SAS took simultaneous measurements.

2.3.1.1 Fourier Transform Infrared Spectroscopy System

The FTIR system was provided by CleanAir Instrument Rental® and was specifically designed to meet the needs of the project. It was located outside between the analytical container and pilot skid. The unit consisted of an enclosure that housed:

- a) MKS® FTIR analyzer
- b) ESC® Data Acquisition 8832
- c) Gaus® 4710 O₂ analyzer
- d) Stream switching valve box
- e) Temperature controllers

- f) Laptop – this ran the system control software for all the instrumentation. The system software provided direct access to the datalogger and operational functions of the FTIR analyzer.

There were three heated lines connected to the enclosure; the supply feed, return feed and the feed to the SAS. Figures 2.7 and 2.8 show the FTIR cabinet and the sample lines going to the flue gas supply and return ports. Also shown in Figure 2.8 is the sample line going to the SAS and the bypass line to vent additional flow from the FTIR cabinet.



Figure 2.7. Front view of the FTIR cabinet.



Figure 2.8. Heated sample lines going to the FTIR cabinet. From bottom left to upper right corner, the sample lines are return, supply, bypass and flow to the SAS.



Figure 2.9. Interior of the front-side of the FTIR cabinet. From top to bottom, the components are: datalogger, O₂ analyzer, control laptop, FTIR analyzer, flow control box and temperature controllers.



Figure 2.10. Interior of the rear-side of the FTIR cabinet.

2.3.1.2 Secondary Analytical System

The SAS was located inside the analytical container and was used to provide redundancy in case of breakdowns or other scenarios when the FTIR system was offline. The system consisted of three different analyzers:

- a) Siemens® NOXMAT 600 for NO and NO₂
- b) Siemens® ULTRAMAT/OXYMAT 6 for O₂ and CO₂
- c) Thermo® 43i for SO₂

Each analyzer was integrated into a rack layout where each one would sample from a common flue gas manifold. Calibration lines to each analyzer were kept separate except for N₂, which was shared from a common manifold. Additional support systems for each analyzer were incorporated into the rack and included a gas conditioning system and solenoid valves to control gas flow for calibration. Gas conditioning was provided by a cooler, which removed water vapor from the flue gas prior to entering the gas analyzers. All gas measurements made in the SAS were on a dry-basis, i.e., without the presence of water vapor. A set of solenoid valves, controlled by the analyzers themselves, were used to direct the flow of calibration gas through the analyzer rack to appropriate analyzer.

The SAS was initially constructed by Tess-Com, Inc®. for other DOE projects, however I re-engineered major components of it to meet the needs of the project. This included installing an SO₂ dilution system, Campbell Scientific® CR10X datalogger and rewiring the analog signals for each analyzer.

2.3.1.3 Analytical System Operational Parameters

The entire analytical system (FTIR and SAS) utilized a set of operational parameters that were maintained throughout the course of the project. These are noted below in Table 2.1.

Table 2.1. Description of the operational settings used on the FTIR system and SAS.

Parameter	Value	Note	Analyzer(s) and/or Analytical System(s)	Application
Supply Flow Rate	7 – 8 act. lpm	Flow to FTIR and SAS systems	FTIR and O ₂ analyzer, SAS	Provide enough flow for analyzer systems
Treated Flow Rate	7 – 8 act. lpm	Flow to FTIR and SAS systems	FTIR and O ₂ analyzer, SAS	Provide enough flow for analyzer systems
Flow Rate to SAS	6 act. lpm	Flow that bypasses the FTIR system	SAS	Provide enough flow to the SAS
Sample Lines Temperature	188 ± 2 °C (370 ± 4 °F)		FTIR	Ensure all species are in the gaseous phase
Internal Lines Temperature	188 ± 2 °C (370 ± 4 °F)		FTIR	Ensure all species are in the gaseous phase
Cabinet Temperature	29 ± 2 °C (85 ± 4 °F)		FTIR	Optimal temperature for instrumentation
Trailer Temperature	24 °C (75 °F)		SAS	Optimal temperature for instrumentation
Bypass Flow Rate	>0 act. lpm		SAS	Maintain positive flow to ensure SAS is sampling flue gas only
Sample Pressure	9 – 12 psig	Pressure setting for pump in SAS	SAS	Deliver required pressure and flow to dedicated analyzers
O ₂ Analyzer Flow Rate	1 act. lpm	Flow delivered to analyzer	Siemens® ULTRAMAT/OXYMAT 6	Required flow rate
CO ₂ Analyzer Flow Rate	1 act. lpm	Flow delivered to analyzer	Siemens® ULTRAMAT/OXYMAT 6	Required flow rate
NO _x Analyzer Flow Rate	0.5 act. lpm	Flow delivered to analyzer	Siemens® NOXMAT 600	Required flow rate
SO ₂ Analyzer Flow Rate	1 act. lpm	Flow delivered to analyzer	Thermo® 43i	Required flow rate
Sample Probes Temperature	93 °C (200 °F)		FTIR and O ₂ analyzer, SAS	Freeze protection, help ensure all species are in the gaseous phase



Figure 2.11. Upper front-side of the SAS. From top to bottom are the rotameters, sample pressure gauge, O₂/CO₂, NO_x and SO₂ analyzers.

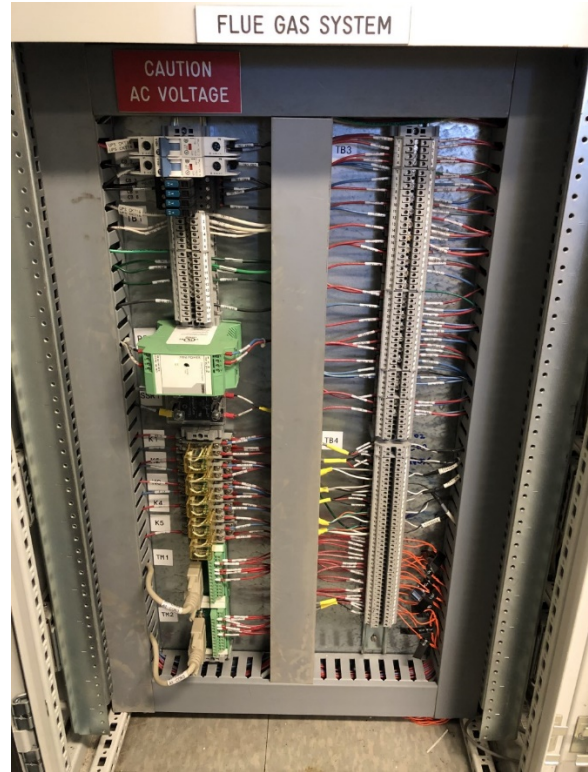


Figure 2.12. Lower front-side of the SAS. This is the wiring to control the calibration solenoids, record analyzer faults and gas concentrations.

2.3.1.4 Analytical System Maintenance and Calibration

The analytical system, consisting of the FTIR system and SAS, operated continuously throughout the project except in cases of calibration or routine maintenance. Each system checked and, if needed, calibrated on a regular basis. This was approximately every other day to ensure and verify accuracy. The calibration checks included a zero and span check. Calibration gases were on-site in cylinders located outside of the analytical container. The specific calibration gases, concentrations, and applicable system are shown in Table 2.2. Zero-checks were carried out using Ultra High Purity (UHP) gaseous N₂. For the FTIR system, this consisted of flushing the sample lines with UHP N₂. Once the signal from the GAUS® O₂ analyzer in the FTIR cabinet was stable, i.e., constant over 30 second period, the FTIR could be zeroed. The process was similar for the SAS, however each analyzer had to be checked separately. A zero check was initiated by accessing the control panel on each analyzer. A span-check, using a specific gas at a known concentration, was carried out on each analytical system. The gas concentrations used during span checks were selected to be higher than typically observed measurements in the flue gas. For the FTIR, ethylene (C₂H₄) was used to determine the overall response of the system. An O₂/CO₂ gas mixture was used to check the response of O₂ and CO₂ specifically. If a notable difference, i.e., > 5%, was observed then the FTIR was recalibrated. Each analyzer in the SAS was calibrated with a specific calibration gas as noted in Table 2.2. In a manner similar to the zero check, each analyzer was checked and calibrated separately.

Table 2.2. Description of the calibration gases used for the FTIR system and SAS.

Gas/Mixture	Concentration	Manufacturer	Application	System(s)	Analyzer(s)
N ₂	Pure	Airgas	Zero Check	FTIR/SAS	All
O ₂ /CO ₂	14% CO ₂ , 9% O ₂ , balance N ₂	Linde/Airgas	Span Check	FTIR/SAS	FTIR, OXYMAT/ULTRAMAT 6
NO	250 ppm _v , balance N ₂	Linde	Span Check	SAS	NOXMAT 600
NO ₂	50 ppm _v , balance N ₂	Linde	Span Check	SAS	NOXMAT 600
SO ₂	75 ppm _v , balance N ₂	Linde	Span Check	SAS	43i
C ₂ H ₄	101 ppm _v , balance N ₂	Linde	Overall Response	FTIR	FTIR



Figure 2.13. Calibration gas cylinders next to the analytical trailer. Each gas was regulated and passed through a bulkhead that went to the SAS or remained outside to go to the FTIR system.

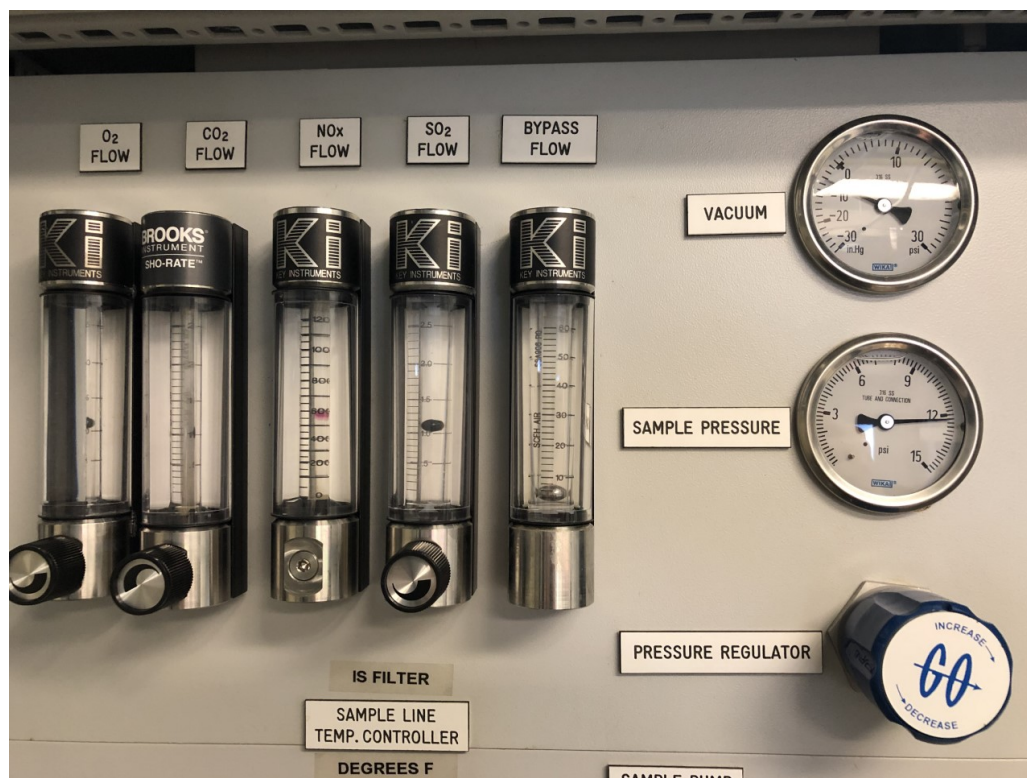


Figure 2.14. Rotameters for each of the gas analyzers in the SAS and the sample pressure regulator. Sample flow was set by the operator.

2.4 Conclusion

The information provided in this chapter provides information on the setup and design of the pilot skid at APP and the WASHU-ESP. Also, a description of the gas composition system was given. This provides the reading with an understanding of the WASHU-ESP and gas measurements, which is relevant for the following chapters of this thesis.

Chapter 3: Modeling and Data Analysis Methods

The purpose of this chapter is to provide the modeling and data analysis methods used in this thesis. Methods presented here provide the detailed approach used in analyzing data collected in March, 2020 in addition to the approach used for modeling. The ensuing model can provide insight to gaseous pollutant formation at a range of conditions – within and beyond the conditions observed during the project. In this chapter, the model purpose, assumptions and simplifications will be discussed followed by a detailed description of the modeling method used in this thesis. Finally, discussion will conclude with the methods used to analyze the FTIR measurement data.

3.1 Model Purpose

In Chapter 2, a description was provided of the FTIR system used to measure the concentrations of gaseous O_2 , CO_2 , CO , H_2O , NO , NO_2 , and SO_2 both upstream and downstream of the ESP. The results from these measurements are presented in Chapter 4. However, this data alone does not provide sufficient evidence if the ESP alters gaseous NO_x , SO_2 , H_2SO_4 and/or HNO_3 flue gas emission rates because they were not made concurrently. It is difficult to determine if any differences between upstream and downstream emission rates are due to the WASHU-ESP, operational fluctuations at APP, or measurement uncertainties. Also, there is a minimal amount of measurement data over a small set of WASHU-ESP operational conditions; i.e., the ESP was tested from a nominal voltage of 5 – 8 kVDC, where in (Bostick 2017) previous studies had tested an ESP up to 18 kVDC.

With the ensuing model, the goal was to evaluate how different variables affect the generation of gaseous NO_x , SO_2 , H_2SO_4 and/or HNO_3 over a range of operational conditions. The research goal was to investigate how ESP voltage (and therefore current), flue gas temperature, flue gas flowrate and photoionization affect emission rates. Furthermore, this

research can help determine emission rates over a broad range of conditions that could be observed at a power plant. As stated in Chapter 1, the emission of NO_x is of particular concern for a PCC plant, given the formation of nitrosamines and nitramines. The model determines the formation of NO_x , in addition to SO_2 , H_2SO_4 and/or HNO_3 , over a range of conditions which has practical importance for operation, reliability and safety of a PCC facility.

3.2 Assumptions and Simplifications

The modeling method presented in this chapter makes use of several assumptions and simplifications. These include the following:

1. Assumptions

- a. The coal type and composition used at Abbott Power Plant were assumed constant throughout the measurement campaign in March, 2020. This was necessary so a constant fuel factor could be used in the calculation of emission rate. A lab analysis from 2018, indicated the coal used at APP had a heating value was consistent with that of bituminous coal (Matthews 2018). This is assumed to be the typical coal type used at APP. As described in US EPA Method 19, bituminous coal has an average fuel factor of 263 L/MJ (liters per mega-joule) at 20 °C (68 °F) (*Method 19 - Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates* 2017). This is the fuel factor describing the volume of gaseous products, on a dry-basis, produced per unit energy consumed during combustion.
- b. The initial concentration of several gas-phase radicals (radicals), ions and other gases with no net electrical charge (gases) used in the model are zero; in other words, there is a negligible inlet concentration into the WASHU-ESP. These include sulfur monoxide (SO), atomic hydrogen ($\cdot\text{H}$), hydroxyl ($\cdot\text{OH}$), triplet state

atomic oxygen ($\cdot\text{O}({}^3\text{P})$), hydroperoxyl ($\cdot\text{HO}_2$), atomic oxygen anion ($\cdot\text{O}^-$), molecular oxygen anion ($\cdot\text{O}_2^-$), ozone anion ($\cdot\text{O}_3^-$), carbon trioxide anion ($\cdot\text{CO}_3^-$), carbon tetroxide anion ($\cdot\text{CO}_4^-$), molecular oxygen cation ($\cdot\text{O}_2^+$), carbon dioxide cation ($\cdot\text{CO}_2^+$), carbon monoxide cation ($\cdot\text{CO}^+$), atomic hydrogen cation (H^+), atomic carbon (C), dicarbon monoxide (C_2O), molecular hydrogen (H_2), atomic nitrogen ($\cdot\text{N}$), singlet state atomic oxygen ($\cdot\text{O}({}^1\text{D})$), nitrous acid (HONO), ozone (O_3), $\cdot\text{HSO}_3$, sulfur trioxide (SO_3), nitrosyl hydride (HNO) and nitric acid (HNO_3). By definition, a radical is an atom, molecule or ion that has an unpaired electron. Furthermore, an ion is an atom or molecule that has a net electrical charge. Gases, as defined above, have no net electrical charge with a few examples being O_2 , N_2 and CO_2 . A full list of all the species used in this thesis is given in Appendix B.

Gaseous SO_3 is assumed to be converted entirely to gaseous H_2SO_4 as in (Jaworowski and Mack 1979) at the temperature range used in this analysis (300 – 400 K). (Jaworowski and Mack 1979) show that flue gas containing 8% by volume H_2O at 478 K, gaseous SO_3 is converted entirely as gaseous H_2SO_4 . Furthermore, (Jaworowski and Mack 1979) show that below 478 K, gaseous H_2SO_4 condenses into H_2SO_4 aerosol. However, in a study at Abbott Power Plant in February 2016 (*Report on the Air Emissions Test Program Conducted for the University of Illinois at the Abbott Power Plant* 2016), Airtech Environmental Services, Inc. measured gaseous H_2SO_4 through EPA Method 8A and reported an average value of 22.5 ppm_v at dry conditions (*Report on the Air Emissions Test Program Conducted for the University of Illinois at the Abbott Power Plant* 2016). This value, while

representing the average of only two trials, will be used as an initial condition for gaseous H_2SO_4 in this analysis.

Gaseous HNO_3 is assumed to not exist in the supply gas upstream of the ESP.

Measurements from the FTIR showed that HNO_3 had an average concentration of 3.88 and standard deviation of 1.12 ppm_v on March 13th during the ESP operation.

However, there was interference between the SO_2 and HNO_3 signals from the FTIR during that time. Given this and a limited data set on March 13th, it is assumed for the purpose of modeling that the gaseous HNO_3 concentration was 0 ppm_v during the course of the project.

- c. The modeled electric field (Eqn. 4) in the WASHU-ESP is assumed as given by Chen and Davidson (2002), at current densities above 10 $\mu\text{A}/\text{cm}$. Chen and Davidson (2002) state the deviation between the actual electric field and the modeled field presented by Eqn. 4 is minimal.
- d. A number of the reaction rate constants, in Appendix B, have a defined temperature range that is outside of the temperature range used in this analysis (300 – 400 K).

2. Simplifications

- a. The modeling methods presented in this chapter are concerned with gas-phase species and reactions only.
- b. The following modeling method in this chapter can be analyzed as a spatially and temporally dependent problem. However, for simplification, it is presented at steady-state i.e., the modeling method is only spatial dependent. Further simplification has been achieved with the spatially dependent parameters used in the modeling method. These parameters have been averaged and are given as

single values for electron number concentration, electron mean energy and residence time.

3.3 Model Structure and Design

The modeling method presented in this chapter is based off the design of the WASHU-ESP used at Abbott Power Plant during the CO₂ capture project in March, 2020. This method describes how the ESP affects the emission rates of NO, NO₂, SO₂, H₂SO₄ and HNO₃. It is a chemical kinetic model, that is dependent on three factors: (1) number concentration of electrons, (2) residence time and (3) flue gas temperature. The formation of gas-phase ions and radicals, and the subsequent formation or decomposition of gaseous NO, NO₂, SO₂, H₂SO₄ and HNO₃, is dependent on the electron number concentration. Residence time is important because it is proportional to the extent of a chemical reaction. Finally, flue gas temperature is needed because several reaction rate constants are temperature dependent. Furthermore, electron number concentration is proportional to the current flowing from the discharge to collection electrodes in the WASHU-ESP and residence time is inversely proportional to flowrate. Photoionization also increases current at a given voltage, thereby increasing the number concentration of electrons (Kulkarni et al. 2002). Figure 3.1 gives a simplified cross-sectional view of the 1st stage of the WASHU-ESP. The discharge and collection electrodes were at a positive voltage and ground, respectively and were horizontally orientated. This produced a positive corona in the 1st stage. A negative corona is typically used in industrial applications because it is more stable than a positive corona (Flagan and Seinfeld 1988). However, a negative corona produces more ozone as noted by Flagan and Seinfeld (1988) and shown in (Jing et al. 2015). Appendices B and C include all of the derivations and code for modeling the emission rate of gaseous NO, NO₂, SO₂, H₂SO₄ and HNO₃.

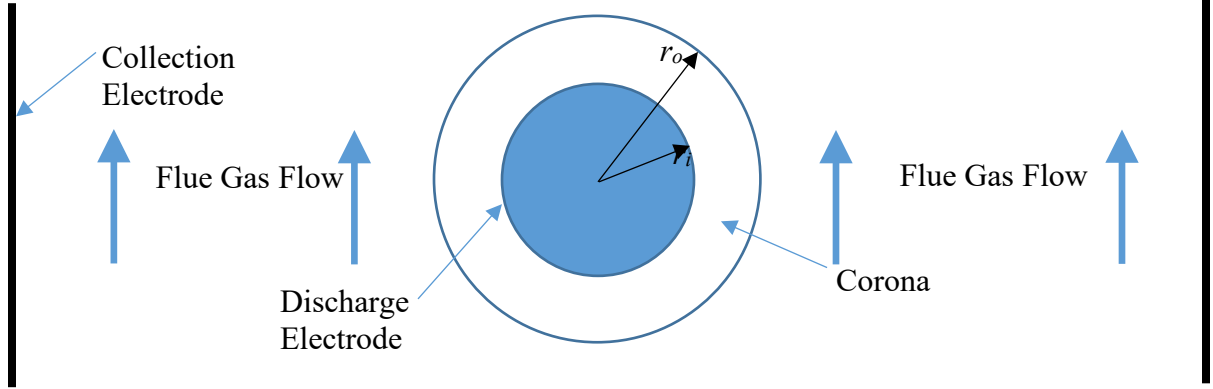
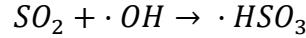
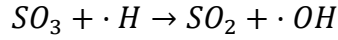
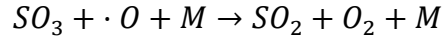
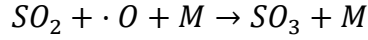
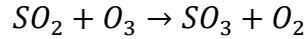
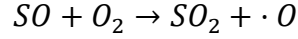


Figure 3.1. Cross-sectional view of the ESP's 1st stage showing the discharge and collection electrodes, flue gas flow direction and corona surrounding the discharge electrode. In this schematic, only one discharge electrode is shown, however the ESP's 1st stage contained 23 adjacent discharge and collection electrodes.

The chemical change modeled in this thesis is initiated by the interaction of high-energy electrons, surrounding the discharge electrodes, with flue gas species similar to the method presented by (Mikoviny et al. 2004). Ions and radicals produced from this interaction can further react to potentially alter the concentration of typical flue gas species including gaseous NO, NO₂, SO₂ as well as HNO₃ and H₂SO₄. The model structure used in this analysis consisted of a system of ordinary differential equations (ODEs) where each ODE described the time rate of change of each species, similar to the method presented in (Mikoviny et al. 2004). All the ODEs presented in this analysis were derived by myself. Furthermore, each of these rate equations were developed from a set of chemical equations, i.e., the rate equation for a particular species was developed from all the chemical equations where that species was either produced or consumed. For example, the rate of formation of gaseous SO₂ in the model is:

$$\begin{aligned} \frac{d}{dt}SO_2(t) = & k_1O_2(t)SO(t) - k_2O_3(t)SO_2(t) - k_3O(t)SO_2(t)N_2(t) + k_4H(t)SO_3(t) \\ & + k_5O(t)SO_3(t)N_2(t) - k_6OH(t)SO_2(t)N_2(t) \end{aligned}$$

This is an ODE describing the time rate of change of SO₂. This equation was developed from all the chemical equations that include SO₂. In terms of this example, those equations are:



These are all the chemical equations, used in the model, describing how SO₂ is produced and consumed. This process was completed for all 35 chemical species in the model and therefore yielded a rate equation for each species. The list of chemical equations totaled 121 and each one had a corresponding reaction rate constant. The full list of chemical species, chemical equations, reaction rate constants, are included in Appendix B.

The code used to model the effect of the ESP on the gaseous constituents of the flue gas was written in *Wolfram Mathematica 12*® (version 12.0.0.0). This code is included in Appendix C as a separate file.

As stated in Chapter 1, the main goal of this thesis is to determine if the ESP alters the NO, NO₂, SO₂, H₂SO₄ and/or HNO₃ emissions. To further break down the specific ESP operating conditions (ESP voltage and current), environmental conditions (flue gas temperature and pressure) and initial conditions (flue gas species concentrations upstream of the ESP) responsible for changing gaseous NO, NO₂, SO₂, H₂SO₄ and/or HNO₃ emission rates, the inputs used in the modeling method are divided into two sections. The first section lists the ESP operational conditions and physical parameters (Tables 3.1 and 3.2 respectively) and the second section describes the flue gas conditions (Table 3.3). Furthermore, Table 3.3 is divided into two regimes. The first regime consists of conditions that were observed during measurement while

the second regime consists of conditions not observed during measurement. Model results from the first regime can be compared to measurement results from the FTIR. Results from the second regime can be used to model how the ESP alters the emission rates of gaseous NO, NO₂, SO₂, H₂SO₄ and/or HNO₃ at conditions beyond what was measured during March 2020. Specifically, the second regime is designed to determine how modeled results change with varying gas flow rate through the ESP and gas temperature. The specific test conditions used in the modeling method presented in this chapter are listed in Tables 3.1, 3.2 and 3.3.

Table 3.1. A list of the various operational characteristics used to model the effect of the ESP on flue gas species. Voltage and Current were measured during March, 2020 from 4.978 - 7.966 kV and 0.278 - 10.39 mA respectively. Current values of 12 through 16 mA are used to model the ESPs effect on flue gas species concentrations beyond the tested current range in March, 2020. For all values of Current, Linear Current Density was calculated using the Number of Discharge Electrodes and Discharge Electrode Length listed in Table 3.2.

Nominal Voltage, V_n (kVDC)	Measured Voltage, V_a (kVDC)	Current, I (mA)	Linear Current Density, i ($\mu\text{A}/\text{cm}$)
5	4.978	0.278	0.207
6	5.974	2.318	1.725
7	6.970	5.716	4.254
7.5	7.468	7.962	5.926
7.75	7.717	9.07	6.75
8	7.966	10.39	7.733
--	--	12	8.931
--	--	14	10.419
--	--	16	11.908

In Table 3.1, I is the measured current in the first stage of the ESP, i.e., the current flowing from the discharge electrode to the collection electrode. The linear current density, i , is the current per unit length of the discharge electrode. This is an important metric used in the modeling and was calculated from the value of I , in addition to the length and number of the discharge electrodes found in Table 3.2.

Table 3.3 lists the various flue gas characteristics that will be used as inputs in the modeling method. These were divided into two regimes – the first regime lists the temperature, pressure, superficial flow rate and supply flue gas composition measured during the project. The purpose of this regime is to determine how well modeled results agree with the measured gas species concentrations exiting the ESP given inputs that are identical to the supply flue gas parameters. The purpose of the second regime is to determine how temperature and superficial flow rate influence the outlet concentration (and emission rate) of gaseous NO, NO₂, SO₂, H₂SO₄ and/or HNO₃ emissions. In this regime, the temperature and superficial flow rate values are 300, 350 and 400 K and 0.15, 0.30, and 0.45 m³/s respectively where all other species constant. The concentration of all the other species is approximately equal to those observed during measurement on March 8th and 13th, 2020.

Table 3.2. A list of the physical parameters describing the 1st stage of the ESP. These are best estimates based off the design of the 1st stage and are used throughout this analysis.

Number of Discharge Electrodes (#)	Discharge Electrode Diameter (m)	Discharge Electrode Length (m)	ESP Cross-Sectional Area (m ²)
23	1*10 ⁻⁴	0.5842	0.3413

Table 3.3. A list of the supply flue gas characteristics used in the model. Regime I_{FG} consists of observed flue gas conditions and species concentrations from March 8th and 13th, 2020. In Regime I_{FG}, the sulfuric acid concentration was based the measurement report provided by (*Report on the Air Emissions Test Program Conducted for the University of Illinois at the Abbott Power Plant* 2016). Regime II_{FG} consists of simulated scenarios used to determine the influence of gas temperature and flowrate on modeled results. In both regimes, Input Flue Gas Composition is given on a wet-basis because several of the parameters used in the modeling method are dependent on the actual, i.e., wet flue gas composition.

	I _{FG}			II _{FG}
	March 8 th	March 13 th – Run No. 1	March 13 th – Run No. 2	Modeled Flue Gas
Temperature (K)	385	383	393	300, 350, 400
Pressure (kPa)	99.457	99.877	100.146	101.325
Superficial Flow Rate (act. m ³ /s)	0.224	0.178	0.291	0.15, 0.30, 0.45
<i>Input Flue Gas Composition (Concentration, wet basis)</i>				
<i>Major Gases (% Volume)</i>				
# of samples	81	13	179	-- ¹
Nitrogen (N ₂)	68.576	69.416	68.523	68.07
Oxygen (O ₂)	8.28	8.70	8.51	8.50
Carbon Dioxide (CO ₂)	7.61	7.77	7.49	7.50
Water (H ₂ O)	14.6	13.2	14.5	15.0
Argon (Ar)	0.934	0.934	0.934	0.934
<i>Trace Gases (ppm_v)</i>				
Nitric Oxide (NO)	165.0	160.2	156.4	160.0
Nitrogen Dioxide (NO ₂)	13.59	13.58	12.35	14.0
Sulfur Dioxide (SO ₂)	79.71	76.51	69.75	75.0
Carbon Monoxide (CO)	218.7	251.6	195.7	225.0
Sulfuric Acid (H ₂ SO ₄)	19.2	19.5	19.2	22.5

¹ The modeled flue gas in regime II_{FG} was not based of measured data unlike the data from regime I_{FG}.

In summary, the modeling method presented in this thesis consists of several parts. Modeling is dependent upon the ESP and supply flue gas characteristics with the latter being divided into two regimes. With this modeling method, the goal was to determine any change the ESP had on the emission rates of gaseous NO, NO₂, SO₂, H₂SO₄ and/or HNO₃.

3.4 Internal Model Parameters

The model was designed to use inputs that could be determined from the ESP operating, conditions, ESP physical configuration and supply flue gas conditions. Other parameters, not used directly as inputs, but used in the modeling method are listed below and are dependent on the data in Tables 3.2 and 3.3. ESP residence time, while not considered as a model parameter, but rather an input, is also dependent on the data from Tables 3.2 and 3.3. For that reason, it is described in section 3.2.3.

Electron Number Concentration: the electron density produced by a corona discharge. This is needed for reactions that produce radicals by dissociative ionization, electron impact, dissociative attachment, associative attachment and ion-electron recombination reactions. The electron number concentration is also a function of linear current density, gas pressure, gas temperature and gas moisture content.

Electron Energy: the mean energy of electrons in the corona. Several of the rate constants used in the model are dependent upon the electron energy.

The electron number concentration, electron energy and gas residence time in the corona discharge of the ESP are given as a mean value i.e., each value has been integrated throughout the corona discharge region and then divided by the cross-sectional area of the region. This approach simplifies modeling from a spatially and temporally dependent analysis to one that is

temporally dependent only. In the following sections, the theory for calculating each parameter is provided.

3.4.1 Electron Number Concentration

The electron number concentration is needed to determine the reaction rate of each chemical species in the flue gas. The method presented in this section for determining electron density (number concentration), closely matches (Chen and Davidson 2002). As indicated in (Chen and Davidson 2002), the electron density in the corona surrounding a wire is dependent upon multiple factors. These include the wire diameter, wire current density, and radial distance from the wire surface as well as gas temperature and pressure. In the following section, the equations for calculating the average electron number concentration in a positive, direct-current corona discharge is described in detail.

The corona electron number concentration can be determined by solving the drift-diffusion equation as noted in (Chen and Davidson 2002).

$$0 = \nabla \cdot (\overline{D_e} \nabla n_e) - \nabla \cdot (n_e (\overline{\mu_e E})) - (\alpha - \beta) n_e \mu_e E \quad [\text{Eqn. 1}]$$

In the radial direction, r , this reduces to,

$$\frac{d}{rdr} \left(r D_e \frac{dn_e}{dr} \right) + \frac{d(r n_e \mu_e E)}{rdr} = -(\alpha - \beta) n_e \mu_e E \quad [\text{Eqn. 2}]$$

The terms α , β , μ_e , D_e , n_e , E are the ionization coefficient, attachment coefficient, electron mobility, diffusion coefficient, electron number concentration, and electric field, respectively.

All variables and units are listed in Appendix B. The electric field between two concentric cylinders is given as Eqn. 3 (Flagan and Seinfeld 1988),

$$E(r) = \frac{q_v}{2\epsilon_0} \left(r - \frac{r_0^2}{r} \right) + \frac{r_0 E_c}{r} \quad [\text{Eqn. 3}]$$

Chen and Davidson (2002) states that the electric field distribution for linear current densities less than or equal to 10 $\mu\text{A}/\text{cm}$ is nearly identical to the case with no space charge, i.e., $q_v = 0$.

For that reason, it is assumed that

$$E(r) = \frac{r_0 E_c}{r}, \text{ for } i \leq 10 \mu\text{A}/\text{cm} \quad [\text{Eqn. 4}]$$

As described in Chen and Davidson (2002), the ionization coefficient (α), attachment coefficient (β), electron mobility (μ_e) and diffusion coefficient (D_e) are dependent upon the local electric field (E), pressure (P) and temperature (T). The transport terms, α , β , μ_e and D_e can be expressed empirically in terms of E , P and T . To accomplish this, *BOLSIG+*, a program used to solve the Boltzmann equation, was used to determine the transport factors, α , β , μ_e and D_e at discrete electric field strengths. Input data for *BOLSIG+*, obtained from the *LXCat* database <https://www.lxcat.net>, consisted of the electron collision cross-sections for H_2O , CO_2 , O_2 , N_2 and Ar – the major components of flue gas. Further description of *BOLSIG+*, the parameters used, and output data in addition to *LXCat* is given in Appendix B. Using data provided by *LXCat*, the *BOLSIG+* solver was able to provide α , β , μ_e and D_e over a range of electric field strengths and at a given temperature, pressure and gas composition.

To determine α , β , μ_e and D_e , a few assumptions need to be made about the composition of the gas, its pressure and temperature. These included a constant gas composition upstream of the ESP. Furthermore, since the purpose of this thesis is to develop a model based on measured data, the actual supply gas composition to the WASHU-ESP was used to determine the transport factors. In order to solve [Eqn. 2], equations for α , β , μ_e and D_e as functions of r needed to be determined. Below, non-linear fit equations were determined for α , β , μ_e and D_e using the discrete data produced from *BOLSIG+*. These were calculated using *Wolfram Mathematica 12*®. A 5th order polynomial was used to fit the data from *BOLSIG+*.

385 K, 99.457 kPa, March 8th gas composition

The equations for α , β , μ_e and D_e can be expressed in terms of r using Eqn. 4.

$$\alpha(r) = r_0 E_c \left[4335 - 0.005879 \left(\frac{1}{r} \right) + 1.773 * 10^{-9} \left(\frac{1}{r} \right)^2 + 1.185 * 10^{-16} \left(\frac{1}{r} \right)^3 - 1.673 * 10^{-23} \left(\frac{1}{r} \right)^4 + 4.898 * 10^{-31} \left(\frac{1}{r} \right)^5 \right] \quad [\text{Eqn. 5}]$$

$$\beta(r) = r_0 E_c \left[-2048 + 0.003007 \left(\frac{1}{r} \right) - 8.6 * 10^{-10} \left(\frac{1}{r} \right)^2 + 1.089 * 10^{-16} \left(\frac{1}{r} \right)^3 - 6.472 * 10^{-24} \left(\frac{1}{r} \right)^4 + 1.468 * 10^{-31} \left(\frac{1}{r} \right)^5 \right] \quad [\text{Eqn. 6}]$$

$$\mu_e(r) = r_0 E_c \left[0.09873 - 2.67 * 10^{-8} \left(\frac{1}{r} \right) + 6.419 * 10^{-15} \left(\frac{1}{r} \right)^2 - 8.05 * 10^{-22} \left(\frac{1}{r} \right)^3 + 4.886 * 10^{-29} \left(\frac{1}{r} \right)^4 - 1.138 * 10^{-36} \left(\frac{1}{r} \right)^5 \right] \quad [\text{Eqn. 7}]$$

$$D_e(r) = r_0 E_c \left[-0.01454 + 1.131 * 10^{-7} \left(\frac{1}{r} \right) - 1.972 * 10^{-14} \left(\frac{1}{r} \right)^2 + 1.955 * 10^{-21} \left(\frac{1}{r} \right)^3 - 9.678 * 10^{-29} \left(\frac{1}{r} \right)^4 + 1.884 * 10^{-36} \left(\frac{1}{r} \right)^5 \right] \quad [\text{Eqn. 8}]$$

All of the equations for α , β , μ_e and D_e are included in Appendix B.

In the method described by Chen and Davidson (2002), [Eqn. 2] requires two boundary conditions to solve for the electron number concentration, n_e , as a function of r . Chen and Davidson (2002) go on to state that those conditions are at the wire surface and edge of the corona. At the wire surface, the electron number concentration is expressed as the current density per unit area, J .

Wire Surface

$$J = e \left[u_e E n_e + D_e \frac{dn_e}{dr} \right]_{r=r_i} \quad [\text{Eqn. 9}]$$

$$J = \frac{i}{2\pi r} \quad [\text{Eqn. 10}]$$

$$n_e(r_i) = \frac{\frac{i}{2\pi r_i e} - D_e(r_i) \frac{dn_e(r_i)}{dr}}{\mu_e(r_i) E(r_i)} \quad [\text{Eqn. 11}]$$

The term, i , is the current per length of wire and e is the elementary charge in Coulombs per electron. The electric field at the surface of the wire, $E(r_i)$, is equated to Peek's onset field as in Chen and Davidson (2002) – this is the field required to produce a glow corona as described in (Turner et al. 2002). Peek's onset field can be determined by the method presented in Hartmann (1984) which includes the dependence on temperature, pressure and humidity. That method is presented below:

$$E_c = E(r_i) = E_s(r_i, \delta_c, H) = E_0(\delta_c, H) \left(1 + \frac{A_0}{r_i^{B_0}} f(r_i, \delta_c, H) g(r_i) \right) \quad [\text{Eqn. 12}]$$

$$E_0(\delta, H) = E_0(1, 0) \delta_c (1 + \alpha_H \sqrt{H}) \quad [\text{Eqn. 13}]$$

$$f(r_i, \delta, H) = \frac{(1 - A_H \sqrt{H})(1 - A_\delta(\delta_c - 1))}{r_i^{-(B_H H + B_\delta(\delta_c - 1))}} \quad [\text{Eqn. 14}]$$

$$g(r_i) = r_i^{-a_2(1,0) \ln(r_i) + a_4(1,0) \ln(r_i)^3} \quad [\text{Eqn. 15}]$$

$$\delta_c = \frac{P}{760} \frac{293}{273 + T} \quad [\text{Eqn. 16}]$$

Where $E_0(1, 0) = 3 \times 10^6$ V/m ((Chen and Davidson 2002) quotes 3×10^6 V/m as the value most agreed upon by researchers. (Hartmann 1984) originally gives this value as 2.463×10^6 V/m, however for consistency, this analysis will use 3×10^6 V/m). From (Hartmann 1984), $\alpha_H = 1.603 \times 10^{-2}$, $A_0 = 0.13824$, $B_0 = 0.43823$, $A_H = 2.472 \times 10^{-2}$, $A_\delta = 0.4967$, $B_H = 3.340 \times 10^{-4}$, $B_\delta =$

3.134×10^{-2} , $a_2(I,0) = 9.103 \times 10^{-3}$, $a_4(I,0) = 8.995 \times 10^{-5}$. Furthermore, r_i is the radius of curvature of the wire (m), δ_c is the ratio of air density at actual conditions to air density at standard conditions, i.e., 760 torr (1 atm) and 20 °C. The water content, in g/m³, is given by H .

Corona Edge

The second boundary condition for solving the drift-diffusion equation [Eqn. 2], is at the outside edge of the corona plasma where the electron number concentration is assumed equal to the amount produced by photoionization as stated by (Chen and Davidson 2002). At the corona edge, the electron number concentration is given as:

$$n_e(r_0) = \gamma_p \int_a^{r_0} \alpha(r) g(r) e^{-\mu(r_0-r)} n_e(r) dr \quad [\text{Eqn. 17}]$$

$$g(r) = g_{\text{radial}}(r) g_{\text{axial}}(r) \quad [\text{Eqn. 18}]$$

$$g_{\text{radial}}(r) = \frac{1}{\pi e^{-\mu(r_0-r)}} \int_0^{\pi - \sin^{-1}(a/r)} e^{-\mu(r_0^2 + r^2 - 2r_0 r \cos \phi)^{1/2}} d\phi \quad [\text{Eqn. 19}]$$

$$g_{\text{axial}}(r) = \frac{2}{\pi e^{-\mu(r_0-r)}} \int_0^{\pi/2} e^{-\frac{\mu(r_0-r)}{\cos \phi}} d\phi \quad [\text{Eqn. 20}]$$

Here, γ_p , is the photoionization coefficient and μ is the absorption coefficient of photons.

(Zheng, Zhang, and He 2011) has provided a numerical approach to determining γ_p and μ for air in a positive corona discharge. In their analysis,

$$\gamma_p = \left[0.04 + \frac{12.137}{E_0/N} \right] q \quad [\text{Eqn. 21}]$$

$$q = \frac{\delta_q}{\delta + \delta_q} \quad [\text{Eqn. 22}]$$

$$\delta = \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right) \quad [\text{Eqn. 23}]$$

Where $P_0 = 760$ Torr, $T_0 = 293$ K and $\delta_q = 0.04$. The Lochschmidt constant, N , is given as,

$$N = \frac{P}{k_b T} \quad [\text{Eqn. 24}]$$

With k_b as the Boltzmann constant. Furthermore, (Zheng, Zhang, and He 2011) describes the absorption coefficient as,

$$\mu(\rho) = \frac{f(\rho)}{[1 - \int_0^\rho f(\rho') d\rho']} \quad [\text{Eqn. 25}]$$

$$f(\rho) = \frac{\exp\left(-\frac{\kappa_1 \rho N}{N_0}\right) - \exp\left(-\frac{\kappa_2 \rho N}{N_0}\right)}{\rho \ln\left(\frac{\kappa_2}{\kappa_1}\right)} \quad [\text{Eqn. 26}]$$

Where ρ is the radial distance from the photon emission point, ρ' is a dummy integration variable, $\kappa_1 = 5.6 \text{ cm}^{-1}$ and $\kappa_2 = 320 \text{ cm}^{-1}$.

With the boundary conditions specified and the values for the transport terms given as functions of E , the corona electron number concentration as a function of radial distance, r , can be specified for a given temperature, pressure, moisture content and linear current density.

Integrated over the entire region, the average electron number concentration becomes:

$$n_{e \text{ avg}} = \frac{1}{\pi(r_i^2 - r_o^2)} \int_{r_o}^{r_i} 2\pi r n_e(r) dr \quad [\text{Eqn. 27}]$$

In this analysis, the linear current density was calculated from the measured 1st stage current.

3.4.2 Electron Energy

In addition to the electron number concentration, the model also requires the electron energy to determine how much the ESP affects the gaseous composition of flue gas. As in the previous section, electron energy must be expressed in terms of radial distance, r . Fortunately, the *BOLSIG+* solver provides the mean electron energy in terms of electric field strength. Substituting the electric field E with r yields, for the following trial,

385 K, 99.457 kPa, March 8th gas composition

$$\bar{\epsilon}(r) = r_0 E_c \left[-1.444 + 3.062 * 10^{-6} \left(\frac{1}{r} \right) - 4.727 * 10^{-13} \left(\frac{1}{r} \right)^2 + 4.699 * 10^{-20} \left(\frac{1}{r} \right)^3 - 2.307 * 10^{-27} \left(\frac{1}{r} \right)^4 + 4.437 * 10^{-35} \left(\frac{1}{r} \right)^5 \right] \quad [\text{Eqn. 28}]$$

All of the equations for the mean electron energy are found in Appendix B.

As stated by Chen and Davidson (2002), the electron energy distribution function is governed by the Boltzmann equation.

$$\frac{\partial F}{\partial t} + \vec{v} \cdot \nabla_r F + \vec{a} \cdot \nabla_v F = \left(\frac{dF}{dt} \right)_c \quad [\text{Eqn. 29}]$$

Here, F , is the electron distribution function. Following the method presented by (Chen and Davidson 2002), the electron energy distribution function (EEDF) can be determined. The EEDF describes the probability an electron has a given kinetic energy (u). The upper and lower bounds on the range of kinetic energy, and therefore boundary conditions for [Eqn. 28], is usually given as:

$$f_0(0) = 0$$

$$f_0(\infty) = 0$$

Where f_0 is the EEDF. The mean electron energy is found by integrating the product of the EEDF and the electron energy. *BOLSIG+* defines the mean electron energy as:

$$\bar{\epsilon}(r) = \int_0^\infty \epsilon^{3/2} f_0(u(r)) d\epsilon \quad [\text{Eqn. 30}]$$

The electron kinetic energy is dependent upon the electric field strength.

$$u(r) = q_e V = q_e E(r) d \quad [\text{Eqn. 31}]$$

Where q_e is the electron elemental charge and d is the spacing between the discharge and collection electrodes. In summary, the mean electron energy at a given radial position is found by integrating the EEDF. Integrated over the entire region, the mean electron energy throughout the corona plasma becomes:

$$\bar{\epsilon}_{avg} = \frac{1}{\pi(r_i^2 - r_o^2)} \int_{r_o}^{r_i} 2\pi r \bar{\epsilon}(r) dr \quad [\text{Eqn. 32}]$$

3.4.3 Residence Time

The extent at which the concentration of chemical species change in the WASHU-ESP is also dependent on the residence time inside the corona surrounding the discharge electrode. Using potential flow theory, the residence time of an infinitesimally small parcel of flue gas in the corona region can be determined.

Potential flow is a special case in fluid mechanics, where the flow medium is given as incompressible and inviscid fluid and the resulting flow field has no vorticity. This derivation follows the method presented by Currie (2013). For the case of uniform flow around a circular cylinder perpendicular to its axis, Currie (2013) gives the complex potential of the flow as,

$$F(z) = U \left(z + \frac{a^2}{z} \right) \quad [\text{Eqn. 33}]$$

Where z is a complex number. Taking the derivative, the expression becomes,

$$W(z) = \frac{d}{dz} F(z) = U \left(1 - \frac{a^2}{z^2} \right) \quad [\text{Eqn. 34}]$$

Using Euler's formula, z is expressed as r and ϑ , in two-dimensional cylindrical coordinates,

$$W(z) = U - \frac{Ua^2}{r^2} e^{-2i\theta} \quad [\text{Eqn. 35}]$$

Currie (2013) defines the radial and tangential components of the velocity field as,

$$W(z) = (u_R - iu_\theta) e^{-i\theta} \quad [\text{Eqn. 36}]$$

Using this form, Eqn. 35 can be expressed as,

$$W(z) = U - \frac{Ua^2}{r^2} e^{-i\theta} e^{-i\theta} \quad [\text{Eqn. 37}]$$

Using Euler's formula, Eqn. 37 is expressed as,

$$W(z) = U - \frac{Ua^2}{r^2} (\cos(-\theta) + i\sin(-\theta)) e^{-i\theta} \quad [\text{Eqn. 38}]$$

Therefore,

$$u_R = U - \frac{Ua^2}{r^2} \cos(-\theta) = U \left(1 - \frac{a^2}{r^2} \right) \cos \theta \quad [\text{Eqn. 39}]$$

$$u_\theta = - \left[U - \frac{Ua^2}{r^2} \sin(-\theta) \right] = -U \left(1 + \frac{a^2}{r^2} \right) \sin \theta \quad [\text{Eqn. 40}]$$

$$\begin{aligned} V(r) = \sqrt{u_R^2 + u_\theta^2} &= \sqrt{U^2 \left(1 - 2\frac{a^4}{r^4} + \frac{a^4}{r^4} \right) \cos^2 \theta + U^2 \left(1 - 2\frac{a^4}{r^4} + \frac{a^4}{r^4} \right) \sin^2 \theta} \\ &= \sqrt{4U^2 \left(1 + \frac{a^4}{r^4} \right)} = 2U \sqrt{1 + \frac{a^4}{r^4}} \quad [\text{Eqn. 41}] \end{aligned}$$

Using the definition of velocity, the equation for residence time becomes,

$$t(r) = \frac{\pi r}{2U} \left(1 + \frac{a^4}{r^4} \right)^{-\frac{1}{2}} \quad [\text{Eqn. 42}]$$

Integrated over the entire region, the average residence time becomes:

$$t_{avg} = \frac{1}{\pi(r_i^2 - r_o^2)} \int_{r_o}^{r_i} 2\pi r t(r) dr \quad [\text{Eqn. 43}]$$

3.4.4 Effect of Soft X-ray Photoionization

Soft X-ray (3.5 – 9.5 keV) (Jing et al. 2015) photoionization enhances particle charging by increasing the number of bi-polar ions and electrons in the ESP (Jing et al. 2015). X-rays have sufficient power to ionize gas molecules as well as cause the photoemission of electrons from metal surfaces on the interior of the ESP (Jing et al. 2015). In the studies by (Kulkarni et al. 2002; Jing et al. 2015) the ESP current with X-ray photoionization was always greater than the current without X-ray photoionization. Furthermore, as stated by (Kulkarni et al. 2002), when X-rays are supplied, the number concentration of ions and electrons is higher producing a greater current at any given voltage. In the study by (Jing et al. 2015), it was shown that the electron number concentration increased by a maximum of approximately 5 times with the application of soft X-rays. Exact data is not given; however, an estimate was determined.

With X-ray photoionization, the mean electron number concentrations produced from the data shown in Tables 3.1 and 3.2 are multiplied by 5 in keeping with the study by (Jing et al. 2015). From there, the number concentration, along with other the other parameters and inputs discussed in the preceding sections, is used to determine the effect of X-ray photoionization on the emission rate of NO_x, SO₂, H₂SO₄ and/or HNO₃.

3.5 FTIR Experimental Analysis

This section describes the methods used to analyze the FTIR data. To determine if the gas composition exiting the WASHU-ESP was different than entering, a one-way Analysis of Variance (ANOVA) (Welch 1951) will be used to analyze the data. Furthermore, gas concentration data will be normalized to unit energy to account for variations in temperature and pressure in addition to dilution effects as shown in (*Method 19 - Determination of Sulfur Dioxide*

Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates 2017). These steps are described below in the following sections.

3.5.1 Gaseous Dry Conditions

The data measured by the FTIR is reported in volume per volume units on a wet basis i.e., each gas concentration is measured in the presence of water vapor. This represents the actual flue gas composition. However, since water vapor content changes over time it is necessary to analyze the flue gas composition on a dry basis i.e., with no water vapor present. This correction is described by,

$$c_{dry} = c_{wet} \left(\frac{1}{1 - n_w} \right) \quad [\text{Eqn. 44}]$$

where c_{dry} and c_{wet} are the concentration of a particular species on a dry and wet basis respectively and n_w is the mole fraction of water vapor.

3.5.2 Emission Rate

Even on a dry basis, the effects of dilution are still present in the flue gas. Dilution occurs when air, or another gas, is mixed in with the flue gas after leaving the boiler. To account for this, a correction must be applied. In this analysis, volume per volume, e.g., % volume and ppm_v, data is expressed on a mass per unit energy basis to correct for the dilution and changes in temperature and pressure. However, in order to make this conversion, a standard temperature and pressure (STP) must be used. For this analysis, STP is 293 K and 101.325 kPa. Normalized emission rates are given by the following equation (*Method 19 - Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates* 2017).

$$\dot{m}_E = c_{dry} F_{dry} \left(\frac{20.9}{20.9 - O_2\%} \right) \quad [\text{Eqn. 45}]$$

$\dot{m}_E$ is the emission rate in mass per unit energy, F is the fuel factor and $O_2\%$ is the oxygen concentration without the presence of water, i.e., dry conditions. This factor describes the amount of gas produced per unit energy consumed and it is specific to the type of fuel. As shown in US EPA Method 19, bituminous coal has an average fuel factor of 263 L/MJ at dry conditions and at STP (*Method 19 - Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates* 2017). An analysis from 2018, indicated the coal used at APP had a heating value consistent with that of bituminous coal (Matthews 2018). The fuel type and therefore fuel factor is assumed to be constant.

3.6 Conclusion

This chapter provided the necessary framework and background for the experimental and modeled results shown in Chapter 4. Here, the parameters, structure and physics used in the model were discussed along with assumptions and simplifications. Also, the methods used for analyzing the experimental data are given. The modeled results were calculated using the parameters and design shown in Tables 3.1, 3.2 and 3.3. In the following chapter, a detailed understanding of the role corona discharge has on flue gas composition can be made. Modeled results have been described in terms of varying temperature and flue gas flow rate. Furthermore, with the application of soft X-ray photoionization, a comprehensive analysis can be made on ESPs fitted with photoionizers and the potential implications they can have when used in a PCC plant.

Chapter 4: Results and Discussion

In this chapter, measurement and modeling results are presented to show how the WASHU-ESP effects the emission rates of gaseous NO, NO₂, SO₂, H₂SO₄ and HNO₃. Sections 4.1 – 4.3 include modeling and FTIR experimental results for NO, NO₂ and SO₂ emission rates respectively. The purpose of these sections is to show how the results produced from the modeling method in Chapter 3 agrees with actual measured emission rates obtained during March, 2020. Discussion is then provided to address differences between experimental and modeled results. However, sections 4.4 and 4.5 show how the modeled emission rates of NO, NO₂, SO₂, H₂SO₄ and HNO₃ vary with flue gas temperature and residence time in the WASHU-ESP, respectively. Finally, this chapter concludes with a discussion of the experimental and modeled emission rates and potential impacts on a CO₂ capture facility.

4.1 Experimental and Modeled Results for NO

The following graphs (Figures 4.1 – 4.6) show how the WASHU-ESP effected the emission rate of NO in the flue gas from APP through experimental data. Additionally, modeling has been done to assess how well these results correspond to the actual measurements. Emission rates have been normalized to unit energy consumed during combustion as outlined in Chapter 3.5.2. Graphs are given for the days shown in regime I_{FG} listed in Table 3.3, i.e., March 8th, March 13th Run No. 1 and March 13th Run No. 2. The actual data shown in the graphs are on a per-minute basis corresponding to actual data collected from the FTIR. A line of best fit based off the FTIR data is included as well: a corresponding coefficient of determination, R^2 , is provided and shows how well variance in emission rate is explained by variance in WASHU-ESP current. Tables 4.1, 4.2 and 4.3 provide interpretation of the information shown in Figures 4.1 – 4.6.

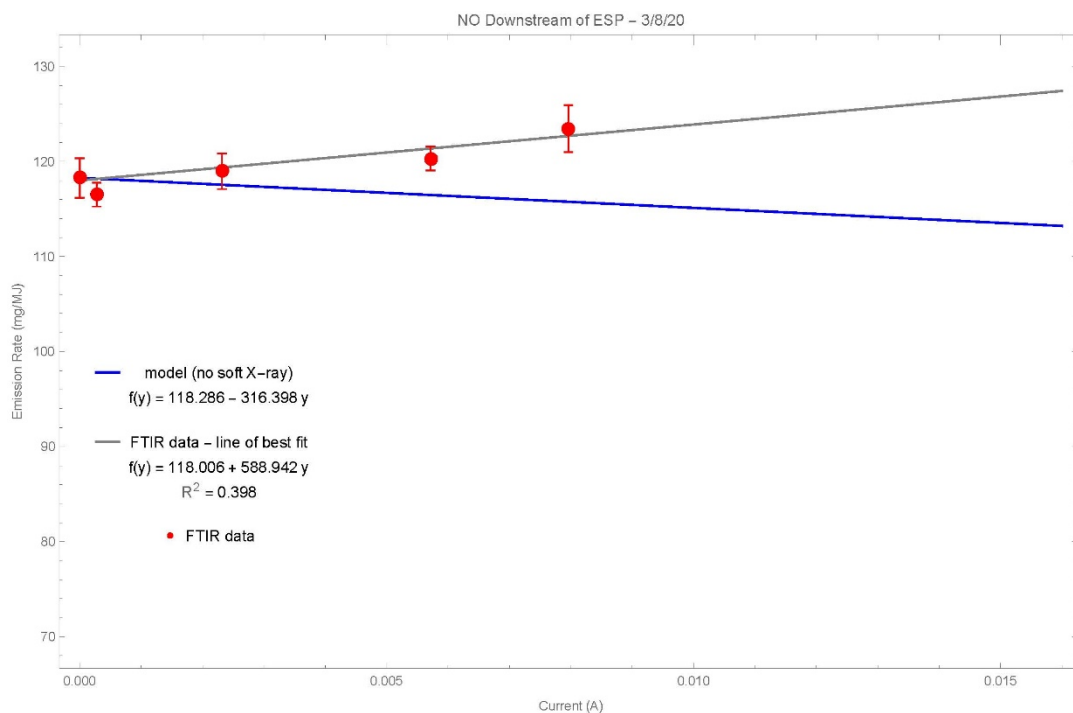


Figure 4.1. Plot showing the emission rate of NO from Abbott Power Plant on March 8th, 2020. The mean and standard deviation of emission rates from the FTIR system (FTIR data) are graphed alongside the modeled results obtained from *Mathematica 12* (model). A line of best fit is included for the FTIR data set. The standard deviation of current was less than 1 % of the mean, and is therefore not shown.

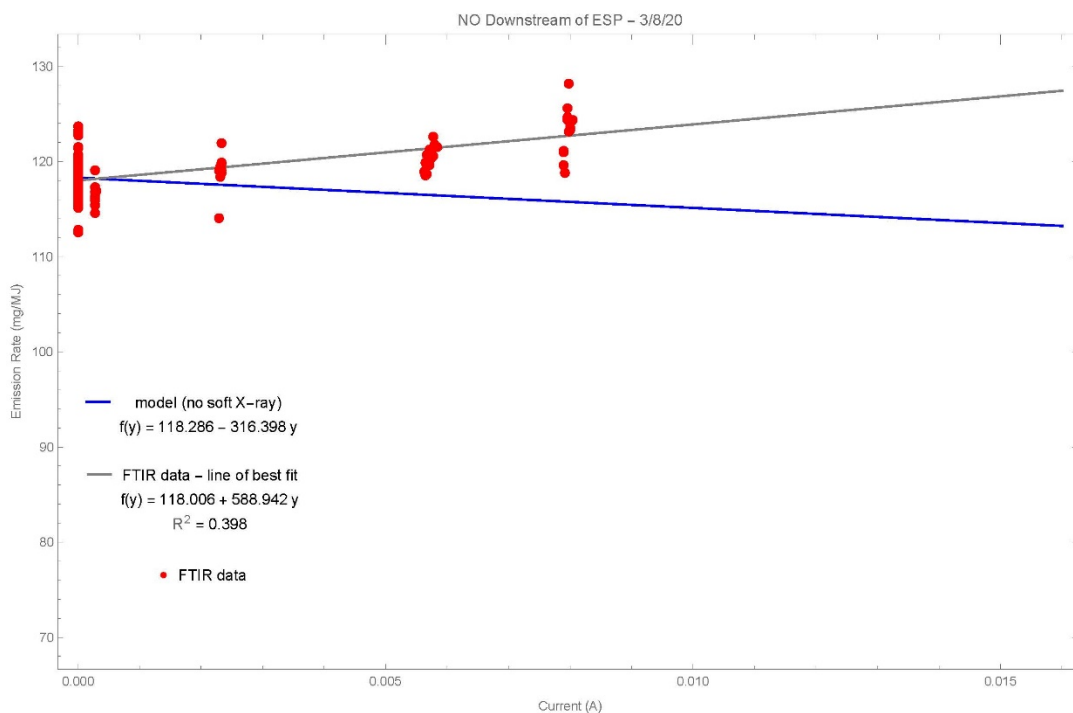


Figure 4.2. Plot showing the emission rate of NO from Abbott Power Plant on March 8th, 2020. Emission rates from the FTIR system (FTIR data) are graphed alongside the modeled results obtained from *Mathematica 12* (model). A line of best fit is included for the FTIR data set.

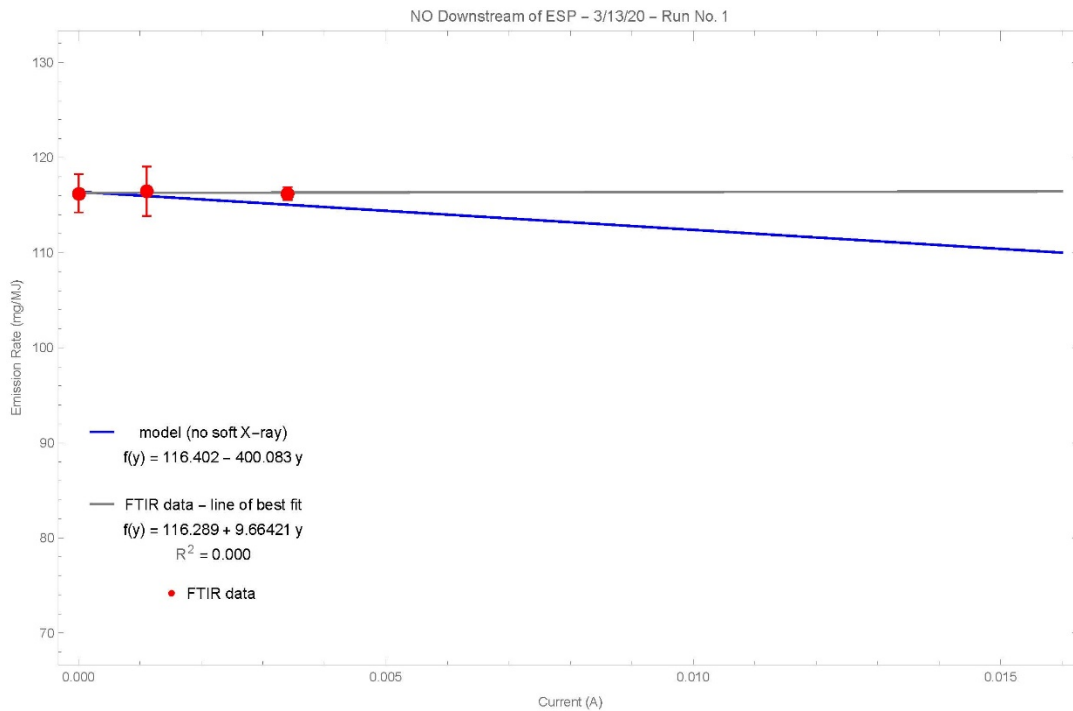


Figure 4.3. Plot showing the emission rate of NO from Abbott Power Plant on March 13th, 2020 – Run No. 1. The mean and standard deviation of emission rates from the FTIR system (FTIR data) are graphed alongside the modeled results obtained from *Mathematica 12* (model). A line of best fit is included for the FTIR data set. The standard deviation of current was less than 1 % of the mean, and is therefore not shown.

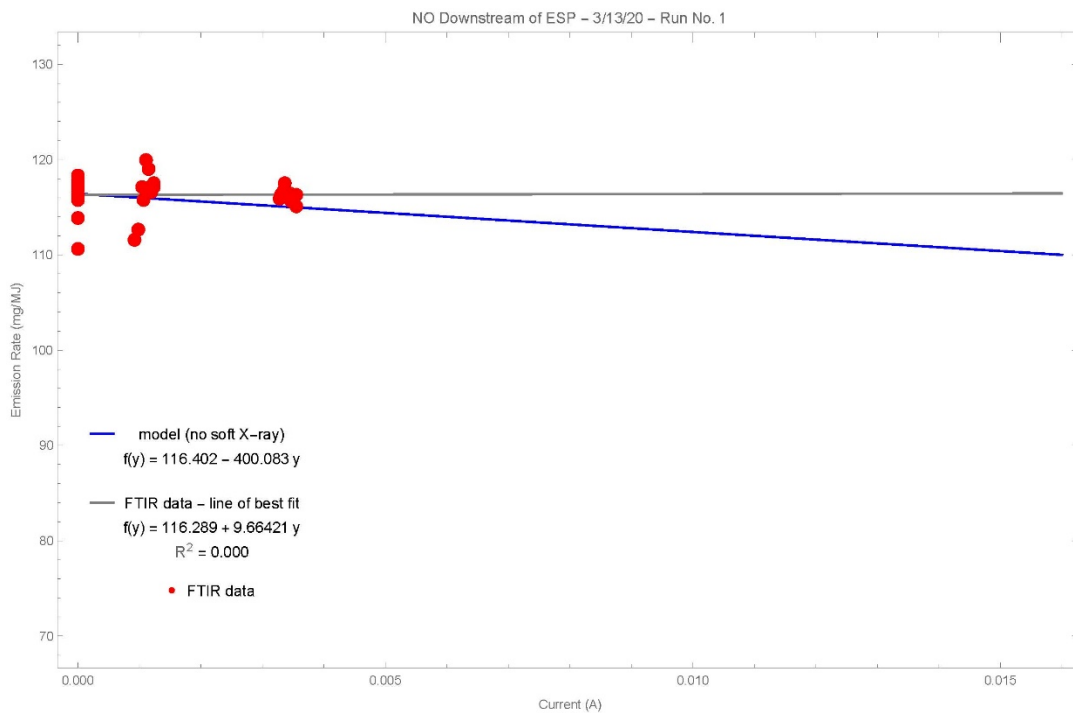


Figure 4.4. Plot showing the emission rate of NO from Abbott Power Plant on March 13th, 2020 – Run No. 1. Emission rates from the FTIR system (FTIR data) are graphed alongside the modeled results obtained from *Mathematica 12* (model). A line of best fit is included for the FTIR data set.

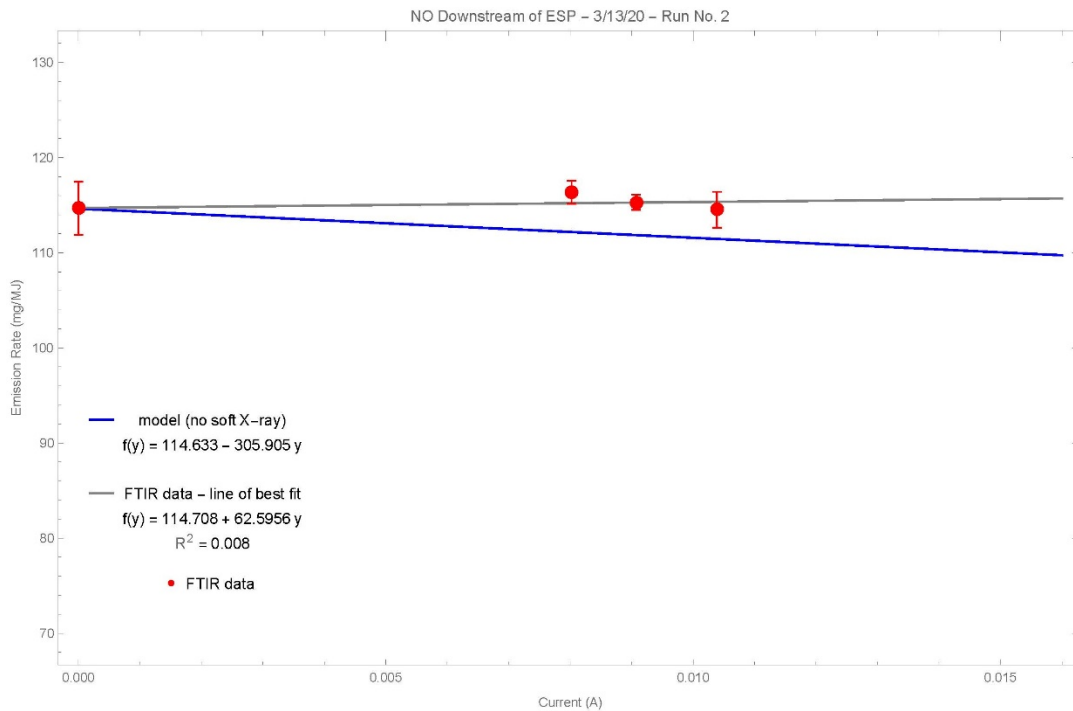


Figure 4.5. Plot showing the emission rate of NO from Abbott Power Plant on March 13th, 2020 – Run No. 2. The mean and standard deviation of emission rates from the FTIR system (FTIR data) are graphed alongside the modeled results obtained from *Mathematica 12* (model). A line of best fit is included for the FTIR data set. The standard deviation of current was less than 1 % of the mean, and is therefore not shown.

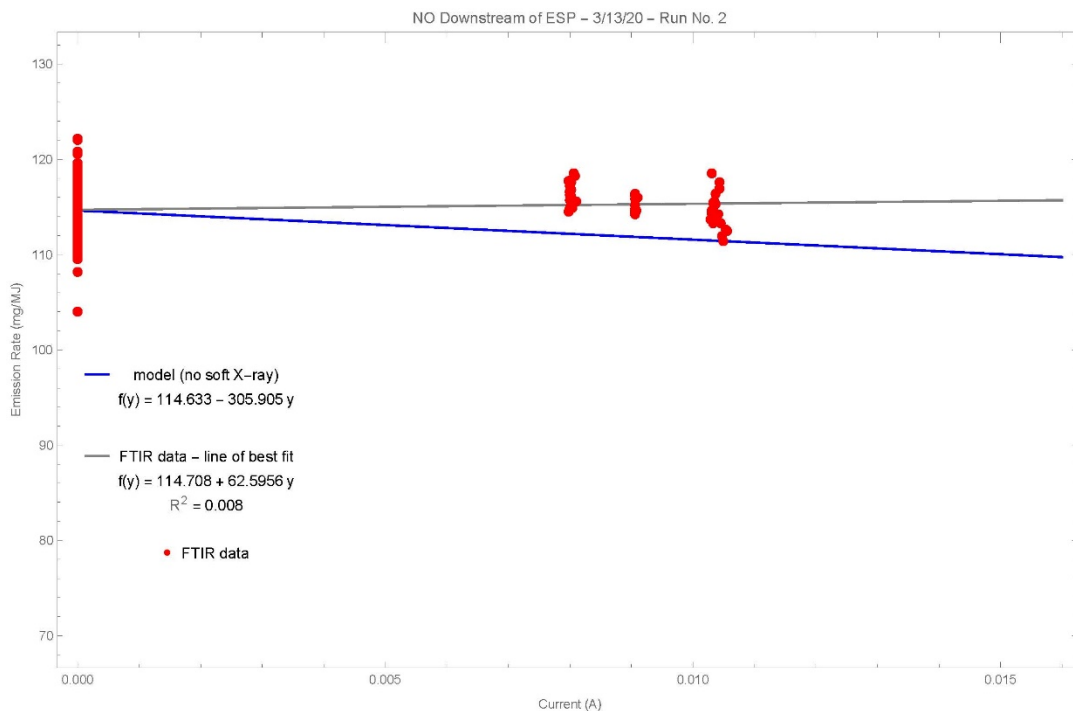


Figure 4.6. Plot showing the emission rate of NO from Abbott Power Plant on March 13th, 2020 – Run No. 2. Emission rates from the FTIR system (FTIR data) are graphed alongside the modeled results obtained from *Mathematica 12* (model). A line of best fit is included for the FTIR data set.

Table 4.1. Summary of NO emission rates from experimental and modeled data¹.

Scenario	Equation of line – model	Equation of line slope – model	Line of best fit – FTIR data	Line of best fit slope – FTIR	Average difference ² (%)	R- squared ³
March 8 th , 2020	$f(y) = 118.286 - 316.398y$	negative	$f(y) = 118.006 + 588.942y$	positive	5.8	0.398
March 13 th , 2020 – Run No. 1	$f(y) = 116.402 - 400.083y$	negative	$f(y) = 116.289 + 9.66y$	positive	2.8	0.000
March 13 th , 2020 – Run No. 2	$f(y) = 114.633 - 305.905y$	negative	$f(y) = 114.706 + 62.596y$	positive	2.7	0.006

¹ The data presented here are not indicative of how the WASHU-ESP would perform in all test cases. Rather, these results are for a given set of test conditions shown in Table 3.3.

² The average percent difference between the equation of the line from the model and line of best fit from the FTIR measurements. This was calculated over 0 – 16 mA and then averaged.

³ R-squared for the line of best fit – FTIR data.

Table 4.2. NO emission rate percent changes from experimental and modeled data¹.

Scenario	Percent change – model ² (%)	Percent change – FTIR data ³ (%)
March 8 th , 2020	-4.3	8.0
March 13 th , 2020 – Run No. 1	-5.5	0.1
March 13 th , 2020 – Run No. 2	-4.3	0.9

¹ The data presented here are not indicative of how the WASHU-ESP would perform in all test cases. Rather, these results are for a given set of test conditions shown in Table 3.3.

² The modeled percent change of NO emission rate calculated between 0 and 16 mA.

³ The experimental percent change of NO emission rate calculated between 0 and 16 mA.

The results shown in Table 4.1 describe how well NO emission rate predicted by the model agrees with experimental data. In all test cases, the model showed that the NO emission rate would decrease however, measured NO concentrations were shown to increase. The coefficient of determination, R^2 , values were very low, indicating that variance in emission rate is not due to variance in WASHU-ESP current. These results tend to indicate that 1) the WASHU-ESP had little to no effect on NO emission rate or 2) there was an effect, however it is not noticeable due to changes in emission rate upstream of the WASHU-ESP. This conclusion is further supported by the data in Tables 4.2 and 4.3. Table 4.2 provides data on how the modeled emission rate changed from 0 – 16 mA. Measured data was extrapolated, giving a line of best fit for emission rate from 0 – 16 mA. For all test days, the model showed that NO emission rate decreased 4.7 % on average, ranging from -4.3 to -5.5 %. On the other hand, measured results showed that emission rate increased 3 % on average, ranging from 0.1 to 8.0 % – these results were not consistent during testing.

Table 4.3. ANOVA of NO emission rates¹.

Scenario	p-value ²	Significant treatments ³ (kV)	Significant treatments (mA)	All treatments ⁴ (kV)
March 8 th , 2020	<0.0001	5, 7, 7.5	0.278, 5.716, 7.962	5, 6, 7, 7.5
March 13 th , 2020 – Run No. 1	0.9564	--	--	5, 6
March 13 th , 2020 – Run No. 2	0.0552	7.5	7.962	7.5, 7.75, 8

¹ The data presented here are not indicative of how the ESP would perform in all test cases. Rather, these results are for a given set of test conditions shown in Table 3.3.

² The p-value was determined as part of the ANOVA test. Alpha (significance level) was set at 0.05.

³ Significant treatments were determined from the Dunnett's post-test.

⁴ All treatments tested.

To better elucidate the effect of the WASHU-ESP, through the kinetic mechanism described in Chapter 3, a one-way ANOVA (Welch 1951) test was performed on the FTIR data.

Furthermore, to determine which treatment level had a significant effect on emission rate, Dunnett's test was performed where treatments could be compared against a control (0 kV) group (Dunnett 1955). Table 4.3 provides the results of the ANOVA and Dunnett's test showing which treatments produced NO emissions rates statistically significant from supply emission rates. These treatments are given in terms of voltage and current. The results show no clear trend was observed during the test period. On March 8th, NO emission rate was shown to increase with voltage, with 5, 7, and 7.5 kV producing statistically significant results from the control group. However, data from March 13th – Run No. 1, showed that no treatment produced a statistically significant emission rate despite being tested at a lower flow rate, i.e., higher residence time, where the WASHU-ESP is thought to have a greater effect on emission rate. Data from March 13th – Run No. 2 showed that the 7.5 kV treatment had a tendency to produce a statistically significant emission rate from the control group. Measurements from the FTIR are

limited and were conducted at varying voltages and flow rates, making it difficult to determine how the WASHU-ESP affects NO emission rate.

In conclusion, modeling and experimentation were carried out to determine how the WASHU-ESP affected the emission rate of NO. In all test cases, the model predicted the NO emission rate decreased by about 5 % from 0 to 16 mA. FTIR data, on the other hand, showed NO emission rate increased 3 %, ranging from 0.1 to 8.0 %, from 0 to 16 mA. The low R^2 values and inconsistent results from Dunnett's test indicate that either 1) the WASHU-ESP had no measurable effect on NO emission rate or 2) the effect was not noticeable due to a varying emission rate upstream it.

4.2 Experimental and Modeled Results for NO₂

The following graphs (Figures 4.7 – 4.12) show how the WASHU-ESP effected the emission rate of NO₂ in the flue gas from APP through experimental data. Additionally, modeling has been done to assess how well these results correspond to the actual measurements. Emission rates have been normalized to unit energy consumed during combustion as outlined in Chapter 3.5.2. Graphs are given for the days shown in regime I_{FG} listed in Table 3.3, i.e., March 8th, March 13th Run No. 1 and March 13th Run No. 2. The actual data shown in the graphs are on a per-minute basis corresponding to actual data collected from the FTIR. A line of best fit based off the FTIR data is included as well – a corresponding coefficient of determination, R^2 , is provided and shows how well variance in emission rate is explained by variance in WASHU-ESP current. Tables 4.4, 4.5 and 4.6 provide interpretation of the information shown in Figures 4.7 – 4.12.

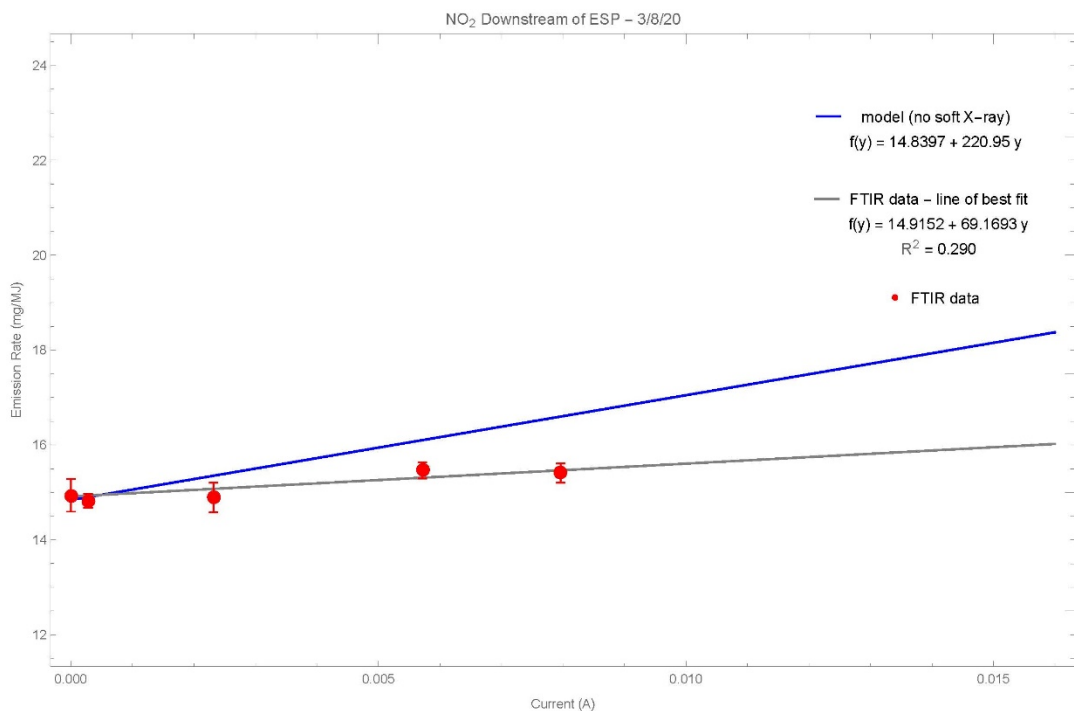


Figure 4.7. Plot showing the emission rate of NO₂ from Abbott Power Plant on March 8th, 2020. The mean and standard deviation of emission rates from the FTIR system (FTIR data) are graphed alongside the modeled results obtained from *Mathematica 12* (model). A line of best fit is included for the FTIR data set. The standard deviation of current was less than 1 % of the mean, and is therefore not shown.

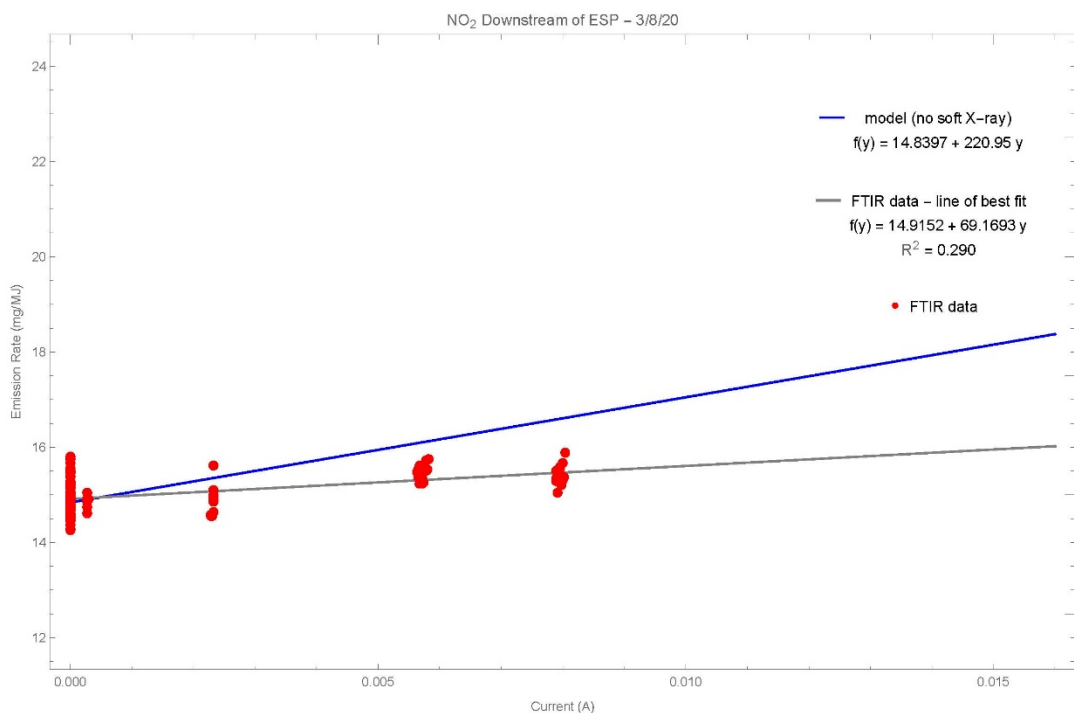


Figure 4.8. Plot showing the emission rate of NO₂ from Abbott Power Plant on March 8th, 2020. Emission rates from the FTIR system (FTIR data) are graphed alongside the modeled results obtained from *Mathematica 12* (model). A line of best fit is included for the FTIR data set.

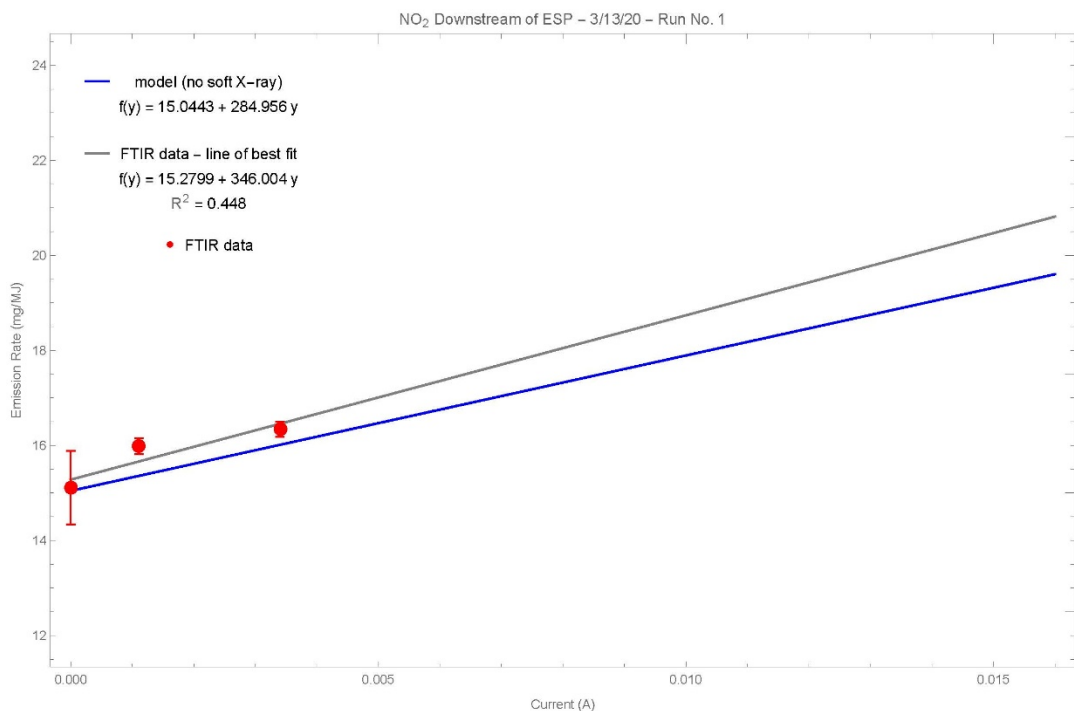


Figure 4.9. Plot showing the emission rate of NO₂ from Abbott Power Plant on March 13th, 2020 – Run No. 1. The mean and standard deviation of emission rates from the FTIR system (FTIR data) are graphed alongside the modeled results obtained from *Mathematica 12* (model). A line of best fit is included for the FTIR data set. The standard deviation of current was less than 1 % of the mean, and is therefore not shown.

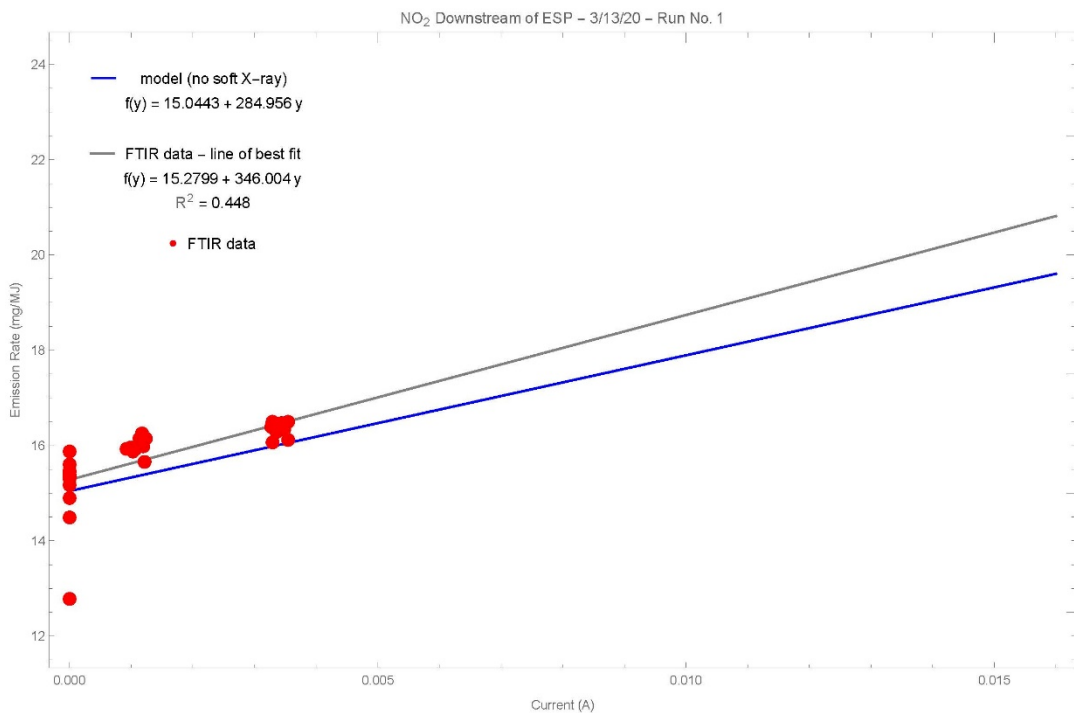


Figure 4.10. Plot showing the emission rate of NO₂ from Abbott Power Plant on March 13th, 2020 – Run No. 1. Emission rates from the FTIR system (FTIR data) are graphed alongside the modeled results obtained from *Mathematica 12* (model). A line of best fit is included for the FTIR data set.

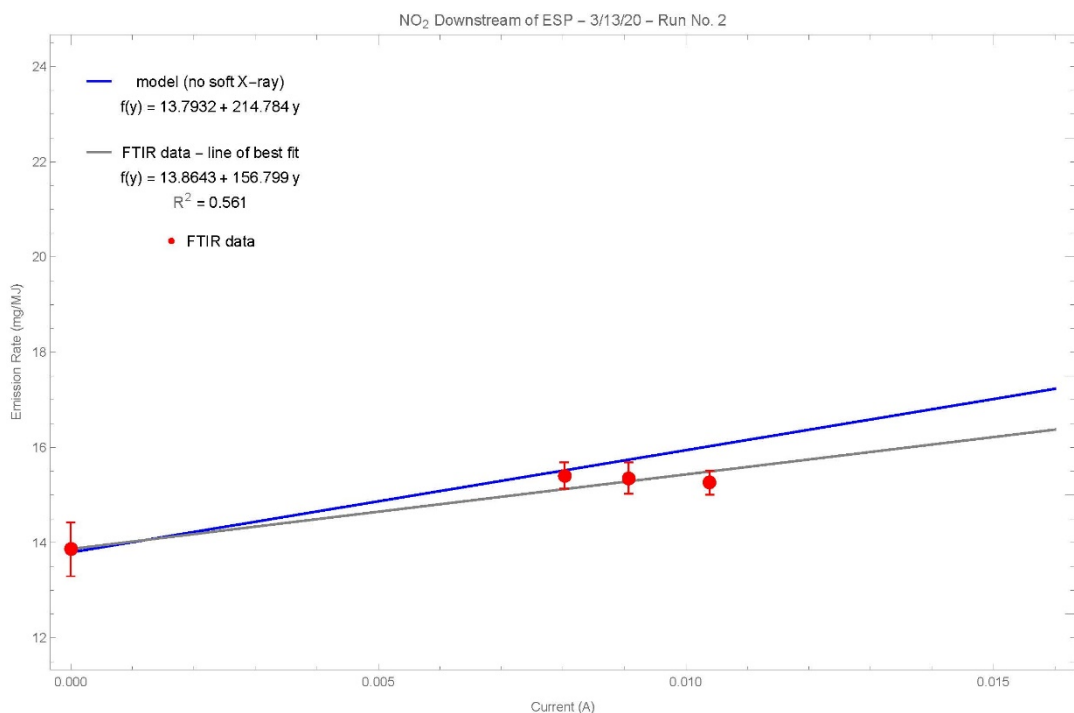


Figure 4.11. Plot showing the emission rate of NO₂ from Abbott Power Plant on March 13th, 2020 – Run No. 2. The mean and standard deviation of emission rates from the FTIR system (FTIR data) are graphed alongside the modeled results obtained from *Mathematica 12* (model). A line of best fit is included for the FTIR data set. The standard deviation of current was less than 1 % of the mean, and is therefore not shown.

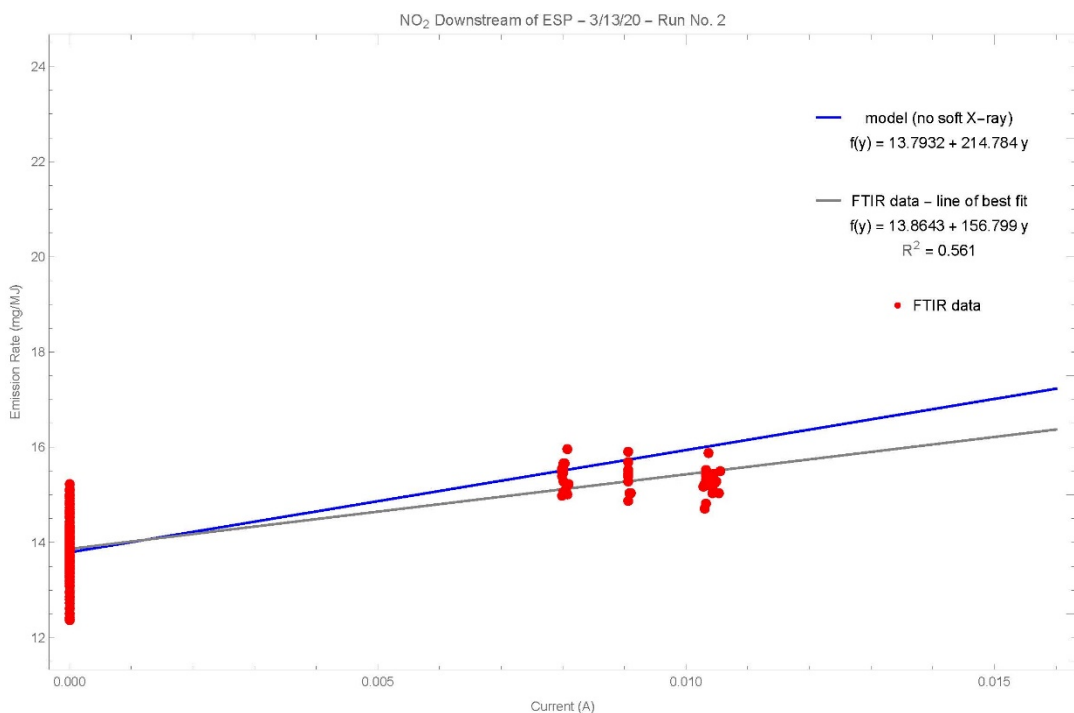


Figure 4.12. Plot showing the emission rate of NO₂ from Abbott Power Plant on March 13th, 2020 – Run No. 2. Emission rates from the FTIR system (FTIR data) are graphed alongside the modeled results obtained from *Mathematica 12* (model). A line of best fit is included for the FTIR data set.

Table 4.4. Summary of NO₂ emission rates from experimental and modeled data¹.

Scenario	Equation of line – model	Equation of line slope – model	Line of best fit – FTIR data	Line of best fit slope – FTIR data	Average difference ² (%)	R- squared ³
March 8 th , 2020	$f(y) = 14.840 + 220.95y$	positive	$f(y) = 14.915 + 69.169y$	positive	6.9	0.290
March 13 th , 2020 – Run No. 1	$f(y) = 15.044 + 284.956y$	positive	$f(y) = 15.280 + 346.004y$	positive	4.0	0.448
March 13 th , 2020 – Run No. 2	$f(y) = 13.793 + 214.784y$	positive	$f(y) = 13.864 + 156.799y$	positive	2.5	0.561

¹ The data presented here are not indicative of how the WASHU-ESP would perform in all test cases. Rather, these results are for a given set of test conditions shown in Table 3.3.

² The average percent difference between the equation of the line from the model and line of best fit from the FTIR measurements. This was calculated over 0 – 16 mA and then averaged.

³ R² for the line of best fit – FTIR data.

Table 4.5. NO₂ emission rate percent changes from experimental and modeled data¹.

Scenario	Percent change – model ² (%)	Percent change – FTIR data ³ (%)
March 8 th , 2020	23.8	7.4
March 13 th , 2020 – Run No. 1	30.3	36.2
March 13 th , 2020 – Run No. 2	24.9	18.1

¹ The data presented here are not indicative of how the WASHU-ESP would perform in all test cases. Rather, these results are for a given set of test conditions shown in Table 3.3.

² The modeled percent change of NO₂ emission rate calculated between 0 and 16 mA.

³ The experimental percent change of NO₂ emission rate calculated between 0 and 16 mA.

The results shown in Table 4.4 describe how well NO₂ emission rate predicted by the model agrees with experimental data. In all test cases, the model showed that the NO₂ emission rate would increase – consistent with measurements. However, the R² values were somewhat low indicating that variance in emission rate is not entirely explained by variance in WASHU-ESP current. These results tend to indicate that 1) the WASHU-ESP had a limited effect on NO₂ emission rate or 2) there was an effect, however it is not entirely noticeable due to changes in emission rate upstream of the WASHU-ESP. This conclusion is further supported by the data in Tables 4.5 and 4.6. Table 4.5 provides data on how the modeled emission rate changed from 0 – 16 mA. Measured data was extrapolated, giving a line of best fit for emission rate from 0 – 16 mA. For all test days, the model showed that NO₂ emission rate increased 26.3 % on average, ranging from 23.8 to 30.3 %. On the other hand, measured results showed that emission rate increased 20.6 % on average, ranging from 7.4 to 36.2 % – these results were not consistent during testing.

Table 4.6. ANOVA of NO₂ emission rates¹.

Scenario	p-value ²	Significant treatments ³ (kV)	Significant treatments (mA)	All treatments ⁴ (kV)
March 8 th , 2020	<0.0001	7, 7.5	5.716, 7.962	5, 6, 7, 7.5
March 13 th , 2020 – Run No. 1	<0.0001	5, 6	0.278, 2.318	5, 6
March 13 th , 2020 – Run No. 2	<0.0001	7.5, 7.75, 8	7.962, 9.07, 10.39	7.5, 7.75, 8

¹ The measurements presented here are not indicative of how the ESP would perform in all test cases. Rather, these results are for a given set of test conditions shown in Table 3.3.

² The p-value was determined as part of the ANOVA test. Alpha (significance level) was set at 0.05.

³ Significant treatments were determined from the Dunnett's post-test.

⁴ All treatments tested.

As in the preceding section, a one-way ANOVA (Welch 1951) test was performed on the FTIR data to better determine the WASHU-ESP's effect on NO₂ emission rate. Furthermore, to determine which treatment level, i.e., WASHU-ESP voltage, had a significant effect, Dunnett's test was performed where treatments could be compared against a control (0 kV) group (Dunnett 1955). Table 4.6 provides the results of the ANOVA and Dunnett's test showing which treatments produced NO₂ emissions rates statistically significant from supply emission rates. These treatments are given in terms of voltage and current. The results indicate a trend was observed during the test period. On March 8th, NO₂ emission rate was shown to increase with voltage, with 7 and 7.5 kV producing statistically significant results from the control group. Furthermore, data from March 13th – Run No. 1, showed that 5 and 6 kV produced a statistically significant emission rate. This is plausible because the WASHU-ESP was tested at a lower flow rate, which would increase the residence time a parcel of gas spends in it, increasing its effect on emission rate. Data from March 13th – Run No. 2 showed that the 7.5, 7.75 and 8 kV treatments produced a statistically significant emission rate from the control group. Measurements from all

the test days showed that most of the treatments produced NO₂ emission rates that were statistically significant from the control groups.

In conclusion, modeling and experimentation were done to determine how the WASHU-ESP affected the emission rate of NO₂. In all test cases, the model predicted that the NO₂ emission rate increased by 26.3 % on average. Similarly, FTIR measurements showed that NO₂ emission rate increased by 20.6 % on average. Dunnett's test also showed that most of the treatments produced statistically significant emission rates. However, R² showed that variance in measured emission rate was not entirely explained by variance in current. Rather, another factor or set of factors were responsible for variance observed in measured NO₂ emission rate. This may be explained by processes upstream of the WASHU-ESP.

4.3 Experimental and Modeled Results for SO₂

The following graphs (Figures 4.13 – 4.18) show how the WASHU-ESP effected the emission rate of SO₂ in the flue gas from APP through experimental data. Additionally, modeling has been done to assess how well these results correspond to the actual measurements. Emission rates have been normalized to unit energy consumed during combustion as outlined in Chapter 3.5.2. Graphs are given for the days shown in regime I_{FG} listed in Table 3.3, i.e., March 8th, March 13th Run No. 1 and March 13th Run No. 2. The actual data shown in the graphs are on a per-minute basis corresponding to actual data collected from the FTIR. A line of best fit based off the FTIR data is included as well – a corresponding coefficient of determination, R², is provided and shows how well variance in emission rate is explained by variance in ESP current. Tables 4.7, 4.8 and 4.9 provide interpretation of the information shown in Figures 4.13 – 4.18.

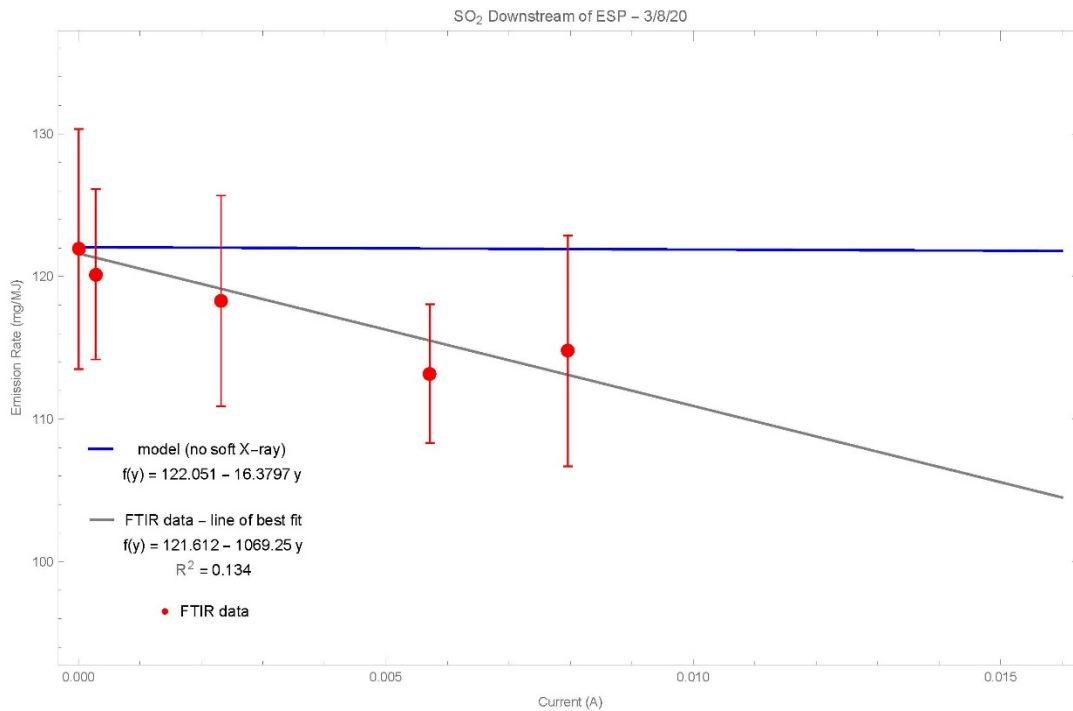


Figure 4.13. Plot showing the emission rate of SO₂ from Abbott Power Plant on March 8th, 2020. The mean and standard deviation of emission rates from the FTIR system (FTIR data) are graphed alongside the modeled results obtained from *Mathematica 12* (model). A line of best fit is included for the FTIR data set. The standard deviation of current was less than 1 % of the mean, and is therefore not shown.

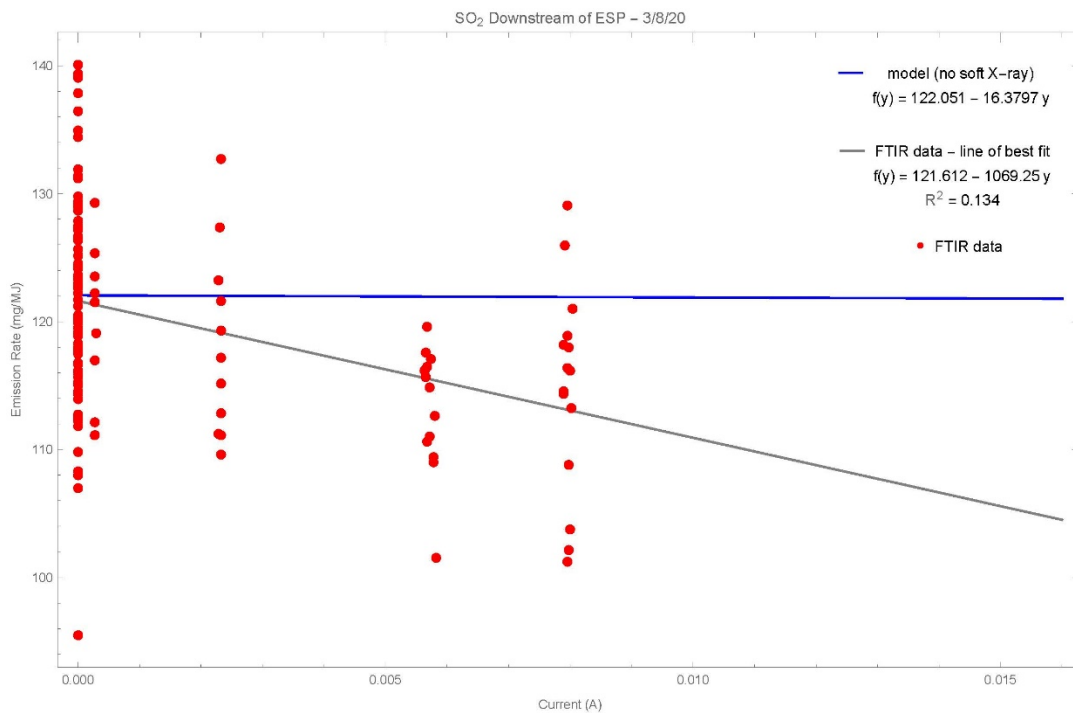


Figure 4.14. Plot showing the emission rate of SO₂ from Abbott Power Plant on March 8th, 2020. Emission rates from the FTIR system (FTIR data) are graphed alongside the modeled results obtained from *Mathematica 12* (model). A line of best fit is included for the FTIR data set.

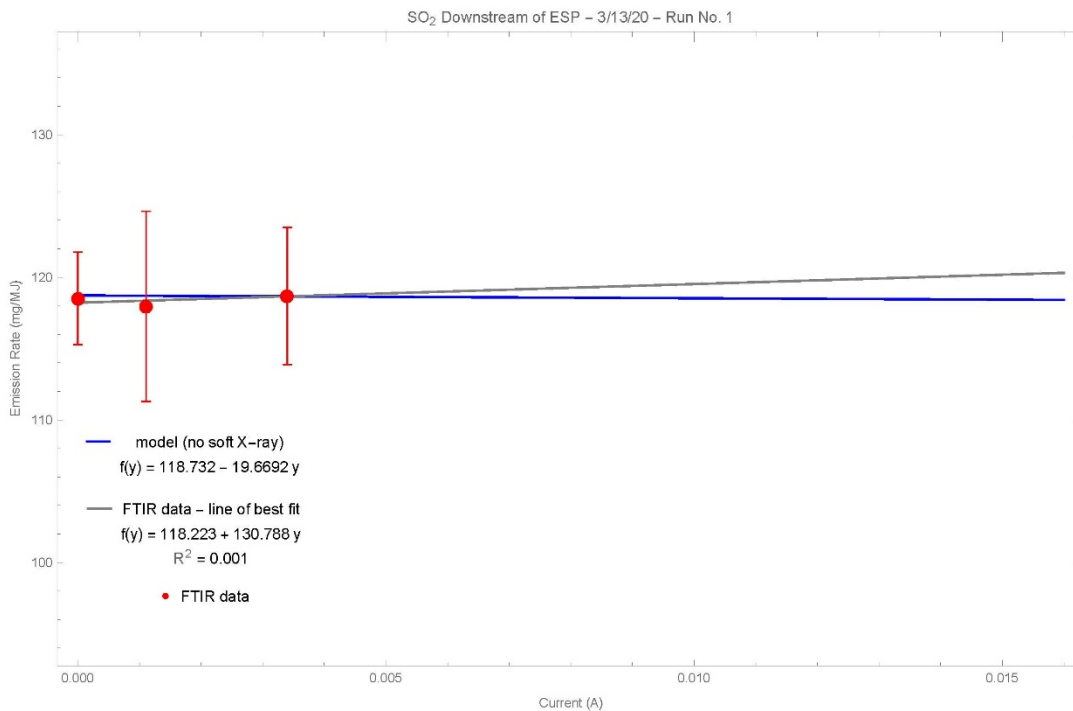


Figure 4.15. Plot showing the emission rate of SO₂ from Abbott Power Plant on March 13th, 2020 – Run No. 1. The mean and standard deviation of emission rates from the FTIR system (FTIR data) are graphed alongside the modeled results obtained from *Mathematica 12* (model). A line of best fit is included for the FTIR data set. The standard deviation of current was less than 1 % of the mean, and is therefore not shown.

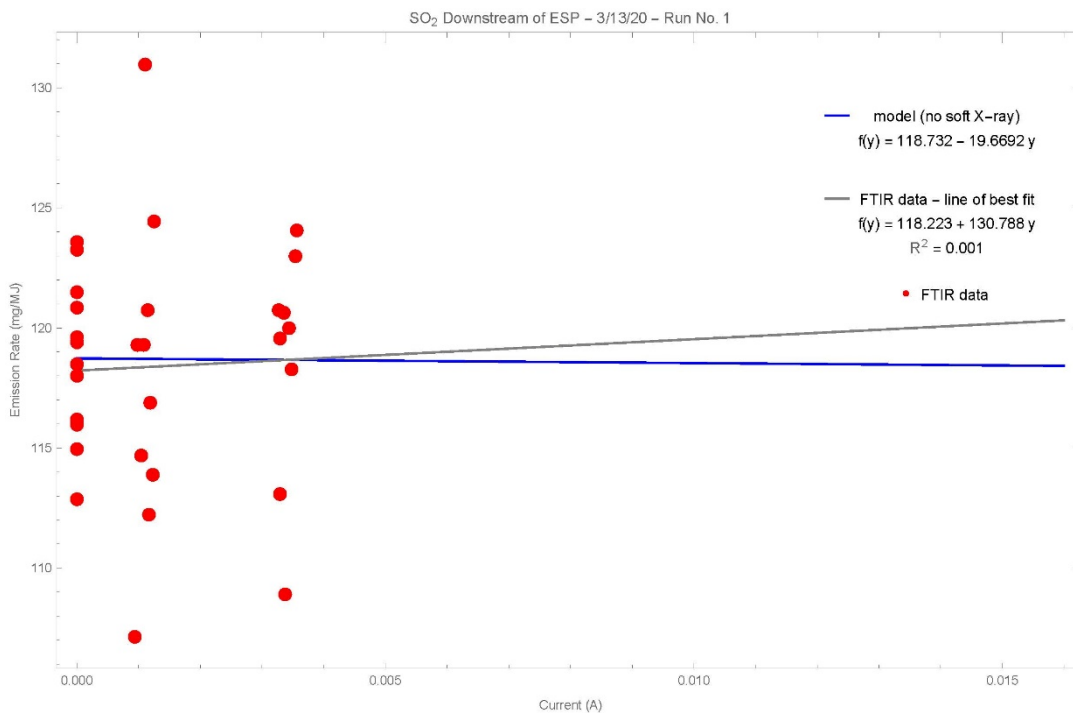


Figure 4.16. Plot showing the emission rate of SO₂ from Abbott Power Plant on March 8th, 2020 – Run No. 1. Emission rates from the FTIR system (FTIR data) are graphed alongside the modeled results obtained from *Mathematica 12* (model). A line of best fit is included for the FTIR data set.

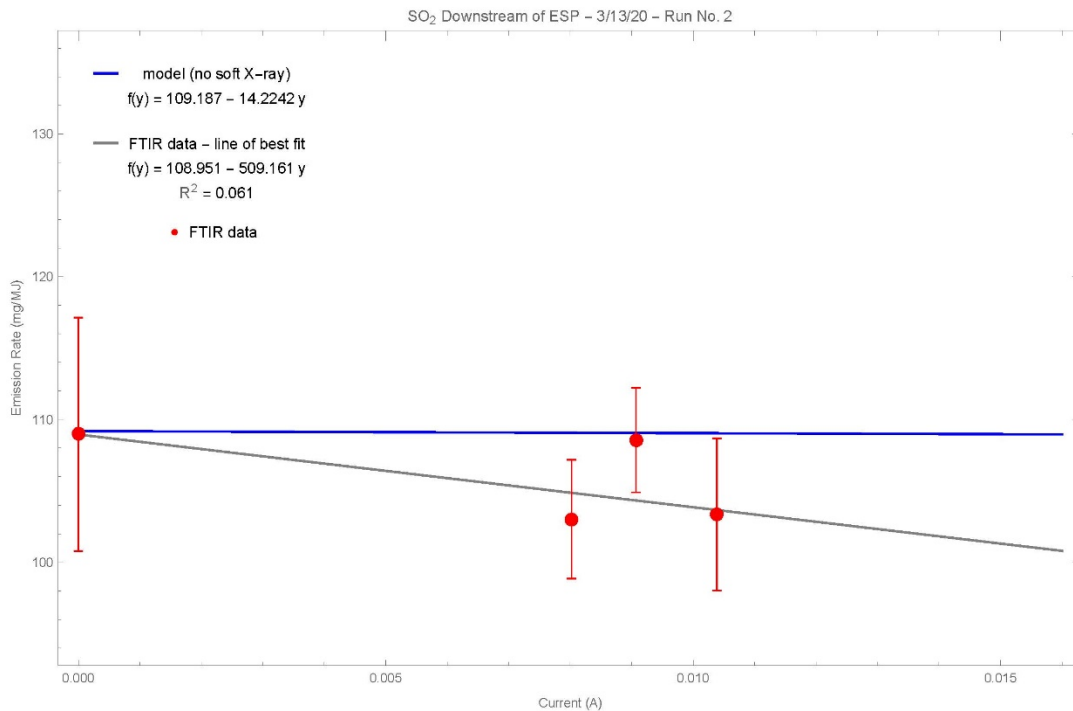


Figure 4.17. Plot showing the emission rate of SO₂ from Abbott Power Plant on March 13th, 2020 – Run No. 2. The mean and standard deviation of emission rates from the FTIR system (FTIR data) are graphed alongside the modeled results obtained from *Mathematica 12* (model). A line of best fit is included for the FTIR data set. The standard deviation of current was less than 1 % of the mean, and is therefore not shown.

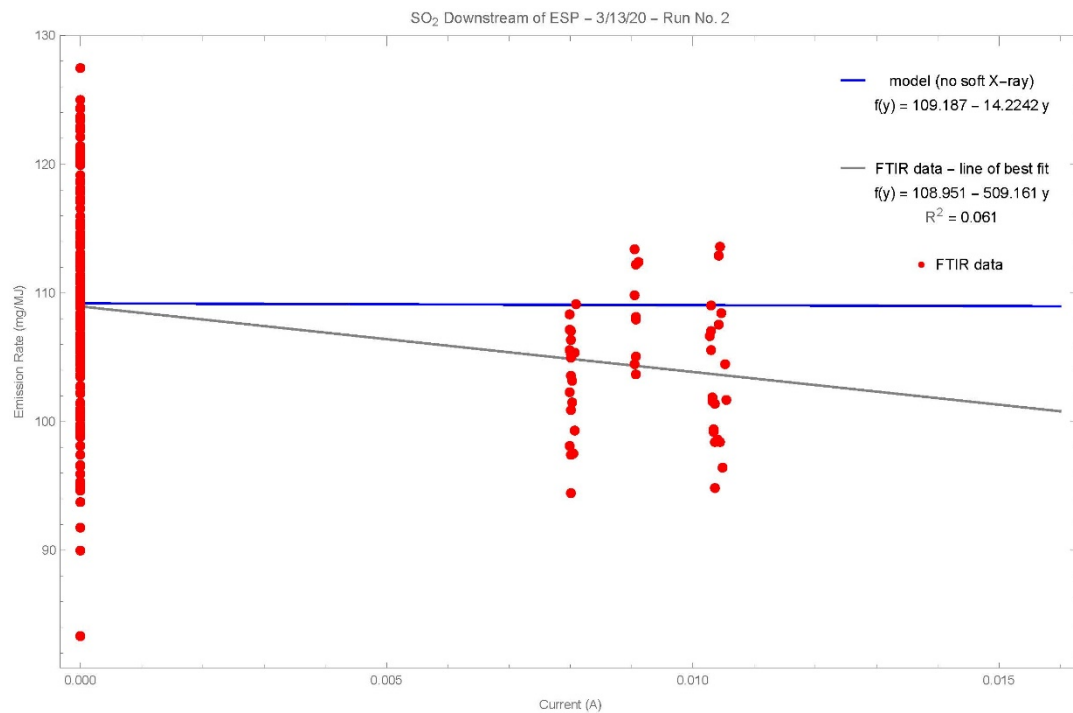


Figure 4.18. Plot showing the emission rate of SO₂ from Abbott Power Plant on March 8th, 2020 – Run No. 2. Emission rates from the FTIR system (FTIR data) are graphed alongside the modeled results obtained from *Mathematica 12* (model). A line of best fit is included for the FTIR data set.

Table 4.7. Summary of SO₂ emission rates from experimental and modeled data¹.

Scenario	Equation of line – model	Equation of line slope – model	Line of best fit – FTIR data	Line of best fit slope – FTIR data	Average difference ² (%)	R- squared ³
March 8 th , 2020	$f(y) = 122.051 - 16.380y$	negative	$f(y) = 121.612 - 1069.25y$	negative	7.6	0.134
March 13 th , 2020 – Run No. 1	$f(y) = 118.732 - 19.669y$	negative	$f(y) = 118.223 + 130.786y$	positive	0.7	0.001
March 13 th , 2020 – Run No. 2	$f(y) = 109.187 - 14.224y$	negative	$f(y) = 106.951 - 509.161y$	negative	5.9	0.061

¹ The data presented here are not indicative of how the WASHU-ESP would perform in all test cases. Rather, these results are for a given set of test conditions shown in Table 3.3.

² The average percent difference between the equation of the line from the model and line of best fit from the FTIR measurements. This was calculated over 0 – 16 mA and then averaged.

³ R² for the line of best fit – FTIR data.

Table 4.8. SO₂ emission rate percent changes from experimental and modeled data¹.

Scenario	Percent change – model ² (%)	Percent change – FTIR data ³ (%)
March 8 th , 2020	-0.2	-14.1
March 13 th , 2020 – Run No. 1	-0.3	1.8
March 13 th , 2020 – Run No. 2	-0.2	-7.6

¹ The data presented here are not indicative of how the WASHU-ESP would perform in all test cases. Rather, these results are for a given set of test conditions shown in Table 3.3.

² The modeled percent change of SO₂ emission rate calculated between 0 and 16 mA.

³ The experimental percent change of SO₂ emission rate calculated between 0 and 16 mA.

The results shown in Table 4.7 describe how well SO₂ emission rate predicted by the model agrees with experimental data. In all test cases, the model showed that the SO₂ emission rate would decrease slightly – inconsistent with measurements. Furthermore, the R² values were very low indicating variance in emission rate is not explained by variance in WASHU-ESP current. These results tend to indicate that 1) the WASHU-ESP had no effect on the SO₂ emission rate or 2) there was an effect, however it is not noticeable due to changes in emission rate upstream of the WASHU-ESP. Chang et al. (1991) showed SO₂ removal rate from a combined dielectric barrier discharge with plasma photolysis became noticeable when residence time was on the order of 1 second. This is consistent with the modeled results, considering residence time in the WASHU-ESP was on the order of 1 millisecond. This conclusion is further supported by the data in Tables 4.8 and 4.9. Table 4.8 provides data on how the modeled emission rate changed from 0 – 16 mA. Experimental data was extrapolated, giving a line of best fit for emission rate from 0 – 16 mA. For all test days, the model showed that SO₂ emission rate decreased 0.2 % on average, ranging from -0.2 to -0.3 %. On the other hand, measured results showed that emission rate decreased 6.6 % on average, ranging from -14.1 to 1.8 % – these results were not consistent during testing.

Table 4.9. ANOVA of SO₂ emission rates¹.

Scenario	p-value ²	Significant treatments ³ (kV)	Significant treatments (mA)	All treatments ⁴ (kV)
March 8 th , 2020	0.0005	7, 7.5	5.716, 7.962	5, 6, 7, 7.5
March 13 th , 2020 – Run No. 1	0.9433	--	--	5, 6
March 13 th , 2020 – Run No. 2	0.0173	7.5	7.962	7.5, 7.75, 8

¹ The data presented here are not indicative of how the WASHU-ESP would perform in all test cases. Rather, these results are for a given set of test conditions shown in Table 3.3.

² The p-value was determined as part of the ANOVA test. Alpha (significance level) was set at 0.05.

³ Significant treatments were determined from the Dunnett's post-test.

⁴ All treatments tested.

As in the preceding section, a one-way ANOVA (Welch 1951) test was performed on the FTIR measurements to better determine the WASHU-ESP's effect on SO₂ emission rate. Furthermore, to determine which treatment level, i.e., WASHU-ESP voltage, had a significant effect, Dunnett's test was performed where treatments could be compared against a control (0 kV) group (Dunnett 1955). Table 4.9 provides the results of the ANOVA and Dunnett's test showing which treatments produced SO₂ emissions rates statistically significant from supply emission rates. These treatments are given in terms of voltage and current. The results indicate SO₂ emission rate decreased at 7 and 7.5 kV, however R² was very low indicating the variance in SO₂ emission rate is not explained by the variance in WASHU-ESP current.

In conclusion, modeling and experimentation were done to determine how the WASHU-ESP affected the emission rate of SO₂. In all test cases, the model predicted the SO₂ emission rate decreased by 0.2 % on average. However, the FTIR showed SO₂ emission rates decreased by 6.6 % on average. Dunnett's test also showed that 2 of the treatments produced statistically significant emission rates. However, R² values showed variance in measured emission rate was

not explained by variance in WASHU-ESP current. Rather, another factor or set of factors were responsible for the variance observed in measured SO₂ emission rate. This was likely due to processes upstream of the WASHU-ESP, such as a slight variation in SO₂ concentration coming from the flue-gas desulfurization unit.

4.4 Modeled Effect of Flue Gas Temperature

The following graphs (Figures 4.19 – 4.23) show how flue gas temperature in the WASHU-ESP would have affected the emission rate of NO, NO₂, SO₂, H₂SO₄ and HNO₃ with and without soft X-ray photoionization. Emission rates have been normalized to unit energy consumed during combustion as outlined in Chapter 3.5.2. Graphs are given for the gas composition shown in regime II_{FG} listed in Table 3.3. Flow rate and water content were kept constant at 0.15 m³/s and 15 % by volume, respectively. Temperature was varied from 300 – 400 K, in 50 K increments. Table 4.10 provide interpretation of the information shown in Figures 4.19 – 4.23. Furthermore, Table 4.11 shows how much the emission rate for NO and NO₂ vary with respect to degrees K. The results shown in this section do not include any experimental data and is solely based on modeled data.

The purpose of this analysis is to better understand how an ESP, utilizing soft X-ray photoionization, responds to temperature change and the implications for NO, NO₂, SO₂, H₂SO₄ and HNO₃ emission rates. This can be of interest, since Dai and Mitch (2014) state that NO and NO₂ concentrations were linearly correlated to the accumulation rate of nitramines and nitrosamines in PCC amine-based solvent.

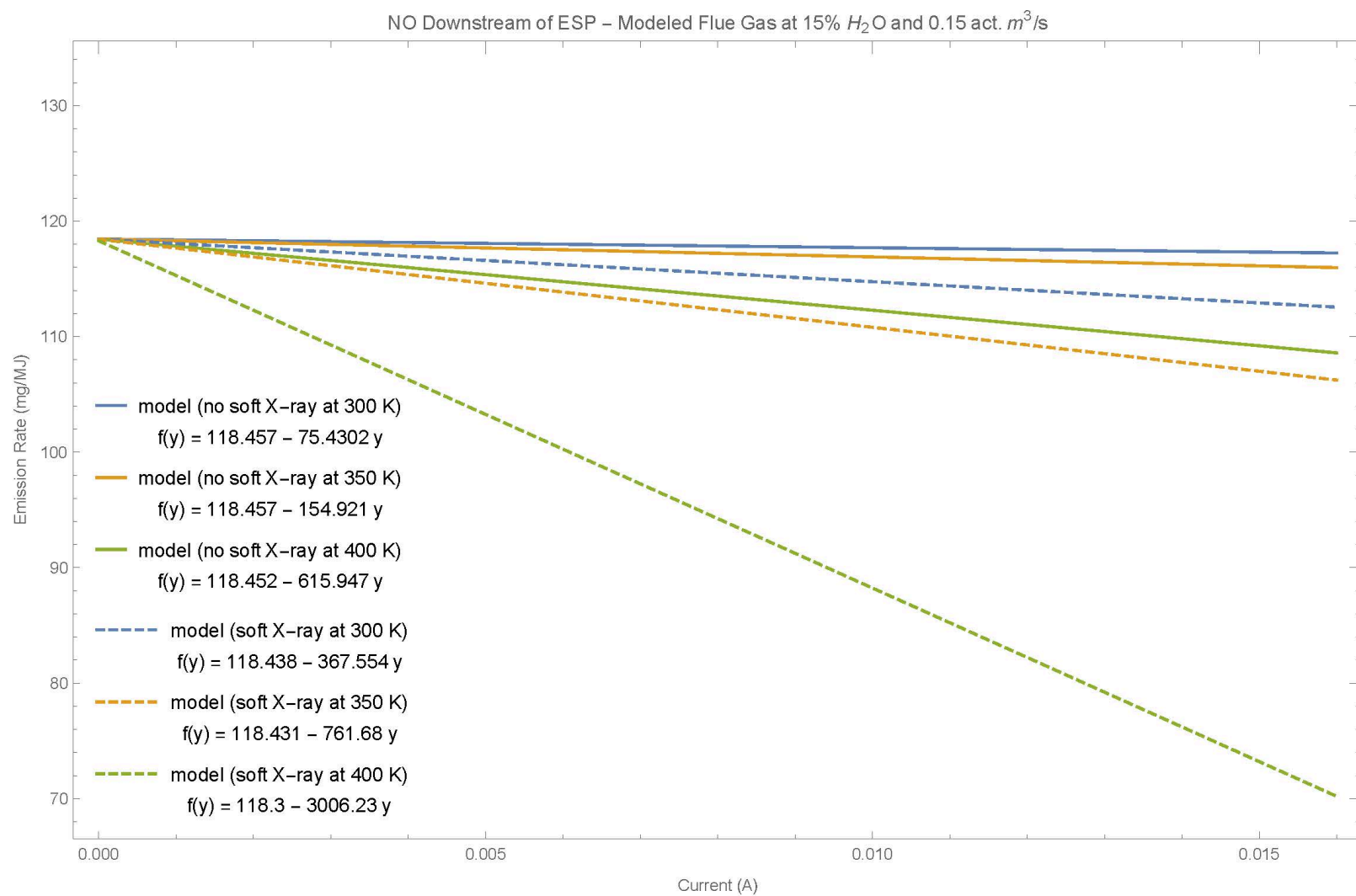


Figure 4.19. Plot showing the modeled emission rates of NO. The emission rate has been calculated with and without the application of soft X-ray photoionization and temperature was varied from 300 – 400 K.

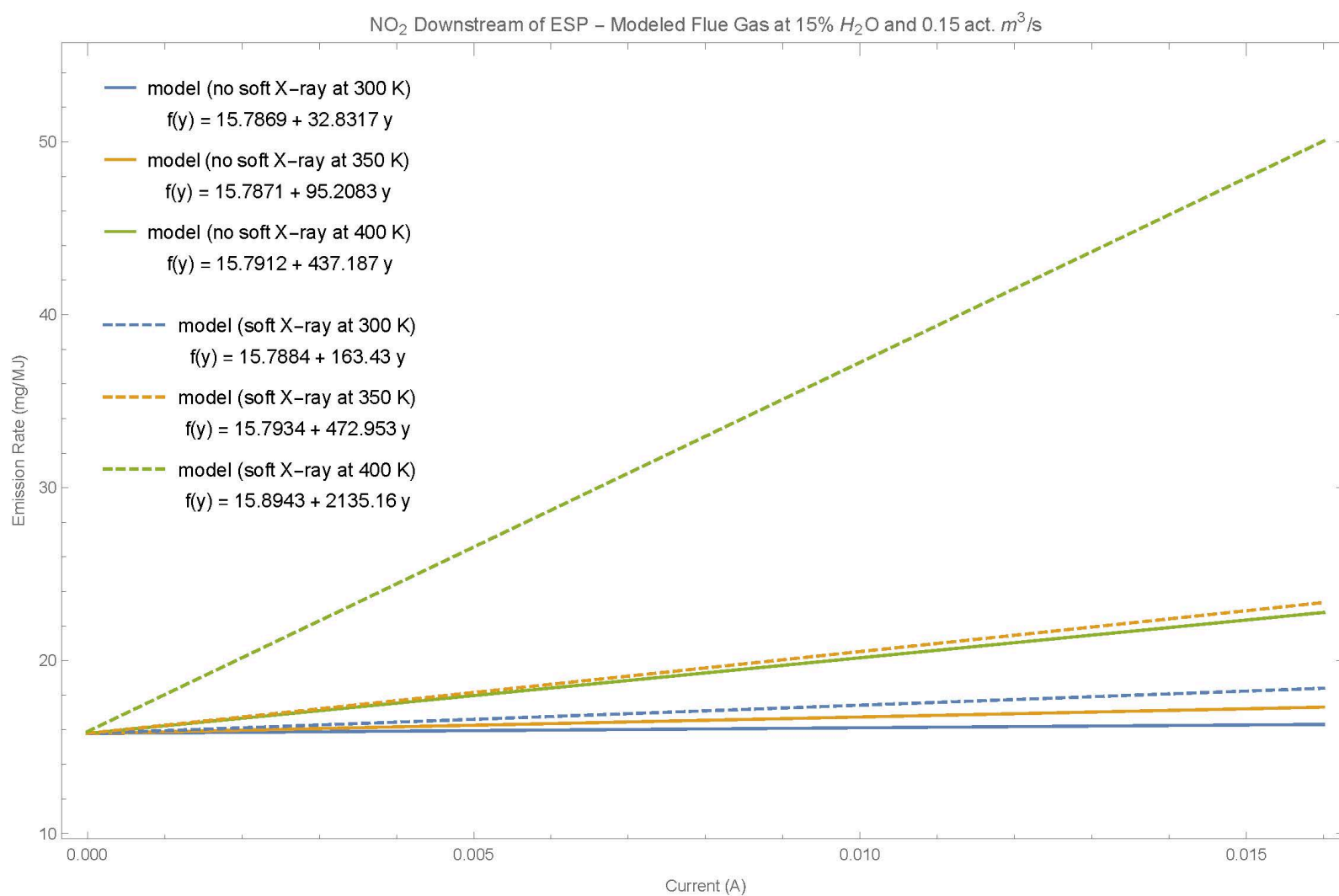


Figure 4.20. Plot showing the modeled emission rates of NO₂. The emission rate has been calculated with and without the application of soft X-ray photoionization and temperature was varied from 300 – 400 K.

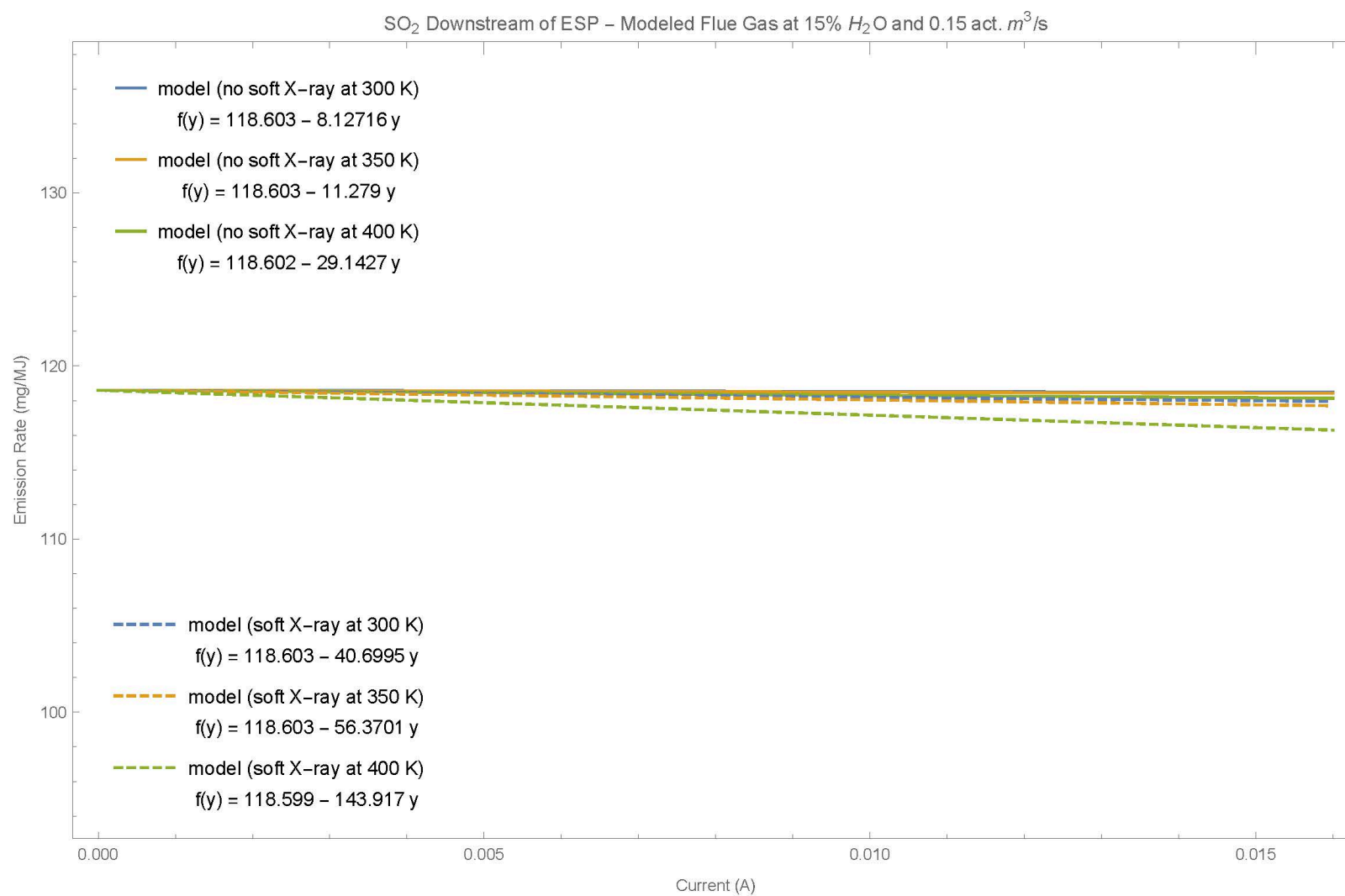


Figure 4.21. Plot showing the modeled emission rates of SO₂. The emission rate has been calculated with and without the application of soft X-ray photoionization and temperature was varied from 300 – 400 K.

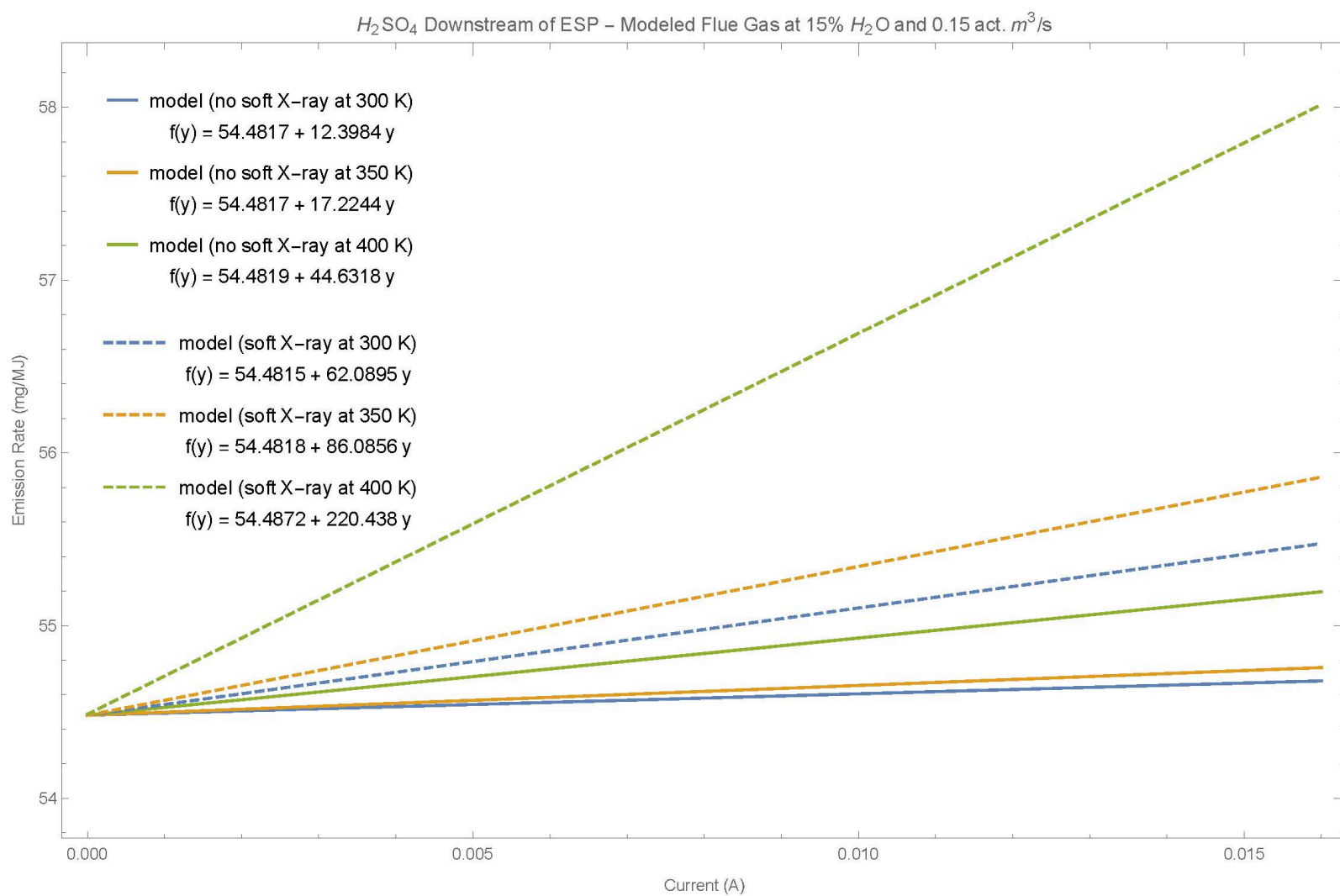


Figure 4.22. Plot showing the modeled emission rates of H_2SO_4 . The emission rate has been calculated with and without the application of soft X-ray photoionization and temperature was varied from 300 – 400 K.

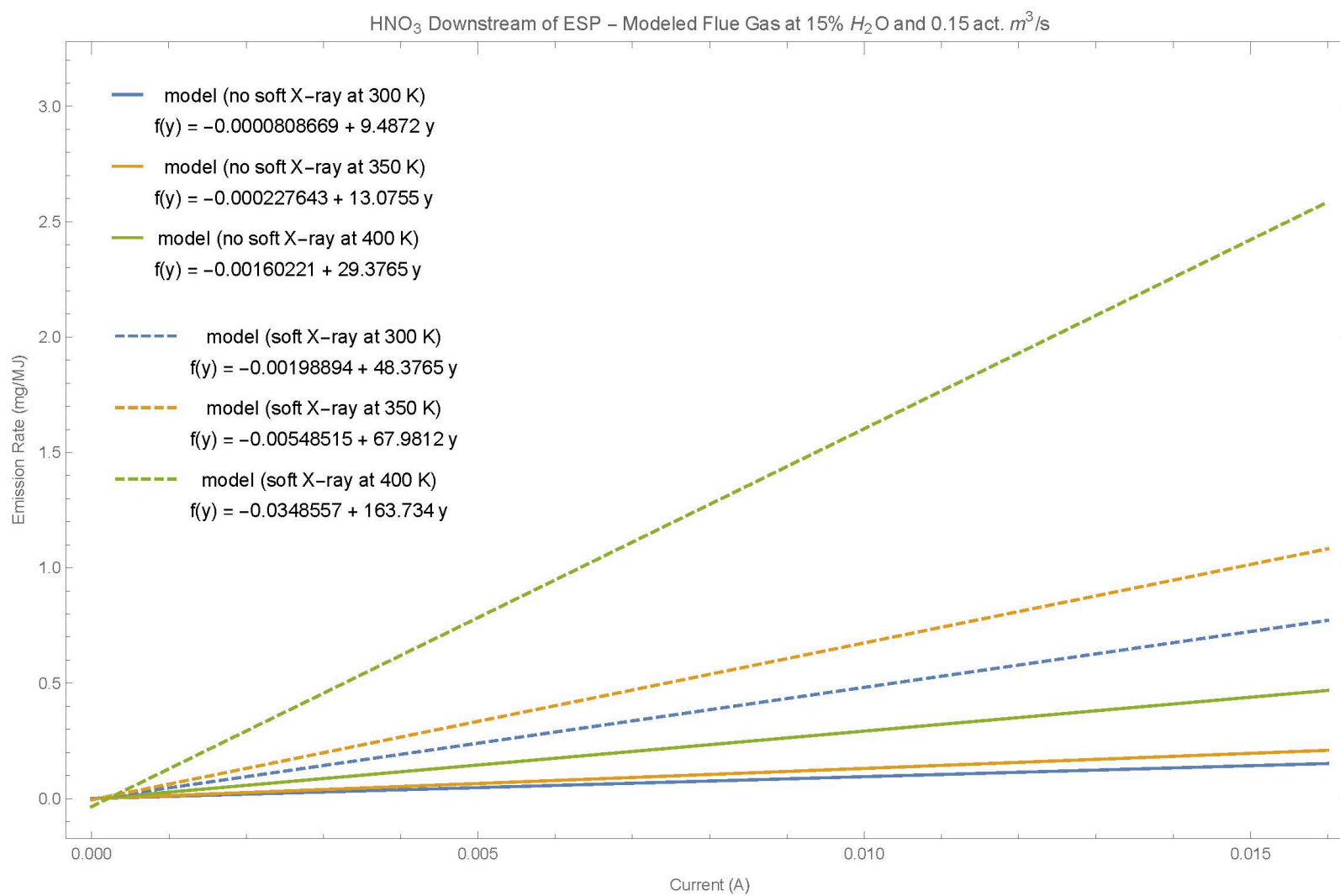


Figure 4.23. Plot showing the modeled emission rates of HNO₃. The emission rate has been calculated with and without the application of soft X-ray photoionization and temperature was varied from 300 – 400 K.

Table 4.10. Change in emission rate in the temperature range of 300 – 400 K¹.

Scenario	Percent change ² (%)				Emission rate ³ (mg/MJ)
	NO	NO ₂	SO ₂	H ₂ SO ₄	HNO ₃
No Soft X-ray, 300 K	-1.0	3.3	-0.1	0.4	0.2
No Soft X-ray, 350 K	-2.1	9.6	-0.2	0.5	0.2
No Soft X-ray, 400 K	-8.3	44.3	-0.4	1.3	0.5
Soft X-ray, 300 K	-5.0	16.6	-0.5	1.8	0.8
Soft X-ray, 350 K	-10.3	47.9	-0.8	2.5	1.1
Soft X-ray, 400 K	-40.7	214.9	-1.9	6.5	2.6

¹ The data presented here are not indicative of how the WASHU-ESP would perform in all test cases. Rather, these results are for a given set of test conditions shown in Table 3.3.

² The modeled percent change of emission rates calculated between 0 and 16 mA.

³ The modeled emission rate at 16 mA.

Table 4.10 shows how much the model predicted a change in emission rate, based off temperature, for gaseous NO, NO₂, SO₂, H₂SO₄ and HNO₃ between 0 and 16 mA with and without soft X-ray photoionization. With all species, an increase in flue gas temperature was shown to increase the change in emission rate. This effect was intensified by soft X-ray photoionization. As shown, NO and NO₂ exhibit the greatest change in emission rate at -40.7 and 214.9 %, respectively at 400 K with soft X-ray photoionization. Without soft X-ray photoionization, the NO and NO₂ change in emission rates fell to -8.3 and 44.3 %, respectively at 400 K. On the other hand, gaseous SO₂, H₂SO₄ and HNO₃ showed a low change in emission rate. The greatest change was observed at 400 K with soft X-ray photoionization. These values were -1.9, 6.5 and 2.6 % for SO₂, H₂SO₄ and HNO₃, respectively. Based on these results, gaseous NO and NO₂ are highly sensitive to temperature.

Table 4.11. Emission rate dependence on flue gas temperature from 300 – 400 K¹.

Scenario	Emission rate normalized to unit temperature ² (mg/MJ-K)	
	NO	NO ₂
No Soft X-ray, 300 – 400 K	0.09	0.06
Soft X-ray, 300 – 400 K	0.42	0.32

¹ The data presented here are not indicative of how the ESP would perform in all test cases. Rather, these results are for a given set of test conditions shown in Table 3.3.

² Emission rate dependence on flue gas temperature calculated at 16 mA.

Table 4.11 shows the dependence of gaseous NO and NO₂ emission rate on temperature from 300 – 400 K with and without soft X-ray photoionization at an ESP current of 16 mA. From these results, it is shown that soft X-ray photoionization has a greater effect in altering the emission rate of gaseous NO and NO₂ compared to no soft X-ray photoionization on a per degree Kelvin change in temperature.

The model results indicated that only gaseous NO and NO₂ were sensitive to flue gas temperature changes from 300 – 400 K. Furthermore, these results showed NO and NO₂ were about 4.7 and 5.3 times more sensitive to flue gas temperature changes when exposed to soft X-ray photoionization, respectively. Under this scenario, the most drastic changes in NO and NO₂ emission rate were observed. In summary, the flue gas temperature inside the WASHU-ESP, ESP current, and the application of soft X-ray photoionization are important factors in determining the change in emission rate for gaseous NO and NO₂.

The effect of temperature on gaseous NO and NO₂ emission rate could be of interest for a CO₂ capture process. As discussed in Chapter 1, particles in the flue gas upstream of a PCC facility can have detrimental effects on the efficiency of a CO₂ capture process. For an amine solvent-based CO₂ capture process, an ESP would be used upstream of a PCC facility to capture particles and reduce solvent loss. However, Dai and Mitch (2014) show that increasing NO and

NO₂ concentrations were linearly correlated to an increase in the accumulation rate of nitramines and nitrosamines in PCC amine-based solvent. The modeling results show that NO₂ emission rate is very sensitive to temperature, and even more so with the application of soft X-ray photoionization.

The temperature of flue gas in an ESP could vary for a number of reasons all stemming from operational characteristics of a power plant. While the WASHU-ESP was tested at similar temperatures (ranging from 383 to 393 K) during the project in 2020, potential temperature variation could be caused by the reheat burner (placement shown in Figure 2.1). The purpose of this analysis was to determine how sensitive emission rates for gaseous NO, NO₂, SO₂, H₂SO₄ and HNO₃ were, given that flue gas temperature can vary.

4.5 Modeled Effect of Flue Gas Flow Rate

The following graphs (Figures 4.23 – 4.28) show how volumetric flow rate through the WASHU-ESP would have affected the emission rate of gaseous NO, NO₂, SO₂, H₂SO₄ and HNO₃ with and without soft X-ray photoionization. Emission rates have been normalized to unit energy consumed during combustion as outlined in Chapter 3.5.2. Graphs are given for the gas composition shown in regime II_{FG} listed in Table 3.3. Temperature and water content were kept constant at 350 K and 15 % by volume, respectively. Flow rate was varied from 0.15 to 0.45 actual m³/s. Table 4.10 provide interpretation of the information shown in Figures 4.19 – 4.23. Furthermore, Table 4.11 shows how much the emission rate for NO and NO₂ vary with respect to degrees K.

The purpose of this analysis is to better understand how an ESP, utilizing soft X-ray photoionization, responds to volumetric flow rate change and the implications for NO, NO₂, SO₂, H₂SO₄ and HNO₃ emission rates. This can be of interest, since Dai and Mitch (2014) state that

NO and NO₂ concentrations were linearly correlated to the accumulation rate of nitramines and nitrosamines in PCC amine-based solvent.

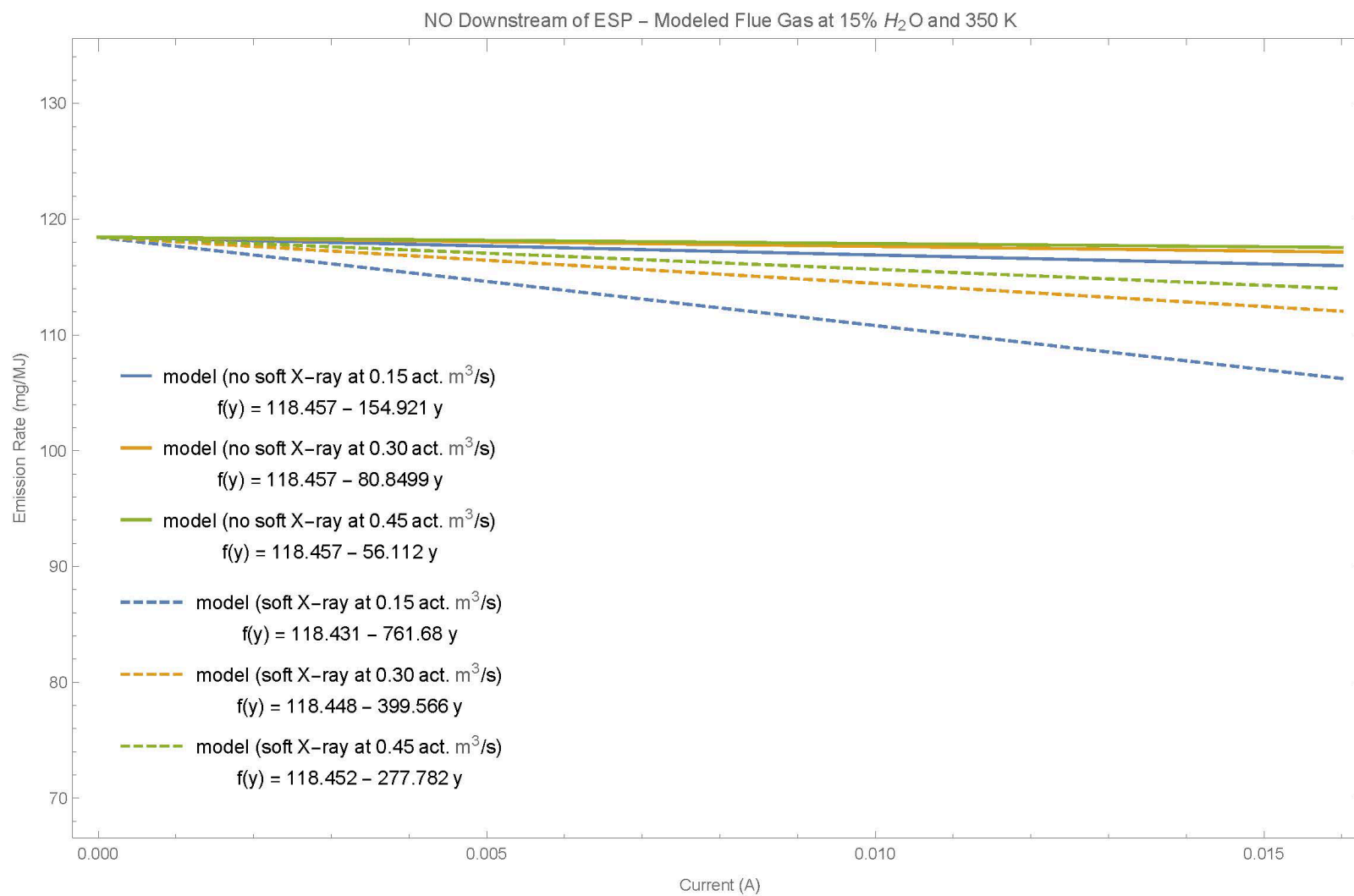


Figure 4.24. Plot showing the modeled emission rate of NO. The emission rate has been calculated with and without the application of soft X-ray photoionization and flow rate was varied from 0.15 – 0.45 act. m^3/s .

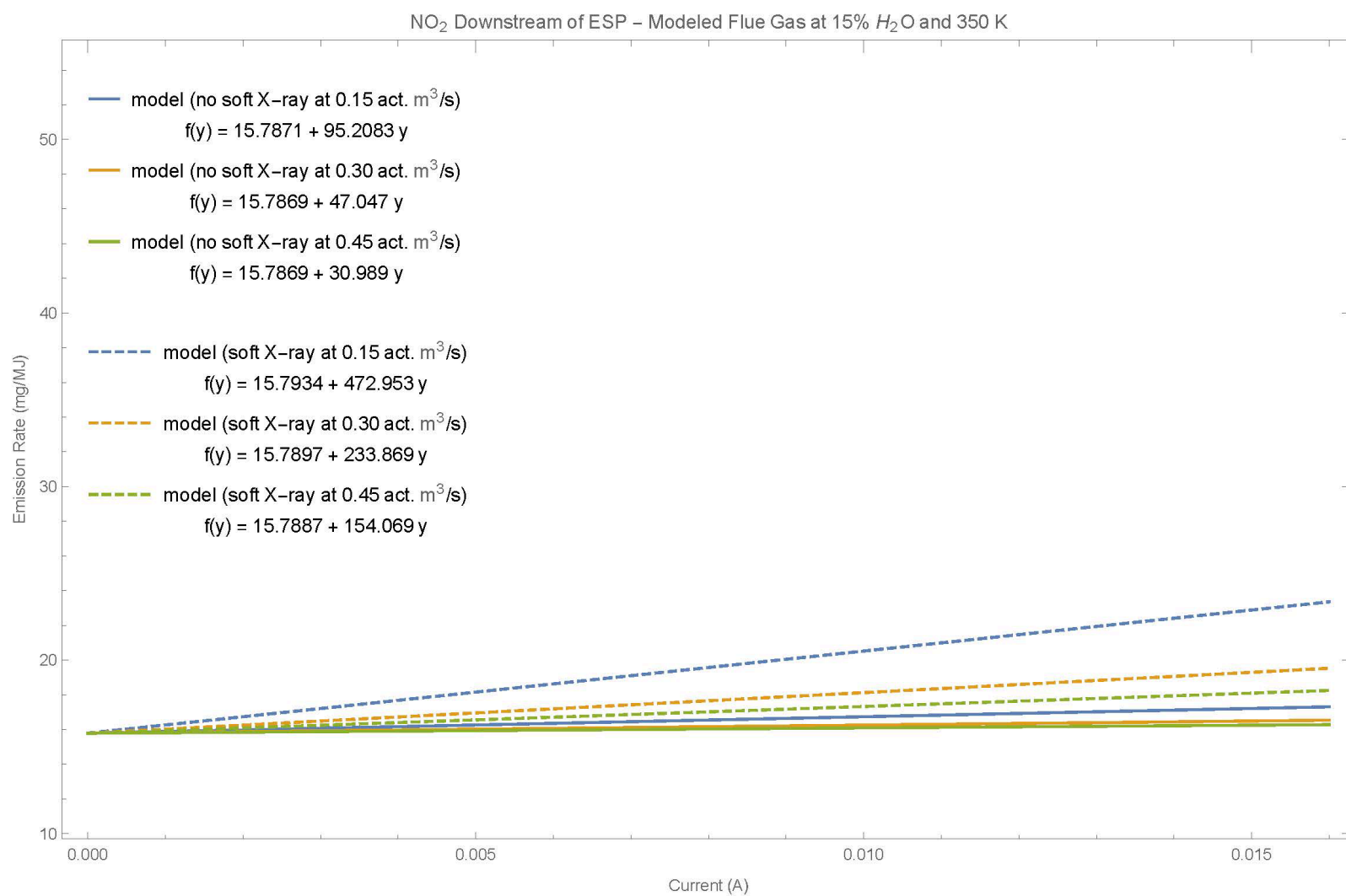


Figure 4.25. Plot showing the modeled emission rate of NO₂. The emission rate has been calculated with and without the application of soft X-ray photoionization and flow rate was varied from 0.15 – 0.45 act. m³/s.

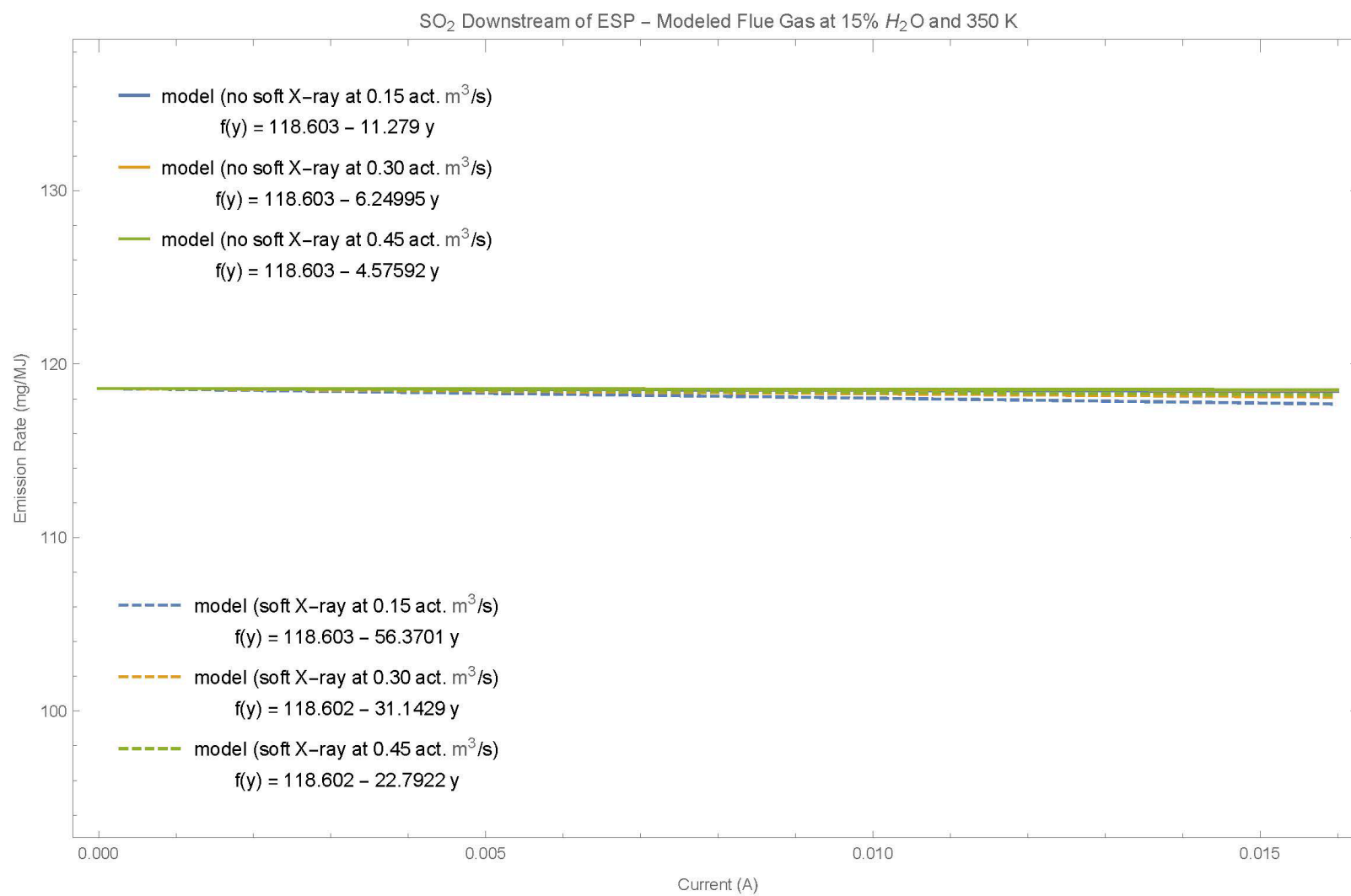


Figure 4.26. Plot showing the modeled emission rate of SO₂. The emission rate has been calculated with and without the application of soft X-ray photoionization and flow rate was varied from 0.15 – 0.45 act. m³/s.

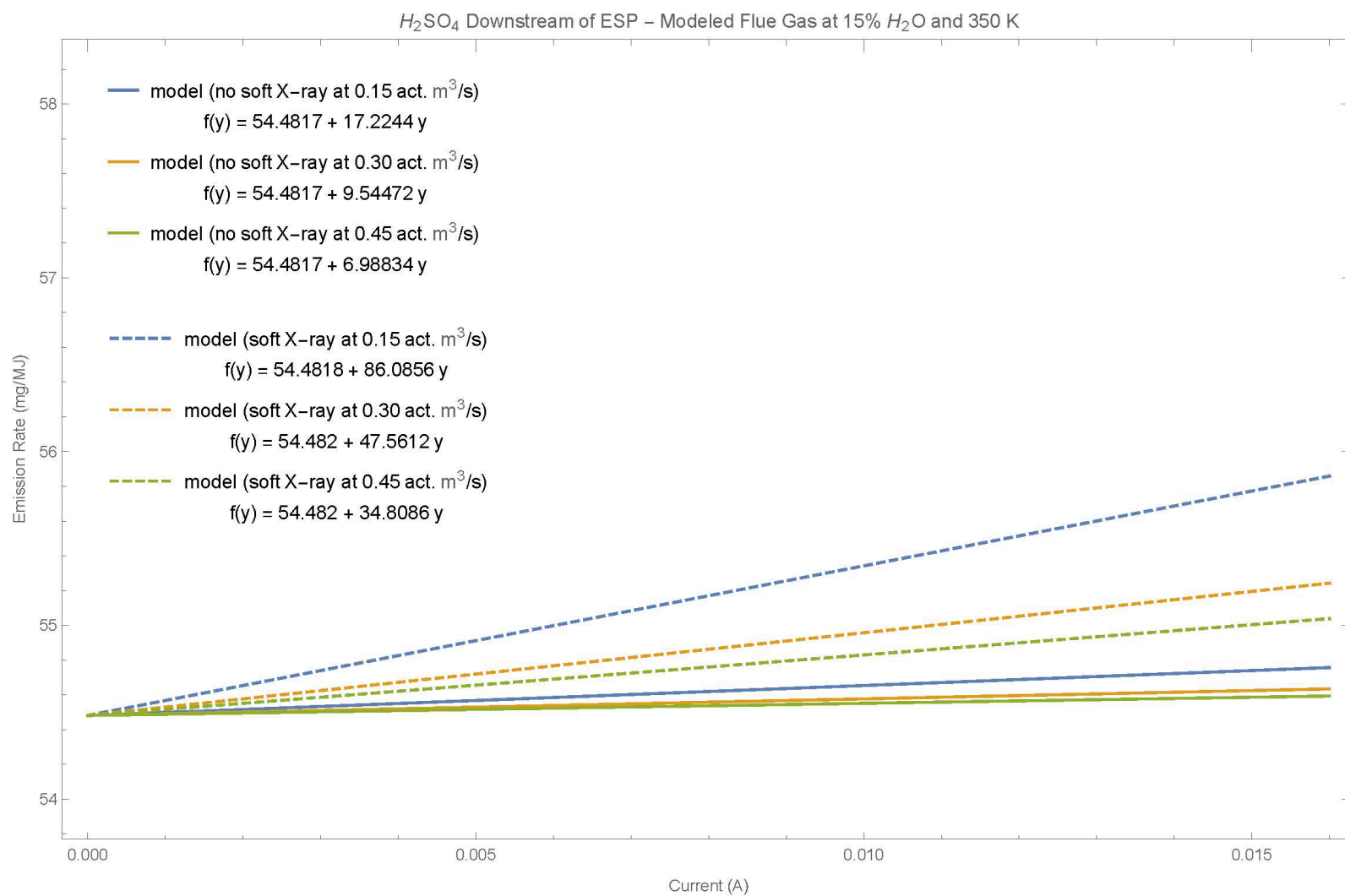


Figure 4.27. Plot showing the modeled emission rate of H_2SO_4 . The emission rate has been calculated with and without the application of soft X-ray photoionization and flow rate was varied from 0.15 – 0.45 act. m^3/s .

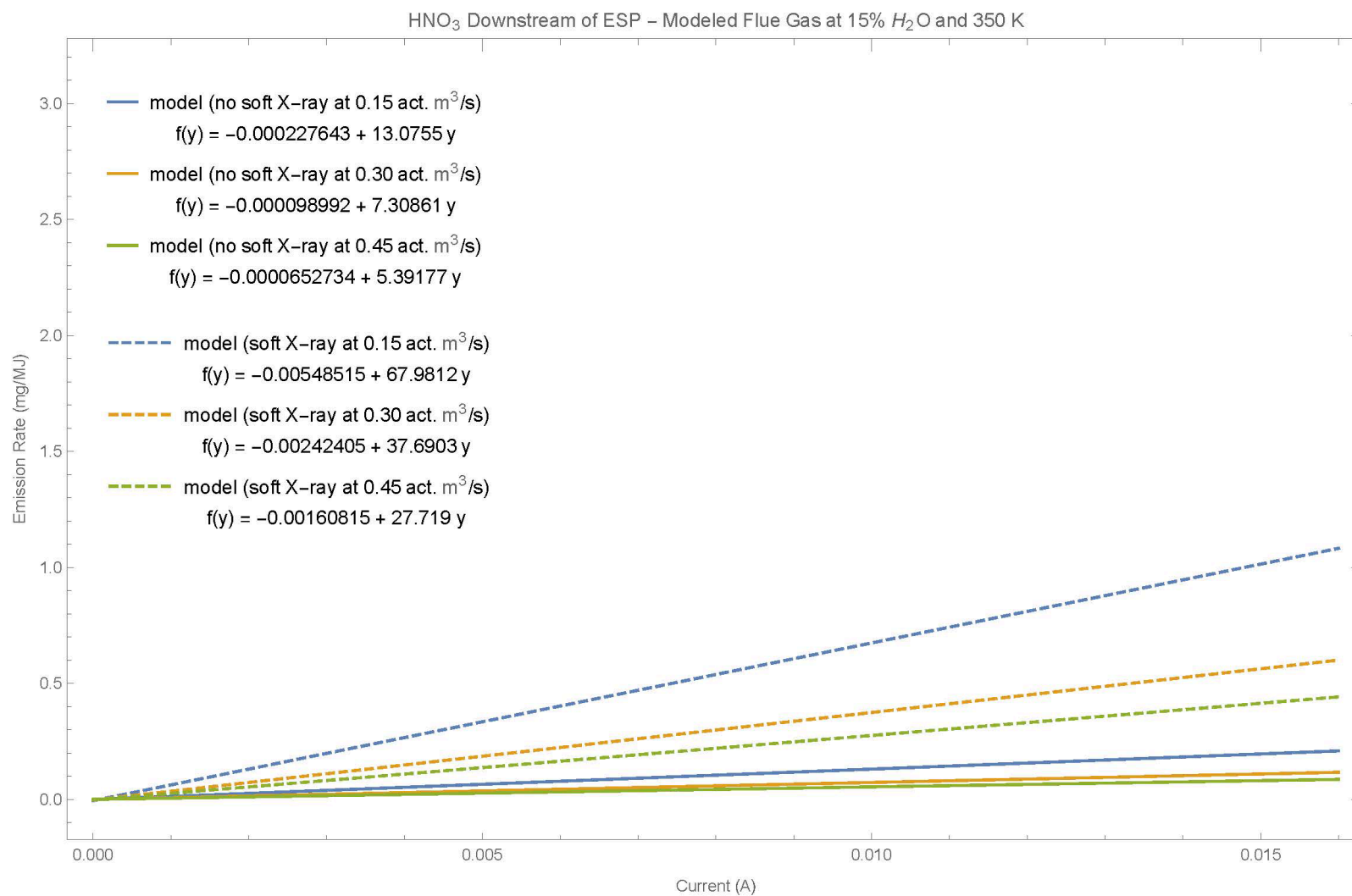


Figure 4.28. Plot showing the modeled emission rate of HNO₃. The emission rate has been calculated with and without the application of soft X-ray photoionization and flow rate was varied from 0.15 – 0.45 act. m³/s.

Table 4.12. Change in emission rate from 0.15 – 0.45 act. m³/s at 350 K and 15 % H₂O¹.

Scenario	Percent change ² (%)				Emission rate ³ (mg/MJ)
	NO	NO ₂	SO ₂	H ₂ SO ₄	HNO ₃
No Soft X-ray, 0.15 act. m ³ /s	-2.1	9.6	-0.2	0.5	0.2
No Soft X-ray, 0.30 act. m ³ /s	-1.1	4.8	-0.1	0.3	0.1
No Soft X-ray, 0.45 act. m ³ /s	-0.8	3.1	-0.1	0.2	0.1
Soft X-ray, 0.15 act. m ³ /s	-10.3	47.9	-0.8	2.5	1.1
Soft X-ray, 0.30 act. m ³ /s	-5.4	23.7	-0.4	1.4	0.6
Soft X-ray, 0.45 act. m ³ /s	-3.8	15.6	-0.3	1.0	0.4

¹ The data presented here are not indicative of how the WASHU-ESP would perform in all test cases. Rather, these results are for a given set of test conditions shown in Table 3.3.

² The modeled percent change of emission rates calculated between 0 and 16 mA.

³ The modeled emission rate at 16 mA.

Table 4.12 shows how much the model predicted a change in emission rate, based off WASHU-ESP flue gas flow rate, for gaseous NO, NO₂, SO₂, H₂SO₄ and HNO₃ between 0 and 16 mA with and without soft X-ray photoionization. With all species, an inversely proportional relationship between volumetric flow rate and change in emission rate was observed. This effect was intensified by soft X-ray photoionization. As shown, NO and NO₂ exhibited the greatest change in emission rate at -10.3 and 47.9 %, respectively at 0.15 act. m³/s with soft X-ray photoionization. Without soft X-ray photoionization, the NO and NO₂ change in emission rates fell to -2.1 and 9.6 %, respectively at 0.15 act. m³/s. On the other hand, gaseous SO₂, H₂SO₄ and HNO₃ showed a low change in emission rate. The greatest change was observed at 0.15 act. m³/s with soft X-ray photoionization. These values were -0.8, 2.5 and 1.1 % for SO₂, H₂SO₄ and HNO₃, respectively. Based on these results, gaseous NO and NO₂ are more sensitive to residence time in the WASHU-ESP.

Table 4.13. Emission rate dependence on flue gas flow rates from 0.15 – 0.45 act. m³/s¹.

Scenario	Emission rate normalized to unit velocity ² (mg-s/MJ-m)	
	NO	NO ₂
No Soft X-ray, 0.15 – 0.45 act. m ³ /s	1.8	1.2
Soft X-ray, 0.15 – 0.45 act. m ³ /s	8.8	5.8

¹ The data presented here are not indicative of how the WASHU-ESP would perform in all test cases. Rather, these results are for a given set of test conditions shown in Table 3.3.

² Emission rate dependence on flue gas temperature calculated at 16 mA. Rate has been normalized to unit velocity.

Table 4.13 shows the dependence of gaseous NO and NO₂ emission rate on volumetric flow rates from 0.15 – 0.45 act. m³/s with and without soft X-ray photoionization at 16 mA. From these results, it is shown that soft X-ray photoionization has a greater effect in altering the emission rate of gaseous NO and NO₂ compared to no soft X-ray photoionization when normalized to unit velocity. Emission rate was normalized to unit velocity because volumetric flow rate does not provide information about residence time i.e., volumetric flow rate is both dependent on velocity and cross-sectional area. Furthermore, velocity is a much easier to measure than residence time. For these reasons, emission rate was normalized to unit velocity and not volumetric flow rate nor residence time. Like Table 4.11, soft X-ray photoionization was shown to enhance the change in emission rate. This effect is about 4.9 and 4.8 times greater for NO and NO₂, respectively.

The model results indicated that only gaseous NO and NO₂ were the most sensitive to change in volumetric flow rate from 0.15 – 0.45 act. m³/s. Furthermore, model results showed NO and NO₂ were about 4.9 and 4.8 times more sensitive when exposed to soft X-ray photoionization, respectively. Modeling under this scenario produced the most drastic changes in NO and NO₂ emission rate. In summary, the volumetric flow rate through the ESP, ESP

current, and the application of soft X-ray photoionization are important factors in determining the change in emission rate for gaseous NO and NO₂.

The effect of volumetric flow rate on gaseous NO and NO₂ emission rate could be of interest for a CO₂ capture process. As discussed in Chapter 1, particles in the flue gas upstream of a PCC facility can have detrimental effects on the efficiency of a CO₂ capture process. For an amine solvent-based CO₂ capture process, an ESP would be used upstream of a PCC facility to capture particles and thereby reduce solvent loss. However, Dai and Mitch (2014) show that increasing NO and NO₂ concentrations were linearly correlated to an increase in the accumulation rate of nitramines and nitrosamines in PCC amine-based solvent. The modeling results show that NO₂ emission rate is sensitive to volumetric flow rate i.e., residence time, and even more so with the application of soft X-ray photoionization.

Volumetric flow rate in an ESP could vary for several reasons all stemming from operational characteristics of a power plant. Also, a CO₂ capture process could require a particular flue gas flow rate. The WASHU-ESP was tested at volumetric flow rates ranging from 0.178 – 0.291 act. m³/s during the project. The purpose of this analysis was to determine how sensitive emission rates for gaseous NO, NO₂, SO₂, H₂SO₄ and HNO₃ were with respect to a given flue gas volumetric flow rate.

Chapter 5: Conclusion

The measurement and modeling results given in the preceding sections show how the WASHU-ESP altered the emission rate of gaseous NO, NO₂, SO₂, H₂SO₄ and HNO₃. The following sections summarize the findings from Chapter 4 and ends with final thoughts and future studies.

5.1 Experimental Results Summary

Chapter 3 showed how the chemical change of gas-phase pollutants can be initiated by the number concentration of electrons in the WASHU-ESP. This is further dependent on the electrical current and whether soft X-ray photoionization is used in the ESP. However, measurements obtained during March 2020 indicated that current was not the only factor affecting emission rate for NO, NO₂ and SO₂. Nevertheless, NO₂ had the highest R² values and most consistent percent change in emission rates over the course of the project (Tables 4.4 and 4.5). Overall low R² values for NO, NO₂ and SO₂, could be caused by a couple of reasons. The first being that; changes in the supply emission rate upstream of the WASHU-ESP were not necessarily accounted for. Since upstream and downstream measurements of emission rate were not done concurrently, changes in upstream emission rate were not necessarily accounted for in the downstream measurements. Furthermore, since emission rate measurements were not made concurrently, any change in the boiler, flue gas desulfurization unit and reheat burner operation may not have been accounted for when taking emission rate measurements during the project. The second reason is that this analysis does not take into account gas-to-particle conversion or vice-versa. Additionally, flue gas moisture content was not controlled. However, during the operation of the WASHU-ESP, moisture only varied between 13.2 and 14.6 %.

In general, the emission rate of gaseous NO, NO₂ and SO₂ did change between upstream and downstream measurements of emission rate. It is not clear though, if these changes were due to the WASHU-ESP or variation in upstream gas composition.

5.2 Modeled Results Summary

The modeling method presented in Chapter 3 was used to calculate the emission rate of gaseous NO, NO₂, SO₂, H₂SO₄ and HNO₃ downstream of the WASHU-ESP. This method was utilized for two reasons 1) to compare against measured data obtained during the project (Sections 4.1 – 4.3) and 2) determine how temperature and volumetric flow rate affect emission rate (Sections 4.4 and 4.5).

In Sections 4.1 – 4.3, the model was used to predict downstream emission rates of gaseous NO, NO₂ and SO₂. Among these predictions, modeled NO₂ emission rate was shown to agree the best with its corresponding measurement. Table 4.4 gives the average percent difference between the modeled and measured emission rate of NO₂. The best agreement was observed in the March 13th – Run No. 2 trial with the average difference between the measured and modeled data at 2.5 %.

In Sections 4.4 and 4.5, temperature and volumetric flow rate were altered independently to determine how each variable affects the emission rates of gaseous NO, NO₂, SO₂, H₂SO₄ and HNO₃ downstream of the WASHU-ESP. Table 4.10 shows that NO and NO₂ were most affected by temperature with NO decreasing by 41 % and NO₂ increasing by 215 % over 0 – 16 mA at 400 K with soft X-ray photoionization. Likewise, Table 4.12 showed that NO and NO₂ were the most affected by volumetric flow rate with NO decreasing by 11 % and NO₂ increasing by 48 % over 0 – 16 mA at 0.15 act. m³/s with soft X-ray photoionization.

The emission rates of gaseous NO and NO₂ were affected the most by temperature, volumetric flow rate and X-ray photoionization. The SO₂, HNO₃ and H₂SO₄ emission rates were not as affected.

5.3 Future Studies and Final Thoughts

In this thesis, research was conducted to determine the effect the WASHU-ESP had on the emission rates of gaseous NO, NO₂, SO₂, H₂SO₄ and HNO₃ in the flue gas from APP. On-site gas composition measurements were performed on the pilot-scale ESP and a model was developed to analyze the effect of the ESP on altering emission rates based on the methods outlined by (Chen and Davidson 2002) and (Mikoviny et al. 2004). Measurements and modeling indicate that NO and NO₂ were the most affected by the corona discharge in the ESP. This may be of concern since NO₂, in particular, can be detrimental to an amine-based post-combustion CO₂ capture process by causing degradation of amine solvent and creating health concerns due to the formation of nitramines and nitrosamines (Dai and Mitch 2014). The modeled results showed that the most notable changes were with NO and NO₂ emission rates at the conditions of 400 K and 0.15 actual m³/s under the presence of soft X-ray photoionization.

Future studies could include the analysis of secondary particle formation downstream of the WASHU-ESP used at APP. Bostick (2017) discussed that H₂SO₄-H₂O aerosol nucleation can occur downstream of the ESP however it would be interesting to investigate if HNO₃ observes the same trend, given that gaseous HNO₃ was shown to generate in the model. Furthermore, a model was developed by the Aerosol and Air Quality Research Laboratory (AAQRL) at Washington University in St. Louis to better understand the effects of a particle size distribution on the emission of solvent from a PCC process (Dhanraj and Biswas 2018). The model, simulated in Aspen Plus, showed that condensation and coagulation, to a lesser extent, are the main sources of solvent loss (Dhanraj and Biswas 2018). While the model shown in this

research only predicts the emission rate of flue gas pollutants formed in an ESP, this could form the basis, with the AAQRL model, of a more comprehensive analysis for determining solvent loss. Finally, additional studies could also include a parametric analysis of the ESP at a range of gas temperatures, flow rates and flue gas water contents to determine the optimal operating conditions for it in a PCC plant setup.

In conclusion, it was shown that the WASHU-ESP can alter the emission rates of NO and NO₂ through a corona discharge especially with the application of soft X-ray photoionization. In this research, the concentration of gaseous pollutants NO, NO₂, SO₂, HNO₃, and H₂SO₄ were measured both upstream and downstream of the WASHU-ESP. The measurements, while useful, were not as consistent and conclusive as the results obtained through the model for a number of reasons. The model was used to determine the effect of the WASHU-ESP on downstream emission rates based on upstream gas composition, gas temperature and volumetric flow rate. It was shown through modeling, that NO and NO₂ can change the most between upstream and downstream of the WASHU-ESP. Furthermore, it was shown that the greatest change occurred at 0.15 act. m³/s, 400 K and in the presence of soft X-ray photoionization. More specifically, it was shown the emission rate of NO decreased and NO₂ increased substantially. The analysis presented in this thesis can help to better understand and optimize the conditions (temperature and volumetric flow rate) to ensure that NO₂ formation is minimized given its potential to degraded the amine-based solvent used in a post-combustion CO₂ capture process.

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Appendix A: Supplementary Material for Chapter 2

The purpose of this appendix is to provide supplementary information for Chapter 2.

This includes additional drawings of the apparatus set-up used at APP.

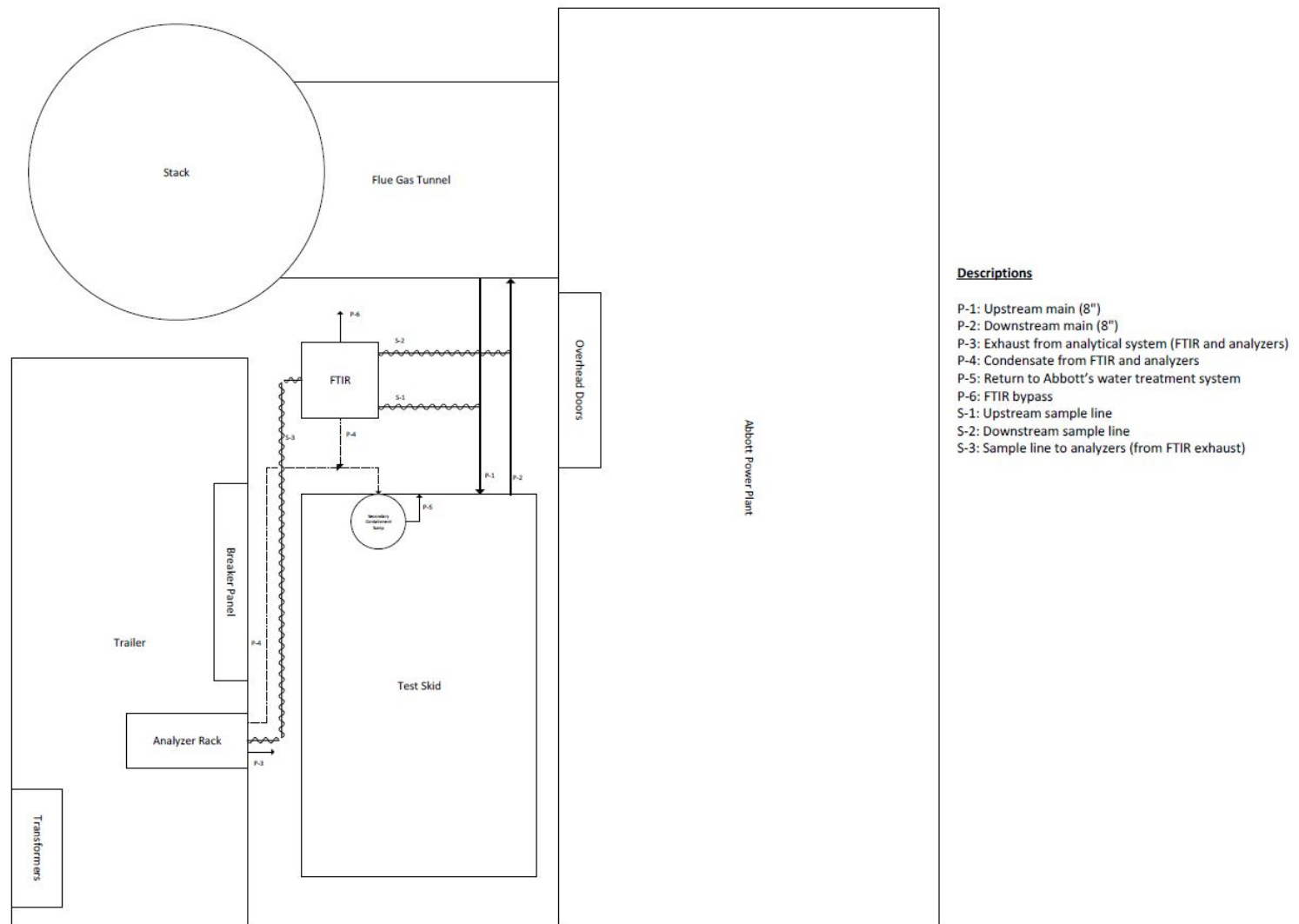


Figure A.1. Overhead view of the equipment (pilot skid, FTIR system and analytical container (trailer)) layout in relation to Abbott Power Plant. This figure was produced by myself (Wyatt Sherlock).

Appendix B: Supplementary Material for Chapter 3

The purpose of this appendix is to provide supplementary information for Chapter 3.

This includes a description of the parameters used throughout the chapter along with the equations and constants used in the model.

B.1 Description of Parameters

In this section, a list of the main parameters used in Chapter 3 are provided along with a description of each one.

Table B.1. A list of the main parameters used in Chapter 3. A corresponding description is given for each one.

Parameter	Description	Units
$\left(\frac{E}{N}\right)(r)$	reduced electric field as a function of radial distance	Vm ²
$\left(\frac{E}{N}\right)_{avg}$	average reduced electric field	Vm ²
$E(r)$	electric field as a function of radial distance	V/m
$N_e(r)$	electron number concentration as a function of radial distance	#/cm ³
$N_{e avg}$	average electron number concentration	#/cm ³
$\bar{\epsilon}(r)$	mean electron energy as a function of radial distance	electronvolt (eV)
$\bar{\epsilon}_{avg}$	mean electron energy throughout corona region	electronvolt (eV)
$t(r)$	corona residence time as a function of radial distance	s
t_{avg}	average corona residence time	s
$\alpha(r)$	Townsend's Ionization Coefficient as a function of radial distance	1/m
$\beta(r)$	Townsend's Attachment Coefficient as a function of radial distance	1/m
$D_e(r)$	electron diffusion coefficient as a function of radial distance	m ² /s
$\mu_e(r)$	electron mobility as a function of radial distance	m ² /(V·s)
T	gas temperature	K

B.2 Chemical Species

In this section, a list of the chemical species used in the model is provided. All of the molecules, ions and radicals listed here are in the gas phase.

Table B.2. A list of the 35 gaseous chemical species used in the model.

No.	Chemical Name	Chemical Formula	Classification
1	Atomic oxygen anion	$\cdot\text{O}^-$	Anion Radical
2	Molecular oxygen anion	$\cdot\text{O}_2^-$	Anion Radical
3	Ozone anion	$\cdot\text{O}_3^-$	Anion Radical
4	Carbon trioxide anion	$\cdot\text{CO}_3^-$	Anion Radical
5	Carbon tetroxide anion	$\cdot\text{CO}_4^-$	Anion Radical
6	Molecular oxygen cation	$\cdot\text{O}_2^+$	Cation Radical
7	Carbon dioxide cation	$\cdot\text{CO}_2^+$	Cation Radical
8	Carbon monoxide cation	$\cdot\text{CO}^+$	Cation Radical
9	Hydrogen cation	H^+	Cation
10	Nitrogen dioxide	$\cdot\text{NO}_2$	Neutral Radical
11	Nitric oxide	$\cdot\text{NO}$	Neutral Radical
12	Ozone	O_3	Molecule
13	Sulfur Monoxide	SO	Molecule
14	Sulfur dioxide	SO_2	Molecule
15	Sulfur trioxide	SO_3	Molecule
16	Sulfuric acid	H_2SO_4	Molecule
17	-- ¹	$\cdot\text{HSO}_3$	Neutral Radical
18	Atomic hydrogen	$\cdot\text{H}$	Neutral Radical
19	Hydroxyl	$\cdot\text{OH}$	Neutral Radical
20	Hydroperoxyl	$\cdot\text{HO}_2$	Neutral Radical
21	Carbon monoxide	CO	Molecule
22	Carbon dioxide	CO_2	Molecule
23	Nitrosyl hydride	HNO	Molecule
24	Nitrous acid	HONO	Molecule
25	Nitric acid	HNO_3	Molecule

Table B.2 Continued

26	Triplet state atomic oxygen	$\cdot\text{O}(^3\text{P})$	Neutral Radical
27	Water	H_2O	Molecule
28	Atomic carbon	C	Atom
29	Dicarbon monoxide	C_2O	Molecule
30	Molecular oxygen	O_2	Molecule
31	Molecular hydrogen	H_2	Molecule
32	Molecular nitrogen	N_2	Molecule
33	Atomic nitrogen	$\cdot\text{N}$	Neutral Radical
34	Singlet state atomic oxygen	$\cdot\text{O}(^1\text{D})$	Neutral Radical
35	Nitrous oxide	N_2O	Molecule

¹ No common name is given for this radical according to the NIST Chemistry WebBook

<https://webbook.nist.gov/chemistry/>

B.3 Chemical Equations and Reaction Rate Constants

In this section, a list of the chemical equations and their corresponding reaction rate constants are provided. The chemical equations are grouped by their classification. These include ionization, dissociative ionization, neutral dissociation by electron impact, dissociative attachment, three-body attachment, associative detachment, ion-molecular, ion-ion recombination, ion-electron recombination, and neutral component reactions. Overall, 121 chemical equations were used in this thesis. These are all gas-phase reactions.

B.3.1 Ionization

Table B.3. A list of the ionizing chemical equations used in this analysis.

No.	Chemical Equation	Reaction Rate Constant	Units	Source
1 ¹	$\text{O}_2 + \text{e} \rightarrow \cdot\text{O}_2^+ + \text{e} + \text{e}$	$f\left(\left(\frac{E}{N}\right)_{avg}, [\text{CO}](t), [\text{CO}_2](t)\right)$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)

Table B.3 Continued

2 ¹	$\text{CO}_2 + \text{e} \rightarrow \cdot\text{CO}_2^+ + \text{e} + \text{e}$	$f\left(\left(\frac{E}{N}\right)_{avg}, [\text{CO}](t), [\text{CO}_2](t)\right)$	cm ³ /molecule-s	(Cenian et al. 1994)
3 ¹	$\text{CO} + \text{e} \rightarrow \cdot\text{CO}^+ + \text{e} + \text{e}$	$f\left(\left(\frac{E}{N}\right)_{avg}, [\text{CO}](t), [\text{CO}_2](t)\right)$	cm ³ /molecule-s	(Cenian et al. 1994)
4 ^{1,2}	$\text{H}_2\text{O} + \text{e} \rightarrow \cdot\text{H}_2\text{O}^+ + \text{e} + \text{e}$	$f(\bar{\epsilon}_{avg})$	cm ³ /molecule-s	(Dolan 1993)

¹ Reaction rate constant included in source code.

² The cation radical $\cdot\text{H}_2\text{O}^+$ does not appear in Section B.2 since it was not a target species of interest nor was needed to derive any rate equations in the source code.

B.3.2 Dissociative Ionization

Table B.4. A list of the dissociative ionization chemical equations used in this analysis.

No.	Chemical Equation	Reaction Rate Constant	Units	Source
5 ^{1,2}	$\text{H}_2\text{O} + \text{e} \rightarrow \text{OH}^+ + \cdot\text{H} + \text{e} + \text{e}$	$f(\bar{\epsilon}_{avg})$	cm ³ /molecule-s	(Dolan 1993)
6 ^{1,3}	$\text{H}_2\text{O} + \text{e} \rightarrow \cdot\text{O}^+ + \text{H}_2 + \text{e} + \text{e}$	$f(\bar{\epsilon}_{avg})$	cm ³ /molecule-s	(Dolan 1993)
7	$\text{H}_2\text{O} + \text{e} \rightarrow \text{H}^+ + \cdot\text{OH} + \text{e} + \text{e}$	$f(\bar{\epsilon}_{avg})$	cm ³ /molecule-s	(Dolan 1993)
8 ^{1,4}	$\text{H}_2\text{O} + \text{e} \rightarrow \cdot\text{H}_2^+ + \cdot\text{O} + \text{e} + \text{e}$	$f(\bar{\epsilon}_{avg})$	cm ³ /molecule-s	(Dolan 1993)

¹ Reaction rate constant included in source code.

² The cation OH^+ does not appear in Section B.2 since it was not a target species of interest nor was needed to derive any rate equations in the source code.

³ The cation radical $\cdot\text{O}^+$ does not appear in Section B.2 since it was not a target species of interest nor was needed to derive any rate equations in the source code.

⁴ The cation radical $\cdot\text{H}_2^+$ does not appear in Section B.2 since it was not a target species of interest nor was needed to derive any rate equations in the source code. The radical $\cdot\text{O}$ is used in the source code as (and assumed to be) $\cdot\text{O}(^3\text{P})$.

B.3.3 Neutral Dissociation by Electron Impact

Table B.5. A list of the neutral dissociation by electron impact chemical equations used in this analysis.

No.	Chemical Equation	Reaction Rate Constant	Units	Sources
9 ^{1,2}	$\text{O}_2 + \text{e} \rightarrow \cdot\text{O} + \cdot\text{O} + \text{e}$	$f\left(\left(\frac{E}{N}\right)_{avg}, [\text{CO}](t), [\text{CO}_2](t)\right)$	cm ³ /molecule-s	(Cenian et al. 1994)

Table B.5 Continued

10 ^{1,2}	$\text{CO}_2 + e \rightarrow \text{CO} + \cdot\text{O} + e$	$f\left(\left(\frac{E}{N}\right)_{avg}, [\text{CO}](t), [\text{CO}_2](t)\right)$	cm ³ /molecule-s	(Cenian et al. 1994)
11 ^{1,2}	$\text{CO} + e \rightarrow \text{C} + \cdot\text{O} + e$	$f\left(\left(\frac{E}{N}\right)_{avg}, [\text{CO}](t), [\text{CO}_2](t)\right)$	cm ³ /molecule-s	(Cenian et al. 1994)
12	$\text{N}_2 + e \rightarrow \cdot\text{N} + \cdot\text{N} + e$	$f\left(\left(\frac{E}{N}\right)_{avg}\right)$	cm ³ /molecule-s	(Lowke and Morrow 1995)
13 ²	$\text{O}_2 + e \rightarrow \cdot\text{O} + \cdot\text{O}(\text{}^1\text{D}) + e$	$f\left(\left(\frac{E}{N}\right)_{avg}\right)$	cm ³ /molecule-s	(Lowke and Morrow 1995)
14 ²	$\text{O}_3 + e \rightarrow \cdot\text{O} + \text{O}_2 + e$	$5*10^{-9}$	cm ³ /molecule-s	(Mikoviny et al. 2004)
15	$\text{H}_2\text{O} + e \rightarrow \cdot\text{OH} + \cdot\text{H} + e$	$6.8*10^{-12}$	cm ³ /molecule-s	(Eichwald et al. 1997)

¹ Reaction rate constant included in source code.

² The radical $\cdot\text{O}$ is used in the source code as (and assumed to be) $\cdot\text{O}(\text{}^3\text{P})$.

³ Reaction rate constant fit to data provided by Lowke and Morrow (1995).

B.3.4 Dissociative Attachment

Table B.6. A list of the dissociative attachment chemical equations used in this analysis.

No.	Chemical Equation	Reaction Rate Constant	Units	Source
16 ^{1,2}	$\text{O}_2 + e \rightarrow \cdot\text{O}^- + \cdot\text{O}$	$f\left(\left(\frac{E}{N}\right)_{avg}, [\text{CO}](t), [\text{CO}_2](t)\right)$	cm ³ /molecule-s	(Cenian et al. 1994)
17 ¹	$\text{CO}_2 + e \rightarrow \cdot\text{O}^- + \text{CO}$	$f\left(\left(\frac{E}{N}\right)_{avg}, [\text{CO}](t), [\text{CO}_2](t)\right)$	cm ³ /molecule-s	(Cenian et al. 1994)
18 ¹	$\text{CO} + e \rightarrow \cdot\text{O}^- + \text{C}$	$f\left(\left(\frac{E}{N}\right)_{avg}, [\text{CO}](t), [\text{CO}_2](t)\right)$	cm ³ /molecule-s	(Cenian et al. 1994)
19	$\text{O}_3 + e \rightarrow \cdot\text{O}^- + \text{O}_2$	$1*10^{-11}$	cm ³ /molecule-s	(Cenian et al. 1994)

Table B.6 Continued

20 ³	$\text{H}_2\text{O} + \text{e} \rightarrow \text{H}^- + \cdot\text{OH}$	$9 \cdot 10^{-11}$	$\text{cm}^3/\text{molecule-s}$	(Lowke and Morrow 1995)
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¹⁷ Reaction rate constant included in source code.

¹⁸ The radical $\cdot\text{O}$ is used in the source code as (and assumed to be) $\cdot\text{O}(^3\text{P})$.

¹⁹ The ion H^- does not appear in Section B.2 since it was not a target species of interest nor was needed to derive any rate equations in the source code.

B.3.5 Three-body Attachment

Table B.7. A list of the three-body attachment chemical equations used in this analysis.

No.	Chemical Equation	Reaction Rate Constant	Units	Source
21 ¹	$\cdot\text{O} + \text{e} + \text{M} \rightarrow \cdot\text{O}^- + \text{M}$	$1 \cdot 10^{-31}$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Cenian et al. 1994)
22	$\text{O}_2 + \text{e} + \text{CO}_2 \rightarrow \cdot\text{O}_2^- + \text{CO}_2$	$3.0 \cdot 10^{-30}$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Cenian et al. 1994)
23	$\text{O}_2 + \text{e} + \text{CO} \rightarrow \cdot\text{O}_2^- + \text{CO}$	$2.0 \cdot 10^{-30}$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Cenian et al. 1994)
24	$\text{O}_2 + \text{e} + \text{O}_2 \rightarrow \cdot\text{O}_2^- + \text{O}_2$	$2.0 \cdot 10^{-30}$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Cenian et al. 1994)

¹ The radical $\cdot\text{O}$ is used in the source code as (and assumed to be) $\cdot\text{O}(^3\text{P})$.

B.3.6 Associative Detachment

Table B.8. A list of the associative detachment chemical equations used in this analysis.

No.	Chemical Equation	Reaction Rate Constant	Units	Source
25	$\cdot\text{O}^- + \text{CO} \rightarrow \text{CO}_2 + \text{e}$	$4.0 \cdot 10^{-10}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
26 ¹	$\cdot\text{O}^- + \cdot\text{O} \rightarrow \text{O}_2 + \text{e}$	$2.0 \cdot 10^{-10}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
27	$\cdot\text{O}^- + \text{O}_2 \rightarrow \text{O}_3 + \text{e}$	$1 \cdot 10^{-12}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)

Table B.8 Continued

28 ¹	$\cdot\text{O}^- + \text{CO}_2 \rightarrow \text{CO}_2 + \cdot\text{O} + \text{e}$	$4.0 \cdot 10^{-12}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
29 ¹	$\cdot\text{O}_2^- + \cdot\text{O} \rightarrow \text{O}_3 + \text{e}$	$3.3 \cdot 10^{-10}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
30	$\cdot\text{O}_2^- + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_3 + \text{e}$	$6.0 \cdot 10^{-10}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
31	$\cdot\text{CO}_3^- + \text{CO} \rightarrow \text{CO}_2 + \text{CO}_2 + \text{e}$	$5.0 \cdot 10^{-13}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)

¹ The radical $\cdot\text{O}$ is used in the source code as (and assumed to be) $\cdot\text{O}(^3\text{P})$.

B.3.7 Ion-Molecular

Table B.9. A list of the ion-molecular chemical equations used in this analysis.

No.	Chemical Equation	Reaction Rate Constant	Units	Source
32 ¹	$\cdot\text{O}^- + \text{O}_3 \rightarrow \cdot\text{O} + \cdot\text{O}_3^-$	$8.0 \cdot 10^{-10}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
33 ¹	$\cdot\text{O}_2^- + \cdot\text{O} \rightarrow \text{O}_2 + \cdot\text{O}^-$	$1 \cdot 10^{-11}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
34	$\cdot\text{O}_3^- + \text{CO}_2 \rightarrow \text{O}_2 + \cdot\text{CO}_3^-$	$5.5 \cdot 10^{-10}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
35 ¹	$\cdot\text{O}_3^- + \cdot\text{O} \rightarrow \text{O}_2 + \cdot\text{O}_2^-$	$2.5 \cdot 10^{-10}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
36 ¹	$\cdot\text{CO}_3^- + \cdot\text{O} \rightarrow \text{CO}_2 + \cdot\text{O}_2^-$	$8.0 \cdot 10^{-11}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
37 ¹	$\cdot\text{CO}_4^- + \cdot\text{O} \rightarrow \cdot\text{CO}_3^- + \text{O}_2$	$2.0 \cdot 10^{-10}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
38	$\cdot\text{CO}_4^- + \text{O}_3 \rightarrow \text{CO}_2 + \text{O}_2 + \cdot\text{O}_3^-$	$1 \cdot 10^{-10}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
39	$\cdot\text{O}^- + \text{CO}_2 + \text{CO}_2 \rightarrow \cdot\text{CO}_3^- + \text{CO}_2$	$9.0 \cdot 10^{-29}$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Cenian et al. 1994)

Table B.9 Continued

40	$\cdot\text{O}^- + \text{CO}_2 + \text{CO} \rightarrow \cdot\text{CO}_3^- + \text{CO}$	$3.0 \cdot 10^{-28}$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Cenian et al. 1994)
41	$\cdot\text{O}^- + \text{CO}_2 + \text{O}_2 \rightarrow \cdot\text{CO}_3^- + \text{O}_2$	$3.0 \cdot 10^{-28}$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Cenian et al. 1994)
42	$\cdot\text{O}^- + \text{O}_2 + \text{M} \rightarrow \cdot\text{O}_3^- + \text{M}$	$1 \cdot 10^{-30}$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Cenian et al. 1994)
43	$\cdot\text{O}_2^- + \text{CO}_2 + \text{M} \rightarrow \cdot\text{CO}_4^- + \text{M}$	$1 \cdot 10^{-29}$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Cenian et al. 1994)
44	$\cdot\text{CO}_2^+ + \text{O}_2 \rightarrow \cdot\text{O}_2^+ + \text{CO}_2$	$5.0 \cdot 10^{-11}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
45	$\cdot\text{CO}^+ + \text{CO}_2 \rightarrow \cdot\text{CO}_2^+ + \text{CO}$	$1.1 \cdot 10^{-9}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
46	$\cdot\text{CO}^+ + \text{O}_2 \rightarrow \cdot\text{O}_2^+ + \text{CO}$	$5.0 \cdot 10^{-10}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)

¹ The radical $\cdot\text{O}$ is used in the source code as (and assumed to be) $\cdot\text{O}(\text{}^3\text{P})$.

B.3.8 Ion-Ion Recombination

Table B.10. A list of the ion-ion recombination chemical equations used in this analysis.

No.	Chemical Equation	Reaction Rate Constant	Units	Source
47 ¹	$\cdot\text{O}^- + \cdot\text{O}_2^+ \rightarrow \cdot\text{O} + \text{O}_2$	$1 \cdot 10^{-7}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
48 ¹	$\cdot\text{O}_2^- + \cdot\text{O}_2^+ \rightarrow \text{O}_2 + \cdot\text{O} + \cdot\text{O}$	$4.2 \cdot 10^{-7}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
49 ¹	$\cdot\text{O}_2^- + \cdot\text{CO}_2^+ \rightarrow \text{O}_2 + \text{CO} + \cdot\text{O}$	$6.0 \cdot 10^{-7}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
50 ¹	$\cdot\text{CO}_3^- + \cdot\text{O}_2^+ \rightarrow \text{CO}_2 + \text{O}_2 + \cdot\text{O}$	$3.0 \cdot 10^{-7}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
51 ¹	$\cdot\text{CO}_3^- + \cdot\text{CO}_2^+ \rightarrow \text{CO}_2 + \text{CO}_2 + \cdot\text{O}$	$5.0 \cdot 10^{-7}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)

Table B.10 Continued

52	$\cdot\text{CO}_4^- + \cdot\text{O}_2^+ \rightarrow \text{CO}_2 + \text{O}_2 + \text{O}_2$	$3.0 \cdot 10^{-7}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
53	$\cdot\text{CO}_4^- + \cdot\text{CO}_2^+ \rightarrow \text{CO}_2 + \text{CO}_2 + \text{O}_2$	$5.0 \cdot 10^{-7}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)

¹ The radical $\cdot\text{O}$ is used in the source code as (and assumed to be) $\cdot\text{O}(^3\text{P})$.

B.3.9 Ion-Electron Recombination

Table B.11. A list of the ion-electron recombination chemical equations used in this analysis.

No.	Chemical Equation	Reaction Rate Constant	Units	Source
54 ^{1,2}	$\cdot\text{O}_2^+ + \text{e} \rightarrow \cdot\text{O} + \cdot\text{O}$	$f(T, \bar{\epsilon}_{avg})$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
55 ^{1,2}	$\cdot\text{CO}_2^+ + \text{e} \rightarrow \text{CO} + \cdot\text{O}$	$f(T, \bar{\epsilon}_{avg})$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)

¹ Reaction rate constant included in source code.

² The radical $\cdot\text{O}$ is used in the source code as (and assumed to be) $\cdot\text{O}(^3\text{P})$.

B.3.10 Neutral Component

Table B.12. A list of the neutral component chemical equations used in this analysis.

No.	Chemical Equation	Reaction Rate Constant	Units	Source
56 ^{1,2}	$\cdot\text{O} + \cdot\text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$	$f(T)$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Cenian et al. 1994)
57 ^{1,2}	$\text{O}_2 + \text{O}_2 + \cdot\text{O} \rightarrow \text{O}_3 + \text{O}_2$	$f(T)$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Cenian et al. 1994)
58 ^{1,2}	$\text{O}_2 + \text{CO} + \cdot\text{O} \rightarrow \text{CO} + \text{O}_3$	$f(T)$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Cenian et al. 1994)

Table B.12 Continued

59 ^{1, 2}	$\text{O}_2 + \cdot\text{O} + \text{CO}_2 \rightarrow \text{O}_3 + \text{CO}_2$	$f(T)$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Cenian et al. 1994)
60 ^{1, 2}	$\text{CO} + \cdot\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}_2$	$f(T)$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Cenian et al. 1994)
61 ^{1, 2}	$\text{CO} + \text{CO} + \cdot\text{O} \rightarrow \text{CO}_2 + \text{CO}$	$f(T)$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Cenian et al. 1994)
62 ^{1, 2}	$\text{CO} + \text{CO}_2 + \cdot\text{O} \rightarrow \text{CO}_2 + \text{CO}_2$	$f(T)$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Cenian et al. 1994)
63	$\text{C} + \text{CO} + \text{M} \rightarrow \text{C}_2\text{O} + \text{M}$	$6.5 \cdot 10^{-32}$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Cenian et al. 1994)
64 ^{1, 2}	$\cdot\text{O} + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2$	$f(T)$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
65 ²	$\text{C} + \text{O}_2 \rightarrow \text{CO} + \cdot\text{O}$	$3.0 \cdot 10^{-11}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
66 ²	$\text{C}_2\text{O} + \cdot\text{O} \rightarrow \text{CO} + \text{CO}$	$8.3 \cdot 10^{-11}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
67	$\text{C}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{CO}$	$3.3 \cdot 10^{-13}$	$\text{cm}^3/\text{molecule-s}$	(Cenian et al. 1994)
68	$\cdot\text{N} + \cdot\text{NO}_2 \rightarrow \cdot\text{NO} + \cdot\text{NO}$	$9.0 \cdot 10^{-12}$	$\text{cm}^3/\text{molecule-s}$	(Lowke and Morrow 1995)
69 ²	$\cdot\text{N} + \cdot\text{NO} \rightarrow \text{N}_2 + \cdot\text{O}$	$5.9 \cdot 10^{-11}$	$\text{cm}^3/\text{molecule-s}$	(Lowke and Morrow 1995)
70 ²	$\cdot\text{N} + \cdot\text{O} + \text{N}_2 \rightarrow \cdot\text{NO} + \text{N}_2$	$1.0 \cdot 10^{-32}$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Lowke and Morrow 1995)
71 ²	$\cdot\text{N} + \text{O}_2 \rightarrow \cdot\text{NO} + \cdot\text{O}$	$1.0 \cdot 10^{-16}$	$\text{cm}^3/\text{molecule-s}$	(Lowke and Morrow 1995)
72	$\cdot\text{N} + \text{O}_3 \rightarrow \cdot\text{NO} + \text{O}_2$	$1.0 \cdot 10^{-16}$	$\text{cm}^3/\text{molecule-s}$	(Lowke and Morrow 1995)

Table B.12 Continued

73 ¹	$\text{O}_3 + \cdot\text{NO} \rightarrow \cdot\text{NO}_2 + \text{O}_2$	$f(T)$	$\text{cm}^3/\text{molecule-s}$	(Ray and Watson 1981)
74 ^{1,2}	$\text{SO}_2 + \cdot\text{O} + \text{M} \rightarrow \text{SO}_3 + \text{M}$	$f(T)$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Atkinson et al. 2004)
75 ^{1,2}	$\text{SO}_3 + \cdot\text{O} + \text{M} \rightarrow \text{SO}_2 + \text{O}_2 + \text{M}$	$f(T)$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Jacob and Winkler 1972)
76 ¹	$\text{SO}_3 + \cdot\text{H} \rightarrow \text{SO}_2 + \cdot\text{OH}$	$f(T)$	$\text{cm}^3/\text{molecule-s}$	(Hindiyarti, Glarborg, and Marshall 2007)
77 ^{1,2}	$\cdot\text{O} + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \cdot\text{OH}$	$f(T)$	$\text{cm}^3/\text{molecule-s}$	(Lifshitz and Michael 1991)
78 ^{1,2}	$\cdot\text{OH} + \cdot\text{O} \rightarrow \cdot\text{H} + \text{O}_2$	$f(T)$	$\text{cm}^3/\text{molecule-s}$	(Atkinson et al. 2004)
79 ^{1,2}	$\text{SO} + \text{O}_2 \rightarrow \text{SO}_2 + \cdot\text{O}$	$f(T)$	$\text{cm}^3/\text{molecule-s}$	(Atkinson et al. 2004)
80 ¹	$\text{SO} + \text{O}_2 + \text{M} \rightarrow \text{SO}_3 + \text{M}$	$f(T)$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Wood and Heicklen 1971)
81 ¹	$\cdot\text{H} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}$	$f(T)$	$\text{cm}^3/\text{molecule-s}$	(Baulch et al. 1992)
82 ^{1,2}	$\text{CO} + \cdot\text{O} \rightarrow \text{CO}_2$	$f(T)$	$\text{cm}^3/\text{molecule-s}$	(W. Tsang and Hampson 1986)
83 ¹	$\text{SO}_2 + \text{O}_3 \rightarrow \text{SO}_3 + \text{O}_2$	$f(T)$	$\text{cm}^3/\text{molecule-s}$	(DeMore et al. 1997)
84	$\text{CO} + \text{O}_3 \rightarrow \text{CO}_2 + \text{O}_2$	$4.0 \cdot 10^{-25}$	$\text{cm}^3/\text{molecule-s}$	(Arin and Warneck 1972)

Table B.12 Continued

85	$\text{H}_2\text{O} + \cdot\text{NO} + \cdot\text{NO}_2 \rightarrow \text{HONO} + \text{HONO}$	$4.14 \cdot 10^{-37}$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(England and Corcoran 1975)
86	$\text{HONO} + \text{O}_3 \rightarrow \text{HNO}_3 + \text{O}_2$	$5.0 \cdot 10^{-19}$	$\text{cm}^3/\text{molecule-s}$	(DeMore et al. 1997)
87 ^{1,2}	$\text{O}_3 \rightarrow \text{O}_2 + \cdot\text{O}$	$f(T)$	$\text{cm}^3/\text{molecule-s}$	(Heimerl and Coffee 1979)
88 ^{1,2}	$\text{O}_3 + \cdot\text{O} \rightarrow \text{O}_2 + \text{O}_2$	$f(T)$	$\text{cm}^3/\text{molecule-s}$	(Atkinson et al. 2004)
89 ¹	$\cdot\text{OH} + \text{O}_3 \rightarrow \cdot\text{HO}_2 + \text{O}_2$	$f(T)$	$\text{cm}^3/\text{molecule-s}$	(Atkinson et al. 2004)
90 ¹	$\cdot\text{HO}_2 + \text{O}_3 \rightarrow \cdot\text{OH} + \text{O}_2 + \text{O}_2$	$f(T)$	$\text{cm}^3/\text{molecule-s}$	(Herndon et al. 2001)
91 ¹	$\text{CO} + \cdot\text{HO}_2 \rightarrow \text{CO}_2 + \cdot\text{OH}$	$f(T)$	$\text{cm}^3/\text{molecule-s}$	(Volman 1996)
92 ¹	$\cdot\text{OH} + \cdot\text{NO}_2 \rightarrow \text{HNO}_3$	$f(T)$	$\text{cm}^3/\text{molecule-s}$	(Atkinson et al. 1997)
93 ¹	$\text{HNO}_3 + \cdot\text{H} \rightarrow \text{H}_2\text{O} + \cdot\text{NO}_2$	$f(T)$	$\text{cm}^3/\text{molecule-s}$	(Boughton, Kristyan, and Lin 1997)
94	$\text{HONO} + \text{HONO} \rightarrow \text{H}_2\text{O} + \cdot\text{NO} + \cdot\text{NO}_2$	$1.0 \cdot 10^{-20}$	$\text{cm}^3/\text{molecule-s}$	(Kaiser and Wu 1977)
95 ^{1,2}	$\text{HONO} + \cdot\text{O} \rightarrow \cdot\text{OH} + \cdot\text{NO}_2$	$f(T)$	$\text{cm}^3/\text{molecule-s}$	(Wing Tsang and Herron 1991)
96	$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$	$1.2 \cdot 10^{-15}$	$\text{cm}^3/\text{molecule-s}$	(Reiner and Arnold 1994)
97 ³	$\cdot\text{OH} + \text{H}_2\text{SO}_4 \rightarrow \cdot\text{HSO}_4 + \text{H}_2\text{O}$	$1.5 \cdot 10^{-14}$	$\text{cm}^3/\text{molecule-s}$	(Anglada, Olivella, and Solé 2006)
98 ¹	$\cdot\text{OH} + \text{SO}_2 + \text{N}_2 \rightarrow \cdot\text{HSO}_3 + \text{N}_2$	$f(T)$	$\text{cm}^3/\text{molecule-s}$	(Atkinson et al. 1992)

Table B.12 Continued

99 ¹	$\text{O}_2 + \cdot\text{HSO}_3 \rightarrow \cdot\text{HO}_2 + \text{SO}_3$	$f(T)$	$\text{cm}^3/\text{molecule-s}$	(Atkinson et al. 2004)
100 ¹	$\cdot\text{OH} + \cdot\text{NO} \rightarrow \text{HONO}$	$f(T)$	$\text{cm}^3/\text{molecule-s}$	(Atkinson et al. 1989)
101 ¹	$\cdot\text{NO} + \cdot\text{H} + \text{M} \rightarrow \text{HNO} + \text{M}$	$f(T)$	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Wing Tsang and Herron 1991)
102 ¹	$\cdot\text{H} + \text{HNO} \rightarrow \text{H}_2 + \cdot\text{NO}$	$f(T)$	$\text{cm}^3/\text{molecule-s}$	(Wing Tsang and Herron 1991)
103	$\cdot\text{OH} + \cdot\text{HSO}_3 \rightarrow \text{H}_2\text{SO}_4$	$1.0 \cdot 10^{-12}$	$\text{cm}^3/\text{molecule-s}$	(Lowke and Morrow 1995)
104	$\cdot\text{OH} + \text{HONO} \rightarrow \cdot\text{NO}_2 + \text{H}_2\text{O}$	$0.5 \cdot 10^{-11}$	$\text{cm}^3/\text{molecule-s}$	(Lowke and Morrow 1995)
105 ¹	$\cdot\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \cdot\text{OH}$	$f(T)$	$\text{cm}^3/\text{molecule-s}$	(Dunlea and Ravishankara 2004)
106 ²	$\cdot\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \cdot\text{O}$	$1.2 \cdot 10^{-11}$	$\text{cm}^3/\text{molecule-s}$	(Lowke and Morrow 1995)
107 ²	$\cdot\text{O}(^1\text{D}) + \text{O}_3 \rightarrow \cdot\text{O} + \cdot\text{O} + \text{O}_2$	$1.2 \cdot 10^{-10}$	$\text{cm}^3/\text{molecule-s}$	(Lowke and Morrow 1995)
108	$\cdot\text{O}(^1\text{D}) + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2$	$1.2 \cdot 10^{-10}$	$\text{cm}^3/\text{molecule-s}$	(Lowke and Morrow 1995)
109	$\cdot\text{O}(^1\text{D}) + \cdot\text{NO} \rightarrow \cdot\text{N} + \text{O}_2$	$1.7 \cdot 10^{-10}$	$\text{cm}^3/\text{molecule-s}$	(Lowke and Morrow 1995)

Table B.12 Continued

110	$\cdot\text{O}(^1\text{D}) + \cdot\text{NO}_2 \rightarrow \cdot\text{NO} + \text{O}_2$	1.4×10^{-10}	$\text{cm}^3/\text{molecule-s}$	(Lowke and Morrow 1995)
111 ²	$\cdot\text{O}(^1\text{D}) + \text{N}_2 \rightarrow \text{N}_2 + \cdot\text{O}$	2.2×10^{-11}	$\text{cm}^3/\text{molecule-s}$	(Atkinson et al. 1992)
112 ²	$\cdot\text{O}(^1\text{D}) + \text{O}_2 \rightarrow \text{O}_2 + \cdot\text{O}$	6.3×10^{-12}	$\text{cm}^3/\text{molecule-s}$	(Lowke and Morrow 1995)
113 ²	$\cdot\text{O}(^1\text{D}) + \cdot\text{O} + \text{N}_2 \rightarrow \text{N}_2 + \text{O}_2$	9.9×10^{-33}	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Lowke and Morrow 1995)
114 ²	$\cdot\text{N} + \cdot\text{NO}_2 \rightarrow \text{N}_2\text{O} + \cdot\text{O}$	3.0×10^{-12}	$\text{cm}^3/\text{molecule-s}$	(Lowke and Morrow 1995)
115	$\cdot\text{O}(^1\text{D}) + \text{N}_2\text{O} \rightarrow \cdot\text{NO} + \cdot\text{NO}$	6.7×10^{-11}	$\text{cm}^3/\text{molecule-s}$	(Lowke and Morrow 1995)
116	$\cdot\text{O}(^1\text{D}) + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}_2$	4.9×10^{-11}	$\text{cm}^3/\text{molecule-s}$	(Lowke and Morrow 1995)
117	$\cdot\text{O}(^1\text{D}) + \text{N}_2 + \text{N}_2 \rightarrow \text{N}_2 + \text{N}_2\text{O}$	3.5×10^{-37}	$\text{cm}^6/\text{molecule}^2\text{-s}$	(Lowke and Morrow 1995)

¹ Reaction rate constant included in source code.

² The radical $\cdot\text{O}$ is used in the source code as (and assumed to be) $\cdot\text{O}(^3\text{P})$.

³ The radical $\cdot\text{HSO}_4$ does not appear in Section B.2 since it was not a target species of interest nor was needed to derive any rate equations in the source code.

B.3.11 Multiple Pathways

Table B.13. A list of the multiple pathway chemical equations used in this analysis.

No.	Chemical Equation	Reaction Rate Constant	Units	Source
118 ^{1, 2}	$\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{P}$	$f(\bar{\epsilon}_{avg})$	$\text{cm}^3/\text{molecule-s}$	(Dolan 1993)
119 ^{1, 3}	$\text{H}_2\text{O} + \text{H}^+ \rightarrow \cdot\text{H} + \text{P}$	$f(\bar{\epsilon}_{avg})$	$\text{cm}^3/\text{molecule-s}$	(Dolan 1993)
120 ^{1, 4}	$\cdot\text{H}_2\text{O}^+ + \text{e} \rightarrow \text{P}$	$f(\bar{\epsilon}_{avg})$	$\text{cm}^3/\text{molecule-s}$	(Dolan 1993)
121 ^{1, 4}	$\text{OH}^+ + \text{e} \rightarrow \text{P}$	$f(\bar{\epsilon}_{avg})$	$\text{cm}^3/\text{molecule-s}$	(Dolan 1993)

¹ P denotes product formed in the reaction.

² Electron ejection reaction.

³ Electron capture reaction.

⁴ Dissociative recombination reaction. The cation radical $\cdot\text{H}_2\text{O}^+$ and cation OH^+ do not appear in Section B.2 since it was not a target species of interest nor was needed to derive any rate equations in the source code.

B.4 LXCat

LXCat, found at <https://www.lxcats.net>, is an open-access on-line database for downloading electron and ion scattering cross-sections, swarm parameters, reaction rates, energy distribution functions, etc. for modeling low temperature plasmas. The data provided by LXCat, is used by *BOLSIG+* to calculate the ionization coefficient, attachment coefficient, electron mobility, diffusion coefficient and mean electron energy used in this analysis. Specifically, electron scattering cross sections were obtained through the PHELPS, MORGAN, SIGLO and TRINITY databases through LXCat.

B.5 BOLSIG+

BOLSIG+, found at <http://www.bolsig.laplace.univ-tlse.fr/index.html>, is a free program that solves the Boltzmann equation for electrons in weakly ionized gases in various types of gas discharges and collisional low temperature plasmas. Input data for the program includes atomic

and molecular cross-sections, gas composition and temperature. The following tables consist of the electron diffusion coefficient, electron mobility, mean electron energy and the Townsend Ionization and Attachment Coefficients as a function of electric field strength. This data was created for the specific gas compositions and temperatures listed in Table 3.3 and was calculated in *BOLSIG+* using the PHELPS, MORGAN, SIGLO and TRINITI databases (Phelps 2013; Morgan 2013; Phelps 2013; Napartovich et al. 2021; Yamabe, Buckman, and Phelps 1983; Phelps and Pitchford 1985; Lawton and Phelps 1978).

B.5.1 – March 8th, 2020

The data shown below has been calculated by *BOLSIG+* based on the March 8th, 2020, scenario listed in Table 3.3. These results are given at 385 K and 101,325 Pa.

Table B.14. A list of the *BOLSIG+* data based on the gas composition and temperature from March 8th, 2020.

E/N (Td)	Diffusion Coefficient*N (1/m/s)	Electron Mobility*N (1/m/V/s)	Townsend Ionization Coefficient α /N (m ²)	Townsend Attachment Coefficient β /N (m ²)	Mean Electron Energy (eV)
50	1.51E+24	1.50E+24	6.70E-26	6.66E-24	1.19
67.95	1.82E+24	1.36E+24	1.50E-24	2.63E-23	1.663
85.9	2.23E+24	1.28E+24	9.30E-24	5.07E-23	2.317
103.8	2.66E+24	1.22E+24	3.07E-23	6.99E-23	2.985
121.8	3.03E+24	1.17E+24	7.19E-23	8.21E-23	3.59
139.7	3.35E+24	1.13E+24	1.37E-22	8.86E-23	4.117
157.7	3.61E+24	1.10E+24	2.28E-22	9.12E-23	4.573
175.6	3.83E+24	1.08E+24	3.45E-22	9.13E-23	4.978
193.6	4.02E+24	1.05E+24	4.89E-22	9.00E-23	5.342
211.5	4.18E+24	1.03E+24	6.59E-22	8.78E-23	5.667
229.5	4.34E+24	1.01E+24	8.54E-22	8.51E-23	5.982

Table B.14 Continued

247.4	4.49E+24	9.95E+23	1.07E-21	8.23E-23	6.292
265.4	4.61E+24	9.79E+23	1.31E-21	7.93E-23	6.577
283.3	4.73E+24	9.63E+23	1.57E-21	7.63E-23	6.846
301.3	4.84E+24	9.49E+23	1.85E-21	7.34E-23	7.114
319.2	4.95E+24	9.35E+23	2.15E-21	7.06E-23	7.376
337.2	5.05E+24	9.23E+23	2.46E-21	6.79E-23	7.631
355.1	5.15E+24	9.11E+23	2.79E-21	6.53E-23	7.884
373.1	5.24E+24	9.00E+23	3.13E-21	6.29E-23	8.132
391	5.34E+24	8.89E+23	3.48E-21	6.05E-23	8.378
409	5.43E+24	8.79E+23	3.84E-21	5.83E-23	8.621
426.9	5.51E+24	8.69E+23	4.21E-21	5.62E-23	8.862
444.9	5.60E+24	8.60E+23	4.59E-21	5.42E-23	9.101
462.8	5.68E+24	8.51E+23	4.98E-21	5.23E-23	9.336
480.8	5.76E+24	8.42E+23	5.37E-21	5.05E-23	9.572
498.7	5.84E+24	8.34E+23	5.77E-21	4.87E-23	9.806
516.7	5.92E+24	8.26E+23	6.17E-21	4.71E-23	10.04
534.6	6.00E+24	8.19E+23	6.57E-21	4.56E-23	10.27
552.6	6.07E+24	8.11E+23	6.98E-21	4.41E-23	10.5
570.5	6.14E+24	8.04E+23	7.39E-21	4.27E-23	10.73
588.5	6.22E+24	7.97E+23	7.81E-21	4.14E-23	10.96
606.4	6.29E+24	7.90E+23	8.22E-21	4.01E-23	11.19
624.4	6.36E+24	7.84E+23	8.64E-21	3.89E-23	11.41
642.3	6.43E+24	7.77E+23	9.05E-21	3.77E-23	11.64
660.3	6.49E+24	7.71E+23	9.47E-21	3.66E-23	11.87
678.2	6.56E+24	7.65E+23	9.89E-21	3.56E-23	12.09
696.2	6.63E+24	7.59E+23	1.03E-20	3.46E-23	12.31
714.1	6.69E+24	7.54E+23	1.07E-20	3.36E-23	12.54
732.1	6.76E+24	7.48E+23	1.11E-20	3.27E-23	12.76
750	6.82E+24	7.43E+23	1.16E-20	3.18E-23	12.98

B.5.2 – March 13th, 2020 – Run No. 1

The data shown below has been calculated by *BOLSIG+* based on the March 13th, 2020 – Run No. 1 scenario listed in Table 3.3. These results are given at 383 K and 101,325 Pa.

Table B.15. A list of the *BOLSIG+* data based on the gas composition and temperature from March 13th, 2020 – Run No. 1.

E/N (Td)	Diffusion Coefficient*N (1/m/s)	Electron Mobility*N (1/m/V/s)	Townsend Ionization Coefficient α /N (m ²)	Townsend Attachment Coefficient β /N (m ²)	Mean Electron Energy (eV)
50	1.54E+24	1.50E+24	6.21E-26	6.10E-24	1.196
67.95	1.82E+24	1.36E+24	1.41E-24	2.42E-23	1.655
85.9	2.23E+24	1.27E+24	8.82E-24	4.69E-23	2.3
103.8	2.64E+24	1.21E+24	2.94E-23	6.50E-23	2.963
121.8	3.01E+24	1.17E+24	6.93E-23	7.65E-23	3.567
139.7	3.33E+24	1.13E+24	1.33E-22	8.27E-23	4.096
157.7	3.59E+24	1.10E+24	2.22E-22	8.51E-23	4.553
175.6	3.81E+24	1.07E+24	3.38E-22	8.53E-23	4.959
193.6	4.00E+24	1.05E+24	4.80E-22	8.41E-23	5.324
211.5	4.16E+24	1.03E+24	6.48E-22	8.21E-23	5.65
229.5	4.31E+24	1.01E+24	8.41E-22	7.96E-23	5.966
247.4	4.46E+24	9.91E+23	1.06E-21	7.70E-23	6.278
265.4	4.59E+24	9.75E+23	1.30E-21	7.42E-23	6.563
283.3	4.70E+24	9.59E+23	1.56E-21	7.14E-23	6.832
301.3	4.81E+24	9.45E+23	1.84E-21	6.87E-23	7.1
319.2	4.92E+24	9.32E+23	2.13E-21	6.61E-23	7.362
337.2	5.02E+24	9.19E+23	2.44E-21	6.36E-23	7.619
355.1	5.12E+24	9.07E+23	2.77E-21	6.12E-23	7.872
373.1	5.22E+24	8.96E+23	3.11E-21	5.89E-23	8.121
391	5.31E+24	8.86E+23	3.46E-21	5.67E-23	8.367

Table B.15 Continued

409	5.40E+24	8.76E+23	3.82E-21	5.46E-23	8.61
426.9	5.48E+24	8.66E+23	4.19E-21	5.26E-23	8.851
444.9	5.57E+24	8.57E+23	4.57E-21	5.07E-23	9.091
462.8	5.65E+24	8.47E+23	4.95E-21	4.90E-23	9.326
480.8	5.73E+24	8.39E+23	5.35E-21	4.73E-23	9.562
498.7	5.81E+24	8.31E+23	5.74E-21	4.57E-23	9.796
516.7	5.88E+24	8.23E+23	6.14E-21	4.42E-23	10.03
534.6	5.97E+24	8.15E+23	6.55E-21	4.27E-23	10.26
552.6	6.04E+24	8.08E+23	6.96E-21	4.13E-23	10.49
570.5	6.11E+24	8.01E+23	7.37E-21	4.00E-23	10.72
588.5	6.18E+24	7.94E+23	7.78E-21	3.88E-23	10.95
606.4	6.26E+24	7.87E+23	8.19E-21	3.76E-23	11.18
624.4	6.32E+24	7.80E+23	8.61E-21	3.65E-23	11.41
642.3	6.39E+24	7.74E+23	9.03E-21	3.54E-23	11.63
660.3	6.46E+24	7.68E+23	9.44E-21	3.44E-23	11.86
678.2	6.53E+24	7.62E+23	9.86E-21	3.34E-23	12.08
696.2	6.59E+24	7.56E+23	1.03E-20	3.24E-23	12.31
714.1	6.66E+24	7.50E+23	1.07E-20	3.15E-23	12.53
732.1	6.72E+24	7.45E+23	1.11E-20	3.07E-23	12.75
750	6.79E+24	7.39E+23	1.15E-20	2.99E-23	12.98

B.5.3 – March 13th, 2020 – Run No. 2

The data shown below has been calculated by *BOLSIG+* based on the March 13th, 2020 – Run No. 2 scenario listed in Table 3.3. These results are given at 393 K and 101,325 Pa.

Table B.16. A list of the *BOLSIG+* data based on the gas composition and temperature from March 13th, 2020 –

Run No. 2.

E/N (Td)	Diffusion Coefficient*N (1/m/s)	Electron Mobility*N (1/m/V/s)	Townsend Ionization Coefficient α /N (m ²)	Townsend Attachment Coefficient β /N (m ²)	Mean Electron Energy (eV)
50	1.52E+24	1.50E+24	6.77E-26	6.75E-24	1.193
67.95	1.82E+24	1.36E+24	1.51E-24	2.65E-23	1.667
85.9	2.24E+24	1.28E+24	9.32E-24	5.08E-23	2.321
103.8	2.66E+24	1.22E+24	3.07E-23	7.01E-23	2.988
121.8	3.03E+24	1.17E+24	7.19E-23	8.21E-23	3.591
139.7	3.35E+24	1.13E+24	1.37E-22	8.86E-23	4.119
157.7	3.61E+24	1.10E+24	2.28E-22	9.11E-23	4.575
175.6	3.83E+24	1.08E+24	3.45E-22	9.13E-23	4.979
193.6	4.02E+24	1.05E+24	4.89E-22	8.99E-23	5.343
211.5	4.18E+24	1.03E+24	6.59E-22	8.77E-23	5.668
229.5	4.34E+24	1.01E+24	8.54E-22	8.51E-23	5.983
247.4	4.49E+24	9.95E+23	1.07E-21	8.22E-23	6.294
265.4	4.62E+24	9.79E+23	1.31E-21	7.93E-23	6.578
283.3	4.73E+24	9.63E+23	1.57E-21	7.63E-23	6.847
301.3	4.84E+24	9.49E+23	1.85E-21	7.34E-23	7.115
319.2	4.95E+24	9.35E+23	2.15E-21	7.06E-23	7.376
337.2	5.05E+24	9.23E+23	2.47E-21	6.79E-23	7.633
355.1	5.15E+24	9.11E+23	2.79E-21	6.53E-23	7.885
373.1	5.25E+24	9.00E+23	3.13E-21	6.28E-23	8.134
391	5.34E+24	8.89E+23	3.48E-21	6.05E-23	8.38
409	5.43E+24	8.79E+23	3.85E-21	5.82E-23	8.623
426.9	5.52E+24	8.69E+23	4.22E-21	5.61E-23	8.864
444.9	5.60E+24	8.60E+23	4.60E-21	5.41E-23	9.103
462.8	5.68E+24	8.51E+23	4.98E-21	5.22E-23	9.338
480.8	5.76E+24	8.42E+23	5.37E-21	5.04E-23	9.574
498.7	5.84E+24	8.34E+23	5.77E-21	4.87E-23	9.808

Table B.16 Continued

516.7	5.92E+24	8.26E+23	6.17E-21	4.71E-23	10.04
534.6	6.00E+24	8.19E+23	6.58E-21	4.55E-23	10.27
552.6	6.07E+24	8.11E+23	6.99E-21	4.40E-23	10.51
570.5	6.15E+24	8.04E+23	7.40E-21	4.26E-23	10.73
588.5	6.22E+24	7.97E+23	7.81E-21	4.13E-23	10.96
606.4	6.29E+24	7.90E+23	8.23E-21	4.01E-23	11.19
624.4	6.36E+24	7.84E+23	8.64E-21	3.88E-23	11.42
642.3	6.43E+24	7.77E+23	9.06E-21	3.77E-23	11.64
660.3	6.50E+24	7.71E+23	9.48E-21	3.66E-23	11.87
678.2	6.56E+24	7.65E+23	9.89E-21	3.55E-23	12.09
696.2	6.63E+24	7.59E+23	1.03E-20	3.45E-23	12.32
714.1	6.69E+24	7.54E+23	1.07E-20	3.36E-23	12.54
732.1	6.76E+24	7.48E+23	1.11E-20	3.27E-23	12.77
750	6.82E+24	7.43E+23	1.16E-20	3.18E-23	12.99

B.5.4 – Modeled Flue Gas, 300 K

The data shown below has been calculated by *BOLSIG+* based on the Modeled Flue Gas scenario listed in Table 3.3. These results are given at 300 K and 101,325 Pa.

Table B.17. A list of the *BOLSIG+* data based on the gas composition and temperature for the Modeled Flue Gas listed in Table 3.3.

E/N (Td)	Diffusion Coefficient*N (1/m/s)	Electron Mobility*N (1/m/V/s)	Townsend Ionization Coefficient α /N (m ²)	Townsend Attachment Coefficient β /N (m ²)	Mean Electron Energy (eV)
50	1.50E+24	1.51E+24	6.77E-26	6.79E-24	1.184
67.95	1.81E+24	1.37E+24	1.53E-24	2.69E-23	1.663

Table B.17 Continued

85.9	2.24E+24	1.28E+24	9.45E-24	5.20E-23	2.32
103.8	2.66E+24	1.22E+24	3.11E-23	7.17E-23	2.99
121.8	3.04E+24	1.18E+24	7.28E-23	8.42E-23	3.598
139.7	3.36E+24	1.14E+24	1.38E-22	9.09E-23	4.123
157.7	3.62E+24	1.11E+24	2.30E-22	9.34E-23	4.578
175.6	3.84E+24	1.08E+24	3.48E-22	9.36E-23	4.983
193.6	4.03E+24	1.05E+24	4.92E-22	9.22E-23	5.336
211.5	4.20E+24	1.03E+24	6.63E-22	8.99E-23	5.673
229.5	4.35E+24	1.01E+24	8.59E-22	8.72E-23	5.988
247.4	4.50E+24	9.97E+23	1.08E-21	8.43E-23	6.298
265.4	4.63E+24	9.81E+23	1.32E-21	8.13E-23	6.582
283.3	4.74E+24	9.65E+23	1.58E-21	7.82E-23	6.853
301.3	4.86E+24	9.51E+23	1.86E-21	7.52E-23	7.121
319.2	4.96E+24	9.38E+23	2.16E-21	7.23E-23	7.383
337.2	5.06E+24	9.25E+23	2.47E-21	6.96E-23	7.637
355.1	5.16E+24	9.13E+23	2.80E-21	6.69E-23	7.89
373.1	5.26E+24	9.02E+23	3.14E-21	6.44E-23	8.139
391	5.35E+24	8.91E+23	3.49E-21	6.20E-23	8.386
409	5.44E+24	8.81E+23	3.86E-21	5.97E-23	8.629
426.9	5.53E+24	8.71E+23	4.23E-21	5.75E-23	8.87
444.9	5.61E+24	8.62E+23	4.61E-21	5.55E-23	9.109
462.8	5.70E+24	8.53E+23	4.99E-21	5.35E-23	9.345
480.8	5.78E+24	8.44E+23	5.39E-21	5.17E-23	9.58
498.7	5.86E+24	8.36E+23	5.78E-21	4.99E-23	9.815
516.7	5.93E+24	8.28E+23	6.18E-21	4.83E-23	10.05
534.6	6.01E+24	8.20E+23	6.59E-21	4.67E-23	10.28
552.6	6.09E+24	8.13E+23	7.00E-21	4.52E-23	10.51
570.5	6.16E+24	8.05E+23	7.41E-21	4.37E-23	10.74
588.5	6.23E+24	7.98E+23	7.83E-21	4.24E-23	10.97
606.4	6.30E+24	7.92E+23	8.24E-21	4.11E-23	11.2
624.4	6.37E+24	7.85E+23	8.66E-21	3.98E-23	11.42
642.3	6.44E+24	7.79E+23	9.07E-21	3.86E-23	11.65
660.3	6.51E+24	7.72E+23	9.49E-21	3.75E-23	11.87

Table B.17 Continued

678.2	6.58E+24	7.66E+23	9.91E-21	3.64E-23	12.1
696.2	6.64E+24	7.61E+23	1.03E-20	3.54E-23	12.32
714.1	6.71E+24	7.55E+23	1.07E-20	3.44E-23	12.55
732.1	6.77E+24	7.49E+23	1.12E-20	3.35E-23	12.77
750	6.84E+24	7.44E+23	1.16E-20	3.26E-23	12.99

B.5.5 – Modeled Flue Gas, 350 K

The data shown below has been calculated by *BOLSIG+* based on the Modeled Flue Gas scenario listed in Table 3.3. These results are given at 350 K and 101,325 Pa.

Table B.18. A list of the *BOLSIG+* data based on the gas composition and temperature for the Modeled Flue Gas listed in Table 3.3.

E/N (Td)	Diffusion Coefficient*N (1/m/s)	Electron Mobility*N (1/m/V/s)	Townsend Ionization Coefficient α /N (m ²)	Townsend Attachment Coefficient β /N (m ²)	Mean Electron Energy (eV)
50	1.51E+24	1.51E+24	6.89E-26	6.91E-24	1.188
67.95	1.82E+24	1.37E+24	1.54E-24	2.72E-23	1.667
85.9	2.24E+24	1.28E+24	9.50E-24	5.22E-23	2.325
103.8	2.67E+24	1.22E+24	3.12E-23	7.20E-23	2.998
121.8	3.04E+24	1.18E+24	7.29E-23	8.44E-23	3.601
139.7	3.36E+24	1.14E+24	1.39E-22	9.10E-23	4.126
157.7	3.62E+24	1.11E+24	2.30E-22	9.35E-23	4.581
175.6	3.84E+24	1.08E+24	3.48E-22	9.36E-23	4.984
193.6	4.03E+24	1.05E+24	4.93E-22	9.22E-23	5.338
211.5	4.20E+24	1.03E+24	6.63E-22	9.00E-23	5.674
229.5	4.35E+24	1.01E+24	8.59E-22	8.73E-23	5.989

Table B.18 Continued

247.4	4.50E+24	9.97E+23	1.08E-21	8.43E-23	6.298
265.4	4.63E+24	9.81E+23	1.32E-21	8.13E-23	6.583
283.3	4.74E+24	9.65E+23	1.58E-21	7.82E-23	6.854
301.3	4.86E+24	9.51E+23	1.86E-21	7.52E-23	7.122
319.2	4.97E+24	9.37E+23	2.16E-21	7.24E-23	7.383
337.2	5.06E+24	9.25E+23	2.47E-21	6.96E-23	7.638
355.1	5.16E+24	9.13E+23	2.80E-21	6.69E-23	7.89
373.1	5.26E+24	9.01E+23	3.14E-21	6.44E-23	8.139
391	5.35E+24	8.91E+23	3.49E-21	6.20E-23	8.386
409	5.44E+24	8.81E+23	3.86E-21	5.97E-23	8.629
426.9	5.53E+24	8.71E+23	4.23E-21	5.75E-23	8.87
444.9	5.62E+24	8.62E+23	4.61E-21	5.55E-23	9.109
462.8	5.70E+24	8.53E+23	4.99E-21	5.35E-23	9.345
480.8	5.78E+24	8.44E+23	5.39E-21	5.17E-23	9.581
498.7	5.86E+24	8.36E+23	5.78E-21	4.99E-23	9.815
516.7	5.93E+24	8.28E+23	6.19E-21	4.83E-23	10.05
534.6	6.01E+24	8.20E+23	6.59E-21	4.67E-23	10.28
552.6	6.09E+24	8.13E+23	7.00E-21	4.52E-23	10.51
570.5	6.16E+24	8.05E+23	7.41E-21	4.37E-23	10.74
588.5	6.23E+24	7.98E+23	7.83E-21	4.24E-23	10.97
606.4	6.30E+24	7.92E+23	8.24E-21	4.11E-23	11.2
624.4	6.37E+24	7.85E+23	8.66E-21	3.98E-23	11.42
642.3	6.44E+24	7.79E+23	9.07E-21	3.86E-23	11.65
660.3	6.51E+24	7.72E+23	9.49E-21	3.75E-23	11.87
678.2	6.58E+24	7.66E+23	9.91E-21	3.64E-23	12.1
696.2	6.64E+24	7.61E+23	1.03E-20	3.54E-23	12.32
714.1	6.71E+24	7.55E+23	1.07E-20	3.44E-23	12.55
732.1	6.77E+24	7.49E+23	1.12E-20	3.35E-23	12.77
750	6.84E+24	7.44E+23	1.16E-20	3.26E-23	12.99

B.5.6 – Modeled Flue Gas, 400 K

The data shown below has been calculated by *BOLSIG+* based on the Modeled Flue Gas scenario listed in Table 3.3. These results are given at 400 K and 101,325 Pa.

Table B.19. A list of the *BOLSIG+* data based on the gas composition and temperature for the Modeled Flue Gas listed in Table 3.3.

E/N (Td)	Diffusion Coefficient*N (1/m/s)	Electron Mobility*N (1/m/V/s)	Townsend Ionization Coefficient α /N (m ²)	Townsend Attachment Coefficient β /N (m ²)	Mean Electron Energy (eV)
50	1.51E+24	1.51E+24	6.99E-26	7.01E-24	1.192
67.95	1.82E+24	1.37E+24	1.55E-24	2.74E-23	1.671
85.9	2.24E+24	1.28E+24	9.53E-24	5.24E-23	2.329
103.8	2.67E+24	1.22E+24	3.13E-23	7.22E-23	3.002
121.8	3.05E+24	1.17E+24	7.30E-23	8.45E-23	3.604
139.7	3.36E+24	1.14E+24	1.39E-22	9.10E-23	4.128
157.7	3.62E+24	1.11E+24	2.30E-22	9.36E-23	4.582
175.6	3.84E+24	1.08E+24	3.48E-22	9.36E-23	4.986
193.6	4.03E+24	1.05E+24	4.93E-22	9.22E-23	5.339
211.5	4.20E+24	1.03E+24	6.64E-22	9.00E-23	5.675
229.5	4.35E+24	1.01E+24	8.59E-22	8.73E-23	5.99
247.4	4.50E+24	9.97E+23	1.08E-21	8.44E-23	6.299
265.4	4.63E+24	9.81E+23	1.32E-21	8.13E-23	6.584
283.3	4.74E+24	9.65E+23	1.58E-21	7.82E-23	6.854
301.3	4.86E+24	9.51E+23	1.86E-21	7.53E-23	7.122
319.2	4.97E+24	9.37E+23	2.16E-21	7.24E-23	7.384
337.2	5.06E+24	9.25E+23	2.47E-21	6.96E-23	7.638
355.1	5.16E+24	9.13E+23	2.80E-21	6.69E-23	7.89
373.1	5.26E+24	9.01E+23	3.14E-21	6.44E-23	8.139
391	5.35E+24	8.91E+23	3.49E-21	6.20E-23	8.386

Table B.19 Continued

409	5.44E+24	8.81E+23	3.86E-21	5.97E-23	8.63
426.9	5.53E+24	8.71E+23	4.23E-21	5.75E-23	8.871
444.9	5.62E+24	8.62E+23	4.61E-21	5.55E-23	9.11
462.8	5.70E+24	8.53E+23	4.99E-21	5.35E-23	9.345
480.8	5.78E+24	8.44E+23	5.39E-21	5.17E-23	9.581
498.7	5.86E+24	8.36E+23	5.78E-21	4.99E-23	9.815
516.7	5.93E+24	8.28E+23	6.19E-21	4.83E-23	10.05
534.6	6.01E+24	8.20E+23	6.59E-21	4.67E-23	10.28
552.6	6.09E+24	8.13E+23	7.00E-21	4.52E-23	10.51
570.5	6.16E+24	8.05E+23	7.41E-21	4.37E-23	10.74
588.5	6.23E+24	7.98E+23	7.83E-21	4.24E-23	10.97
606.4	6.30E+24	7.92E+23	8.24E-21	4.11E-23	11.2
624.4	6.37E+24	7.85E+23	8.66E-21	3.98E-23	11.42
642.3	6.44E+24	7.79E+23	9.07E-21	3.86E-23	11.65
660.3	6.51E+24	7.72E+23	9.49E-21	3.75E-23	11.88
678.2	6.58E+24	7.66E+23	9.91E-21	3.64E-23	12.1
696.2	6.64E+24	7.61E+23	1.03E-20	3.54E-23	12.32
714.1	6.71E+24	7.55E+23	1.07E-20	3.44E-23	12.55
732.1	6.77E+24	7.49E+23	1.12E-20	3.35E-23	12.77
750	6.84E+24	7.44E+23	1.16E-20	3.26E-23	12.99

B.6 Equations for the Ionization Coefficient, α

The ionization coefficient is a parameter needed to calculate the electron number concentration in a corona discharge as shown in (Chen and Davidson 2002). Here, a set of 5th order equations have been fitted to the data provided by *BOLSIG+* (shown in Section B.5). The equations were fitted using *Mathematica 12* and have been expressed as a function of radial distance. Similar to the data provided by *BOLSIG+*, the following equations are for a given gas composition and temperature, however have been further corrected for a specific pressure. The specific flue gas temperature, pressure and composition is listed in Table 3.3.

Table B.20. A list of the fitted equations based on *BOLSIG+* data.

Fitted Equations for the Ionization Coefficient, $\alpha(r)$	
March 8 th , 2020	$r_0 E_c \left[4335 - 0.005879 \left(\frac{1}{r} \right) + 1.773 * 10^{-9} \left(\frac{1}{r} \right)^2 + 1.185 * 10^{-16} \left(\frac{1}{r} \right)^3 \right. \\ \left. - 1.673 * 10^{-23} \left(\frac{1}{r} \right)^4 + 4.898 * 10^{-31} \left(\frac{1}{r} \right)^5 \right]$
March 13 th , 2020 – Run No. 1	$r_0 E_c \left[4356 - 0.005804 \left(\frac{1}{r} \right) + 1.7 * 10^{-9} \left(\frac{1}{r} \right)^2 + 1.247 * 10^{-16} \left(\frac{1}{r} \right)^3 - 1.678 \right. \\ \left. * 10^{-23} \left(\frac{1}{r} \right)^4 + 4.83 * 10^{-31} \left(\frac{1}{r} \right)^5 \right]$
March 13 th , 2020 – Run No. 2	$r_0 E_c \left[4271 - 0.005868 \left(\frac{1}{r} \right) + 1.79 * 10^{-9} \left(\frac{1}{r} \right)^2 + 1.234 * 10^{-16} \left(\frac{1}{r} \right)^3 \right. \\ \left. - 1.755 * 10^{-23} \left(\frac{1}{r} \right)^4 + 5.205 * 10^{-31} \left(\frac{1}{r} \right)^5 \right]$
Modeled Flue Gas – 300 K	$r_0 E_c \left[5759 - 0.005991 \left(\frac{1}{r} \right) + 1.398 * 10^{-9} \left(\frac{1}{r} \right)^2 + 6.423 * 10^{-17} \left(\frac{1}{r} \right)^3 - 7.2 \right. \\ \left. * 10^{-24} \left(\frac{1}{r} \right)^4 + 1.617 * 10^{-31} \left(\frac{1}{r} \right)^5 \right]$
Modeled Flue Gas – 350 K	$r_0 E_c \left[4933 - 0.005988 \left(\frac{1}{r} \right) + 1.631 * 10^{-9} \left(\frac{1}{r} \right)^2 + 8.742 * 10^{-17} \left(\frac{1}{r} \right)^3 \right. \\ \left. - 1.143 * 10^{-23} \left(\frac{1}{r} \right)^4 + 2.995 * 10^{-31} \left(\frac{1}{r} \right)^5 \right]$
Modeled Flue Gas – 400 K	$r_0 E_c \left[4308 - 0.005977 \left(\frac{1}{r} \right) + 1.86 * 10^{-9} \left(\frac{1}{r} \right)^2 + 1.147 * 10^{-16} \left(\frac{1}{r} \right)^3 - 1.71 \right. \\ \left. * 10^{-23} \left(\frac{1}{r} \right)^4 + 5.118 * 10^{-31} \left(\frac{1}{r} \right)^5 \right]$

B.7 Equations for the Attachment Coefficient, β

The attachment coefficient is a parameter needed to calculate the electron number concentration in a corona discharge as shown in (Chen and Davidson 2002). Here, a set of 5th order equations have been fitted to the data provided by *BOLSIG+* (shown in Section B.5). The equations were fitted using *Mathematica 12* and have been expressed as a function of radial

distance. Similar to the data provided by *BOLSIG+*, the following equations are for a given gas composition and temperature, however have been further corrected for a specific pressure. The specific flue gas temperature, pressure and composition is listed in Table 3.3.

Table B.21. A list of the fitted equations based on *BOLSIG+* data.

Fitted Equations for the Attachment Coefficient, $\beta(r)$	
March 8 th , 2020	$r_0 E_c \left[-2048 + 0.003007 \left(\frac{1}{r} \right) - 8.6 * 10^{-10} \left(\frac{1}{r} \right)^2 + 1.089 * 10^{-16} \left(\frac{1}{r} \right)^3 \right. \\ \left. - 6.472 * 10^{-24} \left(\frac{1}{r} \right)^4 + 1.468 * 10^{-31} \left(\frac{1}{r} \right)^5 \right]$
March 13 th , 2020 – Run No. 1	$r_0 E_c \left[-1936 + 0.002805 \left(\frac{1}{r} \right) - 7.932 * 10^{-10} \left(\frac{1}{r} \right)^2 + 9.935 * 10^{-17} \left(\frac{1}{r} \right)^3 \right. \\ \left. - 5.842 * 10^{-24} \left(\frac{1}{r} \right)^4 + 1.311 * 10^{-31} \left(\frac{1}{r} \right)^5 \right]$
March 13 th , 2020 – Run No. 2	$r_0 E_c \left[-2016 + 0.003005 \left(\frac{1}{r} \right) - 8.719 * 10^{-10} \left(\frac{1}{r} \right)^2 + 1.12 * 10^{-16} \left(\frac{1}{r} \right)^3 \right. \\ \left. - 6.75 * 10^{-24} \left(\frac{1}{r} \right)^4 + 1.553 * 10^{-31} \left(\frac{1}{r} \right)^5 \right]$
Modeled Flue Gas – 300 K	$r_0 E_c \left[-2748 + 0.003085 \left(\frac{1}{r} \right) - 6.752 * 10^{-10} \left(\frac{1}{r} \right)^2 + 6.542 * 10^{-17} \left(\frac{1}{r} \right)^3 \right. \\ \left. - 2.975 * 10^{-24} \left(\frac{1}{r} \right)^4 + 5.163 * 10^{-32} \left(\frac{1}{r} \right)^5 \right]$
Modeled Flue Gas – 350 K	$r_0 E_c \left[-2352 + 0.003087 \left(\frac{1}{r} \right) - 7.888 * 10^{-10} \left(\frac{1}{r} \right)^2 + 8.922 * 10^{-17} \left(\frac{1}{r} \right)^3 \right. \\ \left. - 4.735 * 10^{-24} \left(\frac{1}{r} \right)^4 + 9.593 * 10^{-32} \left(\frac{1}{r} \right)^5 \right]$
Modeled Flue Gas – 400 K	$r_0 E_c \left[-2055 + 0.003087 \left(\frac{1}{r} \right) - 9.021 * 10^{-9} \left(\frac{1}{r} \right)^2 + 1.167 * 10^{-16} \left(\frac{1}{r} \right)^3 \right. \\ \left. - 7.08 * 10^{-24} \left(\frac{1}{r} \right)^4 + 1.639 * 10^{-31} \left(\frac{1}{r} \right)^5 \right]$

B.8 Equations for Electron Mobility, μ_e

Electron mobility is a parameter needed to calculate the electron number concentration in a corona discharge as shown in (Chen and Davidson 2002). Here, a set of 5th order equations have been fitted to the data provided by *BOLSIG+* (shown in Section B.5). The equations were fitted using *Mathematica 12* and have been expressed as a function of radial distance. Similar to the data provided by *BOLSIG+*, the following equations are for a given gas composition and temperature, however have been further corrected for a specific pressure. The specific flue gas temperature, pressure and composition is listed in Table 3.3.

Table B.22. A list of the fitted equations based on *BOLSIG+* data.

Fitted Equations for Electron Mobility, $\mu_e(r)$	
March 8 th , 2020	$r_0 E_c \left[0.09873 - 2.67 * 10^{-8} \left(\frac{1}{r} \right) + 6.419 * 10^{-15} \left(\frac{1}{r} \right)^2 - 8.05 * 10^{-22} \left(\frac{1}{r} \right)^3 \right. \\ \left. + 4.886 * 10^{-29} \left(\frac{1}{r} \right)^4 - 1.138 * 10^{-36} \left(\frac{1}{r} \right)^5 \right]$
March 13 th , 2020 – Run No. 1	$r_0 E_c \left[0.09766 - 2.633 * 10^{-8} \left(\frac{1}{r} \right) + 6.288 * 10^{-15} \left(\frac{1}{r} \right)^2 - 7.827 \right. \\ \left. * 10^{-22} \left(\frac{1}{r} \right)^3 + 4.712 * 10^{-29} \left(\frac{1}{r} \right)^4 - 1.088 * 10^{-36} \left(\frac{1}{r} \right)^4 \right]$
March 13 th , 2020 – Run No. 2	$r_0 E_c \left[0.09998 - 2.734 * 10^{-8} \left(\frac{1}{r} \right) + 6.654 * 10^{-15} \left(\frac{1}{r} \right)^2 - 8.455 \right. \\ \left. * 10^{-22} \left(\frac{1}{r} \right)^3 + 5.202 * 10^{-29} \left(\frac{1}{r} \right)^4 - 1.228 * 10^{-36} \left(\frac{1}{r} \right)^5 \right]$
Modeled Flue Gas – 300 K	$r_0 E_c \left[0.07619 - 1.593 * 10^{-8} \left(\frac{1}{r} \right) + 2.934 * 10^{-15} \left(\frac{1}{r} \right)^2 - 2.814 \right. \\ \left. * 10^{-22} \left(\frac{1}{r} \right)^3 + 1.306 * 10^{-29} \left(\frac{1}{r} \right)^4 - 2.324 * 10^{-37} \left(\frac{1}{r} \right)^5 \right]$

Table B.22 Continued

Modeled Flue Gas – 350 K	$r_0 E_c \left[0.08852 - 2.139 * 10^{-8} \left(\frac{1}{r} \right) + 4.575 * 10^{-15} \left(\frac{1}{r} \right)^2 - 5.105 \right.$ $\left. * 10^{-22} \left(\frac{1}{r} \right)^3 + 2.759 * 10^{-29} \left(\frac{1}{r} \right)^4 - 5.72 * 10^{-37} \left(\frac{1}{r} \right)^5 \right]$
Modeled Flue Gas – 400 K	$r_0 E_c \left[0.1009 - 2.771 * 10^{-8} \left(\frac{1}{r} \right) + 6.767 * 10^{-15} \left(\frac{1}{r} \right)^2 - 8.628 * 10^{-22} \left(\frac{1}{r} \right)^3 \right.$ $\left. + 5.328 * 10^{-29} \left(\frac{1}{r} \right)^4 - 1.263 * 10^{-36} \left(\frac{1}{r} \right)^5 \right]$

B.9 Equations for the Diffusion Coefficient, D_e

The diffusion coefficient is a parameter needed to calculate the electron number concentration in a corona discharge as shown in (Chen and Davidson 2002). Here, a set of 5th order equations have been fitted to the data provided by *BOLSIG+* (shown in Section B.5). The equations were fitted using *Mathematica 12* and have been expressed as a function of radial distance. Similar to the data provided by *BOLSIG+*, the following equations are for a given gas composition and temperature, however have been further corrected for a specific pressure. The specific flue gas temperature, pressure and composition is listed in Table 3.3.

Table B.23. A list of the fitted equations based on *BOLSIG+* data.

Fitted Equations for the Diffusion Coefficient, $D_e(r)$	
March 8 th , 2020	$r_0 E_c \left[-0.01454 + 1.131 * 10^{-7} \left(\frac{1}{r} \right) - 1.972 * 10^{-14} \left(\frac{1}{r} \right)^2 + 1.955 \right.$ $\left. * 10^{-21} \left(\frac{1}{r} \right)^3 - 9.678 * 10^{-29} \left(\frac{1}{r} \right)^4 + 1.884 * 10^{-36} \left(\frac{1}{r} \right)^5 \right]$
March 13 th , 2020 – Run No. 1	$r_0 E_c \left[-0.01021 + 1.067 * 10^{-7} \left(\frac{1}{r} \right) - 1.796 * 10^{-14} \left(\frac{1}{r} \right)^2 + 1.723 \right.$ $\left. * 10^{-21} \left(\frac{1}{r} \right)^3 - 8.239 * 10^{-29} \left(\frac{1}{r} \right)^4 + 1.547 * 10^{-36} \left(\frac{1}{r} \right)^4 \right]$

Table B.23 Continued

March 13th, 2020 – Run No. 2

$$r_0 E_c \left[-0.01437 + 1.161 * 10^{-7} \left(\frac{1}{r} \right) - 2.053 * 10^{-14} \left(\frac{1}{r} \right)^2 + 2.064 * 10^{-21} \left(\frac{1}{r} \right)^3 - 1.036 * 10^{-28} \left(\frac{1}{r} \right)^4 + 2.047 * 10^{-36} \left(\frac{1}{r} \right)^5 \right]$$

Modeled Flue Gas – 300 K

$$r_0 E_c \left[-0.01231 + 6.708 * 10^{-8} \left(\frac{1}{r} \right) - 9.015 * 10^{-15} \left(\frac{1}{r} \right)^2 + 6.886 * 10^{-22} \left(\frac{1}{r} \right)^3 - 2.627 * 10^{-29} \left(\frac{1}{r} \right)^4 + 3.942 * 10^{-37} \left(\frac{1}{r} \right)^5 \right]$$

Modeled Flue Gas – 350 K

$$r_0 E_c \left[-0.01416 + 9.133 * 10^{-8} \left(\frac{1}{r} \right) - 1.435 * 10^{-14} \left(\frac{1}{r} \right)^2 + 1.282 * 10^{-21} \left(\frac{1}{r} \right)^3 - 5.723 * 10^{-29} \left(\frac{1}{r} \right)^4 + 1.005 * 10^{-36} \left(\frac{1}{r} \right)^5 \right]$$

Modeled Flue Gas – 400 K

$$r_0 E_c \left[-0.01593 + 1.192 * 10^{-7} \left(\frac{1}{r} \right) - 2.142 * 10^{-14} \left(\frac{1}{r} \right)^2 + 2.188 * 10^{-21} \left(\frac{1}{r} \right)^3 - 1.117 * 10^{-28} \left(\frac{1}{r} \right)^4 + 2.245 * 10^{-36} \left(\frac{1}{r} \right)^5 \right]$$

B.10 Equations for the Mean Electron Energy, $\bar{\epsilon}$

The mean electron energy is a parameter needed to calculate the electron number concentration in a corona discharge as shown in (Chen and Davidson 2002). Here, a set of 5th order equations have been fitted to the data provided by *BOLSIG+* (shown in Section B.5). The equations were fitted using *Mathematica 12* and have been expressed as a function of radial distance. Similar to the data provided by *BOLSIG+*, the following equations are for a given gas composition and temperature, however have been further corrected for a specific pressure. The specific flue gas temperature, pressure and composition is listed in Table 3.3.

Table B.24. A list of the fitted equations based on *BOLSIG+* data.

Fitted Equations for the Mean Electron Energy, $\bar{\varepsilon}(r)$	
March 8 th , 2020	$r_0 E_c \left[-1.444 + 3.062 * 10^{-6} \left(\frac{1}{r} \right) - 4.727 * 10^{-13} \left(\frac{1}{r} \right)^2 + 4.699 * 10^{-20} \left(\frac{1}{r} \right)^3 \right. \\ \left. - 2.307 * 10^{-27} \left(\frac{1}{r} \right)^4 + 4.437 * 10^{-35} \left(\frac{1}{r} \right)^5 \right]$
March 13 th , 2020 – Run No. 1	$r_0 E_c \left[-1.405 + 2.979 * 10^{-6} \left(\frac{1}{r} \right) - 4.463 * 10^{-13} \left(\frac{1}{r} \right)^2 + 4.326 * 10^{-20} \left(\frac{1}{r} \right)^3 \right. \\ \left. - 2.069 * 10^{-27} \left(\frac{1}{r} \right)^4 + 3.874 * 10^{-35} \left(\frac{1}{r} \right)^5 \right]$
March 13 th , 2020 – Run No. 2	$r_0 E_c \left[-1.441 + 3.106 * 10^{-6} \left(\frac{1}{r} \right) - 4.875 * 10^{-13} \left(\frac{1}{r} \right)^2 + 4.935 * 10^{-20} \left(\frac{1}{r} \right)^3 \right. \\ \left. - 2.471 * 10^{-27} \left(\frac{1}{r} \right)^4 + 4.859 * 10^{-35} \left(\frac{1}{r} \right)^5 \right]$
Modeled Flue Gas – 300 K	$r_0 E_c \left[-1.462 + 2.359 * 10^{-6} \left(\frac{1}{r} \right) - 2.809 * 10^{-13} \left(\frac{1}{r} \right)^2 + 2.155 * 10^{-20} \left(\frac{1}{r} \right)^3 \right. \\ \left. - 8.181 * 10^{-28} \left(\frac{1}{r} \right)^4 + 1.218 * 10^{-35} \left(\frac{1}{r} \right)^5 \right]$
Modeled Flue Gas – 350 K	$r_0 E_c \left[-1.458 + 2.754 * 10^{-6} \left(\frac{1}{r} \right) - 3.835 * 10^{-13} \left(\frac{1}{r} \right)^2 + 3.441 * 10^{-20} \left(\frac{1}{r} \right)^3 \right. \\ \left. - 1.528 * 10^{-27} \left(\frac{1}{r} \right)^4 + 2.662 * 10^{-35} \left(\frac{1}{r} \right)^5 \right]$
Modeled Flue Gas – 400 K	$r_0 E_c \left[-1.45 + 3.142 * 10^{-6} \left(\frac{1}{r} \right) - 4.994 * 10^{-13} \left(\frac{1}{r} \right)^2 + 5.113 * 10^{-20} \left(\frac{1}{r} \right)^3 \right. \\ \left. - 2.588 * 10^{-27} \left(\frac{1}{r} \right)^4 + 5.136 * 10^{-35} \left(\frac{1}{r} \right)^5 \right]$

Appendix C: Model Program

The purpose of this appendix is to provide the computer program, developed in *Mathematica 12*, used for determining the emission rate of gaseous species including NO, NO₂, SO₂, HNO₃ and H₂SO₄ after flue gas has passed through an ESP. The ESP may be modeled as utilizing soft X-ray photoionization for additional particle charging. The code is located in the supplementary folder: NovelESP_Gaseous_Species_Formation. In this folder, two files are provided:

- BOLSIG Formatted data.xlsx
- NovelESP_Gaseous_Species_Formation.nb

To use the program, open NovelESP_Gaseous_Species_Formation.nb in *Mathematica* and provide the necessary user-defined inputs. These have been highlighted and an explanation of each variable has been provided in the file.