Quantification of gas and aerosol-phase piperazine emissions by FTIR under variable bench-scale absorber conditions

Steven M. Fulk\textsuperscript{a} and Gary T. Rochelle\textsuperscript{a*}

\textsuperscript{a}The University of Texas at Austin, Mcketta Department of Chemical Engineering, Texas Carbon Management Program, 200 E Dean Keeton St. Stop C0400, Austin, TX 78712-1589 USA

Abstract

Recent pilot-scale CO\textsubscript{2} capture plants have found that amine condensation onto seed nuclei results in very high amine emissions which are very difficult to characterize and control using traditional aerosol removal techniques. Modeling and experiments have shown significant potential to efficiently capture high density, submicron particles in packed columns by adjusting contactor operating conditions. This study presents the influence of operating conditions on total (gas and aerosol) emissions of piperazine (PZ) measured by hot-gas Fourier Transform Infrared Spectroscopy (FTIR) from a bench-scale CO\textsubscript{2} absorber with RSR-0.3 random packing using 0.9 m PZ. Aerosols were created by vaporizing and quickly condensing 0.5 m PZ and 0.05 vol % sulfuric acid (H\textsubscript{2}SO\textsubscript{4}). PZ was inversely proportional to solvent temperature and flowrate, but increased independent of the inlet CO\textsubscript{2} with PZ/H\textsubscript{2}O seed nuclei. PZ emissions were proportional to flowrate and inversely related to inlet CO\textsubscript{2} concentration for H\textsubscript{2}SO\textsubscript{4}/H\textsubscript{2}O condensation nuclei.

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* Corresponding author. Tel.: +1-512-471-7230; fax: +1-512-471-7060.
E-mail address: gtr@che.utexas.edu
1. Introduction

1.1. Emissions from CO₂ Capture Plants

Acid gas removal by absorption/stripping using aqueous amine solvents has been successfully used on an array of industrially relevant applications for many decades. Recently, amine scrubbing has been identified as a crucial piece of technology in the portfolio of CO₂ abatement strategies designed to address climate change. The simplicity of chemically reversible separation of CO₂ has led to significant and fruitful studies involving process optimization by selecting amine solvents which change the thermodynamic and hydraulic performance of the absorber and stripper unit operations in an effort mitigate the drawbacks of a direct-contact, thermal-swing system: energy performance, capital cost, and environmental impact. Proper characterization of solvent performance at the bench-scale has facilitated the construction of numerous thermodynamic and kinetic process models which provide the tools to accurately predict process performance and capital cost of many combinations of solvents and process configurations. However, the omission of pollutants from modeling activities and other complexities of real-life application of these systems can lead to severe degradation of performance, as well as unacceptable emissions by a variety of mechanisms.

Traditional aqueous solvents used to capture CO₂ are continuously exposed to contaminants in the incoming flue gas. In the case of post-combustion carbon capture (PCCC), those pollutants include gaseous combustion byproducts such as O₂ (3-5 vol %), SOₓ, NOₓ, and HCl, post-treatment slippage from selective catalytic reduction (NH₃), flue gas desulfurization (CaCO₃ and CaSO₄), and mercury removal (activated carbon), as well as particulate matter (PM) produced from sublimation of vaporous heavy metals, ash shedding, heterogeneous and homogeneous nucleation, and cenosphere/bursting mechanisms [1]. In addition to inlet impurities, continuous thermal cycling of solvent (40-150 ºC) during the capture/release steps serves to diminish performance through thermal degradation. Out of all the possible pathways for emissions to occur, recent works have identified amine aerosol as not only the dominant emission pathway, but one of the most difficult to measure and to control with wash columns or other conventional countermeasures.

1.2. Previous Aerosol Measurements

Amine-containing aerosols can originate from a variety of sources: physical entrainment of solvent, homogeneous nucleation of amine with other gaseous species, and heterogeneous nucleation/condensation on preformed nuclei such as hygroscopic PM, and most importantly, H₂SO₄ mist formed by reaction and subsequent condensation of SO₃ and H₂O. Several studies have quantified the impact of H₂SO₄ mist and PM on the loss rate of amine in addition to characterizing the particle size distributions and concentrations using a variety of measurement techniques.

A review of aerosol literature in PCCC pilot plants and at the bench-scale shows that very low levels of inlet SO₃ and soot/PM can create seed nuclei on the order of a few nanometers in size at very high densities (10⁵-10⁷ particles/cm³) which lead to excessive amine carryover in absorber exhaust [2, 3, 4]. Kamijo et al. show that 0-3 ppmv of SO₃ can produce 0.4-23.2 ppmv and 0.8-67.5 ppmv for KS-1™ and MEA solvents, respectively [5]. High amine emissions due to aerosol carryover was also confirmed during CO₂ capture tests at Maasvlakte where detailed characterization of the particle phase was attempted using a combination of light extinction measurements, an Aerodynamic Particle Sizer (APS), an Electrical Low Pressure Impactor (ELPI), and the installation of a high efficiency droplet capture device called the Brownian Demister Unit (BDU) [6, 7]. The Sauter mean droplet diameter (D₃₂) at the top of the absorption tower before to the BDU was reported to be 0.76-7.88 μm and decreased to 0.2-1.74 μm at the BDU outlet.

A more recent set of papers from Brachert, Mertens, and Khakharia detailing collaborative aerosol studies at the Karlsruhe Institute of Technology (KIT) clearly verified the direct influence of H₂SO₄ mist as well as soot/PM on the amine slippage rate while providing both inlet and outlet droplet size distribution measurements using the extractive ELPI sampling technique and a condensation particle counter (CPC) in combination with FTIR. Most importantly, it was found that soot concentrations of 10⁶ particles/cm³ and H₂SO₄ mist at a density of 10⁸ particles/cm³ resulted in 200 (74) and 600-1100 (223-409) mg/Nm³ (ppmv) of MEA emissions, respectively [3],
and that the average seed nuclei grew from a few nanometers entering the absorber to nearly 1 \( \mu \text{m} \) at the outlet [2, 4]. Droplet growth was further verified by changing the dilution rate to the ELPI sampling train and observing the shifting size distribution.

Aerosol measurements from pilot plants and smaller-scale tests thus far have demonstrated the clear need to reduce PCCC emissions resulting from inlet condensation nuclei. Though many solutions currently exist, including high density fiber filters and inertial separation methods, the associated pressure drop likely precludes their use in full-scale CO\(_2\) capture facilities. Research in this area must find more cost-effective strategies of capturing aerosols in CO\(_2\) capture units.

### 1.3. Aerosol Abatement by Growth and Capture

Several aerosol researchers have pointed to efficient aerosol removal in packed columns by heterogeneous nucleation (condensation) [8, 9, 10]. By effectively selecting operating conditions, they argue, and experimentally confirm, that high degrees of supersaturation can be achieved which can “activate” aerosol growth and subsequent capture in randomly packed columns. The degree of supersaturation, and the influence of operating conditions, is characterized by the ratio of heat and mass transfer rates, given by the Lewis number. Heidenreich and co-authors demonstrated that high concentrations (10\(^6\) particles/cm\(^3\)) of submicron particles of variable starting composition can be efficiently collected using a two-stage cascade counter-current contactor by increasing the temperature difference between the inlet fluids. In PCCC research, previous modeling of heat and mass transfer of aerosols in CO\(_2\) capture systems have arrived at similar conclusions [11]. It was theorized that by altering the operating conditions or design of the CO\(_2\) capture plant, aerosol capture may be facilitated by condensational growth or evaporative shrinking. Cascaded column designs to remove aerosols through growth conditioning could be readily incorporated into existing water wash towers.

Pilot plant measurements done by Mertens et al. have found similarly conclusive, quantitative linkages between operation of CO\(_2\) capture plants and amine emissions [12]. In the study by Mertens and colleagues, MEA, PZ, and 2-amino-2-methyl-1-propanol (AMP), were measured using FTIR, flame ionization detection (FID), and a manual sampling technique employing a combination of impingers and adsorbents under different steady-state operating conditions. The study showed that amine emissions were positively correlated to the temperature difference across the water wash and negatively correlated to the inlet CO\(_2\) concentration. Their conclusions indicate a strong influence of enthalpy on emissions; however, complex interactions of reaction enthalpy and solvent vapor pressure depression due to CO\(_2\) loading.

The imbalance in rates of heat and mass transfer leads to greater supersaturation in gas-liquid contactors. The creation of supersaturation through influential operation handles can lead to emissions reductions strategies without resorting to costly countermeasures.

### 1.4. Work Objectives

This work seeks to reduce gaseous and amine aerosol emissions from CO\(_2\) capture plants using aqueous amine solvents by investigating the influential process factors including: (1) inlet CO\(_2\) content, (2) solvent flowrate, and (3) inlet solvent temperature. A newly constructed apparatus capable of simulating CO\(_2\) capture using a dilute PZ solvent in the presence of aerosols will be presented. Gas-phase FTIR measurements will clearly demonstrate the effect of operating conditions, most notably the solvent rate, on PZ emissions. The findings of this work can further facilitate better emission reduction strategies from PCCC systems.

### 2. Experimental Methods

An experimental apparatus, analogous to a randomly packed amine-based CO\(_2\) absorber, was constructed with the capability of generating and measuring aerosols as well as performing simultaneous gas-phase composition measurements at multiple sampling points under variable process conditions relevant to CO\(_2\) capture absorbers and water wash columns. Figure 1 shows a simplified process flow diagram of the experimental apparatus.
2.1. Aerosol Growth Column (AGC)

The absorber column built for this study, referred to as the AGC, is a randomly packed CO₂ absorber with a temperature controlled, recirculated solvent.

The inlet gas is made up of a mixture of N₂, taken from a large dewar, and Bone dry, Gr. 3.0 CO₂ (Airgas® CDBD200) regulated using a Y11-N245D320, CGA320 regulator. The N₂ supply is split following an isolation valve into three streams used for the absorber gas supply, the LVI gas supply, and FTIR maintenance, background, and calibration. The N₂ flowrate to the absorber is controlled by an analog 100 SLPM Brooks 5851 I-Series mass-flow controller connected to an NI 9265 4-ch, 20 mA current output module and an NI 9203 8-ch, 20 mA current input module. Connection is made with a 15 pin D-Sub cable at the controller side and crimp pin connections at the NI module side. The NI modules are connected to a cDAQ-9174 USB chassis which is controlled by a user-built LabVIEW™ application with interactive GUI via a laptop and USB 2.0 connection. The flowrate of CO₂ is controlled by a 15 SLPM Brooks 5850 I-Series mass-flow controller using the same NI modules and chassis.

The N₂/CO₂ gas stream is bubbled through a presaturator to approximately maintain H₂O balance within the absorber column. The presaturator for the AGC is constructed of 6” 304SS Sch. 10 pipe with #150 flanges. Temperature is controlled with a screw-plug immersion heater with a relayed temperature controller. The head-space temperature is logged with a separate K-type thermocouple connected to a 4-ch ± 80 mV NI-9211 module. The inlet gas is sparged into the presaturator by a 3/8” straight tube with small drilled holes. The total liquid height in the saturator is maintained at over 20”.

Figure 1: Process flow diagram of the Aerosol Growth Column (AGC), the Liquid Vaporizer and Injector (LVI) aerosol generator, and FTIR sampling system.
A hot gas mixture delivered by the LVI is mixed with the saturated process gas at the outlet of the presaturator in a 3/4” stainless steel tee fitting. Rapid cooling downstream of the LVI/process gas mixing point produces homogenous nuclei prior to entering the absorber column. The aerosol carrying gas is introduced into a flanged tee at the bottom of the column below the packing supports.

The absorption section of the AGC is constructed out of a 1½” 304SS Sch. 10 pipe with flanged ends. Removable lugs and a mesh screen support up to 6’ of packing. The packing used in this study was RSR-0.3 random packing.

Solvent is drawn from a 16 gal SS tight-head drum (The Cary Company 26B6SS) by a Micropump® A-mount suction shoe pump head controlled by a Cole Parmer Console Drive. The flowrate is measured by a rotameter (Omega FL46302). The inlet solvent temperature is controlled by cross exchange with recirculated H2O provided by a Lauda ECO E4G temperature bath. The cross exchanger is a Thermal Transfer Systems AN14-20H plate-and-frame heat exchanger. Solvent is delivered above the packing using hollow-cone spray nozzles (Kyser and Associates 1/4A-316SS2 & 1/4A-316SS-5) connected to a tapped blind flange. The solvent temperature is measured at the flange using a K-type thermocouple. CO2-rich liquid drains through a 1” inner diameter (ID) gravity drain line back into the solvent tank.

The inlet and outlet gas composition can be sampled and analyzed by FTIR using the Process Sampling Unit (PSU) and heated stream switcher. The PSU consists of a heated filter and a heated Teflon® diaphragm pump. The heated stream switcher is a heated enclosure with 3-way valves which can alternately sample up to three FTIR locations. FTIR sample points are constructed from 3/4” threaded pipe tees reduced to 1/4” tubing connection using reducer bushings and Swagelok® adapters. FTIR connections are always insulated using glass wool and connections made to the process are heat-traced with heat tape controlled by AC Variable Autotransformers (variac). Variacs are typically set to 35% of full voltage (120V).

Outlet gas from the absorber runs through a counter-current, pipe-and-tube condenser fed with cooling water to knock out H2O and amine. The cooled gas leaving the exchanger is sent to a 2” pipe tee to reduce the velocity such that condensate and large entrained droplets will be collected and drain to the condensate collection point located at the bottom of the column.

A liquid sampling port consisting of a 3/8” Swagelok® tee with a 12.7 mm OD RESTEK® BTO Septa is located at the inlet of the solvent pump. Liquid samples are drawn using a 2 mL syringe and are transferred to 4 mL (1 dr.) amber vials for subsequent analysis.

2.2. Liquid Vaporizer and Injector (LVI)

The LVI was designed by Air Quality Analytical, Inc. to produce H2SO4 aerosol up to 5 ppmv in a 350 ACFM (pilot-scale) gas stream. The LVI blends hot gas (310 °C) with a metered stream (FMI RH00 pump and FMI VS200 controller) of liquid in an eductor (Air-VAC HAVR062HSS) body. The flowrate of the eductor motive fluid (N2) is controlled by a pressure regulator and is measured using a rotameter adjusted for the supply pressure of 100 psig.

The vaporized material is introduced into the cold, main process gas stream where condensation occurs. Given a high enough supersaturation level, the vaporized liquid should form small, homogeneous aerosol nuclei.

The LVI controls and liquid reservoir (500 mL G45 amber bottle) are contained in a Hoffman 19” x 16” x 14” enclosure. The eductor, air preheater, and tubing are housed in a Wigman 10” x 8” x 4” steel enclosure with a 3/8” 316SS bulkhead outlet fitting. The Wigman enclosure is stuffed with several layers of internal closed-cell silicone foam insulation. The power, control, pressure, and liquid lines between the two enclosures are wrapped in a 15’ woven umbilical line.

2.3. Analytical methods

2.3.1. FTIR

Low resolution FTIR is a powerful quantification tool used to measure species concentrations in the gas or vapor phase. Individual components are distinguished by their absorption of light over a range of particular wavenumbers in the mid-infrared (IR) region (500-4000 cm⁻¹). IR absorption causes molecular vibrations and rotations which are
unique to the structure and bond strength of a particular molecule. IR absorption bands can be used in combination with the Beer-Lambert law to quantify individual species present in complex, multicomponent sample matrices. Absorption is assumed to be proportional to concentration; reference (calibration) spectra for each individual component are multiplied by a scalar and summed across the measured IR range to reproduce the gross spectra measured by the FTIR.

The specific hardware used in this work is the Gasmet™ DX4000 portable FTIR spectrometer. The path length is 5 m and the wavenumber resolution is 8 cm\(^{-1}\). Peripheral equipment including heated sample lines, the heated stream switcher, and the PSU is maintained at 180 °C to prevent condensation during transport and analysis. Calcmet™ software is used for chemometric analysis. Compensations for pressure and temperature on the total gas concentration are made using the onboard cell sensors.

Sample flow is kept at 2-12 SLPM by the PSU connected to the inlet of the FTIR cell. The flowrate to the FTIR optical purge line is kept at 0.1 SLPM by a pressure regulator and a Bird Precision critical orifice (0.004” ID).

Table 1 displays the analysis regions used in this work.

<table>
<thead>
<tr>
<th>Component</th>
<th>Range 1 (cm(^{-1}))</th>
<th>Range 2 (cm(^{-1}))</th>
<th>Range 3 (cm(^{-1}))</th>
<th># of Ref. Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>2475 - 2600</td>
<td>3050 - 3375</td>
<td>--</td>
<td>7</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>910 - 1015</td>
<td>2165 - 2240</td>
<td>2550 - 2750</td>
<td>6</td>
</tr>
<tr>
<td>PZ</td>
<td>2475 - 2540</td>
<td>2680 - 2900</td>
<td>--</td>
<td>11</td>
</tr>
</tbody>
</table>

3. Results and Discussion

The solvent used in this study was gravimetrically prepared by mixing 3 kg of PZ with 10 gallons of tap H\(_2\)O to produce a roughly 0.9-1.0 molal (m, moles/kg H\(_2\)O) solution. The initial solvent PZ concentration and CO\(_2\) loading produced an initial P\(_{CO2}\) of 110.4 ppmv and P\(_{PZ}\) of 2.8 ppmv at 40 °C as measured by FTIR.

The following section details total PZ emissions measurements at the AGC outlet under variable conditions using the solvent described above in the presence of injected aerosol.

3.1. Aerosol Injection and Emissions

The LVI affords a unique opportunity to study aerosols of various starting composition. Liquid solutions containing semi-volatile, and low-volatility species can be vaporized and recondensed as homogeneous aerosols provided a large enough supersaturation during cooling and mixing with the process gas. The LVI also allows for tracers to be added to the aerosol phase such that the partitioning between the gas, droplet, and solvent can be measured.

In this work, two different LVI solutions were used to create inlet aerosol: (1) 0.5 m PZ and (2) 0.05 vol % H\(_2\)SO\(_4\). The LVI N\(_2\) flowrate for all experiments was 1.035 SCFM produced by an eductor inlet pressure of 60 psig which created a vacuum level of 20 in Hg at the eductor suction. The LVI liquid flowrate was set to 1.0 mL/min for all cases. Table 2 shows the composition produced for both the PZ and H\(_2\)SO\(_4\) aerosol cases. These streams were mixed with a constant process gas flowrate of 20 SLPM that was saturated to H\(_2\)O at 40 ± 1 °C.

The presaturator and inlet solvent temperature was set to 40 °C throughout all experiments, even when the solvent temperature was increased.

Reported inlet CO\(_2\) concentrations are calculated by summing the output of the N\(_2\) and CO\(_2\) mass-flow controller outputs, adjusting for H\(_2\)O assuming saturation at the measured presaturator head-space temperature using DIPPR correlations [13], and renormalized to the total flowrate produced by mixing the LVI and saturated process gas. No condensation between the LVI/process gas mixing point and the inlet of the absorber was assumed because no appreciable liquid was ever observed in that line experimentally.
Table 2: LVI composition produced using 0.5 m PZ and 0.05 vol % H₂SO₄, respectively. The LVI product gas is mixed with the process gas (20 SLPM) which is saturated to H₂O at 40 °C.

<table>
<thead>
<tr>
<th>Component</th>
<th>Unit</th>
<th>PZ Aerosol</th>
<th>H₂SO₄ Aerosol</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>vol %</td>
<td>95.7</td>
<td>95.6</td>
</tr>
<tr>
<td>H₂O</td>
<td>vol %</td>
<td>4.3</td>
<td>4.4</td>
</tr>
<tr>
<td>PZ</td>
<td>ppmv</td>
<td>383</td>
<td>--</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>ppmv</td>
<td>--</td>
<td>7.5</td>
</tr>
</tbody>
</table>

3.1.1. Effect of inlet CO₂

The inlet CO₂ concentration was varied between 0-8 vol % during both the PZ and H₂SO₄ aerosol experiments. Figure 2 and Figure 3 show inlet CO₂, outlet CO₂, H₂O, and PZ, and the solvent flowrate. The steady state PZ concentration for the PZ and H₂SO₄ aerosol case was 50-75 and 5-7 ppmv, respectively. The dashed gray lines indicate when the LVI pump was either connected (LVI On) or disconnected (LVI Off). The dead volume in the LVI liquid line causes a response lag of about 3 minutes.

At a solvent rate of 12 GPH and 4 vol % inlet CO₂, PZ jumped from 50 to 100 ppmv for the PZ aerosol case. Further increases in CO₂ concentration appear to cause very small relative differences in outlet PZ measured during PZ aerosol injection. The large, CO₂ concentration independent change in PZ may be attributable to changes in the nucleation environment where an acid (CO₂) and a base (PZ) can fully react and condense in a humid environment. Alternatively, the low concentration of PZ in the solvent may not be supplying sufficient vapor pressure to create large enough saturation changes to cause observable aerosol growth even with the exothermic absorption of CO₂ increasing the solvent temperature. High solvent rates of 6-18 GPH, corresponding to a liquid-to-gas ratio (L/G) of 9.5-28.4 mol/mol, would also dampen any temperature bulging, and consequently saturation changes in the column.

Under identical conditions, but with H₂SO₄ injection, PZ shows less clear behavior. Though PZ initially increases by about 17% as CO₂ is increased from 0 to 4 vol %, an additional doubling of CO₂ to 8 vol % causes a 17% decrease in PZ. Once the solvent flowrate and CO₂ concentrations are lowered from 12 to 6 GPH and 8 to 4 vol %, respectively, outlet PZ increased from 3.5 to 5.5 ppmv. When the inlet CO₂ is turned off, PZ returns to the baseline of 6 ppmv.

Amine emissions respond to the inlet CO₂ concentration depending on the nuclei composition. FTIR measurements showed a near doubling of the outlet PZ when CO₂ was introduced into the AGC for PZ seed nuclei; aerosols produced from H₂SO₄ did not exhibit this behavior. However, emissions do appear to be inversely proportional to CO₂, though the absolute change was quite small in these tests. The predicted effect of CO₂ on aerosol growth is likely dampened under these conditions, i.e., high solvent rates and low solvent concentrations. Further exploration using a more concentrated solvent and lower L/G is required.

3.1.2. Effect of L/G

L/G was varied in this study between 9.5-57.0 mol/mol. Figure 4 and Figure 5 show the effect of L/G changes independent of inlet CO₂ concentrations for the PZ and H₂SO₄ aerosol cases, respectively.
Figure 2: Absorber outlet emissions under PZ aerosol load in response to changing solvent flowrate and inlet CO₂ concentration. Outlet PZ increases sharply with CO₂, but is not correlated to the concentration. PZ is inversely related to solvent rate. Inlet solvent T is 40 °C.

Figure 3: Absorber outlet emissions under H₂SO₄ aerosol load in response to changing solvent flowrate and inlet CO₂ concentration. Outlet PZ shows a weak, inverse correlation to CO₂ concentration and is positively correlated to solvent flowrate. Inlet solvent T is 40 °C.
Figure 4: Absorber outlet emissions under PZ aerosol load in response to changing solvent flowrate. Outlet PZ is inversely proportional to the solvent rate. L/G varies from 9.5-57.0 mol/mol. Inlet solvent T is 40 °C.

Figure 5: Absorber outlet emissions under H₂SO₄ aerosol load in response to changing solvent flowrate. Outlet PZ is proportional to the solvent rate. L/G varies from 9.5-57.0 mol/mol. Inlet solvent T is 40 °C.
Stepwise decrease in solvent rate significantly reduces the outlet PZ measured during PZ aerosol injection experiments. Figure 4 shows that PZ decreases in a proportional fashion. Though this behavior was seen during the variable CO₂ experiments, the degree of reduction in PZ is not nearly as high. A mass balance using the LVI and process gas compositions leads to a total (gas and aerosol) PZ concentration of 231 ppmv. Since the baseline PZ measured at the AGC outlet is 50-75 ppmv, the AGC column is absorbing PZ, as well as possibly capturing PZ-containing aerosol with an efficiency of 67.5-78.4%. It is therefore possible that increasing the solvent rate provides more absorption capacity and greater collection of PZ. In the case of the CO₂ experiment (Figure 2), PZ is not scrubbed with such high efficiency when the solvent rate is increased. CO₂ may be serving to sequester PZ inside the aerosols through reaction. Modeling work has shown that for even conservative CO₂ absorption rates, the absorption rate of CO₂ into amine-containing aerosols is very fast and that the aerosol phase is at a much higher CO₂ loading than the solvent, and therefore has a much lower P*PZ than the solvent. Fast reaction of CO₂, be it during nucleation or upon entering into the absorber, would prevent favorable partitioning of PZ towards the solvent. The CO₂ rich aerosol would then only respond to very large changes in driving forces created by CO₂ absorption at very low liquid rates, or large temperature differences between the inlet gas and liquid.

Figure 5 shows that H₂SO₄ aerosol has opposite behavior compared to PZ aerosols on varying the inlet solvent rate, though the measurement is less clean. Creation of supersaturation might explain the inverse relationship between solvent rate and PZ emissions. The inlet gas is about a 1.5:1 mixture of gases at 310 and 40 °C that cools due to heat loss in the system prior to entering the absorber; therefore, it is expected that the inlet gas temperature is higher than the inlet solvent at 40 °C. If the solvent temperature is raised, then the temperature difference across the column is minimized. Conversely, if the flowrate of the colder solvent is increased, the temperature gradient would be steeper, and cause higher degrees of supersaturation, and consequently more aerosol growth.

L/G affects outlet PZ emissions to a much higher degree than CO₂ for both aerosol cases investigated. Without size distribution measurements of the aerosols, differentiation of absorption and aerosol behavior is nearly impossible, though comparing the H₂O curves to that of PZ does provide some perspective. The outlet FTIR measurement, in the absence of aerosol generation, closely approximates saturated solvent conditions. The variability in these measurements is atypical of system control and heater oscillations. Further, the near parallel behavior of H₂O and PZ indicates that the majority of the measured PZ is in the aerosol phase.

3.1.3. Effect of temperature

The final operation variable explored in this study was the inlet solvent temperature. The temperature was increased from 40 to 50 °C without changing the solvent flowrate and in the absence of CO₂.

Figure 6 and Figure 7 show the change in outlet PZ for the PZ and H₂SO₄ aerosol cases, respectively. PZ emissions dropped by 20% for the PZ aerosol case; distinct trends for the H₂SO₄ aerosols are indistinguishable. Increasing the solvent temperature decreases PZ absorption in the solvent as well as reducing the temperature gradient across the AGC. The PZ absorption or solvent washing and the supersaturation or aerosol growth mechanisms should influence the outlet PZ in opposing directions. Looking back at Figure 4, the H₂O curve increases with solvent flowrate, which would be consistent with the aerosol growth mechanism, but then decreases at higher flowrates, which is consistent with the absorption mechanism. It is possible that both mechanisms are occurring simultaneously, or in the best case, are starting to be captured in the packing.

Results at the time of this study are inconclusive on the effect of solvent temperature on outlet emissions. Particle size distribution measurements are needed to make valid conclusions.
Figure 6: Absorber outlet emissions under PZ aerosol load in response to changing the solvent inlet temperature from 40 to 50 °C. Outlet PZ is inversely proportional to the solvent temperature.

Figure 7: Absorber outlet emissions under H₂SO₄ aerosol load in response to changing the solvent inlet temperature from 40 to 50 °C.
4. Conclusions

A new experimental apparatus was constructed to measure the effects of operating conditions of CO₂ absorbers using aqueous amine solvents on total (aerosol and gas-phase) emissions. Inlet aerosols of variable (0.5 m PZ and 0.05 vol % H₂SO₄) composition were generated by vaporizing a metered liquid stream kept at 1 mL/min sucked through an eductor by a preheated (310 °C) motive N₂ stream at 1.035 SCFM. The solvent flowrate (6-36 GPH), inlet CO₂ concentration (0-8 vol %), and the inlet solvent temperature (40 and 50 °C) were changed independently and the outlet PZ concentration was measured using FTIR.

The baseline outlet gas CO₂ and PZ concentrations relative to the solvent (0.9 m PZ) flowing at 12 GPH was 110.4 and 2.8 ppmv, respectively. Injection of PZ and H₂SO₄ aerosols increased the outlet PZ value to 65 and 6.5 ppmv, respectively.

Increasing the inlet concentration of CO₂ to 4 vol % doubled the measured PZ in the exhaust gas under PZ aerosol load; however, further increase of CO₂ produced very minor relative changes. PZ seems to be inversely related to inlet CO₂ concentration in the case of H₂SO₄ aerosols.

Changes to the solvent flowrate had far greater impact on the exhaust rate of amine. PZ decreased from 75 to 20 ppmv when the solvent rate was reduced from 36 to 6 gpm for the PZ aerosol case in the presence of no inlet CO₂. Solvent rate was found to have the opposite behavior for the H₂SO₄ aerosol case; PZ emissions increased from 6 to 20 ppmv as the solvent rate was increased from 6-36 GPH. Similar behavior was found during multivariable (CO₂ and flowrate) studies, though the absolute changes in measured PZ were much smaller.

Finally, PZ emissions were found to have a reciprocal relationship to inlet solvent temperature for the PZ aerosol case. No clear trend was observed during H₂SO₄ aerosol testing.

Future experiments with higher solvent concentrations should increase the effect of CO₂ interaction with the droplet phase, leading to cleaner distinction of the effects of solvent rate and inlet gas composition. The addition of droplet size analysis and particle counting will allow separation of total emissions into their respective phase contributions.

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