

Anthropogenic Emissions and the Future of Our Atmosphere:

- I. *Cyclohexanol Chemistry and Aerosol Formation in an
Environmental Chamber*
- II. *K₂CO₃-Based Sorbent Development and Testing in a
Packed Bed Reactor for CO₂ Capture*

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The logo for the California Institute of Technology (Caltech), featuring the word "Caltech" in a bold, orange, sans-serif font.

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A b s t r a c t

STUDYING AND MITIGATING ANTHROPOGENIC EMISSIONS

In all human history there has not been a more essential scientific -and political- endeavor than the prevention of the commencing climate catastrophe. Without swift and aggressive intervention, the upcoming century will see dramatic consequences for air quality, food security, and the habitability of entire regions across the globe. Because of the scale and complexity of the crisis, effective climate action must be multifaceted. A non-exhaustive list includes: support and development of green energy to replace combustion fuels, removal and storage of emitted or ambient carbon, reforestation, reducing energy consumption, monitoring and predicting emissions, and then regulation of said emissions. This dissertation contributes work to two of these key areas; monitoring and predicting emissions (Chapter 1) as well as carbon removal from the atmosphere (Chapters 2-4).

Chapter 1 presents experimental studies conducted in an environmental chamber, alongside mechanistic modeling, to quantify aerosol formation from the gas-phase pollutant cyclohexanol. While greenhouse gases like carbon dioxide and methane typically receive the most attention in climate modeling and global monitoring, atmospheric particles also play a critical role in Earth's radiative balance by absorbing and scattering light. Studies on black and brown carbon atmospheric aerosol (so named due to their strong absorption of visible light) indicate they contribute significantly to the global radiative budget, making them of growing interest to climate modelers. A specific class of these particles, secondary organic aerosols (SOA), forms in the atmosphere via the condensation of aged gas-phase emissions. Studies like this one quantify aerosol forming potential with the goal of informing and guiding regulatory policies. Solvents and chemical feed stocks, for example, with large aerosol forming potential should be more carefully stored to prevent evaporation or even replaced with analogous compounds. And unlike greenhouse gases, aerosol have short atmospheric lifetimes which means that proper regulation could result in almost immediate cooling effects once old brown aerosol rain or deposit out. In short, identifying gas-phase pollutants that result in SOA formation will enable faster phase-out of

problematic species from industrial and commercial processes, which if enacted will quickly improve global radiative budgets.

While Chapter 1 focuses on particulate emission prediction to assist in regulation, the following chapters explore novel methods to capture carbon dioxide, the largest single contributor to radiative forcing. Chapter 2 describes the construction and characterization of a mini-industrial scale packed-bed reactor, loaded with K_2CO_3 -impregnated particles for CO_2 capture. Chapters 3 and 4 describe the formulation of durable high-capacity K_2CO_3 -based sorbents using wet activated granulation and extrusion spheronization, respectively. These works were performed to assist in making point source capture economically feasible. While regulation of gas and particle phase emissions is critical to decelerate current heating trends, international infrastructures and energy networks are not prepared for complete decoupling from combustion yet. Thus, in the short-term future, it is necessary to develop supportive technologies that can remove combusted CO_2 from exhaust streams before they are emitted. While the sorbents studied in Chapters 3 and 4 are intended to be used in a point source capture system, like the reactor constructed in Chapter 2, given their favorable properties, K_2CO_3 sorbents also hold promise for deployment in ambient air capture systems.

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Chapter 1

CYCLOHEXANOL OXIDATION AND AEROSOL MASS YIELD

1.1 Abstract

Quantifying individual Volatile Chemical Product (VCP) contributions to urban aerosol poses a great challenge due to their diverse sources and chemical structures. In this work, cyclohexanol chemistry and aerosol mass yield when oxidized by OH in the presence of varying concentrations of NO is examined. Cyclohexanol + OH is determined to have $k_{298} = 1.79 (\pm 0.26) 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, and a cyclohexanone yield of 0.53. NO is found to decrease aerosol forming potential of oxidative products. Under no-NO_x conditions we determined a mass yield (MY) as high as 23(1)%, while under the highest NO_x environment studied here, we determined a wall-loss corrected MY of 13(1)%. These values, which are higher than measured and predicted MY of similar 6-carbon species, indicates the importance of functionalization, and interaction between functional groups (and not just carbon number), on aerosol forming potential.

1.2 Introduction

1.2.1 VOCs and Urban Air Pollution

A growing portion of urban aerosol, in particular secondary organic aerosol, SOA, is sourced from a category of anthropogenic emissions known as volatile chemical products, VCPs.¹ VCPs are a subclass of volatile organic compounds, VOC, that are unique in that they are used, most often as solvents, in everyday household items. These compounds, which can be found in consumer goods like paints, beauty or cleaning products evaporate at varying rates depending on their volatility and use and are then oxidized in the atmosphere.^{2,3} Once oxidized, their product molecules can potentially decrease in vapor pressure (assuming no significant fragmentation has occurred) and condense forming nascent particles, or adhere unto preexisting aerosol surfaces.⁴ A simplified oxidation model for VOCs is presented in Figure 1.1.

The importance of studying urban SOA produced via VCP oxidation is threefold; Firstly, the particles themselves impact human health through deposition into our lungs. High

aerosol exposure in urban regions is responsible for increased mortality and morbidity due to cardiovascular and respiratory diseases.^{5,6} Secondly, oxidation of VOCs in the presence of NO_x, a common pollutant in urban air, results in the formation of tropospheric ozone. Ozone is itself a respiratory irritant, and like SOA can result in increased morbidity due to illness like asthma and pneumonia.^{7,8} Lastly, the effect of SOA on the global radiative budget is of great uncertainty. SOA can impact radiative forcing directly through absorption of light and indirectly by impacting cloud formation by acting as cloud condensation nuclei.⁹ For these reasons, estimating VCP contributions to urban SOA is critical to regulate pollution according to human health and global climate. Unfortunately, predicting VCP contributions to aerosol mass is challenging because they vary greatly in carbon number and functionalization. To date, hundreds of VCPs have been identified, but cost and complexity of laboratory measurements limit the number of molecules that have yet been and will be studied.¹

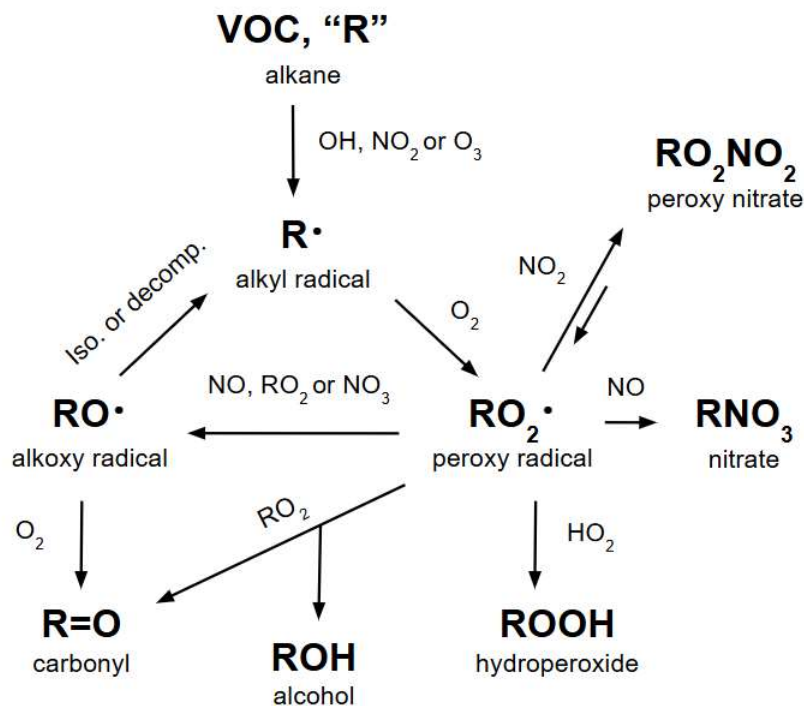


Figure 1.1 displays a general VOC oxidation model. Diagram is adapted from Kroll and Seinfeld.⁴ A generic VOC (alkane) undergoes an H abstraction with an atmospheric oxidant, most commonly OH, to form an alkyl radical. The alkyl radical quickly reacts with O₂ to form a peroxy radical which then reacts with itself or another peroxy radical (RO₂), HO₂, NO or NO₂.

Most of our knowledge about VCP SOA formation result from laboratory data on fundamental compounds. From these data, chemical trends have been identified to help guide predictions. O:C ratio, vapor pressure, and carbon number of the parent molecules have been noted as some of the most critical guiding factors and have even been used as basis sets for aerosol models.¹⁰⁻¹² Aerosol forming potential or mass yield, MY, (new aerosol mass divided by VCP mass reacted) has been found to increase with carbon number, and for simple alkanes ringed and linear isomers have higher potential than branched.¹³ Figure 1.2 displays mass yield as a function of carbon number for linear alkanes.¹⁰ The effect of functional groups on MY has been studied to some extent, but it is challenging to draw general conclusions.^{13,14} Inclusion of functional groups to a carbon backbone enhance MY by decreasing initial vapor pressure, however do make the structure more vulnerable to fragmentation. Identity of the functional group and its location on the molecule have variable outcome on molecule fragmentation.

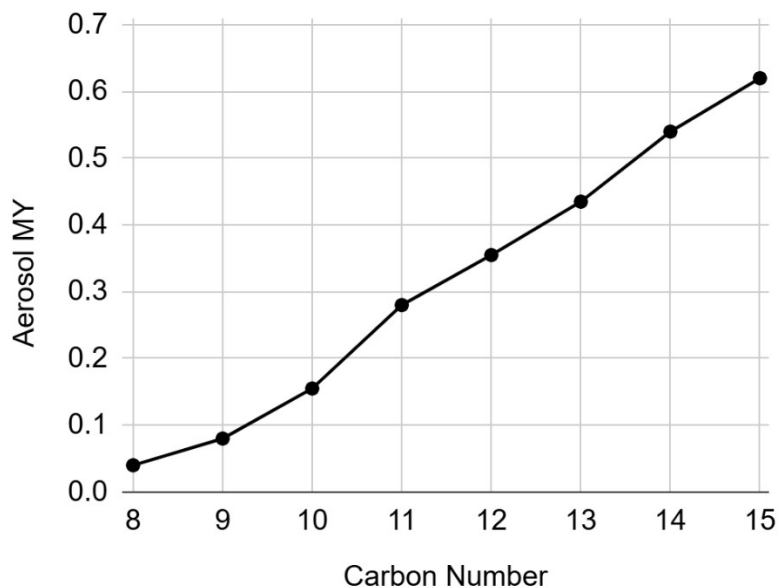


Figure 1.2 displays how carbon number can be used to predict aerosol mass yield for linear alkanes. The black dots display measured values under high-NO_x conditions.

Cyclohexane's (C=6) mass yield is so low that it is not depicted. As carbon number increases so does aerosol mass yield, in a near linear manner. Thus, carbon number is often considered one of the most important characteristics in determining a VOC's mass yield. Figure is adapted from Cappa and Wilson.¹⁰

1.2.2 Cyclohexanol Sources and Significance

Cyclohexanol $\text{HOCH}(\text{CH}_2)_5$ is a clear, viscous liquid at room temperature synthesized via cyclohexane oxidation or hydrogenation of phenol. The primary uses for cyclohexanol is as a chemical feedstock in the formation of larger more complex organic molecules, such as nylon. Unreacted cyclohexanol is also used as a solvent in lacquers and varnishes and a solvent in soaps and detergents.

Cyclohexanol ambient measurements are minimal, which is not unexpected due to the novel nature of VOC and VCP chemistry and the abundance of molecules needing study. A few air quality measurements have been included this VCP and its primary oxidative product, cyclohexanone.^{2,3,15,16} While outdoor detections and measurements may exist, we were only able to find indoor measurements performed on homes,³ newspaper stands,¹⁶ from carpets,² and inside neonatal incubators¹⁵ where they were detected in the 1-10 ppb range. Given its presence in adhesives and paints, it would be reasonable to expect cyclohexanol in any indoor environment, especially newly remodeled homes. Currently, cyclohexanol is estimated to be a small fraction of global VOC emissions, 0.03%.¹ While this means it may not currently contribute hugely to outdoor SOA, it still has the ability to impact indoor air quality greatly due to its abundant use.

Cyclohexanol emissions, especially outdoors, may grow in coming years due to changes in our fuel economy. Depletion of non-renewable fossil fuel stores has galvanized advances in biofuel research. Biofuels come from many sources, including both agricultural and industrial waste, and typically require mixing with other reactants to optimize combustion conditions. Compared to other additives, cyclohexanol has a high energy density, results in shorter ignition delay times and overall assists in creating a neater burn.^{13,17-19} These characteristics make cyclohexanol a desirable biofuel additive. Since biofuels are being considered in the context of a world which wishes to reduce anthropogenic pollution, it is important to also consider how increased cyclohexanol emissions might impact air quality.

1.2.3 Previous Work

To date, no other laboratory measurements have been made regarding MY of cyclohexanol. The OH + cyclohexanol reaction rate has been measured, 1.9 and 2.7×10^{-11} molec cm⁻³,^{20,21} and some products have been identified during oxidation in the presence of NO_x, including an around 50% yield of primary product cyclohexanone.²⁰ Currently, it appears that understanding of the oxidation mechanism of OH + cyclohexanol, especially in the absence of NO_x, is incomplete. The Leeds Master Chemical Mechanism (MCM 3.3) offers an abundance of insight into many chemical mechanisms and can be exported to create kinetic models. In the case of cyclohexanol, the structure activity relationship (SAR) method used to predict its mechanism does not strongly agree with laboratory work, predicting cyclohexanone yield to be only 26% when laboratory results predict 50%.²²

Without laboratory data on the MY of cyclohexanol, the best substitute currently is using intuition and modeling. McDonald et al. used a multigenerational oxidation model that uses statistics to mimic oxidation, functionalization, and decomposition of parent molecules.¹⁰ Using this model assuming high NO conditions and utilizing vapor pressure to predict partitioning into the aerosol phase, they calculated a MY of 2.2%. In this work, we further examine the OH-cyclohexanol oxidation mechanism and evaluate the VCP's aerosol forming potential. To do this, we utilize laboratory MY measurements in an atmospheric chamber, which are interpreted with a kinetic model.

1.3 Methods

1.3.1 Chamber and Instrument Descriptions

All experiments were performed in one of two hanging atmospheric chambers. These chambers and instruments have been utilized in several works, so will only be briefly described here.^{23–26} The chambers, whose walls are composed of fluorinated ethylene propylene (FEP) Teflon, are designed to minimize gas and particle loss to the chamber. While cyclohexanol and cyclohexanone loss to the chamber walls were not observed, particles do deposit on the wall's surface. Corrections for particle wall-loss are discussed in more detail later. Both chambers are temperature controlled and about 18 m³, but one was designated a NO_x-free chamber to minimize trial-to-trial contamination. In addition, each chamber was flushed with filtered air for at least 24 hours between trials.

Aside from particle deposition, another large source of error is the volume change of the chamber due to gas-phase and particle sampling. To minimize error introduced by sampling perturbation, product identification and MY measurements were conducted separately. Product identification of VOC oxidation utilized a chemical ionization mass spectrometer (CIMS) which happens to require the largest sampling rate. In addition to product identification and MY measurements, relative rate measurements were also performed to determine the OH + cyclohexanol rate constant at room temperature. The specific details for each individual trial are listed in Table 1.1.

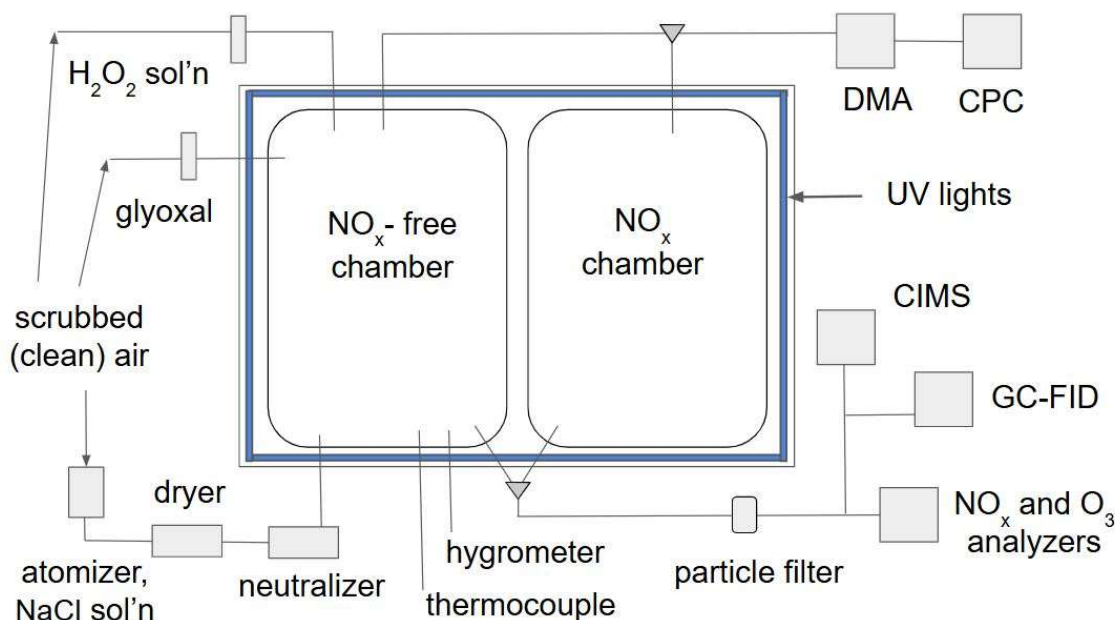


Figure 1.3 displays the two Teflon chamber bags hanging in their UV-lit room. The bags have Teflon-tube ports which allow for controlled injection of gas and particle species as well as gas and particle sampling. While there are other elements connected to these chambers, for example a clean air injection and exhaust port, only those relevant to understanding our experiments are depicted here. Instruments shown include a Scanning Mobility Particle Sizer (SMPS) which is made up of a differential mobility analyzer (DMA) and condensation particle counter (CPC), the NO_x and O₃ monitors, a Gas Chromatograph with Flame Ionization Detection (GC-FID) and the Chemical Ionization Mass Spectrometer (CIMS).

Table 1.1.1 All laboratory experiments.

Trial	Date	VOC(s) Used	[VOC] _i (ppb) ^a	Experiment Type ^b	[NO] _i (ppb)	SA _f ^c (10 ³ μm ² cm ⁻³)	N _f ^c (10 ⁴ cm ⁻³)	V _f ^c (10 ³ μm ³ cm ⁻³)	Length ^d (hrs)
1	10/27/22	cyclohexanol, butanol	-	R.R.	0	0	0	0	3
2	1/8/23	cyclohexanol, n-butanol	-	R.R.	0	0	0	0	3
3	10/25/22	cyclohexane	230	MY	110	1.99 ± 0.04	2.21 ± 0.08	103 ± 2	17
4	9/8/22	cyclohexanol	410	Product ID	0	0	0	0	9
5	8/15/22	cyclohexanol	430	Product ID	80	0	0	0	5
6	7/22/22	cyclohexanol	190	MY	0	1.49 ± 0.01	0.97 ± 0.01	85 ± 1	18
7	7/25/22	cyclohexanol	220	MY	30	2.19 ± 0.03	1.36 ± 0.04	129 ± 2	17
8	7/27/22	cyclohexanol	260	MY	75	1.41 ± 0.05	0.92 ± 0.01	76 ± 3	18.5
9	7/23/22	cyclohexanol	230	MY	120	1.80 ± 0.01	1.07 ± 0.01	108 ± 1	20

^a butanol and n-butanol were not calibrated. R.R. method only requires relative peak intensities. ^b R.R. = relative rate, MY = mass yield experiment, Product ID = product identification experiment. ^c (NH₄)₂SO₄ seed particles were injected for MY experiments prior to oxidation initiation. The 6-sample average seed surface area (SA), particle number (N) and volume (V) immediately before oxidation are provided. ^d The trial length for MY experiments is much longer than R.R and Product ID. It was determined that cyclohexanol and cyclohexane require over 15 hours of oxidation before their MY stabilizes and can be reported.

To mimic photo-oxidative conditions of the atmosphere, broadband UV lights are fitted on the walls of the room in which the chambers reside. For all experiments, H_2O_2 acted as our OH source. Recently measured H_2O_2 and NO_2 photolysis rates of $4.7\text{E-}6$ and $6.2\text{E-}3 \text{ s}^{-1}$ were used to check the validity of measured NO_x concentrations and calculated OH concentrations from our kinetic model. Both the VOC and H_2O_2 were injected by passing N_2 at a rate of 5 L min^{-1} over the sample. For all trials VOCs were injected from a 3-port glass piece with glass wool inside. The glass wool increases injection efficiency of these viscous compounds by increasing surface area. All VOC injections, for all 3 trial types, were $50 \mu\text{L}$ or less, resulting in total VOC chamber concentrations of around 500 ppb. In each trial $200 \mu\text{L}$ of H_2O_2 was heated lightly at 40°C in a water bath to assist evaporation. For NO-containing trials, a ppm-level Airgas mixture was introduced into the chamber at a rate of 5 L min^{-1} until the desired concentration was measured on the Nitrogen Oxide Analyzer.

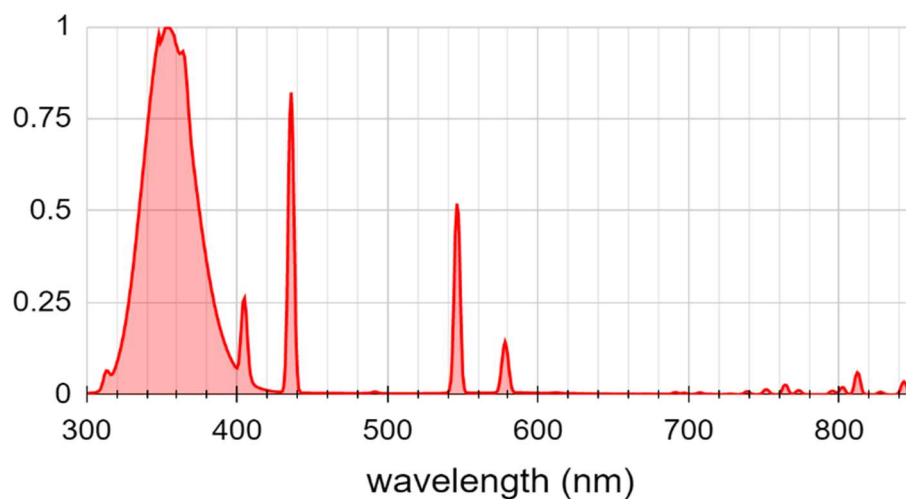


Figure 1.4 displays the intensity spectrum of the atmospheric chamber lights. It can be observed that the most intense light is observed between 300 and 400 nm, a region known to photolyze many atmospheric molecules including NO_3 , NO_2 , and O_3 . This region of light is also responsible for the photolysis of H_2O_2 , our OH source.

In our study three different types of experiments were performed: relative rate trials (RR), product Identification trials (Product ID), and Mass Yield (MY) trials. For rate measurements only the VOCs and OH-source are necessary. Both the VOC and H_2O_2 were injected by passing N_2 at a rate of 5 L/min over the sample. For all trials VOCs were

injected from a 3-port glass piece with glass wool inside. The glass wool increases injection efficiency of these viscous compounds by increasing surface area. All VOC injections, for all 3 trial types, were 50 μL or less resulting in total VOC chamber concentrations of around 500 ppb. In each trial 200 μL of H_2O_2 was heated lightly at 40 $^\circ\text{C}$ in a water bath to assist evaporation. For NO-containing trials, a 100 ppm Airgas mixture in N_2 was introduced into the chamber at a rate of 5 L/min until the desired concentration was measured on the Nitrogen Oxide Analyzer.

For MY trials, a surface for organic matter to condense is necessary. It should be noted that some VOCs when oxidized, can generate seed particles of their own. This was not the case for the compounds studied here, and thus ammonium sulfate particles seeded our experiments. To form these seeds, a 0.06M $(\text{NH}_4)_2\text{SO}_4$ solution was aerosolized, dried, and charge-conditioned with a TSI Model 3088 soft X-ray neutralizer. Figure 1.5 depicts aerosol seed preparation.

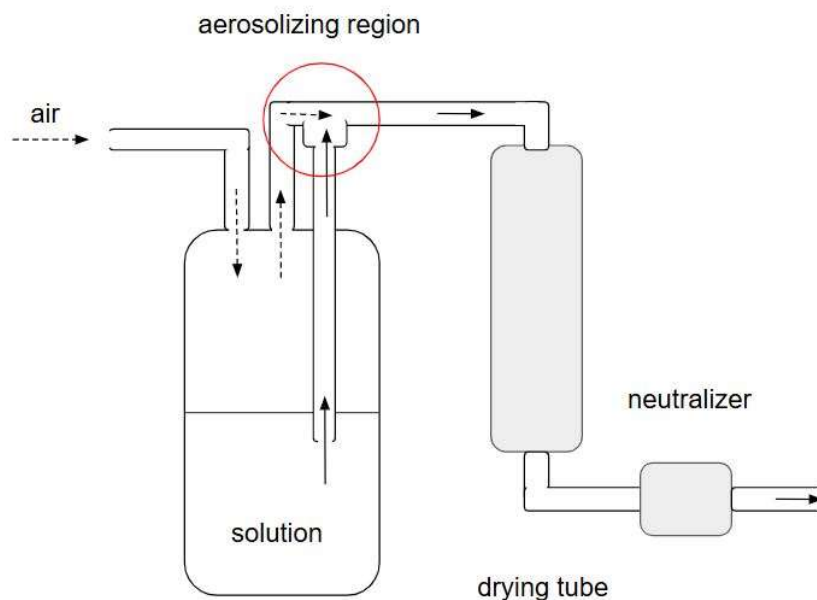


Figure 1.5 depicts how ammonium sulfate seeds are generated from the aqueous solution. Pressurized clean air is blown into the atomizer creating a negative pressure region circled in red. The aqueous solution is then drawn up and met by the air channel. The stream of wet newly formed particles is dried and charge neutralized before it is injected into the chamber.

As noted above, several instruments were utilized to sample the gas and particle phases. For RR trials, only GC-FID monitoring was required to observe decay of cyclohexanol and reference molecules. In all other trials, NO and NO₂ concentrations were monitored via model T200 Teledyne nitrogen oxide analyzer (NO_x Analyzer) while O₃ was monitored via Horiba ambient monitor. For MY trials, particle concentration and size distribution were monitored via scanning mobility particle sizer (SMPS). To minimize chamber-volume loss from sampling, product ID trials were conducted separately from MY trials, and included use of a chemical ionization mass spectrometer (CIMS).

The CIMS used for product identification has been described in previous publications,²⁷ but will be briefly described here. Our chemical ion source, which has been utilized in other atmospheric studies, is CF₃OOCF₃. The compound, which is produced on site and stored in a small metal gas regulator, is diluted with N₂ gas sent through the cylindrical ion source cup which is lined with Polonium-210. The polonium acts as an alpha particle source which collides with N₂, which then emits an electron. The CF₃OOCF₃ acquires this electron and resultantly splits into radical CF₃O•, and our chemical ion, CF₃O⁻. These reactions are described by 1-3.

1. $^{210}\text{Po} \rightarrow \alpha + ^{206}\text{Pb}$
2. $\alpha + \text{N}_2 \rightarrow \alpha + \text{N}_2^+ + \text{e}^-$
3. $\text{e}^- + \text{CF}_3\text{OOCF}_3 \rightarrow \text{CF}_3\text{O}^- + \text{CF}_3\text{O}^\bullet$

CF₃O⁻ has been observed to generally bind to strong and weak acids. The ion has become popular for atmospheric studies for its ability to detect hydroperoxides, an important highly oxidative product from HO_x chemistry, but a challenge to many atmospheric sampling methods. In this work, CF₃O⁻ is used to detect many cyclohexanol oxidative products, including hydroperoxides, alcohols, and nitrates. Unfortunately, products with only ketone or aldehyde groups do not efficiently bind to the ion making some of our products, including the primary ring-opening product 1,6 hexanal undetectable.

GC-FID was primarily used to monitor cyclohexanol concentration (though it was also used for cyclohexane and reference molecules) in the gas phase throughout trials. As it turns out, cyclohexanol does indeed bind with our chemical ion and is observable at m/z 185 and 119. However, m/z 119 is not usable as it also displays signal from CF₃O⁻*H₂O₂

clusters. Upon oxidation of the sample, a product is also observed mass 185, obscuring the cyclohexanol decay curve. The GC-FID was thus determined to be a more appropriate method than the CIMS for monitoring cyclohexanol concentration throughout trials.

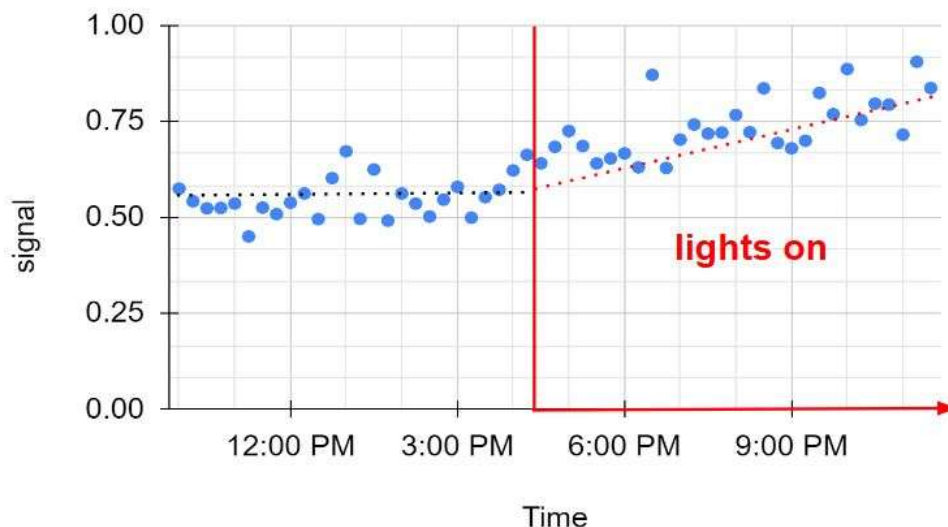


Figure 1.6 shows the raw signal from the CIMS at m/z 185 before and after oxidation of a cyclohexanol sample. m/z 185 signal before photolysis can be assumed to be solely from cyclohexanol ($100\ m/z$) binding to the primary ion, CF_3O^+ ($85\ m/z$). When the lights are turned on, instead of signal decreasing due cyclohexanol reaction with OH it increases due to formation of some oxidative product.

The unmodified portion of the GC-FID is equipped with a HP-5 column (5%-Phenyl methylpolysiloxane, 30m x 0.32mm x 0.25um), which is generally meant for non-polar molecules. It should be noted that this column is not ideal for polar molecules, like cyclohexanol, and its oxidative products. Unfortunately, other measurements were being performed on the environmental chamber at this time and necessitated a dually compatible column. The unideal column choice did not prevent detection or quantification but resulted in poorer chromatography. Polar molecules tend to bleed and produce what is called a “tail” on non-polar columns. This problem can be mitigated by careful integration; being sure to include the entire “tail.” As this GC was designed for small, discrete, liquid samples, the inlet was modified for continuous sampling from the chamber. A 10 mL sized tube of chamber air acts as the “sample” which is injected into the column. Since the sample must be fresh, this 10 mL tube always has chamber air running through it. When the GC is

already running a sample or is preparing to take the sample, the tube flows directly into an exhaust port. When the GC is ready to take the sample, a valve is switched, and the tube is disconnected from the exhaust and connected to the inlet. This system requires a 6-valve system, that has two arrangements depicted in Figure 1.7, one for when the sample is being injected, and one when it is not.

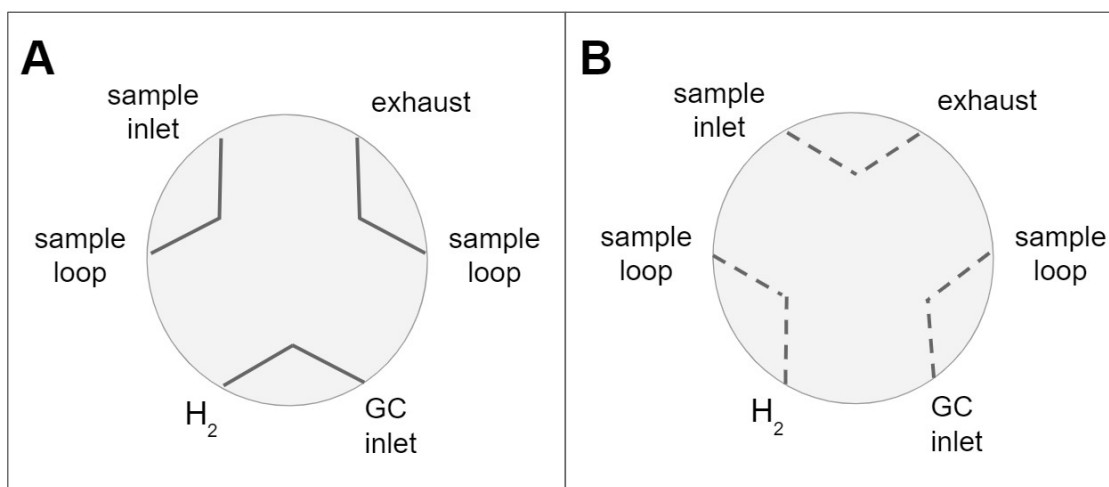


Figure 1.7 depicts the modified inlet of the GC-FID. The inlet is a 6-way valve which at any time is in one of two configurations, A or B. Configuration A is the default in which the sample pulled from the bag (sample inlet) goes straight through the sample loop and into the exhaust. In configuration A only the H_2 gas runs through the GC column. When the GC is prepared to take a sample the valve switches to configuration B and the gas contained in the sample loop closes, mixes with H_2 , and is run through the GC.

The SMPS, which measures our aerosol size distribution, is formed from a 308100 TSI differential mobility analyzer (DMA) and a TSI 3010 condensation particle counter (CPC). The DMA only allows particles within a particular size bin to the exit stream. This stream is then flown into the butanol CPC, which detects and counts the particles by measuring scattered light as the particles are individually passed through a light beam. Because scattering increases with size, the size-selected particles which exit the DMA are grown via butanol condensation in the CPC before they are counted. This minimizes accidental non-detection of smaller particles. To determine the entire aerosol size distribution, the DMA is scanned across all relevant size bins.

1.3.2 Relative Rate Measurements

Due to a discrepancy in the cyclohexanol + OH reaction, we measured this value via relative rate method. The relative rate method states that for cyclohexanol and a reference compound (assuming the only losses are from reaction with OH) the following holds true:

If cyclohexanol and the reference only react with OH via

4. OH + cyclohexanol $\rightarrow$ products
5. OH + reference $\rightarrow$ products

Then the following is true

$$6. \quad \ln \frac{[c-hexol]_0}{[c-hexol]_t} = \frac{k_y}{k_z} \ln \frac{[reference]_0}{[reference]_t}$$

Thus, for a reference compound with a well-known rate constant k_z , k_y can be determined from the slope of the log-log plot. Cyclohexanol and reference compound concentrations were monitored via GC-FID. While it is possible to determine the exact concentration of the reference compound, only the peak area (PA) is truly necessary as the concentration will be the PA multiplied by some scaling factor and is lost in the log-fraction.

1.3.3 Cyclohexanone Branching Fraction

In addition to measuring the cyclohexanol rate constant, we also measured the cyclohexanone forming branching fraction of the cyclohexanol rate constant.

If the only reactions impacting the cyclohexanone concentration are

7. OH + chexol $\rightarrow$ products
8. OH + chexone $\rightarrow$ products

Then the cyclohexanone rate equation is defined below

$$9. \quad \frac{d[chexo]_t}{dt} = k_a \varphi [OH]_t [chexol]_t - k_b [chexone]_t [OH]_t$$

Where φ is the chexone yield, k_a is the cyclohexanol + OH rate constant and k_b is the cyclohexanone + OH rate constant. Both the cyclohexanol and cyclohexanone reaction rates with OH have been measured. While the cyclohexanone measurements are in decent

agreement, cyclohexanol measurements are limited and in poorer agreement. For this reason, we used our own measured rate, presented in the results section.

To assist us in evaluating φ , we need the $[OH]_t$ profiles. We do not have a direct measurement of OH concentration, however we are able to calculate these from the cyclohexanol decay curves. We know that, assuming only OH reacts with cyclohexanol,

$$10. \quad \frac{d[chexo]_t}{dt} = -k_a[OH]_t[chexol]_t$$

We have the time dependent cyclohexanol concentration from the GC data. The cyclohexanol decay curve can be described as an exponential function dependent on $[OH]$. If $[OH]$ in the chamber is also time dependent, then the following relationship can be utilized.

$$11. \quad [chexol]_t = Ae^{-k_a[OH]_t}$$

To make fitting simpler, we will take the log-log plot of the cyclohexanol data,

$$12. \quad \ln[chexol]_t = \ln[A] - k_a[OH]_t$$

The log-log plot can then be easily fit to a polynomial function to determine the slowly varying concentration of $[OH]$ in the chamber during trials. Once we determine $[OH]_t$ for the trials, we see when referring to equation c) that we have values for every variable except for φ . We can then utilize our chemical model code (explained Kinetic Model section) and adjust φ until the modeled data most resembles the experimental data.

Table 1.2. Measured rate constants for OH reactions.

reactions	rate measurements (molecules cm ⁻³)
chexol + OH + O ₂ ^a	1.9x10 ⁻¹¹ , Bradley <i>et al.</i> 2001; 2.7x10 ⁻¹¹ , Berndt <i>et al.</i> 2003
chexone + OH + O ₂ ^b	6.1x10 ⁻¹² , Berndt <i>et al.</i> 2003; 6.5x10 ⁻¹² , Dagaut <i>et al.</i> 1988; 5.35x10 ⁻¹² , Aschmann <i>et al.</i> 2011; 6.36x10 ⁻¹² , Liu <i>et al.</i> 2019

^anote there is about a factor of 2 disagreement between these measurements

^bAll four measurements are in good agreement

1.3.4 Calibrations

Cyclohexanol and cyclohexane concentrations were monitored via GC-FID with a D-5 column. Cyclohexanol and cyclohexane concentrations were needed to determine their respective mass yields under the conditions provided in table 1.1. Cyclohexanone was also monitored on the GC-FID to determine cyclohexanone yield in the oxidation of cyclohexanol, assuming the same sensitivity as cyclohexanol. To calibrate the signal intensities, gas phase samples of the molecules at around 50 ppm, were measured by Fourier transform infrared absorption spectroscopy (19 cm pathlength) using absorption cross sections measured by Pacific Northwest National Laboratory (PNNL). These samples were then diluted with N₂ via flow cell to ambient level concentrations before entering the GC. The dilution cell depicted below was constructed because in small vessels low concentrations of these VOCs (< 1 ppm) appeared to slowly form a phase equilibrium in high surface area containers, complicating measurements.

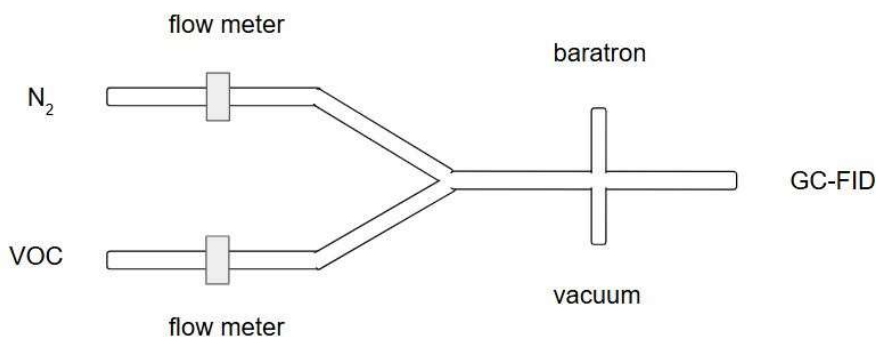


Figure 1.8 shows how 50 ppm VOC samples were diluted for calibration on the GC-FID. Flow meters controlled the flow rates of VOC and N₂. The GC-FID samples at a very small flow rate so excess volume were purged via wall vacuum. The pressure was monitored via baratron to ensure the sample entering the GC-FID remained ~1atm.

1.3.5 Mass Yield Calculations

Aerosol MY, γ , is mass formed divided by the VOC mass, reacted and is unitless. Aerosol mass measurement is not done directly but instead is determined by multiplying the observed volume change, ΔV , by an (often theoretical) particle density, ρ . ΔV is monitored through SMPS (seed volume is subtracted), and Δm_t of the VOC was monitored by GC-

FID. while Aerosol density was not measured in this study, and for our calculations was assumed to be 1.4 g cm^{-3} .²⁸

$$13. \quad \gamma_t = \frac{\rho \Delta V_t}{\Delta m_t}$$

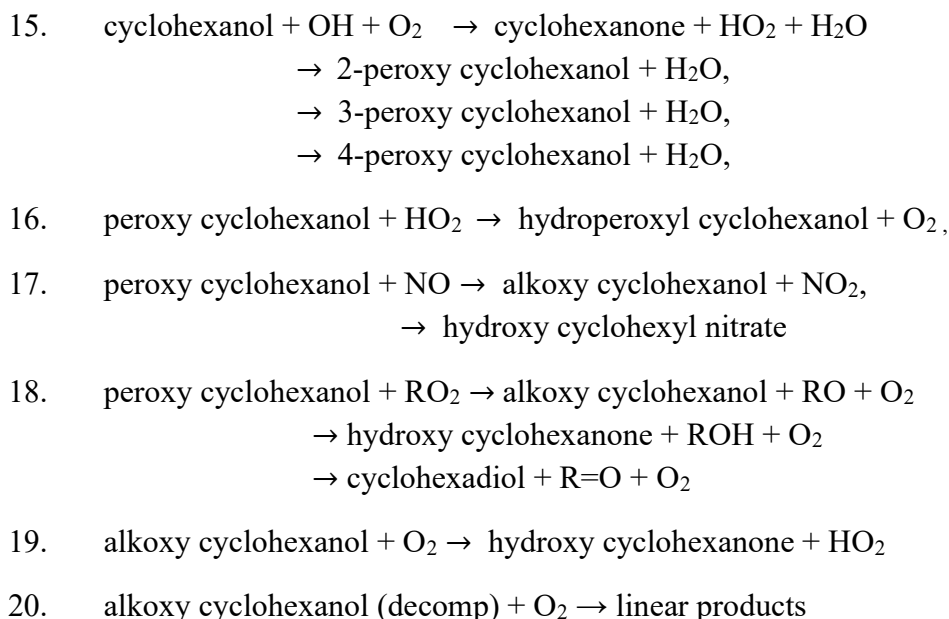
As it takes some time for VOC to oxidize, it is important to allow the system appropriate time for the MY to stabilize. Depending on $[\text{OH}]_t$ in the chamber, as well as the rate constants of the VOC and its products, stabilization can take many hours. Over these lengths of experiments, particle loss due to deposition on the wall, “wall-loss,” is substantial and must be accounted for. Wall-loss corrections were done utilizing protocol and code established by Charan et al 2018.^{23,25,29} In short, the code creates a correction function based off loss statistics from an hour-long pre-reaction period performed before each trial. Theoretically, the particle number concentration varies according to equation (23), where D_p is the particle diameter (measured by the SMPS), $\partial n(D_p, t)$ is the number concentration profile, and $\beta(D_p)$ is called the particle wall deposition coefficient.

$$14. \quad \left(\frac{\partial n(D_p, t)}{\partial t} \right) = -\beta(D_p) \cdot \partial n(D_p, t)$$

$\beta(D_p)$ is dependent on the chamber charge, $\bar{E}$, the chamber eddy diffusion coefficient k_e , Brownian diffusivity of the particles, and the chamber size. It was determined by Charan et al that under standard conditions, it can be assumed that these particular chambers have no charge, i.e. $\bar{E} = 0 \text{ V cm}^{-1}$.²⁹ This was attributed to the fact that these chambers are fully suspended and do not touch any surfaces.²³ k_e , which corresponds to chamber turbulence, was set to 0.005 s^{-1} . The “goodness of fit” for k_e was determined by plotting the pre-reaction period particle population with the correction, varying k_e . A plot with an ideal fit would be perfectly flat (no change in particle volume). For these calculations, it was also assumed that particles that deposit on the wall no longer act as seeds to condensing gas-phase products.

1.3.6 Kinetic Model

To create a kinetic model, it was first necessary to develop an oxidative mechanism (with multiple product generations). Current literature of the oxidative mechanism for the



We see that from just this first oxidation step, many distinct products are formed. The system complexity grows even larger in the chamber, as the first-generation products will continue to react, becoming either larger from additions of oxidative groups or decompose into smaller fragments. Understanding the formation rate of the alkoxy radical, and knowing its resultant fate, are critical to understanding parent-molecule decomposition. To assist in this goal, prior work on analogous molecules were used to predict the second and third generation products in this system, and fill out a more complete chemical mechanism to be inserted into a kinetic model.³⁰

The OH site-dependent abstractions of cyclohexanol and cyclohexanone were derived from the experimental works of Bradley *et al.*, Ceacero-Vega *et al.*, and Aschmann *et al.*^{20,31} Bradley *et al.* unfortunately observed over 100% product yield, so the branching fraction had to be estimated from their results. Their site-dependent OH-yields based on observed product concentrations were reported to be 55, 32, 31, and 8% respectively for the α , β , γ , and δ sites. The α , β , γ , and δ site abstractions result in products P1, and I1-I3 in Figure 1.9. While it may make sense to simply scale each number down equally, Ceacero-Vega *et al.* also measured the cyclohexanone forming path (α -abstraction) of about 55%. This indicates that the 55% should not be adjusted as it was verified by another group. The other values were scaled down to 19, 19 and 7%. It seems likely from the work of Bradley *et al.* that (despite some issues with measuring product concentrations), the other abstractions rates are dominated by symmetry. Put simply, the δ site observes less attack because the other two sites are symmetrically redundant. A similar effect is noted in the reaction of cyclohexanone by Aschmann *et al.* They note that in linear ketones H-atom abstraction from the β -carbon is enhanced due to formation of a hydrogen-bonded transition state. This transition state is not available to the ring-locked cyclohexanone thus simple structure-activity relationships suggest another branching distribution guided by symmetry, i.e. 40, 40 and 20%. The over-all rate constants measured for these two reactions are available in Table 1.2.

While little other mechanistic work is available for cyclohexanol, a lot can be learned from analogous systems. For example, since we are interested in the NO branching fraction of the cyclohexyl peroxy radicals, cyclohexane and cyclohexene are important systems to consider. When cyclohexene reacts with OH, instead of an abstraction it adds to the double bond, forming the ortho-cyclohexanol radical, shown in Figure 1.12. This resultantly reacts with O₂ to quickly form the ortho-cyclohexanol peroxy radical. Aschmann *et al.* studied OH-addition to cyclohexene under high NO conditions (minimizing any RO₂ + RO₂ and RO₂ + HO₂ reaction) to isolate NO + RO₂ chemistry. In this system, they attempted to detect evidence of the 6-membered ring alkoxy radical isomerization depicted in Figure 1.12.³²

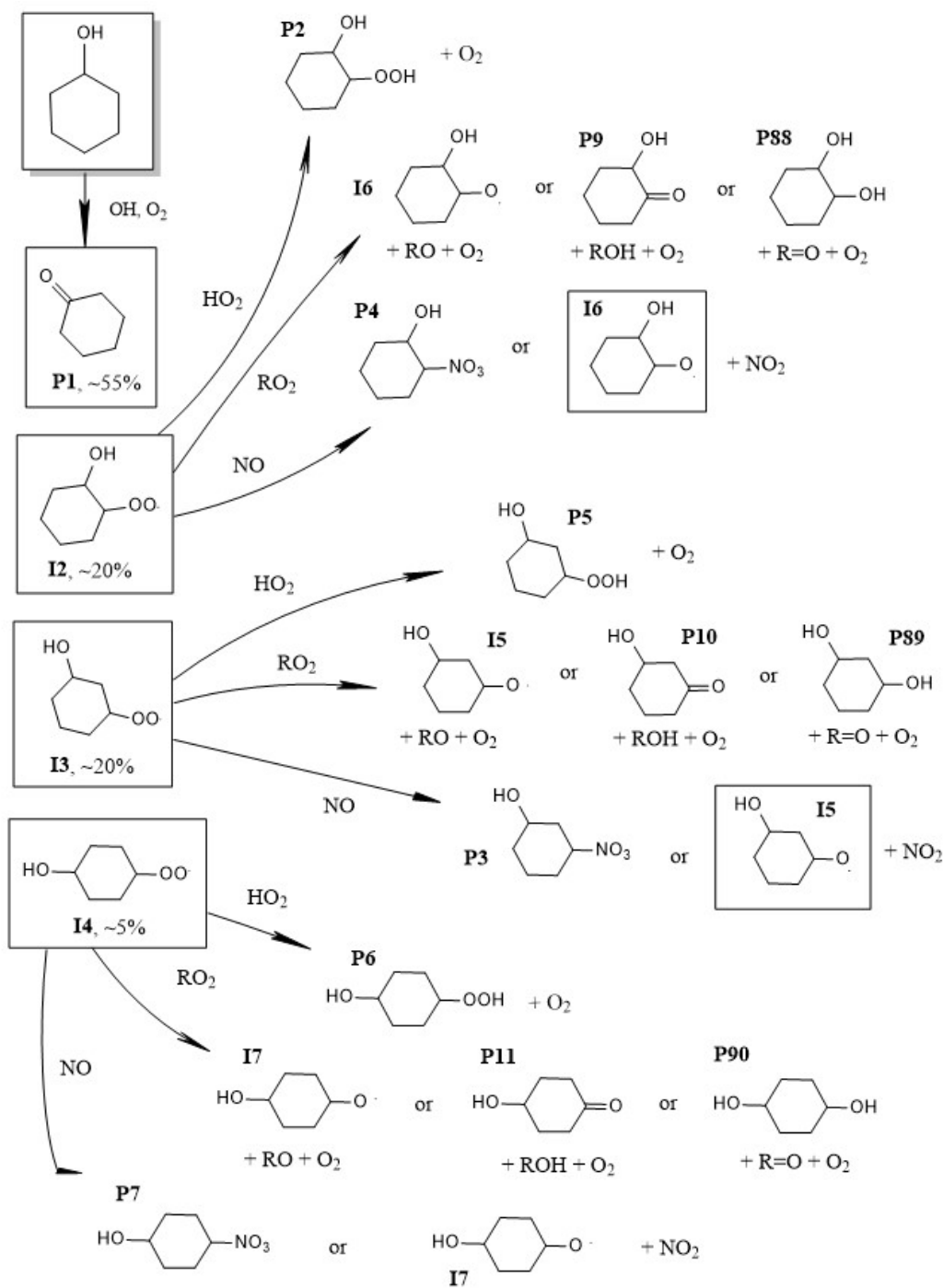


Figure 1.9 shows the formation of cyclohexanone (**P1**) and the three peroxy radical isomers (**I1**, **I2**, **I3**). Reaction of each peroxy isomer with NO , HO_2 , and RO_2 is also shown.

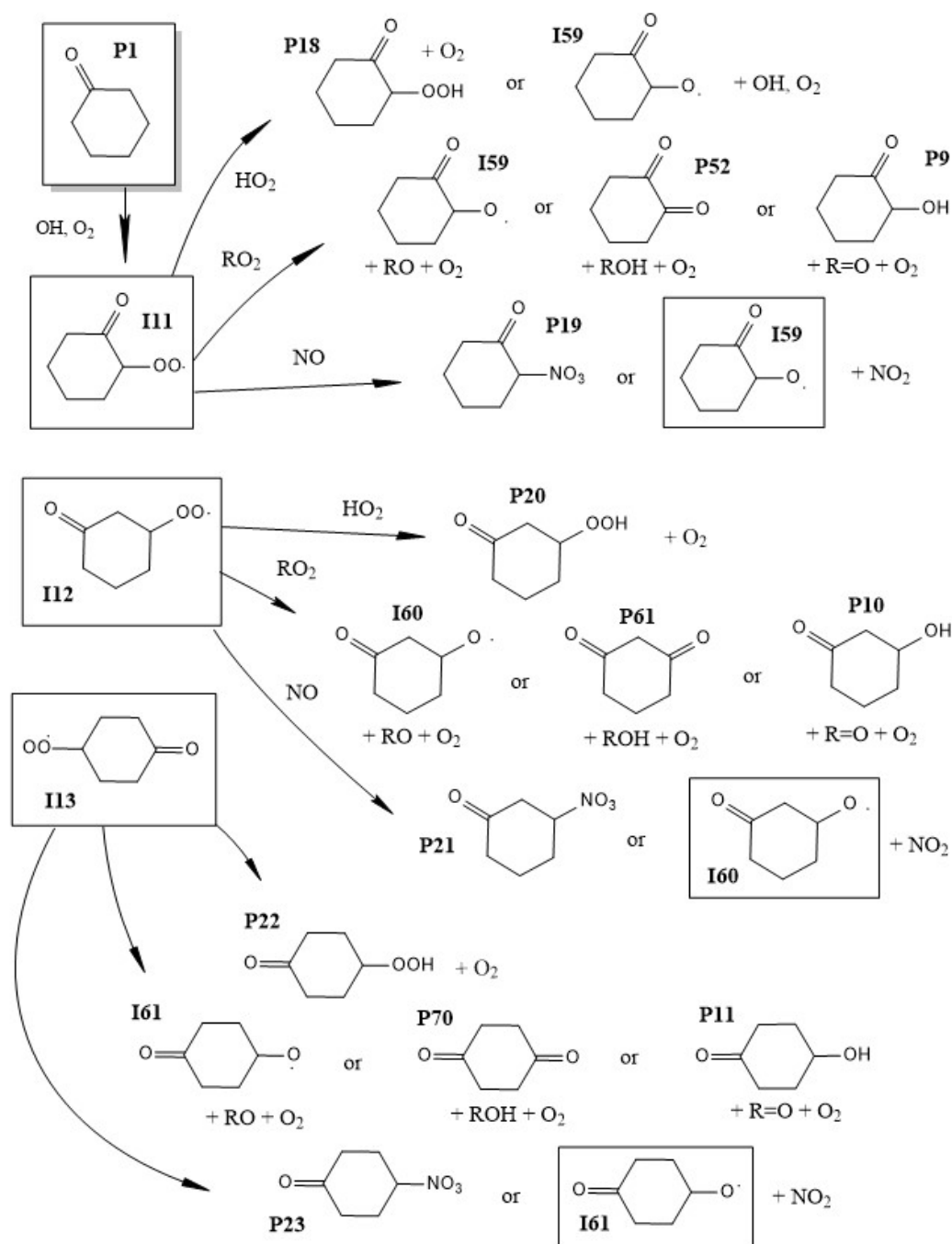


Figure 1.10 depicts an analogous oxidation path as Figure 1.9 but for the primary product of cyclohexanol oxidation, cyclohexanone (P1). Cyclohexanone peroxy radicals, I11-13, are treated similarly in the kinetic model as cyclohexanol peroxy radicals.

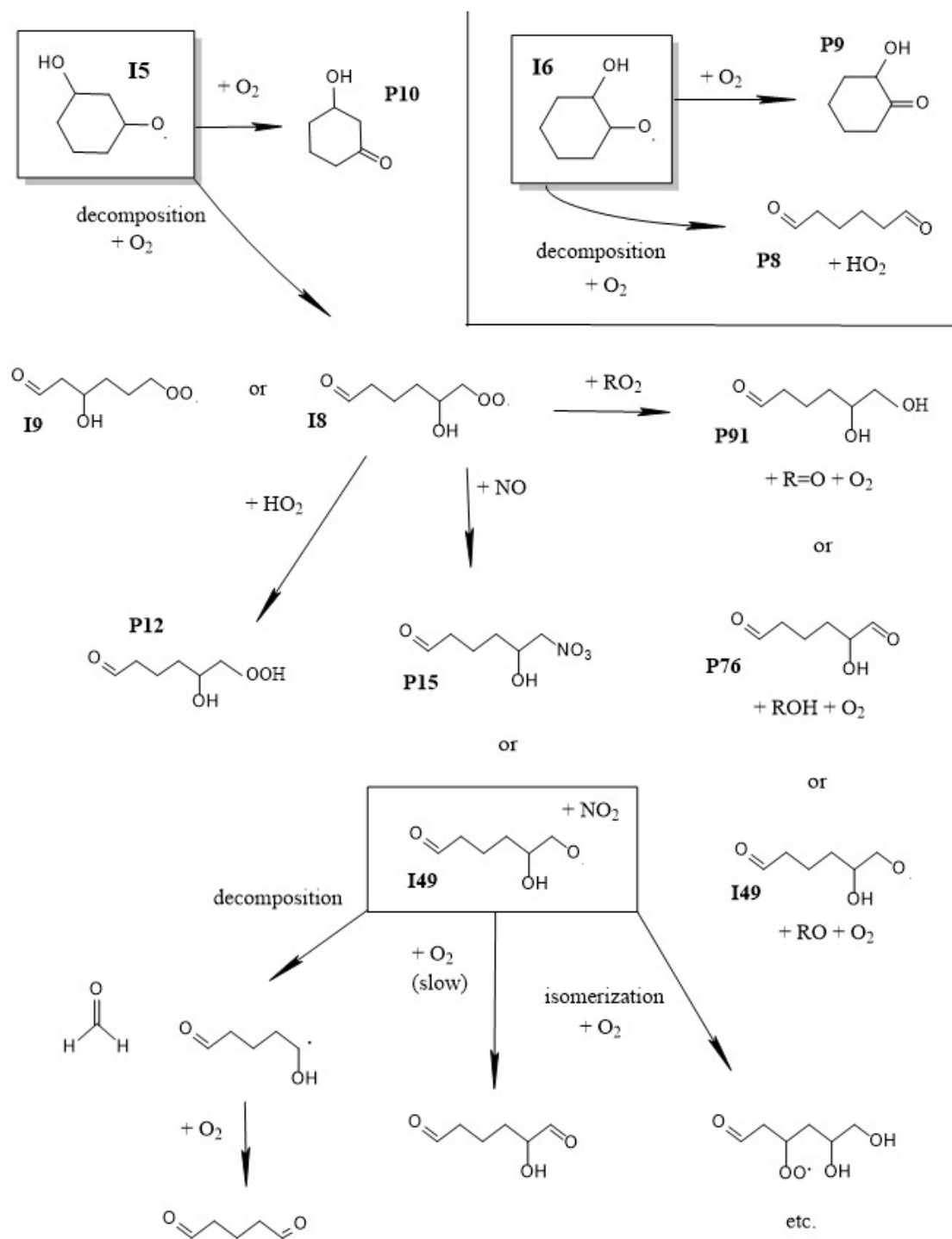


Figure 1.11 demonstrates how location of the alkoxy group might impact its fate. **I6** and **I5**, boxed in Figure 1.9, are further reacted. It is observed that when the alkoxy group is beta to the hydroxy group, it quickly forms the dialdehyde. In contrast, the meta (and not displayed para) position will result in a peroxy radical that can further react.

Table 1.3. Branching fractions selected for model

Reaction	branching	References
OH + cyclohexanol	$\alpha = 0.55,$ ^b $\beta = 0.19$ ^a $\gamma = 0.19,$ ^a $\delta = 0.7$ ^a	Bradley <i>et al.</i> ²⁰ Ceacero-Vega <i>et al.</i> ³³
OH + cyclohexanone	$\alpha = 0.4,$ ^a $\beta = 0.4,$ ^a $\gamma = 0.4$ ^a	Aschmann <i>et al.</i> ³¹

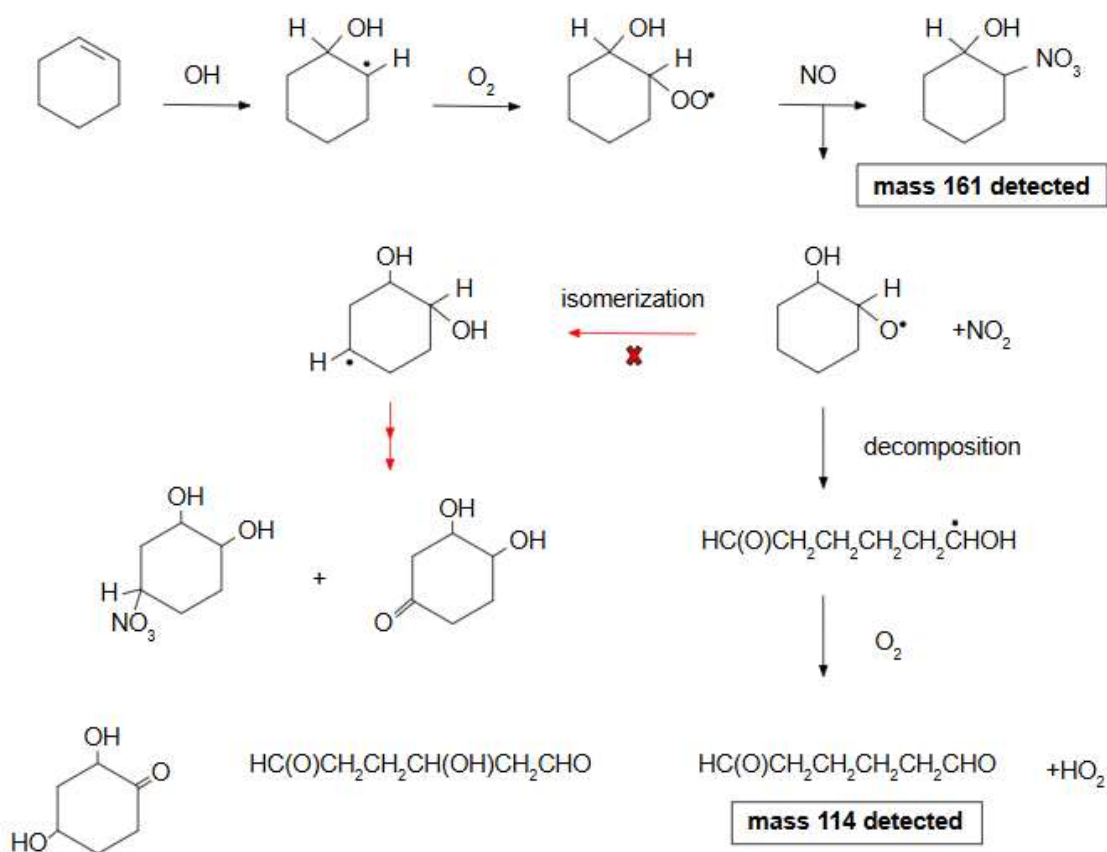
^a adjusted value^b taken directly from reference

Figure 1.12 was adapted from Aschmann *et al.* 2012 and depicts the predicted fate of cyclohexene when reacted with OH. This system is analogous to cyclohexanol when OH attacks the ortho position and thus can be used to help guide our kinetic model. While Aschmann *et al.* predicted the possibility of isomerization of the alkoxy radical, they found that the 6-membered ring was too strained. Thus the primary fate of the alkoxy is decomposition, with a small amount reacting with O_2 to form a carbonyl and HO_2 .³²

Aschmann et al. also tried to quantify the nitrate forming branching fraction. Importantly, they found that ortho-cyclohexanol peroxy radical is unable to undergo H-shift isomerization. Decomposition is also so quick that it out-competes O₂ abstraction of H to form a carbonyl. Thus, from this work, we can expect that alkoxy radicals formed from NO reaction with RO₂ primarily decompose. Additionally, they found a nitrate molar yield of only ~5-6%. This means that only a small portion of the NO-reacted cyclohexanol will retain its ringed structure.

Similarly, we consider cyclohexanol + OH under high NO a decent system to predict the fate of non-ortho alkoxy radicals. In this case, since the alkoxy group is not directly neighboring the hydroxyl group we assume the hydroxyl group has little impact on decomposition rate. Perhaps even more important, the hydroxyl group is not neighboring the peroxy group when NO is attacking, which we predicted would impact the nitrate branching fraction. In a similar earlier 2011 study, Aschmann et al carried out a similar set of experiments and found that the cyclohexyl peroxy radical observed a nitrate forming yield of 16%.³¹ This implies that for our kinetic model, nitrate formation is likely 3 times larger for radicals where the peroxy group is not next to the hydroxy group. This is likely due to a slightly higher steric hindrance.

1.4 Results and Discussion

1.4.1 VOC Calibrations

The concentrations of the VOCs and their exact dilutions are provided in Table 1.4. The original concentrated samples were determined by FTIR to be 37.5, 50.5, and 44.2 ppm for chexane, chexone, and chexol, respectively. The fitted FTIR plots are presented in Figure 1.13 A-C, where the red traces are the reference data taken from PNNL, and the blue traces are fits. One uses ordinary least squares (OLS) and the other scales the areas (Integral). The concentrations in the table are the average of these two values. Those samples were then diluted in nitrogen according to the flow ratios displayed below, resulting in a final diluted sample concentrations of 676, 506, and 622 ppb which corresponded to peak areas of 7.03, 4.51, and 6.02, also displayed in Table 1.4.

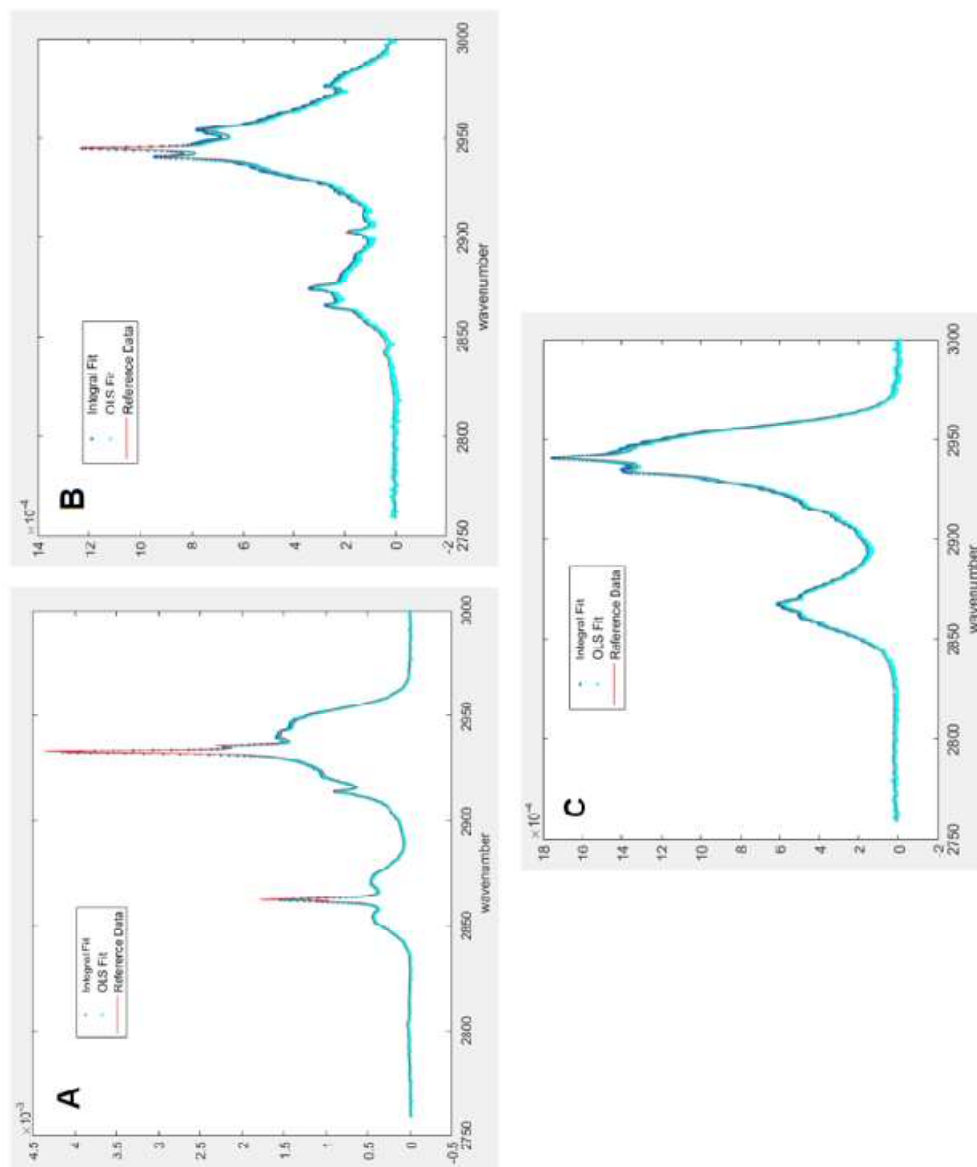


Figure 1.13 A-C displays FTIR fitted plots for cyclohexane, cyclohexanone, and cyclohexanol, respectively. The PNNL reference plot is red while the two fits are in cyan and blue.

Table 1.4. Calibration measurements for all VOCs

VOC	C _{in} (ppm)	F _{VOC} , F _{N₂} (L/min)	C _F (ppb)	PA
chexane	37.5	0.09, 4.9	676	7.03
chexone	86.7	0.03, 5.11	506	4.51
chexol	44.2	0.07, 4.9	622	6.02

A ratio of peak area to concentration shows us that the most sensitive compound to our GC-FID method is cyclohexane, followed by cyclohexanol, then cyclohexanone (chexane > chexol > chexone). Their sensitivities are not hugely different; c-hexane is about 1.15 times as sensitive as chexone. Their sensitivities on the GC-FID seem to not have much to do with their ionization energies. NIST Kinetic Webbook shows that the first ionization energies for c-hexane and chexol are around 10 eV while chexone is a little lower, around 9.2 eV. We would expect the lower ionization energy VOC, chexone, to be easier to ionize and thus be the most sensitive, but this is not what we observe. For this reason, we believe that the column stationary phase ((5%-phenyl)-methylpolysiloxane, known as DB-5) has more to do with the relatively higher observed sensitivity of c-hexane as it is meant for non-polar molecules. Better retention of c-hexane by the column can be qualitatively observed as it has a more narrow peak in the chromatograph.

1.4.2 Measured Concentration Profiles

While many products and reactants were not able to be quantified throughout the run, several species which are critical for testing the model were measured by the GC-FID and NO_x and Ozone analyzers. Figures 1.14 displays the measured concentration profiles, determined by GC-FID, for cyclohexanol (top) and cyclohexanone (bottom). O₃, NO, and NO₂ concentrations were retrieved by the commercial analyzers and are displayed in Figure 1.16. Ideally, for easier comparison, the MY trials would have been run at the same cyclohexanol concentrations (with matching PAs). Unfortunately, the low (<50%) injection efficiency of the compound made uniform injections challenging.

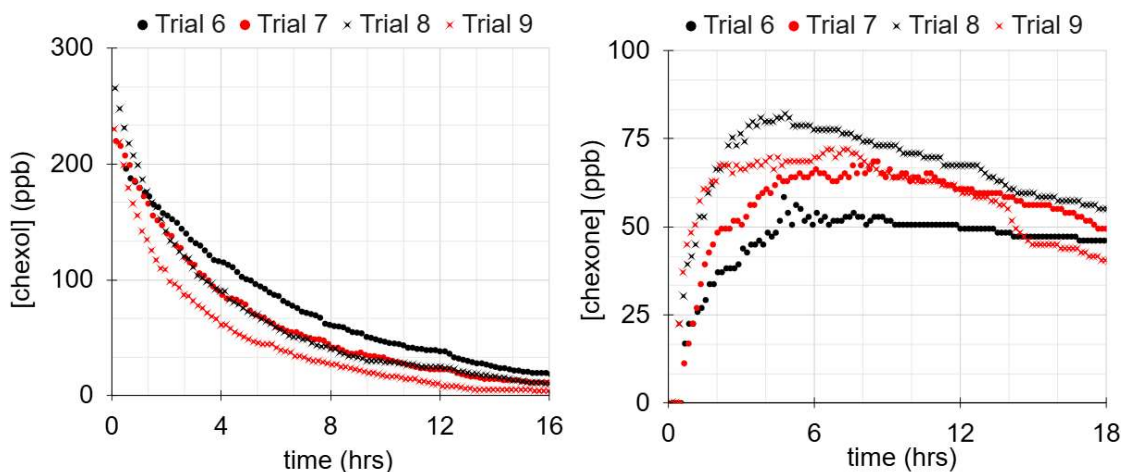


Figure 1.14 left panel displays the decreasing cyclohexanol concentration for the four MY experiments, trials 6, 7, 8, and 9. While the starting concentrations are not the same, some general trends are noticeable. The exponential decay rate is NO dependent. Trial 6, which was run under 0-NO conditions, has the shallowest slope while Trial 9, run at over 100 ppb, has the steepest slope. The right panel shows the cyclohexanone growth curves.

Even so, some general trends can be noticed from the cyclohexanol decay curves. First, the $[\text{NO}]_i$ concentration impacts the rate at which cyclohexanol is reacted. This can be understood by the OH-reforming reactions that are introduced when NO_x is present. NO can react with peroxy radicals to form an alkoxy radical and NO_2 . This NO_2 can be photolyzed, forming odd oxygen, which will mostly form O_3 , reforming the NO. When NO is not reacting with RO_2 , another likely reacting partner is HO_2 , reforming OH. To summarize, when NO is introduced, it can react with RO_2 to result in an O_3 , or it can react with HO_2 to reform OH. This simplification of course, is a very short explanation of the HO_x and NO_x cycles present in our system and ignores many reservoir species.

- a) $\text{NO} + \text{RO}_2 \rightarrow \text{NO}_2 + \text{RO}$
- b) $\text{NO}_2 \rightarrow \text{NO} + \text{O}$
- c) $\text{O} + \text{O}_2 \rightarrow \text{O}_3$
- d) $\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH}$

Next, we observe that ozone formation is proportional to concentration of NO introduced. This again, is predicted by the above equations as NO_2 photolysis results in the formation

of O_3 . Without NO present, $RO_2 + RO_2$ and $HO_2 + RO_2$ dominate, resulting in no odd oxygen. NO_2 concentrations, shown in Figure 1.16, for trials 7-9 are understandably largest at the beginning. Over time we see that NO is not reformed very quickly, as NO_2 undergoes slow photolysis.

Figure 1.16 displays the greatest limitation of this work. NO concentrations for Trials 7-8 are only high at the very start of the trial. Figure 1.15 shows the percentage of cyclohexanol reacted with time and indicates that by the time the NO has been reacted away beyond our limit of detection, less than 25% of the cyclohexanol in the chamber has reacted. This means that for the remaining 75%, the $RO_2 + RO_2/RO_2 + HO_2$ regime will dominate, with only small contributions from NO which is reformed by the slow photolysis of NO_2 . Ideally, NO concentration would be stable throughout the trial and be a better representation of atmospheric conditions.

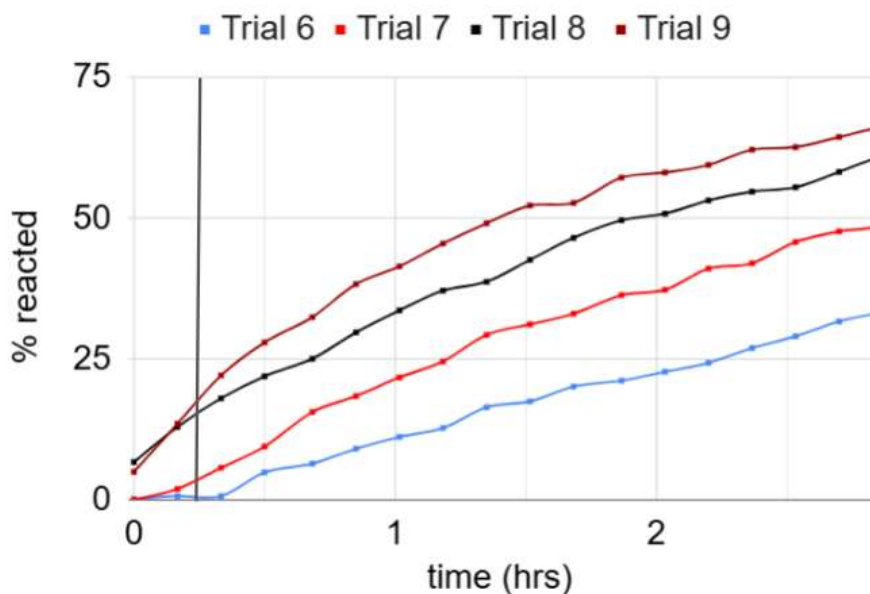


Figure 1.15 displays the reacted percentage of cyclohexanol for all Trials for the first 3 hours. This plot can be related to Figure 1.16, to indicate that by the time most of the NO has reacted to NO_2 , less than 25% of the cyclohexanol has reacted. In other words, for Trials 7-9, all NO is reacted before 0.25 hours, as shown in Figure 1.16. This region is indicated by a thin gray line. The remaining 75%+ of unreacted cyclohexanol in these trials were reacted under a low NO regime.

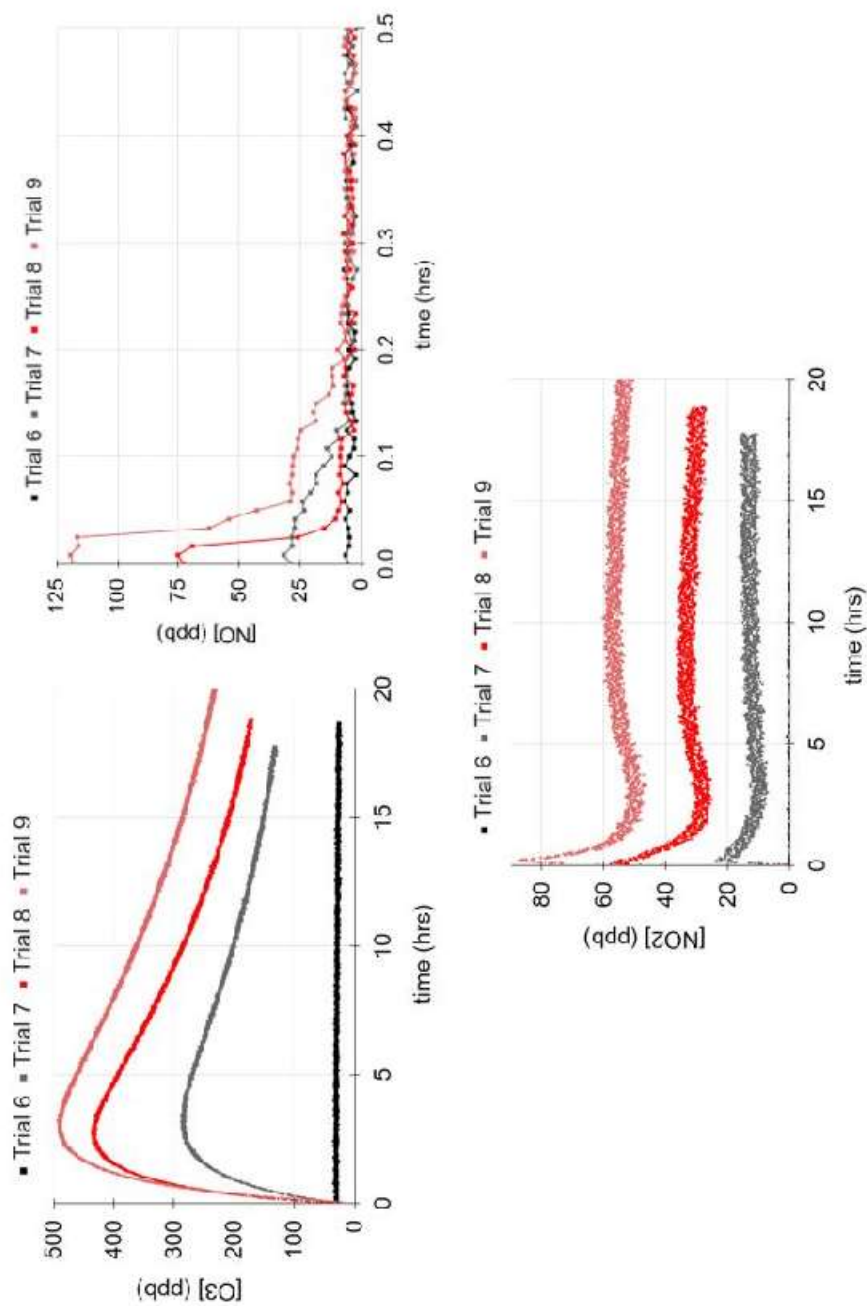


Figure 1.16 shows the O_3 , NO , and NO_2 data, respectively. As is further explained in-text, the most notable trends are the increase in O_3 formation with $[NO]_t$ and the quick depletion of NO in trials 7-9. Alternatively, one can observe the absence of NO as the large reservoir of NO_x , which is not photolyzed quick enough to regenerate significant concentrations of NO after its initial first reaction.

1.4.3 Relative Rate

The OH + chexol rate was determined in reference to two compounds, butanol and butanal. These compounds were selected because they were readily available, easy to evaporate, and have rates which are just below and above that of cyclohexanol. The plotted log-log plots of the reference versus cyclohexanol yielded slopes of 2.12 and 0.689 for butanol and butanal respectively and are displayed in Figure 1.17. We then took these values and multiplied them by their corresponding literature measured rates shown in Table 1.5. The average of these two experimentally determined values was $1.79 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. This value, closer to that measured by Bradley *et al.* than Berndt *et al.*, was then used going forward to estimate the cyclohexanone branching fraction.

Table 1.5. Relative rate data for cyclohexanol + OH

	slope	Lit Value	References	Rate
butanol	2.12	8.47, 8.98, 8.31×10^{-12}	Yujing and Mellouki, 2001 ³⁴ Sime et al, 2020 ³⁵ Wallington and Kurylo, 1987 ³⁶	18.2×10^{-12}
butanal	0.69	24.1, 23.8, 28.8×10^{-12}	Renbaum-Wolff and Smith, 2012 ³⁷ D'Anna et al, 2001 ³⁸ Albaladejo et al, 2002 ³⁹	17.6×10^{-12}

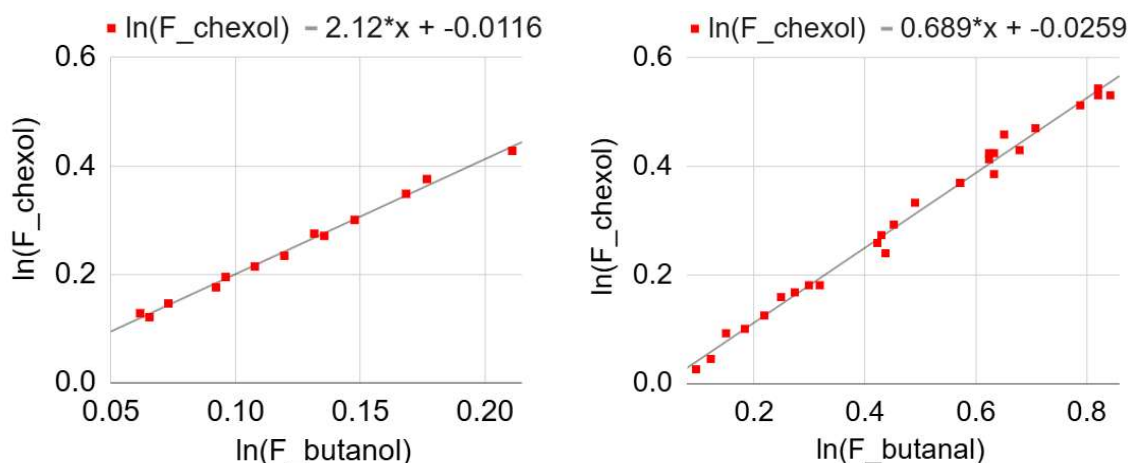


Figure 1.17 shows the log-log plots for the butanol and butanal relative rate measurements of chexol + OH. The slopes are multiplied by the reference reaction rate to determine a corresponding chexol + OH rate, displayed in Table 1.5.

1.4.4 Cyclohexanone Branching Fraction

As described in the methods section, to estimate the cyclohexanone-forming branching fraction first the $[\text{OH}]_t$ profile for each trial is required. In figure 1.19 the natural log of concentration was plotted against time and fitted to a polynomial function which is a slowly changing function of $[\text{OH}]_t$.

Polynomials of degrees 2, 3 and 4 were considered, but only degree 4 was able to fit the plateauing observed by the end of each of the trials, again depicted in figure 1.14. The decrease in the change in [chexol], or plateauing in Figure 1.14, can be attributed to the loss of both chexol and OH, impacting the overall rate. The OH profiles plotted in Figure 1.18 were calculated by taking the fitted polynomials from Figure 1.19 (excluding the constant offset) and dividing them by the overall chexol + OH rate, determined in this work. Again, the justification for this procedure is provided in the methods section in more detail.

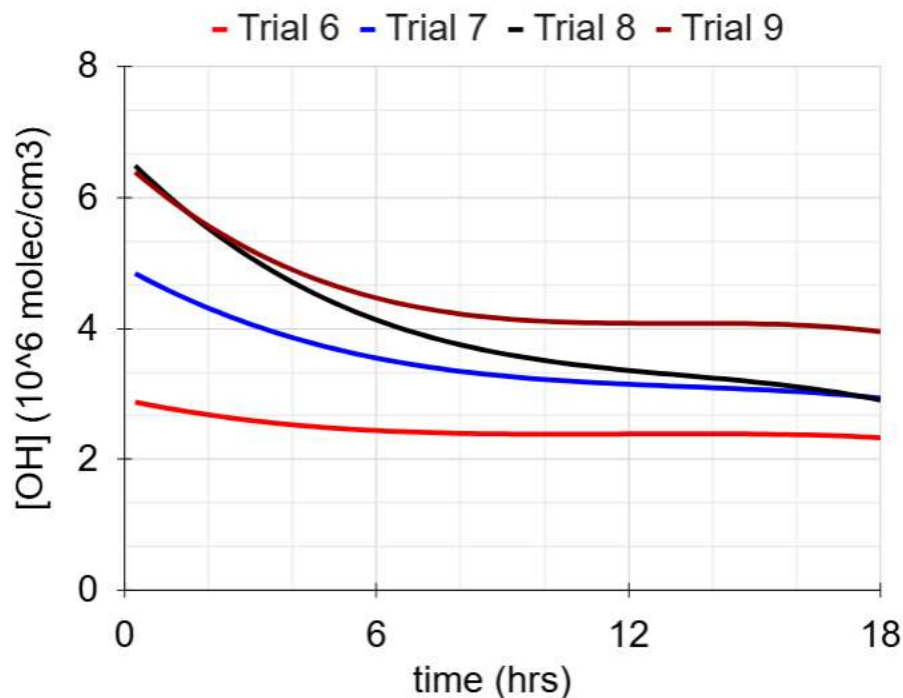


Figure 1.18 displays the calculated $[\text{OH}]_t$ profiles for the four trials. At the start of the trial, when NO is still present in large amounts, $[\text{OH}]_t$ is at its highest, likely because it is being regenerated by $\text{HO}_2 + \text{NO}$. After the first few hours, the $[\text{OH}]_t$ appears to stabilize.

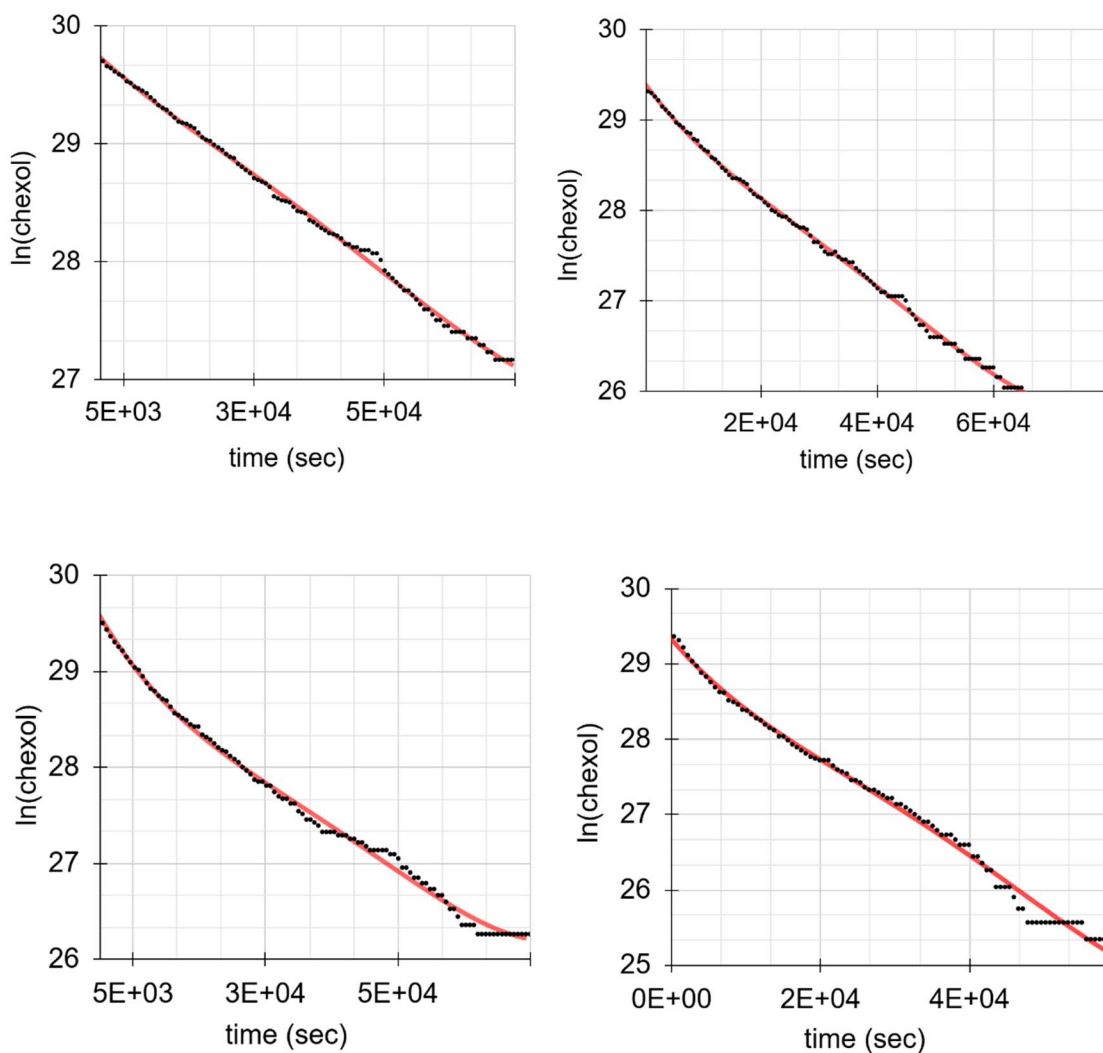


Figure 1.19 shows the $\log [\text{chexol}]$ plots fitted to 4th degree polynomials for Trials 6-9. The polynomials represent slowly varying functions of $[\text{OH}]_t$ and were used to determine the profiles plotted in Figure 1.18. Trials 6-9 are shown, in order, on the top left, top right, bottom left and bottom right panels.

$$\text{Trial 6} = 29.3 - 5.13\text{E-}05x + 6.67\text{E-}10x^2 - 1.59\text{E-}14x^3 + 1.23\text{E-}19x^4$$

$$\text{Trial 7} = 29.4 - 8.67\text{E-}05x + 1.74\text{E-}09x^2 - 3.37\text{E-}14x^3 + 2.31\text{E-}19x^4$$

$$\text{Trial 8} = 29.6 - 1.17\text{E-}04x + 3.15\text{E-}09x^2 - 5.99\text{E-}14x^3 + 4.15\text{E-}19x^4$$

$$\text{Trial 9} = 29.3 - 1.15\text{E-}04x + 2.75\text{E-}09x^2 - 5.84\text{E-}14x^3 + 4.13\text{E-}19x^4$$

What we found by plotting these profiles, displayed in Figure 1.18, is that while the $[\text{OH}]_t$ does stabilize eventually, for the first several hours while the cyclohexanol is still very active, it is quite unstable. In other words, as we expected, when calculating the cyclohexanone-forming branching fraction it would be a poor assumption that $[\text{OH}]_t$ is constant throughout the trial. To fit the cyclohexanone data, we thus took the $[\text{OH}]_t$ profiles plotted in Figure 1.18 and fixed them into our kinetic model. While most other molecule concentration profiles in the model are constantly adjusting to each other in accordance with the inserted rate equations, it is possible to fix a couple profiles. It should be noted that in theory, we could run the model with an initial $[\text{H}_2\text{O}_2]$ and a measured H_2O_2 photolysis rate, but this does introduce error as in our current set-up we are unable to know the concentration of H_2O_2 pre-photolysis. For this reason, fixing the calculated $[\text{OH}]_t$ profiles is preferred.

The models were then run forward with their corresponding starting concentrations of chexol, and our calculated chexol reaction rate. Unfortunately, the $\text{OH} + \text{chexone}$ rate and ϕ are correlated when fitting. This would not matter except that the literature is not in perfect agreement on the $\text{OH} + \text{chexone}$ rate (Table 1.2). To address this, we performed phi fits for a range of $\text{OH} + \text{chexone}$ rates. This means that for each trial several rate and phi pairs were tested. The variable fits for Trials 6 and 9 are exemplified in Figure 1.20. $\text{OH} + \text{chexone}$ rates of 5.35 , 6.08 and $6.5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ were tested and ϕ was adjusted manually in the model to minimize error between the fit and the plotted data.

Table 1.6. Cyclohexanone rate vs. ϕ fit.

Trial	5.35×10^{-12}	$k=6.08 \times 10^{-12}$	6.5×10^{-12}
6	<u>0.53^a</u>	0.55	0.57
7	<u>0.52^a</u>	0.53	0.54
8	<u>0.52^a</u>	0.54	0.55
9	<u>0.54^a</u>	0.55	0.57

^afinal chosen phi fit values are underlined for each Trial

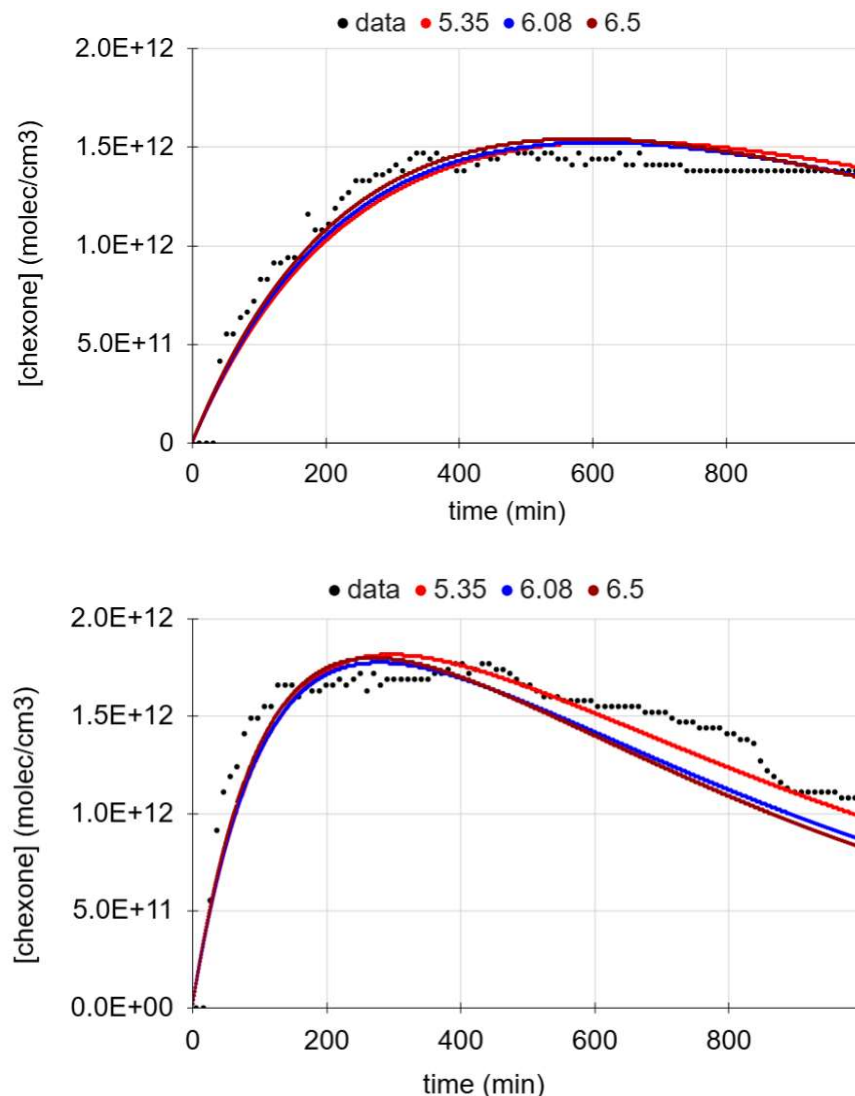


Figure 1.20 shows how rate and ϕ were varied for Trials 6 and 9 data (top and bottom respectively). The chexone data is plotted in black against the fitted model data for chexone + OH rates of 5.35 (red), 6.08 (blue) and $6.5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ (dark red). The modeled data plotted is the best fit ϕ (presented in Table 1.6) for that rate. The lowest assumed k value, in red, appears to fit our experimental data best for both high and low $[\text{NO}]$.

We can see in Figure 1.20 that at the beginning of each trial (200 minutes) the overall OH + chexone rate picked doesn't hugely impact the "goodness of fit." Over the rest of the trial however, the lower OH + chexone fits in red better resemble the data, meaning lower OH + chexone rates perform better. If the actual chexone + OH rate is closer to 5.35, then the best-fit chexone branching fractions for these trials spanned between 0.52 and 0.54.

Assuming a k of $5.35 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, Trials 6-9 were fit to $\phi = 0.53$, 0.52 , 0.52 and 0.54 , respectively, as shown in Table 1.6. Thus, we report and average ϕ of approximately 0.53 . This value is very close to the 55% reported by Ceacero-Vega *et al.* and Bradley *et al.* Figure 1.21 shows Trial 7 fit to 5.35×10^{-12} and $\phi = 0.52$, as well as its small residuals of $\pm 10\%$.

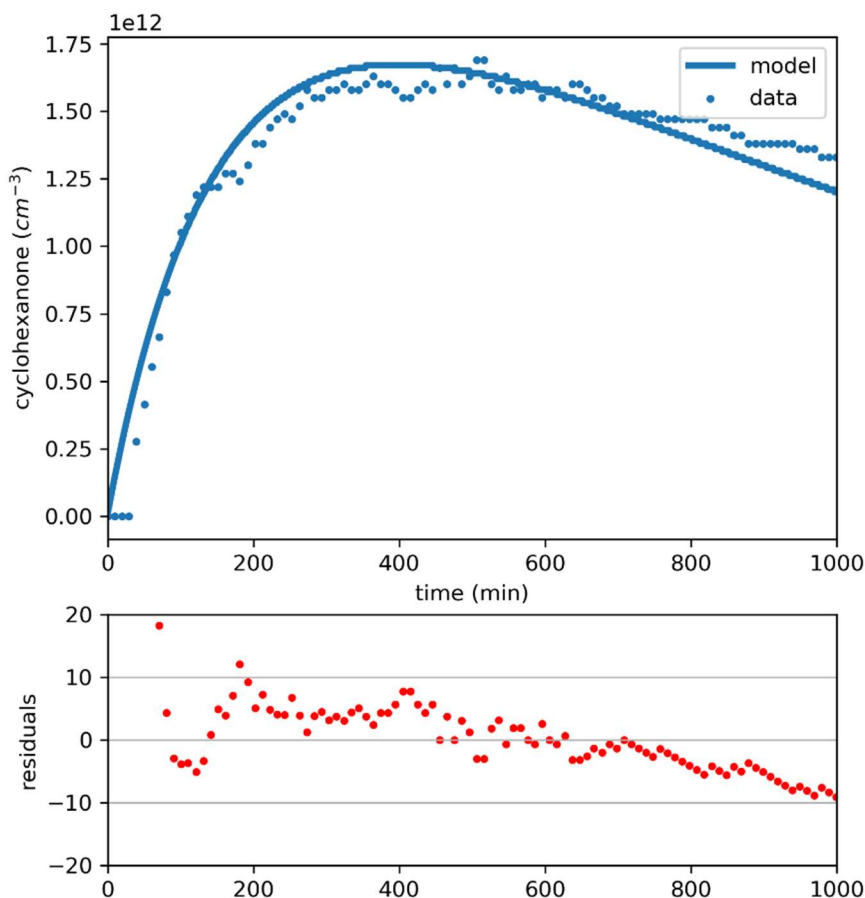


Figure 1.21 displays on the top panel experimental cyclohexanone concentration against modeled cyclohexanone concentration for Trial 7, assuming the optimal ϕ , 0.52 . The residuals are plotted on the bottom panel and typically range within $\pm 10\%$.

1.4.5 HO₂ and RO₂ Concentrations

Oxidation of cyclohexanol begins with an OH attack followed by reaction with O₂. Assuming the product is a peroxy radical (cyclohexanone will undergo another attack by OH), that peroxy radical's fate will be determined by the relative abundances and rates of

HO₂, RO₂, and NO. Our first insight into the [HO₂] throughout the trials was to look at its precursor, H₂O₂. H₂O₂ was injected in abundance in all trials, and by the end of an 18-hour reaction period is expected to be ~50% depleted, as shown in Figure 1.22. Note again, that because the CIMS was unable to be run during MY measurements, we must extrapolate from Trials 4 and 5, the Product ID Trials. Figure 1.22 shows m/z 120 signal normalized to m/z 86 for Trials 4 and 5. m/z 120 results from CF₃O*HDO₂ and m/z 86 results from ¹³CF₃O⁻. ¹³CF₃O⁻ and HDO₂ are used instead of CF₃O⁻ and H₂O₂ to avoid oversaturation issues. Unfortunately, we did not have a way to calibrate the H₂O₂ concentration, so all that can be said is that H₂O₂ was not depleted by the end of the trial. From this we can conclude that there is probably not a huge time dependence of [HO₂], like there is for [NO].

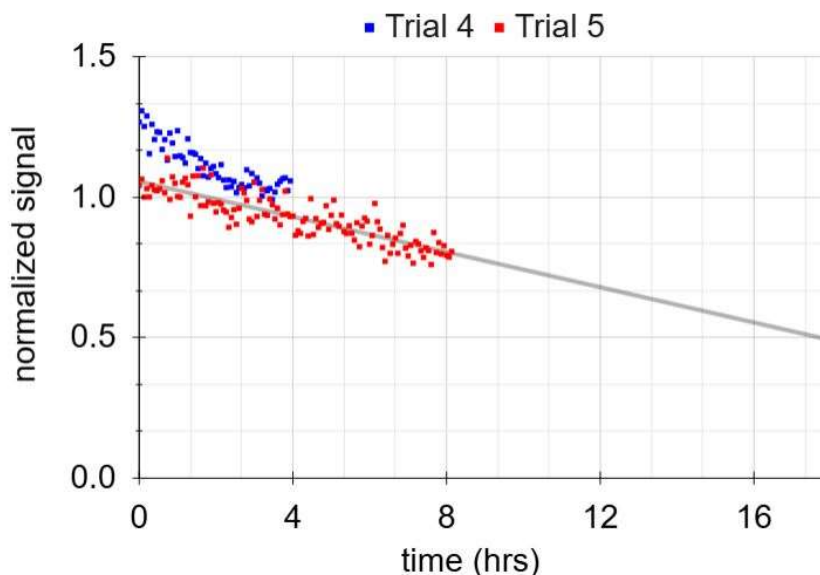


*Figure 1.22 shows a normalized signal for m/z 120 during the product ID trials and extrapolates further to the length of a MY trial. m/z 120 is known to result from CF₃O*HDO₂ and can be used as a measure of [H₂O₂] over the photolysis period.*

Figure 1.22 informs us that H₂O₂ is not depleted by the end of the photolysis period, but without calibration it did not allow us a way to determine actual HO₂ concentration. Again, our model can be utilized here to try and better understand the chemical environment of our trials. For each trial we ran a corresponding model (like we did to determine the branching fraction) with appropriate starting chexol and NO concentrations and fixed [OH]

profiles. In Figure 1.23, the modeled results for $[HO_2]$ and $[RO_2]$ are plotted. The $[RO_2]$ concentration is the sum of all the unique predicted RO_2 species in our model. Unfortunately, one of the limitations of our model is that not all the reactions of RO_2/HO_x are accounted for. $RO_2 + RO_2$ and $RO_2 + HO_2$ chemistry (excluding ROOR forming path) for all cyclohexanol and cyclohexanone-peroxy radicals have been included.

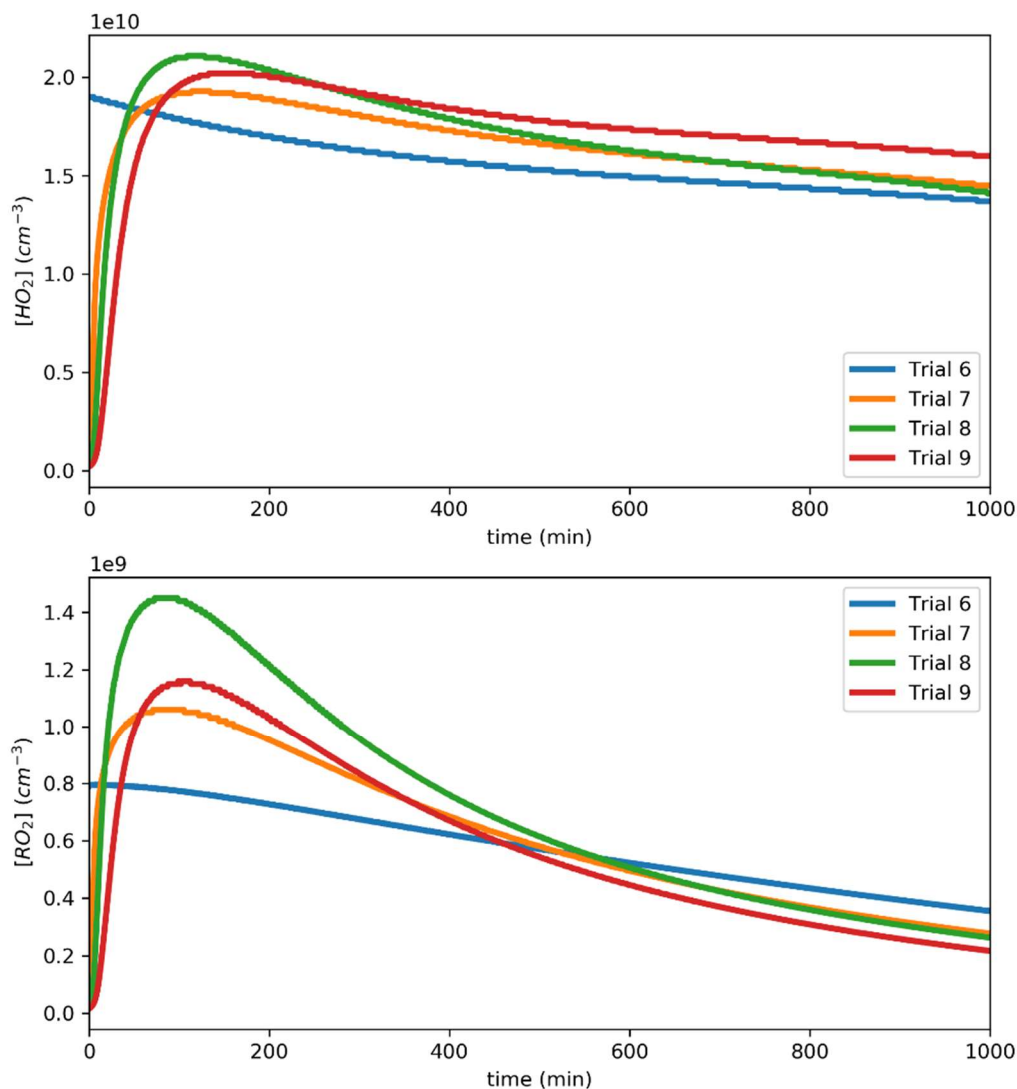


Figure 1.23 depicts the model-generated HO_2 and RO_2 concentration profiles for Trials 6-9. As is explained in-text, NO is observed to delay the appearance of both HO_2 and RO_2 by reacting with them at the start of photolysis. The $[RO_2]$ maximum is largest for trial 8, likely because it has the largest starting concentration of VOC, displayed in Figure 1.14.

Figure 1.23 shows that the presence of NO influences the starting concentrations of RO₂ and HO₂. We observed this in our OH profile as well; the reaction of NO with HO₂ regenerated OH at the beginning of the trial, giving a boost to [OH] at the start. Correspondingly, HO₂ concentration is noticeably (in our model) depressed at the start of the trial when NO is introduced. While the maximum [HO₂] achieved during the trial is not directly related to the [NO]_i, the delay time for it to reach that maximum is proportional to [NO]_i. In other words, Trial 9 takes the most time to reach its maximum because there is more NO to react with the initially formed HO₂, whereas Trial 6 which has no NO is at its maximum at the start of photolysis.

NO also creates a delay in the buildup of RO₂ in the system, for the same reason, in that it is reacting with it to form either RNO₃ or RO. Once the NO is mostly reacted away within the first hour of the experiment, RO₂ proceeds to react more slowly with itself and HO₂. The same trend in the delay to reach maximum is observed but more noticeably, Trial 8 has significantly more RO₂ present at the start. This is likely a direct result of Trial 8 having a higher concentration of VOC injected. Thus, in Table 1.7 the largest factor influencing differences in the HO₂:RO₂ of the chamber is starting VOC concentration; Trial 8 has the lowest average HO₂:RO₂. Despite this slight difference, we can conclude from this analysis that the trials occur under similar HO_x/RO_x regimes and the primary difference across trials is in fact the [NO]_i. We calculated that there is around 0.5 ppb HO₂ and 30 ppt RO₂ on average throughout these trials.

Table 1.7. HO₂ and RO₂ Modeled Concentrations for Trials 6-9.

Trial	[chexol] _i ppb	[NO] _i ppb	[HO ₂] _{ave} molec cm ⁻³	[RO ₂] _{ave} molec cm ⁻³	HO ₂ :RO _{2ave}
6	190	0	1.60 x10 ¹⁰	5.8 x10 ⁸	27.6
7	220	30	1.71 x0 ¹⁰	6.2 x10 ⁸	27.4
8	260	75	1.70 x10 ¹⁰	7.2 x10 ⁸	23.6
9	230	120	1.74 x10 ¹⁰	5.95 x10 ⁸	29.4

1.4.6 Product Identification

While cyclohexanol and cyclohexanone were monitored on the GC-FID, their products were too oxidized to be observed on the GC (non-polar column, DB-5). Instead, all other products were identified via CIMS. The binding molecule can associate with the 85 m/z parent ion CF_3O^- (and isomers), the 19 m/z fragment F^- , or both. Our instrument is capable of scanning between 50 and 450 m/z and can do so in about 3.5 minutes. This is a reasonable acquisition time when considering the typical 10-minute span between GC measurements. To assist in identifying the detected masses, we screened for the distinct 94 products predicted by our kinetic model. Some of these products do not contain functional groups which will bind to the chemical ions. It should also be noted that many of these compounds are isomers. After removing products that will not bind to the chemical ions and accounting for redundancy due to isomers, we anticipated observing product growth for 16 unbound masses. Since these 16 masses can bind with either CF_3O^- or F^- , anticipated products may be found at 32 different m/z. To help distinguish these many products and better understand the two chemical environments, product masses were collected under no-NO and high-NO conditions.

Figures 1.24 and 1.25 show together 56-295 m/z for both the no-NO and NO-containing product ID runs. The signal strength on the y-axis is simply the average signal at the end of the run minus the average starting signal. This is meant to assist in removing background signals. The model-predicted mass locations are labeled A-P in Figures 1.24 and 1.25 according to Table 1.8. All predicted masses are shown except P, at 307 m/z. The potential identities of other masses pinpointed in Figures 1.24 and 1.25 are discussed later in-text. The full mass spectrum can be useful in identifying some major products and comparing product distribution under no-NO and NO-containing conditions, however some signals plotted are potentially due to noise and not necessarily product growth. For a product to be considered “detected” we considered a limit of detection of around 95% confidence. For a given mass, we determine the standard deviation for 10 and 15 points prior to photolysis. If the average signal at the end of oxidation is more than twice that standard deviation, then the molecule is considered detected. Thus, while Figures 1.24 and 1.25 may appear to show substantial signal at a given mass, it is possibly due to a noisy background.

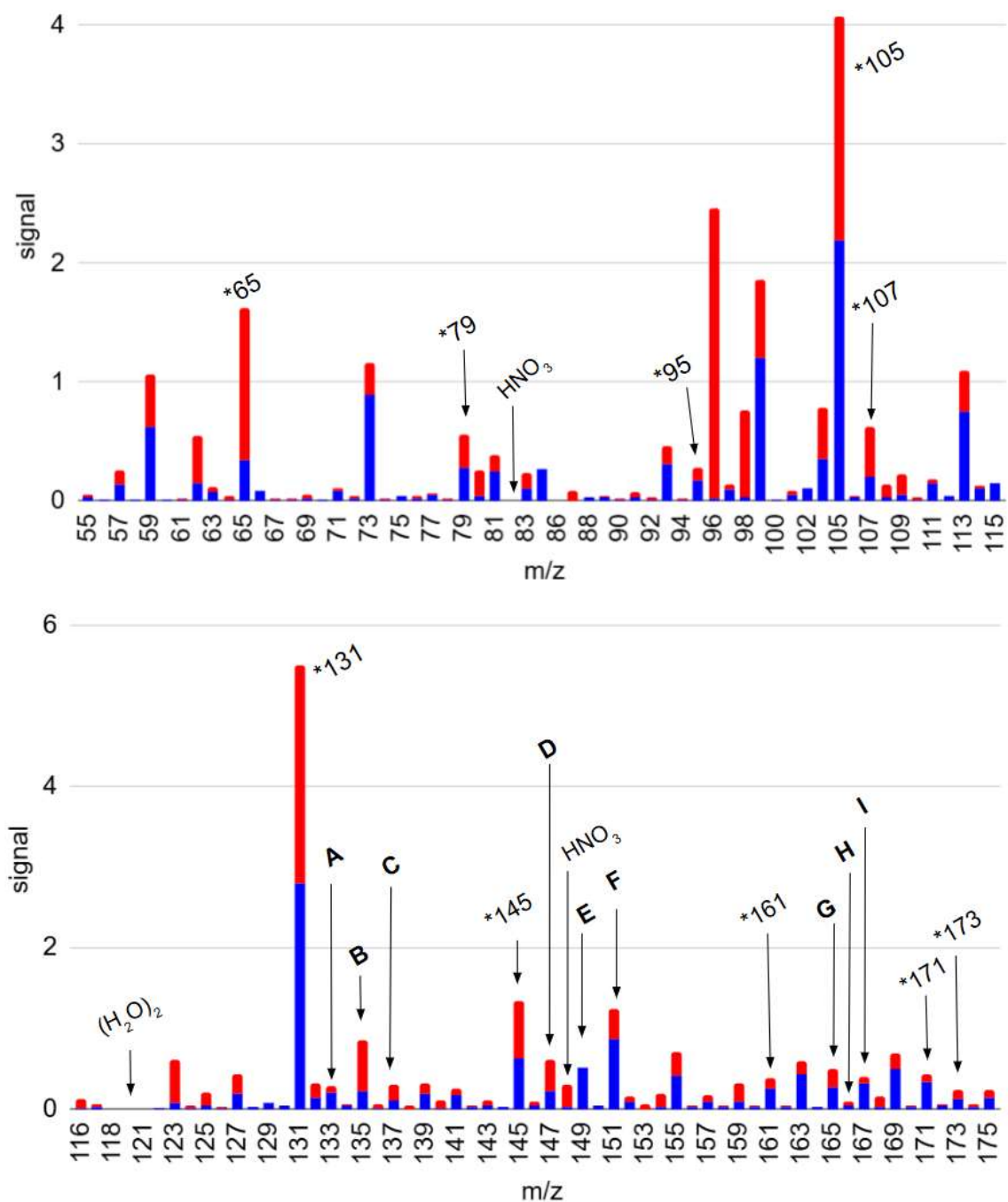


Figure 1.24 shows detected ions m/z 56-175 at the end of Trials 4 (no-NO) and 5 (yes-NO). Trials 4 and 5, which are labeled in blue and red respectively, are stacked on top of each other to assist in indicating which products are observed for both conditions. 82 m/z is from HNO_3 , 121 from $(\text{H}_2\text{O})_2$ while 120 is likely from D and ^{13}C isomers of H_2O_2 (complexed with CF_3O^-); all three signals are larger than the scale and as they are not cyclohexanol oxidation products, were removed for this image to prevent clutter.²⁷ Letters correspond to Table 1.8, numbered masses are discussed in text.

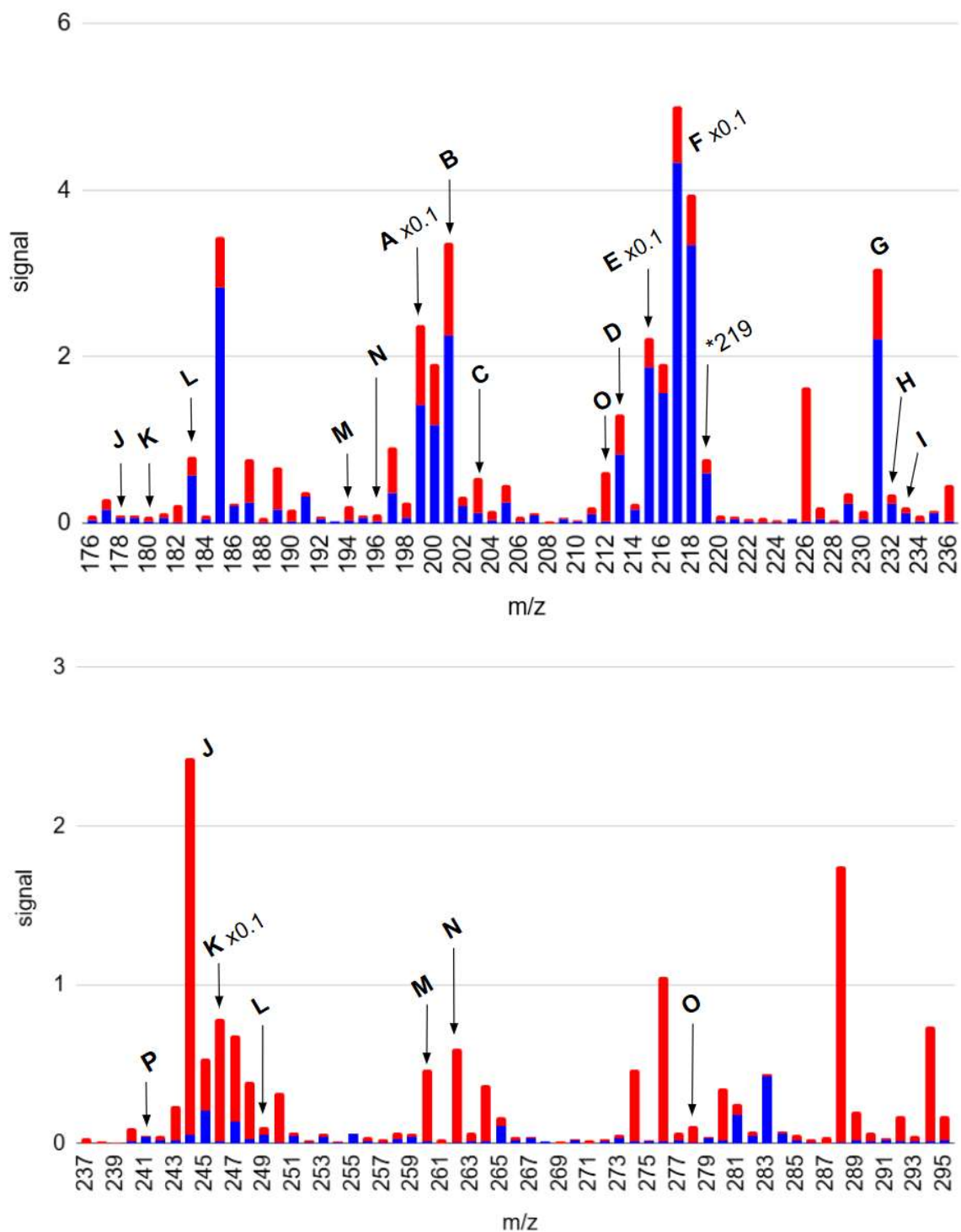


Figure 1.25 shows detected ions m/z 176-295 at the end of Trials 4 (no-NO) and 5 (yes-NO). Trials 4 and 5, labeled in blue and red respectively, are stacked to assist in indicating which products are observed for both conditions. Some signals for products A, E, F and K were scaled down by a factor of 10 ($\times 0.1$) to better fit the Figure.

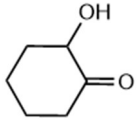
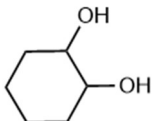
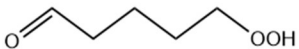
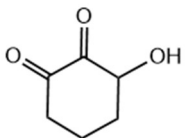
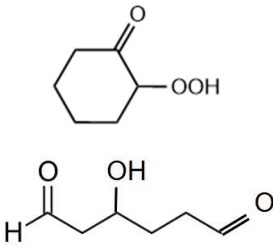
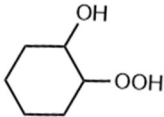
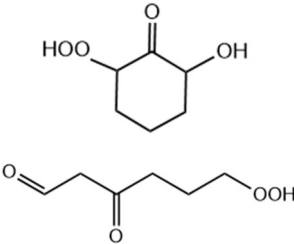
Masses above 300 m/z were observed, but only for the NO-containing Trial, 5. While literature predicts that some peroxy radicals self-react to form ROOR, this pathway was not included in this work's current kinetic model. These 300+ m/z masses are unlikely to result from ROOR for two reasons. First, they were only observed in the presence of NO, and we would expect to see more ROOR without the presence of NO, in a RO_2+RO_2 dominant regime. Also, ROOR tends to photolyze readily, and are unlikely to survive detection. Since these 300+ m/z are only observed when NO is present, we expect they result from highly oxidized products with multiple NO_3 groups.

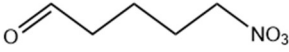
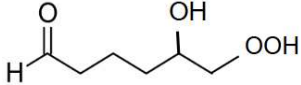
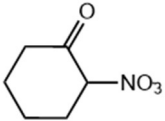
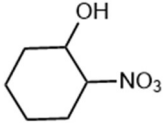
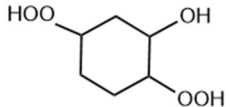
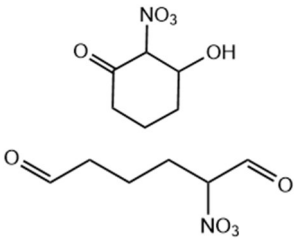
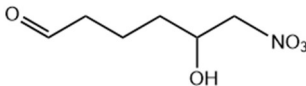
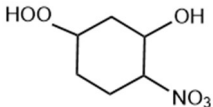
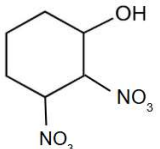
Again, according to our predicted chemical mechanism, we expected product growth at 16 different un-bound masses, corresponding to 32 different potential m/z (+19 or +85). Table 1.8 displays information regarding the 16 un-bound masses, including the isomer formula and unbound mass, their 2 expected masses (F^- and CF_3O^-) and whether they were detected under the no-NO and high-NO conditions. Table 1.8 illustrates potential structures for the 16 predicted un-bound masses. For relevant predicted masses, an example of both a cyclic and linear isomer is offered. Even if non-zero signal was observed in Figures 24 and 25, it must pass the previously described criteria of 95% confidence to be considered detected.

Under no-NO conditions (Trial 4) 8 predicted products were detected, while under moderate NO conditions (Trial 5) all 16 products detected. It should be noted again that since each molecule has different binding efficiency to the chemical ions, their signal strength alone cannot be used to determine the abundance or even relative abundance of the products.

One way we can further validate our predicted product identity is by plotting the mass's raw CIMS signal (proportional to concentration) curve against one produced by our kinetic model. Unfortunately, we were unable to calibrate any of the products detected via CIMS. Because the products detected by CIMS are not calibrated, we scaled the experimental curve(s) and plotted them on the same graph as the modeled curve(s) to compare their shapes and defining features. Often both F^- and CF_3O^- bound masses were detected for a predicted product. In addition, both cyclic and linear products are possible, thus up to four curves were plotted, 2 experimental and 2 modelled.

Table 1.8. Observed masses from predicted mechanism.

Ref.	Formula & Mass	# Iso.	Representative Structure(s)	Pred. Masses	Trial 4	Trial 5
A	$C_6H_{10}O_2$ 114	3		133 199	- Y	- Y
B	$C_6H_{12}O_2$ 116	3		135 201	Y Y	Y Y
C	$C_5H_{10}O_3$ 118	1		137 203	- -	- Y
D	$C_6H_8O_3$ 128	6		147 213	Y Y	Y Y
E	$C_6H_{10}O_3$ 130	6 3L, 3C		149 215	Y Y	Y Y
F	$C_6H_{12}O_3$ 132	3		151 217	Y Y	Y Y
G	$C_6H_{10}O_4$ 146	16 6L, 10C		165 231	Y Y	Y Y

H	$C_5H_9O_4N_1$ 147	1		166 232	- -	Y Y
I	$C_6H_{12}O_4$ 148	3		167 233	Y Y	Y Y
J	$C_6H_9O_4N_1$ 159	3		178 244	- -	- Y
K	$C_6H_{11}O_4N_1$ 161	3		180 246	- -	- Y
L	$C_6H_{12}O_5$ 164	6		183 249	Y Y	Y Y
M	$C_6H_9O_5N_1$ 175	13 3L, 10C		194 260	- -	Y Y
N	$C_6H_{11}O_5N_1$ 177	3		196 262	- -	- Y
O	$C_6H_{11}O_6N_1$ 193	10		212 278	- -	Y Y
P	$C_6H_{10}O_7N_2$ 222	6		241 307	- -	- Y

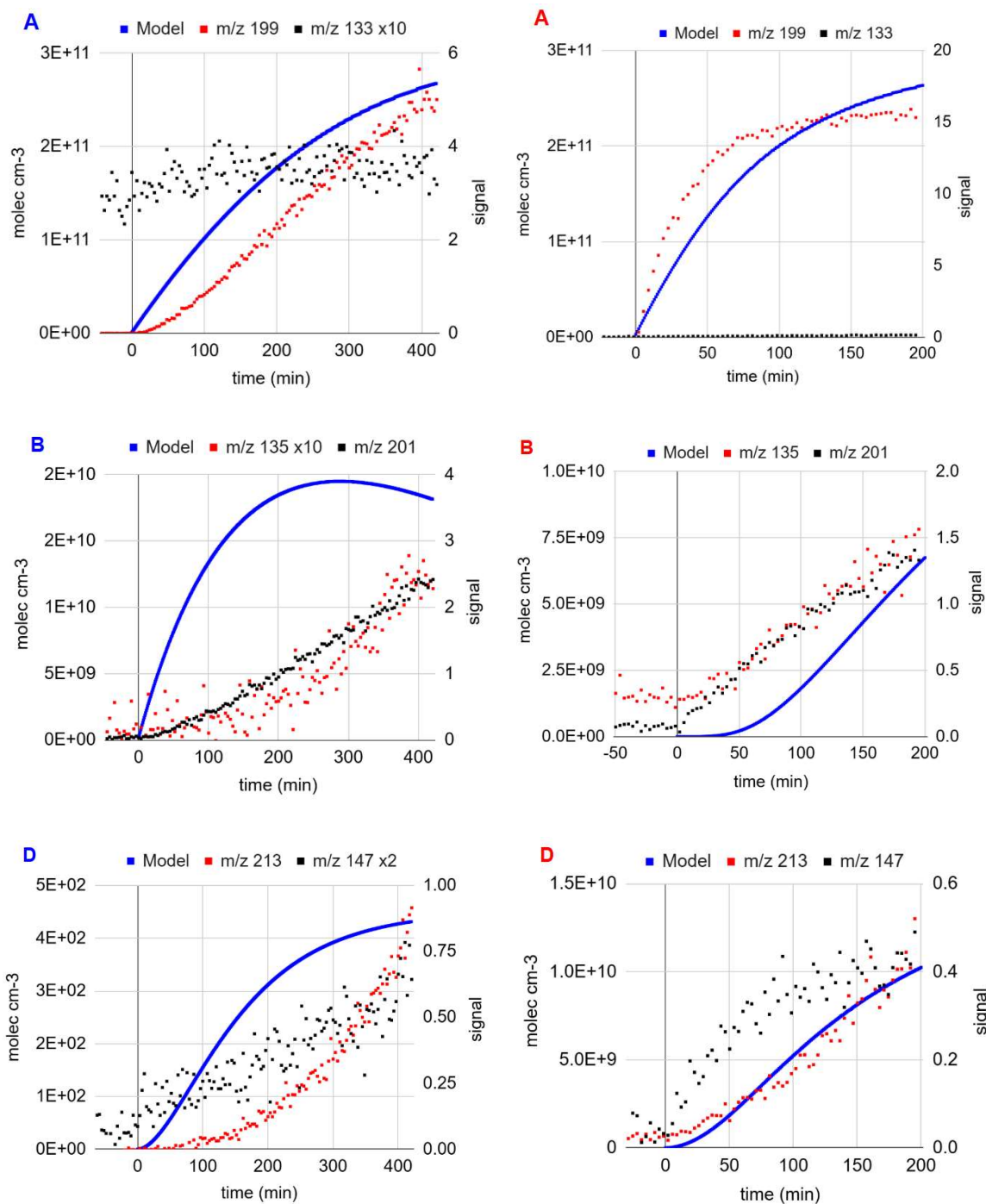


Figure 1.26 displays modeled concentrations versus measured ion signals corresponding to products A, B and D in Table 1.8. On the left side (letters in blue) are data for Trial 4 (no-NO) while Trial 5 is on the right (letters in red). For product A only one mass ($M + CF_3O$) was detected, while both masses were detected for products B and D under both NO and no-NO conditions. Product B fits most poorly to the model of the 3 presented; under no-NO the model predicts a curve, while the detected signal is linear in appearance.

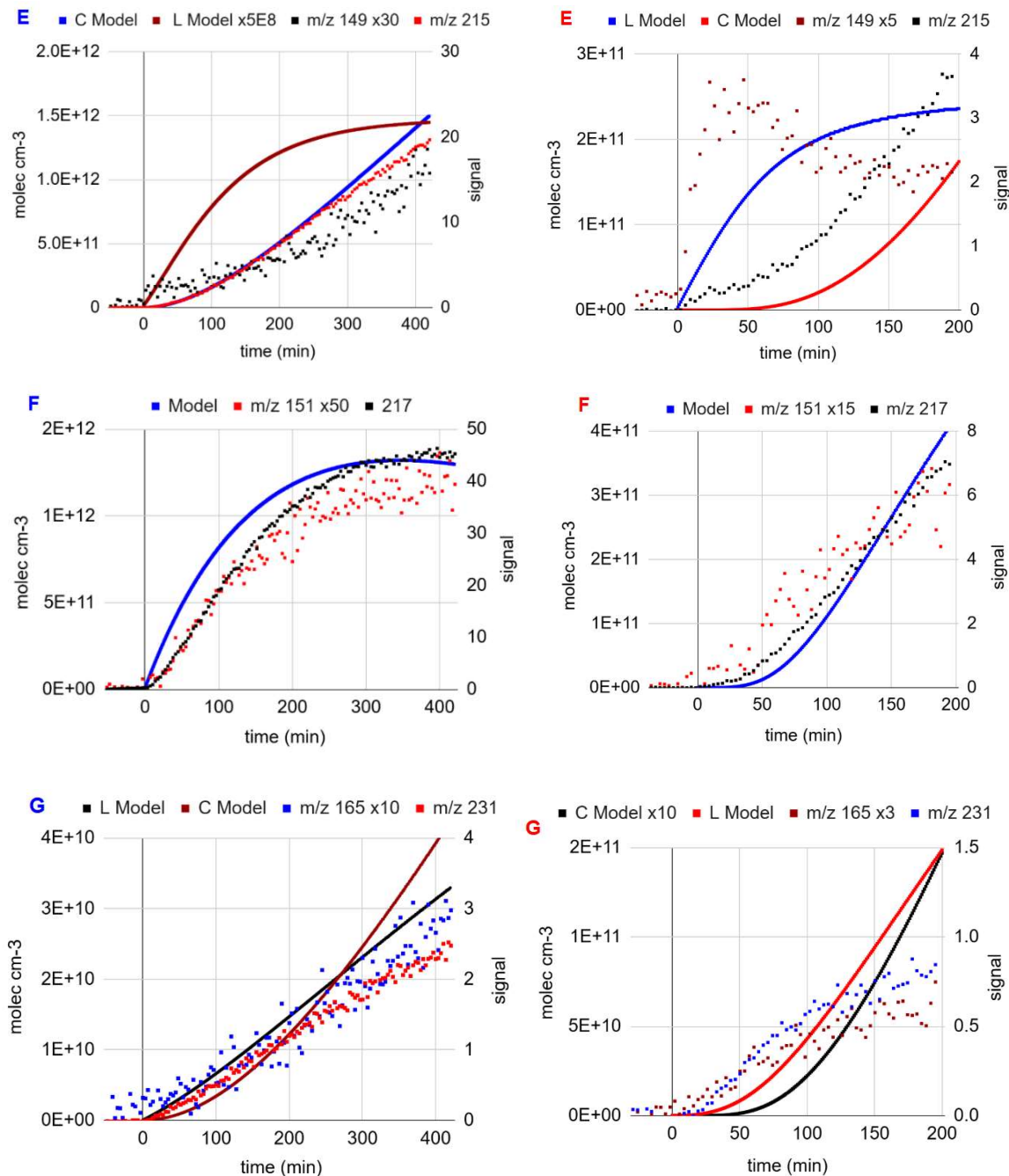


Figure 1.27 displays modeled concentrations versus measured ion signals corresponding to products E, F and G in Table 1.8. On the left side (letters in blue) are data for Trial 4 (no-NO) while Trial 5 is on the right (letters in red). Both the F^- and CF_3O^- bound versions of E, F and G were detected in both NO and no-NO environments. The best fit product of these 3 by the model was product F. The model predicted well the initial curve of F under no-NO, which becomes more linear as NO was added. Utilizing the curves predicted for the cyclic and linear products for E, it appears that the linear isomers bond more strongly to F^- while the cyclic isomers may bond more strongly to CF_3O^- .

A total of 24 modeled vs measured plots were thus produced (8 products detected under no-NO, 16 products detected in the presence of NO). These 24 plots are presented across Figures 1.26-1.29. In the case of no-NO conditions (Trial 4), our kinetic model was able to well-mimic the curve for 4 of the 8 observed masses: A, E, F and G. Of the 16 predicted products detected under Trial 5 (NO-containing) 12 have experimental curves which match those produced by the model: A, B, D, E, F, I, J, K, M, N, O and P. As multiple isomers contribute to the signal observed by the mass spectrometer, all similar isomer concentrations are summed for the “Model” curves. For example, ortho, meta, and para hydroxy cyclohexanone contribute to Ref A, so their modeled concentrations were summed. Again, each isomer will have a different binding efficiency, so this is an estimate. When a product has both linear and cyclic isomers, these modeled concentrations were plotted separately from each other, as they are generated from very different mechanistic paths. Linear isomers are labeled “L Model” while cyclic isomers are labeled “C Model.”

In Figure 1.26 products A, B and D are plotted under NO and no-NO conditions. Interestingly, the modeled concentrations match closest to the signals observed for the NO containing Trial, Trial 5. This is unexpected as more pathway to production of most products are increased when NO is present, and thus we would expect more error to be introduced. The no-NO plot for product A gives a clear example of when one bound mass was detected (m/z 199) while the other was not (m/z 133). The m/z curves for product D from Trial 5 (yes-NO) indicate there may be another isomer that was not predicted by the model. This is because the curves for m/z 147 and 213 are very different in shape.

Similarly, in Figure 1.27 the NO and no-NO modeled vs experimental curves are presented for products E, F and G. Under no-NO both masses for product E match the cyclic isomers modeled curve. However, when NO was added, we see m/z 147 and m/z 215 split into two distinct shapes. m/z 215 continues to resemble the cyclic curve while m/z 149 better resembles the linear isomers curve. The kinetic model appears to do a very good job of mimicking the production of product F, as the model was able to predict the shapes for both Trial 4 and Trial 5 data, despite their having very different curves. While product G signal is likely the result of both cyclic and linear isomers these plots were not able to distinguish the two.

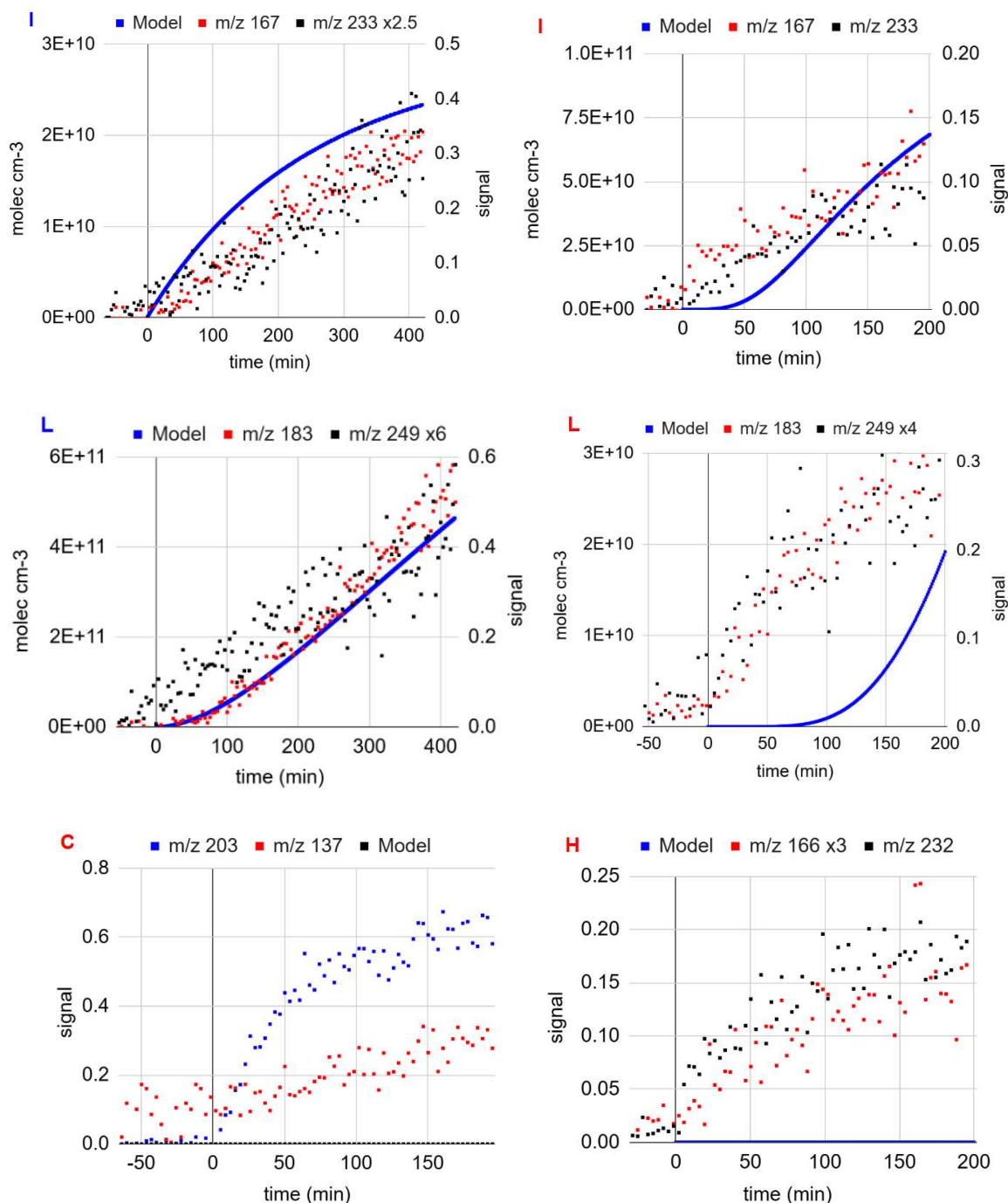
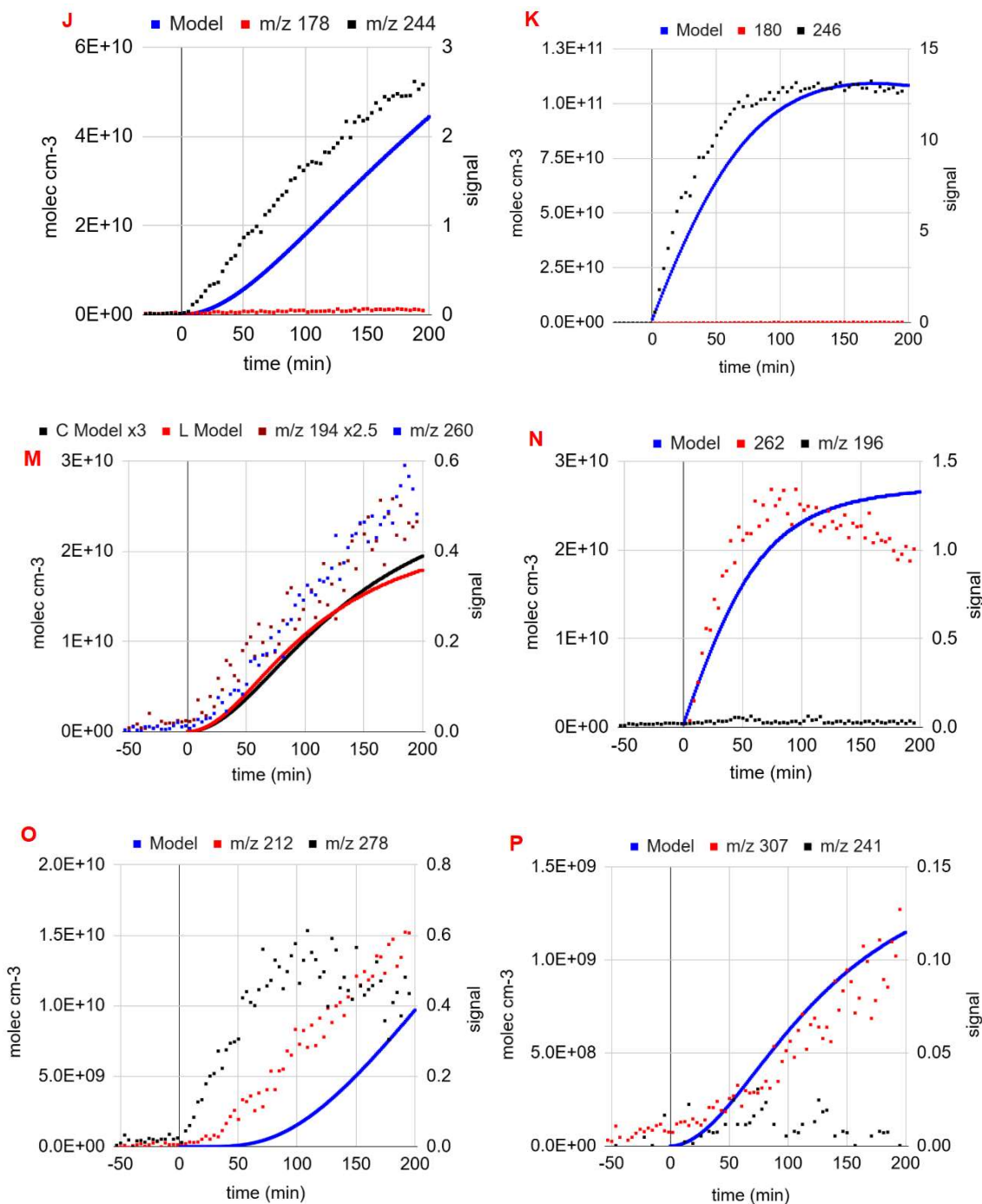


Figure 1.28 displays modeled concentrations versus measured ion signals corresponding to products I, L, C and H. Products I and L are shown under both no (left panels with blue letters) and NO (right panels in red letters) conditions. While for product C it may look as if m/z 137 is growing, large uncertainty before photolysis makes it challenging to confirm that the signal is from real growth and not just drift in the background. Notably, modeled results for C and H did not predict significant growth of these products despite their being detected. This suggests that kinetic constants in the model may require adjustment.



In Figure 1.28 four product modeled versus measured ion curves are presented: I, L, C and H. Products I and L were detected under both NO-containing and no-NO conditions and thus are plotted under both. Products C and H were both only detected in the presence of NO (Trial 5). Both C and H are linear species resulting from ring-decomposition. This suggests that NO increases the likelihood of ring destruction, which makes intuitive sense as a large path from NO-reaction is formation of alkoxy radical (reaction 17). Our model does not predict substantial growth of these two species, indicating the biggest flaw in our kinetic model. For example, product C is expected to primarily result from ortho-alkoxy cyclohexanone decomposition and successive oxidation. There are likely other parent molecules whose decomposition result in product C that are missing from this model.

In Figure 1.29, six products only observed in the presence of NO are presented; all of which contain a nitrate group. Of these, J, K, N and P are only detected when bound to CF_3O^- . It is possible that these products do bind to F^- as well, but just less efficiently, and the current in-chamber concentrations are too low to detect these complexes. There are only 7 nitrate-containing predicted products (H in Figure 1.27 also contains a nitrate group); 4 only bind to CF_3O^- , and 3 bind to both. Future studies employing this chemical ion should anticipate significantly better detection of nitrate groups via CF_3O^- complexation compared to F^- . Product O contains two distinct curves for the CF_3O^- and F^- complexes, indicating their may be an additional isomer not predicted by our model.

In addition to the 16 product isomers we predicted via our kinetic model, we also attempted to identify other remaining peaks, identified in Figures 1.24 and 1.25. We suspect that a mass at 131 m/z might be ethanol, $\text{C}_2\text{H}_6\text{O}$ ($46 + 85$ m/z), but a bound mass of 131 may also result from a heavier molecule complexing with F^- ($112 + 19$ m/z). The likelihood that the mass 131 results from ethanol was further demonstrated when a matching growth curve was identified at 65 m/z ($46 + 19$ m/z). Similarly, we strongly believe that 145 and 79 m/z result from acetic acid ($\text{C}_2\text{H}_4\text{O}_2$), 173 and 107 from 4-hydroxy butanal ($\text{C}_4\text{O}_2\text{H}_8$), and lastly 105 and 171 from butanedial ($\text{C}_4\text{H}_6\text{O}_2$).

Less evidence is available for m/z 219, which may result from malic acid ($\text{C}_4\text{H}_6\text{O}_5$). Masses at 285 and 153 ($219 + 66$ and -66) are undetected, providing no further support or opposition of its identity.

Similarly, m/z 308 ($C_6H_{11}O_7N_2$) may arise from a linear version of product P (one more hydrogen), but no signal was found at 374 or 242. The lack of detectable mass at 242 m/z (the F- bound complex) would not be surprising for a nitrate-containing product, as evidenced by J, K, N and P. Lastly, we believe that a highly oxidized product with two nitrogen groups is responsible for a peak at 322 ($C_6H_9O_8N_2$), with again no detected signal at 256 or 388 m/z .

1.4.7 Mass Yields

An OH-initiated cyclohexane experiment (Trial 3, Table 1.9) was conducted to evaluate the validity of our calculations, as cyclohexane MY has been previously measured. Shown in Table 1, 230 ppb of cyclohexane was oxidized in $[NO]_i = 110$ ppb. Using the protocol discussed in section 1.35, cyclohexane was found to have an uncorrected MY of 1.9 and a corrected MY of 9.8%. The cyclohexane MY curve is presented in Figure 1.30, alongside the MY plots for Trials 6-9. Unfortunately, long oxidation periods were required to fully deplete VOCs, resulting in large particle wall-loss corrections. Thus, in this work, we will consider uncorrected and corrected MYs to be lower and upper bounds of the “real” MY.

Table 1.9: Cyclohexanol Mass Yield

Trial	$[NO]_0$ (ppb)	VOC reacted (%)	chamber V_f (%)	$[OH]_{ave}$ (molec/cm ³) ^a	MY uncorrected ^b (%)	MY corrected ^b (%)
3	110	86	91	-	1.9(0.3)	9.8(0.7)
6	0	92	91	2.4E6	14(1)	23(1)
7	30	96	91	3.1E6	6.5(0.3)	18(1)
8	75	96	90	3.6E6	13(1)	20(1)
9	120	98	89	4.0E6	4.0(0.3)	13.(1)

^a $[OH]$ was calculated according to the procedure described in 2.3.3.

^b Uncertainty is the standard deviation of the last 15 points, which span over about an hour and a half.

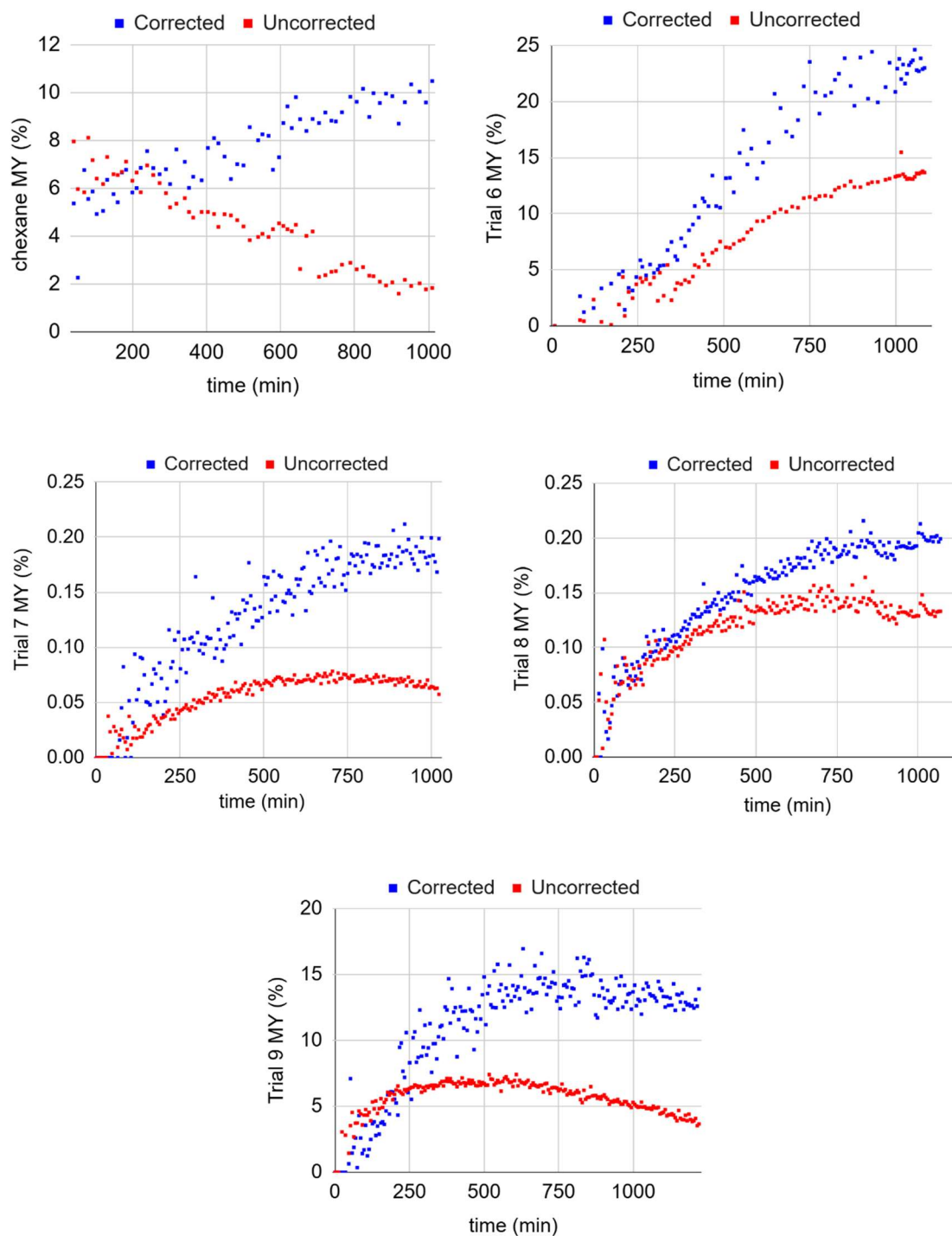


Figure 1.30 shows the MY plots for Trials 3 (cyclohexane) and 6-9 (cyclohexanol), whose details are provided in Tables 1.1 and 1.9. Note that MY is a function with time, and the MY reported in Table 1.9 were taken once the corrected curves stabilized. Trial 8 is a particularly clean example of a curve where MY increased until a stabilized region around 500 min+. A MY reported prior to approximately 500 min would be an underestimation.

Lim and Ziemann experimentally determined a MY of 4% for cyclohexane. Due to the difference in our systems these results are not directly comparable. Among other factors, their chamber is a smaller size (5.9 m³ versus our 18 m³), utilized a different aerosol seed (dioctyl sebacate versus ammonium sulphate), is run at higher VOC concentrations (10 ppm vs 230 ppb), and with methyl nitrite providing a constant source of NO. Despite these experimental differences, the Lim and Ziemann value falls within our measured range, highlighting that our cyclohexanol MY measurements, which are calculated in the same manner, are reasonable.

For the cyclohexanol MY measurements, four experiments (Trials 6-9) were performed with [NO]_i ranging from 0 to 120 ppb. These results are plotted in Figure 1.30, with further details provided in Table 1.9. Additionally, the four cyclohexanol MY results are depicted against the McDonald theoretical cyclohexanol MY, as well as the mass yield of a large linear alkane (dodecane)⁴⁰ which has what is considered a high mass yield in Figure 1.31.

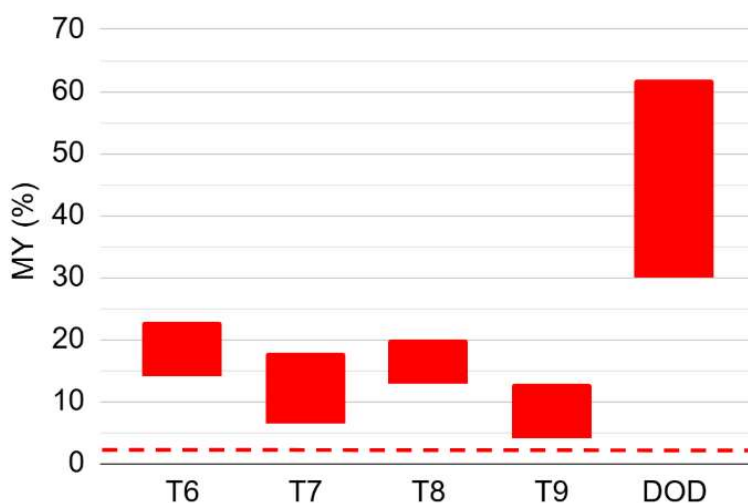


Figure 1.31 plots our MY results from Trials 6-7 against the McDonald et al. theoretical MY (dotted line = 2.2%) and the experimentally determined MY of the 12-carbon linear alkane, dodecane. Dodecane has twice as many carbons as cyclohexanol, and has what is considered a notably high yield for comparison. Cyclohexanol can have a surprisingly large MY depending on its oxidative environment, and certainly has a large MY than that predicted by the McDonald et al. model.

Notably, the McDonald theoretical value of 2.2% does not address how NO (or lack thereof) may impact aerosol formation and is provided as a universal value. It should also be noted that their multigenerational oxidative model predicts cyclohexanol and cyclohexane to have the same low MY. Our results show that cyclohexanol, at least under these conditions, have a much higher mass yield than that predicted by the McDonald *et al.* oxidative model.

How cyclohexanol oxidation chemistry and thus MY might compare to cyclohexane is not as obvious as it might seem at first glance. While the addition of an OH-group can be expected to increase MY due to the drop in vapor pressure, it has also been found that some oxidative groups are sites vulnerable to fragmentation and can accelerate decomposition, lowering MY, especially in the presence of NO.¹⁴ In the case of cyclohexanol, it appears that the cyclic nature of the species protects the molecule, allowing the hydroxy group to enhance aerosol forming potential.

We also found that [NO] does impact cyclohexanol aerosol formation, with no-NO conditions being as high as 22.9% (corrected value). As indicated in section 1.4.5, this aerosol formed in a HO₂+RO₂ dominant environment. The two “moderate” starting NO cases, Trials 7 and 8, show a minor deflation in aerosol forming potential, while the high starting NO trial, Trial 9, saw a reduction in MY of almost half. This wide range of observed MY stresses the importance of oxidative environment when evaluating aerosol forming potential, and highlights the complexity needed of predictive models.

1.5 Conclusion

Though particulate pollution from cars is being mitigated, VCP emissions continue to grow as a source of urban aerosol. These molecules are present in all urban life; from cleaning products to personal care products, to the paints and varnishes we use to color our cars and houses. To reduce comorbidities resulting from poor air quality, it is important to monitor and reduce these VCP-derived aerosol. It is unrealistic to expect urban communities to reduce use of these products; instead, we need to carefully select active ingredients and solvents that are not just minimally toxic in their original form, but also have minimal aerosol forming potential. The challenge to making these decisions is there are so many VCPs, ranging in size and functionality, that performing laboratory measurements of all

these molecules under all possible atmospheric conditions is unreasonable. As a result, the atmospheric community is developing a variety of methods to predict aerosol forming potential, like volatility basis sets and statistical oxidation models.^{1,11} In the case of cyclohexanol we observe how multiple functionalization can have interacting effects. The cyclic nature of cyclohexanol protects the molecule from fragmentation, and thus the hydroxy group reduces the vapor pressure, and does not appear to greatly enhance fragmentation to the point of lowering MY. This work, like other recent works on oxidized VCPs,²³ stresses that things like O:C ratios and carbon number alone are sometimes unable to adequately predict aerosol forming potential of parent molecules. VCPs should not be ruled out of scrutiny based on carbon number alone. Continued laboratory and mechanistic modelling of parent molecules can hopefully bridge our gap in understanding how molecule structure can be used to predict MY under a variety of atmospheric conditions.

In the present work, we also observed that kinetic modeling and chemical ion detection when utilized in tandem can provide further support for product identification. In the case of our CF_3OOCF_3 ion source which creates two chemical ions, F^- and CF_3O^- , coplotting of signals can help distinguish isomer structures (cyclic versus linear). Lastly, we note that careful calibration techniques are critical for any future studies evaluating MY of intermediate volatility organic compounds (I-VOCs). We observed that I-VOCs like cyclohexanol are liable to stick to even Teflon materials like atmospheric sampling bags and tubes. Effects of sticking can be minimized if the I-VOC is kept in large concentrations and diluted into the sampling instrument in real time via flow cell.

1.6. Future Works

Any future atmospheric chamber studies of this length (10+ hours) should employ a different procedure for maintaining $[\text{NO}]$ in the chamber. Ideally, slow pulses of NO can be introduced to maintain the concentration throughout the oxidation period. This would be very different from our work in which one pulse introduced the NO at the start, which was depleted within 30 minutes. Additionally future studies on cyclohexanol using a similar system would benefit from calibrating the CIMs to some of the primary and secondary products. However, many of these are not commercially available and would yield challenges to synthesis and storage, such as products containing hydroperoxide or

nitrate groups. If kinetic modeling of this system is improved and better supported by ion signal curves, it may be possible to avoid need for calibration. In either case, it would help to increase ion signal over-all, as some of the products could not be confidently detected. We do not recommend simply increasing cyclohexanol starting concentration, as this will shift the regime to favor $\text{RO}_2 + \text{RO}_2$ chemistry more heavily, to a degree which may not resemble atmospheric conditions. In fact, atmospherically measured concentrations of cyclohexanol are already much lower than used in this study (~ 200 ppb). Lower concentrations, though preferable, are undetectable via the GC column utilized. Instead, may be better to increase the chemical ion source, CF_3OOCF_3 . The impact of cyclohexanol concentration on aerosol mass yield is likely also of interest. To study lower concentrations of cyclohexanol via the gas phase sampling GC-column described would require installation of a more polar column.

1.7 Citations

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*. Chapter 2***CENTENNIAL REACTOR DESIGN AND TESTING WITH K_2CO_3
IMPREGNATED ZEOLITE****2.1 Abstract**

In the following chapter the construction and validation of a prototype industrial scale “Centennial” reactor is discussed. The reactor is a two-tower system designed by Mitico, a carbon capture company founded in 2022 out of Caltech, to continuously capture CO_2 . This is accomplished as one tower undergoes an absorption cycle, the other tower releases CO_2 in a regeneration cycle. Two different K_2CO_3 -impregnated zeolite sorbents were tested and cycled; PureAir “rock-type” impregnated by the manufacturer and ADCOA spherical pellets impregnated on-site by Mitico. PureAir zeolite, was found to have the higher of the two capacities, with our highest trial capacity reaching 0.3 mmol g^{-1} sorbent capture for the 112 kg load. The impact of different regeneration temperatures and gas identities (N_2 , CO_2 , H_2O) on sample cyclability were also explored. It was found that steam can lower the required energy for regeneration, and results in a faster and more complete regeneration. While ultimately capture capacities were lower than desired, major design flaws and quirks were identified for the purpose of bettering future reactor designs.

2.2 Introduction**2.2.1 Carbon Capture**

As the impacts of climate change become ever more prominent in political discussions, globally governments have made concerted efforts to minimize greenhouse gas emissions and find usage for them, i.e. storage through chemical fixation.¹ Of the many greenhouse gases, which includes fluorinated gases, nitrous oxide (N_2O) and methane, by far the most abundant is CO_2 which is expected to represent about 80% of annual emissions.² CO_2 is emitted in abundance for combustion energy and as a manner of eliminating unwanted materials. For example, CO_2 is emitted from coal and natural gas power plants, but it is also emitted when municipal solid waste is burned, a common practice in many countries.^{3,4} CO_2 is also a by-product in many chemical reactions in industrial processes, like cement

production. Fossil fuel burning powerplants however, are estimated to be the single largest source of CO₂ production, representing a third of global annual emissions.⁵

As CO₂ sources are various and their originating processes are often challenging to replace with carbon neutral or negative alternatives, elimination of widespread CO₂ production is impossible, at least in the near future. Thus, it is necessary to find ways to capture CO₂, and store or utilize it. While capturing CO₂ may not naturally benefit corporate entities under an unregulated capital system, many governments have incentivized sequestration by offering carbon credits to companies who manage their emissions or delivering carbon tax penalties to those that do not.⁶ In general, CO₂ capture can be categorized as ambient/direct air (DAC) or point source capture (PSC). Both capture types experience their own sets of challenges. In the case of DAC, the primary challenge is creating a system which can overcome the thermodynamic difficulty of reacting with a molecule that makes up less than 0.1% of the atmosphere. To increase the uptake rate of CO₂ into the reacting material, fans are used to pull in ambient air.

While green energy can be used to power these fans, operating costs for direct air capture are expected to be high as a result. Estimates for 2030 DAC systems are expected to range from \$600-1,000 USD per net tonne of CO₂ captured.⁷ Heirloom is one of the first to-market DAC companies; it is California-based and utilizes limestone tray stacks to chemically capture CO₂. Their earliest sales in 2021 is a good measure of current market limitations; with costs as high as \$2000 per net ton captured.⁸ The limestone, Ca(OH)₂, reacts with CO₂ to form CaCO₃. When CaCO₃ is heated, it releases CO₂ leaving behind CaO, which can be hydrated to reform Ca(OH)₂.⁷ This chemical reactivation via temperature swing is a common strategy in both DAC and PSC.

PSC is as it sounds; sequestration of CO₂ from a point source emitter, most often flue stacks on top of powerplants. Flue stacks have very high exhaust flow rates, between hundreds and thousands of m³/ph depending on the design.⁹ In addition, the CO₂ is present in much larger concentrations, typically between 4 and 15% by volume.¹⁰ For this reason, the primary challenge to PSC is that absorbers must have very high capture capacities and reaction rates.



Figure 2.1 depicts the real Heirloom DAC facility in Brisbane California, 2023.⁸ $\text{Ca}(\text{OH})_2$ powder is laid out on vertical stacks to minimize land requirements and maximize sorbent-air exposure from fans.

Materials with low capture capacities pose concern to economic costs as they will need to be replaced/recycled more frequently or be used in larger quantities. Materials with low reaction rates necessitate long residence times through the material, again increasing the size of the capture system (in the case of a reactor, the height) and compounding system complexity. While there are many materials under development that provide fast and efficient capture, other material qualities must be balanced as well. Properties that impact industrial feasibility include cost of material production, cost of regeneration and material lifetime (if the material is to be cycled) and toxicity to name a few. Two of the leading directions for selective CO_2 capture are metal organic frameworks (MOFs) and amine solvents. To illustrate the current state of the field of carbon capture, we will briefly discuss MOF and amine-based capture.

In the early 2000s, advancements in high porosity materials and synthetic tuning of pore environments allowed for MOFs to be applied to CO_2 related-problems.¹¹ Design elements that are common amongst MOFs intended for reversible CO_2 capture include square or hexagonal channels that are designed to allow CO_2 (and only CO_2) navigation, hydrophobic pores, open metal sites to interact with CO_2 , and other heteroatom functionalization of the backbone like amino groups, again to interact with the CO_2 .^{11,12} Zeolites are an inorganic

silica and alumina based naturally occurring solid that can form in a variety of 3D structures. Zeolites are one of the earliest developed metal-oxide frameworks of interest to catalytic and capture technology.¹³ Due to their high capacity and reversible absorption, zeolites are used as molecular sieves and structurally tuned depending on their application. Zeolites were one of the first simple materials with notable selective CO₂ capture and are often used as a basis of comparison to other capture materials. Zeolite 13X, for example, generally captures around 5mmol CO₂ per gram however they also capture other small gases like H₂O, O₂ and N₂.¹⁴ MOFs can easily reach this capacity at standard pressures, and even higher capacities at higher pressures.¹⁵ Unfortunately, MOFs also experience selectivity issues observed by zeolite. In addition to their high cost of production, insufficient CO₂ selectivity is one of the biggest challenges that prevent current use of MOFs for carbon capture.¹⁵

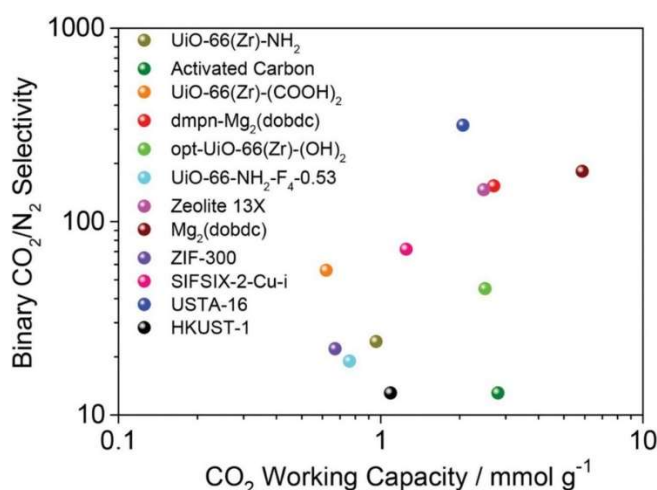
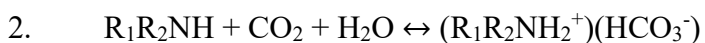
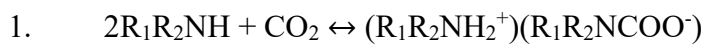


Figure 2.2 is borrowed from Younas et al and displays CO₂ capture capacity for a variety of studied MOFs against their selectivity in CO₂/N₂ mixtures.¹⁵

The most common carbon capture method that currently occupies about 60% of the carbon capture market is amine scrubbing.¹⁶ Before its use in carbon capture to help mitigate climate change, amine scrubbing was used to purify industrial gas streams of compounds like hydrogen sulphide (H₂S) for safety reasons, which is why it is also called acid-gas decontamination. When amines react with CO₂, they do so according to lines 1 and 2; where line one displays formation of carbamate and line 2 displays formation of bicarbonate. The reaction preference between these two paths differs depending on the

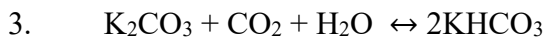
amine identity, especially if it is primary, secondary or tertiary. Tertiary amines, for example, can only undergo the reaction 2.¹⁷



Amine scrubbing is currently the most economically viable method of CO₂ capture, as amines are cheap and easy to produce, and controlled release of the CO₂ requires only a small temperature swing. Capture typically occurs between 40 and 70°C, while release occurs between 100 and 150°C, a temperature that can easily be achieved at most industrial plants by repurposing waste-heat.¹⁸ Despite these advantages, amine scrubbing cannot be the only long-term solution to CO₂ management because accidental release of amines presents its own environmental concerns. While amine towers utilize traps to minimize losses, amine vapours and aerosol still readily escape. Additionally as amines degrade over time due to oxidation, they also form other compounds such as organic acids, ammonia, and amides which corrode equipment and are themselves environmentally hazardous.^{17,19}

2.2.2 K₂CO₃-Based Sorbents

New materials are needed to replace amine-based CO₂ capture to prevent future environmental complications brought on by amine emissions. To be able to compete with amine scrubbing, the capture material must possess many properties including cheap and simple production, a low-cost regeneration, and a long use time before needing to be replaced to name a few. Solid alkali-metal based sorbents have been identified and begun to be explored in the last few decades.²⁰ Some metal oxides and carbonates that have been considered include MgO, CaO, and K₂CO₃.^{20,21} In the following work we explored the capture capability and feasibility of K₂CO₃-based sorbents on a small industrial scale (a small packed bed reactor, not a bench scale measurement). K₂CO₃ is considered over other alkali-metal materials due to its comparably low regeneration temperature. Most metal oxides are heated to >500°C, while in comparison under atmospheric conditions K₂CO₃ regenerates at around 120°C+ depending on the utilized support and gas conditions, but typically hovering around 155°C.^{22,23} The simplified reaction is provided in line 3; K₂CO₃ reacts with CO₂ under humid conditions to reversibly form KHCO₃.²⁰



The biggest challenge to K_2CO_3 -based sorbents is that despite their high theoretical capacity of 7.25 mmol CO_2/g K_2CO_3 (compare this to zeolite, around 5 mmol CO_2 per gram), actual CO_2 conversion often is capped at around 50% that. This is primarily due to poor morphological structure of the raw K_2CO_3 that results in pore-clogging.²⁴ In addition, due to the very deliquescent nature of K_2CO_3 salt, their stability in humid environments is often quite low.²² For these two reasons, support structures are needed to provide ample surface area for reaction, and to prevent dissolution of the material and thus mass loss while cycling. Recently most efforts in developing K_2CO_3 -based solid sorbents have been focused on finding a viable support for industrial scalability. Some of the options considered in the literature include carbon nanofibers, TiO_2 , Al_2O_3 , SiO_2 , cement and clay.²⁴

There are primarily two approaches to adhering K_2CO_3 to its support. Wet-activated granulation, like what is primarily used for clays and cements, describes a process in which support/binding dry powders are mixed with K_2CO_3 and water. The slurry can then be shaped into pellets then dried or dried to be crushed and sieved into the appropriate size particles. When dried low temperatures superficial water is baked off, and at high temperatures ($>300^\circ\text{C}$) calcination may even convert carbonates and hydroxides to metal-oxides, or recrystallize the mixture, increasing material strength.²⁵ Alternatively, impregnation describes a process in which a covalently bonded network, typically a metal oxide particle like Al_2O_3 , is submerged in K_2CO_3 solution. Dissolved K_2CO_3 slowly traverses the pores until the solution reaches an equilibrium. The particles are then removed from the solution and dried. While there are many benefits to granulation-formulated materials, as will be discussed in Chapter 3, for the purpose of testing the Centennial reactor we chose to utilize impregnated zeolite beads. The primary benefit of utilizing an impregnated media is that there is no concern the structure the K_2CO_3 is adhered to will dissolve or break apart. As this work involves the construction and calibration of the new reactor system, it was important that the testing material be as chemically simple as possible by providing a strong support for the K_2CO_3 .

2.3 Methods

2.3.1 Reactor Design and Construction

The Centennial packed bed reactor, with which this work was performed, is the first industrial prototype that utilized Mitico's potassium carbonate-based sorbent. It is the test-system of a family of reactors which will be installed on top of industrial exhaust vents to capture CO₂ from post-combustion flue gas. The entire structure referred to as the Centennial reactor is multiple tandem systems that make controlled capture and release of CO₂ possible. The system generates a laboratory "flue gas," controls that flue gas composition and flow rate, regulates temperature, pressure and humidity in the tower, and detects and captures data related to CO₂ capture and release. Generation of the laboratory flue gas mimic was a non-trivial aspect of the work, as will be explained in the following section. Figure 2.3 provides a simplified diagram of the main points of interest in the centennial system.

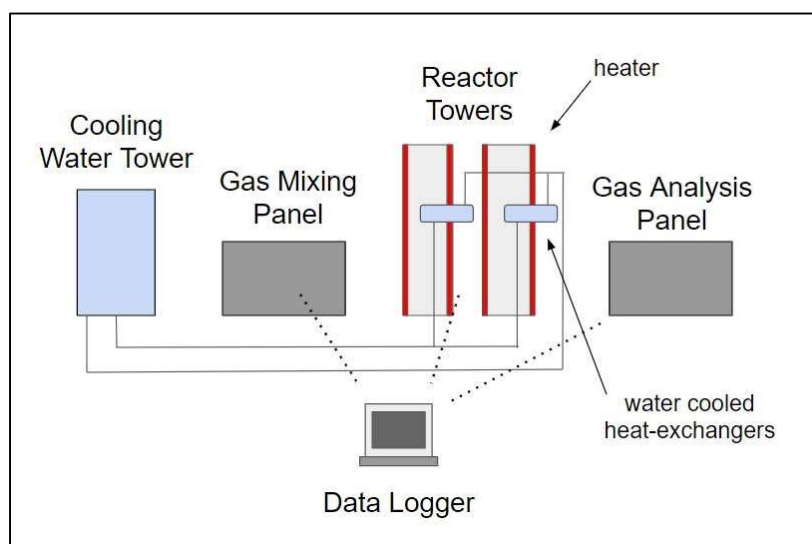


Figure 2.3 displays an overview of the most critical components to the Centennial reactor. The three subsystems that will be explored in more detail in the following sections are the gas mixing Panel, the packed bed towers, and the gas analysis panel. Also shown in the above image is the cooling water system, the internal tower heater, and the data logger.

Centennial was assembled at Mitico's 2023-2024 headquarters, an industrial warehouse in Los Angeles, California. Assembly began Spring of 2023 and was completed Fall of that year, excluding some minor modifications carried out in late 2023 and early 2024. The two

reactor towers were purchased from a commercial supplier and mounted on a modular process skid for easier mobility. All other system components were constructed around the skid, which was placed near the black “X” in Figure 2.4. To make the reactor work requires an elaborate network of electronics, plumbing and gas regulation subsystems, not all of which will be discussed in detail. For example, to generate enough steam to provide humid flue gas at high flow rates necessitated utilization of a commercial steam generator which itself requires a deionized water source. A water sampling network with multiple reverse osmosis filters are maintained to provide the steam generator with a constant flow of clean water. Another subsystem not explored in this thesis is wastewater management. When the towers are in operation, lines must be continuously drained of any condensed vapours resulting from absorption or regeneration. However, the site did not allow for easy gravity drainage from all active sites, thus electronic drains were installed to collect and move wastewater. In the following sections we will explore in further detail the flue gas generation at the gas mixing panel, the packed bed towers, and the gas analysis panel.



Figure 2.4 shows the Centennial site prior to construction. Black tape was used to outline the approximate total system size. The black “X” indicates the approximate site the skid-mounted towers were placed. Component placement was optimized according to the location of the water supply (the white sink), site drainage (the black tube by the sink), and power supply (transformer and electrical control panels, grey).



Figures 2.5 and 2.6 display the complete Centennial system from two different angles. The cooling tower is around the open door (1) in Figure 5, and thus not displayed. In Figure 5, the tower control panels (2) are displayed on the reactor front, as well as compressed gases on the right (3), which are used to generate different flue gas conditions. In between the towers and cylinders sits a steam generator (4) used primarily to humidify the flue gas. Occasional trials were conducted where steam was also utilized for CO₂ regeneration. In Figure 6 the gas mixing (5) and gas analysis (6) panels are visible. An in-line heater (7) is available near the tower control panels and provides extra temperature control for injected flue gas. One of the water-cooled heat exchangers (8) also illustrated in Figure 2.3, is visible to the left of the gas mixing panel.

2.3.2 Gas Mixing Panel

Centennial is designed to be flue gas agnostic, meaning that it can capture CO₂ from many industrial processes. For example, in a natural gas combined cycle powerplant CO₂ concentrations are very dilute, about 4% in the outlet stream. Alternatively, a pulverized coal power plant may have exiting CO₂ concentrations as high as 15%.¹⁰ Powerplants, depending on their energy source and combustion conditions, can also be highly humidified, with most post-combustion streams having absolute humidities between 5 and 15% H₂O.²⁶ One challenge to creating carbon capture materials is though they must be employed under a variety of industrial conditions, the composition of the gas can affect the performance of the material in many ways. For example, pure K₂CO₃ has a lower capture capacity at lower concentrations of CO₂ because of a shift in the reaction equilibrium. This was observed by Luo *et al.*, who found an absorption capacity of 6.24 mmol g⁻¹ when the flue gas was 1% CO₂ and a capacity of 6.92 mmol g⁻¹ while at 100 %CO₂.²⁷ Hydration levels of the material, active or inactive, may also impact the rate at which CO₂ is captured. If H₂O is blocking pores, dissolving material, and overall creating greater flow resistance it can impede reaction with CO₂. On the other hand, readily accessible water may expedite the 3-molecule reaction to form bicarbonate.²⁷

Since the material performance will vary depending on the flue gas composition, it is important for any study to have a well-defined flue gas. To accomplish this, we constructed a flue gas mixing panel. The panel was constructed of a perforated carbon steel sheet for its easy mounting capability and large weight capacity. During initial system testing, which included leak testing and monitoring gas flows through the tower, two Omega FMA-1600 series mass flow controllers were utilized to mix CO₂ and N₂ from Airgas compressed gas cylinders. During this phase only low flow rates between 5 and 25 lpm were needed. Figure 2.7 shows this initial set-up, including a sampling line that sends mixed but not yet humidified flue gas to a Servomex 4900 Multigas (CO₂) Analyser. While it is redundant to send samples of known mixtures through to the CO₂ analyser, later compressed air was utilized to increase flow to industrially relevant rates greater than 50 lpm and necessitated use of an external concentration measurement. Once the gas was mixed and verified against the CO₂ analyser, it was humidified and sent to the reactor inlet.



Figure 2.7 shows the original perforated panel design. Two mass flow controllers set the flow of CO₂ (1) and N₂ (2) coming from pressurized cylinders. Around 2 lpm of the mixed “flue” gas is sent to a CO₂ analyser (5) via another mass flow controller (4) to monitor composition changes in real time. Again, this is not as necessary when flue gas is generated by controlled gas mixes, but later compressed ambient air was used instead of N₂ to increase flow rates. A pressure relief valve (3) can be used in case of an emergency shutdown. Once the gas is mixed and analysed it is sent to a junction (6) that introduces water vapor from the steam generator.

As previously stated, industrial flue gas absolute humidities span between 5 and 15% water, and reaction kinetics and sorbent capacity are dependent on humidity levels. However, maintaining near constant humidity levels in gas streams, especially at high flow rates is not trivial. The Antoine equation²⁸ for water dictates that at 50°C, air can hold a little over 10% water. Thus, we hoped to generate flue gas of around 50°C or more. It should be noted that gas greatly above the optimal absorption temperature of 65°C, which can hold up to 25% water, would also introduce issues, as it would shift the equilibrium towards the reverse (regeneration) reaction.

The heat from the steam injected into the line was not on its own enough to heat the gas stream to 50°C so heating tape was wrapped around the humidification junction depicted

in Figure 2.7. The Cellkraft E-1500 Precision Steam generator can produce steam at a set flow rate, or it can be set to an operating mode that uses a hygrometer and internal Proportional-Integral-Derivative (PID) loop to maintain an average set humidity. It was determined that temperature fluctuations in the warehouse and flow rate fluctuations from the air compressors introduced too much instability to use a set steam flow rate, thus we utilized PID operation mode.

Before actual packed-bed absorption testing the original mixing panel shown in Figure 2.7 was used for general operational testing. First, N₂ between 0 and 25 lpm was injected into the tower under different operational configurations (to be explained in the following section) to test for leaks. Leaks were identified by comparing entering tower flow rates to exiting tower flow rates and located on the skid by bubble test method. CO₂ containing samples were then injected to ensure that no unexpected empty tower absorption unto surfaces occur, again by comparing the concentration at the inlet to that at the exit. Lastly, humidified samples were injected into the tower to ensure tower drainage was functional and properly removing condensed vapours.

As we increased testing flow rates to mimic industrial flue gas conditions, it was clear that it was not possible to replace N₂ tanks fast enough. Thus, when this initial round of testing was complete, the compressed N₂ was replaced with compressed air from two 15-gallon DeWalt Electric Air compressors. Additionally, all the quarter inch lines displayed in Figure 2.7 were replaced with half inch lines.

2.3.3 Packed Bed Towers and Operational Procedures

Centennial was designed to continuously cycle absorbing material, therefore after an absorption phase saturated material must be regenerated in the tower (opposed to being unloaded and regenerated elsewhere). But because the capture system must continuously capture CO₂ exiting an industrial vent, while saturated material is regenerating a fresh reactor bed must be available for capture. Thus, to perform continuous CO₂ capture necessitates (at minimum) a two-tower system, which we will refer to as “A” and “B.”

In short, while tower A is performing capture, Tower B can regenerate its sorbent and prepare for another absorption period. To accomplish this, a collection of valves is controlled by the tower's operating system and progress each tower through 3 phases: absorption, regeneration, and cooling.



Figure 2.8 displays the front of the two-tower reactor on its mounting skid. The left control panel (1) is used to set and monitor each tower's operating phase (absorption, regeneration, and cooling). The right control panel (2) sets the towers' temperatures. At the bottom of the tower, a set of matching pressure relief membranes are visible (3) that open when tower exceeds pressures of 20 atmospheres. In between towers A and B is an inline heater (4) that can be used to maintain or increase flue gas temperature.

To simply explain typical Centennial operation, we will describe a complete cycle within a singular tower. During the absorption phase the tower is heated, usually to 65°C, at which point the flue gas is injected. In the trials performed here, ~100kg loads of K₂CO₃-impregnated zeolite were found to absorb for approximately 1 to 3.5 hours (variation will be explained in the results and discussion section). Saturation is observed when outgoing CO₂ concentration equals that of the incoming concentration on the CO₂ analysers.

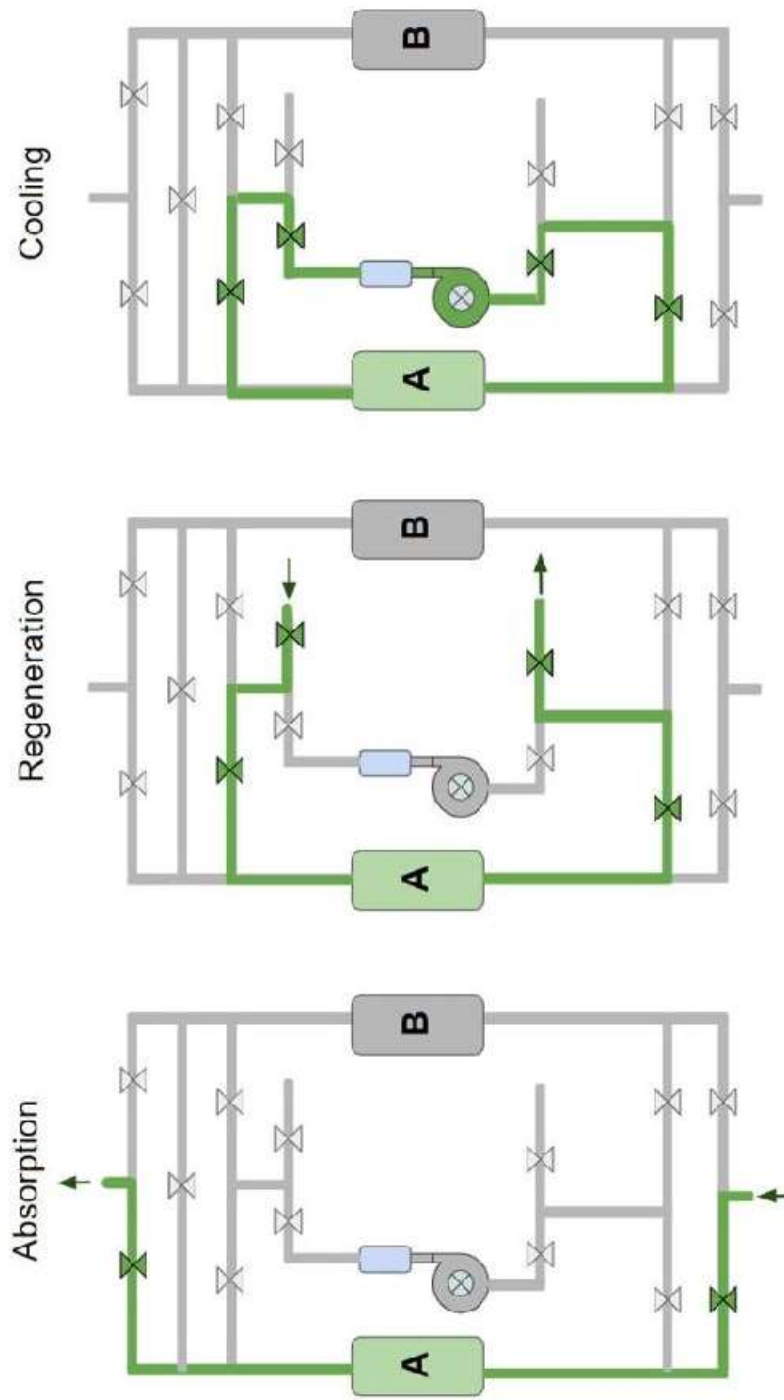


Figure 2.9 visualizes the three phases of a complete cycle in reference to tower A. Valves are illustrated by the hourglass shape, and the cooling fan and heat-exchanger are located between towers A and B and highlighted in green during the cooling phase. The tower is designed such that flue and purge gases enter and exit through different channels to allow for simultaneous running of the towers. During the absorption phase flue gas enters through the bottom of the tower and exits through the top of the tower, while during the regeneration phase purge gas enters through the top and exits through the bottom. During the cooling phase the air is circulated.

Typically, the absorption phase is held for at least half an hour after the CO₂ analysers first indicate sample saturation. When the absorption phase ends, flue gas injection in that tower is halted, and the tower is heated to prepare for sorbent regeneration. Once the tower has reached the desired regeneration temperature (can vary, will be explained in the results section), a purge gas can be injected. While in an ideal open-air system a purge gas may not be necessary, the reactor has long and narrow lines that may trap CO₂ during regeneration. During the regeneration phase once the purge gas is introduced the outcoming CO₂ is again monitored on a Servomex analyser. Regenerated CO₂ is observed as an increase in CO₂ concentration/volume of the exiting gas.

Typically, regeneration is the longest step as it takes multiple hours to heat the tower, especially depending on how much moisture the sorbent absorbed due to the high heat capacity of water. Challenges in accurately measuring low CO₂ concentration towards the end of regeneration phases made it difficult to assign when regeneration was truly “complete.” For this reason, the length of regeneration period varied sometimes taking as long as 40 hours for N₂ and CO₂, but taking only about an hour with steam, as explained in the results section. After the regeneration phase ends the tower is at around 160°C and must be cooled before another absorption cycle can begin. During the cooling phase the tower heater shuts off, and the system valves reconfigure to create a loop as shown in Figure 2.9. An internal fan (Redbo 2GH210-H16) circulates tower air at 98 m³ph, through one of the water-cooled heat exchangers. The rate at which the tower can be cooled is primarily determined by the fan rate and the water temperature, which for our system was about 20°C.

During operation, sensors inside the towers help assess system and material performance. Each tower has a cylindrical reactor region that is 1.8 meters long with an inner diameter of 0.27 meters. Surrounding these reactors are the heating elements, which are then surrounding with a layer of fiberglass insulation. At the very bottom of each tower is a condensate trap that is monitored via pH meter. The pH probe was installed to monitor sorbent leaching which occurs due to condensation that dissolves K₂CO₃ and will be discussed further in the results section. At the top, middle and bottom of each tower are thermocouples, pressure gauges, as well as humidity sensors. At just the top and bottom of

the towers are mass flow meters. The thermocouples were used primarily to monitor tower heating and cooling rates during the regeneration and cooling phases. The thermocouples, for example, helped identify heat sinks that would prevent sorbent from regenerating to completion. In early tests runs, it was determined that the middle of the tower heated much faster than the top and bottom, despite the heating elements running the full reactor length. Thus, extra fibre glass insulation was installed on both the top and bottom to minimize the temperature differential. The RH probes assist monitoring in two ways. During the absorption phase, the RH meters assure that flue gas is properly humidified upon arrival to the reactor. During the regeneration and cooling phases, the RH meter should be monitored to evaluate sample “wetness.” A sample that is very wet, which will read as a high or even 100% RH, will take longer to heat due to the high heat capacity of water. In addition, when the sorbent is too wet it risks losing active material due to the previously mentioned issue of leaching. The pressure gauges should be monitored regularly to ensure that the reactors do not become dangerously over-pressurized from a lapse in procedure or system malfunction. They are also used to measure the sorbent-dependent pressure drops. Lastly, flow rate measurements are necessary to calculate total absorbed CO₂.

2.3.4 Gas Analysis Panel

During the absorption and regeneration phases, the exiting gas streams are navigated towards a gas analysis panel. As can be seen in Figure 2.9, it is necessary to have the treated and regenerated gas exit through different paths so that both towers can be run simultaneously. Ideally, the gas analysis panel would be equipped with two CO₂ analysers so that exiting treated flue gas and regenerated gas can also be analysed simultaneously while both reactors are loaded. At the time of data collection however, the gas analysis panel was equipped with one CO₂ analyser, labelled (6) in Figure 2.10. For this reason, during the data collection described in this chapter, only one tower was run at a time. The PureAir and ADCOA zeolites were run in towers B and A, respectively, so that both reactors were tested for potential system issues.

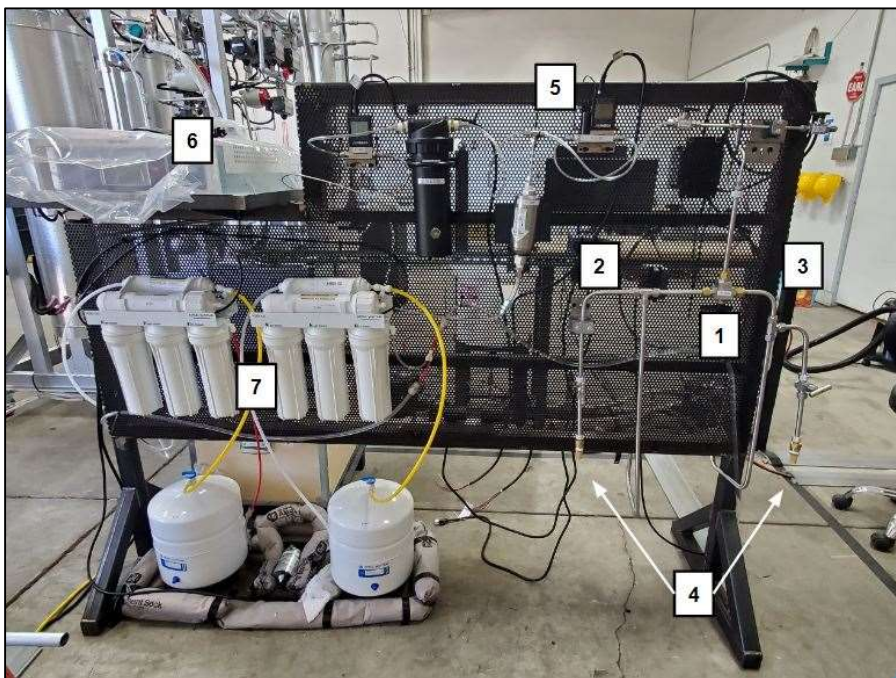


Figure 2.10 displays the gas analysis panel at the start of testing. The valve (1) is switched to select the exiting treated flue gas (3) or the regenerated CO_2 (2). Since the CO_2 analyser, which is this picture is bagged, (6) can only measure flow rates of up to 2.5 lpm, vent valves (4) were installed to release excess gas. Due to the very large flow exiting the towers during the absorption phase, positive pressure prevents outside air from mixing significantly with sampled gases. A flow controller (5) sets the analyser (6) flow rate. Condensers and desiccants were installed after the flow meter (5) to protect the analyser. The tower humidity meters indicated that treated flue gas was almost completely dry by the time it exited the towers. On the other hand, regenerated gas was quite wet, and later another larger condenser/drying tube was installed near (2).

2.3.5 Impregnated Zeolite, Preparation and Loading

At the time that these towers were constructed and tested, a higher capture capacity sorbent was being developed in parallel via wet activated granulation method, as explained further in Chapter 3. For the purpose of tower testing and development, a first-generation material was utilized; K_2CO_3 impregnated zeolite beads. To keep K_2CO_3 in the solid phase requires at minimum some sort of support material. This is because K_2CO_3 is very deliquescent in humid conditions and has an incredibly high solubility, of over 1 g/mL at room temperature. In addition to resistance to moisture, supporting material should also provide porosity. While K_2CO_3 has a very high theoretical capture capacity of $7.24 \text{ mmol CO}_2 \text{ g}^{-1} \text{ K}_2\text{CO}_3$, measured capture capacities of pure K_2CO_3 tend to be substantially lower due to

poor pore formation during crystallization.^{27,29} For example, K_2CO_3 calcined from the hydrate ($K_2CO_3 \cdot 1.5H_2O$) at $200^\circ C$ with no support only achieves about half of the theoretical capture efficiency.²⁹ Alternatively, K_2CO_3 supported by 65 mass percent γ -alumina has been observed to increase that capture to 70% the theoretical value.²⁵ As will be further explored in chapters 3 and 4, the support material and how it is bonded to K_2CO_3 (water content, calcination temperature, material density etc.) can alter sorbent capacity, sometimes allowing it to reach near theoretical values.

Impregnated zeolite was selected for first generation sorbent testing primarily because of its high surface area and known resilience in humid environments. For example, $3\mu m$ diameter 13X zeolites prepared from bentonite clays have an observed surface area of around $900 m^2 g^{-1}$. Assuming a crystal (non-bulk) density of around $1.5 g cm^{-3}$, a nonporous material of the same diameter would have a surface area of around $1 m^2 g^{-1}$. Thus, the zeolite microstructure increases the surface area by about 3 orders of magnitude! Due to its use in many industrial and commercial systems as a molecular sieve, zeolite beads are also relatively cheap, making it amenable to large-scale (multiple kg) testing. Again, due to their popular use, zeolite beads are commercially available in many sizes.

Sorbent particle size must be carefully matched to the tower design. On one hand, smaller particles are preferable due to higher surface area:volume ratio, which results in slightly faster chemical reactions. On the other hand, particles which are smaller can create too much frictional resistance, resulting in large pressures drops according to the Ergun Relation, equation 4.³⁰ Pressure drops are an issue for a couple of reasons. First, to increase pressure usually requires greater energy consumption by using electric pumps. Pressure drops also correspond to a decrease in reactor residence time, which in turn results in lower reaction efficiencies. Lastly, too great of pressure drops can result in channelling, leading to uneven reaction conditions.

$$4. \quad -\frac{dP}{dx} = \alpha \frac{(1-\varepsilon)^2 \mu}{\varepsilon^3 D_p^2} v + \beta \frac{(1-\varepsilon) \rho}{\varepsilon^3 D_p} v^2$$

The Ergun equation predicts pressure drop (P) of a given material packing length (x). The pressure drop is dependent on the particle diameter (D_p), the porosity or void fraction of the bed (ε), the incoming fluid velocity or superficial velocity (v), as well as the fluid (flue gas) density (ρ), fluid viscosity (μ), and viscous resistance (α) and formal resistance (β) coefficients of 150 and 1.75. Most of these variables cannot be modified for the system as they are inherent properties of the flue gas. The tower height must be selected according to the anticipated capture efficiency of the material. For example, slower reacting materials will need a comparably taller tower than quickly reacting materials to obtain a similar capture efficiency as they need to interact with more material. Thus, the simplest variable to adjust to reduce pressure drop is D_p .

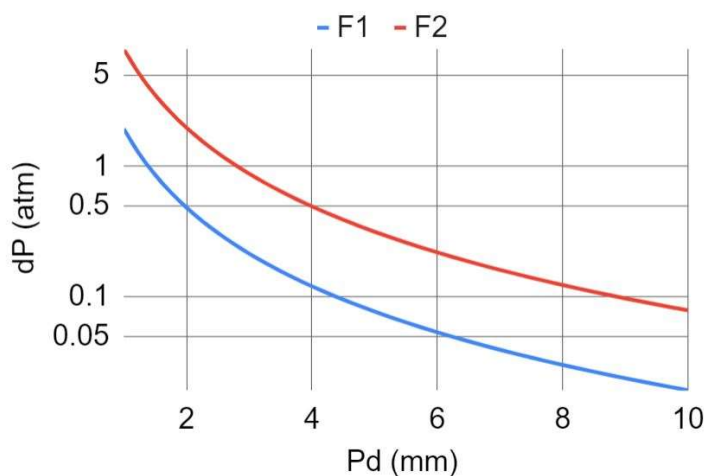


Figure 2.11 displays the expected pressure drop curve according to the Ergun equation for two different flow rates in the centennial tower. F1 and F2 are equal to 6 and 12 m^3ph . They were converted to linear flow by dividing by the reactor cross-sectional area as well as the void fraction. These curves were calculated assuming a 40% void fraction.

The relationship between D_p and pressure drop for two different flow velocities is expressed in Figure 2.11. The incoming velocity for most trials we performed is approximately 6 m^3ph , which with a reactor diameter of 0.266 m and assumed void fraction of 40% corresponds $v = 0.075 \text{ m s}^{-1}$. μ and ρ of the flue gas can be approximated to that of ambient air, so $1.8 \times 10^{-5} \text{ kg m}^{-1}\text{s}^{-1}$ and 1.2 kg m^{-3} , respectively. Considering a reactor height of 1.8 m, we can plot the pressure drop as a function of P_d . The pressure drop relation for a total flow rate of 6 m^3ph is labelled Flow 1 or “F1.” Flow rates exiting power plant flue

stacks can easily be double that, so we also plot the pressure drop curve for 12 m³ph, labelled “F2.” Higher flow rates result in larger frictional forces, thus, to obtain similar pressure drops towers with higher flow rates will require larger particles. For example, in Figure 2.11 the 6 m³ph flow observes a pressure drop of 0.1 atm for a particle around 4 mm, while the 12 m³ph tower will observe the same drop for a 9 mm particle.

In an ideal system, where no chemical reactions are happening, the change in pressure will directly result in a change in flow rate according to conservation of mass, equation 5. Here, m_{in} (and similarly out) is mass flow rate, A is the cross-sectional area, v_{in} is the linear velocity, and ρ_{in} is the gas density. Thus, the change in the linear velocity of the fluid can be estimated to be inversely proportional to the density change in the fluid. The change in density is, at constant temperature, proportional to the change in pressure. So, a decrease in pressure of 10% results in an increase in flow rate by 10%. Again, this is assuming conservation of mass, which we know is not true for our system where both CO₂ and H₂O are reacting.

$$5. \quad m_{in} = m_{out} = Av_{in}\rho_{in} = Av_{out}\rho_{out}$$

In conclusion, to prevent substantial pressure drop a support bead size of at least 4mm was selected for impregnation. Impregnation of zeolite samples is theoretically a simple procedure; expose the support material to the active material by submerging it in concentrated K₂CO₃ solutions, then dry them before use.³¹ Ideally, K₂CO₃ can penetrate the entire depth of the particles and multiple layers adhere to its surface. Impregnation duration and solution concentration can both impact the resultant activated particle capacity and kinetics. Too concentrated of a solution causes fast adhesion onto the particle once it is submerged, and this creates thick but superficial impregnation. Superficial impregnation means that the active material resides mostly on the surface and makes the material more susceptible for leeching and thus material loss. This is not ideal, since the sorbents are meant to be cycled potentially hundreds of times. Additionally, superficial and fast adhesion can contribute to pore clogging, which reduces surface area and thus also reduces sample capacity and kinetics. On the other hand, solutions which are not concentrated enough do not adhere enough active material to the support material. Lastly, it takes time

for active material to attach to the support surface. To ensure proper adhesion all sorbents formed at Mitico were submerged for around 24 hours which is standard for incipient wetness impregnation.^{31,32}

To verify the solution concentration selected for large-scale sorbent testing was optimized, small-scale samples were tested and compared in terms of their capacities. For impregnation of small-scale samples, 100g of 4mm ADCOA 13X zeolite beads, shown in Figure 2.12, were submerged in 500g solutions ranging between 15 and 45g K_2CO_3 g⁻¹ H₂O. After 24 hours samples were drained and superficially dried for an hour at 95°C, and then more thoroughly dried at 190°C for two hours. This two-step drying method was selected as rapid initial drying before the addition of the 95°C step caused the particles to crack, likely due to explosive water release. The zeolite impregnation was visually confirmed as the beads changed colour from beige to paler beige (K_2CO_3 is white).



Figure 2.12 displays the Mitico-prepared ADCOA spherical zeolite (left) as well as the PureAir-prepared rock-type zeolite (right).

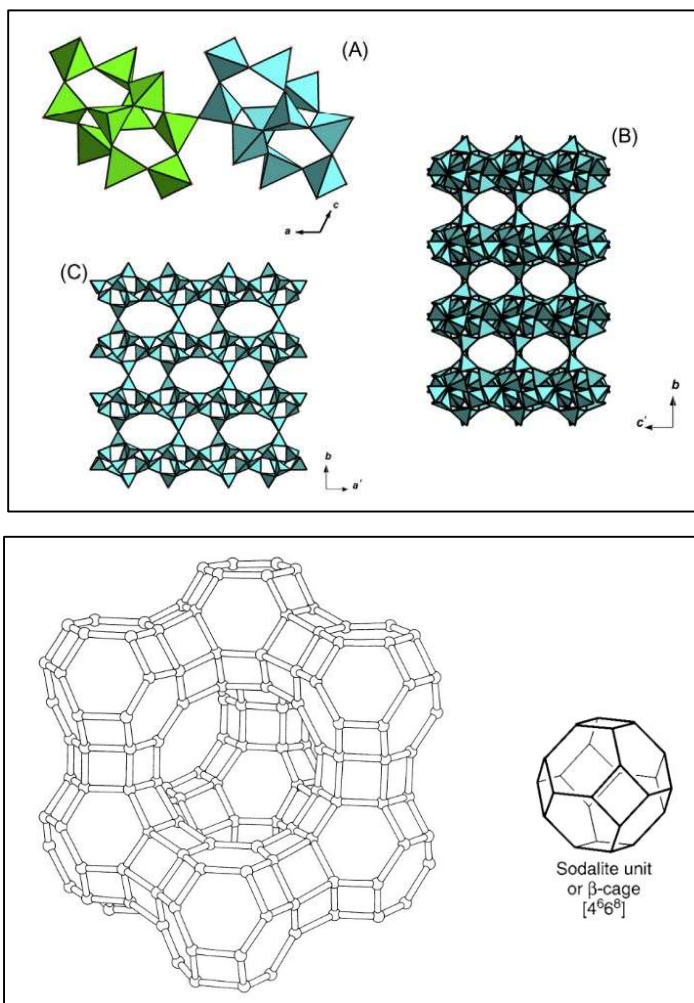
In addition to the Mitico-prepared spherical 13X zeolite beads another sample comprised of Clinoptilolite zeolite, which we refer to as rock-type, was purchased and impregnated by PureAir to be tested. The impregnation methods for the rock-type Clinoptilolite zeolite thus are proprietary. The goal in testing two different zeolite samples is to quantify the effect of zeolite source and impregnation method on resultant sorbent capacity and kinetics. Despite both the spherical and rock-type sorbents being zeolites, we do not expect them to have the same capture properties. Zeolites can vary greatly in both structure and chemical

composition, which results in differences in colour, density, pore size, and compressive strength.^{33,34}

Zeolites are similar to clays in that they are aluminosilicates containing exchangeable cations. They also have the ability to hold large amounts of water, up to 20% of their mass in humid environments.³³ However clays are phyllosilicates, meaning that they are 2D sheets that make 3D structures by layering.³⁴

Unlike clays, zeolites have crystallographic 3D order, specifically zeolites are tetrahedral.³⁴ Connected tetrahedra can form a variety of unique structures, but they all fall under a system that can be used to classify them according to their structural elements, known as the Meier and Olsen framework.³³ This framework identifies secondary building units that makes different crystals more easy to identify. For example, clinoptilolite (the PureAir rock-type) is primarily made up of the 10-node 4-4-1-1 subunit, also known as the heulandite subunit.³⁵ These subunits are primarily connected via mirror planes forming what is known as the heulandite series (IUPAC code HEU). Heulandite is structurally the same as clinoptilolite except heulandite contains samples with $\text{Si:Al} < 4$ and the clinoptilolite series refers to those with $\text{Si:Al} > 4$.³⁶ Clinoptilolite, as a member of the HEU series, contains 3 types of large channels made up of 8 and 10-membered rings, depicted in the top panel of Figure 2.13.³⁶ Clinoptilolite is also naturally occurring, and contains both primary and secondary porosity, where the primary porosity refers to that determined by crystal structure and secondary refers to natural imperfections like fractures.³⁷

Zeolite 13X on the other hand, which the ADCOA beads are made of, is industrially made and primarily composed of structural unit called a sodalite or β -cage in an arrangement that forms what is called the faujasite series (IUPAC code FAU).³³ Sodalite cages are defined by a surface which is composed of six 4-rings and eight 6-rings. In the FAU series sodalite cages are joined together via double-six rings, like carbon in a diamond. This creates a “super cage” with four 12-ring openings as shown in the bottom of Figure 2.13. Zeolite X refers to a synthetic FAU with lower Si:Al , typically around 1. As Si-O bonds are shorter than Al-O bonds, ~ 1.6 vs $1.8 \text{ \AA}$, enriching zeolites in either Si or Al modifies the pore size. 13X is often called NaX as it is also primarily composed of sodium ions.



The top panel of Figure 2.13 is borrowed from Gatta and Lotti and depicts the HEU series from 2 different orientations (B and C). Also shown in the top panel is two heulandite subunits side by side (A).³⁶ The bottom panel of Figure 2.13 depicts a sodalite unit, borrowed from McCusker and Baerlocher, as well as the full FAU super cage.³³

These structural and compositional differences result in different pore sizes and effective surface area. Clinoptilolite tends to secondary porosity that is more mesoporous, with pores on the order of 50nm,³⁷ while zeolite 13X is considered to be microporous with pores on the order of around 1nm. We expect these differences, especially the pore size, to impact many aspects of the impregnated product. Differences we expect include how much active material can be loaded, how deeply the active material can penetrate the particles, how fast the loaded K_2CO_3 can react with CO_2 , how fast and how completely the $KHCO_3$ can be regenerated to K_2CO_3 . These effects may be caused by simple sterics (larger openings makes for better mobility) or chemical effects (for example, larger pores may hold larger

amounts of water). We even expect differences in the longevity of the material; differences in pore size may result in substantial variation in material leaching.

As mentioned in Section 2.3.4, the rock-type and ADCOA 13X zeolites were run in separate trials in towers B and A respectively. The ADCOA impregnation method resulted in beads which had taken up 20% their original dry mass in K_2CO_3 after optimization. This means for every 100 g ADCOA beads, 20 g of K_2CO_3 can be loaded resulting in a dry mass of 120 g after impregnation and drying. The rock-type loading efficiency is unknown due to its proprietary nature, but PureAir said to have also optimized their loading efficiency. Future work on Clinoptilolite samples would benefit from noting the loading efficiency to know the total mass of active material loaded into the tower. These samples were loaded using cotton long underwear to gently convey particles into the reactor bed, preventing fragmentation. Minimal fragmentation was visually confirmed when the towers were later unloaded. The entire 1.8m reactor length was loaded for both trials, to normalize is respect to volume. The rock-type and ADCOA beads ultimately had total loaded masses of 111.6 and 100.8 kg, respectively.

2.3.6 Calculations

The sensors before, along, and past the reactor (discussed in sections 2.3.2-2.3.4) were ultimately used to characterize and quantify the effectiveness of the absorption and regeneration cycles. The raw sensor data was primarily used to calculate three types of data; capture efficiency, total CO_2 captured, and a 2nd order kinetic rate constant. Capture efficiency compares the amount of CO_2 injected to how much was absorbed at a single point in time. Ideally, around 100% capture would occur for almost the entire capture period with a very steep transition to 0%. This sort of efficiency curve is correlated to, but not the same as, the capture kinetic constant. A fast overall absorption rate constant should result in a high capture efficiency, unless for some reason there is little CO_2 or H_2O available in the flue gas stream. CO_2 captured is put simply, the total injected CO_2 minus the exiting (non-captured) CO_2 .

To calculate **capture efficiency** (moles captured/moles injected, shown in equation 8 requires the amount of CO_2 injected at a point in time (N_{inj}) as well as the moles captured

at that same point in time (N_{capt}). It should be noted that the gas that enters at some time “t” really exits the tower and is sampled at some point “t+dt” where “dt” is the residence time through the reactor and entering/exiting lines. The reactor ($\sim 0.1 \text{ m}^3$ packing volume) residence time at the flow rates used ($\sim 5 \text{ m}^3/\text{hr}^{-1}$) was estimated to be about 1.5 minutes. We estimate the total “dt” for the gas stream entering at time “t” to exit is about 2 minutes. Since absorption usually occurs over several hours, the error associated with sampling injected and exiting CO_2 at the same time was considered minimal. To be clear; for capture efficiency calculations, each injected and exiting pair was calculated for the same time “t.”

Sampling is done in 10 second intervals, thus moles injected during a sampling period is defined by equation 6, where $F_{\text{CO}_2, \text{inj}}$ is the volumetric flow rate, 4 slpm, which is always the same in our trials as it is injected via flow controller. t_{samp} is the sampling period, which when multiplied by the flow rate determines the volume of flow injected in litres and can be converted to moles via relationship with the ideal gas constant, R. Since the flow is in slpm, P and T are standard pressure and temperature.

Moles captured is moles injected, determined by equation 6, minus moles exiting. The moles exiting the tower is calculated according to equation 7. This equation takes the same form as equation 6, except that the flow rate of CO_2 exiting the tower must be determined by the total flow exiting the tower, F_{tower} and the fraction of CO_2 in the stream, $\%_{\text{CO}_2}$, measured on the exiting gas panel via CO_2 analyser. Condensers (Figure 2.10) and later desiccant tubes were installed prior to the analyser inlet to protect it, thus the $\%_{\text{CO}_2}$ is inherently a RH = 0 measurement. This did become an issue later when we attempted to calculate regenerated CO_2 as the exiting stream is inherently wet. This means that the $\%_{\text{CO}_2}$ is artificially higher during regeneration cycles than it is in reality as water vapor was intentionally removed. However, for absorption cycles, RH meters at the tower exit confirmed the gas stream was always dry once exiting the column at the location where F_{tower} is measured. This is not unexpected as the absorption reaction requires both CO_2 and H_2O , and zeolite is a known desiccant, meaning it physisorbs water.

6. $N_{inj} = F_{CO_2, inj} (t_{smp}) \left(\frac{P}{RT} \right)$
7. $N_{exit} = F_{tower} (\%CO_2) (t_{smp}) \left(\frac{P_{tower}}{R T_{tower}} \right)$
8. $N_{eff} = \frac{N_{capt}}{N_{inj}} = \frac{N_{inj} - N_{exit}}{N_{inj}}$

To calculate **CO₂ captured**, we can utilize equations 6 and 7, i.e. $N_{capt} = N_{inj} - N_{exit}$. It is important to note this calculation determines CO₂ captured over the 10 second sampling period. Total capture is calculated by summing over the total absorption period. CO₂ captured can be expressed in moles, kg, kg kg⁻¹ sorbent or kg m⁻³ reactor. While academic literature often normalizes capture by the mass of sorbent, in an industrial setting it is often more useful to consider the volume of material that can be loaded, since the reactor size is fixed once it is constructed but the material density can change.

In addition to these two calculations, we attempted to determine a **2nd order rate constant** for each absorption cycle of the two trials. This calculation was performed early in the cycle at the point of highest observed absorption to better accommodate our assumptions, which includes that there was negligible diffusion limitation, the available reacting solid K₂CO₃ is constant, and there is no back reaction. If we assume that the absorption is 3-body one-step mechanism but with a constant solid K₂CO₃ (K₂CO₃ activity is assumed unchanging) then equation 3 implies equation 9, a bimolecular rate. As will be explored more thoroughly later in section 2.4, there is significant evidence that H₂O hydration does not occur simultaneously with CO₂ addition. We acknowledge that this framework, though necessary to attempt to quantitatively compare rates across and within trials, ultimately simplifies a very complex chemical mechanism.

$$9. \quad \frac{d[CO_2]_t}{dt} = \frac{d[H_2O]_t}{dt} = -k[CO_2]_t [H_2O]_t$$

Equation 8 is ultimately used to derive equation 16, which can be utilized to calculate a 2nd order rate constant, k. First, equation 9 is simply rearranged and integrated to form equation 10. Without more information equation 10 is very challenging to integrate; however, if we consider the stoichiometric relationship in equation 3, equation 11 follows. Using equation 11 we can rewrite equation 10 as equation 12. Equation 12

simplified is of the form shown in equation 13, where $c = [H_2O]_0 - [CO_2]_0$. Expression 14 yields equation 15 when $[H_2O]_t$ is substituted back in. As is shown in equation 16, utilizing this framework of assumptions we can calculate a bimolecular rate constant for the absorption reaction in the tower using only the initial and final concentrations of CO_2 and H_2O (mol m^{-3}).

$$\begin{aligned}
 10. \quad & \int \frac{1}{[CO_2]_t [H_2O]_t} d[CO_2]_t = \int -k dt \\
 11. \quad & [H_2O]_t = [H_2O]_0 - ([CO_2]_0 - [CO_2]_t) = [H_2O]_0 - [CO_2]_0 + [CO_2]_t \\
 12. \quad & \int_{[CO_2]_0}^{[CO_2]_f} \frac{1}{([CO_2]_t)([CO_2]_t + [H_2O]_0 - [CO_2]_0)} d[CO_2]_t = -k(\tau - 0) \\
 13. \quad & \int \frac{1}{x(x+c)} dx = \int \frac{c^{-1}}{x} + \frac{-c^{-1}}{(x+c)} dx = \frac{\ln(x) - \ln(x+c)}{c} \\
 14. \quad & \frac{(\ln[CO_2]_f - \ln[CO_2]_0 + \ln([CO_2]_0 - [CO_2]_0 + [H_2O]_0) - \ln[CO_2]_f + [H_2O]_0 - [CO_2]_0)}{([H_2O]_0 - [CO_2]_0)} = -k \tau \\
 15. \quad & \frac{(\ln[CO_2]_f - \ln[CO_2]_0 + \ln[H_2O]_0 - \ln[H_2O]_f)}{([H_2O]_0 - [CO_2]_0)} = -k \tau \\
 16. \quad & k = \left\{ \ln \left(\frac{[CO_2]_0}{[H_2O]_0} \right) + \ln \left(\frac{[H_2O]_f}{[CO_2]_f} \right) \right\} ([H_2O]_0 - [CO_2]_0)^{-1} \tau^{-1}
 \end{aligned}$$

The initial undiluted CO_2 concentration ($[CO_2]_{und}$, mol s^{-1}) is given by the mass flow controller connected to the CO_2 compressed gas cylinder. The initial diluted concentration ($[CO_2]_0$, mol m^{-3}) needed to calculate k is dependent on the total flow (F_{total} $\text{m}^3 \text{s}^{-1}$), which is measured at the bottom of the reactor after the CO_2 stream is mixed with air and hydrated via the steam generator described in section 2.3.2. The initial H_2O concentration can be determined by the RH meter and temperature probe at the bottom of the reactor. The August–Roche–Magnus, equation 18, can be used to approximate the saturation vapor pressure in hPa, where T is in kelvin. Then the absolute vapor pressure is proportional to the measured relative humidity. The initial H_2O concentration ($[H_2O]_0$, mol m^{-3}) can be calculated according to equation 19.

$$\begin{aligned}
 17. \quad & [CO_2]_0 = \frac{[CO_2]_{und}}{F_{total}} \\
 18. \quad & VP_{sat} = 6.11 \exp \left(\frac{17.63}{T + 243.04} \right) \\
 19. \quad & [H_2O]_0 = VP_{sat} \left(\frac{\%RH}{100} \right) \left(\frac{1}{RT} \right)
 \end{aligned}$$

Lastly, the final concentrations of CO₂ and H₂O are needed to calculate the rate constant. The final concentrations can both be calculated if the amount of CO₂ reacted is known. The amount of CO₂ reacted ($\Delta[\text{CO}_2]$, mol m⁻³) is determined by the signals on the CO₂ analysers according to equation 20 where the signals before and after reactor are noted S₀ and S_f, respectively. Due to stoichiometric equivalence, $\Delta[\text{CO}_2]$ is the same as $\Delta[\text{H}_2\text{O}]$. Then the final concentrations of both CO₂ and H₂O are just the initial minus the amount reacted, written for CO₂ in equation 21.

$$20. \quad \Delta[\text{CO}_2] = [\text{CO}_2]_0 \left(\frac{S_i - S_f}{S_i} \right) = \Delta[\text{H}_2\text{O}]$$

$$21. \quad [\text{CO}_2]_f = [\text{CO}_2]_0 - \Delta[\text{CO}_2]$$

2.4 Results and Discussion

2.4.1 Raw Data

The rock-type operation, labelled Trial 1 in table 2.1, ran from 9/25-10/20/23 in tower B. There was a total loaded sorbent mass of 111.6 kg, completing 8 cycles. Trial 1 was terminated early because it was determined that further insulation was required to prevent condensation during steam regeneration, which was attempted for the first time in Trial 1, cycle 7. The ADCOA beads, noted Trial 2, ran from 10/24-12/11/23 in tower A with a total loaded mass of 100.8 kg, completing 13 cycles. Two more steam regenerations were attempted in Trial 2 (after modifications to prevent condensation), with an added drying step before cooling down. This drying step utilized a 30-minute burst of compressed air to liberate excess water from the reactor walls as well as superficial water from the sorbent.

Table 2.1: Trials overview

Trial	Material	Impregnation	Tower Tested	Mass loaded	Run Dates	Cycles
1	“rock-type” Clinoptilolite	by PureAir	B	111.6 kg	9/25-10/20/23	8
2	spherical beads 13X ADCOA	by Mitico	A	100.8 kg	10/24-12/11/23	13

*Impregnation of the ADCOA beads and loading procedure for both Trials 1 and 2 are described in section 2.3.5

During the absorption period around 5 to 6 m³ph of mixed flue gas was injected into the bottom of the tower. The compressed air tanks do generate some variation in the flow rate, as shown in Figure 2.14, on the bottom panel. As the flue gas enters the bottom of the tower, we measure a pressure less than one atmosphere. Since the flue gas is generated in a closed system using a steam generator it is possible to form flue gas below atmospheric pressure. There may also be some sort of vacuuming force between the mixed flue gas and the tower bottom. Since the reactor is full of a hygroscopic sorbent, and the flue gas is between 15-25% H₂O at any time, we hypothesize this may result in a low-pressure region at the tower bottom.

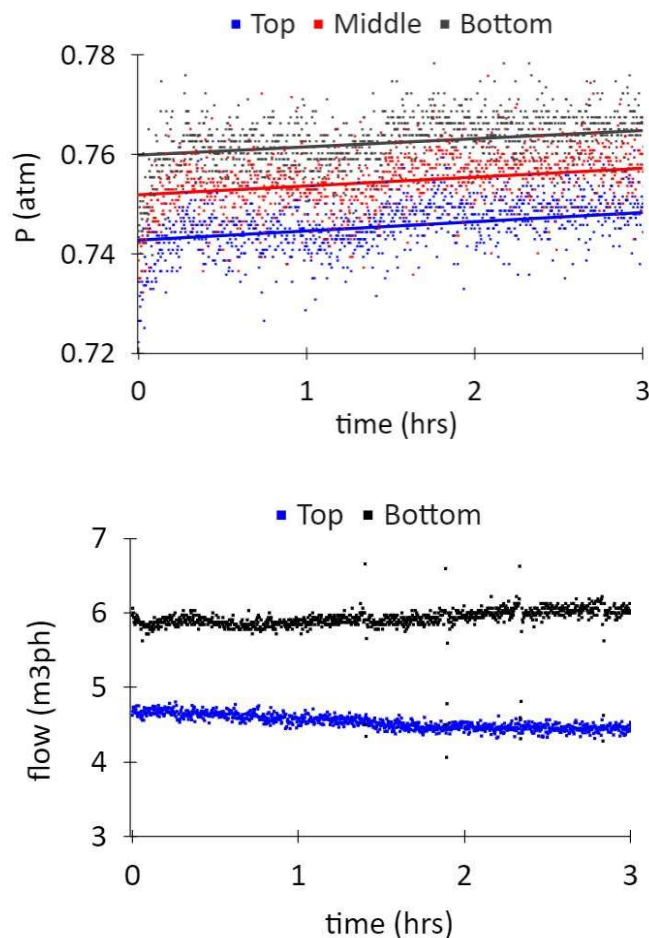


Figure 2.14 displays the pressure and flow profiles for Trial 2, Absorption 7. These profiles are typical of what was observed across all trials and absorption cycles. The top panel displays the pressure profile measured along the tower. The bottom panel shows that instead of a flow rate increase, we observed a decrease.

A pressure drop on the order of 1500-2500 Pa, or 0.015-0.025 atm is observed from the bottom to the top of the tower for both trials (both sorbents), which makes sense given that despite being different shapes the materials are of similar size. For 4 mm diameter spheres with an initial volumetric flow rate of 6 m³/ph, we calculated a drop in pressure of approximately 0.1 atm or around 10,000 Pa when the void fraction is assumed to be 40% (see Figure 2.11). As our measured pressure drop is around an order of magnitude smaller, we expect that our void fraction is much higher than 40%. If we assume a void fraction of 50%, we calculate a pressure drop of approximately 3000 Pa, which is much closer to our measured value which fluctuates between 1500 and 2500 Pa. A void fraction of around 50% is on the higher end of what can be expected for a typical cylindrical reactor packing when the material randomly loaded, and indicates that a more optimal packing procedure is probably desired for industrial setting to optimize the mass loaded.³⁸

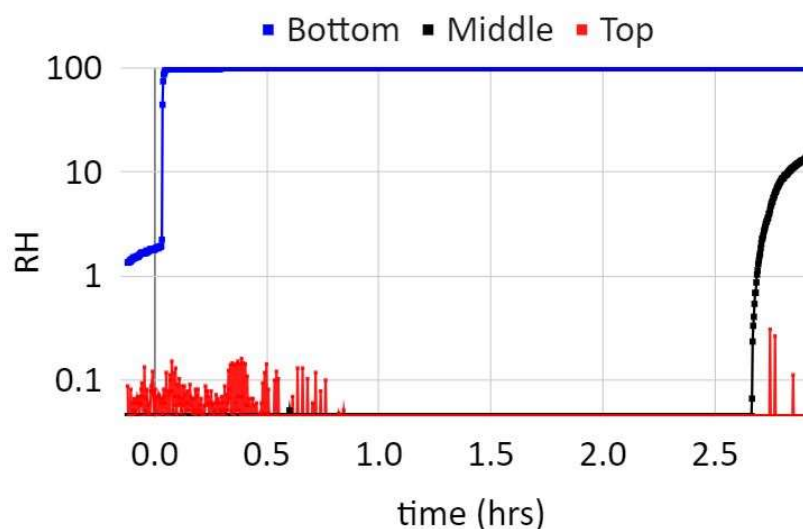


Figure 2.15 displays the RH meter outputs from along tower B during Trial 1 absorption 8. The plot shows the few minutes prior to start of the absorption period (time < 0), and the rapid increase in RH at the bottom of the tower once the flue gas is injected. Despite some minor variations in the baseline at the start and end of the trial, the top RH sensor consistently detects an essentially dry stream throughout the absorption period, meaning that the exiting gas was dry. The middle sensor began to increase towards the end of the trial, indicating that after about 2.5 hours the bottom-middle of the tower was becoming saturated with water.

Under a non-reacting flue gas system, we would expect the flow rate to increase as the pressure drops. Instead, we observe a drop in volumetric flow rate from 6 to around 4.5 m³ph. This corresponds well to a loss in CO₂ and H₂O from the flue gas due to uptake by the coated zeolite; CO₂ and H₂O_(g) comprise about 5 and 10-25% of the volume, respectively. While the sorbent very quickly becomes saturated with CO₂, as shown by the data collected on the CO₂ analyser (Figure 2.16, left panel), the zeolite can absorb water for much longer before it becomes saturated (assuming it was dried before recycling). The slow saturation of the zeolite was observed by the RH meters along the tower, for example Figure 2.15.

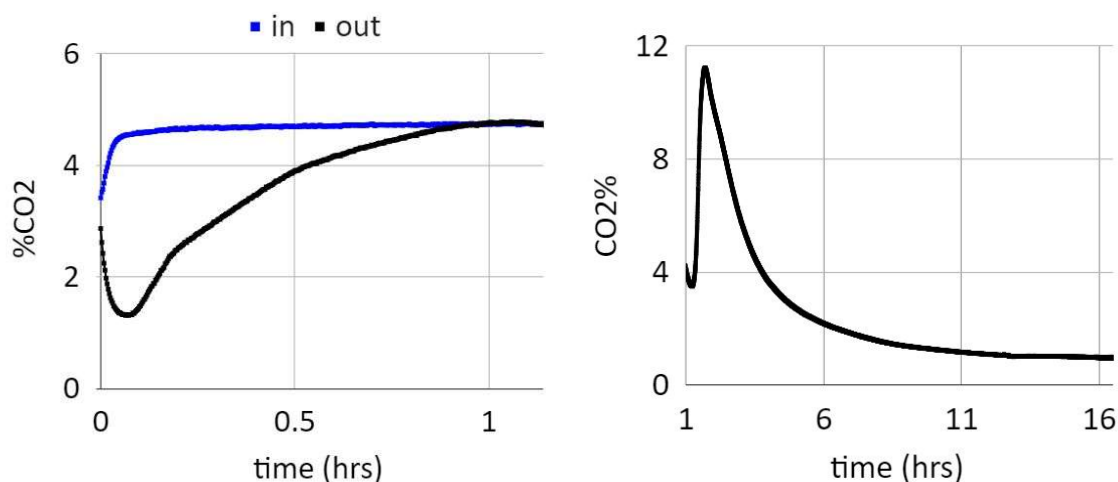


Figure 2.16 displays an example of the absorption breakthrough point on the left panel.

The data is taken from Trial 2, absorption 5, and is also an example of sub-optimal capture as the outgoing CO₂ concentration never drops near 0 (100% capture efficiency). The right panel shows the CO₂ exponential decay resulting from regeneration with N₂ as a purge gas. The data is taken from Trial 2, regeneration 2. The slow decrease towards 0% made it challenging to determine a clear cut-off to end regeneration. Regeneration length was varied to determine its impact on the following absorption cycle.

The total length of each period (absorption, regeneration and cool down) was not constant across cycles. The length of the absorption period was held at minimum until “breakthrough,” where the final and initial signals on the CO₂ analysers are the same. An example of the breakthrough is shown in Figure 2.16 on the left panel. While absorption indicates completion in a clear manner, regeneration depending on the purge gas identity, is more challenging to determine.

For this reason, a variety of regeneration lengths were tested in both Trial 1 and 2, as shown in Table 2.2. The regeneration durations listed include time required to heat the tower, which was especially important in the case of steam.

Table 2.2: Trial details

Trial	Cycle	Regen Details	Trial	Cycle	Regen Details
1	1	CO ₂ @ 5 slpm, 36 hrs	2	4	CO ₂ @ 5 slpm, 51 hrs
	2	CO ₂ @ 5 slpm, 42 hrs		5	N ₂ @ 5 slpm, 24 hrs
	3	CO ₂ @ 5 slpm, 31 hrs		6	CO ₂ @ 5 slpm, 18 hrs
	4	CO ₂ @ 5 slpm, 27 hrs		7	N ₂ @ 5 slpm, 28 hrs
	5	N ₂ @ 5 slpm, 66 hrs		8	H ₂ O @ 65 gpm, 1.5 hrs
	6	CO ₂ @ 5 slpm, 67 hrs		9	N ₂ @ 5 slpm, 40 hrs
	7	H ₂ O @ 65 gpm, 3.5 hrs		10	H ₂ O @ 65 gpm, 2.5 hrs
2	1	N ₂ @ 5 slpm, 73 hrs		11	N ₂ @ 5 slpm, 28 hrs
	2	N ₂ @ 5 slpm, 17 hrs		12	N ₂ @ 5 slpm, 28 hrs
	3	N ₂ @ 5 slpm, 24 hrs			

In both Trials 1 and 2 three different gases were used to regenerate the sorbent, N₂, CO₂ and steam. While the heating of the reactor to 160°C+ will initiate the regeneration reaction, a purge gas is needed to push gaseous products (CO₂ and H₂O) through the lines. In theory, no purge gas is needed if infinite time is available for products to diffuse out, but this is not possible in an industrial setting. In addition, for commercial reactors no gas can be used as a purge unless it is easily removed after the sorbent is regenerated or does not reduce the purity of the final product significantly. For this reason, the two purge gases that are being considered for scale-up are CO₂ and H₂O. A small flow rate of CO₂ in theory can

help push released CO₂ out of the reactor without reducing the stream purity. At a substantially high temperature, the backwards reaction should be minimal, so the CO₂ should not be recaptured. Alternatively, steam can be used and condensed out of the stream once the CO₂ is regenerated. Use of steam does necessitate active prevention of condensation in the tower, making its use a little more challenging to engineer. The obvious benefit of using steam instead of CO₂ in an industrial setting is that no CO₂ is reused in the regeneration process. For our studies N₂ is used as standard because it does not partake in the capture reaction and should go right through the material (it also minimally physisorbs to zeolites).

For regeneration using N₂, the analyser was calibrated to 10% CO₂. The accuracy of the CO₂ analyser is dependent on how close the experimental value is to the calibration point. As regeneration nears completion, and closer to 0%, the analyser becomes less accurate/sensitive to the small decreases in CO₂ concentration. In the case of regeneration trials when N₂ is used as a purge gas, outgoing CO₂ % curve is an exponential decay, shown in Figure 2.16 on the right panel. This made it very challenging to determine when the regeneration should be considered complete. The impact of the length of regeneration phase (which at the same time is also a drying phase as the material is heated) for N₂ purge is more thoroughly explored in section 2.4.2. A flow rate of 5 slpm was selected as higher flow rates caused substantial heat dissipation from the tower, resulting in longer heating times and temperature fluctuations.

The same flow rate of 5 slpm was used to purge with CO₂. The CO₂ analyser could not be used to approximate the end of the regeneration as it was for purge with N₂ (shown in Figure 2.16, right panel) as it will always show around 100%. Instead, a flow meter was installed after a desiccant tube on the gas analysis panel (Figure 2.10) to measure changes in the total amount of CO₂ exiting the tower. The flow rate initially (first few hours) sits well below 5 lpm, indicating the possibility of further absorption by the material. While at first this may seem unreasonable, as we observed CO₂ breakthrough (like in Figure 2.16, left panel) it should be recalled that the absorption capacity of K₂CO₃ has been found to be dependant on the amount of CO₂ in the gas stream. As was mentioned in section 2.3.2, *Luo et al.* found an absorption capacity of 6.24 mmol g⁻¹ when the flue gas was 1% CO₂ and a

capacity of 6.92 mmol g^{-1} while pure CO_2 due to a shift in the reaction equilibrium.²⁷ Thus we would anticipate that during the pure CO_2 flush, the material will absorb about 10% more CO_2 before reaching its new higher capacity. Additionally, while the CO_2 was flushed in the tower at $t=0$, the tower did not reach its maximum temperature for regeneration of 160°C until about 2 hours in.

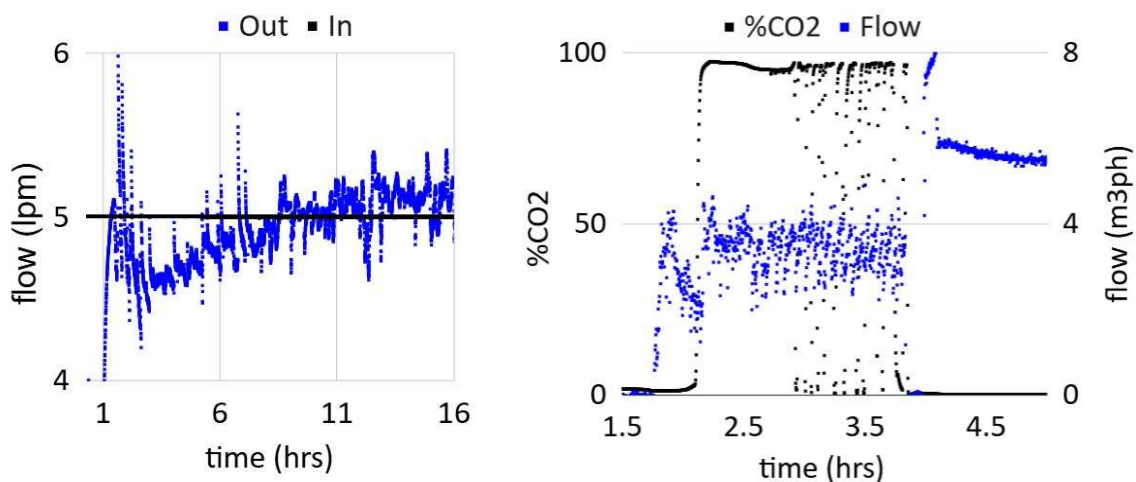


Figure 2.17 on the left panel displays the flow profile exiting the tower from Trial 2 cycle 6 during a CO_2 purged regeneration. As is discussed further in the main text, there is a small period in which the flow rate exiting is below 5 lpm, indicating further CO_2 absorption. This however, can be expected due to an increased absorption capacity at higher concentrations of CO_2 . On the right panel, a steam purged regeneration from Trial 2 cycle 10 is displayed. The steam flows for about 15 minutes before a change is observed in the exiting $\text{CO}_2\%$. A near 100% CO_2 flow was observed on the analyser for over an hour before dropping down to 0. This indicates a fast and efficient regeneration.

Due to this extra absorption period when CO_2 is used to purge the regeneration, like the N_2 purge it appears that a complete regeneration takes many hours to complete under these conditions. Industrial scalability requires that the regeneration phase take a similar length to complete as the absorption phase. The raw data suggests that absorption for these trials take on average less than 3 hours, while N_2 and CO_2 purged regenerations take 10+ hours. This will be discussed further in the capture results section, 2.4.2. It may be possible to increase the regeneration efficiency and decrease the phase length by increasing the purge gas flow rate. But as was described earlier, above about 5 lpm caused substantial heat

dissipation with this reactor design. Future study of purge gas flow rate on purge efficiency would require injected purge gas to be closer to 160°C; for these measurements it was closer to 100°C. In fact, the temperature of the entering purge gas likely has a significant effect on the regeneration as well. One can imagine that cold purge gas will steal heat from the hotter sorbent upon collision, potentially slowing the regeneration of the sorbent. The K_2CO_3 system and absorption/regeneration mechanism are clearly quite complex and depend on surrounding gas conditions, as evidenced by the change in absorption capacity with % CO_2 . The impact of purge gas flow rate as well as temperature clearly requires further study, but is beyond the scope of the current work.

In addition to CO_2 , in this work steam was also considered as a potential industrially scalable purge gas for the regeneration phase. The raw data from one of the steam regeneration trials is presented in the right panel of Figure 2.17. It should be noted that the actual steam did not get injected until about 1.5 hours into the phase. During this time the tower was being heated from its absorption phase temperature of 70°C to about 110°C. This temperature was selected as the minimum temperature to begin steam injection to reduce the possibility of condensation in the tower. Once this was reached, steam was injected at a steam generator set point of 65 gpm, which corresponded to a measured flow rate of approximately 4 m^3/ph , or more than 60 lpm. This high flow rate was selected as the steam generator used had an optimal injection rate between 50 and 100 gpm, with a more stable rate at around 65+ gpm setting. Figure 2.17 right panel shows that there was a short, 15-minute delay after steam was injected before the CO_2 began appearing on the exiting analyser at around 100% purity. Then, after about 1.5 hours of high purity CO_2 showing up on the exiting analyser, the % CO_2 dropped. To confirm that the regeneration was complete, the steam generator was then set to 100 gpm which can be observed in Figure 2.17 right panel as an increase in flow rate, while % CO_2 remained at 0. Based off these raw data, steam regeneration appears preferable over CO_2 as a purge gas for industrial use. This is due to the clear end (compared to Figure 2.17 left panel) and complete regeneration, as well as the phase's brevity. In section 2.4.2, the regeneration conditions' impact on following capture capacities will be discussed, and further compare the industrial scalability of CO_2 to steam.

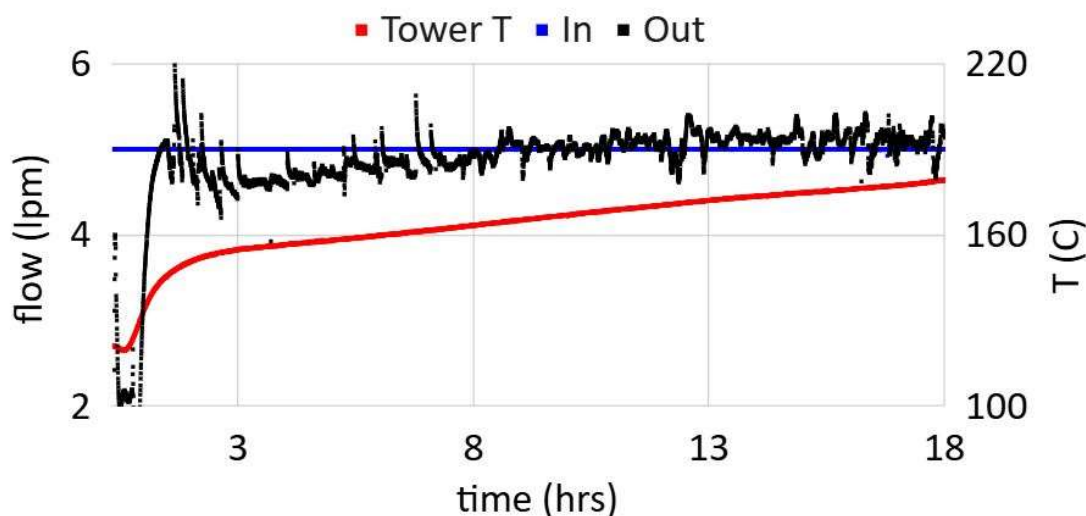


Figure 2.18 shows an expanded version of the data from Figure 2.17, on the left panel. From 8 to 18 hours there is no significant or obvious increase in the flow rate of CO_2 exiting the tower compared to that entering (shown in blue), indicating, if any, a very slow regeneration. This profile can be more directly compared to the 5 lpm N_2 purge shown in Figure 2.16, right panel. Despite using the same flow rate, N_2 appears to purge the regenerated gas faster than CO_2 .

It should be noted that the 60+ lpm of steam is clearly a lot higher than the 5 lpm CO_2 and N_2 injections, which complicates the comparison of the purge gas identity on regeneration efficiency. It is possible that at 60+ lpm, CO_2 would be just as efficient at purging the regenerated CO_2 as steam. However, a 60 lpm purge of CO_2 for just an hour (assuming the length to completion is similar or better than steam) would require injecting around 7 kg of CO_2 into the tower. As will be discussed further in section 2.4.2, this is even larger than the amount captured during one cycle during these experiments. Recycling captured CO_2 for purge purposes, especially in such large quantities, may pose engineering challenges for scalability.

One of the biggest challenges we observed when using CO_2 as a purge gas is determining when the regeneration was complete. This is better depicted in Figure 2.18, an expanded view of the data from Figure 2.17, left panel. The same strange absorption region previously discussed in Figure 2.17 is displayed before the 8-hour mark, but from 8 to 18 hours the exiting CO_2 hovers around 5 lpm (the initial purge flow rate). At 5 lpm, it appears

that the regenerated CO_2 does not significantly add to the overall measured CO_2 flow, indicating a slow and steady regeneration. This will be further quantified in section 2.4.2. However, it indicates a clear challenge; future studies which want to use CO_2 as a purge need to be able to measure a clear end of regeneration, which may require a substantially higher purge flow rate to speed up the process. For comparison, the N_2 regeneration was performed at the same low 5 lpm flow rate, but experienced an obvious maximal regeneration point, depicted in Figure 2.16 on the right panel. While the “end” of regeneration was still challenging to determine from the Figure 2.16 decay curve, there was a much more obvious maximal regeneration region between 1 and 6 hours.

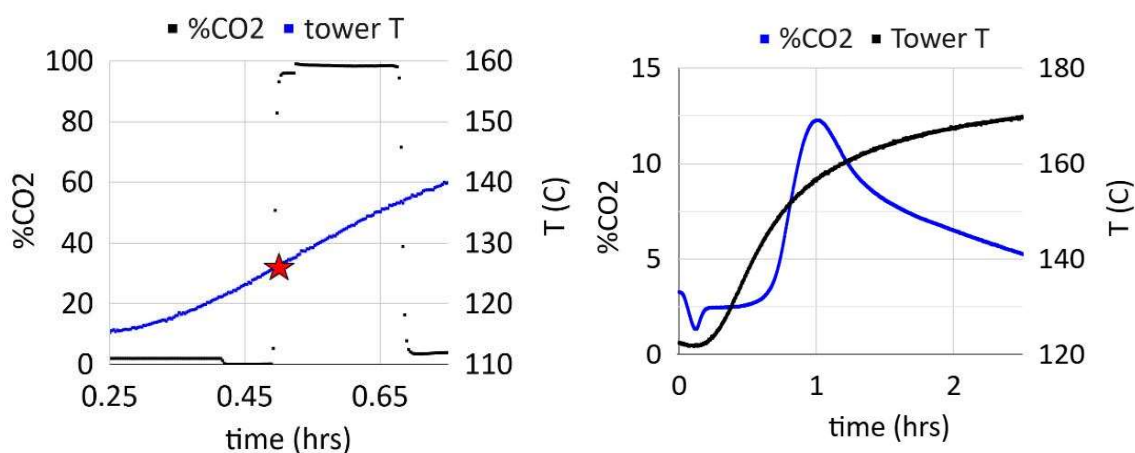
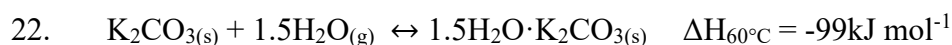


Figure 2.19 compares the temperature needed to regenerate the material under steam (left panel) versus N_2 (right panel) purge gas. The left panel and right panel data is taken from Trial 2 cycle 8 and Trial 2 cycle 1, respectively. In both panels, the CO_2 profile exiting the tower (black) is displayed against the temperature profile (blue), and tower temperature refers to the temperature taken in the middle of the tower. The red star in the left panel indicates the region where a burst of CO_2 began to exit the tower, which occurred at a tower temperature of around 125°C . When N_2 was used as a purge some regeneration occurred at around 130, but substantial regeneration begins at $140^\circ\text{C}+$.

Another benefit we found to using steam as a purge gas was that regeneration was noted to occur at a significantly lower temperature than anticipated. During the N_2 purged regenerations, our zeolite-supported K_2CO_3 sorbents typically began to substantially desorb at temperatures above 140°C . An example of this is shown in the right panel of Figure 2.19. On the other hand, when steam was introduced, we saw fast regeneration occur

at a temperature of around 125°C, depicted in the left panel of Figure 2.19. Literature on the K_2CO_3 reaction mechanism gives insight to this purge-gas dependent desorption temperature. As will be discussed further in Chapter 3, there is substantial evidence that reaction 3 occurs in a multistep mechanism, with potentially multiple hydrated intermediates. One reaction pair that has been considered is presented in equations 22 and 23 below.³⁹ Zhao *et al.* suggested saving energy of regeneration by reforming $1.5\text{H}_2\text{O} \cdot \text{K}_2\text{CO}_3$ instead of K_2CO_3 . It should be noted that K_2CO_3 hydrates are complex, as they can dehydrate at temperatures above 100°C depending on the pressure and humidity conditions.⁴⁰ Despite this, humidity swing to decrease the regeneration temperature is feasible, as Rodríguez-Mosqueda *et al.* were able to successfully regenerate 50% of captured CO_2 with wet air at bench scale.⁴¹ Thus, there is precedence in the literature to observe, as we did, a decrease in the required temperature for regeneration when substantial water is present.



2.4.2 Capture Results

While the raw sensor data gives some insight into the effectiveness of each regeneration, in this section we will present capture capacities, capture efficiencies, and calculated capture kinetics during the maximal efficiency period to compare regeneration conditions in a quantitative manner. In addition to being able to more directly compare the impact regeneration conditions have on the following absorptions, with these data we will also be able to observe the effects of cycling on material durability.

Table 2.3: Trial 1 Capture Capacities

Cycle	1	2	3	4	5	6	7	8
CO_2 Capt. (kg)	0.32	+0.21 ^a	0.52	- ^b	0.57	0.94	1.4	0.28
Cap. (kg m^{-3})	3.2	+2.1 ^a	5.2	- ^b	5.7	9.4	14.	2.8

^a note that the CO_2 compressed gas cylinder ran out before breakthrough occurred

^b data acquisition for cycle 4 crashed; the data was lost

Table 2.3 displays the captured CO₂ as well as the capture capacity for Trial 1, the rock-type zeolite. The capture capacity is simply the CO₂ captured divided by the tower volume; it can be used to estimate how large a tower may need to be scaled in future designs. It should be considered that tower dimensions must be scaled carefully to avoid pressure drop and flow tunnelling, but this is beyond the scope of the current work.

The first obvious trend in this data is that over many cycles (excluding for a moment, cycle 8) the material does not drop in capacity. The material could lose activity over time if disintegration/degradation causes pore closure or if the material leeches K₂CO₃. These data affirm that the current tower design and support material does not cause substantial degradation/leeching within 8 cycles. It is challenging to quantify exactly how long the material would need to last without replacement for it to be commercially viable. The lifetime of the material impacts the cost of capture, but further, even if a material is very cheap, operating a tower becomes cumbersome if it requires frequent loading/unloading. Conversations with potential customers indicate that materials that have a lifetime less than about a month are undesirable. Assuming a tower completes 2 cycles a day, the material would need to last about 60 cycles.

There are essentially two groupings of capacities that were measured in Trial 1. Cycles 1-5 and 8 captured about half a kg of CO₂ or less, while cycles 6 and 7 stood out with higher capacities. Unfortunately, the data for cycle 4 was lost as the data acquisition device crashed. Additionally, the captured CO₂ for cycle 2 is a lower bound, as the CO₂ cylinder ran out in the middle of the absorption cycle. The efficiency curve for cycle 2 (Fig 2.20) shows that the material was close to saturation regardless. Absorptions 1-5 and 8, despite having similar low capacities, had prior regenerations performed with all three purge gas types (see Table 2.2). While the goal was to determine the impact (if any) of different purge gases on the regeneration efficiency, we determined that for Trial 1 other factors may have obscured any potential differences across cycles. We attribute the lower capacities seen in cycles 1-5 and 8 to primarily two factors: incomplete regeneration and overly wet material, both of which result from us not yet optimizing operating procedures. For example, the first absorption was performed after the material was loaded into the tower. Before

absorption 1, the material was dried for over a day with a purge gas flow rate of 2 lpm N_2 , during which the tower hovered around $140^{\circ}C$. This drying was intended to drive off water, as the RH meters indicated the loaded material was wet, but in retrospect it is highly likely that during manufacturing/packaging/traveling the material also became somewhat saturated with CO_2 . This was rectified in Trial 2 by increasing the purge flow rate to 5 lpm and tower set temperature to $190^{\circ}C$ before the first absorption.

During Trial 1, we also were still optimizing procedure related to the absorption phase. While we observed CO_2 breakthroughs typically around 3 or less hours into absorption, we allowed the flue gas to flow for up to 12 hours in some cases to test other tower subunits. During prolonged absorption phases, eventually the material became quite wet, as evidenced by the RH meter data for the middle tower probe, shown in Figure 2.21. The regeneration phase if long enough, could help dry the material. This was likely true in the case of cycles 6 and 7, which had 65+ hours each of drying (Table 2.2).

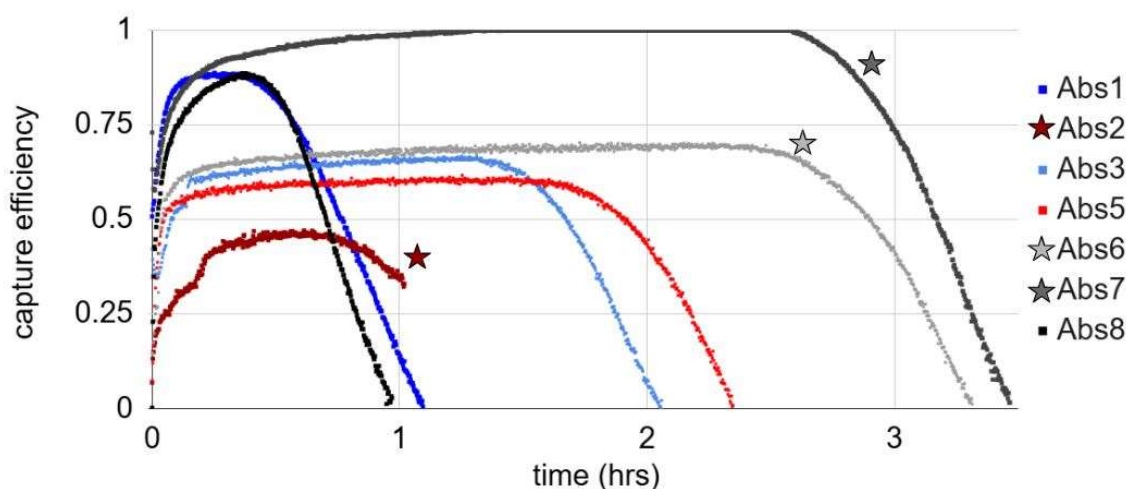


Figure 2.20 displays the efficiency curves for each of the absorption cycles in Trial 1. Cycles 6 and 7 observed the longest capture periods, with maximal capture efficiency occurring for about 3 hours. Alternatively, cycle 2 performed the worst, with the lowest maximal efficiency of less than 50%, and dropping at less than one hour into the absorption period.

Alternatively cycle 8, which performed very poorly, occurred after our first attempt at steam regeneration (regeneration 7) which appeared to have condensation issues. Thus, in conclusion, while Trial 1 absorption 1 likely performed poorly due to CO₂ saturation during manufacturing/packaging/shipping, cycles 2-5 and 8 appear to have performed poorly due to water saturation of the sorbent. How increase in absorbed water reduces capacity cannot be studied thoroughly with this system, but most likely is related to pore blocking. More complex analytical techniques are necessary to diagnose what physical/chemical mechanisms are driving this capacity drop and should be explored in future works.

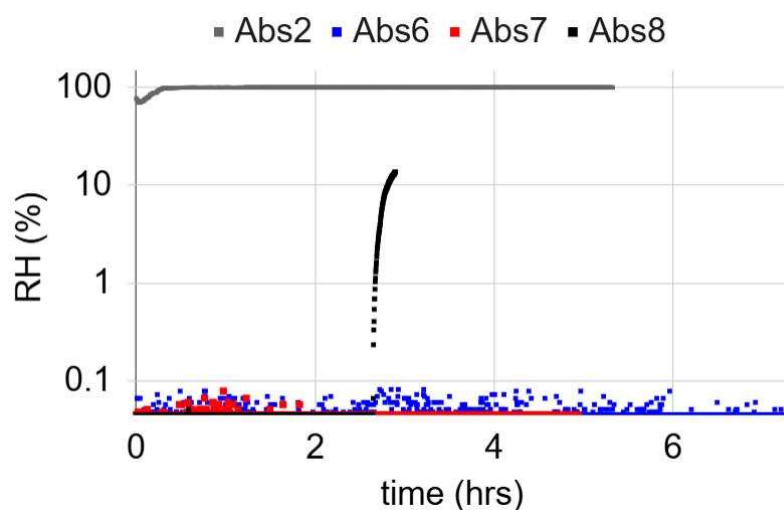


Figure 2.21 displays the RH data from the middle tower sensor during Trial 1, absorption phases 2, 6, 7, and 8. Absorption 2 performed the worst in terms of efficiency and capacity of any cycle in Trial 1 and was the most wet by far. The middle RH meter (grey) sat near 100% during the entire absorption 2 period. Absorption 8 occurred after a steam regeneration and began to display signs of water saturation at the tower midpoint at around 2.5 hours (black). Absorption 8 also performed poorly in terms of capacity and efficiency. In comparison, absorptions 6 and 7 performed the best in terms of total capacity and did not indicate signs of water saturation during their entire phases.

The decrease in sorbent activity can also be observed as changes in the capture efficiency profile (Figure 2.20) or the calculated 2nd order rate constant (Table 2.4). As is explained in more detail in section 2.3.6, the efficiency profile shows what fraction of the injected CO₂ at a given moment was taken up by the tower. If all mass injected at a given moment was absorbed (the CO₂ analyser on the tower exit reads 0%), then the efficiency will be 1.

In addition to having the largest capture capacity cycle 7 also showed the greatest maximal efficiency, reaching near 1 for most of the absorption phase. Interestingly, cycles 8 and 1 have the second and third highest maximal efficiencies, but only for a short period of time before they drop, thus explaining their low capacities. Cycle 2 had the lowest maximal efficiency; at its best capturing less than 50% of the injected CO₂. The kinetic data in Table 2.4 is in general agreement with the trends observed in the capture data and efficiency profiles. We had hoped that these data may also be used to discriminate optimal tower temperature for this system, but there unfortunately were no clear trends between calculated rate and middle-tower temperature. This may be further evidence that the one-step mechanism in which H₂O and CO₂ are simultaneously reacted is a poor assumption.

Table 2.4: Trial 1 Calculated Kinetic Constants

Cycle	1	2	3	4	5	6	7	8
k ^a (m ³ mol ⁻¹ s ⁻¹)	1.4(0.5) ^c E-2	5.2(0.9) E-3	4.5(0.8) E-3	-	8.5(0.8) E-3	1.2(0.5) E-2	2.0(0.6) E-1	7.6(0.8) E-3
Temp ^b (°C)	45.5 (0.7) ^c	46.3 (0.9)	55.1 (1.0)	-	43.3 (0.6)	42.3 (0.7)	34.1 (0.6)	56.0 (0.5)

^a note that the kinetic constant can be calculated at any point in the absorption. We chose times near the start of the maximal efficiency period

^btemperature of reaction is assumed to be that measured at the middle tower probe

^cuncertainty is the standard deviation of 4 measurements, 1 minute apart

While the RH meters have proven quite critical in monitoring tower operations, future tower designs would benefit from minor changes to their layout. The bottom tower RH meter is located right by the flue/purge gas entrance and basically indicates the humidity of the entering gas stream. The next RH meter is in the middle of the tower and was used to determine when the material became saturated with water. Unfortunately, it measures the RH of the gas surrounding the material, not the wetness of the material itself. Because zeolite is a very good desiccant, the RH meter only appears to read non-zero values when the zeolite is almost fully water saturated. Additionally, if no gas is being moved through the tower (flow rate = 0), then the RH meter also reads 0, even when the material is very wet. The RH meter at the very top of the tower almost always reads 0, because the tower

saturates from the bottom up. For this reason, to help monitor tower wetness, it would be useful to mount an RH meter between the bottom and middle of the tower. Future designs may even investigate more direct manners of monitoring material wetness.

Table 2.5 displays the capture capacities measured for Trial 2, the 13X ADCOA bead zeolite. During Trial 1, many operational issues were identified and resultantly avoided or modified for Trial 2. To avoid over-wetting the sorbent, once capture was completed (indicated by the exit CO₂ concentration equalling that entering the tower) the flue gas was immediately shut off. During N₂ and CO₂ purged regeneration cycles, RH was closely monitored to ensure significant drying had occurred. As previously mentioned, the middle tower RH meter was our best indicator of material wetness. After CO₂-purged regenerations, a final compressed air pulse was used to evacuate remaining CO₂ before the tower entered the cooling phase. This was to prevent reabsorption of the CO₂ remaining in the tower after CO₂-purged regeneration. Lastly, after steam-purged regenerations compressed air was utilized again, but in this case to evacuate water that might condense during the cool down phase. While during N₂ and CO₂ purged regenerations drying occurs over many hours at a low flow rate, during steam-purged regenerations the following compressed air pulse spurs drying. In summary, multiple procedural changes were instituted so that Trial 2 had more consistent sorbent conditions than Trial 1. As a result, we were better able to compare the regeneration abilities of the different purge gases, N₂, CO₂ and steam.

Table 2.5: Trial 2 Capture Capacities

Cycle	1	2	3	4	5	6	7	8
CO ₂ Capt. (kg)	0.56	0.52	0.43	0.51	0.14	0.33	0.20	0.33
Cap. (kg m ⁻³)	5.6	5.2	4.3	5.1	1.4	3.3	2.0	3.3

Cycle	9	10	11	12	13
CO ₂ capt. (kg)	0.37	0.32	- ^a	0.25	0.27
Cap. (kg m ⁻³)	3.7	3.2	- ^a	2.5	2.7

^adata acquisition for cycle 11 crashed; the data was lost

Despite our optimized procedure, the best performing cycle of Trial 2 observed a total CO₂ capture of 0.56 kg, which is less than half that of Trial 1, which was 1.4 kg. Since the Trial's total sorbent mass loaded were similar (111.6 and 100.8 kg for Trial 1 and 2 respectively), we hypothesize that the rock-type Clinoptilolite had a higher mass percent of K₂CO₃ than the 13X (which was around 20%). Unfortunately, the supplier did not provide the mass loaded, however it would not be unreasonable to expect Clinoptilolite to support more K₂CO₃ than 13X. As discussed in section 2.3.5, 13X is a commercial produced zeolite with very regular primary structure and pores that are around 1nm. On the other hand, clinoptilolite is a naturally occurring zeolite with secondary structure and has a range of pore sizes, scaling as large as 50nm.³⁷ Larger pores may enable clinoptilolite to hold more K₂CO₃ than 13X. In addition, larger pores may prevent pore clogs during absorption (pore clog/closure will be discussed further in Chapter 3), increasing availability and activity of K₂CO₃.

Unlike Trial 1, Trial 2 observed a decrease in material activity over cycling, with a starting capacity of 0.56 kg CO₂ and a final cycle 13 capacity of 0.27 kg. The capacity drop appears to occur around cycle 5. Notably, the regeneration 4, which occurred directly before cycle 5, was the first regeneration of Trial 2 without a N₂ purge. Cycles 1-4 were all performed after a N₂ purge to determine the variation in measured capture under conditions which were as similar as possible. The standard deviation across cycles 1-4 was 0.05 kg, 11% of the average. It can be extrapolated that most of our capacity measurements have an error of around 10%. Cycles 5 and 7, which occurred after CO₂ regeneration, had the lowest capacities of the Trial. While cycle 9, which occurred after steam regeneration, also had a low capacity, it compares well to neighbouring post-N₂ cycles. This is depicted in Figure 2.22. While cycle 11 was also performed after a steam regeneration, unfortunately the data acquisition device again malfunctioned, and the data for that cycle was lost. Capacity measurements from cycles 12 and 13, both performed after N₂-purged regenerations, did not decrease significantly. Thus, we can still conclude that steam regeneration under these new procedures did not harm material activity overtime.

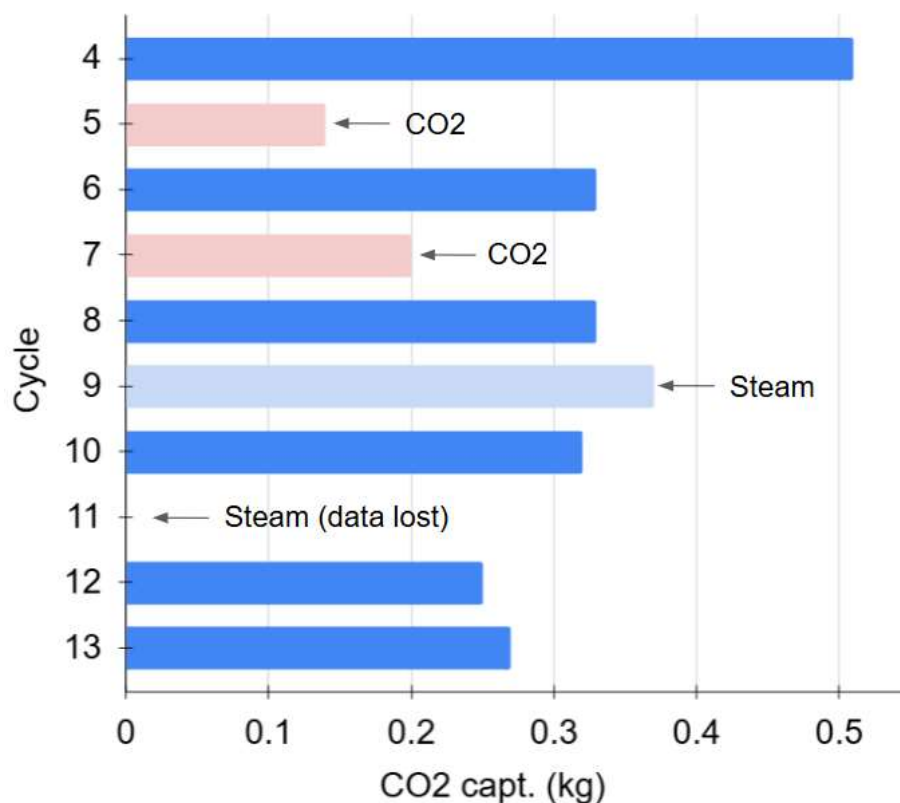


Figure 2.22 visualizes the CO₂ captured for cycles 5-13 from Table 2.5. The post-N₂ regenerated cycles are shown in blue, post CO₂ and steam cycles are shown in light red and light blue respectively. Unfortunately, the second post-steam cycle data, cycle 11, was lost. As the material does appear to degrade in activity overtime, the post-N₂ cycles in-between CO₂ and steam regeneration cycles can be used for comparison to observe the impact of these two purge gases. Cycles 4, 6, and 8 neighbour the post-CO₂ cycles while 8 and 10 neighbour the post-steam cycle. Using these as comparison, steam performs similarly to N₂, while CO₂ does worse by nearly 50%.

Figures 2.23, 2.24 and 2.25 display capture efficiency curves for Trial 2. Unlike the Trial 1 curves (Figure 2.21), whose trends are overshadowed by issues with tower wetness, Trial 2 data shows differences in regeneration effectiveness according to purge gas type. First, Figure 2.23 displays the first four cycles, all post-N₂ purge, and contrasts them to a curve from Trial 1. The four Trial 2 curves are very similar in shape, which agrees well with their similar capture capacities. Notably, their maximal efficiency region is short lived and drops consistently throughout absorption in comparison to Trial 1. This may be evidence of pore-clogging, which makes K₂CO₃ in the particle center harder to access.

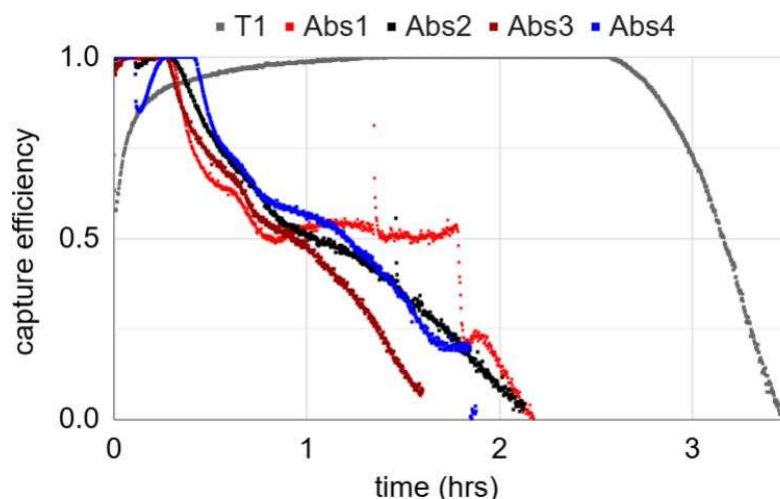


Figure 2.23 compares the first four cycle efficiencies of Trial 2 to each other, as well as the highest performing absorption of Trial 1, which was cycle 7 (labelled T1). Absorptions 1-4 are very similar in profile, which agrees with their similar absorption capacities listed in Table 2.5. They contrast greatly with the profile from Trial 1, which is very smooth and proceeds for over 3 hours where most of the cycle observes a fairly unchanging measured efficiency.

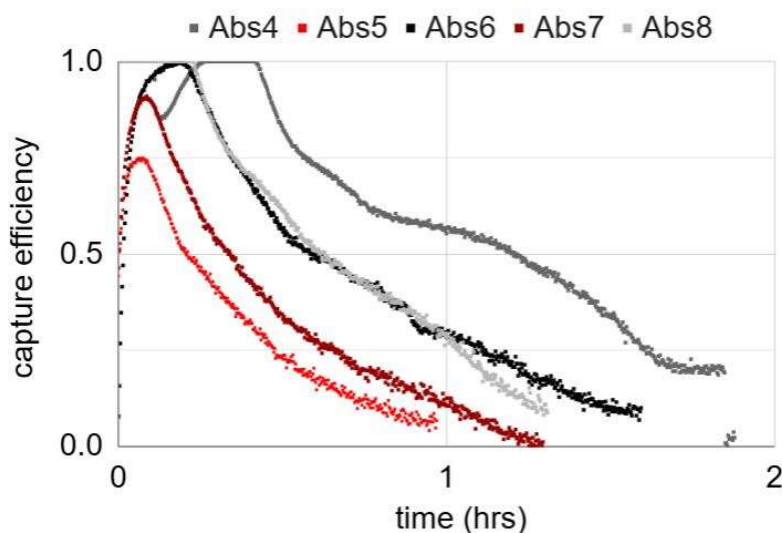


Figure 2.24 displays the post-CO₂ absorption efficiency profiles, Abs5 and Abs7, shown in light and dark red respectively. They are directly compared against the neighbouring post-N₂ cycles Abs4, Abs6 and Abs8. While Abs4 (in medium grey) outdoes all other presented cycles, likely because it was performed earliest and the material appears to degrade over cycling, absorptions 5 and 7 both perform substantially worse than the latest presented cycle, cycle 8 (in light grey).

In Figure 2.24, the efficiency curves for the post-CO₂ regenerated absorptions are directly compared against the neighbouring post-N₂ absorptions. Interestingly, the shape of the profiles are quite similar; a sharp increase with a short-lived maximal efficiency period, followed by a slow decay to 0%. Notably, both post-CO₂ curves indicate the material performed worse than even the latest neighbouring absorption cycle, cycle 8. Figure 2.25 compares the only post-steam cycle with surviving data, Abs9, against its neighbouring post-N₂ curves. The data from Abs11 (the other post-steam cycle) was unfortunately lost, but the Abs12 and Abs13 curves which immediately followed continued to observe similar efficiencies as those prior, indicating that no substantial material change occurred due to steam-regeneration. While issues from Trial 1 gave us concern that steam regenerations give opportunities for condensation and thus leaching of K₂CO₃, the largest drop in capacity and efficiency occurred between Abs4 and Abs5, when the first CO₂ purge of Trial 2 was performed. It is possible that the CO₂-purge initiated significant material degradation, but how is currently unclear without material characterization techniques such as Brunauer–Emmett–Teller (BET) or Scanning Electron Microscopy (SEM).

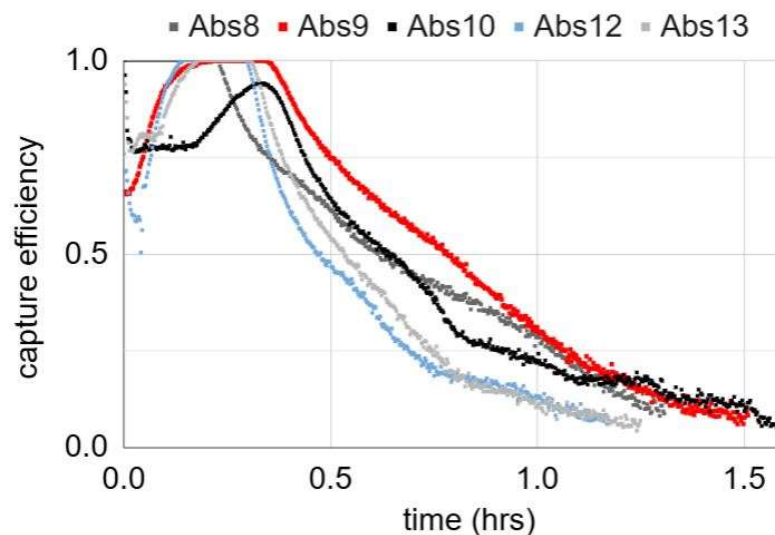


Figure 2.25 displays the efficiency curves for absorptions 8-13. Absorptions 9 and 11 were performed after steam-purged regenerations but unfortunately the data from absorption 11 was lost. Abs9 outperformed its prior and successive absorptions, 8 and 10, indicating that steam as a purge was very effective. While the data from Abs11 was lost, the following absorption efficiency curves appear very similar to all those prior.

Table 2.6: Trial 2 Calculated Kinetic Constants

Cycle	1	2	3	4	5	6	7
k ^a (m ³ mol ⁻¹ s ⁻¹)	1.3(0.2) ^c E-2	5.7(1.2) E-2	2.9(0.1) E-2	2.7(0.1) E-2	3.3(0.2) E-3	1.0(0.4) E-2	1.8(0.1) E-3
Temp ^b (°C)	27.4 (0.1) ^c	50.1 (0.2)	46.0 (0.3)	41.0 (0.1)	41.3 (0.2)	43.0 (0.2)	40.5 (0.1)

Cycle	8	9	10	11	12	13
k ^a (m ³ mol ⁻¹ s ⁻¹)	5.8(0.9) E-3	9.6(0.4) E-3	3.5(0.2) E-3	-	3.8(1.4) E-2	1.3(0.3) E-1
Temp ^b (°C)	40.4 (0.2)	41.2 (0.1)	38.0 (0.3)	-	47.9 (0.1)	48.0 (0.2)

^a calculated at times near the start of the maximal efficiency period

^b temperature of reaction is assumed to be that measured at the middle tower probe

^c uncertainty is the standard deviation of 4 measurements, 5 seconds apart. These are notably more closely spaced than points selected for Table 2.5. This is because the maximal efficiency period was much shorter.

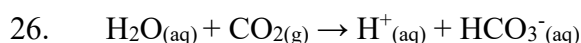
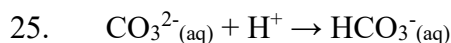
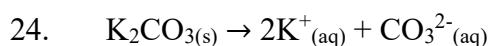
Table 2.6 shows the calculated rate constants for these absorptions. Like Table 2.4, the rate was calculated at the region of highest efficiency, which for each cycle in Trial 2 lasted just a few minutes. Also, like Table 2.4 the results are not elucidating in the same way that the capacity measurements and efficiency profiles are. For example, cycles 12 and 13 both occurred after N₂-purge regenerations and occurred at the same measured mid-tower temperature but have rates that are an order of magnitude apart. It is possible that there was a temperature gradient in the tower, meaning that the reaction doesn't occur at the reported temperature, it occurs under a temperature range. The bottom and top probes typically measure different values than the mid tower probe that are more indicative of the temperature of the gas stream entering and exiting the tower. Thus, to be more confident in the temperature distribution of the material more probes may be useful in future designs. On the other hand, as mentioned earlier, it may be that the single-step capture mechanism is a very poor assumption. A more complex mechanistic model may be necessary to accurately compare cycle kinetics.

The theoretical capacity of pure K_2CO_3 is 7.25 mmol g^{-1} , and the expected mass loaded of the 13X was about 20% based on the density change after impregnation. The total mass loaded during Trial 2 was 100.8 kg, meaning that 20.16 kg of K_2CO_3 was present. Assuming all of this was available for capture, this would result in a captured CO_2 mass of 6.43 kg. Our highest observed CO_2 mass captured was 0.56 kg, meaning that we captured only about 9% of the theoretical capacity of this material was reached.

Typical pilots plants capturing point source carbon from powerplants hope to capture about 1-tonne (1000 kg) of CO_2 a day.⁴² Even if the material is cycled every hour, this system would capture less than one tenth that goal at its current size. Comparatively, the clinoptilolite (Trial 1) captured 1.4 kg during its best run, absorption 7. Additionally, as previously discussed Trial 1 operating conditions were not yet optimized, meaning that it may have performed even better. It appears that clinoptilolite may provide a better support than 13X zeolite. We hypothesize that the bigger pores, provided via naturally forming secondary structure, allows for greater mass loading and availability of K_2CO_3 .

2.4.3 Additional Diagnostic Data

In addition to CO_2 capture data, we monitored other operational variables during these trials that will impact future designs. One variable of great importance is the pH of the condensed liquids exiting the tower bottom. While condensation should be avoided as much as possible, as the flue gas contains around 15% $\text{H}_2\text{O}_{(\text{g})}$ and we performed some regenerations with superheated steam; ultimately, some liquid will condense and exit out the tower bottom. In addition to rusting of the tower, two chemical processes will impact the pH of the exiting liquid: leaching and acidification. Material leaching describes carbonate ion dissolution, resulting in a pH increase according to reactions 24 and 25. Alternatively, acidification occurs when gaseous CO_2 dissolves into the liquid water according to equation 26.



By monitoring the pH exiting the tower, we hoped to identify if there were specific phases (absorption, regeneration and cooling) or purge gas conditions that exacerbated either of these processes. We anticipated seeing an increase in pH due to leaching during the cooling phase or during steam regeneration. We also expected a decrease in pH due to acidification during CO₂-purged regeneration. Instead, we observed rapid changes in pH during the absorption phases in which pH generally increased, indicative of leaching. Absorption phases occur at temperatures less than the boiling point of water (typically less than 70°C), while regeneration occurs at 100°C+, and cooling begins at temperatures of 100°C+. Thus, it makes sense that more condensation occurs during the absorption phase comparatively, which results in greater leaching of carbonate ions from the sorbent. It would be beneficial in the future to measure the volume condensed after each phase, even collecting these samples for further analysis. This is clearly not reasonable to do for day-to-day industrial working conditions but would be useful to optimize operational procedures before regular use.

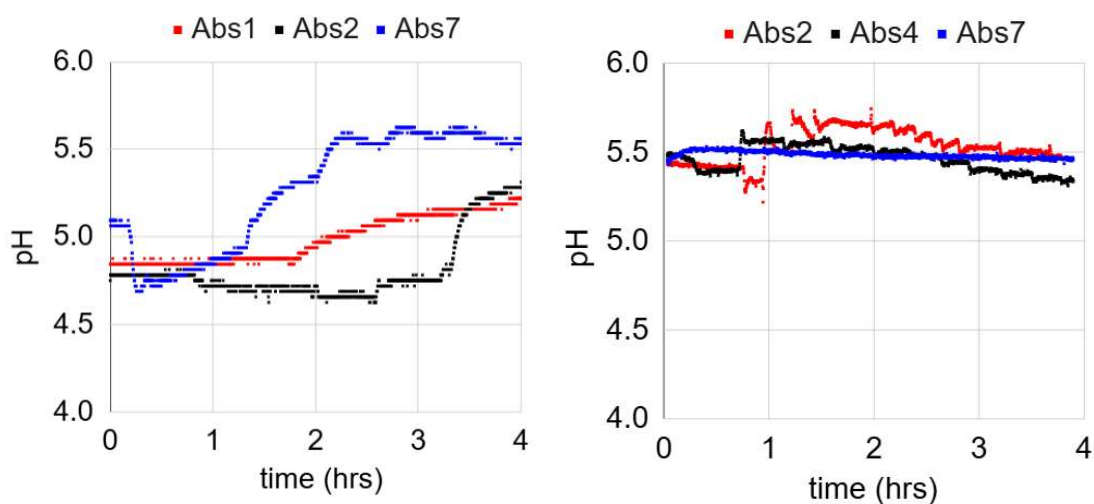


Figure 2.26 shows data from Trial 1 on the left panel and Trial 2 on the right panel. They are presented with the same scale of pH 4 to 6 for the first four hours of absorption.

In addition to finding that larger pH changes occurred during absorption phases, we also found that Trial 1 observed significantly larger pH increases than Trial 2. This agrees with our understanding that the material during Trial 1 was generally more wet due to flaws in operational procedure. This difference is visualized in Figure 2.26.

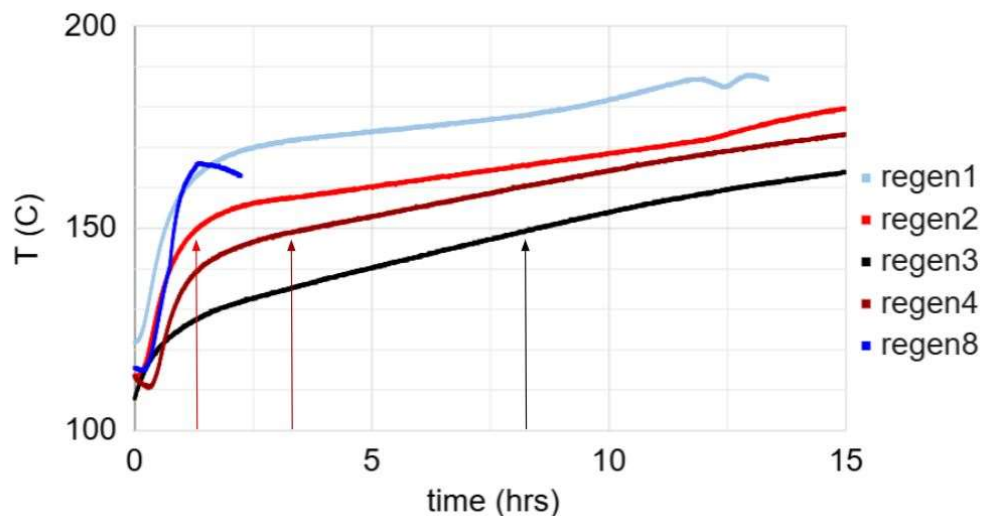


Figure 2.27 displays some mid-tower temperature ramps during the regeneration of sorbent from Trial 2. Regenerations 1-3 were performed with N_2 at 5 lpm, regeneration 4 was performed with CO_2 also at 5 lpm, and regeneration 8 was performed with steam at 65 gpm. Even across regenerations 1-3 (which utilized the same purge gas and flow rate) we observed large variability in time for the tower to warm to 150°C. The fastest tower heating of all 13 cycles occurred via steam-induced regeneration (dark blue) and took less than an hour. The wiggle-curve at the end of regen1 is the result of the tower heater turning off and on to maintain an average temperature of 185°C.

One of the greatest challenges to providing similar regeneration conditions is setting tower temperature. During Trial 1 the in-tower heater was initially set to 165°C, but it was determined that by setting it to a higher temperature the heating occurred significantly faster, thus for all Trial 2 runs the in-tower heater was set to 185°C. While the heater could reach 250°C, the RH meters throughout the tower are only viable to temperatures up to 200°C, after which they break. In general, it is difficult to find RH meters that can withstand high temperatures; this may be a challenge for manufacturing if larger temperature gradients are needed to heat the tower more quickly.

There was a large variability in the time it took for the tower to reach the minimum temperature in which regeneration could be expected, which should be around 150°C. We expect flow rate and purge gas identity to impact the heating time, as gases have different thermal conductivities and heat capacities. However, even across the three N_2 cycles presented in Figure 2.27 we see a large variability in the time to heat to 150°C. Fast tower

heating is highly desirable to increase the number of cycles (thus total CO₂ captured) a tower is capable in a day. It is also important that the length of the absorption phase vs the regeneration and following cooling phase be very similar to maximize tower efficiency. One can imagine, for example, that if an absorption only requires two hours but to regenerate and cool the material requires a total of twenty, there is a lot of idle time in which the tower is not absorbing. So, while the mere 30 minutes to heat up observed for regenerations 1 and 8 are very scalable, the longer heating times, for example eight hours for regeneration 3, may cause an issue. It is possible that the temperature of the warehouse had an impact on the heat up time of the tower, as during the operational period the temperature could fluctuate between 5-30°C, which is quite large. While this may appear problematic for a laboratory study, it does resemble real conditions as reactor towers will be installed outdoors on top of flue stacks and will be subjected to variable temperatures. It is also possible that while we attempted to dry the tower to similar degrees throughout Trial 2, that we ultimately were not entirely successful. Increased water content in the sorbent would increase its heat capacity, causing an increase in the time to heat the material. More work is necessary to pinpoint the primary causes of this variability. However, another benefit to using steam as the purge gas is that it is highly efficient at transferring heat.

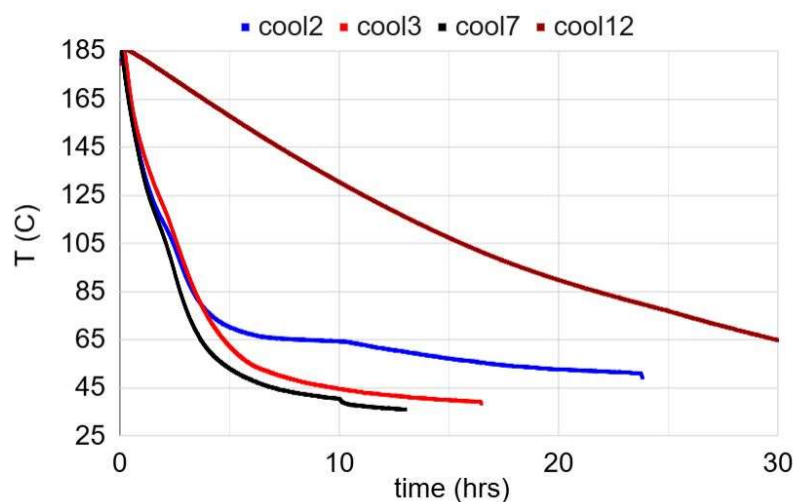


Figure 2.28 displays some cooling profiles from Trial 2. Tower temperature should be a maximum of 65°C before flue gas is injected for absorption. Cooling phases 2, 3, and 7 were performed with the cooling fan and heat exchangers while cooling phase 12 did not.

Lastly, to maximize the number of daily full tower cycles, the cooling phase must also be optimized. For the current tower design, sorbent composition, and flue gas flow rate absorption phases typically require about three hours to completion. Assuming steam is used as the purge, regeneration phases typically take about one hour to complete at which point they will need to be cooled before a new absorption can occur. Thus, for the current design, a cooling period of around 2 hours to 65°C is optimal. As previously mentioned, (section 2.3.3), the cooling phase is currently assisted by an internal fan (Redbo 2GH210-H16) which circulates tower air at 98 m³ph, while two water-cooled heat exchangers (shown in Figure 2.3) remove system heat at a water flow rate of approximately 0.8 m³h⁻¹ and a total heat exchanging area of 0.1m². The water used in this system comes from the exit of a cooling water tower circuit (we recycle the cooling water), which is about 10-20°C depending on ambient conditions. When the fan is inactive, and the tower is allowed to cool naturally, it takes up to 30 hours. As depicted in Figure 2.28, when the cooling phase is active it takes between 5 and 10 hours for the material to cool from 185 to 65°C. To cut idle time larger heat exchanging area may be necessary to reduce cooling time in future adaptations.

2.5 Conclusion

A two-tower packed bed reactor for the purpose of K₂CO₃-based carbon capture was constructed and tested. The towers are a little smaller than industrial size, approximately 1.8 m tall, 0.1 m³ internal volume, with the capability of holding around 100 kg of impregnated zeolite sorbent. Two Trials, each utilizing a different type of zeolite, clinoptilolite and 13X, were cycled under varying conditions. Both temperature and humidity swing regenerations were attempted at temperatures ranging between 125 and 200°C. It was determined that steam assisted in lowering the temperature needed for material regeneration, which has been observed at the laboratory scale for other K₂CO₃ based sorbents. Sorbent dampness appears to negatively affect material capacity, which may continue to challenge future tower designs and operational procedures. Of the two materials the natural zeolite, clinoptilolite, observed higher performance, which may be a result of larger pores. A total of 8 and 13 cycles were successfully completed without large

losses of material activity, indicating potential of zeolite as a support in the future of K_2CO_3 -based capture.

2.6 Future Works

While sorbent formulation improvement is still under development, some immediate changes can be made to the reactor diagnostics systems. It was determined that the internal reactor humidity levels and overall saturation levels of the sorbent greatly impacted absorption capacity and kinetics. More humidity meters can be added along the reactor length to assist in monitoring these levels. Unfortunately, the model used here appeared sensitive to the operational temperatures, which can reach as high as 200°C , breaking the sensors. A more robust sensor model would be ideal, otherwise the sensor ports will need to be redesigned to isolate them from high temperatures. If this proves to be a challenge, it may even be necessary to design particle sampling ports along the length of the reactor. Then, throughout operation small particle samples can be directly removed and analysed for water content. On the bench scale, each sorbent formulation will need to be characterized, to determine the saturation levels at which performance suffers, defined by the mass of water absorbed by a given mass of dry particles. The “drying” phase will need to be added in between regeneration and cooling phases (or added into an extended regeneration phase) to bring particles below the identified maximal saturation level. It is possible that flue gas streams may even need to be somewhat dried to prevent quick oversaturation of sorbent with water. While some amount of water is necessary for the capture to proceed, the optimal flue stream humidity has yet to be determined. Similarly, the impact of total flow rate and CO_2 partial pressure on the sorbent is another avenue that requires investigation.

2.7 Citations

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Chapter 3

K₂CO₃ SORBENT DEVELOPMENT VIA WET-ACTIVATED GRANULATION

3.1 Abstract

In the following chapter, we present bench-scale testing results for several prototype granulated (uncalcined) K₂CO₃-based formulations developed by Mitico. Optimized formulations are desired for eventual scale-up and use in a packed bed reactor system for point source carbon capture, as described in Chapter 2. While many categories of additive materials were considered, including binders and potential catalysts, we found that sorbents composed primarily of the active material, inert supports, and desiccants resulted in materials that had simultaneous sufficient activity and material durability. Material activity was evaluated via capacity and kinetic evaluation over multiple cycles. Material durability was defined by its ability to maintain particle structure over cycling and exposure to humidity. We present our findings on the beneficial effects of adding Al₂O₃, CeO₂, CaCO₃ (supports and fillers), CaCl₂, and Zeolite 13X powder (desiccants) to K₂CO₃ granulate sorbents. Na₂CO₃, MgCl₂, Clinoptilolite zeolite powder, and a Mg-Al silicate were also considered, but found to be less effective than their analogues.

3.2 Introduction

3.2.1 Previous work on K₂CO₃ sorbents

Hot carbonates, in addition to other solvents, have been used for decades in oil refineries, ammonia manufacturing, and coal and natural gas purification plants to remove acidic gases in a process called gas “scrubbing” or “sweetening.”¹ In fact, amine scrubbing for CO₂ and H₂S removal from acidic gas streams was patented in 1930, but wasn’t significantly applied to small scale coal and gas-fired power plants until the 1980s and 1990s.² As discussed in Chapter 2, temperature requirements to swing amine solutions are minimal, but other environmental impacts of amine use are significant. Accidental release of amines and their oxidized/degraded products make such systems hazardous, and thus an unideal solution to the carbon capture problem.^{3,4} Alternatively, the Benfield process, currently utilized in hundreds of plants globally, uses 20-30% by mass solutions of non-

toxic non-volatile K_2CO_3 and is less environmentally detrimental. Unfortunately, K_2CO_3 solutions observe slower reaction kinetics.^{5,6} Assuming potassium or sodium carbonates are the sole reacting species present the net reaction is presented in line 1, where of all steps (2-4) the rate limiting step is line 3.^{6,7}

1. $CO_{2(g)} + CO_3^{2-}(aq) + H_2O(l) \rightarrow 2HCO_3^-(aq)$
2. $H_2O(l) \rightarrow H^+(aq) + OH^-(aq)$
3. $CO_{2(g)} + OH^-(aq) \rightarrow HCO_3^-(aq)$
4. $CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq)$

To enhance the rate of line 3, promoters are added to the solution, reactor temperature is increased, and most importantly reactor vessels are pressurized to around 70 atmospheres.^{5,8} Thus, while the Benfield process does not emit toxic gases to the degree that amine based processing does, pressurizing hot corrosive solutions comes with its own set of safety and environmental concerns.

As K_2CO_3 -based solutions have expanded in usage for carbon capture, simultaneously interest in the solid-phase reaction with CO_2 has increased, showing much potential. In the past two decades significant work has been made in elucidating the more complex “dry” chemistry, which is notably much faster. Note, dry chemistry refers to the fact that the K_2CO_3 sorbent is in the solid phase, opposed to being dissolved as in the Benfield process, but in fact is still exposed to water vapor. Recall from Chapter 2 that K_2CO_3 reacts in the presence of water with CO_2 to form $KHCO_3$ via the net reaction, line 5. The forward rate is maximal around 60°C while the forward reaction is initiated at temperatures as low as 120 °C, but typically around 155°C.^{9,10}

5. $K_2CO_{3(s)} + CO_{2(g)} + H_2O(g) \leftrightarrow 2KHCO_{3(s)}$
6. $K_2CO_{3(s)} + 1.5H_2O(g) \rightarrow K_2CO_3 \cdot 1.5H_2O(s)$
7. $K_2CO_3 \cdot 1.5H_2O(s) + CO_{2(g)} \rightarrow 2KHCO_{3(s)} + 0.5H_2O(g)$
8. $2K_2CO_{3(s)} + 2.5H_2O(g) + CO_{2(g)} \rightarrow K_4H_2(CO_3)_3 \cdot 1.5H_2O(s)$
9. $K_4H_2(CO_3)_3 \cdot 1.5H_2O(s) + CO_{2(g)} \rightarrow 4KHCO_{3(s)} + 0.5H_2O(g)$
10. $2K_2CO_3 \cdot 1.5H_2O(s) + CO_{2(g)} \rightarrow K_4H_2(CO_3)_3 \cdot 1.5H_2O(s) + 0.5H_2O(g)$

Earlier (mid-1990s) work on the K_2CO_3 dry reaction mechanism by Hirano *et al.* and Hayashi *et al.* showed X-ray Diffraction (XRD) evidence of a stable K_2CO_3 -hydrate intermediate, $1.5\text{H}_2\text{O} \cdot \text{K}_2\text{CO}_3$ (reactions 6-7).^{11,12} Further work and XRD assignments by Zhao *et al.* gave evidence for a second reaction mechanism (lines 8-9) through hydrate $\text{K}_4\text{H}_2(\text{CO}_3)_3 \cdot 1.5\text{H}_2\text{O}$.¹³ Both hydrates were verified by Luo *et al.*, and are hypothesized to form together under most relevant flue gas conditions.¹⁴ Luo *et al.* suggest that the overall reaction might progress through a two-step hydration instead, according to line 10.¹⁴

Currently, there does not appear to be conclusive work which can predict branching fractions for the two (possibly three) paths. Due to the complexity of this mechanism, it is very difficult to define a kinetically accurate rate law that can be used to calculate rate constants to be compared across differing reaction conditions. As a flawed rate law/constant derivation is better than none what-so-ever, the following work continued to use the bimolecular rate constant derivation described in Chapter 2 Section 3.6 to compare sorbent reaction rates.

These mechanistic insights do however indicate that excess humidity, despite its challenges to sorbent structure/durability, may positively impact the speed of reaction. In short, if the material is fully hydrated (via line 6) before any flue gas is introduced, then initial hydrate formation step may be “skipped.” Unfortunately, reaction kinetics are not only defined by the chemical mechanism. Luo *et al.*, like many others, have seen that physical accessibility of reacting material is also a great challenge to the K_2CO_3 system. For example, they observed via SEM imaging that at higher CO_2 concentrations, the surface reacted so quickly that the interior K_2CO_3 became inaccessible due to pore clogging. Thus, even though theoretically we would chemically expect higher CO_2 capacities at higher CO_2 concentrations (due to equilibria shift described in Chapter 2 Section 3.2), we might observe lower reaction rates depending on the pore structure.

Due to the deliquescent nature of K_2CO_3 as well as its naturally low porosity, current work on K_2CO_3 -based sorbents focuses on formulating materials that can provide adequate support (to minimize material leaching, observed as capacity/mass loss) and maximize surface area. Metal oxides and carbon bonded networks are quite common in the literature.

CaO, MgO, TiO₂, ZrO₂, Al₂O₃, SiO₂, activated carbon, carbon nanotubes, and carbon honeycomb just to name a few, have all been considered and studied.^{9,10,15–17} For example, in their work with TiO₂ and ZrO₂ Lee *et al.* generated impregnated beads and found that to maintain their physical properties over cycling, including bulk density and attrition resistance, they needed to be first calcined at temperatures above 500°C.¹⁶ Unfortunately, calcination of the TiO₂ resulted in the formation of K-Ti alloys, significantly reducing the capacity.¹⁶ Despite the benefits of thermal stability, ZrO₂ currently is not ideal to be the bulk material support as high purity ZrO₂ can be twice as expensive as TiO₂ and similar metal oxides.^{18,19} Additionally, impregnation methods generally have lower K₂CO₃ loading maximums; it appears ZrO₂ was found to load about 30% K₂CO₃ by mass.

Meis *et al.* found that activated carbon, which is essentially charcoal and thus is very economical, observed decently high capacities on first absorption. However charcoal loses about half its capacity on successive cycling (regeneration of 150°C).¹⁰ They found better regeneration using carbon nanofibers grown from synthesis gas using a Ni/SiO₂ catalyst to approximately 1mm in length (much smaller diameter).¹⁰ Small batch preparation of carbon nanofibers make it unclear how such a material would be scaled. Of those materials studied, Al₂O₃ seems a very promising support with good regenerability, high mass loading capability, high porosity (translating to fast kinetics) and low cost.^{15,20–22} There is some variability in the material traits depending on which Al₂O₃ phase is used (commonly used are α , γ and δ). While some success has been made, thus far none of these additives alone, prepared as described in the literature, are an obvious solution to the deliquescent nature of K₂CO₃.

3.2.2 Granule Manufacturing Strategies

While solid particulate sorbents for the purpose of CO₂-capture are emerging technologies, many other commercial products take the form of small granules, including but not limited to prescription drugs, fertilizer, detergents, pet litter, and feed pellets for livestock. Uniform particle generation strategies developed for these other commercial products can be utilized for carbon capture sorbent scale-up. However, it is not as simple as taking a particle production method and simply applying it to the K₂CO₃ system. As will be further described in this chapter, as well as Chapter 4, material processing can have a large impact

on the final properties of a sorbent, including durability/strength, capacity and kinetics. Additionally, some processes are more expensive than others. The cost-intensive nature of other aspects of carbon capture (like storage and mobilization) currently rules out more expensive methods.

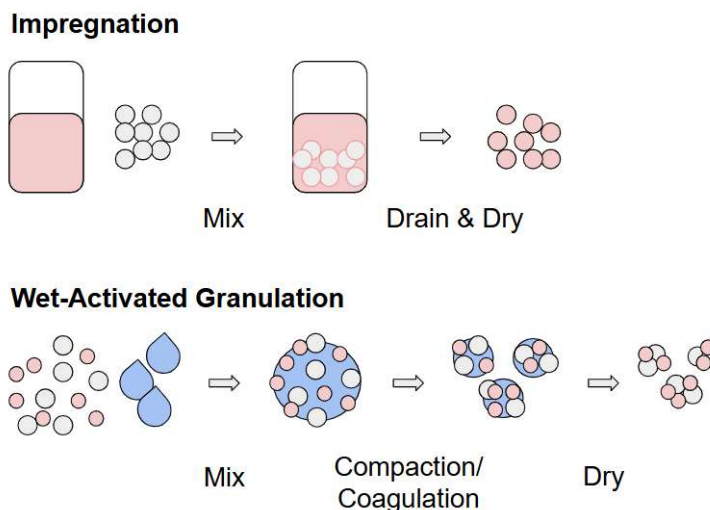


Figure 3.1 visually contrasts two methods for supporting active materials on uniform particles. Impregnation describes the process of soaking already prepared uniform porous particles in solvent concentrated with the active material (shown in light red). Wet-activated granulation takes dry active material and support material and mixes them with a solvent, eventually compacting it and forming particles. These can then be dried of the solvent.

In Chapter 2 Section 2.2, we briefly describe the difference between impregnation and wet granulation, which employ very differing strategies to support an active material on/in uniform particles.²³ Impregnation, which is far more common in the literature, takes already prepared (ideally durable, porous, uniform and inert) particles and submerges them in a solution concentrated with the dissolved material of interest, i.e. active material. The mixture is allowed time to settle, during which the dissolved active material slowly deposits onto the particles. Ideally if they are porous enough, the active deposits throughout their entire depth and not just superficially. On the other hand, wet granulation takes a powder/dust support material and mixes with the dry active in the presence of some solvent. In wet granulation active material is bonded into the support material in a “native” manner; the active material is already present when the particle is formed. The solvent is often water

but can be other liquids such as alcohols or acetone. The purpose of the solvent is to physically bring the dry materials closer together and initiate van der Waals and/or ionic bonding. Afterwards the material is dried so that the solvent evaporates. To help strengthen the material a binder is often added. Additionally, the material can be heated at a higher temperature during a process often referred to as calcination. If higher temperatures are utilized, the particles may continue to strengthen via new (covalent) bonds formed during phase changes. Calcination temperatures must be carefully selected, as if an additive melts it may destabilize the particle structure.

While in theory impregnation is arguably simpler to streamline on a large scale and can be very cost effective, it comes with many limitations. First, impregnated particles cannot easily be recycled as they deteriorate over time. If leaching of the active material was the only problem, the material could simply be reimpregnated, but fast heat cycling does eventually cause cracking/dunting for most metal-oxides (like clays and zeolites).²⁴ If the material cracks and deteriorates it must be discarded and replaced.

Secondly, impregnated materials may have less activity due to clogging and insufficient active loading. As the active material is not “native” to the particle, sufficient deposition is required for significant mass loading onto the support medium. Inherently, the dissolved active material interacts with the superficial layers of the particle first and must traverse porous channels to deposit deeper into the particle. Unfortunately, each active material/particle system is different, and it is challenging to avoid clogging. At lower active dissolved concentrations, it is easier to avoid clogging (allowing material to potentially penetrate deeper into the particle), however lowering the concentration may decrease the amount of active that deposits overall by shifting the deposition equilibrium. In short, it is challenging to achieve a very large mass loading as well as deep penetration at the same time. Shallow penetration results in increased leaching of active material, and low mass loading reduces activity. In the case of the Mitico-developed 13X zeolite investigated in Chapter 2, a mass loading of only about 20% was achieved when the solvent solution concentration was optimized. To reduce size requirements for future CO₂-capturing packed bed towers, it is necessary to increase the sorbent's K₂CO₃ mass loaded.

Alternatively, during granulation, any amount of K_2CO_3 can be loaded into the material, if when mixed it will granulate. Wet granulation is the most common granulation method due to its simplicity and flexibility. It should be noted that dry granulation is also used in some commercial processes. For example, pharmaceutical “slugs” are created through compression of dry powder into slug molds. Most dry granulation techniques are done in small batches and require complex industrial machinery that necessitate larger industrial space and maintenance.²⁵ While this process lends itself to drug manufacturing, the costs and complications make it less desirable for CO_2 capture. Technically there are also many variations to the simple wet granulation presented in Figure 3.1. For example, some utilize freeze/spray granulation, which takes a wetted granulation mixture and sprays droplets into liquid N_2 .^{25,26} It is also possible, for certain more malleable formulations, to extrude the wetted mixture and spheronize it into beads.²⁷ This process will be further explored in Chapter 4.

3.2.2 Requirements for Industrial Scalability

Considering the benefits of wet-activated granulation, which includes increased loading potential, this process was selected for the next phase of Mitico sorbent development. While the primary goal these studies was to identify formulations with increased absorption capacity, it is critical to always keep in mind other necessary traits for a sorbent to be economically viable for scale-up. Any additives must be cheap (or used in very small quantities); ideally the most expensive material in the sorbent would be K_2CO_3 . In the third quarter of the 2024 fiscal year, for example, K_2CO_3 powder cost around 1500-1600 USD per metric ton in the United States and Europe.²⁸ In comparison, TiO_2 during that same period cost 2500+ USD per metric ton in the US and Europe, and thus would not make for an ideal additive.²⁹

Ideally, the material additives or the processes required for production will be non-toxic. One of the major downsides to other popular forms of carbon capture, like amine scrubbing, is their environmental impact. Non-toxic materials also make loading and unloading protocols easier, and thus more desirable for commercial use.

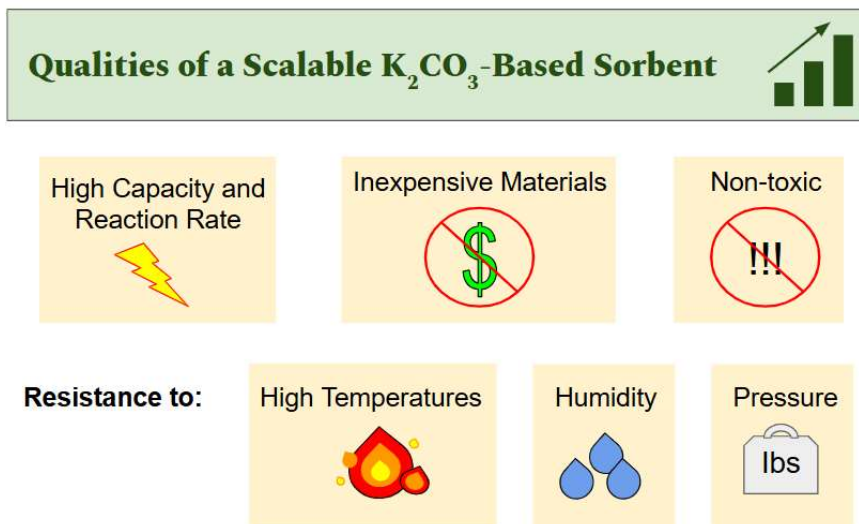


Figure 3.2 visualizes the primary challenges that must be addressed to design an economically viable and competitive K_2CO_3 -based sorbent. While current academic literature focuses heavily on achieving high capacity and reaction rates, the sorbent must possess many other physical properties that are often not considered.

There are also many physical constraints; the material must be able to endure the weight of the tower, survive loading, and remain durable in a humid environment. Thermal cycling to temperatures of almost 200°C are necessary to release the CO_2 once captured, thus the material must also not burn or melt at these temperatures. To make matters more complicated, while some organics may not typically decompose at 200°C on their own, K_2CO_3 creates a strongly basic environment when wetted, and may induce base-catalyzed chemistry, reducing temperature of decomposition. Evidence for base-catalyzed decomposition will be further explored in Chapter 4. Lastly, when the material is wetted, it should not be susceptible to clumping, to avoid pressure drop.

3.3 Methods

3.3.1 Granulation Procedure

K_2CO_3 -based sorbents made via wet-activated granulation method are presented and their properties compared. The particles were generated as follows: first, 500 g of dry materials were massed and mixed dry in a KitchenAid bowl-lift stand mixer with a flat beater for 5 minutes. Next, deionized water was added slowly over the course of another 5-10 minutes while mixing, typically around 20% of the dry mass. The wet-mixing period ended when

particle formation was significant, with an intent of forming particles of around 3 mm in diameter. This size range is of interest to minimize pressure drop in the packed bed reactor described in Chapter 2 and similar future designs. If only small agglomerates formed, typically more water was added (and more time was spent mixing) to increase cluster size. The particles were spread in a thin layer onto a tray and loaded into a counter-top convection oven. There, they were baked at 190°C with an internal fan for 2 hours. Once removed from the tray they were sieved. The saved and tested size range was 2.36-4.75 mm. For some formulations, the particles fused and had to be broken apart with a hammer. The particles had varying shape, especially if they had to be crushed. There was no way to normalize for shape differences across samples.



Figure 3.3 shows an example of particles formed from this process. The left panel shows wet particles still in the bowl of the stand mixer. On the right are the particles spread thin on a baking sheet after 2 hours in the convection oven. Wet granulation is a robust process; while the particles formed may not have regular size and shape distributions, coagulation through mixing and compaction works for most formulations (and worked for all formulations presented here).

3.3.2 Additive Selection and Formulations

Each formulation contains one (or more) of 10 additives: α and γ -Al₂O₃, CeO₂, CaCO₃, Na₂CO₃, CaCl₂, MgCl₂, 13X and clinoptilolite zeolite powder, and a Magnesium aluminum (Mg-Al) silicate. Most materials tested here are not laboratory grade, and for good reason. Economic viability necessitates that the material properties of additives be robust and not dependent on super high purities. If a material loses characteristic traits easily to small contaminations, then it is undesirable for process scale-up.

Anhydrous K_2CO_3 was purchased through Oakwood Chemical, with grains less than 44 microns. Of all the materials purchased we considered the K_2CO_3 source most important in impacting the final quality of the particles formed. Large K_2CO_3 crystals had been attempted previously and were found to not mix well, forming visibly heterogeneous particles. Additionally, hydrous grains must be dried prior to use to accurately determine the mass % composition. α and γ - Al_2O_3 were selected for testing as they appear promising in the literature when used via impregnation method, but less information is available regarding their use in other K_2CO_3 particle formation methods. The α - Al_2O_3 tested is a “rock polish,” from Rock Shed Products, and range in grain sizes between 500 and 180 microns. The γ - Al_2O_3 tested is 99.9% purity with diameters around 20-nm purchased by SkySpring Nanomaterials. It was challenging to find lower grade γ - Al_2O_3 , as the α phase is more common for polishing as it is courser. Two CeO_2 sources were used. One, noted “high grade” in Table 3.1, was purchased from Gold Label Detailing and is white. The other, noted “low grade” was purchased from Gordon Glass and is red, indicating substantial impurities from other earth metals like iron oxide.

CaCO_3 and Na_2CO_3 were considered alongside Al_2O_3 and CeO_2 as potential inert supports/fillers. They are notably different in that they are, like K_2CO_3 , salts of carbonate. They are, however, significantly less deliquescent. The solubilities of K_2CO_3 , Na_2CO_3 and CaCO_3 are 111, 30.7 and ~ 0 g per 100g water at 25 °C, respectively.³⁰ It was hypothesized that CaCO_3 and Na_2CO_3 might provide strength through ionic bonding with the active material. CaCO_3 was purchased through Earthborn Elements and is food grade. Anhydrous Na_2CO_3 was reagent grade and purchased from Aldon. CaCl_2 and MgCl_2 were considered as potential desiccants as they are commonly used to absorb moisture in industrial and commercial settings, for example in road de-icing. CaCl_2 is generally considered more effective. Food grade CaCl_2 powder was purchased through Assencia, and food grade MgCl_2 was, like CaCO_3 , purchased through Earthborn Elements. 13X and clinoptilolite were also explored, recognizing their potential to act as both a desiccant and a secondary support material. The 13X is crushed ADCOA beads, less than 180 microns. Clinoptilolite was from Stellar Chemical Corp, less than 400 microns grain size. Lastly, Mg-Al Silicate, “Van Gel B” was purchased from Vanderbilt Minerals.

Table 3.1: Formulation details of all sorbents

Ref	Formulation (mass %)	Water Added (% dry mass)	Bulk Density (g/mL)
A1	30 K ₂ CO ₃ 70 α -Al ₂ O ₃ , rock polish	24.6	1.14
A2	40 K ₂ CO ₃ 60 α -Al ₂ O ₃ , rock polish	22.9	0.72
A3	45 K ₂ CO ₃ 55 α -Al ₂ O ₃ , rock polish	22.7	0.67
A4	50 K ₂ CO ₃ 50 α -Al ₂ O ₃ , rock polish	23.8	0.66
A5	55 K ₂ CO ₃ 45 α -Al ₂ O ₃ , rock polish	24.4	0.66
A6	60 K ₂ CO ₃ 40 α -Al ₂ O ₃ , rock polish	24.9	0.66
A7	65 K ₂ CO ₃ 35 α -Al ₂ O ₃ , rock polish	26.3	0.64
B1	50 K ₂ CO ₃ 50 γ -Al ₂ O ₃ , 20 nm lab grade	99.5	0.42
B2	50 K ₂ CO ₃ 50 CeO ₂ , high grade	19.2	0.92
B3	50 K ₂ CO ₃ 50 CeO ₂ , low grade	23.4	0.79
B4	50 K ₂ CO ₃ 25 Al ₂ O ₃ , rock polish 25 CeO ₂ , high grade	21.9	0.64
B5	50 K ₂ CO ₃ 50 CaCO ₃	20.9	0.90
B6	50 K ₂ CO ₃ 50 Na ₂ CO ₃	20.8	0.71
B7	60 K ₂ CO ₃ 40 CaCl ₂	34.3	0.62
B8	50 K ₂ CO ₃ 50 13X, size < 180 microns	25.8	0.75

Ref	Formulation	Water Added (% dry mass)	Bulk Density (g/mL)
C1	65 K ₂ CO ₃ ; 15 CaCl ₂ 20 Al ₂ O ₃ , rock polish	23.8	0.66
C2	50 K ₂ CO ₃ ; 15 MgCl ₂ 35 Al ₂ O ₃ , rock polish	20.6	0.75
C3	50 K ₂ CO ₃ ; 15 CaCO ₃ 35 Al ₂ O ₃ , rock polish	35.2	0.85
C4	50 K ₂ CO ₃ ; 15 CaCO ₃ 15 Clinoptilolite 20 Al ₂ O ₃ , rock polish	26.3	0.72
C5	50 K ₂ CO ₃ ; 15 CaCO ₃ 15 Mg-Al Silicate 20 Al ₂ O ₃ , rock polish	24.2	0.80
C6	50 K ₂ CO ₃ ; 15 CaCO ₃ 15 Zeolite 13X 20 Al ₂ O ₃ , rock polish	26.6	0.71
C7	70 K ₂ CO ₃ ; 20 CaCl ₂ 10 Al ₂ O ₃ , rock polish	21.4	0.67

Samples A1-A7 were generated with the intention of observing the impact of K₂CO₃% mass on total absorption capacity. As K₂CO₃ has poor pore formation, it was possible that capacity change would not be linear with K₂CO₃ mass added. Samples B1-B8 were manufactured to test the physical properties, capacity, and kinetics of binary mixtures with the additives of interest. Note that MgCl₂, Clinoptilolite, and Mg-Al silicate are not tested in the B series, however their properties will be compared to their analogues (CaCl₂ and 13X) in the C series. An attempt was made to have all the B series made with 50% K₂CO₃ to make comparing their respective capacities/kinetics simpler. B7 was made with 60% K₂CO₃ instead of 50% because a 50/50 mixture was hard to granulate. All the A and B series samples were run on the mini reactor. The B series was additionally humidity tested, and the granulation quality and relative durability noted. The C series forms trinary/quaternary mixtures of materials to test their synergy and was additionally cycled.

3.3.3 Testing Procedures

Three different stations were utilized to test the sorbent properties: a mini reactor (left panel of Figure 3.4), a humidification cell, and an auto-cycler (right panel of Figure 3.4). Before a sample was reacted, humidified or cycled it was first loaded into a 2cm diameter, 13cm long stainless-steel cylindrical cell. To prevent sample from falling out either side of the cell, a small ball of glass wool was placed on either end. In addition, to ease removal of sample from the cell after use, a thin Amazon Basics silicon baking mat was wrapped inside the wall of the cylinder. Approximately 20g of sample can then be loaded and was tapped repeatedly to minimize void fraction.

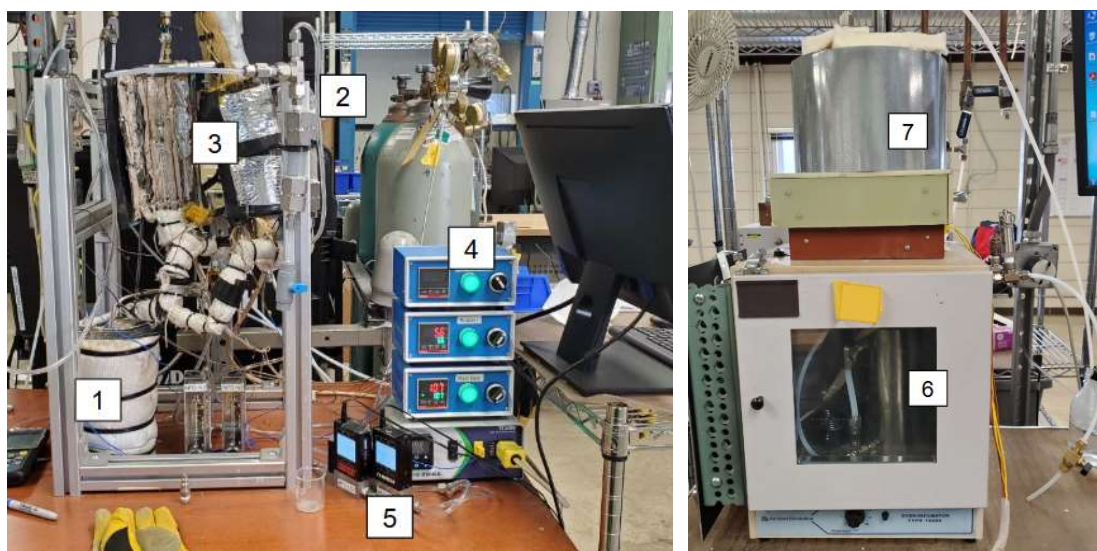


Figure 3.4 displays the mini reactor on the left panel and the auto cycler on the right. In the mini reactor the “flue” gas is injected by Omega mass flow controllers (5). The bubbler (1) is wrapped in fiberglass to help maintain temperature controlled via PID (4). The reactor (3) is also wrapped in fiberglass and controlled via PID (4). Unreacted water is removed via desiccant tube and drain valve (2). The auto cycler is also equipped with a bubbler (6) which is used during the absorption phase and bypassed during regeneration and cooling. The sorbent cell sits inside the “hat” (7) which controls the temperature.

The primary testing station utilized was the mini reactor (left panel of Figure 3.4), which consists of a bubbler, a cell mount (as well as gas connections), and a Hiden Analytical Quadrupole Mass Spectrometer (QMS) controlled by MASsoft 10. The bubbler, which is used in all three systems, is custom-made to hold over a liter of water which is temperature controlled via a Proportional–integral–derivative (PID) controller to 55°C.

During reaction, 150 ccm of 10% CO₂ in Argon (provided by Airgas) is injected into the bubbler via FMA-2606A Omega mass flow controller where the stream is humidified to 15% absolute humidity. This temperature/absolute humidity was selected to have excess water in the “flue” stream so that the reaction is CO₂-limited. The humidified “flue” stream exits the bubbler and enters the sample cell, which itself is heated to 65°C via PID controller. The temperature increase from the bubbler to the cell also helps prevent condensation of water vapor. The reacted gas enters a desiccant tube (non-CO₂-absorbing) and drain valve (closed during reaction) to remove any unreacted water before it enters the QMS.

The humidification cell is essentially the mini reactor without a QMS attached; a 15% absolute humidity stream at 150 ccm through a sorbent cell held at 65°C. Since no reaction needs to occur, a more economical pure N₂ stream is used instead of a CO₂ in Argon mixture. The purpose of the humidity cell is to expose the samples to a prolonged humid environment. While during absorption the mini reactor does expose the material to moisture, a significant portion of that moisture is converted to KHCO₃, and when the reaction is complete the experiment terminates. As each material reacts for different lengths depending on their capacity and kinetics this means that some finish reacting significantly faster than others. The humidity cell provides a more standard comparison for how the material responds to moisture over a 6-hour period. Ideally, the material maintains its shape and structure though wetted. When materials begin to clump or K₂CO₃ begins to visibly dissolve the sorbent is considered inadequate.

Lastly the auto cycler (shown in the right panel of Figure 3.4) is self-explanatory; it is set up to perform many absorptions and desorptions in succession automatically. It is also like a mini reactor without a QMS attached. However, in addition to the absorption phase which utilizes 10% CO₂ (pre-humidification), it is also set up to regenerate with a 150 ccm N₂ stream at 180°C. The system currently has no way of detecting when absorption is complete, so the phase is set to 2 hours. The regeneration phase is 3 hours, with a cooldown period which typically takes about 3 hours (the cycler detects when the sorbent cell reaches 65°C). The regeneration phase is long enough that it essentially also acts as a drying phase. The presented sorbents are technically clusters (not covalently bonded as they are not calcined) thus after enough exposure to water and force they will eventually dissolve and

crumble. It is not necessary to have material that is completely insoluble, just resistant enough that it maintains shape and structure during the absorption phase. On the industrial scale, a drying phase can and should be implemented between absorption cycles to prevent leaching.

The capacity and second order rate calculation are essentially the same as was performed for the packed bed reactor, described in Chapter 2, Section 3.6, except that the %CO₂ is measured via QMS instead of CO₂ analyzer. In short, the CO₂ captured is determined via line 11, and the rate constant is calculated via line 12. In line 11, $N_{inj,t}$ is the total moles of CO₂ injected during a time t , and $N_{exit,t}$ is the exiting moles during that same time. Thus, the difference is the moles captured during that time. The total moles captured are the summation over the capture period. Line 12 shows that to calculate the rate constant requires the CO₂ and H₂O concentrations before ($[CO_2]_0$ and $[H_2O]_0$) and after ($[CO_2]_f$ and $[H_2O]_f$) the sorbent cell as well as the resonance time (τ). As the rate constant can be calculated at any point in the reaction, the first stable point of highest efficiency was selected for each sample. More details on these derivations are available in Chapter 2, Section 3.6. To calculate %CO₂ the QMS utilizes an internal standard, the CO₂:Ar ratio. Sampling is performed approximately every 20-25 seconds.

$$11. \quad \text{CO}_2 \text{ captured} = \sum_0^f (N_{inj,t} - N_{exit,t})$$

$$12. \quad k = \ln \left(\frac{[CO_2]_0}{[H_2O]_0} \right) + \ln \left(\frac{[H_2O]_f}{[CO_2]_f} \right) ([H_2O]_0 - [CO_2]_0)^{-1} \tau^{-1}$$

Replicates were not performed on most samples, making standard error hard to define. Based on a reference formulation (not listed here) replicated 5 times, we determined that the standard deviation in the capacities is approximately 10%. The 5 replicates were all performed on dry sample, were uncycled material, at the same temperature and humidity exposure. The standard deviation of the calculated rate constant tends to be a bit larger, on the order of 15%. We consider sample deviation error, but it should be noted that it is quite possible that some variation across samples is real, considering the irregularities in the particle shapes and sizes.

3.4 Results and Discussion

The calculated capacities, % K_2CO_3 reacted, as well as calculated rate constants are presented for the A, B and C series of sorbents. Capacity is listed two ways, $\text{mg CO}_2 \text{ g}^{-1}$ sorbent, and $\text{mg CO}_2 \text{ mL}^{-1}$ sorbent. When generating scalable sorbents both values should be considered. The mass dependent value is better for comparing the chemical efficiency of each formulation. However, ultimately reactors are designed with a finite volume and more dense materials are typically preferable (assuming the chemical activities are the same across densities) because they can fit more mass in the reactor. If a material has a low density but high mass-dependent capacity this results in a lower density-dependent capacity. Given that manufacturing process, like %water, mix time and mixing speed, does impact material density, some formulations may be further improved through optimization.

Table 3.2: Capacities and rate constants of A1-A7

Ref	$\text{K}_2\text{CO}_3 : \alpha\text{-Al}_2\text{O}_3$	Cap (mg/g) ^a	Cap (mg/mL) ^a	% reacted ^b	k ($\text{m}^3 \text{ mol}^{-1} \text{ s}^{-1}$)
A1	30 : 70	84	96	88	0.121
A2	40 : 60	135	97	105	0.070
A3	45 : 55	146	98	102	0.054
A4	50 : 50	167	110	104	0.046
A5	55 : 45	171	113	97	0.040
A6	60 : 40	195	129	103	0.040
A7	65 : 35	209	134	101	0.030

^aCapacity is listed in mg CO_2 per g or mL sorbent (not K_2CO_3). mL sorbent is bulk density rather than individual particle density.

^bThe theoretical capacity of a pure K_2CO_3 sorbent is $319 \text{ mg CO}_2 \text{ g}^{-1} \text{ K}_2\text{CO}_3$.

In addition to the listed capacities, %reacted is also used a measure of K_2CO_3 availability. % reacted is the actual measured capacity divided by the mass-normalized theoretical capacity. For example, A1 has a mass normalized theoretical capacity of 95.7 mg g^{-1} sorbent (30% of $319 \text{ mg g K}_2\text{CO}_3$). It should be noted that some of our calculated %reacted are over 100%. We consider it unlikely that we observed significant physisorption or chemisorption from material other than K_2CO_3 (which would explain a real value over

100%). Instead, we recognize that our error is on the order of 10%, as described in section 3.3.3, and this likely means that about 100% of the K_2CO_3 present reacted.

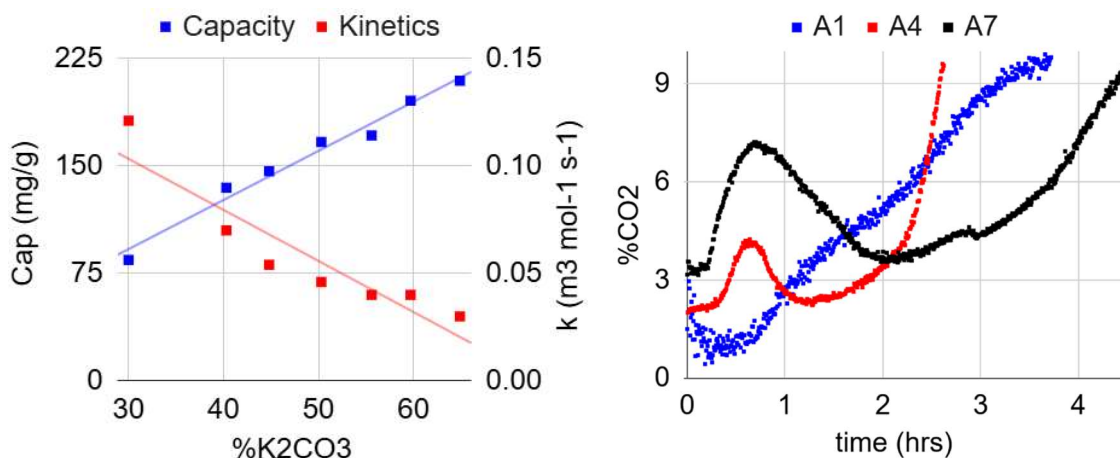


Figure 3.5 displays the capacity and kinetics for the A series on the left panel, and kinetic curves for A1, A4 and A7 on the right panel. Increases in K_2CO_3 shown on the x-axis of the left panel correspond to decreases in Al_2O_3 , as they are binary mixtures. While capacity increases (linearly) with K_2CO_3 , we simultaneously observe a clear decrease in rate of reactions. The kinetic curves (right panel) give some more insight into what may cause this kinetic decrease. As Al_2O_3 is removed, a hump grows in hinting again that the mechanism is more complex.

The calculated results for the A series are listed in Table 3.2, and the mass-dependent capacities and rate constants are plotted in left panel of Figure 3.5. The mass dependent capacities ($mg\ CO_2\ g^{-1}\ sorbent$) increase nearly linearly as K_2CO_3 is added. The largest amount of K_2CO_3 tested was a 70:30 mixture as anything higher could not granulate and became slurries. Al_2O_3 , even in low amounts, appears to provide sufficient surface area to make all the K_2CO_3 available for reaction, as indicated by the %reacted column of Table 3.2. In the K_2CO_3 range tested in the A series, the only sample that appears to have reactivity less than 100% is the lowest concentration sample, 30% K_2CO_3 . Our expected error as described in Section 3.3 is expected to be around 10%. Assuming an error of 10%, 88 +/- 9% reactivity is reasonably high to suspect this sample is still in trend with the other formulations.

As the amount of Al_2O_3 decreases, so does the calculated rate (Table 3.2, Figure 3.5, left panel). By plotting the kinetic curves (Figure 3.5, right panel), it becomes clear that there is not just a uniform decrease in reaction rate. Instead, as Al_2O_3 decreases a hump appears, and grows larger as Al_2O_3 is further decreased. This hints at a more complex mechanism with a rate limiting step. Eventually, whatever process is causing the hump subsides, and the curve returns to its original lowest point. For example, in A4 the CO_2 curve begins at approximately 80% capture (2% CO_2 exiting) before a hump grows in, decreasing the capture efficiency to around 60% (4% CO_2 exiting) at 30 minutes. By an hour into capture, the A4 curve returns to approximately 80% capture.

This temporary rate decrease resembles the work of Luo *et al.* on pure K_2CO_3 samples. They found through XRD analysis and SEM imaging that slow transformation of $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$ and $\text{K}_4\text{H}_2(\text{CO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ to KHCO_3 caused an increase in surface occlusion. Once the surface transformed to KHCO_3 , resistance appeared to decrease, allowing for further reactivity of K_2CO_3 . Al_2O_3 appears to increase porosity such that these intermediate products do not block reactivity of unreacted K_2CO_3 . Future works might also use SEM to image the surface of these samples after reaction to monitor occlusion and verify this hypothesis.

Table 3.3 lists the capacities and rate constants for the B series, which investigates mostly binary mixtures (excluding B4 which is ternary) of other additives. The metal oxides (B1-B4) unsurprisingly outperformed the other additives in terms of capacity and rate. However, activity differences were noted even across the metal oxide mixtures tested. The mass and density dependent capacities of these four samples are presented in Figure 3.7, alongside A4 which also had 50% K_2CO_3 and utilized $\alpha\text{-Al}_2\text{O}_3$. Figure 3.7 shows that for the wet granulation method, our $\alpha\text{-Al}_2\text{O}_3$ performs similarly to $\gamma\text{-Al}_2\text{O}_3$ and both CeO_2 grades when considering mass-dependent capacity. However, CeO_2 forms much denser material, making both the low and high grade CeO_2 sorbents more reactive per volume. The $\gamma\text{-Al}_2\text{O}_3$ formed the least dense material of all those tested, 0.42 gm/mL, resulting in a very low-density dependent capacity. We suspect that the density of the resultant sorbent is mostly due to the very fine grade of particles formed (20 nm), whereas all other additives were present in grain sizes on the order of 100+ microns.

Table 3.3: Capacities and rate constants of B1-B8

Ref	Formulation	Cap (mg/g)	Cap (mg/mL)	% reacted ^b	k (m ³ mol ⁻¹ s ⁻¹)
B1	50:50 γ -Al ₂ O ₃	150	63	94	0.057
B2	50:50 CeO ₂ , H grade	142	131	89	0.028
B3	50:50 CeO ₂ , L grade	158	125	99	0.06
B4	50:25:25 Al ₂ O ₃ , CeO ₂	164	105	103	0.084
B5	50:50 CaCO ₃	76	68	47	0.022
B6	50:50 Na ₂ CO ₃	89	63	56	0.034
B7	60:40 CaCl ₂	11	7	6	0.008
B8	50:50 13X	113	85	71	0.026



Figure 3.6 displays examples of unstable material after exposure to the humidification cell. The left shows what particle clumping looks like. The right shows dissolved/deteriorated sorbent. Both samples are from the A series and have an appearance typical of sorbents which do not contain dessicant.

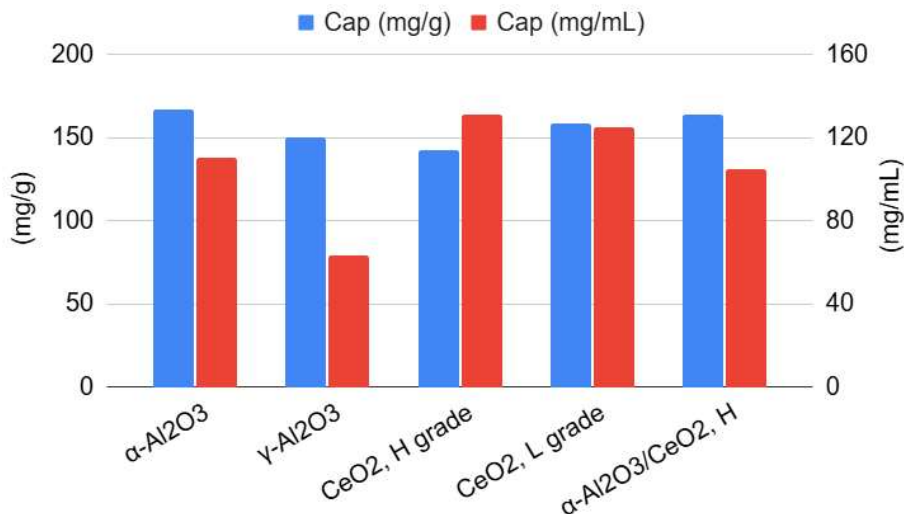


Figure 3.7 compares the mass dependent and volume dependent capacities of A4 (50/50 with α -Al₂O₃) to the other 50% K₂CO₃ metal oxide formulations, B1-B4. CeO₂ sorbents are very dense, resulting in high density-dependent capacities. Though γ -Al₂O₃ performs similarly in mass-dependent capacity to the other sorbents presented, it has a very low density, giving it a low density-dependent capacity. We hypothesize this is mostly due to the small grain size (20 nm).

The other additives tested in the B series, CaCl₂, CaCO₃, NaCO₃, and zeolite 13X, all displayed significantly lower mass-dependent and density-dependent capacities, as expected. More interesting is how these additives impacted other granule properties. The sample strength, shape, and response to humidity were observed. CaCl₂ did not granulate well, and clearly had a greatly adverse effect on capacity and kinetics (likely by inhibiting the formation of intermediate K₂CO₃-hydrates), but greatly increased the longevity when exposed to humidity, and even improved dry strength. CaCO₃ granulated well and provided the material compressive strength (when dry) and displayed moderate resistance to humidity. The ionic bonding networks formed between K₂CO₃ and CaCl₂ and CaCO₃ are likely responsible for their greater compressive strengths. The strength CaCO₃ provided is also intuitive as CaCO₃ is used in concrete for similar reasons. NaCO₃ observed similar capacity and kinetics to CaCO₃ and was decently strong (when dry). But, likely due to its much higher solubility, NaCO₃ granulated poorly and was not resistant to humidity. 13X granulated well, but did not have much compressive strength compared to formulations with CaCl₂ and CaCO₃. That said, 13X was able to lend substantial resistance to humidity without the huge capacity drop seen when CaCl₂ is used.

In summary, from series A we concluded that large quantities of K_2CO_3 (30% by mass is common in the literature) could be loaded to the sorbent, if sufficient porous support was present. While the A series did not survive a single absorption cycle or humidity test (see Figure 3.6), it did confirm that mass-dependent capacity does in fact increase linearly within our target $\text{K}_2\text{CO}_3\%$ range. We also note a substantial kinetic block (the hump in Figure 3.5) grows in at masses above 50%. From the B series we concluded that CaCO_3 benefits the dry strength of the material but could not act as the bulk support due to significant reduction in capacity. CaCl_2 and 13X provide humidity resistance which prevents K_2CO_3 from dissolving under the time scales we consider relevant for reaction in a tower. However, CaCl_2 appears to be so desiccating that in large amounts it outcompetes K_2CO_3 at bonding with water and deactivates the sorbent. It is possible that chemical desiccation as is observed with CaCl_2 , and physical desiccation, as is 13X, have very different effects on K_2CO_3 activity. This should be investigated in future works.

We utilized these findings to propose potentially synergistic combinations of additives, which resulted in the C series. In series C, we also investigated the desiccating properties of MgCl_2 (C2), a CaCl_2 analogue, and Clinoptilolite and a Mg-Al silicate (C4 and C5), 13X analogues. As all the C series survived initial absorption and humidity testing, they were resultantly cycled. As MgCl_2 is known to not be as strong of a desiccant as CaCl_2 , it was hypothesized that it might not have as strong of a deactivating effect on the sorbent. Simultaneously, we suspected it may not be able to provide as much humidity resistance, thus C1 and C2 were formulated to compare the effectiveness of CaCl_2 versus MgCl_2 . C2 was prepared with 15% less K_2CO_3 in anticipation of these trends, then both were cycled. As is shown in Figure 3.8, C1 and C2 were each cycled 22 times. While C1 observed some loss of material strength during cycling, C2 suffered much more decomposition, indicated by a large portion of the surviving mass being dust (right panel, Figure 3.8). At the time this observation was made, there was not a procedure in place for quantitatively comparing survivability of the material. Future works might measure and compare the sample mass remaining in the original sieved size regime (2.36-4.75 mm) to the dust fraction. Similarly, future works might determine the mass lost by measuring the sorbent mass before and after cycling, as dissolved/leached K_2CO_3 was observed to occasionally coat the glass wool.

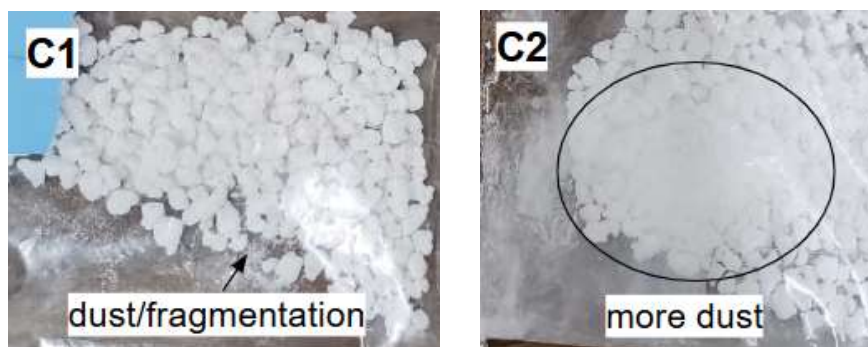


Figure 3.8 displays samples C1 and C2 after 22 cycles in the auto cycler. Despite being prepared with 15% less K_2CO_3 , the $MgCl_2$ sorbent was much weaker, with much of the material crumbling into dust. It was concluded that for a $MgCl_2$ based sorbent to be as durable as those formed with $CaCl_2$ would require even more of the mass fraction to belong to $MgCl_2$ perhaps taking place of the porous support (Al_2O_3 here).

Table 3.4: Capacities and rate constants of C1-C7

Ref	Formulation	Cap (mg/g)	Cap (mg/mL)	% reacted ^b	k ($m^3 mol^{-1} s^{-1}$)
C1	65 K_2CO_3 ; 15 $CaCl_2$ 20 Al_2O_3	118	78	57	0.024
C2	50 K_2CO_3 ; 15 $MgCl_2$ 35 Al_2O_3	76	57	48	0.048
C3	50 K_2CO_3 ; 15 $CaCO_3$ 35 Al_2O_3	139	118	88	0.031
C4	50 K_2CO_3 ; 15 $CaCO_3$ 15 Clinpt.; 20 Al_2O_3	90	65	57	0.053
C5	50 K_2CO_3 ; 15 $CaCO_3$ 15 Mg-Al Silicate 20 Al_2O_3	118	78	57	0.024
C6	50 K_2CO_3 ; 15 $CaCO_3$ 15 13X; 20 Al_2O_3	100	71	63	0.067
C7	70 K_2CO_3 ; 20 $CaCl_2$ 10 Al_2O_3	93 133 ^a	62 89 ^a	41 59 ^a	0.034 0.074 ^a

^aIn addition to first cycle absorption, C7 was also measured after 24 cycles

Similarly, C3-C6 were formulated to test the desiccating ability of 13X and its analogues. Again, one way in which these samples differ from those with CaCl_2 and MgCl_2 is these additives manage moisture through physisorption, instead of forming salt-hydrates. Since B8 (50/50 with 13X) was found to have less than desirable dry strength, CaCO_3 was also added. C3-C6 samples are presented after 33 cycles on the auto cycler (Figure 3.9). C3 contains just CaCO_3 (15%) and Al_2O_3 (30%) as additives, C4, C5 and C6 has 15% Clinoptilolite, Mg-Al silicate or 13X added, respectively (Al_2O_3 is 20 instead of 35%). It is clear from visual inspection that C6 significantly outperformed the other materials when cycled. Surprisingly, C4 and C5 seemed to perform equally as poor as C3, which did not have any desiccant. By the dusty look of the material (apposed to materials which clump) and their poorer ability to granulate, it may be that the K_2CO_3 does not bind as strongly to these as 13X. It may also be as simple as 13X was more effective at controlling moisture. Unfortunately, without other characterization techniques it is challenging to assess why the 13X analogues did so poorly.



Figure 3.9 displays samples C3-C6 after 33 cycles on the auto cycler. C6, which contains 13X exited the cycler with minimal decomposition, clumping, or dust formation.

Lastly, C1 was taken a step further to form C7, which contained what we believe is the absolute maximum amount of K_2CO_3 that can be stabilized this way, 70%. Before testing, it was unclear whether the benefits (theoretical capacity) of having such a high amount of K_2CO_3 outweighed the large amount of CaCl_2 (deactivating) that would be needed to stabilize the material. When the material was removed from 24 cycles, it very much resembled C1 after 22 cycles. Despite having 5% more active material than C1, the increase in CaCl_2 resulted in a 15% drop in %reacted, thus the overall capacity was still less C1 (see Table 3.4). This insight may be important for future development; maximizing the amount of K_2CO_3 loaded alone may not be the best strategy for creating a sorbent with maximal capacity.

After cycling, C7 was reintroduced to the mini reactor for what would be its 25th cycle. The results were quite eye opening- the capacity and kinetics of the material both improved significantly (see Table 3.4). At first, this may not be intuitive, however it has been observed Beving *et al.* that repeated hydration cycling of raw K_2CO_3 resulted in microcracking, which stimulates surface area increase, and in the case of raw K_2CO_3 even particle expansion (loss of density).³¹ These microcracks improved the reactivity such that the material no longer observed the “hump” (see Figure 3.10) characteristic of what we believe is surface occlusion by $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$ and $\text{K}_4\text{H}_2(\text{CO}_3)_3 \cdot 1.5\text{H}_2\text{O}$.¹⁴

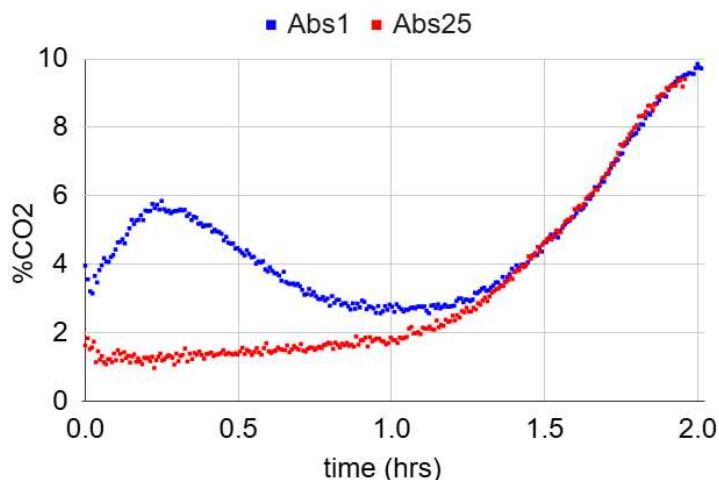


Figure 3.10 displays the kinetic profile for C7 during its first absorption cycle against its 25th absorption cycle. The characteristic “hump” observed across most of the samples appears to have disappeared. We attribute this to microcracking.³¹

To further test how the $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$ and $\text{K}_4\text{H}_2(\text{CO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ intermediate products and bound water in general impact the reaction rate, some samples underwent mini reactor testing after hydration. Two B4 samples were exposed to 150 ccm of humidified N_2 for 35 minutes, and 90 minutes respectively (Figure 3.11). Unfortunately, the mass of water absorbed by the samples were not noted and should be monitored in future works.

It appears that a minimal amount of hydration achieved by the 35-minute exposure decreased the “hump” substantially, improving the overall capture rate while minimally impacting the capacity (164 and 158 $\text{mg CO}_2 \text{ g}^{-1}$ sorbent, dry and 35-min exposure respectively). However, 90-minute exposure appears to exceed this beneficial hydration period, in fact lowering both the kinetics and capacity significantly (122 $\text{mg CO}_2 \text{ g}^{-1}$ sorbent). The decrease in capacity due to excess hydration was also observed for the impregnated zeolite samples used in the packed bed reactor in Chapter 2. It is very likely that this is a property inherent of K_2CO_3 itself and not just the supporting material; as K_2CO_3 becomes excessively wet not only does it become unstable, the K_2CO_3 shifts from a primarily “dry” chemistry regime (lines 5-10) to a wet one (lines 1-4).

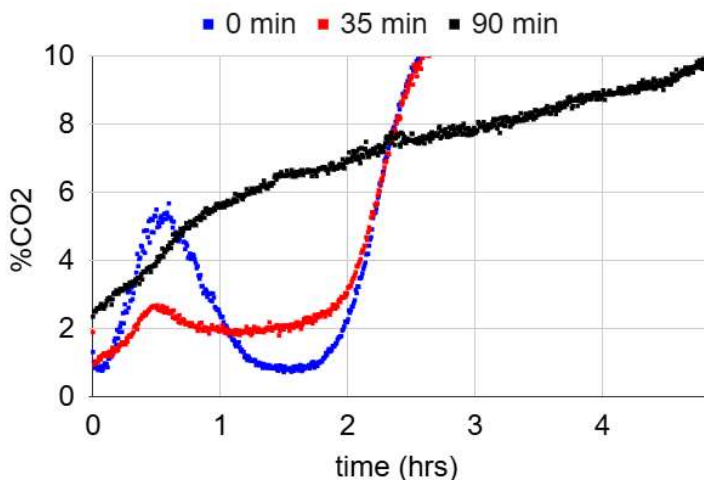


Figure 3.11 displays B4 mini reactor curves when reacted dry (0 min), lightly wetted (35 min) and heavily wetted (90 min). When dry, the material appears to experience occlusion around 30 minutes. After a 30-min hydration this occlusion period is greatly minimized, though the overall highest efficiency period (around 1.5 hours) is a bit lower than when the material was dry. In comparison to both of these, the 90-min hydrated sample was very slow, taking almost twice as long to reach breakthrough.

3.5 Conclusions

Three series of K_2CO_3 -based wet granulated sorbents for carbon capture (A, B and C series) were manufactured and tested in a bench scale mini reactor. Positive activity in terms of capacity and kinetics were found for samples that contained Al_2O_3 or CeO_2 , but they were not stable when exposed to humid flue gas on their own. CaCO_3 appears to increase dry strength though this should be further quantified, perhaps with a durometer. Desiccants like CaCl_2 and zeolite 13X help control in-particle moisture, resulting in sorbents which can maintain their structures of 20+ cycles when regenerated/dried with N_2 . At larger mass loadings (50%+) of K_2CO_3 desirable to carbon capture, kinetic hindrances might occur due to the low porosity of K_2CO_3 .

In this work we have observed that low amounts of pre-reaction hydration might give $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$ and $\text{K}_4\text{H}_2(\text{CO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ formation a head start to prevent significant surface build up and occlusion by these intermediate products. However, this may only benefit kinetics within a certain hydration range, which once breached appears to harm CO_2 diffusion, decreasing reaction rate. Lastly, K_2CO_3 -based granulate sorbents appear to have the potential to improve in both capacity and kinetics when cycled due to microcracking.

3.6 Future Works

Further characterization of the particles in general might benefit this work by verifying observations, for example expectations of microcracking over cycling. Preferred methods for observing surface area and microstructure changes are BET and SEM respectively. Future works might also characterize other sorbent changes when cycled, for example compressive strength, mass loss or changes in particle density. Changes in particle density seem particularly important, as engineers might have to consider particle expansion over continued operation. Current literature on K_2CO_3 -based sorbents focus heavily on reactivity and appear to neglect characterization of particle stability from a mechanical perspective. Any improvements in characterizing and quantifying sorbent mechanical stability would benefit this field.

Something that was only briefly touched up here is how grain size/source of additives used impact final sorbent quality. Future works might consider analyzing the properties of their additives more closely, like their grain size or contaminant sources (perhaps through ICP-MS). Based on the density of sorbent produced by 20-nm Al_2O_3 (B1), grain size of additives at the very least may impact final sorbent density and may perhaps even impact reactivity or stability.

Lastly, while these sorbents appear promising in their ability to be dry cycled (N_2 -purged regeneration), their ability to survive steam regeneration, like the impregnated sorbents in Chapter 2, has not yet been verified. Should these materials struggle to maintain their structure when undergoing steam-regeneration, it may be beneficial to explore calcination of these materials to form covalent bonding networks between neighboring support grains.

3.7 Citations

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Chapter 4

BENTONITE-K₂CO₃-BASED SORBENTS MADE BY EXTRUSION-SPHERONIZATION

4.1 Abstract

In the following chapter, K₂CO₃-based particle sorbents were prepared by extruding and spheronizing mixtures of bentonite clay and KHCO₃. KHCO₃ was utilized to improve quality of sorbent extrusion-spheronization and was converted to the reactive ingredient K₂CO₃ via activation at 180°C. Bentonite, which was employed as a binder and support, was found to have appropriate plasticity to compress through our screw driven extruder. We also found improved humidity resistance for samples calcined above 500°C, likely due to phase change not unlike pottery “firing.” While more data is needed, it appears the calcined bentonite physisorbs CO₂ and is not regenerable at 180°C. By cycling two of our prepared sorbents (B4 and B5 with 50% bentonite and 25/25% bentonite and Al₂O₃, respectively) it appears that supporting active material with Al₂O₃/bentonite mixtures would compromise material stability and capacity. Our overall best performing material, B5, had a capture capacity of 142 and 165 mg g⁻¹ sorbent before and after 40 cycles, respectively. In addition, SEM imaging was utilized to understand the physical processes that result in material degradation over cycles. A K₂CO₃ “leach and recrystallization” model is discussed as a primary source of material deterioration. The Hunt lab will continue to investigate bentonite-KHCO₃-based sorbents due to their favorable properties and demonstrated scalability.

4.2 Introduction

4.2.1 Extrusion-Spheronization Method

As has already been thoroughly illustrated in Chapters 2 and 3, K₂CO₃-based sorbent development is of great interest to the field of carbon capture. Chapters 2 and 3 respectively demonstrate the feasibility of K₂CO₃ sorbent formation through impregnation and wet granulation methods. While impregnation may be easy to scale-up (assuming an appropriate support is acquired), the amount of active material that can be loaded is often limited. Wet activated granulation is also simple to scale and has the added benefit that it

is easier to load larger amounts of active material. However, spherical particles of uniform size are rarely attainable through typical granulation methods. Instead, the resultant dried heterogeneous granules must be size selected via sieving.^{1,2} In the process of sieving, large amounts of the product can be lost, making this procedure somewhat inefficient. Instead of drying and sieving the wetted mass after mixing, some materials are capable of being uniformly sized and shaped through a process called extrusion-spheronization (ES), displayed in Figure 4.1. ES has been utilized for over 50 years to make uniform pellets, particularly in drug manufacturing. The first two steps are the same as wet granulation; dry and then wet mixing.³ However, once the materials are wetted and mixed, instead of drying them, they are extruded into uniform diameter cylinders/rods. There are several types of commercial extruders, including screw, sieve and basket, roll, and ram extruders, but they essentially all work the same; pressure is applied to the wetted mass until flows through an orifice called the “die.”⁴ Once extruded, the rods are introduced to a grooved friction plate which rotates, inducing further deformation. The frictional forces cause the rods to break and very quickly the now small broken rods spheronize. It should be acknowledged that not all formulations are capable of ES processing; they must be “plasticky” in nature, i.e. be moldable.

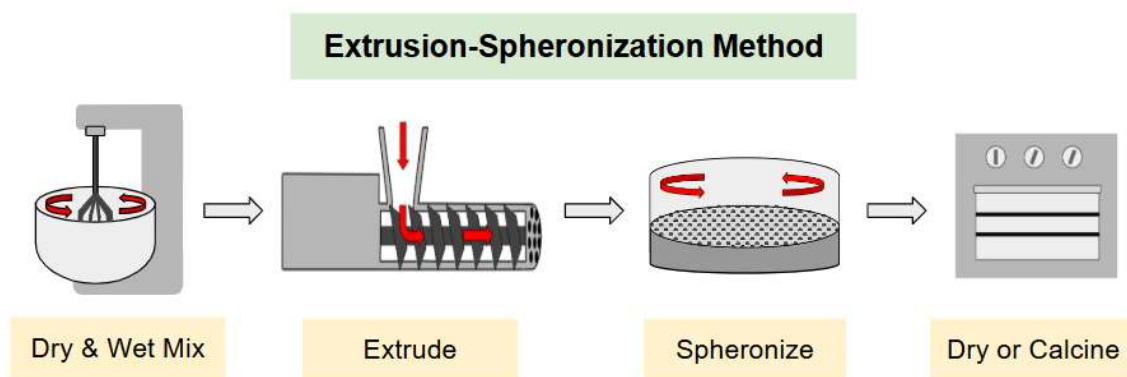


Figure 4.1 displays the 4-step process involved in ES particle manufacturing process. The first step (or two steps, as dry mixing is typically performed before solvent is added) is the same as wet granulation. However, instead of being dried and sieved to generate a homogeneously sized product, the irregularly sized granulated is then loaded into an extruder. The one show here utilizes a giant screw, which when spun compacts the mix and pushes the mix through the die. The extrudate is then loaded into the spheronizer, where the rods brake and deform into spheres, which can then be dried or even calcined.

If a wetted mass is too firm, sandy, or soggy for example it will not be capable of ES processing. The spherionized material can then be dried, or even calcined. Some important variables that can impact the quality of the resultant particles include extrusion pressure and speed, the surface geometry of the friction plate, the plate size and rotation speed, and the die size to name a few.⁴ The die hole size, for example, is a key parameter in determining the particle diameter. However, if the material is sufficiently wet and it is spherionized for too long, these particles can grow larger than the original die size, and even become irregular once more through essentially a second wet granulation period. In general, particles formed from ES are denser than those formed via wet granulation as they essentially undergo a second compaction when extruded.

4.2.2 Previous Works

To date, only a few published works are available which utilize extrusion or ES methods to make K_2CO_3 -based rod pellets or spherical particles, see Table 4.1.⁵⁻⁷ (It should be noted that pellets can be formed if the material is extruded and cut instead of spherionized). As noted by Wang *et al.* in their 2019 study on Urea-templated K_2CO_3 pellets, most sorbents, regardless of formation method, currently suffer from material fragmentation and attrition. Fast material degradation in an industrial/commercial setting would require frequent sorbent replacement which increases capture costs, hindering chances of scale-up.⁶ However, it is challenging to find supporting additives that prevent material degradation that simultaneously lend themselves to ES method, and help maintain the porous structure needed for capture. In their work on Urea-templated K_2CO_3 pellets, Wang *et al.* summarize the challenge, “Support materials play significant roles in improving CO_2 sorption performance of potassium-based sorbents, as they promote the dispersion of active component for enhanced K_2CO_3 utilization and provide active sites and porosity for efficient CO_2 sorption... material that possesses a double functionality as both support and binder would be the preferred choice in the preparation of pellets.”⁶ In general, while compaction of the ES method improves particle stability in other systems, like CaO-sorbents, it simultaneously can jeopardize porosity.^{6,8} To counter the effects of compaction, some have used pore-forming templates such as sacrificial organics. When heated, these additives are meant to burn and decompose, leaving behind pockets to increase surface area.^{6,8,9}

Table 4.1: Summary of extruded K₂CO₃-sorbents from literature

Sorbent	Preparation	Abs	Regen	Capacity ^a (mg CO ₂ g ⁻¹ sorbent) ^{bc}	Ref
35 K ₂ CO ₃ 50 Al ₂ O ₃	syringe-squeezed, dried @300°C for 2 hrs	100 ml min ⁻¹ 15% CO ₂ , 10% H ₂ O, 75% N ₂	N ₂ 180°C, 25 min	A1- 70 A10- 70	[5]
35 K ₂ CO ₃ 65 Calcium Aluminate Cement				A1- 20 A10- 20	
35 K ₂ CO ₃ 65 Kaolin Clay				A1- 40 A10- 60	
35 K ₂ CO ₃ 65 Fly Ash				A1- 25 A10- 25	
35 K ₂ CO ₃ 65 Portland Cement				A1- 15 A10- 15	
50 K ₂ CO ₃ 50 Al ₂ O ₃	mini-extruder, 1000 rpm 3 mins spherionized, 300°C for 6 hrs	500 mL min ⁻¹ 10% CO ₂ 10% H ₂ O 60°C	-	A1- 100	[6]
50 K ₂ CO ₃ 35 Al ₂ O ₃ , 15 Urea				A1- 140	
50 K ₂ CO ₃ 45 Al ₂ O ₃ , 5 Urea				A1- 115	
70 K ₂ CO ₃ 15 Al ₂ O ₃ , 15 Urea				A1- 105	
14 K ₂ CO ₃ ^a 86 carbon nanotubes (CNT)	plunger extruder with 1.5mm die 80 °C 2 hrs 120 °C 6 hrs 500 °C	2.3 L min ⁻¹ wet air, 380–420 ppm CO ₂ 5 mbar H ₂ O 30 °C, 6 hrs	Argon 100 mL min ⁻¹ 150 °C 1 hr	A1- 30 A10- 25	[7]
28 K ₂ CO ₃ ^a 72 CNT				A1- 48 A10- 48	
42 K ₂ CO ₃ ^a 58 CNT				A1- 58 A10- 68	
56 K ₂ CO ₃ ^a 44 CNT				A1- 55 A10- 78	

^aThe listed %K₂CO₃ are estimated as the formulation is made from potassium acetate slurry. ^bIf the material was tested after cycling N times, the final absorption “AN” is also listed ^cThe noted capacity results are estimated from plotted figures.

In Table 4.1 previous K_2CO_3 -based sorbents made through extrusion or ES method are compared.⁵⁻⁷ It should be noted that the formulations presented in Table 4.1 are not the only ones tested in each work, simply those we wish to highlight. Qin *et al.* made syringe-extruded pellets using 4 different binders that also act as support materials; calcium aluminate cement, so-called “Portland” cement (made mostly of calcium silicates), fly ash (a powder residue from coal), and kaolinite clay.

For a mass loading of 35% K_2CO_3 , of the four binders tested kaolinite clay had the largest compressive strength (~ 25 MPa), observed negligible mass loss over 12 cycles, and also observed the highest capacity which even increased over time likely due to increase in number of pores, as the pore symmetry remained the same.⁵ Al_2O_3 -based samples were also prepared for comparison, and while were noted to unsurprisingly have higher capacities (~ 70 mg g^{-1} sorbent for 35% loading) observed attritional losses of nearly 40% of 12 cycles. Wang *et al.* created ES particles via mini extruder made of Al_2O_3 and a urea sacrificial template to increase pore sizes. While their total capacities were much higher, potentially due to larger loading of K_2CO_3 (35 vs 50%), it should also be noted that mini extruders generate particles on the order of 100s of nm, not the mm needed for industrial use. They did see significant increase in porosity with the addition of Urea, which resulted in a large increase in capacity.

Derevschikov *et al.* prepared composite pellets from carboxylated carbon nanotubes (CNT) and potassium acetate paste. Potassium acetate is likely used instead of the active form, K_2CO_3 , in the interest of having a “self-sacrificing” active material. Like urea, which was used by Wang *et al.* to carve out pockets to increase surface area, potassium acetate also decomposes when heated to $500^\circ C$, forming K_2CO_3 and gaseous by-products which might form pores. These samples were also not spherionized, but were extruded through a larger (more industrially relevant size) die resulting in 1.5 mm diameter pellet rods. The addition of CNT did significantly reduce the material susceptibility to thermal oxidative corrosion compared to Al_2O_3 , one of the leading high capacity supports. Unfortunately, despite some of the Derevschikov samples having similar active material mass loadings to those produced by Wang *et al.*, these samples had significantly lower capacities. In this way, it appears they traded thermal stability for some of their capacity.

4.3 Methods

4.3.1 Additive Selection and Formulations

In the following work the capacity, thermal stability, and humidity resistance of ES sorbents primarily supported/bound by bentonite clay were explored. In addition to utilizing bentonite as the material support and binder, the effect of using KHCO_3 as a source of K_2CO_3 was also explored. KHCO_3 was considered for use in ES production as an alternative to K_2CO_3 because it has a much lower solubility, around 20 g g^{-1} water versus 110 g g^{-1} water at 20°C .^{10,11} Early test mixtures using bentonite and K_2CO_3 were determined to be too wet to extrude or spheronize, even at low added water volumes. When wetted, K_2CO_3 tends to attain a syrupy texture while KHCO_3 is sandier due to incomplete dissolution.

Previous work on unsupported K_2CO_3 calcined from KHCO_3 indicates that decomposition of KHCO_3 appears to increase material porosity and capacity.¹² While 0.02 mm (unsupported) grains of K_2CO_3 without pretreatment only observed 29% of the theoretical predicted capture, grains of the same size calcined from KHCO_3 observed a conversion of 93%.¹² Thus in addition to the preferable extrusion capability KHCO_3 provides, we anticipated that particles formed from KHCO_3 might also have increased surface area and thus capacity.

As presented in the works of Qin *et al.*, kaolinite clay provided thermal and cycling stability in their syringe-extruded pellets.⁵ We found that kaolinite may be too slick to lend itself to extrusion in a screw-driven industrial extruder utilized here. This galvanized our interest in exploring other types of clay, specifically bentonite. Generally speaking, all clays including both kaolinite and bentonite are “2D” sheets that layer to create their “3D” structure.¹³ The sheets are constructed of silica, alumina and oxygen bonded networks in tetrahedral or octahedral coordination. Aluminosilicates, like clays, are charge deficient, and the more Si that is replaced by Al, the more charge deficient the material is. To balance the material charge, cations and water are trapped between the layers.¹⁴ Thus clay layers are held together by electrostatic forces and ionic bonds between interlayer cations. These flexible and hydrophilic sliding layers give clay its plastic-like behavior; when clays are wetted and untreated they are highly moldable, making them great binders.¹³

Table 4.2: A and B series sorbent compositions and preparation conditions

Ref	Estimated Composition (%)	Composition Before Activation (%) ^{a,b}	Preparation
A1	50 K ₂ CO ₃ , 50 Bent.	50.0 K ₂ CO ₃ , 50.0 Bent. + 14.2 H ₂ O	Extr. 45 Hz 2mm die, Sph. 15 Hz 30 sec, 180°C 24 hrs
A2	50 K ₂ CO ₃ , 50 Bent.	35.5 K ₂ CO ₃ , 17.2 KHCO ₃ 47.3 Bent. + 11.1 H ₂ O	
A3	50 K ₂ CO ₃ , 50 Bent.	10.7 K ₂ CO ₃ , 46.7 KHCO ₃ 42.8 Bent. + 9.6 H ₂ O	
A4	50 K ₂ CO ₃ , 50 Bent.	59.9 KHCO ₃ , 40.1 Bent. + 11.7 H ₂ O	
A5	85 K ₂ CO ₃ , 15 Bent.	15.0 K ₂ CO ₃ , 74.4 KHCO ₃ 10.6 Bent., + 7.5 H ₂ O	Extr. 35 Hz 2mm die (not Sph. baked, or further tested)
A6	75 K ₂ CO ₃ , 25 Bent.	15.0 K ₂ CO ₃ , 65.0 KHCO ₃ 20.0 Bent., + 7.5 H ₂ O	
A7	60 K ₂ CO ₃ , 40 Bent.	12.5 K ₂ CO ₃ , 54.2 KHCO ₃ 33.3 Bent., + 7.5 H ₂ O	
B1	50 K ₂ CO ₃ , 45 Bent. 5 CaCl ₂	10.7 K ₂ CO ₃ , 46.5 KHCO ₃ 38.5 Bent., 4.3 CaCl ₂ + 15.4 H ₂ O	Extr. 35 Hz 2mm die, Sph. 15 Hz 15 sec, 180°C 24 hrs
B2	50 K ₂ CO ₃ , 25 Bent. 15 Al ₂ O ₃ , 10 CaCl ₂	10.7 K ₂ CO ₃ , 46.5 KHCO ₃ 21.4 Bent., 12.8 Al ₂ O ₃ 8.6 CaCl ₂ , + 13.4 H ₂ O	Extr. 45 Hz 2mm die, Sph. 15 Hz 30 sec, 180°C 24 hrs
B3	same as B2	same as B2	same as B1 + 600°C 2 hrs
B4	same as A3	same as A3	same as A3 + 600°C 2 hrs
B5	50 K ₂ CO ₃ , 25 Bent. 25 Al ₂ O ₃	10.7 K ₂ CO ₃ , 46.5 KHCO ₃ 21.4 Bent., 21.4 Al ₂ O ₃ + 8.0 H ₂ O	Extr. 45 Hz 2mm die, Sph. 15 Hz 15 sec, 180°C 24 hrs, 600°C 2 hrs

^aThe material masses before activation of KHCO₃ @180 °C were selected assuming 100% of the KHCO₃ converts to K₂CO₃ resulting in the estimated (final) composition.

^bWater added is listed as a percentage of the dry mass total. For example, A1 had a total dry mass of 584 g and we added 90 g of water thus the H₂O% was 15.5

The primary difference between kaolinite and bentonite is that they have 1:1 and 2:1 layer structure respectively, meaning that for every octahedral sheet there is one or two tetrahedral sheets.¹⁵ This structural difference has implications for their physical properties other than texture including, water swelling potential, pH, mineral content, pore size, temperature at which dehydration, dihydroxylation and recrystallization occurs.¹⁵ We found bentonite, which in comparison to kaolinite has greater potential to accept and release water, to have better plasticity for extrusion.¹³ Thus, the impacts on %bentonite and %KHCO₃ on extrusion quality were examined via a set of preliminary formulations noted series A, whose compositions and preparation details are presented in Table 4.2. While series A extruded well, they were found to have weak resistance to humidity.

The B series of sorbents also presented in Table 4.2 were thus produced, with the hopes of creating an ES-friendly composition that was also resistant to humidity. Note that in Table 4.2 there are two columns expressing material composition of the presented sorbents. The first column “estimated composition” represents the target composition after activation of the KHCO₃ at 180°C. In the decomposition of KHCO₃, half as much K₂CO₃ is produced due to the net reaction, line 1. Additionally, the molar mass of K₂CO₃ and KHCO₃ are 138.2 and 100.1 g mol⁻¹ approximately. Thus, if KHCO₃ is intended to be utilized instead of K₂CO₃, you must use approximately 1.45 times the mass of K₂CO₃ that would have been used. Thus, the dry mass compositions, labeled “compositions before activation” appear deflated compared to their activated counterparts. This conversion also assumes that 100% of the KHCO₃ will convert to K₂CO₃, but this has not yet been verified.



K₂CO₃ and KHCO₃ were both purchased from Oakwood Chemical. K₂CO₃ was purchased anhydrous with a grain size smaller than 0.044 mm (325 mesh). Bentonite clay was purchased from Bulk Apothecary. Again, bentonite is a naturally occurring sedimentary rock which can contain many impurities including quartz, feldspar, carbonates, and even pieces of zeolites.^{16,17} Bentonites also vary in the types of minerals they contain, for example sodium, calcium and a sodium-calcium mixture are quite common.¹⁸ It should be noted that the bentonite clay utilized in this set of studies was not chemically characterized. The Al₂O₃ tested is a “rock polish,” from Rock Shed Products, and range in grain sizes

between 500 and 180 microns. A few samples contained CaCl_2 as a desiccant stabilizer (refer to Chapter 3), which was purchased through Assencia and is “food grade”.

Once the dry masses were assembled for a sorbent, they were dry mixed for 1 minute in a KitchenAid bowl lift stand planetary mixer with a flat beater. Then deionized water was slowly added over 5 minutes while mixing. For most sorbents water equivalent to about 10% of the total dry mass was added. The mixture was considered sufficiently saturated when shear force can be applied via hand and the sorbent no longer crumbles, but instead stays in two solid pieces. The wetted mixture is then loaded into our screw-typed extruder (see Figure 4.1). The extrusion frequency required to appropriately compact the sorbent and create sufficiently “full” extrudate (meaning that the diameter of the exiting rod is the same size as the die used) was determined via trial and error. Sorbent rods exiting the extruder die is displayed in Figure 4.2 on the left panel.



Figure 4.2 displays extrudate exiting the die on the left panel, and sorbent pellets in the middle of spheronization on the right. The extrudate depicted in the left panel is sample A7, which used around a 33% (not yet activated) dry mass of bentonite with a 7.5% dry mass of water added. These “noodles” represent the border of what rods might look like and still be spheronizable. To create fuller noodles more water might be added, or a higher extrusion rate utilized.

The extrudate rods were collected and loaded into the spheronizer, where all samples were spun on the friction plate at 15 Hz (see Figure 4.2, right panel). The length of time necessary to break apart the rods into short cylinders and fully spheronize the sorbent was again determined via trial and error. If the material is spun for too long or too fast the

pieces coagulate into granules that can be much larger than the original die diameter, and even become greatly irregular in shape. After spheronization, samples were baked at 180°C to induce transformation of KHCO_3 to K_2CO_3 and remove excess water. Some samples underwent a second heat treatment, a calcination step at 600°C for 2 hours.

4.3.2 Testing and Calculations

To test the absorption capacity of the samples, a replicate reactor of those used by Mitico was assembled in the Hunt laboratory. In short, the reactor consists of a reactor chamber/cell mounted on a bubbler, which connects to a Hiden Analytical Quadrupole Mass Spectrometer (QMS) controlled by MASsoft 10. The bubbler maintains a temperature of 55°C by utilizing a heating tape controlled via Proportional–integral–derivative (PID) and hydrates the “flue gas” to approximately 15% absolute humidity. Before absorption is initiated, the sample is massed and loaded into the reactor cell which is a 5-inch long 2 cm diameter stainless steel cylinder with a small glass wool ball on either end to protect sample from exiting. The sample cell is heated by another heating tape maintaining 65°C via PID. A baseline (0% CO_2) is produced by flowing dry N_2 (purchased from Airgas) into the cell. When the absorption begins, the N_2 is shut off, and a “flue gas” mixture of 10% CO_2 in Argon (purchased from Airgas) is injected into the bubbler at 150 ccm via FMA-2606A Omega mass flow controller. There the gas is humidified and then injected into the reactor, where the exiting gas is dried via desiccant tube and then analyzed by the QMS. The % CO_2 in the stream is determined by internal standardization; the CO_2 :Ar ratio. The total CO_2 captured is determined via line 2, where $N_{\text{inj},t}$ is the total moles of CO_2 injected during a time t , and $N_{\text{exit},t}$ is the exiting moles during that same time. Thus, the difference is the moles captured during that time. The QMS samples approximately every 20-25 seconds, so the total capture capacity is the sum of capture over all sampling periods.

$$2. \quad \text{CO}_2 \text{ captured} = \sum_0^f (N_{\text{inj},t} - N_{\text{exit},t})$$

The Hunt laboratory at the time of this dissertation does not have the capability to easily regenerate or cycle sorbents. Of the samples presented here, two were cycled 40 times; B4 and B5. The cycling was performed at Mitico HQ on their auto cycler, described in Chapter 3, Section 3.3.

In addition to capacity measurements, Scanning Electron Microscopy (SEM) was utilized to monitor surface texture changes before and after calcination, before and after reaction with CO_2 , and before and after cycling. For samples imaged after reaction, careful effort was taken to remove water from the hydrated particles without initiating the regeneration reaction and reconverting KHCO_3 (captured CO_2) to K_2CO_3 . Unfortunately, particles compared in this work (before and after reaction, for example) are not the exact same particle, but instead from the same sampling batch.

4.4 Results and Discussion

From the A series of sorbents, samples A1-A4 were generated to test the impact of using KHCO_3 in place of K_2CO_3 on extrusion and spheronization. To do this, the “activated” (after KHCO_3 converts to K_2CO_3) mass % of bentonite was held constant at 50%. After activation, all samples should in theory have a total dry mass of K_2CO_3 equal to 50%, however varying degrees of that K_2CO_3 will have originated from KHCO_3 conversion. In samples A1-A4, 0, 25, 75 and 100% of the final amount of K_2CO_3 present originated from KHCO_3 , respectively. Sample A1 required the most water to extrude properly, which makes sense given that only K_2CO_3 was used, and K_2CO_3 is highly soluble in water.



Figure 4.3 shows A1 and A4 after ES on the left and right panels, respectively. Note how A1 maintained a rod-like shape after spheronization due to material stiffness. Extrudate rods or “noodles” also did not break into consistent sizes, generating a variety of granulate lengths. While A4 did not generate perfect spheres after ES, they were more uniform in size and more spherical in shape.

It is very likely that large amounts of the water added went directly to dissolving K_2CO_3 and were not taken up by the bentonite, making it more challenging to increase its plasticity. While the large quantity of bentonite present helped control the undesirable slickness of the K_2CO_3 , it was clear from prior trial formulations that with less bentonite the material would have been unable to extrude. The wetted mixture appeared quite stiff, and while it was able to break into smaller pieces in the spheronizer, the material was so stiff it did not lose its rod-like shape (see Figure 4.3, left panel).

A2 which had 25% of its final K_2CO_3 originate from $KHCO_3$ extruded similarly to A1 but was found to be slightly less stiff, and thus experienced more centrifugal force induced plastic deformation and observed the beginning steps of spheronization. A3 and A4 both spheronized more easily than A1 and A2, not producing perfect spheres, however producing a more uniform size distribution and rounded shape. A4 (Figure 4.3, right panel) was determined to be crumblier than A3; it appears that the slick nature of K_2CO_3 can act somewhat like another binder in small amounts by helping keep granulate grains closer together. For most following formulations a “75:25” rule ($KHCO_3$: K_2CO_3) like A3 was adopted.

It was determined after these formulations were created that a fairer comparison could have been made if they had all be formed with the same amount of water, in addition to utilizing the same extrusion and spheronization speed. Unfortunately, the ES-method is a bit of an art in that most “optimal” conditions are found by trial and error. The “optimal” extrusion and spheronization conditions for all these samples would vary greatly. Regardless, by comparing these four formulations it was clear that the highly deliquescent nature of K_2CO_3 makes it more challenging to apply to the ES method directly in large concentrations. Additionally, it was noted that the temperature increases due to dissolution when water is added is much lower for $KHCO_3$ than K_2CO_3 for the same mass. This offers another benefit to scaling up formulas with $KHCO_3$ substitute.

Samples A5-A7 were similarly formulated to test the limits of bentonite-supported extrusion. In short, we hoped to determine what the maximal amount of active mass is in which we can still extrude/spheronize quality particles. From A1-A4 and other prior non-

extrudable attempts, we determined bentonite plasticity does the “heavy lifting.” We hoped to determine if it was possible for the active material to still extrude, even when (activated) mass loadings approached 60, 70, or even 80%. We observed that larger mass loadings on the order of 75%+ are highly unlikely to extrude using bentonite alone as a binder (see Figure 4.4). While further testing is necessary, we did observe A7, which had a K_2CO_3 mass load of 60%, extruded reasonably full noodles. By adjusting the $K_2CO_3/KHCO_3$ ratio and %water added, it should be possible to formulate ES-friendly sorbents with active mass loads as high as 60%.



Figure 4.4 displays A6 and A7 after attempted extrusion on the left and right panels respectively. A6 was formulated with an (activated) K_2CO_3 mass load of 75%. Despite its inability to remain in aggregate pieces (it immediately fell apart) the material was quite wet, indicating further water would not improve shape. A7 on the other hand was able to maintain desirable shape with a K_2CO_3 mass load of 60%.

All samples in the A-series were found to be very susceptible to humidity and generally weak, so it was determined that the next step in developing a bentonite supported/bound sorbent was to increase resistance to humidity and tensile strength. The B-series began by adding $CaCl_2$ as a desiccant support (see Chapter 3). Sample B1 and B2 both have $CaCl_2$ added and were tested on the Hunt lab absorption reactor. Those results are presented in Table 4.3. The 5% $CaCl_2$ present in B1 was not found to sufficiently support the sorbent in humidity resistance, so that amount was doubled in B2. As $CaCl_2$ was found to cause strong material deactivation (see Chapter 3) Al_2O_3 was added to the mix to surface area and hopefully maintain material activity. B2 was unable to maintain sorbent shape (they squished) when reacted, thus the rest of the B2 batch was calcined at 600°C.

Table 4.3: B series capacity measurements and measured densities

Ref	Estimated Composition/ heat treatment	Capacity (mg CO ₂ g ⁻¹ sorbent) ^a	% reacted (actual/ theoretical) ^b	Density (g mL ⁻¹) ^c
B1	50 K ₂ CO ₃ , 45 Bent. 5 CaCl ₂ 180°C 24 hrs	115	72.3	0.76
B2	50 K ₂ CO ₃ , 25 Bent. 15 Al ₂ O ₃ , 10 CaCl ₂ 180°C 24 hrs	92.3	57.9	0.83
B3	B2 +600°C 2 hrs	58.8	36.9	0.85
B4	50 K ₂ CO ₃ , 50 Bent. 180°C 24 hrs 600°C 2 hrs	124.1 55.9 ^a	77.8 35.0 ^a	0.83
B5	50 K ₂ CO ₃ , 25 Bent. 25 Al ₂ O ₃ 180°C 24 hrs, 600°C 2 hrs	142.2 165.1 ^a	89.1 103.5 ^a	0.83

^aIn addition to the first absorption measurement, the capacities of B4 and B5 were also determined after 40 cycles on the Mitico auto cycler

^bThe theoretical capacity of a 50% K₂CO₃ sorbent is ~160 mg CO₂ g⁻¹ K₂CO₃

^cBulk density, not individual particle density is listed

The physical changes upon calcination were remarkable, yet unsurprising. Clays are known to recrystallize at high temperatures, creating stronger covalently bonded 3D networks (instead of stacked 2D sheets). The recrystallization temperatures of clays differ, literature on bentonite suggests it occurs around 500°C.¹⁹ The calcination (essentially “firing”) of bentonite is so effective at increasing tensile strength and resistance to humidity/water, that samples B3-B5 became insoluble in water, shown in Figure 4.5. The transformation was also observed via SEM imaging. Prior to calcination clear 2D clay sheets can be seen, while after calcination the layers appear to merge, flattening the particle surface (Figure 4.6). Unfortunately, calcination did result in a large drop in sorbent capacity and kinetics (for kinetic changes observe Figure 4.7). B2 and B3 have capacities of 92.3 and 58.8 mg CO₂ g⁻¹ sorbent respectively.

To further optimize capture capacity B4 and B5 were formulated and tested as CaCl_2 was deemed unnecessary to provide humidity resistance once the material is calcined. Again, upon calcination bentonite-containing samples are highly resistant to water-based attrition and have noticeably greater tensile strength. Thus, it was determined that future samples (B4 and B5) were unlikely to benefit from the addition of CaCl_2 or other desiccants. In uncalcined granulates, the desiccants provide support at the cost of capacity, likely by preventing formation of K_2CO_3 -hydrate intermediate products (see Chapter 3).

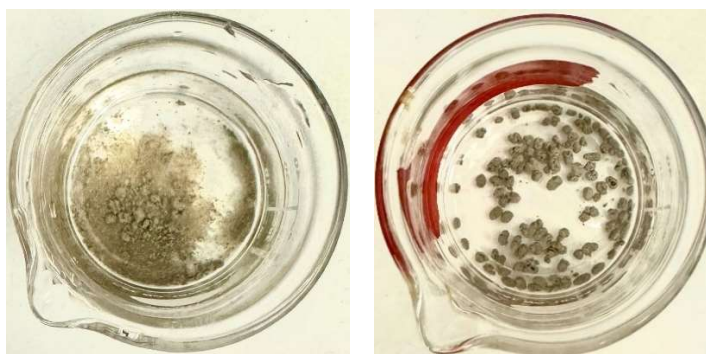


Figure 4.5 displays A3 (left) and B4 (right) each in a graduated cylinder of water. A3 (after activation) is 50/50 K_2CO_3 and bentonite heat treated at 180°C for 24 hours. B4 is A3 but after an additional 2-hour calcination at 600°C . A3 completely dissolved within 5 minutes of water exposure, while B4 was left overnight and remained visually unaffected.

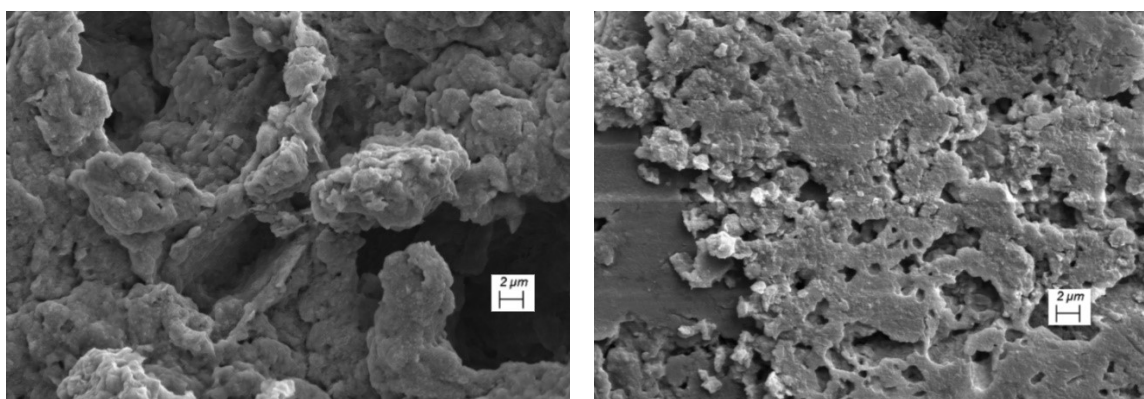


Figure 4.6 displays 2,000X magnification of the particle surface before (A3, left) and after (B4, right) calcination at 600°C , with a 2-micron segment for size. Very large morphological changes occurred during calcination. On the left we observed plated clay sheets stacked on top of each other. On the right, after calcination, the particle surface looks much flatter. These images and all SEM images presented here were taken by Ricardo Hernandez and Jordan Threat at Caltech.

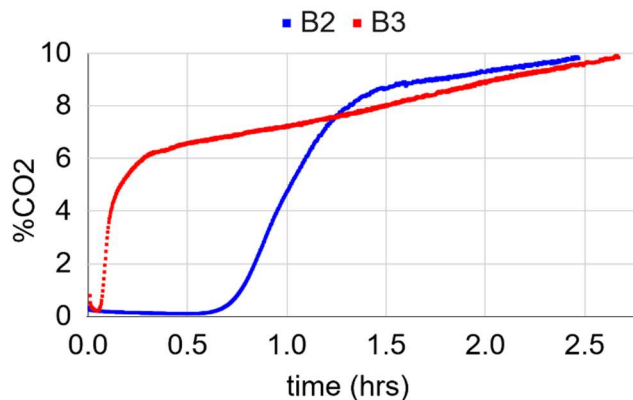


Figure 4.7 displays the absorption curve for samples B2 and B3. While B3 exhibits greater durability than B2, this appears to have come at the expense of the sorbent's reactivity. Not only does B3 have a lower capacity (see Table 4.3) but compared to B2 which showed near 100% capture efficiency for 30 minutes of its 2.5-hour reaction, B3 spends most of the reaction at 40% or lower capture efficiency.

It is possible that when calcined, CaCl_2 recrystallizes, restructuring neighboring K_2CO_3 and reducing its availability. For example, in the solution phase, dissolved K_2CO_3 reacts with CaCl_2 to form CaCO_3 precipitate and KCl . A reaction like this, but in the solid phase at higher temperatures, might explain the large drop in capacity between B2 and B3.

On the other hand, the bentonite dehydration and phase change may have shrunk the pores enough to not only slow the reaction (shown in Figure 4.7) but also cause pore clogging, making some unreacted K_2CO_3 unavailable. Future work might attempt to relate heat treatment, including calcination, to pore size distribution via Brunauer–Emmett–Teller (BET) measurement. For samples presented here, even large macropores (see Figure 4.8) appear to become fully covered in a shell of reacted K_2CO_3 after absorption. It is unclear from these images alone how much surface resistance is increased by reacted K_2CO_3 . It is however clear, how widespread the coverage of KHCO_3 (or other products) is on the particle surface after absorption. In their work on unsupported (pure) K_2CO_3 crystals Luo *et al.* attributed these geometric structures which block pores to both $\text{K}_4\text{H}_2(\text{CO}_3)_3 \cdot 1.5\text{H}_2\text{O}$ and KHCO_3 , confirmed via x-ray diffraction analysis.²⁰

To further test how the heat treatment procedure can alter the particle surface, a stepwise calcination ($100^\circ\text{C} \rightarrow 180^\circ\text{C} \rightarrow 350^\circ\text{C} \rightarrow 500^\circ\text{C}$) was performed and can be compared to

the two step ($180^{\circ}\text{C} \rightarrow 600^{\circ}\text{C}$) particle surface. The flattened yet irregular looking surfaces shown in Figures 4.6 and 4.8 are typical of the two-step calcination. (The stepwise treated sample was not yet absorption tested, and thus is not listed in the formulations tables). The composition and preparation are the same as A3/B4 except for the multi-step heat treatment. As it was determined that bentonite recrystallization should occur at 500°C , this was used as the final temperature instead of 600°C .¹⁹

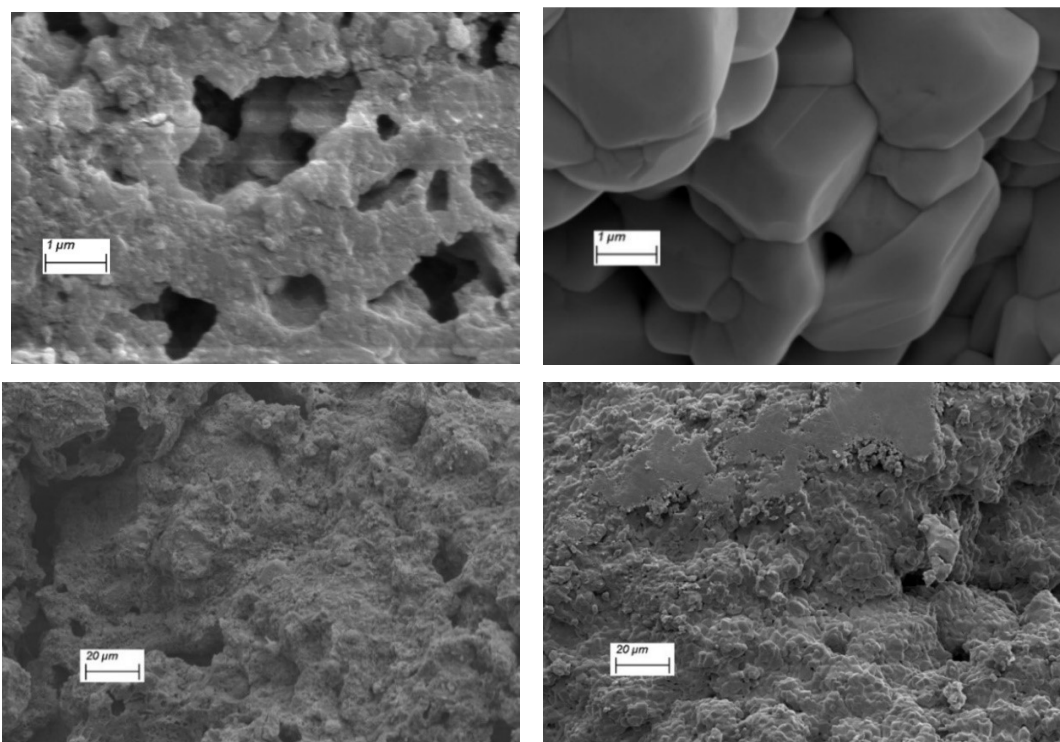


Figure 4.8 displays an example of the particle surface (B4) before (left panels) and after (right panels) reaction with CO_2 . The top panels were taken at 2,000X magnification, with a 1-micron segment for size, while the bottom panels were taken at 500X magnification with a 20-micron segment for size.

The stepwise heating was designed to break up the different physical/chemical processes so they might occur successively instead of simultaneously. Some of the anticipated chemical/physical changes include- evaporation of superficial water, evaporation of deep intraparticle water (including K_2CO_3 -hydrates and water trapped between clay layers), decomposition of KHCO_3 , dihydroxylation of bentonite layers, desorption of trapped organic contaminants, recrystallization of bentonite.

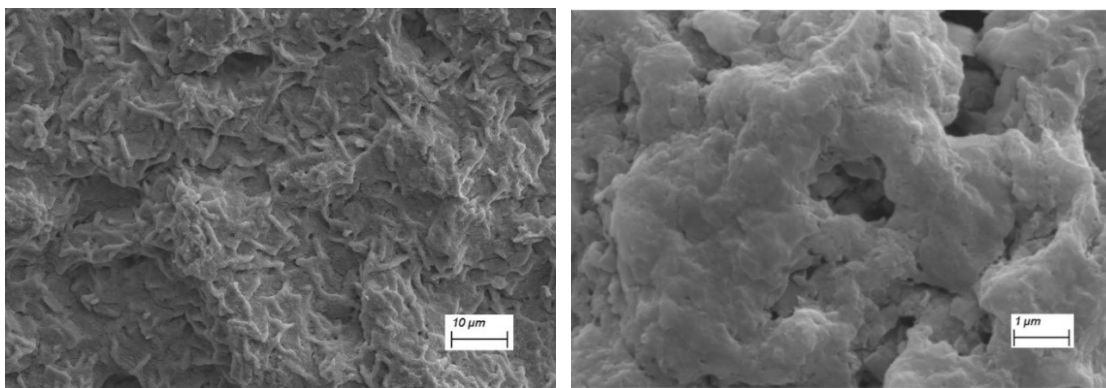


Figure 4.9 displays the morphological result of the stepwise calcination ($100^{\circ}\text{C} \rightarrow 180^{\circ}\text{C} \rightarrow 350^{\circ}\text{C} \rightarrow 500^{\circ}\text{C}$). These images can be directly compared to Figures 4.6 and 4.8 as the stepwise sample was otherwise formulated/prepared the same as sample B4. The left and right panels display the particle at 1,000X and 10,000X magnification, respectively. A 10-micron and 1-micron segment are offered in each panel for size.

The result of the stepwise heating is shown in Figure 4.9. Compared to the random mars-like surface of the two step calcined sorbents depicted in Figures 4.6 and 4.8, the stepwise heated sample has a uniform appearance. SEM visualization indicates macropores greater than 1-micron in size seem less abundant. This can be expected as when multiple chemical/physical processes are happening at once they may result in explosive pocket formation while the material calcines the final morphology. In a stepwise heating procedure, each process might occur more slowly, with a more controlled release of trapped gases. By the time the final morphology is sealed (the 500°C) all the gases are evacuated (the 350°C step). The impact of these morphological differences requires further characterization through absorption and BET measurements at minimum.

To test the longevity of calcined bentonite, samples B4 and B5 were cycled 40 times. It should be noted that the regeneration step was performed with 150 ccm N_2 at 180°C , in other words a dry regeneration. The capacities of B4 and B5 on their 1st and 41st absorptions are presented in Table 4.3. Recall that B4 and B5 each have an “activated” mass loading of 50% K_2CO_3 . The rest of B4 is supported by calcined bentonite while B5 was supported by a 25/25 mixture of bentonite and Al_2O_3 . While their initial absorption capacities are quite comparable (124 and 142 $\text{mg CO}_2 \text{ g}^{-1}$ sorbent, respectively), after cycling their capacities are quite different. After 40 cycles, the absorption capacities of B4 and B5 are 60 and 165 $\text{mg CO}_2 \text{ g}^{-1}$ sorbent, respectively. In summary, while B4 (only bentonite) decreased in

capacity by about half, B5 (contains 25% Al_2O_3) increased in capacity by about 15%. While it would be simple to attribute the decrease in absorption capacity of B4 to material attrition, it has been noted that under certain conditions bentonite can be transformed into zeolites, materials well known for their capability to physisorb CO_2 . In their work, Chen *et al.* calcined NaOH-infused bentonite to form zeolite 13X.²¹ Due to the basicity of K_2CO_3 -containing wetted mixtures, it is possible that a similar process is occurring here, transforming our bentonite into 13X or another zeolite capable of physisorbing large amounts CO_2 . Thus, while the initial B4 absorption would be large due to both chemical and physical absorptions, successive absorption cycles would observe reduced capacities as regeneration of physisorbed CO_2 may require temperatures greater than 180°C or much lower pressures.²² Searching the surfaces of calcined unreacted samples with large amounts of bentonite (like B4), we were able to visually identify smooth and geometric looking surfaces, shown in Figure 4.10. While zeolites take many forms, in general they are smooth and geometric in appearance as their pores primarily microporous and will not show up on most SEM images.^{21,23} We strongly believe these structures, presented in Figure 4.10, to be evidence of zeolite formation. This would also explain why sample B4 would decrease in capacity with cycling under these regeneration conditions. To properly assign the identity of the (pre-reaction, thus not products of K_2CO_3) smooth geometric shapes would likely require Energy dispersive X-ray (EDX) or X-ray diffraction analysis.

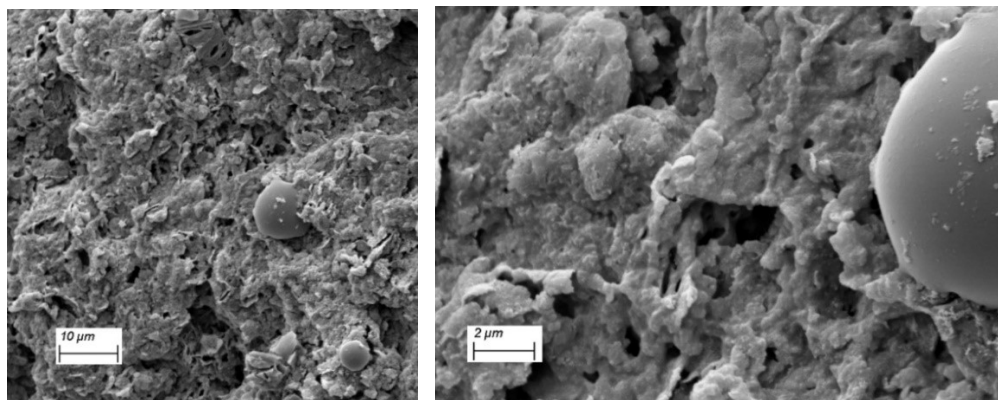


Figure 4.10 displays round, smooth, geometric structure on the surface of unreacted, calcined bentonite-containing samples. These structures are believed to be some kind of zeolite. The left and right panels were taken at 1,000X and 5,000X magnification respectively, with 10-micron and 2-micron segments for size.

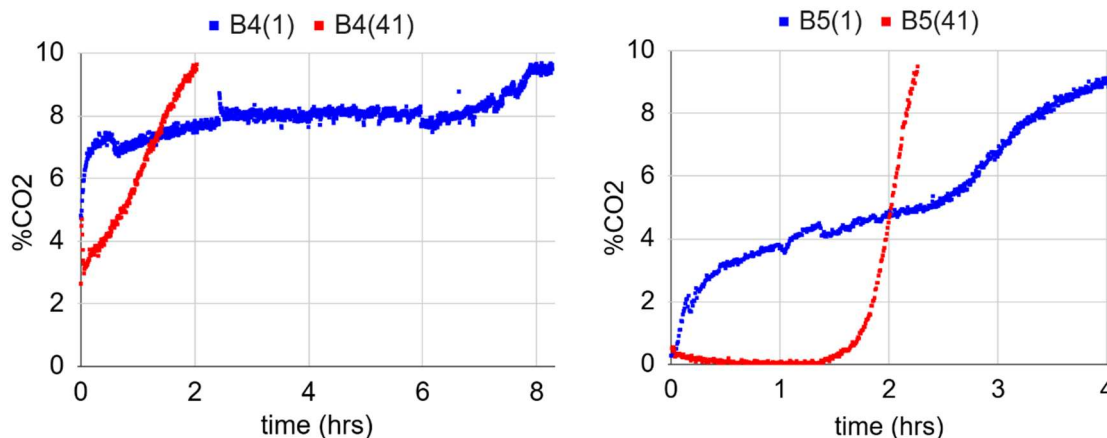


Figure 4.11 displays the absorption curves for B4 (left panel) and B5 (right panel) before and after 40 cycles on the Mitico auto cycler. B4, which is calcined (activated) 50/50 K_2CO_3 and bentonite has a very slow absorption curve before cycling. After cycling the kinetics, or reaction efficiency, improved, but the overall capacity was much lower (see Table 4.3). B5, which is calcined 50/25/25 K_2CO_3 /bentonite/ Al_2O_3 has a comparably much faster first absorption curve. However, what is even more note-worthy is how much the curve improved after 40 cycles, with a capacity that even increased (Table 4.3).

Unlike B4, which suffers from capacity issues possibly resulting from zeolite formation and unregenerated physisorption, B5 performs quite well before and after cycling. Not only did the capacity improve, but the kinetic change is very remarkable. Cycling resulted in what is the ideal structure; most of the absorption period occurs at 100% reaction efficiency, before quickly saturating. Future work will investigate how pore size distribution and overall surface area changes for calcined bentonite/ Al_2O_3 mixtures.

Of the two samples after 40 cycles, B5 (which contains 25% Al_2O_3) is physically weaker and visually shows more signs of deterioration. SEM imaging indicates massive morphological changes and formation of macropores in both B4 and B5 (Figure 4.12). Interestingly, B5 (and B4 to a minor extent) grew crystallites which we assume are K_2CO_3 . These anemone-looking spikes are primarily found near crevasses on the surface where larger chunks of sorbent have apparently broken off. We believe that these spikes might weaken the particle structure, causing physical deterioration as they grow. We thus propose a “leach and recrystallization” model of material deterioration, where K_2CO_3 leached during wet absorption cycles forms crystallites during dry periods which can weaken the material over cycles. Further investigation of this hypothetical process is needed.

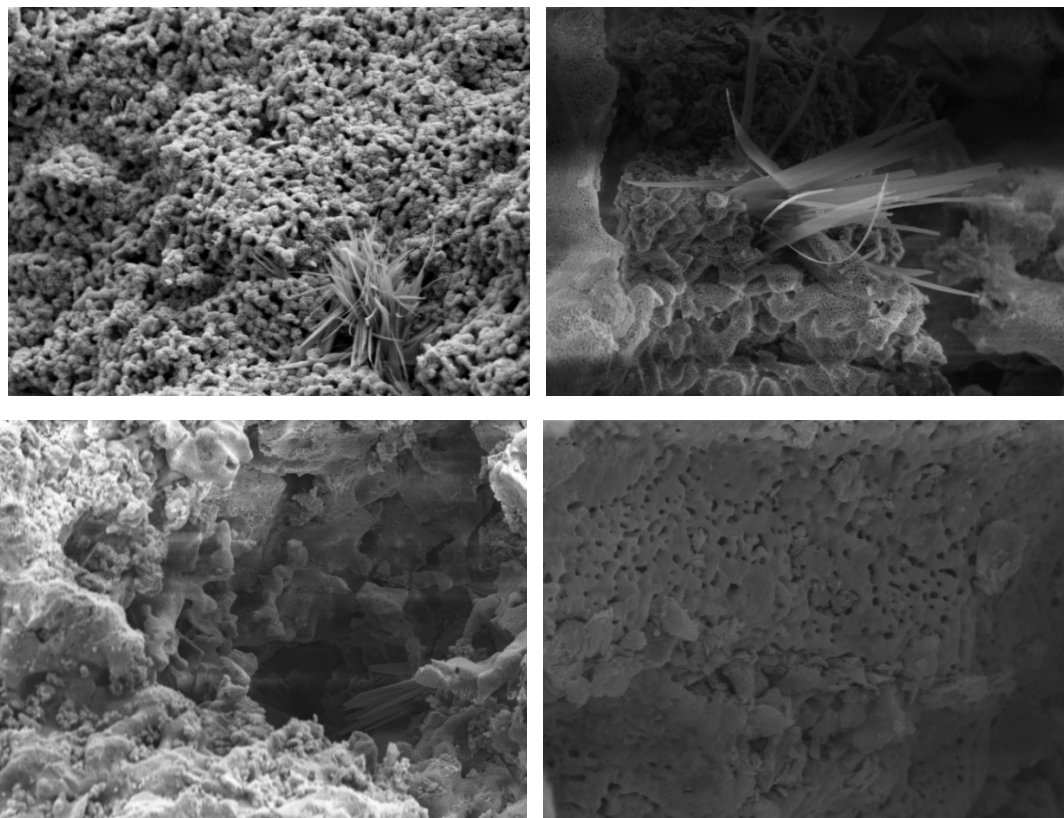


Figure 4.12 presents some preliminary SEM images of samples B4 and B5 after 40 cycles. Anemone-like (hypothetically K_2CO_3) crystallites are shown in the top two panels and the bottom left panel. Surface pores are visualized in the bottom right panel. The top left, top right, bottom left and bottom right panels were taken at 1,000X, 1,000X, 500X, and 5,000X magnification, respectively.

4.5 Conclusions

K_2CO_3 -based sorbents for CO_2 point source capture were prepared (primarily) from wet mixing and extrusion-spheronization of $KHCO_3$ and bentonite. Bentonite clay was used as a binder to provide plasticity to sorbent mixtures so that they could be pushed through a screw-type extruder. $KHCO_3$ was found to produce sorbent mixtures that extruded more easily than K_2CO_3 , likely due to its lower solubility. Activation of samples prepared from $KHCO_3$ is necessary to drive off CO_2 and essentially regenerate K_2CO_3 before they can be reacted. We activated samples at $180^\circ C$. While bentonite containing samples baked at $180^\circ C$ were not resistant to humidity, and thus undesirable for scale-up, calcination of bentonite at temperatures higher than $500^\circ C$ results in recrystallization that increases tensile strength and makes the sorbent no longer soluble (highly resistant to water). Calcined particles prepared only from the active material and bentonite were found to have

a high capacity on their first absorption ($124 \text{ mg CO}_2 \text{ g}^{-1}$ sorbent), while cycled capacity ($56 \text{ mg CO}_2 \text{ g}^{-1}$ sorbent) dropped significantly. Literature on bentonite treatment suggests recrystallization can form zeolites, which can physisorb CO_2 and are unlikely to release it under our regeneration conditions. SEM imaging supports this possibility by identifying smooth geometric structures which appear to be zeolite. On the other hand, calcined samples formed from both bentonite and Al_2O_3 have great potential, as they are durable, and have high cycled capacity ($165 \text{ CO}_2 \text{ g}^{-1}$ sorbent after 40 cycles). A sorbent “leach and recrystallization” model of particle deterioration was proposed, suggesting that K_2CO_3 crystals which increase in size as material leaches is one of the primary causes of material deterioration.

4.6 Future Works

Extrusion-spheronization of bentonite/ K_2CO_3 sorbents show great potential for scalability. The Hunt lab will continue to investigate the properties of calcined bentonite sorbents, particularly using Al_2O_3 as an added support to provide extra surface area. We are interested in determining how Al_2O_3 /bentonite mixtures might be further optimized for capacity, kinetics and durability. To do this, further characterization of all samples is needed. BET surface area measurements, particularly as samples are cycled, will be incredibly useful and should be correlated to material reactivity. We hope to attempt steam-regeneration on the samples to determine how that might impact their longevity. SEM imaging also shows that multiple heating steps results in a different surface morphology even for samples of the same composition. Impact of firing/calcination conditions (such as length, number of steps or humidity) should be explored.

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