Waste-Derived Activated Carbon Adsorbent Materials for Landfill Gas Purification (#1393115)

Ryan Thomas, Mitch Guirard, Masoud Jahandar Lashaki

Department of Civil, Environmental and Geomatics Engineering
Florida Atlantic University
Boca Raton, FL 33431

The Air & Waste Management Association's 116th Annual Conference & Exhibition

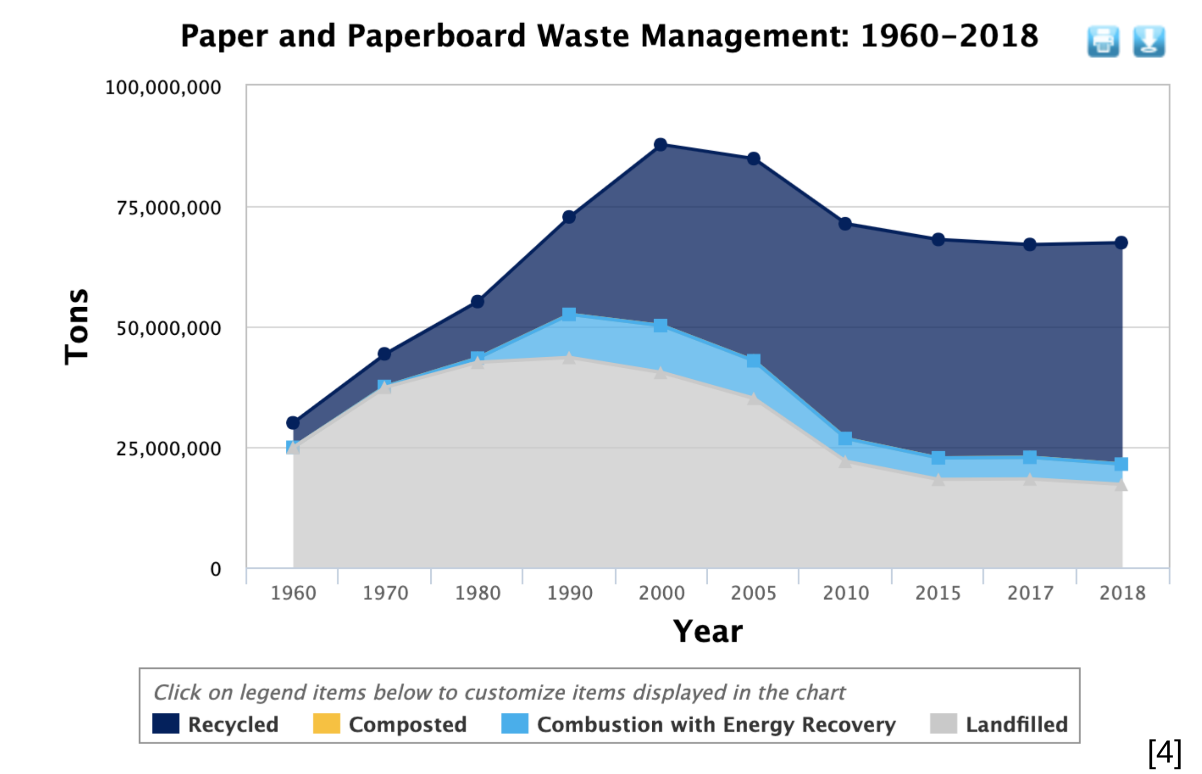
Orlando, FL (June 2023)

Abstract

A large percentage of the waste entering landfills is easily biodegradable organics such as food waste, paper waste, and yard waste. Once buried, such organic matter will undergo anaerobic decomposition and produce landfill gas as a byproduct, which is comprised of roughly 50% methane, 40% carbon dioxide, and 10% other impurities such as water vapor, ammonia, and hydrogen sulfide. Due to its high methane content, this gas can be purified into renewable natural gas and used as a carbon-neutral fuel. However, current purification processes are highly energy intensive and require multiple steps to remove all impurities. For these reasons, the potential of paper waste-derived activated carbon for removal of carbon dioxide and hydrogen sulfide from landfill gas was investigated. Activated carbon materials were prepared by carbonizing paper waste followed by acid treatment to remove ash, mixing with aqueous phase potassium hydroxide, and activation via microwave heating. The resulting adsorbent materials were modified with both tetraethylenepentamine and diethanolamine to potentially increase the carbon dioxide uptake. All modified and unmodified adsorbents were evaluated using thermogravimetric analysis to determine their equilibrium uptake of carbon dioxide. Adsorbent screening was conducted in conditions mimicking that of landfill gas, namely temperature of 40 °C and 40% carbon dioxide. All modified materials underperformed their unmodified counterparts. Performant materials were identified as those achieving uptakes greater than 3 wt.%. The best performing material achieved an uptake of 5 wt.% and maintained 97% of its uptake during 100 successive adsorption-desorption cycles. Column-breakthrough experiments demonstrated that the final candidate achieved complete removal of both carbon dioxide and hydrogen sulfide, suggesting viability for larger scale landfill gas purification.

Waste Generation and Management

- Paper is the third largest contributor to landfills [1]
- Paper can only be recycled 5-7 times [2]
- Paper is easily contaminated and cannot be recycled (pizza boxes, paper plates, tissues, etc.) [3]



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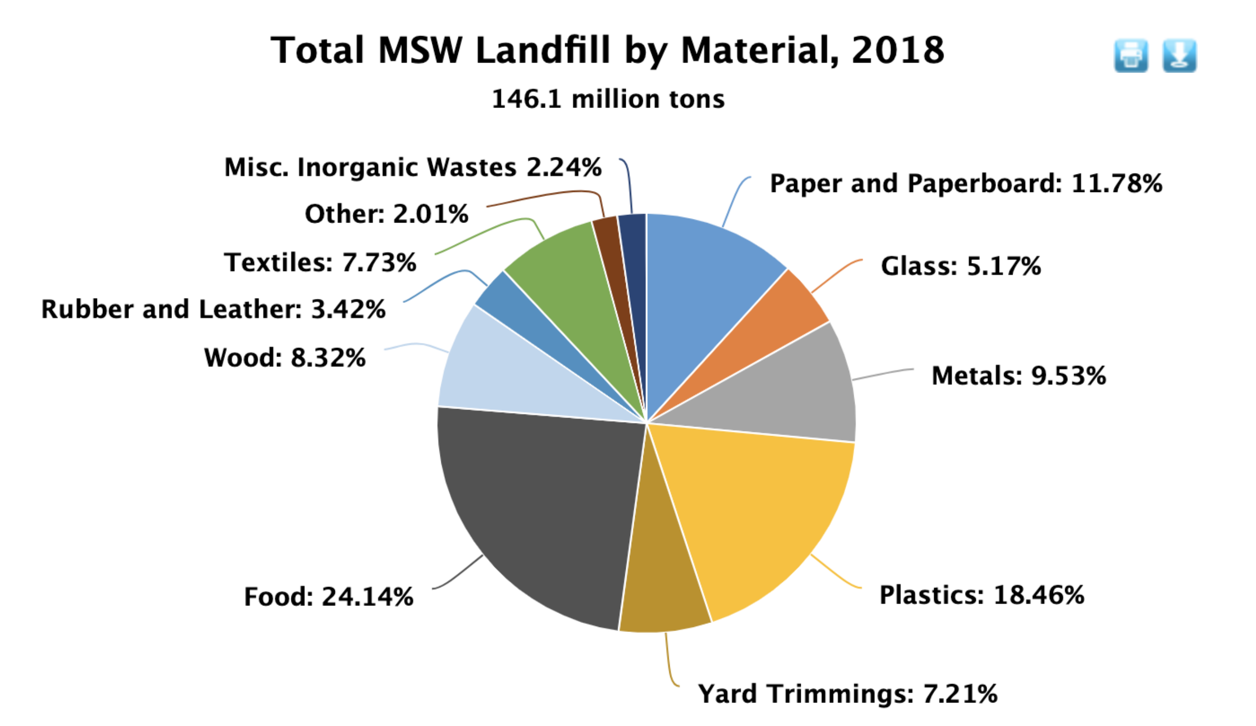
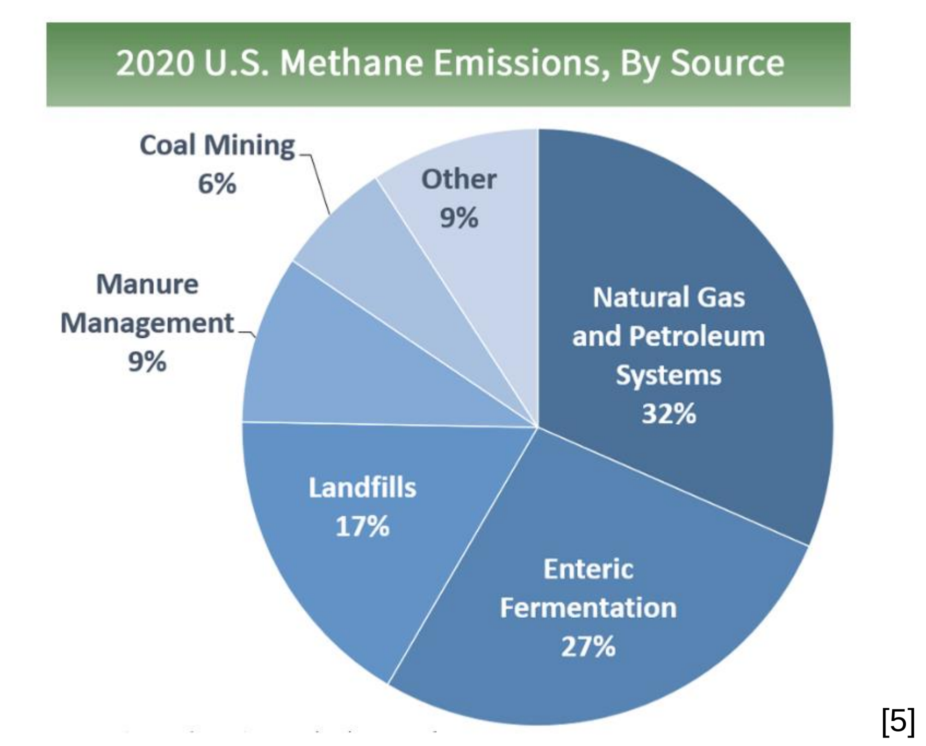


[1]

Methane and Landfill Gas (LFG)

- Methane (CH_4) makes up 11% of all GHG emissions [5]
- CH_4 is 25 times more potent of a GHG than CO_2 [5]
- Landfills are third largest emitters of methane [5]



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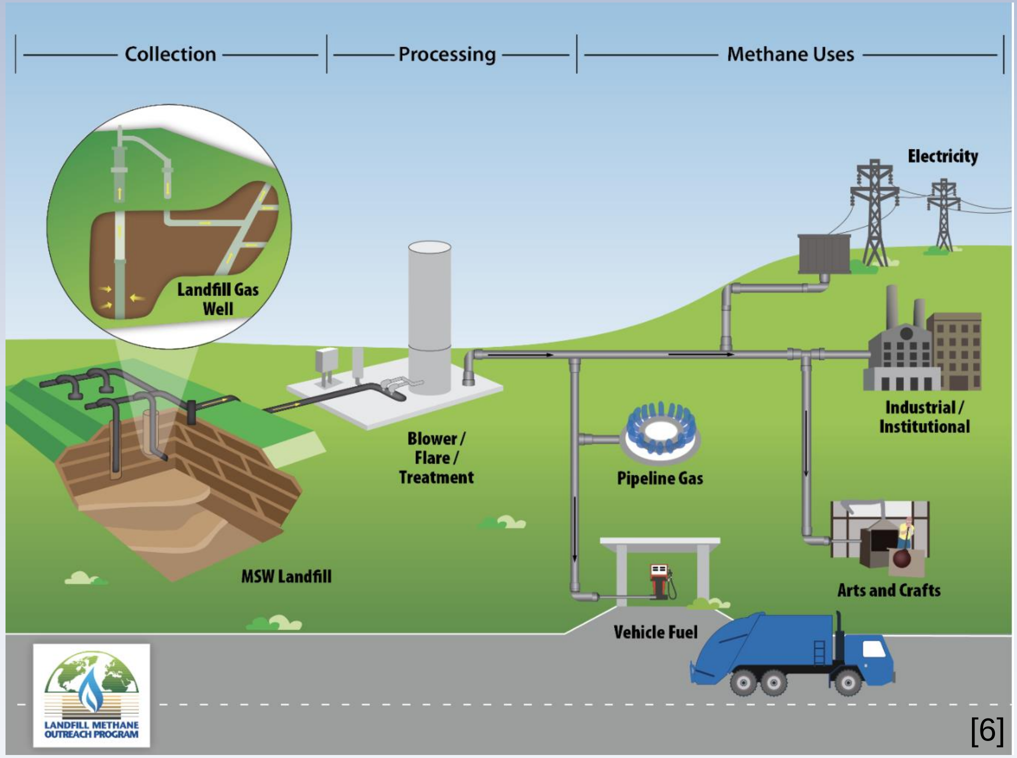


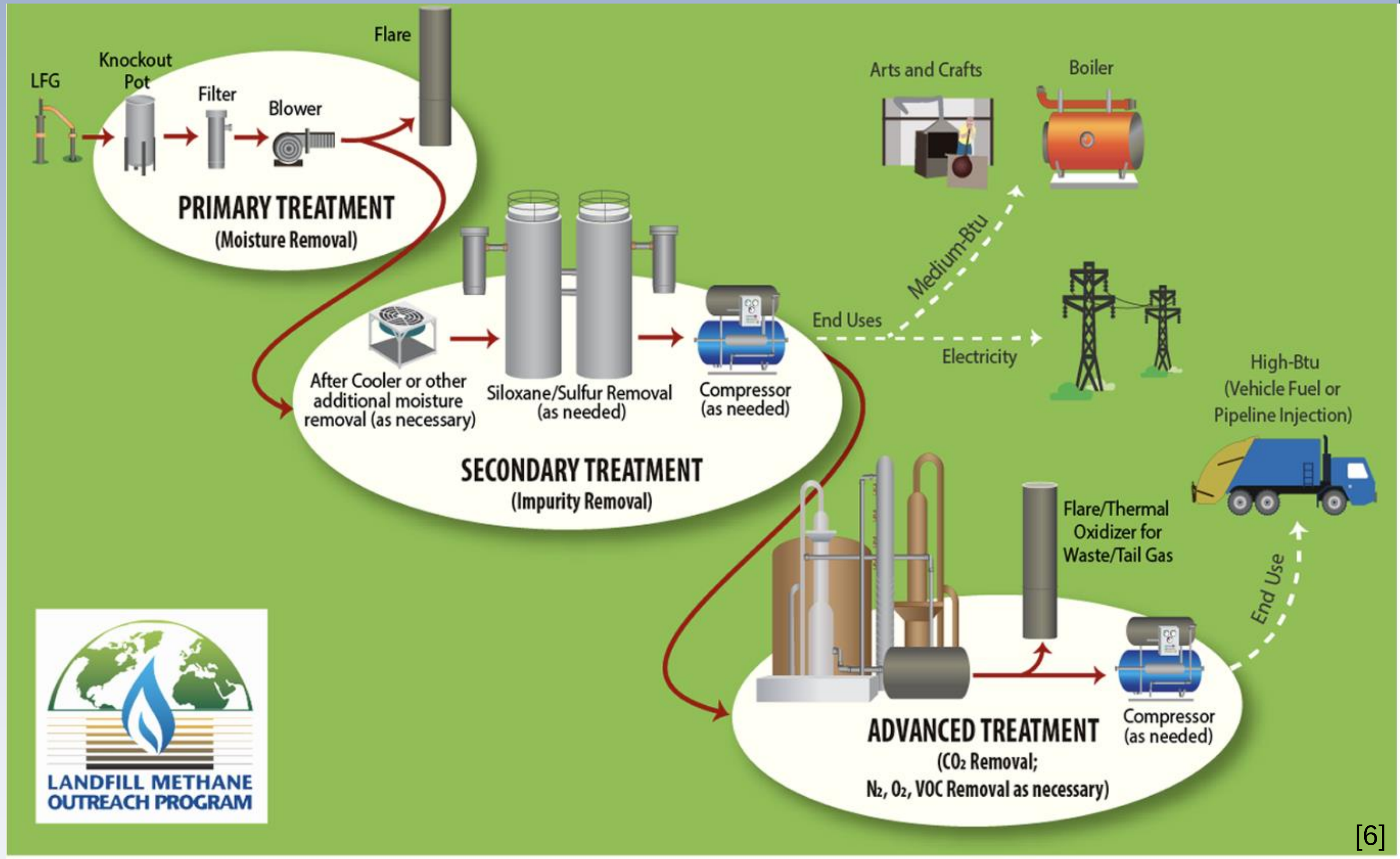
[6]

LFG Collection and Control

LFG uses [6]

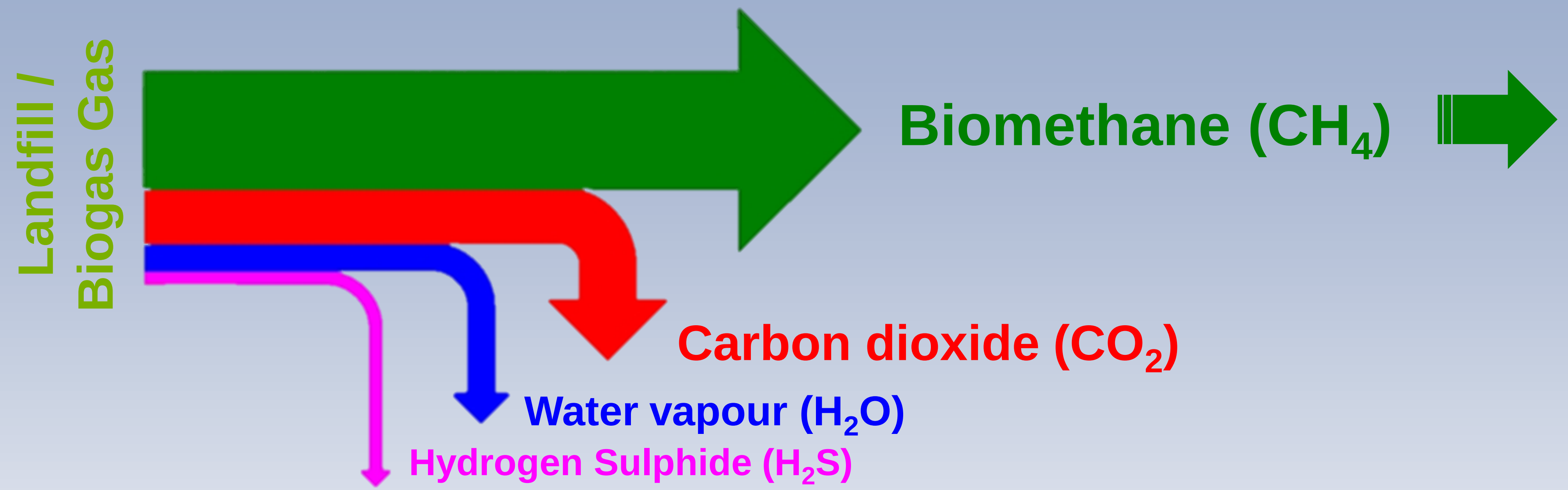
- Flare
- Electricity generation/cogeneration
- Direct use of medium-BTU gas
- Renewable Natural gas

Operational LFG to energy sites [7]	Candidate LFG to energy sites [7]
538	470
1,434 MW generation	957 MW generation potential



[6]

Landfill Gas and Biogas Purification



RNG

Renewable Natural Gas

Need for Integrating and Intensifying Process

- Integrating- Combining multiple processes into one
- Intensifying- Creating a more energy efficient process for the same outcome

Cyclic Adsorption-Desorption process

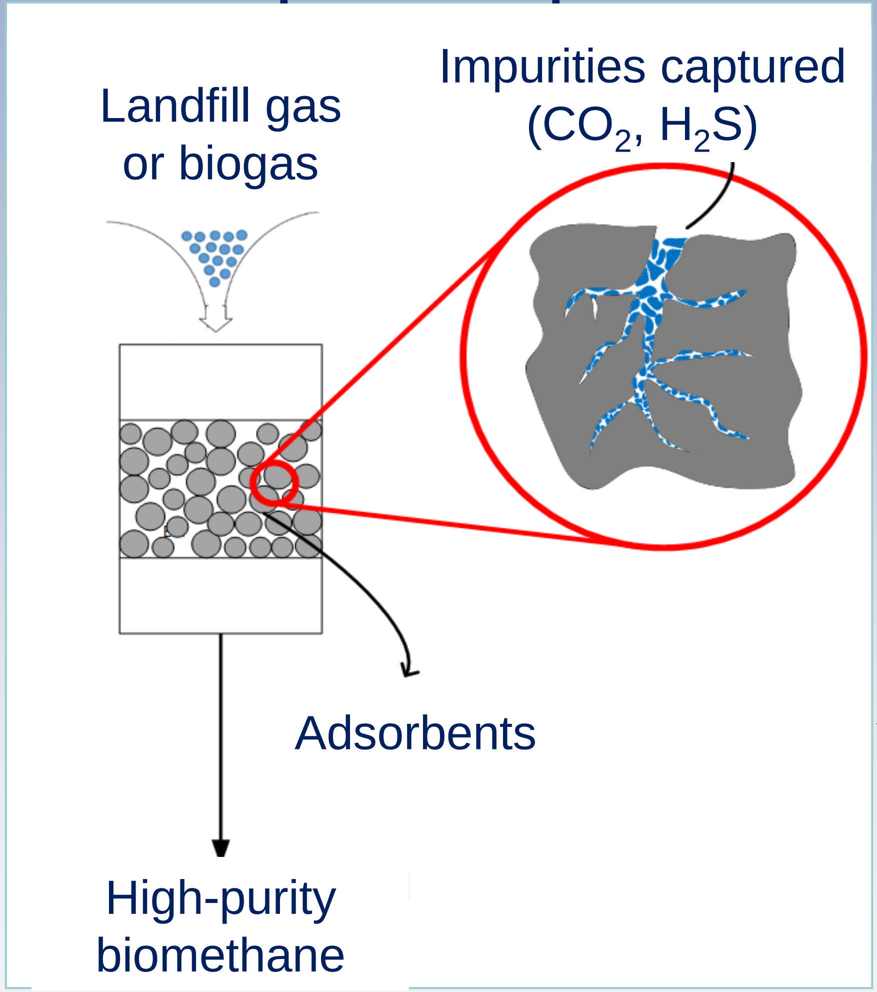
Pore Sizing

- Macropores (>50 nm)
- Mesopores (2-50 nm)
- Micropores (<2 nm)

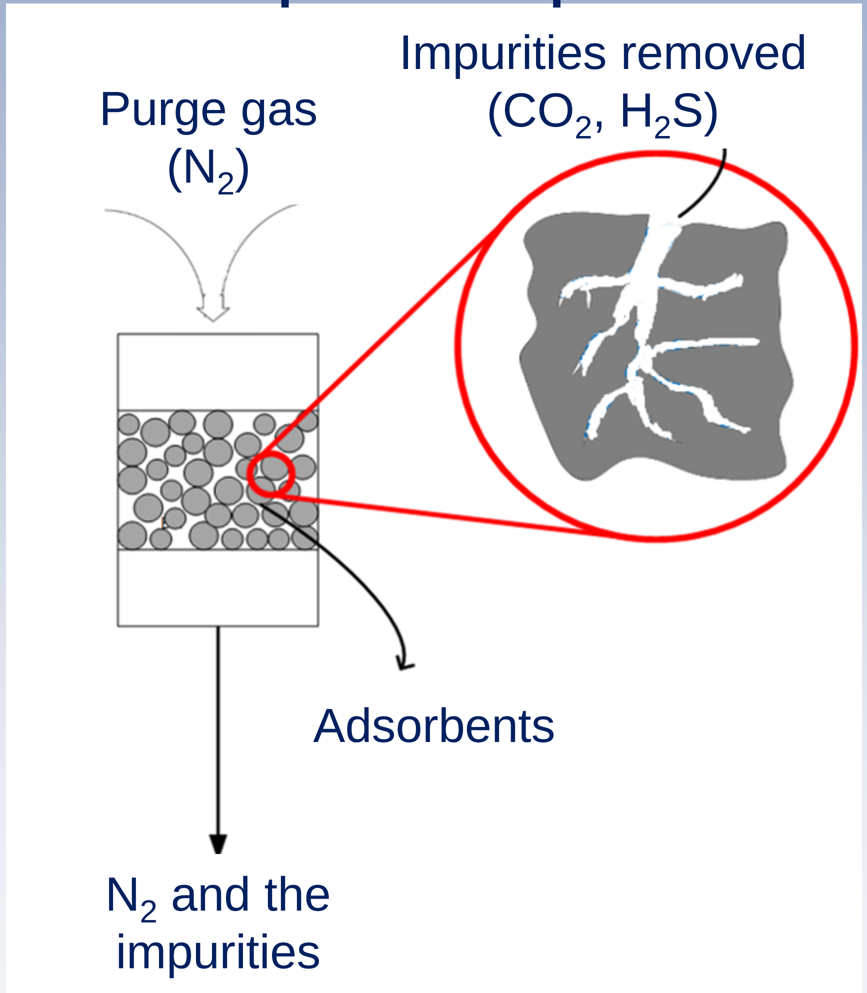
Adsorbents

- Zeolites
- Silica
- Activated carbon

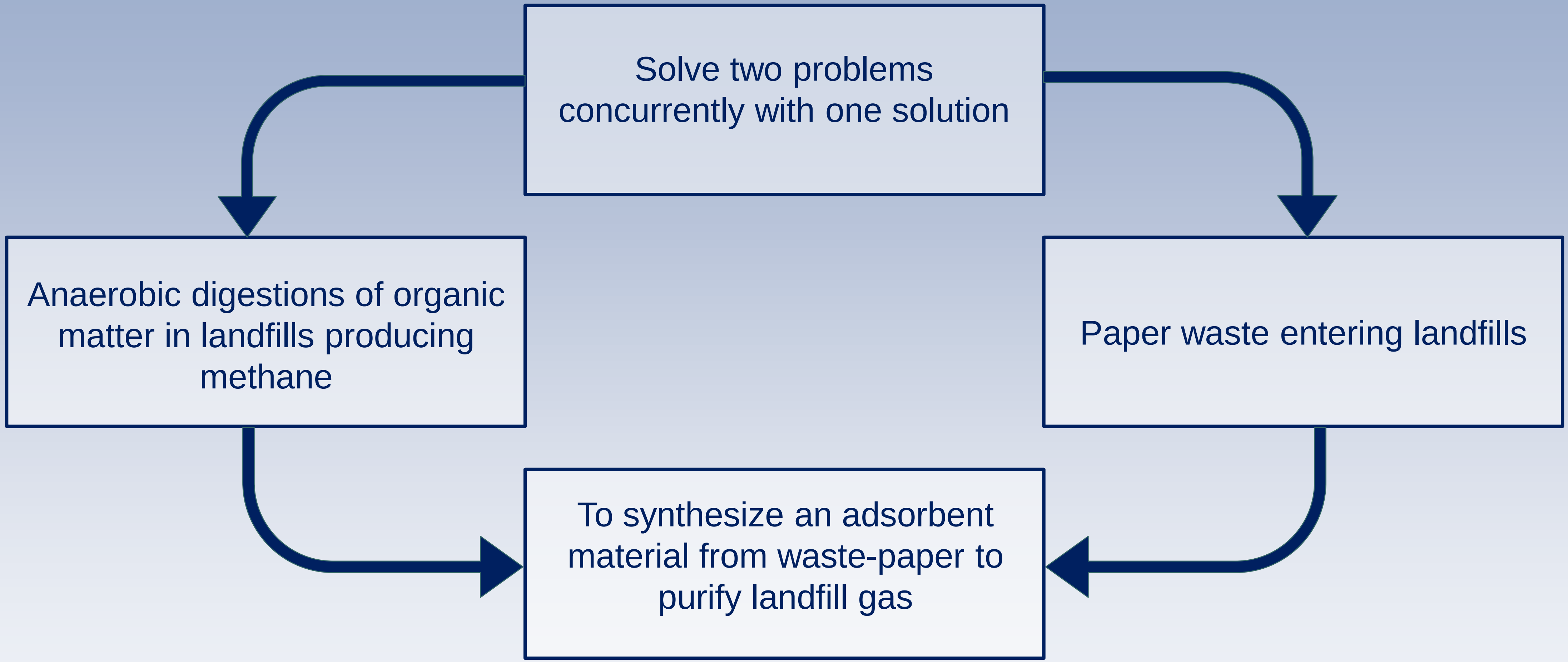
Adsorption of Impurities



Desorption of Impurities



Objective


Solve two problems concurrently with one solution
Anaerobic digestions of organic matter in landfills producing methane
Paper waste entering landfills
To synthesize an adsorbent material from waste-paper to purify landfill gas

Materials and Procedures

Carbon- Derived from mixed paper waste

Activation- Microwave radiation utilized to enhance porosity for adsorption

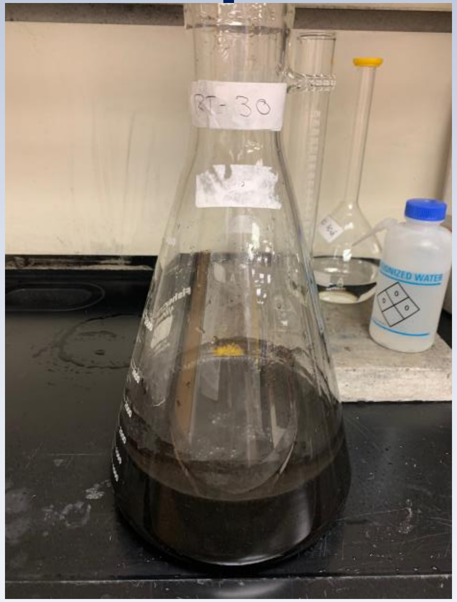
Amine Modification- Tetraethylenepentamine (TEPA), Diethanolamine (DEA)

Sample Testing- CO2 uptake screenings, adsorption kinetics

Best Performing Sample Testing – Performance stability, column breakthrough

Methodology – Carbonization/Acid Treatment

Cut up waste-paper and carbonize at 500°C → Grind carbonized material → Acid treat with 1 M HCL for 2 hours → Filter, rinse with DI water, and dry → Sieve with 100-mesh screen

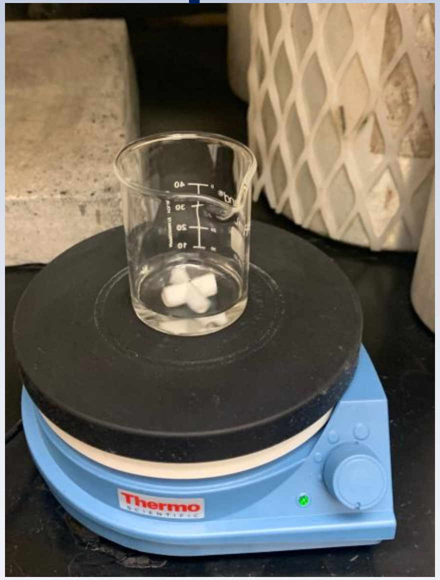


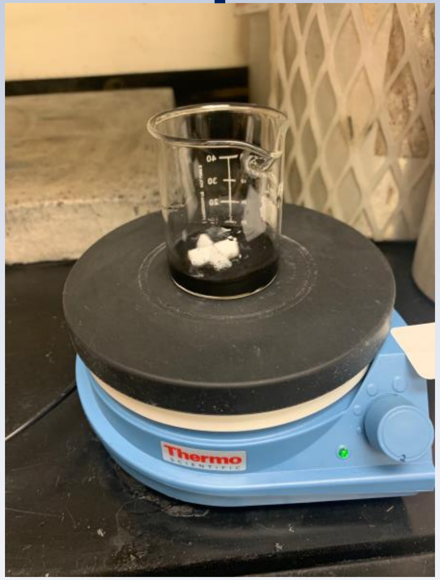
Methodology - Activation

Mix carbon precursor with aqueous phase KOH → Place in Microwave and purge with humid nitrogen → Activate with desired microwave duration (750 watts) → Collect and rinse (neutralize) with 1 M HCl, DI water, and dry in oven

Methodology – Amine Modification

Dissolve amines in methanol → Add carbon and mix thoroughly until methanol is volatilized out → Collect sample → Name (A-B-C-D-E)





Naming Convention

A = Precursor
- Commercial Activated Carbon (AC)
- Carbonized Paper Waste (P)

B = KOH:Carbon ratio
- 1
- 1.5

C = Activation time
- 2, 4, 6, 8, 10, 15, 20 minutes

D = Amine type
- Tetraethylenepentamine (T)
- Diethanolamine (D)

E = Amine loading Wt%
- 20
- 30

Note: (N=None)

Testing Methods

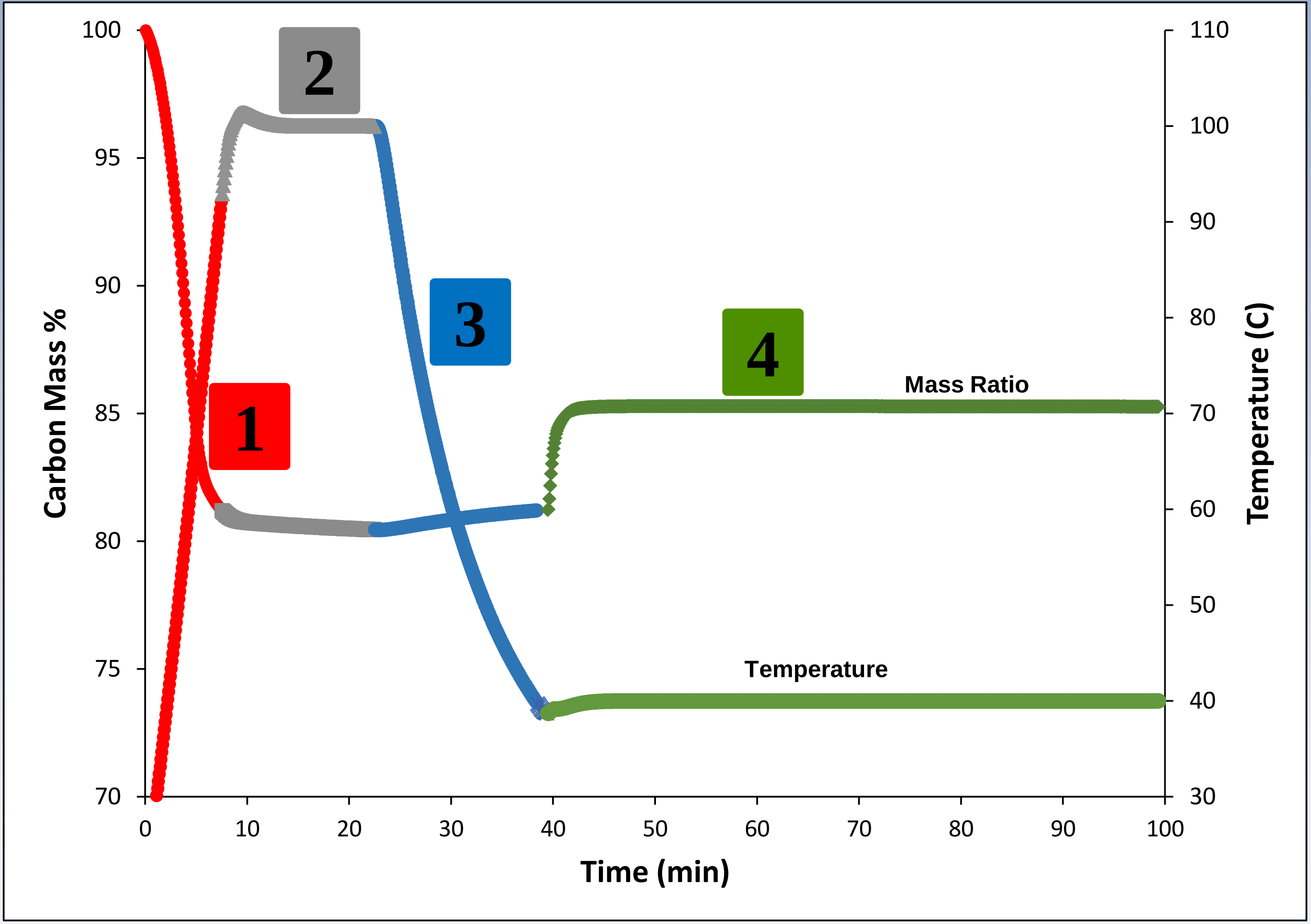
TGA

1.) Preheating: Sorbent is pre-heated to 100°C to remove impurities, while N_2 is being used as a purge gas.

2.) Isothermal: Temperature is kept at 100°C for 15 minutes under N_2 purge to ensure material is flushed of impurities.

3.) Cooling: Temperature is lowered to 40°C while under N_2 purge.

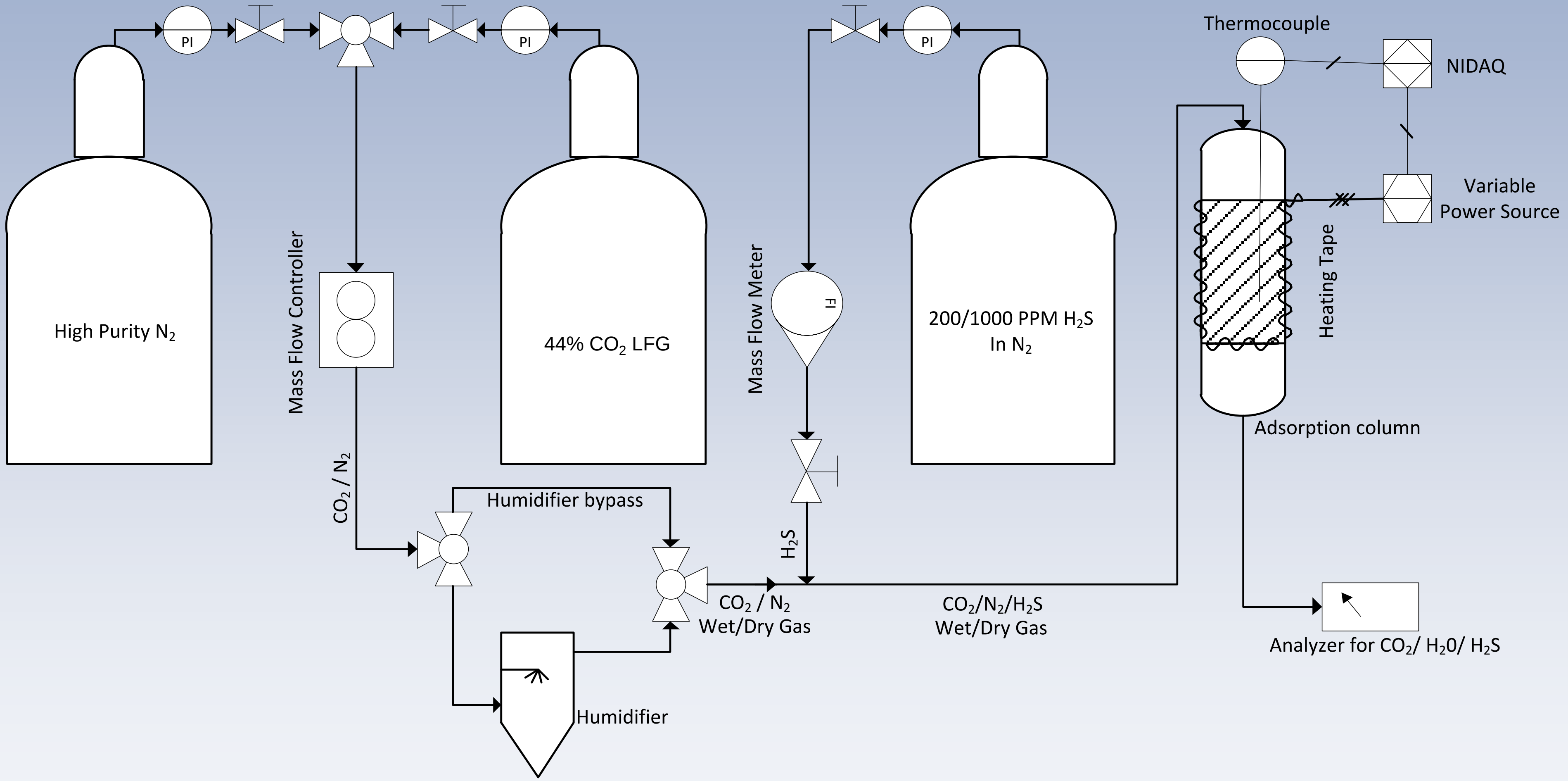
4.) Adsorption: Purge gas is switched to 40% CO_2 in N2, and temperature remains constant at 40°C for 1 hour.



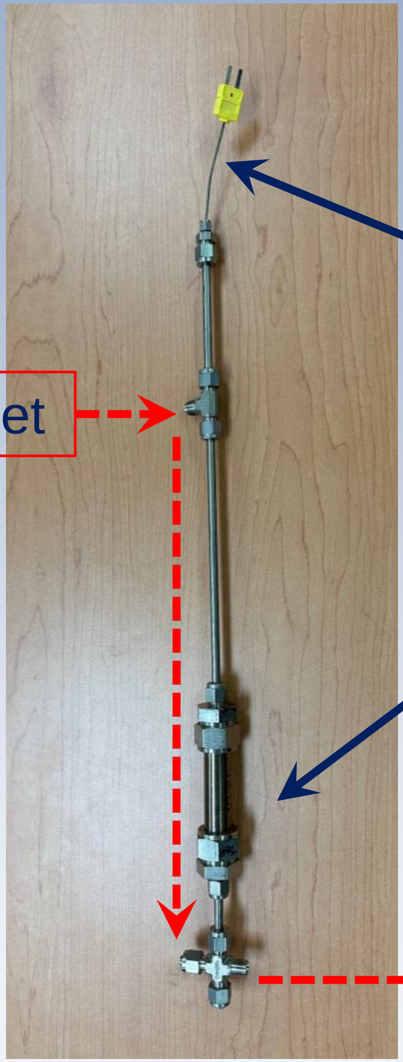
Testing Methods

Breakthrough Test

- Track effluent concentration on target impurity
- Tests a larger batch (2 grams) compared to TGA analysis



Breakthrough Test



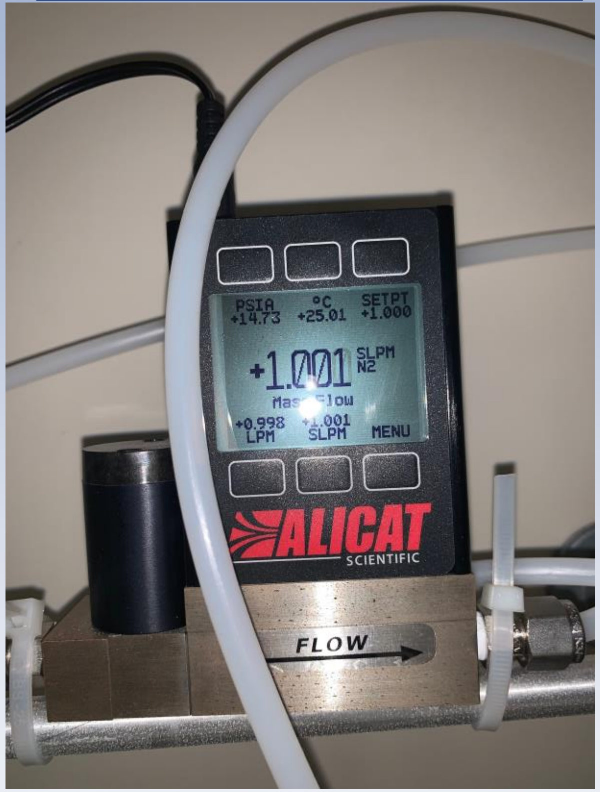
Thermo-couple

Inlet

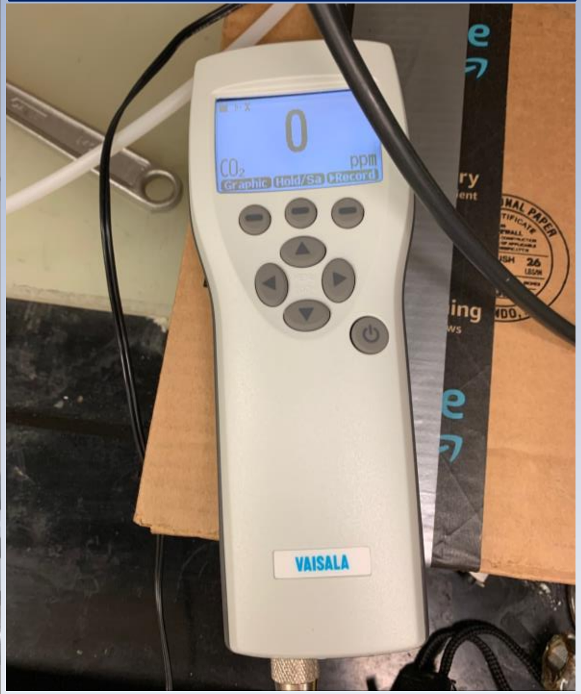
Sample Reactor

Outlet

Mass Flow Controller



CO_2 Detector Probe

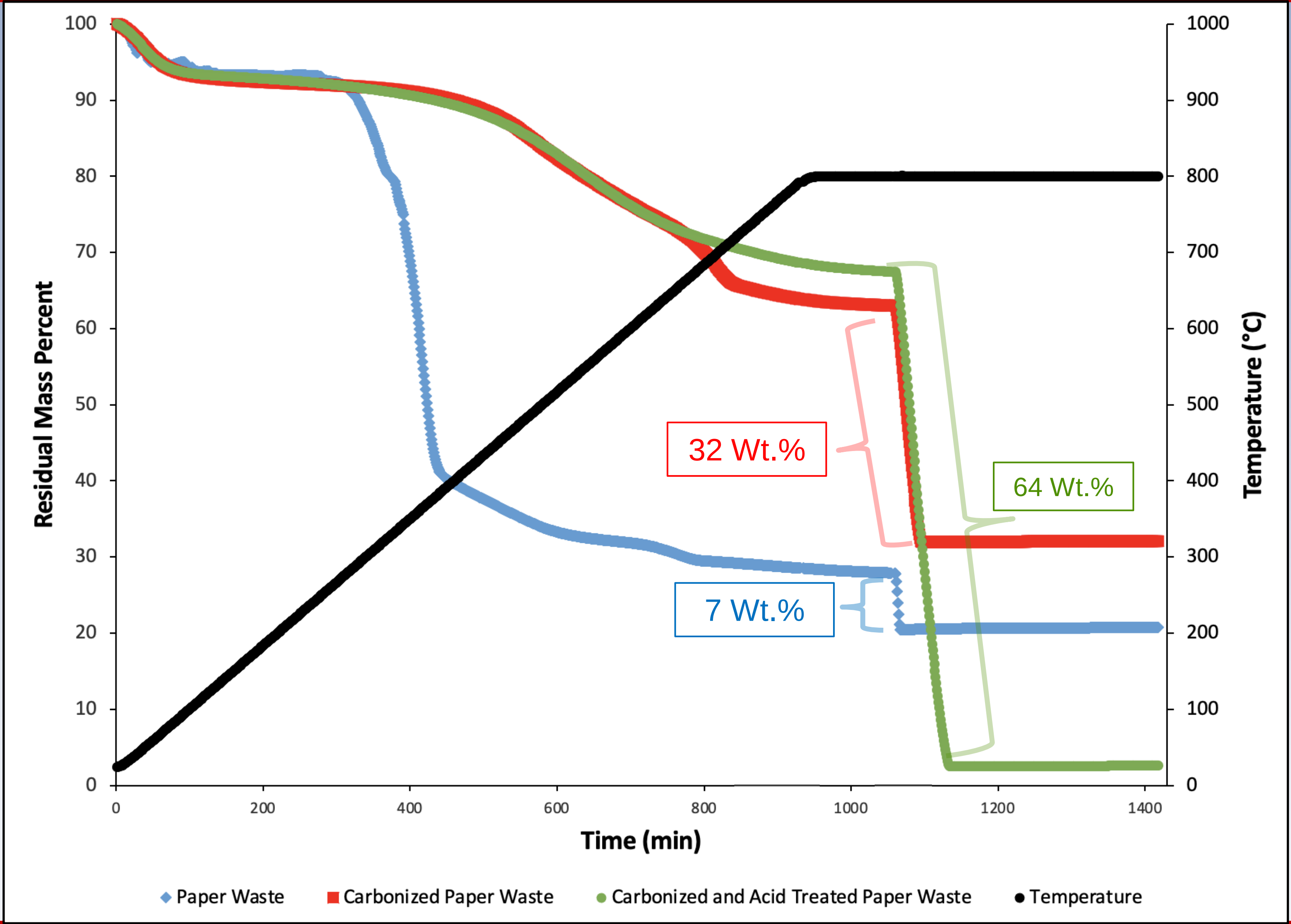


PID Analyzer (H_2S)

RESULTS

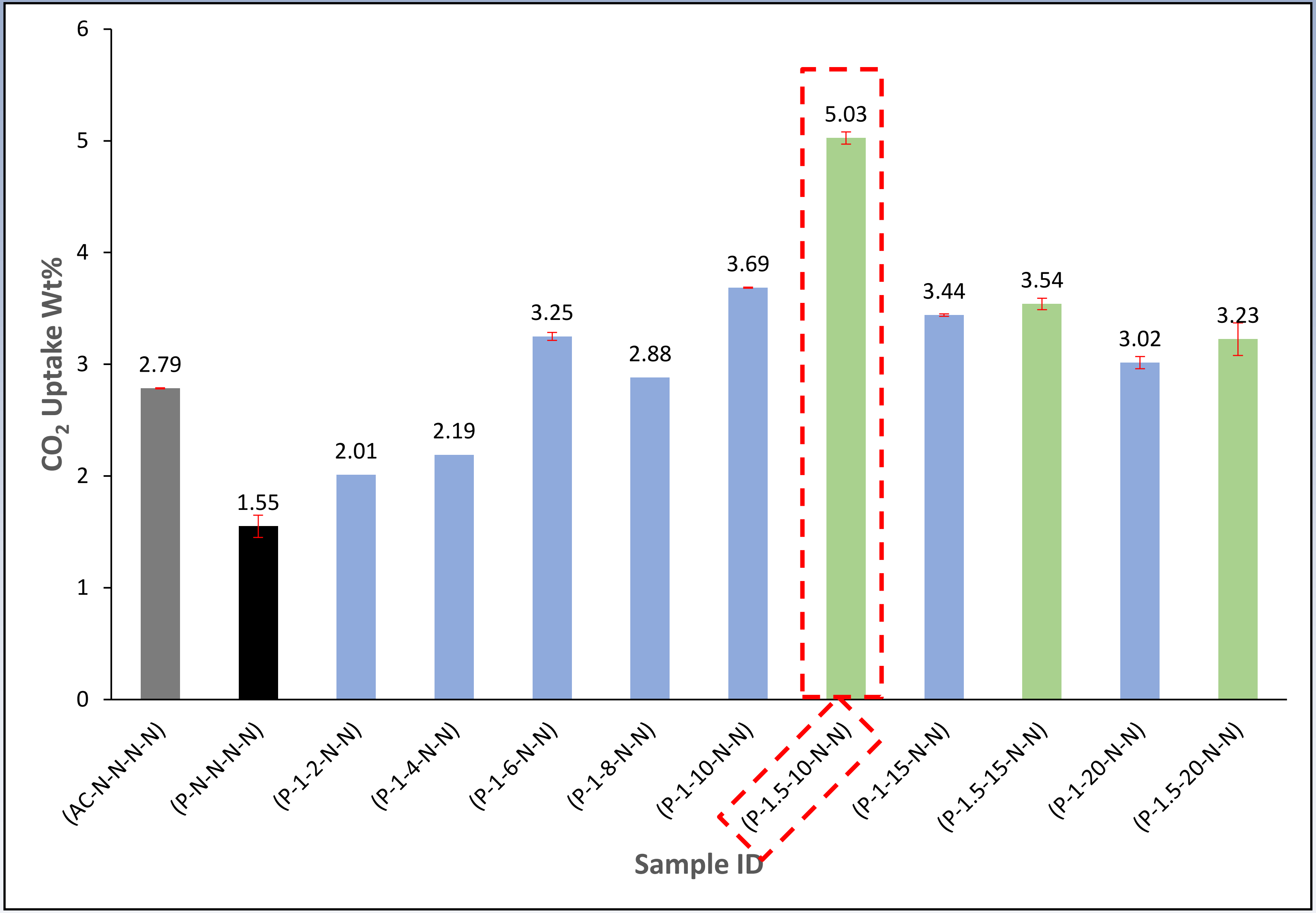
TGA Temperature Profile for Ash Content Determination

- 53% decrease in volatiles from carbonization
- 93% decrease in ash content after acid treatment

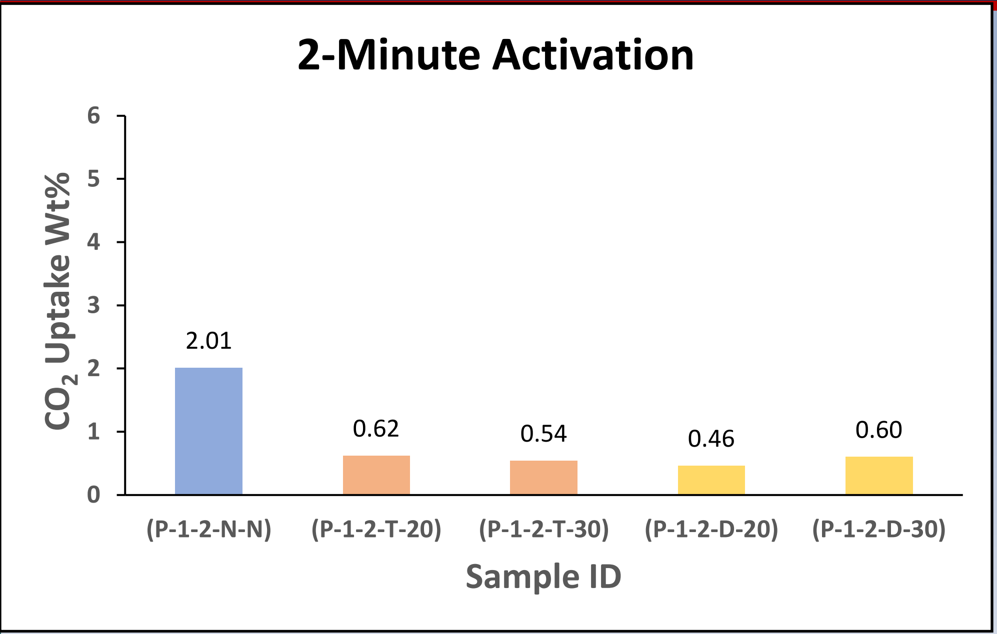


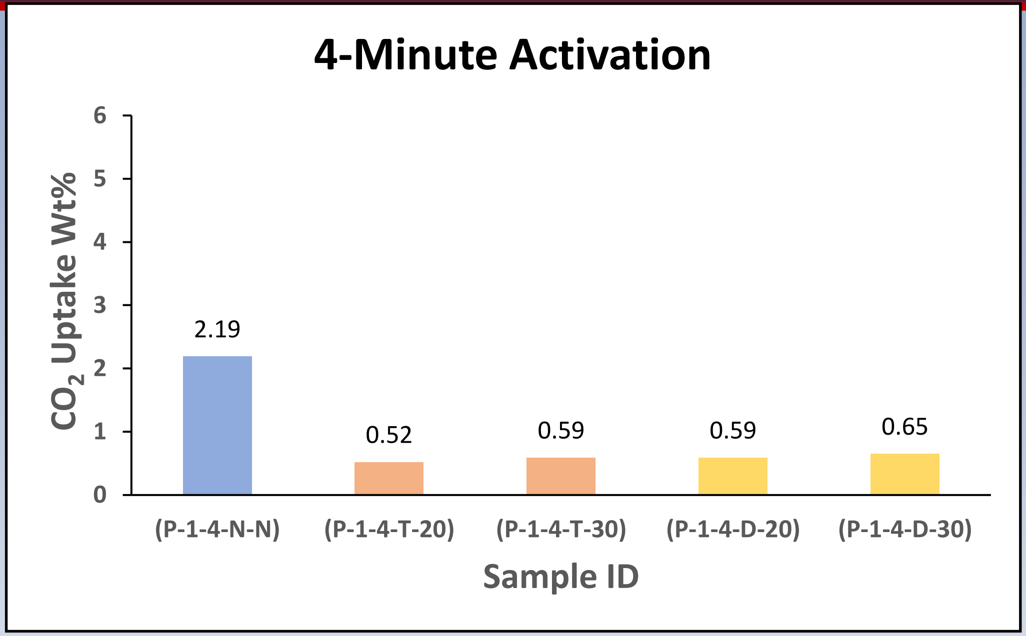
Adsorption Capacities of Unmodified Samples

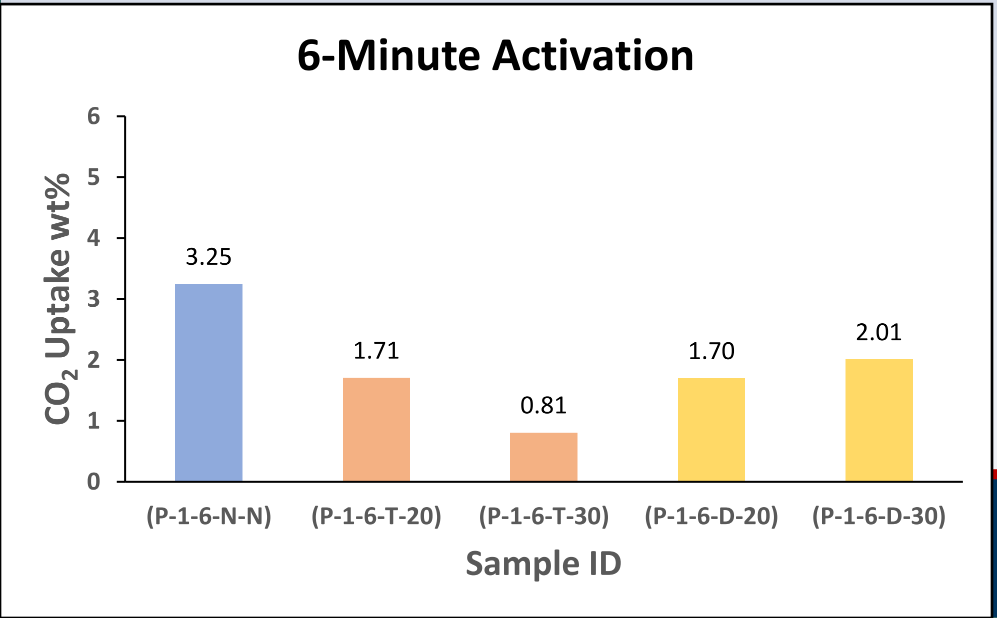
- No significant increase in adsorptive properties until 6 minutes of activation
- Plateau beyond 6 minutes
- Maximum uptake occurred at 10 minutes for both KOH ratios

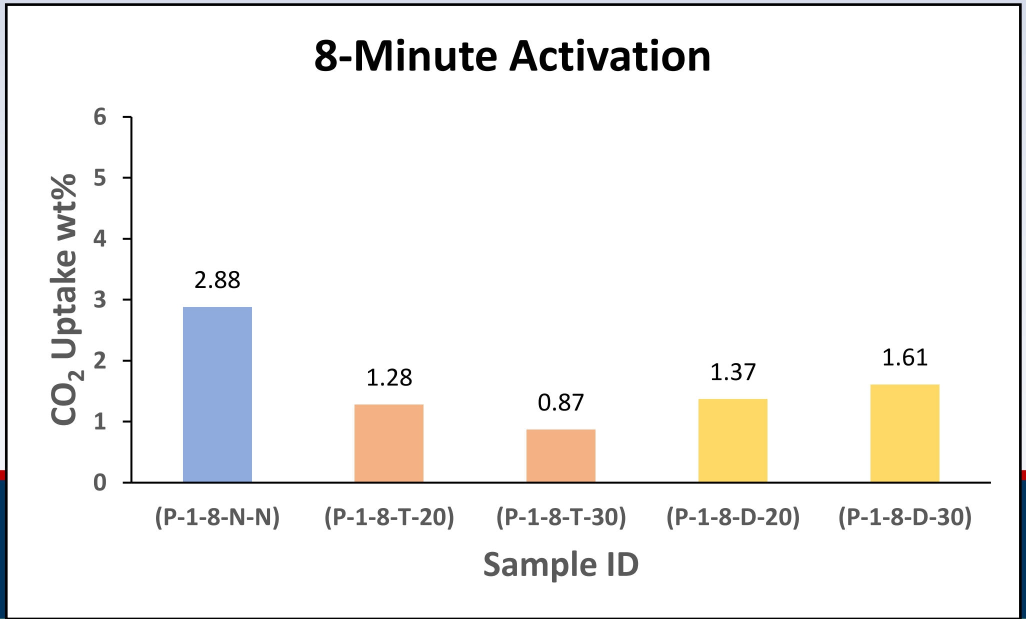


CO_2 Uptake Screening for Amine-Modified Samples



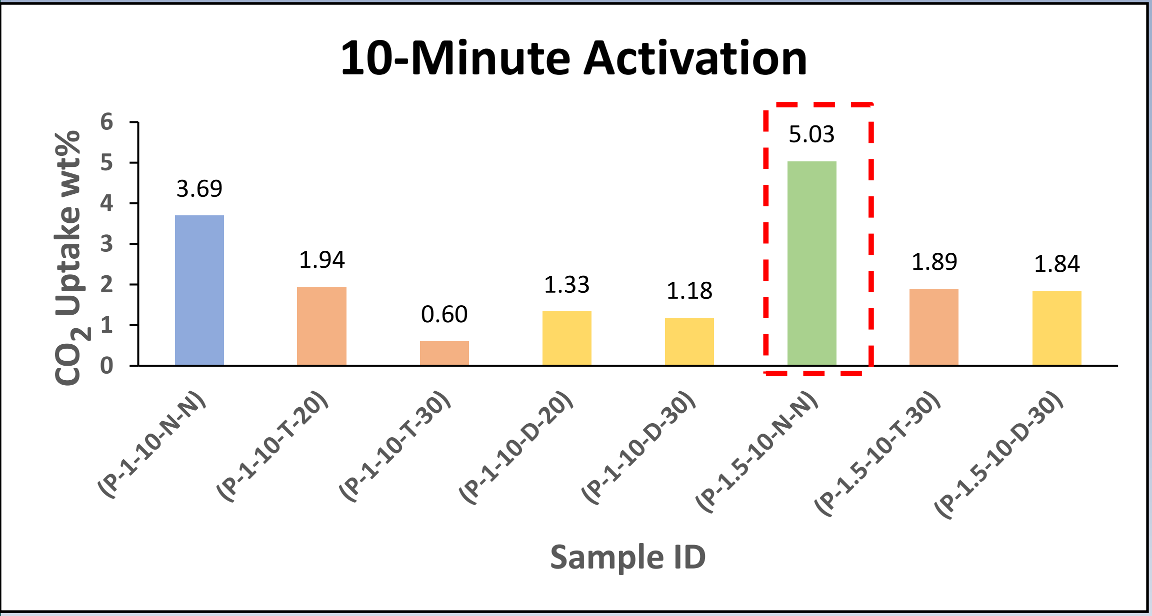


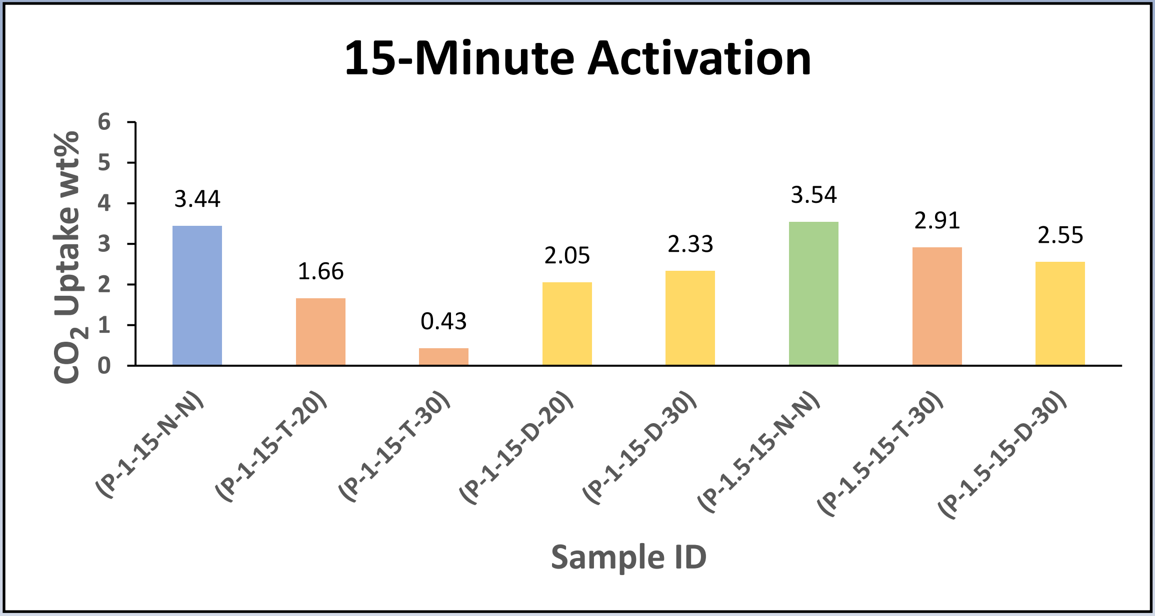


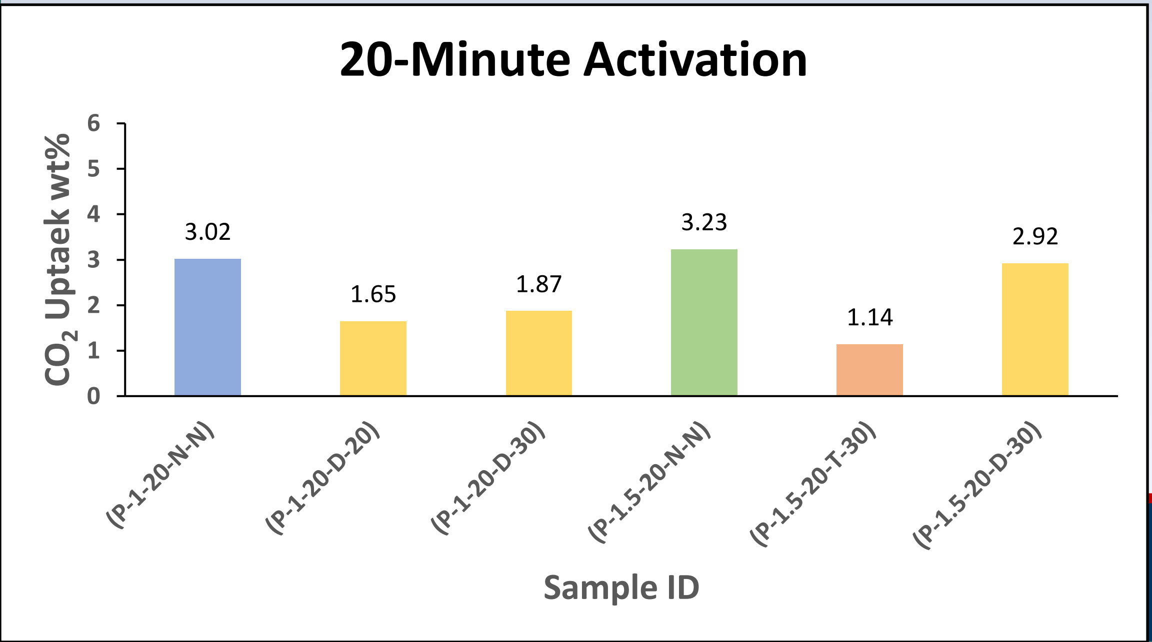


- All unmodified samples outperform their amine-modified counterparts
- Amine samples had significantly lower CO_2 uptakes

Amine Samples

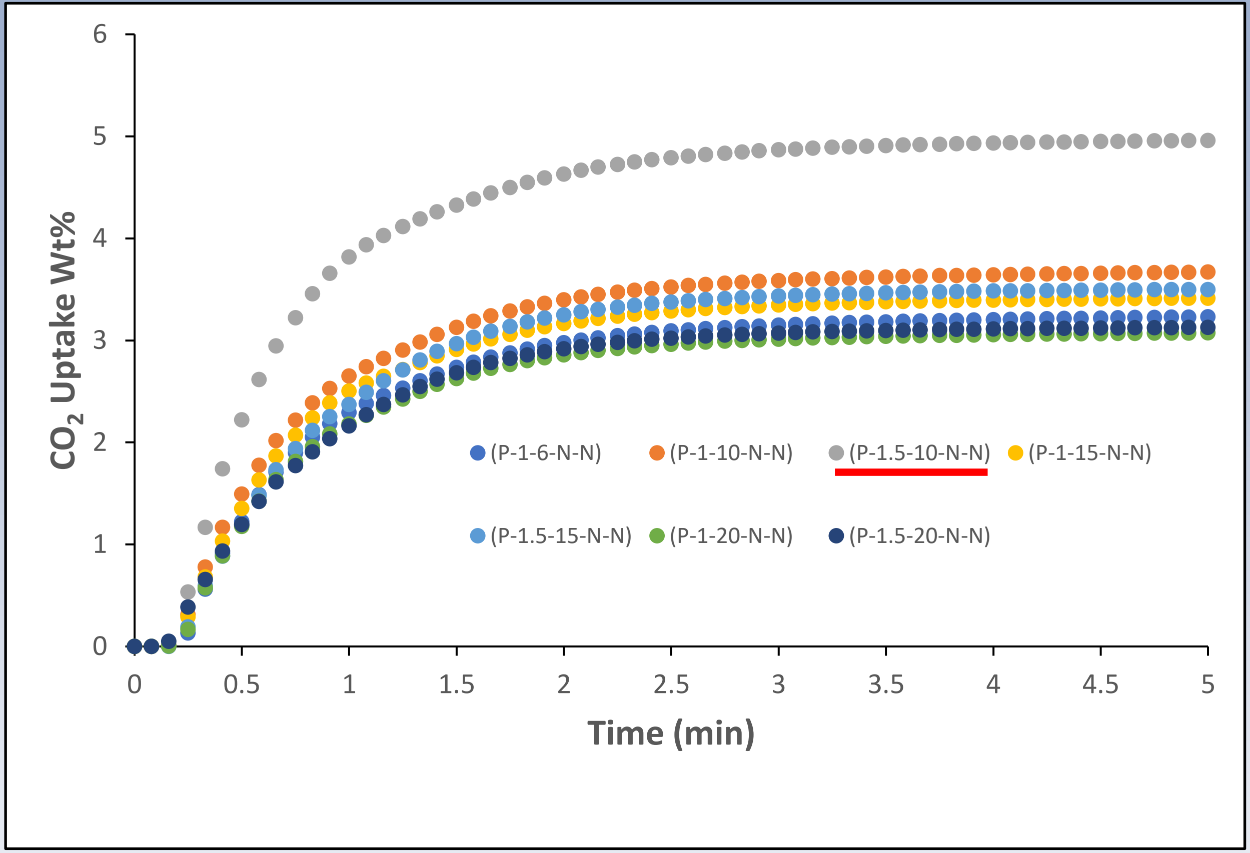


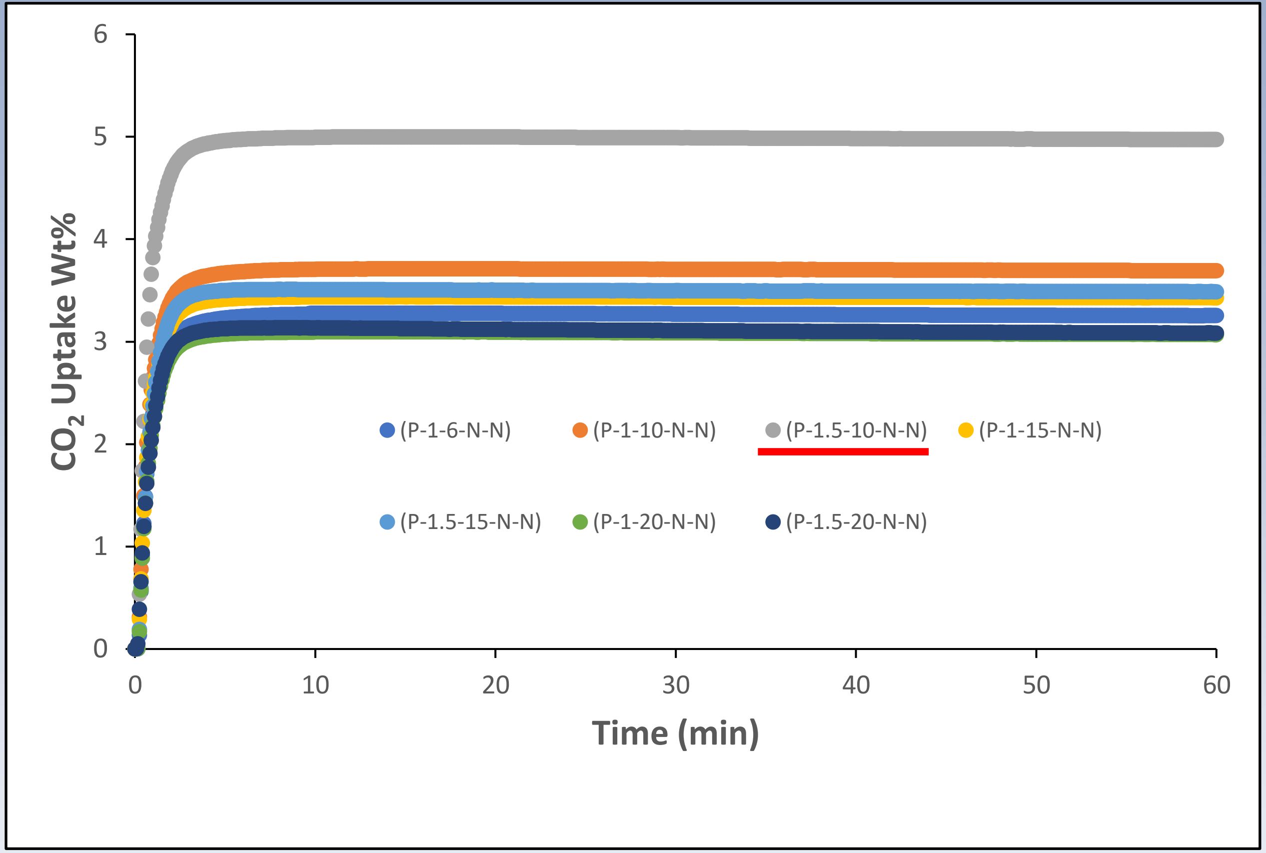




- All unmodified 1.5:1 samples outperformed the 1:1 samples of the same activation duration
- All unmodified samples outperform amine-modified counterparts

CO_2 Adsorption Kinetics

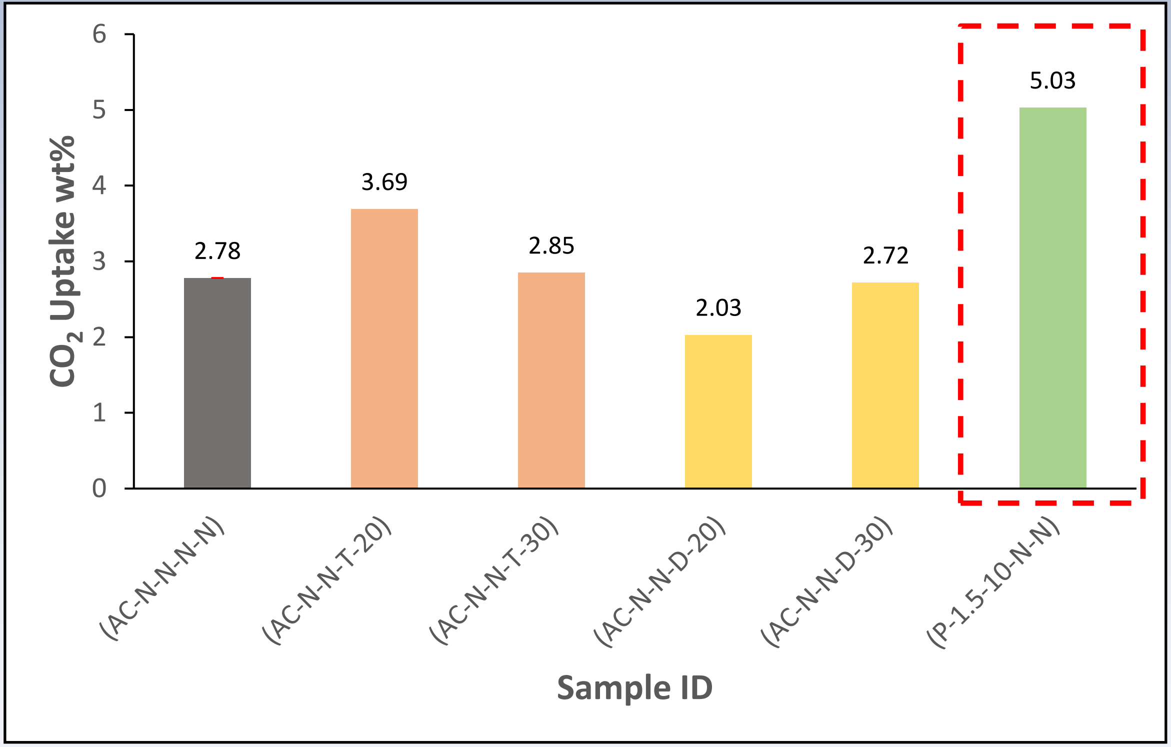


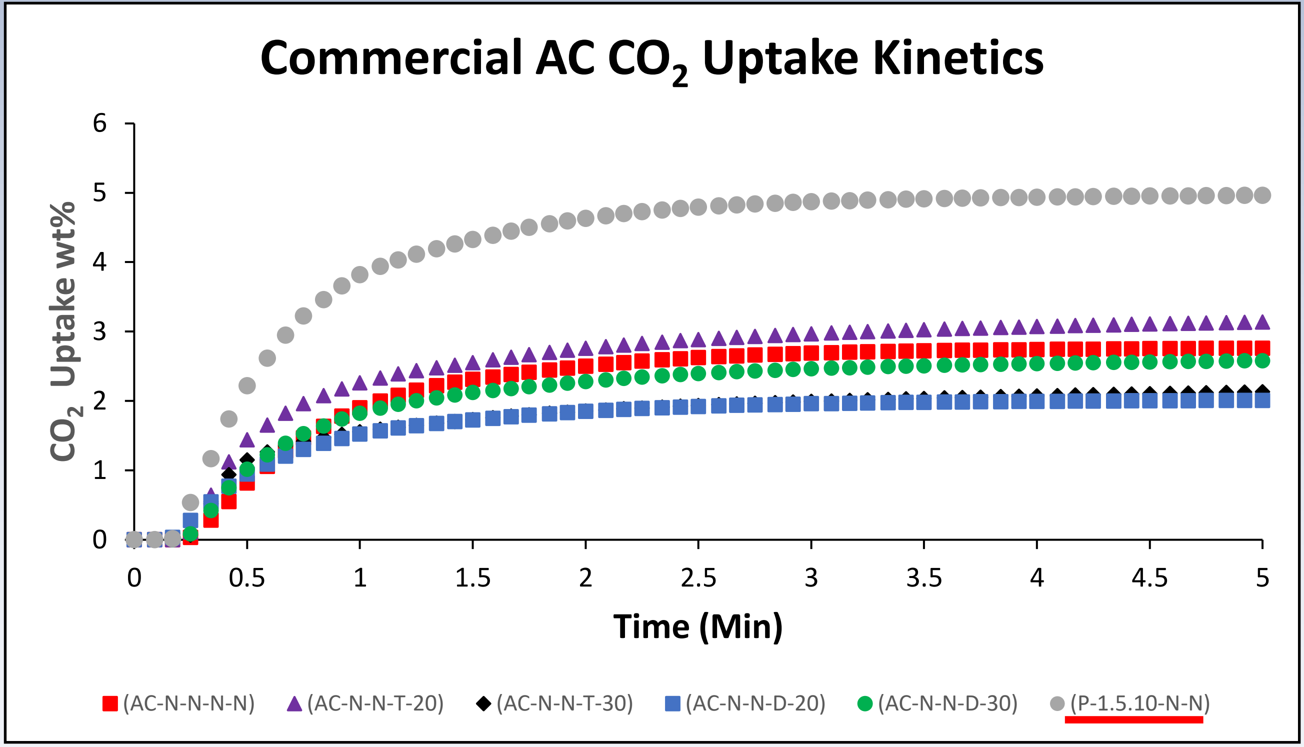


- 1.5:1 KOH samples outperformed their 1:1 KOH counterparts
- All samples reached equilibrium within 2 minutes of CO_2 exposure

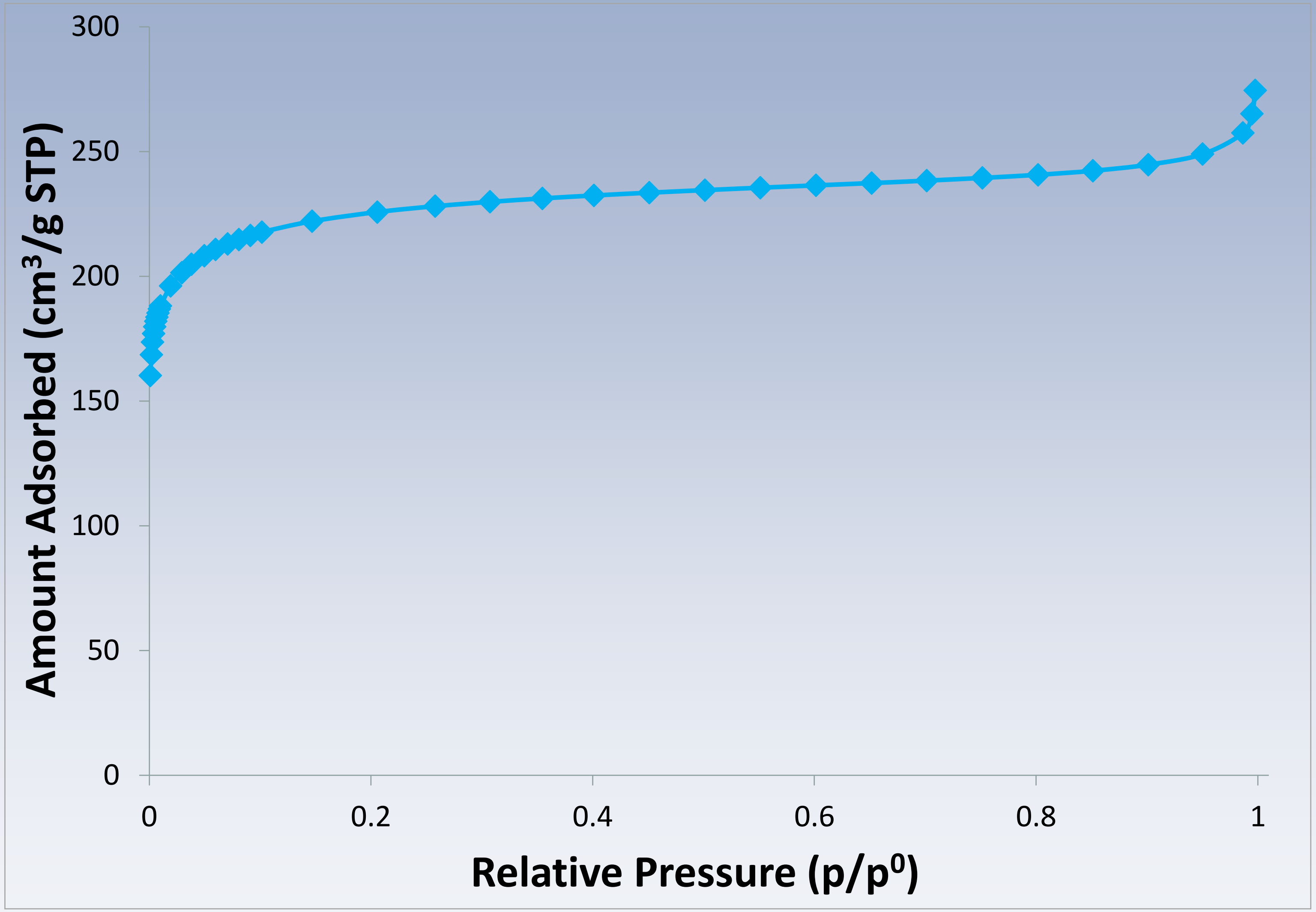
Commercial Activated Carbon Samples

- TEPA modification outperformed unmodified counterpart
- DEA showed no significant increase in CO_2 uptake
- Adsorption kinetics follow the same trend as CO_2 uptake screening





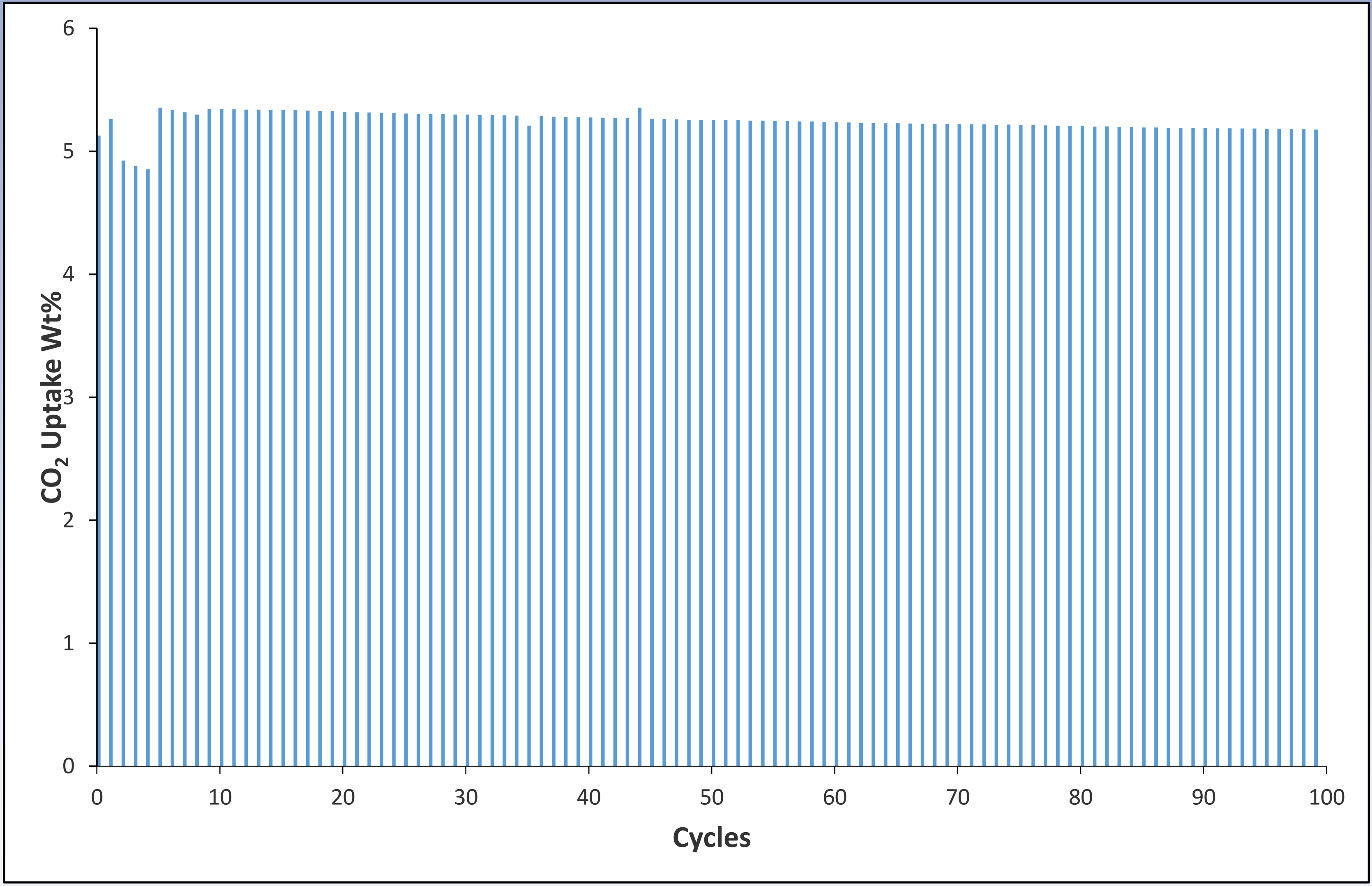
Nitrogen Adsorption Isotherm and Textural Properties



- Type I adsorption isotherm
- BET surface area of 722 m^2/g
- Micropore volume of 0.409 cm^3/g (based on NLDFT)
- Most micropores (0.397 cm^3/g) were smaller than 9.5 Å, which are effective for CO_2 capture
- Total pore volume of 0.444 cm^3/g (based on NLDFT)

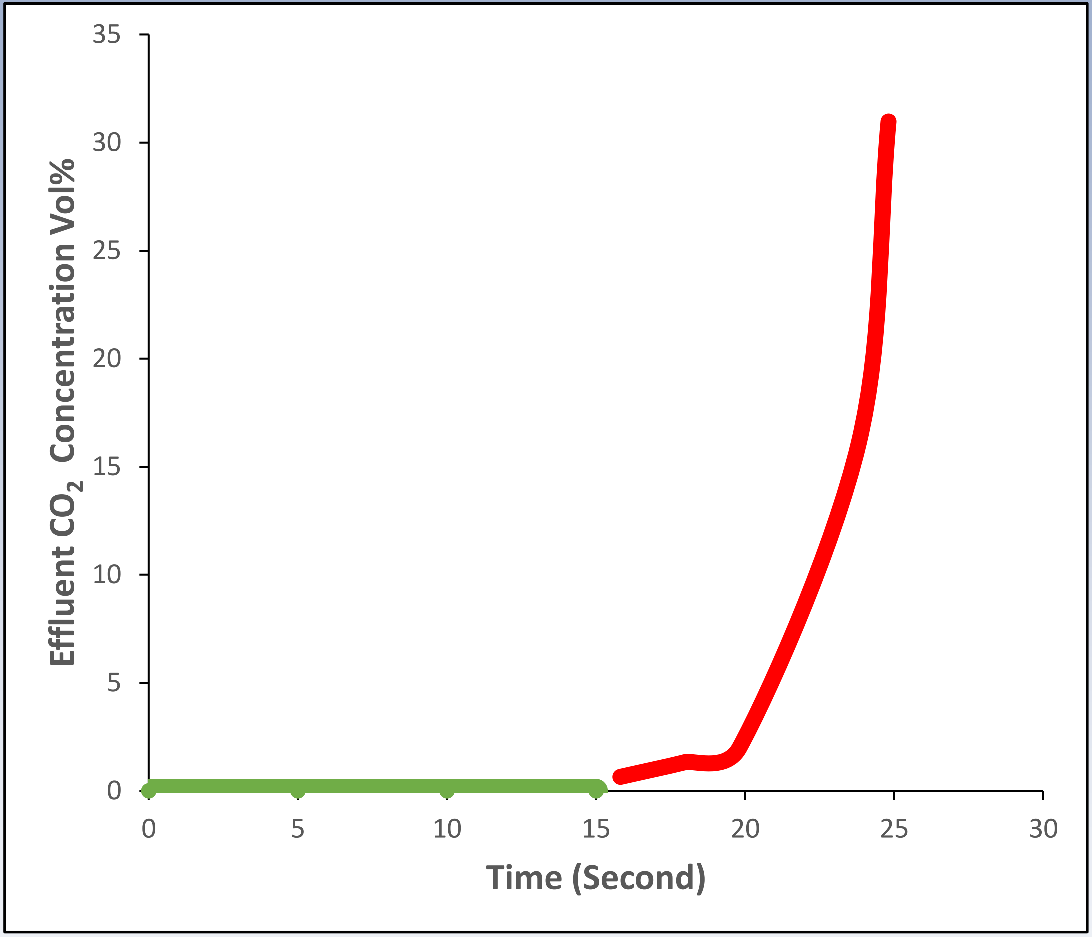
Cyclic Performance Stability (P-1.5-10-N-N)

- Best sample was tested
- Shows regenerative abilities
- 120°C purge temperature
- 5 minute CO_2 cycle time
- Materials CO_2 uptake remained stable after 100 cycles



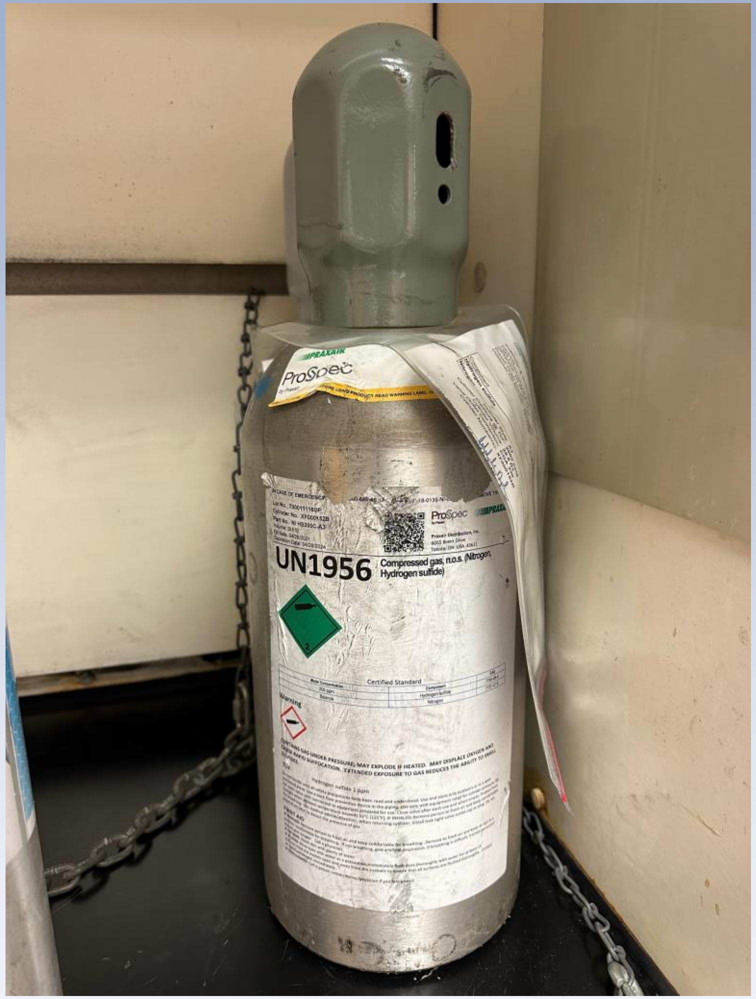
CO_2 Column Breakthrough Test (P-1.5-10-N-N)

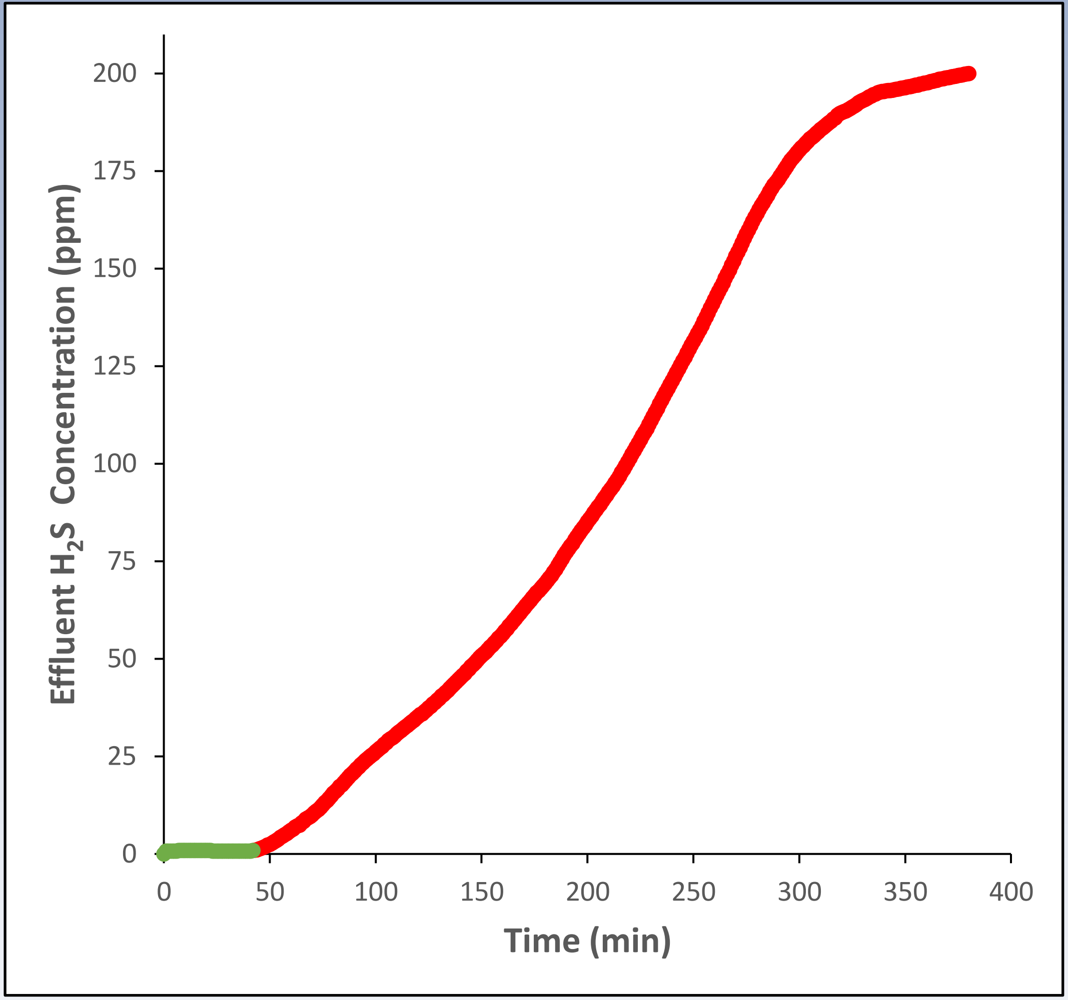
- Commercially available landfill gas (44% CO_2)
- Different gas than TGA data is based on (40% CO_2)
- Tested at 40°C
- Two grams of (P-1.5-10-N-N)
- Flow rate of 1 L/min



H_2S Column Breakthrough Test (P-1.5-10-N-N)

- Feed gas 200 ppmv H_2S in N_2
- Tested at 40°C
- Two grams of (P-1.5-10-N-N)
- Flow rate of 0.5 L/min
- No breakthrough until 42 minutes of exposure





Summary

The objective of purifying landfill gas with a waste-derived activated carbon was investigated.

The activated carbon tested was derived from paper-waste.

Seven samples with equilibrium CO_2 uptake greater than 3% were identified

The best performing candidate showed stable performance over 100 adsorption/desorption cycles

The 1.5:1 KOH sample which underwent 10 minutes of microwave activation and had no amine modification (P-1.5-10-N-N), performed the best across all screenings

Acknowledgements

Florida Department of Environmental Protection

Department of Civil, Environmental and Geomatics Engineering

Air & Waste Management Association
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References

1. https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/national-overview-facts-and-figures-materials
2. https://archive.epa.gov/wastes/conserve/materials/paper/web/html/faqs.html
3. https://lbre.stanford.edu/pssistanford-recycling/frequently-asked-questions/frequently-asked-questions-contamination
4. https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/paper-and-paperboard-material-specific-data
5. https://www.epa.gov/ghgemissions/overview-greenhouse-gases
6. https://www.epa.gov/lmop/basic-information-about-landfill-gas
7. https://www.epa.gov/lmop/project-and-landfill-data-state

THANK YOU FOR LISTENING

Any Questions?