UPISC UNIVERSITY OF PITTSBURGH INFRASTRUCTURE SENSING COLLABORATION WORKSHOP

NATIONAL ENERGY TECHNOLOGY LABORATORY

# Advanced Sensors for In-Situ Amine Degradation Monitoring in Post-Combustion Carbon Capture

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## Introduction

- Reducing the $CO_2$ emissions is paramount to meet the decarbonization goal of net-zero emissions by 2050
  - Post-combustion carbon capture offers a variety of advantages:[1-4]
    1. Retrofitted to existing coal fired power plants
    2. Suitable for natural gas fired power plants
    3. Power generation can be achieved even if the carbon capture process is down for maintenance unlike the pre-combustion process
- Chemical absorption is a widely used post-combustion method[1–4]
  - The most common chemical absorbers are amine-based solvents:
    1. These solvent systems degrade losing carbon capture efficiency over time
    2. Monoethanolamine (MEA) is the most studied
- **Objective**
  - **In situ real-time monitoring of amine degradation will optimize operational control, carbon capture efficiency, and reduce the overall cost**

## Point Source Carbon Capture (PSCC)

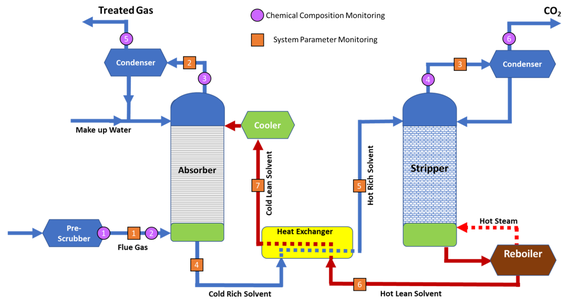


**Figure 1.** Pictorial representation of PSCC system with system parameter and chemical composition monitoring locations indicated.

**Amine Degradation Mechanisms**[1,5-9]
- Oxidative: absorber, cross exchanger
- Thermal: stripper
- Caused by flue gas contaminants

**National Carbon Capture Center (NCCC) Slipstream Solvent Test Unit (SSTU)**

**Problem Statement:** 1) Solvent degradation is hindering large-scale deployment of amine-based carbon capture. Amine solvent degradation associated costs can be significant compared with the cost to monitor. 2) Existing monitoring methods usually involve sampling from the process lines and sending samples to laboratories for analysis using expensive instruments.

## References

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## State-of-the-Art Monitoring

### Physical Parameters

**Table 2.** Physical monitoring parameters for PSCC[2-6]

| Location | Equipment | System Parameter Monitoring |
|---|---|---|
| 1,2,3 | Pressure Gauge | Pressure of Gas and Liquids |
| 1,2 | Volumetric Flow Rate | Rate of Gaseous Flow |
| 4,5,6,7 | Viscosity | Flow Rate of Solvent |
| 4,5,6,7 | Temperature | Temperature of Solvent |

Monitoring locations for Tables 2 & 3 are indicated in Figure 1.

**Technology Gap**
- Cost of analysis instrument
- Periodic sampling
- Point sensing
- Sensitivity to low-concentration degradation products
- Lack of monitoring of trace toxic metals

### Chemical Parameters

**Table 3.** Chemical monitoring parameters for PSCC[2-6] and potential equipment cost[10]

| Location | Equipment | Chemical Composition Monitoring | Potential Cost |
|---|---|---|---|
| 1 | pH Meter | Basicity | $3,000 |
| 1 | UV | $SO_2$, $NO_2$ | $10,000 |
| 1 | Total Organic Carbon Analyzer | $CO_2$ | $3,000 |
| 2,5,6 | FTIR | $CO_2$, $H_2O$, $NH_3$, NO, $NO_2$, $SO_2$, $CH_2O$, $C_2H_4O$, Amines | $100,000 |
| 2,5,6 | NDIR | $CO_2$ | $20,000 |
| 2 | Paramagnetic | $O_2$ | $8,000 |
| 3,4 | GC/MS | $CO_2$, $O_2$, $N_2$, $H_2O$ | $100,000 |
| 3,4 | LC/MS | $CO_2$, $O_2$, $N_2$, $H_2O$ | $50,000 |
| 2,4 | Electric Conductivity | $O_2$ content | $1,000 |
| 5,6 | Single Ion Monitoring | Mass Spectrometry | < $50,000 |
| 5,6 | Electric Low-Pressure Impactor | Aerosol Measurements (Size Distribution and Count) | |

## Key Parameters for Amine Degradation Monitoring

### Direct Monitoring

**Amine Solvent Color Change**[9]
- Amine degradation leads to color changes

**Amine Concentration in Water**[5,8]

**pH Change**[11]
- Indicates $CO_2$ loading; $CO_2$ dissolution into water; heat stable salt neutralization

**Degradation Products Detection**[8]
- Nitrate, sulfate salts, nitrosamine, ammonia gas


**Figure 2.** Examples of an amine solvent system degradation over time.[9]

### Indirect Monitoring

**Temperature Monitoring**[8]
- Related to thermal degradation

**$O_2$ Monitoring**
- Oxidative: absorber, cross exchanger
- $O_2$ concentration: 5-10 ppm in solvents

**Monitoring of Flue Gas Contaminants**
- SOx, NOx, etc.

**Toxic Trace Metal Ion Monitoring**
- Trace Metals: Hg, As, Se, Cr

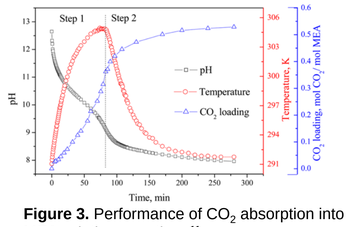



**Figure 3.** Performance of $CO_2$ absorption into MEA solution over time.[11]

## In-Situ Optical Fiber Sensors Installation at NCCC

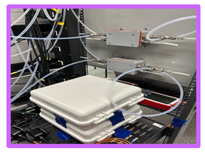
- **Gas Phase:**
  Installed $CO_2$ Sensors
  - 2 Locations
    - Before & After Absorber
- **Liquid Phase:**
  Installed Amine Sensors
  - 4 Locations
    - Cold & Hot Rich
    - Hot & Cold Lean

**Installation of Amine Degradation Sensors onto SSTU in March 2024**

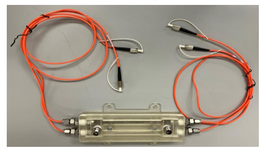
## Optical Fiber $CO_2$ Sensor

### Real-Time Monitoring of $CO_2$ Capture Efficiency

**Original Prototype $CO_2$ Sensor**



**Updated 3D-Printed Prototype $CO_2$ Sensor**



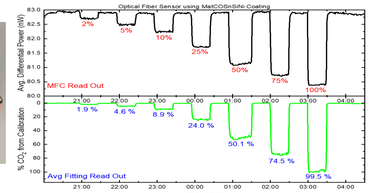



**Figure 4.** $CO_2$ optical fiber sensor calibration.

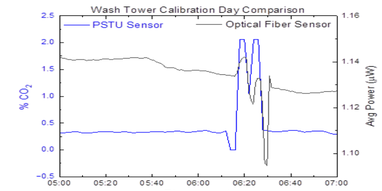


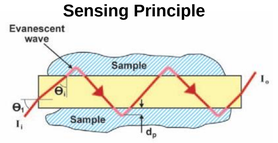

**Figure 5.** $CO_2$ sensing results of Pilot Solvent Test Unit (PSTU) gas flow after absorber and water tower.

- Real-time monitoring of $CO_2$ concentrations in flue gas and after absorber
- Calibrated $CO_2$ sensor in lab
- Upgraded $CO_2$ sensor prototype design using 3D printing
- Blank reference fiber for temperature correction

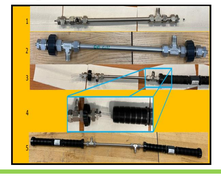
## Optical Fiber Amine Degradation Sensor

### In-situ Monitoring of Amine Degradation

**Sensing Principle**




**Amine Degradation Sensor Prototype**



**Lab Investigation of Amine Degradation Indicators for Quantitative Monitoring**

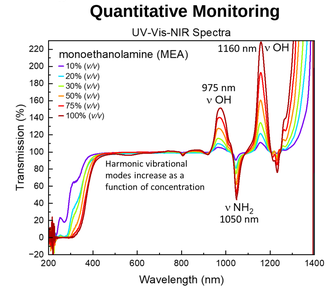



**Figure 6.** UV-Vis-NIR spectra of MEA vs. water content.

## Summary

In-situ monitoring with NETL's sensor capabilities has been developed and deployed into the post-combustion carbon capture streams at National Carbon Capture Center (NCCC). These sensors will provide feedback on the carbon capture efficiency, solvent health, and reduce operational costs.

1. Developed optical fiber-based sensors for amine degradation and $CO_2$ monitoring.
2. Installed optical fiber-based sensors into the slipstream solvent test unit (SSTU) at NCCC.
3. Updated previous $CO_2$ design to 3D-printed $CO_2$ sensor for ease of deployment and reduction in sensing volume.
4. Revised amine prototype design to improve resistance of ferrules to amine exposure.
5. Working on quantitative calibration of amine degradation sensor in the lab.

**Next Steps:**
1. NCCC solvent flow under $CO_2$ capture conditions will resume, following ongoing repairs to the SSTU solvent line.
2. Monitor long-term $CO_2$ capture performance and solvent degradation.
3. Verify optical fiber results against chemical analysis of aliquots and NCCC capture efficiency data.