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)

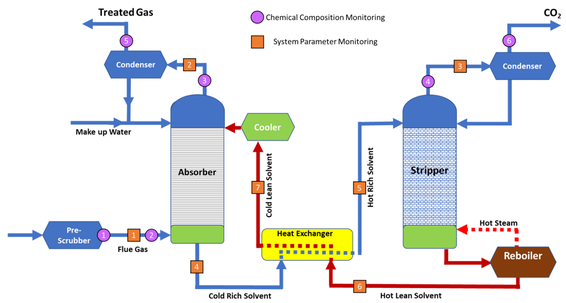

Figure 1. Pictorial representation of PSCC system with system parameter and chemical composition monitoring locations indicated.

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

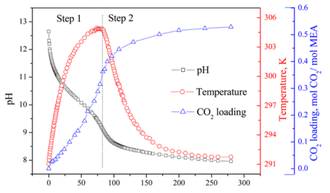


Figure 3. Performance of CO_2 absorption into MEA solution over time.[11]

In-Situ Optical Fiber Sensors Installation at NCCC

➢ **Gas Phase:**
Installed CO_2 Sensors
- 2 Locations
  - Before & After Absorber

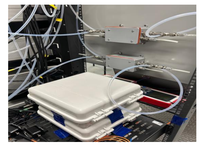
➢ **Liquid Phase:**
Installed Amine Sensors
- 4 Locations
  - Cold & Hot Rich
  - Hot & Cold Lean

Installation of Amine Degradation Sensors onto SSTU in March 2024

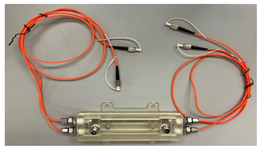
Optical Fiber CO_2 Sensor

Real-Time Monitoring of CO_2 Capture Efficiency

Original Prototype CO_2 Sensor



Updated 3D-Printed Prototype CO_2 Sensor



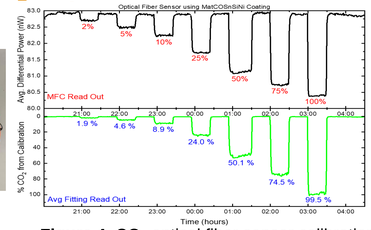


Figure 4. CO_2 optical fiber sensor calibration.

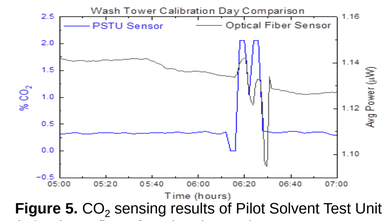


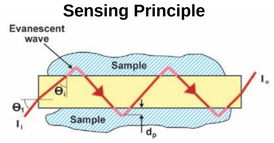
Figure 5. CO_2 sensing results of Pilot Solvent Test Unit (PSTU) gas flow after absorber and water tower.

- 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

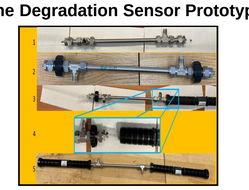
Optical Fiber Amine Degradation Sensor

In-situ Monitoring of Amine Degradation

Sensing Principle



Amine Degradation Sensor Prototype



Lab Investigation of Amine Degradation Indicators for Quantitative Monitoring

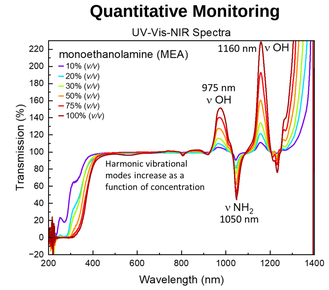


Figure 6. UV-Vis-NIR spectra of MEA vs. water content.

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.