UPISC UNIVERSITY OF PITTSBURGH INFRASTRUCTURE SENSING COLLABORATION WORKSHOP

NATIONAL ENERGY TECHNOLOGY LABORATORY

Review of 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 emission 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 their carbon capture efficiency over time
  2. Monoethanolamine (MEA) being 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)

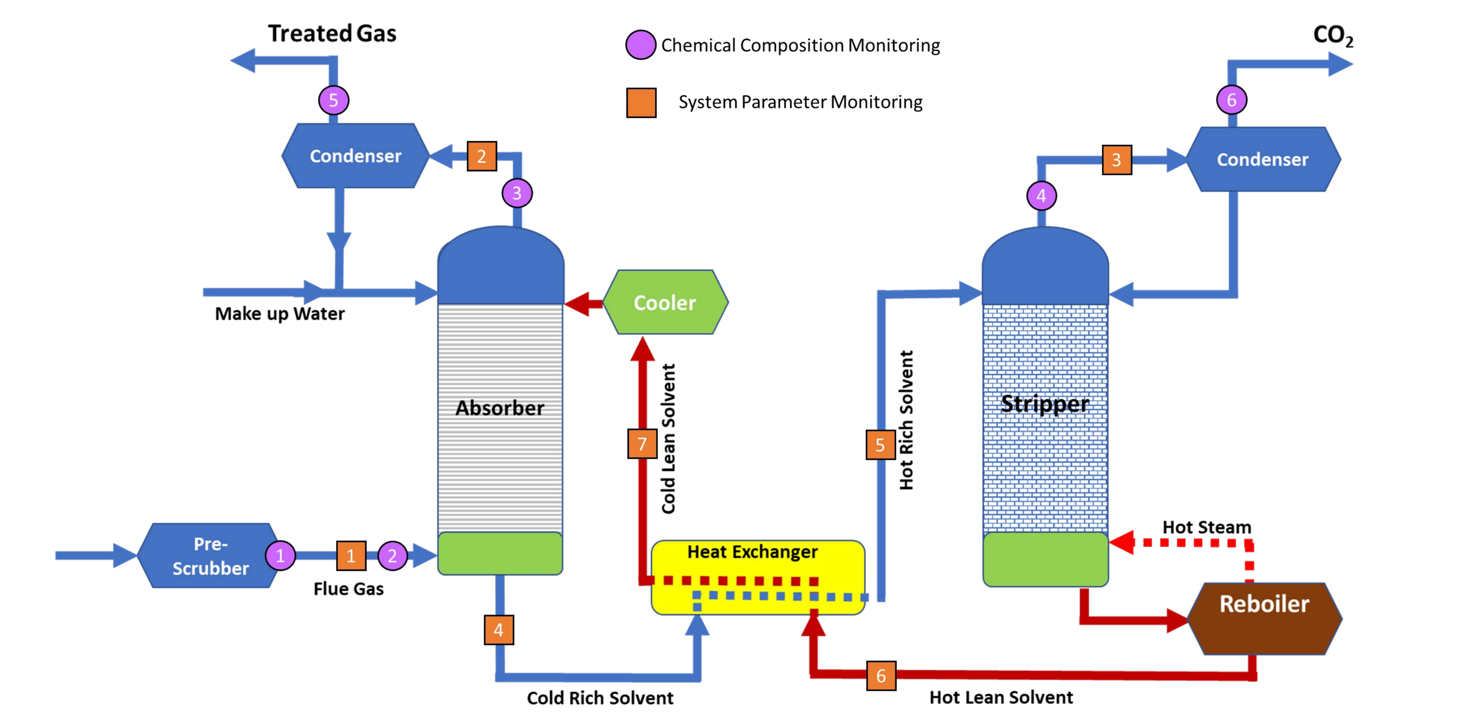

Figure 1. Pictorial representation of PSCC system with system parameter and chemical composition monitoring locations indicated

Amine Degradation Mechanisms[1,5-9]

- Oxidative: absorber, cross exchanger
- Thermal: stripper
- Caused by flue gas contaminants

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.

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Industry Monitoring Necessities

Table 1. Industrial monitoring requirements both current and future

Current Monitoring Requirements	Emerging Monitoring Requirements
• Density of Solvent • Viscosity of Solvent • Temperature • CO_2 Capture Efficiency • Chemical Composition • Pressure • pH • Amine Concentration	• Water Mass Balance • < 1 % Nitrosamine Concentration • NH_3 Concentration in Water Wash • SO_3 Impact on Aerosol • Ammine Carryover • Trace Metal: Mercury, Arsenic, Selenium, Chromium • pH Changes • Following Distinct Functional Groups • Color Change of Solvent • Electrochemical Changes

Technology Gap

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

Table 2. Potential equipment cost for PSCC monitoring[10]

Equipment	Cost ($)
pH Meter/Automatic Titrator	$3,000
UV Gas Sensor	$10,000
Total Organic Carbon Analyzer	$3,000
Fourier-Transform Infrared Spectroscopy (FTIR)	$100,000
Nondispersive Infrared Sensor (NDIR)	$20,000
Paramagnetic O_2 Analyzer	$8,000
Gas Chromatography–Mass Spectrometry (GC/MS)	$100,000
Liquid Chromatography–Mass Spectrometry (LC/MS)	$50,000
Electric Conductivity	$1,000
Single Ion Monitoring	< $50,000
Electric Low-Pressure Impactor	Aerosol Measurements (Size Distribution and Count)

Hardware Concerns

- Direct component analysis is prohibitively expensive
- Multiple sites need to be monitored continuously
- Self-contained systems are preferred due to hazardous solvent/contaminant properties
- Hardware must be capable of running on multiple month timescale

State of the Art Monitoring

Physical Parameters

Table 3. 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 Table 2 and Table 3 are indicated in Figure 1.

Chemical Parameters

Table 4. Chemical monitoring parameters for PSCC[2-6]

Location	Equipment	Chemical Composition Monitoring
1	pH Meter	Basicity
1	UV	SO_2, NO_2
1	Total Organic Carbon Analyzer	CO_2
2,5,6	FTIR	CO_2, H_2O, NH_3, NO, NO_2, SO_2, CH_2O, C_2H_4O, Amines
2,5,6	NDIR	CO_2
2	Paramagnetic	O_2
3,4	GC/MS	CO_2, O_2, N_2, H_2O
3,4	LC/MS	CO_2, O_2, N_2, H_2O
2,4	Electric Conductivity	O_2 content
5,6	Single Ion Monitoring	Mass Spectrometry
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

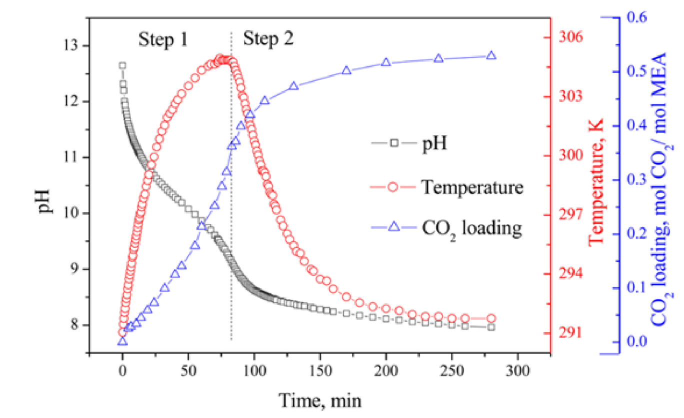

Figure 3. Performance of CO_2 absorption into MEA solution over time[11]

NETL Sensor Capabilities

Long-distance Distributed Optical Fiber Sensors

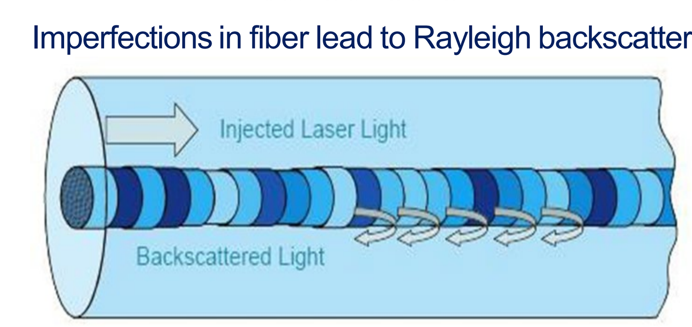

Figure 4. Fiber optic representation of Rayleigh backscattering

Passive Wireless Surface Acoustic Wave Sensors

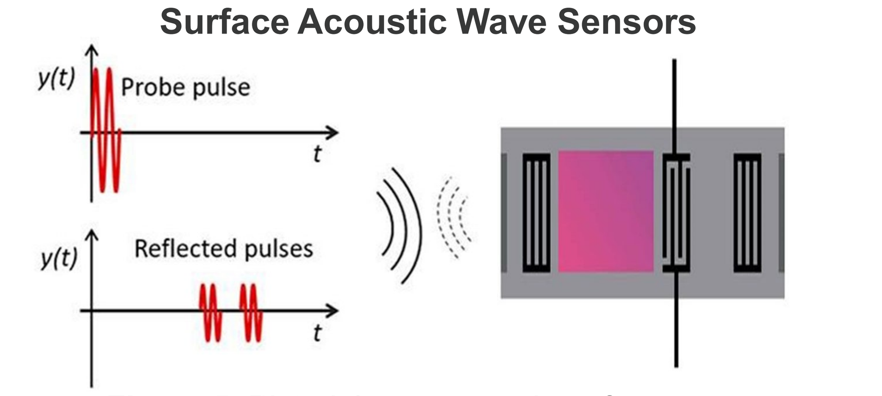

Figure 5. Pictorial representation of a surface acoustic wave sensor

Electrochemical Sensors

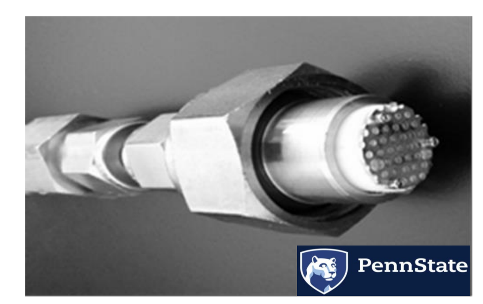

Figure 6. Picture of electrochemical sensor

LIBS: Laser Induced Breakdown Spectroscopy

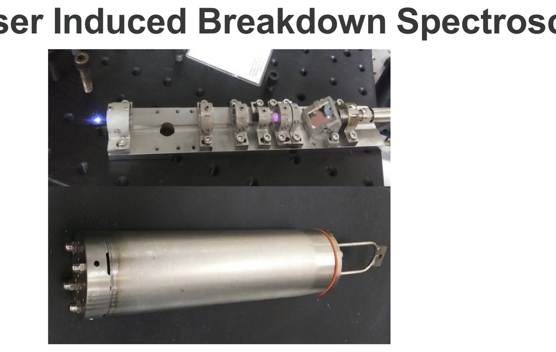

Figure 7. Picture of a LIBS probe

Summary

In-situ monitoring with NETL's sensor capabilities can be developed for deployment into the post-combustion carbon capture streams. These sensors will provide feedback on the carbon capture efficiency, solvent health, and reduce operational costs.

Project Achievement:
1. Identified key indicators for amine degradation as sensing targets.
2. Surveyed and selected low-cost existing sensor technologies for these targeted indicators, instead of expensive full-on laboratory chemical analysis
3. Interviewed industry stakeholders such as The National Carbon Capture Center (NCCC) and Ion Clean Energy to learn the monitoring needs for post-combustion carbon capture process.
4. A report is prepared on monitoring needs, sensor technology survey, and recommendation for cost-effective online monitoring of amine degradation

Next Step:
Pilot-scale testing of NETL-developed optical fiber sensors for amine degradation and CO_2 monitoring at NCCC.