

Review of Sensors for In-Situ Amine Degradation Monitoring in Post-Combustion Carbon Capture

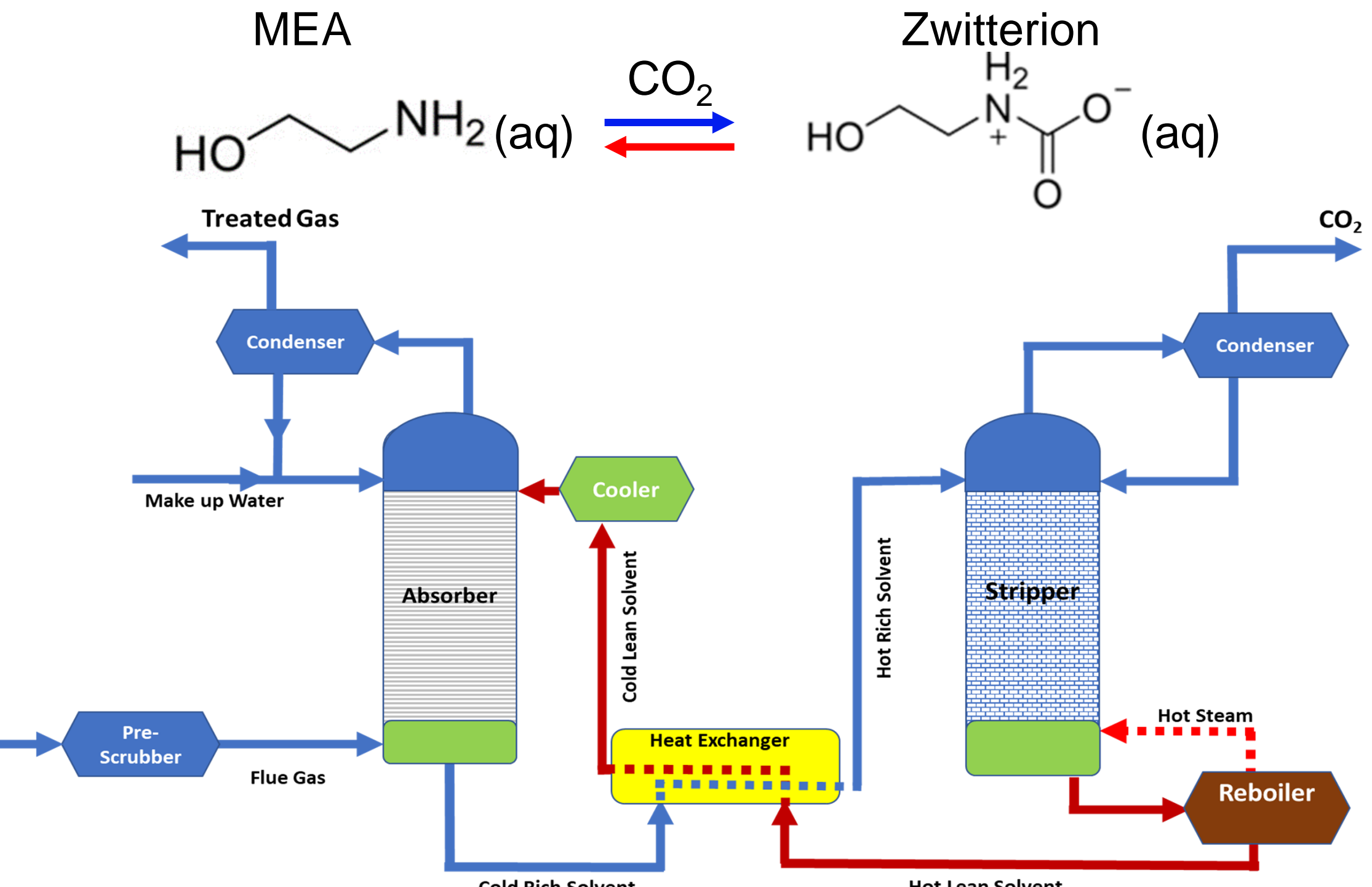
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Introduction

- Carbon dioxide emission comes from the chemical combustion process
 - A human-made source is produced in fossil-fuel power plants
- Reducing the CO₂ emissions is paramount
 - Post-combustion carbon capture offers a variety of advantages:
 - Retrofitted to existing coal fired power plants
 - Suitable natural gas fired power plants
 - Power generation can be achieved even if the carbon capture process is down for maintenance
- Chemical absorption is a widely used post-combustion method¹⁻⁴
 - The most common chemical absorbers are amine-based solvent
 - Monoethanolamine (MEA) being the most studied
- Solvent system degrades losing its carbon capture efficiency over time
 - Identifying key indicators of amine solvent degradation will optimize operational control and carbon capture efficiency

Point Source Carbon Capture (PSCC)



- ### Amine Degradation Mechanisms
- Oxidative degradation
 - Absorber and heat exchanger
 - Thermal degradation
 - Stripper
 - Degradation can be caused by flue gas contaminants
 - SO_x, NO_x, halogenated compounds, hydrocarbons, and other impurities

- ### Amine Degradation Consequences
- Increase the solvent viscosity and surface tension
 - Lead to corrosion, fouling, and foaming
 - Reduce capture capacity and efficiency
 - Increase costs
 - Monitoring: send samples to laboratories
 - Replenishment of chemicals
 - Equipment and maintenance

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Key Parameters for Degradation

Direct Monitoring

- #### Amine Solvent Color Change
- Colorless
 - Pure amines
 - Yellow coloration
 - Cyclization, dealkylation, oxidation, oligomerization or coupling
 - Dark brown coloration
 - Heat stable salt formation
- #### Amine Concentration in Water
- Viscosity/flow rate, dielectric constant, electrical conductivity
- #### pH Change
- Indicates CO₂ loading; CO₂ dissolution into water; heat stable salt neutralization
 - Amine performance indication



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

- #### Degradation Products Detection
- Nitrate, sulfate salts, nitrosamine, ammonia gas

Indirect Monitoring

- #### Temperature Monitoring
- In the stripper, 100 °C – 160 °C are typical operation temperatures (T) for various amine absorbents
 - Degradation increases significantly when T increases
 - In the absorber, T changes at different CO₂ loading, and can be used for amine absorption efficiency indicator
- #### O₂ Monitoring
- Oxidative: absorber, cross exchanger
 - O₂ concentration: 5-10 ppm in solvents
- #### Monitoring of Flue Gas Contaminants
- SO_x, NO_x, etc.
- #### Toxic Trace Metal Ion Monitoring
- Trace Metal: Hg, As, Se, Cr

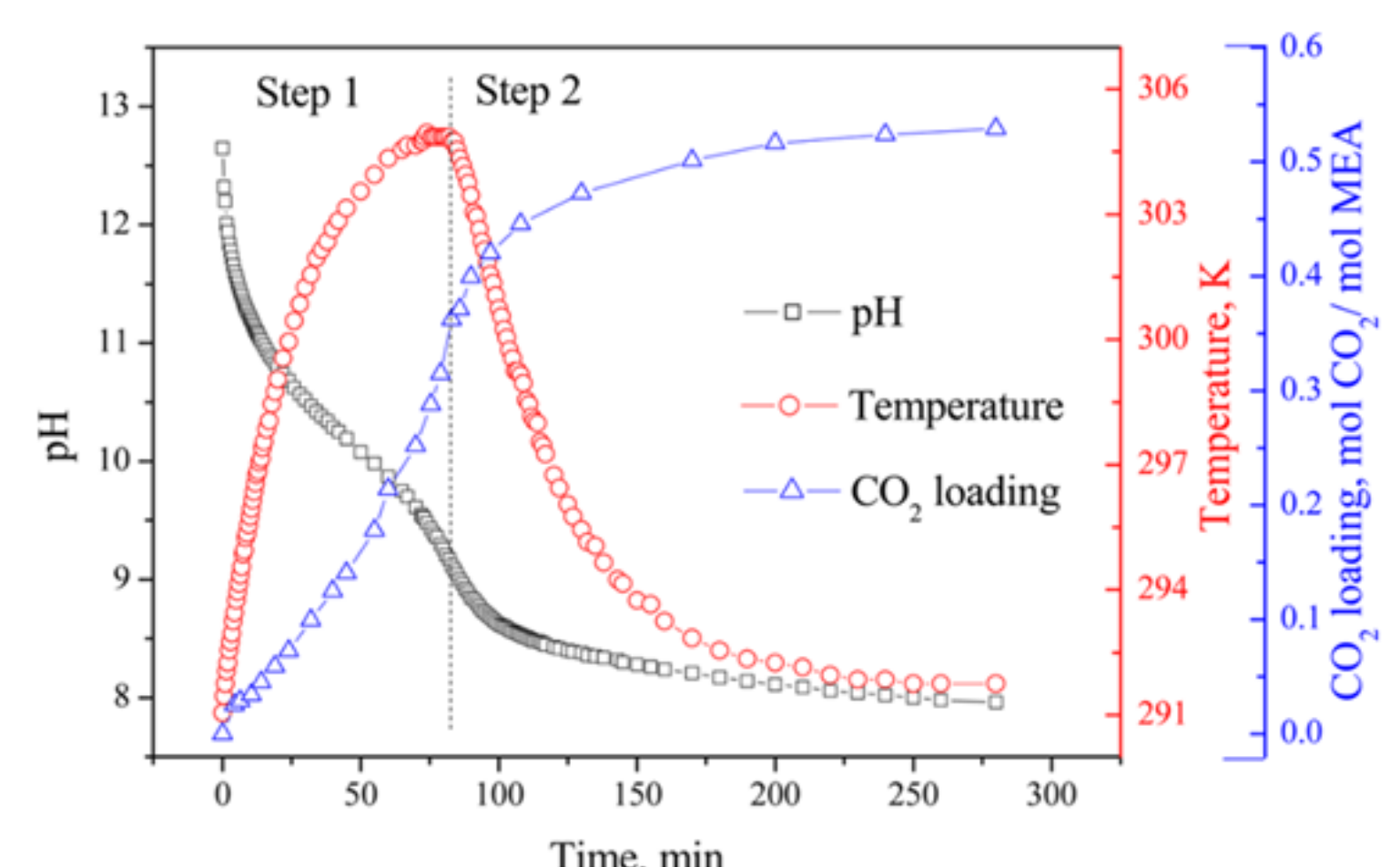


Figure 3. Performance of CO₂ absorption into MEA solution over time.¹³

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pH Monitoring

- pH sensing optical fiber for distributed measurements
- Three current options for pH sensitive coatings based on conditions
 - Oxides and calcined pH sensitive polymer coatings

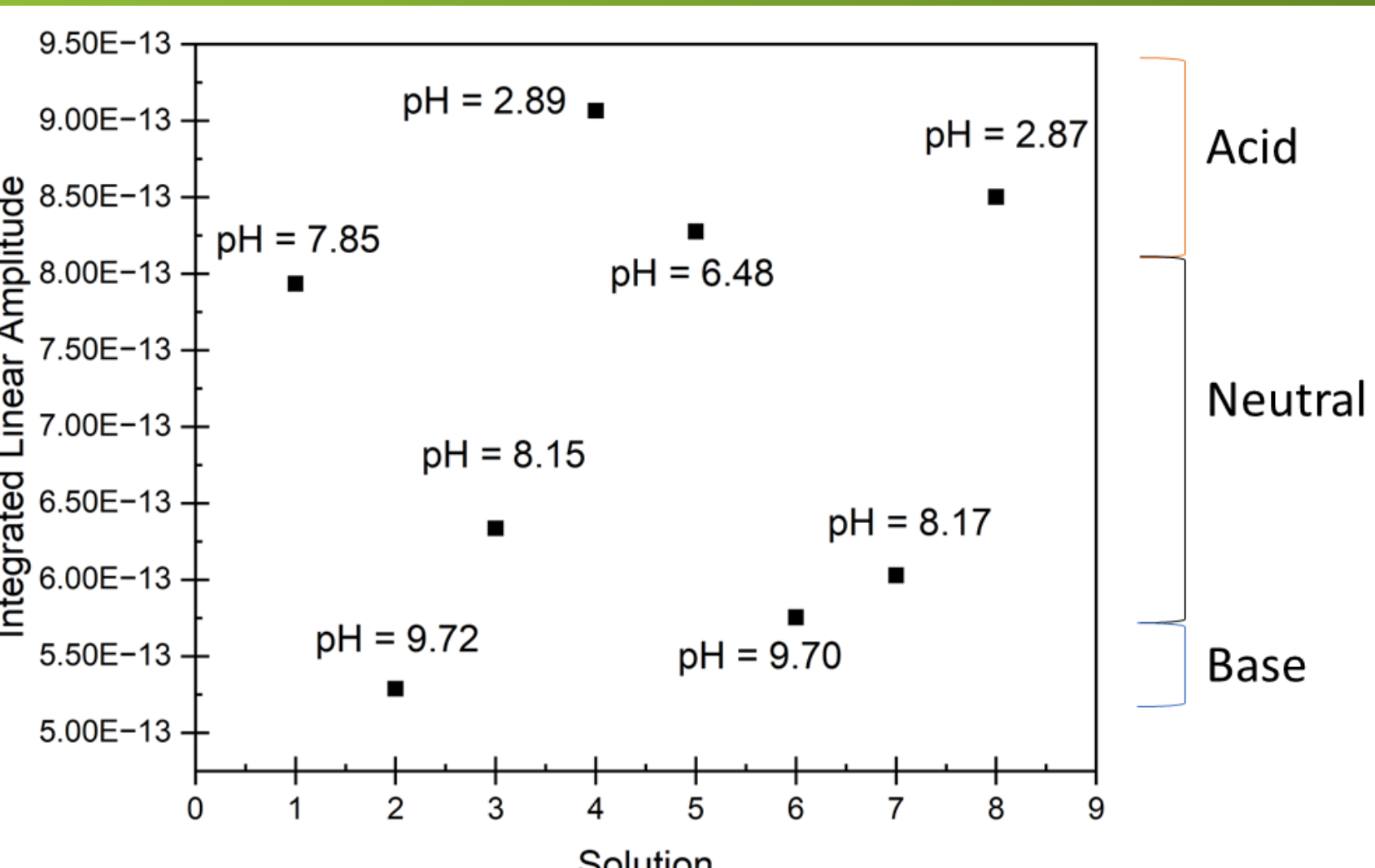


Figure 4. Distributed pH Monitoring at 80 °C.

Colorimetric Analysis

- ### 30% v/v MEA
- CO₂ bubbled for two days and heated at 40 °C
 - Heated for two days at 120 °C
 - 300-600 nm changes in reflection
- Colorimeter operates on reflected light through a bifurcated fiber bundle
 - Glass fiber sensor tip is heat and chemically resistant at capture system conditions

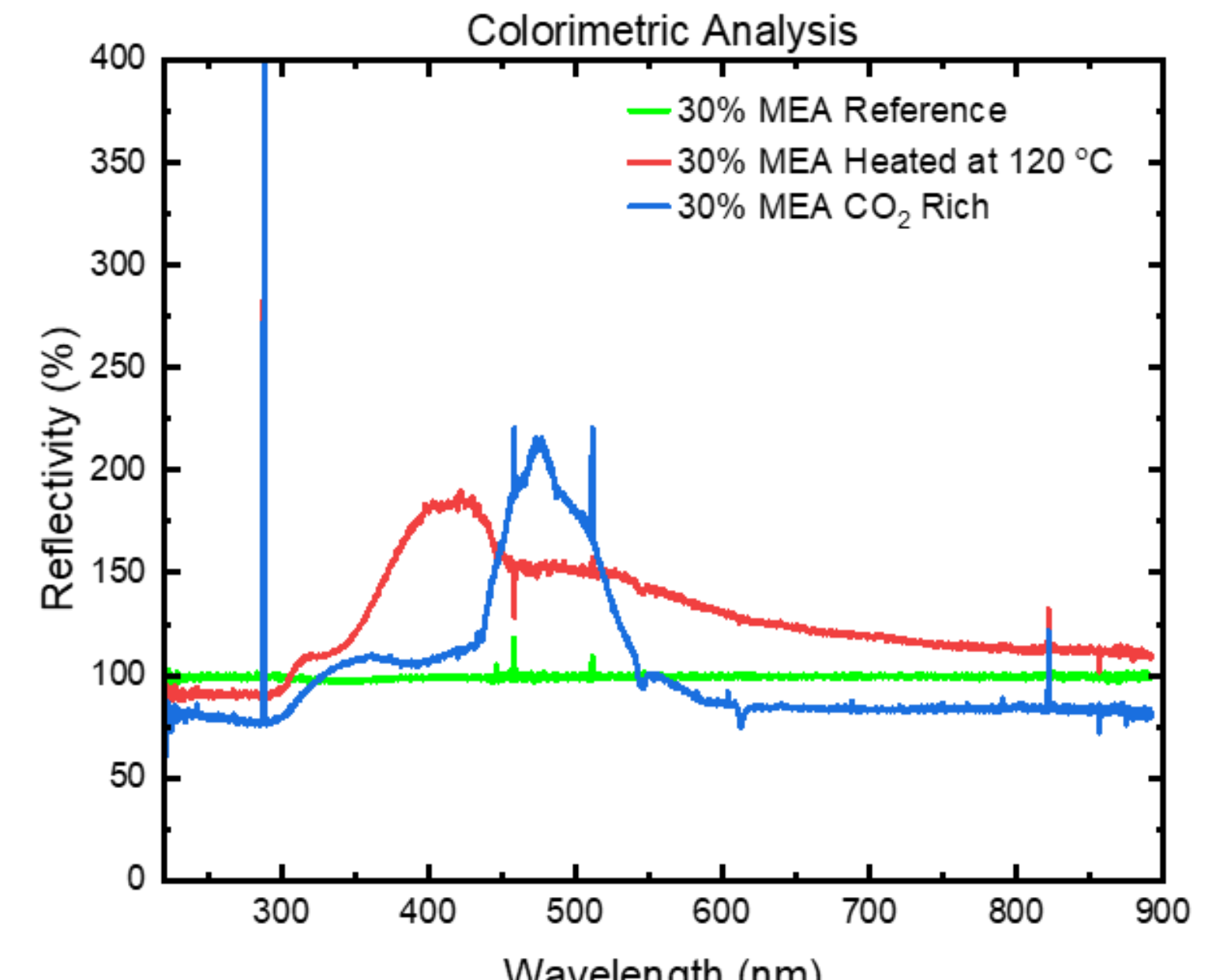


Figure 5. Colorimetric analysis of 30% MEA.

CO₂ Monitoring

- Sorbent matrix coated optical fiber gas sensor
- Good selectivity of CO₂ over other atmospheric gases
- Reversible sensing with rapid response time

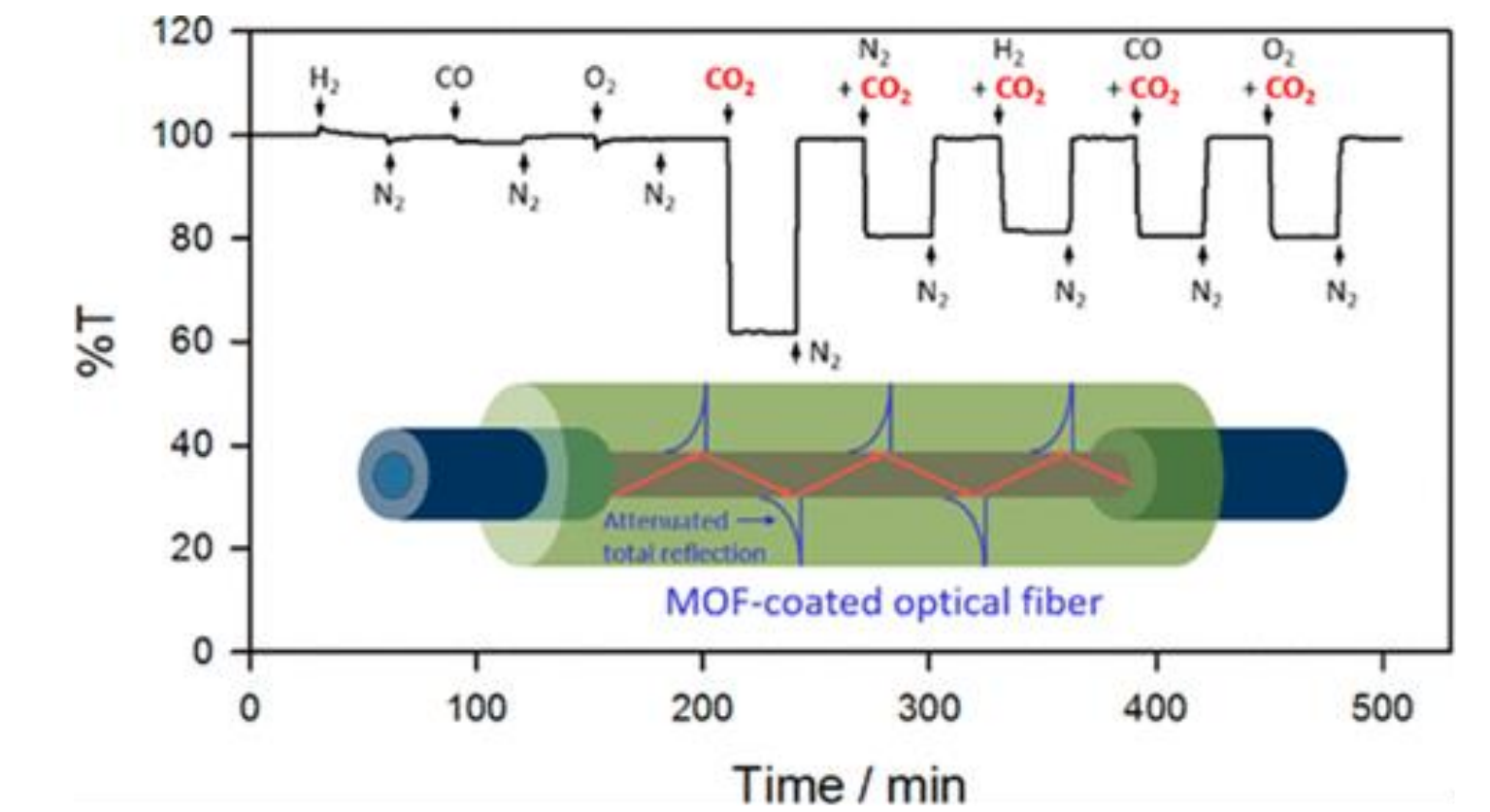


Figure 6. Pictorial representation of a coated MOF optical fiber sensing for carbon dioxide.¹⁰

Summary

- In-situ monitoring with fiber optic sensors can be developed for deployment into the post-combustion carbon capture streams (CO₂ Monitoring, Colorimetric Analysis, and pH Monitoring)
- These sensors will:
 - Reduce operational costs
 - Provide feedback on the carbon capture efficiency and solvent health through:
 - Monitoring the CO₂ capture efficiency in multiple location both in aqueous and gas phase
 - Evaluation of the degradation of the amine solvent system as the color changes
 - Monitoring the loading and unloading of CO₂ for the amine solvent system as the pH changes through cyclization between the absorber and stripper