# Safeguarding Amines from Oxidation by Enabling Technologies

## primary project goal

The University of Texas at Austin is developing technologies to safeguard amine-based carbon dioxide ($CO_2$) capture processes from solvent loss by oxidation. The project team is evaluating strategies to minimize amine oxidation in advanced second- and third-generation solvents caused by two of the most significant impurities: oxygen and nitrogen dioxide ($NO_2$). These effective technologies will reduce the cost and environmental risk of solvent-based carbon capture systems by addressing the effects of flue gas impurities on solvent loss and will make significant progress toward achieving $30/tonne of $CO_2$ captured by 2030.

## technical goals

- Develop technology to overcome amine oxidation processes which includes nitrogen sparging, optimizing time and temperature with dissolved oxygen, optimizing time and temperature at the bottom of the stripper, and in the presence of adsorbed soluble iron.
- The technology will support capture using second- and third-generation solvents from fossil fuel-fired power plants.
- Baseline experiments will consist of gas-fired turbine conditions using 5 molar (m) piperazine and the advanced flash stripper (PZAS). Further experiments will extend this work to hydroxyl-ethyl-piperazine (HEP), the blend of amino-methyl-propanol (AMP)/PZ, and other amines.

## technical content

The University of Texas at Austin has been developing a $CO_2$ capture process (PZAS) using 5 m (30 wt%) PZ with the advanced flash stripper (AFS) (Figure 1). This solvent and process (PZAS) serves as the baseline for this project on solvent loss. Five molar PZ absorbs $CO_2$ two times faster and has 1.36 times greater capacity than 30 wt% monoethanolamine (MEA). The AFS requires 15–20% less heat than a simple stripper. The PZAS system has been demonstrated at National Carbon Capture Center (NCCC) coal conditions (0.5 megawatt [MW]) and natural gas combined cycle (NGCC) conditions (0.3 MW) to require a heat duty less than 2.1 gigajoules (GJ)/tonne $CO_2$ removed.

The PZAS process is representative of second-generation amine scrubbing technology for $CO_2$ capture. It is fully published and represents a valuable case study with results that will be useful for proprietary second-generation processes, such as those offered by MHI and Shell/Cansolv. This technology sheet describes general approaches to minimizing oxidation and addresses the specific objectives of this project.

**program area:**
Point Source Carbon Capture

**ending scale:**
Small Pilot

**application:**
Post-Combustion Power Generation PSC

**key technology:**
Solvents

**project focus:**
Reduce Solvent Loss in Amine-Based $CO_2$ Capture Processes

**participant:**
University of Texas at Austin

**project number:**
FE0031861

**predecessor projects:**
N/A

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**start date:**
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**percent complete:**
58%

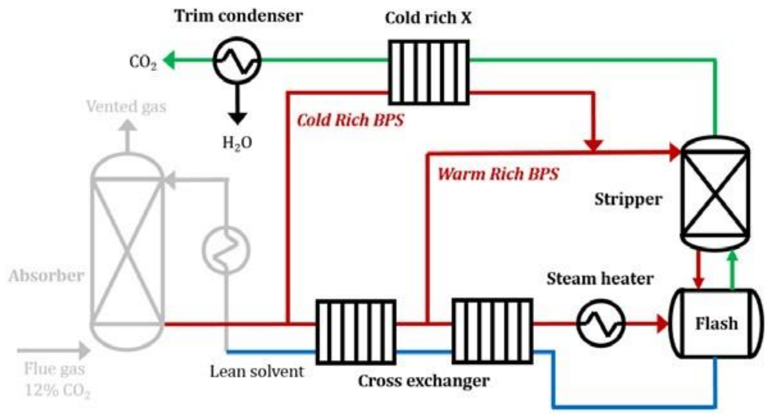


Figure 1: PZAS process.

Early bench-scale work showed that MEA, ethylenediamine, and other amines readily oxidize at 40–60°C when there is sufficient mass transfer to dissolve 0.05–0.21 bar oxygen ($O_2$) and some dissolved iron to initiate the free radical reaction. A necessary prerequisite for low oxidation is to select amines resistant to oxidation at 40–60°C. MHI, Shell/Cansolv, and other developers of second-generation amines have claimed that their solvents are resistant to oxidation. This project will evaluate PZ, HEP, and AMP/PZ, which have previously been shown to be resistant to oxidation.

Figure 2 shows the oxidation rate of PZ in four pilot plants as the accumulation of nitrogen degradation products. An important objective of this proposed work is to understand why there is less oxidation at the University of Texas Separations Research Program (UT-SRP) and NCCC-AFS so that those conditions can be applied to reduce oxidation at other sites, with other solvents, and with other process configurations. Four features may be responsible for low oxidation and represent opportunities that can be used commercially:

- There was no $NO_2$ in the flue gas at SRP and NCCC-AFS, so eliminating $NO_2$ may be an effective method of minimizing oxidation.
- The AFS provides flashing of the hottest solvent that removes dissolved oxygen before it reaches the maximum time and temperature in the stripper sump.
- The average residence time of hot lean solvent in the stripper sump is less than two minutes at UT-SRP and NCCC-AFS, which may minimize oxidation of amine by $Fe^{+3}$.
- Dissolved iron was less than 0.02 micromoles (mM) at UT-SRP and less than 0.10 parts per million (ppm) at NCCC-AFS.

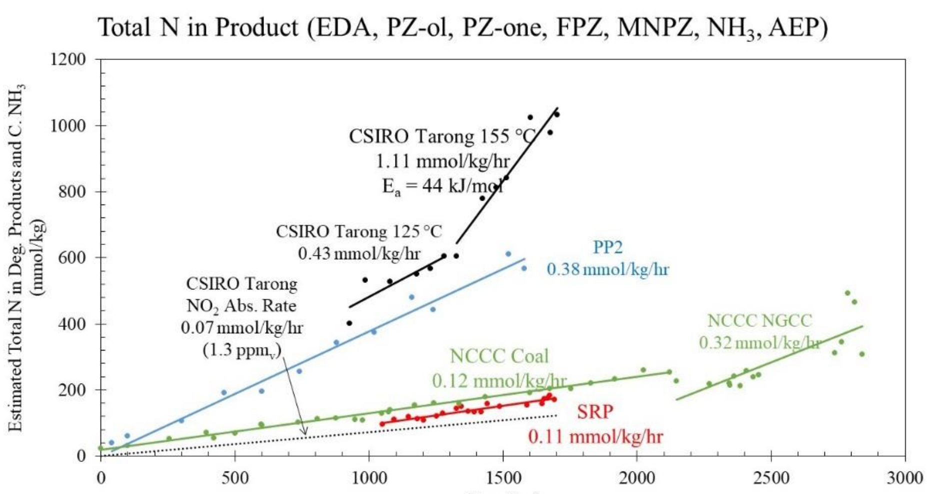


Figure 2: Total nitrogen quantified in degradation products and estimated cumulative ammonia at SRP, PP2, Tarong, and NCCC.

If an amine is resistant to oxidation at absorber conditions, rich solvent leaving the absorber sump will be saturated with oxygen at the absorber temperature (T) and $P_{O2}$. When heated to stripper T in the cross exchanger, the faster kinetics at elevated T will result in oxidation in the rich line before the dissolved oxygen is removed by stripping or flashing. Researchers have demonstrated that PZ and methyldiethanolamine (MDEA)/PZ will oxidize by this mechanism.

The University of Texas at Austin has demonstrated, using bench-scale testing, that nitrogen sparging in the rich solvent can reduce oxidation by a factor of 3.5–4.5 when the rich solvent is exposed to 150°C for 30 seconds without prior stripping (Figure 3). These results also establish that oxidation requires residence time at elevated temperatures and would be negligible at absorber T. It appears that oxidation could be reduced by operating the stripper at lower temperatures.

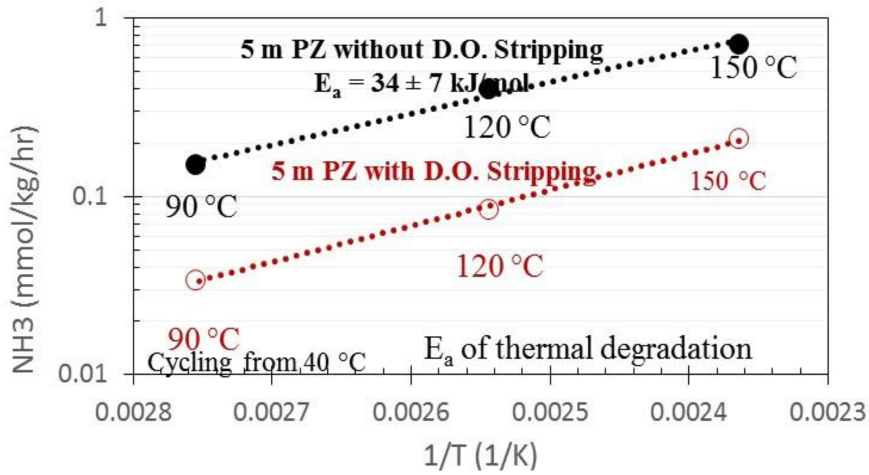


**Figure 3: $N_2$ sparging reduces oxidation in high-temperature oxidation reactor (HTOR) by a factor 3.5–4.5. Cycling from 40°C with 0.1 mmol $Fe^{+2}$/kg. At 40°C absorption/40°C stripping, the ammonia ($NH_3$) production rate (0.025 mmol/kg-hr) would be negligible. (Nielsen, 2018)**

In a pilot plant or larger-scale system, it is probable that oxidation by dissolved oxygen will occur in the hot liquid holdup between the cross exchanger and the top of the stripper where the oxygen will be removed. With a typical commercial simple stripper, the holdup in the rich feed line could be 40 sec (200 ft of pipe at 5 ft/s). However, in advanced configurations such as the AFS, the rich solvent feed can be 10–25°C colder than the stripper sump, thus reducing the oxidation rate by this mechanism, as seen at UT-SRP (Figure 2).

## technology advantages

- Create environmentally friendly solvent processes for $CO_2$ capture.
- Safeguard second- and third-generation solvents from $O_2$ and $NO_2$ oxidation, reducing solvent degradation and extending solvent lifetime.

## R&D challenges

- Using research and development (R&D) corrosion loop test results to design SRP pilot modifications for residence time tests.

## status

The University of Texas at Austin developed an ultraviolet visible (UV-Vis) measurement technique as a method for evaluating metal ion (iron) species in amine solvents. Their experimental data allowed them to estimate adsorption rates and isotherms for PZ oxidation products on carbon in degraded samples. During this work, researchers also designed and developed new corrosion loop test skid and designed SRP pilot modifications for residence time tests. The project conclusions on $Fe^{+2}$/$Fe^{+3}$ was the $Fe^{+3}$ solubility in PZ varies solvent degradation from 0.02–2 mM. Carbon bed treatment reduced ammonia ($NH_3$) production at the NCCC and in HTOR. Carbon bed treatment removed 3 mM of "soluble" iron from the NCCC solvent system. All the "soluble" Fe must be removed to reduce oxidation. Carbon bed treatment also removed PZ degradation products that adsorb at 320 and 540 nm. In addition, greater than 0.01 m PZ protects carbon steel from corrosion at the absorber temperature.

## available reports/technical papers/presentations

Rochelle, G., "Safeguarding Amines from Oxidation by Enabling Technologies," Presented at 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 13, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Rochelle_amine.pdf*

Rochelle, G., Closmann, F., "Safeguarding Amines from Oxidation by Enabling Technologies," Budget Period 1 Review Meeting presentation, Pittsburgh, PA, May 10, 2021. *https://netl.doe.gov/projects/plp-download.aspx?id=10928&filename=Safeguarding+Amines+from+Oxidation+by+Enabling+Technologies.pdf*.

Closmann, F., "Safeguarding Amines from Oxidation by Enabling Technologies," Project kickoff meeting presentation, Pittsburgh, PA, June 10, 2020. *https://netl.doe.gov/projects/plp-download.aspx?id=10927&filename=Safeguarding+Amines+from+Oxidation+by+Enabling+Technologies.pptx*.