Reducing the Degradation of Carbon Capture Solvents

primary project goal

Pacific Northwest National Laboratory (PNNL) is conducting research to mitigate common mechanisms of solvent degradation and byproduct formation in carbon dioxide (CO_2) capture processes. Research and development (R&D) efforts focus on studying the effects of steel interfaces on oxidation and nitrosation for both aqueous and water-lean solvents and studying the molecular underpinnings of solvent degradation (e.g., hydrolysis, nitration, oxidation) and design new formulations that are resistant to these chemical degradations.

technical goals

- Develop fundamental understanding of degradation mechanisms for multiple solvent components on steel interfaces such that oxidative degradations from oxygen (O_2) and nitrogen oxide (NO_X) can be mitigated.
- Study the effects of steel interfaces on oxidation and nitrosation for up to six solvents from aqueous and water-lean classes (three from each).
- Develop experimental and computational studies of solvent degradation for neat solvents and then solvents in the presence of 304 carbon and 316 stainless steels uncoated or treated with urethane or imidazole coatings.
- Downselect solvents/conditions for confirmation testing in PNNL's small-scale continuous testing platform.
- Evaluate two CO_2BOLs, including N-(2-ethoxyethyl)-3-morpholinopropan-1-amine (2-EEMPA), as an additive in commercial aqueous solvents with the aim of fast-tracking commercialization for aqueous solvents.
- Perform an initial techno-economic analysis (TEA) based on the material property measurements.
- Develop molecular model and batch testing to ascertain degradation/byproduct behavior for the most viable aqueous blends identified in the earlier tasks.

technical content

Commercial and pre-commercial solvents for CO_2 capture from flue gas sources have advanced considerably over the years. R&D has focused on lowering overall regeneration energy via solvent chemistry advances and related process development. Additionally, work on quantifying and reducing solvent degradation was undertaken in the previous DOE-funded Field Work Proposal (FWP)-72396. Solvent degradation not only impacts solvent costs, but can ultimately hinder fielding if hazardous products are formed (e.g., carcinogenic nitrosamines). The purpose of this research is to leverage prior PNNL investigations on the fundamental understanding of degradation mechanisms of multiple solvent components. PNNL's molecular modeling experts provide mechanistic insights to observed degradation pathways and potential chemistry for additives or process modifications for ultimate mitigation. Other degradation measurements for solvents, such as data from SINTEF's solvent degradation test rig, are also used for validation. Further, there is interest in understanding the impacts of intentional dilution of PNNL's water-lean CO_2BOLs in aqueous solvent blends as a means of commercially fast-tracking those solvents. This fast-track approach requires an understanding of solvent performance impacts, as well as any unique degradation/byproduct impacts.

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Post Combustion Power Generation PSC

key technology:
Solvents

project focus:
Methods for Mitigating Mechanisms of Solvent Degradation

participant:
Pacific Northwest National Laboratory (PNNL)

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FWP-77217

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FWP-72396

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54%

PNNL's previous work in FWP-72396 showed a previously undiscovered solvent degradation that occurs on the interfaces of stainless steels. In this study, PNNL had discovered direct chelation of specific chemical motifs of carbon capture solvents directly coordinating to stainless steel interfaces and chemically activating them for degradations such as hydrolysis and oxidation (Figure 1). It is believed that the chromium oxide (CrO) coating that makes stainless steel corrosion resistant acts as the catalyst for oxidative degradation reactions with O_2 and NO_X. Chromium oxides are known oxidative catalysts for alcohols and amines, and unsurprisingly, previous studies indicated that the structural motifs that showed the highest deactivation in the presence of steels were those that contained alcohols and imines, with the former present in all alkanolamines and the latter in the CO_2BOL alkanol guanidine solvent class. The finding that steel interfaces directly coordinate and activate specific chemical moieties means that all carbon capture solvents are susceptible to these degradations. Learning how to stop these catalytic activations for decomposition reactions provides a new means to increase solvent lifetime for all solvent-based processes. Thus, this research effort aims to shut down this newly discovered mechanism of catalytic decomposition by steel interfaces for both aqueous and water-lean solvents by simply passivating the interface with durable organic coatings. Further, if the CrO coating on stainless is the culprit, passivation of a less expensive carbon steel (304) with a chemically durable organic coating could result in significant cost-savings for infrastructure and avoid the use of costly 316 stainless steel.

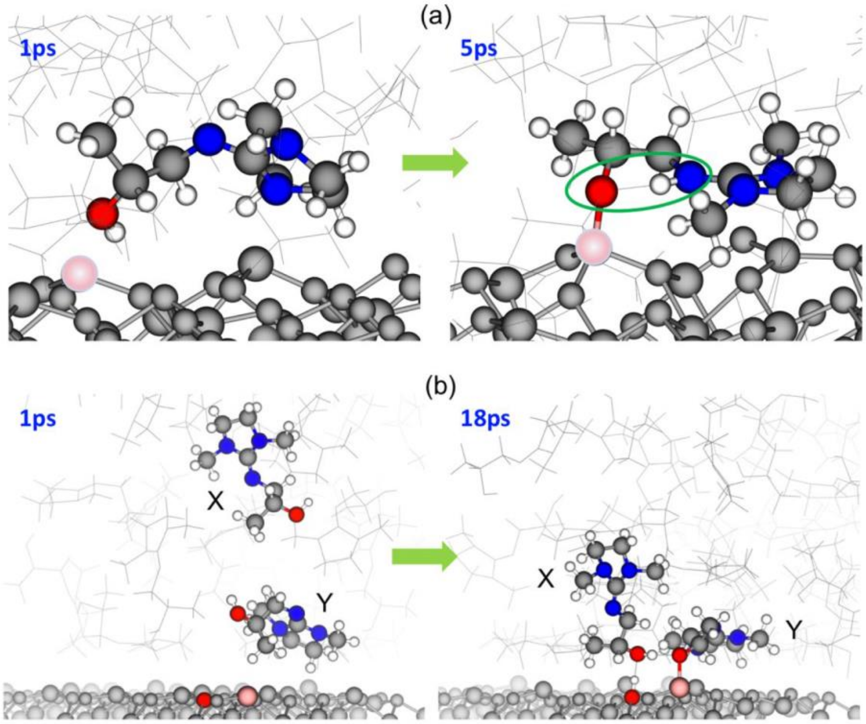

Figure 1: Representative interfacial activation of a water-lean solvent by stainless steel. 1-IPADM-2-BOL/hematite(steel) interface: (a) structure of a molecule right at the solid surface at 1 picosecond (ps) and 5 ps of an Ab initio molecular dynamics (AIMD) simulation, the surface atom in pink indicates the iron atom that assists the proton transfer from the OH group to an N atom of the same molecule; (b) structure of two molecules X and Y at 1 ps and 18 ps of the same AIMD simulation, surface atoms O (red) and Fe (pink) directly assisted the proton transfer from X to the surface and from Y to X. Most of surface atoms and surround molecules are in grey for clarification.

The project team showed that they could increase solvent lifetime by as much as 50% by simply removing contact with a steel interface. The retardation of chemical degradation of solvents was achieved by removing the steel interfaces that were acting as catalysts for the degradation reactions. Thus, removal or passivation of the interface had the effect of increasing the degradation activation energies (thermal, oxidation, hydrolysis) for three solvents by approximately 2,000–3,000 calorie (cal)/mol. PNNL aims to show that comparable retardation could be achieved for other modes of amine degradation in solvent-based post-combustion CO_2 capture processes.

Reactions of carbon capture solvents with NO_X remains a challenge for solvent developers as nitrosation results in the formation of potentially carcinogenic nitrosamines. Often, nitrosation cannot be avoided, and multiple solvent formulations have had to be used with caution (e.g., piperazine, 2-AMP) or outright abandoned (e.g., a subcomponent in an experimental Fluor solvent) due to unacceptable levels of nitrosamine formation. Nitrosation occurs via an oxidation reaction, which PNNL hypothesizes to be catalyzed by stainless steel interfaces, not just dissolved metals that accumulate in the solvents from corrosion. Nitrosamines are specifically problematic for secondary amine chemical moieties, which are often utilized due to their more favorable energetics as compared to primary amines such as monoethanolamine (MEA). Thus, if nitrosation could be mitigated by coating steel interfaces, previously established energetically favorable and cost-effective solvents could be revitalized and rapidly expedited for commercialization.

Mechanistic studies are being performed systematically with dissolved metal catalysts to determine which, if any, catalyze the nitrosation reaction. With this data, PNNL is designing new aqueous amine formulations that have different functional groups that would disfavor nitrosation. PNNL is also performing experimental and computational studies of solvent degradation for neat solvents and solvents in the presence of 304 carbon and 316 stainless steels that are both uncoated and treated with urethane or imidazole coatings. The goal is to confirm that coated 304 steels do not catalyze oxidative degradations and are resistant to corrosion.

There is interest in using PNNL's water-lean CO_2BOLs solvents to initially enable more conservative concentrations in aqueous blends, despite the outstanding performance with minimal water. The logic in this interest is that one commercialization barrier is the risk to technology providers of using a new solvent in water-lean form in existing/initial commercial equipment. Fluor used this approach when developing their latest Econamine FG+ solvent, which increased the solvent concentration from approximately 30% up to 50%. PNNL is assessing two CO_2BOLs as active additives to commercial aqueous solvents with water loading ranging from 50–80%. The project team is utilizing molecular modeling and batch testing to ascertain degradation/byproduct behavior. The most viable aqueous blends are then being subjected to steady-state continuous testing using simulated coal-derived flue gas. By using a CO_2BOL solvent as an active ingredient in an aqueous system, higher initial concentrations would be achievable, along with the prospect to drive those loadings up to greater than 90% over time, reducing the overall commercialization risk.

There are four primary goals of this project:

- Mitigate the mechanism of catalytic oxidative decomposition by steel interfaces for both aqueous and water-lean solvents that have been assessed in various platforms, including the SINTEF degradation test rig, by simply passivating the interface with novel monolayer coatings.
- Enable utilization of cheaper carbon steel (304) by modifying the surface with chemically novel monolayer organic coatings, resulting in significant cost-savings for infrastructure by avoiding the use of costly 316 stainless steel.
- Evaluate water-lean CO_2BOLs as active ingredients in next-generation aqueous solvent systems, utilizing higher initial concentrations with the goal to increase loadings up to greater than 90% over time, thus reducing the overall commercialization risk of water-lean solvents.
- Perform steady-state continuous flow testing using PNNL's laboratory-continuous flow system (LCFS) for the best-performing aqueous and water lean solvents to demonstrate, for at least for 72 hours, achieving 90% capture from simulated coal-derived flue gas (15% CO_2, 84% N_2 with sulfur oxide [SO_X], NO_X, O_2) and validate TEA projections.

technology advantages

- Potential to shut down oxidative decomposition by steel interfaces through passivation of the liquid-solid interface.
- Enable utilization of less-expensive carbon steel (304).

R&D challenges

- Demonstrate a minimum of 72 hours of continuous flow testing achieving greater than 95% capture from simulated coal-derived flue gas.

status

PNNL is currently working on identifying candidate steel coatings and batch testing multi-solvents and additives, along with coated and uncoated steels. Additionally, molecular modeling is being developed concurrently to theoretically study the solvent properties; these are being correlated to the experimental test data being collected from the small-scale continuous testing apparatus.

available reports/technical papers/presentations

Koech, P., “Reducing the Degradation of Carbon Capture Solvents,” Project kickoff meeting presentation, Pittsburgh, PA, February 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11576&filename=Reducing+Degradation+of+Carbon+Capture+Solvents.pptx*.

Koech, P., “Reducing the Degradation of Carbon Capture Solvents,” NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Koech.pdf*.