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Reclaiming Methods to Mitigate Iron Accumulation in Piperazine for Carbon Capture

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Abstract

Amine scrubbing for post combustion carbon capture (PCCC) is a mature and robust technology essential to the global reduction of CO_2 emissions. Oxidation of amine solvents remains one of the largest obstacles to broader deployment of amine scrubbing for PCCC. Solvent makeup costs associated with oxidation are estimated to be as much as 10% of the cost of the entire capture process.[1] Piperazine (PZ), a second generation amine solvent, exhibits significantly less oxidation than other solvents such as monoethanolamine (MEA).[2] However, in the presence of metal catalysts such as Fe, PZ oxidizes more readily.[3,4,5,6] The purpose of this paper is to complete a comprehensive review of the current state of amine reclaiming in PCCC as it relates to metal removal and to present new results regarding the effectiveness of reclaiming PZ during temperature-cycled bench-scale oxidation experiments.

From bench- and pilot-scale experiments, Fe has been shown to be solubility-limited by the products of PZ oxidation.[7] As PZ oxidizes and these products accumulate, the solubility of Fe increases, and the increased Fe concentration speeds up the rate of oxidation, forming a positive feedback loop. When Fe is removed from solution, it returns rapidly because the source of Fe from stainless steel corrosion will always be abundant enough to replenish the Fe removed.[7] It is hypothesized that to prevent runaway oxidation the degradation products that solubilize Fe must be removed by some method of batch or online solvent reclaiming or treatment. Furthermore, it is proposed that proactively reclaiming the solvent will prevent the accumulation of degradation species or Fe from occurring. Testing the oxidation mitigation from early and continuous treatment of mildly degraded amine has not yet been investigated. Reclaiming methods include thermal reclaiming, vacuum distillation, electrodialysis, ion exchange, and carbon treating.[8] Based on a literature review, these methods have been tested on MEA and some other amine solvents and blends, but the effectiveness of solvent reclaiming on PZ has not been thoroughly studied.[8,9,10,11,12,13,14,15,16]

The Texas Carbon Management Program (TxCMP) has been actively investigating the potential for carbon treating to reduce metal and degradation product concentrations in PZ.[17] The treatment is tested in the High Temperature Oxidation Reactor (HTOR), an apparatus designed to mimic the conditions in actual systems by cycling solvent between low and high temperatures. Wu demonstrates the potential of carbon treating to reduce the presence of metals and oxidation products in PZ scrubbing, however, it is not known how carbon treating of PZ compares to other reclaiming strategies.[17] TxCMP has also previously attempted pilot- and bench-scale testing of PZ thermal reclaiming with some success, but key issues were identified at the pilot-scale, including the precipitation of PZ causing full system shutdowns. Results from pilot-scale reclaiming of PZ will be published publicly for the first time in this review. At the bench-scale, thermal reclaiming removed 95% of nitrosamines from PZ when operated at 150 °C with

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a 10 min residence time.[18] The effect of thermal reclaiming on degradation products and metal concentrations was never fully determined. In techno-economic studies of amine reclaiming, distillation, ion exchange, and electrodialysis were assumed to recover 95, 99, and 98% of amine, respectively.[7,19,20] However, no experimental studies have ever proven that these levels of amine recovery are possible for PZ. The economic viability of reclaiming is most sensitive to the cost of solvent makeup, so lower recovery rates could make a given reclaiming method infeasible.[20]

The results of bench-scale thermal and ion exchange reclaiming and their effect on oxidation mitigation in the HTOR will be presented and compared to previous HTOR campaigns with carbon treatment and without any solvent management. Ion exchange resins are currently being screened to determine the optimal resin to use to continuously reclaim PZ during an HTOR campaign. The optimal resin will remove degradation products and catalytic metals such as Fe, while maintaining PZ levels. Solvent and resin are combined and continuously stirred in a covered beaker for a few hours. The concentration of degradation products and PZ are measured using ion chromatography, except aldehydes such as piperazinol (PZOH) which are analyzed with high performance liquid chromatography (HPLC) with UV-Vis detection. Metal concentrations are measured with inductively coupled plasma optical emission spectroscopy (ICP-OES). Early results revealed that a weak cationic exchange resin removed 50% of PZ. Anionic exchange resins should be able to remove negatively charged degradation products, and subsequently Fe without retain a high percentage of PZ. Moser et al. found an anionic exchange resin removed more Fe compared to cationic exchange resins tested, because the Fe may be present in solution as a negatively charged chelating complex.[21] A thermal reclaimer is being built based on designs from Fine (see Fig. 1).[20] Solvent will be fed to a heated round bottom flask through a burette. The reclaimer will be operated at 150 °C and contains a pressure relief valve to control pressure build up. A fritted glass column is attached to the flask where vapor condenses on the walls and can travel out the distillate drain. A condenser at the top of the column refluxes any vapor that leaves the column. The main deviation from the original design is to operate the condenser at 70 °C using a heated circulating water bath to avoid PZ precipitation at lower temperatures and to scale-up the design to be able to reclaim 1-3 L of solvent. Both ion exchange and thermal reclaiming will be tested with caustic treatment to improve the recovery of amine.[13,19,20]

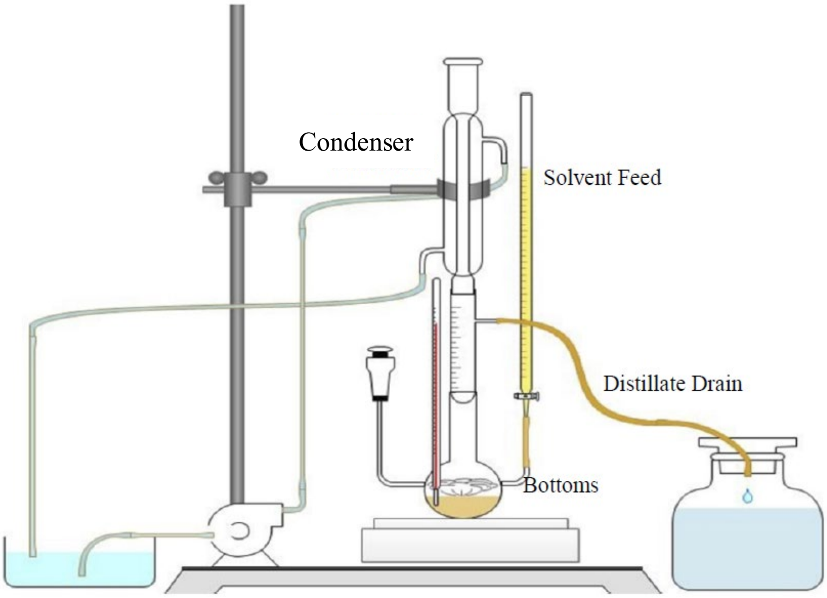

Figure 1: Design for bench-scale thermal reclaimer.[20]

Keywords: amine scrubbing; amine reclaiming; thermal reclaiming; ion exchange

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