IEAGHG 8th Post Combustion Capture Conference

16th to 18th September 2025 Marseille, France

Continuous Two Stage Thermal Reclaiming of Monoethanolamine

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Abstract

For satisfactory long-term operation of an amine capture plant all impurities formed by degradation or added from the flue gas need to be removed at the same rate as they are formed, i.e. the solvent eventually needs to be in a composition that is, on average at least, stable. This long-term stabilised solvent composition also needs to perform satisfactorily with respect to factors such as capture capacity, energy efficiency and corrosion potential in order to achieve satisfactory operation, maintenance and costs.

Impurity removal can be achieved through solvent management strategies such as thermal reclaiming, process that separates the working solvent from produced degradation products by exploiting differences in volatility of the species involved. Despite being widely implemented, this technology is still far from being fully understood and optimised [1]. This presents a challenge, as further development is urgently needed given the rapid expansion of the CO_2 capture field and the substantial financial investments in capture plants.

A key function of any reclaiming system is to remove all introduced or generated impurities from an active amine capture process, ensuring that the circulating solvent remains at an acceptable purity level indefinitely. Maintaining solvent health for sustained operation can be achieved. In current capture test campaigns, thermal reclaiming is typically employed between operational runs or when specific degradation products, such as heat-stable salts, reach a critical concentration threshold [2,3]. Industrial practice [e.g. Sherman FEED] is, however, to continuously removing impurities from the amine solvent, a mode of operation that avoids the significant disruptions to performance when reclaiming is taking place at relatively high rates and the ‘saw tooth’ solvent purity profile between reclaiming periods. It is evident that a plant with a stable solvent composition will also be easier for operators to control and maintain since it should always respond in the same way.

A standalone two-stage thermal reclaimer has been developed at the University of Sheffield for testing of conditions of effective continuous thermal reclaiming of monoethanolamine solvent with the aim to maintain the solvent health without any long-term degradation product accumulation [4], in line with UK permitting guidance that requires the solvent on a plant to run using fully representative flue gases over a period of at least 12 months [5].

This reclaimer study will utilize both synthetically degraded amine solvent and solvent that has previously been used in an industrial setting. The synthetically degraded solvent will contain known concentrations of commonly found degradation products from oxidative degradation such as monoethanolamine formate (CAS 53226-35-0) and ethanolamine acetate (CAS 54300-24-2) heat-stable salts and thermal degradation products such as, HEEDA (N-(2-Hydroxyethyl) ethylenediamine, CAS 111-41-1), and HEIA (N-(2-Hydroxyethyl) ethylene urea, CAS 3699-54-5). This controlled composition will allow for a clear assessment of the effectiveness of the reclaiming method in removal of less volatile degradation products. The solvent previously used on an operating commercial plant will undergo the same reclaiming process, with the efficiency of this reclaiming process evaluated in terms of

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MEA recovery and degradation product elimination. The overall results from this study and the optimum operational conditions for continuous reclaiming will be documented to aid future solvent management strategies and reclaimer designs.

The first stage of operation, the setup for which is shown in **Figure 1**, has three main variables. The setpoint of the temperature of the reclaimer can be adjusted, and the flow rate of the blowdown pump from the bottom of the reclaimer and the addition of water into the first stage of the reclaimer can be modified through the pump set flow rate. The level in the reclaimer is kept constant using a weir overflow. The reclaimer will initially test at 2.4 bar(a), in line with recent work for the required stripper conditions to achieve a lean solvent loading for ultra-high capture rates [6], as in continuous operation, the reclaimer will vent to the desorber to recover the reclaimer thermal energy input.

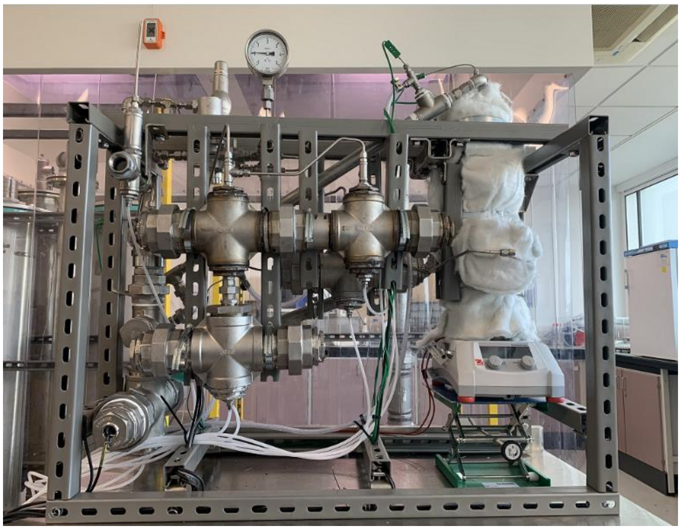

Figure 1: First Stage Reclaimer

Second stage reclaiming of the blowdown from the first stage reclaimer will be conducted off-line in batch mode with the main emphasis to maximise amine recovery while also not using excessive energy and not returning an excessively high proportion of the more volatile impurities back into the system. This stage will be operated in 3 steps a) a filling/concentration stage, b) an amine recovery stage and c) a residue concentration stage [7]. Tests will assess the relative performance of both atmospheric pressure and sub-atmospheric pressure operation, with the objective of achieving satisfactory reclaiming efficiency while minimising solvent thermal degradation. The apparatus for the second stage off-line reclaimer is shown in **Figure 2**.

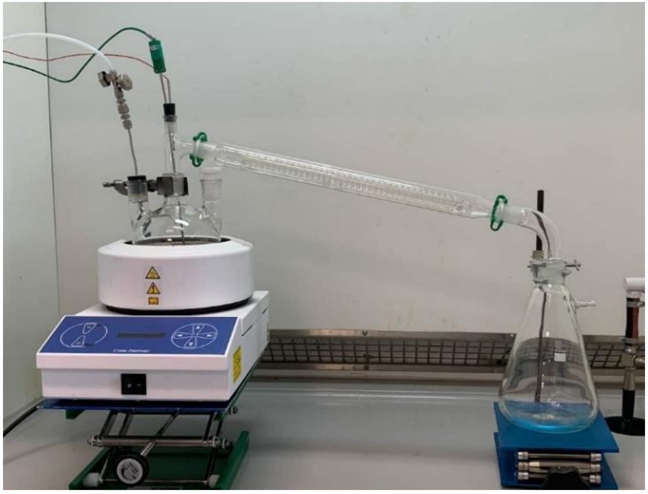

Figure 2:Second Stage Reclaimer

Caustic addition for heat-stable salt neutralisation will be tested in both the first and second stages of this reclaiming operation to determine the optimum procedure for the greatest amine recovery, energy efficiency and operability of the units.

If continuous reclaiming can be economically implemented, the solvent consumption of a plant can be reduced. Recent cost estimates for MEA solvent losses are 2 kg MEA/tCO2, at a cost basis of around $1.14/kg MEA [8]. Maintaining low levels of impurities in the solvent may also play a vital role in extending the lifespan of future capture projects through reduced corrosion rates.

In this study, amine recovery and the relative amounts of degradation products of interest such as HEEDA and HEIA are measured using gas chromatography. Amine concentration will also be monitored in real time via a novel monitoring technique developed at the University of Sheffield called HAPTICS [9]. The concentration of heat-stable salts will be analysed using a conductometric titration experiments. In addition to these analytical techniques, the vapour which is condensed in thermal reclaiming is collected, which will allow a complete MEA balance to be made.

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Keywords: Solvent Management; Reclaiming; Degradation; Monoethanolamine; MEA; Amine; SMART; Thermal Reclaiming;