ACT LAUNCH Project No 299662

Lowering Absorption process UNcertainty, risks and Costs by predicting and controlling amine degradation

D.3.1.4 Report describing the foaming tendencies and results from the iron solubility measurements

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Written By	Maxime François, Andreas Grimstvedt, Max Lukas Teschner, Quyen Lily Dinh, Hanna K. Knuutila	
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Introduction

While amine-based carbon capture has been shown to be effective in capturing CO_2, there are several challenges associated with this technology. One of the main challenges is solvent degradation, which refers to the chemical decay of the amine solution over time. This degradation can reduce the effectiveness of the amine in capturing CO_2 and increase the cost of the process. One factor that can impact amine degradation is the presence of iron in the amine solution potentially catalysing the oxidative degradation.

Another potential challenge with amine-based carbon capture is foaming in the absorber, which refers to the formation of small bubbles in the amine solution. Foaming, which depends on the solvent, and typically occurs after some time and is often thought to be caused by some degradation compounds, can reduce the efficiency of the process and increase its cost by increasing pressure drop and requiring regular addition of anti-foaming agents to mitigate the formation of bubbles.

This work aims to investigate these two related phenomena that affect the performance of the capture process. This report briefly describes this work's motivation and experimental methodology, which focuses on the influence of many parameters on the solubility of iron or other metals.

Iron solubility set-up and protocol

The solubility of a solid refers to the maximum amount of the solid that can dissolve in a specific amount of solvent to form a homogeneous solution. While precipitation is a process in which solid particles are formed from a solution. This occurs when the concentration of a dissolved substance exceeds its solubility limit, and the excess solid separates from the solution and forms a precipitate.

There are some previous works on iron solubility in MEA by Fytianos et al. [1] and Fischer [2]. However, the results are rather scattered. In the work by Fytianos, the iron solubility in fresh and loaded (0.4 mol_{CO2}/mol_{MEA}) 30wt% MEA was reported to be 120 mg/L at 25°C, about 80 mg/L at 45°C and about 30 mg/L at 60°C. In Fischer's work, 9 molal MEA (equivalent to about 35wt%) was used. The results of Fischer are quite different, with a high solubility (about 800 mg/kg) at 24°C with a loading of 0.44, and a low one (under 40 mg/kg) at 45 and 62°C with the same loading.

Solubility measurements reported in the literature for iron in amine solution were so far carried out by gradually pouring solid iron sulphate into a solution of MEA [1-2]. Dissolution proved to be quite slow, lengthening the duration of the experiment and increasing the probability of degradation that could distort the solubility measurements.

In the current work, water containing a large amount of dissolved metal was brought into contact with an amine solution. The solubility of iron in an aqueous amine solution is much lower than in pure water. Consequently, the dissolved iron must precipitate in order to meet the solubility limit in the aqueous amine solution.

A jacketed and closed reactor of 1L was used to conduct iron solubility experiments. A water-bath was used to control the temperature. The stirring of the reactor contents was ensured by a Teflon half-moon, connected to a Teflon shaft driven by a motor located above the reactor (it is imperative to avoid the presence of metallic elements in contact with the amine solution). A picture of the set-up is shown in Figure 1.

Typically, a 50wt% MEA solution was prepared. Additionally, water was mixed with iron sulphate heptahydrate ($FeSO_4, 7H_2O$) to make a concentrated iron solution (1g/L Fe element). After inerting the reactor with nitrogen and setting the water-bath to the desired temperature, both solutions were added to the reactor to obtain 500mL of a 30wt% MEA solution. The stirring was then turned on. Excess iron that cannot be solubilised by the aqueous amine solution will precipitate gradually during the experiment. Samples are taking out after 24h and 48h.
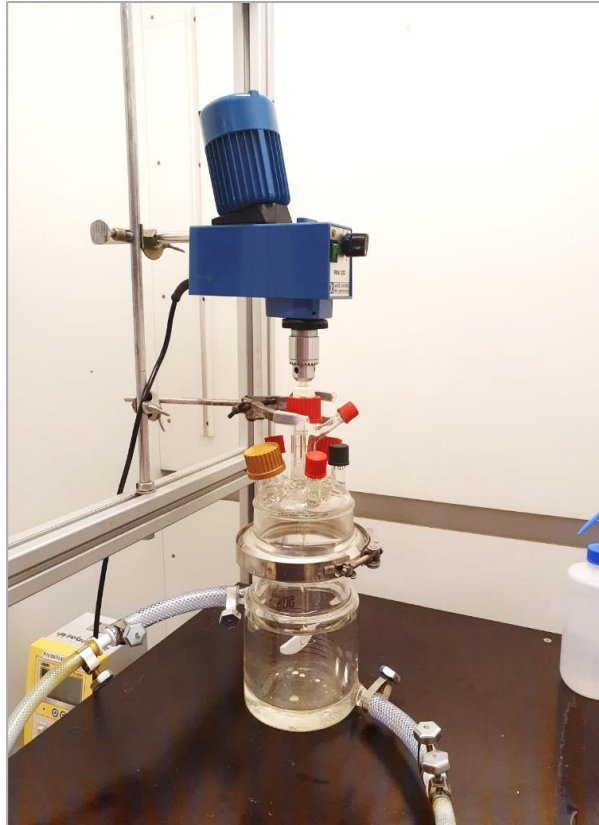
Figure 1: Iron solubility experimental setup picture

Foaming set-up and protocol

The foaming experiments consisted of blowing nitrogen gas into the solution to be studied and measuring the height of foam formed, and comparing it with other solutions. This provided a qualitative measure of the foamability of a solution.

The experimental set-up consists of a jacketed bottle with a capacity of approximately 1L. A water bath was used to control the temperature within the bottle via the jacket. Two thermocouples were used to monitor the temperature within the reactor and the jacket. In operation, the reactor was topped by a lid into which a long tube with a sinter was inserted. This tube passing through the plug supplied nitrogen gas, causing foaming. A flowmeter was used to control the flow of nitrogen. A picture of the set-up is shown in Figure 2.
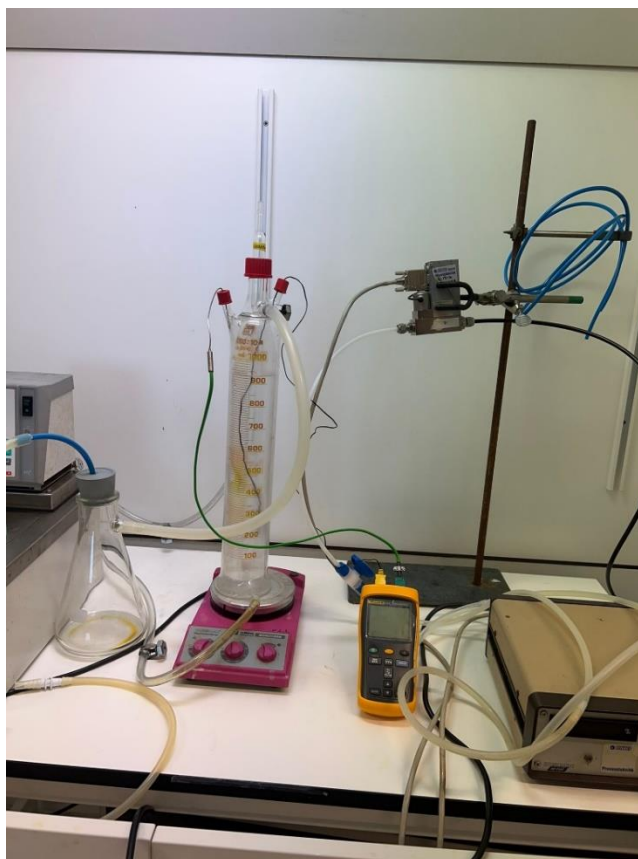
Figure 2: Foaming experimental setup picture

Samples taken were analysed using various techniques. Amine titration was used to determine alkaline content, using sulphuric acid with a G20 Compact Titrator (Mettler Toledo, Switzerland). The sulphuric acid solution used was prepared from a Titrisol® ampoule (Merck, Germany). When necessary, the CO_2 loading of the samples was determined using a Total Organic Carbon (TOC) Analyzer (Shimadzu, Japan). In the case of degraded samples, LC-MS, using a method developed by SINTEF, was used to analyse the amount of degradation products. Finally, the metal content of the samples was analysed by ICP-MS (Inductively coupled plasma mass spectrometry) by SINTEF.

Using the described setups and procedures, the influence of temperature, CO_2 loading, amine, amine concentration, pH, oxidation state of iron in solution, type of counter ion, and presence of degradation products in the solution on the solubility of iron in amine solution was investigated. For the foamability study, the influence of amine concentration, temperature, CO_2 loading, presence of iron and copper and type of degradation were investigated. A short study was also carried out on the effect of activated carbon treatment on the foamability of degraded solvent.

A journal manuscript is being prepared and the published paper will be made available through the LAUNCH website as soon as possible.

References

[1]   G. Fytianos, Corrosion and degradation in MEA based post-combustion CO2 capture, Doctoral thesis, NTNU, Norway (2016)
[2]   K.B. Fischer, Corrosion of Stainless and Carbon Steel in Aqueous Amine for CO2 Capture, Thesis, University of Texas; USA (2019)