Quantitative in-line measurement of CO_2 loading in amine gas scrubbers

Benefits at a glance
- Optimization of gas scrubber operation
- In-line monitoring of liquid phase during absorption and regeneration
- Quantification of CO_2 loadings

Introduction

The absorption of gas components like hydrogen sulphide (H_2S) and carbon dioxide (CO_2) is an established treatment option to clean various "acid gases." The process of gas cleaning using amines involves a complex relationship between physical parameters as well as chemical reactions. Amine scrubbers are well established in several industrial segments to clean these components from off-gas and synthesis gas. Furthermore amine scrubber approaches have also found use in the preparation of special gases like sewage gas, landfill gas, biogas, and methane.

The current investigations concentrated on detergent mixtures of methyldiethanolamin (MDEA), mono or ethanol amine (MEA), 2-(2-Aminoethoxy)ethanol (Diglycolamine® DGA) and water. These detergent mixtures are already commercially used for the simultaneous absorption of hydrogen sulphide and carbon dioxide from special gas flows.

Raman spectroscopy is a well established technique for chemical reaction monitoring due to the high information content of the Raman spectrum. The use of fiber optic probes and compact Raman systems has allowed the potential of laboratory Raman spectroscopy to be realized in industrial manufacturing settings for a wide variety of industries. In this study, a Raman analyzer was evaluated in order to verify if Raman spectroscopy can be used to directly monitor on-line the chemical composition and allow quantifying the CO_2 loadings in an amine scrubber.

Experimental

The experimental investigations were conducted in 2007 using the amine scrubber at the "Institut für Energie- und Umwelttechnik e.V." (Germany)[1]. The test facility permits the simultaneous investigation of absorption and desorption in a closed cycle with absorption pressure up to 26 bar. The absorption column (height of 4.7 m and inside diameter of 0.312 m) and the desorption column (height of 5.76 m and inside diameter of 0.316 m) are filled with modern, structured packages from Sulzer Chemtec.[1]

A Raman analyzer with a 785 nm laser, coupled with a fiber optic Raman probe employing immersion sampling, was used to make the reported measurements. Raman spectra were acquired within seconds using approximately 180mW of laser power.

Figure 1: Gas scrubber facility IUTA.

Results

During the absorption process several changes in the Raman spectra can be observed.[2]

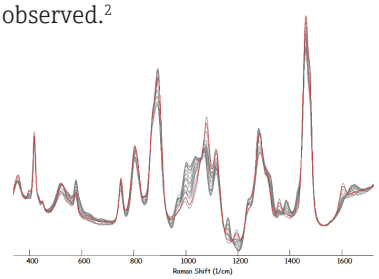

Figure 2: DGA - Raman spectra for absorption process

ⓘ All Raman analyzers and probes referenced in this application note are Endress+Hauser products powered by Kaiser Raman technology.

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An amine specific band at 1610cm^{-1} diminishes over time indicating the consumption of DGA while a band at 1021cm^{-1} shows formation of the bicarbonate (HCO_3^-) species.

For process monitoring, CO_2 was bubbled through a solution containing 30% DGA in water at 25°C. Raman spectra were recorded every 30 seconds and specific bands for loaded and unloaded CO_2 containing solution were monitored over time. After 30 minutes, the CO_2 gas was stopped and the solution was heated to 90°C leading to regeneration of the process solution. Figure 3 shows the absorption – desorption process of DGA monitored using in-line Raman spectroscopy.

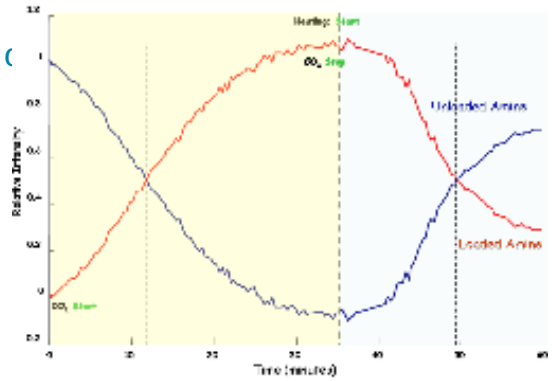

Figure 3: Absorption-desorption process monitoring

For calibration, samples of different CO_2 loadings in 15%, 30% MEA and 30% DGA at 25°C were produced using a specially constructed apparatus at the University of Duisburg[2]. The absorber is equipped with a vacuum pump and N_2 gas inlet for evacuation of air and drying of the vessel. After filling the absorber with the desired amine solution, a mass flow controller (MFC) allows precise addition of defined quantities of CO_2 gas into the stirred solution. Using this approach, 12 sample sets of different CO_2 loadings in MEA and DGA were prepared. After equilibrium, each concentration was measured 20 times using the Raman equipment noted above.

A PLS chemical model was constructed from the Raman spectral information using a multivariate data analysis package (Grams PLS/IQ). The initial model was subsequently validated using a set of 15 validation samples.

In Figure 4 a calibration plot for data from CO_2 loadings in MEA at 25°C is shown. The data is very repeatable, resulting in a calibration with R2=0.99987. A corresponding validation set confirmed the accuracy of the prediction model.

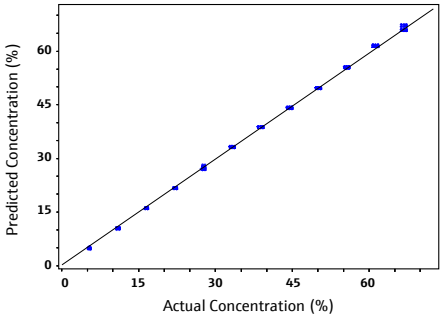

Figure 4: MEA calibration curve for CO_2 loadings at 25°C

Conclusion

The process of gas scrubbing using CO_2 and different aqueous amine solutions can be monitored successfully using Raman spectroscopy.

The loaded and regenerated liquid phase can be monitored using Raman immersion optics directly in-line.

A quantitative PLS model was be established for different CO_2 loadings and this model was used for quantitative in-line monitoring of CO_2 loading.

Further investigations using different type of washing solutions and conditions are part of ongoing work at IUTA and the University of Duisburg (Dec. 2007).

Reference

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