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研究指導	エクセルギー工学				
研 究 題 目	滴定による酸・塩基度の定量化に基づく CO ₂ 分離回収用化学吸収劣化液の運転特性予測 Performance prediction of degraded CO ₂ capture solution based on total acidity/alkalinity quantified by titration				

1. Introduction

Post-combustion CO₂ capture (PCC) technologies, especially the chemical absorption method by aqueous amine solutions, are technically mature and have a wide range of applications to reduce greenhouse gas emissions and contribute to climate change mitigation. One of the critical issues preventing the rapid deployment of amine-based PCC is the degradation of amines over the long-term operation. Oxidative and thermal degradation are the two main causes of amine degradation and result in generation of a variety of degradation compounds. These products often lead to a decrease in loading capacity or alteration in solution physical properties, and entail operational issues such as increases in operating costs, foaming probability and corrosion rates. Therefore, it is worthwhile to analyze the type and the concentration of degradation products and investigate their effects on the process performance.

From the previous studies in the laboratory [1], simulated degraded amine solution was made by adding weak acids to fresh amine solution in accordance with the composition of real degraded amine solution to investigate the effects of the representative degradation compounds on the solution properties. However, the results showed that the simulated degraded solution could not reproduce the main properties of actual degradation amine solution completely. One of the reasons of this non-reproducibility might be dominantly caused by unidentified degraded compounds which was not added to the simulated degraded solution. Namely, although the simulated degraded solution could reproduce the composition of representative acid compounds which can be identified by Ion Chromatography (IC) analysis, it could not simulate the concentration of unknown acidic compounds, which cannot be identified by IC but might exist and dominantly affect the solution properties.

In this research, a holistic approach quantifying the total acidity/alkalinity without the identification of all degradation compounds by titration was proposed, and a simulated degraded solution which has the same acidity/alkalinity with a real degraded solution was prepared. As a real degraded solution, the degraded aqueous amine solution of monoethanolamine (MEA), which were made by 750 hours continuous operation of a bench-scale, 10kg-CO₂/day capture apparatus in the laboratory, were used. The composition of the degraded solution measured by titration was reflected to that of the simulated one. Moreover, the CO₂ capture experiments for simulated degraded solution and real degraded solution after 750 operational hours were performed to confirm the effects of the total acidity/alkalinity on the simulation of real degraded solution through the comparison of the solutions' process performance.

2. Titration method to measure total acidity/alkalinity

A titration analysis established by a patented method [2], which has been improved and calibrated based on the measured pH value and the volume change of the titrants, was employed to analyze the total acidity/alkalinity in aqueous amine solutions. It consists mainly of the excessive addition of a strong acid into the solution to release loaded CO₂ and the base titration using such treated solution. The accuracy of the quantification method by titration has been measured by repeated experiments and can be controlled within an acceptable range of 10%. The total HSS concentration in real degraded solutions obtained by this method were taken as a reference for preparing the corresponding simulated solution. The pH change with excessive acid addition and the base titration curve are shown in the following Figure 1.

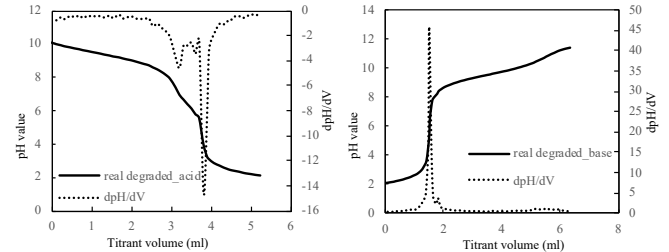


Figure 1-(a) acid titration of real degraded solution

Figure 1-(b) base titration of real degraded solution

3. CO₂ capture experiment and evaluation of process performance

The CO₂ capture experiments were conducted using fresh solution, the real degraded solution after 750 operational hours, and the simulated degraded solution. The purpose of this experiment is to evaluate the reproducibility of simulated degraded solution by comparing the process performance of the absorbents under the same operating conditions. Figure 2 shows the breakdown of the regeneration energy and the results of the CO₂ capture rate. Figure 3 shows the axial distribution of CO₂ loading of the absorber. Figure 4 shows the partial pressure of the water vapor and CO₂ at the top of the stripper.

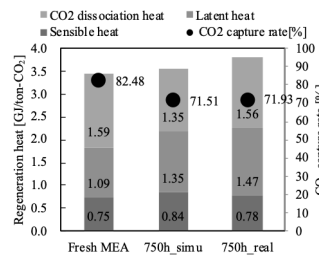


Figure 2 Breakdown of regeneration energy and CO₂ capture rate

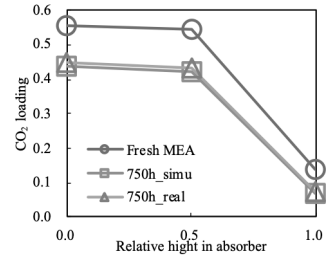


Figure 3 CO₂ loading profile in the absorber

The simulated degraded solution can simulate the operating characteristics of the real degradation solution relatively compared to previous trial by Park's, especially for the CO₂ capture rate and CO₂ loading, while there remains the difference on the detailed heat distribution. It was indicated that the difference between the actual degradation compounds and the HSS added to the simulated solution might cause the alteration of the enthalpy of desorption, which results in a decrease in the regeneration energy for CO₂ desorption. As can be seen from Figure 4, for the simulated degraded and the real degraded solution, the partial pressure of H₂O was near the saturated vapor pressure, respectively. These results indicate the excessive water vaporization and consist with marked increase in latent heat in Figure 4.

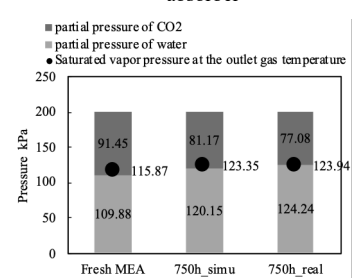


Figure 4 Partial pressure of the water vapor and CO₂ in the stripper

Reference:

- [1]. Park, S. (2017), Waseda University, M.S. Thesis.
- [2]. JPA 2014185913-000000 熱安定性塩 公開特許