HOLISTIC DEVELOPMENT OF A LOW-ENERGY AMMONIA-BASED PROCESS FOR CO_2 CAPTURE WITH SOLID FORMATION

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Key Words: CO_2 capture, continuous crystallization, crystallization kinetics, reactive absorption.

Absorption-based gas treatment processes allow removing CO_2 from flue gas streams of large CO_2-point sources, e.g. coal and natural gas fired power plants, cement plants, and steelworks, and make CO_2 available at conditions suitable for geological storage. Therefore, it represents a key option in the portfolio of measures required to mitigate climate change and a valuable bridging technology that can support the shift towards a renewable-based supply of energy and chemicals. Among existing options, the chilled ammonia process (CAP) is a promising solution on the verge of commercialization. In the CAP, a cold ammonia solution absorbs CO_2 from the flue gas in an absorption tower. The resulting CO_2-rich solution releases CO_2 upon moderate heating, while the (partially) regenerated ammonia solution can be recycled to the absorption section. At several points in the process flow-scheme, the liquid composition may exceed the solubility of the intermediate compounds at the relevant temperature. Solid formation can lead to clogging of process units. On the other hand, the formation of solids can increase the CO_2 uptake capacity of the solvent with beneficial effects on the specific energy demand per unit of mass of CO_2 captured. We have developed a so-called controlled solid formation-CAP (CSF-CAP), which successfully reduces the energy demand by exploiting solid formation. The new process controls the formation, separation, and subsequent dissolution of solids in a dedicated process section, whereas the absorption and stripping columns are kept free of solids. Our holistic process development strategy comprises (i) thermodynamics and (ii) kinetics, (iii) process synthesis, (iv) process integration, and (v) process optimization.

The work on thermodynamics makes use of phase diagrams of the CO_2-NH_3-H_2O system to map the process streams and analyze criticalities with respect to solid formation and opportunities for optimization. The analysis showed that the energetic optimization pushes the solvent composition towards the solubility limit. In the CSF-CAP, the CO_2-rich solution is cooled down in a crystallizer to form solid ammonium bicarbonate (BC). The generated suspension is separated in a hydro-cyclone into (i) a rich slurry, which is sent to the regeneration unit, and (ii) a clear solution, which is sent to the top of the absorber. Due to the solid formation and separation, the latter stream can be introduced at lower temperature enabling a more effective control of the NH_3 slip to the gas. The investigation of the kinetics considers both mass transfer and solid formation. On the one hand, pilot plant tests of the CO_2 absorber have been carried out in order to study the reactive absorption process. On the other hand, the crystallization kinetics of BC in aqueous solution has been measured. The experimental investigation of this system is complicated by the evaporation of CO_2 and NH_3 from the solution as well as by the decomposition of the salts. Therefore, a temperature-controlled batch reactor, in which the volume of the vapor phase is minimized to limit the influence of the VLE on the liquid composition, has been developed. Metastable zone width data have been obtained, and BC growth kinetics has been modelled from the concentration profile during batch cooling seeded crystallization experiments with the help of a population balance model.

The synthesis of the solid handling section has been developed combining mass, energy and population balances for the crystallization and dissolution into a rigorous rated-based model. Several process configurations, where mixed suspension mixed product removal (MSMPR) are coupled with scraped surface heat exchangers (SSHE) crystallizers, have been compared by optimizing the process productivity and energy needs. As a result, different optimal crystallization trajectories have been identified.
Our optimization approach relies on a performance assessment based on the irreversibilities of the process as objective function. Equilibrium-based process simulations under the assumptions reported by Sutter et al. [1] led to an efficiency improvement of 17% in the CSF-CAP with respect to the conventional CAP. In our presentation, we will show our latest results on absorption kinetics, BC growth rate modelling, optimized flow scheme for the solid handling section, and optimal operating conditions of the process found for different flue gas compositions and CAP configurations.

[1] D. Sutter, M. Gazzani and M. Mazzotti, *Faraday Discuss.*, 2016, 192, 59-83