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KOH-BASED MODIFIED SOLVAY PROCESS: OPTIMIZATION AND KINETICS STUDIES

By

Aya Abdel-Hamid Ismail Mourad

Faculty Advisor

Prof. Ali Hassan Al-Marzouqi, Department of Chemical and Petroleum Engineering

College of Engineering

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Abstract

While desalination of seawater is important for meeting the water demand, the technology produces large volumes of reject brine and CO_2, causing environmental pollution. Solvay process (based on ammonia, NH_3) and modified Solvay process (based on calcium oxide, CaO) try to manage these wastes. However, more attention is needed to overcome different limitations of these processes such as, alkaline solubility, operating temperature, maintaining high pH value, and low sodium (Na^+) removal efficiency, which does not exceed 35%. The aim of this work is to introduce an alternative alkaline, namely potassium hydroxide (KOH) and investigate its ability to overcome these limitations.

A preliminary study was conducted to compare the effectiveness of KOH with that of CaO. All experiments were conducted in a novel inert particle spouted bed reactor. It was observed that KOH entails very high solubility and maintains a high level of pH in comparison with CaO. In addition, the combined reaction was more spontaneous in case of the KOH.

Further investigations were carried out to optimize the operating conditions using response surface methodology (RSM) analysis. Under a 10 °C temperature, 2.1 barg gauge pressure, 848.5 ml/min CO_2 gas flow rate, 110 g/l KOH concentration, a maximum CO_2 uptake of 0.58 g/g KOH, maximum Na^+removal of 44.1%, chloride (Cl^-) removal of 40.1%, and almost 100% calcium (Ca^{2+}) and magnesium (Mg^{2+}) removal was achieved. The characterization of the collected solids revealed production of valuable products, particularly sodium bicarbonate ($NaHCO_3$), potassium bicarbonates ($KHCO_3$), Magnesium hydroxide ($Mg(OH)_2$), calcium carbonate ($CaCO_3$) and potassium chloride (KCl).

The conventional process is preferred to be operated under low temperatures (10-20 °C), whereas reject brine is usually discharged from desalination plants at relatively high temperatures (40–55 °C). Therefore, the proposed process was optimized to investigate the ability of KOH to reduce brine salinity at high temperatures. The results demonstrated that a good CO_2 uptake of 0.50 g CO_2/g KOH and maximum Na^+ reduction of 45.6% were obtained at a gauge pressure of 2 bar, gas flowrate of 776 ml/min, and KOH concentration of 30 g/l, and at high temperature of 50 °C.

These optimal conditions were then adopted to investigate the reaction kinetics. A near first-order overall reaction rate with respect to CO_2 concentration was established, whereby the reaction rate constant (k) was $\sim$ 0.0003 mol/l. min.

Multi-stage treatment process was examined to achieve an additional reduction in ions removal. Three different methods were investigated. The first method evaluated the effectiveness of adding ammonium bicarbonate (NH_4HCO_3) in reducing $NaHCO_3$ solubility. The $Na^+$and Cl^-concentrations were reduced by 56.2% and 40%, respectively. In the second method, the addition of extra KOH in subsequent stages was investigated. There was an ~47.3% improvement in CO_2 uptake as compared to the first method. Furthermore, the percentages of $Na^+$and Cl^- removal were increased to 65% and 64.5%, respectively. In the third method, the recovery of Ca^{2+} and Mg^{2+} were approximately 76.3% and 94.6%, respectively, following the pre-treatment step (filtration). Reducing these ions decreased the competitive reactions, resulting in higher cumulative CO_2 uptake from all stages to 108.2 g CO_2/1000 ml, which was 8.3% more than the second method.

Finally, the dynamic behaviour of the reactor was evaluated using step changes in the inlet gas and liquid flow rates. The results are promising in terms of the reactor system's adaptability to large-scale processes.

Keywords: Desalination, reject brine, CO_2 capture, modified Solvay process, KOH, response surface methodology, kinetics, multi-stage, hydrodynamics