5-2022

KOH-BASED MODIFIED SOLVAY PROCESS: OPTIMIZATION AND KINETICS STUDIES

Aya Abdel-Hamid Mourad
United Arab Emirates University, 200834607@uaeu.ac.ae

Recommended Citation

Mourad, Aya Abdel-Hamid, "KOH-BASED MODIFIED SOLVAY PROCESS: OPTIMIZATION AND KINETICS STUDIES" (2022). *Dissertations*. 232.
https://scholarworks.uaeu.ac.ae/all_dissertations/232

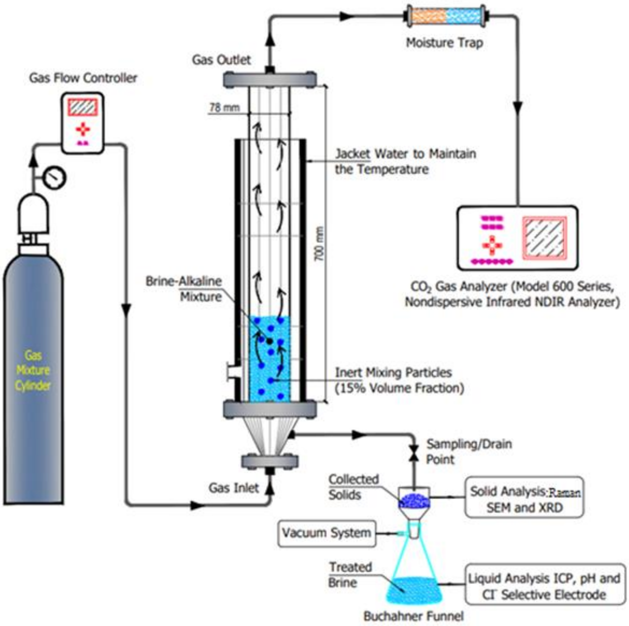
جامعة الإمارات العربية المتحدة
United Arab Emirates University

DOCTORATE DISSERTATION NO. 2022:5

College of Engineering

KOH-BASED MODIFIED SOLVAY PROCESS: OPTIMIZATION AND KINETICS STUDIES

Aya Abdel-Hamid Ismail Mourad



May 2022

United Arab Emirates University

College of Engineering

KOH-BASED MODIFIED SOLVAY PROCESS: OPTIMIZATION AND KINETICS STUDIES

Aya Abdel-Hamid Ismail Mourad

This dissertation is submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering

May 2022

United Arab Emirates University Doctorate Dissertation
2022: 5

Cover: Schematic diagram of the inert particle spouted bed reactor (IPSBR) system.

(Photo: By Aya Abdel-Hamid Mourad)

Print: University Print Service, UAEU 2022

Declaration of Original Work

I, Aya Abdel-Hamid Ismail Mourad, the undersigned, a graduate student at the United Arab Emirates University (UAEU), and the author of this dissertation entitled "*KOH-Based Modified Solvay Process: Optimization and Kinetics Studies*", hereby, solemnly declare that this dissertation is my own original research work that has been done and prepared by me under the supervision of Professor Ali H. Al-Marzouqi, in the College of Engineering at UAEU. This work has not previously formed the basis for the award of any academic degree, diploma or a similar title at this or any other university. Any materials borrowed from other sources (whether published or unpublished) and relied upon or included in my dissertation have been properly cited and acknowledged in accordance with appropriate academic conventions. I further declare that there is no potential conflict of interest with respect to the research, data collection, authorship, presentation and/or publication of this dissertation.

Student's Signature: Aya Mourad

Date: ___17/05/2022___

Advisory Committee

1) Advisor: Ali H. Al-Marzouqi

Title: Professor

Department of Chemical and Petroleum Engineering

College of Engineering

United Arab Emirates University

2) Co-advisor: Mohamed Al-Marzouqi

Title: Professor

Department of Chemical and Petroleum Engineering

College of Engineering

United Arab Emirates University

3) Co-advisor: Mohammednoor Al Tarawneh

Title: Associate Professor

Department of Chemical and Petroleum Engineering

College of Engineering

United Arab Emirates University

4) Co-advisor (External): Muftah El-Naas

Title: Professor

Gas Processing Center, College of Engineering

Qatar University, Qatar

Approval of the Doctorate Dissertation

This Doctorate Dissertation is approved by the following Examining Committee Members:

1) Advisor (Committee Chair): Ali H. Al-Marzouqi
Title: Professor
Department of Chemical and Petroleum Engineering
United Arab Emirates University

Signature Ali Hassan   Date 17/05/2022

2) Member: Munjed Maraqa
Title: Professor
Department of Civil & Environmental Engineering
United Arab Emirates University

Signature Munjed Maraqa   Date 17/05/2022

3) Member: Muhammad Tahir
Title: Assistant Professor
Department of Chemical and Petroleum Engineering
United Arab Emirates University

Signature   Date 17/05/2022

4) External Member: Paul Chen:
Title: Associate Professor
Department of Civil and Environmental Engineering
National University of Singapore

Signature   Date 17/05/2022

This Doctorate Dissertation is accepted by:

Acting Dean of the College of Engineering: Professor Mohamed Al-Marzouqi

Signature Mohamed AlMarzouqi

Date June 24, 2022

Dean of the College of Graduate Studies: Professor Ali Al-Marzouqi

Signature Ali Hassan

Date June 24, 2022

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 ~ 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

Title and Abstract (in Arabic)

تفاعل السولفاي المعدل (Modified Solvay Process) المبني علي هيدروكسيد البوتاسيوم (potassium hydroxide, KOH) : دراسات التحسين والـحركية (Kinetics)

الملخص

بم أن تحلية مياه البحر مهمة لتلبية الطلب علي المياه، فإن التكنولوجيا المستخدمة تنتج كميات كبيرة من المحلول الملحي (مياه عالية الملوحة) و CO_2 أيضا، مسببا تلوث بيئي. تفاعل السولفاي (Solvay Process) المبني علي الأمونيا (ammonia, NH_3) وتفاعل السولفاي المعدل المبني على أكسيد الكالسيوم (calcium oxide, CaO) تحاول التحكم في تلك الملوثات. ومع ذلك، المزيد من الاهتمام مطلوب للتغلب على القيود المختلفة لتلك التفاعلات مثل الـذائبية القلوية، درجة حرارة التشغيل، الحفاظ على قيمة عالية لدرجة الحموضة وكفاءة إنخفاض تركيز الصوديوم (sodium, Na^+)، الذي لا يتجاوز 35%. الهدف من هذه الدراسة هو تسليط الضوء والتعريف بإستخدام مركب قلوي بديل، وهو هيدروكسيد البوتاسيوم (potassium hydroxide, KOH) والتحقيق في قدرته على التغلب على تلك القيود. أجريت دراسة أولية لمقارنة فعالية هيدروكسيد البوتاسيوم مع فعالية أكسيد الكالسيوم. أجريت جميع التجارب في (a novel inert particle spouted bed reactor). وقد لوحظ أن هيدروكسيد البوتاسيوم يستلزم ذوبانية عالية جدًا ويحافظ على مستوى عالٍ من درجة الحموضة مقارنةً بـأكسيد الكالسيوم. بالإضافة إلى ذلك، كان التفاعل المشترك أكثر تلقائية في حالة هيدروكسيد البوتاسيوم. تم إجراء المزيد من البحث لتحسين شروط التفاعل بإستخدام طريقة (RSM). عند درجة حرارة 10 درجات مئوية، قياس ضغط 2.1 بار، معدل تدفق الـ CO_2 848.5 مل / دقيقة، تركيز هيدروكسيد البوتاسيوم 110 جم / لتر، الحد الأقصى لإمتصاص ال CO_2 بلغ 0.58 جم / جم هيدروكسيد البوتاسيوم، والحد الأقصي لإزالة الـ Na^+ 44.1%، وإزالة الكلوريد (chloride, Cl^-) 40.1%، و تم إزالة الكالسيوم (calcium Ca^{2+}) و الماغنيسيوم (magnesium, Mg^{2+}) بنحو 100%. تحليل المنتجات الصلبة أظهر إنتاج مواد قيمة، وخاصة بيكربونات الصوديوم (sodium bicarbonate, $NaHCO_3$) وبيكربونات البوتاسيوم (potassium bicarbonates, $KHCO_3$)، وكلوريد البوتاسيوم (potassium chloride, KCl). يفضل تشغيل العملية التقليدية عند درجات حرارة منخفضة (10 إلي 20 درجة مئوية)، في حين يتم تفريغ المحلول الملحي (reject brine) من محطات التحلية عادة عند درجات حرارة عالية نسبيًا (40 إلي 55 درجة مئوية). ولذلك، تم تحسين التفاعل المقترح للتحقق من قدرة هيدروكسيد البوتاسيوم على تقليل تركيز المحلول الملحي (brine salinity) عند درجات الحرارة العالية بإستخدام طريقة (CCD-RSM). أظهرت النتائج أن

إمتصاصٍ جيد للـ CO_2 يبلغ 0.50 جم CO_2 لكل جم هيدروكسيد البوتاسيوم و الحد الأقصى لتقليل الـ Na^+ هو 45.6% عند مقياس ضغط 2 بار، وتدفق غاز 776 مل / دقيقة، وتركيز هيدروكسيد البوتاسيوم هو 30 جم / لتر، وعند درجة حرارة عالية تبلغ 50 درجة مئوية. ومن ثم، تم تطبيق شروط التفاعل المُحسَّنة تلك للتحقق من حركية التفاعل (reaction kinetics). تم تحديد أول معدل تفاعل كلي مع الحفاظ علي تركيز الـ CO_2، حيث كان ثابت معدل التفاعل (k) تقريبا (0.0003 mol/l. min). تم تقييم المعالجة متعددة المراحل لتحقيق انخفاض إضافي في التخلص من الأيونات. تم التحقيق في ثلاث طرق مختلفة. قيمت الطريقة الأولى فعالية إضافة بيكربونات الأمونيوم (ammonium bicarbonate, NH_4HCO_3) في تقليل ذوبانية الـ $NaHCO_3$. تركيز كلا من الـ Na^+ و Cl^- قل بنسبة 56.2% و 40% علي التوالي. في الطريقة الثانية، تم التحقق من إضافة المزيد من هيدروكسيد البوتاسيوم في المراحل اللاحقة. كان هناك نسبة تحسن تقريبا 47.3% في إمتصاص الـ CO_2 عن الطريقة الأولى. علاوة على ذلك، زادت نسبة التخلص من كلا من الـ Na^+ و Cl^- إلي 65% و 64.5% علي التوالي. في الطريقة الثالثة، كان معدل إسترداد كلا من الـ Ca^{2+} و Mg^{2+} تقريبا 76.3% و 94.6% علي التوالي، بعد خطوة المعالجة المسبقة (filtration). أدى تقليل هذه الأيونات إلى تقليل التفاعلات التنافسية، مما أدى إلى معدل إمتصاص تراكمي أعلي من جميع المراحل إلى (108.2 g CO_2 / 1000ml)، وهو ما يزيد بنسبة 8.3% عن الطريقة الثانية. أخيرًا، تم تقييم السلوك الديناميكي للمفاعل بإستخدام تغييرات مرحلية في معدل تدفق الغاز والسائل. النتائج واعدة من حيث قابلية الـ (reactor system) لتفاعلات ذات مقياس كبير.

مفاهيم البحث الرئيسية: تحلية، المحلول الملحي المركز (reject brine)، إمتصاص ثاني أكسيد الكربون CO_2، عملية السولفاي (Solvay Process) المعدلة، هيدروكسيد البوتاسيوم، منهجية الـ (response surface)، معدل التفاعل (kinetics)، متعدد المراحل، الديناميكا المائية.

List of Publications

(ORCID ID: 0000-0002-2706-1386)

This dissertation is based on the work presented in the following papers.

I. Aya A-H. Mourad, Mohammad, A.F., Altarawneh, M., Al-Marzouqi, A.H., El-Naas, M.H., Al-Marzouqi, M.H. (2021). Effects of potassium hydroxide and aluminum oxide on the performance of a modified solvay process for CO_2 capture: A comparative study. International Journal of Energy Research, 45(9): 13952-13964. https://doi.org/10.1002/er.6737

II. Aya A-H. Mourad, Mohammad, A.F., Al-Marzouqi, A.H., El-Naas, M.H., Al-Marzouqi, M.H., Altarawneh, M. (2022). CO_2 and ions removal through reaction with potassium hydroxide in desalination reject brine: Statistical optimization. Chemical Engineering and Processing-Process Intensification, 170: 108722. https://doi.org/10.1016/j.cep.2021.108722

III. Aya A-H. Mourad, Mohammad, A.F., Al-Marzouqi, A.H., El-Naas, M.H., Al-Marzouqi, M.H., Altarawneh, M. (2021). KOH-Based Modified Solvay Process for Removing Na Ions from High Salinity Reject Brine at High Temperatures. Sustainability, 13(18):10200. https://doi.org/10.3390/su131810200

IV. Aya A-H. Mourad, Mohammad, A.F., Al-Marzouqi, A.H., Altarawneh, M., Al-Marzouqi, M.H., El-Naas, M.H. (2022). Carbon dioxide capture through reaction with potassium hydroxide and reject brine: A kinetics study. International Journal of Greenhouse Gas Control. (Submitted and under review).

V. Aya A-H. Mourad, Mohammad, A.F., Al-Marzouqi, A.H., Altarawneh, M., Al-Marzouqi, M.H., El-Naas, M.H. (2022). A Process for CO_2 Capture and Brine Salinity Reduction through Reaction with Potassium Hydroxide: A Multi-stage Evaluation. Journal of Natural Gas Science and Engineering. (Submitted and under review).

Author’s Contribution

The contribution of Aya Abdel-Hamid Ismail Mourad to the papers included in this dissertation was as follows:

I. Conceptualization, had main responsibility for the experimental work, writing–original draft and editing, and evaluation of results.

II. Methodology, data collection and processing, software, formal analysis, and writing the first draft.

III. Experimental procedures, data analysis, visualization, and manuscript writing and editing.

IV. Data curation, evaluation of results, visualization, and manuscript writing.

V. Data collection and processing, analysis of results, investigation, and writing the original draft.

Author Profile

Aya Abdel-Hamid I. Mourad was awarded her BSc degree (2013) and M.Sc. degree (2017) in Chemical Engineering from the United Arab Emirates University (UAEU). She was honored from her Highness Sheikha Fatima Bint Mubarak as a distinguished undergraduate student of 3.9 GPA (excellent with honor) in 2014. She was also honored from his highness Sheikh Saif Bin Zayed Al Nahyan as a distinguished graduate student of 3.87 GPA (excellent with honor) in 2019. In 2020, she got the Merit Fellowship award for maintaining an excellent GPA during her PhD study at UAEU. She has more than nine years of academic and professional experience. In, 2013, she worked as a graduate teaching assistant in the UAEU. She then worked as a process engineer for two years (from 2014 to 2016) in Technip France-Abu Dhabi Company, in the field of Oil & Gas Industry. She was involved in Fronxperiencest End Engineering Design (FEED) and Engineering Procurement and Construction (EPC) Projects in Offshore and Onshore Oil & Gas facilities including Greenfield and Brownfield Projects. She is currently working as an instructor at the Abu Dhabi Polytechnic-Institute of Applied Technology (UAE) since 2016. Over the period of her work, she gained a high level of skills and capabilities in teaching. She published many scientific papers in top 5% and 10% journals. All publications are of high impact to the community of UAE. It is always her intention to develop herself and to gain new experiences as she believes that there is always room for self-improvement, both personally and professionally.

Acknowledgements

I am very pleased to record that, words are insufficient to express my gratitude to my supervisor Prof. Ali H. Al-Marzouqi for his constant support, encouragement, and generous assistance. His guidance has been total, never lacking, and enjoyable beyond words.

I would also like to thank my internal advisory committee members, Prof. Mohamed Al-Marzouqi and Dr. Mohammednoor Al Tarawneh for their many valuable and constructive suggestions on my research.

Extended gratitude goes to my external co-advisor Prof. Muftah El Naas, Qatar university, whose support and advice throughout the thesis work was immensely appreciated and a key element to the successful accomplishment of the work.

I would like to thank the chair and all members of the Department of Chemical and Petroleum Engineering at the United Arab Emirates University (UAEU) for assisting me all over my studies and research. I wish to record my heartfelt thanks to my colleague Dr. Ameera Mohammad, Department of Chemical and Petroleum Engineering at UAEU, for providing guidance and support during my PhD work. Her ever-ready availability for my experimental work has made every stage very easy and enjoyable.

I would like also to acknowledge my employer, Institute of Applied Technology - Abu-Dhabi Polytechnic (ADPOLY), for permitting me to continue my PhD studies as a part-time student. Special thanks go to Prof. Mufeed Batarseh, head of the Academic Support Department-ADPOLY, for his continuous cooperation.

Finally, and most importantly, I am deeply indebted to my great father, Prof. Abdel-Hamid Mourad, and my lovely and wonderful mother Wafaa, who contributed, aided, encouraged, and provided me with all the strength I needed throughout my years of study and the process of researching and writing my dissertation. This accomplishment would not have been possible without their assistance. I would also like to thank, in particular, my beloved husband, Eng. Ahmed Mourad, and loving sons, Saif and Faris who provided me with all the support and strength to complete this work. Words fail me to acknowledge the support given by them. In addition, special thanks are extended to my lovely brother (Dr. Bahaa) and my wonderful sister (Eng. Ameera) to all for their kind assistance and support.

Dedication

To my beloved parents, husband, and sons

Table of Contents

List of Tables

List of Figures

List of Abbreviations

$AlCl_3$	Aluminum chloride
Al_2O_3	Aluminum oxide
AMP	2-amino, 2-methyl, propanol
ANOVA	Analysis of variance methodology
Ba^{2+}	Barium
C	Concentration (g/l)
Ca^{2+}	Calcium
$CaCl_2$	Calcium chloride
$CaCO_3$	Calcium carbonate
CaO	Calcium oxide
$Ca(OH)_2$	Calcium hydroxide
CCD	Central composite design
CCU	Carbon capture and utilization
CCS	Carbon capture and storage
CFD	Computational fluid dynamics
CI	Confidence interval
CKD	Cement kiln dust
Cl^-	Chloride
CO_2	Carbon dioxide
CO_3^{2-}	Carbonates
3D	Three-dimensional

DEA	Diethanolamine
EDS	Energy-dispersive X-ray spectroscopy
F	Flowrate (ml/min)
FTIR	Fourier transform infrared
G	Gibbs free energy (kJ/mol)
GCC	Gulf Cooperation Council
GHG	Greenhouse gas emissions
H	Enthalpy (kJ/mol)
H_2	Hydrogen gas
H_2O	Water
HCO_3^-	Bicarbonates
ICP	Inductively coupled plasma
IPSBR	Inert-particles spouted-bed reactor
K^+	Potassium
KCl	Potassium chloride
K_2CO_3	Potassium carbonate
$KHCO_3$	Potassium bicarbonate
KOH	Potassium hydroxide
M	Method
MDEA	N-methyl diethanolamine
MEA	Mono ethanolamine
Mg^{2+}	Magnesium

$MgCl_2$	Magnesium chloride
$MgCO_3$	Magnesium carbonate
$Mg(OH)_2$	Magnesium hydroxide
Na^+	Sodium
NaCl	Sodium chloride
Na_2CO_3	Sodium carbonate
$NaHCO_3$	Sodium bicarbonate
NaOH	Sodium hydroxide
NH_3	Ammonia
NH_4^+	Ammonium
NH_4Cl	Ammonium chloride
NH_4HCO_3	Ammonium bicarbonate
OH^-	Hydroxide ions
P	Pressure (bar)
PZ	Piperazine
R	Reaction rate (mol/l.min)
RSM	Response surface methodology
S	Stage
SEM	Scanning Electron Microscopy
T	Temperature (°C)
UAE	United Arab Emirates
XRD	X-ray Diffraction

Greek letters

τ_p	Time constant (min)
t_d	Dead time (min)
Δ	Change in thermodynamic property

Chapter 1: Introduction

1.1 Overview

It is estimated that by 2025, more than half of the world's countries could face water stress or scarcity, whereas up to 75% of the world's population will be able to face water scarcity by 2050 [1]. Consequently, desalination technology is an attractive option for addressing potable water demand. At the end of 2017, there were 19,372 desalination plants worldwide with a total desalination capacity of roughly 99.8 Mm^3 /day [1]. It is worth mentioning that Gulf Cooperation Council (GCC) countries depend primarily on desalinated water to meet their industrial and domestic needs [2, 3]. Over the last few years, United Arab Emirates (UAE) had a significant growth in its desalination capacity. The production of desalination plants in UAE increased from 7 Mm^3 in 1973 to 1,750 Mm^3 in 2015, and currently there are 266 desalination plants in operation [4]. Despite the fact that desalination produces freshwater, a crucial environmental issue is the reject brine (water with high salts concentration) coproduced from desalination processes [5]. Approximately 1.5 l of reject brine is produced for every 1 l of potable water produced by desalination [6]. Furthermore, another type of waste discharge associated with desalination plants is the emission of carbon dioxide (CO_2) into the atmosphere, which contributes to global warming and climate change [7].

Desalination technology cannot be operated sustainably without addressing the aforementioned environmental concerns. Therefore, the management of discharge brines became a very crucial environmental challenge. The most common methods of reject brine disposal are surface water discharge, deep well injection, evaporation ponds, and land disposal [8]. Reject brine is commonly disposed of into the sea, but in the long term, that could result in harmful effects for the aquatic species and also pollute the water [9]. On the other hand, carbon capture and storage (CCS) is used to sequestrate CO_2, while carbon capture and utilization (CCU) relates to the production of valuable products [9]. However, these conventional technologies entail numerous limitations such as safety concerns, high capital costs, extensive energy requirements, non-universal application, and low efficiency [10-15]. Hence, viable and cost-effective management systems are needed to reduce environmental pollution.

The most efficient way of managing these wastes is to treat these pollutants in a single reaction, namely the modified Solvay process [9]. The proposed process is an effective, economic and environmental friendly approach [9]. However, the available literature [9] shows that more attention is required to overcome different limitations of this process such as, alkaline solubility, operating temperature, and maintaining high pH value. Another challenge is the low salinity reduction of the treated brine, which results in a low overall desalination efficiency [9]. This dissertation focuses on introducing a new alkaline, namely potassium hydroxide (KOH) to investigate its effectiveness to overcome these limitations for a further improvement in the productivity and sustainability of modified Solvay process. Most current technologies directly capture CO_2 from atmosphere by reaction with strong alkaline solutions, such as KOH, due to its strong binding affinities with CO_2 [16]. In addition, the proposed process aims to recover valuable solid products from high salinity water, such as, $NaHCO_3$, potassium bicarbonate ($KHCO_3$), and potassium chloride (KCl), which can be used in many industrial applications [17]. Along the same line of enquiry, the current study sets out to present underpinning thermochemical parameters for the overall reaction. Additionally, parametric sensitivity analysis is carried out to optimize the operating conditions and thereby maximize CO_2 capture and ions removal from high-salinity brines. Furthermore, the ability of the new alkaline to manage brine waste and capture CO_2 at relatively high temperatures (close to brine temperature) is investigated. The kinetic parameters governing the CO_2 capture process through reactions with KOH are also investigated under different operating conditions. Based on the optimized conditions, multi-stage desalination process is investigated for a further reduction in brine salinity. In addition, the dynamic behaviour of the reactor is evaluated to examine the flexibility and applicability of the reactor for large-scale processes.

This project is expected to contribute to the development of an efficient technology for brine desalination and CO_2 capture. The outcomes of the project are expected to be useful for power generation plants, desalination plants, oil refineries, natural gas purification, gas separation in the petrochemical industries, production of nickel-Zinc battery systems [18], and fertilizer industry.

1.2 Statement of the Problem

While desalination of seawater has enabled communities to flourish in the arid conditions of the desert, the by-product of desalination, reject brine, affects the health of marine ecosystems, and it is often directly pumped out to the sea by desalinization plants. Once brine is pumped to the sea it sinks to the sea floor, reducing oxygen levels and destabilizing marine biodiversity [19]. Brine management is a very important aspect of desalination plants considering that it has a substantial environmental impact on both flora and fauna, on sea and land [20]. The total production of brine around the world is 142 Mm^3/day [21]. In the UAE, 42% of the potable water comes from desalination plants; these plants have 14% of the world's total production of brine water [22]. The disposal of reject brine from desalination plants is the greatest environmental and economic challenge associated with water desalination. Reject brine can deteriorate water quality if not disposed of properly [9]. The reject brine is commonly disposed of into the sea, but in the long term, that could result in harmful effects for the aquatic species and also pollute the water [6]. Despite advances in desalination process technology, there is a need for further improvements in the disposal of reject brine. Most of the traditional brine management methods are still suffering from some drawbacks such as the contamination of ground water, salinization of soil and high capital and operational cost [9]. Reject brine consists of many useful ions, such as sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+) and chloride (Cl^-) that can be converted into many useful compounds [9]. These compounds have diverse applications in the industrial sector [23, 24]. Hence, there is a great potential for researchers and scientists to analyze reject brine from the utilization point of view rather than just for its disposal. Another type of waste discharge associated with industries in general and the desalination industry specifically in Middle East is the release of CO_2 into the atmosphere [25, 26]. CO_2 is believed to have the greatest adverse impact on the observed greenhouse effect. Power plants based on coal, oil, and natural gas contribute for approximately 60% of the total CO_2 emissions to the atmosphere [27]. In fact, the rise in the average earth surface temperature is known to correlate well with the amount of CO_2 in the atmosphere. As high levels of CO_2 are also released into the atmosphere by the desalination industry, growing concerns related to climate change have created a further impetus for alternative waste management methods [9, 26]. For example, various desalination methods adopted in the UAE are estimated to be responsible for a discharge of 15,846 tons of CO_2 per day [7]. Industries are rapidly progressing towards innovative technologies to handle the carbon emission. The CCS approach is used for the sequestration of CO_2 and CCU approach is used for the production of value-added products [9, 28]. However, CCS technology has several environmental and technical disadvantages [29, 30]. In addition, CCU requires large amounts of energy to induce reactions. Among existing CCU technologies, the process for converting CO_2 into calcium carbonate ($CaCO_3$) requires high temperature and high pressure as reaction conditions [31].

The combined reaction of reject brine and CO_2 not only manages these pollutants simultaneously, but also results in the formation of value-added products [9]. Hence the concept of “waste to resource generation” is also materialized [9]. The valuable components in the reject brine can react with CO_2 in the presence of a catalytic medium to form value-added products i.e. carbonate salts [24]. “Solvay process” has been considered the primary process for simultaneous treatment of reject brine and capture of CO_2 to form useful biproducts. Ammonia (NH_3) is used as a catalytic medium in this reaction to absorb CO_2 in the presence of sodium chloride (NaCl) to form $NaHCO_3$ and ammonium chloride (NH_4Cl) [8, 32-35]. Although NH_3 was used as a catalyst to enhance the reaction rate by increasing the pH, NH_3 is environmentally hazardous and its recovery is costly [24]. Several modifications have been made to the traditional "Solvay process" in order to improve its performance in terms of energy consumption for NH_3 regeneration [9]. El-Naas et al. [24] modified the Solvay process by replacing NH_3 with 1 to 2% calcium oxide (CaO), which provided better results with respect to pH value, CO_2 capture, and ions reduction. In addition, many other useful products were produced such as soluble calcium chloride ($CaCl_2$) and a precipitate of $NaHCO_3$, which makes the modified Solvay process a more economical viable process and more environmentally friendly.

A major challenge of the Solvay and modified Solvay processes is the limited Na^+ removal which does not exceed 35% [24, 32], and could be related to the associated chemical reactions or to the reactor’s mixing properties, and hydrodynamics or mass transfer limitations. In the chemical reactions involved in the traditional and modified Solvay processes, the presence of metal carbonates such as magnesium carbonate ($MgCO_3$) in the brine may compete with NH_3 and CaO, reducing their availability for reaction with CO_2 and brine salts. Another challenge of the Solvay as well as the modified Solvay processes is the high solubility of $NaHCO_3$ and accordingly the low overall desalination efficiency [9].

Furthermore, the low solubility of CaO in the reject brine is considered as another limitation [24]. The solubility of CaO in reject brine is almost 2 g/l. Adding extra amounts of CaO beyond the solubility limits is required to maintain high pH value through the reaction, CO_2 capture, and metal ions reduction. It was reported that the optimum CaO amount is 20 g/l. Adding more than 20 g/l of CaO resulted in the formation of $CaCO_3$ and thus competing with the formation of $NaHCO_3$ [24]. On the other hand, adding less than 20 g/l CaO significantly reduced the percentage reduction of Na^+ ions in reject brine. This is due to the reduction in the pH value, which decreased the solubility of CO_2 in reject brine [24]. It was also reported that CO_2 capture does not seem to be affected by increasing the CaO concentration beyond 20 g/l, as pH level (12.5) maintained the same beyond this level. This indicates that the CO_2 capture is mainly related to pH level in contrast to Na^+ removal, which is related to both pH level and CaO concentration [24]. Therefore, further investigation is needed to overcome the CaO solubility limits and thus improve the percentage reduction of Na^+ in reject brine.

Moreover, the Solvay and modified Solvay processes are facing another limitation related to the operating temperature of the reaction. In general, it was concluded from all the previous studies [9] that the modified Solvay processes based on different types of alkaline and wastes are preferred to be operated under low temperatures (10-20°C), where the low temperature increases the solubility of CO_2 gas and enhances the precipitations of metallic salts. However, it is worth mentioning that brine is usually rejected from desalination plants at relatively high temperatures (40-55°C) [36]. Hence, there is a need to overcome the temperature limitation and to be able to capture CO_2 and mange reject brine without any further cooling.

It is also important to note that the kinetics of modified Solvay process have not yet been thoroughly studied, which could significantly help in improving and enhancing the rate of the reaction and overall performance of the process [9].

Current research focuses on introducing a new alkaline, namely KOH to investigate its effectiveness and ability to overcome these limitations for a further improvement in the overall performance of the modified Solvay process.

1.3 Relevant Literature

1.3.1 Water Scarcity

The distribution of water resources on Earth is not favorable, as seawater constitutes about 96.54% of the total, while freshwater constitutes only 2.53% [37]. In recent years, many countries have faced severe water crises due to the reduction in groundwater availability [9]. As the world's population rises, the availability of water resources is increasingly threatened. Additionally, households and agriculture utilize a large volume of groundwater, which might contribute to water shortages [9]. Several measures are being taken to reduce the stress on the water supply, including conservation of water, repair of existing infrastructure, and modification of distribution systems. However, these measures can only improve the available water resources, not increase their availability. This encourages countries to utilize seawater through desalination, which demands greater investment in water procurement [9].

1.3.2 Desalination Technology

The Middle East is considered a leader in large-scale seawater desalination. The GCC countries produce more than 60% of all desalinated water produced worldwide. Within the Middle East, the UAE is suffering from water shortage due to the fast-growing population and the expansion of industrial and agricultural activities. The UAE produces about 13% of the world desalinated water production due to the economic and demographic development [22]. Globally, the highest proportion of desalted water is produced through membrane processes, i.e., 63.7%, while 34.2% is produced through thermal desalination processes [9].

1.3.3 Environmental Impact of Desalination

The output of the desalination approach is clean water, reject brine or concentrate stream with high salt concentration, and greenhouse gas emissions (GHG). GHG comes from the burning of fossil fuels for thermal energy and electricity generation. The primary component of GHG is CO_2 [38-40]. The disposal of reject brine from desalination plants is the greatest environmental and economic challenge associated with water desalination. The reject brine is usually disposed into the sea, but in the long term, that could result in harmful effects for the aquatic species and also pollute the water [6]. The economic and environmental concerns associated with reject brine limit the economic performance of the desalination industry [26]. Another type of waste discharge associated with the desalination industry specifically in Middle East is the release of CO_2 into the atmosphere. CO_2 is the major contributor to global warming as it is relatively more persistent in the atmosphere than other gases [41]. The high consumption of coal and fossil fuels releases large volumes of CO_2 into the atmosphere [42]. Power plants based on coal, oil, and natural gas contribute approximately 60% of the total CO_2 emissions to the atmosphere [27]. Hence, removing CO_2 from flue gases can effectively reduce the volume of carbon entering the atmosphere. Desalination technology cannot be operated sustainably unless the aforementioned environmental concerns are addressed.

1.3.4 Reject Brine Management

Although technological advances have resulted in the development of new and highly efficient desalination processes, little improvements have been achieved in the management and handling of the major by-product waste of most desalination plants. Regulatory authorities usually do not allow direct disposal of reject brine if the concentrations of contaminants and primarily metals exceed concentration-based discharge limits [43]. The disposal of reject brine represents major environmental challenges to most desalination plants, and it is becoming more costly [44]. This is especially true for inland desalination plants where brine disposal could reach 15% of the overall desalination cost [45]. The most common methods of reject brine disposal include surface water discharge, deep well injection, evaporation ponds, and land disposal. These methods have safety concerns, high costs, and low productivity making them less feasible for long term usage [9-15]. For instance, evaporation ponds suffer from many drawbacks including the need for huge areas and the possibility of contaminant leakage into soil and groundwater [8]. Currently, options for reject brine treatment are limited and most treatment methods have been developed in laboratories and their feasibility at the industrial scale is unclear [9].

1.3.5 CO_2 Capture

Widely used methods for CO_2 capture include adsorption, absorption, membrane-based processes, and application of biotechnological materials [9, 46-49]. However, these methods face several technical and economic barriers that must be overcome before it can be implemented on a large scale [29, 30].

In addition, the conversion of CO_2 to various products is energy intensive (CCU), as it requires large amounts of energy to induce reactions [31].

1.3.6 Combined Reaction

There is an urgent need to develop a new process for the management of desalination reject brine that can be used by coastal as well as inland desalination plants. Reject brine comprises many metal ions, such as Na^+, Mg^{2+}, Ca^{2+}, K^+, and Cl^-. These components can be converted into many useful products which have various important industrial applications [9]. Therefore, reject brine can be classified as a “resource” instead of a “waste” byproduct. Hence, there is a great potential for researchers and scientists to analyze reject brine from the utilization point of view rather than just for its disposal. Recent studies analyzed the recovery of valuable salts and chemicals from brine to assess the sustainability of brine treatment processes [50, 51]. However, high costs are incurred in scaling- up extraction, and further improvements are needed [52]. A cost effective and energy efficient way is to manage these pollutants (reject brine and CO_2 emission) together in a single reaction. The presence of valuable metal ions in the reject brine can react with CO_2 in the presence of an alkaline medium, resulting in the formation of value-added products.[9].

1.3.7 Parameters Affecting the Reaction

1.3.7.1 Effect of pH Value

A high pH is required in the combined process to capture CO_2 and remove salt from reject brine at the same time. The pH, which is a key parameter in this process, determines the composition of the products and overall progress of the reaction. A higher pH increases the CO_2 solubility in water and increases the saturation rate of salt with respect to the CO_2. In addition, a high pH reduces the solubility of the metallic components of salt and increases precipitation, thus improving the efficiency of CO_2 capture and salt removal [9, 24, 32]. The ideal pH level reported in the literature resides between 10 and 12 [23]. To increase the pH level, various alkaline components are often added into the mixture. Various alkaline oxides and amines were previously used to adjust the pH of the combined process [9].

1.3.7.2 Effect of Alkaline Type

The Solvay process was named after Ernest Solvay who was the first to develop the process in 1860. It is initially developed for the manufacture of sodium carbonate (Na_2CO_3), where NH_3 is used as a catalytic medium to absorb CO_2 in the presence of NaCl to form a precipitate of $NaHCO_3$ and soluble NH_4Cl [32-35, 53], according to Equation (1.1). $NaHCO_3$ is then heated to form the washing soda (Na_2CO_3); whereas NH_4Cl solution is mixed with calcium hydroxide ($Ca(OH)_2$) and heated to recover NH_3 according to Equations (1.2) and (1.3), respectively [32].

$$NaCl + NH_3 + CO_2 + H_2O \rightarrow NaHCO_3 + NH_4Cl \tag{1.1}$$

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O \tag{1.2}$$

$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O \tag{1.3}$$

Mohammad et al. [32] optimized the Solvay process with respect to CO_2 capture and Na^+ reduction by applying response surface methodology (RSM) for optimization. Optimal conditions were achieved at a gas flow rate of 1.54 l/min, a temperature of 19°C, and a molar ratio of NH_3 to NaCl of almost 3.3:1; these parameters resulted in a maximum Na^+ reduction of 33% and CO_2 capture efficiency of 86%. On the other hand, NH_3 is a relatively hazardous substance to both human health and the environment. Furthermore, NH_3 regeneration is regarded as an energy-intensive step that significantly raises the overall operating cost of the process [24, 32], in addition to its high volatility at the operating temperature [41, 54].

Different modifications have been made to the "Solvay process" in order to improve its performance. Alternative solvents to NH_3 are considered as major developments in the conventional Solvay process, as they overcome the aforementioned drawbacks associated with NH_3 [9]. Different types of amines i.e. 2-amino, 2-methyl, propanol (AMP), mono ethanolamine (MEA), diethanolamine (DEA), N-methyl diethanolamine (MDEA), and piperazine (PZ) are proved to be effective replacements to NH_3 [9, 10, 55, 56]. Amine recovery is a challenging task that needs to be addressed [57]. Generally, to achieve the maximum recovery of amine, two methods are considered. In the first method, the precipitation of amine salts is achieved with a cooling filtrate, followed by the reaction of precipitates with lime. This causes the formation of $CaCl_2$ and $CaCO_3$ and releases amine that can be reused for CO_2 absorption. In the second method, the desorption of filtrate was performed to remove the absorbed CO_2. The maximum desorption temperature was found to be 120°C for 0.6 M NaCl and 30 wt% AMP. Then, with the injection of lime and sodium aluminate, the chloride ions converted into calcium chloroaluminate, which has several applications and the amine can be separated for re-utilization [9, 10].

Recently, El-Naas et al. [24] modified the Solvay process by replacing NH_3 with CaO according to Equation (1.4). $Ca(OH)_2$ is produced following the addition of CaO to the brine, after which it reacts with CO_2 to produce $NaHCO_3$ and soluble $CaCl_2$, which can be utilized in many industrial applications [24, 58]. The experiments were carried out using a novel inert particle spouted bed reactor (IPSBR). The results demonstrated that the spontaneity of the CO_2 reaction with $Ca(OH)_2$ is higher than that of the conventional Solvay process, Equation (1.1). The parametric sensitivity studies were conducted using central composite design (CCD) approach-based RSM analysis to evaluate the impact of the most important parameters on process performance and to determine the optimum operating conditions.

The results indicated that at optimum operating conditions (temperature, gas flow rate, pressure, and CaO concentration of 20°C, 1 l/min, 1 atm, and 20 g/l, respectively) an optimum CO_2 uptake value of 0.92 g CO_2/g CaO and a reduction in Na^+ ion of 30% were achieved. More reduction in Na^+ up to 35% was reported by the addition of ammonium bicarbonate (NH_4HCO_3) [24], which confirmed its effectiveness in reducing $NaHCO_3$ solubility. It was also reported that under the same optimum conditions, the reaction sustained a pH value of 11.8, compared to the Solvay process pH of 11.2. Therefore, the modified process entails the dual benefit of reducing brine salinity and CO_2 capture. In addition, the modified process eliminates the need for NH_3 recovery, which is an energy intensive step in the traditional Solvay process.

$$2NaCl + 2CO_2 + Ca(OH)_2 \rightarrow CaCl_2 + 2NaHCO_3 \quad (1.4)$$

However, it was reported that increasing the concentration of CaO beyond 20 g/l does not increase the pH, but can result in an increase in the mass transfer resistance between the reactants [24]. Therefore, the process is designed in a manner to optimize the concentration of the alkaline component needed to enhance the pH. The process can be improved by investigating a new alkaline that that is highly soluble and can maintain a high pH value.

1.3.7.3 Effect of Temperature

In addition to the effects of alkaline type and solution pH, reaction temperature has a significant impact on the process performance because it controls the solubility of CO_2, precipitation of metal ions in the brine, and composition of the final products [9]. In general, increasing the temperature causes an increase in product solubility, a decrease in CO_2 capturing and metal removal efficiency, and a change in product composition. Therefore, the temperature must be optimized to obtain the desired composition of product and other mentioned factors. In case NaCl is present as the main constituent in the reject brine, $NaHCO_3$ is obtained as the main product and its solubility increases as the temperature increases as shown in Figure 1.1, which ultimately decreases the precipitation of the desired product. [9, 59]. Additionally, high temperatures also decrease the CO_2 solubility, which lowers its capturing efficiency. Hence, in general, high temperatures are not beneficial to this process. El-Naas et al. [24] found that an increase in temperature from 10°C to 50°C causes almost 50% decrease in CO_2 removal efficiency for NaCl rich brine. In addition, the increase in temperature reduces the sodium removal efficiency, from 35% to < 5% as the temperature increases from 20°C to 50°C. Another study reported by S. Palitsakun et al. [60] described the effect of temperature, NaCl concertation, NH_3 concentration, and CO_2 flow rate on the CO_2 capturing efficiency using NH_3 base absorbent in a bubble column. The authors observed a reduction in CO_2 capturing efficiency with increased temperature, and this decline becomes even more significant with an increase in the gas flow rate, which is due to the reduced gas residence time. A CO_2 capturing efficiency of about 70% was achieved at a temperature of 38°C, 3.0 M initial concentration of NaCl and CO_2 gas flow rate of 500 ml/min. After 3 h of reaction time, approximately 10% increase in efficiency was observed by reducing the gas flow rate to 300 ml/min, while keeping the other parameters constant [60].

In addition, a higher temperature enhances the evaporation of volatile basic absorbents, such as NH_3, resulting in a decrease in the pH of the solution, ultimately resulting in lower CO_2 absorption. Therefore, an optimum gas flow rate and ambient temperature are required to maximize the efficiency of CO_2 capture and metal removal [9].

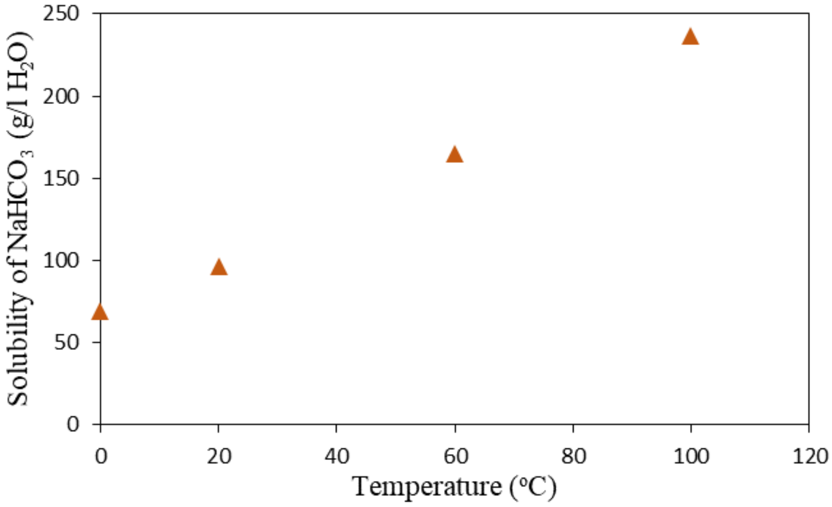


Figure 1.1: Solubility of $NaHCO_3$ in grams (g) per liter of water as a function of temperatures (°C) [9, 59]

The spontaneity of the NH_3-based Solvay process was compared to the CaO-based modified Solvay process using Gibbs free energy change (ΔG) with temperature. Figure 1.2 clearly shows that Equation (1.4) is a more spontaneous reaction than Equation (1.1) at all temperatures. The ΔG change becomes more negative with reduced temperature and Equation (1.4) is more favorable to produce a high quantity of products. The CaO based Solvay process not only avoids the hazardous effects from the traditional Solvay process, but it achieves better performance in terms of CO_2 capture, Na^+ removal and energy consumption. It can be noted from Figure 1.2 that ΔG difference between Equations (1.1) and (1.4) reduces with an increase in temperature. Moreover, the spontaneity of these two reactions decreases with temperature [9, 24].

It is worth mentioning that reject brine is usually discharged from desalination plants at relatively high temperatures (40–55°C) [36]; however, the combined process requires low temperatures (10–20°C) to increase CO_2 capture and improve ion removal [9]. Hence, there is a need to overcome the temperature limitation and to be able to operate the process effectively without any further cooling.

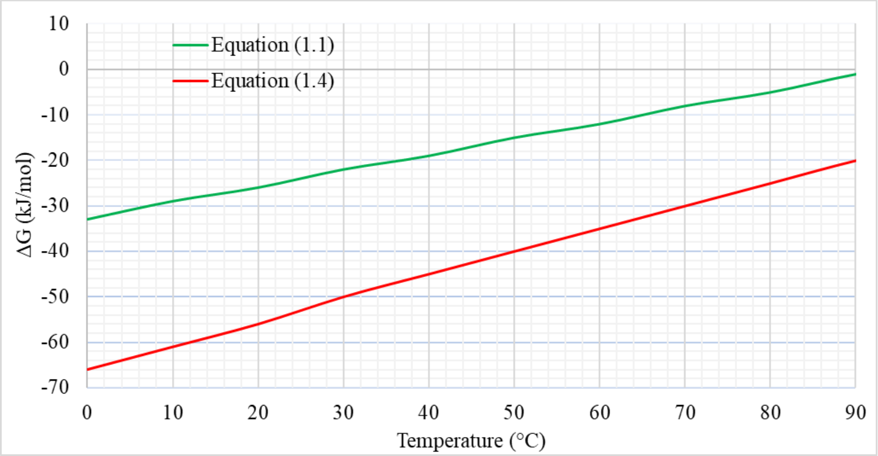


Figure 1.2: Thermodynamic comparison of Equations (1.1) and (1.4) [9, 24]

1.3.7.4 Effect of Salt Type and Concentration

It is also important to note that the type and concentration of salt determines the product type and its percentage yield [9]. Normally, in the Solvay process, NaCl dominant brine is utilized to obtain precipitation of $NaHCO_3$ [8, 10, 61, 62], whereas nesquihonite, dolomite, hydromagnesite, lansfordite, artinite, dypingite are the most common products formed from the treatment of Mg-rich reject brine [23, 62-66]. In the case of magnesium chloride ($MgCl_2$) dominant brine utilized to capture CO_2, the final products and capturing efficiency of CO_2 are different from the NaCl based brine. The CO_2 capturing efficiency for Mg^{2+} and Na^+ rich brine ranges from 29 to 99% [9]. The reaction rate decreases with increased salinity. With high salinity (magnesium rich), there is a formation of chlorartinite minerals, which are soluble carbonates not recommended to capture the CO_2. At low magnesium salt concentration, nesquehonite and lansfordite precipitation takes place. They are stable enough to hold carbon dioxide for relatively longer periods [65].

In the current research, the brine utilized contains high concentration of NaCl. Therefore, $NaHCO_3$ is the main products from the Solvay and modified Solvay processes. However, the high solubility of $NaHCO_3$ limits the overall performance of the process [9]. It is critical to investigate factors other than temperature and pressure that can increase $NaHCO_3$ precipitation. Investigating a new alkaline with high solubility may reduce mass transfer limitations and improve $NaHCO_3$ precipitation for a further increase in the productivity and sustainability of the modified Solvay process.

1.3.7.5 Reaction Kinetics of CO_2 Using Various Chemical Solvents

In chemical processes, the mass transfer from gas bubbles to the surrounding liquid or vice versa is an important factor. This absorption process in the presence of a chemical reaction usually takes place in the liquid phase. One of the most important factors for decreasing the cost of regeneration is the use of an effective solvent with low regeneration energy requirements. In addition, the solvent should possess rapid reaction kinetics and high absorption capacity [67]. The overall CO_2 absorption can be categorized into physical and chemical absorption [68, 69]. Physical absorption takes place as the CO_2 is diffused from the gaseous phase into the liquid phase through an interface which can be described by the two-film theory. This method is commonly described by a mass transfer coefficient which relates the mass flux to a concentration difference and is a function of the material properties and flow conditions. Reactive chemical absorption can be explained as a process in which the CO_2 reaction occurs in the liquid phase (film or bulk) [9]. For Solvay reactions in which CO_2 reacts with NH_3 (Equation (1.1)), the instantaneous rate of reaction controlled by diffusion is as follows [70]:

$$\text{Rate} = K_{NH_3} C_{NH_3} C_{CO_2} \tag{1.5}$$

Abdel-Aal et al. [71] developed a numerical algorithm to evaluate the unreacted NH_3 concentration. The numerical values were compared with experimental data. There was a good agreement between the experimental and numerical results. It was concluded that the resistance to mass transfer was present only in the liquid side (liquid diffusion-controlled). Therefore, bubble column reactor was the best choice for the process because liquid–diffusion controlled required more contact time to reach satisfactory results. El Hadri et al. [72] investigated the use of six types of amines—five tertiary amines and one secondary amine (2-ethylaminoethanol, 2EAE) in terms of CO_2 capture efficiency. The thermodynamic and kinetic characteristics of the six amines for absorbing CO_2 were analyzed. The kinetics of CO_2 absorption by the above-mentioned amines was measured at a temperature range of 25 to 40°C and a concentration range of 5 to 800 mol/m^3 using stopped-flow equipment. The obtained constant of the second-order reaction rate illustrated that the 2EAE (2-ethylaminoethanol) has better thermodynamic, CO_2 absorption, and kinetic properties compared with the conventional amine-based solvent (i.e., MEA), and, as such, 2EAE could be utilized as an alternative to MEA.

It is also worth mentioning that the kinetics of modified Solvay process have not yet been investigated deeply that may help to a large extent in improving and enhancing the rate of the reaction. This can also help with scaling up the process to an industrial level.

Table 1.1 shows a summary of studies on the combined process with a prime focus on reaction temperature, metal removal efficiency, CO_2 capture efficiency, and a summary of main products [9].

Table 1.1: Summary of carbon dioxide capture and brine desalination studies [9]

Author	Reactants	Reaction Temperature	Metal removal efficiency	CO_2 Capture Efficiency	Main Products	Advantages	Challenges
Kang et al., 2020 [56]	Industrial wastewater (Ca^{2+}, Mg^{2+} and Na^+ rich ions) is carbonated in the presence of MEA	25°C (process temperature) 70°C (ethanol removal) 200°C (water removal)	50.1 mol % (Na^+)	~44.29 mole % Efficiency = CO_2 (product)/CO_2 (supply))	$CaCO_3$ $MgCO_3$ $NaHCO_3$	Separation of both $Ca^{2+}$and Mg^{2+} ions, average metal removal efficiency	To achieve multiple products with high purity, Regeneration of MEA, Low CO_2 capturing efficiency
Palitsakun et al., 2019 [60]	Carbonation of ammoniated brine (NaCl)	20°C	N/A	> 91 % (Efficiency = CO_2 (concentration in outlet gas)/CO_2 (concentration in inlet gas))	$NaHCO_3$ Na_2CO_3 NH_4HCO_3 Ammonium carbonate	High CO_2 capturing efficiency	Separation and purification of products, Regeneration of NH_3
Galvez-Martos et al., 2018 [63]	Reject brine (Mg^{2+} rich and a significant concentration of Ca^{2+}) is carbonated in the presence of alkaline media (Sodium hydroxide (NaOH))	20-60°C	67-97% (Ca^{2+}) 21-83% (Mg^{2+})	N/A	$CaCO_3$ Nesquihonite Dolomite Hydromagnesite family	Separation of multiple ions, high metal removal efficiency	To achieve multiple products with high purity, Regeneration of alkaline media (NaOH)

Table 1.1: Summary of carbon dioxide capture and brine desalination studies [9] (Continued)

Author	Reactants	Reaction Temperature	Metal removal efficiency	CO_2 Capture Efficiency	Main Products	Advantages	Challenges
Dindi et al., 2018 [73]	Mixed metal oxides (mixed magnesium/aluminum oxides) are used to capture CO_2 and reduce the salinity of reject brine	25ºC (Regeneration temperature of mixed metal oxides lies from 400-800 ºC)	20% (Na^+)	~42 % Capture efficiency = %CO_2 (exist gas)/%CO_2 (inlet gas)	$NaHCO_3$	High purity of product	Regeneration of mixed metal oxide, Low metal removal efficiency, Low CO_2 capturing efficiency, High energy cost
Imbabi et al., 2018 [23]	Reject brine (Mg-based ions) is reacted with cement kiln dust (CKD) to capture CO_2	20-70ºC	59-95% (Mg^{2+})	51-91% CO_2 yield [mass %] = Mg yield * R, where R is the CO_2 / Mg molar ratio in the product formed)	lansfordite nesquehonite artinite dypingite	High CO_2 capturing efficiency, Utilization of industrial waste as an alkaline media	Separation and purification of products, Noticeable fouling of industrial equipment
Zhang et al., 2018 [74]	CO_2 mineralization using artificial brine ($CaCl_2$, $MgCl_2$ and NaCl) reacted with NaOH in the presence of nickel-based nanoparticles	25-50ºC	>50% (Ca^{2+})	87.8% without catalyst and 96.7% with catalyst (Efficiency = CO_2 (product)/CO_2 (supply))	$CaCO_3$ (calcite, aragonite)	High CO_2 capturing efficiency	Separation and purification of products, Regeneration of alkaline media (NaOH)

Table 1.1: Summary of carbon dioxide capture and brine desalination studies [9] (Continued)

Author	Reactants	Reaction Temperature	Metal removal efficiency	CO_2 Capture Efficiency	Main Products	Advantages	Challenges
Bang et al., 2017 [75]	CO_2 mineralization using reject brine (containing Mg^{2+} and Ca^{2+} ions) in the presence of alkaline media (NaOH)	Ambient temperature	99% (Ca^{2+}) 86% (Mg^{2+})	>86% CO_2 (Efficiency = CO_2 (product)/CO_2 (supply))	Hydromagnesite calcite	Separation of multiple ions, high CO_2 capturing efficiency,	Regeneration of alkaline media (NaOH), Separation and purification of products
Mohammad et al., 2016 [32]	Ammoniated brine is used to capture CO_2 and CaO is used to regenerate NH_3	19°C	33% (Na^+)	86% (Efficiency = CO_2 (concentration in outlet gas)/CO_2 (concentration in inlet gas))	$NaHCO_3$ NH_4Cl	High CO_2 capturing efficiency	Regeneration of NH_3, Separation and purification of products, Low metal removal efficiency
El-Naas et al., 2017 [24]	Reject brine is reacted with CaO to capture CO_2	20°C	35% (Na^+)	99% (Efficiency = CO_2 (moles captured)/CO_2 (moles loaded))	$NaHCO_3$ $CaCl_2$ $CaCO_3$	High CO_2 capturing efficiency	Low metal removal efficiency

Table 1.1: Summary of carbon dioxide capture and brine desalination studies [9] (Continued)

Author	Reactants	Reaction Temperature	Metal removal efficiency	CO_2 Capture Efficiency	Main Products	Advantages	Challenges
De Carvalho Pinto et al., 2016 [64]	Ammoniated brine is used to capture CO_2 and steel slag is used to regenerate NH_3	≥20°C	>89% (Ca)	8.1 wt% of the initial CO_2 effectively captured and converted into $CaCO_3$ (Efficiency = CO_2 (product)/CO_2 (supply))	$NaHCO_3$ $CaCO_3$ NH_4Cl	High metal removal efficiency	Low CO_2 capturing efficiency, Separation and purification of products
Shim et al., 2016 [76]	NaOH could be produced from NaCl electrolysis reacted with CO_2	Ambient temperature	N/A	CO_2 absorption rate is >95.0%, CO_2 absorption rate = volume percent of CO_2 captured by volume percent of CO_2 in the inlet gas *100	$NaHCO_3$	High purity of the product, High CO_2 capturing efficiency	High energy expenditure, complex reactor design
Ibrahim et al., 2019 [77]	Reject brine is reacted with steel-making dust (BHD) to capture CO_2	24°C	N/A	0.22g CO_2/g BHD	$MgCO_3$ $CaCO_3$	Utilization of steel-making waste Attainment of high purity main products	Low CO_2 capturing efficiency

In the light of the above literature review, it can be concluded that the combined reaction of reject brine and CO_2 not only alleviates the environmental pollutants simultaneously, but also produces a variety of useful products. However, some operating parameters limit the overall performance of the modified Solvay processes. A parametric evaluation provides valuable insight into the effects of various factors.

The low solubility of the alkaline used in the modified Solvay process is one of the most important factors that can significantly affect the process [9]. For instance, the solubility of CaO in reject brine is almost 2 g/l. Adding extra amounts of CaO beyond the solubility limits is required to maintain high pH value through the reaction, CO_2 capture, and metal ions reduction. It was reported that the optimum CaO amount is 20 g/l. Adding more than 20 g/l of CaO resulted in the formation of $CaCO_3$ and thus competing with the formation of $NaHCO_3$, according to Equation (1.6). In addition, $CaCO_3$ scale causes fouling of process equipment. On the other hand, adding less than 20 g/l CaO significantly reduced the percentage reduction of Na^+ ions in reject brine. This is due to the reduction in the pH value, which decreased the solubility of CO_2 in reject brine. It was also reported that CO_2 capture does not seem to be affected by increasing the CaO concentration beyond 20 g/l, as pH level (12.5) maintained the same beyond this level. This indicates that the CO_2 capture is mainly related to pH level in contrast to Na^+ removal, which is related to both pH level and CaO concentration. Therefore, further investigation is needed to overcome the solubility limits of CaO and hence improve the percentage reduction of Na^+ in reject brine.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (1.6)$$

Temperature is another important parameter. It is also worth mentioning that the traditional Solvay process and other modifications that are based on different types of alkaline material are effective in the reduction of reject brine salinity and the capture of CO_2 under low temperatures (10–20°C) [9]. At low temperatures solubility of CO_2 is higher, which enhances the precipitation of metallic salts [9]. However, brine is commonly discharged from desalination plants at relatively high temperatures of 40–55°C [36]. To the best of the author's knowledge, no previous work has optimized the Solvay or modified Solvay processes to achieve high CO_2 capture and ion removal at relatively high temperatures.

In addition, the high solubility of the main product ($NaHCO_3$) is regarded as a significant challenge for Solvay and modified Solvay processes, and accordingly the low Na^+ removal [9]. This is clear from the summarized studies on the combined process in Table 1.1, which illustrates the metal removal efficiency.

More research is required to improve the reduction of brine salinity and increase the recovery of some metal ions in the form of high purity, valuable products. Several studies have been striving to recover the divalent ions such as Ca^{2+} and Mg^{2+} from seawater and brine prior to the post-treatment process, as it could enhance the overall performance of the process [9, 78-83]. Rahardianto et al. [84] reported that when reverse osmosis was combined with accelerated precipitation softening, the recovery of low-salinity brackish water was optimized, with total product water recovery of up to 98% due to concentration reductions in scale-forming ions of more than 90%, 95% and 78% for Ca^{2+}, barium (Ba^{2+}) and strontium (Sr^{2+}), respectively.

Furthermore, the experimental data that represents the kinetics of CO_2 reactions in the modified Solvay process requires further investigation [9], which will aid in greatly improving and enhancing the rate of the reaction, and thus the overall performance of the process. This can also assist to scale up the process to an industrial level.

According to the literature, the modified Solvay process based on CaO is more effective, economical, and environmentally friendly than the conventional Solvay process based on NH_3 or other types of amines. However, the aforementioned limitations (Sections 1.2 and 1.3), such as alkaline solubility, pH value, operating temperature, and low Na^+ removal resulted in a low overall desalination efficiency.

This research focuses on introducing a new alkaline, namely KOH to investigate its ability to overcome these limitations for a further improvement in the productivity and sustainability of the modified Solvay process. Most current technologies directly capture CO_2 from atmosphere by reaction with strong alkaline solutions, such as KOH, due to its strong binding affinities with CO_2 [16]. Bandi et al. [85] investigated the absorption of CO_2 by adding KOH inside a packed column with a total height of 2 m. It was concluded that the CO_2 absorption from ambient air was around 70%. Lendzion-Bielun et al. [86] investigated the effect of KOH treatment on the surface properties of activated commercial carbon to improve the adsorption capacity of CO_2. They reported an increase in the concentration of hydroxyl groups on the surface, which led to an increase in the uptake value of CO_2 by 14% at 0°C. In another study performed by Keith et al. [87] aqueous KOH solution was combined with calcium caustic recovery loop to capture about 1 Mt-CO_2/year from ambient air in an industrial plant. Detailed engineering and cost analysis were studied. It was reported that the levelized cost was about 94 to 232 \$/t-CO_2 captured from the atmosphere. Lombardia et al. [88] studied the effects of capturing CO_2 from landfill gas by the addition of KOH and producing useful products. It was mentioned that adding extra amounts of KOH resulted in the production of K_2CO_3. However, potassium bicarbonate (undesired) was obtained by adding extra amounts of CO_2. About 98% of CO_2 capture was reached under a KOH concentration of 53%, a solution flow rate of 60 l/h, and almost a constant temperature between 40°C and 45°C. Mohammad et al.

[89] analyzed the effect of modified activated alumina with sodium hydroxide (NaOH) and KOH on the CO_2 adsorption efficiency. By using 2.0 g of adsorbent, under optimum conditions (20°C and 6 bar), the results indicated that the highest CO_2 adsorption was 0.147 g/g for KOH (concentration of 30%) in comparison with 0.131 g/g for NaOH (concentration of 30%).

1.4 Research Objectives

To the best of the author’s knowledge, the KOH-based Solvay process has never been investigated in the available literature. Hence, the proposed research is considered novel since for the first time KOH is utilized in the modified Solvay process. The overall reaction of the modified Solvay process based on KOH as the alkaline material can be described using Equation (1.7). It is also important to note that all the experiments were carried out in a novel inert particle spouted bed reactor (IPSBR) developed by El-Naas et al. [90, 91].

$$NaCl + CO_2 + KOH \rightarrow NaHCO_3 + KCl \tag{1.7}$$

The combined reaction of reject brine and CO_2 not only manages these pollutants simultaneously, but also results in the formation of value-added products such as KCl and $NaHCO_3$. These solids can be used in further environmental and industrial applications [17]. It is also important to note that the production of 1 mole of CaO from $CaCO_3$ can produce 1 mole of CO_2, as shown in Equation (1.8) [24]. However, in the presence of NaCl and according to the Modified Solvay process (Equation (1.4)), $Ca(OH)_2$ can capture 2 moles of CO_2 which may affect the total amount of CO_2 captured. KOH can be produced from the electrolysis of the KCl solution, as illustrated in Equation (1.9) [17] with no CO_2 production, which is an advantage of using KOH.

$$CaCO_3 \rightarrow CaO + CO_2 \tag{1.8}$$

$$2\ KCl + 2\ H_2O \rightarrow 2\ KOH + Cl_2 + H_2 \quad (1.9)$$

Experimental screening, thermodynamic analysis, statistical analysis and optimization, as well as solid characteristics for the main involved reaction are needed to evaluate the efficiency of the proposed process. Accordingly, the objectives of this research are the following:

1. To investigate the potential of KOH as an alternative alkaline on the overall performance of the modified Solvay process and to compare its effectiveness with that of CaO in terms of pH, alkaline solubility, CO_2 capture, ion reduction, and thermochemical parameters.

2. To perform a parametric study to optimize the underlying operating parameters such as temperature, gas flow rate, pressure, and KOH concentration.

3. To investigate the ability of the KOH-based Solvay process to manage the two wastes at a relatively high temperature of 50°C, as reject brine is typically discharged from desalination plants at relatively high temperatures (40–55°C).

4. To study the kinetics of CO_2 reactions in the modified Solvay process based on KOH to acquire a model that best describes the underlying reaction kinetics.

5. To evaluate the multi-stage treatment process with the addition of NH_4HCO_3 to reduce the solubility of $NaHCO_3$ for a further reduction in Na^+ ions from high-salinity brines and to increase the CO_2 capture efficiency under optimal operating conditions.

6. To investigate the dynamic behavior of the IPSBR using step changes in the inlet gas and liquid flow rate. To assess the reactor system's flexibility, stability, and adaptability for large-scale processes.

Chapter 2: General Discussion

2.1 Research Design

Current research focuses on introducing a new alkaline (KOH) to investigate its ability to overcome the limitations associated with the modified Solvay process based on CaO (Chapter 1) for a further improvement in the productivity and sustainability of the modified Solvay process. The outcomes of this work have been published in Papers I to V.

2.1.1 Preliminary Study for KOH as a New Alkaline (Paper I)

A preliminary study was conducted to compare the effectiveness of other alkaline and amphoteric oxides, namely KOH and aluminum oxide (Al_2O_3), respectively, with that of CaO in terms of thermodynamic properties, pH value, solubility, CO_2 capture, ions reduction.

Thermodynamic Analysis:

The thermodynamic analysis for the three reactions illustrated in Equations (2.1), (2.2), and (2.3) was performed using quantum chemical calculations [92]. Gaussian16W software was utilized using the CBS-QB3 composite method [93, 94]. The latter initially executes all the geometry optimizations and frequency calculations for all illustrated reactants and products in reactions (2.1), (2.2), and (2.3) at the B3LYP/CBSB7 level of theory. This is followed by successive single point energies at higher theoretical levels. It is very important to note that all the preferred properties should be assessed at the minimum energy geometries. In the following step, the obtained values of the vibrational frequencies and rotational constants from the Gaussian16W software were used to compute thermodynamic partition functions, from which Gibbs free energy (ΔG) and enthalpy (ΔH) for Equations 2.1–2.3 as a function of the temperature were determined. Thermochemical computations were carried out using ChemRate code [95].

$$2NaCl + 2CO_2 + Ca(OH)_2 \rightarrow 2NaHCO_3 + CaCl_2 \quad (2.1)$$

$$NaCl + CO_2 + KOH \rightarrow NaHCO_3 + KCl \quad (2.2)$$

$$6NaCl + 6CO_2 + Al_2O_3 + 3H_2O \rightarrow 6NaHCO_3 + 2AlCl_3 \quad (2.3)$$

Impact of the Alkaline/Metal Oxide Amount on the Initial pH Value and Temperature:

From previous research works [9, 24, 58], it was concluded that the pH value impact on the CO_2 capture and ions reduction from brine is rather very significant. The high pH value plays a significant role, as it enhances the solubility of CO_2 and increases the precipitation of valuable solid products [9]. Several experimental runs were conducted to investigate the effect of KOH, CaO, and Al_2O_3 concentrations on the brine solution pH before it reacts with CO_2.

The solubility of CO_2 mainly depends on the system's temperature. It was experimentally observed that increasing the temperature decreases the CO_2 solubility, which negatively affects the process performance [9]. Therefore, the effect of the different added amounts of alkaline/metal oxide on the solution (without CO_2) temperature was examined. It is also important to mention that the temperature was measured instantaneously.

Alkaline/Metal Oxide Impact on the CO_2 Capture Efficiency and Ions Removal:

El-Naas et al. [24] investigated the CaO effect on the CO_2 removal (Equation (2.1)) under the optimized temperature of 20°C, gas flowrate of 1 l/min (10% CO_2), and 20 g of CaO/l. In this research, the effect of KOH and Al_2O_3 on CO_2 capture and ions deduction percentage was examined under the same operating conditions and stochiometric concentrations of 70.57 g/l and 21.4 g/l, respectively. The experiments were conducted for each species separately until CO_2 reached the saturation point, and the results were compared to those of CaO. The structural and chemical characteristics of the precipitated solids were analyzed.

2.1.2 Statistical Optimization for KOH-Based Modified Solvay Process (Paper II)

The Preliminary results have confirmed the high reactivity and effectiveness of KOH in capturing CO_2 and managing reject brine. In this study, parametric sensitivity analysis has been carried out to optimize the operating conditions and thereby maximize CO_2 capture and ions removal from high-salinity brines.

The optimization of the modified Solvay process based on KOH was carried out according to the Response surface methodology (RSM)- central composite design (CCD) approach as implemented in Minitab 19.0 [96-98]. RSM is suitable for fitting a quadratic surface and aids in optimizing the process parameters with a minimum number of experimental runs [98-101]. In this study, RSM was utilized to select the CCD in order to design a sequence of experiments to study the influence of the operating parameters on responses. The affecting factors are determined based on the screening experiments which show the approximate range for each factor where the optimal conditions could be located. A full-factorial CCD design was employed to investigate the effects of independent factors (i.e., pressure, feed gas flow rate, KOH concentration, and temperature) on responses (i.e., CO_2 uptake and ion reduction in reject brine) throughout the IPSBR. Table 2.1 lists the values of these independent parameters at each level. A total of 31 experimental runs were generated to analyze the impacts of the operating parameters on responses.

Experimental results were fitted following second-order polynomial equations to evaluate the relative influence of each factor on the studied responses. Moreover, analysis of variance (ANOVA) was implemented to validate the adequacy of the models developed. The response optimizer in RSM was used to determine the optimum operational conditions; its performance was evaluated based on the desirability parameter (d), that ranges from 0 to 1 [101, 102]. An optimal solution may be reached by the proposed model when the desirability value approaches its maximum (i.e., close to 1). For the purpose of this research, response optimizer requested targets were adjusted to maximize responses, CO_2 uptake, and the percentage of ions reduction. The predicted optimal responses were validated experimentally. The characterization of the collected solid products at optimum conditions were investigated.

Table 2.1: Independent factors and their levels

Levels	Feed gas Flow rate	KOH Concentration	Temperature	Gauge Pressure
Units	l/min	g/l	°C	barg
Tag	F	C	T	P
Level -α	400	30	10	1.0
Level -1	700	50	20	1.5
Level 0	1000	70	30	2.0
Level +1	1300	90	40	2.5
Level +α	1600	110	50	3.0

It was reported previously [24] that inert particles create vigorous mixing and circular motion inside the reactor, thereby enhancing the gas–liquid interfacial area and improving mass and heat transfer between the two phases. In this study, the impact of the mixing particle volume fraction on CO_2 uptake and percentage of ion reduction was addressed under optimized conditions. The mixing particle volume fractions employed were in the range of 0–25%.

2.1.3 Ability of KOH-Based Solvay Process for Removing Na Ions from High Salinity Reject Brine at High Temperatures (Paper III)

Based on the literature review in Chapter 1, temperature has been found to be a vital parameter that significantly affects the combined process in terms of metal solubility and CO_2 uptake. Notably, low temperature conditions are generally preferred to achieve high CO_2 capture and ion removal from reject brine. However, brine is commonly discharged from desalination plants at relatively high temperatures of 40–55°C [36]. To the best of the author’s knowledge, no previous work has attained the optimization of the KOH based Solvay process to achieve high CO_2 capture and ion removal at high temperatures.

Three-dimensional (3D) graphs were used to illustrate the relationship between the independent variables, namely temperature, pressure, flowrate, and KOH concentration, and the responses of 31 previous experimental runs (Section 2.1.2). The responses of the 31 experimental runs were mentioned in Papers II and III. It was observed that under certain conditions and at high temperatures up to 50°C, effective Na^+ removal can still be obtained. As a result, the developed RSM model in Minitab software (Section 2.1.2) was targeted toward the highest ions percentage reduction while keeping the temperature constraint at 50°C. RSM's performance was assessed using the high desirability parameter (d), which should be close to 1 [101, 102]. The predicted responses under the optimized conditions were experimentally validated. Furthermore, the structural and chemical characteristics of the precipitated solids were investigated.

2.1.4 Kinetics Study for KOH-based Modified Solvay Process (Paper IV)

The kinetics of CO_2 reactions in the modified Solvay process based on KOH have never been investigated experimentally, even though the findings yielded would contribute to the reaction rate enhancement. This gap in extant knowledge is addressed in the present study by changing the CO_2 concertation, reaction temperature, operating pressure, CO_2 gas flow rate, and KOH concertation, one at a time, while fixing the values of other parameters at their previously established optimal values. The outcome of this set of experiments was to acquire a model that best describes the underlying reaction kinetics. As the optimal parameter values for the KOH-based modified Solvay process were determined as a part of our previous work (Section 2.1.2) [103], these values were adopted here when investigating the reaction kinetics. The kinetic parameters and corresponding ranges are tabulated in Table 2.2.

Table 2.2: Kinetic parameters and corresponding ranges

Parameters	Unit	Symbol	Conditions range				
CO_2 concentration	%	-	3	10	15	-	-
Temperature	°C	T	10	20	30	40	50
Pressure	bar	P	1	2	3	4	5
KOH concentration	g/l	C	30	70	110	150	190
CO_2 flow rate	ml/min	F	400	800	1200	1600	2000

2.1.5 Multi-Stage Treatment for KOH-Based Modified Solvay Process (Paper V)

It was reported previously that the precipitation and high recovery of metal ions from the modified Solvay process depend on many parameters, most importantly temperature, pH and CO_2 gas flow rate [9, 17, 24, 103, 104]. Although some metal ions could be reduced, other ions could not be recovered effectively under the same optimum conditions, such as Na^+ and Cl^- which represents the highest percentage of metals in high salinity reject brines [9].

From the presented literature review (Section 1.3), it can be concluded that the pre-treatment of some metal ions from reject brine and produced water has enhanced the overall recovery efficiency of the post-treatment processes. Furthermore, the addition of NH_4HCO_3 for the modified Solvay process based on CaO increased the Na^+ reduction from 30% to 35% [24].

Consequently, the objective of this work was to evaluate the multi-stage treatment process for a KOH-based modified Solvay process to achieve a further reduction in ion removal from high-salinity brines and to increase the CO_2 capture efficiency in comparison with previous results obtained under optimal operating conditions [103]. Three different methods were investigated.

In the first method, the effect of adding NH_4HCO_3 was studied in a total of four stages. The whole system was operated under the optimum operating conditions. It was reported previously [53] that adding NH_4HCO_3 decreased the solubility of $NaHCO_3$, where the high solubility of this component limits precipitation even at a high pH and low temperature. By increasing the concentration of NH_4HCO_3 (Equation (2.4)) and thus the concentration of (HCO_3^-), Equation (2.5) would shift to the left, lowering the solubility of $NaHCO_3$.

$$NH_4HCO_{3(aq)} \leftrightarrow NH_4^+ + HCO_3^- \tag{2.4}$$

$$NaHCO_{3(aq)} \leftrightarrow Na^+ + HCO_3^- \tag{2.5}$$

The same procedures followed in method 1 was applied in method 2, with the difference of adding a specific amount of KOH after each stage to maintain a high pH value. In the third method, the effect of the pre-treatment step was investigated on the overall performance of the process, where the filtration of the solution (reject brine + KOH) was applied before the reaction with CO_2 to remove the divalent ions (Ca^{2+} and Mg^{2+}). This was followed by the same procedures as method 2.

Additionally, the collected solid products were characterised to evaluate their composition and major physical and chemical properties.

2.1.6 Continuous Operation of IPSBR (Paper V)

It is also important to note that the reactions occur in a novel inert particle spouted bed reactor (IPSBR) developed by El-Naas et al.[90, 91]. Consequently, the objective in the current research is to investigate the dynamic behavior of the IPSBR using inlet gas flowrate (800 ml/min to 2400 ml/ min) and liquid flowrate (10 to 30 ml/min) step changes, where a KOH-based modified Solvay process was performed. The continuous experiments were conducted under the previously determined optimum conditions [103]. The step changes in the reactor's inlet gas flow rate and liquid flowrate to a higher or lower level were used to evaluate the reactor's dynamic behavior, while keeping the other parameters constant. The dead time and time constant were measured to quantify the process's responsiveness, adaptability and ease of control [105].

2.2 Data Collection

Descriptions of the used materials, brine samples, analytical techniques, reactor configuration, and experimental procedures in the investigation of the CO_2 capture and ions removal are presented in the following sections. More details are mentioned in Papers I to V.

2.2.1 Materials

CaO (99.9% purity), KOH (85-100% purity), and Al_2O_3 (99.9% purity) were obtained from Scientific Progress Medical and Scientific Equipment Company, UAE. In addition, the particle size of CaO and Al_2O_3 were <1.0-µm APS powder, and KOH had a particle size between 5 and 7 mm. NH_4HCO_3 with a purity of 99% was acquired from EuroLab Chemicals, Belgium. Three gas cylinders with different CO_2 concentrations

(3, 10, and 15% CO_2/air) were purchased from Abu Dhabi Oxygen Company, UAE. Samples of real reject brine were provided by a multistage flash desalination unit in Abu Dhabi, UAE.

2.2.2 Analytical Techniques

2.2.2.1 Liquid Analysis

Different analytical instruments were used to determine the characteristics of the fresh and treated brine, where liquid was separated from precipitated solids by vacuum filtration after each experimental run. Brine pH and salinity were measured using pH and conductivity meter (HACH portable pH meter (Model HQ11D53000000) and HACH portable conductivity meter (Model HQ14D.99.000000)), respectively. Standard solutions were used to calibrate the device. The ions content (Na^+, Ca^{2+}, Mg^{2+}, K^+) were measured using inductively coupled plasma spectrometry (Varian 710-ES ICP optical emission spectrometer). An appropriate dilution factor was used for all samples because of the high ion concentrations. The ICP calibration was accomplished by analyzing solutions of multiple element standards, and after analyzing every six unknown samples, a reference sample was tested to evaluate the analysis quality and performance [106]. Chloride ions were analyzed by HACH HQ40D portable multimeter equipped with a Cl^- ion selective electrode (HACH Intellical™ ISECL181). To enhance the accuracy of each reading, chloride ionic strength adjustment buffer powder pillows were utilized. The average and standard deviation of ion concentrations for actual fresh reject brine samples are illustrated in Table 2.3. The reject brine samples displayed an average salinity of 72,640 mg/l. All readings were determined by considering the averaged value for three collected samples.

Table 2.3: Chemical composition and pH value of the reject brine

Na^+ mg/l	Cl^- mg/l	Ca^{2+} mg/l	Mg^{2+} mg/l	K^+ mg/l	pH
23,063±7	48,330±4	933±3	2,675±6	877±4	8.02 ± 0.01

2.2.2.2 Solid Characteristics

After each experimental run, the collected solid samples were dried and grinded to identify their characteristics. The structural and chemical characteristics of the precipitated solids were examined using XRD, SEM, Raman, and FTIR spectroscopy. More details about these analytical techniques are provided in Papers I to V.

XRD analysis:

The structural properties for the collected samples were investigated using an X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54$ Å). The analytical XRD diffraction peaks for the collected solids were identified based on the theoretical intensity of the three most intense peaks for that mineral in a pure state [107, 108].

SEM analysis:

The surface morphology, texture, and shape of samples were characterized using Scanning Electron Microscopy (SEM). Samples were first gold coated with a 300 Å gold layer. Then samples were analyzed in three different areas. Average energy-dispersive X-ray spectroscopy (EDS) analysis was then performed to detect the main elements in each collected sample.

Raman analysis and FTIR analysis:

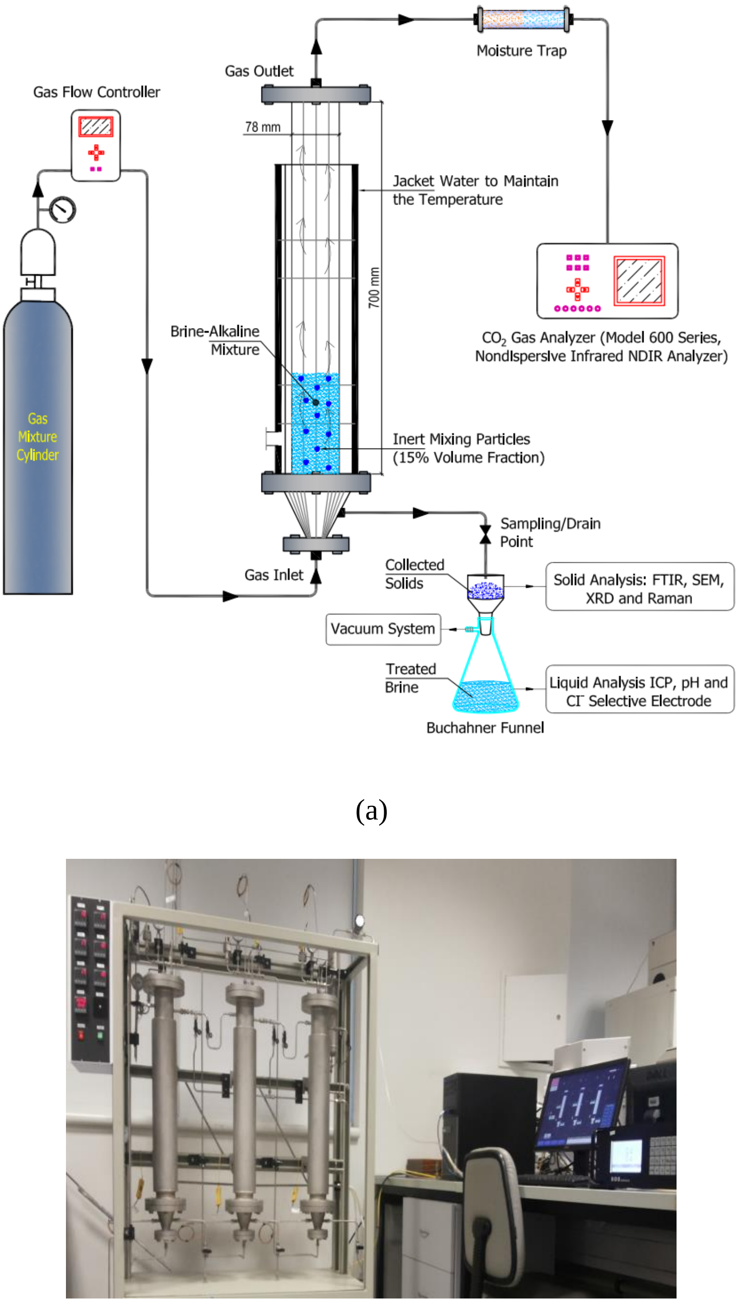
Raman spectroscopy and FTIR were implemented to confirm the structure and effective functional groups of the collected solids, respectively.

2.2.3 Experimental Apparatus (Papers I to V)

In each experimental run, a pre-defined amount of alkaline/metal oxide was mixed with 1 l of reject brine using a magnetic stirrer to ensure a uniform distribution of alkaline/metal oxides in the reject brine. The pH of the mixture was recorded before reaction with CO_2 gas. All experiments were performed in a novel inert particle spouted bed reactor (IPSBR). More details about the reactor system can be found in previous studies [77, 91, 102, 109, 110]. The reactor consists of a cylindrical vessel with a conical base, inert particles, a jacket to control the temperature, a mass flow controller, and a CO_2 gas analyzer. The reactor had a port for liquid sampling and drainage at the bottom. Figure 2.1 (a) and (b) shows a schematic diagram and real picture of the reactor. Table 2.4 shows the dimensions of the reactor and particle specifications follow analogues values previously reported by El-Naas et al. [24].

Table 2.4: Reactor dimensions and inter particles specifications [90, 91]

Reactor material	Stainless steel
Reactor internal diameter	78 mm
Reactor height	700 mm
Reactor total volume	3000 ml
Orifice diameter	2 mm
Inert particles material	Polymethyl methacrylate
Particle average size	13 mm
Particle average weight	0.511 g/particle
Particle sphericity	0.62
Particle wet density	1.022 g/cm^3
Particle volume	0.5 cm^3/particle
Particle surface area	4.92 cm^2/particle



(a)

(b)

Figure 2.1: IPSBR system (a) Schematic diagram and (b) real picture of the IPSBR system [103]

2.2.4 Experimental Procedures (Papers I to V)

Initially, the IPSBR system was filled with the prepared solution and exposed to a continuous gas flow through an orifice at the bottom of the reactor (semi-batch mode). The flow rate of the gas was controlled by a mass flow controller. To determine the amount of CO_2 captured, the outlet gas stream was passed through a CO_2 gas analyzer. The gauge pressure was controlled using a back pressure regulator valve installed at the reactor outlet. At the end of each experiment, the internal pressure was gradually reduced to atmospheric pressure. Each experiment was ended when the designated saturation point was reached, i.e., where the CO_2 concentration at the outlet was equal to its inlet value. At the end of each experiment, the contents of the reactor were drained and the treated brine liquid was separated from precipitated solids by vacuum filtration using a Buchner funnel setup. It is important to note that the solution samples (5 ml) for the kinetics investigation were collected at 15-minute intervals. The pH value of the treated brine was recorded. Ion concentrations of treated brines were measured using ICP spectrometry (Section 2.2.2.1). The percentage of ion (Ca^{2+}, Na^{+}, K^{+}, Mg^{2+}, Cl^{-}) reduction, CO_2 moles reacted, CO_2 capture efficiency, and CO_2 uptake, were calculated using Equations (2.6), (2.7), (2.8), and (2.9), respectively [103]. Solid characteristics were investigated using the analytical techniques discussed in Section 2.2.2.2.

$$\text{Ion removal \%} = \frac{C_i - C_f}{C_i} * 100 \qquad (2.6)$$

where $C_i$is the initial concentration of ions in the feed brine (mg/l) and C_f is the final concentration of ions in the treated brine (mg/l).

$$\text{Moles of } CO_2 \text{ reacted} = \frac{\int_0^t \text{volume of } CO_2 \text{ captured (l/min).dt}}{\text{Molar volume of } CO_2 \text{ (l/mol)}} \qquad (2.7)$$

$$CO_2 \text{ capture efficiency} = \frac{\text{Moles of } CO_2 \text{ captured (mol/min)}}{\text{Moles of } CO_2 \text{ (mol/min) loaded to the reactor}} *100 \qquad (2.8)$$

$$CO_2 \text{ uptake} = \frac{\text{mass of } CO_2 \text{ reacted}}{\text{mass of KOH used}} \quad (2.9)$$

The inert particle volume fraction was obtained using Equation [77] as follows:

$$\text{Inert particle volume fraction} = \frac{\text{volume of particles}}{\text{volume of reject brine}} * 100\% \quad (2.10)$$

The reaction rate (R) is defined as the change in the amount of a reactant per unit time per unit volume of reaction mixture [111], as indicated below:

$$R = \frac{\text{Change in reactant concentration}}{\text{corresponding change in time}} \quad (2.11)$$

2.2.4.1 Experimental Procedures for Multi-Stage Treatment Process (paper V)

As previously stated in Section 2.15, three different methods were performed during the multi-stage process. The methodology followed for each method is described in detail below.

First Method (M1):

In the first method, the reject brine is passed through a total of four stages. In the first stage (M1-S1), a brine sample of 1000 ml was mixed properly with 110 g/l KOH alkaline (optimum concentration) using a magnetic stirrer. IPSBR system was filled with the prepared solution and exposed to a continuous gas flow through an orifice. The outlet CO_2 is continuously monitored and measured using a CO_2 gas analyzer. The whole system was operated under the optimum conditions. When the experiment reached the saturation point, the reactor content was drained and filtrated. The ions in the liquid were analyzed by using the same technique mentioned in Section 2.2.2.1. In the second stage (M1-S2) the effect of adding NH_4HCO_3 was tested. It is important to mention that the added amount of NH_4HCO_3 (40 g/l) was selected on the basis of the screening experiments. It was found that adding NH_4HCO_3 gave the maximum Na^+ reduction (56%), as no further reduction in Na^+ was observed by increasing the concentration of NH_4HCO_3 more than 40 g/l. This amount was considered in further stages of the treatment. After adding NH_4HCO_3 to the treated effluent from S1, it was mixed under room temperature with brine for 15 min at a mixing rate of 50 rpm. The mixture was then kept in the refrigerator at 7ºC for 24 h to ensure maximum $NaHCO_3$ precipitation. The recovered solids from this mixture were then collected using Buchner filtration, dried and analyzed using the same techniques described in Section 2.2.2.2. The treated brine was collected and sent to the next stage. In M1-S3, the treated liquid from S2 was inserted to the IPSBR and reacted with CO_2 under the optimum operating conditions for a further treatment step. The treated brine was then mixed again with NH_4HCO_3 and the same procedures applied for M1-S2 were followed. This stage was repeated until no precipitates and CO_2 capture were observed, which occurred during the fourth stage (M1-S4). Figure 2.2 demonstrates the flowchart for M1 stages. The liquid analysis and solid characteristics were investigated by using the mentioned analytical techniques in Section 2.2.2. The percentage of ion reduction, CO_2 capture efficiency, and CO_2 uptake were calculated using Equations (2.6), (2.7-2.8), and (2.9), respectively [103].

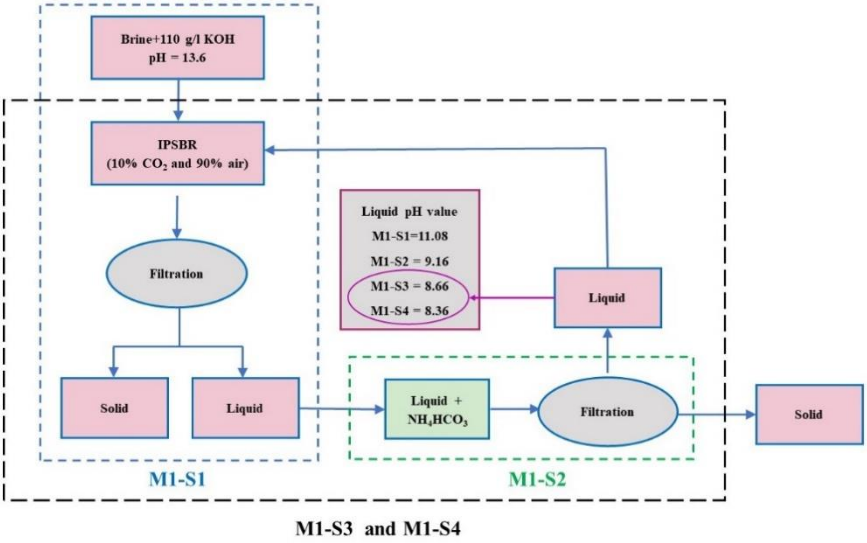


Figure 2.2: Flowchart for the subsequent stages of M1

Second Method (M2):

The same procedures that were applied in the first method were followed for the second method. Nevertheless, after the addition of NH_4HCO_3 and the filtration step, a specific amount of KOH was added to the liquid to increase its pH value to the same value (13.6) in the initial prepared solution. The treated effluent was then recycled to the IPSBR for further reaction with CO_2. The objective of adding KOH was to enhance the pH value as it increases the solubility of CO_2 and decreases the solubility of salt's metallic components, thus increasing precipitation of products.

Consequently, a high pH improves the efficiency of CO_2 capture and salt removal. All the experimental runs were operated under the optimum conditions. The stages were completed when no further ion reduction was observed, which occurred during the fourth stage (M2-S4). The amount of KOH added in S3 was 70 g/l, and the amount added in S4 was 100 g/l. Figure 2.3 demonstrate the subsequent stages of M2. Liquid analysis and solid properties were investigated using the analytical techniques described in Section 2.2.2. Equations (2.6), (2.7-2.8), and (2.9) were used to calculate the percentage of ion reduction, CO_2 capture efficiency, and CO_2 uptake, respectively [103].

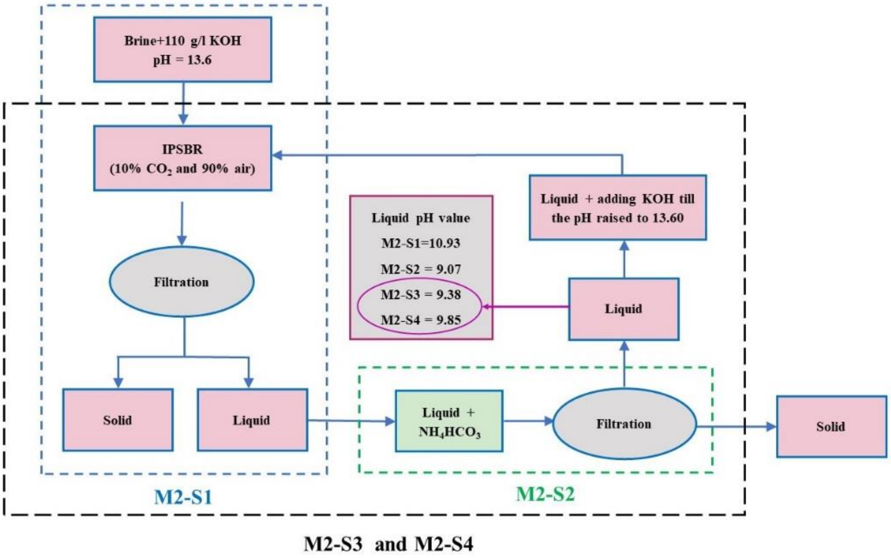


Figure 2.3: Flowchart for the subsequent stages of M2

Third Method (M3):

In this method, the effect of the pre-treatment of brine before any exposure to CO_2 capture was investigated on the process performance in terms of CO_2 capture and metal ion reduction percentage. At the first stage (M3-S1), a total amount of 110 g KOH was added to 1000 ml of reject brine and mixed at room temperature with the brine for 15 min at a mixing rate of 50 rpm. The mixture was left covered at room temperature for almost 2 h until no more precipitation of solids was observed. The solution was then filtered using a Buchner funnel set-up. The collected solids were dried for 24 h at a temperature of 120°C. In M3-S2, the treated solution was inserted into the reactor to react with CO_2 under the optimum operating conditions. The reaction was stopped at the saturation point, and the reactor was drained. NH_4HCO_3 was added in M3-S3 by the same steps shown in the previous two methods (M1 and M2). Afterwards, the solids were separated from the liquid by filtration. For further treatment, KOH was added to the treated brine, similar to the procedure followed in M2 to increase the pH to the same value as S1 (pH = 13.60). Then, in M3-S4, the whole solution was inserted into the reactor for a further reaction with CO_2. This was repeated until no more ions reductions were detected. This occurred during the fifth stage (M3-S5). The amount of KOH added in S4 was 70 g/l, and the amount added in S5 was 100 g/l. The subsequent stages of M3 are shown in Figure 2.4.

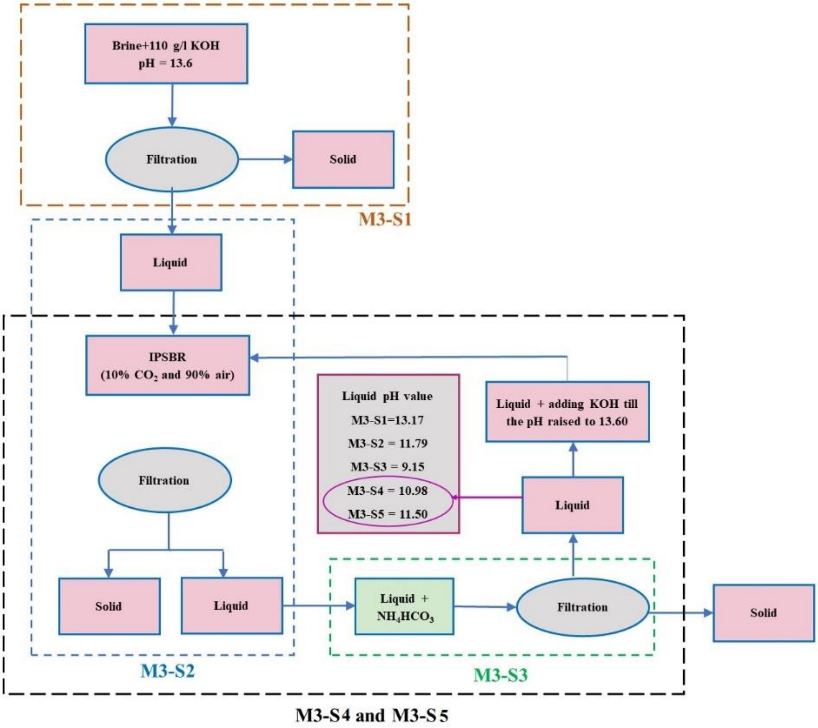


Figure 2.4: The subsequent stages of M3

2.2.4.2 Experimental Procedures for Continuous Operation of IPSBR (Paper V)

Step changes in the reactor's inlet gas and liquid flow rates to higher or lower levels were used to evaluate the reactor's dynamic behaviour while keeping the other parameters constant. The feed gas was bubbled through the reactor, whereas the liquid was fed at the top of the reactor and controlled by a piston pump. The gas effluent from the top was passed through a moisture trap and then to a CO_2 gas analyser. The continuous experiments were conducted under the optimal conditions. First, each experiment was performed for at least 3 h to achieve a steady state in CO_2 capture. Each parameter was then subjected to a step change in independent tests (gas flow rate increased from 800 to 2400 ml/min; liquid flow rate increased from 10 to 30 ml/min). A second steady-state condition of CO_2 capture was achieved and maintained for at least another 3 h. Each parameter was then reset to its previous value to achieve the third steady-state condition.

CO_2 capture efficiency was calculated using Equations (2.7) and (2.8). The dead time (t_d) and time constant (τ_p) were measured to describe how quickly the process responds, how adaptable it is, and how easy it is to control the overall process [105].

The dead time (t_d) is defined as the time interval between the gas and liquid flow rate step change and the first change or response in the CO_2 capture efficiency. The reactor time constant (τ_p), which describes the speed with which the measured CO_2 capture % responds to step changes in the gas and liquid flowrates. More specifically, it represents the time needed for the CO_2 capture % to reach 63.2% of its total and final change [91, 105, 112]. Equations (2.12) and (2.13), were used to calculate the t_d and τ_p, respectively.

$$t_d = t_1 - t_2 \tag{2.12}$$

$$\tau_p = t_{63.2\%} - t_2 \tag{2.13}$$

where t_1 denote the time at which the step change occurs, t_2 denote the time when the measured CO_2 capture efficiency responds to the step change for the first time and $t_{63.2\%}$ denote the point at which the measured CO_2 capture efficiency equals 63.2% of the total final change.

2.3 Overview of the Main Findings

2.3.1 Preliminary Study for KOH as a New Alkaline (Paper I)

The aim of this work was to compare the effectiveness of other alkaline and amphoteric oxides, namely KOH and Al_2O_3, respectively, with that of CaO in terms of thermodynamic properties, pH value, solubility, CO_2 capture, ions reduction, and type of produced solids [17]. For comparison purposes, the reactor was operated under the same optimized conditions that were previously reported by El-Naas et al. [24] where the CaO (20 g/l) was investigated. All experiments were performed under the same conditions, and stoichiometric quantities were utilized for the KOH and Al_2O_3. The results indicated that most of the ions removal based on the KOH and CaO were very close. The combined reaction was very fast in case of the KOH, and many valuable products were observed, such as KCl, in the form of crystals, as KOH was capable of maintaining a high level of pH throughout the reaction. It is not recommended to use Al_2O_3 in further studies as it did not result in any CO_2 capture and Na^+ removal, which is due to its lack of solubility and low pH level (~8.7) at the onset of the reaction. However, it demonstrated that it can be used as a coagulant to remove Mg^{2+} ions in the reject brine solution in the form of Clinohumite.

Thermodynamic Properties:

Thermodynamic properties for all illustrated Equations (2.1), (2.2), and (2.3) were obtained using quantum chemical calculations (Gaussian16W software). It was observed that the modified Solvay process is not spontaneous with Al_2O_3 in comparison with the other alkaline solids over the whole temperature range (0–100°C). It is also important to note that using KOH in the modified Solvay reaction renders it more spontaneous (more negative ΔG) than when using $Ca(OH)_2$ at all the temperatures.

Impact of the Alkaline/Metal Oxide Amount on the Initial pH Value:

Figure 2.5 demonstrates the investigation of the KOH, CaO, and Al_2O_3 concentrations effect on the brine solution pH before it reacts with CO_2. The results show that potassium and calcium hydroxides can maintain high pH values of more than 10 in comparison with Al_2O_3, where the pH value was not changed. It is worth mentioning that based on the stoichiometric ratio for KOH (Equation 2.2), 70.57 g/l should be utilized, which means that the process can be conducted with great performance without using all the required amount of KOH, as the pH reached its optimal value (13.6) under 70.57 g/l. There was no remarkable difference between the mass addition and pH change when Al_2O_3 was added. Therefore, it was decided to run the experiment at a stoichiometric mass of 21.4 g/l of Al_2O_3. Figure 2.5 reveals that the maximum pH value was reached at 4.00 g/l of added CaO. It was reported previously [24] that 20 g/l of CaO is the optimal amount at which the CO_2 capture and ions removal rates reach their optimum values.

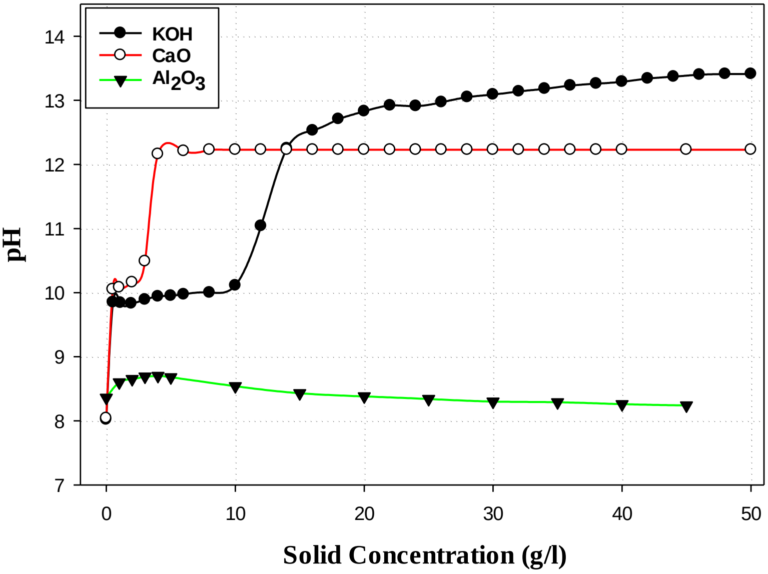


Figure 2.5: Effect of the alkaline/metal oxide mass on the pH of brine before carbonation for the added oxides

Alkaline/Metal Oxide Solubility:

It was also observed that the KOH entails very high solubility in comparison with the CaO. All the used quantities were dissolved in high quantities compared with CaO. However, Al_2O_3 was found to have no solubility in the reject brine among the three buffer solutions justifying its poor performance in CO_2 capture.

Alkaline/Metal Oxide Impact on the CO_2 Capture Efficiency:

It was reported that almost 0.92 g CO_2/g CaO was achieved by adding 20 g of CaO. It is very important to note that this added amount of CaO is less than the stoichiometric quantity but exceeds the solubility limit. It was reported previously that an extra amount was added to maintain high pH level [24]. It was also concluded that the CO_2 uptake was ~0.32 g CO_2/g KOH when 30 g of KOH was tested. In addition, adding the stoichiometric amount of KOH (70.57 g/l) enabled to reach almost the same uptake of 0.31 g CO_2/g

KOH. The same uptake value at different stoichiometric ratios can be explained in terms of the capacity limit of KOH in absorbing specific mass of CO_2 under same operating conditions. Moreover, the CO_2 removal was examined using Al_2O_3, but there were no detected results regarding the capturing of CO_2.

Impact of the Alkaline/Metal Oxide Stoichiometric Amount on the Reaction pH Level:

It is important to sustain a high pH value until the Solvay process reaches the saturation state. It is also important to note that the pH value can control the types of the formed products [9]. For example, the carbonic acid ions initially existed in the form of carbonates $CO_3^{2-}$and bicarbonates HCO_3^- in the pH ranges of pH > 10.5 and 6.5 < pH < 10.5, respectively [113]. It was observed from a previous study that the pH reached its maximum value of almost 11.8 when CaO was utilized at the optimal amount of 20 g/l [24]. Therefore, $CaCO_3$ was observed when more CaO was added to the system. The formation of $CaCO_3$ competed with the formation of $NaHCO_3$. It is also worth mentioning that this pH value (11.8) almost remained constant until the end of the reaction. It is also important to note that raising the CaO concentration more than 20 g/l, did not enhance the pH level anymore, but instead hindered the mixing inside the reactor and reduced sodium removal.

In the current study, the effect of adding of 70.57 g/l KOH was investigated. It can be observed that the maximum reached pH value was 12.9, and it decreased along the reaction time until reaching a value of approximately 9.8, at which the process reached full saturation with CO_2. The changing rate of the pH value was also observed when Al_2O_3 was added at a stoichiometric amount of 21.4 g/l. It was reported that the maximum reached pH value was almost 8.7, which negatively affects the solubility of the CO_2 gas.

Impact of the Alkaline/Metal Oxide Type on the Ions Removal:

The effect of Al_2O_3/KOH/CaO on the ions deduction percentage was investigated, as illustrated in Figure 2.6, for a temperature of 20°C, a gas flow rate (10% CO_2) of 1 l/min, and amounts of 21.4 g Al_2O_3/l, 20 g CaO /l, and 70.57 g KOH /l. The experiments were conducted for each species separately until CO_2 reached the saturation point. At first glance, the reduction percentage of the Cl^- ions was almost the same (36%) when using calcium and potassium hydroxides. However, the poorest performance was observed when Al_2O_3 was used, as only ~ 8% of the Cl^- ions was reduced. It can also be noted that there was a slight decrease in the Na^+ reduction percentage when KOH was utilized instead of CaO. The lowest reduction was for Al_2O_3, where the Na^+ ions reduction was ~ 3%. It is very clear from the figure that the maximum ions removal was for the Mg^{2+} ions, as reductions of almost 98% and 96% were attained for the CaO and KOH alkaline, respectively. There was a remarkable decline to around 24% when Al_2O_3 was used. Although Al_2O_3 has no reactivity and solubility in the brine, it can be utilized as a coagulant for removing magnesium cations in the reject brine solution. It was also observed that utilizing KOH as an alkaline removed almost 97% of Ca^{2+}ions.

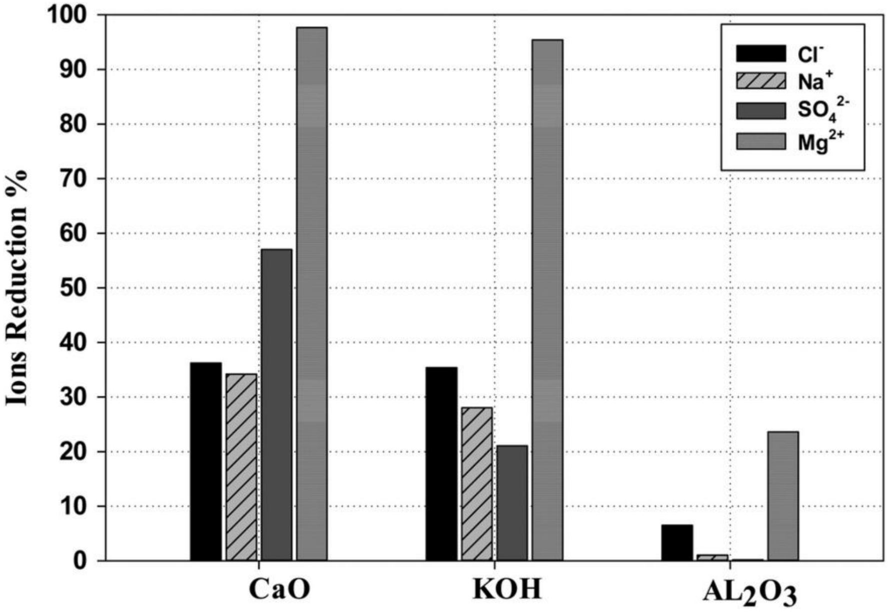


Figure 2.6: Ions reduction in effluent brine reacted with a CO_2-air gas mixture with different alkaline/metal oxide. The time needed to reach full CO_2 saturation was 525 min, 330 min, 25 min for CaO, KOH, and Al_2O_3, respectively

Characterization of the Produced Solids:

Figure 2.7 shows the main mineral components resulting from the reaction when KOH was used. XRD peaks at 28.3°, 40.6°, and 50.1° confirmed the production of KCl in the precipitated solids [114]. It is worth mentioning that after the samples were collected, it was found that some of the crystals started to be formed, as demonstrated in Figure 2.8 (a). The formation of KCl crystals were confirmed by using SEM after they were grown in a brine solution for 24 hr. The average EDS analysis for the formed crystals shows that the main elements are potassium, and chloride with mass percentage of 96-98%, which confirms the production of KCl crystals. Figure 2.8 (b) illustrates that the produced KCl crystals in this process have sharp edges and apexes. The production of KCl crystals has many advantages in different fields. In addition, KOH can be produced from the electrolysis of the KCl solution, as illustrated in Equation (2.14) [115] with no CO_2 production, which is an advantage of using KOH.

$$2\ KCl + 2\ H_2O \rightarrow 2\ KOH + Cl_2 + H_2 \tag{2.14}$$

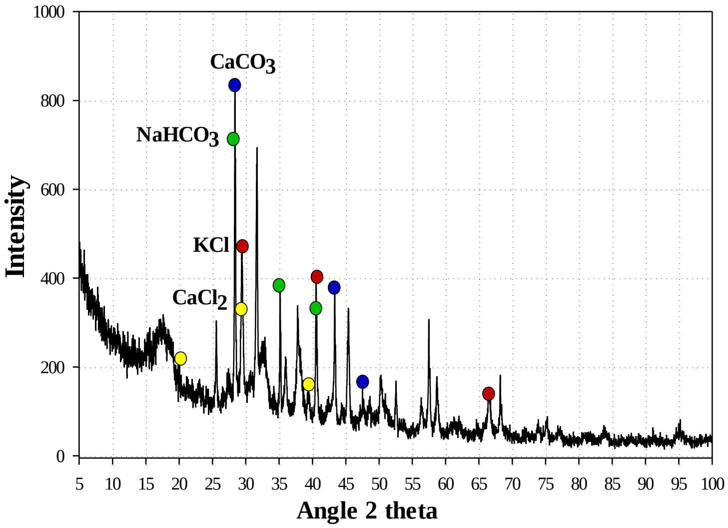
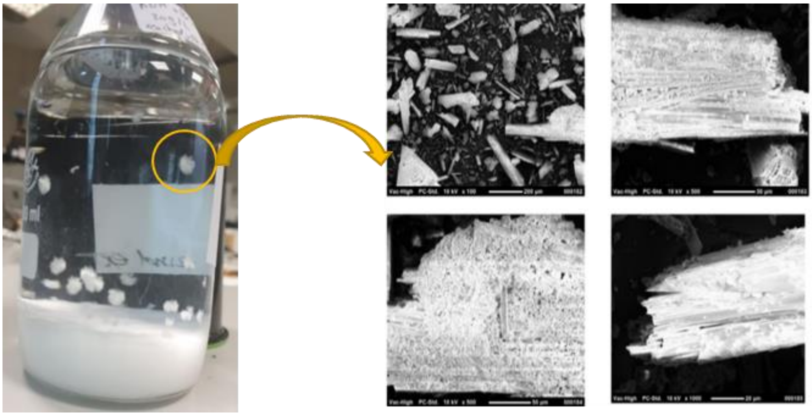


Figure 2.7: X-ray diffraction pattern for the solids produced from the reaction between brine and CO_2 with different alkaline/metal oxide for KOH from 5 to 100° 2 θ



(a) (b)

Figure 2.8: Solid products (a) Solid products when KOH was added and (b) SEM analysis of the same solid products

In summary, the results showed a promising future for KOH as a buffer to be used in the treatment of brine and in CO_2 capture. Further investigations in terms of the parametric analysis were required to optimize the process parameters for the purpose of maximizing the CO_2 capture and the metal removal from solutions in the presence of KOH.

2.3.2 CO_2 Capture and Ions Removal through Reaction with Potassium Hydroxide in Desalination Reject Brine: Statistical Optimization (Paper II)

In this study, parametric sensitivity analysis was carried out to optimize the operating conditions and thereby maximize CO_2 capture and ions removal from high-salinity brines. RSM analysis using the CCD approach was implemented to statistically determine the impact of important operating conditions, including KOH concentration (30–110 g/l), CO_2 gas flow rate (400–1600 ml/min), gauge pressure (1–3 barg), and temperature (10–50°C) on key response process output variables, such as CO_2 uptake and ions reduction. These analyses demonstrated that under the optimized conditions at a temperature of 10°C, gauge pressure of 2.1 barg, CO_2 gas flow rate of

848.5 ml/min, KOH concentration of 110 g/l, and an inert mixing particle volume fraction of 15%, a maximum CO_2 uptake value of 0.58 g/g KOH, maximum Na^+ removal of 44.1%, Cl^- removal of 40.1%, Ca^{2+} removal of 100%, and Mg^{2+} removal of 99.8% were achieved.

RSM Analysis for CO_2 Uptake and Ions Removal:

Tables S1, S3, S4, S5, and S6 (Paper II) present the experimental and predicted results for CO_2 uptake, Na^+, Cl^-, Mg^{2+}, and Ca^{2+}, respectively under different operating factors designed by the RSM-CCD. To relate the measured CO_2 uptake and ions removal to specific variables, a full quadratic model was fitted to the data. Moreover, the high R^2 value (> 0.90) reveals that the regression model fits the data. The insignificant lack of fit (p-value > 0.05) affirms that the model fits well to the experimental data [101]. More details about the developed quadratic models are given in Paper II.

ANOVA was used to evaluate the statistical significance of the developed models such that the model is considered statistically significant when the p-value is <0.05 at the 95% confidence level [102, 116, 117]. Table S2 (Paper II) shows that pressure is the only factor that exerts a significant effect on CO_2 uptake. Moreover, the importance of the fitted regression models, main parameters, and their interactions were assessed using ANOVA as shown in Tables S7, S8, S9, and S10 (Paper II) for percentage reductions of Na^+, Cl^-, Mg^{2+}, and Ca^{2+}, respectively. The results depict that the independent parameters of temperature and flow rate had a significant effect on the Na^+ and Cl^- removal. It was also observed that all independent factors had a significant effect on the removal of Mg^{2+} ions. However, the gas flow rate was detected as the only major factor influencing the Ca^{2+} removal.

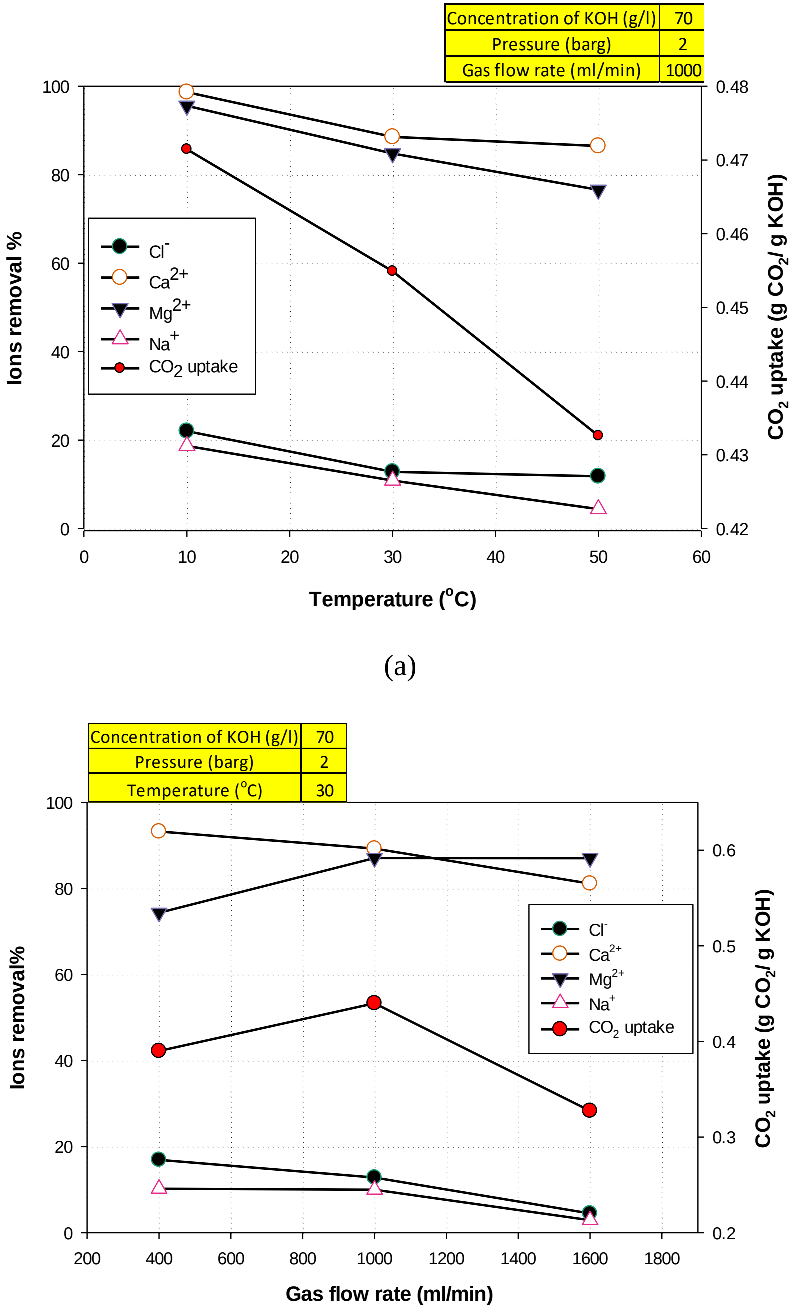
Process optimization and validation:

Optimization was accomplished in Minitab by obtaining individual desirability values for each response. Table 2.5 shows the optimum conditions, confidence interval (CI), and desirability function. The desirability value is almost 1, confirming an optimal performance for the studied factors [102].

Table 2.5: Optimum conditions and fitted responses for CO_2 uptake combined with ion removal

Optimum operating conditions		Response	Fits	95% CI	Composite desirability
C (g/l)	110	CO_2 uptake (g CO_2 / g KOH)	0.542	(0.363, 0.760)	0.984
P (barg)	2.1	Na^+% reduction	41.7	(34.00, 49.41)	
F (ml/min)	848.5	Cl^-% reduction	23.6	(19.58, 27.56)	
T (°C)	10	Mg^{2+}% reduction	97.6	(88.83, 100)	
		Ca^{2+}% reduction	99.5	(87.77, 100)	

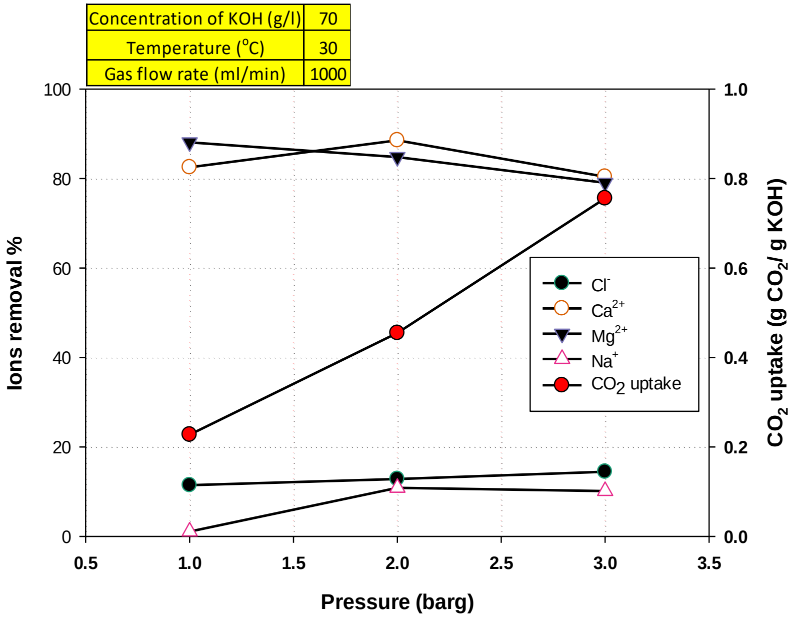
Low temperatures increase CO_2 solubility, causing a decrease in ion solubility by increasing solid precipitation [24], as shown in Figure 2.9 (a). According to Equation (2.2) and as demonstrated in Figure 2.9 (b), a high gas flow rate can positively influence CO_2 uptake values by enhancing the reaction rate and shifting it toward the products. However, flow rates higher than 1000 ml/min appeared to have a negative effect on CO_2 uptake, which can be explained by decreasing the gas residence time in the reactor and hence decreasing the reaction rate. Consequently, an intermediate value of gas flow rate was predicted by the response optimizer. Furthermore, pressure exhibits a linear relationship with CO_2 uptake and a limited effect on ion removal as illustrated in Figure 2.9 (c). Therefore, a gauge pressure value of ~2.1 barg was fitted by Minitab.



(a)

(b)

Figure 2.9: Effects of (a) temperature, (b) gas flow rate, and (c) pressure on CO_2 uptake and ions removal



(c)

Figure 2.9: Effects of (a) temperature, (b) gas flow rate, and (c) pressure on CO_2 uptake and ions removal (Continued)

The optimum conditions were experimentally validated under the same predicted conditions. The results obtained for CO_2 uptake, Na^+, Cl^-, Mg^{2+}, and Ca^{2+} percentage removal were 0.56 g CO_2/g KOH, 38.8%, 36.1%, 99.8%, and 100%, respectively. These results all reside within the CI of 95% as presented in Table 2.5, confirming the ability of the model to predict process performance at several operating parameters.

Influence of inert mixing particle volume fraction:

El-Naas et al. [24] concluded that the optimum condition of CaO-based modified Solvay process was achieved for an inert particles volume fraction of ~6.6%. Therefore, the above-mentioned experiments were conducted based on a particle volume fraction of ~6%. In the current study, the impact of the mixing particle volume fraction was addressed under the optimized conditions (Table 2.5). The mixing particle volume fractions employed were in the range of 0%–25%. The inert particle volume fraction was obtained using Equation (2.10) [77] . The optimum conditions were improved at mixing particle percentages of 15% compared with 6%, while no improvement was detected beyond 15%. Under these conditions, the maximum CO_2 uptake was ~0.58 g CO_2/g KOH, and the maximum reductions of Na^+, Cl^-, Ca^{2+}, and Mg^{2+} were 44.1%, 40.1%, 100%, and 99.8%, respectively.

It is also worth mentioning that the K^+ reduction was almost 63.5%. Despite the fact that KOH was used as the primary alkaline (110 g KOH/l brine), high reduction percentages were achieved in the treated brine, confirming KOH 's high reactivity.

Characterization of the Produced Solids:

The collected solids were characterized using SEM, XRD and FTIR (Paper II). Obtained spectra by these surface characterization techniques confirm the production of valuable solid products, such as $NaHCO_3$, $KHCO_3$, K_2CO_3, and KCl.

The produced solids have many applications in diverse industrial fields. $NaHCO_3$ can be used as a pH-buffering agent, baking soda, and cleaning agent. In addition, it can be utilized as a desulfurization agent in flue gas treatment [24, 76, 118]. The salt (KCl) is widely used as a major ingredient in the production of potassium-fertilizers [108, 119]. It also has some medical applications [120]. Moreover, K_2CO_3 and/or $KHCO_3$ are widely used as cleaning and emulsifying agents, respectively [121].

Cost estimation:

It is important to note that the modified Solvay process based on different alkaline metals, such as CaO and KOH, resulted in a net positive economic benefit by eliminating the associated cost with NH_3 regeneration in the traditional Solvay process [24]. According to El-Naas et al. [24] , the modified Solvay process eliminates all NH_3 regeneration energy requirements, which are estimated to be about 30% of total operating energy. Furthermore, by eliminating the work required for steam consumption and compression, which accounts for approximately 70% of the total equivalent work, the modified process significantly reduces the equivalent work.

Table 2.6 summarizes the estimated cost of consumed alkaline materials for traditional and modified Solvay processes. It also shows the operating conditions, CO_2 capture efficiency, and sodium reduction percentage. It is worth noting that the cost of consumed KOH is approximately 66% and 94% less than that of the consumed CaO and NH_3, respectively. Although KOH has a lower CO_2 uptake than some other alkaline, it is superior in high metal ions reduction. Due to its high reactivity and good ions removal compared to other alkaline metals, KOH could be a good alternative, making it more competitive in the global market. It is also important to note that the investigations confirmed the effectiveness of the modified Solvay process based on KOH to operate under a relatively high temperature that is near the actual reject brine temperature without prior cooling (Section 2.3.3) [104]. Therefore, using KOH can eliminate all energy requirements associated with cooling the brine discharge from desalination units. This demonstrates the novelty of the KOH-based modified Solvay process.

Table 2.6: Summary of combined process studies under different operating conditions

Reference	Alkaline	Alkaline solubility (g/l)	T (°C)	P (bar)	Na^+ reduction %	CO_2 capture efficiency/ CO_2 uptake	Cost (US$/$m^3$ treated gas)
Mohammad et al.[32]	NH_3	-	19	1	33	86%	7.0
El-Naas et al. [24, 58]	CaO	2 (at 20°C)	20	1	35	0.92 g CO_2/g CaO	1.28
Current Study	KOH	1210 (at 25°C)	10	2.1 barg	44.1	0.58 g CO_2/g KOH	0.43

2.3.3 KOH-Based Modified Solvay Process for Removing Na Ions from High Salinity Reject Brine at High Temperatures (Paper III)

Temperature is a vital parameter that significantly affects the combined process in terms of metal solubility and CO_2 uptake. Notably, low temperature conditions are generally preferred to achieve high CO_2 capture and ion removal from reject brine. However, brine is commonly discharged from desalination plants at relatively high temperatures of 40–55°C [36]. Therefore, in this study, an RSM-based CCD approach using Minitab 19.0 was implemented to predict and optimize the effects of the important factors on the responses by holding the temperature at 50°C. It was concluded that a CO_2 uptake of 0.50 g CO_2/g KOH and maximum removal rates of Na^+, Cl^-, Ca^{2+}, and Mg^{2+} of 45.6%, 29.8%, 100%, and 91.2%, respectively, were obtained at a gauge pressure, gas flowrate, and KOH concentration of 2 bar, 776 ml/min, and 30 g/l, respectively, and at high temperature of 50°C. These results confirm the effectiveness of the process in salinity reduction at a relatively high temperature that is near the actual reject brine temperature without prior cooling (Paper III).

Impact of Independent Factors on CO_2 uptake and Ions Removal from Reject Brine:

The relation between the independent variables, i.e., temperature, pressure, flowrate, and KOH concentration, and responses was represented using three-dimensional (3D) plots (Paper III). Figure 2.10 demonstrates the impact of the interaction between temperature and pressure on the CO_2 uptake. As a general conclusion, the uptake increases with pressure at a constant temperature. This is for the studied ranges of temperature (10–50°C) and gauge pressure (1–3 bar). These results were achieved under a constant gas flowrate of 1000 ml/min and a KOH concentration of 70 g/l.

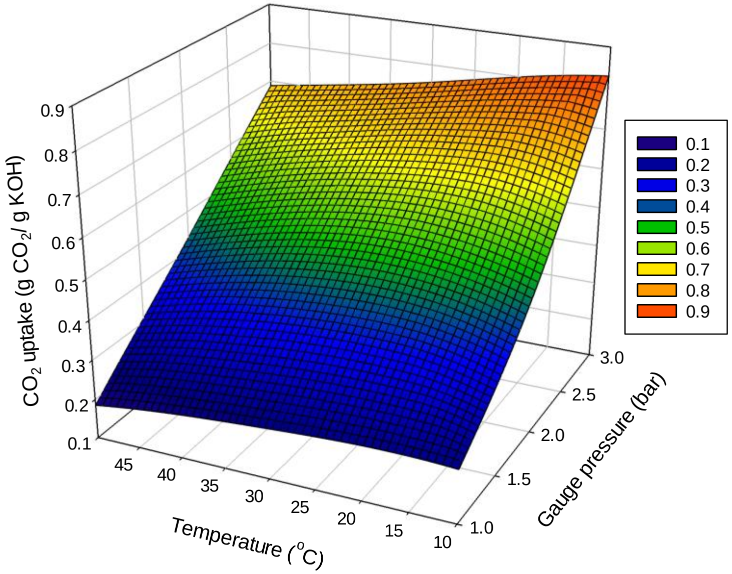


Figure 2.10: Response surface plots of the effect of temperature and pressure on CO_2 uptake

Figure 2.11 depicts the effect of the interaction between temperature and KOH concentration on the Na^+ removal, which was evaluated under a constant gauge pressure of 2 bar and a gas flowrate of 1000 ml/min. The maximum Na^+ removal efficiency was achieved at a low temperature and a high concentration of 110 g/l, which was beyond the stoichiometric value (70.57 g/l). Moreover, a good Na^+ removal efficiency can still be achieved at high temperatures and low KOH concentrations (30 g/l).

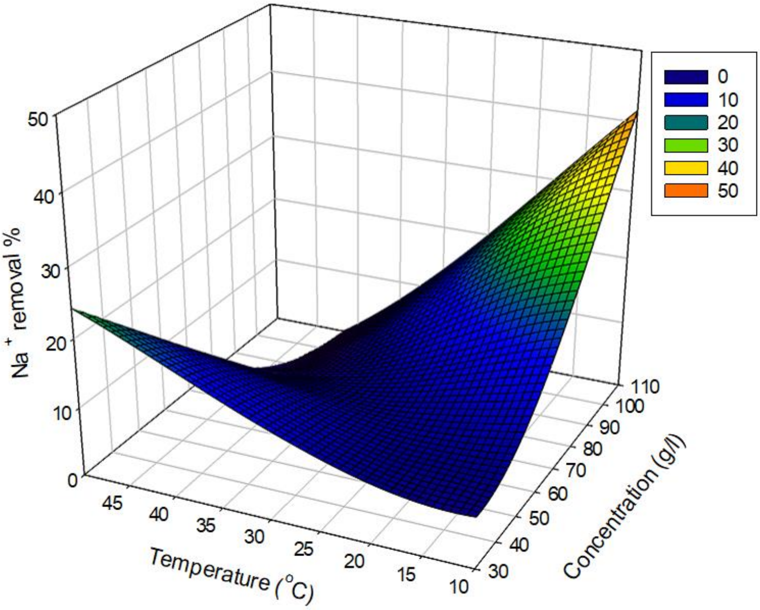


Figure 2.11: Surface response plots of the effect of temperature and KOH concentration on Na^+ reduction in reject brine

Process Optimization and Validation:

The previously developed RSM-based CCD model (Paper II) for the responses of the 31 experimental runs performed in the previous study (2.3.2) was implemented. The response optimizer was used to predict the optimum conditions to achieve the maximum ions reduction by holding the temperature at 50°C. The developed RSM model predicted that the maximum ion reduction can be achieved at a KOH concentration, gauge pressure, and gas flowrate of 30 g/l, 2.0 bar, and ~776 ml/min, respectively, under a constant temperature of 50°C. A high desirability value of almost 0.85 confirms the optimal performance of the studied parameters [102].

The predicted operating conditions and corresponding responses were experimentally verified. Na^+, Cl^-, Mg^{2+}, and Ca^{2+} show a reduction efficiency of up to 45.6%, 29.8%, 91.2%, and 100%, respectively. All the obtained results were within the 95% CI range, confirming the ability of the model to predict the performance of the process at several operating parameters. Notably, under the same operating conditions, CO_2 uptake reached up to 0.5 g CO_2/g KOH, which still constitutes a good level of CO_2 capture.

Figure 2.12 demonstrates the response optimization plot obtained via Minitab software. It is noticed that a high KOH concentration has a negative effect on the Na^+, Cl^-, and Mg^{2+} reduction. However, it can positively affect the reduction in Ca^{2+} ions. The figure also shows a negligible influence of pressure on the Na^+ removal percentage. It is worth noting that the optimum reduction for all ions except Ca^{2+} can be achieved at a high temperature (50°C). Moreover, the figure reveals that a low gas flowrate has a good impact on ions removal, except for Ca^{2+} ions, on which it has a negative impact. Therefore, the optimum reduction for all ions can be achieved at an intermediate gas flowrate value of 776 ml/min.

The hot K_2CO_3 process (hot pot process) [122, 123] can explain the realization of good CO_2 capture and Na^+ reduction at a relatively high temperature (50°C). A high temperature ensures a high solubility of the produced K_2CO_3, and simultaneously, a high pressure maintains CO_2 gas solubility in the solution, facilitating the reaction described in Equation (2.15) [122] to proceed. HSC Chemistry 6.1 software [124] was used to perform a thermodynamic analysis for Equation (2.15). The analysis indicates that the reaction is spontaneous for the whole temperature range (0 to 100°C) as indicated by the negative ΔG.

$$K_2CO_3 + CO_2 + H_2O \leftrightarrow 2KHCO_3 \qquad (2.15)$$

Moreover, a low KOH concentration (30 g/l) favors the formation of HCO_3^-, resulting in the formation of $KHCO_3$ and $NaHCO_3$. At 50°C, both $KHCO_3$ and $NaHCO_3$ are soluble. However, owing to its high lattice energy, $KHCO_3$ has higher solubility than $NaHCO_3$ [125]. This causes the treated solution to be oversaturated with HCO_3^-; therefore, $KHCO_3$ starts to compete against $NaHCO_3$, resulting in a high precipitation of $NaHCO_3$ (Paper III).

Notably, the K^+ reduction efficiency reached up to 79%. Although KOH was used as the main alkaline material at high concentrations, a high reduction efficiency was still achieved in the treated brine, confirming the high efficiency of the reaction under the optimized conditions.

The structural and chemical characteristics of the produced solids were investigated (XRD, SEM, and FTIR analysis), confirming the presence of valuable products such as $NaHCO_3$, $KHCO_3$, and KCl.

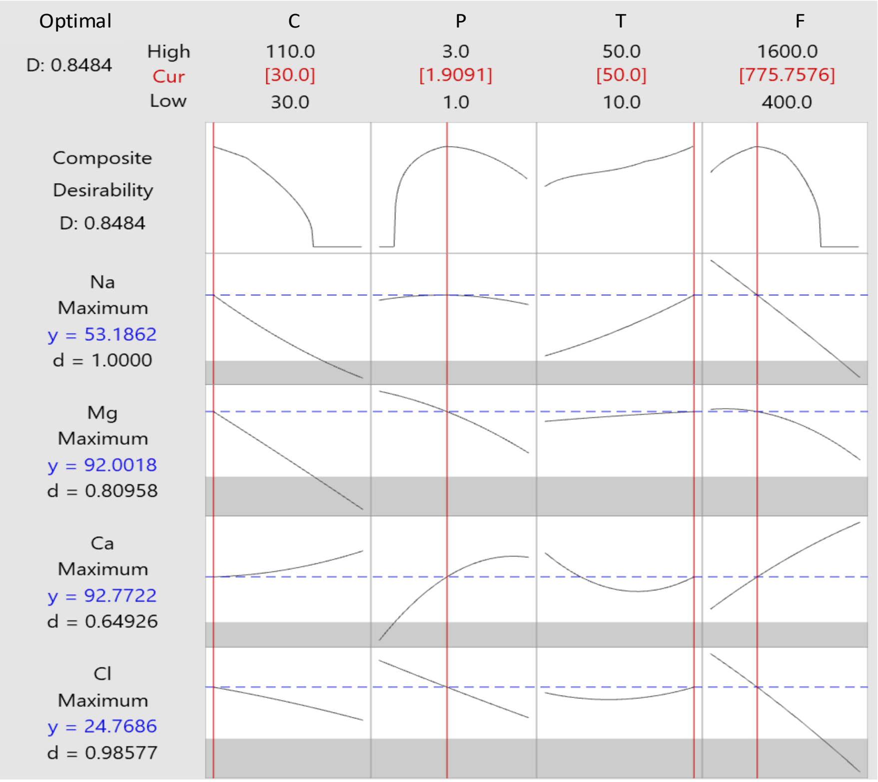


Figure 2.12: Response optimization plot

Following the achievement of the optimal conditions for the KOH-based modified Solvay process, the reaction kinetics for the process were investigated under these optimal conditions.

2.3.4 Carbon Dioxide Capture through Reaction with Potassium Hydroxide and Reject Brine: A Kinetics Study (Paper IV)

It was reported previously that the optimum conditions were obtained at a gauge pressure, gas flow rate, temperature, KOH concentration, and CO_2 inlet concertation of 2.1 bar, 848.5 ml/min, 10°C, 110 g/l, and 10%, respectively (Section 2.3.2). In the current study, the reaction kinetics of KOH-based modified Solvay process were investigated. The operating parameters were selected based on the previously obtained optimal conditions, i.e., CO_2 inlet concentration (3–15%), temperature (10−50°C), KOH concentration (30–190 g/l), CO_2 gas flow rate (400–2,000 ml/min), and total applied pressure (1−5 bar). To investigate their influence on the reaction rate, each of these parameters were varied in turn while keeping others at their respective optimal values. The results revealed that the overall reaction rate is directly proportional to the increase in the inlet CO_2 concentration. However, the selected range of reaction temperature and KOH concentration exerted no influence on the overall CO_2 absorption rate, which remained nearly constant within the selected ranges for these parameters. In summary, under the chosen operating conditions, a first-order overall reaction rate with respect to the inlet CO_2 concentration was established, whereby the reaction rate constant (k) was ~ 0.0003 mol/l. min.

Figure 2(a) presented in Paper IV illustrates the cumulative CO_2 moles reacted per 1 l brine as a function of CO_2 inlet concentration (3, 10 and 15% CO_2) while adopting the optimized conditions (800 ml/min CO_2 flow rate, 10°C temperature, 110 g/l KOH concentration, and 2 barg total pressure). As can be seen from the graph, increasing the inlet CO_2 concentration has a direct effect on the reaction rate. The slope displayed in Figure 2(a) (Paper IV) represents the reaction rate, reflecting the change in CO_2 concentration in unit time. The cumulative CO_2 moles reacted was calculated using Equation 2.7.

The graph illustrated in Figure 2.13 confirms that the reaction rate is a function of inlet CO_2 concentration (3%, 10%, and 15%) and the power trend line provides a good fit to the experimental data (with $R^2 = 1$). The process is almost first-order with respect to inlet CO_2 concentration, which is expected, given that according to Equation (2.2), as the concentration of one of the reactants increases, the reaction shifts toward the product side, and the reaction rate and conversion increase.

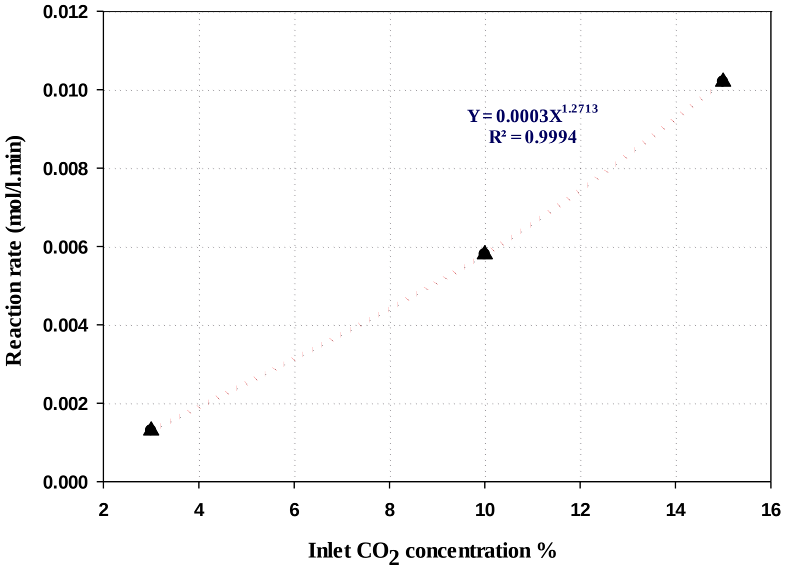


Figure 2.13: Change of reaction rate with inlet CO_2 concertation at the optimal conditions of 110 g/l KOH concentration, 800 ml/min gas flow rate, 10°C temperature, and pressure of 2 barg

The effect of temperature on the reaction kinetics was also examined, and the findings are reported in Figure 2.14. For this experiment, five temperature values (10, 20, 30, 40, and 50°C) were explored, while the remaining factors were kept constant. The findings indicated that this selected range of temperatures does not influence the reaction rate, which is in line with the results reported previously [103, 104].

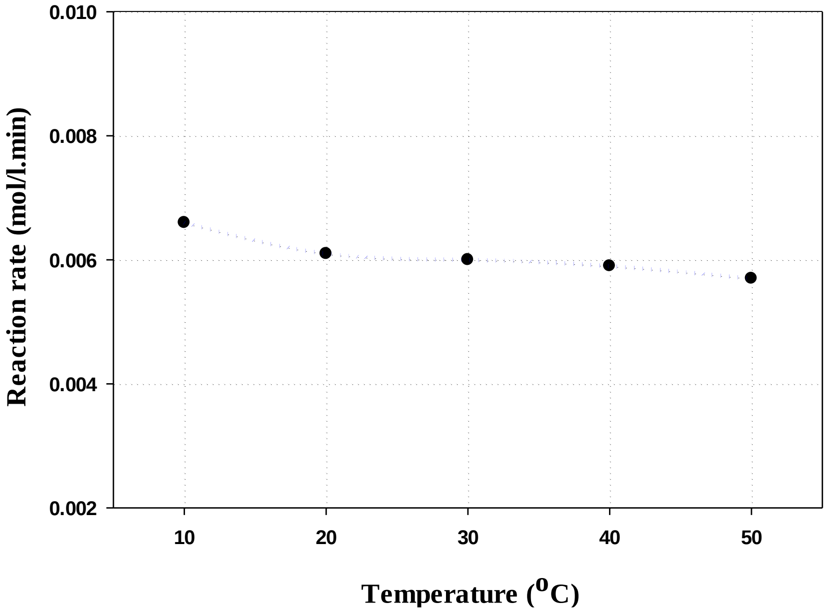


Figure 2.14: Effects of temperature on the reaction rate at a pressure, KOH concentration, inlet CO_2 concentration %, and gas flow rate of 2 barg, 110 g/l, 10%, and 800 ml/min, respectively

Figure 2.15 illustrates the influence of KOH concentration (30–190 g/l) at a constant gauge pressure of 2 bar, temperature of 10°C, constant gas flow rate of 800 ml/min, and inlet CO_2 concentration of 10% on the overall rate of reaction. As can be seen from the graph, within the selected range, the effect of KOH concentration has almost no impact on the reaction rate. This observation confirms the low mass transfer limitations, indicating that the process is mainly limited by the diffusivity and reactivity of CO_2 into the solution.

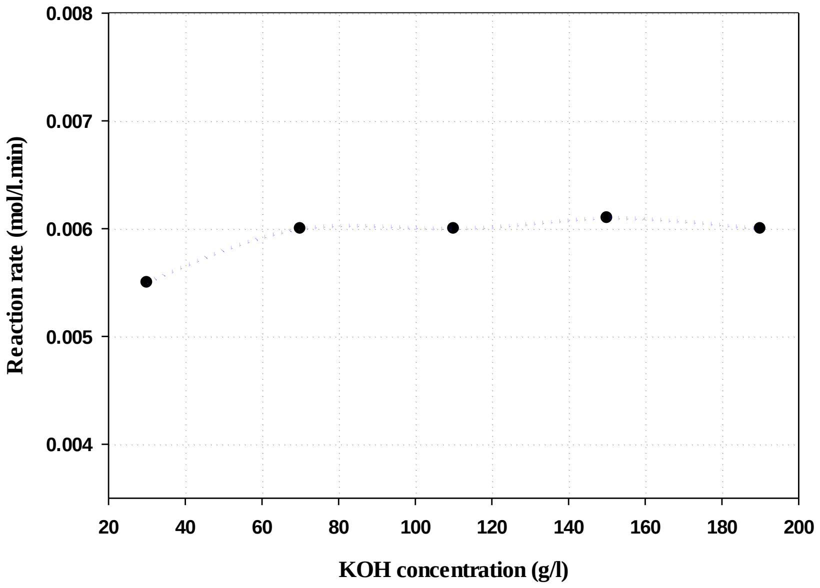


Figure 2.15: Effects of KOH concentration on the reaction rate at a pressure, CO_2 inlet concentration %, temperature, and gas flow rate of 2 barg, 10%, 10°C and 800 ml/min, respectively

As confirmed by Figure 2.16 and Figure 2.17, respectively, the relationship between CO_2 flow rate and reaction rate, as well as pressure and reaction rate, is linear with power of ~ 1 ($R^2 > 99\%$). These results were expected, as greater pressure allows more CO_2 to be solubilized. Increasing the flowrate means adding more amount of CO_2 in the solution. As indicated by Equation (2.2), this also influences the reaction rate, shifting it toward the product and reaching the optimal CO_2 uptake in less time.

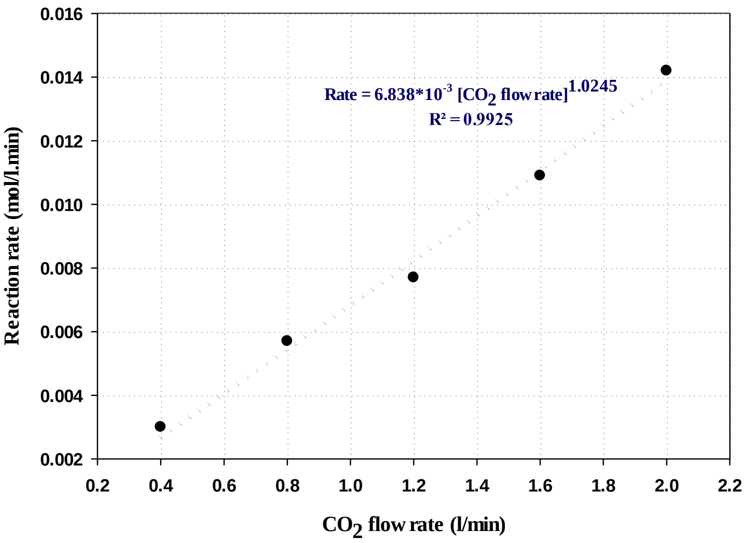


Figure 2.16: Effects of CO_2 flow rate on the reaction kinetics at KOH concertation, CO_2 inlet concentration, temperature, and pressure of 110 g/l, 10%, 10°C, and 2 barg, respectively

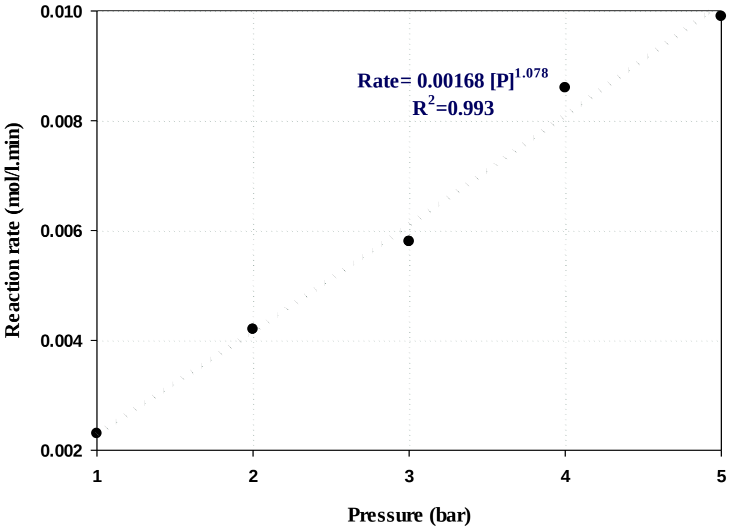


Figure 2.17: Effects of total applied pressure on the reaction kinetics at KOH concertation, CO_2 inlet concentration %, temperature, and gas flow rate of 110 g/l, 10%, 10°C, and 800 ml/min, respectively

Kinetics Model (Paper IV):

As the reaction rate increases with increasing concentration of reactants, the rate for the reaction given by Equation (2.2) is generally represented by a power law:

$$R = k[CO_2]^x[OH^-]^y \tag{2.16}$$

where k is the reaction rate constant, $[OH^-]$ and $[CO_2]$ represent the concentrations of OH^- ions and inlet CO_2, respectively, and x and y correspond to the order of reaction with respect to $[CO_2]$ and $[OH^-]$, respectively.

According to the results presented, CO_2 inlet concentration has a direct effect on reaction kinetics, where the rate order is almost first-order with respect to CO_2 inlet concentration (3, 10, and 15%), as shown in Figure 2.13. Figure 2.16 and Figure 2.17 confirmed the direct impact of CO_2 flow rate and pressure on the rate of reaction. On the other hand, as revealed in Figure 2.15, the reaction rate is independent of the selected KOH concentration range, and thus follows the zero-order kinetics with respect to KOH concentration. As a result, the overall rate of reaction which is zero-order with respect to $[OH^-]$ and a near first-order with respect to $[CO_2]$ is given by:

$$R= k[CO_2]^{1.27} \tag{2.17}$$

The constant k in the rate equation is unique for every chemical reaction and depends mainly on the reaction temperature [111]. In the present study, the rate of reaction was found to be almost constant within the selected temperature range (10−50°C) and under the same operating conditions (pressure of 2 barg, gas flow rate of 800 ml/min, inlet CO_2 concentration of 10%, and KOH concentration of 110 g/l). Moreover, the values of kinetic rate constant (k) for the five temperatures (10, 20, 30, 40, and 50°C) adopted here were obtained by substituting the CO_2 concentration of 10% and the rate value corresponding to each temperature (Figure 2.14) into Equation (2.17). A nearly constant value of k (0.0003 mol/l.min) was obtained irrespective of temperature.

2.3.5 Multi-Stage Treatment for Modified Solvay Process Based on Potassium Hydroxide for High-Level Reject Brine Salinity Reduction and CO_2 Capture (Paper V)

The objective of this research was to evaluate the multi-stage treatment for a modified Solvay process based on KOH to achieve an additional reduction in ion removal from high-salinity brines and an increase in CO_2 capture than was previously obtained under optimal operating conditions (Section 2.3.2). Three different methods were investigated. The first method evaluated the effectiveness of adding NH_4HCO_3 in reducing the solubility of $NaHCO_3$. Even though the Na^+ and Cl^- concentrations were reduced by 56.2% and 40%, respectively, the total CO_2 uptake slightly improved by 1.2%. In the second method, the addition of extra KOH in subsequent stages was investigated to overcome the pH reduction observed in the first method. There was a 47.3% improvement in CO_2 uptake from 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+} was approximately 76.3% and 94.6%, respectively, following the pre-treatment step (filtration), followed by the same stages as in the second method. Reducing these ions decreased the competitive reactions and thus increased CO_2 solubility and reactivity with KOH, 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.

A summary of the overall reduction in ions and CO_2 uptake (g CO_2/ 1000 ml brine) from the three methods (M1, M2, and M3) are illustrated in Table 2.7.

Table 2.7: Summary of ions reduction % and CO_2 uptake of brine for the three methods

Stages	Na^+%			Cl^-%			CO_2 uptake (g CO_2/ 1000 ml brine)		
	M1	M2	M3	M1	M2	M3	M1	M2	M3
S1	38	38.9	1.1	35	36.1	3	63	59.7	-
S2	56	49.8	38.9	38.9	40.4	36.6	-	-	84.5
S3	56.07	60.7	47.1	39.5	58.7	39.9	3	17.5	-
S4	56.2	65	54.6	40	64.5	53	1.8	22.7	7.5
S5	-	-	57.7	-	-	60.1	-	-	11.1
Total	-	-	-	-	-	-	67.8	99.9	108.2

CO_2 capture efficiency and ions removal percentage by M1:

Figure 2.18 shows a significant increase in Na^+ removal from ~38% in S1 to 56% in S2, followed by a constant removal percentage in the following stage as there was no more Na^+ reduction. These results confirmed the effectiveness of NH_4HCO_3. Adding NH_4HCO_3 decreased the solubility of $NaHCO_3$, according to Equations (2.4) and (2.5).

Furthermore, Table 2.7, illustrates that the addition of NH_4HCO_3 had almost no effect on the CO_2 uptake (g CO_2 / 1000 ml of brine) in the further stages (S3 and S4). The total CO_2 uptake from M1 was 67.8 g CO_2 / 1000 ml of brine. More details about the findings are demonstrated in Paper V.

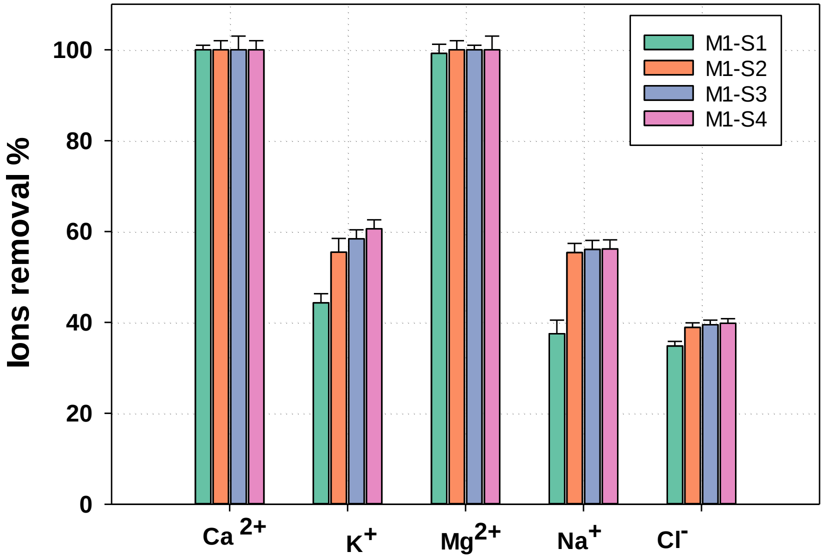


Figure 2.18: Ion reduction % for M1-S1, M1-S2, M1-S3 and M1-S4

CO_2 capture efficiency and ions removal percentage by M2:

In M2, there was a 15.7% and 61.2% improvement in Na^+ and Cl^- reduction from the first method, respectively. Moreover, the total CO_2 uptake reached almost 99.9 g CO_2/1000 ml of brine in M2, compared with only 67.8 g CO_2/1000 ml of brine in M1, which is approximately a 47.3% improvement. This result shows the effectiveness of adding more KOH in subsequent stages, because high pH values increase CO_2 solubility and the precipitation of valuable solid products. Table 2.7 summarizes the total CO_2 uptake and ions reduction from each stage. More information on the findings can be found in Paper V.

CO_2 capture efficiency and ions removal percentage by M3:

In M3, there was a considerable enhancement in the total CO_2 uptake in the early stage (S2), with a value of 84.5 g CO_2/1000 ml brine compared with 59.7 g CO_2/1000 ml in M2-S1, a difference of approximately 41.5%. This is due to the effect of the pre-treatment step (filtration) in M3, where

Ca^{2+} and Mg^{2+} were removed by ~ 76.3% and 94.6%, respectively. These ions behave as inhibitors, and their reduction decreased competitive reactions by increasing CO_2 solubility and reactivity with KOH. In addition, the cumulative CO_2 uptake at the final stage for M3 was 8.3% higher than that for M2, as shown in Table 2.7. On the other hand, the total reduction in Na^+ and Cl^- percentages were decreased in M3 by almost 11.2% and 6.8%, respectively, when compared to M2. This is due to a decrease in the total salinity of the brine. According to Equation 2.2, as salinity decreases, the reaction shifts to the left side (Le Chatelier principle), resulting in a decrease in total Na^+ and Cl^- percentages.

By comparing M2 with M3, the results illustrate that the highest Na^+ and Cl^- removal were achieved by M2. However, if high CO_2 uptake, and early recovery of Ca^{2+} and Mg^{2+} as pure solids were preferred, M3 would be the best option.

Collected solids characteristics:

The recovery of the ions was also confirmed from the solid characteristics analysis (Section 2.2.2.2). The XRD analysis for the collected solids from M2-S3 confirmed the recovery of $NaHCO_3$, KCl and $KHCO_3$ solids as shown in Figure 2.19. The presence of $NaHCO_3$ and $KHCO_3$ confirms the effectiveness of adding NH_4HCO_3. It is worth noting that the precipitation of K^+ in the form KCl and $KHCO_3$ confirms the high reactivity of KOH with CO_2, although it was used as the primary alkaline at high concentrations.

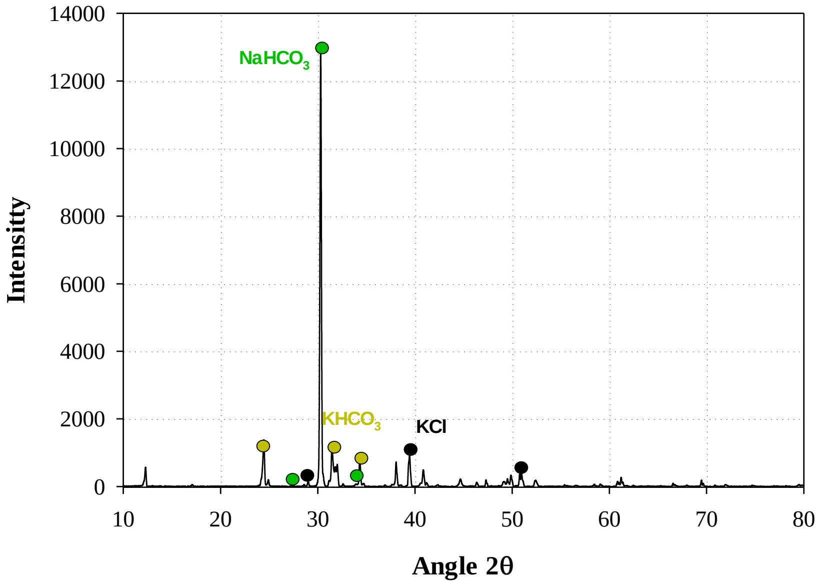
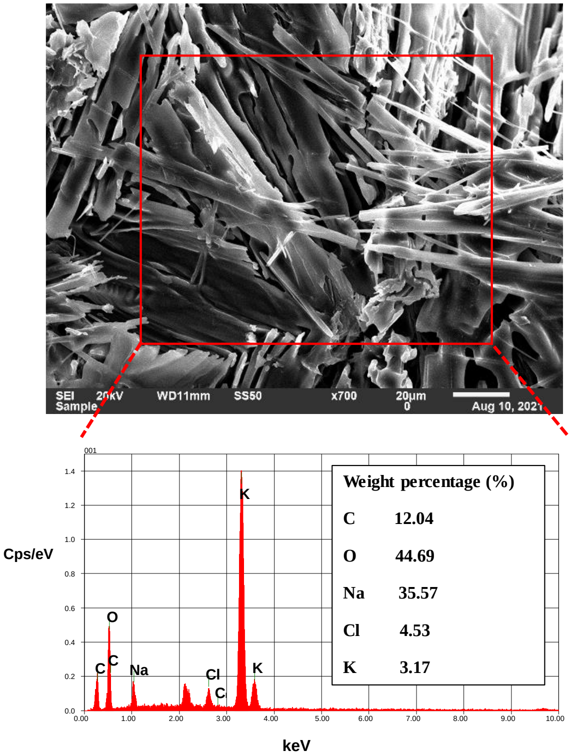


Figure 2.19: X-ray diffraction patterns of dried and collected solids from M2-S3

Figure 2.20 shows SEM images and the EDS analysis for the M3-S4 tested sample. The EDS analysis confirmed the high percentage recovery of Na^+ in the form of $NaHCO_3$. The presence of KCl and $KHCO_3$ was also confirmed. Lack of any spiky type solids shows that most of the NH_4HCO_3 added has been converted to $NaHCO_3$ and $KHCO_3$. Figure 2.21 illustrates the crystals formed at M3-S4.



Weight percentage (%)	
C	12.04
O	44.69
Na	35.57
Cl	4.53
K	3.17

Figure 2.20: Results from SEM and EDS analyses for the M3-S4 collected solids

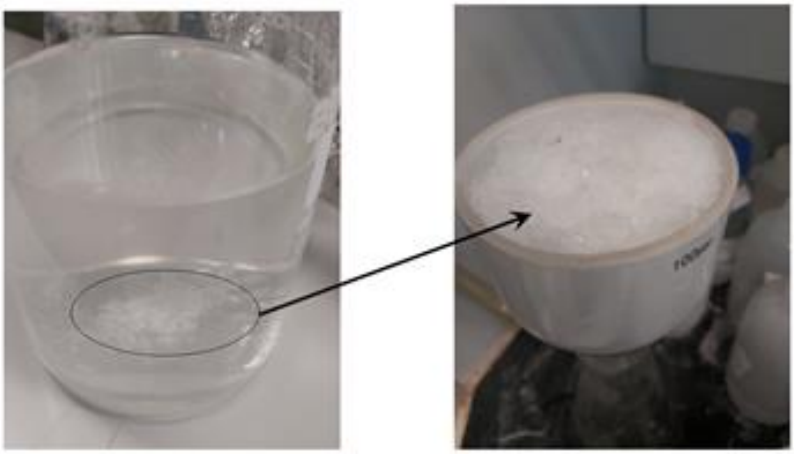


Figure 2.21: The recovery of the crystals formed in M3-S4

2.3.6 Continuous Operation of IPSBR (Paper V)

It is important to note that the reactions occur in a novel inert particle spouted bed reactor (IPSBR) developed by El-Naas et al. [90, 91]. Therefore, the objective of the current work was to investigate the dynamic behavior of the IPSBR using inlet gas flow rate and liquid flow rate step changes, where a KOH-based modified Solvay process was performed. Continuous flow experiments were conducted under the previously determined optimum conditions (Table 2.5-Section 2.3.2). The results were very promising in terms of the reactor system's flexibility and applicability for large-scale processes.

The decrease or increase in CO_2 capture efficiency caused by the step changes in gas and liquid flow rates is shown in Figures 2.22 and 2.23. It is shown that the efficiency of CO_2 capture increases as the gas flow rate decreases. The opposite has been observed for increasing the liquid flow rate.

According to Equation (2.2), the above results were expected because it has previously been reported [103, 104] that a high gas flow rate can positively influence CO_2 uptake by increasing the reaction rate and pushing it toward the products. However, flow rates greater than 1000 ml/min appeared to have a negative effect on CO_2 uptake, which can be explained by decreasing the gas residence time in the reactor and thus the reaction rate. Consequently, an intermediate value of gas flow rate (848.5 ml/min) was predicted by the response optimizer (Section 2.3.2).

Increasing the liquid flow rate positively affects the CO_2 capture rate due to increasing the volume of fresh solution (brine + 110g/l KOH) that contacts the gas at every time unit. This fresh solution has a high pH value and contains a high level of metal ions, which ensures the high reactivity of CO_2 during the treating time.

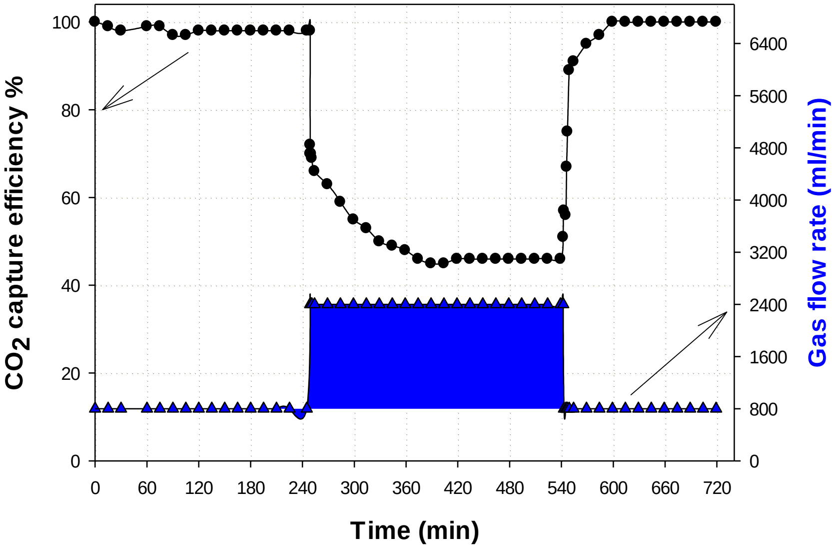


Figure 2.22: CO_2 capture versus reaction time as a function of gas flow rate at the conditions of 110 g/l KOH concentration, and 10°C temperature, and pressure of 2 barg

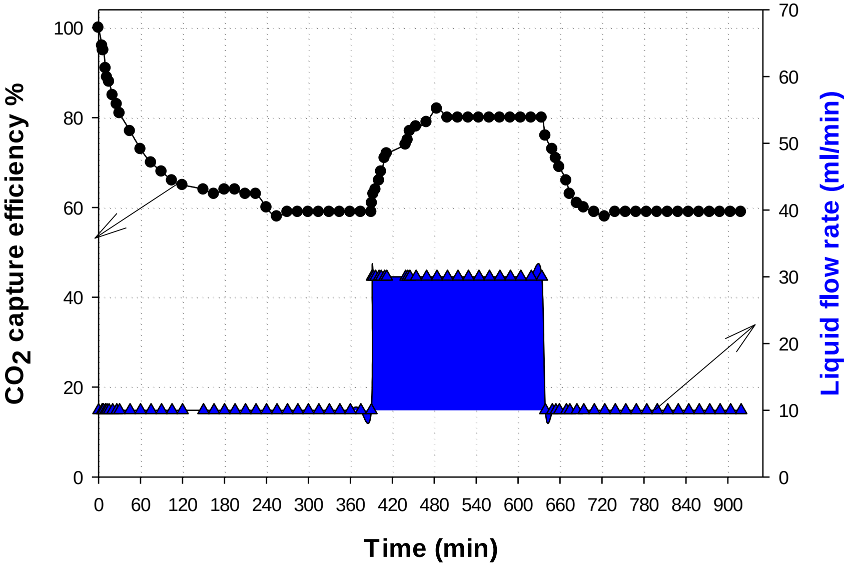


Figure 2.23: CO_2 capture versus reaction time as a function of liquid flow rate at the conditions of 110 g/l KOH concentration, and 10°C temperature, and pressure of 2 barg

Figure 2.24 shows that the dead time (t_d) is less than the reactor time constant (τ_p) in all experiments, indicating tight and simple overall process control [126].

The above results showed that the CO_2 capture efficiency % was in a steady state and stabilized for at least 3 h at different operational conditions. Additionally, the t_d was less than τ_p in all experiments. These findings are promising in terms of the reactor system's flexibility and applicability to large-scale processes [91].

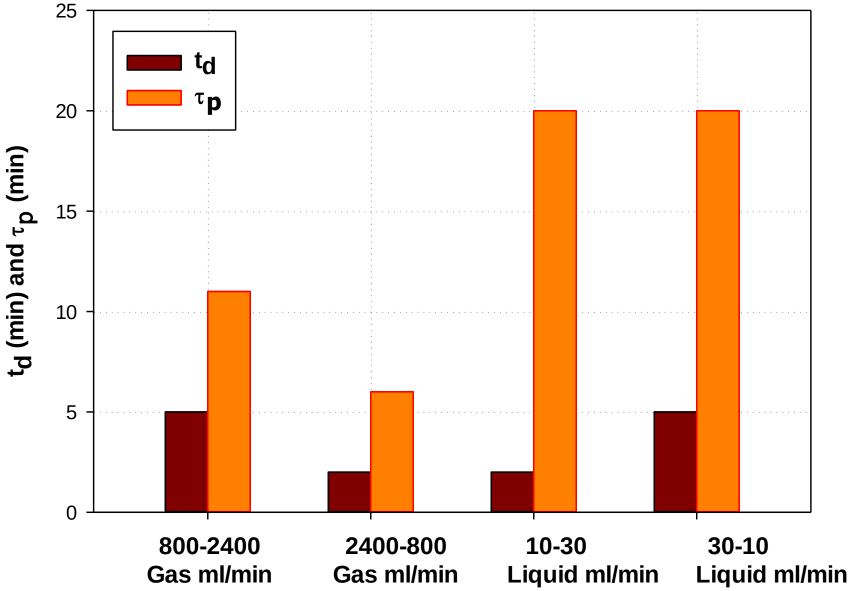


Figure 2.24: t_d and τ_p for the performed step change experiments

Chapter 3: Conclusion and Future Perspectives

Solvay and modified Solvay processes are facing some limitations such as, alkaline solubility, operating temperature, maintaining a high pH value, and low Na^+ removal, which does not exceed 35%, resulting in a low overall desalination efficiency. The research presented in this dissertation introduces a new alkaline, namely KOH to investigate its ability to overcome these limitations for further improvement in the productivity and sustainability of the modified Solvay process.

A preliminary investigation was conducted to compare the effectiveness of a modified Solvay process based on KOH to CaO results obtained in previous studies. All experiments were performed under a temperature of 20°C, gas flow rate of 1 l/min, CaO concentration of 20 g/l (optimum amount), and KOH concentration of 70.57 g/l (stochiometric amount). Experiments were conducted in a novel inert particle spouted bed reactor. It was observed that KOH entails very high solubility in comparison with CaO. The obtained results also demonstrated that most of the ions removal based on the KOH and CaO were very close. Moreover, KOH was capable of sustaining a high level of pH (~13.6) throughout the reaction (Paper I).

Initial results revealed that KOH is a promising alkaline material, which can significantly accelerate CO_2 capture efficiency and treat reject brine. Further investigations in terms of the parametric sensitivity analysis were conducted to optimize the process parameters for the purpose of maximizing the CO_2 capture and the metal removal from solutions in the presence of KOH. The optimization of KOH-based modified Solvay process was investigated to obtain the maximum CO_2 uptake and ions recovery from reject brine. CCD-RSM approach was utilized to predict and optimize the parameters of four key factors, namely, KOH concentration (30-110 g/l), gauge pressure (1–3 barg), temperature (10–50°C), and CO_2 gas flow rate (400–1600 ml/min). The experimental results were represented by a second-order regression model and the predicted responses agreed well with the experimental results ($R^2 > 0.95$). The optimum operating conditions were found to be KOH concentration of 110 g/l, gauge pressure of 2.1 barg, CO_2 flow rate of 848.5 ml/min, and temperature of 10°C. Under these conditions, the maximum CO_2 uptake was ~0.58 g CO_2/g KOH, and the maximum reductions of Na^+, Cl^-, Ca^{2+} and Mg^{2+} were 44.1%, 40.1%, 100%, and 99.8%, respectively. The effect of the mixing particle volume fraction was also examined between 0 and 25%, such that the optimum conditions were improved at mixing particle percentages of 15%, while no improvement was detected beyond 15%. The collected solids were characterized using SEM, XRD and FTIR. Obtained spectra by these surface characterization techniques confirm the production of valuable solid products, such as $NaHCO_3$, $KHCO_3$, K_2CO_3, $CaCO_3$, $Mg(OH)_2$, and KCl (Paper II).

It is known that the temperature is an important parameter that affects the performance of the combined process. Generally, the increase in temperature causes increase in the solubility of product, decrease in the CO_2 capturing and metal removal efficiency. Hence a lower temperature is required to increase the CO_2 capturing and metal removal efficiencies. However, brine is commonly discharged from desalination plants at relatively high temperatures of 40–55°C. One important motivational point of this work is to examine the performance of KOH-based modified Solvay process at high temperatures. The optimization was performed under different operating conditions to obtain the maximum CO_2 capture and ion recovery from reject brine at a relatively high temperature of 50°C. An RSM-based CCD approach using Minitab 19.0 was implemented to predict and optimize the effects of four important factors on the responses, namely, KOH concentration (30–110 g/l), gauge pressure (1–3 bar), temperature (10°C –50°C), and CO_2 gas flowrate (400–1600 ml/min). The responses of 31 experimental runs were properly represented using 3D surface response plots. A response optimizer was used to predict the optimum conditions to achieve the maximum responses by holding the temperature at 50°C. The predicted optimum conditions were obtained at a gauge pressure, gas flowrate, and KOH concentration of 2 bar, 776 mL/min, and 30 g/l, respectively. The predicted responses under these conditions were experimentally validated, and the results showed a good agreement with the predicted values. The experimental results showed that under the optimized conditions and at 50°C, a maximum CO_2 uptake of ~0.50 g CO_2/g KOH and maximum reduction efficiencies of Na^+, Cl^-, Ca^{2+}, and Mg^{2+} of 45.6%, 29.8%, 100%, and 91.2%, respectively, were achieved. Under these operating conditions, the reaction rate was relatively high, and a new reaction occurred. This can be explained by the hot pot process of K_2CO_3, during which the pressurized CO_2 reacts with soluble K_2CO_3 at high temperatures to form $KHCO_3$. $KHCO_3$ starts to compete against $NaHCO_3$, resulting in a high precipitation of $NaHCO_3$. The solid products were characterized using SEM, XRD, and FTIR analysis. All the results confirmed the production of valuable products with diverse industrial applications, such as $NaHCO_3$, $KHCO_3$, K_2CO_3, and KCl (Paper III).

Understanding the reaction kinetics is essential for controlling reactions and obtaining the desired outcomes. For example, production can be improved by ascertaining how fast products are formed and identifying factors that cause reactions to slow down. Therefore, reaction kinetics of the KOH-based modified Solvay process were studied in a novel IPSBR system. The operating parameters were selected based on the previously obtained optimal conditions, i.e., CO_2 inlet concentration (3–15%), temperature (10−50°C), KOH concentration (30–190 g/l), CO_2 gas flow rate (400–2,000 ml/min), and total applied pressure (1−5 bar). To investigate their influence on the reaction rate, each of these parameters was varied in turn while keeping others at their respective optimal values. Temporal changes in ion reduction and pH were also examined during each experimental run. The findings revealed a direct relationship between rate of reaction and CO_2 inlet concentration. In addition, the same trend of variation was attained by the changing gas flow rate and total applied pressure. On the other hand, no change in the reaction rate was observed when the reaction temperature increased from 10°C to 50°C. Moreover, the rate was independent of the selected range of KOH concentrations. As a result, the overall reaction rate was first-order with respect to CO_2 concentration, and the reaction rate constant (k) was ~ 0.0003 mol/l. min within the operating conditions chosen (Paper IV).

Though acceptable efficiency has been achieved by utilizing the single stage process, a multi-stage treatment process was also investigated to check its impact for further improvement in the overall performance of the KOH-based modified Solvay process in terms of CO_2 capture and ions reduction. At the optimum conditions, a single-stage treatment process achieved a maximum CO_2 uptake of 67 g CO_2/1000 ml of treated brine, a maximum Na^+ reduction of 44.1%, Cl^- reduction of 40.1%, Ca^{2+} reduction of 100%, and Mg^{2+} reduction of 99.8%. The current multi-stage treatment process consists of three methods. The first method tested the effect of adding NH_4HCO_3 on Na^+ removal, which increased to 56.2%. Nevertheless, CO_2 uptake slightly increased to 67.8 g CO_2/1000 ml of treated brine. In M2, more KOH was added in subsequent stages to overcome the pH reduction caused by each treatment stage. This resulted in a considerable increase in the reduction of Na^+ and Cl^- to 65 and 64.5%, respectively. Additionally, CO_2 uptake reached 99.9 g CO_2/1000 ml of treated brine. The effect of filtration on the solution prior to reaction with CO_2 was assessed in M3. At this stage, it was found that 94.6% recovery of Mg^{2+} in the form of $Mg(OH)_2$ and

~76.3% removal of Ca^{2+} were achieved. This had a positive effect on CO_2 uptake, as it reached its maximum value of 84.5 g CO_2/1000 ml of treated brine directly from the second stage without an additional treatment step. In addition, the cumulative CO_2 uptake from all stages was almost 108.2 g CO_2/1000 ml of treated brine. These results showed that the new, proposed multi-stage desalination process has the potential to significantly improve the desalination of reject brine with a high salinity, which may be used in different industrial applications. Moreover, solid products were characterized using SEM, XRD, FTIR and Raman analysis (Paper V).

It is worth noting that, the reactor system's dynamic behaviour was also investigated using step changes in gas flow rate (800 - 2400 ml/min) and liquid flow rate (10-30 ml/min). The dead time and reactor time constant were calculated for each transient state condition. In all cases, the dead time was less than the reactor time constant, showing tight and simple overall process control (Paper V).

Based on the experimental and analytical studies conducted in this work, there are many challenging issues to be considered for the future:

- Industrial solid waste can be used instead of commercial alkaline to increase the pH and generate valuable products with a wide range of applications. Wood ash is considered as nontoxic waste, it contains alkaline material in the form of potassium carbonate (K_2CO_3) and KOH, often referred to as pearl potash and potash, respectively. These compounds are highly soluble in water and react with it to produce hydroxide ions with a pH as high as 12 [127]. Charcoal industry produces significant amounts of wood ash waste, as well as pulp and paper mills industries. Further investigations are required to examine the effect of the wood ash wastes (tree limbs/palm fronds) to increase the productivity and sustainability of the modified

Solvay process based on KOH. Exploring the effect of this waste can be a new research dimension in this area.

- Further improvement in the multi-stage process is required for enhancing the purity of the produced solids. Mohammad et al. [128] developed a novel technique, namely, a multi-stage desalination process, where a combination of chemical and electrocoagulation processes were implemented at different stages. This method was applied for the modified Solvay process based on CaO. In each stage, a specific metal ion was recovered in high purity. The electrocoagulation process was used to recover most of the ammonium (NH_4^+) content as NH_3 gas. Moreover, Ca^{2+} ions in the form of $CaCl_2$ was recovered as $Ca(OH)_2$ resulted from the electrolysis of water. Moreover, hydrogen (H_2) and chlorine (Cl_2) gases were produced. It is also important to implement the developed multi-stage [128] for the KOH-based modified Solvay process. This will increase the purity of the produced solids. In the current work, some of the KCl was produced as a form of crystals, which can be easily recovered by filtration. However, still some of the KCl is dissolved in the solution. Therefore, the electrocoagulation process can be applied to recover the dissolved KCl as a form of KOH. Furthermore, NH_4^+ resulted from the addition of NH_4HCO_3 in the multistage treatment (Section 2.3.5) can be converted into NH_3 gas. This could result in high recovery for K^+ ions up to 100% recovery. The proposed multi-stage process has the potential to result in further improvement in the productivity and sustainability of the process.

- Recently, Mohammad et al. [129] investigated the effect of new oil-adsorbent material produced by the modified Solvay process based on CaO. The solids are mostly made up of $NaHCO_3$, $CaCl_2$, $Mg(OH)_2$, and K_2CrO_3. It was determined that the developed adsorbents can be utilized in oil spill cleanup. The utilization of the recovered solids by the KOH-based modified Solvay process is another interesting area of research. The solid characteristics analysis of the current work confirmed the existence of $NaHCO_3$, KCl, $KHCO_3$, K_2CrO_3, and $Mg(OH)_2$ which could be examined to check its ability as oil adsorbent material.

- The IPSBR hydrodynamics was simulated previously by Mohammad et al. [102, 109, 110] using ANSYS computational fluid dynamics software (CFD). Based on the developed model, it is recommended to utilize Ansys Chemkin-Pro simulator to select the appropriate kinetics models for the proposed process. The continuous operation of the process can be validated experimentally by knowing the inlet parameters of the reactor and the kinetics model predicted experimentally. Such simulation work will produce more accurate and realistic data for further scale up process.

- Purity of the collected solids and the purification process need to be addressed and investigated for more clear utilization process. Utilization of the recovered solids in industrial and/or environmental applications requires more investigations and more comprehensive characterizations.

- The treated brine is within a salinity value of ~ 39,225 ppm. Accordingly, treated brine has less impact on the operational infrastructure units compared to the feed brine (75,000-80,000 ppm). On an industrial scale, treated brine could be used in thermoelectric-power industry to cool electricity-generating equipment. Also, it can be used in enhanced oil recovery, mining, and some industrial operations. The aim is to optimize the process to reach much lower salinity so that it can be used for brackish water irrigation.

- There are multiple parameters in the study to achieve the optimized performance such as concentrations of salts, temperature, and ionic strength. It is recommended to use equilibrium model(s) such as MINEQL to determine the better operational conditions.

- A pilot study will be carried in the future for scale up. Currently, there is an existing pilot plant in which the CaO-based modified Solvay process is implemented. The pilot plant produces a clean air gas (~free of CO_2). In addition, the recovered solids are mainly $NaHCO_3$ and $CaCO_3$ mixture with a weight percentage around 20% $NaHCO_3$ and 80% $CaCO_3$, which could reach a selling benefit of 10 $US/Kg for $NaHCO_3$ and 5 $US/Kg for $CaCO_3$ after a specific purification process. The scale-up process could be tested for the new alkaline (KOH), and hence further feasibility study will be carried out based on the optimum operating conditions for the proposed process.

References

[1] A. Panagopoulos, K. J. Haralambous, and M. Loizidou, "Desalination brine disposal methods and treatment technologies-A review," *Science of the Total Environment,* vol. 693, 2019, doi: 10.1016/ j.scitotenv.2019.07.351.

[2] N. Ghaffour, T. M. Missimer, and G. L. Amy, "Technical review and evaluation of the economics of water desalination: current and future challenges for better water supply sustainability," *Desalination,* vol. 309, pp. 197-207, 2013.

[3] N. Ghaffour, "The challenge of capacity-building strategies and perspectives for desalination for sustainable water use in MENA," *Desalination and Water Treatment,* vol. 5, no. 1-3, pp. 48-53, 2009.

[4] A. S. Alsharhan and Z. E. Rizk, "Water Desalination: Environmental Impacts and Brine Management," in *Water Resources and Integrated Management of the United Arab Emirates*: Springer, 2020, pp. 455-470.

[5] J. Swaminathan, "Design and operation of membrane distillation with feed recirculation for high recovery brine concentration," *Desalination,* vol. 445, pp. 51-62, 2018.

[6] S. Lattemann and T. Höpner, *Seawater desalination: Impacts of brine and chemical discharge on the marine environment*. Balaban Desalination Publications L'Aquila, Italy, 2003, http://1 43. 233. 204. 254: 508 / publications.asp (accessed Feb. 20, 2022).

[7] J. Liu, S. Chen, H. Wang, and X. Chen, "Calculation of carbon footprints for water diversion and desalination projects," *Energy Procedia,* vol. 75, pp. 2483-2494, 2015.

[8] M. H. El-Naas, A. H. Al-Marzouqi, and O. Chaalal, "A combined approach for the management of desalination reject brine and capture of CO_2," *Desalination,* vol. 251, no. 1-3, pp. 70-74, 2010.

[9] J. Mustafa, A.H. M. Aya, A. H. Al-Marzouqi, and M. H. El-Naas, "Simultaneous treatment of reject brine and capture of carbon dioxide: A comprehensive review," *Desalination,* vol. 483, 2020, doi: https://doi.org/10.1016/j.desal.2020.114386.

[10] A. Dindi, D. V. Quang, and M. R. Abu-Zahra, "Simultaneous carbon dioxide capture and utilization using thermal desalination reject brine," *Applied Energy,* vol. 154, pp. 298-308, 2015.

[11] B. K. Pramanik, L. Shu, and V. Jegatheesan, "A review of the management and treatment of brine solutions," *Environmental science: water research & technology,* vol. 3, no. 4, pp. 625-658, 2017.

[12] O. Ogunbiyi *et al.*, "Sustainable brine management from the perspectives of water, energy and mineral recovery: A

comprehensive review," *Desalination,* vol. 513, 2021, doi: https://doi.org/10.1016/j.desal.2021.115055.

[13] A. Ghalavand, M. S. Hatamipour, and Y. Ghalavand, "Clean treatment of rejected brine by zero liquid discharge thermal desalination in Persian Gulf countries," *Clean Technologies and Environmental Policy,* vol. 23, no. 9, pp. 2683-2696, 2021.

[14] X. Zhang, W. Zhao, Y. Zhang, and V. Jegatheesan, "A review of resource recovery from seawater desalination brine," *Reviews in Environmental Science and Bio/Technology,* vol. 20, no. 2, pp. 333-361, 2021.

[15] A. Panagopoulos and K. J. Haralambous, "Environmental impacts of desalination and brine treatment-Challenges and mitigation measures," *Marine Pollution Bulletin,* vol. 161, 2020, doi:https://doi.org/10.1016/j.marpolbul.2020.111773.

[16] A. Gambhir and M. Tavoni, "Direct air carbon capture and sequestration: how it works and how it could contribute to climate-change mitigation," *One Earth,* vol. 1, no. 4, pp. 405-409, 2019.

[17] Aya A-H. Mourad, A. F. Mohammad, M. Altarawneh, A. H. Al-Marzouqi, M. H. El-Naas, and M. H. Al-Marzouqi, "Effects of potassium hydroxide and aluminum oxide on the performance of a modified solvay process for CO_2 capture: A comparative study," *International Journal of Energy Research,* vol. 45, no. 9, pp. 13952-13964, 2021.

[18] E. M. Jost, "Nickel-zinc battery system having an aqueous electrolyte consisting of potassium hydroxide and potassium carbonate,"ed: Google Patents, 1969.

[19] A. D. Khawaji, I. K. Kutubkhanah, and J. M. Wie, "Advances in seawater desalination technologies," *Desalination,* vol. 221, no. 1-3, pp. 47-69, 2008.

[20] M. O. Mavukkandy, C. M. Chabib, I. Mustafa, A. Al Ghaferi, and F. AlMarzooqi, "Brine management in desalination industry: From waste to resources generation," *Desalination,* vol. 472, 2019, doi: https://doi.org/10.1016/j.desal.2019.114187.

[21] Z. Zhongming, L. Linong, Y. Xiaona, Z. Wangqiang, and L. Wei, "UN warns of rising levels of toxic brine as desalination plants meet growing water needs." 2019, http://resp. llas. ac.cn/ C666/handle/ 2XK7JSWQ/ 109063 (accessed Feb. 23, 2022).

[22] A. Mohamed, M. Maraqa, and J. Al Handhaly, "Impact of land disposal of reject brine from desalination plants on soil and groundwater," *Desalination,* vol. 182, no. 1-3, pp. 411-433, 2005.

[23] M. S. Imbabi, F. P. Glasser, J. L. G. Martos, G. Jauffret, and J. Morrison, "Method of Sequestering Carbon Dioxide," ed: Google Patents, 2018.

[24] M. H. El-Naas, A. F. Mohammad, M. I. Suleiman, M. Al Musharfy, and A. H. Al-Marzouqi, "A new process for the capture of CO_2 and reduction of water salinity," *Desalination,* vol. 411, pp. 69-75, 2017.

[25] F. Levihn, "CO_2 emissions accounting: Whether, how, and when different allocation methods should be used," *Energy,* vol. 68, pp. 811-818, 2014.

[26] J. Mustafa, A. H. Al-Marzouqi, M. H. El-Naas, and N. Ghasem, "Electrodialysis based waste utilization methodology for the desalination industry," *Desalination,* vol. 520, 2021, doi: https://doi.org/10.1016/j.desal.2021.115327.

[27] K. M. K. Yu, I. Curcic, J. Gabriel, and S. C. E. Tsang, "Recent advances in CO2 capture and utilization," *ChemSusChem: Chemistry & Sustainability Energy & Materials,* vol. 1, no. 11, pp. 893-899, 2008.

[28] F. A. Rahman *et al.*, "Pollution to solution: Capture and sequestration of carbon dioxide (CO_2) and its utilization as a renewable energy source for a sustainable future," *Renewable and Sustainable Energy Reviews,* vol. 71, pp. 112-126, 2017.

[29] N. S. Siefert and S. Litster, "Exergy and economic analyses of advanced IGCC–CCS and IGFC–CCS power plants," *Applied energy,* vol. 107, pp. 315-328, 2013.

[30] R. Baciocchi, A. Corti, G. Costa, L. Lombardi, and D. Zingaretti, "Storage of carbon dioxide captured in a pilot-scale biogas upgrading plant by accelerated carbonation of industrial residues," *Energy Procedia,* vol. 4, pp. 4985-4992, 2011.

[31] B. Dou, Y. Song, Y. Liu, and C. Feng, "High temperature CO_2 capture using calcium oxide sorbent in a fixed-bed reactor," *Journal of hazardous materials,* vol. 183, no. 1-3, pp. 759-765, 2010.

[32] A. F. Mohammad, M. H. El-Naas, M. I. Suleiman, and M. Al Musharfy, "Optimization of a solvay-based approach for CO_2 capture," *International Journal of Chemical Engineering and Applications,* vol. 7, no. 4, pp. 230-234, 2016.

[33] K. E. Børseth, "Method for desalination of water and removal of carbon dioxide from exhaust gases," ed: Google Patents, 2007.

[34] P. Grauer and F. Krass, "Method and device for binding gaseous CO_2 to sea water for the flue gas treatment with sodium carbonate compounds," ed: Google Patents, 2010.

[35] B. R. Constantz, K. Farsad, and M. Fernandez, "Desalination methods and systems that include carbonate compound precipitation," ed: Google Patents, 2010.

[36] Q. Liu and M. M. Maroto-Valer, "Studies of pH buffer systems to promote carbonate formation for CO_2 sequestration in brines," *Fuel Processing Technology,* vol. 98, pp. 6-13, 2012.

[37] G. Congjie and C. Guohua, "Desalination Technology and Engineering Handbook," ed: Beijing: Chemical Industry Press, 2004.

[38] P. K. Cornejo, M. V. Santana, D. R. Hokanson, J. R. Mihelcic, and Q. Zhang, "Carbon footprint of water reuse and desalination: a review of greenhouse gas emissions and estimation tools," *Journal of Water Reuse and Desalination,* vol. 4, no. 4, pp. 238-252, 2014.

[39] A. Linda and H. Singh, "Geological Carbon Capture and Storage as a Climate-Change Mitigation Technology," in *Advances in Carbon Capture and Utilization*: Springer, 2021, pp. 33-55.

[40] C. E. Finke, H. F. Leandri, E. T. Karumb, D. Zheng, M. R. Hoffmann, and N. A. Fromer, "Economically advantageous pathways for reducing greenhouse gas emissions from industrial hydrogen under common, current economic conditions," *Energy & Environmental Science,* vol. 14, no. 3, pp. 1517-1529, 2021.

[41] J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried, and R. D. Srivastava, "Advances in CO_2 capture technology—the US Department of Energy's Carbon Sequestration Program," *International journal of greenhouse gas control,* vol. 2, no. 1, pp. 9-20, 2008.

[42] B. Bolin and E. Eriksson, "Changes in the carbon dioxide content of the atmosphere and sea due to fossil fuel combustion," *The atmosphere and the sea in motion,* vol. 1, pp. 30-142, 1959.

[43] M. Fahim, T. Alsahhaf, and A. Elkilani, "Chapter 17—Environmental Aspects in Refining," *Fundamentals of Petroleum Refining; Elsevier: Amsterdam, The Netherlands,* pp. 423-455, 2010.

[44] J. Truesdall, M. Mickley, and R. Hamilton, "Survey of membrane drinking water plant disposal methods," *Desalination,* vol. 102, no. 1-3, pp. 93-105, 1995.

[45] P. Glueckstern and M. Priel, "Optimized brackish water desalination plants with minimum impact on the environment," *Desalination,* vol. 108, no. 1-3, pp. 19-26, 1997.

[46] N. Khurana, N. Goswami, and R. Sarmah, "Carbon Capture: Innovation for a Green Environment," in *Advances in Carbon Capture and Utilization*: Springer, 2021, pp. 11-31.

[47] A. Kapoor, E. Poonguzhali, N. Dayanandan, and S. Prabhakar, "Applications of Membrane Contactors for Water Treatment," *Applied Water Science Volume 1: Fundamentals and Applications,* pp. 361-381, 2021.

[48] J. Godin, W. Liu, S. Ren, and C. C. Xu, "Advances in recovery and utilization of carbon dioxide: A brief review," *Journal of Environmental Chemical Engineering,* vol. 9, no. 4, 2021, doi: https://doi.org/10.1016/j.jece.2021.105644.

[49] T. Huang, M. Alyami, N. Kashab, and S. Nunes, "Engineering membranes with macrocycles for precise molecular separations," Journal of Materials Chemistry A, vol.9, pp. 18102-18128, 2021, doi: https://doi.org/10.1039/D1TA02982G.

[50] G. Juby, A. Zacheis, W. Shih, P. Ravishanker, B. Mortazavi, and M. Nusser, "Evaluation and selection of available processes for a zero-liquid discharge system for the Perris, California," *Ground Water Basin*, 2008, https://www.usbr.gov/ research/ dwpr/ reportpdfs/ report149.pdf (accessed Feb. 1, 2022).

[51] M. Wang, A. Lawal, P. Stephenson, J. Sidders, and C. Ramshaw, "Post-combustion CO_2 capture with chemical absorption: A state-of-the-art review," *Chemical engineering research and design*, vol. 89, no. 9, pp. 1609-1624, 2011.

[52] M. Petersková, C. Valderrama, O. Gibert, and J. L. Cortina, "Extraction of valuable metal ions (Cs, Rb, Li, U) from reverse osmosis concentrate using selective sorbents," *Desalination*, vol. 286, pp. 316-323, 2012.

[53] M. H. El-Naas, "Reject brine management," *Desalination, trends and technologies*, pp. 237-252, 2011.

[54] N. Dave, T. Do, G. Puxty, R. Rowland, P. Feron, and M. Attalla, "CO_2 capture by aqueous amines and aqueous ammonia–A Comparison," *Energy Procedia*, vol. 1, no. 1, pp. 949-954, 2009.

[55] A. Dindi, D. V. Quang, N. El Hadri, A. Rayer, A. Abdulkadir, and M. R. Abu-Zahra, "Potential for the simultaneous capture and utilization of CO_2 using desalination reject brine: amine solvent selection and evaluation," *Energy Procedia*, vol. 63, pp. 7947-7953, 2014.

[56] D. Kang, Y. Yoo, and J. Park, "Accelerated chemical conversion of metal cations dissolved in seawater-based reject brine solution for desalination and CO_2 utilization," *Desalination*, vol. 473, 2020, doi: https://doi.org/10.1016/j.desal.2019.114147.

[57] R. R. Luna, "Process for producing sodium bicarbonate from natural soda salts," ed: Google Patents, 1994.

[58] E.-N. Muftah, "Process for capture of carbon dioxide and desalination," ed: Google Patents, 2018.

[59] N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*. Elsevier, 2012.

[60] S. Palitsakun, A. Seubsai, and K. Sudsakorn, "CO_2 capture in the form of thermally stable solid compounds using ammoniated brine," *Songklanakarin Journal of Science & Technology*, vol. 41, no. 5, pp. 984-991, 2019.

[61] R. Hoffman and A. Follows, "Method of producing sodium carbonate and bicarbonate spherules from brine," ed: Google Patents, 1974.

[62] J. P. Detournay and F. Coustry, "Process for producing sodium bicarbonate for flue gas desulphurization," ed: Google Patents, 2012.

[63] J.L. Galvez-Martos, A. Elhoweris, J. Morrison, and Y. Al-horr, "Conceptual design of a CO_2 capture and utilisation process based on calcium and magnesium rich brines," *Journal of CO_2 Utilization,* vol. 27, pp. 161-169, 2018.

[64] P. de Carvalho Pinto, T. Da Silva, F. Linhares, F. De Andrade, M. de Oliveira Carvalho, and G. De Lima, "A integrated route for CO_2 capture in the steel industry and its conversion into $CaCO_3$ using fundamentals of Solvay process," *Clean Technologies and Environmental Policy,* vol. 18, no. 4, pp. 1123-1139, 2016.

[65] C. De Vito, V. Ferrini, S. Mignardi, M. Cagnetti, and F. Leccese, "Progress in carbon dioxide sequestration via carbonation of aqueous saline wastes," *Periodico di Mineralogia,* vol. 81, no. 3, pp. 333-344, 2012.

[66] V. Ferrini, C. De Vito, and S. Mignardi, "Synthesis of nesquehonite by reaction of gaseous CO_2 with Mg chloride solution: Its potential role in the sequestration of carbon dioxide," *Journal of hazardous materials,* vol. 168, no. 2-3, pp. 832-837, 2009.

[67] T. Sema *et al.*, "Comprehensive mass transfer and reaction kinetics studies of CO_2 absorption into aqueous solutions of blended MDEA–MEA," *Chemical engineering journal,* vol. 209, pp. 501-512, 2012.

[68] X. Luo, A. Hartono, and H. F. Svendsen, "Comparative kinetics of carbon dioxide absorption in unloaded aqueous monoethanolamine solutions using wetted wall and string of discs columns," *Chemical engineering science,* vol. 82, pp. 31-43, 2012.

[69] G. Puxty, R. Rowland, and M. Attalla, "Comparison of the rate of CO_2 absorption into aqueous ammonia and monoethanolamine," *Chemical Engineering Science,* vol. 65, no. 2, pp. 915-922, 2010.

[70] M. S. P. Danckwerts, "The absorption of CO_2 into solutions of alkalis and amines, with some notes on hydrogen Sulphide and carbonyl Sulphide," *Institution of Chemical Engineers,* pp. 176-178, 1966.

[71] H. Abdel-Aal, A. Ibrahim, M. Shalabi, and D. Al-Harbi, "Chemical separation process for highly saline water. 2. System analysis and modeling," *Industrial & engineering chemistry research,* vol. 35, no. 3, pp. 805-810, 1996.

[72] N. El Hadri, D. V. Quang, E. L. Goetheer, and M. R. A. Zahra, "Aqueous amine solution characterization for post-combustion CO_2 capture process," *Applied Energy,* vol. 185, pp. 1433-1449, 2017.

[73] A. Dindi, D. V. Quang, I. AlNashef, and M. R. Abu-Zahra, "A process for combined CO_2 utilization and treatment of desalination reject brine," *Desalination,* vol. 442, pp. 62-74, 2018.

[74] N. Zhang, R. M. Santos, S. M. Smith, and L. Šiller, "Acceleration of CO_2 mineralisation of alkaline brines with nickel nanoparticles catalysts in continuous tubular reactor," *Chemical Engineering Journal*, vol.377, 2018, doi: 10.1016/j.cej.2018.11.177.

[75] J. H. Bang, Y. Yoo, S. W. Lee, K. Song, and S. Chae, "CO_2 mineralization using brine discharged from a seawater desalination plant," *Minerals,* vol. 7, no. 11, 2017, doi: https://doi.org/ 10.3390/ min7110207.

[76] J. G. Shim, D. W. Lee, J. H. Lee, and N. S. Kwak, "Experimental study on capture of carbon dioxide and production of sodium bicarbonate from sodium hydroxide," *Environmental engineering research,* vol. 21, no. 3, pp. 297-303, 2016.

[77] M. H. Ibrahim, M. H. El-Naas, R. Zevenhoven, and S. A. Al-Sobhi, "Enhanced CO_2 capture through reaction with steel-making dust in high salinity water," *International Journal of Greenhouse Gas Control,* vol. 91, 2019, doi: 10.1016/j.ijggc.2019.102819.

[78] M. A. Osman, M.H. El-Naas, and S. Al-Zuhair, "Electrocoagulation treatment of reject brine effluent from Solvay process," *Desalination and Water Treatment,* vol. 163, pp. 325-335, 2019.

[79] A. Pérez-González, R. Ibáñez, P. Gómez, A. Urtiaga, I. Ortiz, and J. Irabien, "Recovery of desalination brines: separation of calcium, magnesium and sulfate as a pre-treatment step," *Desalination and Water Treatment*, vol. 56, no. 13, pp. 3617-3625, 2015.

[80] R. Y. Ning, A. Tarquin, M. Trzcinski, and G. Patwardhan, "Recovery optimization of RO concentrate from desert wells," *Desalination,* vol. 201, no. 1-3, pp. 315-322, 2006.

[81] A. Rahardianto, B. C. McCool, and Y. Cohen, "Accelerated desupersaturation of reverse osmosis concentrate by chemically-enhanced seeded precipitation," *Desalination,* vol. 264, no. 3, pp. 256-267, 2010.

[82] M. Badruzzaman, J. Oppenheimer, S. Adham, and M. Kumar, "Innovative beneficial reuse of reverse osmosis concentrate using bipolar membrane electrodialysis and electrochlorination processes," *Journal of Membrane Science,* vol. 326, no. 2, pp. 392-399, 2009.

[83] N. Melián-Martel, J. Sadhwani, and S. O. P. Báez, "Saline waste disposal reuse for desalination plants for the chlor-alkali industry: The particular case of pozo izquierdo SWRO desalination plant," *Desalination,* vol. 281, pp. 35-41, 2011.

[84] A. Rahardianto, J. Gao, C. J. Gabelich, M. D. Williams, and Y. Cohen, "High recovery membrane desalting of low-salinity brackish water: Integration of accelerated precipitation softening with membrane RO," *Journal of Membrane Science,* vol. 289, no. 1-2, pp. 123-137, 2007.

[85] A. Bandi, M. Specht, T. Weimer, and K. Schaber, "CO_2 recycling for hydrogen storage and transportation—electrochemical CO_2 removal and fixation," *Energy conversion and management,* vol. 36, no. 6-9, pp. 899-902, 1995.

[86] Z. Lendzion-Bieluń *et al.*, "Surface characteristics of KOH-treated commercial carbons applied for CO_2 adsorption," *Adsorption Science & Technology,* vol. 36, no. 1-2, pp. 478-492, 2018.

[87] D. W. Keith, G. Holmes, D. S. Angelo, and K. Heidel, "A process for capturing CO_2 from the atmosphere," *Joule,* vol. 2, no. 8, pp. 1573-1594, 2018.

[88] L. Lombardia, A. Corti, E. Carnevale, R. Baciocchi, and D. Zingaretti, "Carbon dioxide removal and capture for landfill gas up-grading," *Energy Procedia,* vol. 4, pp. 465-472, 2011.

[89] N. K. Mohammad, A. Ghaemi, and K. Tahvildari, "Hydroxide modified activated alumina as an adsorbent for CO_2 adsorption: experimental and modeling," *International Journal of Greenhouse Gas Control,* vol. 88, pp. 24-37, 2019.

[90] E. N. Muftah, "System for contacting gases and liquids," ed: Google Patents, 2017.

[91] M. H. El-Naas, A. F. Mohammad, M. I. Suleiman, M. Al Musharfy, and A. H. Al-Marzouqi, "Evaluation of a novel gas-liquid contactor/reactor system for natural gas applications," *Journal of Natural Gas Science and Engineering,* vol. 39, pp. 133-142, 2017.

[92] M. Altarawneh and B. Z. Dlugogorski, "Introducing quantum chemistry in chemical engineering curriculum," *Journal of Chemical Education,* vol. 95, no. 9, pp. 1562-1571, 2018.

[93] M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, and J. Cheeseman, "Gaussian 16. Wallingford: Gaussian," ed: Inc, 2016, https://gaussian.com/citation/ (accessed Feb. 6, 2022).

[94] J. A. Montgomery Jr, M. J. Frisch, J. W. Ochterski, and G. A. Petersson, "A complete basis set model chemistry. VII. Use of the minimum population localization method," *The Journal of Chemical Physics,* vol. 112, no. 15, pp. 6532-6542, 2000.

[95] V. Mokrushin, V. Bedanov, W. Tsang, M. Zachariah, V. Knyazev, and V. ChemRate, "1.19," *NIST: Gaithersburg, MD,* 2002.

[96] R. H. Myers, D. C. Montgomery, and C. Anderson-Cook, "Process and product optimization using designed experiments," *Response surface methodology,* vol. 2, pp. 328-335, 2002.

[97] T. Ölmez, "The optimization of Cr (VI) reduction and removal by electrocoagulation using response surface methodology," *Journal of Hazardous Materials,* vol. 162, no. 2-3, pp. 1371-1378, 2009.

[98] B. K. Körbahti and M. Rauf, "Application of response surface analysis to the photolytic degradation of Basic Red 2 dye," *Chemical Engineering Journal,* vol. 138, no. 1-3, pp. 166-171, 2008.

[99] K. Y. Kim and J. W. Seo, "Shape optimization of a mixing vane in subchannel of nuclear reactor," *Journal of Nuclear Science and Technology,* vol. 41, no. 5, pp. 641-644, 2004.

[100] J. Antony, *Design of experiments for engineers and scientists*. Elsevier, 2014.

[101] Aya. A-H. Mourad, N. M. Ghasem, and A. Y. Alraeesi, "Modelling and simulation of hydrogen production via water gas shift membrane reactor," *Int. J. Chem. Eng. Appl,* vol. 9, no. 4, 2018, doi: 10.18178/ijcea.2018.9.4.709.

[102] A. Mohammad *et al.*, "CFD and statistical approach to optimize the average air velocity and air volume fraction in an inert-particles spouted-bed reactor (IPSBR) system," *Heliyon,* vol. 7, no. 3, 2021, doi: https://doi.org/10.1016/j.heliyon.2021.e06369.

[103] A. H. I. M. Aya, A. F. Mohammad, A. H. Al-Marzouqi, M. H. El-Naas, M. H. Al-Marzouqi, and M. Altarawneh, "CO_2 capture and ions removal through reaction with potassium hydroxide in desalination reject brine: Statistical optimization," *Chemical Engineering and Processing-Process Intensification,* vol. 170, 2022, doi: 10.1016/j.cep.2021.108722.

[104] Aya. A-H. Mourad, A. F. Mohammad, A. H. Al-Marzouqi, M. H. El-Naas, M. H. Al-Marzouqi, and M. Altarawneh, "KOH-Based Modified Solvay Process for Removing Na Ions from High Salinity Reject Brine at High Temperatures," *Sustainability,* vol. 13, no. 18, 2021, doi: https://doi.org/10.3390/su131810200.

[105] J. Lefebvre, M. Götz, S. Bajohr, R. Reimert, and T. Kolb, "Improvement of three-phase methanation reactor performance for steady-state and transient operation," *Fuel processing technology,* vol. 132, pp. 83-90, 2015.

[106] A. Virgilio, D. Schiavo, J. A. Nóbrega, and G. L. Donati, "Evaluation of standard dilution analysis (SDA) of beverages and foodstuffs by ICP OES," *Journal of Analytical Atomic Spectrometry,* vol. 31, no. 6, pp. 1216-1222, 2016.

[107] M. M. Hluchy, "The value of teaching X-ray techniques and clay mineralogy to undergraduates," *Journal of Geoscience Education,* vol. 47, no. 3, pp. 236-240, 1999.

[108] M. Database. http://www.webmineral.com/ (accessed Feb. 3, 2021).

[109] A. F. Mohammad *et al.*, "Computational fluid dynamics simulation of an Inert Particles Spouted Bed Reactor (IPSBR) system," *International Journal of Chemical Reactor Engineering,* vol. 18, no. 5-6, 2020, doi: https://doi.org/10.1515/ijcre-2020-0025.

[110] A. F. Mohammad *et al.*, "Comprehensive Optimization of the Dispersion of Mixing Particles in an Inert-Particle Spouted-Bed Reactor (IPSBR) System," *Processes,* vol. 9, no. 11, 2021, doi: https://doi.org/10.3390/pr9111921.

[111] H. S. Fogler, *Elements of Chemical Reaction Engineering* (Prentice Hall International Series in the Physical and Chemi). Pearson Education, 2016.

[112] B. Liptak, "Process control and optimization. Instrument engineers' handbook. Chapter 6 Control valve selection and sizing, vol. 2," ed: CRC Press, 2005.

[113] P.C. Chen, "Absorption of carbon dioxide in a bubble-column scrubber," in *Greenhouse Gases-Capturing, Utilization and Reduction*: InTech, 2012, pp. 95-112.

[114] What is new. http://webmineral.com/whatsnew.shtml#.YqjjhnZBw 2x (accessed November, 2019).

[115] L. C. Curlin, T. V. Bommaraju, and C. B. Hansson, "Alkali and chlorine products, chlorine and sodium hydroxide," *Kirk-Othmer Encyclopedia of Chemical Technology*, 2000, doi: 10. 1002/ 047123 8961. 0308121503211812. a01.

[116] Y. L. Gao and X. R. Ju, "Statistical prediction of effects of food composition on reduction of Bacillus subtilis As 1.1731 spores suspended in food matrices treated with high pressure," *Journal of food engineering,* vol. 82, no. 1, pp. 68-76, 2007.

[117] H. Zhao and H. R. Hu, "Optimal design of a pipe isolation plugging tool using a computational fluid dynamics simulation with response surface methodology and a modified genetic algorithm," *Advances in Mechanical Engineering,* vol. 9, no. 10, 2017, doi: 10.1177/ 1687814017715563.

[118] Y. h. Lee, D. w. Kim, S. i. Shin, and S. g. Oh, "Preparation of Au colloids by polyol process using $NaHCO_3$ as a buffering agent," *Materials chemistry and physics,* vol. 100, no. 1, pp. 85-91, 2006.

[119] J. A. Stewart, "Potassium sources, use, and potential," *Potassium in agriculture,* pp. 83-98, 1985.

[120] S. R. Smith, P. E. Klotman, and L. P. Svetkey, "Potassium chloride lowers blood pressure and causes natriuresis in older patients with hypertension," *Journal of the American Society of Nephrology,* vol. 2, no. 8, pp. 1302-1309, 1992.

[121] M. Mahmoudkhani and D. W. Keith, "Low-energy sodium hydroxide recovery for CO2 capture from atmospheric air—Thermodynamic analysis," *International Journal of Greenhouse Gas Control,* vol. 3, no. 4, pp. 376-384, 2009.

[122] P. Feron, *Absorption-based post-combustion capture of carbon dioxide*. Woodhead publishing, 2016.

[123] F. K. Ayittey, C. A. Obek, A. Saptoro, K. Perumal, and M. K. Wong, "Process modifications for a hot potassium carbonate-based CO_2 capture system: a comparative study," *Greenhouse Gases: Science and Technology*, vol. 10, no. 1, pp. 130-146, 2020.

[124] A. Roine, "HSC-software Ver. 3.0 for thermodynamic calculations," in *Proceedings of the International Symposium on Computer Software in Chemical and Extractive Metallurgy*, 1989: Elsevier, pp. 15-29.

[125] D. C. Engel, G. F. Versteeg, and W. P. van Swaaij, "Solubility of hydrogen in aqueous solutions of sodium and potassium bicarbonate from 293 to 333 K," *Journal of Chemical & Engineering Data*, vol. 41, no. 3, pp. 546-550, 1996.

[126] B. G. Liptak, *Instrument Engineers' Handbook, Fourth Edition, Volume Two: Process Control and Optimization* (Instrument Engineers' Handbook). CRC Press, 2005.

[127] E. Serafimova, M. Mladenov, I. Mihailova, and Y. Pelovski, "Study on the characteristics of waste wood ash," *Journal of the University of Chemical Technology and Metallurgy*, vol. 46, no. 1, pp. 31-34, 2011.

[128] A. F. R. Mohammad, "Multi Stage Modified Solvay Process for CO_2 Capture and Reject Brine Desalination," 2021, https:// limo.libis.be/ primo-explore/ fulldisplay? docid= LIRIAS3637696 & context= L&vid= Lirias & search_scope= Lirias&tab= default_tab & fromSitemap= 1 (accessed Feb. 7, 2022).

[129] A. F. Mohammad *et al.*, "Effective and sustainable adsorbent materials for oil spill cleanup based on a multistage desalination process," *Journal of Environmental Management*, vol. 299, 2021, doi: https://doi.org/10.1016/j.jenvman.2021.113652.

List of Other Publications

(ORCID ID: 0000-0002-2706-1386)

Mustafa, J., Aya A-H. Mourad, Al-Marzouqi, A. H., El-Naas, M. H. (2020). Simultaneous treatment of reject brine and capture of carbon dioxide: A comprehensive review. *Desalination*, *483*, 114386. https://doi.org/10.1016/j.desal.2020.114386

Mohammad, A. F., Aya A-H. Mourad**,** Galiwango, E., Lwisa, E. G., Al-Marzouqi, A. H., El-Naas, M. H., Van der Bruggen, B. Al-Marzouqi, M. H. (2021). Effective and sustainable adsorbent materials for oil spill cleanup based on a multistage desalination process. Journal of Environmental Management, 299, 113652. https://doi.org/10.1016/j.jenvman.2021.113652

Mohammad, A. F., Aya A-H. Mourad, Mustafa, J., Al-Marzouqi, A. H., El-Naas, M. H., Al-Marzouqi, M. H., Van der Bruggen, B. Al Musharfy, M. (2021). A CFD Investigation on the Effect of IPSBR Operational Conditions on Liquid Phase Hydrodynamics. 2021: IEEE, pp. 153-157, https://doi: 10.1109/ICREGA50506.2021.9388292.

Mohammad, A., Aya A-H. Mourad, Al-Marzouqi, A. H., El-Naas, M. H., Van der Bruggen, B., Al-Marzouqi, M.H., Alnaimat, F., Suleiman, M., Al Musharfy, M. (2021). CFD and statistical approach to optimize the average air velocity and air volume fraction in an inert-particles spouted-bed reactor (IPSBR) system. Heliyon, 7(3), e06369. https://doi.org/https://doi.org/10.1016/j.heliyon.2021.e06369.

Mohammad, Ameera F., Aya A-H. Mourad, Mustafa, J., Al-Marzouqi, A. H., El-Naas, M. H., Al-Marzouqi, M.H., Alnaimat, F., Suleiman, M. I., Al Musharfy, M., Firmansyah, T. "Computational fluid dynamics simulation of an Inert Particles Spouted Bed Reactor (IPSBR) system" International Journal of Chemical Reactor Engineering, vol. 18, no. 5-6, 2020, pp. 20200025. https://doi.org/10.1515/ijcre-2020-0025.

Mohammad, A. F., Aya A-H. Mourad, Al-Marzouqi, A. H., El-Naas, M. H., Bruggen, B. V. D., Al-Marzouqi, M. H., Alnaimat, F., Al Musharfy, M. (2021). Comprehensive Optimization of the Dispersion of Mixing Particles in an Inert-Particle Spouted-Bed Reactor (IPSBR) System. *Processes*, *9*(11), 1921. https://doi.org/10.3390/pr9111921.

Mustafa, J., Mohammad, A. F., Aya A-H. Mourad, Al-Marzouqi, A. H., El-Naas, M. H. (2021). Treatment of saline wastewater and carbon dioxide capture using electrodialysis. In *2021 6th International Conference on Renewable Energy: Generation and Applications (ICREGA)* (pp. 158-162). IEEE. https://doi.org/10.1109/ICREGA50506.2021.9388277

UAE UNIVERSITY DOCTORATE DISSERTATION NO. 2022:5

While desalination of seawater is important for meeting the water demand, the technology produces large volumes of reject brine (high salinity water) and CO_2, causing environmental pollution. Solvay and modified Solvay processes 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 removal efficiency, which does not exceed 35%. The aim of this work is to introduce an alternative alkaline, namely KOH and investigate its ability to overcome these limitations for a further improvement in the productivity of the process.

Aya Abdel-Hamid Mourad received her PhD from the Department of Chemical and Petroleum Engineering at UAE University, UAE. She received her MSc from the Department of Chemical and Petroleum Engineering at UAE University, UAE.

www.uaeu.ac.ae