Effects of potassium hydroxide and aluminum oxide on the performance of a modified solvay process for CO₂ capture: A comparative study

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Summary

In a previous work, the overall performance of modified Solvay process was investigated in the absence of ammonia, where carbon dioxide and brine treatments were accomplished in a single reaction and in the presence of calcium hydroxide (Ca(OH)₂). In this study, the impact of alkaline and amphoteric oxides, namely potassium hydroxide (KOH) and aluminum oxide (Al₂O₃), on the pH level, CO₂ capture capacity, ions reduction, and type of produced solids was investigated at a temperature of 20°C and a gas flow rate of 1 L/min. At the stoichiometric ratio and less than the solubility limit, the KOH/brine mixture achieved a CO₂ uptake of 0.31 g CO₂/g KOH. In comparison, about 0.92 g of CO₂ was captured by 1 g of CaO when CaO was added to the brine in an amount that was more than the solubility limit but less than the stoichiometric ratio. Moreover, the percentage of the ions reduction for the KOH and CaO was almost the same except for the sulfate ions, as the best removal was for the CaO. The poorest CO₂ capture and ions removal occurred with the Al₂O₃. X-ray diffraction was used to identify most of the solid products, and the obtained results proved that KOH is a promising alkaline for the combined process. In addition, potassium chloride crystals were produced when KOH was utilized, which is a very valuable product, and it can also be easily separated. Although Al₂O₃ showed no reactivity, it revealed good results in terms of magnesium ions recovery and could be considered as a coagulant for recovering magnesium ions in the reject brine solution.

KEYWORDS

alkaline, aluminum oxide, ammonia, brine, CO₂ capture, DFT, potassium chloride, potassium hydroxide
1 INTRODUCTION

The traditional Solvay process is based on using ammonia (NH₃) to form sodium bicarbonate (NaHCO₃) through the reaction of carbon dioxide (CO₂) with sodium chloride according to Reaction (1), producing soluble ammonium chloride (NH₄Cl) and insoluble sodium bicarbonate (NaHCO₃).¹ ² In order to recover NH₃, Ca(OH)₂ is mixed with NH₄Cl according to Reaction (2), which contributes additional costs to the overall process.³ In a modified Solvay process, El-Naas⁴ replaced ammonia with calcium oxide (CaO), which provided better results with respect to pH value, CO₂ capture, and ions reduction.⁴ In addition, many other useful products were produced such as soluble calcium chloride (CaCl₂) and a precipitate of NaHCO₃ (Reaction 3).

\[
\text{NaCl} + \text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{NaHCO}_3 + \text{NH}_4\text{Cl} \quad (1) \\
2\text{NH}_4\text{Cl} + \text{Ca(OH)}_2 \rightarrow \text{CaCl}_2 + 2\text{NH}_3 + 2\text{H}_2\text{O} \quad (2) \\
2\text{NaCl} + 2\text{CO}_2 + \text{Ca(OH)}_2 \rightarrow 2\text{NaHCO}_3 + \text{CaCl}_2 \quad (3)
\]

El-Naas⁴ optimized the modified Solvay process for the capture of CO₂ and desalination of reject brine.³ At a temperature of 20°C, a pressure of 1 atm, a gas flow rate of 1 L/min, and a CaO concentration of 20 g/L, the CO₂ capture efficiency and sodium (Na) reduction reached up to 99% and 35%, respectively.³ Several studies have explored the effect of pH on CO₂ capture and salt removal.³ ⁵ ⁶ ⁹ Various alkaline oxides were previously used to adjust the pH of chemical processes.

Potassium hydroxide (KOH) has strong CO₂-binding affinities and has been reported to be effective for capturing CO₂ from ambient air.¹⁰ Bandi et al¹¹ investigated the absorption of CO₂ by adding KOH inside a packed column with a total height of 2 m. It was concluded that the CO₂ absorption from ambient air was around 70%. Lendzion-Bieluń et al¹² investigated the effect of KOH treatment on the surface properties of activated commercial carbon to improve the adsorption capacity of CO₂. They reported an increase in the concentration of hydroxyl groups on the surface, which led to an increase in the uptake value of CO₂ by 14% at 0°C. In another study performed by Keith et al,¹³ aqueous KOH solution was combined with calcium caustic recovery loop to capture about 1Mt-CO₂/year from ambient air in an industrial plant. The detailed engineering and cost analysis were studied. It was reported that the levelized cost was about 94 to 232 $/t-CO₂ captured from the atmosphere. Lombardia et al¹⁴ studied the effects of capturing CO₂ 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 K₂CO₃. However, potassium bicarbonate (undesired) was obtained by adding extra amounts of CO₂. About 98% of CO₂ 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 al¹⁵ analyzed the effect of modified activated alumina with sodium hydroxide (NaOH) and KOH on the CO₂ adsorption efficiency. By using 2.0 g of adsorbent, under optimum conditions (20°C and 6 bar), the results indicated that the highest CO₂ adsorption was 0.147 g/g for KOH (concentration of 30%) in comparison with 0.131 g/g for NaOH (concentration of 30%). Dindi et al¹⁶ studied the effective capture of CO₂ by utilizing the mixed-metal oxides of Mg-Al-layered double hydroxide, and it was reported that it had a good impact on the chloride ions removal (70%) and sodium elimination (20%). Moreover, the absorption of CO₂ was achieved, and it was about 0.082 g of CO₂ per g of carbonated solution. In another study conducted by Kameda et al,¹⁷ it was concluded that Mg-Al oxide displays a noticeable impact on removing chloride ions. Likewise, it was revealed that the efficiency of the Cl⁻ removal primarily depends on the type of cations in the solution and the amount of deployed mixed oxides.

The bauxite residue is simply considered as waste, and it is mainly produced in aluminum industries. It consists of a mixture of many oxides. Therefore, it has high alkalinity, which results in a negative impact on the environment. Hence, many studies were conducted to manage such residues in order to reuse them in other beneficial applications.¹⁸ Dilmore et al¹⁹ examined the sequestration of CO₂ in the presence of bauxite residues and brine obtained from an oil field. More than 9.5 g CO₂/L of bauxite residues and brine mixture was sequestered, and the volume ratio of the bauxite residue to brine was 90 to 10 at 20°C and 0.689 MPa. The majority of the products were dawsonite as well as calcite. Dilmore et al²⁰ successfully sequestered a considerable quantity of CO₂ from oil-field brine and different alkaline materials (eg, bauxite residues). The maximum CO₂ sequestration capacity was observed when flue gas desulfurization spray dryer ash was utilized, as it contains a great amount of Ca(OH)₂. Although bauxites showed an intermediate CO₂ sequestration ability, Soong et al²¹ integrated bauxite residues and brine waste to examine their effect on capturing CO₂ (6.6 g) and removing sulfur oxide (SO₂). The results indicated that more than 99.9% of the SO₂ and CO₂ was sequestered at a temperature of 140°C, a bauxite residue to brine mixture ratio of 80:20 v/v, and a pressure of 3.85 MPa. The capturing of CO₂ via red mud waste (high alkaline material) was also studied by
Jones et al., and it was found that around 15 000 000 t of CO2 could be removed through such wastes, which are located near industrial aluminum zones in Australia. However, it was stated that further investigation is still needed to enhance the capturing of CO2. In a recent study, Ibrahim et al. examined the use of steel-making Bag House Dust (BHD) as a potential source of CaO in the modified Solvay process. An optimum CO2 uptake of 0.22 g CO2/g BHD was obtained under a temperature of 24°C and pressure of 1 atm. In another study conducted by Moioli et al., potassium taurate was used as an absorbent for CO2 removal and confirmed that this absorbent has less energy consumption comparing to the traditional amine aqueous solutions. The energy was reduced from 4.4 MJ/kg CO2 to 2.4 MJ/kg CO2.

The aim of this work is to compare the effectiveness of other alkaline and amphoteric oxides, namely KOH and Al2O3, respectively, with that of CaO in terms of pH, CO2 capture, and ions reduction. The reaction productions (NaHCO3, CaCl2, and potassium chloride (KCl)) have many applications in diverse industrial fields. NaHCO3 can be used as a pH buffering agent, CaCl2 can be utilized as a growth enhancer for different types of plants. Moreover, KCl is used in the production of crop fertilizers and has some other medical applications. Along the same line of enquiry, the current study sets out to present underpinning thermochemical parameters for the overall reactions accomplished using quantum chemical calculations based on the optimized structures for all the species.

2 | UTILIZATION OF DIFFERENT ALKALINE AND METAL OXIDE IN THE MODIFIED SOLVAY PROCESS

In a previous study conducted by El-Naas et al., CO2 was reacted with concentrated brine in the presence of Ca(OH)2 according to Reaction (3). It is important to note that Ca(OH)2 is directly produced once calcium oxide is added to the brine. This method was then extended to other alkaline solutions. In the current study, CO2 was contacted with brine in the presence of KOH and Al2O3. The corresponding reactions are shown by Equations (4) and (5), respectively. It is worth mentioning that CaO and Ca(OH)2 are also available as waste products that can be utilized and neutralized through the modified Solvay process. On the other hand, KOH is considered to be as a by-product of the manufacturing of hydrochloric acid (HCl) and chlorine. In addition, most of the obtained wastes from water management processes and bauxite industries contain significant amounts of aluminum/iron oxides. Therefore, potassium and aluminum oxides were utilized in this study to investigate their impact on the modified Solvay process.

$$\text{NaCl} + \text{CO}_2 + \text{KOH} \rightarrow \text{NaHCO}_3 + \text{KCl} \quad (4)$$

$$6\text{NaCl} + 6\text{CO}_2 + \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 6\text{NaHCO}_3 + 2\text{AlCl}_3 \quad (5)$$

3 | COMPUTATIONAL THERMODYNAMIC PROPERTIES

In this study, thermodynamic properties were obtained using quantum chemical calculations. Gaussian16W software was utilized using the CBS-QB3 composite method. The latter initially executes all the geometry optimizations and frequency calculations for all illustrated reactants and products in reactions (3), (4), and (5) 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. Figure 1 reveals the optimized structures for the reactants and products of the above-mentioned reactions.

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 ($\Delta G$) and enthalpy ($\Delta H$) for reactions (3) to (5) as a function of the temperature were determined. Thermochemical computations were carried out using ChemRate code.\(^3\)\(^5\) Figures 2A,B illustrate the changes in $\Delta G$ and $\Delta H$ with the temperature, respectively, for the three reactions.

Figure 2A portrays that the Solvay process is not spontaneous with Al$_2$O$_3$ in comparison with the other alkaline solids, because of the positive $\Delta G$ over the whole temperature range (0°C-100°C). It is also important to note that using KOH in the modified Solvay reaction renders it more spontaneous (more negative $\Delta G$) than when using Ca(OH)$_2$ at all the temperatures. The derived free energy for Reaction (3) and the previously obtained values by El-Naas et al\(^3\) through HSC Chemistry 6.1 software are $-61.3$ and $-56$ kJ/mol, respectively, at 20°C. Both considered reactions based on Ca(OH)$_2$ and KOH are exothermic, as demonstrated in Figure 2B. However, using Al$_2$O$_3$ led to a positive value of $\Delta H$ (endothermic). Inspection of enthalpy trends in Figure 2B demonstrates a temperature-independent profile for the three reactions. Entropic contribution gradually increases the computed Gibbs free energy values in Figure 2A. Nonetheless, the non-spontaneous nature of Reaction (5) remains unchanged with temperature.

4 | EXPERIMENTAL METHOD

Descriptions of the used brine and alkaline/metal oxide samples, experimental procedures, and analytical techniques in the investigation of the CO$_2$ capture and ions removal are presented in the following sections.

4.1 | Brine and alkaline/metal oxide samples

A brine sample with a mean salinity (based on sodium chloride) of 73, 540 mg/L and a pH value of 8.36 was collected from a multistage flash desalination unit in a local desalination plant. There were six main ions in the brine samples: sodium (Na$^+$), magnesium (Mg$^{2+}$), calcium (Ca$^{2+}$), potassium (K$^+$), chloride (Cl$^-$), and sulfate (SO$_{4}^{2-}$), and they have average concentrations of 24 280, 2856, 1482, 905, 37 582, and 6051 ppm, respectively. The used CaO, KOH, and Al$_2$O$_3$ were obtained from Scientific Progress Medical and Scientific Equipment Company, UAE. CaO and Al$_2$O$_3$ have a same purity of 99.9%, while KOH has a purity between 85% and 100%. In addition, the particle size of CaO and Al$_2$O$_3$ is <1.0-μm APS powder, and KOH has a particle size between 5 and 7 mm. The used gas contained 10% CO$_2$ and 90% air, and it was purchased from the Abu Dhabi Oxygen Company. All the above-mentioned companies/plants are located in the UAE.

4.2 | Experimental procedures

Figure 3 shows a schematic diagram of the reactor. More details about the experimental apparatus can be found in previous studies.\(^3\),\(^4\),\(^36\),\(^37\) The system operated under a semi-batch mode, where the reactor was charged with 1000 mL of a premixed solution consisting of reject brine
and alkaline/metal oxide solutions (KOH/Al2O3). A magnetic stirrer was used to ensure a uniform distribution of alkaline/metal oxides in the reject brine. Then, the liquid was subjected to a continuous flow of bubbled gas until saturation. For comparison purposes, the reactor was operated under the same optimized conditions that were previously reported by El-Naas et al., where the CaO was investigated. The reactor was maintained at a temperature of 20°C through the reactor jacket, and the gas flow rate was controlled at 1 L/min. Solution samples were collected every 15 minutes, and the pH for each sample was measured through a digital pH meter. After the end of the experimental run, the solid was separated from the liquid and dried. Different analytical techniques were utilized to determine and identify the contents of all the samples. Moreover, a CO2 gas analyzer was employed to observe the amount of the removed CO2 from the effluent gas.

4.3 Analytical methods

The brine solution was collected and filtrated from the solids at the end of each experiment to determine its metal concentrations (Ca2+, Na+, K+, Mg2+) using inductively coupled plasma (ICP) spectrometry (Varian 710-ES ICP optical emission spectrometer). The analysis of the chloride ions (Cl−) was performed using a HACH HQ40D portable multimeter equipped with a chloride ion selective electrode (HACH Intellectual ISECL181). To enhance the reading accuracy, chloride ionic strength adjustment buffer powder pillows were utilized. Moreover, the sulfate (SO4−2) analysis was carried out using a HACH spectrophotometer (HACH-Lange DR5000). In all runs, appropriate dilution with high concentration was performed for the samples. In addition, standard solutions were utilized for the calibration of all instruments.

After filtration, all solid products were dried at 110°C in an oven for 2 days. Then, the dried solids were identified using a powder X-ray diffractometer (XRD). In order to determine the surface morphology, texture, and shape of the produced solids, a scanning electron microscope (SEM) was employed at three different areas. The sample was coated with a thin gold film prior to conducting the SEM analysis. The average energy dispersive spectra (EDS) analysis was then performed to detect the main elements in the sample.

5 RESULTS AND DISCUSSION

5.1 Impact of the alkaline/metal oxide amount on the initial pH value

From previous research works, it was concluded that the impact of pH on the CO2 capture capacity and ions reduction from the brine is rather significant. In addition,
it was reported that the ultimate pH range for this process is from 10 to 12. The high pH value plays a significant role, as it enhances the solubility of CO$_2$ and increases the precipitation of valuable solid products. Figure 4 demonstrates the investigation of the KOH, CaO, and Al$_2$O$_3$ concentrations effect on the brine solution pH before it reacts with CO$_2$, respectively. The addition of KOH significantly increased the pH until it remained constant at a value of approximately 13.6 at a concentration of 35 g/L. It is also worth mentioning that based on the stoichiometric ratio for KOH (Reaction 4), 70.57 g/L should be utilized (1 KOH:1 NaCl), 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. Therefore, the KOH influence was examined based on a value which is less than the stoichiometric amount at an intermediate value of 30 g/L at which the pH was still maintained at a value of 13. The results are depicted in Section 5.4. There was no remarkable difference between the mass addition and pH change when Al$_2$O$_3$ was added. Therefore, it was decided to run the experiment at a stoichiometric mass of 21.4 g/L of Al$_2$O$_3$ (1 Al$_2$O$_3$:6 NaCl). Figure 4 reveals that adding more calcium oxides remarkably enhanced the pH of the solution until it remained the same. The maximum pH value was reached at 4.00 g/L of added CaO. Based on the conducted optimization study by El-Naas et al., it was concluded that 20 g/L of CaO is the optimal amount at which the CO$_2$ capture and ions removal rates reach their optimum values. In summary, the results of the aforementioned analyses show that potassium and calcium hydroxides can maintain high pH values of more than 10 in comparison with Al$_2$O$_3$, where the pH value was not changed.

5.2 Impact of the alkaline/metal oxide amount on the temperature

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. It was also previously reported that the optimum temperature is 20°C in the case of utilizing Ca(OH)$_2$. Therefore, the effect of the different added amounts of alkaline/metal oxide on the solution (without CO$_2$) temperature was examined and depicted in Figure 5. It is also important to mention that the temperature was measured instantaneously. At first glance, temperature slightly increased when calcium and aluminum oxides were added. In contrast, when KOH was utilized, the temperature remarkably increased until a value of 46°C, after which the temperature remained constant. These results well agree with those reported in Section 5 (thermodynamics analysis), as they confirm that the KOH ensued in a highly exothermic reaction. The use of CaO resulted in an incremental increase in the temperature. However, adding different amounts of Al$_2$O$_3$ did not change the solution temperature. In order to maintain the system at the optimum temperature (20°C), as reported before by El-Naas et al., a water jacket was connected, as illustrated in Figure 4. It was also observed that the KOH

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**Figure 4** Impact of the alkaline/metal oxide mass on the pH of brine before carbonation for the added oxides [Colour figure can be viewed at wileyonlinelibrary.com]

**Figure 5** Brine temperature at different solid concentration (CaO, Al$_2$O$_3$, and KOH) [Colour figure can be viewed at wileyonlinelibrary.com]
entails very high solubility in comparison with the CaO. All the used quantities were dissolved in high quantities compared with CaO. However, Al2O3 was found to have no solubility in the reject brine among the three buffer solutions justifying its poor performance in CO2 capture.

5.3 Alkaline/metal oxide impact on the CO2 capture efficiency

El-Naas et al.3 investigated the CaO effect on the CO2 removal (Reaction 3) under the optimized temperature of 20°C, gas flowrate of 1 L/min, and 20 g of CaO/L. In this research, the CaO uptake was examined under the same conditions. It was concluded that the process reached a steady state after 525 minutes, where the CO2 uptake attained its maximum level. About 0.92 g of CO2 was captured per g of CaO added. It is very important to note that the added amount of CaO (20 g per liter of brine) is less than the stoichiometric quantity but exceeds the solubility limit. The stoichiometric amount depends on the molar ratio between reactants and products in the balanced equation, while solubility limits indicates the maximum amount of a substance that can be dissolved in the solvent. It was mentioned that an extra amount was added to maintain high pH level and reach high CO2 reduction and solid precipitation. In this study, the KOH buffer was tested (Reaction 4) under the same temperature, gas flowrate, and KOH amounts of 30 and 70.57 g/L, as shown in Figures 6 and 7. From the figures, it can be seen that saturation with CO2 was quickly reached (285 minutes) by adding 30 g/L of KOH compared with adding the stoichiometric amount of 70.57 g/L, which took around 330 minutes to reach full saturation. It was also concluded that the CO2 uptake was ~0.32 g CO2/g KOH when 30 g of KOH was tested. In addition, adding the stoichiometric amount of 70.57 g/L enabled to reach almost the same uptake of 0.31 g CO2/g KOH. The same uptake value (~0.3 g CO2/g KOH) at different stoichiometric ratios can be explained in terms of the capacity limit of KOH in absorbing specific mass of CO2 under same operating conditions.

It is important to note that the production of 1 mol of CaO from CaCO3 can produce 1 mol of CO2, as shown in Reaction (6).3 However, in the presence of sodium chloride as well as other ions in the brine and according to the modified Solvay process (Reaction (3)), Ca(OH)2 can capture 2 mol of CO2 which may affect the total amount of CO2 captured. The use of a solid waste as a source of Ca(OH)2, such as steel dust, can capture 0.22 g CO2/g BHD without contributing to the generation of CO2.23 KOH can be produced from the electrolysis of the KCl solution, as illustrated in Reaction (7)29 with no CO2 production, which is an advantage of using KOH.

\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \quad (6)
\]

\[
2\text{KCl} + 2\text{H}_2\text{O} \rightarrow 2\text{KOH} + \text{Cl}_2 + \text{H}_2 \quad (7)
\]

Moreover, the CO2 removal was examined using Al2O3, but there were no detected results regarding the capturing of CO2, so it is not recommended to use it in the combined process of the CO2 removal and brine treatment.
The moles of the CO$_2$ removal during a time interval were calculated using Equation (8):

$$\text{Moles of CO}_2 \text{ removal} = \frac{\int_0^t \text{volume of CO}_2 \text{ captured (L/min)} dt}{\text{Molar volume of CO}_2 \text{ (L/mol)}} \quad (8)$$

5.4 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. As mentioned above, more pH drives high CO$_2$ solubility and more precipitation of valuable solids. It is also important to note that the pH value can control the types of the formed products. 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 $6.5 < \text{pH} < 10.5$, respectively. 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. Therefore, CaCO$_3$ was observed when more CaO was added to the system, as this enhanced the pH value and made it more than 10. It is also worth mentioning that this value almost remained constant until the end of the reaction. In the current study, the effect of adding two different amounts of KOH is revealed in Figure 8. As an overall trend, the pH value for the 70.57 g/L (stoichiometric value) is higher than that of 30 g/L. In the case of 70.57 g/L, it can be observed that the maximum reached pH value was almost 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$_2$. However, the maximum value of the pH was almost 12.5 when less amount of KOH (30 g/L) than the stoichiometry amount was used. This value started to gradually decline until reaching a value of around 9.8. Consequently, it was predicted that different types of solids can be produced due to the formation of CO$_3^{2-}$ and HCO$_3^{-}$. Further parametric studies are still needed to examine the effect of adding excess amounts of KOH buffers on the pH value. However, it is expected that the pH value would be maintained at a value of more than 13 with the extra KOH amounts. The changing rate of the pH value was also observed when Al$_2$O$_3$ 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 and hence the overall performance of the Solvay process.

5.5 Impact of the alkaline/metal oxide type on the ions removal

The effect of Al$_2$O$_3$/KOH/CaO on the ions deduction percentage was investigated, as illustrated in Figure 9, for a temperature of 20°C, a gas flow rate (10% CO$_2$) of 1 L/min, and amounts of 21.4 g Al$_2$O$_3$/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. The time needed to reach full CO$_2$ saturation was 525, 330, and 25 minutes for CaO, KOH, and Al$_2$O$_3$, respectively. At first glance, the reduction percentage of the chloride ions was almost the same (36%) when using calcium and potassium hydroxides. However, the poorest
performance was reported when Al₂O₃ was used, as only ~8% of the chloride ions was reduced. However, the maximum reduction proportion in the sulfate ions (58%) was obtained from the addition of CaO, and it decreased to almost 20% and 0% in the case of KOH and Al₂O₃, respectively. It can also be noted that there was a slight decrease in the sodium reduction percentage when KOH was utilized instead of CaO. For example, the deduction percentage was 35% for CaO, and it slightly declined to approximately 29% with KOH. The poorest percentage was for Al₂O₃, where the Na⁺ ions reduction was only ~3%. It is very clear from the figure that the maximum ions removal was for the magnesium 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 Al₂O₃ was used. Although Al₂O₃ has no reactivity and solubility in the brine, it can be utilized as a coagulant for removing magnesium cations in the reject brine solution.

A further illustration of the ions removal is shown in Figure 10, which also provides additional information regarding the calcium ions removal using KOH as alkaline in brine through CO₂ capture. A good reduction of almost 97% was reported for the Ca²⁺ ions. In summary, the results showed a promising future for KOH as a buffer to be used in the treatment of brine and for CO₂ capture. It is expected that better results can be attained concerning the ions removal and brine treatment with excess KOH. In this study, the optimum CaO amount was compared with the stoichiometric KOH amount, which encouraged a statistical and optimization study for using KOH as a buffer in the modified Solvay process.

5.6 Potassium ions removal with the KOH buffer

It is important to assess the amount of potassium ions remaining in the brine solution after treatment with the KOH buffer. Table 1 demonstrates the reduction in the potassium ions when KOH was used as a buffer with a stoichiometric amount of 70.57 g/L. It was mentioned before in Section 4.1 that the potassium ions concentration in fresh brine was 905 ppm. Based on the stoichiometric amount (Reaction (4)), it was decided to dissolve 70.57 g/L of KOH buffer with the brine solution. Therefore, the concentration of the potassium ions sharply increased to almost 50 062 ppm. After the reaction with CO₂ and reaching the saturation point, it was observed that the potassium ions concentration declined to 42 322 ppm, which corresponds to a deduction of 15.5%.

This is due to the formation of potassium carbonate (K₂CO₃) solids, which are discussed in detail in the coming section. A further reduction in the potassium ions was reported due to the formation of KCl crystals. As a result, a total of ~30.1% reduction from potassium ions was achieved (refer Table 1), which is equivalent to 35 000 ppm. However, the treated brine was still not suitable for human consumption, as it contained high concentrations of potassium and other ions. However, it can be used in the production of nickel-zinc battery systems, as their electrolytes consist of an aqueous solution of KOH and K₂CO₃. It was also demonstrated that when the electrolyte was comprised of KOH and K₂CO₃ solutions, the conductivity of the system was enhanced, and the lifetime of the battery became much better than before.

![Figure 10](https://example.com/figure10.png)
5.7 | Characterization of the solid product with different alkaline/metal oxide

Figure 11 illustrates the results of XRD for the produced solids from the reaction between the brine and CO$_2$ and in the presence of CaO/KOH/Al$_2$O$_3$. The analytical XRD diffraction peaks for the collected solids was identified based on the theoretical intensity of the most three intense peaks for that mineral in a pure state.$^{41,42}$ All the results were obtained at 20°C, a gas flow rate of 1 L/min, and at stoichiometric quantities. Figure 11A confirms the obtained results before by El-Naas et al.,$^3$ where NaHCO$_3$, calcium chloride, and calcium bicarbonate were detected. The product was expected to have CaCO$_3$ because the addition of extra CaO increased the pH to more than 10, which increased the carbonates (CO$_3^{2-}$) formation. All these products are very valuable and have many industrial applications.$^2,^3$ The scanning electron microscopy of the reaction products is shown in Figure 12. The SEM analysis confirmed the formation of CaCO$_3$ and CaCl$_2$, as average EDS analysis for the solid sample shows that the main elements are calcium, carbon, oxygen, and chloride with mass percentage of 35% to 47%. It is also clearly visible from Figure 12 that the formation of CaCl$_2$ almost has a flat surface.$^{43}$ In addition, CaCO$_3$ formed has an amorphous texture and irregular shape.$^{44,45}$ A further aggregation of the CaCO$_3$ was also detected as shown in the figure.

Figure 11B shows the main mineral components resulting from the reaction when KOH was used (Reaction (4)): NaHCO$_3$, CaCO$_3$, KCl, and CaCl$_2$. XRD peaks at 28.3°, 40.6°, and 50.1° confirmed the production of KCl in the precipitated solids.$^{42}$ 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 13A. The formation of KCl crystals was confirmed by using SEM after they were grown in a brine.
solution for 24 hours. The average EDS analysis for the formed crystals shows that the main elements are potassium, and chloride with mass percentage of 96% to 98%, which confirms the production of KCl crystals.

Figure 13B illustrates that the produced KCl crystals have sharp edges and apexes. The production of KCl crystals has many advantages in different fields. For example, 95% of the fertilizers in the USA are...
supplied in a form of KCl\textsuperscript{27} for the majority of crops. In addition, KCl can be easily separated from the brine solution without any need for additional separation units because of its crystallized form. It can be reused also in the production of potassium hydroxides through the electrolysis process,\textsuperscript{29} which confirms the sustainability of this promising alkaline (KOH) to be used as a main reactant in the modified Solvay process. However, the XRD of the produced solid from the reaction with the Al\textsubscript{2}O\textsubscript{3} illustrates that, the main produced product was Al\textsubscript{2}O\textsubscript{3}, still it proved that this amphoteric oxide is capable to treat and manage the magnesium ions in the brine and recover on a coagulated form such as Beusite and Clinohumite. Figure 11C reveals the XRD for the obtained products from this reaction (Reaction (5)).

6 | CONCLUSIONS

In this study, the potential of utilizing different alkaline/metal oxide with desalination brine for the simultaneous CO\textsubscript{2} capture and brine treatment was investigated. KOH and Al\textsubscript{2}O\textsubscript{3} were identified and compared with the obtained CaO results from a previous study using CO\textsubscript{2} capacity, ions reduction, and quality of the precipitated products. All experiments were performed under the same conditions, and stoichiometric quantities were utilized for the KOH and Al\textsubscript{2}O\textsubscript{3}. The obtained results demonstrated that the CO\textsubscript{2} capture capacity and 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\textsubscript{2}O\textsubscript{3} in further studies as it did not result in any CO\textsubscript{2} capture, which is due to its lack of solubility and low pH level (\textasciitilde 8.7) at the onset of the reaction. However, it demonstrated that it can be used as a coagulant to remove magnesium ions in the reject brine solution. An amount of \textasciitilde 24% reduction in the magnesium ions was observed. Further investigations in terms of the parametric analysis are required to optimize the process parameters for the purpose of maximizing the CO\textsubscript{2} capture and the metal removal from solutions in the presence of KOH.

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DATA AVAILABILITY STATEMENT

Data available on request from the authors.

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