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Dual-Purpose Solvay-Dow (Magnesium) Conceptual Process

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Abstract

The proposed process basically combines two decades old processes (Solvay and Dow Magnesium) for the manufacture of soda ash and magnesium, respectively into a single process that also produces "partially-desalinated" water. It does so by subjecting salt brines first, to ammonia causing two simultaneous actions: 1) the absorption of ammonia forming what is called "ammoniated brine", and 2) the precipitation of magnesium ions, found in the brine, as magnesium hydroxide, $Mg(OH)_2$, which is filtered and separated. Next, carbon dioxide is introduced through the bulk of ammoniated brine, brine saturated with ammonia, causing the chemical conversion of both Na^+ and Cl^- into $NaHCO_3$ and NH_4Cl, respectively. Soda ash (Na_2CO_3) and ammonium chloride (NH_4Cl) come as products, along with partially desalinated water. This process is identified as "brine desalting", because of the drastic reduction of the salt content in brine. This part was experimentally tested before by the author and coworkers. Magnesium chloride ($MgCl_2$) is obtained, next, by reacting ammonium chloride (NH_4Cl) with $Mg(OH)_2$. In this double reaction, ammonia will be regenerated and recycled back to the process: $2NH_4Cl + Mg(OH)_2 \rightarrow Mg(Cl)_2 + 2NH_3 + 2H_2O$. Magnesium chloride is the raw material for making magnesium metal. This makes an additional economic value to the proposed process. The present contribution offers this conceptual scheme as an amalgamation of both Solvay/Dow (Magnesium) processes.

Subject Areas

Green Chemistry

Keywords

Magnesium Chloride, Soda Ash, Magnesium Metal, Ammonium Chlorid

1. Introduction

A separation process was proposed by Abdel-Aal *et al.* [1] [2] [3] which utilizes a series of chemical reaction sequences in order to separate NaCl from highly-saline water resources (sodium chloride-rich brines). The process involves bubbling of CO_2 gas into ammoniated brines, thus converting Na^+ and Cl^- into $NaHCO_3$ and NH_4Cl, respectively. Bubble columns were used as chemical reactors. Detailed experimental findings are reported by Ibrahim [4]. More than 80% NaCl conversion was achieved for saturated brines, leading to the production of partially desalinated water along with valuable chemical products, namely, soda ash and NH_4Cl.

When it comes to the Solvay process [5] [6] [7] [8] [9], it could be stated that while the soda ash is the main product in this process, it is a by-product in the proposed process. The main product is partially-desalted water that contains ammonium chloride, which may be called "fertile" water, to be used for agriculture purposes.

2. Proposed Process

Our proposed process follows the idiom of "killing two birds with one stone". Sea oceans are a virtually inexhaustible source of magnesium [10] [11] [12] [13]. About one pound of magnesium is recovered from each hundred gallon of sea water.

The main two steps involved in the proposed process are:

1st: Adding ammonia to our system will trigger the precipitation of magnesium, in the brine, as magnesium hydroxide $Mg(OH)_2$ which is separated first as an intermediate product. Simulateously, brine will get sturatred with ammonia forming what is called "ammoniated brine".

2nd: Bubbling carbon dioxide gas into the ammoniated brine, will initiate a set of chemical reactions described as follows:

3. Main Reactions

- Primary reactions: Takes place between CO_2 and NH_3:
  (a) $CO_2 + NH_3 \rightarrow NH_2COOH$ [carbamic acid]
  (b) $NH_3 + NH_2COOH \rightarrow NH_4^+ + NH_2COO^-$ [carbamate]
  The net reaction is: $CO_2 + 2NH_3 \rightarrow NH_2COO^- + NH_4^+$.
- Secondary reaction s: In the bulk of the solution, the carbamate hydrolyses comparatively slowly to bicarbonate:

$$NH_2COO^- + H_2O \rightarrow NH_3 + HOCOO^-.$$

- Product formation reactions

3.1. Soda Ash

In the presence of NaCl, the following instantaneous reaction takes place:

$$NH_4 + HCO_3^- + NaCl \rightarrow NaHCO_3 + NH_4Cl.$$

This leads to the precipitation of sodium bicarbonate leaving ammonium chloride in

a partially desalinated water (pdw). Sodium bicarbonate ($NaHCO_3$) precipitates from the reaction is converted to the final product, sodium carbonate Na_2CO_3 by calcination (160˚C - 230˚C), producing water and carbon dioxide as byproducts:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2.$$

3.2. Magnesium Chloride

Part of the partially desalinated water contining ammonium chloride is added separately to magnesium hydroxide forming magnesium chloride along with the regeneration of ammonia gas, to be recycled:

$$Mg(OH)_2 + 2NH_4Cl \rightarrow MgCl_2 + 2NH_3 + 2H_2O.$$

The modified process, which could be named Modified Solvay Process (MSP) is schematically illustrated in Figure 1.

4. Final Thoughts on the Duel-Purpose (Solvay-Dow) Process

A bird's eye view on the MSP compared to current one (shown in Figure 2) indicates some interesting observations:

- For the current Solvay process, CO_2 and $Ca(OH_2)$ are produced by burning lime stone using metallurgical coke:

$$CaCO_3 \rightarrow CaO + CO_2.$$

Next, Quick lime, CaO, is slacked by water: $CaO + H_2O \rightarrow Ca(OH)_2$.

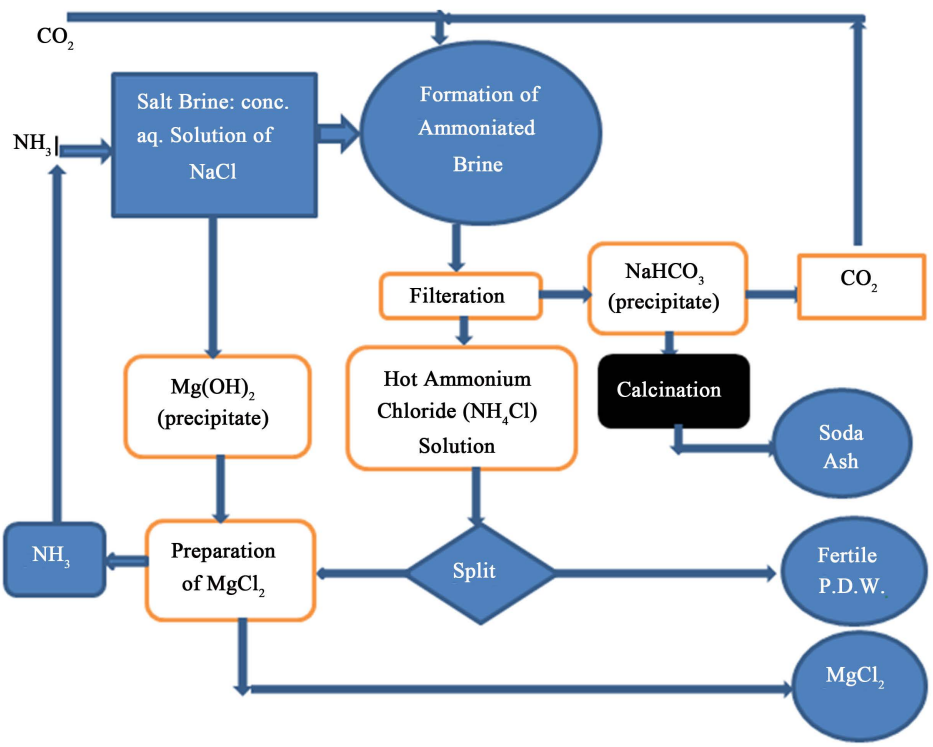

Figure 1. Process flow diagram for the Modified Solvay Process (MSP).

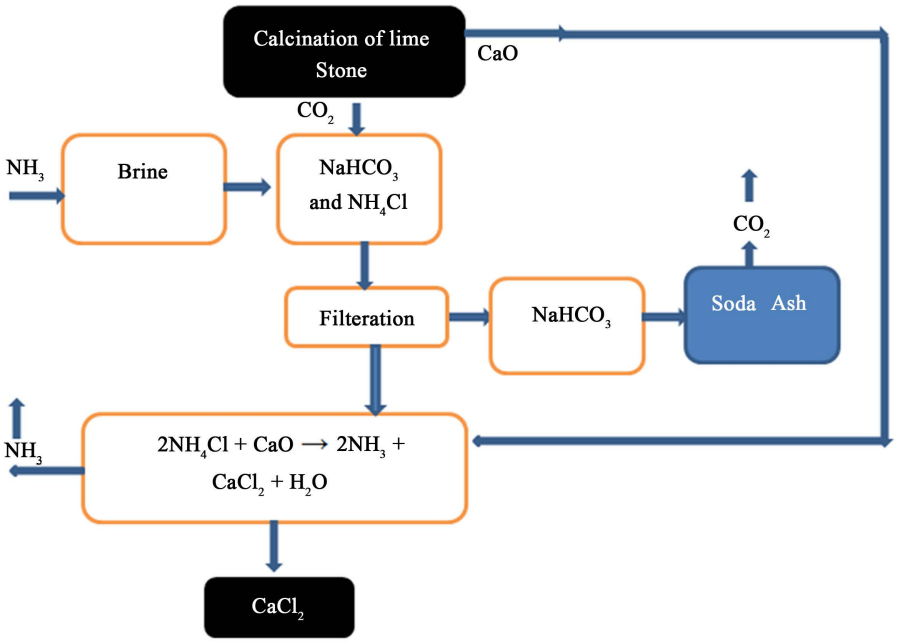

Figure 2. Conventional solvay process.

- In the proposed process, the source of CO_2 could be the combustion of fossil fuels in power generation and water desalination plants.
- In the Solvy process, $CaCl_2$ is produced as a waste; and arrangements are done for its disposal.
- The extraction of magnesium as magnesium chloride from sea water by the Dow process implies the precipitation of magnesium as magnesium hydroxide first by slurrying with calcined dolomite and then converting it to magnesium chloride by reacting it next, with hydrochloric acid.

5. Conclusions

The proposed process comprises two simultaneous operations: brine desalting and magnesium recovery. It offers a scheme that provides three products, soda ash, magnesium chloride and partially desalted water, as compared to one product by the Solvay process. Regeneration of ammonia is accomplished in the absence of CaO used in the Solvay process as indicated before.

The option of producing fertile water, (partially desalted water) containing NH_4Cl could be a feasible choice to be sold as a fertilizer for rice crops [14].

The proposed process offers a novel scheme, different from the well-known Dow process, for the extraction of magnesium chloride from sea water by eliminating the use of hydrochloric acid [15]. The separation of magnesium chloride as a byproduct adds an economic value to the proposed process.

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