CHEMICAL DESALTING OF SALINE WATER USING AMMONIA AND CARBON DIOXIDE: DEVELOPMENTS IN PROCESS SYNTHESIS

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Keywords: Ammonia, carbon dioxide, soda ash, saline water, Solvay, desalination

Conveersion of both Na^+ and Cl^- found in saline water into separable chemical products was achieved by bubbling ammonia through brine followed by the chemical reaction with carbon dioxide gas. The products obtained are soda ash (Na_2CO_3) and ammonium chloride (NH_4Cl) along with partially desalted water. A development is introduced in the process synthesis to allow for ammonia to be recycled rather than consumed, since ammonia plays a key role in this staged chemical reaction sequence. A conceptual flow scheme for the modified process is presented along with the production- consumption analysis. A comparison is made between the proposed method and the Solvay process.

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Introduction

Innovations in chemistry have a great effect on separation and processing in chemical industries. As a matter of fact, many important chemical revolutions center about the discovery of new reaction paths, such as the one we are considering in this paper.

Taking the case of Solvay process,[1] it is the major industrial process for the production of *soda ash* (sodium carbonate). The ammonia-soda process was developed into its modern form by Ernest Solvay during the 1860s.[2] The ingredients for this process are readily available and inexpensive: salt brine (from inland sources or from the sea) and limestone (from mines). A similar approach was followed by Abdel-Aal,[3] but with different objectives. The target is to desalinate highly-saline water resources using ammonia and carbon dioxide and to produce at the same time, soda ash and other chemicals. Clearly it could be stated that while in Solvay process soda ash is the main product, it is considered a by-product in the proposed process leaving the partially desalted water be the main product.

Main Reactions

The basic reactions involved could be visualized to take place as follows:

Reaction between CO_2 and NH_3 can be described as:

$$CO_2 + 2NH_3 \rightarrow NH_2COO^- + NH_4^+ \qquad (1)$$

In the bulk of the solution, the carbamate hydrolyses comparatively slowly to bicarbonate:

$$NH_2COO^- + H_2O \rightarrow NH_3 + HOCOO^- \qquad (2)$$

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

$$NH_4^+ + HCO_3^- + NaCl \rightarrow NaHCO_3 + NH_4Cl \quad (35)$$

This leads to the precipitation of sodium bicarbonate leaving ammonium chloride in a partially desalinated solution.

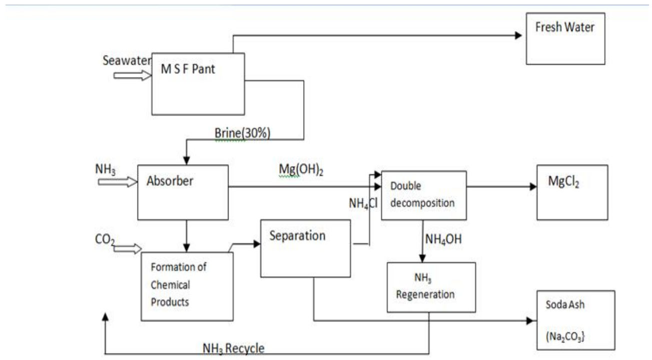

Fig.1 BLOCK FLOW DIAGRAM FOR THE PROPOSED PROCESS

Process Synthesis with Modifications

Sea oceans are a virtually inexhaustible source of magnesium. About one pound of magnesium is recovered from each hundred gallon of sea water. Adding ammonia to our system will trigger the precipitation of magnesium as magnesium hydroxide $Mg(OH)_2$ which is separated as an intermediate product, as shown in Figures 1 and 2. This is a turning point in our process synthesis that will lead to formation of NH_3 to be recycled as given by equation (6):

$$2NH_4Cl + Mg(OH)_2 \rightarrow MgCl_2 + 2NH_3 + 2H_2O \qquad (4)$$

The separation of magnesium chloride as a product adds an economic value to the process.

 DOI: 10.17628/ECB.2013.2.352

Table 1. Consumption- Production Analysis for the Chemical Desalting Process

	Species											
Reactions	**Reactants**					**Products**						
	NH_3	**H_2O**	**CO_2**	**$MgCl_2$**	**NaCl**	**NH_4OH**	**$Mg(OH)_2$**	**$NaHCO_3$**	**Na_2CO_3**	**NH_4Cl**	**CO_2**	**PDW**
No.1	-4	-4				+4						
No.2				-1		-2	+1			+2		
No.3			-2		-2	-2		+2		+2		
No.4.								-2	+1		+1	
Net	-4	-4	-2	-1	-2	0	+1	0	+2	+4		

Reaction-1 $4 NH_3 + 4H_2O \rightarrow 4NH_4OH$ (use 4 moles of NH_3)

Reaction-2 $2NH_4OH + Mg(Cl)_2 \rightarrow Mg(OH)_2 + 2NH_4Cl$

Reaction-3 $2 NH_4OH + 2CO_2 + 2NaCl \rightarrow 2NaHCO_3 + 2NH_4Cl$ (use 2 moles of NH_4OH)

Reaction-4 $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

Consumption-Production Analysis

The process involves the following reactions:-

$$NH_3 + H_2O \rightarrow NH_4OH \quad (5)$$

$$2NH_4OH + MgCl_2 \rightarrow Mg(OH)_2 + 2NH_4Cl \quad (6)$$

$$NH_4OH + CO_2 + NaCl \rightarrow NaHCO_3 + NH_4Cl \quad (7)$$

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O \quad (8)$$

The consumption-production analysis is figured out as indicated in Table 1.

For process synthesis, material balance flow rates of the raw materials in and the products out could be readily calculated using any convenient basis for the flow rate input of saline brine containing 25-30 % sodium chloride as a saturated solution.

It should be noted that the number of moles of H_2O shown above are provided by the saline water upon admitting the ammonia gas into it. For CO_2 gas, it is recommended to use 2 moles as given in equation (3) above. Partially desalted water PDW is obtained as a product, after separating the soda ash and magnesium chloride.

Comparison between the Solvay Process and the Proposed Process

This comparison is done along a set of important operating parameters as given in Table 2.

Important Notes:

For Solvay process, metallurgical coke burns lime stone, $CaCO_3$ to give : $CaO + CO_2$. Quick lime, CaO is slacked by water: $CaO + H_2O \rightarrow Ca(OH)_2$

For the proposed process, the source of CO_2 is the combustion of fossil fuels in power generation and water desalination plants.

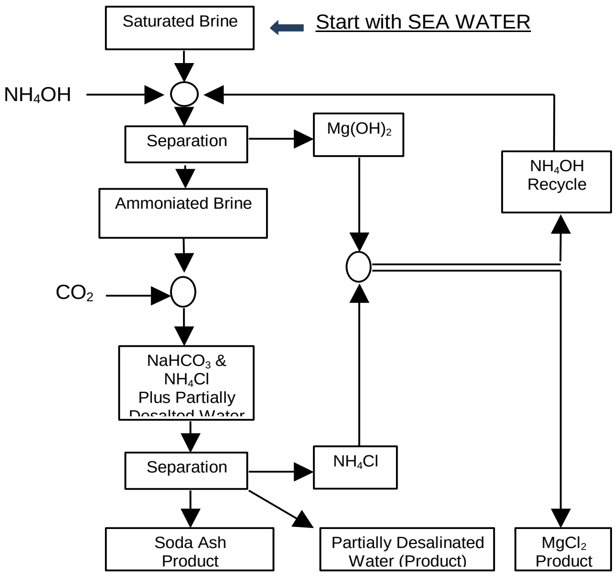

Figure 2. Modified Process Synthesis

Discussions and Conclusions

The proposed process offers a scheme that provides three products as compared to one product only by the Solvay process. Magnesium chloride is an important product for the manufacture of magnesium metal.

Table 2. The Solvay Process versus The Proposed Process

Parameters	**Solvay**	**Proposed**
Raw Material	Salt brine (rock salt) Lime stone Metallurgical coke NH_3 (recycle)	Salt rine/desalination brine CO_2 NH_3 (recycle)
Reactions for NH3 regeneration	$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + 2H_2O$	$2NH_3 + Mg(OH)_2 \rightarrow MgCl_2 + 2NH_3 + 2H_2O$
Products	Soda ash	Soda ash $MgCl_2$ Partially desalted water (PDW)

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As a matter of fact, one can claim that the proposed process could compete with the well-known Dow process,[4] Fertilizer Manual[5] for the extraction of magnesium chloride from sea water.

The process synthesis suggested in this paper focuses on the use of ammonia as a recycle reagent. An excess of say 5-10% ammonia should be considered as a makeup to compensate for losses. Regeneration of ammonia is accomplished in the absence of $Ca(OH)_2$ used in the Solvay process as indicated in the above comparison.

The option of producing fertile water or PDW (partially desalted water) containing NH_4Cl, to be used for agriculture purposes, still exists. Salt content in this water is reduced from initial brine concentration of 25% to about 7%. Although the salt content of the irrigation water affect the crop production[6], the produced ammonium chloride could be used as a fertilizer, so this question requires further investigations. Ammonium chloride is an excellent fertilizer used in the Far East for rice crops, and is recommended as an extremely good source of both N and Cl^- for coconut, oil palm, and kiwifruit.[4]

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Received: 13.01.2013.

Accepted: 11.02.2013.