Byproduct salt recovery from solid industrial effluent of hydrazine manufacturing plant

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A typical hydrazine manufacturing unit employing ureas as raw material, generates solid effluent containing NaCl, Na_2CO_3, NaOH, moisture and traces of hydrazine. A process has been worked out to recover NaCl and Na_2CO_3 as pure products from this effluent by converting the system to the three component encompassing NaCl-Na_2CO_3-H_2O and employing the phase equilibria for this ternery system. The process developed is environmentally friendly with zero discharge. The technical and economical details of the process are described in the paper.

1. INTRODUCTION

There are many processes for the manufacture of hydrazine. Out of these processes, the one which is more economical, employing simple unit operations, resulting in low investment is well adapted for small to medium scale production. Such process employs urea as raw material as source of nitrogen, and the process may be represented by the equation: [1]

$$(NH_2)_2CO + NaOCl + 2NaOH \longrightarrow N_2H_4 + NaCl + Na_2CO_3 + H_2O$$

The alkali is always in excess for the reaction to go to completion, and hence, the solid mixture remaining on separation of hydrazine contains sodium chloride, sodium carbonate, sodium hydroxide and moisture.

The typical pristine solid waste sample collected from the filtration unit of the hydrazine manufacturing plant in Faridabad, India has the following chemical composition, after convertion of NaOH to Na_2CO_3 by carbonation:

NaCl	31.2%
Na_2CO_3	56.0%
Moisture	12.5%

A simple cost effective process has been developed to separate sodium chloride and sodium carbonate into individual species having the best purity for its direct application to the other user industry for these chemicals.

2. PRINCIPLE OF THE PROCESS

Fig.1 shows the phase diagram of the ternery system NaCl-Na_2CO_3-H_2O on a triple coordinate graph [2,3]. ABC is an isotherm for 35°C and XYZ is the isotherm for 75°C. Point B and Y are their respective invariant points. Fig.2 is the phase diagram for the system drawn on rectangular coordinate to facilitate the understanding of the principle of the process.

The point B represents composition of saturated solution at 35°C. On heating the solution to 75°C, the point B is in the triangle Na_2CO_3-Y-Z, which constitutes the Na_2CO_3 solid phase plus solution. The Na_2CO_3 is thus separated. By adding the solid waste containing sodium carbonate and sodium chloride, the composition of which is represented by Point P, the composition at the solution in Point B is moved on line BP, towards P. The composition of the solution intended to attain is that of invariant point Y. To do this, the amount of waste to be added is fixed by bringing point B to M. BM is the amount of solids to be added to get the solution composition of Y. Sodium chloride from the solid goes into solution in this process. The solid sodium carbonate separated is removed by filtering the slurry hot.

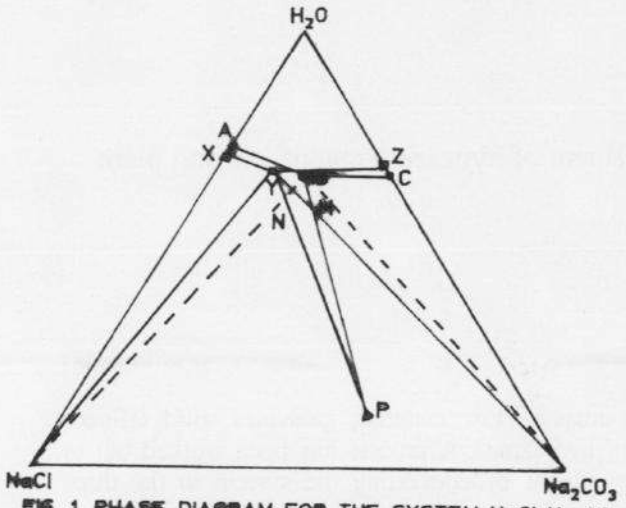

FIG. 1. PHASE DIAGRAM FOR THE SYSTEM NaCl-Na_2CO_3 -H_2O ON TRIPLE COORDINATE

35°C isotherm
75°C isotherm
Unit gm / 100gm Solution

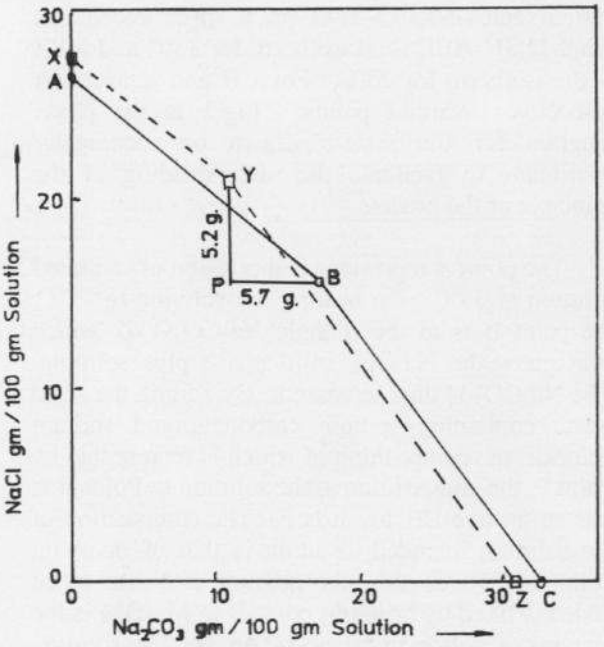

FIG. 2. PHASE DIAGRAM FOR THE SYSTEM NaCl-Na_2CO_3-H_2O ON SQUARE COORDINATE

35°C isotherm
75°C isotherm

On cooling the solution of composition Y to 35°C, the location of point Y falls in the field of NaCl-B-A, which constitutes solid phase field of NaCl plus solution. The solid waste is added to the solution to bring the composition of solution at B, the invariant point of isotherm at 35°C.

The process of addition is represented by line YP. The solid sodium chloride separated is removed by filtration. The amount of the solids to be added to alter the composition and the amount of the component separated in each cycle are shown in Table-1A and 1B.

3. THE PROCESS DESCRIPTION

The solution saturated with respect to both, sodium chloride and sodium carbonate is prepared by dissolving the solid waste in the water. The solution is heated to 75°C in a jacketed vessel equipped with agitator and the calculated quantity of solid waste is added in the solution. The contents are stirred for ten minutes and then filtered using the centrifuge. The solid is washed with the saturated solution of sodium carbonate to remove the adhering impurity of sodium chloride.

The hot filtrate is taken back to the jacketed vessel, and the calculated quantity of the solid waste is added to it. The content is stirred, and cooled by the cooling water circulated through the jacket. The content is filtered at 35°C, using the centrifuge. The solid separated is sodium chloride, which is washed with saturated solution of sodium chloride to remove the adhering impurity of sodium carbonate. Table-1A and 1B details the material balance of the process. Fig.3 shows the block diagram of the process.

4. ECONOMIC EVALUATION

Basis:

I. 6 tonnes of solid waste treatment per day.
II. 24 hrs/day plant operation
III. 300 days/year plant operation.

(a) Total project cost: 12,00,000 Indian Rs.

(b) Total cost of plant operation per day: 3500 Indian Rs.

(c) Quantity of value added products generated/day:

I. Soda ash (Na_2CO_3) - 3 T
II. Sodium chloride - 1.8 T

Table-1A
Material Balance of the process – Na_2CO_3 recovery

	INPUT				OUTPUT			
	SOLUTION		SOLID WASTE		SOLUTION		SOLID PRODUCT	
Temp.	35°C				75°C			
Qty.	100 g		16.66 g		100 g		18.0 g	
Composition	%	Total	%	Total	%	Total	%	Total
NaCl	15.7	15.7	31.12	5.2	20.9	20.9	1.10	0.2
Na_2CO_3	16.8	16.8	56.0	9.3	11.1	11.1	83.3	15.0
Combined + Free moisture	67.5	675	12.5	2.1	68	68	14.4	2.6

Table-1B
Material Balance of the process – NaCl recovery

% = gm/100 gm solution

	INPUT				OUTPUT			
	SOLUTION		SOLID WASTE		SOLUTION		SOLID PRODUCT	
Temp.	75°C				35°C			
Qty.	100 g		10.2 g		100 g		8.7 g	
Composition	%	Total	%	Total	%	Total	%	Total
NaCl	20.9	20.9	31.2	3.2	15.7	15.7	96.5	8.4
Na_2CO_3	11.1	11.1	56.0	5.7	16.8	16.8	2.3	0.2
Combined + Free moisture	68	68	12.5	1.3	67.5	67.5	1.2	0.1

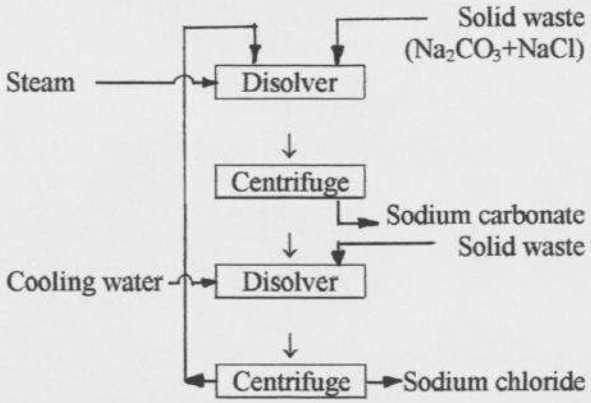

Fig.3 Block diagram of the process for the separation of NaCl and Na_2CO_3 from the solid waste.

(d) Market value of the products obtained:
I. Soda ash : 24,000 Indian Rs.
II. Sodium chloride : 720 Indian Rs.

(e) Net gain = (d) – (b)
= 24720 – 3500
= 21220 Indian Rs.

The proposed process is economically viable and offers attractive profitability.

4. CONCLUSION

A cyclic process for the recovery of sodium carbonate and sodium chloride from the solid waste of the hydrazine manufacturing process has been developed. The process is technically feasible, economically viable and environmentally friendly.

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