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Research Paper

ECONOMIC FEASIBILITY STUDY OF SODIUM BICARBONATE AND SODA ASH PRODUCTION FROM NA$_2$SO$_4$

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An interesting alternate process has been recently outlined for the manufacture of soda ash from sodium sulfate, a process route that is interesting to extend the abandoned Leblanc process. This article presents the techno-economic analysis of sodium sulfate for the suggested alternate process. Two different cases namely, procurement of Na$_2$SO$_4$ from market resources and onsite production of Na$_2$SO$_4$ (and HCl) from sea salt and sulfuric acid have been considered. The economic analysis yielded valuable conclusions. Firstly, for both the cases, producing baking soda is more economical than producing soda ash. Secondly, for soda ash production, the processes are not economically competitive with a profit after tax value of –26.65 M$ for offsite Na$_2$SO$_4$ procurement and –24.73 M$ for onsite Na$_2$SO$_4$ procurement. Sensitivity analysis also inferred to the magnitude of reduction/enhancement in raw material/product prices respectively. Few experimental investigations highlighted the scope for further experimental investigations for the said process route.

Keywords: Soda ash, Sodium sulfate, Techno-economic analysis, Sulfuric acid, Leblanc process

INTRODUCTION

Next to sulfuric acid and ammonia, soda ash (sodium carbonate) is the third largest manufactured chemical in the world. Comparatively, baking soda (Sodium bicarbonate), a byproduct of the soda ash industry also enjoys good market demand. While soda ash is commercially used for the production of glass, inorganic chemicals, soaps, synthetic detergents and processed food, baking soda is primarily used as a leavening agent and in medicines. The world production capacity of soda ash and baking soda is estimated to be 42 million tons in 2005 (Web 1) and 1 million tons in 2001 (Holleman and Wiberg, 2001) respectively. Today, more than 90 % of soda ash and baking soda are manufactured using Solvay's process.

Despite being cost effective for the manufacture

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of both soda ash and baking soda, Solvay's process is disadvantageous from the pollution abatement perspective. Solvay's process produces huge quantities of $CaCl_2$ which does not have much market value. Other waste streams produced in the process contain lower quantities of $CaCO_3$ and other impurities of limestone. In addition, magnesium and calcium ions in the brine solution are removed as carbonates which are also regarded as additional waste products. An alternative for the Solvay's process is the Dual and Hou's process in which ammonia is not recovered, but is transformed into ammonium chloride product, which can be sold as a fertilizer component. In addition, it is important to note that apart from enhanced utility usage, the Dual process requires purer brine solution and does not eliminate the generation of waste carbonate products in the brine purification step.

Existing trends in chemical process industries indicate a strong bias towards integrated processing, co-generation, and minimization of waste product generation. Process intensification coupled with techno-economic analysis enables the selection of most potential physical and chemical transformation routes that maximize process efficiency and minimize waste generation and energy consumption. Considering the necessity to address theoretical and experimental investigations for the alternative route, this work presents a preliminary techno-economic analysis of soda ash and baking soda production from sodium sulfate. Amongst several alternate routes for soda ash and baking soda production, a critical review of the industrial processes for soda ash indicates a partial utilization of the modified Leblanc process to initially produce Na_2SO_4 and HCl from NaCl and H_2SO_4 (Fuentes, 2004) .

Eventually, Na_2SO_4 can be used as the source for the production of baking soda (and soda ash) and $(NH_4)_2SO_4$ (Bichel *et al.*, 2008). Compared to the Solvay's process, the alternate process has certain advantages. Firstly, pure chemicals are used as raw materials and therefore, further purification steps are eliminated, and waste generation is reduced. Secondly, all products namely HCl, baking soda, soda ash and ammonium sulfate have good market value compared to their raw-materials. Thirdly, the process allows the simultaneous removal of SO_x and NO_x from flue gases using regenerated sodium bicarbonate/carbonate solutions along with the production of fertilizers (Mortson and Telesz, 2001).

Despite possessing the above advantages, techno-economic analysis and profitability studies of the process have not been carried out so far. Considering this aspect, this article addresses the techno-economic analysis of soda ash and baking soda production from Na_2SO_4 using the following hierarchal procedures:

a) To prepare a conceptual process flow sheet for the production of baking soda and soda ash from Na_2SO_4. Two sub-cases are considered, namely, onsite generation of Na_2SO_4 from NaCl and H_2SO_4 (modified Leblanc partial process); and, offsite procurement of Na_2SO_4 from the market.

b) To develop a mass balance model for the conceptual process flow sheet using the technical information presented (Fuentes, 2004, Bichel *et al.*, 2008).

c) To carry out sizing and costing analysis for the process using conceptual design methods.

d) To evaluate the economic competitiveness of the flow sheet by carrying out profitability and
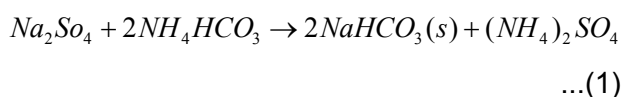
pay out period analysis. If the process is not competitive, the economic analysis shall identify possible variations in the cost of raw materials that would make the process economically viable.

e) To carry out experimental investigations to validate the feasibility of crucial steps in the soda ash production process from Na_2SO_4 and identify the most challenging tasks in the process.

f) In the next section, we present a brief description of the suggested process using the information available (Fuentes, 2004; Bichel *et al.*, 2008).

PROCESS DESCRIPTION

Alternate Soda Ash Production Process

The primary reactions associated with alternate process for soda ash production are (Fuentes and Jose, 2004):

$$Na_2So_4 + 2NH_4HCO_3 \rightarrow 2NaHCO_3(s) + (NH_4)_2SO_4$$
$$...(1)$$

$$2NaHCO_3 \xrightarrow{\text{Calcination}} Na_2CO_3 + H_2O + CO_2 \quad ...(2)$$

In the above reaction scheme, both soda ash and ammonium sulfate possess better market value than sodium sulfate.

Based on the description (Fuentes, 2004) Figure 1(a) presents the Process Block Diagram (PBD) for the process. Using sodium sulfate and ammonium bicarbonate, the process enables the production of sodium bicarbonate and ammonium sulfate using four crystallizers (units 1, 2, 4 and 5), four solid-liquid separators (S1-S4) and a reactor (unit 3). A brief account of the process is presented below.
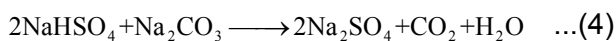
To realize the main reaction, the raw-materials are mixed in unit 1 at the desired charge ratio in an aqueous medium and room temperature and pressure conditions to produce sodium bicarbonate (solid) and ammonium sulfate. Eventually, the solid-liquid separator S1 separates the sodium bicarbonate solid product from the aqueous mixture. The mother liquor from S1 enters unit 2 along with double salt of ammonium sulfate and sodium sulfate obtained from unit S2. Cooling the mixture at freezing conditions enables the precipitation of combined salt of ammonium bicarbonate and Glauber's salt. The separated mother liquor from unit S2 is subjected to acid treatment in unit 3 so as to facilitate the removal of residual bicarbonate. Mother liquors from units 3 and 5 are sent to unit 4 where cooling crystallization is facilitated to precipitate the double salt of sodium sulfate and ammonium sulfate. S3 unit facilitates the separation of the double salt from the mother liquor which is eventually sent to unit 5. Unit 5 involves evaporative crystallization (at 100 °C) to produce ammonium sulfate precipitate. Unit S4 facilitates the separation of the ammonium sulfate product from the mother liquor. A purge stream is facilitated in the process to achieve desired purities of the products. The obtained sodium bicarbonate product is sent to a furnace to facilitate the decomposition to soda ash.

A similar process that exists as on date is the IMC chemicals facility in Trona which enables the recovery of sodium sulfate, soda ash and borax from mixed brine by a carbonation route. The plant is reported to capture upto 800 tonnes of CO_2 per day (Web 7).

Onsite Generation of Na_2SO_4

The chemical transformation route for the onsite generation of sodium sulfate is taken as a variant

of Leblanc process reaction using sea salt and sulfuric acid to produce HCl and NaHSO$_4$ at lower temperature (Bichel *et al.*, 2008). The variant chemical transformation route taken in this work is due to extreme reaction temperature in Leblanc process (about 1000-1100 °C) that offers serious constraints in safety and design issues. On the other hand, the variant process involves the partial consumption of soda ash generated from the alternate process involving reactions (1) and (2) to neutralize acid and acid sulfate to sodium sulfate. The primary reactions involved in the variant sodium sulfate production process are:

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl \qquad ...(3)$$

$$2NaHSO_4 + Na_2CO_3 \longrightarrow 2Na_2SO_4 + CO_2 + H_2O \quad ...(4)$$

$$H_2SO_4 + Na_2CO_3 \longrightarrow Na_2SO_4 + CO_2 + H_2O \qquad ...(5)$$

Of the above reactions, it is important to note that the stoichiometric requirement for soda ash (Na$_2$CO$_3$) in both Equations (4) and (5) is less than that getting produced in reaction (2). This is due to the fact that the only unreacted H$_2$SO$_4$ in Equation (3) would get neutralized with soda ash and only 0.5 mole of soda ash is required for generation of one mole of sodium sulfate in Equation (4).

Figure 1(b) presents the schematic of the variant of Leblanc process that generates sodium sulfate and HCl. The steps involved in the process include :

(a) Reaction of sulfuric acid and sodium chloride in the HCl Reactor to obtain a liquor containing hydrochloric acid and acid sodium sulfate (Equation 3).

(b) Separating the hydrochloric acid from the liquor containing the hydrochloric acid, acid sodium sulfate and an excess of sulfuric acid by evaporation in the Evaporator unit.

(c) Condensation of the vaporized HCl product by cooling around 80 °C to 125 °C to obtain a solution of water and hydrochloric acid at a concentration of 28% to 32% (w/w).

(d) Addition of sodium carbonate as neutralizing agent to the mother liquor in the Neutralizer unit constituting sodium hydrogen sulfate and sulfuric acid to produce sodium sulfate (Equations 4-5).

Literature data available for the phase equilibrium calculations in the process model has been collected (Bichel *et al.*, 2008). Figure 2(a) and 2(b) illustrate Janecke diagrams representing the phase equilibrium scenarios for bicarbonate precipitation from reactants and combined salt precipitation respectively. In these diagrams, X and Y axis represent charge fraction of bicarbonate ion and sodium ion evaluated as:

X axis:

Charge fraction of HCO_3^-

$$= \frac{\text{moles of } HCO_3^-}{\text{moles of } HCO_3^- + 2 \times (\text{moles of } SO_4^{2-})}$$

Y axis:

Charge fraction of Na^+

$$= \frac{\text{moles of } Na^+}{\text{moles of } Na^+ + \text{moles of } NH_4^+}$$

Figure 2 is utilized to locate the feed point on the plane such that the reactants anion and cation charge fractions co-ordinate falls within in the enclosure of the sodium bicarbonate saturation plane. Similarly, Figure 2(c) (Bichel *et al.*, 2008) presents temperature-composition diagram in which the charge fractions co-ordinate should fall within the ammonium sulfate plane so as to produce pure ammonium sulfate as a solid product.

Figure 1: Process Block Diagrams for the Production of (a) Soda Ash from Sodium Sulfate (Bichel *et al.*, 2008) and (b) Sodium Sulfate from NaCl and H_2SO_4 (Fuentes and Jose, 2004)
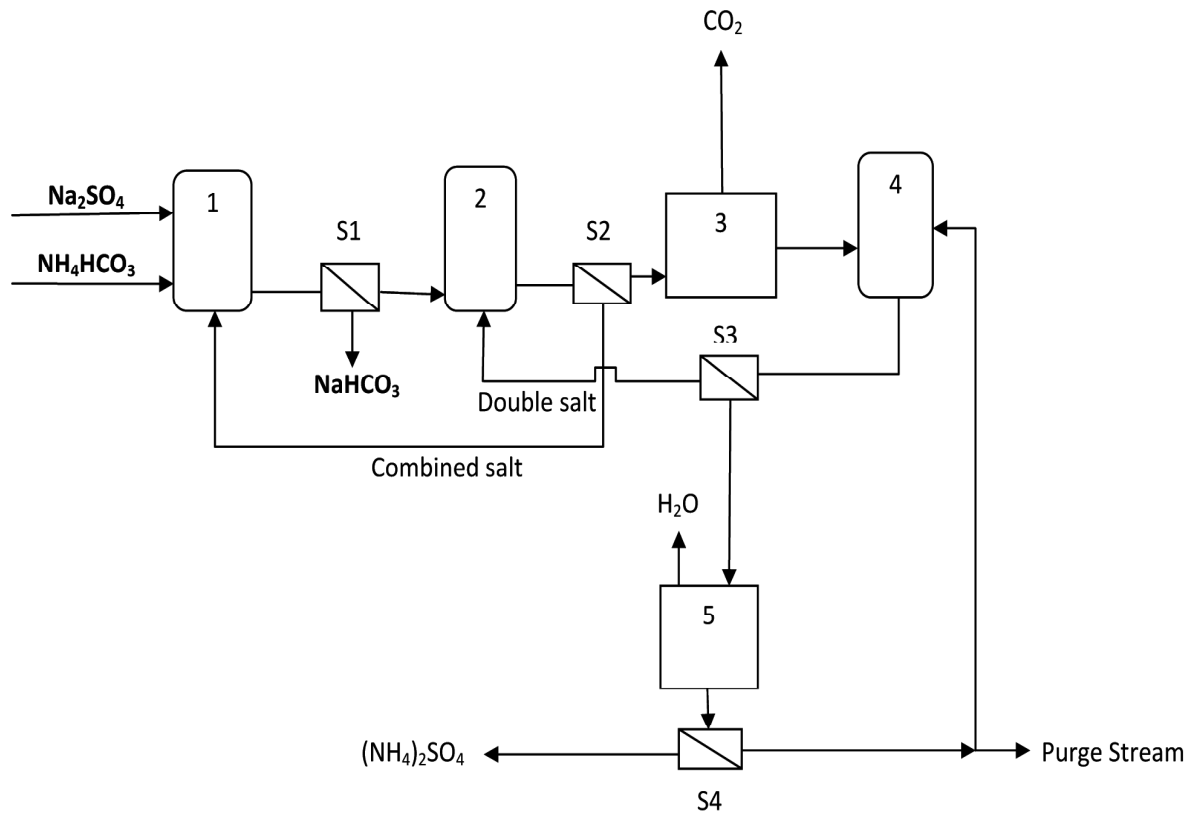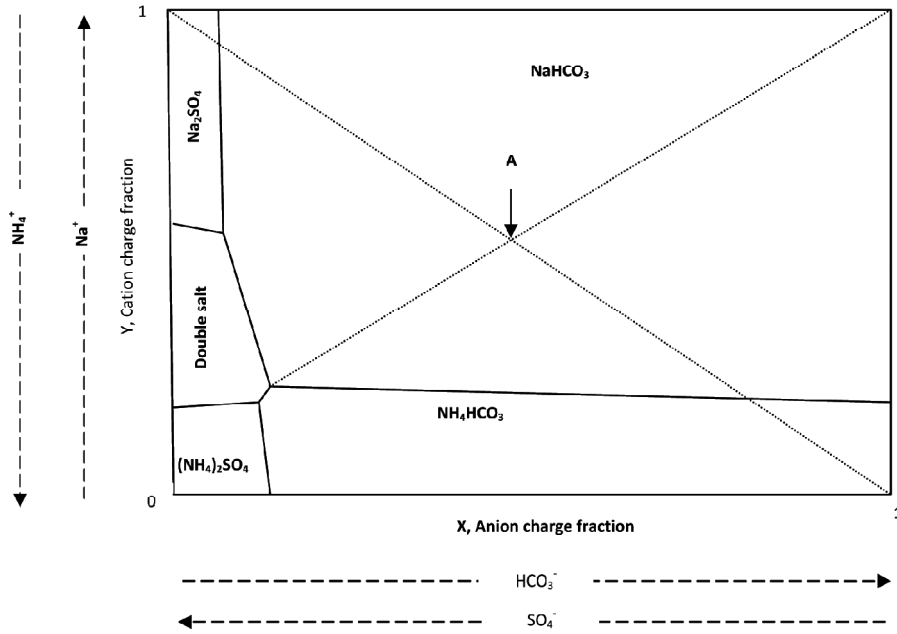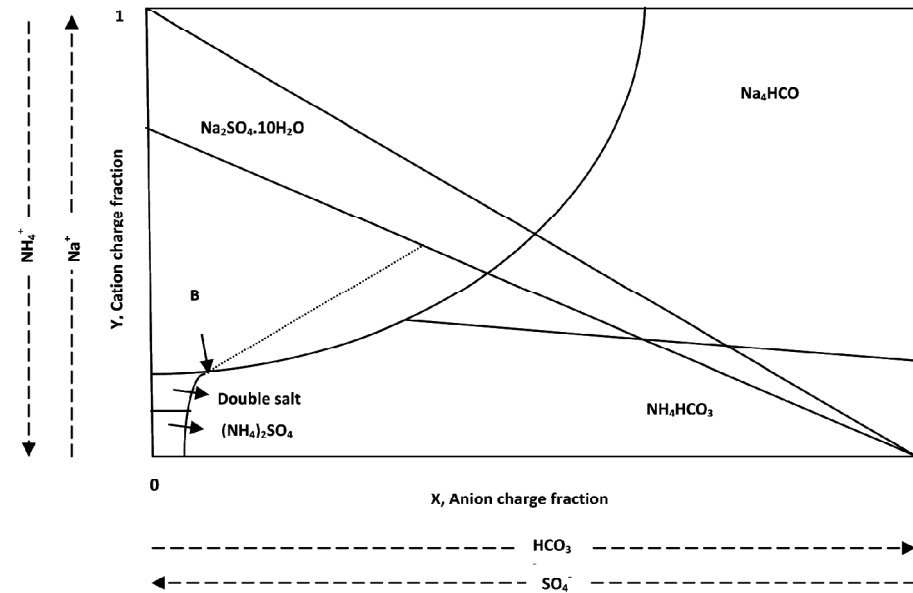

(a)
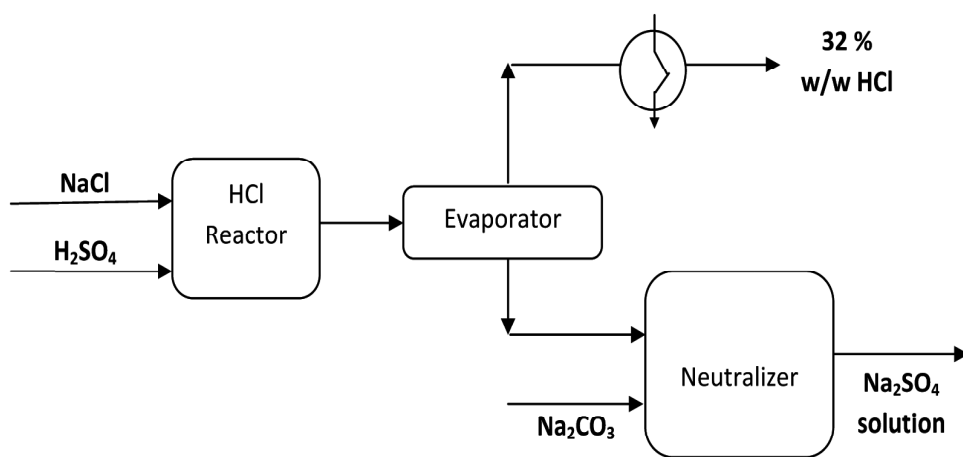
(b)

**Figure 2: Janecke Phase Equilibrium Diagrams for the Mass Balance of
(a) Sodium Bicarbonate Crystallizer (at 35 °C) (b) Combined Salt Crystallizer (at 0 °C) and
(c) Ammonium Sulfate Product Evaporator at 100 °C (Bichel *et al.*, 2008), Points A, B and C
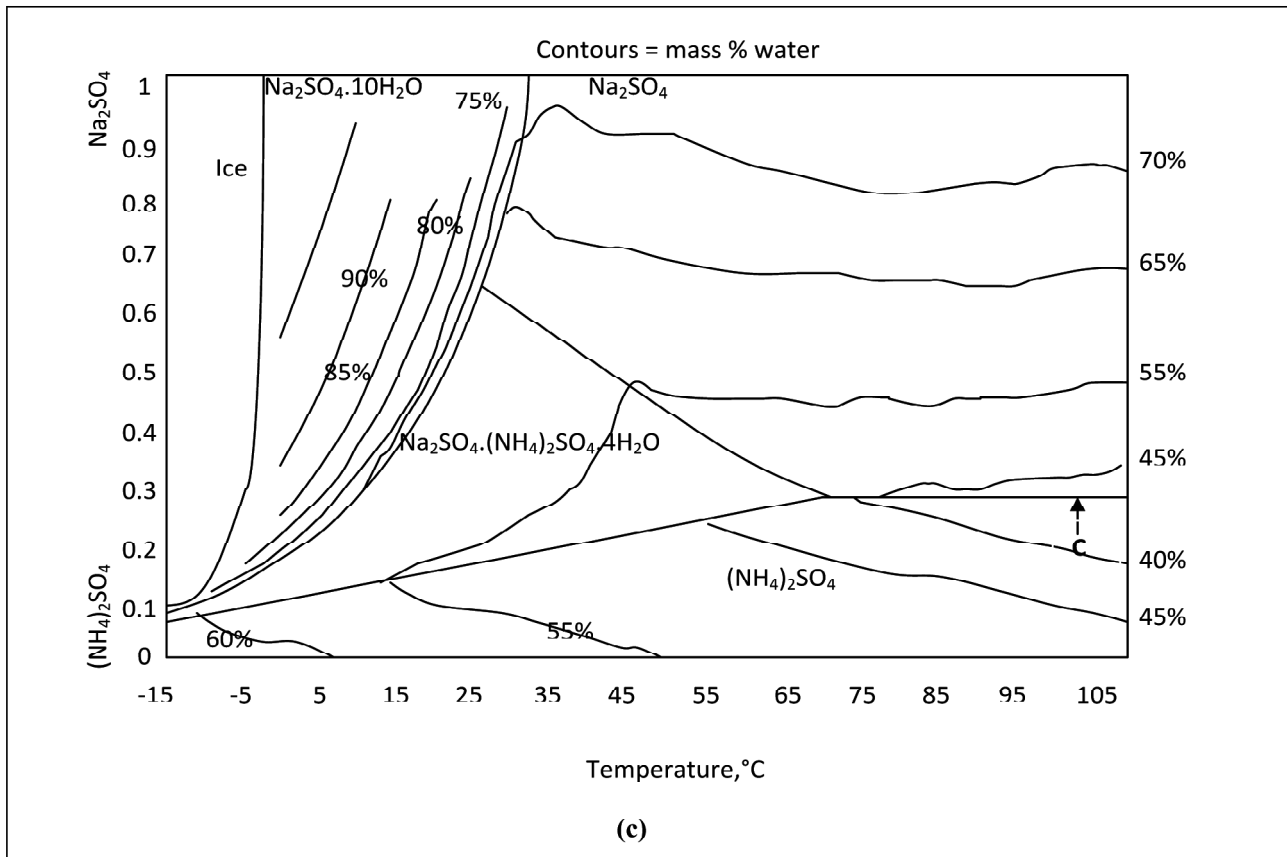from These Graphs Correspond to the Co-ordinates that are Used to Solve the Process Model**

(a)

(b)

Figure 2 (Cont.)

(c)

SIMULATION MODEL

Since the variant of Leblanc process involves simple stoichiometric calculations, the mathematical formulation is exclusively dealt for the production of soda ash from sodium sulfate. The hierarchical procedure for the development of mathematical model involves identification of appropriate operating conditions and product specifications followed by development of process unit models. Finally, the simulation model is solved for maximum conversion without contamination of products using the information obtained from Janecke phase equilibrium diagrams phase presented later in the article. In this work, energy balances were ignored and hence the economic analysis indicates a gross representation of the soda ash production cost.

Pure raw materials are chosen as feeds to the simulation problem with the product specification that both sodium sulfate and ammonium sulfate are at least 99% pure. The assumptions considered for mathematical formulation are:

a) Water is present as required for equilibrium precipitation in each process unit.

b) Fixed operating conditions exist for all equipments.

Though phase equilibrium diagrams define the approximate distribution of components distributed between solid and liquid phases, the existence of two recycle streams in the process flow sheet illustrated in Figure 1 demands the inclusion of phase equilibrium calculations in the

simulation model. The following sub-section presents phase equilibrium calculations that are built in the simulation model to evaluate distribution of components in different process units (crystallizers) between solid and liquid phases that are updated until recycle streams flow rates converge.

Phase Equilibrium Model (Thomsen, 1997)

The mass balance model requires phase equilibrium calculations to obtain respective tie lines for the Identification of compositions corresponding to phase and product distributions. A brief account of necessary equations in the phase equilibrium model is presented in Appendix A. Using the phase equilibrium model, relevant phase Janecke diagrams (Figure 2) were evaluated and these were similar to those presented in the literature.

Mass Balance Model

The goal is to precipitate sodium bicarbonate, so the composition of the feed has to be adjusted such that the plot of the reactants anion and cation charge fractions fall on sodium bicarbonate saturation plane shown in Figure 2.

In order to precipitate maximum $NaHCO_3$, feed should lie at point A , the intersection of the two dotted lines in Figure 2(a). The coordinates of point A is (0.477, 0.523).

$$\therefore 0.477 = \frac{Fo_2 + F_2^5}{Fo_2 + F_2^5 + 2 \times (Fo_1 + F_2^4)} \qquad ...(6)$$

Mother liquor will lie at a point whose co-ordinates is (0.135, 0.218).

$$\therefore 0.135 = \frac{F_1^2}{F_1^2 + 2 \times (F_1^1 + F_1^3)} \qquad ...(7)$$

$$0.218 = \frac{2 \times F_1^1}{F_1^2 + 2 \times (F_1^1 + F_1^3)} \qquad ...(8)$$

Material balance of unit 1 gives the following equations:

$$F_1^3 = (Fo_1 + F_2^4) - F_1^1 \qquad ...(9)$$

$$Po_1 = 2 \times F_1^3 \qquad ...(10)$$

In unit 2, to maximize precipitation of combined salt, mother liquor should reach at point B (0.072, 0.18) in Figure 3.

$$\therefore 0.072 = \frac{F_2^2}{F_2^2 + 2 \times (F_2^1 + F_2^3)} \qquad ...(11)$$

$$0.18 = \frac{2 \times F_2^1}{F_2^2 + 2 \times (F_2^1 + F_2^3)} \qquad ...(12)$$

Let the feed to unit 2 has the coordinates (c, d).

$$\therefore c = \frac{F_1^2}{F_1^2 + 2 \times (F_1^1 + F_1^3 + 2 \times F_4^6)} \qquad ...(13)$$

$$d = \frac{2 \times [F_1^1 + F_4^6]}{2 \times (F_1^1 + F_1^3) + F_1^2 + 4 \times F_4^6} \qquad ...(14)$$

And the precipitate has coordinates (g, h).For no contamination of precipitate,

$$g = \frac{F_2^5}{F_2^5 + 2 \times F_2^4} \qquad ...(15)$$

$$h = 1 - g \qquad ...(16)$$

As all these points (mother liquor, feed and precipitate) should lie on a line,

$$\therefore \frac{0.072 - c}{0.18 - d} = \frac{0.072 - g}{0.18 - h} \qquad ...(17)$$

Material balance of unit 2 gives:

$$F_2^2 = F_1^2 - F_2^5 \qquad ...(18)$$

$$F_2^1 = F_1^1 - F_2^4 \qquad ...(19)$$

Material balance of unit 3 gives:

$$Fo_3 = 0.5 \times F_2^2 \qquad ...(20)$$

$$Po_3 = F_2^2 \qquad ...(21)$$

$$F_3^3 = F_2^3 + 0.5 \times F_2^2 \qquad ...(22)$$

$$F_3^1 = F_2^1 \qquad ...(23)$$

In unit 4, feed point will lie on Y axis in Figure 3 as there is no HCO3- in the feed. Let this point be (0, j).

Figure 3: Cost Contribution of Various Units to the Total Plant Purchase Cost (a) Onsite Na$_2$SO$_4$ and (b) Offsite Na$_2$SO$_4$
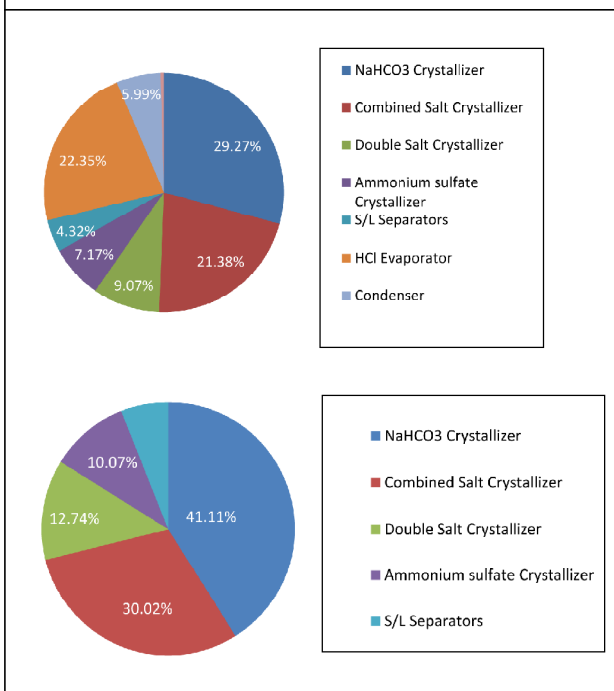
$$\therefore j = \frac{2 \times (F_5^1 + F_3^1)}{2 \times (\in \times F_5^1 + F_3^1 + F_3^3 + \in \times F_5^3)} \qquad ...(24)$$

where $\in$ is fraction of amount being recycled to unit 4.

And for no contamination of double salt precipitate, precipitation should stop at point (0, 0.10).

$$\therefore 0.10 = \frac{2 \times (F_4^1)}{2 \times (F_4^1 + F_4^3)} \qquad ...(25)$$

Material balance of unit 4 gives:

$$F_4^6 = (F_3^1 + \in \times F_5^1) - F_4^1 \qquad ...(26)$$

$$F_4^3 = F_3^3 + \in \times F_5^3 - F_4^6 \qquad ...(27)$$

In unit 5, feed should lie in (NH$_4$)$_2$SO$_4$ precipitation plane. For maximum precipitation of (NH$_4$)$_2$SO$_4$ without contamination, mother liquor should lie on the equilibrium line of Na$_2$SO$_4$ and (NH$_4$)$_2$SO$_4$ in Figure 4.

$\therefore$ At 100 ^{0}C, coordinates of mother liquor is C (100, 0.263) in Figure 4.

$$0.263 = \frac{F_5^1}{F_5^1 + F_5^3} \qquad ...(28)$$

Figure 4: Profitability Analysis of (a) Baking Soda Process Plant With and Without Na$_2$so$_4$ Onsite Management (b) Soda Ash Process Plants With Feed Price Variation

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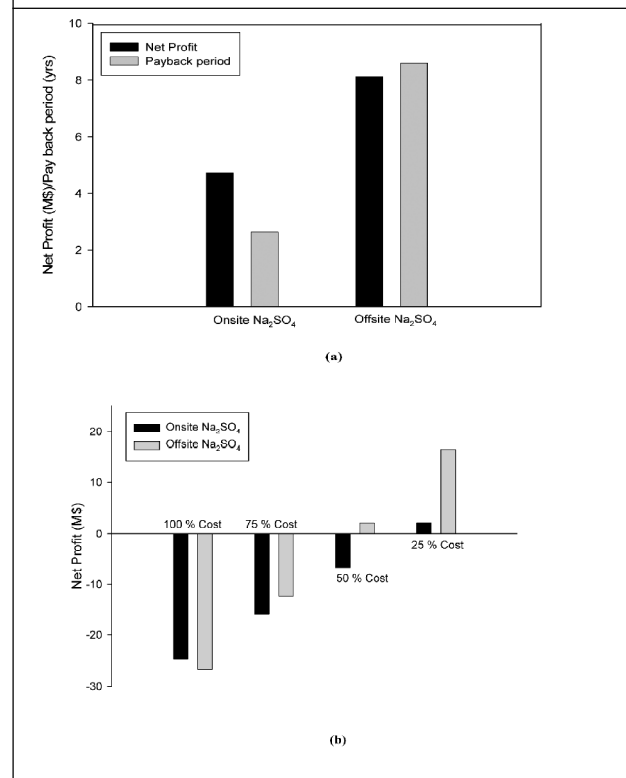
Material balance of unit 5 gives:

$$Po_2 = F_4^3 - F_5^3 \qquad ...(29)$$

$$F_5^1 = F_4^1 \qquad ...(30)$$

Here variables are:

$Fo_1,$ $Fo_2,$ $Fo_3,$ $F_1^1,$ $F_1^2,$ $F_1^3,$ $F_2^1,$ $F_2^2,$ $F_2^3,$ $F_2^4,$ $F_2^5,$ $Po_1,$ $Po_3,$ $c,$ $d,$ $g,$ $h,$ $F_3^1,$ $F_3^3,$ $F_4^1,$ $F_4^3,$ $F_4^6,$ $j,$ $\in,$ $F_5^1,$ F_5^3

Total variables = 26

Input variable = 1 (Fo_1)

Unknown variables (Output variables)

$$= 26 - 1 = 25$$

Total number of equations = 25

Here constraints are $j \leq 0.18$

And $0 \leq \in \leq 1$

SOLUTION METHODOLOGY

The simulation model along with phase equilibrium expressions and relevant physical and process parameters is solved using excel solver assuming non-negative model, quadratic estimates, central derivates and Newton search techniques. The sizing and costing models as well as profitability analysis models are applied after obtaining the mass flow rates of various units in the process flow sheets from the mass balance model, as these models don't involve iterative evaluations. The basis for all calculations is 10-100 tons/h of sodium sulfate as feed. Since simulation data is missing presently, different feed flow rates of sodium sulfate are considered in this work to generate data for reference purposes in the near future to aid process design and development issues. However, for economic appraisal, the feed input is taken as 50 tons/h of sodium sulfate for offsite procurement case and 20.6 tons/h of sodium chloride, 34.5 tons/h of

sulfuric acid and 54 tons/h of ammonium bicarbonate for onsite generation case.

SIZING AND COSTING MODELS

The process flow sheets constitute good number of crystallizers. Therefore, a conceptual process model for the sizing and costing of various crystallizers has been formulated using the following procedure.

The product capacity '$\dot{m}_{cv}$' based on the crystallizer volume is evaluated using the expression:

$$\dot{m}_{cv} = \frac{\dot{M}_c}{V} = \frac{1}{2} a_T G \rho_c = \frac{3\varphi_T}{L_{32}} G \rho_c \qquad ...(31)$$

The growth rate and residence time are evaluated using the expressions:

$$G = \frac{\beta}{3\alpha} k_d \frac{\Delta c}{\rho_c} \qquad ...(32)$$

$$\tau = \frac{V}{\dot{V}_a + \dot{V}_b} \qquad ...(33)$$

The costs of sodium carbonate, combined salt and double salt crystallizers are evaluated using the following expression:

$$C_p = 217 f W^{0.58} \qquad ...(34)$$

where 15 < W < 100 Klb/h of crystals

The cost of ammonium sulfate crystallizer is evaluated using the expression:

$$C_p = 1.218 f \exp(4.868 + 0.3092 \ln W + 0.0548(\ln W)^2) \qquad ...(35)$$

where 10 < W < 100 Klb/h of crystals.

PROFITABILITY ANALYSIS

Conceptual sizing and costing procedures have

been adopted to design and evaluate unit process costs using short cut methods (Cisternas *et al.*, 2006; Mersmann, 2001; Douglas,1988) for various process units in both process flow sheets. Physical properties required for these calculations are presented in Table 1. Crystallizer design parameters to aid sizing and costing calculations are summarized in Table 2. Various sizing and costing parameters evaluated for various crystallizers for the profitability analysis are summarized in Table 3.

Relevant costs of different feed/product materials are presented in Table 4 (Web 2, Web 6). Conventional approaches are adopted to evaluate different associated costs and payback period of various process plants (Couper, 2003).

RESULTS AND DISCUSSION

Simulation Model

Simulation results obtained for the case where sodium sulfate is procured from the market are summarized in Tables 6(a)-6(c) corresponding to 10, 50, and 100 tons/h of sodium sulfate basis respectively. For all cases, a 100% is not achieved due to the purging of about 20% of mother liquor from unit 5, a case that cannot be avoided due to the fact that the feed in unit 4 corresponds to Glauber's salt precipitation region which leads to the co-precipitation of both Glauber's salt and combined salt. The evaluated process stream flow rates are anticipated to serve as conceptual benchmarks for future research into the suggested process.

Table 1: Physical Properties of Different Commodities (Wagialla *et al.*, 1992)		
Commodity	**Density (kg/m³)**	**Heat of Crystallization (kJ/mol)**
Sodium Sulfate	1468 (Solid)	
Ammonium Sulfate	1769 (solid)	–6.8
Ammonium Bicarbonate	1580 (solid)	
Hydrochloric Acid	1160 (32% w/w)	
Sulfuric Acid	1840 (98% w/w)	
Sodium Chloride	2160 (solid)	
Sodium Bisulfate	2742 (anhydrous)	
Sodium Bicarbonate	2211 (solid)	–4.1
Stainless Steel 304	8000	

Table 2: Design Parameters for Crystallizer Sizing and Costing (Cisternas *et al.*, 2006)					
Type of Crystallizer	$m_T (Kg/m^3)$	$\Phi_T (m_c^3/m_{sus})$	τ (h)	$\dfrac{\Delta C}{\rho_c}$	L_{50}
Forced Circulation	200-300	0.1-0.15	1-2	10^{-4}-10^{-2}	02-0.5
Draft Tube Baffled Crystallizer	200-400	0.1-0.2	3-4	10^{-4}-10^{-2}	0.5-1.2
Fluidized Bed	400-600	0.2-0.3	2-4	10^{-4}-10^{-2}	1-5 (10)

Table 3: (a) Sizing; and (b) Costing Model Calculations for Various Crystallizers (Cisternas *et al.*, 2006)

a. Sizing

Parameters	Sodium Bicarbonate Crystallizer	Combined Crystallizer	Salt Double Crystallizer	Salt Ammonium Sulfate Crystallizer
k_d (m/s)	0.0001	0.0001	0.0001	0.0001
α	1	1	1	1
β	6	6	6	6
Φ_r	0.1	0.1	0.1	0.05
ρ_c (kg/m^3)	2211	1768	1600	1769
$\dfrac{\Delta c}{\rho_c}$	0.0002	0.0002	0.0002	0.0002
L_{32} (mm)	1	1	1	0.5
G (m/s)	4×10^{-8}			
M_c (kg/s)	14.9	9.893212395	1.94	3.67
V (m^3)	552	391	101	173
τ (h)	4	3.5	6	2

b. Costing Model Calculations

Parameters	Sodium Bicarbonate Crystallizer	Combined Crystallizer	Salt Double Crystallizer	Salt Ammonium Sulfate Crystallizer
Type of crystallizer		Internal Draft		External Forced Circulation
Mode of operation			Continuous	
Mode of supersaturation		Reaction		Evaporation
Material of construction			Stainless type 304; Material factor =2.5	
Rate of crystal formation (Klb/h)	116	67.5	15.4	29.1
C_p (K$)	8514	6244	2650	2095
Multipliers for installed cost			1.9	
Installed cost K$ (= 1.9 x C_p)	16248	11863	5035	3980

Table 4: Prices of Different Commodities (Web 2, 6, 2012)	
Commodity	Price($)/Ton
Sodium Chloride	47
Sulfuric Acid (98%)	30
Ammonium Bicarbonate	71.5
Sodium sulfate	110
Sodium carbonate	165
Ammonium Sulfate	165
HCl (31% w/w)	94

Economic Feasibility

Table 5 summarizes the feed, product and process specifications for the economic feasibility study in this work. The economic feasibility case corresponds to 50 tons/h of sodium sulfate for offsite procurement case and 20.6 tons/h of sodium chloride, 34.5 ton/h of H_2SO_4 and 54 tons/h of ammonium bicarbonate for onsite sodium sulfate procurement. The conversion with respect to sodium ion is 92.3% and with respect to carbonate ion is 95.8% for both the cases.

Table 5: Design Specifications for Feed, Product and Processes in the Simulation Study

Component	Sodium Sulfate Procured from Market	Onsite Generation of Sodium Sulfate
Feeds	Sodium sulfate: 50 ton/h Ammonium Bicarbonate: 54 ton/h	Sodium Chloride: 20.6 ton/h Sulfuric acid: 35.4 ton/h Ammonium bicarbonate: 54 ton/h
Products	Sodium bicarbonate: 16 ton/h Ammonium sulfate: 12 ton/h	Soda Ash: 16 ton/h Ammonium sulfate: 12 ton/h Hydrochloric Acid: 13 ton/h
Product Purity	Sodium Bicarbonate: 100% Ammonium Sulfate: 100%	Soda Ash: 100% Ammonium Sulfate: 100% Hydrochloric Acid: 32% w/w
Conversion	With respect to Na^+ = 92.3 %, With respect to HCO_3^- = 95.8 %	

Table 6: Simulation Results Obtained for Different Input Rates of Sodium Sulfate (a) 10 tons/h, (b) 50 tons/h, and (c) 100 tons/h

	a				
Stream*	Unit 1	Unit 2	Unit 3	Unit 4	Unit 5
Fo_1	10.00	0.00	0.00	0.00	0.00
Fo_2	10.54	0.00	0.00	0.00	0.00
Fo_3	0.00	0.00	0.29	0.00	0.00
F_1	3.02	1.03	1.03	0.46	0.46
F_2	2.08	0.46	0.00	0.00	0.00
F_3	8.34	3.99	4.37	3.84	1.20
F_4	0.00	4.51	0.00	0.00	0.00
F_5	0.00	1.62	0.00	0.00	0.00
F_6	0.00	0.00	0.00	1.40	0.00
Po_1	10.61	0.00	0.00	0.00	0.00
Po_2	0.00	0.00	0.00	0.00	2.65
Po_3	0.00	0.00	0.26	0.00	0.00

Table 6 (Cont.)

Stream*	Unit 1	Unit 2	Unit 3	Unit 4	Unit 5
b					
Fo_1	50.00	0.00	0.00	0.00	0.00
Fo_2	52.72	0.00	0.00	0.00	0.00
Fo_3	0.00	0.00	1.43	0.00	0.00
F_1	15.11	5.17	5.17	2.30	2.30
F_2	10.41	2.30	0.00	0.00	0.00
F_3	41.68	19.95	21.87	19.21	5.98
F_4	0.00	22.54	0.00	0.00	0.00
F_5	0.00	8.11	0.00	0.00	0.00
F_6	0.00	0.00	0.00	6.99	0.00
Po_1	53.04	0.00	0.00	0.00	0.00
Po_2	0.00	0.00	0.00	0.00	13.23
Po_3	0.00	0.00	1.28	0.00	0.00
c					
Fo_1	100.00	0.00	0.00	0.00	0.00
Fo_2	105.44	0.00	0.00	0.00	0.00
Fo_3	0.00	0.00	2.85	0.00	0.00
F_1	30.21	10.33	10.33	4.59	4.59
F_2	20.82	4.60	0.00	0.00	0.00
F_3	83.35	39.91	43.75	38.41	11.96
F_4	0.00	45.09	0.00	0.00	0.00
F_5	0.00	16.22	0.00	0.00	0.00
F_6	0.00	0.00	0.00	13.98	0.00
Po_1	106.09	0.00	0.00	0.00	0.00
Po_2	0.00	0.00	0.00	0.00	26.45
Po_3	0.00	0.00	2.56	0.00	0.00

Note: *All rates are in ton/h.

Cost contributions of various equipments for the two candidate process flow sheets are summarized in Figures 3(a) and 3(b) for both onsite and offsite management of Na_2SO_4 respectively. It can be observed that when Na_2SO_4 and HCl are produced onsite, the cost of the crystallizers contributed about 67% to the total cost of the process equipment, which amounts to about 29.02 M$ for the chosen capacity. On the other hand, for the offsite Na_2SO_4 procurement case, the total cost contribution is mainly due to the crystallizers in the process for a total investment cost estimate of 20.8 M$. Thereby, it can be envisaged that about 8.2 M$ is required to set up the Na_2SO_4 onsite management. A comparison of various economic parameters for

the alternative process with Solvay's process and Dual process are presented in Table 7. The table also presents a projected estimate of the economic parameters for the prices in 2012, by using an update factor, which is evaluated using M&S index values. As indicated in the table, the alternative process offers lower capital investment than the conventional processes but offers substantially higher production costs with respect to them.
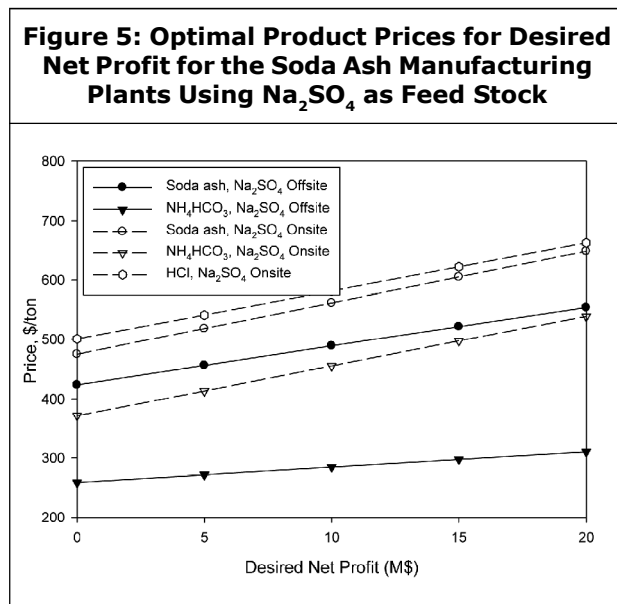
Table 7: Comparison of Economic Parameters of the Alternate Soda Ash Process with Solvay's and Dual Process (Wagialla *et al.*, 1992)

Process	Capital Investment $/ton of Soda Ash	Total Production Cost $/ton of Soda Ash
Na_2SO_4 offsite process	466.27	482.88
Na_2SO_4 onsite process	653.86	569.75
Solvay's process (1992)	829	186.51
Dual process (1992)	1029.5	284.23
Solvay's process (2012)	1341.8	301.88
Dual process (2012)	1666.4	488.6

Figure 4(a) presents the results obtained after the comprehensive profitability analysis for the case when only baking soda is produced in the plant and the production of soda ash is not considered. It can be observed that procuring Na_2SO_4 from the market sources enabled a net profit of 8.11 M$ which reduced to 4.72 M$ when Na_2SO_4 is produced onsite. The corresponding payback period values correspond to 2.64 and 8.6 years for offsite and onsite Na_2SO_4 cases respectively. In summary, it is apparent that the alternative process is economically competitive for the production of baking soda.

Figure 4(b) corresponds to the profitability analysis for the case of producing soda ash from Na_2SO_4. It can be observed that when existing prices of the raw materials (sodium sulfate and ammonium bicarbonate) are considered, negative net profit values (−26.64 M$ for offsite and −24.73 M$ for onsite Na_2SO_4 case) are obtained and the process is not economically feasible. Therefore, other interesting scenarios have been explored that correspond to the economic competence of processes in which the prices of the raw materials are substantially reduced. The results obtained for these cases are also illustrated in the same figure. It can be observed that the offsite Na_2SO_4 case corresponded to a net profit of 2.13 M$ for a reduction in the raw material prices to 25% of the existing values. However, the onsite Na_2SO_4 case corresponds to a better economic performance as the process achieved positive net profit for a reduction of raw materials cost to 50% of the existing values and a net profit of 16 M$ for the case of raw materials price reduction to 25%. Thereby, profitability analysis studies conveyed surprising inferences, namely: (a) Production of baking soda is economically favored by the alternative process and shall be operated without an onsite Na_2SO_4 and HCl plant; and (b) soda ash cannot be manufactured using either process routes with the existing market prices of various commodities.

With the poor economic competence of the alternate process for soda ash production, further interesting case studies have been considered. While the first case as indicated in Figure 4 (b) is the reduction in raw material prices, the second case corresponds to the projection of optimal prices of various products to make the processes

economically favorable. Several optimization problems have been formulated to consider the optimization of product prices for the desired net profit values. The results obtained from such studies are presented in Figure 5. As indicated, the costs of various products are anticipated to enhance substantially to drive the process from an economic perspective. For the case of Na_2SO_4 production, and for existing prices of 260 $/ton for soda ash, 165.34 $/ton for ammonium sulfate and 300 $/ton for HCl, the desired optimal prices for various commodities varied in the range of 474.7-648 $/ton for soda ash, 371.8-538.7 $/ton for ammonium sulfate and 500-662.7 $/ton for HCl. However, for the case of offsite Na_2SO_4 procurement, the desired optimal prices varied in the range of 423.65-553.92 $/ton for soda ash and 258.9-310.4 $/ton for ammonium sulfate. Thereby, the economic evaluations strongly inferred that the production of HCl onsite is not economically favorable and shall be avoided.

Figure 5: Optimal Product Prices for Desired Net Profit for the Soda Ash Manufacturing Plants Using Na_2SO_4 as Feed Stock

CONCLUSION

Based on an alternative process for soda ash production from Na_2SO_4, this work addressed the techno-economic issues for baking soda/soda ash production. Two alternatives namely, onsite and offsite management of Na_2SO_4 have been considered in the study. Theoretical investigations with the process and economic model inferred very significant conclusions. Firstly, with the existing raw materials and product prices, the alternate process is only economical to produce baking soda but not soda ash, despite considering the production of HCl as an additional product to improve the economic competence. Secondly, the alternative process only enabled profits when the prices of the raw materials were reduced to 50% of the existing values and when HCl production was considered. Further, an optimal cost production of the products has also been carried out in this work that indicated that HCl production does not reduce towards a relaxation for futuristic prices of desired products.

The considered process and economic model in this work has considered the production of baking soda from sodium sulfate and ammonium bicarbonate. From a process perspective, the inferred conclusions may be completely different when ammonia, CO_2 and sodium sulfate are considered as raw materials, given the fact that ammonium bicarbonate would be more expensive than using equivalent amounts of ammonia and CO_2. However, experimental data and kinetic models of the same are not available and further research is recommended.

Finally we conclude that the process considered in this work requires considerable experimental investigations towards process development and engineering studies and can further consolidate modeling efforts to realistically evaluate its competence.

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APPENDIX A

Phase Equilibrium Model

The equilibrium between an aqueous phase and the solid salt $K_k A_\alpha . n H_2 O$ (s) consisting of 'k' cations (K), 'α' anions (A) and 'n' water molecules can be described by the equation :

$$K_k A_\alpha . n H_2 O(s) \longleftrightarrow k K(aq) + \alpha A(aq) + n H_2 O \qquad \text{...(A1)}$$
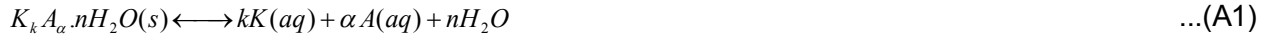
At equilibrium, the chemical potential of the solid salt is equal to the sum of the chemical potentials of the salt's constituent parts. The condition for equilibrium therefore is:

$$\mu_{K_k A_\alpha n H_2 O(s)} = k \mu_K + \alpha \mu_A + n \mu_w \qquad \text{...(A2)}$$

The above equilibrium condition can be expressed in terms of the standard chemical potentials and the activities of ions and water :

$$k \mu_K^{\infty,m} + \alpha \mu_A^{\infty,m} + n \mu_w^0 - \mu_{K_k A_\alpha n H_2 O(s)} = -RT \ln(K_{K_k A_\alpha n H_2 O}) \qquad \text{...(A3)}$$

where, $K_{K_K A_\alpha n H_2 O} = a_K^k a_A^\alpha a_w^n \qquad \text{...(A4)}$

is the solubility product of the salt, $a_i = m_i \gamma_i$ for the ions and $a_w = x_w f_w$ for the water. The activity of solid salt is set equal to 1 because the solid salt is in its standard state.

At equilibrium, the composition of the liquid phase can be calculated from equation:

$$K_k = \prod_i a_i^{\upsilon_{k,i}}, k = 1....s \qquad \text{...(A5)}$$

An s-salt saturation point has to fulfill the above condition for all s salts.

In the above equation, "a" is activity, "$\upsilon_{k,i}$" is the stoichiometric coefficient of component 'i' in salt 'k'.

The equilibrium condition for the chosen system can be written as:

$$K_{K_K A_\alpha n H_2 O} = a_K^k a_A^\alpha a_{H_2 O}^n = (m_K x_w f_K)^k (m_A x_w f_A)^\alpha (x_w f_w)^n \qquad \text{...(A6)}$$

$$= M_w^{-(k+\alpha)} (x_K f_K)^k (x_A f_A)^\alpha (x_w f_w)^n$$

Relevant chemical potentials of different ions associated to phase equilibrium calculations in the simulation model are presented in Table A1.

APPENDIX A (CONT.)

Table A1: Chemical Potential of Different Species for Phase Equilibrium Calculations(Thomsen, 1997)	
Species	**Chemical Potential (J/mol)**
Na+	–26,189
$HCO_3^{–}$	–58,685
$NaHCO_3$	–85,186
NH_4^{+}	–7,937
SO_4^{2-}	–74,463
$(NH4)_2SO_4$	–9,1571.3

NOMENCLATURE

C_p	Purchase Cost, $
V	Volume of crystallizer, m^3
f	Activity coefficient at standard state.
Fo_m	Flow rate of fresh feed 'm', where m $\in$ [Na_2SO_4, NH_4HCO_3,H_2SO_4], tons/h.
F_i^k	Flow rate of component 'k' in output stream of unit 'i',
	where k $\in$ [NaCl, H_2SO_4, Na_2SO_4, NH_4HCO_3, $(NH_4)_2SO_4$, $Na_2SO_4.10H_2O$,
	NH_4HCO_3, $Na_2SO_4.(NH_4)_2SO_4.4H_2O$], tons/h.
Po_n	Flow rate of product 'n', where n $\in$ [$NaHCO_3$, $(NH_4)_2SO_4$, HCl], tons/h.
M_c	Mass flow rate of crystallized substance, kg/s.
ρ_c	Density of crystallized substance, kg/m^3.
L_{32}	Average crystal size, mm.
k_d	Mass transfer coefficient (diffusion controlled), m/s.

NOMENCLATURE (CONT.)

φ_T	$Volumetric\ hold\ up = \dfrac{Volume\ of\ crystals}{Volume\ of\ slurry}$
Δc	Supersaturation, kg/m³
a_T	$Volumetric\ surface\ = \dfrac{6\varphi_T}{L_{32}}$
P_{oj}	Yearly Production of product "j", tons.
$\$_j^P$	Price of Product "j", \$/ton.
F_{ok}	Yearly consumption of feed "k", ton.
$\$_k^f$	Price of feed "k", \$/ton.
$\dot{V}_a, \dot{V}_b$	Volumetric feed flow rates of components a and b respectively, m³/s.
α and β	Volume and surface shape factors, respectively.