

Antisolvent Crystallisation as an Alternative to Evaporative crystallisation for the Production of Sodium Chloride

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A comparison has been made between the antisolvent crystallisation of NaCl with diisopropylamine and the traditional four effect evaporative crystallisation of NaCl. Calculations demonstrated that for a 1 Mton/y salt production plant with an on-site integrated steam power plant the reduction in energy costs can be 29 % if antisolvent crystallisation is applied. The estimated fixed capital costs however, are 8 to 55 % higher for the antisolvent crystallisation of NaCl, depending on the used process configuration. A disadvantage of the antisolvent crystallisation of NaCl is that the crystals are generally small, tend to agglomerate and are contaminated with the antisolvent. The quality of the product can be strongly improved in a two step process. In a first step $\text{NaCl} \cdot 2\text{H}_2\text{O}$ is formed by antisolvent crystallisation, which can be recrystallised in purer brine in a second step. In this two step process large and pure NaCl crystals can be produced at the expense of increased major operating costs.

1. Introduction

In industry sodium chloride is produced by multiple effect evaporative crystallisation. To reduce the energy consumption in the production of sodium chloride this water evaporation step can be substituted by the addition of an antisolvent that reduces the solubility of the salt. Weingaertner et al. (1991) demonstrated that the reduction in energy costs by applying antisolvent (or extractive) crystallisation can be as high as 63 % compared to a three-effect evaporation plant. Weingaertner used DiisoPropylAmine (DiPA) as the antisolvent, which is partially miscible with water [2]. The crystallisation was carried out at -5°C in the single liquid phase area and the DiPA was recovered from the spent mother liquor by increasing its temperature to a value in the two liquid phase area. However, in his calculations Weingaertner did not acknowledge the fact that the mixing of DiPA and water is strongly exothermic and that at a crystallisation temperature of -5°C not the NaCl but the $\text{NaCl} \cdot 2\text{H}_2\text{O}$ crystal modification is formed. This

modification is not a suitable end product because it is unstable at room temperature. Furthermore the estimated heat of crystallisation of -17 kJ/mole for $\text{NaCl} \cdot 2\text{H}_2\text{O}$ (-1.6 kJ/mole for NaCl) significantly contributes to the energy consumption within the process.

Apart from the reduction in the energy consumption, the purity and size of the NaCl crystals formed by antisolvent crystallisation is of paramount importance, since the salt is used in electrolysis plants and for consumption. Continuous crystallisation experiments of NaCl demonstrated that the quality of the formed crystalline material is generally poor. The antisolvent uptake of the sodium chloride can be as high as 630 ppm [3] and the crystals are generally small and agglomerated. However, a high quality product can be obtained in a two step process. In the first step $\text{NaCl} \cdot 2\text{H}_2\text{O}$ is formed by antisolvent crystallisation, which can be recrystallised in purer brine in a second step. Experiments showed that such a recrystallisation can

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produce large single crystals with antisolvent uptakes of 6 ppm or less [4].

In this work estimates of the energy consumption and the fixed capital costs of the production of NaCl, either via the antisolvent crystallisation of NaCl or via the antisolvent crystallisation of $\text{NaCl} \cdot 2\text{H}_2\text{O}$ and a recrystallisation step, are presented concisely and compared with the conventional four effect evaporative crystallisation process. Detailed information on the designs and costs estimations can be found in [5].

2. The Diisopropylamine- H_2O -NaCl System

Liquid-liquid and solid-liquid equilibrium experiments demonstrated that the amine diisopropylamine is a suitable antisolvent for the crystallisation of NaCl. It reduces the sodium chloride solubility significantly and forms a two liquid phase area with brine close to room temperature.

The $\text{NaCl} \cdot 2\text{H}_2\text{O}$ solubility in mixtures of DiPA and water is plotted in Figure 1. In the solubility plot, also solubilities measured by Weingaertner et al. (1988) are displayed. These values, that were determined in the temperature range of -12.5 to -3.9 °C fall approximately on the same line as the solubilities measured at a constant temperature of -12 °C [5]. This demonstrates the fact that the solubility of the salt in DiPA-water mixtures is only a weak function of temperature and is mainly determined by the DiPA concentration.

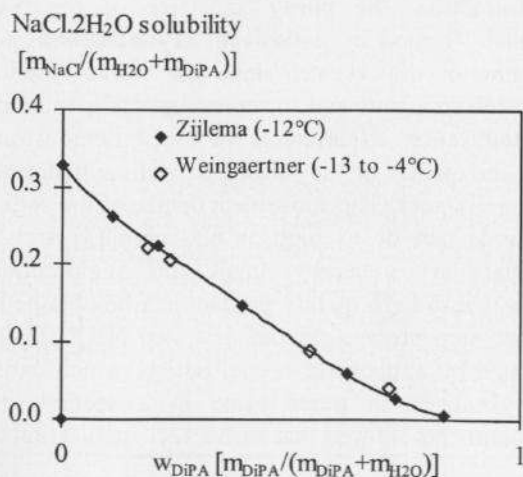


Figure 1. Solubility of $\text{NaCl} \cdot 2\text{H}_2\text{O}$ in DiPA- H_2O .

In Figure 2 the two-phase envelopes of the binary DiPA- H_2O mixture and the ternary DiPA- H_2O mixture saturated with NaCl are displayed. The lower critical solution temperature (LCST) of DiPA- H_2O was estimated at 27 °C. Below this temperature there is one single liquid phase present regardless of the concentration of the amine. The LCST as well as the mutual solubilities of the DiPA and the water in the two liquid phase area, decrease in the presence of sodium chloride. The LCST of the DiPA- H_2O system saturated with NaCl was estimated to be -11.7 °C.

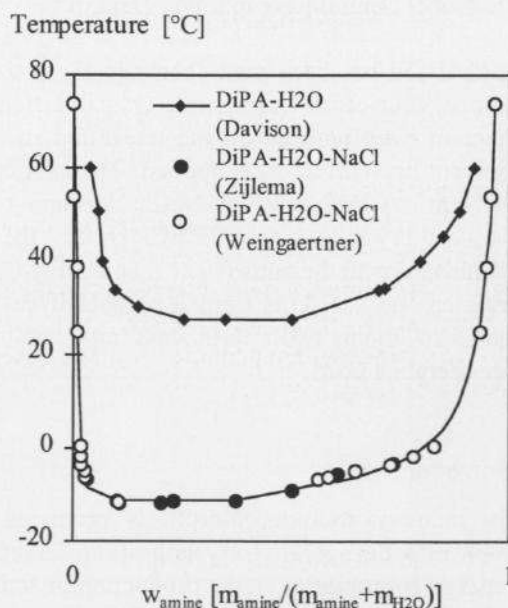


Figure 2. Liquid-liquid equilibria of the binary DiPA- H_2O system [2] and the DiPA- H_2O system saturated with NaCl [1,3].

The experimentally determined enthalpies of mixing of DiPA- H_2O mixtures are presented in Figure 3. All measurements were carried out in the single liquid phase area at temperatures varying between 272 - 298 K. The results demonstrate that the mixing process is strongly exothermic, indicating that the amine-water interactions are strong compared to the water-water and amine-amine interactions.

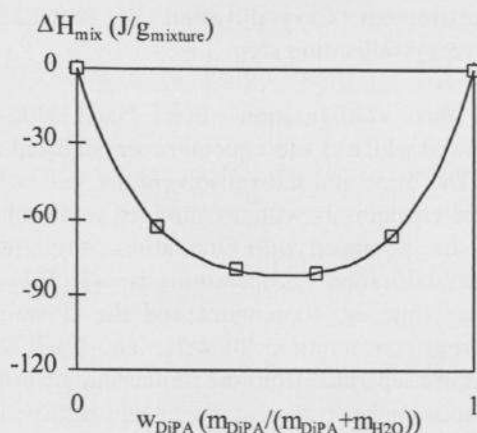


Figure 3. Enthalpies of mixing of DiPA-H₂O.

3. Process Configurations

Two different process configurations for the production of sodium chloride by antisolvent crystallisation have been investigated. One is to crystallise NaCl directly by adding the antisolvent to the brine at a temperature above the NaCl-NaCl·2H₂O transition temperature. A block scheme for this option is displayed in Figure 4.

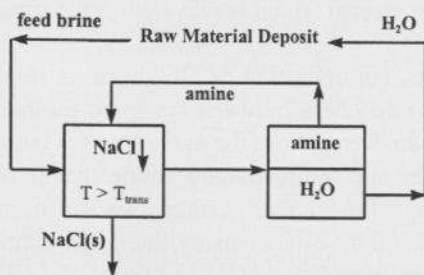


Figure 4. The antisolvent crystallisation of NaCl.

The saturated brine from the raw material deposit is mixed with the amine in the crystalliser. The salt is separated from the spent mother liquor and the antisolvent is recovered by a temperature induced liquid-liquid phase separation. Traces of the amine that remain in the aqueous phase after the liquid-liquid phase separation are removed by extraction (not indicated in Figure 4). The recovered antisolvent and water can be reused. The second option is to crystallise NaCl·2H₂O by antisolvent crystallisation and a consecutive recrystallisation step (Figure 5).

The crystallisation is preferably carried out at amine concentrations exceeding 75 wt%. Under these conditions the NaCl solubility is very low and consequently high yields can be obtained. A disadvantage of crystallising at high antisolvent concentrations is however, that the NaCl concentration in the spent mother liquor will be very low resulting in increased mutual solubilities of the amine and the water in the two liquid phase area. Therefore the liquid-liquid phase separation temperature needs to be high in order to get a good separation between the amine and the water, resulting in a large temperature difference between the crystallisation and the antisolvent recovery sections within the process. This is unfavourable, because an extensive heat exchanger network will be required to heat the spent mother liquor to the antisolvent recovery temperature and to cool the recovered antisolvent to the crystallisation temperature.

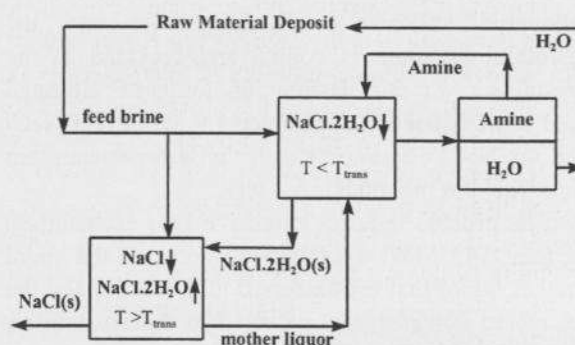


Figure 5. The antisolvent crystallisation of NaCl·2H₂O and a consecutive recrystallisation step.

4. Flow Sheet Design

Flow sheets have been designed for 1 Mton/year salt production plants. Since the raw brine purification will essentially be the same as in the evaporative crystallisation process it has been omitted. The required electricity and steam in the processes can be obtained from an on-site integrated steam power plant.

4.1 Direct Antisolvent Crystallisation of NaCl

Saturated brine from the mine and antisolvent are fed to the crystallisation section consisting of four identical crystallisers with a combined total volume of 970 m³. The crystallisers are equipped with circulation refrigerators, which serve to remove the enthalpies of mixing and crystallisation. The crystalliser antisolvent concentration is 80 wt%, the temperature 0.3 °C and the residence time 100 minutes. The crystalliser suspension is fed to two continuous pusher type centrifuges. The remaining mother liquor is heated to a temperature of 74 °C, which is well above the critical temperature of the system, and fed to a settler with a surface area of 360 m². The DiPA is removed from the aqueous phase by extraction with octane in five rotating disc contactors of 11 meter in length and 4.0 meter in diameter. The resulting octane - DiPA mixture is then distilled in a 54-stage distillation column of 27 meter in length with a diameter of 3.4 meter. The recovered antisolvent of the settler and the distillation column is cooled and recycled to the crystalliser. In this design 566 ton/h of saturated feed brine is needed to produce 1.0 Mton/year NaCl and the NaCl concentration in the water stream that is recycled to the mine is 6.4 wt%.

The process requires extensive heat exchanging. In total 143 MW is exchanged between the spent mother liquor that is transferred to the settler and the recovered amine that is recycled to the crystalliser. This corresponds with ca. 29000 m² of heat exchanger area with a temperature difference of 5 °C at both ends. This is by far the largest contribution to the total amount of heat exchanger area required. The area can be reduced to ca. 20000 m² by increasing the mean temperature difference to 7 °C. In addition to this 46 or 48 MW has to be removed in refrigerators using NH₃ as the coolant. The heat produced in the condensers of the refrigerators can be used in a heat pump to heat the settler feed to 74 °C. This however, requires additional investments. Alternatively steam can be applied for this purpose, which will, however, raise the energy costs.

4.2 Antisolvent Crystallisation of NaCl.2H₂O and a recrystallisation step

In this configuration first NaCl.2H₂O is crystallised which is subsequently recrystallised into NaCl. The brine and the antisolvent are fed to four identical crystallisers with a combined total volume of 820 m³, equipped with circulation refrigerators. The crystallisation temperature is -5 °C, the residence time ca. 40 minutes and the crystalliser antisolvent concentration 80 wt%. The NaCl.2H₂O crystals are separated from the mother liquor in four continuous pusher type centrifuges and resuspended in fresh feed brine. The recrystallisation takes place in a single 150 m³ crystalliser at a temperature of 0.5 °C. The residence time here is ca. 20 minutes. The NaCl crystals are separated from the mother liquor in two continuous pusher type centrifuges. The remaining mother liquor is transferred to the antisolvent crystalliser. The spent mother liquor from the antisolvent crystalliser is treated in the same way as in the direct antisolvent crystallisation of NaCl in almost identically sized equipment. Again 566 ton/h saturated feed brine is needed to produce 1 Mton/year and the NaCl concentration in the water stream which is recycled to the mine is 6.2 wt%.

In this configuration ca. 26000 m² is required to exchange 135 MW between the spent mother liquor that is transferred from the antisolvent crystalliser to the settler and the recovered amine that is recycled to the crystalliser. This surface area can be reduced to ca. 18000 m² by increasing the mean temperature difference from 5 to 7 °C. In addition 55 MW has to be removed in refrigerators using NH₃ as the coolant.

5. Costs Estimation

The costs of the major equipment items of the antisolvent crystallisation processes have been calculated by estimating the total delivered costs (or FOB costs) of the major equipment items with the help of various cost databases. From the delivered costs the fixed capital costs were calculated by using a Lang factor of 4 (fixed capital = Lang factor · delivered costs). These fixed capital costs of the major equipment items are given in Table 1 (route I corresponds to the direct formation of NaCl and

route II to the formation of $\text{NaCl} \cdot 2\text{H}_2\text{O}$ followed by a recrystallisation).

Table 1
FOB costs ($\cdot 10^3$ USD) of the major equipment items.

Item	route I	route II
Crystallisers	1754	1772
Centrifuges	211	635
Hydrocyclones	365	187
Settler	837	753
Distillation Column	478	469
Extraction Column	3686	3585
Total	7331	7401

An item not covered in Table 1 are the costs involved in the exchange of heat. Several heat exchanging configurations have been investigated; i.e. different mean temperature differences between the exchanging streams from and to the antisolvent crystalliser and heat pump or steam based heating of the settler feeds. The consequences of these options for the costs of heat exchange equipment are given in Table 2.

Table 2
FOB costs ($\cdot 10^3$ USD) of heat exchange equipment.

Configuration	route I	Route II
Heat pump, $\Delta T = 5^\circ\text{C}$	31937	36158
Heat Pump, $\Delta T = 7^\circ\text{C}$	29956	32897
Steam, $\Delta T = 5^\circ\text{C}$	23821	25023
Steam, $\Delta T = 7^\circ\text{C}$	19411	21547

With an estimated fixed capital costs of $5 \cdot 10^6$ USD for the brine purification section, the costs of the utilities DiPA and octane of $5 \cdot 10^6$ USD and the figures listed in Tables 1 and 2, the total fixed capital costs were calculated (Table 3). With a fractional discount rate (or cost of capital) of 10%, 15% of the total fixed capital has to be recovered

yearly in order to earn back the investment made at the start of the project in a period of 10 years time (the capital charges). For comparison also the investments and energy costs for a conventional four effect evaporative process are given [7].

6. Discussion

The costs estimations show that, irrespective of the selected process route, the production costs in evaporative crystallisation are still cheaper. This is mainly due to the higher fixed capital costs of the antisolvent crystallisation processes. However, the calculations demonstrate that the direct antisolvent crystallisation of NaCl is only 9 to 20% more expensive than evaporative crystallisation. This is encouraging. Therefore, when taking into account the limited accuracy of cost estimations performed at this stage of a project, there is a need for more accurate estimations of the fixed capital costs.

There are several possibilities to reduce the fixed capital costs in antisolvent crystallisation:

- By reducing the temperature difference between the crystallisation and antisolvent recovery sections of the process by using a different antisolvent or by applying different or additional separation methods for the recovery of the antisolvent.
- A reduction in the FOB costs of the heat exchange equipment, by for instance replacing shell and tube type heat exchangers by more efficient types of heat exchangers, could significantly reduce the total fixed capital costs.

An important disadvantage of the antisolvent crystallisation process is that it requires the presence of large quantities of an organic substance that can be flammable, toxic, chemically instable in a closed loop process and environmentally polluting.

An advantage is that the process is carried out at atmospheric pressure, whereas in the evaporative crystallisation of NaCl water is evaporated at pressures below atmospheric pressure in three of the four effects [8].

Furthermore, an advantage of evaporative crystallisation is that the NaCl yield generally approaches 100 % since practically all the water is evaporated from the feed brine. In antisolvent crystallisation a yield of 100 % is undesired, since the absence of dissolved NaCl in the spent mother

Table 3

Costs involved in the production of NaCl by antisolvent or evaporative crystallisation for a 1 Mton/year plant.

process route	antisolvent recovery	ΔT_m (°C)	fixed capital ($\cdot 10^6$ USD)	capital charge (USD/ton)	energy costs (USD/ton)	major operating costs (USD/ton)
AS crystallisation NaCl	heat pump	5	167	24.7	8.2	32.9
		7	160	23.7	9.4	33.1
	steam	5	135	20.0	10.7	30.7
		7	117	17.3	12.7	30.0
AS crystallisation NaCl.2H ₂ O and Recrystallisation	heat pump	5	185	27.4	10.5	37.9
		7	172	25.4	11.0	36.4
	steam	5	140	20.7	14.4	35.1
		7	126	18.6	15.2	33.8
evap. cryst. NaCl	-	-	108	16.0	11.5	27.5

liquor increases the mutual solubilities of the antisolvent and the water at the antisolvent recovery conditions, giving rise to extremely large recycles of relatively wet antisolvent.

An advantage of the antisolvent crystallisation process could be that it contains a large bleed stream, i.e. the aqueous phase from the antisolvent recovery that is recycled to the raw material deposit. The presence of this bleed limits the build up of the impurities SO_4^{2-} , Ca^{2+} and Br^- in the system, and probably reduces the uptake of these impurities in the salt product.

Another important factor with respect to impurities is the uptake of antisolvent in the product. One of the major disadvantages of DiPA is the fact that it contains nitrogen. In order to avoid the formation of NCl_3 during electrolysis, the maximum allowable DiPA concentration is in the ppm range. Non nitrogen containing antisolvents such as alcohols or ethers would be more acceptable as an impurity.

7. Conclusions

Calculations demonstrated that energy costs in the production of sodium chloride can be reduced by 29% if antisolvent crystallisation is applied. The estimated fixed capital costs, which are dominated by the costs involved in heat exchange, are 8 to 55% higher for the direct antisolvent crystallisation of NaCl depending on the used process configuration.

A disadvantage of the direct antisolvent crystallisation of NaCl is that the crystals are generally small, tend to agglomerate and are contaminated with the antisolvent. Large and pure

NaCl crystals can be produced at the expense of increased major operating costs, if $\text{NaCl} \cdot 2\text{H}_2\text{O}$ is formed by antisolvent crystallisation, which can be recrystallised in purer brine.

8. Acknowledgements

The authors would like to acknowledge Novem BV and Akzo Nobel for their support.

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