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Eutectic freeze crystallization from the ternary $\text{Na}_2\text{CO}_3\text{--NaHCO}_3\text{--H}_2\text{O}$ system

A novel scraped wall crystallizer for the recovery of soda from an industrial aqueous stream

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A B S T R A C T

Eutectic freeze crystallization was tested in a scaled up version of a scraped cooled wall crystallizer on an industrial aqueous sodium carbonate–sodium bicarbonate waste stream containing traces of molybdenum. A heat transfer rate of 5 kW m^{-2} was maintained in the crystallizer. Sodium carbonate decahydrate with molybdenum content below 1 ppm and pure ice were produced by continuous crystallization at -3.8°C by operating within the metastable zone width of bicarbonate. At -4.0°C bicarbonate started to co-crystallize. The bimodal size distribution of the mixture resulted in poor filtration and purity of the salt product.

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1. Introduction

One of the common petrochemical industrial waste streams is a dilute aqueous stream containing carbonate, bicarbonate and various trace impurities. Such streams are normally acid treated to neutralise the carbonates, and are disposed after further purification. An example of such a waste stream is the incinerator stream from AVR industries. The current treatment of this incinerator stream starts by neutralisation with sulphuric acid followed by adsorption of sodium molybdate on an ion exchange column. The resulting sodium sulphate solution is discarded into the environment and the molybdenum is recovered as a concentrated sodium molybdate solution by desorption with caustic.

An alternative route to treat these carbonate containing streams is by the cooling crystallization process of eutectic freeze crystallization (EFC). Example of development of an eutectic freeze process can be found in Stepakoff et al. (1974).

The operating conditions of the EFC process are chosen in such a way that ice and salt are crystallized simultaneously. Due to the difference in density between salt, ice and mother liquor, ice floats to the top and salt settles at the bottom of the crystallizer. The unit operations of crystallization and separation are thus combined in one piece of equipment. The advantages of EFC over the current treatment are that acid dosage is no longer required, and that pure ice and carbonate salts are obtained as valuable products. The impurities present at ppm levels in the feed stream can be recovered more easily from the bleed stream after concentration by the EFC process.

In this paper the recovery of carbonate salts from an aqueous solution containing sodium carbonate, sodium bicarbonate and trace impurities by a continuous EFC process is described. The performance of a scaled up version of a new type of EFC crystallizer under realistic process conditions at AVR industries is reported. Details of the crystallizer design are reported elsewhere (Rodriguez Pascual et al., 2009).

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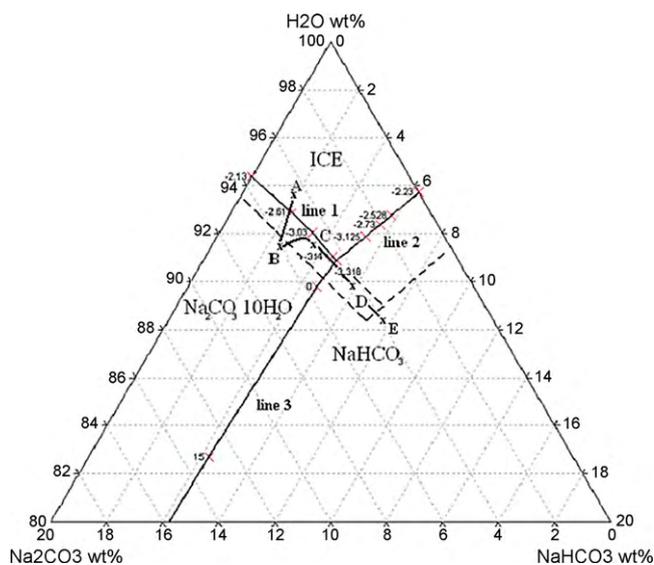


Fig. 1 – Projected ternary phase diagram of sodium bicarbonate, sodium carbonate and water with the three eutectic solubility lines.

2. Methods and materials

2.1. Selection of the process conditions

For selection of the process conditions where ice and either soda, bicarbonate or a mixture of the two are formed, an accurate ternary sodium bicarbonate–sodium carbonate–water phase diagram is needed. The relevant part of this phase diagram is given in Fig. 1 (Rodríguez Pascual et al., 2009).

The three eutectic solubility lines in this ternary phase diagram projected along the temperature axis, represent the conditions where two solid phases are in equilibrium with the solution. The eutectic temperature of sodium bicarbonate, ice and pure sodium bicarbonate solution lies at -2.23°C , the eutectic temperature of sodium carbonate decahydrate, ice and pure sodium carbonate solution at -2.1°C . The third three-phase line of solid bicarbonate, solid sodium carbonate decahydrate in a pure sodium carbonate–sodium bicarbonate containing solution is depicted from -3.318°C to 20°C .

The three eutectic phase lines meet in the quadruple point at -3.318°C , where sodium bicarbonate, sodium carbonate decahydrate, ice and a sodium bicarbonate–sodium carbonate containing solution are in equilibrium.

In a batch EFC process the AVR industrial solution is first cooled down from point A producing ice, and after trespassing the metastable region (point B) soda is produced. Because heat of crystallization is released and supersaturation is consumed, the solution composition and temperature will go to a point close to the solubility line-1 (point C). Upon further decrease in temperature the solution composition closely follows the two phase line-1. As long as no bicarbonate is formed, the crystallization of only soda can be continued within the metastable zone of the bicarbonate (point D). By working in this region the production of soda and ice can be increased substantially. If the metastable region is trespassed (point E) bicarbonate crystallizes, and the solution approaches the quadruple point and a mixture of bicarbonate and soda settles with a low filterability and low added value. Although working in this metastable region includes a risk because of the potential crys-

tallization of bicarbonate, it can be controlled. If the solution starts to become milky due to the formation of bicarbonate crystals the feed flow is increased without stopping the continuous process. By increasing the feed flow the concentration of bicarbonate decreases and the total composition returns to point C where only soda and ice are produced. Once the bicarbonate has been washed out of the system via the salt outlet, the process can be brought back to the maximum production point D. For streams rich in sodium bicarbonate EFC can be performed at a point on the sodium bicarbonate–ice line resulting in the crystallization of sodium bicarbonate and ice.

2.2. Scaled up version of the SCWC-2

Important criteria for the design of an EFC crystallizer are a high heat transfer rate, a low torsion force on the shaft exerted by the scrapers and stable operation over a prolonged period of time. The total heat transfer rules the production rate and should be as high as possible to keep the installation sufficiently small. In-line measurement of torque and heat transfer rate during the process indicate if a not removable ice scale layer starts to form on the heat exchanging surface. This allows remaining in a safe operating region under the selected process conditions.

A scaled up version of the SCWC-2 prototype was needed to achieve the high production rates of ice and soda from the industrial AVR stream (Fig. 2). The prototype can easily be scaled up by stacking more heat exchanger (HE) modules on top of each other. By doing this the necessary torque to drive the scrapers and the size of the crystallizer remain acceptable. In our case two HE modules sufficed, each consisting of two vertical concentric cylinders that are scraped from both sides. This crystallizer has a volume of 180 l and an outside

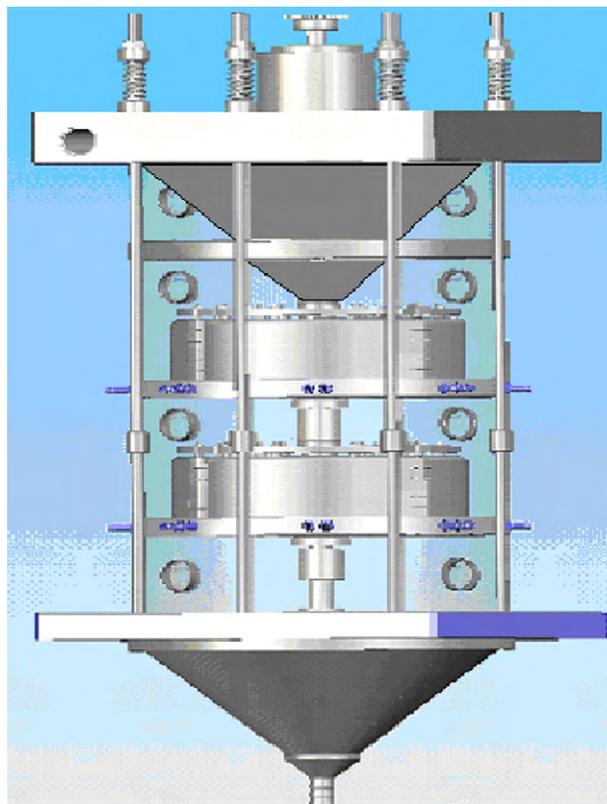


Fig. 2 – Scaled up version of the SCWC-2 with two HE modules.

wall made of transparent PMMA with a total HE surface area of 0.76 m².

In this scaled up version the gravitational ice and salt separation is also not hampered due to the sufficiently large gap between the HE cylinders. To better control the prevention of ice scaling the temperature of the inner and outer cylinder can be controlled independently.

The gap between the HE modules allows the radial separation of ice and salt crystals, which facilitates their gravitational separation. It also improves mixing in the middle section of the crystallizer and flattens the radial temperature profile.

Based upon experience with previous models much attention was paid to the unhampered transport of ice from the crystallizer (Van der Ham et al., 2004; Gencelli et al., 2005). At the top of the crystallizer a conically shaped plastic cylinder is fixed to the rotating shaft. This cone directs the ice layer at the top part of the crystallizer towards the exit pipe. The conical shape of the bottom of the crystallizer prevents building up of salt at the bottom.

2.3. Pilot plant

The flow sheet of the transportable pilot plant is presented in Fig. 3. The incinerator stream (BD) enters a 500l buffer tank, from which the carbonate containing solution is pumped into the crystallizer with a membrane pump. For all other process streams Watson Marlow peristaltic pumps are used because of their high accuracy, reliability and good performance with slurries. The flow rates of the process streams and of the cooling liquid are measured with an accuracy of ± 0.25 l/h by magnetic flow transmitters manufactured by Rosemount Fisher. Before entering the crystallizer the solution is pre-cooled in a plate heat exchanger from Alfa Laval with a 6.6 m² surface area. The cooling machine has a 10 kW cooling capacity at 0 °C, uses freezium (43% potassium formate in water) as a coolant and was supplied by Tamson Instruments B.V. The temperature of the cooling liquid was controlled with an accuracy of 0.1–0.5%. The temperatures of all streams as well as the temperature within the crystallizer and in the separator are measured with an accuracy of ± 0.01 °C by PT-100 sensors connected to an ASL F250 precision thermometer with a resolution of ± 0.001 °C. The separator has a volume of 120l. The belt filters for the salt and the ice were supplied by Larox-Pannevis and have a surface area of 0.75 m² and 2.25 m² respectively. In order to prevent cold losses into the environment all equipment is well isolated. For automatic data acquisition a Rosemount Delta-V system was used.

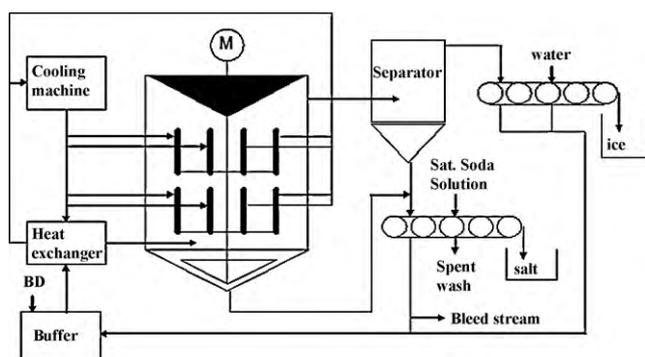


Fig. 3 – Flow sheet of the pilot used at AVR.

2.4. Experimental procedure

Under continuous operation the buffer tank is fed with the BD stream, with the recycled filtrate and with the wash liquor from the belt filters. The flow from the buffer tank to the crystallizer is cooled to a temperature close to the operating temperature in the crystallizer. The slurry in the crystallizer is cooled by the heat flux through the vertical heat exchangers.

The overflow of the crystallizer consists of ice slurry with minor amounts of the salt and is pumped to the separator. The overflow of the separator consisting of ice slurry is pumped to the ice belt filter. On the belt filter the ice is filtered and washed with cold water. The bottom flow of the crystallizer is combined with the bottom flow from the separator and pumped to the salt belt filter. On this filter the salt, that depending on the operating temperature is either sodium carbonate decahydrate or a mixture of sodium carbonate decahydrate and sodium bicarbonate, is filtered and washed with a saturated sodium carbonate solution. The spent wash solution was kept apart and not recycled into the process. After each residence time samples were taken from all process streams. Ice slurry samples taken before the belt filter were filtered over a cooled glass filter, and part of the ice crystals were washed with cold water. Salt slurries before the belt filter were filtered over a glass filter, and part of the salt crystals was washed with saturated soda solution. Ice/salt slurries samples from the middle of the crystallizer were separated in a cooled separation funnel and filtered to measure the salt, ice and solution percentages. The samples were analysed by ICP-AES and by ion chromatography. The carbonate–bicarbonate content of salt, ice and solutions were determined by titration. Scanning electron microscope pictures of the sodium decahydrate, sodium bicarbonate and mixed product were taken.

3. Results and discussion

3.1. Crystallizer performance

The main limitation on the heat transfer rate of a scraped wall crystallizer is the maximum temperature difference that can be applied between the cooling plates and the solution before excessive ice scaling occurs. The maximum temperature difference between solution and heat exchanger surface without the formation of an ice scaling layer on the heat exchanger depends mainly on the type and concentration of the ions in solution, and is difficult to predict even for pure systems (Vaessen et al., 2002; Pronk et al., 2006). The presence of a non-crystallizing solute can affect the water activity and consequently the freezing point of ice, having a positive effect on the maximum temperature difference that can be applied. In this case the non-crystallizing bicarbonate helps to achieve a higher temperature difference. A preliminary EFC experiment showed that at a temperature difference of 8 °C and a heat transfer rate of 7 kW m⁻² over 3 h runtime, the torque on the axis of the crystallizer increased above the upper limit of 200 N m. So for the experiments at AVR a temperature difference of 6 °C resulting in a heat transfer rate of 5 kW m⁻² was chosen.

The heat transfer rate was calculated from the temperature difference over the cooling plates and the coolant flow through the cooling plates. For all experiments at AVR (runtime up to 10 h) the torque on the crystallizer axis and the heat transfer rate indicated that no excessive scaling took place. A heat transfer of 5 kW m⁻² was maintained in the experiments.

Table 1 – Experimental operating conditions.

Experiment no.	1	2
Crystallizer (200l)		
Flow from buffer (l/h)	200	200
Temperature (°C)	−3.8	−3.8
Heat transfer rate (kW m ^{−2})	5	5
Bottom flow to BF salt (l/h)	50	50
Overflow to separator (l/h)	150	150
Residence time (h)	1	1
Ice production rate (kg/h)	30	30
Salt production rate (kg/h)	2.5	2.5
Separator (120l)		
Flow from crystallizer (l/h)	150	150
Bottom flow to BF salt (l/h)	60	60
Overflow to BF ice (l/h)	90	90
Temperature (°C)	−3.8	−3.8
Residence time (min)	48	43
Process in		
Flow BD into buffer (l/h)	35	35
Kluu Wiish wrtti iiro (l/h)	3	3
Process out		
Bleed stream (l/h)	16	16
Ice from belt filler (kg/h)	22	22
Salt from belt filter (kg/l)	1.5	2
Flow wash liquid salt (l/h)	2	2
Run time (h)	5	5
Salt product (kg)	5.8	6.7
Sodium carbonate (%)	37	36.7
Sodium bicarbonate (%)	0.8	0.2
Molybdenum (ppm)	13	64

Table 2 – Na₂CO₃ and NaHCO₃ concentrations in the process solutions.

	Na ₂ CO ₃ (wt%)	NaHCO ₃ (wt%)
Experiment 1		
BD stream	4.1	41
Feed solution	4.2	5.5
Crystallizer solution	4.3	5.5
Experiment 2		
BD stream	4.6	4.4
Feed solution	44	5.8
Crystallizer solution	5.0	5.7

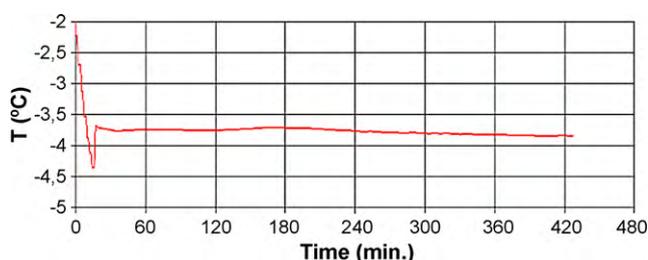
**Fig. 5 – Na₂CO₃·10H₂O product after washing.**

3.2. Process characteristics

Two types of experiments were carried out, one where ice and sodium carbonate decahydrate were produced and a second type where ice, and a mixture of sodium carbonate decahydrate and sodium bicarbonate were produced.

The BD stream from AVR entered the buffer tank at 35 l/h with a concentration of about 4 wt% Na₂CO₃ and 4 wt% NaHCO₃. The solution from the buffer tank was fed into the crystallizer at 200 l/h and because of the recycling of process streams the concentration in the buffer tank was higher than that of the BD. The residence time of the feed solution in the crystallizer was 1 h and the production rate was 30 kg/h for ice and 2.5 kg/h for salt in both experiments. The operating conditions during sodium carbonate decahydrate production are given in Table 1 and the crystallizer temperature during operation of experiment 2 is shown in Fig. 4.

The BD stream from AVR mainly contains Na₂CO₃ and NaHCO₃ with concentrations fluctuating between 2–4 wt% and 1–4 wt% respectively, and because of these variations a real steady state operation does not exist. As a result of that Table 2 presents the average concentrations of the BD, feed and crys-

**Fig. 4 – Temperature in the crystallizer during operation.**

tallizer solutions after five residence times of two experiments where only sodium carbonate decahydrate was produced.

In both cases the temperature in the crystallizer was kept at −3.8 °C with an average solid content of 15 wt% (1.26 wt% Na₂CO₃·10H₂O and 14 wt% ice) in the crystallizer. So we are operating as explained above within the metastable bicarbonate region. The purity of the salt product was 99% with less than 1% of sodium bicarbonate. In the pilot plant the mother liquor was apparently not sufficiently washed out on the belt filters, which explained the high molybdenum content found in the salt after drying (Table 1). The same product washed in situ on more accurate lab scale equipment showed that the uptake of molybdenum in soda crystals was below 1 ppm. SEM pictures of the product are shown in Fig. 5. The ice product after washing was sufficiently pure to be recycled into the plant.

If the temperature in the crystallizer was decreased to −4 °C bicarbonate started to crystallize, and the system approached the quadruple point. The NaHCO₃ crystals are needles that fill up the voids between the large Na₂CO₃·10H₂O crystals, resulting in poor filtration properties. The product from the belt filter as shown in Fig. 6 consisted of 17 wt% NaHCO₃ and 50 wt% Na₂CO₃·10H₂O with 25 wt% mother liquor that contained 350 ppm molybdenum. In this figure the washed soda crystals are partially dissolved, while the bicarbonate needles kept their shape.

To avoid simultaneous crystallization of both salts the feed stream can be increased until point C in Fig. 1 is reached as explained above, and bicarbonate is washed out of the crystallizer.

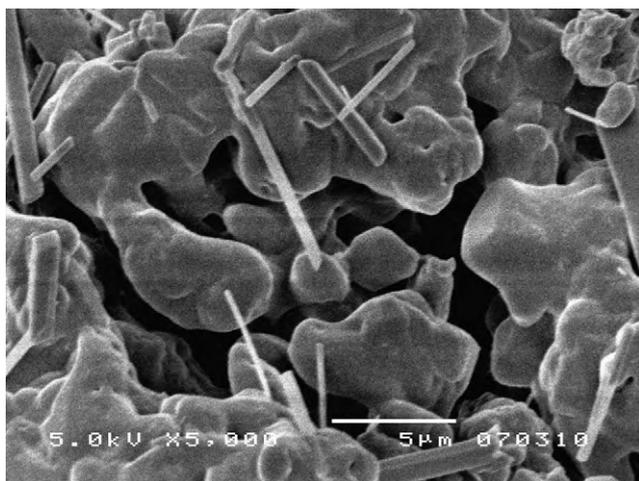


Fig. 6 – A mixture of the $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and NaHCO_3 after the belt filter.

4. Conclusions

Eutectic freeze crystallization (EFC) of carbonate–bicarbonate containing industrial (waste) streams is a promising new technology. The scaled up version of the SCWC-2 was successfully tested at AVR in a skid-mounted pilot plant that was connected to the carbonate containing blow down stream. The heat transfer inside the crystallizer was maintained at 5 kW m^{-2} . The in-line torque and heat transfer measurements in the crystallizer were effective in detecting early ice scale formation on the cooling surface of the heat exchangers leading to efficient control of the ice scraping process.

The ice product after washing was sufficiently pure to be recycled into the plant. Operating at -3.8°C within the metastable bicarbonate zone width resulted in sodium carbonate decahydrate as the sole product with good filtration

properties and a low molybdenum content. If the temperature was decreased to -4.0°C bicarbonate started to crystallize, and the system approached the quadruple point. The mixed sodium carbonate–sodium bicarbonate product had poor filtration properties due to a bimodal size distribution resulting in a high molybdenum content.

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