Evaporative Crystallization of Anhydrous Sodium Carbonate at Atmospheric Conditions

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A new process for the production of superdense anhydrous soda ash uses a mixture of water and a high-boiling second solvent to lower the transition point at which anhydrous (Na_2CO_3) and monohydrous sodium ($Na_2CO_3 \cdot H_2O$) carbonate are in equilibrium to below the atmospheric boiling point. The stable conditions for anhydrate were first established by measuring the water activity in saturated mixtures of water and ethylene glycol. With the results, fed-batch evaporative crystallization experiments were carried out. Both the water activity and the crystallization measurements showed that anhydrous soda was stable in boiling mixtures containing more than 22.5 wt. % ethylene glycol (on a salt-free basis). A subsequent continuous evaporative crystallization experiment produced anhydrous soda ash with a bulk density of 1,550 kg/m^3, which is substantially higher than that of any other atmospherically crystallized soda.

Introduction

Anhydrous soda ash (annual world production of about 35 million tons) is often produced from trona ore using the so-called monohydrate process. The trona or "sesquicarbonate" ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) is mined and crushed to form particles with an average diameter of 6 mm (Habashi, 1980) that are calcined at 300°C. This raw soda is dissolved in water and clarified to remove all insoluble material. The clear brine is then fed to the crystallization section which usually consists of a cascade of three evaporative crystallizers.

Because the crystallization of soda is carried out at atmospheric or subatmospheric pressures, the product from these evaporators is monohydrate. In order to remove the crystal water, the monohydrous product is treated in a second calciner that is usually operated at about 150°C. The product from this calciner is rather porous and has a bulk density of about 600 to 800 kg/m^3, depending on the amount of water that is fed to the calciner together with the monohydrate. Often, the "monohydration" process is applied to increase the bulk density to approximately 1,000 kg/m^3 (which is still much lower than the crystal density of 2,533 kg/m^3). The difference between so-called light and dense soda ash can easily be distinguished in Figures 1 and 2.

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This article describes an alternative new process where a water-miscible organic (anti)solvent is added during evaporative crystallization to produce anhydrous sodium carbonate at atmospheric pressure. The antisolvent used is ethylene glycol. First, the conditions are established at which anhydrous soda is expected to be formed. Then, fed-batch evaporative crystallization experiments are performed to establish the feasibility of the new process.

Figure 3 is shown in order to clearly distinguish between the monohydrate process and the proposed so-called "mixed-solvent" process. Starting with trona as raw material, the high-density soda product can be obtained using either one of the two processes. After calcining of the trona and dissolution of the raw soda (which is the same for each of the processes), the monohydrate process can be used, resulting in the production of monohydrous soda. The monohydrous product then has to be calcined and subjected to the so-called monohydration process in order to obtain the desired product. Application of a mixed solvent in the alternative route gains anhydrous soda in a one-step evaporative crystallization process. From Figure 3, it can be seen that the use of this process leads to the removal of the second calciner from the flowsheet! Since this step requires a large energy input, the proposed process might provide an energy-saving alternative to the conventional option.

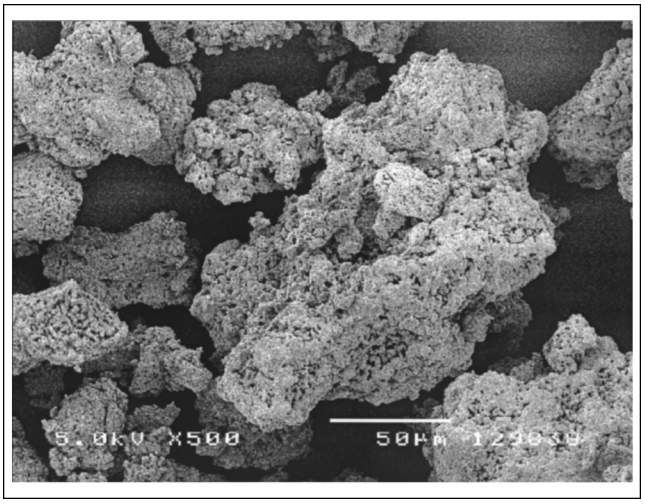

Figure 1. Light soda ash with a bulk density of about 550 kg/m^3.

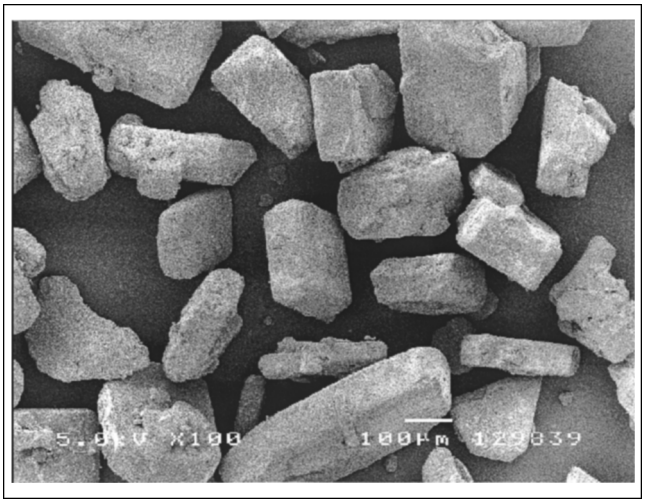

Figure 2. Dense soda ash that has been subjected to a densification step in a calciner with a bulk density of 1,050 kg/m^3.

Finally, note that this new process might be a valuable alternative for the water-removal from hydrated products in energy-intensive calciners.

Anhydrate Stability

The stability of sodium carbonate anhydrate in mixtures of water and ethylene glycol has been discussed by Oosterhof et al. (2001). The transition curve that was constructed in this work is given once more in Figure 4. Furthermore, the vapor pressure data given in that article were used to calculate the boiling point of each mixture of water and glycol, using Clausius-Clapeyron

$$\ln(p) = a + \frac{b}{T} \quad \text{or} \quad T_{\text{boil}} = \frac{b}{\ln(1013) - a} \tag{1}$$

where p is the pressure in mbar and T is the temperature in Kelvin. In Figure 4, the atmospheric boiling points are also given as a function of the weight fraction glycol in the mixture. The influence of the antisolvent is obvious: the transi-

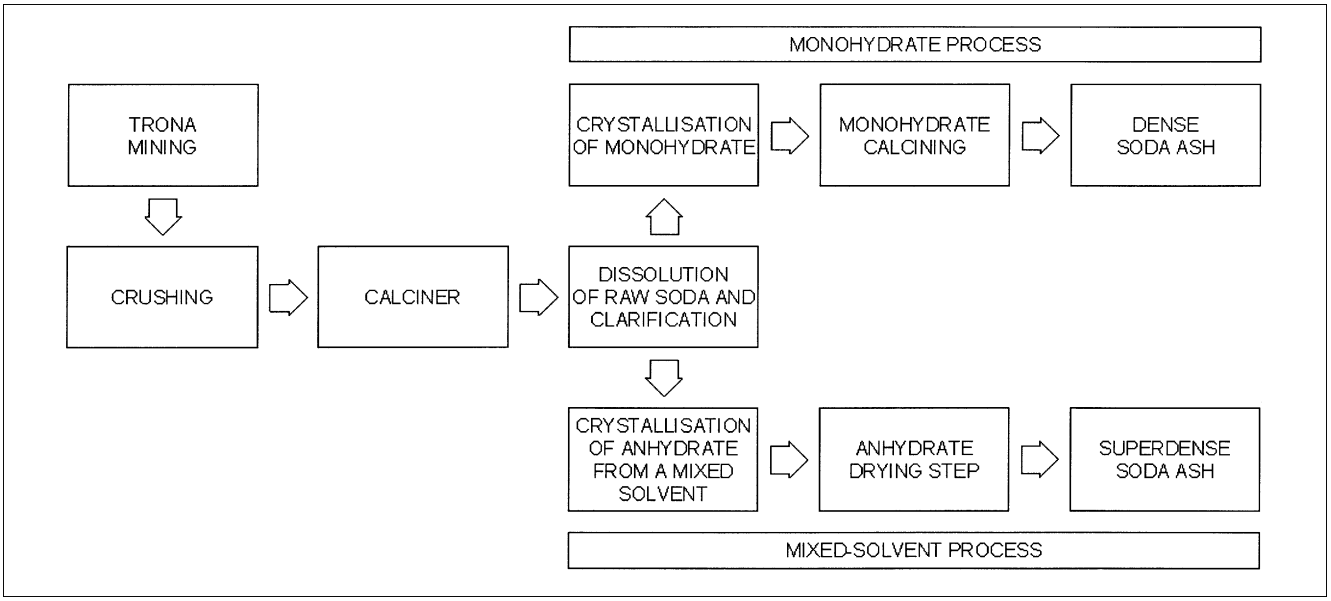

Figure 3. The monohydrate and the mixed solvent process.

Crushing, calcining and dissolution are the same for both options, but due to the direct crystallization of anhydrous soda in the new process (bottom), the second calcining step can be replaced by a drying step.

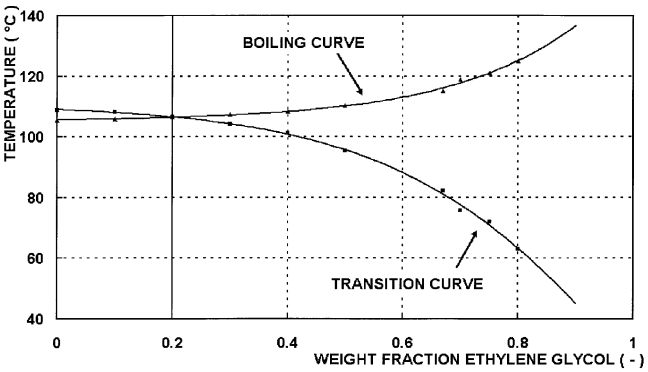

Figure 4. Transition and boiling temperature for aqueous mixtures of ethylene glycol, saturated with soda.

In mixtures containing more than 20 wt. % (salt-free) glycol, anhydrate is stable in the boiling solution. All markers are from vapor pressure measurements by Oosterhof et al., (2001), just as the calculated transition curve.

tion temperature is decreased, while the boiling point is increased (ethylene glycol has a boiling point of 198°C).

In an aqueous solution saturated with soda, the transition temperature is located above the boiling temperature of the solution: this is shown on the vertical axis in Figure 4 (109°C vs. 104.8°C). When a sufficient amount of glycol is added to the mixture, the transition temperature is lower than the boiling point. The minimum wt. % glycol needed is approximately 20 wt. %, according to Figure 4. This means that anhydrous soda (or AH) can be crystallized by means of evaporative crystallization when at least 20 wt. % glycol is present in the crystallizing mixture. Sodium carbonate monohydrate (or MH) will be produced if the solution contains less glycol.

It should be noticed, however, that the point of intersection of the two curves in Figure 4 is very sensitive with respect to the temperature: a small inaccuracy in the measured temperatures may result in a significant shift of the glycol concentration at which the curves cross.

Experimental Studies

It was the aim of the fed-batch experiments to grow crystals from a boiling solution that contained a carefully selected concentration antisolvent—in this case the nonvolatile compound ethylene glycol. All evaporative crystallization experiments were carried out in a jacketed 1.5 L stainless steel vessel that was heated with a Lauda C6 thermostat. It was assumed that only water evaporated and 18 wt. % soda brine was added to compensate for the evaporated water, thus ensuring a constant glycol concentration and a continuous addition of soda needed for growth of the (anhydrous) soda crystals. Distilled water, ethylene glycol (Merck, minimal 99% pure) and soda (Akzo Nobel dense soda ash, minimal 99% pure) were used.

Control

Both the crystallizer and the storage vessel (containing an 18 wt. % aqueous soda solution) are placed on balances. During the experiments, the readings of the balances are sent to the computer that compares the values and adjusts the speed of the pump to maintain a constant glycol concentration throughout the experiment.

The dosage controllers are used to monitor the change in weight on the balances. When both scales are tarred at the start of the experiment

$$m_C = 0 \quad \text{and} \quad m_S = 0 \tag{2}$$

in which m_C and m_S are the weights on the crystallizer and the storage scales (gram). Since only water evaporates from the crystallizer, the amount of water that needs to be added to maintain a constant glycol concentration can be calculated. However, the water that is added contains dissolved soda, which means that the value of m_C at equilibrium will increase during the experiment since the added soda remains in the crystallizer. When the brine in the storage vessel contains c° wt. % soda, the following relation can be used to describe when the crystallizer is at equilibrium, that is, when the glycol concentration is constant

$$m_C = -\frac{c^\circ}{100} \cdot m_S \tag{3}$$

When $m_C > -c^\circ/100 \cdot m_S$, not all added water has evaporated yet, but, when $m_C < -c^\circ/100 \cdot m_S$, too much water has already been removed. In the former case, the pump speed has to be decreased; in the latter case, it has to be increased.

Notice that Eq. 3 can only be applied when anhydrous soda is crystallized; if monohydrate is produced, water is removed from the solution by evaporation and crystallization. In this case, Eq. 3 is replaced by

$$m_C = -\frac{c^\circ}{100} \cdot \frac{M_{MH}}{M_{AH}} \cdot m_S \tag{4}$$

in which M_{MH} and M_{AH} are the molar weights of monohydrate (124 g/mol) and anhydrate (106 g/mol). Evaluation of the crystal product has to provide information whether the appropriate equation (3 or 4) has been used during the experiment.

Automation

Two Systag Midilab dosage controllers are connected to the process computer on which a copy of the process control software Fix/MMI is running. Each dosage controller is also connected to a scale. The dosage controller reads the weight that is on the balance and sends the data to the computer. The computer calculates the set point for the scale on which the crystallizer is placed using the value of the storage-vessel scale and compares it with the actual mass on the crystallizer-scale. The first dosage controller uses this information to adjust the pumping speed of the Watson Marlow 505Du peristaltic pump. This controller is also used to collect data from the Lauda C6 thermostat: the actual temperature in the crystallizer.

The Fix/MMI software acts as a graphical interface to the automated system: it is used to start and stop the experi-

Table 1. Fed-Batch Evaporative Crystallization Experiments*

x_{EG}	c^* (wt. %)	Water (g)	EG (g)	Na_2CO_3 (g)	T_{boil} (°C)	T_{trans} (°C)
0.0	30.0	1,500	0	643	105.7	109.1
5.0	26.9	1,425	75	552	105.9	108.7
10.0	24.1	1,350	150	475	106.0	108.2
15.0	21.5	1,275	225	411	106.3	107.5
20.0	19.1	1,200	300	355	106.5	106.7
25.0	17.0	1,125	375	308	106.8	105.7
30.0	15.1	1,050	450	267	107.2	104.4

*Estimated solubility at the boiling point, composition of the samples, and the boiling and transition temperature of the samples.

Table 2. Experiment: Solubility, Boiling Temperature and Amount of Crystal Water in the Product, with Calculated Transition Temperature for Samples

x_{EG}	c^* (wt. %)	Crystal Water (mol H_2O/mol Na_2CO_3)	T_{boil} (°C)	T_{trans} (°C)
0.00	30.9	2.83	104.8	109.1
0.05	28.6	0.85	105.0	108.7
0.10	27.1	1.23	105.4	108.2
0.15	24.8	0.93	105.4	107.5
0.20	25.1	1.53	106.2	106.7
0.25	20.5	0.70	106.2	105.7
0.30	19.3	0.55	106.8	104.4

ments, to enter data (like the wt. % soda in the brine and the PID parameters used for the control of the pump) and to collect experimental data: the masses on the balances, the crystallizer temperature, and the speed of the pump are logged continuously and stored in the program's database. Furthermore, all alarm messages from the system are depicted on the screen.

Evaporative crystallization experiments

Several crystallization experiments were carried out in mixtures with varying glycol concentrations, ranging from 0 to 30 wt. % at their respective atmospheric boiling points. All wt. % mentioned are on a salt-free basis. All experiments were carried out in duplicate.

At the start of each experiment, the thermostating oil was heated to 150°C. When this temperature was reached, the crystallizer was charged with 1500 g of solution (water and glycol) in which an amount of soda was dissolved (see Table 1) to reach saturation at the boiling temperature. This amount was based on the solubility concentration in the specified mixture at 90°C, which was the highest temperature at which solubility data are available (Oosterhof, 1999). Both balances were tarred and, when the crystallizer content had reached the boiling temperature, water was added to compensate for the evaporated water. Then, the experiment was started: the FIX/MMI software was started and 18 wt. % brine was added from the storage vessel to the crystallizer to replace the evaporated water.

During the experiment, the actual crystallizer temperature was measured with a calibrated pT100 thermometer to establish the exact boiling point of the solution with an accuracy of 0.1°C. The experiment was stopped when approximately 100 g of soda (anhydrous or monohydrous) was produced. A longer duration of the experiment might cause too much evaporation of the glycol, resulting in a lower value of x_{EG}. (Note that x_{EG} is defined as the mass of ethylene glycol, divided by the sum of the masses water and ethylene glycol.) Experimental vapor-liquid equilibrium data (Gmehling et al., 1988), however, report very low glycol concentrations in the vapor above binary water-glycol mixtures with comparable compositions and temperature: the vapor contains maximally 0.5 wt. % glycol. This means that, during the fed-batch experiment in which about 500 grams of water is evaporated, only 2.5 grams of glycol is removed from the crystallizer. At low glycol concentrations, this amount is even smaller, resulting in a negligible shift to lower values of x_{EG}.

At the end of each experiment, two samples of approximately 10 mL were taken from the crystallizer. The crystals were removed from the slurry, and the clear liquid was placed in an oven for 24 h (150°C) to evaporate all water and glycol. From the decrease in sample weight, the soda solubility at the solutions' boiling point was calculated. This solubility was used instead of the value mentioned in Table 1 during the duplicate experiments.

Another sample of about 250 mL was taken for analysis of the crystal product. It was filtrated and washed with ethanol and placed in a centrifuge to remove all adhering mother liquor. Part of the solid sample was placed in an oven at 150°C for 24 h. The amount of crystal water in the samples was calculated from the decrease in weight. Scanning electron microscopy (SEM) pictures were taken to study the morphology of the product; the difference between mono- and anhydrate is easily distinguished.

Results and Discussion

A total of 14 experiments was carried out in the fed-batch setup. All experimental results are given in Table 2. The measured solubilities, the boiling temperatures, and the stoichiometric amount of crystal water in the samples are averaged values.

Solubility

The measured solubilities are given in Table 2 and also in Figure 5. From the graph, it can be seen that, below $x_{EG} \approx 0.30$, the solubility of soda (mono- or anhydrous) is almost linearly dependent on the weight fraction glycol in the mixture. The accuracy of the measurements was found to be rather good: the standard deviations in the results were smaller than 0.4 wt. % and the experimental solubility of soda in pure water agreed well with the values from literature: 30.9 vs. 30.8 wt. %.

Boiling temperature

Figure 5 and Table 2 also contain the temperatures at which the crystallizing mixtures were boiling during the experiments. The boiling temperature was also found to be approximately linearly dependent on the weight fraction glycol in the mixture. These experimental data, however, indicate an intersection with the transition curve at a slightly higher weight fraction glycol, that is, at $x_{EG} \approx 0.225$ than the value of 0.20 in Figure 4.

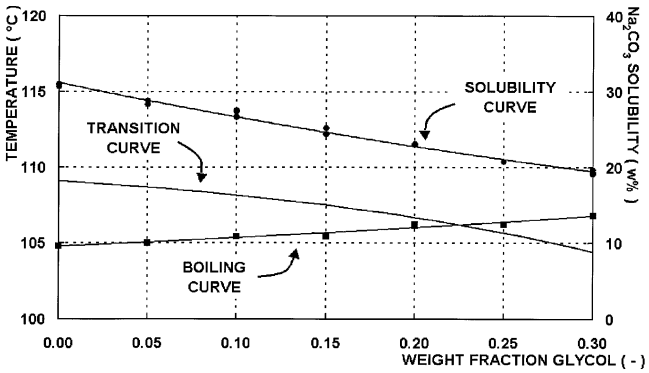

Figure 5. Experiment: measured boiling temperature, measured solubility of soda at boiling temperature, and calculated transition temperature as a function of the weight fraction ethylene glycol in the mother liquor.

Stable hydrate

Table 2 gives the average values for the stoichiometric amount of crystal water in the product of each experiment. Notice that the amount of crystal water in all samples is higher than expected; no clear distinction between anhydrous and monohydrous soda can therefore be made.

This inaccuracy is due to the fact that all crystals still contain adhering wash liquid when they are placed in the oven. Also, significant evaporation of water occurs when the slurry is filtered during sampling, resulting in the precipitation of monohydrate crystals since the solid-liquid separation is carried out at much lower temperatures. It is thus necessary to discriminate between both hydrates by means of visual observation.

SEM pictures

Three SEM photographs are shown in Figures 6, 7 and 8. The first picture (Figure 6) shows monohydrate that was crystallized from an aqueous solution. Elongated, monohydrous crystals can be distinguished.

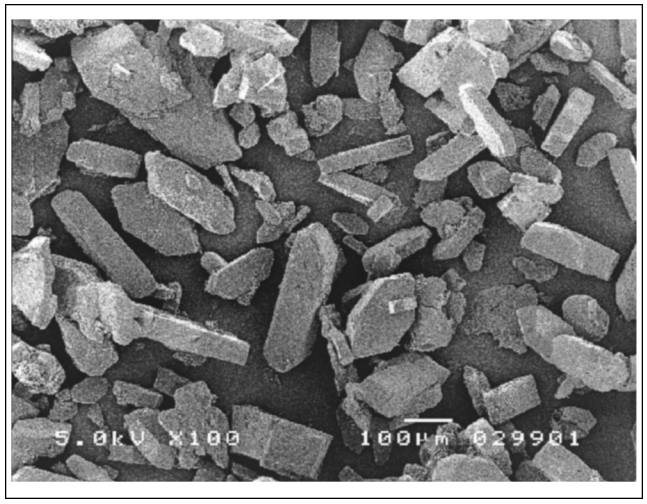

Figure 6. Monohydrous soda produced from an aqueous solution (without any ethylene glycol) at 104.8°C.

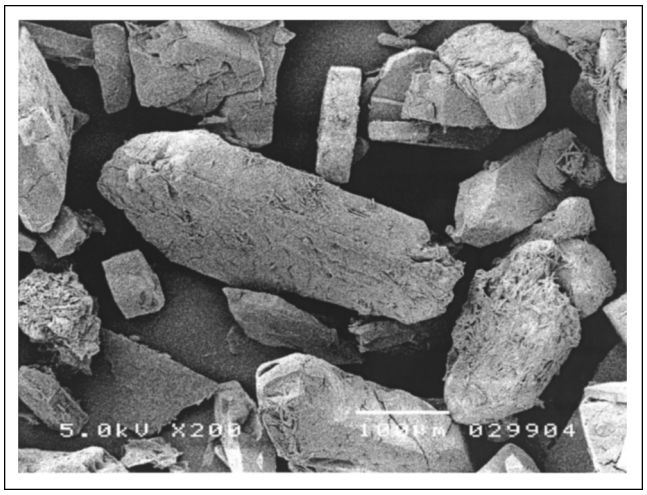

Figure 7. Monohydrous soda produced from an aqueous solution containing 5 wt. % ethylene glycol ($x_{EG} = 0.05$) at 105°C.

Similar crystals are observed in the SEM photograph in Figure 7. These crystals were crystallized from a mixture containing 5 wt. % glycol and dried at 150°C. The habit of the dry product is identical to that of the Figure 6. However, a closer look reveals the microporous structure of the crystals which is due to the removal of the crystal water from the product during the drying process.

This drying step, in the industrial monohydrate process usually performed in a calciner, is the cause of the low bulk density of the conventional soda ash.

The third SEM photograph in Figure 8 depicts anhydrous soda that was directly crystallized at atmospheric pressure

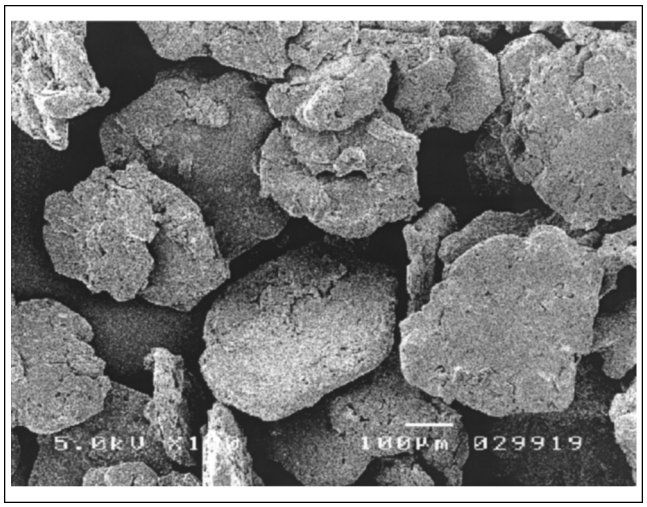

Figure 8. Anhydrous soda, produced from an aqueous solution containing 30 wt. % ethylene glycol ($x_{EG} = 0.30$) at 106.8°C.

Notice the obvious difference in morphology between these and the monohydrous crystals.

from a mixture containing 30 wt. % of glycol. During this evaporative crystallization experiment, anhydrate was stable because the transition temperature was located below the boiling point.

Further analysis of the SEM photographs revealed the anhydrous soda habit only in samples that were taken from mixtures with 25 and 30 wt. % glycol. During all other experiments, monohydrous soda was found to be crystallized. From the graph of 5, it can be seen that this is exactly what was expected: monohydrate is stable below $x_{EG} = 0.225$ and anhydrate above.

Conclusions regarding the fed-batch experiments

During the crystallization experiments, data were collected concerning the solubility of soda in mixtures of water and glycol, the boiling temperature of these mixtures, and the stable phase that was formed. From the experimental boiling temperatures and the calculated transition curve, the minimum glycol concentration to form anhydrate at atmospheric pressure was calculated to be 22.5 wt. % (on a salt-free basis).

It was not possible to determine which hydrate was stable from gravimetric analysis (or "weight loss"). However, from analysis of the SEM photographs, anhydrous soda was found to be stable in boiling mixtures with 25 and 30 wt. % glycol. Mixtures containing 20 wt. % or less glycol were found to contain monohydrate only.

Continuous Evaporative Crystallization

One final exploratory experiment was carried out to determine the quality of continuously crystallized anhydrate. A 2-L jacketed stainless steel vessel (with four baffles and an overflow outlet) was used. The reactor was heated with a Laude C6 thermostatic bath containing silicon oil. A mixture of water, ethylene glycol, and soda ($x_{EG} = 0.25$ and 16 wt. % dissolved soda) was added to the crystallizer with a flow rate of 45 g/min. Due to the high temperature of the silicon oil (150°C), water evaporated and soda crystallized. Stirring was provided with a Heidolph turbine stirrer (1,000 rpm, which was sufficient to keep the particles suspended).

The amount of water that evaporated was estimated by comparing the weight of the slurry that was collected from the overflow outlet with the feed to the reactor. Approximately 10 grams of water per minute were found to evaporate. From these data, a slurry residence time of 70 min and an anhydrate production of 3.7 g/min were calculated.

Slurry samples were taken from the outlet with 60-min intervals. After filtering and washing with methanol, the anhydrate was dried in an oven (24 h at 150°C).

In Figure 9 a SEM photograph of the sample that was taken from the crystallizer after five residence times is given. The size of the particles ranges from 50 to almost 500 μm. Rounded edges of the larger crystals show that the particles were prone to attrition. The smaller particles still have the hexagonal shape that is characteristic for anhydrate. Measurement of the weight loss on heating also showed that the product was anhydrous. Weighing of a carefully determined volume of crystals revealed a bulk density of 1,550 kg/m^3 which is very high, much higher than the values reported for commercially available soda. The product also had very good flowability.

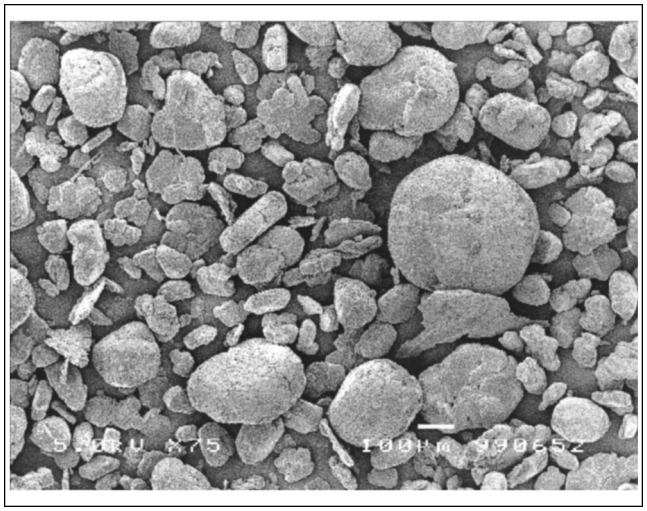

Figure 9. Continuously crystallized anhydrous soda ash with a bulk density of 1,550 kg/m^3.

Conclusions

Fed-batch evaporative crystallization experiments were carried out at ambient pressure in mixtures with varying glycol concentrations. At glycol concentrations of 25 and 30 wt. %, anhydrous soda was found to be stable; in mixtures containing 20 wt. % or less, glycol monohydrate was crystallized. These observations agreed well with the results from the calculated transition curve. The stable hydrate was determined visually from SEM photographs. An exploratory crystallization experiment showed that it is possible to produce anhydrous soda in a continuous mode with a very high bulk density of 1,550 kg/m^3, which is much higher than values reported for commercially available dense soda.

Literature Cited

Dutch Association of Cost Engineers, *Prijzenboekje*, 18th ed., Misset, Arnhem (1995).

Garrett, D. E., *Natural Soda Ash—Occurrences, Processing and Use,* Van Nostrand Reinhold, New York (1992).

Gmehling, J., U. Onken, and J. R. Rarey-Nies, "Vapor-Liquid Equilibrium Data Collection—Aqueous Systems (Suppl. 2), DECHEMA, Frankfurt, Germany (1988).

Habashi, F., *Handbook of Extractive Metallurgy, Vol. IV*, Wiley-VCH, Weinheim, Germany (1980).

Hall, R. S., J. Matley, and K. J. McNaughton, "Process Equipment," *Chem. Eng.*, **5**, 81 (1982).

Meijer, J. A. M., R. M. Geertman, H. Oosterhof, and G. J. Witkamp, "Production of Water-Free Soda," Patent Application No. 97204081.0-1218 (1997).

Oosterhof, H., G. J. Witkamp, and G. M. van Rosmalen, "Some Antisolvents for Crystallisation of Sodium Carbonate," *J. Fluid Phase Equil.*, **155**, 229 (1999).

Oosterhof, H., G. J. Witkamp, and G. M. van Rosmalen, "Antisolvent Crystallisation of Anhydrous Sodium Carbonate at Atmospheric Conditions," *AIChE J.,* in press (2001).

Perry, J. H., *Chemical Engineers' Handbook*, 7th ed., McGraw-Hill, New York (1997).

Rant, Z., *Die Erzeugung von Soda nach dem Solvayverfahren; eine Verfahrenstechnische Darstellung*, Enke, Stuttgart, Germany (1968).

Thomas, R., "Freight Market Report," *Int. Bulk J.*, **1**, 51 (1999).

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