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Comparison of Theoretical and Measured Composition of Brine During Salt Precipitation and Resulting Co-Crystals

C. Booth, V. Thoss, L. Jones, G. Tizzard, Bangor University

Comparison of theoretical and measured composition of brine during salt precipitation and resulting co-crystals

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Salt Production

Keywords: Sea salt production, Brine cation analysis, Single Crystal X-ray diffraction

Abstract

The evaporation of sea water results in the formation of different precipitates, usually following the order CaSO_4 , NaCl , and MgSO_4 . Depending on the brine composition, NaCl can precipitate as either 'lamellose' (flaky) or 'hopper-faced' (pyramidal) crystals.

The crystallisation sequence of brine was investigated based on: theoretical ion concentration calculated from specific gravity values and ion concentrations obtained through Ion Chromatography (IC). It was found that as specific gravity of the seawater increased and decreased throughout a production cycle, the ion concentration varied.

It was observed that the concentration of calcium ions decreases during the production process due to the precipitation of calcium carbonate and calcium sulphate. As the calcium ion concentration decreased, the sodium and magnesium ion concentrations were shown to increase and the precipitation of sodium chloride was observed.

Single crystal X-Ray Diffraction (XRD) analysis on both 'lamellose' (flaky) and 'hopper-faced' (pyramidal) crystals were shown to contain (as co-crystals with NaCl) $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, respectively.



Figure 1: 'Lamellose' and 'Hopper Faced' sea salt.

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C. Booth, V. Thoss, L. Jones, G. Tizzard, Bangor University

Introduction

Evaporating sea water has been a method of salt production since prehistoric times. Traditionally sea salt is produced in a saltern which utilizes heat from the sun to evaporate seawater in large ponds next to the sea shore^{1,2}. Current production processes still include the use of salterns, but have also taken a more technical approach using open-pan salt making with other heat sources and vacuum pan evaporation³.



Figure 2: Location of the Menai Straits in the UK indicated with a red circle. Insert show satellite image of Menai Strait with location of Halen Môn Ty. Halen marked with red dot.

Gourmet sea salt company Halen Môn has been operating on the Isle of Anglesey on the shore of the Menai Strait since 1997 (Fig. 2). The Menai Strait is a stretch of tidal water between the

Comparison of Theoretical and Measured Composition of Brine During Salt Precipitation and Resulting Co-Crystals

C. Booth, V. Thoss, L. Jones, G. Tizzard, Bangor University

mainland of Wales and the Isle of Anglesey⁴. Brine is produced by evaporation from seawater pumped from the Menai Strait to Ty Halen (Halen Môn's production site). The brine is then concentrated in open pans with an intermittent overhead heating pattern. Generally, this process produces two different morphologies of sea salt: mainly 'lamellose' type (flaky) and 'hopper-faced' (pyramidal) crystals later in the production process.

The aim was to analyse a production cycle from starting the cycle until the first harvest by taking liquid samples from the surface of the open pan every four hours. The first 24 hours of the production cycle were monitored using bulk and chemical composition analysis techniques. Bulk analysis techniques include: Specific gravity (S.G)⁵, pH and conductivity. Chemical composition analysis included: theoretical⁶ and measured ion concentration using ion chromatography⁷. Single crystal X-ray Diffraction (XRD) was used to investigate the structures of 'lamellose' and 'hopper-faced' crystals.

Results and Discussion

Specific Gravity measurements

Figure 3 shows that throughout the sampling period, the S.G increased from 1.174 to 1.239 due to the brine solution being concentrated, which led to higher concentration of salts thus affecting the density of each sample. Because of the constant evaporation of the brine combined with the loss of NaCl as a solid via precipitation, the theoretical ion composition as reported by Balarew⁸ was used to aid interpretation of the results. Balarew used density to predict precipitates occurring. In this study, density was measured and converted into specific gravity and compared to Balarew's predictions (Table 1). Based on his observations, sodium chloride precipitation was expected to occur between 5:00 and 8:00 hours. The sample taken at 1:00 was an outlier but is included for completeness of results. From 9:00 to 1:00, Balarew's S. G. predicted gypsum as the main precipitate. However, as the seawater is pre-concentrated to brine using evaporation before entering the crystalliser, calcium salts had already been partly removed through crystallisation.

Sample	Specific gravity	Predicted co-crystals according to C. Balarew ⁸
ultra-pure water	1.000	
9.00	1.174	gypsum
13.00	1.198	gypsum
17.00	1.214	gypsum
21.00	1.216	gypsum
01.00	1.159	gypsum
05.00	1.230	Pure Sodium Chloride

Comparison of Theoretical and Measured Composition of Brine During Salt Precipitation and Resulting Co-Crystals

C. Booth, V. Thoss, L. Jones, G. Tizzard, Bangor University

8.00	1.239	Sodium Chloride and Magnesium sulfate
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Table 1: Specific gravity measurements and the corresponding predicted co-crystallites

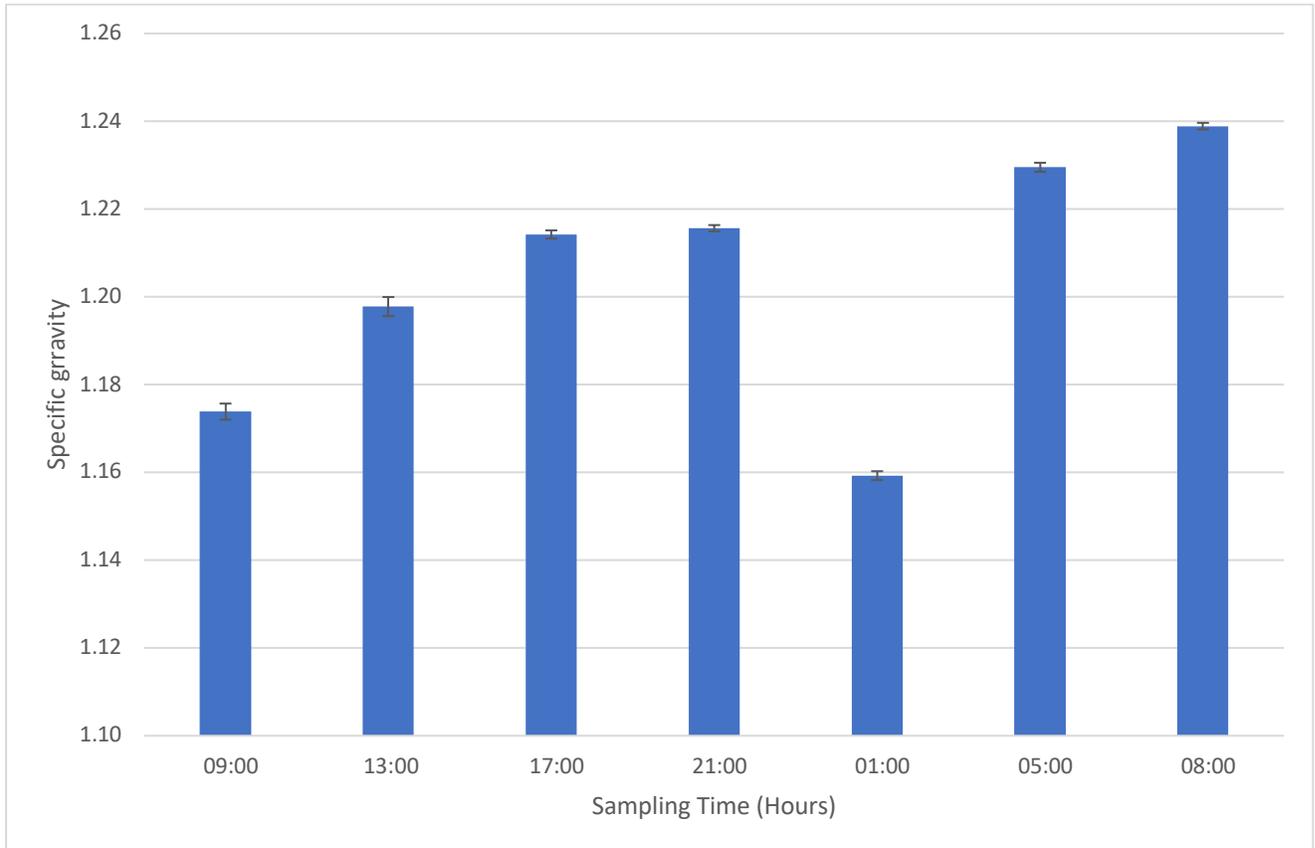


Figure 3: Specific gravity measurements during sampling period.

pH measurements

Figure 4 shows that pH increased during the first four hours from 8.15 to 8.28 and then decreased throughout the duration of sampling from 8.28 to 7.69. The increase of pH may be due to the increased concentration of calcium salts early on, which were precipitated later and their reduction decreased the pH. This decrease may also be attributed to the increasing concentration of magnesium salts which are slightly acidic.

Comparison of Theoretical and Measured Composition of Brine During Salt Precipitation and Resulting Co-Crystals

C. Booth, V. Thoss, L. Jones, G. Tizzard, Bangor University

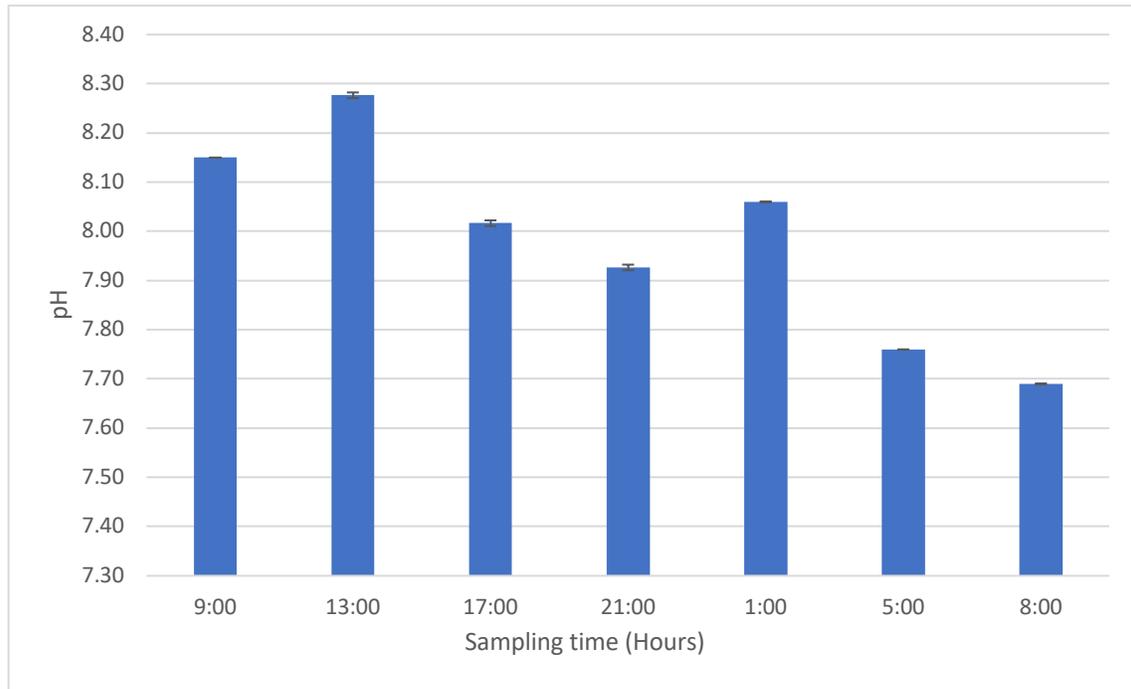


Figure 4: pH measurements during sampling period.

Conductivity Measurements

Conductivity was investigated (Fig. 5) and shown to have an reverse trend to pH with decreasing conductivity in the first four hours of sampling from 655,700 to 590,100 μS . For the next 19 hrs of sampling the conductivity was observed to increase from 5901,000 to 905,100 μS as the brine was concentrated which subsequently led to the ion concentration in solution to be increased. The marked decrease at 13:00 hrs could be due to precipitation of calcium sulfate, as predicted by Balarew⁸, in addition other studies also showed calcium sulfate being one of the early salts to precipitate when sea water is concentrated⁸.

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C. Booth, V. Thoss, L. Jones, G. Tizzard, Bangor University

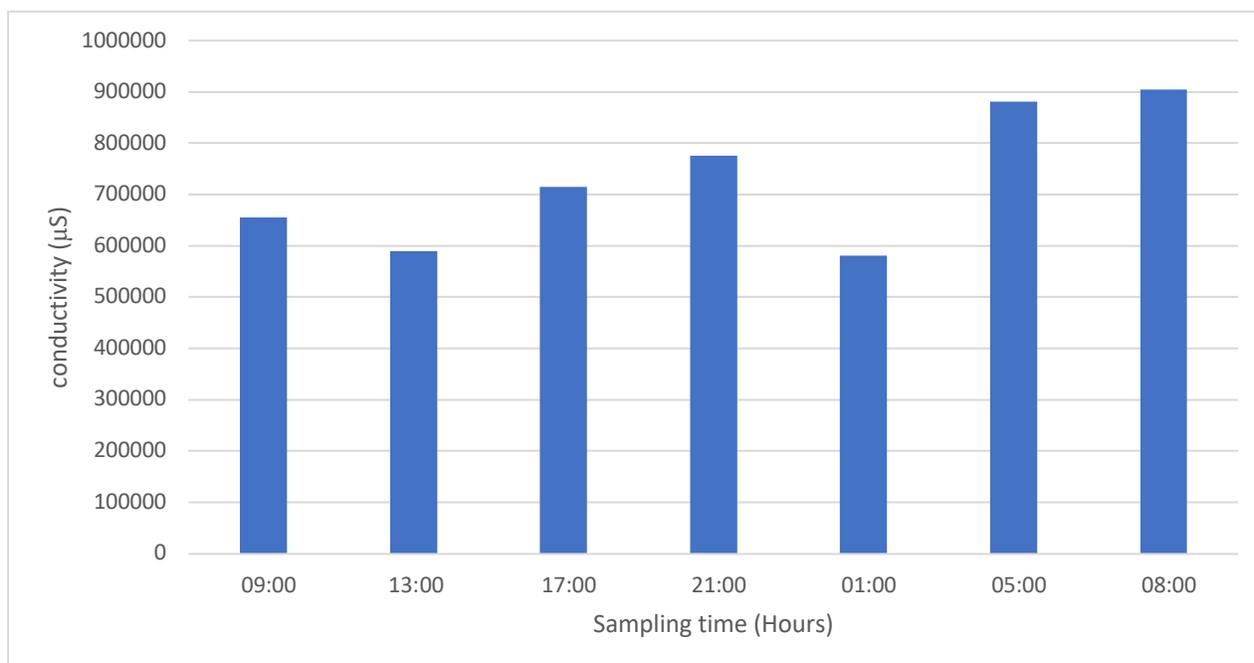


Figure 5: Conductivity measurements during sampling period.

Ion Chromatography and theoretical ion concentrations

Ion chromatography (IC) was used to quantify the amount of sodium, magnesium and potassium ions in liquid samples taken from the crystalliser. The concentration of calcium in diluted samples, as was required to allow the application of IC, was below the detection limit. This was caused by a combination of removal of calcium salts during the production of brine and precipitation early on in the cycle. Figure 6 shows that the concentration of sodium generally increased in the first 8 hours of sampling then decreased during the next 15 hours starting between 17:00 to 01:00 hours, mostly likely due to the precipitation of sodium chloride. Both the magnesium and potassium ion concentration was increasing over the sampling period (Fig 7).

As it was not possible to record the precipitation that had occurred at every sampling time, combined with the increase in concentration due to evaporation, the theoretical values⁶ were plotted against the actual measurements (Fig 7). Taking account of the measurement error, predominantly derived from the necessary dilution, there was close agreement for the sodium concentrations with sometimes higher theoretical values (9:00, 13:00, and 5:00) and sometimes lower (17:00, 21:00 and 8:00). The potassium concentration was generally higher for the measured samples compared to the theoretical concentrations. There was an increasing trend over time. The magnesium concentration also showed an increasing trend over the cycle. As shown in Table 1, magnesium was expected to have precipitated at the last sampling point in the cycle as the S. G. fell in the range given by Balarew for precipitation of magnesium sulfate. In this 24hr cycle only 'lamellose' crystals were produced.

Comparison of Theoretical and Measured Composition of Brine During Salt Precipitation and Resulting Co-Crystals

C. Booth, V. Thoss, L. Jones, G. Tizzard, Bangor University

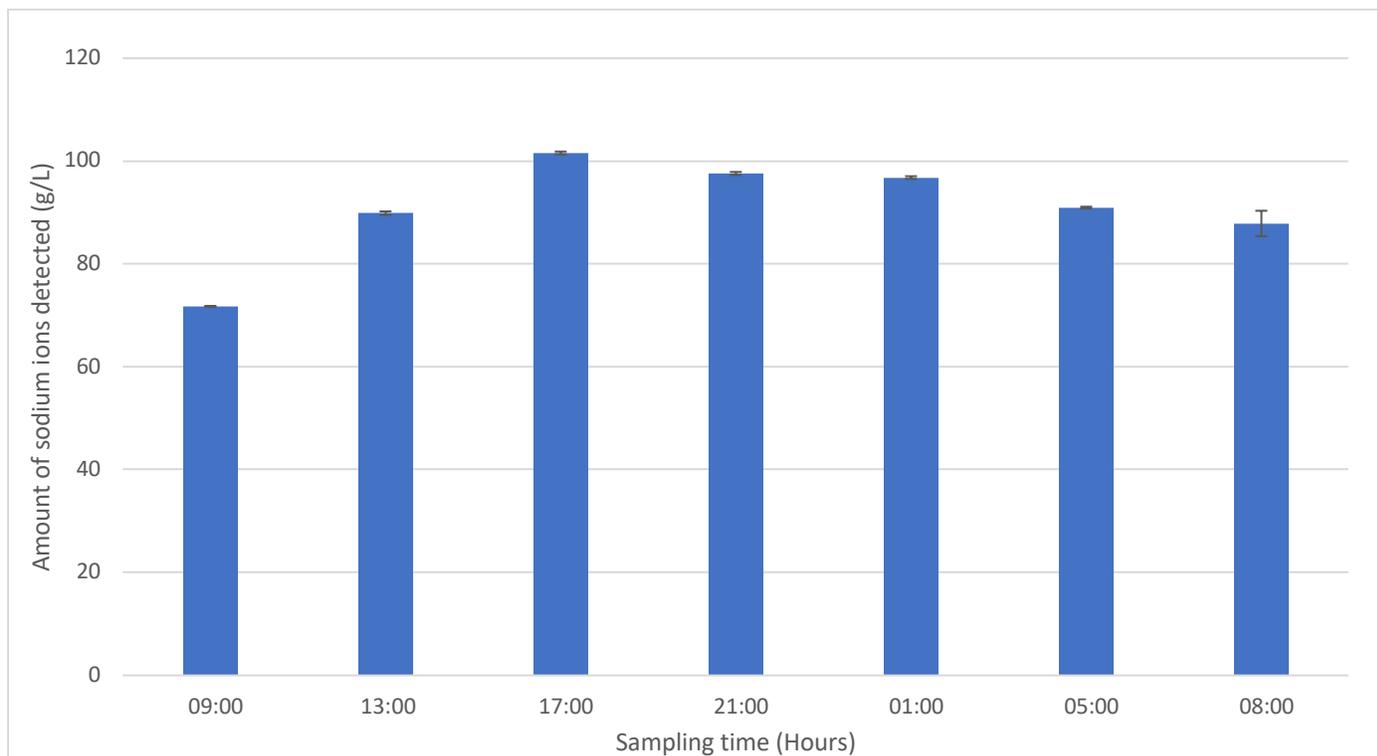


Figure 6: Sodium ions detected during the sampling time.

Comparison of Theoretical and Measured Composition of Brine During Salt Precipitation and Resulting Co-Crystals

C. Booth, V. Thoss, L. Jones, G. Tizzard, Bangor University

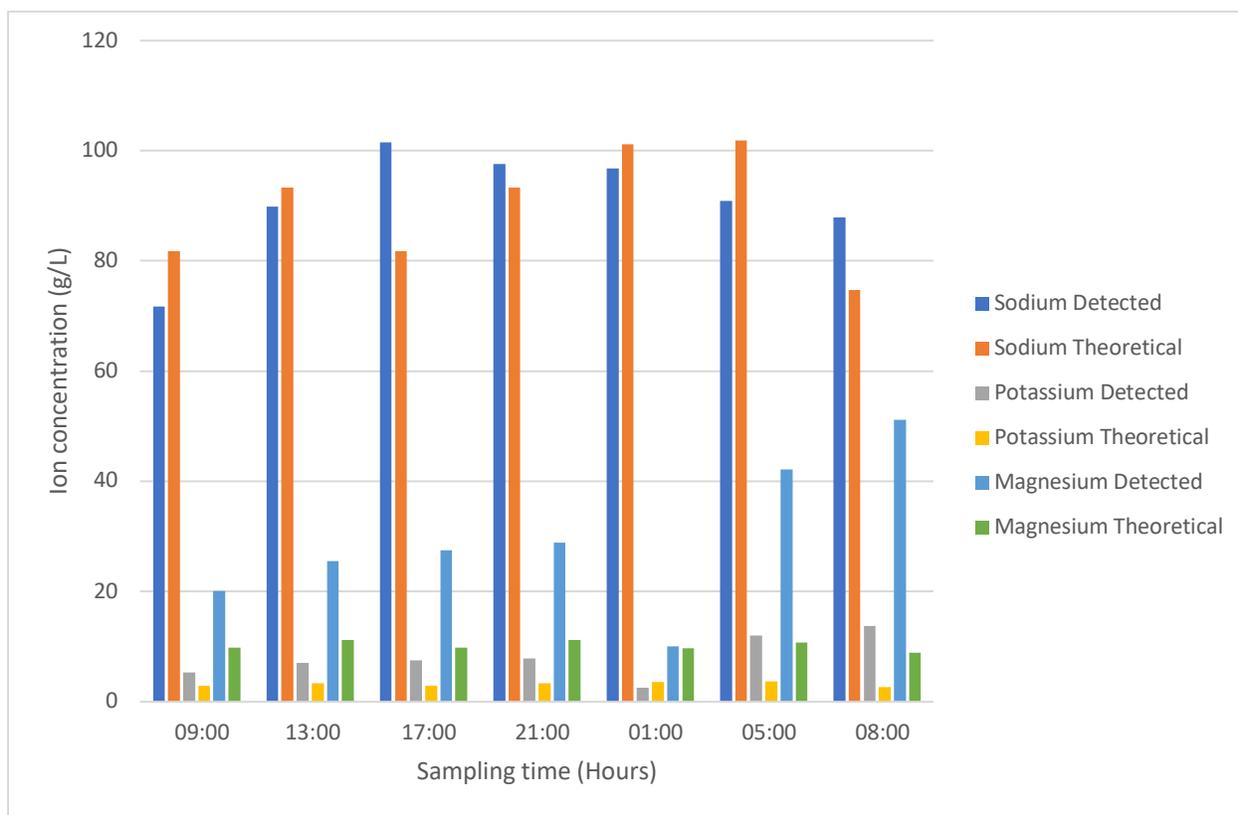


Figure 7: Comparison of theoretical and detected ions.

Single X-ray diffraction studies

In relation to the precipitated sodium chloride, the main morphology observed during the production of sea salt are 'lamellose' crystals, termed flaky. Infrequently, the formation of 'hopper-faced' crystals was observed (Fig 1). This study investigated the differences between both morphologies using single crystal X-ray diffraction. The 'hopper-faced' crystal morphology is also termed pyramidal crystal. Both 'hopper-faced' and 'lamellose' sea salt crystals were examined under a microscope using cross-polarised light. In both cases the predominant NaCl crystals did not extinguish under cross-polarised light (unit cell collections confirmed the presence of NaCl). Both morphologies also contained a significantly smaller proportion of single crystals that extinguished under cross-polarised light. The extinguishing crystals within the 'hopper-faced' crystal were found to be $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ which were embedded in the pyramidal structure. It is hypothesised that the $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ is templating the macroscopic 'hopper-faced' crystal structure. Likewise, the extinguishing crystals within the 'lamellose' crystalline sample were found to be $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$. No peaks associated with either sulphate salts were observed in the powder X-ray diffraction spectra of either salt batch. This is attributed to their (as expected) low quantities and high purity within each salt sample.

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

$\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$

Comparison of Theoretical and Measured Composition of Brine During Salt Precipitation and Resulting Co-Crystals

C. Booth, V. Thoss, L. Jones, G. Tizzard, Bangor University

Formula ^a	H ₁₄ O ₁₁ S ₁ Mg ₁	H ₁ O _{4.5} S ₁ Ca ₁
<i>M_w</i>	246.48	154.16
Crystal System	Orthorhombic	Trigonal
Space group	P2 ₁ 2 ₁ 2 ₁	P3 ₁ 2 ₁
<i>a</i> /Å	6.80150(10)	6.9537(9)
<i>b</i> /Å	11.8933(3)	6.9537(9)
<i>c</i> /Å	11.9323(2)	6.3693(7)
<i>α</i> /°	90	90
<i>β</i> /°	90	90
<i>γ</i> /°	90	120
<i>V</i> /Å ³	965.23(3)	266.72(8)
<i>Z</i>	4	3
<i>T</i> /K	100	100
<i>λ^b</i> /Å	0.71073	0.71073
<i>D_c</i> /g cm ⁻³	1.696	2.879
<i>μ</i> (Mo-Kα)/ mm ⁻¹	0.441	2.234
Meas./indep.(<i>R_{int}</i>) refl.	2196 / 2177 (0.0201)	401 / 372 (0.0356)
Restraints, Parameters	0, 169	0, 35
wR2 (all data)	0.0488	0.1019
<i>R</i> ¹ ^{d,e}	0.0185	0.0556
Goodness of fit on <i>F</i> ²	1.093	1.182

Table 3: X-ray crystallographic data obtained from the needle-like cross-polarised light extinguishing crystals within 'hopper-faced' (left) and 'lamellose' (right) salt samples.

Methods

Experimental set-up

The crystallizer was filled with brine and heated by overhead gas heaters on constant temperature for 2 hours, then subjected to a heating pattern of: 16 min on (heating) and 4 min off (cooling). All samples were kept at room temperature.

Comparison of Theoretical and Measured Composition of Brine During Salt Precipitation and Resulting Co-Crystals

C. Booth, V. Thoss, L. Jones, G. Tizzard, Bangor University

Specific Gravity measurements

Specific gravity was calculated with data obtained from an Ohaus pioneer PA124 balance. Ultrapure water was chosen as the reference material. 500 μl of each sample at 25 $^{\circ}\text{C}$ \pm 0.5 $^{\circ}\text{C}$ were micro-pipetted onto a 4 d.p. balance. Each sample was measured five times and the specific gravity was calculated by dividing the average by the average weight of 500 μl of de-ionised water at 25 $^{\circ}\text{C}$ \pm 0.5 $^{\circ}\text{C}$.

pH measurements

pH was measured using a Orion 5* multimeter equipped with a pH electrode. The pH electrode was calibrated using Hanna buffer solutions (4.01, 7.01 and 10.1) with a slope gradient of 97.5%. The samples were stirred as pH was determined. The temperature of the samples were kept at 25 $^{\circ}\text{C}$ \pm 0.5 $^{\circ}\text{C}$.

Conductivity measurements

Samples were analysed for conductivity using a Orion 5* multimeter and a 4-cell conductivity graphite electrode in a 50ml plastic centrifuge tube equipped with a stirrer bead. The electrode was calibrated using two different concentration sodium chloride solutions provided from Hanna: 7,230 ppm (12.9 mS cm^{-1}) and 692 ppm (1413 μScm^{-1}). The conductivity of the ultra-pure water was determined to be 10.48 μS . 50 μL of each sample were diluted by a factor of 1,000 to 50 ml with ultrapure water. The samples were stirred as conductivity was measured. Each sample was kept between 25 $^{\circ}\text{C}$ \pm 0.5 $^{\circ}\text{C}$.

Ion Chromatography measurements

Cationic IC analysis was carried out using an Dionex ICS-2100 using a Dionex CERS 500 2mm suppressor and an Dionex IonPactm CS12A RFICtm column operating at a flow rate of 0.24 mL/min and column temperature of 30 $^{\circ}\text{C}$. The mobile phase was methanesulfonic acid (Dionex EGC MSA). Samples were detected using a conductivity detector. Samples were diluted by a factor of a thousand.

Calibration curves were constructed using in-house materials for sodium, potassium and magnesium ions using calibration solutions in a linear range of 2.5 - 200 ppm ($r^2 > 0.99$).

XRD Measurements

Single crystal diffraction studies were carried out at the National Crystallography Centre (University of Southampton, England, UK) on a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ Super Bright molybdenum rotating anode generator with HF Varimax optics (100m focus). Powder X-ray diffraction studies were carried out at the School of Chemistry at Bangor University, using a PANalytical Philips X'Pert 3040/60 diffractometer at 45 kV and 35 mA between 5 and 60 $^{\circ}$ 2 θ using Ni-Filtered Cu-K $_{\alpha 1}$ radiation ($\lambda = 1.5405 \text{ \AA}$).

Conclusions

To conclude, the first twenty-four hours of an open pan sea salt production process were investigated in order to assess the compositional changes in the brine using bulk and chemical composition analysis. Specific gravity was measured and increased throughout the sampling period due to evaporation therefore the concentration of dissolved ions increased as well.

Comparison of Theoretical and Measured Composition of Brine During Salt Precipitation and Resulting Co-Crystals

C. Booth, V. Thoss, L. Jones, G. Tizzard, Bangor University

Conductivity was measured in diluted samples and found to generally increase during the sampling period due to the increase in dissolved salt concentration. pH was measured and found to increase until 1pm then generally decreased until 8am, hypothesised to be due to the precipitation of salt which changed the relative concentrations of certain ions in solution, particularly magnesium. Ion chromatography determined the sodium ion content to have increased to peak until 5pm and then decreased during the latter sampling period, Potassium and magnesium ion concentration increased throughout the sampling period. There was good agreement between reported theoretical ion concentrations⁶ and specific gravity values⁸ for sea salt production. Sea salt obtained using an open pan production process resulted in 'lamellose' crystals, which contained needles of $\text{CaSO}_4(\text{H}_2\text{O})_{0.5}$. Rarely were 'hopper-faced' crystals formed, however, they contained crystals of $\text{MgSO}_4(\text{H}_2\text{O})_7$. During the first 24 h only 'lamellose' crystals precipitated.

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