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DOI

[10.1039/D0CE01011A](https://doi.org/10.1039/D0CE01011A)

Publication date

2020

Document Version

Accepted author manuscript

Published in

CrystEngComm

Citation (APA)

Marques Penha, F., Zago, G. P., & Seckler, M. M. (2020). Strategies to control product characteristics in simultaneous crystallization of NaCl and KCl from aqueous solution: Seeding with NaCl and KCl . *CrystEngComm*, 22(44), 7590-7600 . <https://doi.org/10.1039/D0CE01011A>

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STRATEGIES TO CONTROL PRODUCT CHARACTERISTICS IN SIMULTANEOUS CRYSTALLIZATION OF NaCl AND KCl FROM AQUEOUS SOLUTION: SEEDING WITH NaCl AND KCl

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ABSTRACT

In this work, we approach simultaneous crystallization of NaCl and KCl from its aqueous solution by concomitantly seeding both salts. Experiments were designed based on the ternary system phase diagram. Mother-liquor concentration was chosen near the eutonic condition at its boiling temperature. The seeds for each compound had different sizes but the amounts were calculated to provide nearly equal surface areas for each material. Elementary phenomena were assessed and chemical composition in different particle size ranges within the products was analysed. Despite the presence of seeds from each component in the suspension under crystallization, the formation of mixed composition polycrystalline particles was observed. Seeding protocol involving much larger KCl than NaCl seeds resulted in an easily separable product with two distinct populations. In general, segregation of the salts through the size ranges followed the trend induced by seeding, highlighting the possibility of retrieving relatively pure solid fractions of each salt.

1. Introduction

Current well-designed treatment of wastewaters from different industries mainly involve the removal of suspended particles and biological stabilization. Resulting stream contains salts in a wide range of solubility which may not have sufficient quality to enable water reuse in industrial processes. In order to reuse the water, additional treatment is required depending on the effluent conditions and the aim of reuse. The most common processes for this purpose are based on membrane separation, such as reverse osmosis and reverse electrodialysis^{1,2}. However, besides pure water, these processes also generate a highly concentrated brine, which is not compatible with disposal quality standards^{3,4}. In addition, many industries such as food processing, paper, textile manufacture and livestock directly generate saline effluents that need as well to be treated before disposal⁵. For this purpose, crystallization has shown to be technically feasible and has been used to enable Zero Liquid Discharge^{1,6–10}.

Although the main efforts in these treatments are towards water reuse, the salts dissolved in the effluents also require attention, as during crystallization they become particulate materials to be subsequently separated by filtration or centrifugation. These solids can become a saline resource if properly separated in pure streams^{11,12}. The challenge lies in the multicomponent nature of the effluents, which implies that, at some point on a crystallization operation, more than one compound will be simultaneously crystallized. The product from such operation will most likely be a combination of single particles of each compound and mixed composition polycrystalline particles, in different proportions. Mixed composition particles will probably have little or none industrial use, turning into solid waste. Thus, research is needed to design processes that, beyond water reuse, enable the recovery of different components comprising saline effluent streams as particulate products, preferably monocomponent particles.

In previous studies^{13,14} we highlighted the possibility of simultaneously crystallising NaCl and KCl in a single evaporative crystallizer while controlling elementary phenomena to yield particulate products with tailored characteristics. The design was based on the phase diagram and seeding strategies using each salt as seed separately. When NaCl was seeded¹³, a nucleation event was observed close to the eutonic point, which was associated with KCl. KCl new particles were found in high proportions on NaCl surfaces, comprising mixed composition particles. These particles can be formed through agglomeration and heterogeneous nucleation on NaCl surface, which may

induce epitaxial growth. Single crystals of both salts were also seen in different proportions to each experimental condition but, regardless of the condition, in lower proportions than the mixed composition polycrystals. In general, single crystals yield was favoured by low supersaturations conditions, i.e. low evaporation rates and high seed surface area (smaller seeds in high contents). On the other hand, when KCl was seeded¹⁴, although polycrystalline particles were still formed, NaCl nucleation in solution was enhanced, thus, increasing the proportion of single component particles. Segregation of the components in different size ranges was clearer than for the experiments seeded with NaCl. KCl and NaCl size fractions were found with purities higher than 90 and 75 wt%, respectively. However, the single component particles were preferentially formed under high supersaturation conditions, i.e. low seed surface areas. KCl seeds also generated high proportions of secondary nuclei, which ‘contaminated’ the size ranges rich in NaCl, hampering the separation. Overall, heterogeneous nucleation of a deposit-crystal on a substrate – mixed composition particles generators – and secondary nucleation were identified as the limiting phenomena to the separation. Both phenomena are influenced by seed size, seed content and supersaturation.

Recently, our group studied the simultaneous crystallization of sodium chloride and calcium sulphate hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), in both unseeded and seeded conditions, in a batch evaporative crystallizer^{15,16}. Both salts are commonly found in industrial effluents, and its simultaneous crystallization can occur in wastewaters from oil refineries¹⁷. We have found that, for unseeded batches, the primary particles of both salts are formed by primary nucleation that agglomerates after reaching a certain size. Consequently, the product is polydispersed in all particles ranges. Most of the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ remained in the smaller size ranges, indicating the possibility of product separation into its primary components. Agglomeration was lower at low supersaturations, resulting in a more uniformly sized product. As for the seeded batches, we found that calcium hemihydrate does not act as substrate for NaCl heterogeneous nucleation. Instead they agglomerate and deposit on NaCl surfaces, inhibiting NaCl particles from agglomerating with each other. Seeding with $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ reduces the mean size and increases product size dispersion, whilst NaCl seeding was found to ease the separation of both salts in downstream separation.

The results for simultaneous crystallization in both systems suggest that particulates morphological properties could be tuned to minimise the formation of mixed composition polycrystalline particles to ease their separation and use as economically valuable components.

In this study, an approach for the simultaneous crystallization of NaCl-KCl from its aqueous system was developed by seeding both salts concomitantly in the crystallizer. The aim is to inhibit nucleation events, hence minimising the formation of mixed composition polycrystalline particles. Double seeding was investigated in a solution near the eutonic concentration. Different seed sizes were applied to each component, aiming to induce a product comprised by two particle populations, which would be separable simultaneously by size and composition on downstream operations. Despite seed size differences, surface areas promoted by each compound were equal.

2. Theoretical background – Double seeding

Solids content is a relevant parameter in crystallization from solutions to control nucleation (both primary and secondary), growth and agglomeration¹⁸. Usually, seeding strategies are monocomponent. Consequently, only the seeded salt has its supersaturation held at low levels, whilst the supersaturation for the other is left to increase up to an event of primary nucleation. In this context, the influence of seeding both compounds on the residual supersaturation is discussed as follows.

The driving force for crystallization is supersaturation. Supersaturation ratio (S) can be calculated as a function of the solute concentration (c) and its equilibrium concentration (c^*):

$$S = \frac{c}{c^*} \quad (1)$$

It is noteworthy that this simplification is only valid for low supersaturation, i.e. if c and c^* are not far apart from each other. These conditions are usually fulfilled for compounds with narrow metastable zones, such as moderately soluble salts¹⁸. When more than one solute is crystallized simultaneously, the supersaturation with respect to each compound must be considered.

In evaporative crystallization, solvent removal tends to increase the supersaturation with respect to all crystallizing compounds. Crystal growth of a given compound, on the contrary, reduces the supersaturation with respect to that compound. If the crystal surface area available for growth is large, the solution will follow a pathway close to equilibrium, as the supersaturation will be quickly consumed by crystal growth.

Figure 1 gives a schematic representation of the phase diagram of the ternary system NaCl-KCl-H₂O to allow the assessment of the effect of seeding on the residual supersaturations. The orange and the blue lines represent respectively the NaCl and the KCl solubilities, whereas the large black dot represents the eutonic condition (Point E). Point A represents the solution composition after a given amount of solvent is evaporated from an eutonic solution (Point E), prior to nucleation. The points A, B, I and F were arbitrarily represented in the diagram but it is noteworthy to mention that the position of point A was, on purpose, exaggerated to ease the visualization and facilitate the addition of all other points. Point B is representative of a crystallising solution in the presence of KCl excess surface area (excess surface area is considered here as enough area to suppress primary nucleation and will be referred from this point only as surface area), in the same evaporation rate. As it can be noticed, point B is derived from point A, which moves closer to the KCl solubility line due to preferential KCl crystallization. Similarly, point F represents a batch where NaCl surface area is available, as it lies closer to the NaCl solubility line. Finally, point I is representative of a batch in which surface area from both salts is available for crystal growth, as it is closer to both solubility lines and, consequently, closer to the eutonic point. For instance, when KCl area is present, NaCl concentration remains the same ($y_B = y_A$). The same goes for NaCl surface areas, where KCl concentration is constant ($x_F = x_A$).

Figure 1. Schematic representation of the operation point for different seeded batches.

The presence of surface area available for growth on a solution under crystallization may be promoted by adding crystal seeds. In this way, primary nucleation is avoided, whilst secondary nucleation and agglomeration are hindered. Seeding only one of the salts may move the operation point from A to the direction of B or F, if KCl or NaCl, respectively, are seeded. Thus, seeding both salts will move the operation point towards I. Thus, the proximity of the operation point with the solubility line is a function of the surface area: the higher the area, the closer to the equilibrium will be the process. The increase of surface area may be promoted by adding higher amounts of seeds and/or by adding smaller seeds.

Next, the supersaturation ratios can be compared for each crystallising compound (S_{NaCl} and S_{KCl}) for a number of conditions. Considering a supersaturated solution with composition B, i.e. in the presence of KCl surface area, the supersaturation ratio for KCl is determined by the intersection of the evaporation line OB with the KCl solubility line, i.e. $S_{KCl}^B = x_B / x_C$. Similarly, the supersaturation ratio for NaCl in this condition is $S_{NaCl}^B = y_B / y_D$. Supersaturation ratios for representative operating points presented in Figure 1 are summarised in Table 1.

Table 1. Qualitative assessment of the supersaturation in each condition.

Condition	Point	S_{NaCl}	S_{KCl}
Unseeded	A	$S_{NaCl}^A = y_A / y_E$	$S_{KCl}^A = x_A / x_E$
Seeded with KCl	B	$S_{NaCl}^B = y_B / y_D$	$S_{KCl}^B = x_B / x_C$
Seeded with NaCl	F	$S_{NaCl}^F = y_F / y_G$	$S_{KCl}^F = x_F / x_H$
Seeded with KCl and NaCl	I	$S_{NaCl}^I = y_I / y_E$	$S_{KCl}^I = x_I / x_E$

Now, the supersaturations at the condition with no surface area available for growth, i.e. with the highest supersaturation (composition A), are compared with other conditions. It can be seen in Figure 1 that seeding only with KCl drastically reduces this salt supersaturation, as expected. Thus,

$$S_{NaCl}^B = S_{NaCl}^A \text{ and } S_{KCl}^B \ll S_{KCl}^A$$

Analogously, for seeding with NaCl only,

$$S_{NaCl}^F \ll S_{NaCl}^A \text{ and } S_{KCl}^F = S_{KCl}^A$$

For double seeding, both supersaturations are drastically reduced by promoting both NaCl and KCl surface area available for molecular growth:

$$S_{NaCl}^I \ll S_{NaCl}^A \text{ and } S_{KCl}^I \ll S_{KCl}^A$$

It is noteworthy that seeding with any single salt in an eutonic solution only reduces the supersaturation with respect to that salt, although it also has an effect on the supersaturation of the other salt. Although the presence of seeds could reduce the energy barrier to nucleation and trigger heterogeneous nucleation, this effect is not related to supersaturation. Therefore, the double seeding advantage relies mostly on the decrease of the residual supersaturation for both salts, favouring molecular growth mechanisms.

3. Experimental section

3.1. Materials

Analytical grade reagents (NaCl and KCl) and distilled water were used to prepare fresh solutions for each experiment. Ethanol (Purity > 99.5 %) was used to wash crystal samples after filtration.

3.2. Experimental setup

The experimental setup is described in details in our previous works^{13,14}, yet it is summarized here to ease reading. A jacketed glass crystallizer (0.5 L) provided with baffles and mechanical stirring was used. Evaporation was promoted and maintained constant by a fluid circulating on the crystallizer's jacket, heated by a thermostatic bath at a constant temperature ($T_{\text{jacket_bath}} = 142.5\text{ }^{\circ}\text{C}$, Lauda, Eco RE 620). Temperature was monitored by a Pt-100 thermocouple in direct contact with the solution/suspension. Evaporated solvent was condensed in a condenser open to atmosphere also connected to a thermostatic bath ($T_{\text{condenser_bath}} = 1\text{ }^{\circ}\text{C}$) and collected in a scale to monitor the evaporation rate by plotting the mass of condensate as a function of time (plots not shown). Measured evaporation rate was found to be constant at 0.003 min^{-1} for all the experiments.

3.3. Phase diagram and experimental procedure

Equilibrium for sodium and potassium chloride aqueous solution was determined with OLI Studio thermodynamic simulation software (OLI Studio 9.6). For each experiment, weighted solid salts and water were placed on the crystallizer. Initial solution concentration refers to the eutonic condition at $109.5\text{ }^{\circ}\text{C}$ ($0.360\text{ g}_{\text{KCl}}\cdot\text{g}_{\text{H}_2\text{O}}^{-1}$ and $0.273\text{ g}_{\text{NaCl}}\cdot\text{g}_{\text{H}_2\text{O}}^{-1}$) and was chosen to ensure complete dissolution of solids in close proximity to the eutonic condition ($0.362\text{ g}_{\text{KCl}}\cdot\text{g}_{\text{H}_2\text{O}}^{-1}$ and $0.275\text{ g}_{\text{NaCl}}\cdot\text{g}_{\text{H}_2\text{O}}^{-1}$) before the boiling temperature was reached. At this point, seeds were added according to Table 2. After seeding, temperature was increased to start evaporation. A slight dissolution of the seeds due to temperature increase ensures that the system remains saturated in both salts and initiates the crystallization at the eutonic point.

Table 2. Experimental parameters for the experiments performed with NaCl and KCl seeds.

Experiment	Seed dominant size (μm)		Seed content (wt%)	
	NaCl	KCl	NaCl	KCl
E ₀	-	-	-	-
E ₁	275	550	35.3	64.7
E ₂	550	275	68.6	31.4
E ₃	327	327	52.1	47.9
E ₄	152	655	20.2	79.8

The amounts of seeds was chosen as 10 wt% of the total mass of the system, aiming high segregation based on our previous work^{3,4}. To induce the formation of multimodal products, the size of NaCl and KCl seeds were different in each experiment (except for E₃), yet the superficial area provided by each salt was calculated to be equal. An unseeded experiment was also performed. All experiments were performed with 0.003 min⁻¹ evaporation rate, based on the initial amount of solvent (min⁻¹: $\frac{g_{\text{evaporated}}}{g_{\text{initial_solvent}} \cdot \text{min}^{-1}}$). Batch evaporation was carried on up to removal of 50 wt% of the initial water.

Slurry samples were pipetted during crystallization, to monitor particle development, at 10, 25 and 50 wt% of evaporated water. Samples were filtered under vacuum, washed with ethanol, and oven dried at 50 °C overnight.

3.4. Seeds preparation

NaCl seeds were obtained by sieving the analytical grade reagent. KCl seeds were obtained through batch cooling crystallization from solutions, as described in previous work¹⁴. Seeds produced in the batches were filtered, washed in ethanol, dried at 50 °C overnight and then sieved. Seeds in the size ranges of interest (see Table 2) were then stored. It should be highlighted that, since the classification of the seeds was done through sieving, the sizes shown on the table are the average size from the consecutive sieves. The particle size distribution of the seeds for every experiment is shown in Figure 2.

3.5. *Particle characterisation*

Samples of dried crystals were characterised by Scanning Electronic Microscopy (SEM - JEOL JSM-7401F) coupled with Energy Dispersive X-ray Spectroscopy (EDS). Particle size distribution of the yield (Sample 3) of each experiment was analysed through sieving. Each size range obtained through sieving was analyzed for its chemical composition through argentometry and the results were expressed in terms of NaCl proportion (%). The population coefficients of variation (CV), dominant sizes (L_D) and segregation index (SI) was calculated as described in our previous work¹³.

4. Results and discussion

Particle Size Distributions (PSD) for the experiments are shown in Figure 2. The coefficients of variation (CV) and dominant sizes (L_D), both theoretical and experimental, are compiled in

Table 3.

Figure 2. Population density of the product of (a) the unseeded (E_0) batch, and for the seeds and the product of experiment seeded with: (b) NaCl seeds of 550 μm and KCl seeds of 275 μm (E_1); (c) NaCl seeds of 275 μm and KCl seeds of 550 μm (E_2); (d) 327 μm seeds of both salts (E_3); (e) NaCl seeds of 152 μm and KCl seeds of 655 μm (E_4). Note that for the seeded experiments, product distribution is displayed on the primary axis and seeds distribution on the secondary axis.

Table 3. Coefficient of variation (CV) and dominant sizes (L_D) for the experimental conditions tested.

Seeds	CV (%)	L_D (μm)	Experiments	CV (%)	L_D (μm)	L_{NaCl} (μm) ²	L_{KCl} (μm) ²	L_{ave} (μm) ²
NaCl - 152	8.5	161	E₀	17	394 / 612 ¹	-	-	-
275	7.0	270	E₁	18	661	426	707	608
327	9.0	304	E₂	11	647	737	410	634
550	7.5	544	E₃	19	615	463	445	455
KCl - 275	7.5	268	E₄	25	681 / 334 ¹	272	813	-
327	8.0	320						
550	7.0	544						
655	6.0	635						

¹ Primary peak / Secondary peak – ² Theoretical values

Figure 22a shows that the unseeded condition presented a relatively large bimodal distribution ($CV = 17\%$), with the primary peak in much higher proportion than the secondary peak (primary and secondary peaks refer to the peaks with the highest and subsequent higher proportion of crystals). The proportion of particles larger than the dominant size of the primary peak suggests the formation of polycrystalline particles, since the proportion of crystals comprising a population in the range of 700 to 850 μm is not expected for single crystal molecular growth. The width of the secondary peak suggests that new particles are constantly being formed by secondary nucleation – since supersaturation is held at relatively low level – which would not allow successive primary nucleation events. The influence of evaporation rate in the results was taken into account in previous work¹³, where two different evaporation rates were tested. From these first evaluations, an optimal evaporation rate was derived to provide minimal agglomeration and secondary nucleation.

Due to the lack of seeds, supersaturation is higher for this experiment than for the seeded ones, points A and I, respectively, in Figure 1. The first crystals arise in the crystallizer due to primary nucleation. Although the system reaches eutonic condition right at the beginning of the experiment, it is unlikely that both salts nucleate at the same time, since the metastable zone width varies to each compound. The first component to nucleate may seem unimportant, since both salts will inevitably be generated. Yet, if NaCl arises in solution prior to KCl, it can be inferred that most polycrystalline particles generated are comprised by both salts and formed by heterogeneous nucleation of KCl on NaCl surface¹³. If KCl nucleates prior to NaCl, the generation of mixed composition polycrystalline particles by heterogeneous nucleation of NaCl in KCl is known to be less favourable¹⁴. As the supersaturation promoted by the evaporation rate is relatively low – according to previous studies – agglomeration would not be favoured^{13,14}.

Figure 3a shows the SEM-EDS analysis for the unseeded experiment (E_0). On Sample 1, the major presence of NaCl confirms that this salt was the first to nucleate. It was also observed that KCl is seen mainly as microcrystals adhered to NaCl surfaces, confirming the formation of mixed composition polycrystals. On the following samples, NaCl growth and an increase in KCl proportion was seen, as expected. Some single composition particles of both salts can be seen in all samples, yet, the higher proportion of polycrystalline mixed composition particles in comparison with single crystals can also be confirmed in Figure a – Sample 3. It is noteworthy that, despite the similarity between the two compounds, no formation of solid solutions or significant isomorphic substitution of Na^+ and K^+ ions into, respectively, KCl's and NaCl's crystal lattices is expected, as it only occurs for temperatures much higher than those used in this work^{19,20}.

Figure 3. SEM images of Samples 1, 2 and 3, respectively 10, 25 and 50 % of total water removed for (a) the unseeded (E_0) batch and for the seeds and the product of experiment seeded with: (b) NaCl seeds of 275 μm and KCl seeds of 550 μm (E_1); (c) NaCl seeds of 550 μm and KCl seeds of 275 μm (E_2); (d) 327 μm seeds of both salts (E_3); (e) NaCl seeds of 152 μm and KCl seeds of 655 μm (E_4). KCl crystals identified through EDS are presented in red, NaCl crystals in green and the particles in grey were not analysed.

PSDs for the KCl 550 μm seeds and the NaCl 275 μm seeds (E_1) is shown in Figure 2b. It is noteworthy that the PSDs for the seeds are shown separately for each salt – not as a bimodal seeding – and normalised regarding the mass, as the mass was calculated to promote approximately equal surface areas (instead of seeding the same mass-proportion for both salts). The seed contents used in each experiment are shown in Table 2. This information is relevant for the PSDs analysis. The smaller seeds are present in much lower amounts, which can influence on the survival of the peak. For instance if there is an enlargement of both peaks, the one with the lower proportion might easily disappear by joining a higher proportion peak. Thus, the resulting peaks will not present the same proportion as the normalised peaks shown for the seeds.

The product of E_1 displayed unimodal distribution with a size dispersion higher than the unseeded condition ($\text{CV} = 18\%$), instead of the expected bimodal product. Distribution enlargement may occur due to significant formation of polycrystalline particles and secondary nucleation. This is consistent with SEM analysis (Fig. 3b). As smaller NaCl seeds were added here, the epitaxy-generated mixed composition polycrystals of KCl in NaCl might present irregular morphologies that merges with intermediate size ranges – between dominant and seed size ranges –, contributing for the large unimodal distribution formation. Also, large KCl seeds added in this experiments are prone to breakage and abrasion, which promotes secondary nucleation and aid on the enlargement of the distribution. Despite not being individually measured, NaCl and KCl crystals observed in Figure 3b - Sample 3 are clearly in different size ranges that somewhat matches calculated values seen in Table 3. Yet, due to the enlargement of the distribution, both crystals end up comprising the same peak in the PSD.

Figure 3b also shows some mixed composition polycrystalline particles in all samples along with single crystals and monocomponent polycrystals of both salts. Low supersaturation, promoted not only by the relatively low evaporation rate but also by the available surface area from both salts, should preference for crystal growth over nucleation and agglomeration. Yet, despite the low supersaturation, the formation of polycrystals of mixed composition indicates heterogeneous nucleation of the salts on foreign surfaces. Monocomponent polycrystalline particles observed in the product were most likely added to the system as seeds (mainly KCl seeds), rather than formed during evaporation. Sample 3 shows a majority of mixed composition particles in large sizes.

The PSDs for the seeds and for the products of the experiment seeded with NaCl seeds of 550 μm and KCl seeds of 275 μm (E_2) can be seen in Figure 2c. Despite the double seeding, product distribution was unimodal and relatively large ($\text{CV} = 11\%$). The PSD peak is sharp, with a large dominant size (647 μm) - comparable to the calculated weighted average shown in Table 3 - and a weak tendency can be seen towards the formation of particles higher than the dominant size. A small proportion of particles between 200 and 450 μm was also observed.

Figure 3c displays SEM-EDS images for E_2 . Sample 1 shows single particles of both salts along with some mixed composition polycrystals. The proportion of polycrystals decreases on Sample 2 and Sample 3 when compared to single crystals of each component. Evidences of epitaxial growth (mainly KCl crystals on NaCl's surface) were observed. It is noteworthy in Sample 3 that the single crystals of both salts present similar sizes. Although the average calculated product size (Table 3) matches the experimental dominant peak, salts should have considerable different sizes. This evidences that NaCl growth is somewhat hindered in the process, which probably increased its presence in intermediate size ranges as part of polycrystalline mixed composition particles.

The comparison between the experiments with opposite seeding strategies (E_1 and E_2) allows interesting insights. For instance, on E_2 the proportion of particles smaller than 450 μm can be neglected (Fig. 2c), while for E_1 there is a higher proportion of smaller particles in the same size range (Fig. 2b). This can be directly related to the seeding characteristics on E_1 - the large seeds are KCl and the small seeds are NaCl. Large seeds are known to be more prone to breakage, i.e. increasing secondary nucleation. On the contrary, for E_2 , the large seeds were NaCl, which despite the size presents higher resistance (tougher and less ductile) than KCl²¹. Consequently, less secondary nuclei are generated from NaCl than from KCl, i.e. less secondary nucleation takes place on E_2 when compared with E_1 . This hypothesis can be confirmed by the PSDs (Fig. 2b - E_1 and 2c - E_2). In addition, round-edged and damaged crystals on Sample 3 of experiment E_1 contrast well-formed edges of both salts crystals seen for E_2 (Fig. 3b and 3c).

Particle size distribution for the experiment seeded with 327 μm seeds of both salts (E_3) is shown on Figure 2d. As the size range for both seeds is the same, PSD for the seeds are almost fully overlapped. Product also displayed unimodal distribution, much larger than the added seeds. Dominant size for the product of this experiment (E_3) is around 600 μm , higher than the expected (Table 3). A relatively high proportion of particles higher than the dominant size can be seen. The proportion of particles smaller than the dominant size is practically constant for

all size ranges, except for particles under 80 μm , where an increase in the proportion can be observed. This evidences the continuous formation of secondary nuclei, permeating all size ranges. The obtained dominant size larger than expected indicates a tendency towards the formation of polycrystalline particles, most likely with mixed composition, since the low supersaturation is supposed to inhibit agglomeration.

SEM-EDS analysis for E_3 is presented in Figure 3d. It is possible to see evidences of epitaxial growth in all samples. Polycrystalline particles can be seen at Sample 1 in the same proportion as single crystals. It is noteworthy on Samples 1 and 2, that both polycrystalline complexes are seen: comprised by crystals with similar sizes from the same compound and by crystals with very different sizes from both salts. On Sample 3, both mixed composition and monocomponent particles are seen. In general, particles identified as KCl are larger than NaCl particles, although both were seeded in the same size range. Single component polycrystalline particles may have derived from agglomerates present in the seeds, rather than formed by an unexpected agglomeration, as the experimental conditions here lead to a low supersaturation.

Since the conditions tested up to this point were not able to induce a bimodal distribution, the strategy for E_4 was to seed NaCl and KCl in very different size ranges – NaCl, 152 μm and KCl, 655 μm . Figure 2e**Error! Reference source not found.** shows the PSD for the seeds and the product of E_4 . Product presents a bimodal distribution with a (primary) higher proportion peak around 680 μm and a (secondary) lower proportion peak near 330 μm . Distribution peaks are not fully distinct, as a considerable proportion of particles populate the intermediate size (~ 450 μm). Proportions of the two peaks is compatible with the seeds introduced in the experiment (again note that the seeds distributions showed in the figures are normalised with respect to the masses). As the seed content was calculated so that both salts provided the same surface area, the mass of NaCl seeds added was about four times lower than KCl's. A slight increase in particles smaller than 100 μm is also observed. It is likely that each peak, primary and secondary, corresponds to the grown seeds of KCl and NaCl, respectively. Dominant peaks, however, do not match the product size calculated through the mass balance, possibly due to mixed composition polycrystalline particles and/or particles generated by secondary nucleation (< 100 μm).

SEM-EDS images presented in Figure 3e qualitatively confirm the existence of the two distinct populations in E_4 . Sample 1 shows mostly single particles of each component. Signs of breakage on large crystals, identified as KCl can also be seen since Sample 1. On Sample 2 an increase

in size can be noticed for both salts. Some mixed composition polycrystalline particles are present but single particles remain the majority. Sample 3 shows higher proportion of single component particles and a relatively low proportion of mixed composition polycrystals. Only the large crystals can be stated as predominantly comprised by KCl, despite some rare epitaxial evidences. Smaller size ranges are comprised by crystals of both materials and the intermediate sizes presented high proportion of irregular sized particles.

In spite of the epitaxial growth evidences in both directions (NaCl on KCl and KCl on NaCl) mentioned in literature²² and seen on our previous works^{13,14}, to all the conditions in this work, it is possible to observe that the growth of KCl over NaCl is proportionally higher than the opposite. As the crystallizer is stirred, the possibility of local supersaturation-induced phenomena can be neglected. Thus, this may be explained by the higher residual supersaturation for KCl than for NaCl. On our previous works, only one salt was seeded inducing a higher supersaturation for the unseeded salt. When NaCl was exclusively seeded, KCl deposits on the NaCl seeds were observed, as predictable, since a KCl nucleation event was expected on the presence of a foreign surface. Yet, in addition to heterogeneous nucleation, the evaporation generated supersaturation on this work was also higher than the one chosen for the present work, so that agglomeration, after KCl nucleation in solution, may also play a role on the depositing of KCl on NaCl's surface. On the same way, for KCl-only seeding strategies, NaCl deposits were seen on KCl seeds after a NaCl-related nucleation event. Yet a higher proportion of NaCl nucleation in solution and lower formation of mixed composition polycrystals was verified, probably related to low evaporation rates that inhibited agglomeration. Here, both salts were seeded. However, the solubility for KCl at the boiling temperature of the eutonic concentration is higher than for NaCl ($0.362 \text{ g}_{\text{KCl}} \cdot \text{g}_{\text{H}_2\text{O}}^{-1}$ and $0.275 \text{ g}_{\text{NaCl}} \cdot \text{g}_{\text{H}_2\text{O}}^{-1}$). Therefore, a higher residual supersaturation is expected for KCl, culminating on an enhancement of the nucleation rate. An increase in primary nucleation rate of KCl was also reported by Akl et. al²³ in the presence of dissolved NaCl. In our case, besides dissolved NaCl, there is also NaCl crystal surface area available, so that the primary nucleation is heterogeneous. Lower residual supersaturation for NaCl lowers the nucleation rate for this salt, prioritizing the occurrence of molecular growth.

In addition, according to literature²⁴, growth rates for KCl and NaCl are within the same order of magnitude ($10^{-7} \text{ m} \cdot \text{s}^{-1}$), when under similar relative supersaturations in their binary aqueous systems. On the other hand, different study reported that, for NaCl–KCl–H₂O system under cooling crystallization, with seeds of both salts and in eutonic conditions, an enhancement of

KCl growth rates, while NaCl's growth rates are decreased, compared respectively to KCl-H₂O and NaCl-H₂O systems²². The seeding strategy proposed in the present work aims at lowering both salts residual supersaturations. Considering the different growth rates observed in crystallization under eutonic systems, it would be expected that, when smaller seeds added were from KCl, the resulting particles of both compounds would comprise the same size range, hampering the segregation of the compounds. From the experiment seeded with large seeds of NaCl and small seeds of KCl (E₂), SEM-EDS Sample 3 (Figure 3c) analysis shows same-sized single crystals of both salts, which would point towards KCl higher growth rates. When seeding both salts in the same size (E₃), although unimodal seeds were added, results were expected to be bimodal. Indeed, as a result of the interaction of both salts at the eutonic condition, in SEM-EDS final product analysis, particles identified as KCl are usually larger than NaCl particles. This again points out to different growth rates. However, a bimodal PSD was not obtained. Thus, despite these evidences, it was not possible to confirm that KCl growth rates are higher than for NaCl.

Since the produced crystalline particles are, regardless of their composition, typically cubic and transparent, each batch was classified into fractions of different particle size ranges. The chemical composition was analysed for each size range of the products. The results are displayed in Figure 4. The composition of each size range is expressed in NaCl proportion and is shown along with particle size distribution, to enable the assessment of the composition and the proportion of each size range. It is also shown in Figure 4 the average proportion of NaCl on the whole product, i.e. product composition before sieving. Therefore, it is possible to verify segregation of each size fraction regarding the total yield. Segregation index is shown on Table 4. The composition results are discussed referring to the dominant sizes and the average NaCl proportion. Thus, when the composition differs from the average it is referred as segregated, and the terms large, intermediate and small refers to the dominant sizes. When there is more than one distribution peak, the dominant sizes will be specified.

Table 4. Segregation indexes.

Experiment	Segregation Index
E ₀ (unseeded)	0.33
E ₁ (KCl 550 µm and NaCl 275 µm seeds)	0.70
E ₂ (KCl 275 µm and NaCl 550 µm seeds)	0.20
E ₃ (KCl and NaCl 327 µm seeds)	0.61

E₄ (KCl 655 μm and NaCl 152 μm seeds)

3.20

Figure 4. NaCl proportion for each size range, Populational density, Cumulative particle distribution and average NaCl proportion in the final sample for the experiments with (A) no seeds, (B) 275 μm NaCl seeds and 550 μm KCl; (C) 550 μm NaCl and 275 μm KCl; (D) NaCl and 327 μm KCl; and (E) NaCl 152 μm and KCl 655 μm .

Overall, the composition of the small ($< 150 \mu\text{m}$) size ranges are richer in KCl, in purities higher than 88 % (except for E₄, 73 %). Yet, these small size ranges do not represent significant proportion of the product. The large size ranges (above 650 μm) are also highly segregated in terms of KCl, with purities ranging from 79 to 91 % (except for E₀ and E₂). When NaCl large seeds and KCl small seeds were added (Fig. 4C), even though enhanced NaCl proportion is

expected, only around 50 % was found. NaCl was found in higher purities mostly on intermediate size ranges (between 390 and 550 μm), with purities around 75 % for E_3 and E_4 , approximately 70 % for E_2 and 60 % for E_1 . It is worth to mention that the size fractions above 650 μm account for half of the total mass of the sample for E_0 and E_3 , and for over 70 % of the total product for E_1 , E_2 and E_4 .

Moreover, dominant sizes of every peak show segregation that can be related to seeding, except for the seeding of NaCl large seeds to which no segregation was observed on the dominant size. Also, the size ranges that can be related to the evolution/development of the NaCl seeds added on the experiments are also segregated, richer in NaCl. When NaCl seeds were much smaller than KCl seeds, each peak presented high segregation in one salt, directly related to the added seeds.

The expressive presence of KCl on the small size ranges is an evidence of major generation of secondary nuclei by this salt, due to the physical properties aforementioned. This was also seen on our previous work for experiments seeded with NaCl only¹³ and KCl only¹⁴. When KCl seeds were smaller than NaCl, segregation index ($SI = 0.20$) was the lowest, as both salts ended the batch with similar sizes. When NaCl and KCl seeds were the same size (Fig. 4D), it can be seen that, although unimodal, the lower part of the PSD peak (between 390 and 550 μm) is richer in NaCl, whilst the upper part (over 600 μm) is richer in KCl. This evidences that NaCl growth might be hindered or that KCl has a higher growth rate of KCl in simultaneous crystallization²².

Segregation was more effective for KCl large seeds and NaCl small seeds (Fig. 4B and E), respectively 84 and 91 % for KCl and 69 and 75 % for NaCl. Segregation was also seen to enhance with the increase in the size difference of the seeds, where the distribution peaks matched the segregation of the salts. Extrapolation of these results would lead to experiments seeded with KCl only¹⁴. In this previous works, KCl only seeding also led to bimodal PSDs, with one primary peak (high proportion) related to KCl and a secondary peak (lower proportion) related to NaCl, both with high purities, comparable to the ones achieved here.

It should be noted that in a batch evaporative crystallization, the evaporation rate along with extension of the evaporation – which was arbitrated as the removal of 50 wt% of the total water – also plays a role, as they dictate the residence time of the particles in the crystallizer. For higher residence times, crystals keep growing as the solution level decreases. The volume ratio between the solid and liquid phase increases and as a consequence, collision between particles

and particle-crystallizer and stirrer also increases. Therefore, secondary nucleation also increases. That will account for an increase in the number of particles in all size ranges, mixing different composition particles and hampering the segregation. Thus, considering the potential for application in desalination processes, the extent of evaporation has to be considered in order to enable downstream separation of NaCl from KCl by size classification.

5. Conclusions

The elementary phenomena were assessed for batch simultaneous crystallization from a aqueous solution of potassium and sodium chloride in the eutonic concentrations, seeded with both salts concomitantly, in different ratios but with the same surface area.

Relatively low supersaturation was generated by low evaporation rate coupled with a high surface area of both salts. Even so, evidences of heterogeneous nucleation and epitaxial growth were seen in both ways (NaCl in KCl and KCl in NaCl) and in different proportions. Higher occurrence of KCl deposits on NaCl substrates was verified and were related to KCl's higher residual supersaturation on the evaporative crystallization at the eutonic condition.

Although particle size distributions were mainly unimodal, which hinders simultaneous separation of the product by size and composition, it was possible to verify the segregation of the salts in the size ranges analysed. In general, segregation followed the trend induced by seeding, especially on experiments where small seeds of NaCl and large seeds of KCl were added. When the smaller seeds added were from KCl, the resulting particles of both compounds comprised the same size range, hampering the segregation of the compounds. When KCl added seeds were much larger than NaCl's, a bimodal particle size distribution was obtained with each peak related to one of the salts highly segregated. Even so, to some extent, mixed composition particles and evidences of epitaxial growth were seen in all conditions.

The results showed that, even with the formation of mixed composition particles, it is possible to retrieve separated solid fractions of both salts with relatively high purities and amounts from the simultaneous crystallization of multicomponent solution. Therefore, simultaneous crystallization may represent a pathway to process intensification in saline wastewater treatments, enabling the recovery of not only the water, but also the solids as useful raw materials.

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