Agglomeration and dispersion characteristics of particles in simultaneous crystallization of NaCl and Na$_2$SO$_4$ in liquid and air phase

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Abstract. Simultaneous crystallization of multiple salt occurs during evaporative crystallization of industrial high-salt wastewater, making it difficult to separate multiple salt components due to agglomeration, thus forming solid waste. To investigate the main stages of simultaneous crystallization agglomeration phenomenon and the possibility of recovering pure components, agglomeration and dispersion of particles in simultaneous crystallization of NaCl and Na$_2$SO$_4$ under different crystallization orders in liquid and air phase are investigated in this paper. The results show that crystal agglomeration occurs mainly in the air phase, and the simultaneous crystallization of NaCl and Na$_2$SO$_4$ in liquid rarely results in agglomeration, and there are great differences in crystal morphology and size between NaCl and Na$_2$SO$_4$, which can be considered for separation of the two by physical means.

1.Introduction

Water consumption is large in industry, accompanying with the discharge of a large number of saline effluents. In order to reduce the impact of industrial wastewater, it is desirable to develop desalination processes that aim at water reuse. Currently, the main technology of desalination is the membrane separation, such as reverse osmosis or electrodialysis. These processes, although producing freshwater, usually generate a highly concentrated brine [1], which contains the salts originally presented in the feed wastewater. To avoid the negative environmental impact, interest in salt recovery of hypersaline effluent has increased.

Crystallization has been a technically feasible alternative, which is used for both fresh water and salt recovery, such as evaporative crystallization [1], membrane-assisted crystallization [2] and eutectic freeze crystallization [3]. In recent decades, scholars have successively applied these crystallization technologies to recovery a variety of useful and valuable substances from high-salinity wastewater, such as NaCl [4], Na$_2$SO$_4$ [5], etc. However, current research has focused more on the crystallization of just one solute from a multicomponent solution, especially when the content of this solute is much higher than that of other solutes. Due to the multicomponent nature of the concentrate, it implies that two or more components will crystallize simultaneously. The simultaneously crystallized particle products may consist of single particles of each component and polycrystalline particles of mixed components. Mixed-component particles are difficult to purify and may end up as solid waste [6]. One potential treatment is to conduct the simultaneous crystallization in such a way that valuable components will be crystallized as individual particles, which may be separated by a physical separation operation to recover the pure component.

NaCl and Na$_2$SO$_4$ are prevalent in several industrial saline wastewater generated from the coal chemical [7], textile [8] and seawater desalination [9]. The simultaneous crystallization of NaCl and Na$_2$SO$_4$ is inevitable in the practical wastewater treatment. In this paper, the evaporation and simultaneous crystallization of NaCl-Na$_2$SO$_4$-H$_2$O ternary system are investigated. The agglomeration and dispersion of crystalline particles in liquid and air phase are examined to explore the feasibility that the two crystals can be separated when crystallized simultaneously.

2.Materials and methods

2.1. Materials

Reagents used were of analytical grade, including sodium chloride (NaCl, purity 99.5%), sodium sulfate (Na$_2$SO$_4$, purity 99%), anhydrous ethanol (purity 99.5%). And solutions were prepared by deionized water.

2.2. Methods

In order to observe the simultaneous crystallization of NaCl and Na$_2$SO$_4$, 2 pure solutions and 3 mixed solutions with different mass ratios were prepared. The
compositions were specified in Table 1. Each of 3 mixed solutions represents 3 different crystallization orders. To investigate the effect of concentration on the simultaneous crystallization of NaCl and Na₂SO₄, 20 g solution from each of the five samples were taken and placed in five 65mm glass dishes respectively. Evaporation was carried out in a constant temperature of 25°C ± 3°C. Two series of experiments were carried out. Series I investigated the agglomeration and dispersion of crystalline particles in liquid phase. During evaporation, the samples in the glass dishes were carefully observed at intervals under the optical microscope without filter drying operation. Series II investigated the agglomeration and dispersion of crystalline particles in air phase. 5 samples were filtered at the end of evaporation and washed with anhydrous ethanol before being placed in a blast drying oven at 50°C for 8 h. Then the samples were stored in a desiccator for further characterization.

<p>| Table 1. Composition of the 5 original solutions |</p>
<table>
<thead>
<tr>
<th>Sample</th>
<th>NaCl (g)</th>
<th>Na₂SO₄ (g)</th>
<th>H₂O (g)</th>
<th>Crystallization sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>52.5</td>
<td>0</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>30</td>
<td>150</td>
<td>Na₂SO₄ crystallized first</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>20</td>
<td>150</td>
<td>Almost simultaneous crystallized</td>
</tr>
<tr>
<td>4</td>
<td>35</td>
<td>15</td>
<td>150</td>
<td>NaCl crystallized first</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
<td>10</td>
<td>150</td>
<td></td>
</tr>
</tbody>
</table>

2.3. Analysis

Stereomicroscopy microscope (SZ66AN, Chongqing Aote Optical Instrument Co. Ltd., China) and image analysis software (OPTPRO Imaging Series) were used to observe the crystal shape and size characteristics. The composition and structure of the particulate crystals were analyzed by X-ray diffraction (XRD, D8 ADVANCE, Bruker, Germany).

3. Results and Discussion

3.1. Agglomeration and dispersion characteristics of particles in simultaneous crystallization of NaCl and Na₂SO₄ in liquid phase

The crystalline particles of samples 1 and 2 are pure NaCl crystals and pure Na₂SO₄ crystals, respectively, as shown in Fig. 1. All microscopy tests have two magnifiers, i.e., the higher magnification is required to examine the morphology of some specific crystals, whereas the smaller one allows the analysis of the overall crystallization. The NaCl crystals are cubic in shape and develop hopper habit which depressed middle and higher surrounding morphology, accompanied by obvious growth threads, can be clearly seen in the magnification Fig. 1A2. The Na₂SO₄ generated under the present experimental conditions (relative humidity of 42.7%) is anhydrous Na₂SO₄, and the common crystalline shape is bipyramidal and their aggregates, as shown in Fig. 1B2.

Fig. 1. Microscope image of pure NaCl and Na₂SO₄ crystals in liquid phase

Fig. 2 shows the results of evaporative crystallization of mixed solutions (samples 3-5) with different mass ratios. The results of evaporative crystallization of sample 3 are shown in Fig. 2A. At the initial crystallization moment (t=143 min), there are only Na₂SO₄ crystals, which are bipyramidal and needle-like, presumably the needle-like habit at the early stage of the process is due to the high supersaturation at the beginning of crystallization. When t=171 min, small NaCl crystals can be observed, indicating that the solution concentration has reached the eutectic condition. Continued evaporation resulted in the growth of Na₂SO₄ and NaCl crystals (t=223 min). It can be seen that the Na₂SO₄ crystals and NaCl crystals are dispersed from each other in the liquid and there is little agglomeration.

Fig. 2. Microscope images of evaporative crystallization of sample 3-5 at different times in liquid phase
Fig. 2B shows the results of evaporative crystallization of sample 4. At $t=132$ min, a small amount of NaCl and Na$_2$SO$_4$ crystals can be observed, indicating that these two crystals crystallized almost simultaneously. When $t=166$ min, both crystals become larger in size. When evaporated to 200 min, the maximum size of NaCl crystals are observed to be 1.1 mm with obvious growth threads. The crystal size distribution are wide, ranging from 50 to 1100 μm for NaCl and from 50 to 950 μm for Na$_2$SO$_4$. However, at initial concentration close to the eutectic concentration, NaCl has slightly more large crystals than Na$_2$SO$_4$. It is noteworthy both NaCl and Na$_2$SO$_4$ crystals are independent single crystals and dispersed from each other with little agglomeration in the process.

Fig. 2C shows the results of evaporation crystallization of sample 5. At $t=131$ min, the crystallization product is NaCl. when $t=190$ min, a small amount of Na$_2$SO$_4$ can be seen to precipitate, indicating that the evaporation reached the co-saturation state. When the evaporation $t=220$ min, fine Na$_2$SO$_4$ crystals with crystal sizes of 40-150 μm are dispersed among the large NaCl crystals with crystal sizes between 300-1000 μm. At this point, it can be found that NaCl and Na$_2$SO$_4$ also do not appear to agglomerate under the condition that NaCl crystallizes first. However, due to the limited area of the evaporation dish, the gap between the large NaCl crystals become smaller and smaller during the growth process, leading to slight adhesions between the crystals.

3.2. Agglomeration and dispersion characteristics of particles in simultaneous crystallization of NaCl and Na$_2$SO$_4$ in air phase

At the end of evaporation, particles are filtered from the sample solution, dried and observed by optical microscope, with results shown in Fig. 3.

![Fig. 3. Visual and microscopy observations for NaCl and Na$_2$SO$_4$ crystals in air phase](image)

It could be seen that all five samples display severe agglomeration in the dried particles. The number of Na$_2$SO$_4$ single crystals and NaCl single crystals in the dried crystalline particles is small as shown in Fig. 3C-3E. The agglomerates may consist of single-component particles or mixed-component particles with a wide range of particle size distribution and irregular shape. This leads to the difficulty in separating the two crystals when NaCl and Na$_2$SO$_4$ crystallize simultaneously. The proportion of single-component particles of NaCl and Na$_2$SO$_4$ is much smaller than the proportion of multi-component particles compared to the crystalline particles in liquid of Fig. 1-2. This indicates that uncontrolled agglomeration can easily occur during the drying process due to the interparticle forces, such as van der Waals, viscous, or liquid-bridge forces\[10, 11\]. Most importantly, solid crystalline bridges are formed, when the solute concentration in the remaining mother liquor increases through water evaporation and reaches supersaturation and crystallizes in the spaces between the wet filter cakes\[12\].

![Fig. 4. XRD diffraction pattern of 5 samples in air phase](image)

The dried crystals are characterized by X-ray diffraction and the results are shown in Fig. 4. Fig. 4A-4E show the XRD patterns of samples 1-5, respectively. The comparison with the standard XRD spectrum of NaCl show that the evaporation product of sample 1 was pure NaCl. The diffraction peak of the evaporation product of sample 2 matched with the diffraction peak of anhydrous Na$_2$SO$_4$. The XRD patterns of the crystallization products of the mixed solutions (sample 3-5) is compared with that of pure NaCl (sample 1) and pure Na$_2$SO$_4$ solution (sample...
2). It can be found that the products crystallized from the mixed solutions show almost the same diffraction patterns with sample 1 and sample 2, indicating the crystallization products are NaCl and Na₂SO₄. Therefore, no double salt or solid solution are generated in the process.

4. Conclusions

In this paper, agglomeration and dispersion characteristics of particles in simultaneous crystallization of NaCl and Na₂SO₄ in liquid and air phase are studied by static evaporation method under different mass ratios of mixed solutions. The experimental results show that NaCl and Na₂SO₄ crystallized simultaneously does not form double salt or solid solution. The agglomeration of NaCl and Na₂SO₄ occurs mainly in air phase, and the crystalline particles in liquid are mostly single crystals of both components with little agglomeration, and there are great differences in crystal morphology and size between NaCl and Na₂SO₄, which makes the effective separation of NaCl and Na₂SO₄ crystallized simultaneously possible.

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References


