SIGNIFICANCE OF THE PAPER :

A NEW TECHNOLOGY FOR THE CRYSTALLIZATION OF DEAD SEA POTASSIUM CHLORIDE

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In Jordan about 90% of the Potassium Chloride(KCl) is produced as fertilizer grade of about 96% purity , which is also used as a raw material for the production of potassium sulfate(K_2SO_4) fertilizer.In Jordan it is still needed to raise the purity of KCl and get a fine crystal size distribution(CSD) in order to meet the required agricultural specifications since the finer the feed crystals the easier and faster the achievement of pure potassium sulfate fertilizer.

ABSTRACT

The aim of this article is to introduce a new technology for the production of Dead Sea potassium chloride. The new technology depends on using the power of ultrasound waves during a crystallization process to enhance potassium chloride precipitation and to improve the end-use properties of the produced crystals. This environmentally clean technology, which is called sonocrystallization, has received very intensive research in the past few years. It was used in this study to modify the crystallization process of potassium chloride from the decomposition of Dead Sea carnallite. Two crystallization runs were done; the first was performed without the application of ultrasound waves and the second was performed with this application. The effect of sonication on the crystallization process time and on crystal size distribution as well as on the purity of the crystals was studied. It was found that the required time for the un-sonicated process was about 150 min. This time was reduced to about 50 min when sonication was applied. The produced crystals were sieved, and the crystal size distribution (CSD) was determined for the two runs. For the sonicated process, **finer but more uniform crystals were obtained** with a mean average size of 0.2643 mm in comparison with 0.5727 mm for the un-sonicated process. The produced crystals were found to be **of** 96.07% **KCl** for the un-sonicated process and **this purity was improved to** 97.31% **KCl** by the application of ultrasound waves. Based on the results of this study, it seems to be feasible and economical to scale up the proposed technology for industrial applications.
Keywords: Carnallite decomposition; Improved crystallization; Potassium chloride precipitation; Sonocrystallization

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A New Technology for the Crystallization of Dead Sea Potassium Chloride

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The aim of this article is to introduce a new technology for the production of Dead Sea potassium chloride. The new technology depends on using the power of ultrasound waves during a crystallization process to enhance potassium chloride precipitation and to improve the end-use properties of the produced crystals. This environmentally clean technology, which is called sonocrystallization, has received very intensive research in the past few years. It was used in this study to modify the crystallization process of potassium chloride from the decomposition of Dead Sea carnallite. Two crystallization runs were done; the first was performed without the application of ultrasound waves and the second was performed with this application. The effect of sonication on the crystallization process time and on crystal size distribution as well as on the purity of the crystals was studied. It was found that the required time for the un-sonicated process was about 150 min. This time was reduced to about 50 min when sonication was applied. The produced crystals were sieved, and the crystal size distribution (CSD) was determined for the two runs. For the sonicated process, finer but more uniform crystals were obtained with a mean average size of 0.2643 mm in comparison with 0.5727 mm for the un-sonicated process. The produced crystals were found to be of 96.07% KCl for the un-sonicated process and this purity was improved to 97.31% KCl by the application of ultrasound waves. Based on the results of this study, it seems to be feasible and economical to scale up the proposed technology for industrial applications.

Keywords Carnallite decomposition; Improved crystallization; Potassium chloride precipitation; Sonocrystallization

Introduction

Sonochemistry, or the application of power ultrasound to chemical processes, has received very intensive research and development in the past few years, both with respect to its range of application and its implementation at industrial manufacturing scale. This interest arises from the need for environmentally clean technology that offers possibilities for cleaner chemical processes with improved product yield and quality. One of the sonochemistry applications is the use of ultrasound waves to control the course of a crystallization process, which is known as sonocrystallization.

Recent studies on sonocrystallization have shown that the application of ultrasound waves to a crystallizing system can modify and improve both the

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crystallization process and the product end properties. Thus, crystallization appears to be an obvious area in which ultrasonic application could be beneficial. Sonocrystallization has been used successfully to manipulate crystal size distribution and, hence, to modify solid-liquid separation, washing and product purity, product bulk density, and powder flow characteristics (Cains et al., 1998). In contained, sterile operations, such as in pharmaceuticals and fine chemicals manufacture, the use of ultrasound is advantageous in eliminating the need to add seed crystals (McCausland et al., 2001). Sonocrystallization has also been used to accelerate crystallization processes, that is, to run a complete crystallization process in a shorter time compared with the same process under no sonication (Li et al., 2003).

Theory of Sonocrystallization

Induced cavitation is the primary phenomenon from which most sonochemical effects are derived. When the liquid medium is exposed to ultrasound waves, cycles of compression (positive pressure) and refraction (negative pressure) occur. If the negative pressure in the refraction cycle is sufficiently large, the tensile forces bring about void or bubble formation by shearing the liquid continuum apart. At this point, the liquid may break down and bubbles and cavities will continue to develop. These bubbles will grow in size until the next compression cycle occurs during which these bubbles are forced to contract. As a result, many of these bubbles will collapse, producing a shock wave, which is estimated to be in the order of several thousands of atmospheric pressures (Mason and Lorimer, 1988). In sonocrystallization, it is assumed that cavitational collapse creates a nucleation site analogous to that from a trace particle or a surface imperfection (McCausland et al., 2001). Also, ultrasound as an external force will provide a significant amount of impact on the crystals and this will decrease crystal aggregation and agglomeration, resulting in a smaller crystal average size (Kim et al., 2002). It was found that the application of different frequencies of ultrasound waves during the crystallization process usually results in a higher population density of smaller crystals (Bartels and Furman, 2002). Sonocrystallization has a considerable effect on crystal size distribution to the degree that some investigators suggested the use of sonication to control the crystallization process to get a certain required crystal size distribution (Omar and Ulrich, 1999). Also, it was found that organometallic reactions could proceed more rapidly by the application of sonocrystallization than under conventional conditions (Bartels and Furman, 2002; McCausland and Cains, 2002).

In this study, the power of ultrasound was applied for potassium chloride production from the decomposition of Dead Sea carnallite. The effect of ultrasound waves on the crystallization process time as well as on the end-use properties of the product (crystal size distribution and crystals purity) was compared with the effects on crystals obtained under no sonication.

Crystallization of Potassium Chloride from Dead Sea Carnallite

Worldwide production of potassium chloride exceeds 40 million tons, with a growth rate of about 3.2% per year. Virtually all commercial KCl is extracted from natural sources mainly from seawater. More than 90% of the total KCl consumption is used for fertilizer production (Mining, Minerals and Sustainable Development Project, 2002). Other uses of KCl include as a food additive, a supplement to animal feed,

and in the production of potassium hydroxide. In pharmaceutical products, KCl is used for prophylaxis and treatment of hypokalemia, in electrolyte replenishment solutions for general medical use and kidney dialysis, and in digitalis intoxication (Mining, Minerals and Sustainable Development Project, 2002).

Production of Jordanian potassium chloride from Dead Sea water, by the Arab Potash Company, exceeds 1.8 million tons per year. The Dead Sea is the world saltiest sea, with an average salinity of 370 g of salt/kg of water, compared with the ocean's average of 40 g of salt/kg of water. KCl content in Dead Sea is about 12.3 g KCl/kg water. Potassium chloride production from Dead Sea water passes in a series of steps. First, water from the Dead Sea is pumped into a series of solar evaporation ponds. The resulting deposit consists of carnallite ($KCl{\cdot}MgCl_2{\cdot}6H_2O$) and sodium chloride (NaCl). Usually, two types of carnallite result, coarse and fine. This raw material is then used to produce potassium chloride, magnesium chloride, magnesium oxide, hydrochloric acid, caustic soda, chlorine, and magnesium metal. At the company, there are two crystallization units, the hot crystallization unit and the cold crystallization unit. The new $125 million cold crystallization unit is based on new technology operating the crystallization process at ambient temperature and is less energy-intensive than the widely used hot crystallization unit. The process also consumes less water but requires a higher grade of carnallite feed.

The first step in potassium chloride production in the cold crystallization unit is the addition of water to the carnallite in order to dissolve the magnesium chloride ($MgCl_2$). This water causes the carnallite to decompose to its components. As is shown in Figure 1, if the $MgCl_2$ concentration is at or near the triple-saturation point (the point at which the solution is saturated with all carnallite, NaCl, and KCl), the KCl solubility is suppressed to the point where most of it will precipitate. For maximum recovery, the crystallizing mixture must be saturated with carnallite

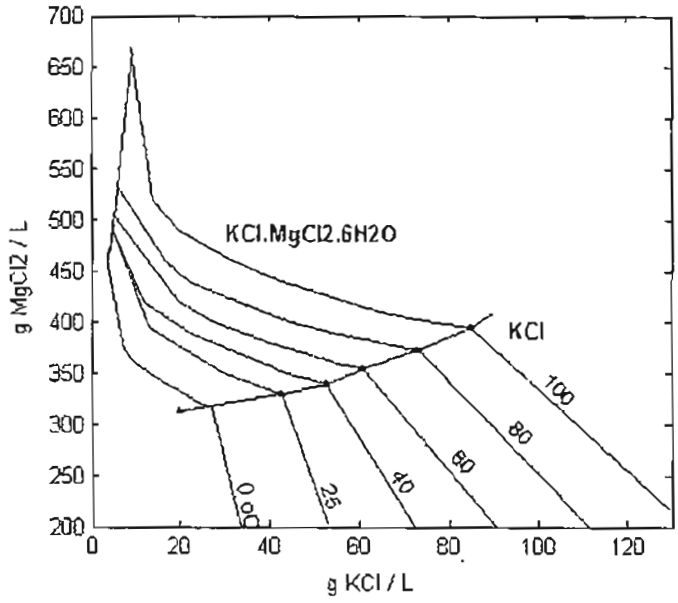

Figure 1. Solubility curves of carnallite/KCl system in the presence of NaCl (3%).

at its triple-saturation point. If the mixture is not saturated, more KCl will dissolve in the water. Industrially, the crystallizer is usually fed with both coarse and fine carnallites such that 10% carnallite remains in the slurry. This can be achieved by adjusting addition of process water.

In this study, crystallization of potassium chloride from Dead Sea carnallite samples was performed in a batch-scale, well-mixed crystallizer at ambient temperature. The crystallization process was done twice; one without the application of the ultrasound waves and the other with this application. As indicated above, the crystallization process time and the end-use properties of the produced KCl of the two runs were compared.

Apparatus and Experimental Procedure

The experiments were carried out in a 1 L batch-scale, well-mixed crystallizer. The crystallizer was initially fed with 1 L brine, 106 g of fine carnallite, and 250 g of coarse carnallite. Process water was added to adjust about 10% excess carnallite over saturation (the resulting mixture then is a slurry). This is similar to the triple-saturation point conditions at the Arab Potash Company crystallizer, which is operated at ambient temperature. The mixing rate was adjusted to 250 rpm. At the initial time, a 1 mL liquid sample was withdrawn from the crystallizer and taken for analysis using atomic absorption spectroscopy. After that, samples were withdrawn periodically during the run of the experiment and analyzed for Mg metal concentration. This will give an idea about the carnallite decomposition since Mg concentration will increase as more carnallite decomposes. At the end of each run, the precipitated crystals were separated by filtration, dried, weighed, and screened using mesh analysis to determine crystal size distribution (CSD). Also, 1 g of the precipitated crystals was dissolved in 20 mL of distilled water, and the solution was analyzed to determine the purity of the resulting crystals, also using atomic absorption spectroscopy analysis. The previous procedure was repeated twice; in the first run no ultrasound waves were applied and in the second run ultrasound waves were applied using a transducer of 2000 W output power. The ultrasound waves were applied in an on-off cycle of 2 s of application and 9 s without application for a total time of 150 min. It is recommended not to increase the continuous exposure time more that this, in order not to heat the solution by the ultrasound waves. The experimental setup is shown in Figure 2. The ultrasound generator is a Weber Ultrasonics

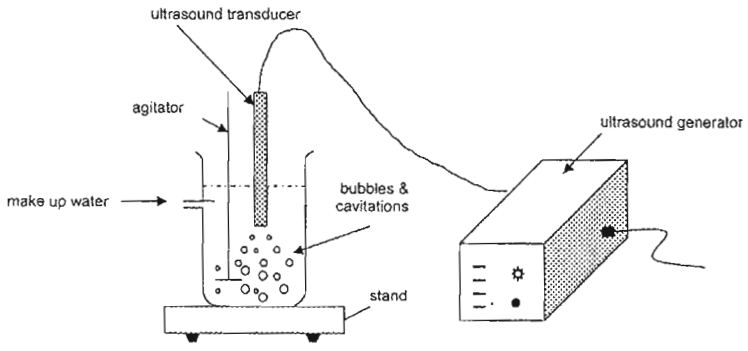

Figure 2. Sketch of experimental setup.

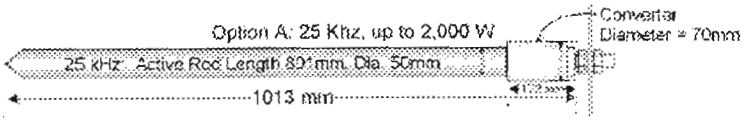

Figure 3. Ultrasound transducer (Sonopush Mono1500 SPM, 25 kHz).

1500-SP, 25 kHz, and the transducer is a Sonopush Mono1500 SPM, 25 kHz, with the dimensions and specifications shown in Figure 3. The transducer is able to generate an intense cavitation field along its surface area as well as from the tip for a distance of around 30 cm. Such a transducer has an excellent service life due to a solid radiating element made of a titanium alloy that protects it from cavitational erosion.

Results and Discussion

Effect of Sonication on Crystallization Process Time

Figure 4 shows the concentration of Mg metal versus time. This concentration increases with time as a result of the carnallite decomposition. In the first run, in which no sonication was applied, the time required for the concentration to reach its maximum was about 150 min. However, when sonication was applied, it was found that the Mg concentration reaches the maximum value after about only 50 min. This means that a reduction of about 100 min of process time was achieved by the application of sonication. This may be explained by the fact that the

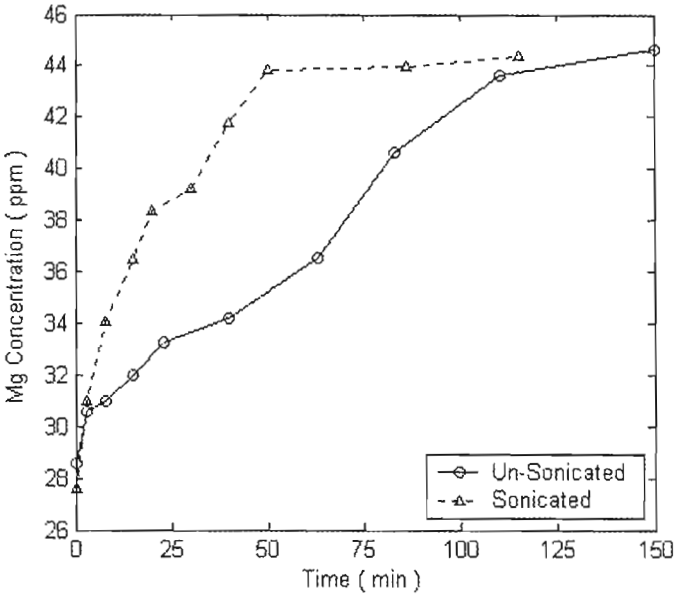

Figure 4. Effect of sonication on Mg concentration.

large number of ultrasonic cavitations work as nucleation sites to initiate the crystallization process of KCl crystals. Also, the ultrasound waves tend to break the agglomerated carnallites, and this enhances the carnallite decomposition rate.

Effect of Sonication on the CSD

Figure 5 shows the CSD of the produced crystals for the two runs. For the un-sonicated run, the crystals of the larger sizes have higher mass fractions than those of the finer crystals since no crystals were retained on the first two smaller meshes. This may be due to the fact that crystals tend to agglomerate to produce larger crystal sizes. For the sonicated crystallization run, the CSD is apparently different since the product contained higher proportions of fine, more uniform crystals in the size range of 0.21–0.425 mm (uniform here means that most of the produced crystals have sizes close to their mean average size). This may be explained by the fact that ultrasound waves tend to eliminate the agglomeration process of the crystals. To represent this mathematically, the mean average size, $\overline{D}$, of the crystals was calculated as follows:

$$\overline{D} = \frac{\sum_{i=1}^{N} d_i \cdot w_i}{\sum_{i=1}^{N} w_i} \tag{1}$$

where d_i is the opening size of mesh i, w_i is the weight of crystals retained on mesh i, and N is the number of meshes.

For the un-sonicated process, the crystals mean average size was found to be 0.5725 mm and that of the sonicated process was found to be 0.2643 mm.

Figure 6 shows the cumulative mass fraction of oversize crystals. Also, it is clear that finer crystals are obtained under sonication since the cumulative fraction is localized within the smaller size ranges.

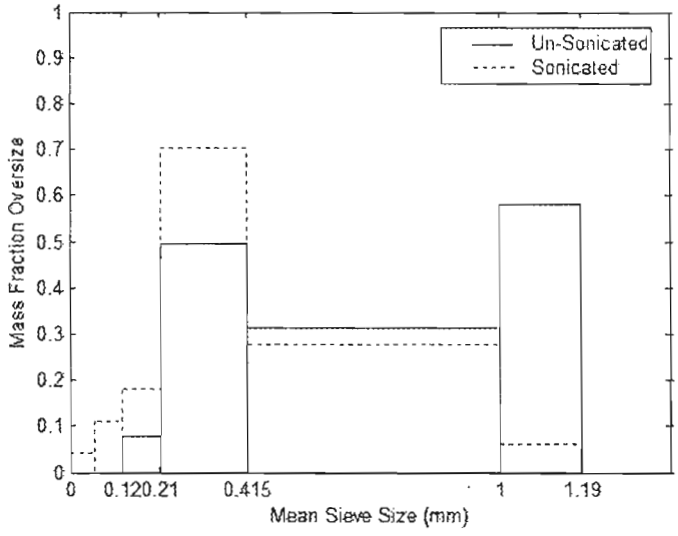

Figure 5. Effect of sonication on the CSD.

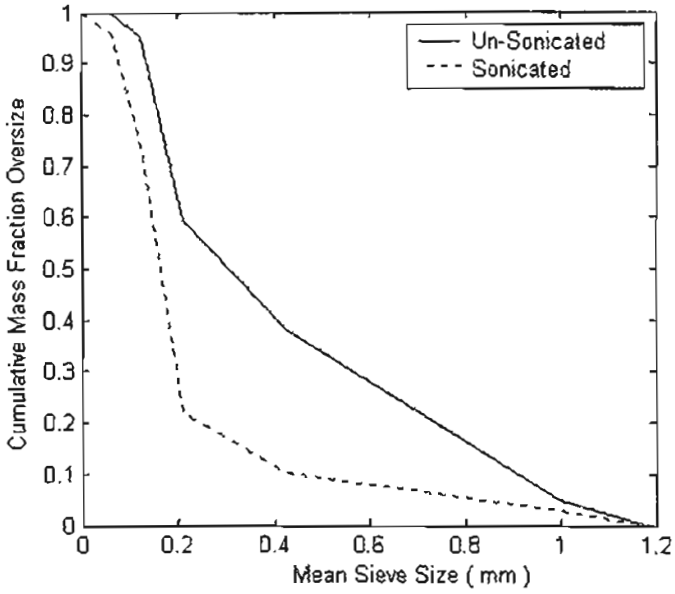

Figure 6. Effect of sonication on the cumulative mass fraction of oversize crystals.

Effect of Sonication on KCl Crystal Purity

As indicated above, the purity of the obtained crystals was determined by dissolving a known amount of the crystals in a known volume of distilled water and then analyzing the solution. For the un-sonicated process, it was found that the purity of the produced crystals was 96.07% KCl and for the sonicated process the purity was 97.31% KCl. As indicated above, this may be explained by the fact that cavitational collapse created by sonication may create a nucleation site analogous to that from a trace particle (such as a tiny undissolved carnalite crystal, a tiny NaCl crystal, or even dust). It is clear then that the application of ultrasound waves has a promising effect in improving crystal end-use properties, especially purity.

Conclusions

The new sonocrystallization technology for the production of KCl from the decomposition of Dead Sea carnallite has shown promising results in significantly

Table I. Comparison between un-sonicated and sonicated crystallization runs

Process	Process time (min)	CSD	Product purity (% KCl)	Mean average size (mm)	Seeding
Un-sonicated crystallization	150	Not uniform	96.07	0.5725	Preferable
Sonicated crystallization	50	Uniform	97.31	0.2643	No need

reducing process time, increasing crystal purity, and enhancing crystal size distribution. The effects of sonication on the KCl crystallization process are summarized in Table I.

It is concluded that the sonocrystallization process is a promising technology for KCl crystallization; it yields more preferable process conditions and end-use product properties. Based on the above results, it is expected to be feasible and economical to scale up this technology for industrial applications.

Acknowledgment

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