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Crystallization of carnallite from KCl-$MgCl_2$ brine solutions by solvent evaporation process and its structural and mechanical characterization

Jiban PODDER [1], Shaoyu Gao [2], Richard W. Evitts [1*], Robert W. Besant [2], and D. Matthews [3]

[1] Department of Chemical and Biological Engineering,
[2] Department of Mechanical Engineering,
[3] PCS Pilot Plant, Innovation place, Saskatoon, University of Saskatchewan, Saskatoon, SK S7N 5A9, Canada

Abstract

Carnallite crystals have been synthesized from brine solutions at room temperature (23°C) by solvent evaporation growth technique to show the effect of the concentration of potassium chloride (KCl) and magnesium chloride ($MgCl_2$) on the growth, structural and mechanical properties of the crystal. Transparent and pseudo-hexagonal shape carnallite crystals with the dimension of 4 × 5 × 2 mm to 16 × 13 × 3 mm were grown. The crystals were characterized by powder X-ray diffraction and the lattice parameters were found to be a = 9.598 Å, b = 16.141Å and c = 22.519Å, space group: Pnna, Z: 12, $\alpha = \beta = \gamma = 90°$ with the unit cell volume, V = 3488.67Å^3. The lattice parameters are found to be in good agreement with the standard values and the structure of the crystal is orthorhombic. A Vickers micro hardness test was carried out to determine the hardness number and work hardening coefficient of the carnallite crystals.

Keywords: Carnallite crystal; Potassium-magnesium chloride solution; Solvent evaporation; X-ray diffraction, Orthorhombic structu

Introduction

The study of multicomponent brine solutions is an important area of research from extraction point of view by flotation or recrystallization process in the mineral industries. Mined and processed potash is usually 98% pure KCl and widely used as a source of potassium fertilizers. Potash ore is composed of approximately 55% (w/w) NaCl, 40% (w/w) KCl and remaining 5% (w/w) is non-soluble clay and non-clay materials as impurities [(1)]. The most important mineral salts from solution mining are halite, sylvinite and carnallite. Carnallite is an important source of potash, an invaluable fertilizer also. Carnallite occupies the void spaces between halite crystals and exists in the form of microcrystals mostly on the surface of the processed KCl [(2).]

In nature, carnallite is formed with a perfect orthorhombic structure and is sometimes blue, yellow and pink in colour. Carnallite is a hydrated double chloride mineral salts (potassium-magnesium chloride) with six hydrated molecule water ($KMgCl_3 \cdot 6H_2O$) and it only forms in nature under a specific environmental condition in an evaporating sea or sedimentary basin. Carnallite crystals are transparent to translucent, optically biaxial (positive) and anisotropic crystals. Its crystal habits are typically granular and massive, and sometimes fibrous. Individual carnallite crystals are pseudo- hexagonal orthorhombic and tabular but are extremely rare [(3)].

Currently there is lack of data on the crystallization of carnallite in a laboratory. A very small carnallite crystal of 1-2 mm size has grown after a few days in a laboratory [(4)]. Carnallite crystal was synthesized from a solution by slow crystallization at 25°C and determined the lattice parameters and the space group of this crystal [(5)]. The new process of synthetic carnallite production by spent magnesium electrolyte (SME) method was reported and the optimum SME particle size was obtained 0.315 mm [(6)]. So far our knowledge is concerned; no report is available on the growth of pseudo-hexagonal structure of carnallite crystals with a large size under solvent evaporation technique at room temperature. However, from a processing point of view, it is of scientific interest to investigate the carnallite crystal and to find mechanisms to recover KCl from carnallite based on the concentration gradient of the brine solutions. In addition to technological and application point of interest, Carnallite crystals have potential mineral sources. In order to understand the

* Corresponding author Email: Richard.evitts@usask.ca

mechanisms of carnallite formation, we have attempted to grow the carnallite crystals in a laboratory from aqueous solutions by solvent evaporation process at room temperature and investigate the structural and mechanical properties of the crystals.

Materials and Experimantal Procedures

Analar grades KCl, $MgCl_2.6H_2O$ supplied by Fisher Scientific were used and a saturated solution was prepared at 23°C (room temperature) containing 2.5 mole KCl and 90 mole $MgCl_2.6H_2O$ following the Van't Hoff phase diagram [7]. The prepared solution was filtered and kept in a petridish covered with a perforated polythene sheet to permit evaporation of solvent in a dust free environment. Care was taken to provide an atmospheric ambient devoid of gusts of air current. Seed crystals were prepared at room temperature by spontaneous nucleation. After preparing the seed crystals, mixed solutions were prepared with different compositions of KCl and $MgCl_2.6H_2O$ Seed crystals with perfect shape and free from macro defects were used for the experiments.

Characterizations

The amount of chlorine, magnesium, potassium was determined using X-ray fluorescence spectroscopy (XRF). Furthermore, to determine the lattice parameters, a powder XRD analysis were performed using an automated 'X'-Pert PRO MPD Theta-Theta system (PANalytical) X-ray powder diffractometer with 'X' Celerator RTMS (Real Time Multiple Strip) detector and monochromatic CoKα radiation (λ=1.70688 Å) with an operating voltage of 40kV and current of 45 mA. Dried samples for XRF analysis are pulverized in a Retsch ZM-200 rotor mill, the pulverized sample is then pressed at 30,000 pounds pressure in an Angstrom press to form a 40 mm diameter pellet. XRF analysis of the pressed pellets is performed using a PANalytcal PW2424 Magix wavelength dispersive XRF.

Results and Discussion

Crystallization of Carnallite

Good quality transparent defect free seed crystals were grown in a Petri dish by a solvent evaporation technique at room temperature. Optically good crystals having the dimensions of 4 × 5 × 2 mm to 16 × 13 × 3 mm with perfect external morphology were harvested within a period of 3 to 4 weeks and are shown in Figure 1(a), 1(b) and 1(c). Table 1 gives the chemical composition of the synthesized carnallite and the product yield from the solution mixture. To warm up the solutions and for a little bit faster evaporation, a 60 Watt lamp was used and focused to the solutions taken in a Petri dish covered by perforated polythene sheet (as carnallite is an evaporate mineral)

In our experiment we observed that due to the different solubilities of magnesium chloride and potassium chloride in water solvent, the mixed solution began to precipitate out as crystals once saturation has been reached. Carnallite starts to precipitate from mixed solution when temperature is reduced. However, such mixed solutions must be close to saturation before precipitation.

Figure 1. Photographs of (a) carnallite seed crystals, (b) & (c) pseudo-hexagonal carnallite crystals, (d) Seed crystals of magnesium chloride hexahydrate, (e) magnesium chloride hexahydrate crystals.

Table 1. Chemical composition of synthesized carnallite (wt%) by XRD analysis.

Sample	X-ray florescence analysis (%)				X-ray diffraction study (%)
wt% /50 ml water	K	Mg	Cl	H_2O	Product
1.12 (g):110.38 (g) $MgCl_2.6H_2O$	14.70	7.60	39.50	35.47	Carnallite (97.27 %)
1.10 (g) KCl:160.26 (g) $MgCl_2.6H_2O$	0.00	11.72	34.66	53.62	$MgCl_2.6H_2O$ (99.40%)
10.8 (g) KCl: 29.2 (g) $MgCl_2.6H_2O$	15.20	7.23	37.65	39.92	Mixed KCl & $MgCl_2.6H_2O$
Pure carnallite	13.51	8.80	38.16	39.51	100

At the surface of the mixed solution (i.e. air-liquid interface), nucleation of small carnallite crystals will appear after attaining super saturation by the solvent evaporation process. Hence they grow at the edges by additions from the surrounding supersaturated solution, and formed thin square tablets. These tablets typically have depressed centers, as a result of reduced buoyancy as they grow heavier and eventually grow too heavy for the surface tension forces; ultimately they drop on the bottom of the Petri dish. The solubility of KCl is low in concentrated magnesium chloride solutions, so initially very high magnesium chloride concentrations is not suitable for the conversion of carnallite. Therefore, the solubility, temperature and mixing intensity of KCl is an important in magnesium chloride solutions for the conversion of carnallite. The concentration of KCl-$MgCl_2$ has to be maintained stoichimteric otherwise the KCl may be undersaturated in $MgCl_2$ solutions. If it is undersaturated then the crystals form almost pure hexahydrate magnesium chloride. The lack of produced carnallite crystal could be due to its low crystallization rate. Since magnesium ions exist in aqueous solution normally as $[Mg(H_2O)_6]^{2+}$ and this promotes the formation of salts having six water molecules in their structure. From KCl- $MgCl_2$ brine solutions, high concentrations of Mg^{2+} ions in solution have reversed the charge on the KCl, thus reducing the growth of KCl from the mixed solutions. On the other hand a higher concentration of $MgCl_2$ in solution would reduce the dissolution rate of carnallite and with the addition of more water; carnallite produces a lower level of supersaturation. Under such crystallization conditions, the growth of KCl will be reduced. Thus there are three possible ways to precipitate carnallite from brine, including evaporative concentration of intercrystalline brine, cooling and mixing of brines of appropriate compositions.

Powder X-ray diffraction

The powder XRD pattern of carnallite crystals are shown in Figure 2. The interplanar spacing (d), full width at half maximum (FWHM) and peak intensity (I) of major planes have been identified and are shown in Table 2. The lattice parameters were calculated and presented in Table 3. From the data, it is observed that carnallite crystallizes orthorhombically. The values of lattice parameters for the carnallite crystals are found to be in good agreement with the reported literature [8]. The phase composition and the structure of the synthesized carnallite are similar to those of naturally enriched carnallite in mines.

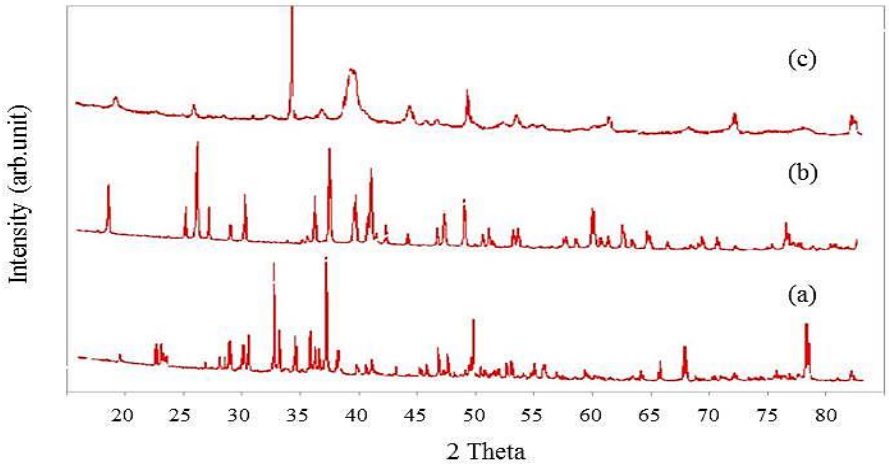

Figure 2. X-ray diffraction spectrum of (a) Possible carnallite $MgKCl_3.6(H_2O)$, (b) $MgCl_2.6H_2O$, (c) Mixed crystal (27% KCl + 73% $MgCl_2.6H_2O$).

Table 2. XRD data on the laboratory grown carnallite.

Sample	h k l	d (A°)	2 Theta	I (%)	FWHM
Synthesized carnallite	130	4.693	21.975	42.4	0.0669
	222	3.873	26.706	35.5	0.0669
	223	3.615	28.652	68.6	0.0669
	224	3.327	31.190	100	0.0612
	225	3.041	34.203	59.3	0.0612
	136	2.931	35.536	82.6	0.0612
	400	2.399	43.775	36.5	0.0612
	402	2.346	44.815	47.3	0.0612
	336	2.218	47.560	13.7	0.0612
	229	2.139	49.433	25.4	0.1020
	406	2.021	52.524	21.3	0.0612
	443	1.989	53.432	23.3	0.0612
	445	1.876	56.935	14.3	0.0612

Table 3. Crystallographic parameters of laboratory grown carnallite

Crystals	Lattice parameters				Unit cell volume (Å)
	a (Å)	b (Å)	c (Å)	Sp.gr.	
Grown carnallite	9.5757	16.1559	22.5268	P2/b2/n2/n	3485.04
Fischer (1973)	9.5980	16.141	22.59	P2/b2/n2/n	3488.67
$MgCl_2.6H_2O$	9.8605	7.1077	6.0745	C12/m1	424.76

The lattice parameters were estimated using the relationship

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \qquad (1)$$

Vickers microhardness studies

Mechanical properties of ore salt crystals in micro range are important for assessing the mineral strength as well as in analyzing the participation of mineral particles during mining. The hardness of a material is a measurement of its resistance to plastic deformation.The micro hardness measurements were carried out by using Vickers Micro hardness Tester, Mode E- 384 fitted with a Vickers diamond pyramidal indenter and attached to a Leitz incident light microscope. During hardness measurements, load variations were applied over a fixed interval of time 10 sec. The indention made on the 001 face of the carnallite crystals at room temperature with the load ranging from 10 g to 200 g. H_V was calculated from equation (2): where, P is the applied load in kg and d is the diagonal length of indentation impression in millimeter and 1.8544 is a constant of geometrical factor for the diamond pyramid. Vickers hardness is a measure of hardness of a material calculated from the size of an impression produced under load by pyramid shaped diamond indentor. The hardness is high at lower loads and then it decreases with increase in load. This may be a result of loosely packed lattice with reduced bond energy due to the introduction of some defects into the matrix of the crystals. The work hardening coefficient *n*, a measure of the strength of the crystal, is computed from the log p-log d plot. The plot of log p-log d yields a straight line and work hardening index or Meyer index, *n* is obtained from the slope of the line for higher loads. According to Meyer's law [9].

$$Hv = 1.8544 \frac{p}{d^2} \ (Kg/mm^2) \qquad (2)$$

$$P = k_1 \, d^n \qquad (3)$$

The value of the slope (n) was found to be less than two (n = 1.15) which reveals that the Vickers hardness increases; indicating their hardening nature and it is in good agreement with the Onistch concept [10].

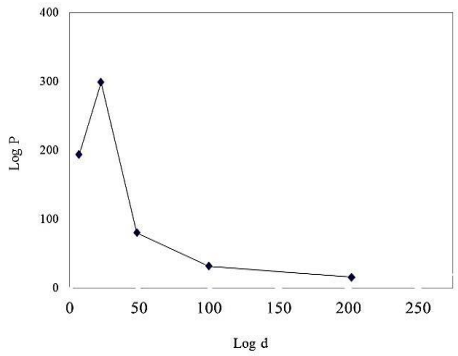

Figure 3. Vickers micro hardness versus applied load.

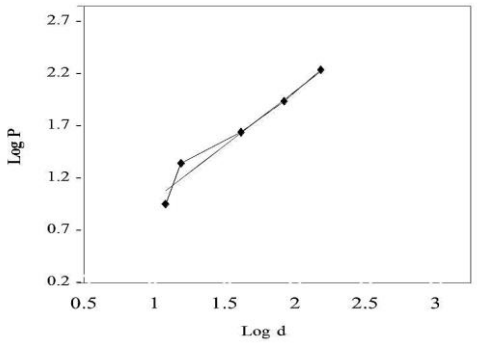

Figure 4. Log p vs. log d for carnallite crystal.

Conclusions

Carnallite crystals have been synthesized from low KCl high $MgCl_2$ concentration of high density aqueous solutions by solvent evaporation technique at room temperature (23°C). The solubility of KCl is found to be lower in mixed KCl-$MgCl_2$ brine solutions due to different ions. Carnallite crystal formed only if the K^+ concentration was found stable in the inter-crystalline brine solutions, otherwise pure heptahydrate magnesium chloride crystal will grow from binary solutions. It was shown that laboratory grown carnallite crystals by solvent evaporation process have pseudo-hexagonal orthorhombic structure. The growth period, surrounding temperature, and KCl-$MgCl_2$ concentration in composition solution are important factors for producing a high yield of carnallite. From application point of view this study could help the modern mineral industries in recovery of KCl from high content of $MgCl_2$ brine solutions where disseminated carnallite and sylvite are widely distributed in the potash ore.

Acknowledgments

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Novelty of the work

Transparent and pseudo-hexagonal shape carnallite crystals with the dimension of 4 × 5 × 2 mm to 16 × 13 × 3 mm have been synthesized by solvent evaporation technique at room temperature, which has not yet been seen in the literature. Structural, morphological, and mechanical properties of carnallite crystals have been studied by XRD, XRF and Vickers microhardness measurements. From industrial application point of view this study will open up a route to the modern mineral industries to recover KCl from high content of $MgCl_2$ brine solutions where disseminated carnallite and sylvite are widely distributed in the potash mines.

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