SCIREA
SCIREA Journal of Chemistry
http://www.scirea.org/journal/Chemistry
March 14, 2017
Volume 2, Issue 1, February 2017

Kinetic Description of the Leaching Mining Process for Carnallite

Yan-Fang MA [1,2], **Kan-She LI** [1*], **Zhi-Hong ZHANG** [2], **Tian-Qi HU** [3], **Jian-Kang WANG** [3]
[1] Xi'an University of Science and Technology, Xi'an 710054, PR China
[2] Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, PR China
[3] University of Chinese Academy of Sciences, Beijing 100049, PR China

*Supported by the Key Laboratory of Comprehensive Utilization of Salt Lake Resources in Qinghai province of China (No. Q-SYS-2014-KF-05) and Qinghai Key S&T Special Projects (No. 2015-GX-A1A).

**Kan-She Li, 58 Yanta Rd., Xian, Shanxi, 710054, P.R. China;
Zhi-Hong Zhang, 18 Xinning Rd, Xining, Qinghai, 810008, P.R. China.

ABSTRACT

Underground leaching mining of carnallite is a mining method with minimal environmental impact. This method involves the leaching of potassium ions from solid carnallite into a liquid phase and subsequent recovery. Herein, we describe research on the effect of temperature on the process of carnallite dissolution, which is a key factor that affects its underground mining. The kinetics of the carnallite dissolution process has been studied, and dissolution kinetic models have been established under isothermal and non-isothermal conditions. The carnallite dissolution process conforms to the Stumm model at 298.15, 323.15 and 348.15K. The dissolution kinetics can be expressed as $(0.0083\mathrm{T}-2.511)A\exp\left(-\frac{\mathrm{E}}{\mathrm{RT}}\right)\mathrm{t}=-\frac{1}{1.4799}(2.23-c)^{1.4799}$ under non-isothermal conditions. The concentration of potassium ions in the process of leaching mining can thereby be predicted. This model may provide guidance for more effective underground leaching mining of carnallite.

Keywords: Carnallite; underground leaching mining; non-isothermal; kinetics.

1. INTRODUCTION

Carnallite, a hydrated chloride of potassium and magnesium that occurs with potassium chloride and sodium chloride, is a soluble potash mineral (Bao Ji-qing et al.,1995). It is widely distributed in Thailand, Laos, South Africa, etc. Carnallite exists in rock formations at a depth of around 1000 m in such areas. Underground leaching mining technology is a common method with minimal impact on the environment that is deployed in salt mines(Wang Ben.,1997; Liang et al.,2012). Potassium ions are leached from solid carnallite into a liquid phase by solid-liquid extraction, and the liquid phase containing potassium ions provides the raw materials for potash. Study of the dissolution kinetics of carnallite can provide theoretical guidance for its leaching mining. Shuping Xia et al. (Xia et al.,1993; Hong et al.,1994; Xia et al.,1993) studied the kinetics and mechanism of crystallization and dissolution of potassium carnallite, and they established dissolution and crystallization kinetic equations in the control situation of a carnallite saturated phase. S. Vyazovkin and Cheng Huai-de et al. (S. Vyazovkin.,1995; M.E. Brown et al.,2000; Cheng et al.,2013; Cheng et al.,2015) studied the dissolution kinetics of carnallite in a seam and established basic dissolution equations. Such literature research work has been mainly focused on carnallite dissolution kinetics in media saturated with potassium chloride. In this paper, based on research on carnallite dissolution kinetics in liquid media not saturated with potassium chloride, a kinetic model of carnallite dissolution under isothermal conditions has been established. Moreover, a kinetic model of carnallite dissolution under non-isothermal conditions is proposed for the first time. With this model, the concentration of K^+ in the process of underground leaching mining of carnallite can be evaluated, which represents an improvement on previous models. It should thus provide theoretical guidance for underground leaching mining.

2. EXPERIMENTAL

2.1 Raw material

Carnallite was obtained from a 775- m-long drilling core from the Democratic Republic of Congo, Africa. Table 1 shows the chemical composition of the carnallite, and Fig. 1 shows its X-ray diffraction pattern.

Table 1. Chemical composition of carnallite.

	K	Mg	Na	Cl
Content	6.77	7.78	17.70	39.11

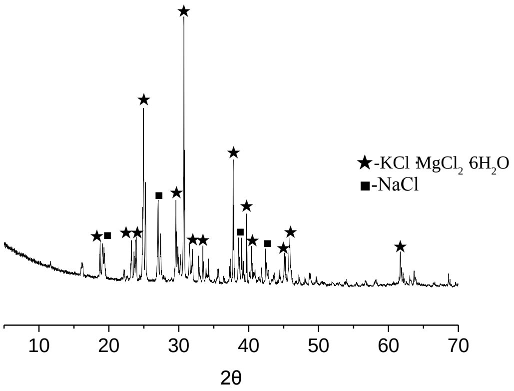


Figure 1. X-ray diffraction pattern of carnallite.

2.2 Experimental procedure

Leaching mining technology involves leaching K^+ from carnallite into a liquid phase. The Na^+, K^+, Mg^{2+}, Cl^--H_2O phase diagram is shown in Fig. 2, in which the solid-phase point of carnallite is A, the liquid-phase point after dissolution is B, and E is the common saturation point of $KCl \cdot MgCl_2 \cdot 6H_2O$, KCl, and NaCl. Reports in the literature have been mainly concerned with the kinetics of carnallite dissolution when the solid phase is in the common saturated zone of carnallite, KCl, and NaCl, that is, the zone A→E in Fig. 2; the research system point is close to E. In the present work, we have studied the kinetics of carnallite dissolution in the zone from the solid point to liquid point, that is, the zone A→B1, B2, and B3; the research system point is close to the common saturated line of KCl and NaCl. The mineral to water ratio in the zone A→E is 0.57:1, whereas in the zone A→B1, B2, and B3 it is clearly different at 1:2.0 to 1:3.0.

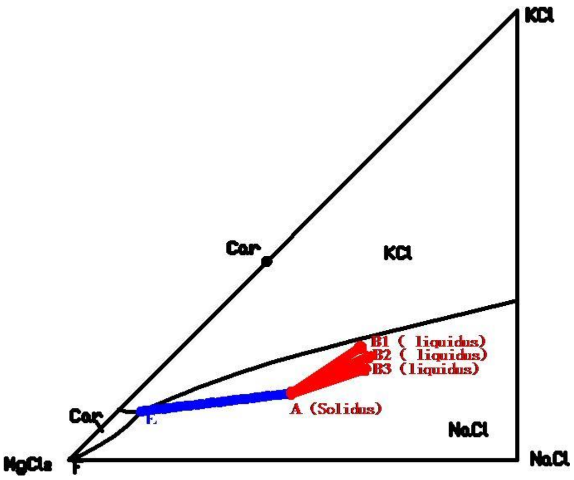
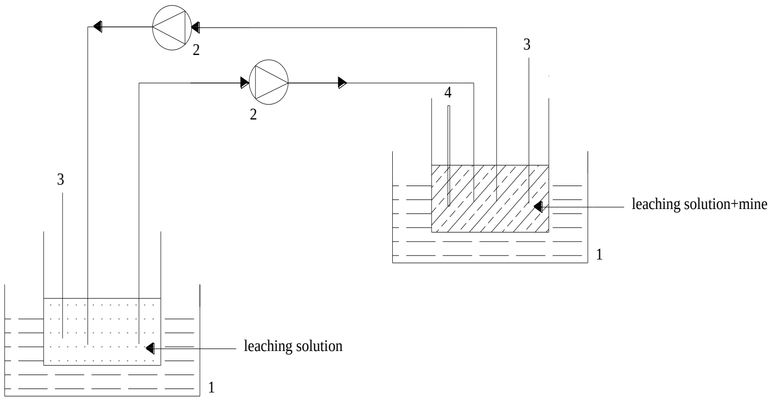


Figure 2. Na+, K+, Mg2+, Cl--H2O phase diagram and points of solid and liquid phase at 25 ℃.

Experimental method: A certain amount of carnallite was weighed and placed in a vessel. The leaching agent and water were added, and the constant temperature water-bath and the velocity of the peristaltic pump were set at the desired levels. The sample was analyzed at timed intervals. The content of K^+ was determined by a quaternary ammonium salt volumetric method; the content of Mg^{2+} was determined by titration with EDTA($C_{10}H_{16}N_2Na_2O_8$); the content of Cl^- was determined by an $Hg(NO_3)_2$ volumetric method; and the content of Na^+ was determined by ion balance subtraction (Qinghai Institute of Salt Lakes, Chinese of Academy of Sciences., 1988).

2.3 experimental process and equipment



1.thermostat water bath 2.peristaltic pump 3.thermometer 4.sample connection

Figure 3. the equipment of experiment

The experiment method: a curtain weighting carnallite is put into vessel and then the water is joined into the vessel, the temperature of thermostat water bath is controlled and the flow rate of peristaltic pump is adjusted, the sample of liquid is analyzed in different dissolved time.figure 3 indicates the equipment of experiment.

Through weighting the raw material, the water joining in vessel has a curtain range and it must be joined without any shutoff.

The method of sampling: setting a sample connection in equipment of experiment and sampling is at regular intervals as setting in the experiment.

3. RESULTS AND DISCUSSION

The key factors that affect dissolution are fluid composition, mineral composition, temperature, the mechanism of fluid mass transfer, environment, and so on (Ni Zhi-yao.,1998;Sergey Vyazovkin et al.,1995;Cheng Yi.,2006;Bao Ji-qing et al.,1995). In this study, we have focused on the effect of temperature on the dissolution of carnallite.

3.1 Dissolution kinetics of carnallite under isothermal conditions

In a certain concentration range, the factors that influence carnallite dissolution rate are mainly temperature, the velocity of the dissolving liquid, and the concentrations of K^+ and Mg^{2+} in the liquid phase. The influence of Mg^{2+} concentration on carnallite decomposition has been studied previously (S.Vyazovkin et al.,1995; Zhang Kai-yong.,2009). In this work, the influence of K^+ concentration in the liquid phase on the dissolution kinetics of carnallite has been studied. Figure 4 shows the concentration of K^+ in the liquid phase at 298.15, 323.15, and 348.15 K at a constant flow rate.

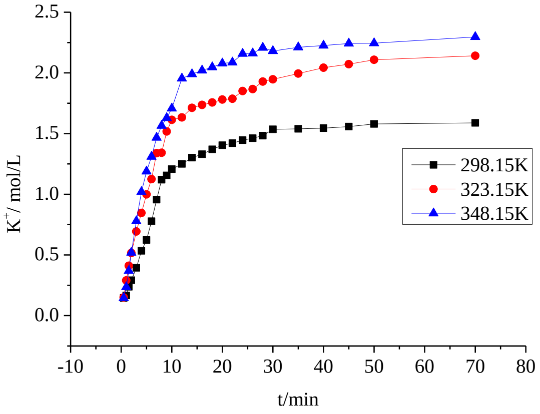


Figure 4. Concentration of K+ in decomposition liquid versus time at different temperatures.

The K^+ concentration in the process of carnallite dissolution clearly increases with increasing temperature.

The dependence of the kinetics of carnallite dissolution on the K^+ concentration could be described using the Stumm model equation (Zhang Kai-yong.,2010):

$$\frac{dc}{dt} = k(c_0 - c)^n \qquad (1)$$

where c_0 is the initial K^+ concentration, c is the K^+ concentration at time t, n is the reaction order, t is the reaction time, and k is the dissolution rate constant.

Table 2 lists the values of k and n calculated using MatLab.

Table 2. Numerical values of *n* and *k*.

Number	Temperature (K)	*n*	*k*
1	298.15	2.6167	0.1936
2	323.15	2.5511	0.1631
3	348.15	2.4732	0.1445

The kinetics of carnallite dissolution was fitted to the K^+ concentration using the model equation:

1) Dissolution kinetic equation in terms of K^+ concentration at 298.15 K:

$$\frac{\mathrm{dc}}{\mathrm{dt}} = 0.1936(1.6572 - \mathrm{c})^{2.6167} \qquad (2)$$

2) Dissolution kinetic equation in terms of K^+ concentration at 323.15 K:

$$\frac{\mathrm{dc}}{\mathrm{dt}} = 0.1631(2.2296 - \mathrm{c})^{2.2551} \qquad (3)$$

3) Dissolution kinetic equation in terms of K^+ concentration at 348.15 K:

$$\frac{dc}{dt} = 0.1445(2.3070 - c)^{2.4732} \qquad (4)$$

Equations (2), (3), and (4) express the kinetics of carnallite dissolution in terms of time and K^+ concentration under isothermal conditions. The kinetic parameters and mechanism functions also had to be studied under non-isothermal conditions in order to fully characterize the process of carnallite dissolution.

3.2 Dissolution kinetics of carnallite under non-isothermal conditions

Equations (2), (3), and (4) describe only specific isothermal processes. However, the process of underground leaching mining of carnallite is non-isothermal. Concentration-temperature-time correlations for carnallite dissolution also had to be obtained, for which it was necessary to study the dissolution kinetics under non-isothermal conditions.

A standard kinetic equation under non-isothermal conditions can be written as (Zhu Jian-rong et al.,2012; Vyazovkin S et al.,1999):

$$\frac{\mathrm{d}\alpha}{\mathrm{dT}} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(c) \qquad (5)$$

where *c* is the concentration in the liquid phase. β is the rate of change of temperature.

$$\beta = \frac{dT}{dt} \qquad (6)$$

Putting Equation (6) into Equation (5), we obtain:

$$\frac{dc}{dt} = A\mathrm{exp}\left(-\frac{E}{RT}\right)f(c) \qquad (7)$$

Integrating Equation (7) on both sides gives:

$$\int\frac{1}{f(c)}\mathrm{dc} = \int A\exp\left(-\frac{E}{RT}\right)dt \qquad (8)$$

The purpose of the kinetic study was to determine the three parameters *E, A,* and *f*(α), which describe the reaction process.

1) Activation energy E

Arrhenius equation:

$$k = A\mathrm{exp}\left(-\frac{E}{RT}\right) \qquad (9)$$

where *k* is the reaction rate constant, *A* is the pre-exponential factor, *E* is the activation energy, R is the molar gas constant, and *T* is the thermodynamic temperature.

Transforming Equation (9):

$$\mathrm{ln}k = \mathrm{ln}A - \frac{E}{R}\times\frac{1}{T} \qquad (10)$$

Equation (10) suggests that a plot of ln*k* against temperature should be a straight line with slope $-\frac{\mathrm{E}}{\mathrm{R}}$ and intercept ln*A*. Figure 5 shows the relationship between dissolution rate constant *k* and temperature.

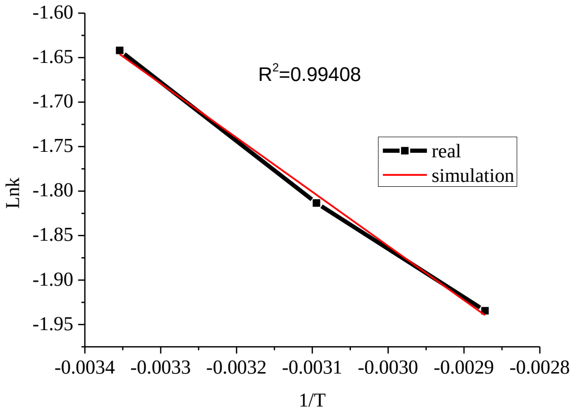


Figure 5. Relationship between ln*k* and 1/T.

The relationship derived from Fig. 4 was:

$$\ln k = -3.688 - 608.75\frac{1}{T} \qquad (11)$$

The reaction rate constant k, E, and A at different temperatures can be obtained from Equation (11). The kinetic effect of the apparent activation energy can be divided into two parts, namely the rate of reaction activation energy and the activation energy model function.

$$-\frac{E_1}{R} = -608.75 \qquad (12)$$

$$E_2 = \frac{RT_2T_1}{T_2-T_1} ln\frac{k_2}{k_1} \qquad (13)$$

$$E = E_1 + E_2 \qquad (14)$$

The dissolution activation energy E_2 between T_2 and T_1 can be obtained from Equation (13), and adding this to E_1 from Equation (12) gives the activation energy E at this temperature.

2) The pre-exponential factor A

$$\ln A_1 = -3.688 \qquad (15)$$

$$\ln A_2 = \ln k + \frac{E}{\mathrm{RT}} \qquad (16)$$

$$A = A_1 + A_2 \qquad (17)$$

A at different temperatures can be obtained from Equations (15), (16), and (17).

3) Mechanism function f(c)

The mechanism function of carnallite dissolution under non-isothermal conditions is inextricably linked with temperature. The K^+ concentration in the solution is only a function of temperature at the same flow rate. Based on a three-dimensional model (Vyazovkin S et al.,1999), Equation (18) gives the mechanism function $f(c)$ of carnallite dissolution under non-isothermal conditions.

$$f(c) = \frac{2.716 - 0.0123T}{2.23 - c^{1.4799}} \tag{18}$$

By calculating the activation energy E, the pre-exponential factor A, and mechanism function $f(c)$, we can express the kinetic equation of carnallite dissolution under non-isothermal conditions as follows:

$$(0.0083T - 2.511)A\exp\left(-\frac{E}{RT}\right)\mathrm{t} = -\frac{1}{1.4799}(2.23 - c)^{1.4799} \tag{19}$$

4) Certification of the model kinetic equation for carnallite dissolution under non-isothermal conditions

Table 3 shows temperatures and dissolution rates obtained from Equation (11).

Table 3. Dissolution rates at different temperatures.

Temperature (K)	ln$k$	K
298.15	-1.6462	0.1928
323.15	-1.8042	0.1646
348.15	-1.9395	0.1438

Table 4 shows activation energies calculated according to Equations (11), (12), and (13).

Table 4. Activation energies.

E_1 (kJ/mol)	E_2 (kJ/mol)	E (kJ/mol)
5.061	5.06	10.12
5.061	29.02	34.08
5.061	17.96	23.02

Table 5 shows the pre-exponential factors calculated according to Equations (15), (16), and (17).

Table 5. Pre-exponential factors.

A_1 (min^{-1})	A_2 (min^{-1})	A (min^{-1})
0.03	0.23	0.26
0.03	0.18	0.20

A_1 (min^{-1})	A_2 (min^{-1})	A (min^{-1})
0.03	0.17	0.19

Figures 6, 7 and 8 show the differences between the experimental and calculated values at 298.15, 323.15, and 348.15 K, respectively.

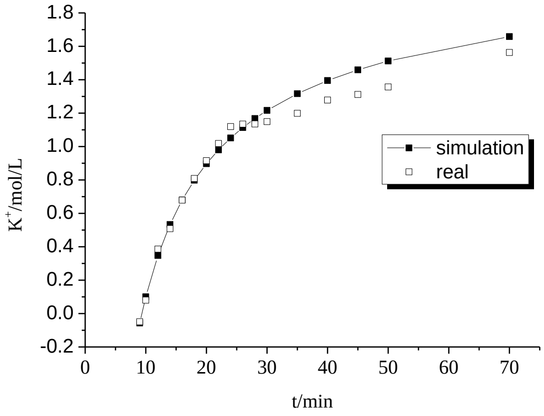


Figure 6. K^+ dissolution kinetics model curve vs. the experimental data at 298.15 K.

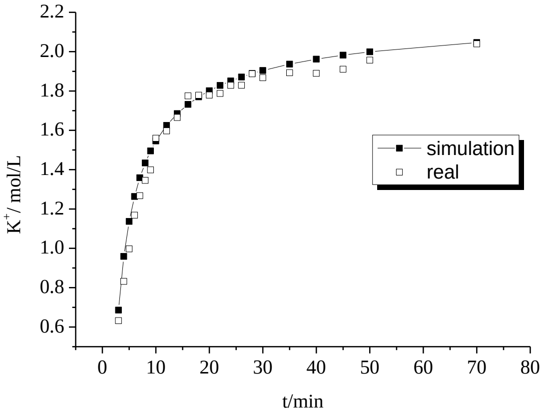


Figure 7. K+ dissolution kinetics model curve vs. the experimental data at 323.15 K.

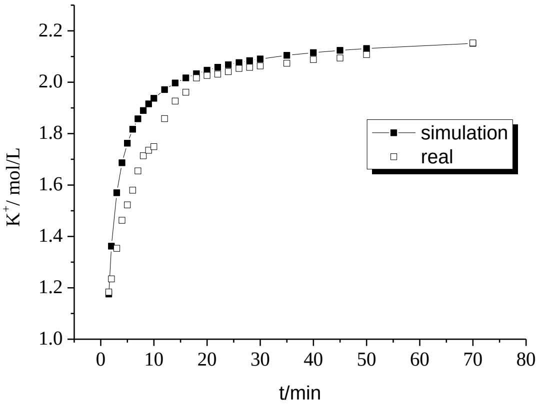


Figure 8. K+ dissolution kinetics model curve vs. the experimental data at 348.15 K.

Comparing the concentrations calculated with the model at different times and experimentally measured values, the error is ≤5%. This shows that the kinetic equation of carnallite dissolution under non-isothermal conditions gives good agreement and that the parameters are reasonable. The kinetic model of carnallite dissolution under isothermal and non-isothermal conditions shows that the dissolution process is controlled by a combination of surface and diffusion effects.

Through experimental measurements of carnallite dissolution under non-isothermal conditions and kinetic evaluation thereof, equations in terms of time, temperature, and concentration of K^+ and a kinetic model have been established. It is hoped that this work will provide theoretical guidance to expedite underground leaching mining.

4. CONCLUSION

1. The process of carnallite dissolution conforms to the Stumm model under isothermal conditions.
2. Temperature has an important influence on the process of carnallite dissolution. With increasing temperature, the reaction order decreases. The process of leaching mining is mainly controlled by a combination of surface and diffusion effects. The relationship between temperature and dissolution rate constant has been established.
3. Through calculation of the activation energy and pre-exponential factor, a kinetic model of carnallite dissolution under non-isothermal conditions has been established. Equations in terms of time, temperature, and concentration of K^+ have been delineated.

4. A theoretical basis for the process of underground leaching mining of carnallite has been elaborated.

5. NOMENCLATURE

c_0	K^+ equilibrium concentration, mol/L
c	K^+ concentration, mol/L
k	dissolution rate constant
t	reaction time, s
n	reaction order
T	reaction temperature, K
R	gas constant
A	pre-exponential factor
E	activation energy, kJ/mol
β	rate of change of temperature, K/s
f(c)	mechanism function

REFERENCES

[1] **Bao Ji-qing, Xia Shu-ping, 1995,** Study on the Dissolution and Transformation of Carnallite in Na_2SO_4 Solution, *Journal of Salt Lake Science,* **3**(3), 40-47.

[2] **Wang Ben, 1997,** Accelerate the development of underground leaching mining technology in China, China Mining Magazine C, 34(6), 8-11.

[3] **Liang Wei-guo, Zhao Yang-sheng, Xu Su-guo, Yu Yan-mei, 2012,** Theoretical Study of in-situ Solution Mining, Journal of Taiyuan University of Technology, 43(3), 382-387.

[4] **Xia Shu-Ping, Hong Xian-lan, 1993,** A Study on the Dissolution Kinetics and Mechanism of Carnallite and KCl, Journal of Salt Lake Science, 1(4), 52-60.

[5] **Hong Xian-lan, Xia Shu-Ping, Gao Shi-yang, 1994**, Dissolution Kinetics of Carnallite, Chinese Journal of Applied Chemistry, 11(3), 26-31.

[6] **Xia Shu-ping, Hong Xian-lan, Gao Shi-yang, 1993,** Study of the principle of carnallite decomposition of potassium chloride process, Journal of Salt and Chemical Industry, 23(2), 10-15.

[7] **S. Vyazovkin, 1995,** The Application of Isoconversional Methods for Analyzing Isokinetic Relationships Occurring at Thermal Decomposition of Solids. Journal of Solid

State Chemistry, 114, 392-398.

[8] **M.E. Brown, M. Maciejewski, S. Vyazovkin, R. Nomen, J. Sempere, A. Burnham, J. Opfermann, R. Strey, H.L. Anderson, A. Kemmler, R. Keuleers, J. Janssens, H.O. Desseyn, Chao-Rui Li, Tong B. Tang, B. Roduit, J. Malek, T. Mitsuhashi, 2000,** Computational aspects of kinetic analysis, Thermochimica Acta, 355, 125-143.

[9] **Cheng Huai-de,Ma Hai-zhou,Zhang Zhi-hong,2013,**Preliminary study on effect of high-magnesium solution on carnallite decomposition, Inorganic Chemicals Industry, 45(1), 21-23.

[10] **Huaide Cheng, Haizhou Ma,Qingyu Hai,Zhihong Zhang,Liming Xu,Guangfen Ran,2015,** Model for the decomposition of carnallite in aqueous solution, International Journal of Mineral Processing, 139, 36–42.

[11] **Qinghai Institute of Salt Lakes, Chinese of Academy of Sciences, 1988,** The analysis method of the brine and salt [M], Beijing: Science Press.

[12] **Ni Zhi-yao, 1998,** Reaction Kinetics Analysis for Mineral Dissolution and Crystallization, Geology-Geochemistry, 26(2), 39-44.

[13] **Sergey Vyazovkin, Wolfgang Linert, 1995,** Detecting isokinetic relationships in non-isothermal systems by the isoconversional method, Thermochimica Acta 269/270, 61-72.

[14] **Cheng Yi, 2006,** A New Kinetic Equation for Non-Isothermal Reaction Process, Chinese Journal of Inorganic Chemistry 22(2), 287-292.

[15] **Bao Ji-qing, Xia Shu-ping, 1995**, Study on effect of NaCl on dissolution of carnallite, Journal of Salt Lake Science, 3(2), 51-58.

[16] **Sergey Vyazovkin, Wolfgang Linert, 1995,** False isokinetic relationships found in the non-isothermal decomposition of solids, Chemical Physics 193, 109-118.

[17] **Zhang Kai-yong, Tang Na, Lian Ying, 2009,** Story on the Decomposition Liquid Concentration Characteristics in the Crystallizer of Potassium Chloride Production by Carnallite Cold-decomposition Method, Journal of Salt and Chemical Industry, 39(1), 3-6.

[18] **Zhang Kai-yong, 2010,** Story on the Decomposition Liquid Concentration Characteristics and Dynamics in Carnallite Cold-decomposition Process”, master's degree thesis of Tianjin University of Science and Technology.

[19] **Zhu Jian-rong, Xiao Xueying, Zhang Zhihong, Dong Shengfa, Ma Yanfang, Zhang Yongfeng, Du Jianning, 2012,** Study on carnallite decomposition of Kunteyi Salt Lake through analysis of components in liquid phase, Inorganic Chemicals Industry, 44(1),

37-39.

[20] **Vyazovkin S, Wight C. A. 1999,** Thermochim. Acta, 341, 53-68.