The Formation of Mathematical Model for CaCl₂ Derived from The Reaction of Ulexite and Hydrochloric Acid by Using Full Factorial Desing Method

Halil DURAK[1,♠], Yaşar GENEL[1], Novruz BASHIROV[2], Genber KERIMOV[3]

[1]Yüzüncü Yıl University, Faculty of Education, Van-TURKEY
[2] Yüzüncü Yıl University, Health Occupation High School , Van-TURKEY
[3] Yüzüncü Yıl University, Başkale Vocatıonal High School, Van-TURKEY

ABSTRACT

One of the significant boron compounds which are common substance in nature is ulexite. Ulexite is a sodium calcium boron hydrate, its chemical formula is $Na_2O2CaO5B_2O_316H_2O$, and it is thick with in Turkey. Lots of products are derived from boron minerals. One of them is boric acid. $CaCl_2$ is used in many fields and this compound can be obtained by different processes. The aim of this study is producing $CaCl_2$ by forming mathematical model for $CaCl_2$ composing in the wake of the interaction of ulexite with hydrochloric acid solution. In the study, full factorial desing method has been used. Some of the parameters used in the process have been pegged, and the others have been regarded as variables. The pegged parameters are particle size, reaction time and stirring speed. Hydrochloric acid concentration, temperature and solid to liquid ratio have been regarded as variable factors in formation of mathematical model. The mathematical model of three-parameter full factorial desing mehtod and the mathematical model of the process have initially been assessed in dimensionless coordinate system, then the available values in the model have been computed by Student criteria, the validity of the formed model has been controlled by Fisher criteria. Henceforwards, the current model of the process has been formed in real coordinate system.

Key words: ulexite, calcium chloride, full factorial desing, mathematical model.

1. INTRODUCTION

Farther than 230 boron minerals exist in nature. The most common ones of them are borax, kernite, colemanite, ulexite, probertite, hydroboracite, inderite, datolite, and szaibelyite (Kirk Othmer, 1992). In the studies, the process of the derivation of calcium chloride and the problems encountered have been researched.

Calcium chloride production as products with interaction of ulexite and HCI seems possible by means of this study we conducted. Calcium chloride is utilised in numerous fields from agriculture to chemical industry (Fusheng et. al., 2011, Alexander et. al., 2006). Most of the studies related to ulexite are pertain to dissolution kinetics and mechanism. In the study conducted, the mathematical modelling of $CaCl_2$ production process, besides boric acid extraction oriented production. The product formed by this modelling method can subsist depending upon the products reacting. Full factorial design method has been used in numerous studies. A. R. Cestari et. al., (2008) have utilised full factorial design method in resolving anionic red dye in aqueous solutions. Özturk and Kavak (2004) have applied full factorial design method in boron removal from aqueous solutions by adsorption. A. P. Rodriquez et. al., (2008) have employed full

factorial design method in crystalizing kluyveromyces lactis β-galactosidase enzyme. Kose (2008) has observed the clearance of colorant from agricultural residue with anion exchanger by means of full factorial design. Özturk and Kavak (2008) have used cerium oxide in aqueous solutions of boron waste, and full factorial design method in the adsorption of boron waste. Y. Seki et. al., (2006) have utilised full factorial design method in the boron removal from aqueous solutions with Al_2O_3 based adsorbants. Salafranga et. al., (1999) have researched the optimization of the supercritical liquid extraction of Iraganox 1076, Irgafos 168 and Chimassob 81 substances with full factorial design method. R. I. Trezona et. al., (2000) have viewed the erosionresistance of automotive polishers with full factorial design method.

It is possible to remove the deficiencies that have appered during getting the correlation in the full factorial design method and classic regression analysis used in this study, and among the coefficients of regression equations used in this study. In the study conducted, the experimental design has been determined by considering the determination of the matter and experimental results. The study consists of several phases. The results gotten after each phase help the determination of next phases of the experiment. Hence the experiment is provided to be controlled optimally. The whole differential parameters can be also changed by experimental design method, and the relations between variables can be assessed. Differently from other research methods, searching the relations between variables in this method raises the productivity of experiments substantially.

2. EXPERIMENTAL

2.1. Materials and Methods

In full factorial design method, the whole combinations of variables at maximum and minimum levels are taken into consideration. The application of full factorial design method is found with the formula of the number of the experiments to be tested for **n** slew levels of **k** slew variables.

$$N = n^k \qquad (1)$$

In the study conducted, there are 3 variable values that is **k**=3. If these 3 factors change at two levels consisting of maximum and minimum, the number of the experiments to be tested should be $N=2^3 = 8$.

Supposing that there are three variables consisting of Z_1, Z_2 ve Z_3 in the study conducted. The range of these factors are as folows:

$$\left. \begin{array}{l} Z_1^{min} \leq Z_1 \leq Z_1^{max} \\ Z_2^{min} \leq Z_2 \leq Z_2^{max} \\ Z_3^{min} \leq Z_3 \leq Z_3^{max} \end{array} \right\} \qquad (2)$$

As is seen, each Z_k changes between its own maximum and minimum values like Z_k^{min} and Z_k^{max} : $Z_k[Z_k^{min}, Z_k^{max}]$, k=1,2,3. as indicated before, 8 experiments

should be held in order to take mathematical model as the number of factors are 3.

Initially the following calculations are done :

$$Z_k^0 = \frac{Z_k^{max} + Z_k^{min}}{2}, \qquad k = 1, 2, 3.$$

$$\qquad (3)$$

$$\Delta Z_i = \frac{Z_k^{max} - Z_k^{min}}{2}, \qquad k = 1, 2, 3.$$

Here the points of Z_1^0, Z_2^0 ve Z_3^0 are called experimental design centre. ΔZ_k - is the changeability value of releant variable. The values of the 8 experiment held in measureless and natural coordinate system have been shown in Table 1. Minimum values of Z_i have been displayed with -1 , and its maximum values with +1. ın compliance with this design, 8 experiments are tested and Y_{exp} basic material values derived from each experiment are added to Table 1.

Henceforwards, mathematical model is formed

$Y_x = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{23}X_2X_3 + a_{123}X_1X_2X_3$ (4)

in dimensionless coordinate system. Coefficient values of model a_0, a_1, a_2, a_3, a_{12}, a_{13}, a_{23} ve a_{123}

$$a_j = \frac{1}{N} \sum_{i=1}^{N} X_{ji} Y_i$$

$$\qquad (5)$$

is computed with the formula above.

Table 1. The plan of full factorial design for three factors

Dimensionless coordinate system(factors in dimensionless system of coordinates)				Natural coordinate system(factor in natural scale)			
Experiment No	X_1	X_2	X_3	Z_1	Z_2	Z_3	Y^{tec}
1.	-1	-1	-1	Z_1^{min}	Z_2^{min}	Z_3^{min}	Y_1
2.	1	-1	-1	Z_1^{max}	Z_2^{min}	Z_3^{min}	Y_2
3.	-1	1	-1	Z_1^{min}	Z_2^{max}	Z_3^{min}	Y_3
4.	1	1	-1	Z_1^{max}	Z_2^{max}	Z_3^{min}	Y_4
5.	1	-1	1	Z_1^{min}	Z_2^{min}	Z_3^{max}	Y_5
6.	1	-1	1	Z_1^{max}	Z_2^{min}	Z_3^{max}	Y_6
7.	-1	1	1	Z_1^{min}	Z_2^{max}	Z_3^{max}	Y_7
8.	1	1	1	Z_1^{max}	Z_2^{max}	Z_3^{max}	Y_8

Then in the experiment station, that is at the points of Z_1^0, Z_2^0 ve Z_3^0, three colleteral experiments are tested, and the values of Y_1^0, Y_2^0 and Y_3^0 out parameters are computed in accordance with them. After that, the mean value of these out parameters are found:

$$\overline{Y}^0 = \frac{\sum\limits_{u}^{3} Y_u^0}{3} \qquad (6)$$

There after

$$S_1^2 = \frac{\sum\limits_{u}^{3} (Y_u^0 - \overline{Y})^2}{3} \quad \text{and} \qquad (7)$$

$$S_{a_m} = \frac{S_1^2}{\sqrt{8}} \qquad (8)$$

's values are computed. By considering the calculated (6), (7) and (8) values, and using Student criteria.

$$t_m = \frac{|a_m|}{S_{a_m}} \qquad (9)$$

with the formula, the values found by the formula in (5) of the mathematical model in (4) are seen from private Styudent criteria table by using P=0,05 condition that they are f=2, $t_p(f)$=4,3 for these values. The values are utilised in the model in (4) by using the formula in (9) if each t_m value is larger than 4,3. The rest, that is the values which are lower than 4,3 are not used. Henceforwards, variences may be in the mathematical models in (4).

Thereafter, the validity of the new model is checked by Fisher criteria :

$$F = \frac{S_2^2}{S_1^2} \qquad (10)$$

Here

$$S_2^2 = \frac{\sum\limits_{i=1}^{8} (Y_i - \overline{Y}_i)^2}{N} \qquad (11)$$

The mathematical model in (4) taken in dimensionless coordinate system is capable of supplying the actual process exactly. To form the valid mathematical model of natural process, the following change of variable formula in model (4) is used :

$$X_j = \frac{Z_j - Z_j^0}{\Delta Z_j} \quad , j=1, 2, 3. \qquad (12)$$

Mathematical model is taken as the follows in natural coordinate system after certain mathematical conversions :

$Y_z = b_0 + b_1 Z_1 + b_2 Z_2 + b_3 Z_3 + b_{12} Z_1 Z_2 + b_{13} Z_1 Z_3 + b_{23} Z_2 Z_3 + b_{123} Z_1 Z_2 Z_3$ \qquad (13)

These b_0, b_1, b_2, b_3, b_{12}, b_{13}, b_{23} ve b_{123} are new values taken as a result of conversion of the formula and values in (12).

2.2. Dissolution studies

Dissolution operation takes place according to the following equation :

Na_2O 2 CaO $5B_2O_3$ $16H_2O + 6HCl \rightarrow 2NaCl_{(aq)} + 2CaCl_{(aq)} + 10H_3BO_{3\ (aq)} + 4H_2O$
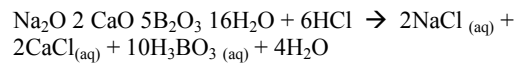
The ulexite used in the study conducted has been supplied from the region of Balıkesir-Bigadiç in Turkey. Boron ore has been segregated into the requested fractions by being sifted through in ASTM class after it is cleaned from the apparent contamination. The chemical analysis and SEM Photograp of ulexite ore has been given in Table 2 and Figure1. The hydrocloric acid used in this study is 37 % bt weight, and it has been supplied from merck. In Tablo 3, the parameters used in the experiment has been shown
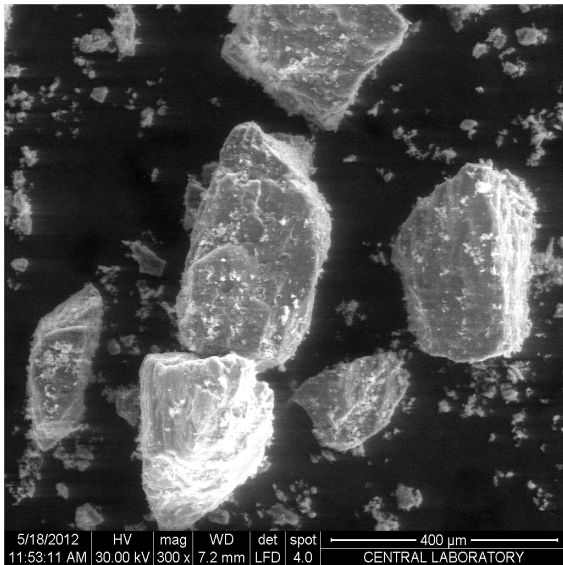
Figure 1. SEM Photograph of ulexite minerals used in this study

Dissolution experiments have been held in 250 mL cylindrical glass batch reactor by usingmechanical mixer. Temperature has been regulated by using a 0,1 ^{0}C sensitivity thermostate. A condenser has been used to prevent the solvent lossoriginating from evaporation. Initially, 100 mL hydrocloric acid has been added to the reactor, and the requested temperature has been watched over by running the mechanical mixer. Then dissolution operation has been embarked on by adding ulexite. When the time is over, the experiment has been halted, and the substance taken from the reactor has been filtered. Henceforwards, B_2O_3, D-mannitol and volumetrik in the substance have been analysed (Scott, 1963). The transformation fraction of the solute B_2O_3 has been retained by being divided into the B_2O_3 ratio in original ore.

Table 2. The chemical analysis of the ulexite used in the study

Component	% Composition
CaO	13.68
B_2O_3	42.24
H_2O	34.18
Na_2O	6.12
MgO	3.15
Others	0.63

Table 3. The parameters used in the experiment

Variable	Range
Concentration (mol/L)	0.5 – 2.0
Solid/liquid ratio (g/mL)	0.02 – 0.1
Tempereture (^{0}K)	293 – 333
Particle size (mm) fixed	1,205
Stirring speed (rpm) fixed	400
Reaction time (min) fixed	5

3. RESULTS AND DISCUSSION

We can set the mathematical model of the process

$Na_2O2CaO5B_2O_316H_2O + 6HCl \rightarrow 2NaCl_{(aq)} + 2CaCl_{2(aq)} + 10H_3BO_{3\,(aq)} + 10H_2O$ (14)
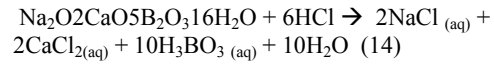
which we have described above.

The mathematical model to be formed of the process will be like (13). Here:

Z_1 – Hydrochloric acid concentration, with mol/L ;
Z_2 – temperature, with ^{0}C ;
Z_3 – solid to liquid ratio has been indicated with g/mL.

(14) reaction time has fixedly been taken 5 minutes for all the experiments.

Range of Z_1, Z_2 and Z_3 parameters are as follows :

$$\left. \begin{array}{l} 0,5 \le Z_1 \le 2 \\ 20 \le Z_2 \le 60 \\ 0,01 \le Z_3 \le 0,02 \end{array} \right\} \quad (15)$$

According to Table 1 that we have given before, the long shot of full factorial desing method and the values of the obtained results of parameters have been displayed in Table 4.

The values of mathematical model to be formed in dimensionless coordinate system by using (5) formula have been found as it has showed in (16) system.

$$\left. \begin{array}{ll} a_0 = 1,099675 & a_{12} = 0,12952 \\ a_1 = 0,059575 & a_{13} = 0,073575 \\ a_2 = 0,202225 & a_{23} = 0,175475 \\ a_3 = 0,616175 & a_{123} = 0,135975 \end{array} \right\} \quad (16)$$

Thus, the folowing mathematical model can be formed in dimensionless coordinate system:

$Y_x = 1,099675+ 0,059575\ X_1 + 0,202225\ X_2 + 0,616175\ X_3 + 0,129525\ X_1X_2 + 0,073575\ X_1X_3 + 0,175475X_2X_3 + 0,135975\ X_1X_2X_3$ (17)

To review the values of (17) model by Student criteria, 3 parallel experiments have been tested at the point of (Z_1^0, Z_2^0, Z_3^0) that is the centre of full factorial desing plan. Our experiment plan centre is the point composing of the coordinates (1,25; 40; 0,015). The results of 3 parallel experiments held at this central point have been found as follows:

$Y_1^0 = 0,8281;\quad Y_2^0 = 0,8327;\quad Y_3^0 = 0,8374$ (18)

Form here

$$\overline{Y}^o = \frac{Y_1^0 + Y_2^0 + Y_3^0}{3} = 0,8327$$

(19)

by using (7) formula, it is found as $S_1^2 = 0,0000144167$ from (8) formula, it is found

$$S_{a_m} = \frac{S_1^2}{\sqrt{8}} = \frac{0,0000144167}{2,82842746} = 0,00000509706$$

As the value of the found S_{a_m} number is small number, all the t_m numbers whose value has been found by (9) formula are larger than $t_p(f)=4,3$ number. This indicates that all the found a_0, a_1, a_2, a_3, a_{12}, a_{13}, a_{23} and a_{123} coefficient values are effective. Thus, all the coefficients of (17) model are useable. For instance, the value of a_0 coefficient can be computed.

$$t_0 = \frac{|a_0|}{S_{a_m}} = \frac{1,099675}{0,00000509706} = 215746,921 \rangle\rangle 4,3$$

(useable).

The following value is taken when this compution is conducted for a_1 coefficient :

$$t_1 = \frac{|a_1|}{S_{a_m}} = \frac{0,059575}{0,00000509706} = 11687,9142 \; \rangle\rangle \; 4,3$$

The usability of the other coefficients have ben designated by this method. Henceforwards, the validity of (17) mathematical model has been controlled by Fisher criteria.

To form the mathematical model of the process in natural coordinate system, it has been benefited from (12) model as follows

$$X_1 = \frac{Z_1 - Z_1^0}{\Delta Z_1} = \frac{Z_1 - 1,25}{0,75} = \frac{4Z_1 - 5}{3}$$

$$X_2 = \frac{Z_2 - Z_2^0}{\Delta Z_2} = \frac{Z_2 - 40}{20}$$

$$X_3 = \frac{Z_3 - Z_3^0}{\Delta Z_3} = \frac{Z_3 - 0,015}{0,005} = 200Z_3 - 3$$

$$(20)$$

After certain mathematical simplifications have been done by using the values in the (20) for the (17) model, the following mathematical model has been composed in natural coordinate system:

$Y_z = 0,76 + 0,528 Z_1 + 0,007 Z_2 + 119,17 Z_3 - 0,019 Z_1 Z_2 - 52,9 Z_1 Z_3 - -0,511 Z_2 Z_3 + 1,813 Z_1 Z_2 Z_3$ (21)

the computed Y_{Zi}^{model} values by using (21) model have been added to the last column of Table 4.

The results of the experiments conducted's relevance to the mathematical models composed in dimensionless coordinate system (17) and natural coordinate system (21) has been given in Figure 2.

As is seen in the figure, the mathematical model formed both in dimensionless coordinate system and in natural coordinate system, and the values of the products derived empirically are rather close to each other. Therefore, the process can be researched far and wide by using the formed mathematical model.

Table 4. Full factorial design plan and resentful values of parameters

Parameters in dimensionless coordinate system										Natural coordinate system			
Experiment number	X_0	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	$X_1X_2X_3$	Y^{exp}	Y_x^{model}	Z_1	Z_2	Z_3	Y_z^{model}
1	1	-1	-1	-1	1	1	1	-1	0,4643	0,4644	0,5	20	0,01	0,4603
2	1	1	-1	-1	-1	-1	1	1	0,4492	0,4491	2	20	0,01	0,4327
3	1	-1	1	-1	-1	1	-1	1	0,5307	0,5307	0,5	60	0,01	0,5185
4	1	1	1	-1	1	-1	-1	-1	0,4898	0,4898	2	60	0,01	0,4387

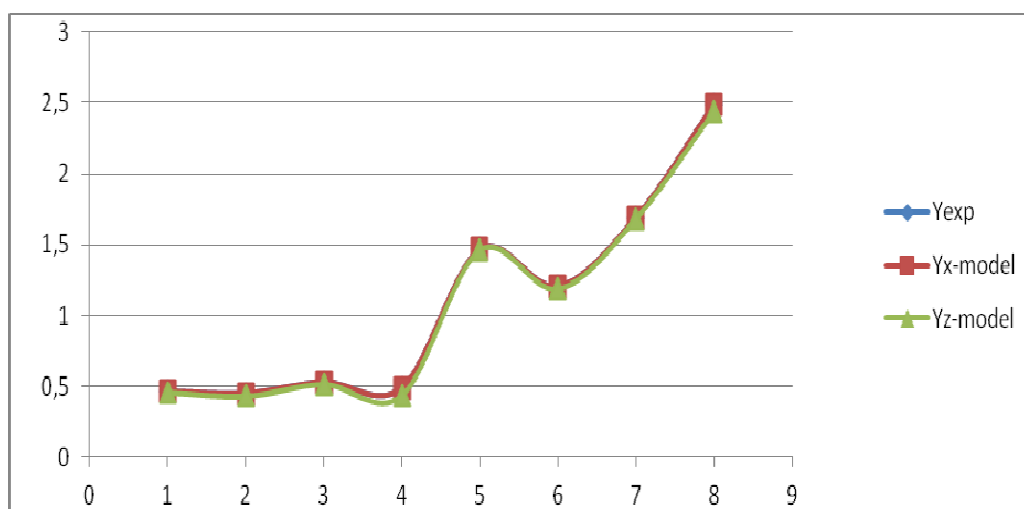| 5	1	-1	-1	1	1	-1	-1	1	1,4705	1,4706	0,5	20	0,02	1,4666
6	1	1	-1	1	-1	1	-1	-1	1,2058	1,2058	2	20	0,02	1,1894
7	1	-1	1	1	-1	-1	1	-1	1,6949	1,6949	0,5	60	0,02	1,6830
8	1	1	1	1	1	1	1	1	2,4922	2,4923	2	60	0,02	2,4414

Figure 2. Graphical display of the validity of the process: Yexp – values received experientially; Yx model- calculated values in dimensionless coordinate system by mathematical model; Yz model- calculated values in natural coordinate system by mathematical model.

4. CONCLUSIONS

In chemistry and chemistry technologies field, the formation of mathematical model of chemical processes matters to. The requested products can be derived in the requested amounts by means of the formed mathematical model. It is benefited from mathematical modelllings in the studies related to the optimization and control of chemical processes.

In the study, full factorial design has been used for the formation of the mathematical model of $CaCl_2$ derivation process from ulexite mineral. First, the testing plan of the experiment has been composed, the experiments have been held by the aforesaid plan, and then the mathematical model of the chemical process has been formed in dimensionless coordinate system. The usability of mathematical model's coefficients has been controlled by Student criteria, and it has been found that all the coefficients are useable. Then, by using private change of variable method, it has been passed from dimensionless coordinate system to natural

coordinate system. The validity of the mathematical model composed in natural coordinate system has been controlled by Fisher criteria.

This mathematical model composed in natural coordinate system which is current for chemical process makes the optimization of the process easy.

$Na_2O2CaO5B_2O_316H_2O + 6HCl \rightarrow 2NaCl_{(aq)} + 2CaCl_{2(aq)} + 10H_3BO_{3\ (aq)} + 10H_2O$
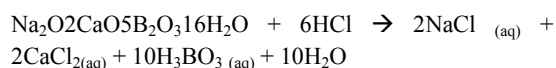
The same parameters have been used for the production of boric acid and calcium chloride in the above chemical process. According to the parameters used,the formed mathematical models by using full factorial design method for calcium chloride production have been displayed as follows:

Calcium Clorur ($CaCl_2$)
Dimensionless coordinate system
Y_x = 1,099675+ 0,059575 X_1 + 0,202225 X_2 + 0,616175 X_3 + 0,129525 X_1X_2 + 0,073575 X_1X_3 + 0,175475 X_2X_3 + 0,135975 $X_1X_2X_3$
Natural coordinate system
Y_z = 0,76 + 0, 528 Z_1 + 0,007 Z_2 + 119,17 Z_3 – 0,019 Z_1Z_2 – 52,9 Z_1Z_3 - 0,511 Z_2Z_3 + 1,813 $Z_1Z_2Z_3$

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