

Optimization of Dissolution of Chevreul's Salt in Ammonium Chloride Solutions

Mustafa Sertçelik, Hacali Necefoğlu, Turan Çalban, Soner Kuşlu

Abstract—In this study, Chevreul's salt was dissolved in ammonium chloride solutions. All experiments were performed in a batch reactor. The obtained results were optimized. Parameters used in the experiments were the reaction temperature, the ammonium chloride concentration, the reaction time and the solid-to-liquid ratio. The optimum conditions were determined by 2^4 factorial experimental design method. The best values of four parameters were determined as based on the experiment results. After the evaluation of experiment results, all parameters were found as effective in experiment conditions selected. The optimum conditions on the maximum Chevreul's salt dissolution were the ammonium chloride concentration 4.5 M, the reaction time 13.2 min., the reaction temperature 25 °C, and the solid-to-liquid ratio 9/80 g.mL⁻¹. The best dissolution yield in these conditions was 96.20%.

Keywords—Ammonium chloride, Chevreul's salt, copper, Factorial experimental design method, optimization.

I. INTRODUCTION

COPPER is usually produced by using cementation or electro-winning methods from the solutions of soluble copper salts [1]. Precipitation of inorganic compounds from aqueous solutions is chemical. Chemical processes can be various due to hydrolytic action, ionic interaction, or reduction. Chevreul's salt is known as a stable mixed-valence sulphite, and attracts much interests due to its intense brick red colour as well as its highly stable mixed-valence state [2]-[5]. The precipitation of Chevreul's salt is a key stage in hydrometallurgical processes and very important in aqueous systems [6]-[8].

In recent years, studies of compounds of this type have been intensified. Chevreul's salt has been obtained by using various methods and reagents [2], [3]. Conklin and Hoffmann have investigated metal ion-sulphur(IV) chemistry and thermodynamics and kinetics of transient iron(III)-sulphur(IV) complexes. Their measurements indicated that sulphite binds the metal through oxygen [9]. Da Silva et al. [10] have examined synthesis, identification, and thermal decomposition of double sulphites like $\text{Cu}_2\text{SO}_3 \cdot \text{MSO}_3 \cdot 2\text{H}_2\text{O}$ (M=Cu, Fe, Mn or Cd). These salts have been obtained by the saturation with

sulphur dioxide gas from the aqueous solutions of M(II) sulphates at room temperature. The thermal behaviour of double sulphites was estimated by thermogravimetry analysis and differential scanning calorimetric methods. They reported that these salts are thermally stable up to 2000 °C, and isostructural with Cu(II) replaced by Mn(II), Fe(II) and Cd(II) ions in $\text{Cu}_2\text{SO}_3 \cdot \text{MSO}_3 \cdot 2\text{H}_2\text{O}$. Çolak et al. [11] obtained 99.78% pure copper powder from the oxidized copper ore belonging to Erzurum-Narman region. They precipitated Chevreul's salt ($\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$) by using ammonia and sulphur dioxide. The best precipitation conditions of Chevreul's salt were found as pH 4, the stirring speed 600 rpm, the temperature 600 °C, passing time SO_2 : reaction time of 1 minute and after passing SO_2 : 6 minutes. de Andrade et al. [12] have studied isomorphous series of double sulphites such as the $\text{Cu}_2\text{SO}_3 \cdot \text{MSO}_3 \cdot 2\text{H}_2\text{O}$ (M=Cu, Fe, Mn or Cd) type. They found that the isomorphous Cu(II) in Chevreul's salt could be replaced by a divalent metal ion, forming an isomorphous series whose properties are strongly dependent on the nature of the M(II) cation. They determined that these mixed valence systems can be used as a model to identify intermediates under atmospheric conditions and to evaluate the role of transition metals as catalysts of S(IV) autoxidation in the conversion of SO_2 in the atmosphere, because of their interesting properties. Innoue et al. [13] synthesized Chevreul's salt by a reaction between CuSO_4 and NaHSO_3 and characterized by X-rays photoelectron spectroscopy (XPS), magnetic susceptibility, Electron paramagnetic resonance (EPR), and electronic spectroscopy. Parker and Muir [14] determined some conditions for precipitation of Chevreul's salt from impure leach solutions. They obtained 75 g of pure particulate copper per unit liter of solutions. Çalban et al. [15] explored the statistical modelling of Chevreul's salt recovery from leach solutions which contains copper. They determined the optimum precipitation conditions of Chevreul's salt using leach solutions. They found as pH 3, temperature 620 °C, stirring speed 600 rpm, reaction time 12 minutes, SO_2 flow rate 358 L.h⁻¹, and concentration of CuSO_4 solution 7.38 g.L⁻¹. Yeşilyurt and Çalban [16] precipitated the Chevreul's salt from mixture of CuSO_4 and Na_2SO_3 solutions. They determined the optimum precipitation conditions as temperature 600 °C, $[\text{SO}_3^{2-}]/[\text{Cu}^{+2}]$ ratio 1.6, pH 3, stirring speed 500 rpm, and reaction time 20 minutes. Giovannelli et al. [17] investigated the surface layers formed on oxidised copper exposed to SO_2 in humid air under hypoxic conditions. Chevreul's salt exhibited orthorhombic symmetry at room temperature. A mechanistic analogy with bronze disease of archaeological artefacts has been indicated. Fischmann et al.

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[18] have studied the upgrading of a chalcopryrite concentrate by copper(II) reaction and unexpected formation of Chevrel's salt. They showed that recovery of copper (II) compound onto a chalcopryrite concentrate can occur quickly at 600°C and at the presence of S(IV). Amazingly, rather than partial conversion of chalcopryrite to a copper sulphite such as chalcocite or covellite, copper was precipitated in the form of Chevrel's salt. This process has an application as a way to increase the copper grade of chalcopryrite concentrates using the leachate from a Galvanox™ leach of flotation tailings. Çalban et al. [19] found the precipitation conditions of Chevrel's salt using $(\text{NH}_4)_2\text{SO}_3$ from synthetic aqueous CuSO_4 solutions. Çalban et al. [20] examined the dissolution kinetics of Chevrel's salt in hydrochloric acid solutions. They found that the dissolution of Chevrel's salt was controlled by diffusion through the ash or product layer. Çalban et al. [21] obtained Chevrel's salt by using synthetic CuSO_4 solutions. At the same time, they have appointed the optimum conditions. Çalban et al. [22] did a study on experimental Chevrel's Salt production methods. They gathered the experimental production methods of Chevrel's salt in one article.

The aim of this study is to dissolve Chevrel's salt by using NH_4Cl solutions. 2^n factorial and orthogonal central composite experimental design methods in the dissolution experiments have used to determine the optimum conditions.

II. MATERIALS AND METHOD

Chevrel's salt samples used in the experiments were precipitated from synthetic CuSO_4 solutions by using the optimum precipitation conditions obtained by Çalban et al. [19]. The produced Chevrel's salt samples were thin. The precipitates were air-dried. Identification of the precipitates with intense brick-red color is made by X-ray powder diffraction (XRD) and Scanning electron microscopy (SEM). XRD and SEM results of the precipitate are demonstrated in Figs. 1 and 2, respectively. The copper amounts in the precipitate and the filtrate were determined complexometrically [23].

The factorial experimental design and the orthogonal central composite design methods were used to determine the experimental plan. As seen from Figs. 1 and 2, the samples were mainly composed of pure Chevrel's salt.

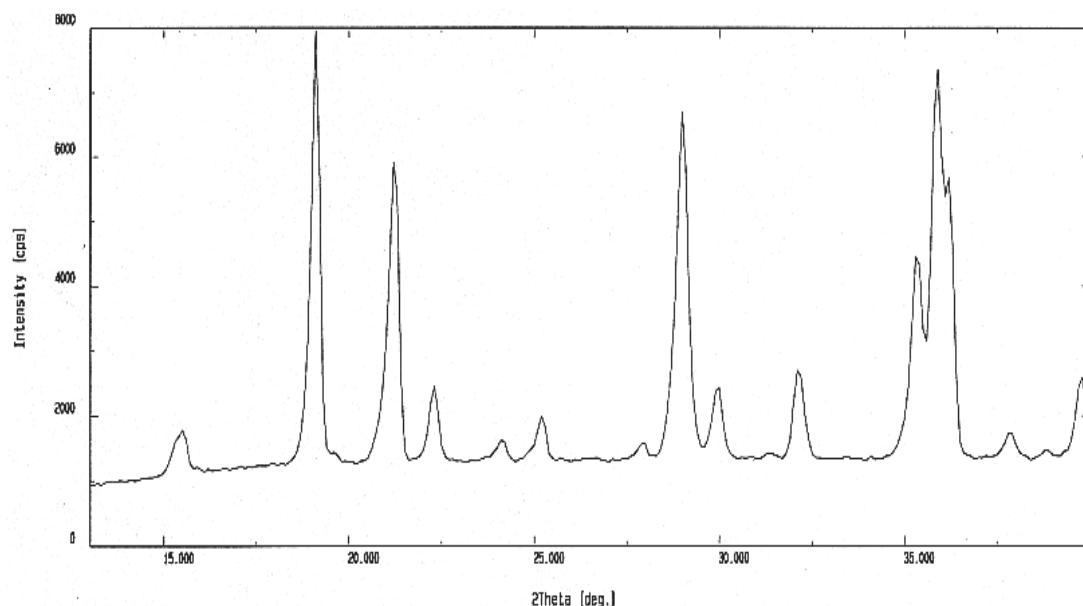


Fig. 1 XRD of Chevrel's Salt [19]

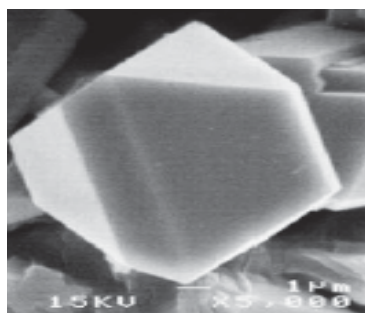


Fig. 2 SEM of Chevrel's salt [19]

III. EXPERIMENTAL PROCEDURE

The experimental design methods are very advantageous in experimental studies. One of the current experimental design methods is the 2^n factorial design. According to this method, the levels of all the variables were determined. In the last step, a regression model based on the experiment results is obtained [24]. 2^n experiments are performed. The levels of parameters are coded as (+1) and (-1). The code of the center point experiments is taken as zero. A variance analysis table (ANOVA) is prepared and tested the effective of each parameter [19], [24]-[29].

The effects of the quadratic terms in ANOVA table are tested by:

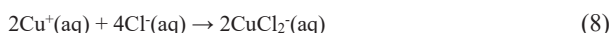
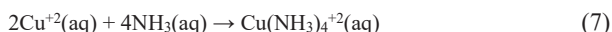
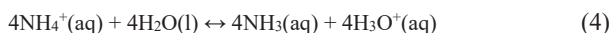
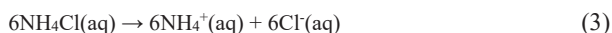
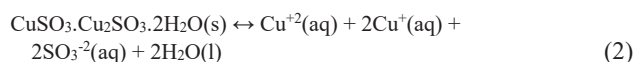
$$LOF_{curv.} = \frac{m_o F(\bar{Y}_1 - \bar{Y}_0)^2}{m_o + F} \quad (1)$$

where $LOF_{curvature}$ (lack of fitting) is the curvature, m_1 is the number of factorial experiments, m_o is the number of center point experiments, \bar{Y}_o is the mean of center point experiments, and \bar{Y}_1 is the mean of factorial experiments.

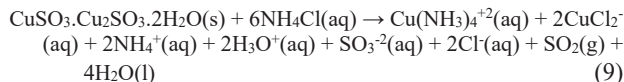
IV. RESULTS AND DISCUSSION

A. Dissolution Reactions

The following reactions occurred during the dissolution of Chevrel's salt in ammonium chloride:



Hence, the overall reaction is:



B. Effects of Parameters

As a result of preliminary experiments, the stirring speed was chosen as a constant parameter since the complete suspension is reached in 600 rpm. After 600 rpm, the effect of the stirring speed is very small. Additionally, the particle size is taken as constant parameter because of precipitating from synthetic $CuSO_4$ solutions. In all of the experiments, the particle size was taken as 0.053 mm. The effects of the parameters on the dissolution were investigated by using the parameter levels given in Tables I and II. Statistical test graphs were given Fig. 3.

TABLE I
PARAMETERS AND THEIR RANGES FOR FIRST-ORDER DESIGN

Parameters	Low Level (-1)	High Level (+1)	Medium Level (0)
X_1 : Ammonium Chloride Concentration (M)	4	5	4.5
X_2 : Solid-to-liquid ratio (g.mL ⁻¹)	1/10	1/8	9/80
X_3 : Reaction temperature (°C)	20	30	25
X_4 : Reaction time (min.)	8	12	10

TABLE II
PARAMETERS AND THEIR RANGES FOR SECOND-ORDER DESIGN

Parameters	Low Level (-1)	High Level (+1)	Medium Level (0)
X_1 : Ammonium Chloride Concentration (M)	3.7	5.3	4.5
X_2 : Solid-to-liquid ratio (g.mL ⁻¹)	0.092	0.133	9/80
X_3 : Reaction temperature (°C)	17	33	25
X_4 : Reaction time (min.)	6.8	13.2	10

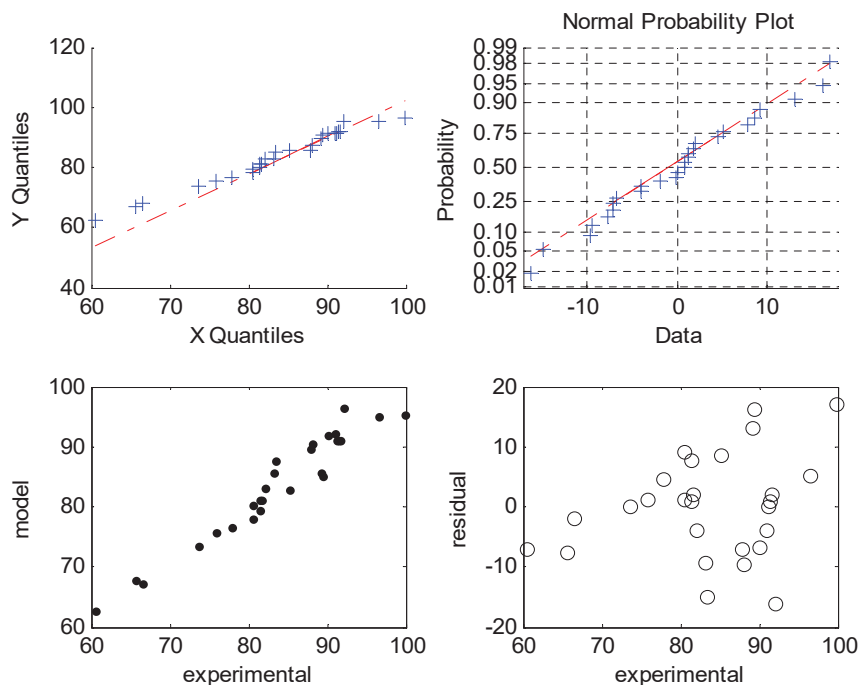


Fig. 3 Statistical test graphs

The fractional conversion Y (%) was defined as:

$$Y(\%) = \frac{(\text{amount of dissolved copper})}{(\text{amount of copper in the sample})} \times 100 \quad (10)$$

TABLE III
EXPERIMENTAL DESIGN MATRIX AND DISSOLUTION YIELDS OF CHEVREUL'S SALT

Exp. No.	X_1	X_2	X_3	X_4	$Y_{\text{experimental}}$	$\hat{Y}_{\text{theoretical}}$	$e_i : Y_i - \hat{Y}_i$
1	+	+	-	-	75.98	76.12	-0.14
2	+	+	+	-	80.56	79.81	0.75
3	+	-	-	+	88.04	90.18	-2.14
4	+	-	+	+	99.79	95.67	4.12
5	-	+	-	-	60.64	63.03	-2.39
6	-	+	+	-	73.57	73.09	0.48
7	-	-	-	+	81.70	80.72	0.98
8	-	-	+	+	91.05	92.57	-1.52
9	-	-	-	-	77.79	77.07	0.72
10	+	+	+	+	87.81	90.19	-2.38
11	-	+	+	+	80.56	78.59	1.97
12	-	-	+	-	83.51	86.84	-3.33
13	+	-	-	-	81.40	81.64	-0.24
14	+	+	-	+	89.48	84.42	5.06
15	-	+	-	+	66.63	66.45	0.18
16	+	-	+	-	83.21	85.05	-1.84
M	0	0	0	0	91.13	91.34	-0.21
M	0	0	0	0	91.67	91.34	0.33
M	0	0	0	0	91.40	91.34	0.06

TABLE IV
ANALYSIS TABLE OF VARIANCE (ANOVA)

Source of Variation	Sum. of Squares	df	Mean Squares	F_0 Ratio	Decision ($\alpha : 0.01$)
X_1	340	1	340	4689.6	Effective
X_2	490	1	490	6758.6	Effective
X_3	310	1	310	4275.8	Effective
X_4	260	1	260	3586.2	Effective
LOF _{curv.}	255.16	1	255.16	3519.45	Effective
Model lack of fit	593.69	11	53.97	744.44	Effective
Exp. Error	0.145	2	0.0725		
Total	2249	18			

$F_{0.99, 1, 2} = 98.5$; $F_{0.99, 11, 2} = 99.40$

TABLE V
EXPERIMENTAL DESIGN MATRIX AND DISSOLUTION YIELDS OF CHEVREUL'S SALT

Exp. No.	X_1	X_2	X_3	X_4	$Y_{Cu}(\%)$
20	-1.607	0	0	0	81.48
21	+1.607	0	0	0	90.06
22	0	-1.607	0	0	85.23
23	0	+1.607	0	0	65.75
24	0	0	-1.607	0	82.02
25	0	0	+1.607	0	96.49
26	0	0	0	-1.607	89.26
27	0	0	0	+1.607	92.20

As seen from the tables, the dissolution yield increased as the ammonium concentration increased from 3.7 M to 4.5 M. After 4.5 M, the concentration of ammonium ions in solution increases. pH of the solution increases due to the increasing free ammonia amount in solution. As a result, dissolved

copper amount decreases, due to the precipitating copper ammonium sulfites.

The effect of the reaction temperature was examined in the range of 17-33 °C. The obtained dissolution results are presented in Tables III and V. As seen from these tables, the dissolution rate of Chevreul's salt increased as the reaction temperature increased. The dissolution of Chevreul's salt was closely linked to the reaction temperature. Additionally, the solubility of Chevreul's salt in aqueous solutions is known to increase up to certain temperatures [22].

The effect of reaction time was studied in the range of 6.8-13.2 min. The dissolution results are presented in Tables III and V. It can be seen that the dissolution yield increased as the reaction time increased because the dissolved Chevreul's salt amount was not maximum in the selected reaction time intervals.

The effect of the solid-to-liquid ratio on the dissolution of Chevreul's salt was investigated in the range of 0.092-0.133-g.mL⁻¹. The dissolution results are given in Tables III and V. As seen from these tables, the dissolution yield decreased as the solid-to-liquid ratio increased.

C. Statistical Analysis on the Dissolution of Chevreul's Salt

The results obtained were analyzed by ANOVA using a MATLAB computer software package. The effect of each parameter was optimized on the full factorial experimental design method. The levels of the parameters were given in Tables I and II. First, the first order model design matrix was prepared. Three central point experiments were added to the experimental plan to estimate the pure experimental error.

The experimental results were given in Table III. Evaluation of the results was shown in Table IV. At the 99% confidence level, all of parameters in the selected level of parameters were found to be effective. Moreover, the effects of the pure quadratic terms were calculated by means of (1). As seen from ANOVA Table (Table IV), the curvature is effective. Therefore, a second order design is necessary.

TABLE VI
ANALYSIS TABLE OF VARIANCE (ANOVA)

Source of Variation	Sum. of Squares	df	Mean Squares	F_0 Ratio	Decision ($\alpha : 0.01$)
X_1	340	1	340	4689.6	Effective
X_2	490	1	490	6758.6	Effective
X_3	310	1	310	4275.8	Effective
X_4	260	1	260	3586.2	Effective
X_1^2	60	1	60	827.5	Effective
X_2^2	500	1	500	6896.5	Effective
X_3^2	10	1	10	137.9	Effective
X_1X_2	70	1	70	965.5	Effective
X_1X_3	40	1	40	551.7	Effective
X_1X_4	20	1	20	275.8	Effective
Model lack of fit	148.85	14	10.63	146.6	Effective
Exp. Error	0.145	2	0.0725		
Total	2249	26			

$F_{0.99, 1, 2} = 98.50$, $F_{0.99, 14, 2} = 99.43$

The second order design matrix and results were presented in Table V. To test the significance of the effect of each

parameter, ANOVA table was prepared, and this table is shown in Table VI. At the 99% confidence level, four parameters in the selected parameter levels were found to be effective.

The full model obtained by the regression analysis is as:

$$Y_{Cu} = 91.47 + 4.04X_1 - 4.88X_2 + 3.88X_3 + 3.51X_4 - 2.31X_{11} - 6.61X_{22} - 0.85X_{33} - 0.23X_{44} + 2.13X_1X_2 - 1.60X_1X_3 + 1.22X_1X_4 + 0.07X_2X_3 - 0.06X_2X_4 + 0.52X_3X_4 \quad (11)$$

The full model given in (11) was chosen as the most suitable model. As seen from this model, the dissolution yield increased as the ammonium chloride concentration, the reaction time, and the reaction temperature increased, but decreased as the solid-to-liquid ratio increased. According to the full model (11), all of the parameters were found to be effective at the 99% confidence level. As seen from Table V (ANOVA), the variables studied individually and in combination affected the dissolution of Chevreul's salt in the ammonium chloride solutions. The ammonium chloride concentration and the solid-to-liquid ratio had the strongest effect on the dissolution. Conversely, the reaction time was less effective at the selected values.

Systematic errors are absent in a well-established model. Normalized residuals depend on the experimental errors, and these values exhibit a normal distribution [19], [24]-[29]. The graphical analysis of the statistical tests is presented in Fig. 3.

V. CONCLUSIONS

- The dissolution of Chevreul's salt increased by increasing the concentration of ammonium chloride.
- The yield of dissolution increased when the ammonium chloride concentration, the reaction temperature, and the reaction time increased, and as the solid-to-liquid ratio decreased.
- The effect of the stirring speed on the dissolution of Chevreul's salt was very small in the chosen stirring speed levels.
- The most effective parameter on the dissolution of Chevreul's salt was the solid-to-liquid ratio.
- At low temperatures, Chevreul's salt can be dissolved in ammonium chloride solutions.
- The best conditions on Chevreul's salt dissolution are the ammonium chloride concentration of 4.5 M, reaction temperature 25 °C, particle size 0.053 mm, solid-to-liquid ratio 9/80-g.mL⁻¹, reaction time of 13.2 min., and stirring speed of 600 rpm. Under these conditions, the dissolution yield was 96.20%.
- In the present study, the dissolution yield increased as the ammonium concentration increased to 4.5 M. After 4.5 M, the concentration of ammonium ions and the pH of the solution increase due to the increasing free ammonia amount in solution. As a result, dissolved copper amount decreases, due to the precipitating copper ammonium sulfites.
- The dissolution of Chevreul's salt was closely linked to the reaction temperature. The solubility of Chevreul's salt

in aqueous solutions increases up to certain temperatures.

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