



Statistical Modelling of Precipitation of Copper Ammonium Sulphite from Synthetic Copper Sulphate Solutions

FATIH DEMIR

Department of Chemical Engineering, Engineering Faculty, Ataturk University, Tr-25240 Erzurum, Turkey

Corresponding author: E-mail: fatihdemir@atauni.edu.tr

Received: 15 July 2013;

Accepted: 23 October 2013;

Published online: 22 March 2014;

AJC-14963

Copper ammonium sulphite was precipitated under optimum conditions by passing SO_2 from a synthetic aqueous copper sulphate solution. Copper ammonium sulphite, $\text{Cu}_2\text{SO}_3 \cdot (\text{NH}_4)_2 \cdot \text{SO}_3$, was characterised by XRD. The effects of parameters such as initial concentration, pH, stirring speed and reaction time were investigated on precipitation. A first-order model was obtained using the 2^4 full factorial design method. It was observed that all parameters on the precipitation of copper ammonium sulphite were effective. The optimum conditions established for maximum copper precipitation at room temperature were: stirring speed 700 rpm, initial concentration 0.8 mol L^{-1} , pH 3.5 and reaction time 15 min. Under these optimum conditions, the percentage of precipitated copper from solution was 99.80.

Keywords: Precipitation, Factorial experimental design, Synthetic copper solutions, Copper ammonium sulphite.

INTRODUCTION

Obtaining copper compounds from aqueous solutions is widely realized with a chemical reaction. They have been produced from aqueous solutions through various technologies. These methods are electrowinning, reduction, segmentation, flotation and the electrolytic extraction process, *etc.*¹⁻⁴

Copper sulphites are of considerable interest in chemistry. Precipitation of mixed valence metal sulphates such as copper ammonium sulphite is important to obtain metals. The mixed valence copper sulphite, $\text{Cu}_2\text{SO}_3 \cdot \text{Cu SO}_3 \cdot 2\text{H}_2\text{O}$, $\text{Cu}_2\text{SO}_3 \cdot (\text{NH}_4)_2\text{SO}_3$ is a model compound characterizing the sulphite structure. This structure indicated that solid metal sulphites and sulphite complexes in solution may play a role as intermediates in various chemical processes. Thus, metal sulphites have been explained as used model compounds in the reactions. For instance, the structures of sulphite ion coordination have strongly influenced the course of the thermal decomposition stable up to 200°C . At the same time, recovery of the precipitation of this complex compound has formed a key stage in the hydrometallurgical processes^{5,6}.

Some studies on the performance of copper ammonium sulphite and the factorial design method in this study were found in the literature. Çolak *et al.*⁷ precipitated as sulphites to produce copper powders from its impure solutions. Copper(I) sulphate solutions were prepared by utilizing these sulphites. The copper powders were produced by thermal disproportionation of copper(I) sulphate at 60°C and 175 mm

Hg pressure in a nitrogen atmosphere. The copper powders produced were obtained with 99.85 % purity.

Çalban *et al.*⁸ oxidized copper ore dissolved under optimum conditions using the 2^n factorial experimental design and orthogonal central composite design methods in the precipitation experiments. They found that the optimum conditions established for maximum copper precipitation were: temperature 62°C , pH 3, stirring speed 600 rpm and reaction time 12 min. Fixed parameters chosen at the initial stage of the reaction were: SO_2 flow rate 358 L h^{-1} and concentration of CuSO_4 solution $7.383 \text{ g Cu L}^{-1}$. They founded that the percentage of copper precipitated from leach solution was 99.92⁸.

Chevreur's salt precipitated from CuSO_4 solutions by means of Na_2SO_3 . Its appropriate precipitation conditions determined as pH-3, $[\text{SO}_3^{2-}]/[\text{Cu}^{2+}]$ ratio-1.6, reaction temperature- 60°C , stirring speed-500 rpm and reaction time-20 min. The precipitate obtained at these conditions contain 49 % copper, with the structure of both tetrahedral coordination of Cu(I) and octahedral coordination of Cu(II) in brick red colour⁹.

In another study, the optimum conditions obtained for maximum copper precipitation were: initial solution concentration 1.14 M, SO_2 feeding rate 329.35 L h^{-1} , reaction time 25 min and initial solution pH 8.5. Under these optimum conditions the percentage of precipitated copper from synthetic aqueous CuSO_4 solutions was 99.95¹⁰.

In this study, synthetic copper sulphate was selectively dissolved under optimum conditions in ammonium sulphate solutions. Copper ammonium sulphite was precipitated by

passing SO₂ from these solutions. The 2ⁿ factorial experimental design method in the precipitation experiments was used to determine the optimum precipitation conditions. The first model, which relates the copper ammonium sulphite [Cu₂SO₃·(NH₄)₂SO₃] precipitation yield to process factors was obtained. It was characterised by X-ray diffraction.

EXPERIMENTAL

Factorial design is the most widely used experimental design to estimate the main effects. In a factorial design the influences of all experimental variables, factors and interaction effects on the response or responses are investigated. In addition, the interaction effects are the 2ⁿ factorial design, when each variable is investigated at two levels. According to the 2ⁿ factorial experimental design method, where the principal steps of experiments are designed, it is often used to obtain first-order models. If the variance analysis indicates that overall curvature is significant, supportive experiments are carried out to develop a second-order model. The principal steps of experiments are designed: determination of response variables, choice of factor levels and statistical analysis of the data. Consequently, the final step of the work is to obtain a statistically regression model^{11,12}.

The main effects and interactions obtained from the regression model are entirely half values obtained from Yates' algorithm. This is due to the response over two levels of each independent variables (from -1 to +1). Coded values of variables are high level +1 and low level -1. Between factor levels, the centre coordinates are zero and that value coincides with the origin of coordinates. A full factorial design was selected to study the influence of the different factors (such as stirring speed, initial concentration, pH and reaction time).

$$\hat{Y} = b_0 + \sum_{i=1}^4 b_i X_i + \sum_{i=1}^n \sum_{j>1}^n b_{ij} X_i X_j \quad (1)$$

where the coefficient b_0 shows the main effects of the factors X_i , b_{ii} and b_{ij} coefficients represent second-order interaction terms. The independent term b_0 represents the response at the zero level of every factor ($X_1 = X_2 = X_3 = X_i = 0$).

With four factors, the 2⁴ full factorial design requires 16 runs. Furthermore, three central replicates were added to the experimental plan in order to estimate pure experimental error. To test the significance of the factor effects, an analysis of variance was conducted at 95 and 99 % confidence intervals. Furthermore, the effects of pure quadratic terms were controlled by means of the following statistic:

$$LOF_{Curv} = \frac{m_0 F(1-0)^2}{m_0 + F} \quad (2)$$

where m_0 is the number of central point experiments, F is the number of factorial experiments, Y_1 the mean of factorial experiments and Y_0 is the mean of central replicates^{13,14}.

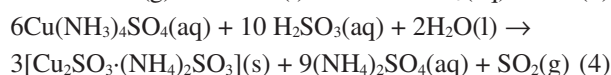
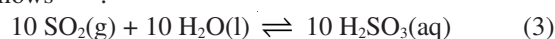
The precipitation process of copper ammonium sulphite was carried out in a glass reactor (500 mL) with three-necks. Copper solution prepared under the optimum conditions was put into the reactor. The reactor was submerged into a water bath with a digital temperature controller (a MEMMERT™) and the content of reactor was stirred with a water-resistant

magnetic stirrer (a IKA™). The probe of a WTW™ pH-meter, which simultaneously measures pH and temperature was immersed into the solution. The reactor was fitted with a back-cooler to prevent loss by evaporation. When the contents of the reactor reached the desired temperature, stirring operation was started at a stable speed, SO₂ gas at a stable flowrate was fed into the reactor with a flow-meter until the pH reached the desired value. Stirring continued along reaction time. At the end of the reaction period, the reactor contents were immediately filtered through Filtrak 389. The chemical structure of precipitated Cu₂SO₃·(NH₄)₂SO₃, with white colour obtained at the end of the first reaction period was characterized by X-ray powder diffraction (Rigaku 2000 JCPDS DMAX (29-1490) diffractometer (XRD) with CuK_α radiation (30 kV and 30 mA and an automatic monochromator) at a scanning rate of 2 h at 2° minute⁻¹ (Fig. 1)⁹. The amount of copper in the precipitate was determined complexometrically¹⁵. Then, the factorial experimental design method was used to determine experimental plan.

RESULTS AND DISCUSSION

Thermodynamic property of copper ammonium sulphite precipitation is related to pH and initial concentration. In addition, SO₂ gas is a versatile reagent capable of precipitating a number of copper sulphates. Some of which can be precipitated selectively from the solution by appropriate adjustments of pH and initial concentration. Copper ammonium sulphite does not form in acidic solutions containing a considerable amount of sulphurous acid. It is necessary to maintain a pH range of 3.5-5, because solubility of copper ammonium sulphite increases at lower pH values.

When copper ammonium sulphite is precipitated from solution, the reactions taking place in the medium can be written as follows^{9,10,16}.



Statistical analysis of the parameters on copper ammonium sulphite precipitation: In order to determine the optimum conditions and derive a model for acid activation with four factors, a full factorial of the type 2⁴ has been used and 16 full factorial design requires 16 runs. Precipitates obtained at all experiments confirmed the generic empirical formula of copper ammonium sulphite. Cu₂SO₃·(NH₄)₂SO₃, because of both its white color and chemical analysis results. The precipitates obtained fitted the theoretical copper and sulphur amounts in copper ammonium sulphite. The precipitation tests of copper ammonium sulphite with sulphur dioxide were studied. The collected data were analyzed with an EXCEL compatible PC using the ANOVA computer software package for the evaluation of the effect of each parameter on the optimization criteria. Experimental parameters for the precipitation process of synthetic copper sulphate solutions, stirring speed (X_1), initial concentration (X_2), pH (X_3) and reaction time (X_4) that were chosen as independent variables to the model, are presented in Table-1. In the light of pre-experiments, two factors; temperature and sulphur dioxide gas flow rate were maintained as constant parameters. Initially, a first-order model

was chosen to fit the experiment data for the small F ratio. Experimental data based on the design was fitted to a first-order polynomial equation as follows:

$$\hat{Y} = b_0 + \sum_{i=1}^n b_i X_i + \sum_{i=1}^n \sum_{j>1}^n b_{ij} X_i X_j \quad (5)$$

where the coefficient b_i shows the main effects of the factors X_i and b_{ij} coefficients represent first-order interactions terms. The independent term b_0 represents the response at the zero level of every factor ($X_1 = X_2 = X_3 = X_4 = 0$).

Furthermore, three central replicates were added to the experimental plan to estimate pure experimental error. To test the significance of the factor effects, an analysis of variance has been conducted at 95 and 99 % confidence intervals. Further-

more, the effects of the pure quadratic terms were controlled by means of the following statistic:

$$LOF_{Curv} = \frac{m_0 F(1-0)^2}{m_0 + F} \quad (6)$$

where m_0 is the number of central point experiments, F is the number of factorial experiments, is the mean of factorial experiments and is the mean of central replicates. The matrix for four variables is varied at two levels (+1 and -1). The higher level of variable was designed as "+" and the lower level was designed as "-". The experiments were usually performed in random order to avoid systematic error. The precipitation of copper ammonium sulphite as % is presented in Table-2. The results of the analysis of variance are given in Table-3.

TABLE-1
FACTOR LEVELS USED IN THE FULL FACTORIAL DESIGN

Factors	Low level (-)	High level (+)	Medium level (0)
X_1 : Stirring speed (rpm)	700	800	750
X_2 : Initial concentration (M)	0.4	0.8	0.6
X_3 : pH	3.5	5	4.25
X_4 : Reaction time (min)	15	30	22.5

TABLE-2
EXPERIMENTAL DESIGN AND COPPER AMMONIUM SULPHITE PRECIPITATION YIELD

Experimental number	X_1	X_2	X_3	X_4	Precipitation yield (Y_i) (%)	Model (Y_{cu}) (%)
1	1	1	1	1	96.00	99.71
2	-1	1	1	1	98.68	94.65
3	1	-1	1	1	94.81	93.42
4	-1	-1	-1	1	88.49	90.11
5	1	1	-1	-1	95.40	91.54
6	-1	1	-1	-1	96.25	99.80
7	1	-1	1	-1	89.89	87.70
8	-1	-1	1	-1	88.21	90.09
9	1	1	-1	1	96.19	96.47
10	-1	1	-1	1	98.42	97.86
11	1	-1	-1	1	87.56	85.63
12	-1	-1	1	1	87.82	87.67
13	1	1	1	-1	98.03	98.57
14	-1	1	1	-1	98.68	99.12
15	1	-1	-1	-1	69.94	76.12
16	-1	-1	-1	-1	91.42	86.22
1*	0	0	0	0	93.33	99.71
2*	0	0	0	0	93.79	94.65
3*	0	0	0	0	92.84	93.42

TABLE 3
ANALYSIS OF VARIANCE

Source of variation	Sum of squares	d.f.	Mean squares	F ratio	Decision ($\alpha = 0.05$)	Decision ($\alpha = 0.01$)
X_1	25.37	1	25.37	112.43	Effective	Effective
X_2	395.11	1	395.11	1750.62	Effective	Effective
X_3	50.58	1	50.58	224.13	Effective	Effective
X_4	25.37	1	25.37	112.43	Effective	Effective
$X_1 X_2$	3.35	1	3.35	14.87	Ineffective	Ineffective
$X_1 X_3$	59.40	1	59.40	263.20	Effective	Effective
$X_1 X_4$	31.50	1	31.50	139.56	Effective	Effective
$X_2 X_3$	20.67	1	20.67	91.62	Effective	Ineffective
$X_2 X_4$	20.90	1	20.90	92.63	Effective	Ineffective
$X_3 X_4$	14.34	1	14.34	63.55	Effective	Ineffective
Curvature	2.96	1	2.96	13.13	Ineffective	Ineffective
Model lack of fit	295.84	5	26.89	119.16	Effective	Effective
Experimental error	0.45	2	0.22			
Total	795.71	18				

$$F_{0.05(1,2)} = 18.51; F_{0.05(5,2)} = 19.30; F_{0.01(1,2)} = 98.50; F_{0.01(5,2)} = 99.30$$

A first model with interaction terms was chosen to fit the experimental data:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_5X_1X_2 + b_6X_1X_3 + b_7X_2X_3 + b_8X_2X_4 + b_9X_3X_4 \quad (7)$$

As seen from Table-3, variance analysis results showed curvature effect. According to these results, the regression first-model was obtained as following:

$$\begin{aligned} \%Y_{Cu} = & 92.40 - 1.25 X_1 + 4.96 X_2 + 1.77 X_3 + 1.25 X_4 \\ & + 0.46 X_1X_2 + 1.92 X_1X_3 + 1.40 X_1X_4 - 1.13 X_2X_3 \\ & - 1.14 X_2X_4 - 0.94 X_3X_4 \text{ (at 95 \% confidence interval)} \end{aligned} \quad (8)$$

Copper precipitated as copper ammonium sulphite from solution: ($\alpha \geq 0.075$) (Y_{Cu}) (%),

$$\begin{aligned} \%Y_{Cu} = & 92.40 - 1.25 X_1 + 4.96 X_2 + 1.77 X_3 + 1.25 X_4 \\ & + 1.92 X_1X_3 + 1.4 X_1X_4 \text{ (at 99 \% confidence interval)} \end{aligned} \quad (9)$$

As the analysis results of variance quadratic terms are effective. With $F = 16$, $m_0 = 3$ and $n = 4$, according to Eq. (7).

As seen from Eq. (7), copper ammonium sulphite precipitation yield increased with increasing temperature, stirring speed, pH and reaction time. The ANOVA of the obtained results shows that all of the variables studied and their combinations affect copper ammonium sulphite recovery from aqueous $NH_3-(NH_4)_2SO_4$ solutions. In Table-3, it is possible to identify that copper ammonium sulphite predominates into the initial concentration of the work. Also, in Table-3, the ANOVA results show effect on copper ammonium sulphite recovery whole parameters. The graphics of tests are presented in Fig. 2a and b).

Conclusion

The optimum conditions of copper ammonium sulphite recovery from aqueous $NH_3-Cu(NH_4)_2SO_4$ solutions was investigated. Experiments were designed according to the 2^n factorial design method. From the experimental results, the optimal conditions for precipitation of copper ammonium sulphite extent of 99.80 % were obtained as the stirring speed 700 rpm,

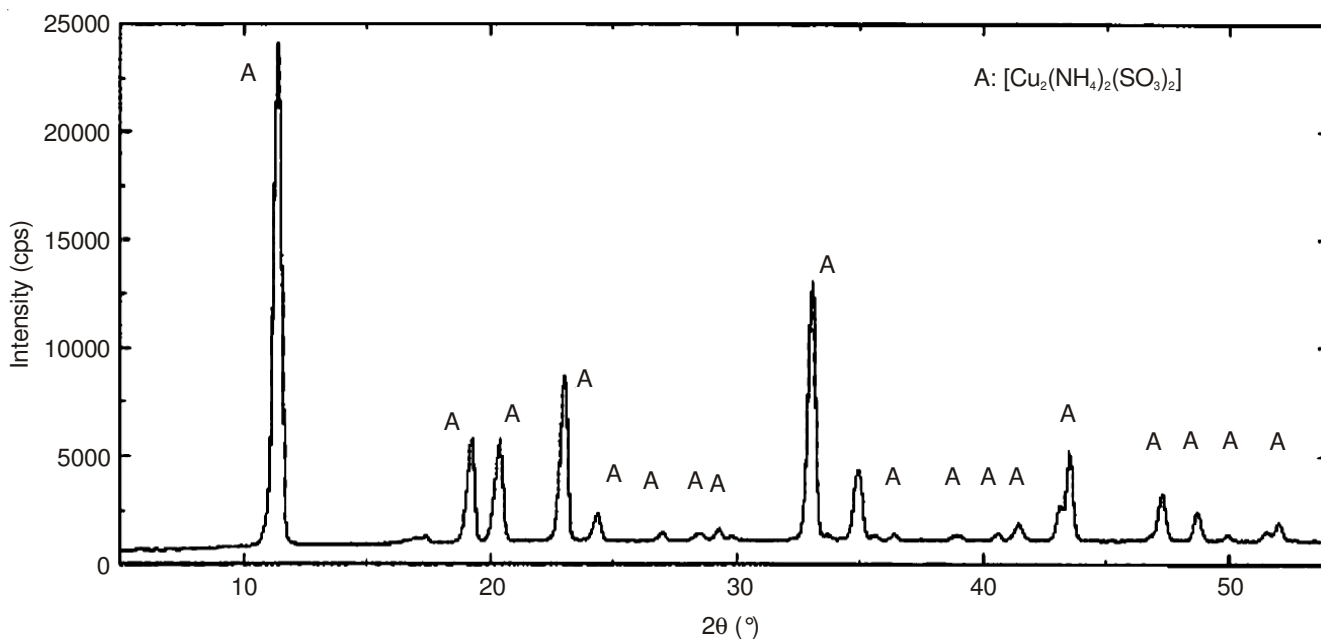


Fig. 1. X-ray diffractogram of $[Cu_2(NH_4)_2(SO_3)_2]$

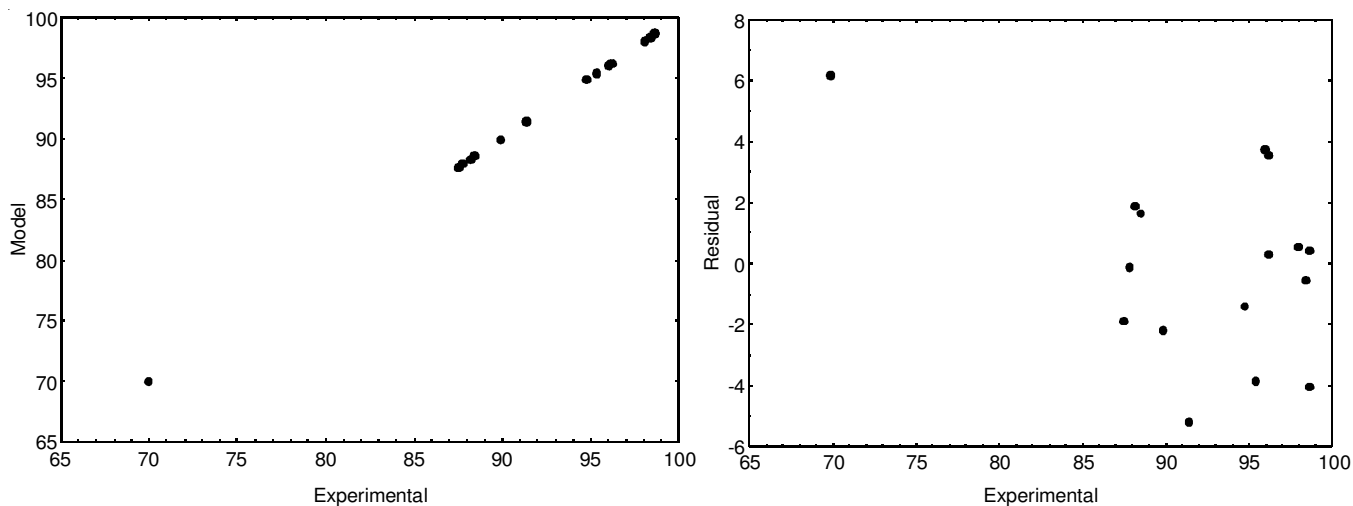


Fig. 2. Statistical test graphics (a and b)

initial concentration 0.8 M, pH 3.5 and reaction time 15 min. Fixed parameters chosen at the initial stage of the reaction were room temperature 20 °C, SO₂ flow rate was 358 L h⁻¹. The correlation coefficient calculated for the first-order model at 92.5 % confidence level has a high value of 0.998. Therefore, the model supports the experimental data very well. It is very efficient and has no systematic errors. The important parameters affecting the precipitation of copper ammonium sulphite were stirring speed, initial concentration, pH and reaction time. The recovery of copper ammonium sulphite increased with the increasing stirring speed, initial concentration, pH and reaction time.

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