

# Experimental Chevreul's Salt Production Methods on Copper Recovery

Turan Çalban, Oral Laçin, Abdüsselam Kurtbaş

**Abstract**—Experimental production methods of Chevreul's salt being an intermediate stage product in copper recovery were investigated on this article. Chevreul's salt,  $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$ , being a mixed valence copper sulphite compound, has been obtained by using different methods and reagents. Chevreul's salt has an intense brick-red color. It is highly stable and expensive. The production of Chevreul's salt plays a key role in hydrometallurgy. Thermodynamic tendency on precipitation of Chevreul's salt is related to pH and temperature. Besides,  $\text{SO}_2$  gaseous is a versatile reagent for precipitating of copper sulphites, Using of  $\text{SO}_2$  for selective precipitation can be made by appropriate adjustments of pH and temperature. Chevreul's salt does not form in acidic solutions if those solutions contains considerable amount of sulfurous acid. It is necessary to maintain between pH 2–4.5, because, solubility of Chevreul's salt increases with decreasing of pH values. Also, the region which Chevreul's salt is stable can be seen from the potential-pH diagram.

**Keywords**—Chevreul's salt, copper recovery, copper sulphite, stage product

## I. INTRODUCTION

COPPER is usually obtained from solutions containing copper. Copper precipitation process can be various due to hydrolytic action, ionic interaction and reduction. In recent years, new copper precipitation methods have been discovered. Besides, the variety of copper compounds precipitated, also increased with time. As a result of that, different copper compounds have been precipitated from aqueous solutions with the help of various technologies and reagents [1].

Chevreul's salt is a very important copper sulfite compound in the hydrometallurgy. It is mixed valence copper sulphite compound. Copper sulphites are of considerable interest in chemistry. Chevreul's salt ( $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$ ), mixed valence copper sulphite is a model compound that characterize the sulphite structure [2]. Chevreul's salt can be obtained by using synthetic or leach solutions containing copper. It is highly stable structure and it has the intense brick-red color. In addition, the precipitation of this complex compound has formed a key stage in hydrometallurgical processes [3]. Also, it is an expensive compound.

T. Ç. is with the Atatürk University, Engineering Faculty, Department of Chemical Engineering, Campus, TR-25240, Erzurum, Turkey (corresponding author to provide phone: 442-231-4578; fax: 442-231-4544; e-mail: turancalban@atauni.edu.tr).

O. L. and A. K. are with the Atatürk University, Engineering Faculty, Department of Chemical Engineering, Campus, TR-25240, Erzurum, Turkey (e-mail: olacin@atauni.edu.tr, akurtbas@atauni.edu.tr).

Thermodynamic tendency of Chevreul's salt precipitation is related to pH and temperature. Besides,  $\text{SO}_2$  gaseous is a versatile reagent capable of precipitating copper sulphite, Using  $\text{SO}_2$  a selective precipitation can be made by appropriate adjustments of pH and temperature. Chevreul's salt does not form in acidic solutions if those solutions contains considerable amount of sulfurous acid. It is necessary to maintain pH range between 2–4.5, because, solubility of Chevreul's salt increases as pH values decrease. Also, the region which Chevreul's salt is stable can be seen from the potential-pH diagram [4].

The production of Chevreul's salt compound by using different methods and reagents has shown encouraging results. Parker and Muir [4] determined the precipitation conditions of Chevreul's salt using different sulphites. They stated that both temperature and the molar ratios of Chevreul's salt and  $\text{CuSO}_4$  were important in the efficiency and stoichiometry of the dissolution reaction. Reference [3] synthesized Chevreul's salt from reaction between  $\text{CuSO}_4$  and  $\text{NaHSO}_3$  and characterized by X-ray photoelectron spectroscopy, magnetic susceptibility, EPR and electronic spectroscopy. Reference [5] investigated synthesis, identification and thermal decomposition of double sulphites like  $\text{Cu}_2\text{SO}_3 \cdot \text{MSO}_3 \cdot 2\text{H}_2\text{O}$  ( $M = \text{Cu, Fe, Mn or Cd}$ ). They reported that these salts were thermally stable up to  $200^\circ\text{C}$  and the structures of sulphite ion coordination strongly influenced the course of the thermal decomposition. Reference [6] dissolved the oxidized copper ore in sulphuric acid. The copper in the leach solution precipitated as 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 pH value was 4, the stirring speed was at 600 rpm, the temperature was at  $60^\circ\text{C}$ , passing time of  $\text{SO}_2$  was at 1 min and reaction time after passing  $\text{SO}_2$  was at 6 min. The appropriate conditions of Chevreul's salt were precipitated. Reference [1] leached the oxidized copper ore in  $\text{NH}_3$ - $(\text{NH}_4)_2\text{SO}_4$  medium that is under optimum conditions. Then, they precipitated Chevreul's salt by passing  $\text{SO}_2$  from these leached solutions. They characterized Chevreul's salt by XRD and SEM. The effects of parameters, such as temperature, pH, stirring speed and reaction time, were investigated on precipitation of Chevreul's salt. They used  $2^n$  factorial experimental design and orthogonal central composite design methods in the precipitation experiments. It was observed that the most effective parameters on the precipitation of Chevreul's salt were temperature, stirring speed and reaction time. The optimum conditions for maximum copper precipitation were found. Those conditions are: the temperature at  $62^\circ\text{C}$ , pH at 3, stirring speed at 600 rpm and reaction time at 12 min. They accepted  $\text{SO}_2$  flow rate at 358

$L.h^{-1}$ , concentration of  $CuSO_4$  solution at  $7.383 \text{ gCu} \cdot L^{-1}$  and they the fixed parameters at the initial stage of the reaction. Under these optimum conditions, the percentage of copper precipitated from leach solution was 99.92. Reference [7] precipitated the Chevrel's salt with  $Na_2SO_3$  reagent from synthetic  $CuSO_4$  solutions. They determined the appropriate precipitation conditions. According to their foundations the appropriate conditions were as the pH at 3,  $SO_3/Cu^{+2}$  ratio as 1.6, the reaction temperature at  $60^\circ C$ , the stirring speed at 500 rpm and the reaction time at 20 min. Reference [8] produced Chevrel's salt by passing  $SO_2$  from synthetic aqueous  $CuSO_4$  solution. They characterized Chevrel's salt by XRD and SEM. They investigated the effects of parameters such as initial solution concentration,  $SO_2$  feeding rate, the reaction time and the initial solution pH on precipitation of Chevrel's salt. They used  $2^n$  factorial experimental design and orthogonal central composite design methods for the optimization of the precipitation experiments. It was observed that the effective parameters on the precipitation of Chevrel's salt were the initial solution concentration, the  $SO_2$  feeding rate, and the initial solution pH. The optimum conditions obtained for maximum copper precipitation were: the initial solution concentration: 1.14 M, the  $SO_2$  feeding rate:  $329.35 \text{ L} \cdot h^{-1}$ , the reaction time: 25 min, and the initial solution pH: 8.5. Constant parameters chosen by them at the initial stage of the reaction were: temperature:  $62^\circ C$ , the stirring speed: 600 rpm, and the reaction pH: 3. The percentage of precipitated copper from synthetic aqueous  $CuSO_4$  solutions under these optimum conditions was 99.95 [9]. They prepared synthetic aqueous  $CuSO_4$  solution at a particular concentration. They precipitated Chevrel's salt by using  $(NH_4)_2SO_3$  solutions prepared at various concentrations. Chevrel's salt was characterized by XRD and SEM analysis. The effects of parameters such as the  $(NH_4)_2SO_3$  concentration, the temperature, the stirring speed and the reaction time were investigated on precipitation of Chevrel's salt.  $2^n$  factorial experimental design and orthogonal central composite design methods in the precipitation experiments were used. Precipitation of Chevrel's salt was the temperature and the stirring speed. The obtained optimum conditions on maximum copper precipitation were: the  $(NH_4)_2SO_3$  concentration: 0.4 M, the temperature at  $60^\circ C$ , the stirring speed was at 700 rpm and 15 min for reaction time. The chosen stationary parameters at the initial stage of the reaction were concentration of the  $CuSO_4$  solution 0.25 M and the pH 4. Under these optimum conditions, the precipitated copper was 98.4%.

## II. EVALUATION OF RESULTS

Chevrel's salt compound has a  $Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O$  formula. It has intense red color and quite a stable structure. It is considered as an intermediate stage product in the recovery of metallic copper. The different compounds and pure copper metal can be obtained by using Chevrel's salt. This salt can also be precipitated from the pure or impure leach solutions containing copper. It has an interesting crystal structure. The crystal structure of Chevrel's salt is firstly published by

Nyberg and Kierkegaard in 1965 [10].  $Cu(I)-S(IV)$ ,  $Cu(II)-S(IV)$  complexes are important in aqueous systems [5,10].  $Cu(I)$  and  $Cu(II)$  cations in Chevrel's salt indicate different bonding characteristics. According to Kierkegaard and Nyberg [10], the crystal structure of Chevrel's salt, can be described in terms of coordination polyhedra:  $SO_3$  trigonal pyramids,  $Cu^I O_3 S$  tetrahedra and  $Cu^{II} O_4 (H_2O)_2$  octahedra. The structure consist of  $SO_3$  trigonal pyramids,  $Cu^I O_3 S$  tetrahedra and  $Cu^{II} O_4 (H_2O)_2$  octahedra linked together with a three dimensional network. When Chevrel's salt is analyzed, its total copper amount is approximately 49.3%. Scanning Electron Micrograph (SEM) photograph of Chevrel's salt was obtained [6]. It is given in Fig. 1.

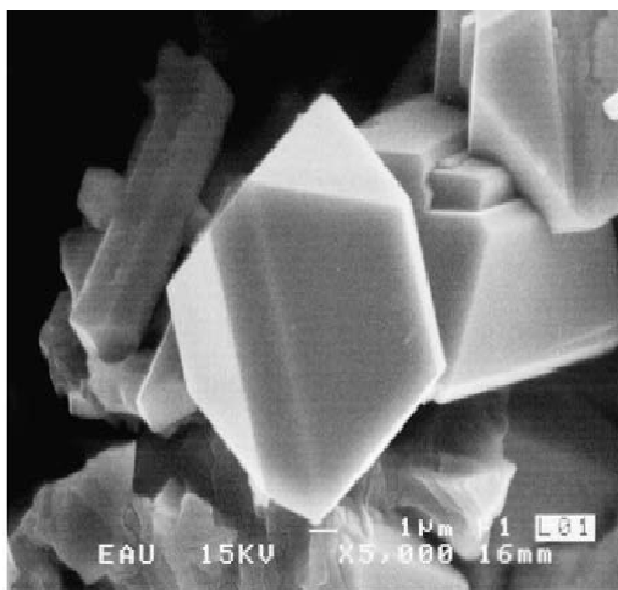


Fig. 1 Scanning electron micrographs (SEM) of precipitates obtained from leach solutions at  $60^\circ C$  [6]

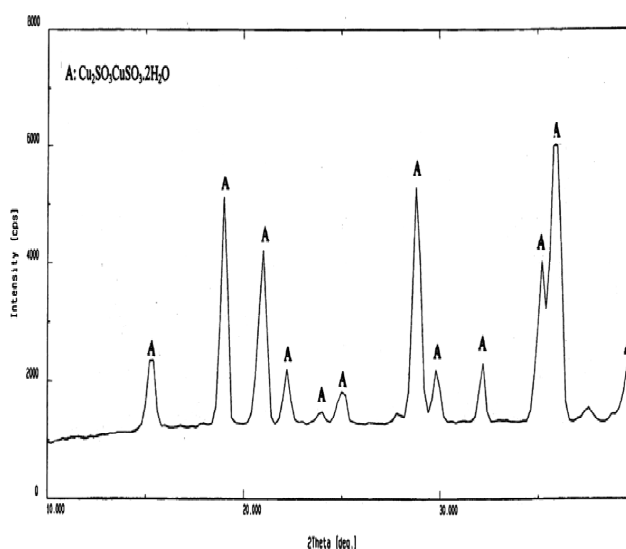


Fig. 2 X-Ray Diffractogram (XRD) of Chevrel's salt obtained by [8]

Chevreur's salt precipitation is related to pH and temperature. Besides, SO<sub>2</sub> gaseous is a versatile reagent capable of precipitating copper sulphite, Using SO<sub>2</sub> a selective precipitation can be made by appropriate adjustments of pH and temperature. Chevreur's salt does not form in acidic solutions if those solutions contains considerable amount of sulfurous acid. It is necessary to maintain pH range between 2–4.5, because, solubility of Chevreur's salt increases as pH values decrease. Also, the region which Chevreur's salt is stable can be seen from the potential-pH diagram [4]. X-Ray Diffractogram (XRD) of Chevreur's salt obtained by [8] is given Fig. 2.

The works done on the precipitation of Chevreur's salt and optimum results obtained on Chevreur's salt recovery are given in Table I.

TABLE I  
THE OPTIMUM CONDITIONS OBTAINED ON CHEVREUR'S SALT PRECIPITATION  
IN RECENT YEARS

Parameters	[6]	[1]	[7]	[8]	[9]
pH	4	3	3	3	4
T(°C)	60	62	60	62	60
The stirring speed (rpm)	600	600	500	600	700
Reagents	NH <sub>3</sub> and SO <sub>2</sub>	SO <sub>2</sub>	Na <sub>2</sub> SO <sub>3</sub>	NH <sub>3</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>3</sub>
Type of initial solution	Leach Solution with H <sub>2</sub> SO <sub>4</sub>	Leach Solution with NH <sub>3</sub> <sup>+</sup> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	Synth. Aq. CuSO <sub>4</sub> Sol.	Synth. Aq. CuSO <sub>4</sub> Sol.	Synth. Aq. CuSO <sub>4</sub> Sol.
The reaction time (min.)	7	12	20	25	15
Precipitated Cu (%)	99.88	99.92	99.41	99.95	98.4

As it can be seen from the examined papers, the most important parameters for precipitation of Chevreur's salt are the pH and the temperature [6]. They investigated the effect of pH by using solutions pH range of 1.5–5. They took as 60°C for the temperature, 400 rpm for the stirring speed and 10 min. for total reaction time, the first minute of which was for the passing time of SO<sub>2</sub> through the solution. So, the precipitation of Chevreur's salt is strongly dependent the pH value of solution. The highest amounts of Chevreur's salt have been obtained at pH 4 value. As well as the pH, the temperature of the solution is significantly effective. Approximately temperature 60°C is the best value for precipitation of Chevreur salt [1], [6]-[9].

The pH of initial solution is also an important parameter for the precipitation of Chevreur's salt. The initial solution pH has a significant effect on the type of precipitation Chevreur's salt does not occur directly in the pHs above 8.5. The nature of precipitation of Chevreur's salt is strongly influenced by the initial solution pH value [1], [6], [8], [9].

#### A. Effect of Temperature on Chevreur's Salt

Table I shows the effect of reaction temperature on the precipitation process. In Table I, the effect of temperature is examined; it is obvious that temperature is an important parameter. As seen from this table, the precipitates obtained at the range of 60-62°C are Chevreur's salt, because their color

are brick red, which is the specific color of Chevreur's salt. Also, according to Table I, when these precipitates obtained, their total copper amount was found to be almost 49.3%. These values have fitted the theoretical copper amount in Chevreur's salt. Furthermore, according to SEM photograph given in Fig. 1, the crystalline structures of precipitate at the range of 60-62°C confirm both tetrahedral coordination of Cu (I) and octahedral coordination of Cu (II) [1], [6]-[9]. The precipitates obtained at the other temperatures are not accepted as Chevreur's salt as their color and structure differ.

#### B. Effect of pH on Chevreur's Salt

The effect of pH on the precipitation of Chevreur's salt was investigated in the pH range of 3–4 and given in Table I. The nature of precipitation of Chevreur's salt is strongly dependent on the pH value. All of the precipitates obtained at pH 3–4 were Chevreur's salt [1], [6]-[9]. However, as it is seen from Table I, the largest amount of precipitate was obtained at pH 4.

#### C. Effect of Stirring Speed on Chevreur's Salt

The effect of the stirring speed on precipitation was investigated for the range of 500–700 rpm (Table I). The precipitates obtained at all of the stirring speeds were Chevreur's salt, and it was found that the amount of precipitate gradually increased until 600 rpm. As it is seen in Table I the effect of the stirring speed on the precipitation of Chevreur's salt was very little when stirring speeds are higher than 600 rpm Effect of Reaction Time on Chevreur's Salt.

The effect of reaction time was investigated for the range of 7–25 minutes (Table I). The precipitates obtained in 7-25 minutes are Chevreur's salt. The effect of reaction time on the precipitation of Chevreur's salt was very small. If the reaction time in acidic solutions is increased, the mass of Chevreur's salt precipitated decreases due to the medium acidity.

### III. CONCLUSIONS

Chevreur's salt compound has a Cu<sub>2</sub>SO<sub>3</sub>.CuSO<sub>3</sub>.2H<sub>2</sub>O formula.

It has intense red color and quite a stable structure.

It is considered as an intermediate stage product in the recovery of metallic copper.

It is an expensive compound.

Chevreur's salt can also be precipitated from the pure or impure leach solutions containing copper.

The crystal structure of Chevreur's salt, can be described in terms of coordination polyhedra: SO<sub>3</sub> trigonal pyramids, Cu<sup>I</sup>O<sub>3</sub>S tetrahedra and Cu<sup>II</sup>O<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub> octahedra. The structure consist of SO<sub>3</sub> trigonal pyramids, Cu<sup>I</sup>O<sub>3</sub>S tetrahedra and Cu<sup>II</sup>O<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub> octahedra linked together with a three dimensional network.

Chevreur's salt is mixed with valence copper sulphite compound. Copper sulphites play an important role in chemistry. Chevreur's salt, (Cu<sub>2</sub>SO<sub>3</sub>.CuSO<sub>3</sub>.2H<sub>2</sub>O) a mixed valence copper sulphite, is a model compound that characterize the sulphite structure.

Chevreur's salt does not form in acidic solutions if those solutions contains considerable amount of sulfuric acid.

As can be seen from the examined papers, the most important parameters for precipitation of Chevreur's salt are the pH and the temperature.

The initial solution pH is an important parameter for the precipitation of Chevreur's salt. The initial solution pH has a significant effect on the type of precipitation.

Chevreur's salt,  $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$ , being a mixed valence copper sulphite compound has been obtained by using different methods and reagents.

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