Experimental Chevreul's Salt Production Methods on Copper Recovery

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***Abstract*—**Experimental production methods of Chevreul's salt being an intermediate stage product in copper recovery were investigated on this article. Chevreul's salt, $Cu_2SO_3.CuSO_3.2H_2O$, 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, SO_2 gaseous is a versatile reagent for precipitating of copper sulphites, Using of 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 ($Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O$), 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.

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Thermodynamic tendency of Chevreul's salt precipitation is related to pH and temperature. Besides, SO_2 gaseous is a versatile reagent capable of precipitating copper sulphite, Using SO2 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 $CuSO_4$ were important in the efficiency and stoichiometry of the dissolution reaction. Reference [3] synthesized Chevreul's salt from reaction between $CuSO_4$ and $NaHSO_3$ 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 $Cu_2SO_3.MSO_3.2H_2O$ (M= Cu, Fe, Mn or Cd). They reported that these salts were thermally stable up to 200°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 ($Cu_2SO_3.CuSO_3.2H_2O$) by using ammonia and sulphur dioxide. The pH value was 4, the stirring speed was at 600 rpm, the temperature was at 60°C, passing time of SO_2 was at 1 min and reaction time after passing SO_2 was at 6 min. The appropriate conditions of Chevreul's salt were precipitated. Reference [1] leached the oxidized copper ore in NH_3-$(NH_4)_2SO_4$ medium that is under optimum conditions. Then, they precipitated Chevreul's salt by passing 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°C, pH at 3, stirring speed at 600 rpm and reaction time at 12 min. They accepted SO_2 flow rate at 358

L.h^{-1}, concentration of $CuSO_4$ solution at 7.383 gCu. 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 Chevreul'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^{o}C, the stirring speed at 500 rpm and the reaction time at 20 min. Reference [8] produced Chevreul's salt by passing SO_2 from synthetic aqueous $CuSO_4$ solution. They characterized Chevreul'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 Chevreul'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 Chevreul'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 L.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^{o}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 Chevreul's salt by using $(NH_4)_2SO_3$ solutions prepared at various concentrations. Chevreul'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 Chevreul's salt. 2^n factorial experimental design and orthogonal central composite design methods in the precipitation experiments were used. Precipitation of Chevreul'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°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

Chevreul's salt compound has a $Cu_2SO_3.CuSO_3.2H_2O$ 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 Chevreul'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 Chevreul'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 Chevreul's salt indicate different bonding characteristics. According to Kierkegaard and Nyberg [10], the crystal structure of Chevreul's salt, can be described in terms of coordination polyhedra: SO_3 trigonal pyramids, Cu^IO_3S tetrahedra and $Cu^{II}O_4(H_2O)_2$ octahedra. The structure consist of SO_3 trigonal pyramids, Cu^IO_3S tetrahedra and $Cu^{II}O_4(H_2O)_2$ octahedra linked together with a three dimentional network. When Chevreul's salt is analyzed, its total copper amount is approximately 49.3%. Scanning Electron Micrograph (SEM) photograph of Chevreul's salt was obtained [6]. It is given in Fig. 1.

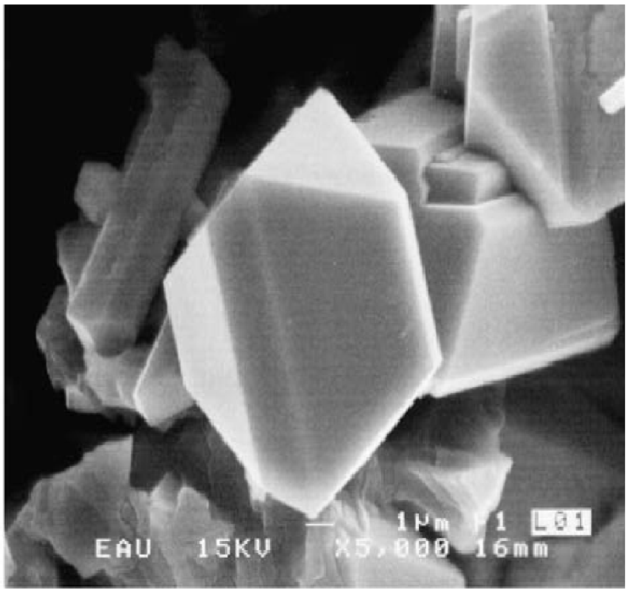

Fig. 1 Scanning electron micrographs (SEM) of precipitates obtained from leach solutions at 60^{o}C [6]

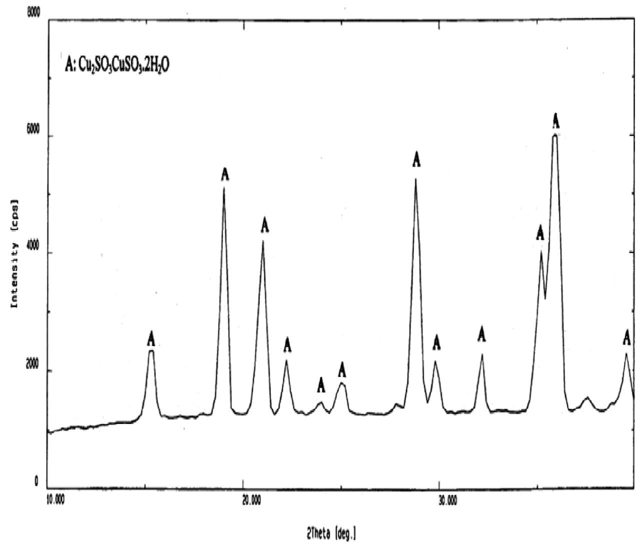

Fig. 2 X-Ray Diffractogram (XRD) of Chevreul's salt obtained by [8]

Chevreul's salt precipitation is related to pH and temperature. Besides, SO_2 gaseous is a versatile reagent capable of precipitating copper sulphite, Using SO2 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]. X-Ray Diffractogram (XRD) of Chevreul's salt obtained by [8] is given Fig. 2.

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

TABLE I
THE OPTIMUM CONDITIONS OBTAINED ON CHEVREUL'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_3 and SO_2	SO_2	Na_2SO_3	NH_3	$(NH_4)_2SO_3$
Type of initial solution	Leach Solution with H_2SO_4	Leach Solution with NH_3+ $(NH_4)_2SO_4$	Synth. Aq. $CuSO_4$ Sol.	Synth. Aq. $CuSO_4$ Sol.	Synth. Aq. $CuSO_4$ 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 Chevreul'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_2 through the solution. So, the precipitation of Chevreul's salt is strongly dependent the pH value of solution. The highest amounts of Chevreul'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 Chevreul salt [1], [6]-[9].

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

A. Effect of Temperature on Chevreul'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 Chevreul's salt, because their color are brick red, which is the specific color of Chevreul'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 Chevreul'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 Chevreul's salt as their color and structure differ.

B. Effect of pH on Chevreul's Salt

The effect of pH on the precipitation of Chevreul's salt was investigated in the pH range of 3–4 and given in Table I. The nature of precipitation of Chevreul's salt is strongly dependent on the pH value. All of the precipitates obtained at pH 3–4 were Chevreul'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 Chevreul'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 Chevreul'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 Chevreul's salt was very little when stirring speeds are higher than 600 rpm Effect of Reaction Time on Chevreul'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 Chevreul's salt. The effect of reaction time on the precipitation of Chevreul's salt was very small. If the reaction time in acidic solutions is increased, the mass of Chevreul's salt precipitated decreases due to the medium acidity.

III. CONCLUSIONS

Chevreul's salt compound has a $Cu_2SO_3.CuSO_3.2H_2O$ 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.

It is an expensive compound.

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

The crystal structure of Chevreul's salt, can be described in terms of coordination polyhedra: SO_3 trigonal pyramids, Cu^IO_3S tetrahedra and $Cu^{II}O_4(H_2O)_2$ octahedra. The structure consist of SO_3 trigonal pyramids, Cu^IO_3S tetrahedra and $Cu^{II}O_4(H_2O)_2$ octahedra linked together with a three dimentional network.

Chevreul's salt is mixed with valence copper sulphite compound. Copper sulphites play an important role in chemistry. Chevreul's salt, ($Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O$) a mixed valence copper sulphite, is a model compound that characterize the sulphite structure.

Chevreul'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 Chevreul's salt are the pH and the temperature.

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

Chevreul's salt, $Cu_2SO_3.CuSO_3.2H_2O$, being a mixed valence copper sulphite compound has been obtained by using different methods and reagents.

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