

The Investigation of Precipitation Conditions of Chevrel's Salt

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Abstract—In this study, the precipitation conditions of Chevrel's salt were evaluated. The structure of Chevrel's salt was examined by considering the previous studies. Thermodynamically, the most important precipitation parameters were pH, temperature, and sulphite-copper(II) ratio. The amount of Chevrel's salt increased with increasing the temperature and sulphite-copper(II) ratio at the certain range, while it increased with decreasing the pH value at the chosen range. The best solution medium for recovery of Chevrel's salt is sulphur dioxide gas-water system. Moreover, the soluble sulphite salts are used as efficient precipitating reagents. Chevrel's salt is generally used to produce the highly pure copper powders from synthetic copper sulphate solutions and impure leach solutions. When the pH of the initial ammoniacal solution is greater than 8.5, ammonia in the medium is not free, and Chevrel's salt from solution does not precipitate. In contrast, copper ammonium sulphide is precipitated. The pH of the initial solution containing ammonia for precipitating of Chevrel's salt must be less than 8.5.

Keywords—Chevrel's salt, copper sulphites, mixed-valence sulphite compounds, precipitating.

I. INTRODUCTION

COPPER is hydrometallurgically produced from the solutions of soluble copper salts [1]. Chemical precipitation depends on hydrolytic action, ionic interaction, or reduction. Recovery of copper sulphites from aqueous solutions containing copper is important in hydrometallurgy [2], [3]. Chevrel's salt is a highly stable mixed-valence sulphites compound [4], [5]. The precipitation of Chevrel's salt is used an intermediate product in hydrometallurgy [6]-[8]. Its precipitation from the aqueous solutions has gained in importance in recent years. Both its precipitating and its dissolution are valuable in the production stage of pure copper metal.

In the last decade, studies on precipitating of this kind of copper compounds have been intensified. Chevrel's salt has been precipitated by using various methods and reagents [2], [3]. Additionally, various solvent reagents have been used for obtaining pure copper metal.

Conklin and Hoffmann investigated the link structure of Chevrel's salt. Besides, they examined the metal ion-sulphur(IV) link structure, thermodynamics of the metal ion species such as Chevrel's salt, and kinetics of iron(III)-

sulphur(IV) complexes. Their measurements indicated that sulphite binds the metal through oxygen [6]. Da Silva et al. [9] synthesized the salt compounds such as $\text{Cu}_2\text{SO}_3 \cdot \text{MSO}_3 \cdot 2\text{H}_2\text{O}$ ($\text{M}=\text{Cu, Fe, Mn or Cd}$). They determined the precipitation, the bond structure, and thermal decomposition of double sulphites in form of Chevrel's salt. These salts have been precipitated from the aqueous solutions by using sulphur dioxide gas. Experiments were performed in the aqueous solutions containing M(II) ions at room temperature. The solutions used in experiments were saturated with sulphur dioxide gas. Thermal behaviour of Chevrel's salt as other sulphites was determined by thermogravimetry analysis and differential scanning calorimetric methods. They proved that all of these salts are stable up to 200 °C. Additionally, they had isostructure with Cu(II) replaced by M(II) (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. [10] obtained the pure copper powders by using oxidized copper ore. The oxidised copper ore was brought from Erzurum-Narman region. The copper content of the ore was 4.48%. They precipitated the Chevrel's salt ($\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$) from leach solutions. They passed the sulphur dioxide gas from the leach solutions with the ammonia. The best precipitation conditions of Chevrel'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 after passing SO_2 : 6 minutes. Then, they dissolved the Chevrel's salt in acetonitril/water system, and obtained 99.78% pure copper powder. de Andrade et al. [7] have precipitated the compounds as $\text{Cu}_2\text{SO}_3 \cdot \text{MSO}_3 \cdot 2\text{H}_2\text{O}$. These compounds were double sulphites in $\text{Cu}_2\text{SO}_3 \cdot \text{MSO}_3 \cdot 2\text{H}_2\text{O}$ ($\text{M}=\text{Cu, Fe, Mn or Cd}$) type. They found that the isomorphous Cu(II) in Chevrel's salt could be replaced by a divalent metal ion. The properties of these isomorphous series were strongly dependent M(II) cation in the compound. They offered that mixed valence compounds being these structure can be used as a model under atmospheric medium. They showed that the structures in Chevrel's salt type can be a very good intermediate. They found that these compounds (mixed valence systems) can be evaluated as catalysts of S(IV) autoxidation in the conversion of SO_2 in the atmosphere. Because the chemical properties of these substances are very convenient in pure metal production. Innoue et al. [11] synthesized the Chevrel's salt using CuSO_4 and NaHSO_3 solutions. They characterized by means of X-rays photoelectron spectroscopy (XPS), magnetic susceptibility, Electron paramagnetic resonance (EPR), and electronic spectroscopy methods. Parker and Muir obtained the Chevrel's salt from impure leach solutions. They identified the appropriate precipitation conditions of Chevrel's salt.

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They roasted the copper concentrates and leached with water to produce copper(II) sulfate solutions. They precipitated the Chevreul's salt from aqueous Na_2SO_3 and $(\text{NH}_4)_2\text{SO}_3$. They dissolved the salt in acetonitrile-water system, and obtained 75 g of pure particulate copper per unit liter of solutions [12]. Çalban et al. [13] precipitated Chevreul's salt from the impure dilute leach solutions obtaining oxidized copper ores. They developed a statistical model on test results. They found the optimum conditions. They determined the precipitation conditions of Chevreul's salt as the pH 3, the temperature 62 °C, the stirring speed 600 rpm, the reaction time 12 minutes, the SO_2 flow rate 358 $\text{L}\cdot\text{h}^{-1}$, and the concentration of CuSO_4 solution 7.383 $\text{gCu}\cdot\text{L}^{-1}$. Yeşilyurt and Çalban [14] recovered Chevreul's salt by means of a mixture of synthetic CuSO_4 and Na_2SO_3 reagent solutions. They determined the optimum copper(II) sulfate solutions with sulfurous acid salts like precipitation conditions as temperature 60 °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. [15] investigated the character of preoxidised copper surfaces and powder copper oxides exposed to SO_2 vapour under an oxygen deprived humid atmosphere. The structure of these copper oxides investigated by X-ray diffraction (XRD) and Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX). They found that Chevreul's salt was a stable product under hypoxic conditions and exhibited an orthorhombic symmetry at room temperature. Fischmann and Dixon [16] observed the unexpected formation of Chevreul's salt as a result of the recovery of aqueous copper(II) onto a chalcopyrite concentrate. They showed that recovery of aqueous copper(II) onto a chalcopyrite concentrate can occur quickly at 60 °C temperature and at the presence of S(IV), in this instance, sulphite. Amazingly, rather than partial conversion of chalcopyrite to a copper sulphite such as chalcocite or covellite, copper was precipitated in the form of Chevreul's salt. Çalban et al. [17] found the optimum precipitation conditions of Chevreul's salt by means of $(\text{NH}_4)_2\text{SO}_3$ reagent from synthetic aqueous CuSO_4 solutions. They found the optimum precipitation conditions as the ammonium sulphite solution concentration 0.4 M, the temperature 60 °C, the stirring speed 700 rpm, the reaction time 15 min., the initial solution concentration 0.25 M, and the reaction pH 4. They found the yield of reaction as 98.40% under these optimum conditions. Çalban et al. [18] examined the dissolution kinetics of Chevreul's salt. They used the hydrochloric acid solution as reagent. They found that the dissolution of Chevreul's salt was controlled by diffusion through the ash or product layer. Çalban et al. [19] obtained Chevreul's salt from synthetic CuSO_4 solutions. They found the optimum precipitation conditions as the initial solution concentration 1.14 M, the SO_2 feeding rate 329.35 $\text{L}\cdot\text{h}^{-1}$, the reaction time 25 min., the initial solution pH 8.5, the temperature 62 °C, the stirring speed 600 rpm, and the reaction pH 3. They found the yield of reaction as 99.95% under these optimum conditions. Çalban et al. [20] did a study on experimental Chevreul's Salt production methods. They gathered the experimental production methods of Chevreul's salt in one article. Guan et

al [21] synthesized Chevreul's salt mesocrystalline microspheres by a facile method. They proposed a Chevreul's salt formation mechanism. They explained that acetic acid played a key role to prepare the Chevreul's salt mesocrystalline microspheres. They found that the mesocrystalline microspheres were composed of sub-microparticles in an oriented fashion, and also, under UV light irradiation, the $\text{Cu}_2\text{SO}_3\cdot\text{CuSO}_3\cdot 2\text{H}_2\text{O}$ mesocrystalline spheres would catalyze the decomposition of the organic dyes in solution. They proved that the big diameters of the microspheres prevented from deactivation of the catalyst via further aggregation and made its post treatment easy.

Apart from the above-mentioned papers, many articles regarding the precipitation of Chevreul's salt have been published recently [22]-[29].

II. PRECIPITATION METHODS OF CHEVREUL'S SALT

Chevreul's salt is precipitated by using sulphite solutions from synthetic CuSO_4 solutions and impure leach solutions with copper. Chevreul's salt has been precipitated from many solutions containing copper(II) ions until now. Many reagents and the aqueous medium to obtain Chevreul's salt have been used. Using of sulfurous acid solutions at certain pH range is the most convenient medium in Chevreul's salt production. Moreover, sulphur dioxide gas-aqueous systems help for the selective precipitation of Chevreul's salt from copper solutions. Soluble sulphite salts in water are used as important precipitating reagents. Na_2SO_3 and $(\text{NH}_4)_2\text{SO}_3$ compounds are the most commonly used salt reagents. Furthermore, Chevreul's salt was obtained from aqueous copper(II) ions on chalcopyrite concentrates in the presence of S(IV) [16]. Chevreul's salt was precipitated in the aqueous copper acetate/ Na_2SO_3 medium at ambient temperature [21].

III. THERMODYNAMIC PROPERTIES OF CHEVREUL'S SALT

Chevreul's salt is a mixed valence copper salt. It is a sulphite compound. This compound contains both copper(I) and copper(II). Copper(I) and copper(II) in the same compound show different crystal structures. These species in Chevreul's salt have different bonding structures. According to Kierkegaard and Nyberg [5], its crystal structure shows a polyhedra coordination structure: $\text{Cu}^{\text{I}}\text{O}_3\text{S}$ tetrahedra, $\text{Cu}^{\text{II}}\text{O}_4(\text{H}_2\text{O})_2$ octahedra, SO_3 trigonal pyramids. These structures linked together with a three dimensional network [5], [7]. The pH of copper solutions containing ammonia is high. Depending on the amount of ammonia in the solution, it consists of copper tetramine complexes. When pH is greater than 8.5, copper binds strongly the ammonia. In this case, because there was no free ammonia in the medium, Chevreul's salt does not occur. Copper ammonium sulphides precipitate instead of Chevreul's salt [10], [19].

The precipitation of Chevreul's salt depends firmly on the temperature of solution. The appropriate temperature range in the sulphurous acid or sulphur dioxide/water medium is 50-70 °C. The precipitation of the Chevreul's salt in this temperature range corresponds to the most sensitive point [10]. The

temperature range for precipitation of Chevreul's salt in the solution containing sulfide salts is larger. Chevreul's salt in soluble sulphite salt solutions precipitates in 50-80 °C temperature range. This case shows that the copper ions in the solution bind more easily the sulphide ions under the influence of the temperature [14]. In the range of these temperatures, the amount of Chevreul's salt formed increases. The temperature on 80 °C has not been tested until now.

The effect of feeding rate of SO₂ gas into leach solution or synthetic CuSO₄ solution in the precipitation process of Chevreul's salt is important. Because SO₂ gas in the aqueous solutions decreases the pH of the solution. The amount of sulphite in the solution leads to an increase. Moreover, the use of soluble salts containing sulphite increases the direct sulphite concentration. Excess of the sulfite ions in the medium leads to easy precipitation of Chevreul's salt. If the number of sulphite ions in solution increases, solution will be much more acidic. Overly acidic environment will begin to dissolve the Chevreul's salt. After a certain amount of sulphite ions, different salts will precipitate.

The effect of initial solution concentration for dilute and concentrated copper solutions is very important. As a result of both dilute and concentrated copper solutions, very pure Chevreul's salt is precipitated by adding SO₂ gas to the aqueous copper solutions. Precipitated amounts of Chevreul's salt depend on the copper content of the solution. Impurities in the form of M(II) in the impure copper solutions precipitate structures similar to the Chevreul's salt. Then, the purity of Chevreul's salt deteriorates. If the amount of sulphite in the solution is adequate, all copper in the solution will precipitate. The concentration of copper has very little effect on the amount of Chevreul's salt precipitated. When the number of the other metal ions is different, the percentages of copper precipitated as Chevreul's salt vary depending on the initial solution concentration.

IV. CONCLUSIONS

- Chevreul's salt is a mixed valence sulphite compound. It contains 49.3% copper by mass.
- Chevreul's salt has a stable structure. It is not decomposed up to 200 °C.
- The best medium for precipitation of Chevreul's salt is SO₂ gas/water. Furthermore, the soluble salts containing sulphite are used as very good precipitating reagents.
- The Chevreul's salt is completely dissolved very fast. As a result of this, copper(II) tetramine complex in the solution forms [30].
- Chevreul's salt cannot be dissolved in the sulphuric acid solutions.
- Chevreul's salt slightly soluble in the solutions containing nitric acid.
- Chevreul's salt reacts with dilute hydrochloric acid. It converts to copper(I) chloride [18], [30].
- Chevreul's salt is used to produce the pure copper powder from synthetic copper sulphate solution and impure leach solutions. Because it is a stable intermediate.
- Chevreul's salt is a model compound for metals in the

form M(II). Particularly, compounds in the form of Cu₂SO₃.MSO₃.2H₂O (M=Cu, Fe, Mn or Cd) have been synthesized [9].

- When pH of the initial solution is greater than 8.5, the copper with ammonia makes a strong binding. In this case, ammonia in the medium is not free, and Chevreul's salt does not precipitate. Copper ammonium sulphide in the solution is recovered [10], [19]. It is a dense white and stable compound. pH of the initial solution for the precipitation of Chevreul's salt must be below 8.5.
- Both copper(I) and copper(II) in Chevreul's salt compound show different crystal structures. Chevreul's salt has a three-dimensional ligament structure [5], [7].
- The precipitation of the Chevreul's salt corresponds to a certain temperature range. Chevreul's salt precipitation temperature range vary depending on the precipitating reagent used. The temperature range in the solutions containing soluble sulphite salts is larger. This case shows that the sulphite ions with the copper ions react more easily [14].
- The precipitation yield increases with increasing the SO₂ or sulphite concentration.
- The most commonly used salt reagents containing sulphite are Na₂SO₃ and (NH₄)₂SO₃.
- When Chevreul's salt precipitated from the copper solutions containing ammonia, ammonium sulfate in the filtered solution occurs. After the ammonium sulfate precipitated from the filtered solution, it can be used as fertilizer. Also, ammonium sulfite forming at the end of the reaction can be used as an important leach reagent in the precipitation of sulfite compounds.
- The important parameters affecting the precipitation of Chevreul's salt have been determined as the temperature, the initial copper concentration, the SO₂ feeding rate, and the initial solution pH, the reaction pH, the reaction time, the used reagent concentration, the stirring speed in the present study.
- The recovery of Chevreul's salt has increased with increasing the initial solution concentration, the SO₂ feeding rate, and the initial solution pH in the studied range.
- Increase of reaction time or the stirring speed did not show an important increase in the yield.

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