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Review

Leaching kinetics of Chevreul's salt in hydrochloric acid solutions

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ABSTRACT

The aim of this study was to investigate the dissolution kinetics of Chevreul's salt in hydrochloric acid [HCl] solutions in a mechanical agitation system and to precipitate Chevreul's salt [$Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O$] using ammonium sulfide [$(NH_4)_2SO_3$] solutions at various concentrations from synthetic aqueous copper(II) sulfate [$CuSO_4$] solutions. Reaction temperature, concentration of HCl, stirring speed and solid/liquid ratio were selected as parameters. The experimental results were successfully correlated by linear regression using Statistica Package Program. Dissolution curves were evaluated in order to test shrinking core models for solid–fluid systems. It was observed that increase in the reaction temperature and decrease in the solid/liquid ratio causes an increase the dissolution rate of Chevreul's salt. The dissolution extent is highly increased with increase the concentration of HCl solutions in the experimental conditions. The activation energy was found to be as 57 kJ/mol. The leaching of Chevreul's salt was controlled by diffusion through the ash or product layer.

Contents

1. Introduction

Generally, precipitation of metals from aqueous solutions is by chemical methods. Chemical precipitation processes can be various due to hydrolytic action, ionic interaction and reduction. In recent years, precipitation methods have been developed. Besides, the variety of compounds of precipitated metal has varied. These type metal compounds have now been produced from aqueous solutions by being used various technologies [1,2]. Precipitation of mixed valence metal sulfites such as Chevreul's salt is very important in the hydrometallurgy of metals. Copper sulfites are of considerable interest in chemistry. The mixed valence copper sulfite, $Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O$, Chevreul's salt is a model compound characterizing the sülfite structure [3]. Precipitation of Chevreul's salt by using synthetic or leach solutions containing copper has interested because of both highly stable structure and the intense red colour. At the same time, the precipitation of this complex compound has formed a key stage in hydrometallurgical processes [4].

Copper is usually produced by cementation or electro-winning methods from solutions of soluble copper salts [5]. Precipitation of

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Nomenclature

b	stoichiometric coefficient
C	concentration of borax decahydrate solution ($mol\ m^{-3}$)
CA_g	concentration of A in the bulk solution ($mol\ m^{-3}$)
D	mean particle size (m)
D_e	diffusion coefficient ($m^2\ min^{-1}$)
E_A	activation energy ($kJ\ mol^{-1}$)
k_d	mass transfer coefficient ($m\ min^{-1}$)
k_s	reaction rate constant for surface reaction ($mol\ min^{-1}$)
k_o	frequency or pre-exponential factor (min^{-1})
L	amount of liquid (mL)
n	mol number (mol)
r	correlation coefficient (–)
R	universal gas constant ($J\ mol^{-1}\ K^{-1}$)
R	initial radius of a solid particle (m)
S	amount of solid (g)
T	reaction temperature (K)
t	reaction time (min)
t^*	reaction time for complete conversion (min)
X	fractional conversion of B_2O_3
W	stirring speed (rpm)
ρ_B	molar density of solid reactant ($mol\ cm^{-3}$)

inorganic compounds from aqueous solutions generally is physical or chemical processes. Chemical processes can be various, like owing to hydrolytic action, ionic interaction or reduction. Precipitation of copper sulphites from aqueous solutions including copper is one of special importance in hydrometallurgical processes [2,3]. 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 [4,5]. The precipitation of Chevreul's salt is a key stage in hydrometallurgical processes and very important in aqueous systems [6–8].

There are many studies in the literature connected with the Chevreul's salt in various solutions. In recent years, studies of compounds of this type have been intensified. Chevreul's salt has been obtained using various methods and reagents [2,3]. Conklin and Hoffmann have researched the metal ion–sulphur(IV) chemistry, thermodynamics and kinetics of transient iron(III)–sulphur(IV) complexes. Their measurements indicated that sulphite binds the metal through oxygen [9]. Silva et al. [10] have examined synthesis, identification and thermal decomposition of double sulphites like $Cu_2SO_3{\cdot}MSO_3{\cdot}2H_2O$ (M = Cu, Fe, Mn or Cd). These salts have been obtained by saturation with sulphur dioxide gas from aqueous solutions of M(II) sulphates at room temperature. The thermal behaviour of double sulphites were estimated by thermogravimetry analysis and differential scanning calorimetric methods. They reported that these salts are thermally stable up to 200 °C, and isostructural with Cu(II) replaced by Mn(II), Fe(II) and Cd(II) ions in $Cu_2SO_3{\cdot}MSO_3{\cdot}2H_2O$. Çolak et al. [11] obtained 99.78% pure copper powder from Erzurum–Narman region oxidized copper containing 4.48% Cu. They precipitated Chevreul's salt ($Cu_2SO_3{\cdot}CuSO_3{\cdot}2H_2O$) 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: 60 °C, passing time SO_2: reaction time of 1 min after passing SO_2: 6 min. de Andrade et al. [12] have researched isomorphic series of double sulphites such as the $Cu_2SO_3{\cdot}MSO_3{\cdot}2H_2O$ (M = Cu, Fe, Mn or Cd) type. They found that the isomorphic Cu(II) in Chevreul's salt could be replaced by a divalent metal ion, forming an isomorphic series which 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] Chevreul's salt synthesized by a reaction between $CuSO_4$ and $NaHSO_3$ and characterized by X-rays photoelectron spectroscopy, magnetic susceptibility, EPR and electronic spectroscopy. Parker and Muir determined some conditions for precipitation of Chevreul's salt from impure leach solutions. They obtained 75 g of pure particulate copper per unit litre of solutions [14]. Çalban et al. [15] researched statistical modelling of Chevreul's salt recovery from leach solutions contained copper. They determined the optimum precipitation conditions of Chevreul's salt using leach solutions. They found as pH 3, temperature 62 °C, stirring speed 600 rpm, reaction time 12 min, SO_2 flow rate 358 $L\ h^{-1}$ and concentration of $CuSO_4$ solution 7.383 $gCu\ L^{-1}$. 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 60 °C, $[SO_3^{-2}]/[Cu^{+2}]$ ratio 1.6, pH 3, stirring speed 500 rpm, and reaction time 20 min. Giovannelli et al. [17] researched an investigation into the surface layers formed on oxidized 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. [18] have investigated upgrading of a chalcopyrite concentrate by copper(II) reaction and unexpected formation of Chevreul's salt. Recovery of aqueous copper(II) onto a chalcopyrite concentrate was shown to be rapid at 60 °C 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. This process has an application as a way to increase the copper grade of chalcopyrite concentrates using the leachate from a Galvanox™ leach of flotation tailings.

The aim of this study was to precipitate Chevreul's salt using $(NH_4)_2SO_3$ solutions at various concentrations from synthetic aqueous $CuSO_4$ solutions and to investigate the dissolution kinetics of Chevreul's salt in hydrochloric acid solutions in a mechanical agitation system. Reaction temperature, concentration of HCl solutions, stirring speed and solid/liquid ratio were selected as parameters on the dissolution rate of Chevreul's salt. There is no study reported in the literature about such a procedure. So that, the kinetic data for the reaction of Chevreul's salt with HCl are very important for industrial application. The dissolution kinetics of Chevreul's salt in ammonium hydrogen sulphate were examined according to the heterogeneous reaction models.

2. Methods and materials

Leaching experiments were conducted under atmospheric pressure conditions. All reagents used in the experiments were prepared from analytical grade chemicals (Merck) and distilled water. A constant temperature water circulator was used in combination with the reactor to maintain the mixture in the reactor at a constant temperature. The experiments were carried out in a 500 mL spherical glass reactor. The reactor was equipped with a reflux condenser to prevent evaporation during heating and a mechanical stirrer to obtain a homogeneous suspension in the reactor. The mechanical agitation experimental system is fairly common, so no illustration of it appears in this paper.