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Technical note

Removal of chloride from simulated zinc sulfate electrolyte by ozone oxidation

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The removal of chloride from simulated zinc sulfate electrolyte by ozone oxidation was investigated. The effects of various process factors including the O_2 flow, bubbling time, reaction temperature, H_2SO_4 and $ZnSO_4$ concentration, and existence of Mn^{2+} were systematically studied. The results showed that with increasing O_2 flow, the chloride removal increased first and then decreased. Increasing both the bubbling time and reaction temperature was beneficial to dechlorination while an increase in the $ZnSO_4$ concentration had an adverse effect. With increasing sulfuric acid concentration, the dechlorination rapidly rose due to the increasing hydrogen ion concentration in electrolyte. Optimum dechlorination process conditions in the absence of Mn^{2+} were obtained as follows: O_2 flow 0.4 $L \cdot min^{-1}$, H_2SO_4 concentration 160 $g \cdot L^{-1}$, Zn^{2+} concentration 40 $g \cdot L^{-1}$, reaction temperature 70 °C, and reaction time 120 min. Under these conditions, the concentration of Cl^- was reduced from 300 to 5 $mg \cdot L^{-1}$. The existence of Mn^{2+} can further accelerate the reaction of ozone with chloride, which was probably through charge-transfer and coordination catalysis mechanism.

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1. Introduction

The roast–leach–purification–electrowin process accounts for almost 80%–85% of primary zinc production in the world (Raghavan et al., 1999). High purity of electrolyte in this process guarantees obtaining high-grade cathode zinc product with low energy consumption while the presence of impurities in electrolyte has a series of negative effects on zinc electrowinning (Boyanov et al., 2004). Chloride ions, one of the major impurities in hydrometallurgical zinc production, can accumulate rapidly and sometimes even reach as high as several thousand milligrams per liter due to recycling of waste electrolyte and usage of high-chlorine content ZnO as a raw material. High concentration chloride ion in acidic environment corrodes not only the equipment and pipeline but also the electrode in the whole electrowinning system. The corrosion to Ag–Pb anode leads to an increase in lead content in the electrolyte, thus reducing the grade of cathode zinc (Liu et al., 2011). At the same time, the anode will become uneven due to the corrosion, which results in increasing electric power consumption. The corrosion to the cathode will accelerate dissolution of the deposited zinc, which reduces current efficiency (Mackinnon et al., 1980). Generally, it's well established that when the concentration of chloride ions in the electrolyte is less than 100 $mg \cdot L^{-1}$, the above adverse effects can be significantly reduced.

Up to now, various dechlorination methods have been adopted, such as silver salt precipitation, Bi_2O_3 method, cuprous chloride precipitation and ion exchange. Both the silver salt precipitation (Wang et al. 2013) and Bi_2O_3 method (Wen 2008; Wu et al., 2014) have a high dechlorination efficiency, but with a poor economy due to the difficulty in recycling of the expensive precipitates AgCl and BiOCl. The cuprous chloride precipitation (Bodson, 1975; Cao et al., 2009; Li et al., 2002) is widely used in industrial production for its high efficiency and relatively low cost due to the availableness of the copper slag discharged from the zinc electrolyte purification section. However, there are still lots of zinc powder and $CuSO_4$ to be added, and the acidity and reaction temperature must be strictly controlled in this process. The ion exchange (Kameda et al., 2003; Liang et al., 2008; Lv et al., 2006) possesses low efficiency and high zinc loss as well as emission of large quantity of chlorine-containing acidic wastewater, which is difficult to dispose of. Recently, Wu et al (2013) studied removal of chloride ions from a simulated zinc electrolyte with electrochemical method, which is based on formation of acid-insoluble precipitate CuCl in a cell. However, the chloride ions can only be reduced from 300 $mg \cdot L^{-1}$ to 136 $mg \cdot L^{-1}$ under optimized process conditions. In our previous study (Zhang et al., 2015), removal of chloride ion from a concentrated phosphoric acid solution by ozone oxidation was studied, and the Cl^- concentration can be effectively reduced from 1000 to 5 $mg \cdot L^{1}$. Therefore, in the present study, the method is adopted to remove chloride ions from zinc sulfate electrolyte.

The reaction between chloride ions and ozone in aqueous solutions has been widely investigated (Haag and Hoigné, 1983; Hoigné et al., 1985; Yeatts and Taube, 1949; Levanov et al., 2003, 2005, 2006, 2008, 2012a,b,c; Razumovskii et al., 2010a,b). Levanov et al. (2003, 2005, 2006, 2008, 2012a,b,c) studied kinetics of the reaction between O_3 and

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Cl^- in acidic solutions systematically. They found that both hydrogen ions and some transitional metal ions can accelerate the reaction remarkably. The mechanism of hydrogen ion enhancement can be expressed as follows (Levanov et al., 2003, 2012b):

$$Cl^- + O_3 \leftrightarrow Cl^- \cdots O_3 \tag{1}$$

$$Cl^- \cdots O_3 + H^+ \leftrightarrow HO_3Cl \tag{2}$$

$$HO_3Cl \rightarrow O_2 + HOCl \tag{3}$$

$$HOCl + Cl^- + H^+ \leftrightarrow Cl_2 + H_2O. \tag{4}$$

From these reactions, a total reaction is formulated as:

$$2Cl^- + O_3 + 2H^+ \rightarrow O_2 + Cl_2 + H_2O. \tag{5}$$

The catalysis of transitional metal ions on the reaction of ozone with chloride ions in acidic solutions includes coordination and charge-transfer catalysis. For the coordination catalysis, its mechanism can be represented as follows (Levanov et al., 2005):

$$M^{m+} + x\,Cl^- + O_3 + n\,H^+ \leftrightarrow H_nMO_3Cl_x \tag{6}$$

$$H_nMO_3Cl_x \rightarrow M^{m+} + O_2 + Cl_2 + H_2O + (x-2)Cl^- + (n-2)H^+. \tag{7}$$

Where, M^{m+} is a transitional metal ion; $H_nMO_3Cl_x$ is an intermediate complex containing the metal ion, hydrogen ion, ozone and chlorine ion, which can decompose and liberate Cl_2 and at the same time regenerate the metal ion.

For the charge-transfer catalysis, a metal ion with dual or multi valence is first oxidized by ozone to its oxidation state. If the redox potential of the metal ion pair is higher than Cl_2/Cl^-, the reaction of metal ion with chloride ions would be possible and usually faster than that of ozone with chloride ions. This is because the former is a homogeneous reaction while the latter is a heterogeneous one. Take Co^{2+} as an example (Levanov et al., 2005), two successive reactions can be written as follows:

$$O_3 + 2Co^{2+} + 2H^+ \rightarrow O_2 + 2Co^{3+} + H_2O \tag{8}$$

$$2Co^{3+} + 2Cl^- \rightarrow 2Co^{2+} + Cl_2. \tag{9}$$

It was noticed that all the studies concerning the reaction between chloride ions and ozone focused mainly on the kinetics and mechanism, and the chloride ion concentration employed was quite high ($\geq 1\ mol \cdot L^{-1}$). Whether the reaction is feasible when applied to remove chloride ion of as low as several hundred milligram per liter from zinc sulfate electrolyte is unknown. Therefore, in this study the effects of various process factors including the O_2 gas flow, reaction temperature and duration, H_2SO_4 and $ZnSO_4$ concentration, and the existence of Mn^{2+} on dechlorination from a simulated zinc sulfate electrolyte were systematically studied at initial chloride concentration of 300 $mg \cdot L^{-1}$ and the mechanism was discussed.

2. Experimental

2.1. Experimental materials and procedure

In hydrometallurgical zinc production, the zinc sulfate electrolyte generally contains Zn^{2+} 40–80 $g \cdot L^{-1}$, H_2SO_4 120–200 $g \cdot L^{-1}$, Cl^- 30–1000 $mg \cdot L^{-1}$ and Mn^{2+} 2–5 $g \cdot L^{-1}$ (Peng et al., 2003). In order to study influence of each of these components except chlorine ion on the dechlorination, a simulated zinc sulfate electrolyte was prepared. The compositions of simulated zinc electrolyte, unless otherwise noted, were H_2SO_4 160 $g \cdot L^{-1}$, Zn^{2+} 40 $g \cdot L^{-1}$, Cl^- 300 $mg \cdot L^{-1}$. During the preparation, all chemical reagents used, including sodium chloride (NaCl), zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$), manganese sulfate ($MnSO_4 \cdot H_2O$) and sulfuric acid (H_2SO_4), were of analytical grade (AR) and all solutions were prepared with distilled water.

A schematic of the experimental apparatus is presented in Fig. 1. Compressed oxygen gas with O_2 purity >99.2% was depressurized, metered and fed to a ozone generator (HY-005, Yifenghong Environmental Protection Technology CO. LTD, ChengDu) with a nominal O_3 output of 5 $g \cdot h^{-1}$. Inside the ozone generator, a discharge tube can ionize the oxygen and produce ozone under an electric field with high voltage and frequency. In this way, a mixed gas containing ozone and oxygen (abbreviated as ozone gas hereafter) can be produced, in which the ozone concentration varied with O_2 flow. The ozone gas was introduced to a 350 ml self-made bubble reactor (height 350 mm, diameter 50 mm) from its bottom through a sand core gas distributor with average hole sizes of 3–4 μm and reacted with the chloride in solution. In each test, 100 mL simulated zinc electrolyte was added to the reactor and preheated in a water bath with temperature fluctuation of ± 1 °C. After preset reaction temperature was reached, the ozone gas was introduced and the reaction was timed. The solution samples were withdrawn periodically to detect the residual chloride concentration. The exhaust leaving the reactor was discharged and absorbed by a KI solution.

2.2. Analysis and characterization

Trace chloride concentration in the simulated zinc electrolyte was determined by visible turbidimetric method (GB/T23945-2009, 2009), in which a series of standard solutions with chloride concentration from 5 to 100 $mg \cdot L^{-1}$ were prepared and compared with the solution samples after addition of an acidic $AgNO_3$ solution. The Cl^- concentration in the samples can be determined between two neighboring chloride standard solutions. Certain amount of oxalic acid was added to eliminate possible color interference of MnO_4^-. When the Cl^- concentration in the samples was over 100 $mg \cdot L^{-1}$, the samples were first diluted to reduce the concentration below 100 $mg \cdot L^{-1}$ and then measured according to the procedure above.

An iodometric method (CJ/T322-2010, 2010) was used to measure the ozone concentrations of the oxygen stream. The ozone in the O_2 stream was sufficiently absorbed with two-stage 2 wt.% KI solutions in series to form I_2. The I_2 concentration was then titrated with 0.3 M

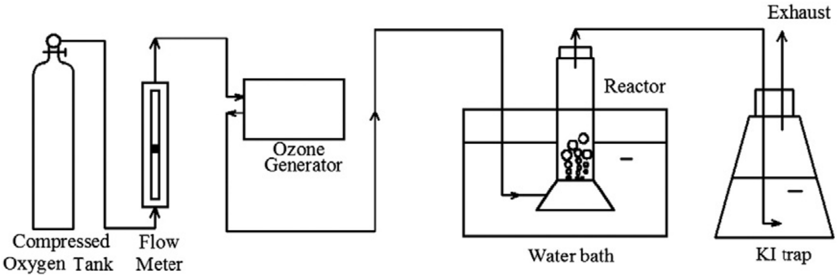

Fig. 1. Schematic of the experimental apparatus.

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