

The characteristics of Zn in highly alkaline wastewater by CO₂ aerated

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Abstract. In the process of CO₂ aerated, the variation of pH value, the characteristics of Carbonate precipitation and hydroxide precipitate by Zn, the adsorption and co-precipitation characteristics with the hydrated oxides of iron and aluminum and calcite have been researched. After CO₂ was aerated to the high alkaline wastewater, the content of Zn after filtering was measured by Inductively Coupled Plasma (ICP), and then analyzed the precipitate by X-ray powder diffraction (XRD). The co-precipitation characteristics of Zn in highly alkaline waste by CO₂ aerated was simulated by PHREEQC. The results showed that CO₂ neutralized the high alkaline waste effectively, and the content of Zn was significantly decreased. The outcome showed that the sediment mainly consisted of CaCO₃ and Zn. With CO₂ continuing aerating, co-precipitation with CaCO₃ created. Iron and aluminum hydroxide can adsorbent Zn, but the phenomenon is not obvious because colloid contains less.

Introduction

Highly alkaline wastewater has a large amount of heavy metals in it. If discharge it into river, it can contribute to pollution. The removal method include that co-precipitation, adsorption, ion-exchange and so on, adsorption based on easy process and well effect receives much concern^[1,2]. Adsorption and co-precipitation are mature technology in the method of wastewater, the result shows that complexes have a strong adsorption to Zn, and Zn can form precipitation by self^[3-6]. The adsorption and co-precipitation can decreased the concentration of heavy metals and remove the specific heavy metal ions^[7-9]. Carbonated technology is a new method, heavy metals can be stabled by it and decrease the toxicity. CO₂ can cause green house effect, but in other words, with Ca²⁺ in the highly wastewater can fix CO₂^[10-13], so the technology not only solve the atmospheric problems but also remove the heavy metals in the solution^[14,15].

1 Experiment

1.1 Method

Aerated CO₂ into wastewater (Table 1), and was continuously stirred using a stirring bar. The pH of the solution was measured by METTLER TOLEDO(FE20) pH meter. The generated solids were collected by filtration through membrane filters (0.45μm inorganic membrane). The filtrate was acidified with 2% nitric acid for analysis of ions with ICP-MS. The solid materials and membrane were dried at 105 °C and then analyzed by XRD. Different concentrate of ions was measured by adding different reagent.

Table 1 The concentration of ions in alkaline wastewater(pH:12.58 Temperture:25 °C)

Ions	Ca	Zn	Fe	Al	Na	K	Cl
Con (mg/L)	512.2	16.82	0.083	2.954	269.143	1577.606	13045.6

1.2 Modeling

The mechanism of heavy metals precipitation in solution was studied by PHREEQC. The balance equation and equilibrium constants of the soluble and precipitated phases in the heavy metals were from databases in PHREEQC2.15.0 (Version 2).

2 Results and discussion

2.1 The results of Zn by ICP

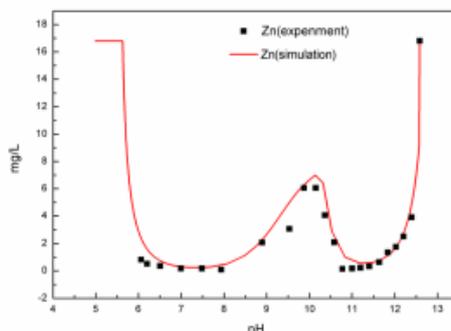


Fig.1 The change of concentration of Zn^{2+}

The precipitation of Zn^{2+} was divided into five stages:

First stage, in the beginning, pH value decreased from 12.58 to 12.39 and the concentration of Zn^{2+} sharply decreased from 16.82mg/L to 3.917mg/L, which reduced to 23.29% of the initial concentration. That because the concentration of OH^- decreased and combined with Zn^{2+} which generated $Zn(OH)_2(s)$.

Second stage, continued on aerating CO_2 , pH value decreased from 12.39 to 10.8, and the concentration of Zn^{2+} decreased from 3.917mg/L to 0.142mg/L. When pH value reached to 10.8, the concentration of Zn^{2+} was 0.142 mg/L, which 0.84% of Zn^{2+} concentration in the initial solution. The results showed that Zn^{2+} reacted with OH^- entirely, $Zn(OH)_2(s)$ was generated.

Third stage, when pH value decreased from 10.8 to 10, the concentration of Zn^{2+} increased gradually. 6.077 mg/L of Zn^{2+} was in the solution when pH value at 10, which 36.13% of Zn^{2+} concentration in the initial solution. Hence, (a) With CO_2 bubbling constantly, pH value decreased gradually, and the concentration of OH^- was reduced, which caused the precipitation of $Zn(OH)_2$ dissolved rapidly. (b) The content of CO_3^{2-} increased, and produced a large amount of $Ca_xZn_{(1-x)}CO_3$. (c) The amount of $Ca_xZn_{(1-x)}CO_3$ was less than the dissolved amount of $Zn(OH)_2$.

Fourth stage, the content of Zn^{2+} was 1% of the initial solution which was 0.106 mg/L at pH value in 7. The removal rate is the largest in this process because large amount of $Ca_xZn_{(1-x)}CO_3$ generated.

Fifth stage, at the pH value was lower than 7, the content of Zn^{2+} increased because $Ca_xZn_{(1-x)}CO_3$ dissolved.

2.2 The simulation of Zn

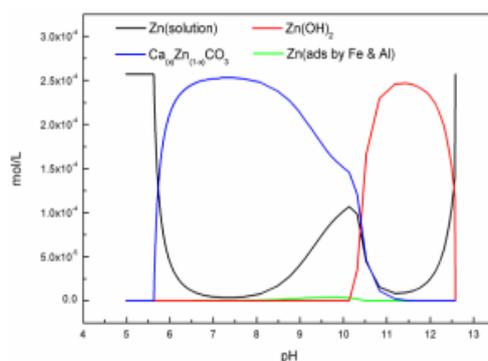


Fig. 2 The concentration of all kinds of Zn in solution

The co-precipitation of Zn^{2+} was divided into three stages:

First stage, when pH value decreased from 12.58 to 10.2, $Zn(OH)_2(s)$ was mainly, Zn^{2+} and $Ca_xZn_{(1-x)}CO_3$ was just a little, Zn was no adsorbed nearly in the solution. Hence, (a) The concentration of Zn^{2+} decreased sharply in the pH value of 12.58 to 11.5. The content of $Zn(OH)_2(s)$ reached the maximum at 2.47×10^{-4} mol/L, which because OH^- reacted with Zn^{2+} with CO_2 aerating. (b) When pH

value decreased from 11.5 to 10.2, Zn^{2+} increased to 1.07×10^{-4} mol/L. The main precipitation transformed from $Zn(OH)_2(s)$ to $Ca_xZn_{(1-x)}CO_3$. $Zn(OH)_2(s)$ decreased to 0 and $Ca_xZn_{(1-x)}CO_3$ increased to 1.46×10^{-4} mol/L correspondingly. That because the amount of $Ca_xZn_{(1-x)}CO_3$ was less than the dissolved amount of $Zn(OH)_2$.

Second stage, Zn^{2+} in the solution was decreased from 1.07×10^{-4} mol/L to 8.12×10^{-6} mol/L at the pH value decreased from 10.2 to 8. And $Ca_xZn_{(1-x)}CO_3$ increased from 1.46×10^{-4} mol/L to 2.48×10^{-4} correspondingly. The result showed that the concentration of CO_3^{2-} increased and a large amount of $CaCO_3$ generated which adsorbed Zn^{2+} and got $Ca_xZn_{(1-x)}CO_3$. When pH value decreased from 8 to 7, the content of Zn^{2+} decreased to 3.73×10^{-6} which 1% of Zn^{2+} concentration in the initial solution.

Third stage, when pH value was lower than 6.5, Zn^{2+} increased at 2.57×10^{-4} mol/L, $Ca_xZn_{(1-x)}CO_3$ dissolved gradually because CO_3^{2-} transform to HCO_3^- with CO_2 aerating. From the result, we concluded that the adsorption of $Fe(OH)_3$ and $Al(OH)_3$ could be ignored. The reason was that the concentration of Ca^{2+} was three magnitudes than that of Al^{3+} and Fe^{3+} , so the effect of $CaCO_3$ adsorption was better than $Fe(OH)_3$ and $Al(OH)_3$.

2.3 The analysis of XRD

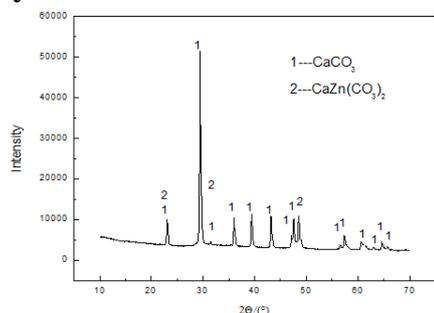


Fig. 3 XRD Diffractogram at pH=7.93

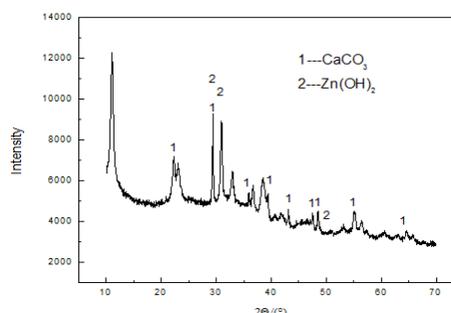


Fig. 4 XRD Diffractogram at pH=12.39

Figure 3 and Figure 4 showed XRD diffractogram of the sediment at pH=7.93 and pH=12.39. At pH=7.93, the diffraction in 23、29.4、31.3、35.9、39.3、43.1、47.1、47.4、48.4、56.5、57.4、62.9、64.6、65.5, which showed that the main component of sediment was $CaCO_3$. The diffraction in 23、31.3、48.4 showed that the sediment was $CaZn(CO_3)_2$ mainly. At pH=12.39, the diffraction in 23、29.4、35.9、39.5、43.2、47.4、48.4、56.5、64.6, which showed that the main component of sediment was $CaCO_3$. The diffraction in 29.4、30.9、50 showed that the sediment contained $Zn(OH)_2$ mainly.

Summary

From the study we concluded that, at the beginning of CO_2 aerating, the pH value decreased and the concentration of Zn^{2+} decreased correspondingly. With CO_2 aerated continually, the content of Zn^{2+} increased, the removal of Zn had a high extent when pH value at 10 to 7, which was 99% and had a good removal effect.

Zn was absorbed by Fe/Al colloid and formed co-precipitation with $CaCO_3$. According to the concentration of Ca^{2+} was three magnitudes higher than Al^{3+} and Fe^{3+} , the adsorption of $Fe(OH)_3$ and $Al(OH)_3$ could be ignored. The adsorption of heavy metals in wastewater by $CaCO_3$ was significantly better than that of Al and Fe.

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