



## Synthesis of Feed-Grade Tribasic Copper Chloride with Alkaline Etching Waste Liquor after the Co-precipitation of Lead and Arsenic

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(Received: 12 July 2010;

Accepted: 9 May 2011)

AJC-9914

A new and effective synthesis of feed-grade tribasic copper chloride was developed using alkaline etching waste liquor. The lead and arsenic in alkaline etching waste liquor were directly removed by co-precipitation with mixed nascent calcium carbonate-ferric hydroxide. The co-precipitation conditions, such as the settling time, temperature, pH and the amount of carrier elements, were investigated. The obtained tribasic copper chloride powder was characterized by XRD and electron microscopy. Results indicated that for 1 L alkaline etching waste liquor at 40 °C and a pH of 8.0, addition of 2.3 g of ferric chloride, 10 g of calcium chloride and 10 g of sodium carbonate led to removal rates for lead and arsenic of 92.4 and 94.6 %, respectively. The contents of lead and arsenic of tribasic copper chloride were 7.4 and 3.5 mg/kg, respectively. Results showed that the synthetic tribasic copper chloride can be used as the feed additive.

**Key Words:** Etching waste liquor, Tribasic copper chloride, Co-precipitation, Lead, Arsenic.

### INTRODUCTION

Over the past ten years in China, production in the field of printed circuit board (PCB) has grown sharply by more than 20 % annually. The most typical method to produce copper printed circuit board uses acid or alkaline etching liquids. It's necessary to develop a sustainable way to treat the waste liquor containing copper.

Copper is an essential element in the biochemical functions for cattle, pig and other animals<sup>1</sup>. The supplemental copper source is critical for the livestock production<sup>2-4</sup>. Tribasic copper chloride ( $\text{Cu}_2(\text{OH})_3\text{Cl}$ , TBCC), as compared with copper sulfate as a copper source in livestock production, possesses several beneficial chemical characteristics such as small particle size, excellent flow, low water solubility, good bioavailability and low toxicity<sup>5-10</sup>.

The reuse of alkaline etching waste liquor for the preparation of the feed additive tribasic copper chloride, can turn waste into useful product<sup>11</sup>. However, the lead and arsenic concentrations of alkaline etching waste liquor were very high and affected the quality of final product due to their well known toxicity. A high content of lead and arsenic in a final product will be detrimental to the animals, making the pretreatment of alkaline etching waste liquor for the removal of lead and arsenic essential.

In this study, a mixed nascent calcium carbonate-ferric hydroxide reagent has been used for the separation and removal of lead and arsenic in the alkaline etching waste liquor due to their synergistic reaction. The effects of the settling time, the temperature, the pH and the amount of carrier elements on the removal of lead and arsenic, were investigated. The obtained tribasic copper chloride powder was characterized by XRD and electron microscopy. The contents of lead and arsenic of final product were assessed.

### EXPERIMENTAL

Etching waste liquor was purchased from Shenzhen Jiepu Electronics Science and Technology Co. Ltd., Shenzhen, China. All the reagents were of analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. A stock solution containing 1 mg/mL of lead was prepared by dissolving 0.1598 g lead nitrate and diluted to 100 mL with 1 %  $\text{HNO}_3$ . A working solution containing 50  $\mu\text{g}/\text{mL}$  of lead was prepared by diluting the stock solution. A stock solution containing 1 mg/mL of arsenic(III) was prepared by dissolving 0.1320 g arsenous trioxide in 100 mL distilled water. A working solution containing 1  $\mu\text{g}/\text{mL}$  of arsenic was prepared by diluting the stock solution. The solutions were prepared weekly and stored in a refrigerator.

The phase structure of tribasic copper chloride crystalline powders was examined by X-ray diffraction (XRD) on a JSM 6480LV diffractometer equipped with graphite monochromatized Cu  $K_{\alpha}$  (40 kV, 20 mA,  $\lambda = 0.154\ 06\ \text{nm}$ ) radiation with the  $2\theta$  angles ranging from  $10\text{-}80^{\circ}$  in steps of  $0.02^{\circ}$  (Japan Electronic Comp., Japan). The surface morphology was observed with by the electron microscope (SCALAR-U2). The purity of tribasic copper chloride is determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Measurements were made using IRIS Intrepid inductively coupled plasma atomic emission spectrometer (Thermo Fisher Scientific Corporation, USA), equipped with two-dimensional cross dispersion system composed by echelle and CID.

**Co-precipitation procedure:** A certain volume of  $0.8\ \text{mol/L}\ \text{CaCl}_2 + 0.8\ \text{mol/L}\ \text{Na}_2\text{CO}_3$  solutions or  $0.15\ \text{mol/L}\ \text{FeCl}_3$  solution was added into  $35\ \text{mL}$  of alkaline waste etching waste liquor which had been heated to different temperatures. The pH of the solution was adjusted by  $\text{NH}_3\cdot\text{H}_2\text{O}$ . After a certain reaction time, the deposition was removed by filtration<sup>12</sup>. The amount of lead and arsenic in the supernatant liquor was determined by ICP-AES and the rates of removal were calculated.

The reaction times of co-precipitation for the removal of lead and arsenic were investigated by adding  $0.8\ \text{mol/L}\ \text{CaCl}_2 + 0.8\ \text{mol/L}\ \text{Na}_2\text{CO}_3$  solution or  $0.15\ \text{mol/L}\ \text{FeCl}_3$  solution to alkaline waste etching liquor; reaction times ranged from  $10\text{-}60\ \text{min}$ .

**Orthogonal design:** The orthogonal experiment with three factors and four levels was carried out and the  $L_9\ (3^4)$  orthogonal table was designed to analyze the removal rate of lead and arsenic from alkaline waste etching liquor. Temperature, pH, the amount of  $0.15\ \text{mol/L}\ \text{FeCl}_3$  solution and the amount of  $0.8\ \text{mol/L}\ \text{CaCl}_2 + 0.8\ \text{mol/L}\ \text{Na}_2\text{CO}_3$  solution were selected as controllable independent variables designated A, B, C and D, respectively. In this study, co-precipitation was accomplished with  $35\ \text{mL}$  of alkaline waste etching liquor. Nine tests were carried out at temperatures of  $25, 40$  and  $55\ ^{\circ}\text{C}$ ; pH values of  $7.5, 8.0$  and  $8.5$ ; volumes of  $0.15\ \text{mol/L}\ \text{FeCl}_3$  solution of  $1, 2$  and  $3\ \text{mL}$  and volumes of  $0.8\ \text{mol/L}\ \text{CaCl}_2 + 0.8\ \text{mol/L}\ \text{Na}_2\text{CO}_3$  solution of  $2.5 + 2.5, 4.0 + 4.0$  and  $5.5 + 5.5\ \text{mL}$ . The test levels are listed in Table-1.

**Synthesis and characterization of tribasic copper chloride:** The synthesis process of tribasic copper chloride is shown in Fig. 1. Purified alkaline etching liquor containing  $120\ \text{g/L}\ \text{Cu}$  and  $6\ \text{mol/L}\ \text{HCl}$  were added dropwise to  $300\ \text{mL}$  deionized water at  $70\ ^{\circ}\text{C}$  in the pH range of  $4.5\text{-}5.5$ . The solution was stirred at a constant rate and the pH adjusted to remain in the desirable range. The synthesized precipitate was filtered and thoroughly washed three times with deionized water. Finally, the samples were dried in vacuum at  $90\ ^{\circ}\text{C}$  for  $2\ \text{h}$ .

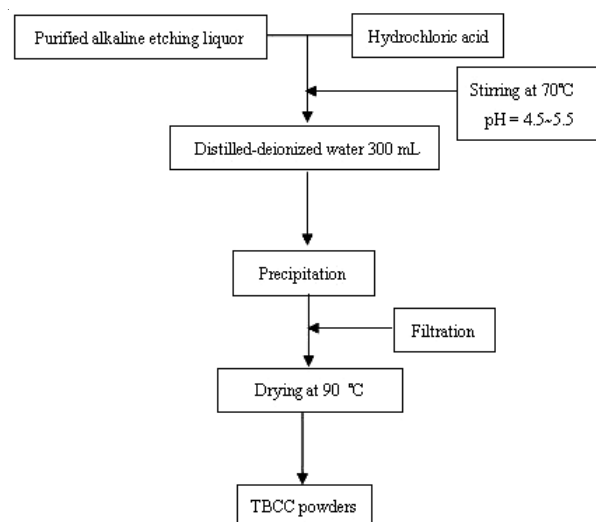


Fig. 1. Flowchart for preparing tribasic copper chloride crystallites

The obtained tribasic copper chloride powder was characterized by XRD and electron microscopy. The contents of copper, lead and arsenic of tribasic copper chloride were determined.

## RESULTS AND DISCUSSION

**Effect of the reaction time of co-precipitation on the removal of lead and arsenic:** Fig. 2 shows that the removal rates of lead and arsenic with  $\text{CaCO}_3$  and  $\text{Fe}(\text{OH})_3$  as the precipitating agents didn't change when the reaction time was increased from  $10\text{-}60\ \text{min}$ . The results indicated that  $\text{CaCO}_3$  and  $\text{Fe}(\text{OH})_3$  can rapidly react with lead and arsenic. For the full co-precipitation, the reaction time of  $20\ \text{min}$  was selected.

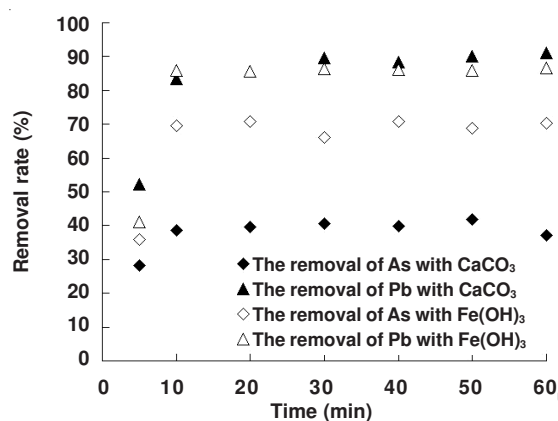


Fig. 2. Effect of the reaction time of co-precipitation on the removal of lead and arsenic. For ◆, the removal of As with  $\text{CaCO}_3$ ; for ▲, the removal of Pb with  $\text{CaCO}_3$ ; for ◇, the removal of As with  $\text{Fe}(\text{OH})_3$ ; for △, the removal of Pb with  $\text{Fe}(\text{OH})_3$ .

TABLE-1  
FACTORS AND LEVELS FOR ORTHOGONAL TEST

Levels	Factors			
	Temperature ( $^{\circ}\text{C}$ ) (A)	pH (B)	Volume of $\text{FeCl}_3$ solution* (mL) (C)	Volume of $\text{CaCl}_2 + \text{Na}_2\text{CO}_3$ solution** (mL) (D)
1	25	7.5	1.0	$2.5 + 2.5$
2	40	8.0	2.0	$4.0 + 4.0$
3	55	8.5	3.0	$5.5 + 5.5$

Notes: \* $0.15\ \text{mol/L}\ \text{FeCl}_3$  solution. \*\* $0.8\ \text{mol/L}\ \text{CaCl}_2$  solution and  $0.8\ \text{mol/L}\ \text{Na}_2\text{CO}_3$  solution.

**Results of orthogonal design:** Detailed spraying conditions and the results tested are listed in Table-2. From the mathematical processing of the data, some conclusions are as follows. First, the analysis of the orthogonal experiment indicated that the factor of the reaction temperature (A) and pH (B) had the greatest influence on the removal of lead and the factor of the amount of 0.15 mol/L FeCl<sub>3</sub> solution (C) had a notable influence on the removal of arsenic. The significance of each factor on the removal of lead and arsenic was  $A \approx B > D > C$  and  $C > B > D > A$ , respectively. Second, the optimal processing parameters of lead removal experiment were A<sub>2</sub>B<sub>3</sub>C<sub>3</sub>D<sub>2</sub>, namely, the reaction temperature is 40 °C, pH is 8.5, the amount of 0.15 mol/L FeCl<sub>3</sub> solution is 3 mL/35 mL alkaline etching waste liquor and the amount of 0.8 mol/L CaCl<sub>2</sub> + 0.8 mol/L Na<sub>2</sub>CO<sub>3</sub> solution is 4.0 + 4.0 mL/35 mL alkaline etching waste liquor. The optimal processing parameters of As removal experiment were A<sub>3</sub>B<sub>3</sub>C<sub>3</sub>D<sub>3</sub>, namely, the reaction temperature is 55 °C, pH is 8.5, the amount of 0.15 mol/L FeCl<sub>3</sub> solution is 3 mL/35 mL alkaline etching waste liquor and the amount of 0.8 mol/L CaCl<sub>2</sub> + 0.8 mol/L Na<sub>2</sub>CO<sub>3</sub> solution is 5.5 + 5.5 mL/35 mL alkaline etching waste liquor.

Subtle differences between optimal processing parameters for Pb and As removal were examined on a factor by factor basis to result in one set of conditions. Although 55 °C was the optimally temperature for removing As, a lot of NH<sub>3</sub> was lost from the system. Due to the weak effect of reaction temperature on the removal of As, the reaction temperature was selected at 40 °C. In addition, there was no notable difference of the amount of 0.8 mol/L CaCl<sub>2</sub> + 0.8 mol/L Na<sub>2</sub>CO<sub>3</sub> solution between 4.0 + 4.0 mL and 5.5 + 5.5 mL for the removal of Pb. The final co-precipitation conditions of As and Pb: 40 °C, pH 8.5 and 3 mL 0.15 mol/L FeCl<sub>3</sub> solution and 5.5 + 5.5 mL 0.8 mol/L CaCl<sub>2</sub> + 0.8 mol/L Na<sub>2</sub>CO<sub>3</sub> solution per 35 mL alkaline etching waste liquor.

When 10 g of CaCl<sub>2</sub>, 10 g of Na<sub>2</sub>CO<sub>3</sub> and 2.3 g of FeCl<sub>3</sub>·6H<sub>2</sub>O were added into 1 L of alkaline etching waste liquor at the co-precipitation conditions described above, removal rates

of 92.4 and 94.6 % for lead and arsenic were obtained, respectively. The results showed that the synergistic effect of CaCO<sub>3</sub> and Fe(OH)<sub>3</sub> was ideal for the co-precipitation of lead and arsenic from alkaline etching waste liquor and could effectively decrease the content of lead and arsenic in the final product.

**Characterization of tribasic copper chloride:** Tribasic copper chloride crystallites were obtained by a complex catalytic liquid phase precipitation route using purified alkaline etching liquor and hydrochloric acid as the starting materials at pH = 4.5-5.5. The purified alkaline etching liquor and hydrochloric acid can react completely by adding dropwise to the deionized water. The tribasic copper chloride sample was analyzed by ICP-AES and determined to contain 59.2 % copper with an overall purity of 99.5 %.

The structure of the obtained tribasic copper chloride was characterized by XRD (Fig. 3). The results showed that a monoclinic structure of tribasic copper chloride with the lattice parameters of  $a = 0.572$  nm,  $b = 0.613$  nm,  $c = 0.565$  nm could be indexed appropriately by diffraction peak positions, which was consistent with the parameters of the bulk tribasic copper chloride (JCPDS 85-1713).

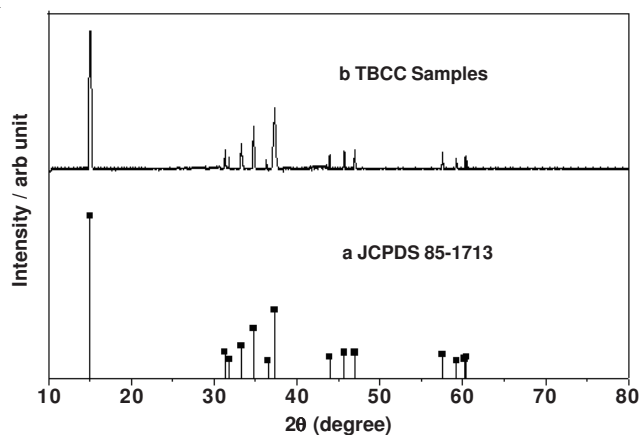


Fig. 3. XRD of the obtained tribasic copper chloride samples

TABLE-2  
LAYOUT OF THE L<sub>9</sub> (3<sup>4</sup>) MATRIX AND RESULTS FOR THE EFFECT OF TEMPERATURE, pH AND THE MOUNT OF PRECIPITATING AGENTS ON THE REMOVAL OF Pb AND AS OF ALKALINE ETCHING WASTE LIQUOR

Test No.	A	B	C	D	Removal rate of Pb (%)	Removal rate of As (%)
1	25	7.5	1	2.5+2.5	58.5	65.8
2	25	8.0	2	4.0+4.0	78.2	83.0
3	25	8.5	3	5.5+5.5	77.7	93.5
4	40	7.5	3	4.0+4.0	81.5	80.7
5	40	8.0	1	5.5+5.5	88.2	82.4
6	40	8.5	2	2.5+2.5	82.4	91.0
7	55	7.5	2	5.5+5.5	74.9	87.0
8	55	8.0	3	2.5+2.5	82.2	92.1
9	55	8.5	1	4.0+4.0	91.9	77.7
N <sub>1</sub>	71.5	71.6	79.5	74.4	—	—
N <sub>2</sub>	84.0	82.9	78.5	83.9	—	—
N <sub>3</sub>	83.0	84.0	80.5	80.3	—	—
R <sub>1</sub>	12.5	12.4	2.0	9.5	—	—
M <sub>1</sub>	80.8	77.8	75.3	83.0	—	—
M <sub>2</sub>	84.7	85.8	87.0	80.5	—	—
M <sub>3</sub>	85.6	87.4	88.8	87.6	—	—
R <sub>2</sub>	4.8	9.6	13.5	7.1	—	—

Notes: N<sub>1</sub>, N<sub>2</sub> and N<sub>3</sub> represent the average of removal of lead on the level of 1, 2, 3, respectively; M<sub>1</sub>, M<sub>2</sub> and M<sub>3</sub> represent the average of removing arsenic on the level of 1, 2, 3, respectively; R<sub>1</sub> and R<sub>2</sub> represent range.

TABLE-3  
ELEMENTS CONTENTS OF TRIBASIC COPPER CHLORIDE POWDER SAMPLES

Elements	Pb	As	K	Na	Mg	Mn	Fe
Content ( $\mu\text{g g}^{-1}$ )	7.4	3.5	89.1	80.1	12.4	1.7	7.9
Standard ( $\mu\text{g g}^{-1}$ )	< 10	< 4	–	–	–	–	–

The obtained tribasic copper chloride crystallites were measured by electron microscopy (Fig. 4). The results showed that the particle size of tribasic copper chloride crystallites were in a range from 50-200  $\mu\text{m}$  (Fig. 4a). A closer examination of the samples indicated that the tribasic copper chloride crystallites had a very smooth surface exhibiting excellent flow characteristic (Fig. 4b).

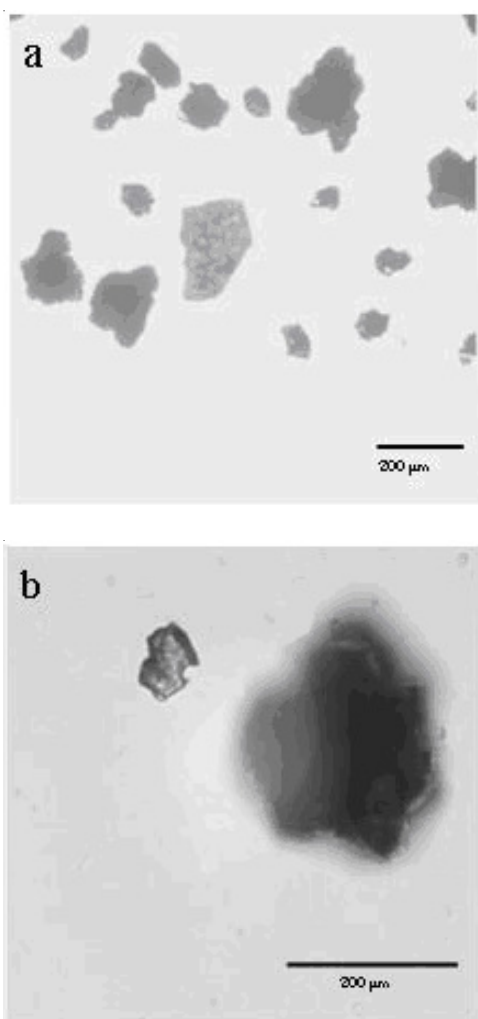


Fig. 4. (a) Electron microscopy of tribasic copper chloride crystallites; (b) magnified image of tribasic copper chloride crystallites

The content of As, Pb, Mg, K, Na, Fe and Mn in tribasic copper chloride crystallites was determined by ICP-AES. Analytical results of impurities of tribasic copper chloride

samples are shown in Table-3. The content of As, Pb, Mg, K, Na, Fe and Mn was 3.54, 7.45, 12.4, 89.1, 80.1, 7.91 and 1.73 mg/L, respectively. The As and Pb content of obtained tribasic copper chloride was less than that of Chinese Chemical industry standards of feed grade copper sulfate<sup>13</sup> indicating the tribasic copper chloride samples were safe to use as the feed additive.

### Conclusion

Lead and arsenic were removed from alkaline etching waste liquor by the co-precipitation effect of  $\text{CaCO}_3$  and  $\text{Fe}(\text{OH})_3$ . The feed grade tribasic copper chloride was obtained by a simple method, which used the purified alkaline etching waste liquor reacted with HCl. Using co-precipitation treatment, the lead and arsenic contents of final tribasic copper chloride were effectively controlled; the industrial waste could be converted to a commercial product and the copper resource recycled.

Future work for this study will focus on the control of particle size of tribasic copper chloride and the enhancement of tribasic copper chloride yield by adjusting the reaction conditions.

### ACKNOWLEDGEMENTS

The authors are grateful for the financial support from the National Natural Science Foundation (No. 50574006) of China.

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