Study on CuS recycling from the waste of AMD bio-treatment

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Abstract. AMD pollution was considered as the world wide problem, Nowadays many technology (especially biotechnology) was researched to purified the waste water. However, the solid waste produced by the procedure was seldom payed attention to. In this research, 4 flocculants were applied to recycle the Cu in the form of CuS to selected the most suitable flocculent and characters for recycling. Besides, solid waste mixture produced by bio-treatment of real AMD was treated to test the performance of the flocculants. The results shows that NPAM takes on a most suitable performance for recycling CuS. The initial pH should be adjusted lower than 2.5, and dosage of NPAM (1% m/m) was 3mL per 500 mL mixture, which contains about 180 mg/L Cu. If the content of Cu was more or less than it in the untreated mixture, the dosage should be adjusted based on the ratio compare with the original Cu content (180 m/L). The recycle ratio of solid waste produced by bio-treatment of real AMD was 78.47%, but the content of CuS was more than 80%, which could be the raw material for smelting Cu. The results could supply a theoretic bases for recycling Cu in the form of CuS.

Introduction

As the Fundao and Santarem mine tailings dams had collapsed in Minas Gerais, Brazil on November 5th, 2015, at least 17 people had been killed and more than 650 km of rivers had been blanketed, and even potable water supplies had been cut off by 62, 000, 000 m^3 sediment and AMD (Acid Mining Drainage) [1]. Mine tailings and AMD have been focused on again by many researchers and government. The treatment and recycle of AMD and tailings become more and more serious problems, especially for AMD. Because of containing strong acid and high concentration of heavy metal ions [2], it may pollute river and soil, leading to aquatic organism death and plant growing inhibition. As a result, purifying AMD has been just around the corner.

Up to now, many researchers have been trying to deal with such wastewater and get some conclusions. [3] use limestone to raise pH of AMD to 4 to precipitate Fe^{3+} firstly, and then precipitate Cu^{2+} as well as other metal ions by piping H_2S. [4] set ferric sulfide as cathode and ferrous waste as anode. The AMD in the channel was formed as a electrochemical loop with cathode and anode, which was applied to raise its pH from 3 to 5.6, and reduce Cu^{2+}, Al^{3+}, Cd^{2+}, Ni^{2+} obviously. [5] treat AMD by SRB in the Microflora of blue-green algae with fertilizer of goat, saw dust and soil as substrate. Within 24h the pH of the wastewater raise from 2.93 to 6.78, 23%-29% of sulfate was reduced, and about 85% of Zn, 88% of Pb,

88% of Cu, 95% of Fe, 71% of Co, 42% of Ni, and 36% of Mn were removed. [6] removed As^{3+} or As^{5+} by mix Sulfate-Reducing Bacteria. After treatment, As^{3+} and As^{5+} was reduced from 1 mg/L to 0.3mg/L and 0.13mg/L. 77% and 55% of them were absorbed by SRB forming precipitate in the part of reduced As^{3+} and As^{5+}, Only 6.6% and 10.5% of which were removed by SRB after 24 h.

Although the technology of AMD treatment is still at the exploration stage, there is a question come to us, how to deal with solid waste. Most of the technology above would form precipitate, in wich the proportion of Cu and Fe were fairly large. If the Cu in the remains could be recycled, not only the solid waste would be reduced, the economy Value also may be created. So in this research some kinds of flocculating agents were tried to applied to separate Cu from the remains in the form of CuS, which was the raw material of smelting Cu.

Methods and materials

Bio-treatment of AMD solid waste. The AMD were selected from $4^{\#}$ tailing pond of Dexing copper mine, Jiangxi, China. Mental composition of it was shown in table 1, which was provided by local analyzer. The AMD was treated by SRB (Sulfate reducing bacteria) with two steps, and solid waste in the first step was produced by the H_2S gas, piped from the second step treatment (Biological treatment), precipitating Cu^{2+}, while iron shavings raised pH of the mixture of solid and water to about 4 initially at the same time.

Table 1 Chemical analysis of the AMD

Item	Value/mg·L^{-1}	Item	Value/mg·L^{-1}
Mo	0.026	Mn	102.5
As	0.741	Pb	0.345
Ca	313.5	Zn	5.178
Cu	185.8	Al	625.5
Fe	485.5	Mg	785.0
pH	2.34	SO_4^{2-}	5789.32

Simulative solid waste of AMD. Since the main heavy metal ions which could be removed as sulfide were Cu^{2+} and Fe^{3+} or Fe^{2+} in the AMD. According to the concentration of Cu and Fe, $CuSO_4 \cdot 5H_2O$ and $FeSO_4 \cdot 7H_2O$ were prepared in 500 mL running water, the pH of which was adjusted by concentrated sulphuric acid to 2 to avoid Fe^{2+} precipitated as $Fe(OH)_2$ or $Fe(OH)_3$. Then it was adjusted again by Na_2S to 4 to simulate solid waste produced by AMD treatment.

Reagents. PAM (Applied by Xinguang chemical product limited company, TP, Renqiu, China) was prepared with running water as its concentration 1% (m/m), including HPAM, CPAM and NPAM. Others were applied by Sinopharm Chemical Reagent Co., Ltd, AR, China. PAC were prepared with running water as its concentration 3% (m/m).

CuS Recycling test. pH of simulated solid waste mixture or bio-treatment of AMD solid waste mixture were adjusted to appropriate value, then stirred for 10 min. Then flocculant

was add in to flocculate and precipitate the solid waste. After that upper liquid was piped out by siphon, and remains were filtered by Medium speed filter paper. When filtration was accomplished the solid remains were cleaned by distilled water, and then sent to air dry oven for drying for 3h at 60 ℃. The solid was spooned out for weighing and Cu content analyze.

Analytical methods. pH was tested by glass combined electrode E-201-C, which was produced by Shanghai instrument electric science instrument Limited by Share Ltd. , connected to the display equipment Orion 818 produced in USA. Cu in the solid was tested according to the method [7]. SEM analyze JSM-5610LV, which was produced by NEC Electronics Corporation, Japan, were used for scanning Bio-treatment of AMD solid waste to view its morphological structure of surface.

Results and discussion

Simulated solid waste recycling by flocculants. As is known that flocculant dosage at about 300~500 g/t normally, so 400 mg/L (6mL prepared flocculants) the flocculants were add in solid mixture to test their abilities. According to Fig. 1, as for filtering time, simulated solid waste mixture flocculated by NPAM was the least. 15 min was enough for separating solid waster form the liquid. Others needed 2h at least. NPAM presents an advantage in aggregating CuS, which makes it separated easily and conveniently.

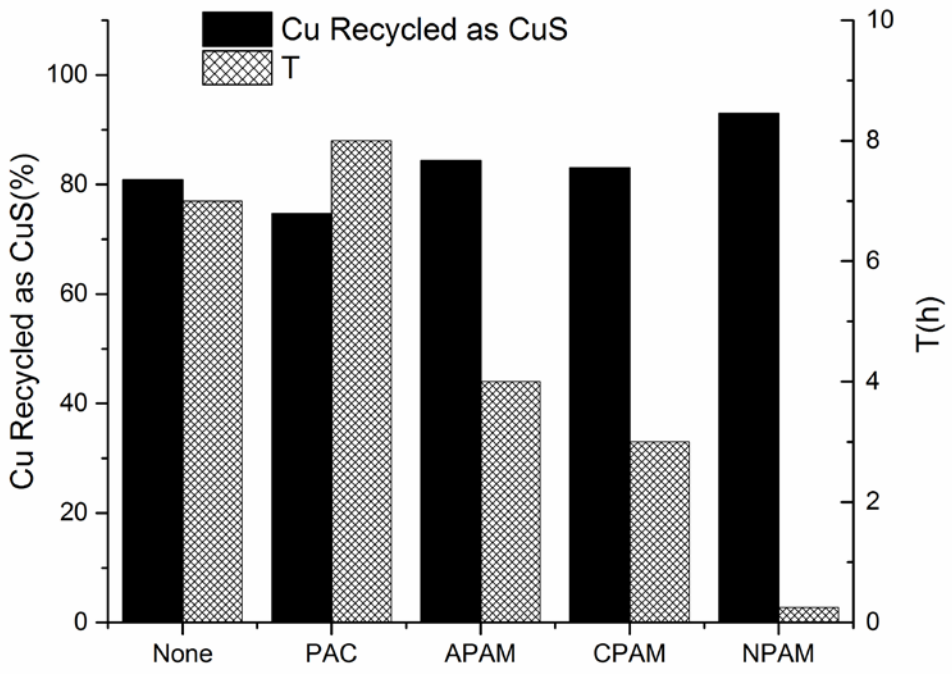

Fig. 1 Simulated solid waste mixture flocculating test by flocculants

All the solid contain about 56.5~57.5% Cu, that is 84.75~86.25% CuS equivalently in the solid, which show that at the pH of 2, CuS take over most part of the black solid, and Fe was dissolved in the liquid. So the value of pH could separate Cu against ferrous compound enough in the mixture.

Although in very sample Cu content was almost the same, the Cu recycling ratios were differed greatly in solid mixture treated by different flocculants. The simulated solid waste mixture treated by NPAM was recycled as much as 92.95% compared with original Cu

weighed in the form of $CuSO_5 \cdot H_2O$, and others were lowed obviously. When PAC added in mixture, it was hydrolyzed and formed like $[Al(OH)_{6-x}(H2O)_x]^{x-3}$. So it couldn't form polymer until it was hydrolyzed to the extent of x=3. However the value of pH was low leading to H^+ was too much to make $[Al(OH)_3(H_2O)_3]$ form, as a result the effect was unsatisfactory . As for APAM, which was fit for the alkaline condition, the recycling ratio was a little lower than NPAM, so as the CPAM which was fit for the flocculation of organic sludge. CuS belongs to the kind of polar molecule, while NPAM also contains much of the polar group, absorbing and uniting CuS in order to make tiny particles enlarge and precipitate at last.

According to the simulated solid waste recycling test shown as Fig. 1, the effect of flocculation was NPAM>CPAM>APAM>PAC. So NPAM was used as the most suitable flocculation to recycle Cu.

Sing factor test. As shown in Fig. 3, the NPAM added in 3mL (1% m/m) was enough to keep CuS recycling ratio more than 90%. Cu contents in the recycled solid were almost the same, which show that CuS recycling ration has no relationship with the dosage of flocculation. However in Fig.4, the tendency was to the opposite, that is when initial pH raised, the CuS recycling ratio were almost the same while if pH was more than 1.5 the CuS content dropped obviously. It shows that CuS content has much relationship with the initial pH in the mixture. As is known that, Fe^{2+} in the water, especially in running water, was easily oxidized, and form colloid $Fe(OH)_3$. When pH in the mixture was more than 4 the $Fe(OH)_3$ would be all precipitated. So at the time when initial pH more than 1.5, part of the $Fe(OH)_3$ must be formed more and more, and precipitated and flocculated with CuS into the recycled solid leading to the CuS content dropped quickly.

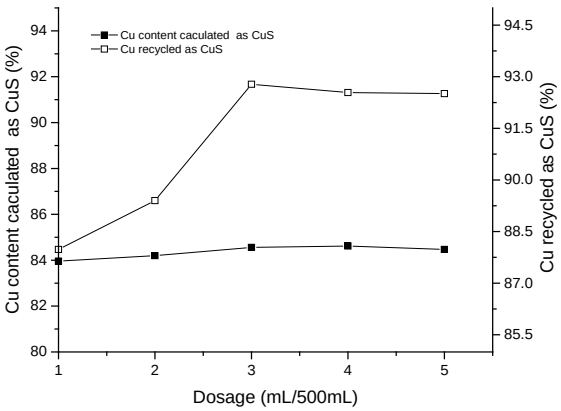

Fig.2 CuS recycled test by dfferent Dosage

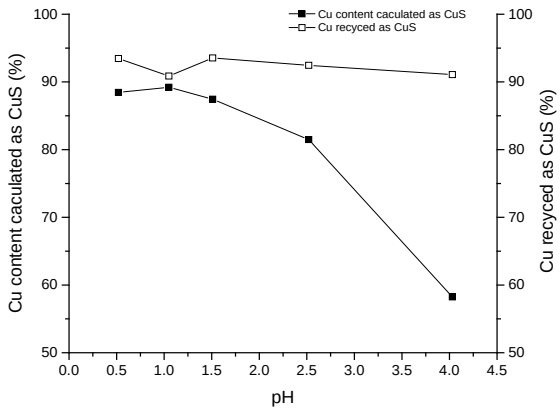

Fig. 3 CuS recycled test by dfferent pH

From the results above, the most appropriate flocculated parameters for recycling Cu was that the initial pH must be adjusted to lower than 1.5, but in order to save the cost, the pH could be adjusted to 2.5 to keep its recycling ration more than 80%, and 3mL flocculants (1% m/m) per 500mL mixture could be used to separate CuS from the solid waste mixture.

CuS recycled test from solid waste mixture produced by real AMD bio-treatment. As shown in Table 1 and 2, because the AMD was continuous treated on 9 days, the Cu^{2+} and other ions was precipitated and accumulated in the mixture, and according to the flow of AMD supplying and Cu^{2+} concentration the amount of Cu^{2+} could be calculated. Based on the simulated solid waste recycling test, the dosage of flocculants must be increased as the ratio comparing with the simulated test.

Table 2 Results of CuS separation from waste mixture produced by real AMD bio-treatment

pH	Dosage /mL·500mL^{-1}	CuS%	Average Cu recycled as CuS/%
2.50	8	81.88	
2.51	8	82.12	78.47
2.51	8	83.23	

The content of CuS was more than 80%, which could be used as the raw material for smelting Cu at the purity. The recycled ratio was a little lower than 80%, which shows that a little bit Cu^{2+} must flow into the second treatment, and was precipitated in it.

Results and discussion

4 kinds of flocculants were tested to precipitating and recycling Cu^{2+} as CuS, NPAM takes on an fantastic performance for separating it from simulated mixture. And according to single factor tests, the most suitable characters for recycling CuS (considering cost saving) was that the initial pH must be adjusted lower than 2.5, and dosage of NPAM (1% m/m) was 3mL per 500 mL mixture, which contains about 180 mg/L Cu. If the content of Cu was more or less than it in the untreated mixture, the dosage should be adjusted based on the ratio compare with the original Cu content (180 m/L). According to the real AMD bio-treatment solid waste flocculation tests, CuS recycled ratio was about 78.47%, but the content of CuS was more than 80%, which can be used as the raw material for smelting Cu. All this results may be supplied a theoretic bases for recycling CuS and shorten the solid waste produced by AMD treatment.

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