

## **Neutralization and flocculation of acid mine drainage with alkaline ore tailing suspension**

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**Abstract**—Laboratory simulations for the neutralization/ flocculation process of the acid mine drainage (AMD) with the alkaline wastewater (AWW) were performed in order to evaluate the impact of AMD on the rivers after the mixing of the AMD and the AWW in river systems and to assess the treatment effect on neutralization of the AMD with the AWW in the wastewater treatment plant.

**Keywords:** acid mine drainage; tailing suspension; wastewater treatment.

### **INTRODUCTION**

The acid mine drainage (AMD) is a major industrial water pollution problem in the Dexing Copper Mine of China because its impact of aquatic life has been very significant. It is characterized by heavy loads of acidity and metal ions, such as Fe and Al in order of magnitude of 2 to 3 g/ L and Cu 0.1 to 0.2 g/ L, as well as higher level sulfate. Whereas, the alkaline wastewater (AWW) possesses heavy loads of alkalinity and solids (Tang, 1992). The solids consist of ore tailing particles arising from the ore dressing plant, and most of the particles are in the size of colloids with a negative surface charge.

Treatment of the AMD and the AWW has become important to protect the aquatic systems. Typical conventional methods use either lime or sodium hydroxide for neutralizing AMD and simultaneous precipitation of mine drainage pollutants. Thanks to the acid - base neutralization/ flocculation technology which makes good use of the alkaline wastewater and destabilization of the precipitated products, it should be possible to neutralize the AMD and to precipitate heavy metals simultaneously.

In this study, jar tests were used first to simulate the neutralization/ flocculation processes in the systems, resulted from the acid mine drainage mixed with the alkaline ore tailing particles. These tests were carried out with synthetic acid mine drainage and alkaline wastewater in order to investigate the possibility and conditions for the neutralization of the two sorts of wastewater

in the treatment plant, and to evaluate the impact of AMD on the river after mixing the AMD with AWW in river system.

## EXPERIMENTAL METHODS AND MATERIALS

### *Preparation of synthetic AWW and AMD*

According to the chemical composition and concentration of cations and anions in AWW and AMD samples collected in field and analyzed by ICP (Table 1), the AMD and AWW used

**Table 1 Comparison of composition and concentration of cations and anions in the AMD and AWW samples and in synthetic AMD and AWW**

Alkaline wastewater (AWW)		
Components	Measured conc., mol/ L	Synthetic conc., mol/ L
Ca <sup>2+</sup>	$5.13 \times 10^{-3}$	$5.00 \times 10^{-3}$
Mg <sup>2+</sup>	$5.31 \times 10^{-3}$	$5.00 \times 10^{-3}$
Na <sup>+</sup>	$7.61 \times 10^{-3}$	$1.20 \times 10^{-2}$
K <sup>+</sup>	$5.05 \times 10^{-3}$	$5.00 \times 10^{-3}$
Fe <sup>3+</sup>	$1.00 \times 10^{-3}$	—
Al <sup>3+</sup>	$1.12 \times 10^{-4}$	—
Cu <sup>2+</sup>	$4.88 \times 10^{-6}$	—
SO <sub>4</sub> <sup>2-</sup>	$1.00 \times 10^{-3}$	$1.00 \times 10^{-3}$
Cl <sup>-</sup>	$1.47 \times 10^{-4}$	$1.50 \times 10^{-4}$
NO <sub>3</sub> <sup>-</sup>	$7.74 \times 10^{-5}$	—
CO <sub>3</sub> <sup>2-</sup>	$5.00 \times 10^{-3}$	$5.00 \times 10^{-3}$
pH	12.0	11.86–12.14
Acid mine drainage (AMD)		
Components	Measured conc., mol/ L	Synthetic conc., mol/ L
Ca <sup>2+</sup>	$6.47 \times 10^{-3}$	$6.50 \times 10^{-3}$
Mg <sup>2+</sup>	$3.38 \times 10^{-2}$	$3.40 \times 10^{-2}$
Na <sup>+</sup>	$2.20 \times 10^{-4}$	$2.20 \times 10^{-4}$
K <sup>+</sup>	$8.28 \times 10^{-4}$	$8.00 \times 10^{-3}$
Fe <sup>2+</sup>	$3.95 \times 10^{-3}$	$4.00 \times 10^{-3}$
Fe <sup>3+</sup>	$1.00 \times 10^{-2}$	$1.00 \times 10^{-2}$
Mn <sup>2+</sup>	$7.30 \times 10^{-4}$	$7.30 \times 10^{-4}$
Al <sup>3+</sup>	$2.00 \times 10^{-2}$	$2.00 \times 10^{-2}$
Cu <sup>2+</sup>	$1.57 \times 10^{-3}$	$1.60 \times 10^{-3}$
Cd <sup>2+</sup>	$1.80 \times 10^{-6}$	—
Pb <sup>2+</sup>	$9.70 \times 10^{-7}$	—
Zn <sup>2+</sup>	$3.80 \times 10^{-5}$	—
SO <sub>4</sub> <sup>2-</sup>	$1.28 \times 10^{-1}$	$1.30 \times 10^{-1}$
Cl <sup>-</sup>	$1.83 \times 10^{-4}$	$1.20 \times 10^{-3}$
NO <sub>3</sub> <sup>-</sup>	$8.10 \times 10^{-4}$	$1.00 \times 10^{-3}$
PO <sub>4</sub> <sup>3-</sup>	$3.77 \times 10^{-3}$	—
pH	2.30	2.13–2.34

in the simulated experiments were synthesized by chemical reagents in laboratory. Composition and concentration of cations and anions in the synthetic AWW and AMD are presented in Table 1.

#### *Preparation of ore tailing suspension (OTS)*

A concentrated suspension of the OTS was size-fractionated by repeated sedimentation to obtain a relatively narrow size distribution. Particle concentration in the concentrated suspension is 39.82 g/L by weighting the solid intercepted on 0.45  $\mu\text{m}$  filter membrane dried. The particle-size distribution is in range of 0.97–3.40  $\mu\text{m}$ , and 80% of the particles are in the range of 0.97–1.46. Mean diameter and volume average diameter are about 1.26  $\mu\text{m}$  and 2.13  $\mu\text{m}$ , respectively. They were determined by a particle analyzer which was called "computerized inspection system (CIS)" manufactured by LOT GmbH / Galai Laboratories LTS. From the result of X-ray diffraction analysis (XRD), the fine-grained OTS mainly consisted of quartz, chlorite, muscovite, montmorillonite, kaolinite and a poorly crystalline Fe and Al oxides (Luan, 1992).

#### *Neutralization experiments*

The experiments were carried out in a jar test apparatus with 250 ml beaker. The synthetic AMD was mixed first with the synthetic AWW with or without ore tailing particles in different concentrations. Rapid mixing rate was maintained at 200 r/min for 30 seconds and slow mixing rate was maintained at 40 r/min for 10 minutes. Then it was statically settled for 10 minutes. At the end of the rapid mixing, the zeta potential of formed hydroxide flocs was determined by a model 501 zeta meter. At the end of the static sedimentation, the turbidity and pH of supernatants were determined by a model 2100A turbidimeter and pH meter, respectively. The particle size and volume of formed hydroxide flocs were measured by the CIS. In addition, the supernatants of about 20 ml were filtered by 0.45  $\mu\text{m}$  membrane. The filtrates were acidified to pH about 2.0 with concentrated  $\text{HNO}_3$ . The concentration of copper ions in the filtrates was analyzed by Perkin-400 atomic absorption spectrophotometer (AAS).

Settling tests were conducted for the formed hydroxide floccus and ore tailing floccus in the neutralization. A 500 ml graduated measuring cylinder (the cylinder height = 210 mm at the 500 ml mark) was used. After mixing the AMD and AWW at different ratios, the mixtures were filled into the cylinder, and then descent time was recorded as a function of the interface between the formed sludge blanket and the clarified supernatant.

## RESULTS AND DISCUSSION

#### *Neutralization / flocculation*

Tests for the neutralization of AMD with AWW were conducted for many times. A typical result in terms of pH of the mixed water vs. the mixing ratio is presented in Fig. 1. Curve A represented the neutralization of AMD with AWW in the absence of ore tailings. It is seen that the amount of AWW required to neutralize AMD is much more than that of base in the normal acid-base neutralization. The mixed water can become neutral only when the mixing ratio of AMD and AWW is up to 1:7 or 1:8. A similar result had also been obtained by the calculation

with the chemical equilibrium model with MINTEQA2 program (Chen, 1992). The high mixing ratio can be explained by considering the effect of hydrolysis-precipitation of iron and aluminum with higher concentrations in AMD, because the acidity generated in AMD is a direct function of iron and aluminum sulfate contents and their reactivities (Barnes, 1968). In the neutralization process, iron and aluminum ions in AMD were rapidly hydrolyzed and precipitated as oxides or hydroxides, and released simultaneously hydrogen ions which were required much more other amount of the alkaline wastewater for neutralization.

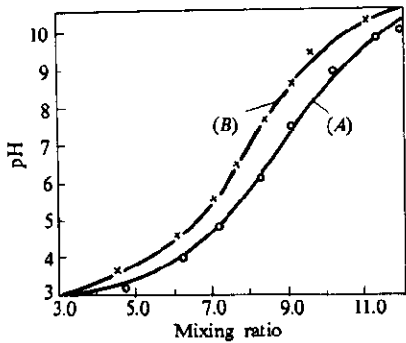


Fig. 1 pH in neutralization of AMD with AWW as a function of the mixing ratio  
 A: in the absence of ore tailings  
 B: in the presence of ore tailings particles

In the chemical process, ferric iron was first precipitated as hydroxide due to its very acid nature. At the concentration of about 1000 ppm Fe(III), the precipitation would start when pH was as low as 2.3, and the residual dissolved concentration of below 1 ppm was detected for pH values above 3.8 (Luan, 1992). Aluminum ions were precipitated as hydroxide at pH above 4.0. The precipitation of other metal ions in AMD could also take place in neutralization. Thus, the precipitated products may be considered as complicated hydroxy-complexes products which mainly consist of iron and aluminum in AMD. When precipitated particulate products were formed, they could aggregate into floc by means of particle collision, and the hydroxide floc could be formed only under

the conditions of slow shear rate or static sedimentation. A typical result of CIS-analysis for the particle size distribution of the hydroxide floc is shown in Fig. 2. Mean diameter of the newly formed hydroxide floc was in the range of 1.0–1.3  $\mu\text{m}$  in neutralization, but their volume average diameter could be up to 10.0–16.0  $\mu\text{m}$ . The hydroxide floc were very easily broken when they were shaken lightly and could aggregate again in the static settling condition.

The aggregation process of the hydroxide floc did not occur readily, and was dependent on the mixing ratio and pH of the mixed waters. Time for formation of the hydroxide floc as a function of pH is given in Fig. 3. When the mixing ratios were above 1:7, the hydroxide floc could be formed rapidly, such as within one minute, and the volume growth of the floc increased also rapidly.

Electrophoretic mobility of newly formed hydroxide floc as a function of pH in the neutralization is given in Fig. 4. Particles of the hydroxide floc were positively charged at low pH values and negatively charged at high pH values, and its isoelectric point ( $\text{pH}_{\text{iep}}$ ) occurred at pH 6.5–6.7. In addition, the electrophoretic mobilities of the hydroxide floc were very low, and most of mobilities were in the range of  $\pm 0.4 \text{ cm} / \mu\text{m} / \text{v} / \text{s}$ . The isoelectric point ( $\text{pH}_{\text{iep}}$ ) of the hydroxide floc obtained in the experiments appears lower than that of the iron or aluminum hydroxide in pure electrolyte solutions published in literature ( $\text{pH}_{\text{iep}} = 8.5\text{--}9.0$  for

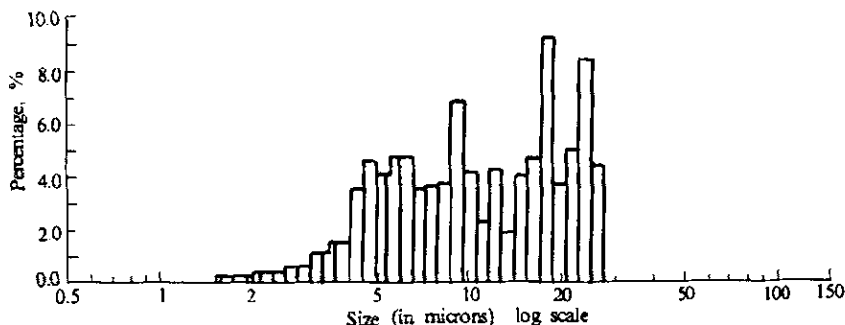


Fig. 2 Particle size distribution (volume density distribution) of new formed hydroxide floccus, Scale range ( $\mu\text{m}$ ): adjusted

aluminum hydroxide and  $\text{pH}_{\text{iep}} = 7.0-7.5$  for iron hydroxide, Singh, 1978). This suggests that under these conditions, the isoelectric point may be determined primarily by precipitate's property and ionization. Because AMD is a complicated solution system containing many kinds of metal ions and anions. In addition, anion concentration in AMD, such as sulfate, has a significant effect on the precipitate charge. According to surface ionization and surface complex reactions (Hohl, 1978), sulfate can decrease the surface charge of the hydroxides or oxides by forming the neutral ( $=\text{MeSO}_4$ ) and negative ( $=\text{MeSO}_4^-$ ) sulfate groups. thus, the specific adsorption of sulfate on the hydroxide surface may be the main reason that leads to the decrease of surface charge of the hydroxide floccus and isoelectric point moving low pH.

This result is in agreement with the result obtained in the study on suspended sediment in Le An River (Luan, 1992). It was found that the suspended oxide particles in the Le An River have a negatively charged surface, suggesting that the surface potential of the hydroxides was partly influenced by these anions capable of specific adsorption on hydroxide surface.

In sedimentation process, when the concentration of coagulated sludge is very high (above 500 mg / L), the particulate settle collectively as a blanket showing a distinct interface between the sludge blanket and the clarified supernatant (Bhargava, 1990).

Data on fall of the interface between the hydroxide floccus and clarified supernatant formed after the mixing, with respect to time for each of different mixing ratios, are presented in Fig. 5. From these plots it was observed that the interface falls had a constant settling velocity within a certain period. The precipitated particles was formed within about 1-2 minutes after mixing, and then they aggregated from small floccus to large floccus by collisions each other and sedi-

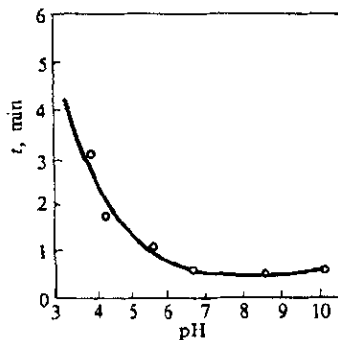


Fig. 3 Time for formation of hydroxide floccus at different pH values

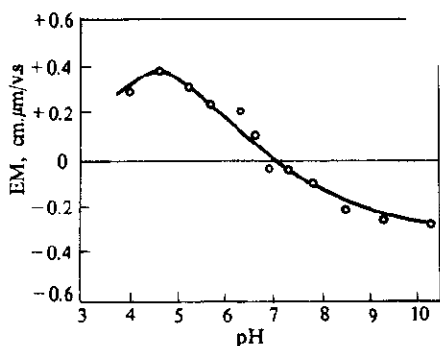


Fig. 4 The electrophoretic mobilities of new formed hydroxide floccus as a function of pH in the neutralization

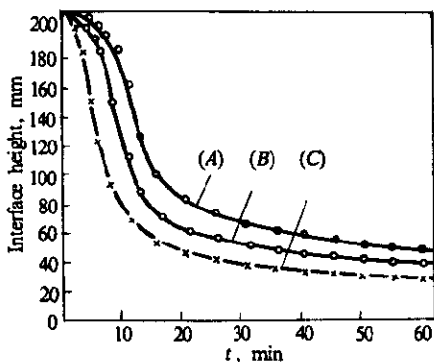


Fig. 5 Interface fall of the hydroxide floccus vs time mixing ratio (A) 1:6.7 (B) 1:8.0 (C) 1:10

mented rapidly. Thus, the interface falls displaced a rapid settling velocity during the transition zone. When the hydroxide sludge entered the compaction zone through the transition zone, the velocity of descent appreciably decreased. But the velocity of interface fall increased with increasing of the mixing ratio. The volumes of the precipitate sludge were 15–30% of the original sample volume, depending on the mixing ratio.

#### Copper removal efficiency

The heavy metals contained in AMD are removed primarily as a mixed metal hydroxide sludge in the neutralization process. Fig. 6 shows the percentage removal of copper from AMD (curve A). Other heavy metals are negligible because their concentrations in AMD are low (0.5–2 mg/L). Prior to the neutralization, concentration of copper in the synthetic

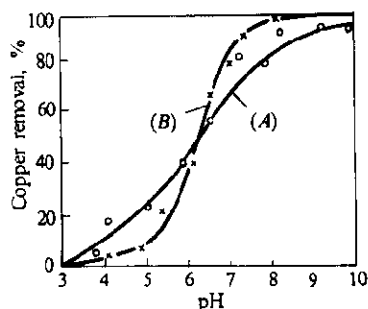


Fig. 6 Removal of copper ion at different mixing ratio in the neutralization (A): in the absence of OTP (B): in the presence of OTP

AMD was about 100 mg/L. The analysis of copper concentration in the mixed wastewater indicated that different removal efficiencies of copper from AMD during the neutralization were observed. Percentage removal of copper from AMD was about 28–98%, depending on the mixing ratio or pH value. Over the mixing ratio of 1:8, the removal efficiency increased to near 100%, only very minimal residual concentration of copper was remained in the mixed wastewater (about 0.05–0.2 mg/L). This can be attributed to the chemical precipitation of Cu(II) at the high pH. About 18–35% of copper ions might be coprecipitated by Fe(III) at pH 3.5–4.5 because the chemical precipitation of Cu(II) did not occur at the low pH

range.

The results show that the neutralization/ precipitation as a removal method of heavy metals from AMD is effective. Coprecipitation of copper ions with the primary precipitates of iron and aluminum hydroxides is also possible when the newly formed precipitate provides a very large reactive surface area for simultaneous adsorption of copper (Singh, 1983).

#### *The effects of ore tailing particles (OTP)*

When AMD was mixed with AWW containing the high concentration of suspended ore tailings, a increase of pH for the mixed wastewater was observed. It can be seen from curve B in Fig. 1 that the pH of the mixed wastewater after the neutralization is shifted to higher pH in the presence of 1500 mg / L of OTP. At the mixing ratio of 1:8, the influence of different concentrations of OTP on the neutralization of AMD is given in Fig. 7. The pH of the mixed wastewater increases with increasing concentrations of OTP. The results illustrate that the acidity in AMD can be neutralized partially by the alkaline OTP. This may be due to the cation exchange or specific adsorption on the surface of the OTP as a result of releasing hydroxyl ions in the mixing process (Davis, 1978).

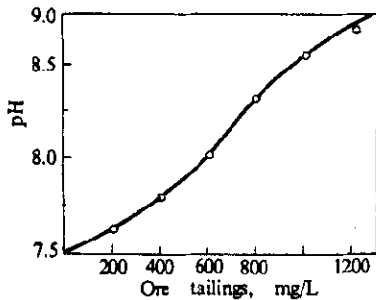


Fig. 7 The influence of concentrations of OTP on pH of the mixed wastewater at mixing ratio of 1:8.0

The effect of fine-grained ore tailing particles on removal of copper ions, as shown in curve B of Fig. 5, shows that at the same mixing ratio, the removal efficiency of copper ion exhibits a tendency of increasing in the presence of higher concentrations of ore tailing particles. Thus, apart from the neutralization on acid load, the OTP can cause a considerable abatement on heavy metal ions in AMD through cation exchange or adsorption.

In the neutralization/ flocculation, electrophoretic mobility and residual turbidity of the ore tailings suspension are shown in Fig. 8.

It is seen from Fig. 8 that the ore tailing particles (curve A) are negatively charged in the experimental pH range (pH 4.10–9.86). At pH 6.0–8.0, the mobilities of the ore tailings particles are in the range of about  $-1.5$ – $-2.0$  cm /  $\mu\text{m}$  / v / s, whereas the mobilities of the floccus

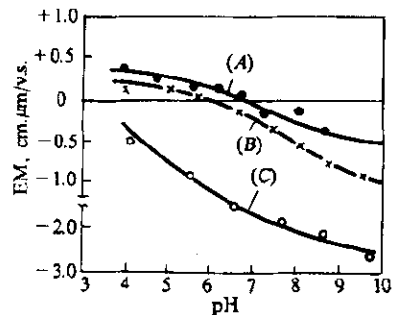


Fig. 8 The electrophoretic mobility of ore tailing particles and its floccus as a function of pH (A): 100 mg / L OTP floccus (B): 800 mg / L OTP floccus (C): ore tailing particles (OTP)

formed in the neutralization/ flocculation have different sign for different concentration of the OTP in suspension. At low concentration (100 mg/ L, (A) in Fig. 8), the changes of mobilities for coagulated ore tailing particles in pH range are approximately consistent with that of the hydroxide floccus as shown in Fig. 4. At high concentration (800 mg/ L, (B) in Fig. 8), the mobility of the ore tailing floccus approaches zero at pH 6.0–6.2, and becomes more negative with increasing pH above 6.2. The observed effect of the ore tailing concentration on the mobility may be related to form hydroxide coating on the ore tailings surface. James and Healy (1972) indicate that the adsorption of soluble hydrolysis products leads to form of a layer or a partial layer of amorphous hydroxide precipitate on the particle surface. Obviously, the mobility of coagulated ore tailing floccus depends on the precipitate coating. As the ore tailing concentration in the mixing process is increased at the constant mixing ratio or pH, the change of mobilities for the coagulated ore tailing floccus reflect the change of the hydroxide coating layer from a completely coated to a partially coated. Thus, the lower charge-reversal point at the higher concentration of the ore tailings is caused by the adsorption and precipitation of positively hydrolysis products on the ore tailing surface which forms a partial coating layer.

The results seem also to show that in the neutralization/ flocculation, the predominant species formed as the coagulant may be the weak positively charged hydroxo-complexes or hydroxides of iron and aluminum because of the effect of specific adsorption of sulfate.

The influence of ore tailing particles on the interface fall of floccus is given in Fig. 9. The results show that increasing concentrations of ore tailing particles can lead to the increase of settling velocity and the volume growth of floccus by means of the adsorption destabilization of hydrolyzed Fe and Al in AMD as well as enmeshment, bridging and adhesion of newly-formed iron and aluminum hydroxids. In addition, it may obviously improve the volume density of precipitated sludge.

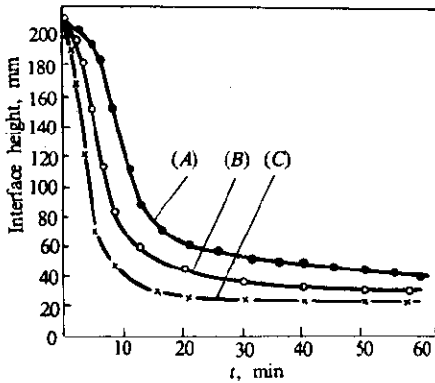


Fig. 9 Interface fall of ore tailing floccus in the neutralization/ flocculation concentrations of TPO (A): 200 mg/ L (B): 400 mg/ L (C): 2000 mg/ L

## CONCLUSION

The experimental results in this report showed that treatment of the acid mine drainage (AMD) by the neutralization/ flocculation using the alkaline wastewater was effective. In addition to neutralization of the acidity from the acid mine drainage, the removal of copper and other heavy metals has been proved to be feasible by the precipitation of hydroxides and coprecipitation with the Fe and Al hydroxides in AMD. The presence of ore tailing particles would help to increase the efficiency of the neutralization and removal efficiency for heavy



metals in AMD.

From the optimal mixing ratio for the neutralization process and from the total load of acid mine drainage and alkaline wastewater (AWW) discharged per year, it is possible to evaluate the treatment capacity for the acid mine drainage and the extent of improvement for the aquatic environment of Dawu River. Thus, the results may be of significance for design of the wastewater treatment plant by mixing two sorts of wastewater to remove the pollutants in AMD, and on assessing the impact of AMD or AWW on aquatic systems after mixing the two sorts of wastewaters in the river.

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