

Pilot test of pollution control and metal resource recovery for acid mine drainage

Bo Yan, Ge Mai, Tao Chen, Chang Lei and Xianming Xiao

ABSTRACT

The study was undertaken in order to recover the metal resources from acid mine drainage (AMD). A 300 m³/d continuous system was designed and fractional precipitation technology employed for the main metals Fe, Cu, Zn, and Mn recovery. The system was operated for six months using actual AMD *in situ*. The chemicals' input and also the retention time was optimized. Furthermore, the material balance was investigated. With the system, the heavy metals of the effluent after the Mn neutralization precipitation were below the threshold value of the Chinese integrated wastewater discharge limit. The precipitates generated contained 42%, 12%, 31%, and 18% for Fe, Cu, Zn, and Mn, respectively, and the recovery rates of Fe, Cu, Zn, and Mn were 82%, 79%, 83%, and 83%, respectively. The yield range of the precipitate had significant correlation with the influent metal content. Using the X-ray diffraction analysis, the refinement for Fe, Cu, and Zn could be achieved through the processes of roasting and floatation. Cost-benefit was also discussed; the benefit from the recycled metal was able to pay for the cost of chemical reagents used. Most important of all, through the use of this technology, the frustrating sludge problems were solved.

Key words | acid mine drainage, fractional selective precipitation, *in situ* pilot test, metal recovery

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NOMENCLATURE

HM	heavy metal
AMD	acid mine drainage
XRD	X-ray diffraction analysis
RES _M	residual M in aqueous phase after precipitation process
CON _M	metal content of precipitate
SDC _M	metal sedimentation cylinder
CRC _M	chemical precipitation reaction cylinder
PCC _M	precipitate concentration cylinder
MOR _M	ratio of the molar precipitant added to the total molar content of a specific metal
Subscript M	denotes a specific metal

INTRODUCTION

Acid mine drainage (AMD) causes severe environmental pollution because of its high heavy metal content and strong acidity (Gokcekus *et al.* 2003). Heavy metals

(HM), including Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn, have the potential to become a major contamination source and are extremely detrimental to the aquatic and soil environment in general (Kim *et al.* 2009; Anju & Banerjee 2010). Most active treatment involves pH adjustment by adding an alkaline material, and removal by precipitation as a result of the formation of oxy/hydroxides. One of the most significant problems in the treatment of AMD is the large volumes of precipitate. The ultimate disposal of AMD precipitate is difficult because of the low economic value of the sludge, substantial difficulties in dewatering, and the high cost of offsite haulage (Dempsey *et al.* 2001; Cui *et al.* 2012). Furthermore, heavy metals like Cu and Zn adsorbed in precipitation are easily extracted if the sludge is exposed to some acid conditions (McDonald & Webb 2006). The heavy metals extracted produce secondary pollution. Dabaoshan Mine, one of the largest copper-sulfide mines in Guangdong Province, produced about 15,000 m³/d of AMD emissions that contaminated surface water, groundwater, and soil in the downstream

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region. The average concentrations of Cu, Zn, and Pb in the surrounding soil were all above the natural soil background levels (Zhao *et al.* 2012). A 15,000 m³/d AMD treatment plant with chemical neutralization precipitation technology was constructed and operated. The quantity of dried precipitate reached 20 t/d and the disposal of the precipitate became a difficult task. A lab-scale comprehensive investigation into the recycling of Fe, Cu, Zn, and Mn from the AMD (Chen *et al.* 2014) was undertaken. With fractional selective precipitation, HMs contained in the effluent were below the threshold value of the Chinese integrated wastewater discharge limits, with Fe, Cu, Zn, and Mn contents of particular settling sludge being 46%, 12%, 31%, and 8.0%, respectively. With this technology, 100%, 86%, 88%, and 80% of Fe, Cu, Zn, and Mn, respectively, was recovered from AMD. Above all, the sludge could be reused and no residues were generated. In this study, an *in situ* pilot-scale fractional precipitation system was constructed and operated to determine the removal rate for the AMD. For the tests, actual AMD was applied to discover the effect of the operating parameters, such as chemicals' input and retention time. The ultimate objective was to optimize the main parameters needed for designing a full-scale treatment plant.

METHODS

Pilot-scale plant design

A typical poly-metallic mine, the Dabaoshan Mine is in northern Guangdong Province, Southern China. A pilot-scale test of 300 m³/d was constructed *in situ* to treat the AMD which was continuously flowing from the mine region. The AMD was oxidized after primary suspended solids (SS) removal with the pre-sedimentation process. Then, Fe, Cu, Zn, and Mn were removed sequentially with a four-step fractional precipitation procedure. The precipitate was concentrated and pressure filtered, the filtrate was re-pumped to the pre-sedimentation cylinder, and the dehydrated precipitate stored for further refinement. The overflow after the Mn removal process was pumped. The main facility had been installed as shown in Figure 1. Five vertical sedimentation cylinders (SDC) were employed for metal precipitation and 1.2 m inclined tubes were added in the cylinders to improve the treatment loading, and the inclination was 60°. A conical hopper was installed at the bottom of each cylinder with an angle of 60° to collect the precipitate. The main structures are illustrated in Figure S1 (available in the online version of this paper). The height and diameter of the chemical reaction cylinders (CRC) installed were 3,200 mm and 500 mm, respectively. Draft-tube horn

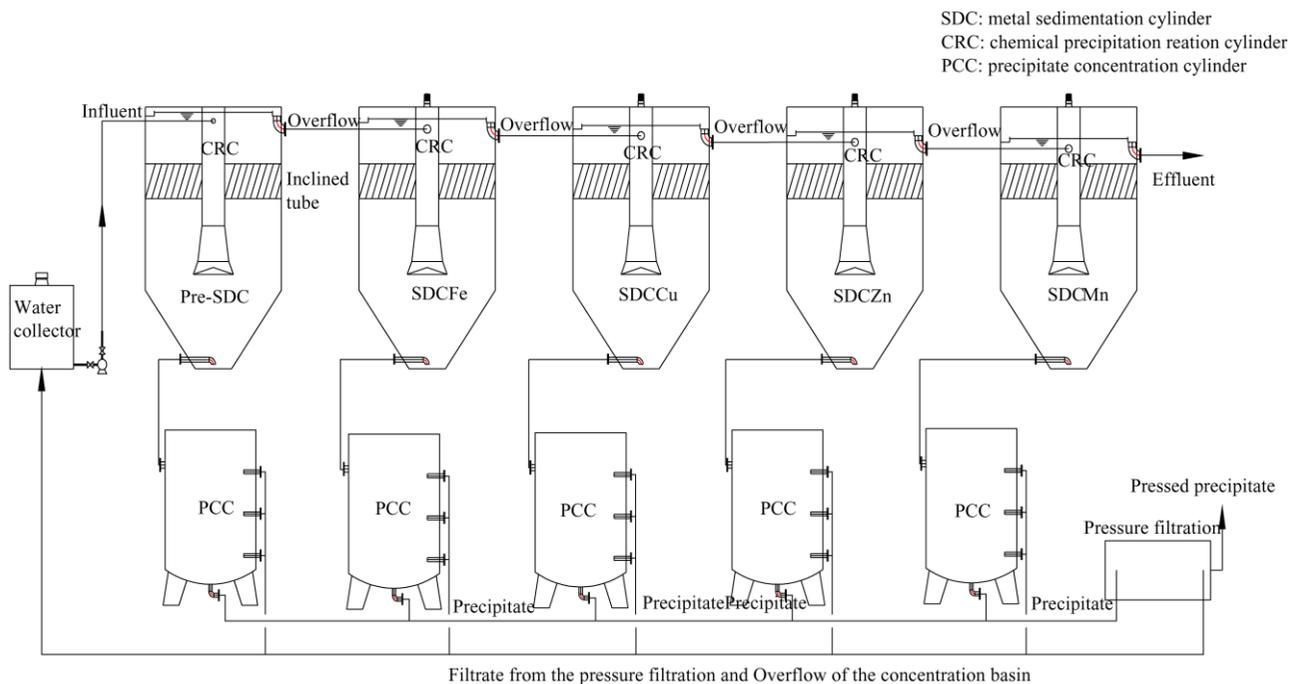


Figure 1 | Pilot-scale continuous flow plant of the fractional precipitation process.

mouths were installed at the bottom of the cylinders and a draft-tube reflection plate installed at the bottom of the horn mouths. The overflow of SDC flowed to the next CRC for its gravitational potential, and the precipitates were pumped to the corresponding concentration cylinder (PCC). The concentrated precipitate was dehydrated with the belt pressure filter. The diameter of SDCs were 3,000 mm, the efficient volume of SDCs were 19.2 m³, 18.4 m³, 17.5 m³, 16.7 m³, and 15.8 m³, respectively. The retention time (h) of the continuous system could be controlled by the influent flow rate. Table 1 shows the retention of the different precipitation cylinders with varied flow rate. The pH value was regulated with the addition of alkaline which was added at the surface of the CRC, the precipitator for Cu and Zn was added at the overflow of SDC_{Fe} and SDC_{Cu}, and the dosage of the reagents was regulated with the flow control pump.

Analysis methods and calculation process

To measure total recoverable and dissolved metals of samples obtained, method 3005A (acid digestion procedure for waters) was used (US EPA 1992), and to measure the metal contents of the precipitate, method 3050A (acid digestion procedure for solids) was used (US EPA 1996). After the digestion process, major metals were determined by the use of an atomic absorption spectrophotometer (AAS, Hitachi ZA3000, Japan), while minor metals at significantly low concentrations were determined through inductively coupled plasma mass spectrometry (ICP-MS) (Angilent 7500, USA) (APHA 2005). The quantification limit for AAS was 0.02 mg/L, while it was 0.5 µg/L for ICP-MS. To measure the Fe(II) concentration on-site, the sample was filtered using a 0.45-µm pore membrane filter, then ferrozine iron reagent was added into the filtrate, and after 3 min Fe(II) was measured by UV-visible absorption (DR 2800, Hach) at 510 nm. The quantification limits of UV-visible absorption is 0.5 mg/L. The pH value of the water was measured by a

glass electrode (E-201, Leici), and the references used were pH buffer fluids (pH 4.00, 6.86, and 9.18). X-ray diffraction (XRD, Rigaku) analysis was used to determine the mineralogical properties of the precipitates from the sludge produced. The XRD was operated at 30 mA and 40 kV, the scanning speed was 5°/min, the step width was 0.02° and the initial and final angles were 3° and 80°, respectively.

The removal rate for the target metal species (RER_M) was obtained using the following equation:

$$\text{RER}_M(\%) = \frac{C_{\text{influent}} - C_{\text{effluent}}}{C_{\text{influent}}} \times 100\% \quad (1)$$

where C_{influent} and C_{effluent} represent the average concentrations of the metal species in the influent and effluent from the corresponding treatment cylinder.

The recovery rate for target metal species (REC_M) was obtained using the following equation:

$$\text{REC}_M = \frac{M_{\text{dp}} \times \text{CON}_M}{C_{\text{influent}} \times Q} \times 100\% \quad (2)$$

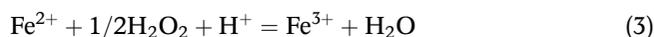
where M_{dp} represents the weight of dried precipitate generated from a specific volume of AMD, and Q is the flow rate of the influent.

RESULTS AND DISCUSSION

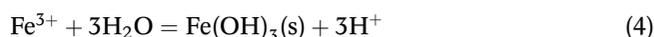
Optimization of the chemicals input and the retention time

Oxidation and precipitation of Fe

As we had investigated, the oxidation of Fe(II) needs to be carried out before the AMD is neutralized for selective removal of Fe (Zvimba et al. 2013). With the addition of H₂O₂, the oxidation of Fe(II) can be expressed as shown in Equation (3):



The oxidized species, Fe(III), is instantly hydrolyzed by the supply of alkalinity to Fe(III) hydroxide compounds which eventually precipitate (Equation (4)):



The effect of the H₂O₂ dosage on the removal rates of Fe, Cu, Zn, and Mn at a pH of 3.7 with flow rate of 10 m³/h is

Table 1 | Retention time under varied flow rate

Flow rate (m ³ /h)	Pre-SDC (h)	SDC _{Fe} (h)	SDC _{Cu} (h)	SDC _{Zn} (h)	SDC _{Mn} (h)
6.5	2.95	2.83	2.69	2.57	2.43
8	2.4	2.3	2.19	2.1	2.0
10	1.92	1.84	1.75	1.67	1.58
12	1.60	1.53	1.46	1.39	1.32
14	1.37	1.31	1.25	1.19	1.13
15	1.28	1.23	1.17	1.11	1.05

illustrated in Figure 2. The removal rate of Fe increased from 69 to 84% when the H_2O_2 dosage increased from 0 to 0.15 mL/L, and reached 97% when the H_2O_2 dosage was 0.3 mL/L; meanwhile, lower removal rates were maintained for Cu, Zn, and Mn. The Cu removal rate dropped to 10% with the addition of H_2O_2 , while the removal rates of Zn and Mn were as little as 1.8% and 0.30%, respectively.

The effect of pH value on RER_{Fe} and CON_{Fe} was investigated at the flow rate of $10 \text{ m}^3/\text{h}$, the H_2O_2 addition was fixed at 0.30 mL/L, and $2 \text{ g}/\text{m}^3$ polyacrylamide (PAM) had been added to accelerate the precipitation process. As shown in Figure 3, with NaOH added, the RER_{Fe} increased gradually, and reached 98% when the pH value was 4.0. On the contrary, the CON_{Fe} declined and RES_{Fe} also declined with the pH value. When CaO had been employed, the trend for RER_{Fe} and CON_{Fe} with the pH value was similar to NaOH being used. The RER_{Fe} and CON_{Fe} was 96% and 42%, respectively,

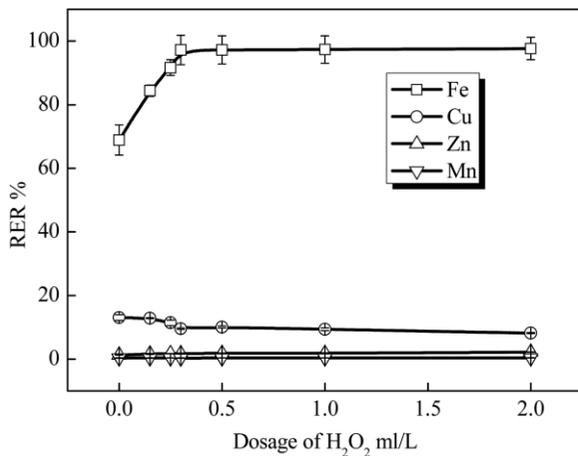


Figure 2 | Effect of the H_2O_2 on the metal removal rate (pH = 3.7, flow rate = $10 \text{ m}^3/\text{h}$).

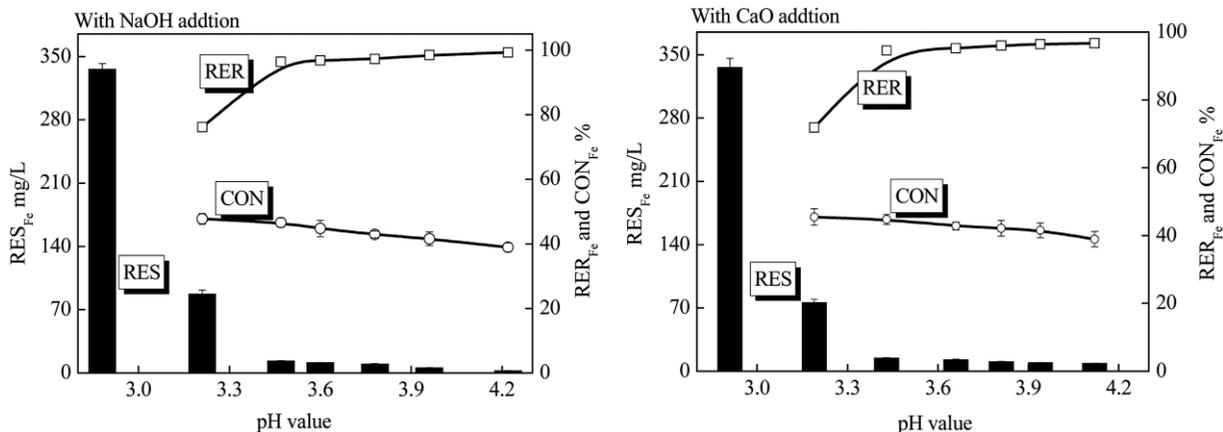


Figure 3 | RES, RER, and CON of Fe precipitation process with varied pH value (flow rate = $10 \text{ m}^3/\text{h}$, $\text{H}_2\text{O}_2 = 0.30 \text{ mL}/\text{L}$).

with a pH value of 3.8. Owing to its low cost, CaO was used for the further neutralization precipitation process.

Precipitation of Cu and Zn with the sulfide addition

Cu could be precipitated prior to Zn and Mn, according to the solubility products of the metal sulfides: Cu_2S (10^{-47}) < CuS (10^{-44}) < Fe_2S_3 (10^{-36}) < ZnS (10^{-23}) < MnS (10^{-15}) < FeS (10^{-19}) (Banfalvi 2006). A 2.0 wt.% Na_2S solution was used as a precipitator and molar ratios of Na_2S to Cu content (MOR_{Cu}) were investigated within a range of 1.5–3.0, the flow rate was $10 \text{ m}^3/\text{h}$, $2 \text{ g}/\text{m}^3$ PAM was added to accelerate the precipitation process. As shown in Figure 4, the RER_{Cu} was only 72% when the MOR_{Cu} was 1.5, the reason for the low RER being that other metal sulfide precipitates generated NiS, CoS, and so on. The fine particle size of CuS under low S^{2-} concentration was another reason (Veeken et al. 2003). The RER reached 97% with MOR_{Cu} of 2.0, and the RES_{Cu} and the CON_{Cu} were 0.41 mg/L and 13%, respectively. With higher MOR, the CON_{Cu} decreased, so the best MOR for Cu precipitation was chosen as 2.0.

The overflow after the Cu removal process was used for the Zn removal, and a 2.0 wt.% Na_2S solution was used as a Zn precipitator, molar ratio range of Na_2S and Zn (MOR_{Zn}) was between 1.0 and 3.02 g/m^3 and PAM was added to accelerate the precipitation process. As shown in Figure 4, with MOR_{Zn} of 1.74, the RES_{Zn} was 1.81 mg/L, and RER_{Zn} and CON_{Zn} reached 94% and 31%, respectively.

Neutralization precipitation for Mn

After the Zn removal process, Mn was 45 mg/L and was the main heavy metal still contained in the drainage. CaO was used to adjust the pH value for the neutralization

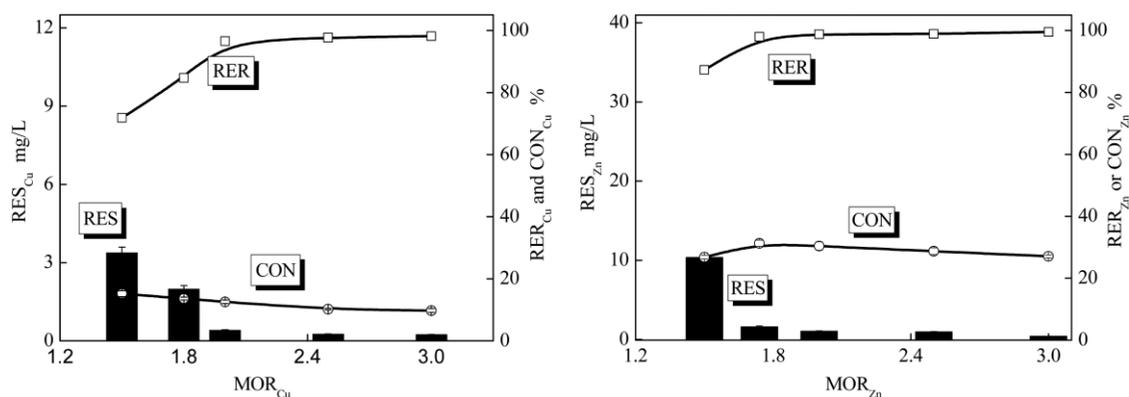


Figure 4 | Effect of MOR for the RES, RER, and CON of Cu and Zn precipitation process (flow rate = 10 m³/h).

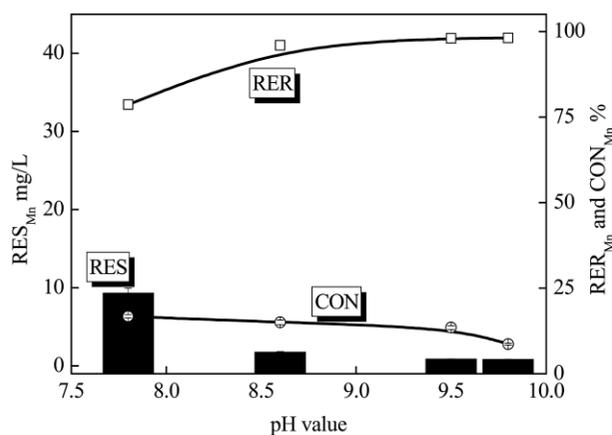


Figure 5 | Effect of pH on the Mn treatment (flow rate = 10 m³/h).

precipitation process. The flow rate was regulated at 10 m³/h, and 2 g/m³ PAM was added to accelerate the precipitation process. As shown in Figure 5, RER_{Mn} was increased with the pH value, and the RES_{Mn} was 0.97 mg/L with a pH of 8.6. The CON_{Mn} decreased with the increased pH value for greater yield of the precipitate.

Retention time optimization

The retention time was the primary factor for the facility design (Al-Sammaraee & Chan 2009), as without sufficient retention time for the precipitation process, alum particles would up flow and the water quality would worsen with increased SS. With the optimized chemicals, the flow rate

Table 2 | Effect of the retention time on the metals' precipitation process

	Retention time (h)	Flow rate (m ³ /h)	pH	Concentration (mg/L)		RER (%)	CON (%)	SS (mg/L)
				Influent	Effluent			
SDC _{Fe}	1.84	10	3.9	317.25 ± 13.69	9.69 ± 0.58	97	41	20 ± 1
	1.53	12	4.0	322.17 ± 3.71	9.85 ± 0.45	97	41	25 ± 1
	1.31	14	3.8	322.5 ± 14.14	13.33 ± 0.07	96	41	28 ± 1
	1.23	15	3.8	325.17 ± 5.72	16.35 ± 0.41	95	41	119 ± 4
SDC _{Cu}	1.75	10	3.9	13.13 ± 0.15	0.45 ± 0.003	97	12	16 ± 1
	1.46	12	4.0	13.58 ± 0.92	0.61 ± 0.001	96	13	15 ± 0
	1.25	14	3.8	14.32 ± 0.22	0.82 ± 0.032	94	13	22 ± 1
	1.17	15	3.8	14.47 ± 1.05	0.93 ± 0.050	94	12	51 ± 2
SDC _{Zn}	1.67	10	4.6	87.70 ± 1.73	1.06 ± 0.02	99	31	18 ± 1
	1.39	12	4.6	84.25 ± 5.30	1.05 ± 0.06	99	29	21 ± 1
	1.19	14	4.6	80.58 ± 1.16	1.13 ± 0.08	99	28	25 ± 2
	1.11	15	4.6	81.39 ± 3.69	1.78 ± 0.01	98	29	49 ± 2
SDC _{Mn}	1.58	10	8.6	58.13 ± 1.43	1.08 ± 0.06	98	7.6	11 ± 0
	1.32	12	8.7	62.05 ± 0.09	1.15 ± 0.08	98	7.6	11 ± 1
	1.13	14	8.6	59.82 ± 3.66	1.32 ± 0.03	98	7.4	27 ± 0
	1.05	15	8.7	60.28 ± 3.54	2.25 ± 0.13	96	5.6	79 ± 2

was regulated from 10 m³/h to 15 m³/h. As shown in Table 2, the retention time has little effect on the RER and also the CON of metals. However, without sufficient retention time, the mass alum particles would up float during the precipitation process and the effluent would turn turbid, changing the SS of the effluent dramatically. The best flow rate for the fractional precipitation was 14 m³/h, and the retention time for SDC_{Fe}, SDC_{Cu}, SDC_{Zn}, and SDC_{Mn} was 1.31 h, 1.25 h, 1.19 h, and 1.13 h, respectively. Effluents photos of each SDB are shown in Figure S2 (available in the online version of this paper).

Removal of other HMs

The flow rate was adjusted to 14 m³/h, and metals contained in the overflow of each SDC are listed in Table 3. Since, for the co-precipitation (Klerk et al. 2012; Bahadir et al. 2014), the RER for As and Cr were high by the neutralization process, the efficiencies reached were 72% and 84%. RER for thiophile elements such as Ni and Co (Chen & Yan 2012) reached 97% and 89%, respectively, with the addition of sulfide. Owing to the discrepancy of the solubility products, RER for Pb and Zn was 98% and 68%, respectively, within the SDC_{Zn}. The residual minor metals were removed with the last neutralization precipitation. Effluent concentration of Cr, Ni, Co, As, Cd, and Pb were lower than 0.01 mg/L, and the RER for these metals were higher than 97%, with the RER for Fe, Cu, Zn, and Mn being 100%, 100%, 100%, and 99%, respectively. The heavy metals of the effluent after the Mn neutralization precipitation were below the threshold value of the Chinese integrated wastewater discharge limit (GB8978-1996).

Continuous operation

The continuous operation of the pilot-scale plant was carried out for 20 days with a flow rate of 14 m³/d. The pH for Fe neutralization and Mn neutralization precipitation were regulated at 3.8 and 8.6, respectively. The MOR_{Cu} and MOR_{Zn} were 2.0 and 2 g/m³, and PAM was added to accelerate the precipitation process. As shown in Figure 6, the mean value of RER for Fe, Cu, Zn, and Mn were 96%, 97%, 98%, and 99%, respectively. The variation for the RER was no more than 5%. The metal content of each effluent was also stable, thus, with this system, the HMs could be removed stably. As shown in Figure 7, the dried precipitate yield of each SDB was 543.52–685.32 g/m³, 86.25–114.78 g/m³, 202.85–233.19 g/m³, and 570.76–768.43 g/m³, respectively. The yield had a significant relationship with

Table 3 | RES and RER of each SDC (flow rate = 14 m³/h, MOR_{Cu} = 2.0, MOR_{Zn} = 2.0)

Items	pH	Fe	Cu	Zn	Mn	Cr	Co	Ni	As	Cd	Pb
Raw AMD mg/L	2.64	361.68 ± 9.11	17.73 ± 0.15	91.07 ± 0.81	66.16 ± 3.28	0.08 ± 0.001	0.38 ± 0.01	0.26 ± 0.02	0.06 ± 0.001	0.36 ± 0.01	1.47 ± 0.10
SDC _{Fe} RES mg/L	3.8	5.61 ± 0.39	15.7 ± 1.18	89.5 ± 4.33	65.9 ± 2.93	0.01 ± 0.001	0.30 ± 0.01	0.25 ± 0.01	0.02 ± 0.001	0.31 ± 0.01	1.18 ± 0.07
SDC _{Fe} RER%	/	98	11	1.7	0.39	88	21	3.9	67	14	20
SDC _{Cu} RES mg/L	3.8	5.58 ± 0.44	0.54 ± 0.02	78.88 ± 5.66	64.72 ± 1.22	0.01 ± 0.00	0.04 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.25 ± 0.01	0.85 ± 0.02
SDC _{Cu} RER %	/	98	97	13	2.2	88	89	96	83	31	42
SDC _{Zn} RES mg/L	4.6	4.25 ± 0.02	0	1.60 ± 0.06	63.69 ± 3.52	0	0	0	0	0.11 ± 0.01	0.61 ± 0.01
SDC _{Zn} RER %	/	99	100	98	3.7	99	100	100	98	69	68
SDC _{Mn} RES mg/L	8.5	0.95 ± 0.05	nd	0.14 ± 0.01	0.93 ± 0.05	nd	0.01 ± 0.00	nd	0	0	0.01 ± 0.00
SDC _{Mn} RER %	/	100	100	100	99	100	97	100	100	100	100

nd, under detection of instrument with the standard method.

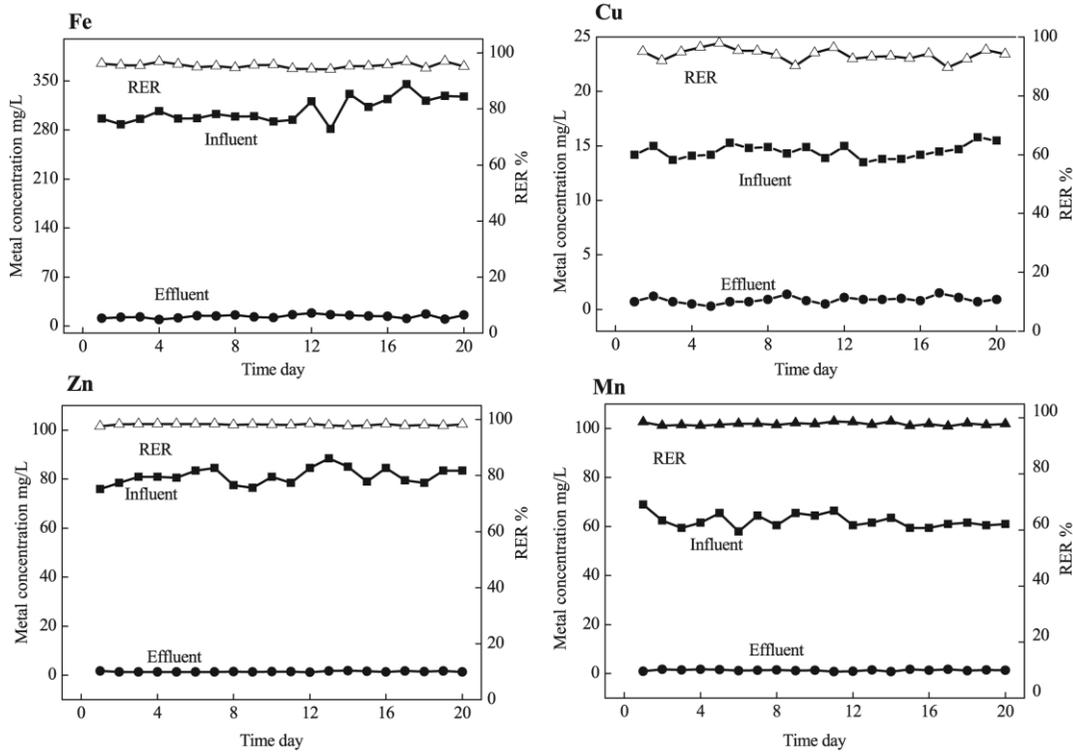


Figure 6 | Removal rate of each precipitation cylinder and metal concentration of the influent and effluent of each cylinder for 20 days (flow rate = 14 m³/h, MOR_{Cu} = 2.0, MOR_{Zn} = 2.0).

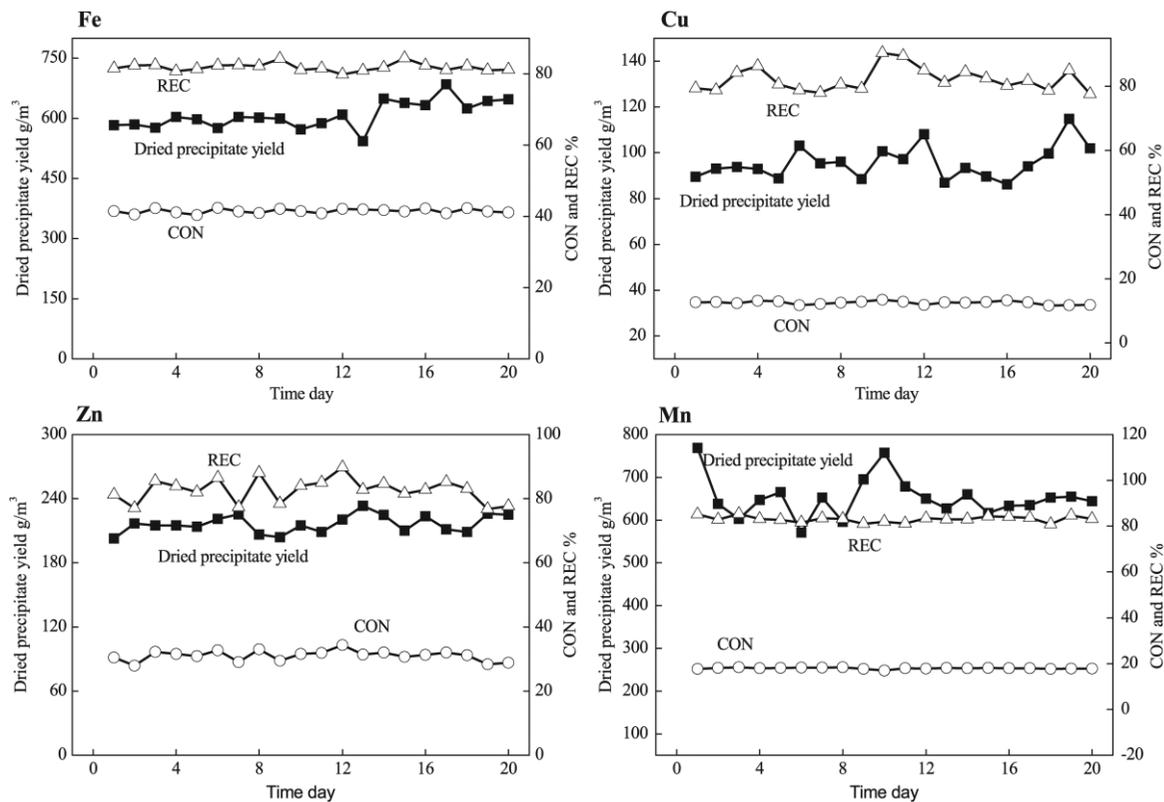


Figure 7 | Variation of metal recovery rate, dried precipitate yield, metal content of the precipitate and water ratio of the pressed precipitate during 20 days (flow rate = 14 m³/h, MOR_{Cu} = 2.0, MOR_{Zn} = 2.0).

the metal content of the influent. The main metal contents of recovered precipitates were 41%, 12%, 31%, and 18% for Fe, Cu, Zn, and Mn, respectively. Recovery rates for Fe, Cu, Zn, and Mn were 82%, 79%, 83%, and 83%, respectively; the reason for the value being lower than RER of each SDC was due to the metal loss during the precipitates pressure filtration process. It can be concluded that, with the four-step fractional selective precipitation treatment, the HMs could be removed stably and the four metals could be recovered. Furthermore, parameters tested for the precipitation process could be used for the engineering design.

Precipitate analysis

Metal contents of the four precipitates are shown in Table 4. The dominating metals of these precipitates were Ca, Mg, Al, Fe, Cu, Zn, and Mn, and the total amount of these metals contained in the neutralization precipitation process

reached 52% and 49%, respectively. However, the total amount was only 33%, and 46% contained in the sulfide precipitation. As previously known, if metals precipitated as sulfides, the mass fraction of all the compounds was only about 58% and 75% through the chemical calculation. Thus, some metals might not combine with sulfide.

Fine powder XRD analysis of the four precipitates is shown in Figure 8. CuS and ZnS were the main phases in the copper and zinc precipitates according to the XRD analysis, but some sulfates like $\text{Al}_2(\text{SO}_4)_3$ existed. The CuS and ZnS have perfect crystal structure by XRD analysis, they are suitable for further floatation refinement process (Avila *et al.* 2011) and the floatation refinement tests that were carried out in our previous study (Chen *et al.* 2014). The mineral phases of Fe precipitate were identified as jarosite ($\text{NaFe}_3(\text{OH})(\text{SO}_4)_2$), MgFeAlO_4 , and FeAlO_4 . The mineral phases were different from a previous study (Regenspurg *et al.* 2004). The goethite (FeOOH) was the main

Table 4 | Metal contents of dried precipitates (flow rate = 14 m³/h, MOR_{Cu} = 2.0, MOR_{Zn} = 2.0)

	Al	Ca	Mg	Fe	Cu	Zn	Mn	Cr	Co	Ni	As	Cd	Pb
Fe precipitate (%)	5.8	2.4	1.7	42	0.23	0.18	0.03	0.01	0.01	0.00	0.00	0.01	0.03
Cu precipitate (%)	7.9	1.6	3.2	0.1	12	5.9	1.9	0.00	0.41	0.38	0.02	0.10	0.52
Zn precipitate (%)	6.3	3.9	2.3	1.0	0.42	31	0.80	0.01	0.03	0.01	0.01	0.11	0.19
Mn precipitate (%)	0.7	15	15	1.0	0	0.46	18	0.00	0.00	0.00	0.00	0.04	0.10

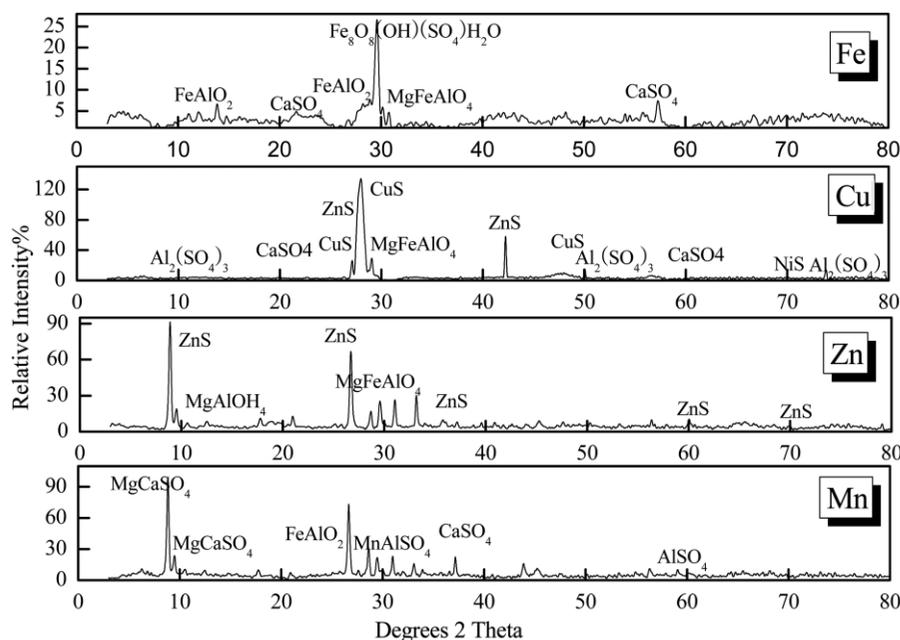


Figure 8 | XRD analysis of precipitates.

Table 5 | Chemical agents used and the cost analysis

Agents	H ₂ O ₂	Ca(OH) ₂	Na ₂ S	PAM
Usage (kg/m ³)	0.300	0.133	0.313	0.02
Unit price (USD/kg)	0.19	0.06	0.47	5.32
Cost (USD/m ³)	0.06	0.09	0.15	0.11

Table 6 | Value of recycled metals

	SDC _{Fe}	SDC _{Cu}	SDC _{Zn}
Mean value of metals contained (g/m ³)	330.17	14.68	80.40
Recovery rate (%)	82	79	83
Mean value of metals recovered (g/m ³)	270.08	11.58	66.99
Price of metals (USD/kg)	0.4	9.67	3.22
Value recycled per tank (USD/m ³)	0.11	0.11	0.22

mineral during the natural neutralization, the main reason for the difference being the reaction time (Kumpulainen *et al.* 2007); the Fe precipitate could be refined with a roasting process (Chen *et al.* 2014). XRD did not reveal the presence of any crystallized minerals of Mn; this would indicate that Mn precipitate was too amorphous, thus, it only can be used for replacement of the cement materials.

Cost-benefit analysis

The cost of chemicals was the main expenditure in the process. As seen from Table 5, the cost of agents used was 0.43 USD per cubic meter AMD.

Based on the previous market investigation (Chen *et al.* 2014), the precipitates can be sold. The value of products was calculated as the metals recycled. As shown in Table 6, the value of the recycled metal was 0.44 USD per cubic meter AMD. The benefit from the recycled metal could pay for the cost of the chemical reagents used. The detailed cost-benefit analysis is shown in the Supplementary material (available in the online version of this paper). Furthermore, with this technology procedure, the frustrating sludge problems were solved. Thus, the fractional precipitation process was a profitable way for pollution control and metal resource recovery of AMD.

CONCLUSION

A pilot-scale fractional precipitation utility was designed and employed for the metal recovery from acid mine drainage.

The system was composed of chemical reaction cylinders, vertical sedimentation cylinders installed with inclined tubes, precipitate concentration cylinders and belt pressure filters. After several months running, it can be concluded that, with neutralization precipitation and the sulfide precipitation process, the pH values for Fe and Mn precipitation were 3.9 and 8.6, respectively, and the MOR for Cu and Zn precipitation was 2.0. Before the Fe neutralization precipitation process 0.30 mL/L H₂O₂ had to be added for Fe(II) oxidation. The SS of the effluent increased with insufficient retention time and the water quality worsened. With the vertical sedimentation cylinders installed with inclined tubes, the best retention times for Fe, Cu, Zn, and Mn were 1.31 h, 1.25 h, 1.19 h, and 1.13 h, respectively. Under the optimized conditions, the heavy metals of the effluent were below the threshold value of the Chinese Integrated Wastewater Discharge Limit (1996). Parameters tested for the precipitation process could be used for engineering design. Furthermore, the recovery rate of Fe, Cu, Zn, and Mn were 82%, 79%, 83%, and 83%, respectively. The main metal content of recovered precipitates (dried) were 42%, 12%, 31%, and 18% for Fe, Cu, Zn, and Mn, respectively. Mineral phases of Fe, Cu, and Zn were detected with the XRD, while the Mn precipitates were too amorphous. The results suggest the refinement of Fe, Cu, and Zn could be realized through a roast and floatation process. As for the cost-benefit analysis, the benefit from the metal recycled could pay for the cost of chemical reagents used, and with this technology procedure, the frustrating sludge problems were solved. Thus the fractional precipitation process was a profitable way for metal resource recovery from a large body of AMD.

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