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Pollution control and metal resource recovery for acid mine drainage

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ABSTRACT

Although the metals contained in acid mine drainage (AMD) are considered environmental pollutants, they may also be valuable resources. The traditional chemical precipitation processes for AMD not only produce large amounts of sludge, but also make it difficult to recycle the waste metals. This study comprehensively investigated the recycling of Fe, Cu, Zn and Mn from AMD. Ferrous ions were first oxidised by 0.15 ml/L 30% H_2O_2, and then a four-step fractional precipitation was applied with the selective addition of $Ca(OH)_2$ and Na_2S solutions. The Fe, Cu, Zn and Mn contents of particular sludges were 45.91%, 11.58%, 31.06% and 7.95% respectively, and the recovery efficiencies of Fe, Cu, Zn and Mn from AMD reached 99.51%, 86.09%, 87.87% and 79.71%, respectively. The metals contained in the effluent were below the Code of Federal Regulations (CFR) limits after the Mn precipitation process. Technology for the complete reuse of the sludge was also tested. Fe oxide red was obtained by roasting the Fe sludge for 30 min at a temperature of 500 °C, resulting in a Fe_2O_3 content of 85.18%. Cu and Zn crude concentrates were generated by a flotation process; the Cu and Zn contents of these concentrates were 35.72% and 55.13% respectively, and the recovery efficiencies of the Cu and Zn were 72.66% and 76.18%, respectively. The Mn sludge obtained can be used in cement mixes to replace 45% of ordinary Portland cement (OPC). Based on the technology tested, a comprehensive metal recovery process is proposed here for the control of metal pollution and metal recovery from AMD.

1. Introduction

Acid mine drainage (AMD) causes severe environmental pollution because of its high heavy metal content and strong acidity (Gray, 1998). Heavy metals, including Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn, have the potential to become major contamination sources and are often extremely detrimental to aquatic and soil environments (Anju and Banerjee, 2010; Kim et al., 2009). As a typical poly-metallic mine, and one of the biggest opencast mines in Southern China, the Dabaoshan Mine region in northern Guangdong province was one of the largest copper mining and refining centres during the Song Dynasty (960–1279 AD) (Chen et al., 2007). The Liwu mud-retaining dam (LWMRD), with a capacity of 20 million cubic metres, was constructed in 1979 to retain the waste rock produced by the mine. However, large quantities of mine tailings have been dumped by illegal miners, and illegal pits have been connected to the LWMRD. Approximately 15,000 m^3/day of AMD has been produced by the LWMRD, contaminating surface water, groundwater and soil downstream from the mine. The heavy metal levels detected have been above the limits set in the Chinese National Standards for Drinking Water (Chen et al., 2007), and the average concentrations of Cu, Zn, Cd and Pb in the surrounding soil have all been above the natural soil background levels (Zhao et al., 2012). Zhuang et al. (2009) found that the heavy metals accumulated in the food crops (rice and vegetables) grown around the mine posed a serious health risk to the local population.

There are currently several methods used to treat AMD, including chemical precipitation, solvent extraction, reverse osmosis, ultrafiltration, electrodialysis, ion exchange/adsorption and wetland treatments (Bruggen and Vandecasteele, 2002; Kongsricharoern and Polprasert, 1995; Lazaridis et al., 2004; USEPA, 2000; Ujang and Anderson, 1996; Mitsch and Wise, 1998). Lime has commonly been used in AMD treatment as a neutraliser and precipitator in chemical precipitation methodology (Pepe et al., 2007). However, metal precipitation investigations have only been carried out in attempts to reduce the metal concentrations to below those of the waste water emission standard requirements. A 15,000 m^3/day AMD treatment plant with chemical precipitation technology was constructed downstream of the LWMRD in 2010. The sludge level reached 100 t/day (with a water content of 80 wt.%), and disposing of it became extremely difficult. The sludge was transported back to the LWMRD, introducing secondary pollution through the dissolution of metal hydroxides and the release of heavy metals from the sludge in the low pH environment. It then became worth considering the recovery of these metals. Selective precipitation has been tested for the recovery of the metal from the industrial waste water (Mauchauffée and Meux, 2007), the waste leaching solution (Innocenzi and Vegliò, 2012) and the mine waste water

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(Hammack and Edenborn, 1992; Hammack et al., 1994). Mechanisms for selective precipitation are based on the difference between the metal compounds' solubility products (Mauchauffée and Meux, 2007). Precipitators commonly used include sodium hydroxide, sodium sulphide and sodium decanoate (Jameson et al., 2010; Mauchauffée et al., 2008; Michalkova et al., 2007; Tokuda et al., 2008). Sampaio et al. (2010) studied the sludge generated in the Zn selective precipitation process, and found that, with the addition of sodium sulphide, sphalerite could be detected in the sludge. This method reduced the overall volume of sludge by 70% compared to the chemical precipitation treatment with no metal recovery process (Silva et al., 2012). Furthermore, the optimization of the precipitation and sludge refinement processes allows the refined sludge to be sold to smelters, which can either recover the metals or use them in paint production (Cibati et al., 2013; Silva et al., 2012). The sludge volume would then be significantly reduced, and the metals could be effectively recycled. The metal recovery efficiencies and the refined products are similar to those reported in studies that have used solvent extraction (Bertuol et al., 2009). The method is easy, economical and does not pose the same environmental threats as those of solvent extraction. Metal recovery efficiencies and the metal contents of the sludge are affected by the metal concentration, pH value and molar ratio between the precipitator and the targeted metal during the selective precipitation process. The metal concentration is, however, lower than that of the leaching solution and the industrial waste water, which is why research into metal recovery from the AMD has been limited (Johnson and Hallberg, 2005). Furthermore, the refining of the precipitate has not been previously investigated. A fractional precipitation process and the precipitate refining process for metal resource recovery from the AMD of the LWMRD were thus investigated in this study.

Nomenclature

$\mathrm{REM_M}$	removal rate of metal from aqueous phase [%]
$\mathrm{RES_M}$	residual M in the aqueous phase after precipitation process [%]
$\mathrm{REC_M}$	recovery rate of metal from the aqueous phase [%]
$\mathrm{CON_M}$	metal content of sludge [%]
$\mathrm{MOR_M}$	ratio of the molar precipitant added to the total molar content of a specific metal
Subscript M	denotes a specific metal

2. Materials and methods

2.1. Water sampling and materials used

Water samples were taken periodically from the LWMRD at a rate of approximately 4 times per month from March 2010 to April 2011. As shown in Fig. 1, all of the samples were collected at the exit of the LWMRD and were then filtered through the 0.45 μm membrane to remove any debris or suspended solids. The samples were stored in closed high-density polyethylene bottles and kept at 4 °C. All of the chemical reagents used were analytical reagent (AR) grade chemicals.

2.2. Precipitation and sludge recovery tests

Precipitation tests were performed within a 2500 ml beaker. The actual liquid volume was 2000 ml, and a mechanical agitator (JJ-1, AoHua) was used for the precipitation chemical reaction, with an agitation rate of 100 rpm used to enhance the precipitation. The precipitator

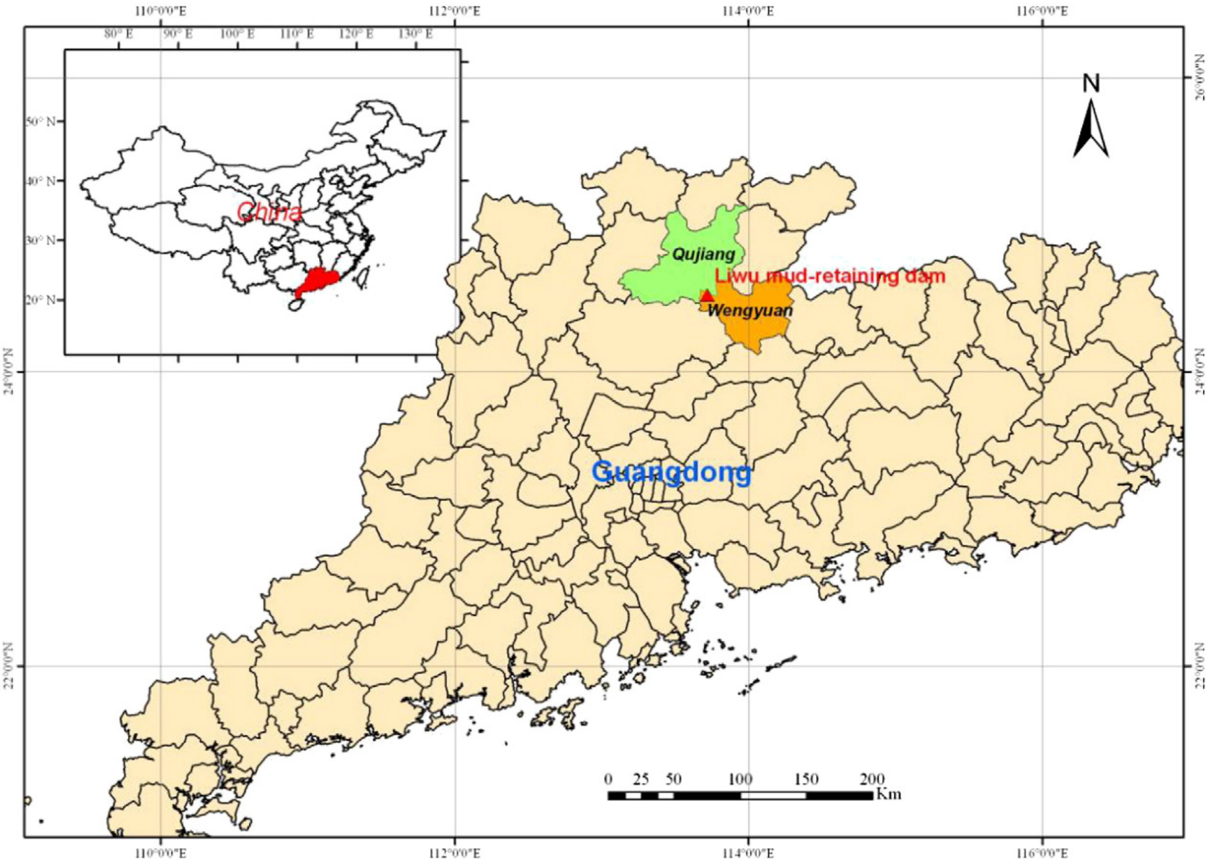

Fig. 1. Sampling location.

was added at the beginning of the agitation as a solution with a certain concentration. Each precipitation test was repeated three times. After each test, the solution was put through a 0.2 μm filter membrane, and the resulting filtrate was used for the next precipitation process, until all the targeted metals were recovered. The sludge was then air dried and roasted in a muffle furnace (DC-B 30/11). A 100 ml flotation machine (XFG5-35) was used to refine the sludge. A powder with over 95% of the volume −0.074 mm in size was obtained through dry grinding with a flight pulveriser. Water was then added to the powder to make a slurry with a pulp density of 25% before the flotation process was carried out. When the sludge was prepared for reuse in construction materials, it was washed with distilled water and dried at 105 °C. Pulverised fly ash (PFA) and ordinary Portland cement (OPC) were mixed with various different proportions of sludge for 10 min in a blender. Water was then added to homogenise the mixture, which was blended for a further 10 min. Specimens were prepared and moulded in cylinders approximately 50 mm in diameter and 80 mm high. They were then removed from the moulds and cured in a moist cabinet at 95% humidity and 20 ± 2 °C. The compressive strengths of the specimens were determined at 3, 7 and 28 days, measuring three specimens per test age. Measurements were obtained with a press testing machine (YES-100). The Chinese standard leaching test (HJ/T299-2007) was applied to the specimens, which were broken down and passed through a 9.5 mm nylon sieve, and the particles leached by a mixed acid solution (concentrated HNO_3 and concentrated H_2SO_4, with the ratio of 1:2) with a pH of 3.20 ± 0.05, for approximately 18 h in a turnover-type shaker.

2.3. Analysis methods

The precipitate samples were filtered and dried at 100 ± 5 °C to a constant weight, and were then digested with 65 wt.% nitric acid for 3 h and made up to a volume of 100 ml for analysis. The digestion and analytical process was repeated with 3 samples. The water samples and the digestion liquid were acidified with nitric acid to a pH of <2 before the metal content analyses. All water samples and digested precipitate samples were analysed for Fe, Ca, Mg, Mn, Zn, Ni, Pb and Cu content according to the Standard Method 3111 (APHA, 2005), using an atomic absorption spectrophotometer (Shimadzu AA-6300C). Minor metals, at significantly lower concentrations, were determined through inductively coupled plasma mass spectrometry (ICP-MS, Agilent 5700), and the arithmetic average of the results was given in the study. The pH value of the water was measured by a glass electrode (E-201, Leici) according to the standard method, 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 particle size distribution of the precipitate was detected with a laser particle size analyser (TopSizer, OMEC).

3. Results and discussion

3.1. Characteristics of the LWMRD AMD and problems with the existing treatment

The characteristics of the AMD from the LWMRD are presented in Table 1, which shows the mean values for all the water samples. The major metal contaminant was Fe, and others such as Cu, Zn, and Mn were also present. Ca concentrations were not included in the table summaries, as the treatment used a large amount of lime, resulting in variable Ca levels in the discharge. The AMD characteristics were significantly affected by rainfall because the LWMRD is located in a subtropical area and the rainfall from April to August is approximately 75% of the annual total. As shown in Table 2, the mean values of Cu^{2+}, Fe^{3+}, Zn^{2+} and Mn^{2+} recorded during this rainy season were almost 75% of mean values during the common season. The mean drainage was 15,000 m^3/day, and approximately 3500 kg of heavy metals were discharged each day. This huge quantity of heavy metals would rapidly destroy the ecological environment through transportation and accumulation processes (Briones, 1987; Kim et al., 2009). However, the majority of metal ions in raw AMD can be recycled as metal resources (Avila et al., 2011), and it was calculated that approximately 4967.55, 220.20, 1206.15, and 994.20 kg/day of Fe, Cu, Zn and Mn, respectively, could be recycled through proper processing.

Table 1
Annual mean value of the metals concentration of the AMD from LWMRD (mg/L, except pH).

pH	Li	Na	Mg	Al	K	Fe	Mn	Cu	Zn
2.43	0.08	3.39	67.01	63.43	5.34	331.17	66.28	14.68	80.41
Cr	Co	Ni	As	Cd	Ba	Pb	V	Rb	Tl
0.08	0.38	0.26	0.06	0.36	0.03	1.47	0.04	0.14	0.01

The process used in the LWMRD AMD plant was neutralization by the addition of lime. The technological process is illustrated in Fig. 2. The pH value was adjusted to be higher than 9.0 to remove the heavy metals by precipitation. The metal contents of the sludge are shown in Table 3. The sludge was dehydrated by a belt filter press, and the mean water mass content was reduced by 80% after the mechanical pressing process. A large amount of lime was added, resulting in a Ca content of approximately 21.18%, with Fe, Zn, Mn and Cu contents at 24.19%, 3.68%, 0.16% and 1.97%, respectively. The metal content at these levels was considered too low for direct recycling to be viable.

Approximately 20 t/day of dried sludge was generated through the neutralization treatment process, delivered to the LWMRD and mixed with AMD. The metals contained in the sludge can then be leached out by the AMD (Matlock et al., 2002; McDonald and Webb, 2006). The pH value of the LWMRD AMD was 2.43, and a sludge leaching simulation test was carried out under the same acidity conditions. The leaching characteristics of the metals contained in the sludge were then investigated, and after 8 h at room temperature the leaching solid to liquid weight ratio was 1:5. The relative amounts of leached metals were determined to be 18.12%, 2.43%, 16.43%, 12.25% and 21.31% for Cu, Pb, Zn, Mn and Fe, respectively.

3.2. Metal recovery from the AMD

The logarithm of the solubility varied linearly with the pH value, and Fe^{3+} settled completely because its hydroxide is at the lowest pH value (Cherry, 1982), unlike other metals, suggesting that separation of Fe^{3+} from the other metals could be realised. Precipitation with a common, soluble sulphide ion produces metal sulphides with extremely low solubility. At a temperature of 25 °C, the solubility products of the metals included the following: Cu_2S (10^{-47}) < CuS (10^{-44}) < Fe_2S_3 (10^{-36}) < ZnS (10^{-23}) < MnS (10^{-15}) < FeS (10^{-19}) (Banfalvi, 2006). It can be concluded that at a low concentration of S^{2-} ions, Cu would be precipitated before Zn and Mn.

Table 2
Mean value of the main metals of LWMRD AMD during different season.

Major metals	Cu	Fe	Zn	Mn
Rainy seasons (mg/L)	12.12	273.01	72.45	52.56
Common seasons (mg/L)	16.51	373.12	86.09	76.13
Mean value (mg/L)	14.68	331.17	80.41	66.28
Total discharge per day(kg/day)	220.20	4967.55	1206.15	994.20

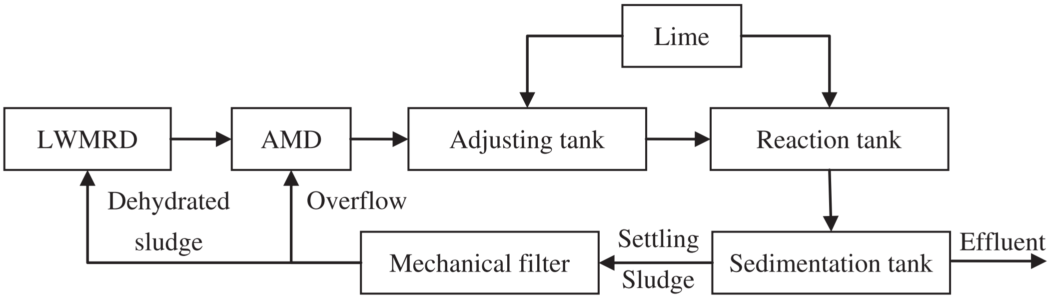

Fig. 2. The technology of the LWMRD AMD treatment plant.

3.2.1. Fe recovery from the AMD

The effect of the pH value on the removal efficiencies of Fe, Cu, Zn and Mn from the AMD was analysed by using 2 wt.% $Ca(OH)_2$ to adjust the pH. As shown in Table 4, the removal efficiencies of Fe were lower than 60% with the pH below 5.0, however Fe^{3+} could be precipitated completely with the pH below 3.5 at 25 °C (Cherry, 1982). The low removal efficiency could be attributed to the existence of Fe^{2+} which was 92.17 mg/L. For its selective removal, the oxidation of Fe^{2+} needs to be carried out before the AMD is neutralised. The oxidiser used is 30 wt.% of H_2O_2, and the effect of this on the removal efficiencies of Fe, Cu, Zn and Mn at a pH of 3.65 is illustrated in Table 5. At a pH value of 3.65, the removal rate of Fe increased from 37.30% to 94.46% when the H_2O_2 dosage was increased from 0 to 0.15 ml/L, and reached 99.51% when the H_2O_2 dosage was 0.3 ml/L. The Cu removal rate dropped to 3.19% with the addition of H_2O_2, while the removal efficiencies of Zn and Mn were as low as 2.15% and 0.37%, respectively.

As described above, Fe was precipitated from the AMD by the addition of H_2O_2 and $Ca(OH)_2$, and sludge containing Fe was obtained. The Fe content of the sludge (CON_{Fe}) was crucial in the removal process. The effect of pH on the Fe removal rate (REM_{Fe}) and the CON_{Fe} was assessed with pH values ranging from 2.8 to 4.0 and an H_2O_2 dosage of 0.30 ml/L. As shown in Fig. 3, the REM_{Fe} increased with increasing pH, while the CON_{Fe} decreased. The CON_{Fe} was 76.83% when the pH was 2.79, thus the proportion of Fe and (OH) was calculated as 1:1. Furthermore, the analysis of diffraction showed that the sludge had no diffraction peaks, indicating that the mineral in the sludge was a kind of amorphous structure. Therefore, it can be concluded that the mineral in the sludge was slightly-crystallized Ferrihydrite. The chemical formula was easy to transform with the ascending pH value (Kumpulainen et al., 2007; Regenspurg et al., 2004). The amorphous sludge was made up of semi-crystalline oxyhydroxides and hydroxysulphates (Munk et al., 2002), and metals could be adsorbed by it, the sorption increasing with the pH value (Lee et al., 2002). The CON_{Fe} values reached 48.46% and 46.13%, the REM_{Fe} values of the AMD were 98.95% and 99.49%, and the residual Fe levels of the AMD (RES_{Fe}) were 3.48 mg/L and 1.69 mg/L at pH values of 3.46 and 3.60, respectively. When the pH was approximately 4.0, the CON_{Fe} decreased from 76.83% to below 40% as the recovery approached 100%. The optimum pH range for Fe removal was thus determined to be 3.5–3.6.

3.2.2. Cu recovery from the AMD

The filtrate remaining after the Fe removal process was used as the source water for the Cu removal process. Cu could be precipitated before Zn and Mn, according to the solubility products of the metal sulphides. A 0.5 wt.% Na_2S solution was used as a precipitator (Xie et al., 2005), and the number of equivalents added was determined from the total dissolved metal content (assuming a 1:1 stoichiometry). Cu removal was investigated within a molar ratio range of Na_2S and Cu (MOR_{Cu}) between 0.8 and 3.2. The pH was not regulated after the Fe precipitation, but was measured as 3.8 before the addition of the Na_2S solution. As shown in Table 6, The REM_{Cu} was only 36.08% when the MOR_{Cu} was 1, and a MOR_{Cu} of 2 was found to be the optimal value for Cu selective precipitation. However, Sampaio et al. (2010) found that with a MOR of 1.1, the REM_{Cu} was approximately 99%. The higher MOR_{Cu} might be due to three reasons. Firstly, as the elemental analysis of the AMD illustrates (Table 1), numerous metals were present, and Ni, Co, Cd, Zn could all be precipitated with the addition of sulphide. As shown in Table 6, the REM_{Zn} was also significantly aligned with the MOR, when the MOR was less than 2.0 and the R was 0.86. Secondly, the Cu concentration was only 5% of that in the Sampaio et al. (2010) test, and it is harder for the supersaturation of the precipitate. Supersaturation, achieved by adding more sulphide, could speed up the precipitation process (Veeken et al., 2003). Furthermore, the feeding of the Na_2S might affect the precipitation process, as König et al. (2006) tested, a precipitator with a titration mode may be more appropriate for lowering the value of MOR, although this is not suitable for large-scale application.

3.2.3. Zn and Mn recovery from the AMD

The filtrate produced from the Cu precipitation step was used as the source water for the Zn and Mn recovery process. Again, a 0.5 wt.% Na_2S solution was used as a precipitator, and the pH was not regulated after Cu precipitation. As shown in Table 7, the REM_{Zn} increased with the MOR_{Zn}, but the CON_{Zn} decreased. The REM_{Zn} and CON_{Zn} reached 97.97% and 31.71%, respectively, with a MOR_{Zn} of 1.5. The remaining Zn content was 1.60 mg/L, and Mn was 63.31 mg/L.

Compared with the Cu sulphide precipitation process, the REM_{Zn} reached 97.95%, with a MOR_{Zn} of 1.5 and 96.58% when the MOR_{Cu} was at 2.0. Metals such as Ni and Co precipitate as sulphides during the Cu and Zn precipitation process. The filtered supernatant after Zn recovery

Table 3
Metal content of the settling sludge generated from the existing treatment process.

Al %	Ca %	Mg %	Fe %	Mn %	Zn %	Cu %	V g/t	Cr g/t
2.78	21.18	14.19	24.19	1.97	3.68	0.16	34.30	913.56
Co g/t	Ni g/t	As g/t	Rb g/t	Cd g/t	Nd g/t	W g/t	Tl g/t	Pb g/t
204.07	nd	156.59	80.78	73.14	nd	nd	nd	155.28

nd means under the detection limit.

Table 4
Effect of neutralization pH on removal efficiencies of metals.

pH value		3.65	4.05	4.59	4.90	5.70	7.51	9.08
Removal rate %	Fe	37.30	41.19	46.13	57.85	93.58	99.81	99.85
	Cu	13.01	25.16	82.56	98.66	99.52	100.00	100.00
	Zn	1.26	1.38	1.63	12.01	82.32	99.32	99.63
	Mn	0.31	3.2	3.8	5.5	26.9	96.1	98.32

Table 5
Effect of H_2O_2 addition on removal efficiencies of metals (pH 3.65).

Dosage of H_2O_2 ml/L		0	0.15	0.25	0.30	0.5	1	2
Removal rate %	Fe	37.30	94.46	98.45	99.51	99.49	99.55	99.68
	Cu	13.01	13.09	11.46	10.86	10.77	9.88	9.82
	Zn	1.26	1.61	1.72	1.75	1.82	1.83	2.15
	Mn	0.31	0.32	0.34	0.30	0.35	0.33	0.37

Table 6
Effects of sodium sulphide addition on Cu recovery.

MOR_{Cu}		0.8	1	1.2	1.4	1.6	1.8	2	2.5	3
REM%	Cu	19.26	36.08	47.24	66.11	71.87	84.68	96.58	99.67	99.96
	Zn	4.55	6.41	7.67	7.69	8.15	8.71	8.87	12.19	14.65
	Mn	0.69	0.99	1.03	1.07	1.07	1.39	1.55	1.78	1.84
CON_{Cu} %		8.28	11.1	11.72	13.91	14.37	15.01	16.5	12.72	8.64

had 5 wt.% $Ca(OH)_2$ added to remove Mn and other remaining heavy metals. As shown in Table 8, the REM_{Mn} increased from 82.45% to 99.19% when the pH value increased from 7.80 to 9.80. The RES_{Mn} was lower than 1.0 mg/L when the pH value exceeded 8.60. At a pH of 8.60, the REM_{Mn} and CON_{Mn} were 98.36% and 7.53%, respectively.

The analysis results for the concentrations of other heavy metals after Mn recovery from the AMD are shown in Table 9. With fractional precipitation, the concentrations of Cr, Ni and Tl contained in the supernatant were reduced to less than the ICP detection limit, while the concentrations of Cu, Zn, Co, As, Ba and Pb were below the Code of Federal Regulations (CFR) (1994) limits. The metals Fe, Cu, Zn and Mn were recycled and enriched in their specific sludge. The volume indices for the Fe, Cu, Zn and Mn sludges were approximately 75 ml/g, 50 ml/g, 45 ml/g and 55 ml/g, respectively. Ba had a slightly higher concentration in the effluent when compared with the influent (Table 1). This could be attributable to metal impurities in the added lime.

3.3. Analysis and use of metal sludges

The sludges generated from the flow were Fe sludge, Cu sludge, Zn sludge and Mn sludge, in sequence. The results of the analysis of these products are shown in Table 10. The dominant metals contained in the products were Al, Mg, Ca, Fe, Mn, Zn and Cu, and the total amounts of these metals contained in the sludges of Fe, Cu, Zn and Mn were 55.51%, 24.37%, 44.73% and 32.54%, respectively. The grades of sludge for Fe, Cu, Zn and Mn were 45.91%, 11.58%, 31.06% and 7.95%, respectively. The precipitation of the other minor metals was not significant because of their low concentrations (Beauchemin et al., 2010). The sludge required some further processing to be used for practical applications.

3.3.1. Roasting refining of the Fe sludge

The Fe content of the sludge was 45.91%, and was precipitated by OH^-, which was generated in the lime hydrolysis. This was too low to use, so a low temperature roasting technique was used for sludge refinement. The Fe sludge was roasted at 500 °C for 30 min, and the resulting Fe content was 59.62%, while the Fe_2O_3 content was 85.18%.

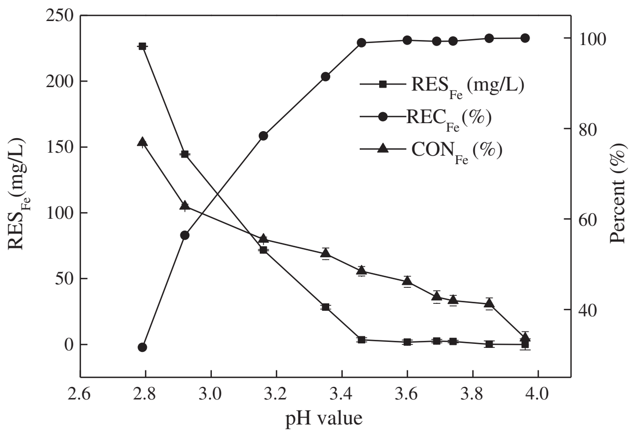

Fig. 3. Effects of pH neutralization on Fe recovery.

Table 7
Effects of sodium sulphide addition on Zn recovery.

MOR_{Zn}		0.8	1	1.3	1.5	2	2.5	3
REM (%)	Mn	0.21	0.42	1.25	1.38	1.43	1.84	2.35
	Zn	52.03	64.21	85.87	97.97	99.58	100	100
CON_{Zn} (%)		37.02	32.45	32.06	31.71	31.41	28	25.74

The weight loss of the sludge was 23%. The Fe_2O_3 content met the first standard of commercial quality for Fe oxide red products, which is 75%, and therefore this is suitable for use in industrial coatings.

3.3.2. Flotation refining of Cu and Zn sludges

The Cu and Zn sludges were generated via conversion to the metal sulphides. The results of the XRD analyses of these are shown in Fig. 4. Using standard XRD reference peaks, it was found that the main components of the Cu sludge were Al_2O_3, CuS and $Fe(OH)_3 \cdot H_2O$, whereas the main components of the Zn sludge were ZnS, Al_2O_3, CaO and $Mg(OH)_2$. These results show that the component materials were crystalline. Based on the XRD analyses of the sludges, it was confirmed that precipitation of the Cu^{2+} and Zn^{2+} ions yielded CuS and ZnS. As calculated from a chemical formula, contents of CuS and ZnS in their specific sludge were 17.37% and 46.35%, respectively. Flotation technology is frequently used for mineral enrichment, and the CuS and ZnS sludges could be refined further by this method (Avila et al., 2011; Pagnanelli et al., 2004; Pestryak et al., 2013). Sampaio et al. (2010) found that with sulphide precipitation, the Cu sludge was covellite, while the Zn was spharelite. The median particle diameters of the Cu and Zn sludges were 7.5 μm and 5.24 μm, respectively. These diameters were close to the boundary grain size for the flotation process, so flocculation flotation was required for the refinement of the Cu and Zn precipitates (Jailton and Jorge, 2005). When the Cu sludge was floated, the pH value of the slurry was adjusted to the 8.0–8.5 range, carboxymethylcellulose, butylxanthate collector, and pine oil frother were then added at 50 g/t, 200 g/t and at 30 g/t sequentially before introducing air via the air supply injection valve at 6.0 l/min. With the flotation tests, the crude concentrates were then collected and analysed. The Cu recovery was 72.66% and the Cu grade was 35.72%. When the Zn sludge was floated, addition of carboxymethylcellulose, butylxanthate collector and pine oil frother were 30 g/t, 240 g/t and 40 g/t. The crude precipitates were collected and analysed. The Zn recovery was 76.18% and the Zn grade was 55.13%. The metal content of the Cu and Zn crude concentrates thus met the required grades for sale.

3.3.3. Mn sludge reuse for cement materials

The Mn sludge could not be used as metal resource because its Mn content was only 7.95%. However, the sludge could be reused in other ways because of its high Ca, Mg and Al content. The total content of

Table 8
Effects of pH on the Mn removal rate.

pH	Mn (mg/L)	Removal rate (%)	CON_{Mn} (%)
7.8	9.30	82.45	8.39
8.6	0.87	98.36	7.53
9.5	0.76	98.57	6.74
9.8	0.43	99.19	4.35

Table 9
Final metal concentrations at the discharge (mg/L, except pH).

pH	Li	Na	Mg	Al	K	Fe	Mn	Cu	Zn
8.43	0.10	4.22	17.01	11.52	5.34	1.05	0.97	0.01	0.16
Cr	Co	Ni	As	Cd	Ba	Pb	V	Rb	Tl
nd	0.01	nd	0.00	0.00	0.08	0.00	0.04	0.14	nd

nd means not detected.

Table 10
Metal contents of dried sludges.

	Unit	Fe sludge	Cu sludge	Zn sludge	Mn sludge
Al	%	1.61	9.49	5.64	5.71
Ca	%	4.93	0.35	2.92	8.1
Mg	%	2.22	1.35	2.61	9.79
Fe	%	45.9	1.07	0.71	0.31
Mn	%	0.27	0.01	0.71	7.95
Zn	%	0.06	0.52	31.1	0.68
Cu	%	0.51	11.6	1.11	nd
V	mg/kg	13.6	23.2	43.8	11.7
Cr	mg/kg	6.77	4.88	6.43	109
Co	mg/kg	7.74	254	317	287
Ni	mg/kg	nd	102.8	316	22.4
As	mg/kg	3.54	2.39	4.66	18.1
Rb	mg/kg	22.1	13.5	16.3	33.1
Cd	mg/kg	8.97	25.4	15.5	47.9
Ba	mg/kg	0.33	11.3	21.6	18.3
Tl	mg/kg	nd	nd	nd	nd
Pb	mg/kg	42.3	59.5	114.0	nd

nd means not detected.

Table 11
Flexural and compressive strength of the specimens.

Mixture ratio(%)			Compressive strength (MPa)			Flexural strength (MPa)		
OPC	PFA	Mn settling sludge	3 days	7 days	28 days	3 days	7 days	28 days
100	0	0	21.6	37.7	40.7	4.7	5.4	5.9
80	5	15	34.1	39.1	44.3	5.6	6.2	7.5
70	5	25	34.5	39.5	42.7	5.6	6.0	7.1
60	5	35	33.7	38.6	41.5	5.3	5.9	7.3
50	5	45	32.9	37.7	40.9	5.6	6.12	7.2
40	5	55	27.7	35.3	38.4	5.2	5.8	6.9

Table 12
Leaching characteristics of the concrete specimens.

Mixture ratio (%)			Leaching contents of heavy metals ($mg \cdot L^{-1}$)					
OPC	PFA	LRT	Cu	Pb	Cd	Cr	Mn	Ni
80	5	15	0.01	0.01	nd	nd	0.03	nd
70	5	25	nd	0.01	nd	nd	0.02	nd
60	5	35	nd	0.01	nd	nd	nd	nd
50	5	45	0.01	0.07	nd	nd	0.04	0.05
40	5	55	0.03	0.07	0.01	nd	0.09	0.01
0	0	100	0.11	0.46	0.02	0.05	0.92	0.04

nd means not detected.

these metals was nearly 23.60%. The Mn sludge was thus blended with ordinary Portland cement (OPC) and pulverised fuel ash (PFA) in appropriate proportions to prepare a cement specimen. PFA was more suitable, as it was able to improve the flow and the mechanical properties of the specimen (Choi et al., 2009). The values of the compressive and flexural strengths of the specimens prepared with different ratios of Mn sludge and OPC are shown in Table 11. An OPC of 42.5 was selected as a reference, in accordance with Chinese Standard GB175-2007. With 45% of the material composed of Mn sludge, the specimen's 28-day compressive strength was almost identical to that of the reference OPC, while the 3- and 7-day compressive and flexural strengths were higher than those of the OPC.

It is also important to consider the possibility of solidification of the heavy metals when waste materials are used in concrete mixes (Malliou et al., 2007). As can be seen from Table 12, adding further OPC reduced the levels of heavy metals that could be leached out. The heavy metal content leached out was low enough to meet the requirements of the Chinese GB5085.3-2007 standard.

3.4. Comprehensive recovery process for the AMD

A four-step fractional precipitation process was conducted to recover the metal from the standard discharge of the LWMRD AMD. The process flow chart is shown in Fig. 5. First, the AMD was oxidised with 30 wt.% of H_2O_2, and Fe precipitation was performed by controlling the pH value in the 3.5–4.0 range with a 2 wt.% $Ca(OH)_2$ solution. The resulting Fe sludge contained an Fe content of 45.91%. Second, the Cu precipitation process was carried out with a 2 wt.% Na_2S solution added, and the resulting Cu sludge had a Cu content of 11.58%. Third, Zn precipitation was performed with the addition of a 2 wt.% Na_2S solution, and the Zn content of the resulting sludge was 31.06%. Finally, precipitation of Mn and all other heavy metals was achieved by controlling the pH value in the 8.0–8.5 range with a 5 wt.% $Ca(OH)_2$ solution. The Mn content of the resulting sludge was 7.95%. Using this method, AMD was processed to achieve a standard discharge that meets CFR requirements.

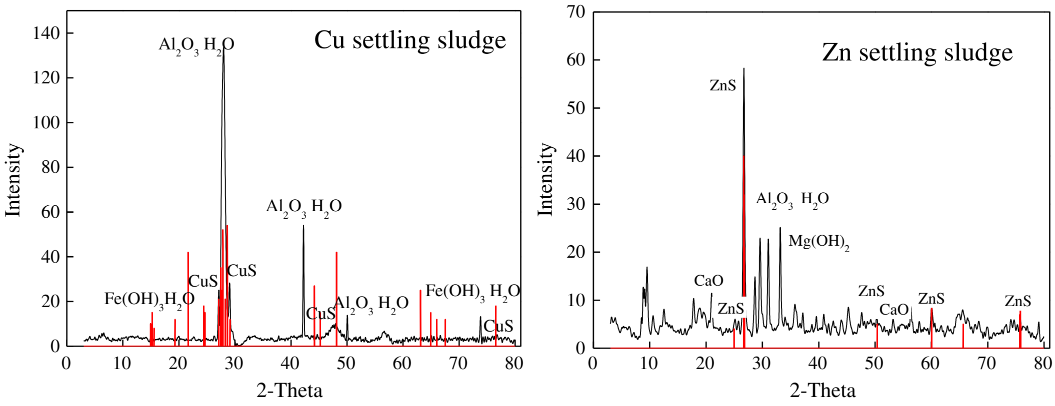

Fig. 4. Mineralogy of Cu and Zn settling sludges.

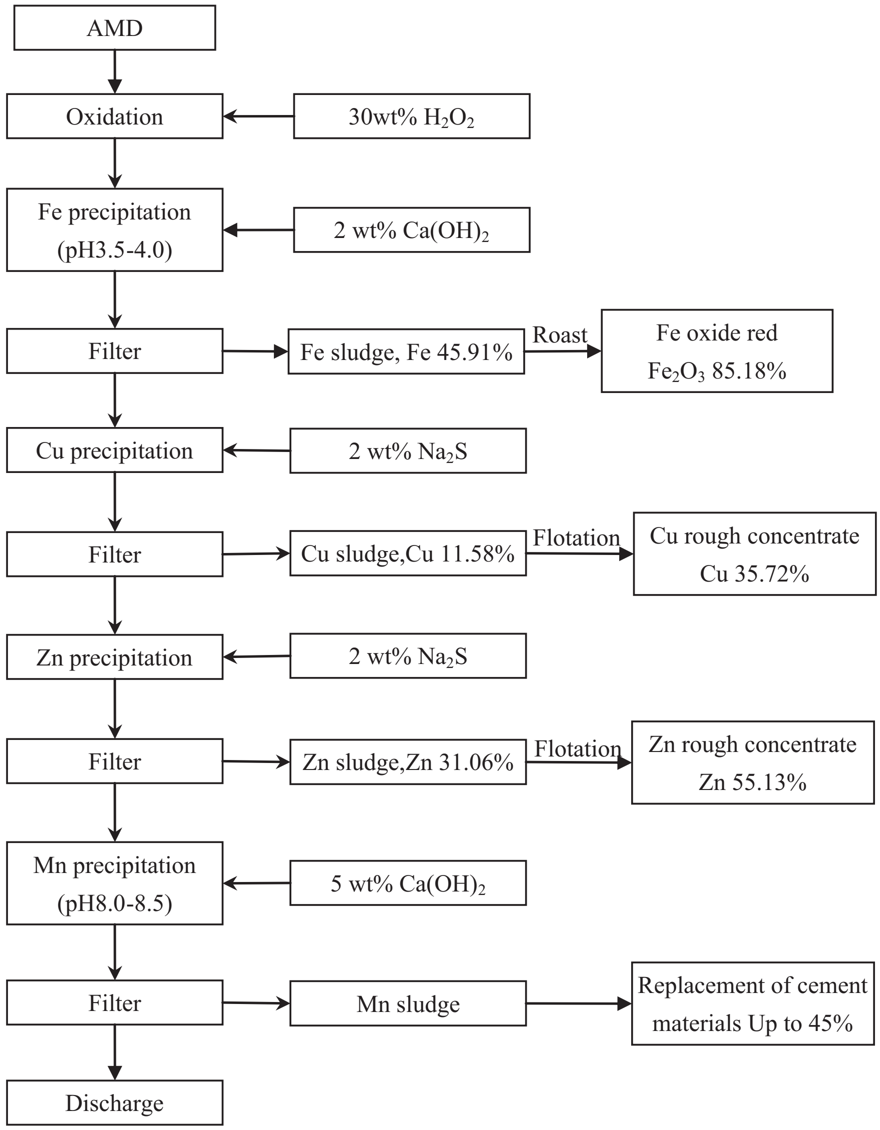

Fig. 5. Flow chart of stepwise recovery of Fe, Cu, Zn and Mn from AMD.

4. Conclusions

Fractional precipitation was used for metal recovery from the AMD. Four particular sludges with high Fe, Cu, Zn and Mn contents were generated in the process, and the use of these sludges for metal recovery was tested. A new and comprehensive technology for wastewater treatment was proposed to reduce pollution and recycle resources from the AMD. Our conclusions are as follows.

(1) Fe was precipitated in the pH range of 3.5–3.6 after ferrous oxidation by the addition of 30 wt.% H_2O_2; Cu was then precipitated by the addition of Na_2S and the MOR_{Cu} of 2; Zn precipitation was performed by the addition of Na_2S with an MOR_{Zn} of 1.5; precipitation of Mn and all other heavy metals was achieved by setting the pH value to 8.5.

(2) The heavy metals contained in the treated effluent were below CFR limits. The recovery efficiencies of Fe, Cu, Zn and Mn were 99.51%, 86.09%, 87.87% and 79.71%, respectively, and the four corresponding types of sludge generated had metal grades of 45.91%, 11.58%, 31.06% and 7.95%, respectively.

(3) The Fe sludge, with an Fe_2O_3 content of 85.18%, can be roasted for use in the coating industry. The Cu and Zn sludges produced were refined to produce copper and zinc concentrates using flotation technology, and the metal contents of the crude concentrates were 35.72% and 55.13%, respectively. The recovery efficiencies of Cu and Zn during the flotation refinement process were 72.66% and 76.18%, respectively. The Mn slag could also be used to replace 45% of OPC in cement materials.

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