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Selectively leaching Cu(Ⅱ) and Ni(Ⅱ) from acid mine drainage sludge by using ethylenediamine-ammonium sulfate①

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[Abstract] A method based on controlling the complexation-precipitation equilibrium of metal ions was proposed to selectively recover nickel and copper from hydroxide sludge formed by lime neutralization of acid mine drainage(AMD). Ethylenediamine(EDA) and ammonium sulfate were chosen as complex reagent and precipitating reagent, respectively, to dissolve target metal hydroxides from sludge and limit useless metal ions in the pregnant solution. Results from both synthetic and natural samples show the excellent selectivity for the target metals(copper and nickel) against Fe(Ⅲ), Ca(Ⅱ) and Mg(Ⅱ), 99% recovery of Cu(Ⅱ) and Ni(Ⅱ) and shorter leaching time can be reached by this process, and the resultant solution can be used for direct electrowinning. The optimum operating conditions are: pH= 9~ 11, ρ(EDA) = 40 g/L, ammonium sulfate 50 g/L, leaching time 5 h(for natural sample) and 2.5 h(for synthetic sludge), liquid to solid ratio being 4 with mechanical stirring at room temperature.

[Key words] ethylenediamine(EDA); AMD sludge; selective extraction; waste treatment; nickel; copper
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1 INTRODUCTION

One environmental problem related to mining company is acid mine drainage (AMD)[1], which is formed by oxidation of sulfides (such as pyrite and chalcopyrite, etc) when they are exposed to air and generally promoted by bacteria such as thiobacillus ferrooxidans and etc[2]. Although AMD from different place differs from each other in their composition, their toxicity, which arise from their acidity and high contents of heavy metals, are similar and must be treated prior to discharge[3]. The common practice in treating AMD is lime neutralization and results in a sludge of mixed metal hydroxides. Unfortunately this kind sludge remains a threat to the surrounding area and will release heavy metals to environment slowly because of the lower chemical stability of metal hydroxides, especially serious when being contacted with low pH water(such as acid rain)[4]. Most of these sludge contain iron, alkaline earth metals (Ca, Mg) and some valuable metals such as copper and nickel. It is a challenge to recover valuable metals as much as possible so that the cost of treatment can be offset and, at the same time, to produce an environment-friendly residue for disposal[5, 6]. There are two basic leach options to recover metals from a sludge . The first would be to acidify the sludge thereby solubilizing all metals, selectively recovering the metals of interests, then re-neutralizing the solution to precipitate the "gangue" metals as a new sludge[7]. The second way would be to selectively leach and recover the valuable metals while rejecting the others. Because of the evident advantage of fewer steps and simple operation for the latter option, organic amine especially polyamine has been investigated in recent years to selectively recover zinc, copper and nickel from sludge. Rao et al[8] performed work in the selective leaching of Zn, Cu and Ni from hydroxide sludge formed in the treatment of AMD by choosing di-ethylene triamine (DETA) as lixiviant. Excellent selectivity was found for extraction of Zn, Cu and Ni from the sludge bearing Fe, Ca, Mg and Al, and the optimum condition was that the molar metal to DETA ratio equals 1∶2 which corresponds to a mass ratio of 1∶3.5. The related work to recover metals from DETA pregnant solution by electrowinning, finished by Felsher et al[9], showed that copper can be electrowon from the Cu-DETA complex at a current density of 155~ 200 A/m^2, a voltage of 2.5 V and a current efficiency of 100%. However, extension of this technique to Ni-EDTA complex proved unsuccessfully due either to the stability of the complex (brought about by the double chelate ring) or to a change in the reduction potential of the nickel, as pointed by Kramer et al[10] in their earlier work of this field. They also suggested the use of ethylenediamine(EDA) over more complex amines, such as DETA, TETA(tri-ethylene tri-amine) and etc to limit these negative factors.

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As the simplest chelating amine the molecular formula of EDA is $NH_2CH_2CH_2NH_2$ with a molecular mass of 68. The advantages of EDA is its higher ratio of functional group of (amine) NH_2 for every carbon chain (C_2H_4) and relatively lower price in market within the polyamines group. Chemical concepts related to the complexation-precipitation process can be seen from the equations as

Sludge formation: $M^{2+}(aq) + 2OH^- \rightarrow M(OH)_2(s)$ (M = Ni, Cu) (1)

EDA disassociation: $EDA + H_2O \rightarrow EDA{-}H^+(aq) + OH^-$ (2)

Sludge dissolution by EDA: $M(OH)_2(s) + m\,EDA \rightarrow M(EDA)_m^{2+}(aq) + 2OH^-$ ($m = 1 \sim 4$) (3)

Possible side reaction: $M(EDA)_m^{2+}(aq) + 2OH^- \rightarrow M(OH)_2(s) + m\,EDA$ (4)

if $m \leqslant 1$, or pH is very high

Precipitation(removing impurity):

$Ca^{2+}(aq) + SO_4^{2-} \rightarrow CaSO_4(s)$

(the same for Mg) (5)

It is no wonder that pH of the leaching system will change during the leaching process, when there is some difference in production of hydroxide between Eqns. (2) and (3). The equilibrium between solid $M(OH)_2$ and aqueous M-EDA complex will be dependent on both free EDA concentration and solution pH. However the latter is not emphasized enough in the previous works, resulting in either very high operating polyamine concentration or non-complete extraction of the target metals, because the solution pH will go up along the dissolution process of $M(OH)_2$.

This communication presents the leaching results using EDA as main complex reagent and ammonium sulfate as precipitating reagent to selectively extract copper and nickel against iron and alkaline earth metals. Batch tests were conducted to establish the optimum conditions such as leaching pH, lixiviants concentration, selectivity over Fe, Ca and Mg.

2 EXPERIMENTAL

Reagents sulfates of zinc, copper, nickel, ferric, ammonium, aluminum and magnesium, and diethyleneamine(EDA) were reagent grade and got from Aldrich-Sigma company. The lime used were provided by Hoover's Company. Purchased solid nickel hydroxide and copper hydroxide(both 99% purity, particle size of 0.030 mm, from Aldrich Company) were studied, from the point of chemistry, to seek the optimum leaching condition such as pH range, EDA operating concentration and etc.

A solution simulating AMD from INCO Corp. (Toronto, Canada) was prepared by containing: 2.5 g/L Fe(Ⅲ), 1.7 g/L Ni(Ⅱ), 1.2 g/L Cu(Ⅱ), 0.15 g/L Zn(Ⅱ), 0.23 g/L Al(Ⅲ) and 0.2 g/L Mg(Ⅱ). This solution was neutralized by "lime milk" until its pH reached 9.5 ~ 10. After centrifuge and throwing away the supernatant a sample was collected and was referred to as "synthetic sample of AMD sludge". Synthetic sample was used to study the technical factors of leaching process such as leaching time, lixiviant concentration, recovery and etc.

A natural sample from Inco Corp was also used and referred to as "natural sample of AMD sludge" after concentrating it by centrifuge technique. Natural sample was used, from the point of technical, economical and environmental issue, to investigate the application feasibility of this technology. The samples used for these experiments as well as their source and the compositions are given in Table 1.

All leaching tests were finished at room temperature (RT) with liquid-solid ratio of 4. In each test 50 g sample and 200 ml EDA solution were poured into a 250 ml beaker and stirred vigorously at a fixed speed by using a Cole-Parmer mechanical stirrer. The leaching recovery was calculated by assaying the residue after solid-liquid separation and drying it at (100 ±5) ℃. Metals concentration in solutions were measured by AAS(atomic adsorption spectroscopy).

3 RESULTS AND DISCUSSION

3.1 pH change during leaching process

Fig. 1 is the pH change curve during the EDA separately leaching of $Ni(OH)_2$ and $Cu(OH)_2$ solid (reagents, Aldrich) at the starting concentration of $\rho(EDA) = 0.05$ mol/L.

Table 1 Sludge samples information

Sample source	Preparation site	Composition/%								
		Ni	Cu	Fe	Zn	Ca	Mg	H_2O	SiO_2	Al_2O_3
Synthetic	In-situ	8.5	7.2	11.3	0.9	13.1	1.2	32.5		
Natural	Inco	7.3	5.8	13.9	1.4	14.9	1.3	28.2	15.7	4.2

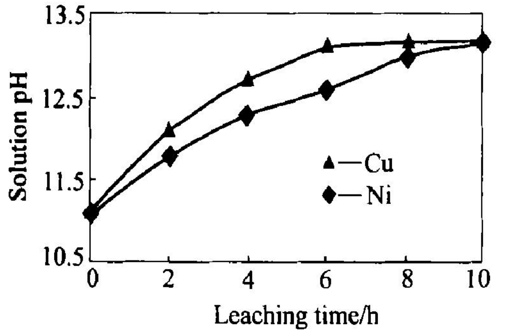

Fig. 1 Solution pH changes in leaching of nickel and copper hydroxide by EDA

Evidently the solution pH value will go up in the leaching process of metal hydroxide because the base strength of the leaching products is greater than that of the primary material(EDA). And the pH curve also reflects that the leaching rate of $Cu(OH)_2$ is faster than that of $Ni(OH)_2$ in the EDA solution during the early stage. This diagram implies that it is necessary to control the solution pH value, otherwise the reverse reaction of precipitation will happen at high pH value and result in non-complete extraction of the target metal hydroxides.

3.2 Optimum leaching pH

Fig. 2 shows the leaching results in 8 h under different controlled pH. In this case molar ratio of EDA to (Cu+ Ni) was fixed at 2, pH was adjusted by ammonium sulfate, and synthetic sample was used as primary material.

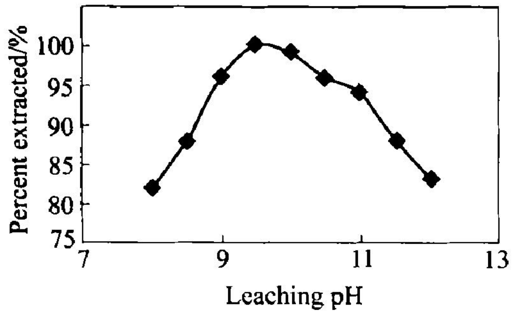

Fig. 2 pH selection during leaching of synthetic sample by EDA

It is easy to understand that the optimum pH value should be 9~ 11, because lower pH value will give rise to free ρ(EDA) decreasing and higher pH value will result in precipitation of aqueous nickel and copper as hydroxides. In fact a buffer solution was formed when ammonium sulfate was used to control calcium concentration in the pregnant solution.

3.3 EDA operating concentration

Fig. 3 is the relationship between concentration of EDA and Cu/Ni recovery.

Clearly EDA operating concentration should be more than 40 g/L in order to gain 99% recovery of the target metals(Cu+ Ni). Obviously iron dissolution is effectively depressed during the EDA leaching media.

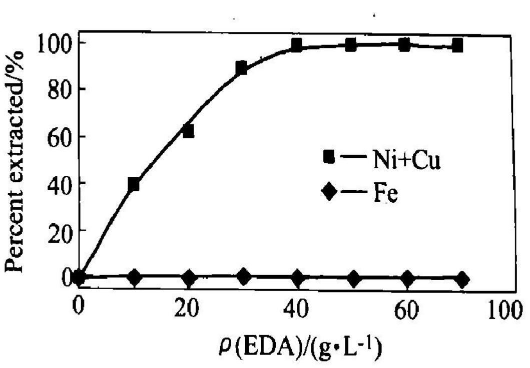

Fig. 3 Extraction of metals from synthetic sample(leaching time 8 h, pH 9~ 10)

3.4 Leaching time

Optimum leaching time can be gotten from Fig. 4 for both synthetic and natural samples at pH 9~ 10 and ρ(EDA)= 40 g/L.

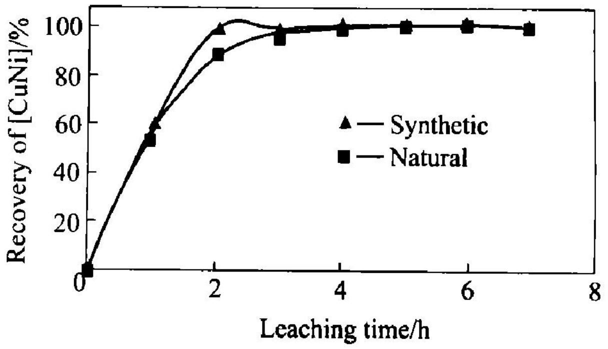

Fig. 4 Selection of leaching time for synthetic and natural samples at pH 9~ 10, ρ(EDA) 40 g/L

Obviously, there are quite different requirement of leaching time for synthetic(2.5 h) and natural (5 h) samples, respectively. Because of the aging effect on natural AMD sludge longer time is needed to extract the target metals compared to the time of the freshly formed sludge(synthetic sample).

3.5 Controlling calcium and magnesium in pregnant solution

Calcium and magnesium in the pregnant solution can be rejected to some extent by using an additive-ammonium sulfate so that the leaching solution can meet the requirements[10] for direct electrowinning, as shown in the Fig. 5.

It can be seen, from Fig. 5 that 50 g/L ammonium sulfate should be added during the leaching process in order to keep ρ(Ca+ Mg) $\leqslant$ 0.5 g/L in the pregnant solution.

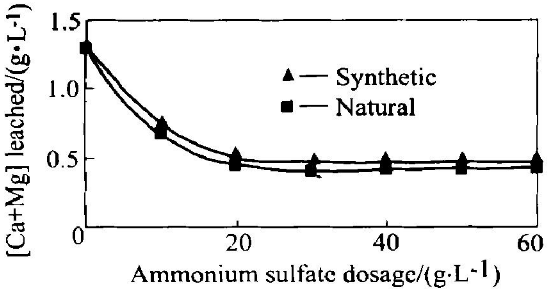

Fig. 5 Relationship between additive dosage and Ca+ Mg in pregnant solution
(pH 9~ 10, ρ(EDA) 40 g/L, leaching time 2.5~ 5 h)

4 CONCLUSIONS

1) EDA-ammonium sulfate system can selectively extract Cu(II) and Ni(II) from Fe(III) and alkaline earth metals in both simulated hydroxide sludge and natural sample formed from lime neutralization.

2) The optimum operating conditions are: pH 9~ 11, ρ(EDA) 40 g/L, ammonium sulfate 50 g/L, leaching time 5 h(for natural sample, 2.5 h for synthetic sludge), liquid to solid ratio being 4 with mechanical stirring at room temperature.

3) The recovery of copper and nickel is higher than 99% and ρ(Ca+ Mg) ≤0.5 g/L in the leaching solution. The resultant solution can meet the requirements for direct electrowinning.

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