



## Short Communication

## A novel strategy achieving enrichment of metal values from and into ammoniacal solutions



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## ABSTRACT

A novel strategy has been proposed to achieve enrichment of metal values from and into ammoniacal solutions through solvent extraction. The extraction equilibria of Cu(II), Ni(II) and Zn(II) in ammoniacal sulfate solution have been examined with  $\beta$ -diketone in the pH range of 6–12. The ammonia stripping behaviors of three metal ions have been studied by consideration of total ammonia, pH and temperature. The results indicate that a special swing phenomenon was found for both extraction and ammonia stripping processes. The loaded organic phases can be successfully stripped with ammoniacal solutions by adjusting total ammonia concentration and pH. Zinc and nickel are more easily stripped than copper. Increasing temperature is beneficial for the ammonia stripping of zinc and nickel but adverse for copper, thus potentially improving the Zn/Cu and Ni/Cu separation. The ammonia stripping isotherm shows that zinc can be efficiently enriched with two counter current stages. Moreover, there is no significant loss of organic phase during stripping. Therefore, direct enrichment of metal values through ammonia stripping has a good prospect for the integrated extraction and electrowinning circuit throughout ammoniacal systems.

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## 1. Introduction

Ammoniacal leaching is a promising method for the recovery of valuable metals (such as, nickel, copper and zinc) from low-grade oxide resources [1], lean complex ores [2], ocean nodules [3] and various secondary resources [4]. In order to separate and recover low concentration metals from ammoniacal leaching liquors, various methods have been proposed and investigated, including precipitation, ion exchange, solvent extraction and membrane separation. Among them, solvent extraction as the preferred technique has been widely used for the recovery of various metals in hydrometallurgy, due to its some advantages of low energy requirement, simple operation, controllable selectivity and easy scale up [5–7]. By integrated with extraction process, the metal values in ammoniacal solutions can be efficiently separated and enriched for the following electrowinning process.

Currently, the general strategy is that the metal ions are stripped from loaded organic phases into sulfuric acid solutions, and then recovered as metal form by electrowinning. For example, Chen et al. successfully recovered zinc from low-grade oxide ores via the ammoniacal leaching–solvent extraction–acidic

electrowinning [1]. Although the acidic electrowinning is very successful in industry, taking account into the metal recovery in ammoniacal systems, there are still some inevitable issues. On one hand, ammonia is easily transferred into organic phases by coextraction, entrainment and microemulsion [8,9]. Once contacting the ammonia loaded organic phase with spent electrolyte, ammonium salt will accumulate and precipitate in electrolyte as the form of double salts, which adversely affects the electrowinning circuit [10]. Thus, ammonia scrubbing procedure is indispensable before the H<sub>2</sub>SO<sub>4</sub> stripping. Meanwhile, the whole process is very complicate because there are two different circuits including ammoniacal leaching–extraction loop and acidic stripping–electrowinning loop. Therefore, if directly enabling enrichment of metal values from and into ammoniacal solutions through solvent extraction, the troubles mentioned above will be effectively resolved and the process can be evidently shortened, which is always pursued in the metallurgical industry.

However, there is little investigation on the ammonia stripping of metal values from the loaded organic phases. And all of them focused on the acidic extraction systems. For instance, in order to recover zinc from chloride medium, Mishonov et al. studied the stripping of Zn(II) from loaded TBP by ammonia/ammonium chloride solution. The obtained strip liquor can be further processed by electrowinning [11]. The ammonia stripping is also an alternative

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for the recovery of nickel from the laterite. A high pressure acid leach–solvent extraction–ammonia stripping route was proposed in BHP Billiton Ravensthorpe project. Following nickel extraction with LIX 84-INS, the loaded organic phase can be stripped by high concentration ammonia solutions [10]. Meanwhile, Wassink et al. found that ammonia stripping of zinc and cadmium from loaded Aliquat 336 was efficient [12]. Although extraction of metal values in ammoniacal solutions is widely studied by LIX54 [13,14], Hostarex DK-16 [15], LIX84I [16], ACORGA M5640 [17], and so on, it's worth noting that there is no report on the ammonia stripping of their loaded organic phases, which is crucial to achieve the recovery of metal values throughout ammoniacal systems.

Herein, we proposed a novel strategy achieving enrichment of metal values from and into ammoniacal solutions through solvent extraction. The extraction behaviors of Cu(II), Ni(II) and Zn(II) in ammoniacal sulfate solution have been examined in the basic pH range using  $\beta$ -diketone extractant. The stripping of loaded organic phases has been studied with the ammoniacal solutions. The stripping, separation and enrichment behaviors of three metal ions have been discussed by consideration of the effect of total ammonia concentration, aqueous pH and temperature, respectively.

## 2. Experimental

### 2.1. Reagents and chemicals

The sterically hindered  $\beta$ -diketone ligand, 4-ethyl-1-phenyl-1,3-octadione (denoted as HA, purity of 98%), was synthesized according to the procedure in our previous work [8]. Toluene (purity > 99.5%) was used as the solvent. All other chemicals were of analytical grade and were used without further purification. Ultrapure water (Millipore MilliQ System, 18.2 M $\Omega$  cm) was used in all experiments. The stock aqueous solutions in the presence of 20 mM Cu(II), Ni(II) or Zn(II) were prepared for extraction by dissolving the corresponding metal sulfate in ammonium sulfate solutions at different pH, respectively. The ammonium sulfate solutions in the absence of metal ions were also prepared for stripping. The aqueous pH was adjusted to the desired value using sodium hydroxide and sulfuric acid. The organic phases were prepared by adding the HA of desired concentration in toluene.

### 2.2. General procedure

The extraction and stripping experiments were carried out in an airtight vial by mixing equal volumes (10 mL) of organic phase with stock aqueous solutions of different pH. Unless otherwise stated, the temperature was maintained at  $25 \pm 0.2$  °C using a thermostat bath. The loaded organic solutions for stripping experiments were prepared by contacting organic solutions of 0.6 M HA with aqueous solutions of pH 12. The stripping solutions are the ammoniacal solutions of 2 M or 4 M total ammonia at various pH conditions. The equilibrium time for both extraction and stripping was set at 40 min. After phase separation, the concentration of Cu(II), Ni(II) and Zn(II) in aqueous phase were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin Elmer 5300DV). The metal concentration in the loaded HA organic phase was calculated by mass balance before and after extraction or stripping. The aqueous pH was measured using a Rex-3C digital pH meter with a combined glass electrode. To obtain the stripping isotherms, the loaded organic phases were equilibrated with the stripping solution at the different phase ratios. The temperature dependency tests for stripping reaction were conducted from 15 to 45 °C. In order to determine the loss of organic phase during stripping process, the fresh organic phase

of 0.6 M HA was mixed with the stripping solution of 4 M total ammonia and different pH. The contents of total organic carbon (TOC) in the ammoniacal solutions before and after equilibrium were measured using a TOC-V<sub>CPH</sub> analyzer from Shimadzu. All results are presented as the average value of triplicate analysis.

## 3. Results and discussion

### 3.1. Extraction of metal ions

The pH effect on the extraction of copper(II), nickel(II) and zinc(II) in ammoniacal solutions with 2 M total ammonia was investigated in the pH range from 6 to 12. The extractant concentration is 0.2, 0.4 and 0.6 M for copper(II), nickel(II) and zinc(II), respectively. As shown in Fig. 1, the extraction processes of three metal ions are highly dependent on the aqueous pH. The dependency of extraction equilibrium on pH presents a special swing effect for each metal. The extraction efficiency for both Zn(II) and Ni(II) shows a gradual increase with the increase of aqueous pH, and reach the maximum at pH 7.5 and 8.0, respectively. Subsequently, it separately declines to the minimum at pH of 9.6 and 9.3. The minimum extraction efficiency is only 8.3% for zinc and 34.7% for nickel. However, when continuously increasing the pH, it's worth noting that the extraction efficiency can again increase, and even rapidly reaches up to 100% at pH 11.8 and 10.9 for Zn(II) and Ni(II). Although HA ligand especially favors for extraction of copper than nickel and zinc at the pH of lower than 10, when using a lower extractant concentration, the extraction efficiency of Cu(II) still shows a similar trend with pH change. Furthermore, the swing effect of extraction equilibrium indicates that the metal ions can be selectively stripped from the loaded organic phases with an appropriate ammoniacal solution, thus enabling the enrichment of metal values from and into ammoniacal solutions.

The analogous phenomena have been widely found for both extraction and adsorption processes of metal ions in ammoniacal solutions. For example, this special extraction behavior had been presented for the extraction of nickel and zinc via various extractants, such as LIX54 [13,14], Hostarex DK-16 [15] and Acorga M5640 [17]. Osseo-Asare found that the adsorption behavior of

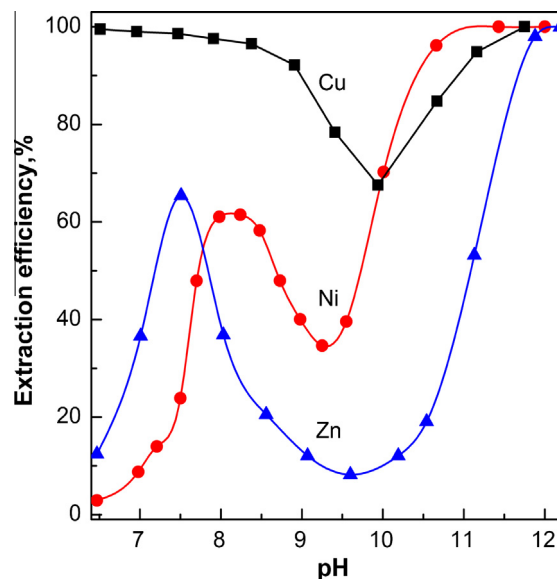


Fig. 1. Effect of aqueous pH on extraction of valuable metals. Aqueous phase: 20 mM metal ions and 1 M  $(\text{NH}_4)_2\text{SO}_4$ , respectively; organic phase: 0.2 M HA for Cu(II), 0.4 M HA for Ni(II), 0.6 M HA for Zn(II); aqueous/organic phase ratio of 1:1.

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