

# Selective extraction of zinc from sulfate leach solution of zinc ore<sup>①</sup>

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**Abstract:** Selective extraction of zinc from sulfate leach solution of zinc ore was studied. D2EHPA dissolved in 260<sup>#</sup> kerosene was used as extractant. The pH-extraction isotherms show the extraction order of D2EHPA for metals is  $\text{Fe}^{3+} > \text{Zn}^{2+} > \text{Ca}^{2+} > \text{Al}^{3+} > \text{Mn}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Mg}^{2+}$  ( $\text{pH}_{0.5}$ ). This confirms that  $\text{Fe}^{3+}$  is preferentially extracted before the extraction of zinc. Extraction experiments were carried out with varying the extractant content, equilibration time, aqueous pH and phase ratio, and the solvent extraction of zinc with sodium salt of D2EHPA were also investigated. Some impurity co-extracted into the zinc loaded organic phase was efficiently removed by scrub, and the  $\text{Fe}^{3+}$  was hardly stripped from organic phase by sulfuric acid, hence zinc was separated from  $\text{Fe}^{3+}$  by selective stripping. A pregnant zinc sulfate solution with low contaminants was obtained by selective solvent extraction.

**Key words:** solvent extraction; zinc; stripping; D2EHPA

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## 1 INTRODUCTION

Solvent extraction was regarded as a highly efficient technique of separation and purification. It has been widely applied in metal extraction and recovery during hydrometallurgical process and environmental protection<sup>[1-4]</sup>. Solvent extraction has been commercially used in the extraction of uranium, rare noble metals, copper, cobalt and nickel, which was typically presented by the technique of leach-solvent extraction-electrowinning. Presently, the copper production from solvent extraction has been accounted for more than 20% of the total copper production in the world<sup>[5]</sup>. With the escalating depletion of mineral resource and the increasing demand for environmental protection, solvent extraction will play a more important role in treating low-grade ore, refractory oxidized ore and poly-metal complicated ore, and in recovery of metals from waste stream and secondary materials.

Researches on zinc solvent extraction were frequently reported. However, most methods were to remove minim zinc impurity from solution in the industrial background. Only several factories produced zinc with solvent extraction in the world<sup>[6-9]</sup>. The reasons are the efficient zinc extractant had not been found, and the price of zinc metal was too low. This is why zinc solvent extraction was lagged behind that of copper.

The solvent extraction electrowinning technique was characterized by short flow sheet, simple operation, low cost and light pollution. If solvent extraction can separate zinc from other impurities and re-

place the purification processes, the zinc hydrometallurgical process will be greatly shortened<sup>[10-12]</sup>. In this paper, selective extraction of zinc from sulfate leach solution of zinc ore was presented.

## 2 EXPERIMENTAL

### 2.1 Materials

D2-Ethythexyl phosphoric acid (D2EHPA) and 260<sup>#</sup> kerosene were obtained from Suzhou Refinery. The sulfate leach solution of zinc-oxidized ore contained 19.83 g/L zinc, 0.44 g/L irons, 0.8 g/L calcium, 4.5 g/L silica. For the determination of pH-extraction isotherms, the solution containing a single metal ion with the mass concentration of 3.0 g/L was prepared by the corresponding AR grade sulfate.

### 2.2 Procedures of extraction experiment

The extraction experiments were carried out in separatory funnels shaken mechanically. The pH of aqueous solution was adjusted to a desired value by adding dilute NaOH/H<sub>2</sub>SO<sub>4</sub> solution. The organic phase and aqueous phase were mixed at a predetermined ratio and shaken for a predetermined time. The mixture was allowed to disengage into two phases within 15 min and the aqueous phase was separated. The equilibrium pH was measured, and the metal content in the aqueous phase was determined by titrimetric method. The metal content in the organic phase was determined by mass balance since the original metal content before extraction had been known.

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In the scrubbing and stripping procedures, the zinc loaded organic phase was contacted with zinc sulfate solution with low and high acidity separately. All experiments were done at  $(25 \pm 1)^\circ\text{C}$ .

### 3 RESULTS AND DISCUSSION

#### 3.1 pH-extraction isotherms

The extraction of some metals varying with equilibrium pH in sulfate medium (pH-extraction isotherms) is shown in Fig. 1, where the extractant content is 10% (volume fraction), the O/A ratio is 1:1, and the contact time is 10 min.

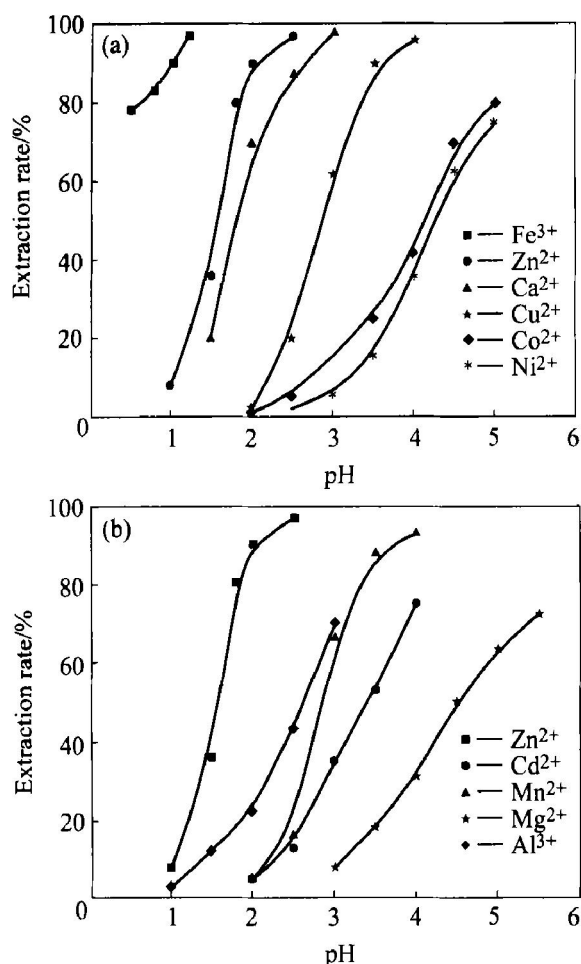


Fig. 1 D2EHPA pH-extraction isotherms for some metals

The typical feature of the phosphate-type extractant is that the strongly extraction of iron (III), which is shown in Fig. 1(a). While the equilibrium pH is above 1.20, the Fe<sup>3+</sup> is almost completely extracted, however, the zinc extraction is just about 15% at this pH. In the pH range of 1.8–2.5, the zinc extraction rate varies from 80% to 97% and the calcium extraction rate from 60% to 90%; while the copper extraction rate only varies from 2% to 20%, and the cobalt and nickel extraction are negligible. It can be seen from Fig. 1(a) that in the pH range of 2.0–2.5 zinc can be efficiently separated from copper,

cobalt and nickel. However, it is difficult to separate zinc from iron(III) and calcium. From Fig. 1(b) it can be seen that zinc is easily separated from cadmium, manganese and magnesium at the pH value of about 2.0. At the pH value of 2.0 the aluminum extraction rate is about 20%, while the extraction of cadmium, manganese and magnesium are negligible. The extraction order obtained from Fig. 1 is  $\text{Fe}^{3+} > \text{Zn}^{2+} > \text{Ca}^{2+} > \text{Al}^{3+} > \text{Mn}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Mg}^{2+}$  ( $\text{pH}_{0.5}$ ), where the  $\text{pH}_{0.5}$  means the pH value at which the metal extraction rate reach 50%.

In the purification processes of zinc hydrometallurgy, the impurities including iron, copper, cadmium, cobalt and nickel etc. should be removed to avoid their deleterious effect during zinc electrowinning. The results show that zinc could be easily separated from the metal ions above except iron (III). At the pH value of about 2.0, portion of calcium and aluminum are extracted, but low contents of calcium and aluminum have no effect on zinc electrowinning. So, if the iron extracted to the zinc loaded organic phase is controlled, a pregnant zinc sulfate solution suitable for electrowinning can be obtained by solvent extraction.

#### 3.2 Influence of extraction conditions

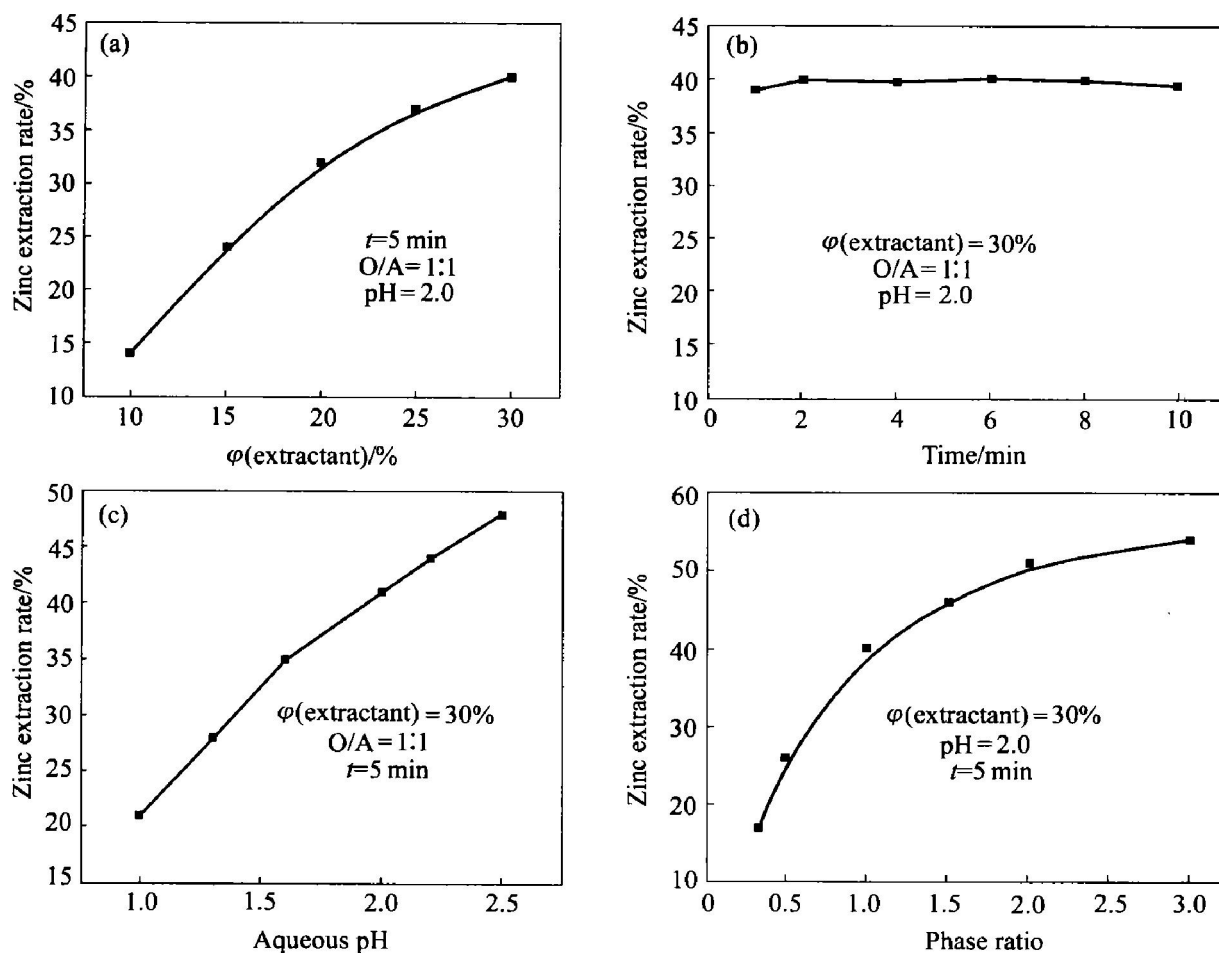
Solvent extraction experiments are carried out varying the extractant content, equilibration time, pH and phase ratio. The iron in the leach solution is almost completely extracted and portion of calcium is also extracted, which is consistent with the above results. The main purpose of these experiments is to investigate the influence of varying extraction conditions on the extraction rate of zinc.

##### 3.2.1 Influence of extractant content

The influence of initial extractant content on the extraction of zinc is studied in the range of 10%–30% (volume fraction). It is observed that the extraction rate increases from 14% to 40% with the increase of extractant content (Fig. 2(a)). Usually the highest content of extractant during solvent extraction is 30%. If the extractant content is higher than 30%, the viscosity of organic phase will increase and the disengagement become difficult. The appropriate extractant content should be 30% in these experiments.

##### 3.2.2 Influence of equilibration time

The results presented in Fig. 2(b) reveal that the equilibration time of zinc extraction is very short. The extraction equilibrium is reached in 2 min, which indicates zinc extraction with D2EHPA is fast. With the increase of contact time, the zinc extraction does not increase any more. However,



**Fig. 2** Influence of extractant content(a), equilibrium time(b), aqueous pH(c) and phase ratio(d) on zinc extraction

it is observed an increasing number of impurities are co-extracted with the increase of time. So the contact time should be 2–3 min. In the following experiments, the contact time is kept at 5 min to ensure the zinc extraction equilibrium.

### 3.2.3 Influence of aqueous pH

Extraction of zinc is studied within the initial aqueous pH range of 1.0–2.5 (Fig. 2(c)). The zinc extraction increases remarkably as the pH value increase. While the pH value increase from 1.0 to 2.5, the zinc extraction rate increases from 21% to 48%. The pH value of leach solution is usually controlled at 2.0–2.5, at which the impurities in the solution are in low levels.

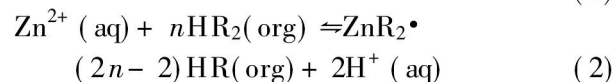
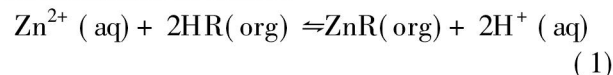
### 3.2.4 Influence of phase ratio

The influence of phase ratio (O/A) on zinc extraction is shown in Fig. 2(d). From the ratio range of 1:3 to 3:1, the zinc extraction rate increases from 17% to 54%. The increase of phase ratio means that there are more extractant involved in zinc extraction, as a result the extraction rate increases.

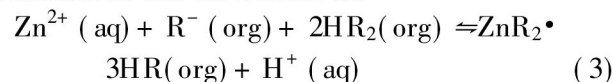
### 3.2.5 Influence of sodium salt of D2EHPA

Extraction of zinc from aqueous sulfate solution using D2EHPA is low. It is due to the poor cation exchange property of the extractant. The hydrogen is released and the pH value decreases during solvent ex-

traction, which held back the extraction reaction. D2EHPA in the kerosene diluent is present predominantly as dimer rather than as monomer, which will influence the metal extraction. The zinc extraction can be illustrated as follow:



To enhance the zinc extraction, the extractant is neutralized by adding concentrated sodium hydroxide. A stoichiometric quantity of NaOH is added to the extractant in kerosene and mixed intimately to form a single phase. The sodium salt of extractant exists as monomer in kerosene, and the extractant that can not neutralized still exists as dimer. Then the reaction of zinc extraction can be written as:



The influence of saponification rate on zinc extraction is listed in Table 1. It can be seen the extraction rates are greatly increased by using the sodium salt of D2EHPA. At the saponification rate of 80%, the zinc extraction rate increases to 98.2%. However, the equilibrium pH value increases with the in-

crease of co-extracted impurities. For example, at the pH of 1.0 the calcium extraction is low, and at the pH of 3.2 the calcium extraction rate is 96.3%. At high equilibrium pH, other harmful impurities such as copper, cobalt and nickel may be extracted too.

**Table 1** Influence of saponification rate on zinc extraction

Saponification rate/ %	Initial pH	Equilibrium pH	Extraction rate/ %		
			Zn	Fe	Ca
60	2.0	2.75	88.6	98.71	83.7
70	2.0	2.90	94.0	98.71	90.5
80	2.0	3.20	98.2	98.74	96.3

$\varphi(\text{D2EHPA}) = 30\%$ ;  $\text{O/A} = 1:1$ ; contact time 5 min

### 3.3 Scrubbing

In solvent extraction, the co-extraction of impurities is inevitable even if using the efficient extractant; and it is more familiar in treating high metal content solutions. Therefore, to obtain the pregnant metal solution with low contaminants, the loaded organic must be scrubbed to remove the co-extracted impurities.

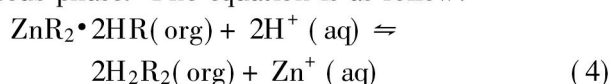
The loaded organic phase is prepared to contain 10 g/L zinc, 0.5 g/L iron, 0.62 g/L calcium, and 0.08 g/L silica. The scrubbing solution is zinc sulfate solution, which contained 30 g/L zinc, and the pH value is 1.5. To keep water balance, the high phase ratio (O/A) is likely to use. The influence of phase ratio on the scrubbing is listed in Table 2. It is seen the co-extracted calcium and the entrainment of silica in loaded organic can be removed by scrubbing, and the phase ratio (O/A) of 10:1 is acceptable. The iron can't be removed by scrubbing.

**Table 2** Influence of phase ratio(O/A) on scrubbing

O/A	Component of loaded organic after scrubbing/(g·L <sup>-1</sup> )			
	Zn	Fe	Ca	Si
5/1	11.1	0.495	Minim	Minim
10/1	10.6	0.497	Minim	Minim
20/1	10.4	0.498	0.001	Minim
30/1	10.1	0.498	0.070	Minim

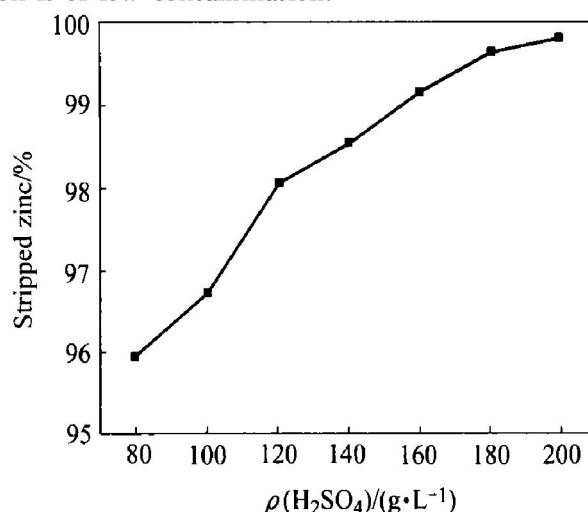
### 3.4 Selective stripping

The stripping is the reverse process of extraction, in which zinc in organic phase is transferred to aqueous phase. The equation is as follow:



Hence the aqueous phase in stripping must be of high acidity to keep the equilibrium move rightwards.

The solution usually is the electrolyte raffinate. The prepared zinc loaded organic phase contained 8.1 g/L zinc, 0.43 g/L iron(III), and minimum of calcium and silica. The prepared aqueous solution contained 30 g/L zinc. The influence of acidity on zinc stripping is shown in Fig. 3. The stripping rate increases with the increase of acidity. When the acidity is 120 g/L H<sub>2</sub>SO<sub>4</sub>, the stripping rate is 98.07%, so the excessive acidity of more than 120 g/L H<sub>2</sub>SO<sub>4</sub> is not necessary. It is interested that the iron in the loaded organic phase is hardly stripped by sulfuric acid, even in the high acidity of 200 g/L H<sub>2</sub>SO<sub>4</sub>. Therefore zinc is likely to be separated from iron by selective stripping. The chemical components of the zinc pregnant solution are listed in Table 3. It is seen that the solution is of low contamination.

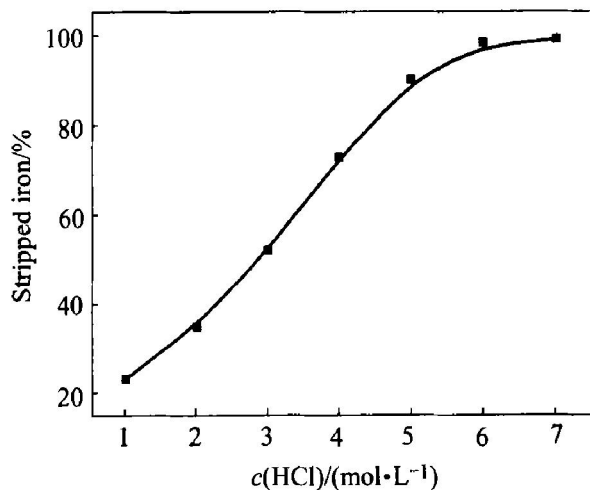


**Fig. 3** Influence of H<sub>2</sub>SO<sub>4</sub> content on zinc stripping  
(Phase ratio 1:1; contact time 5 min)

**Table 3** Chemical component of zinc pregnant solution (g/L)

Zn	Fe	Cu	Mn	Co
55	2	0.04	15	0.02
Cd	CaO	Ni	MgO	
0.08	14	Minim	Minim	

Though the iron content in the leach solution is low, it will accumulate in the recycled organic, which decreases the loading capacity of the extractant. Hence the recycled organic must be treated periodically to remove the iron(III). Galvanic stripping is a method to remove Fe<sup>3+</sup>, in which the Fe<sup>3+</sup> is reduced to Fe<sup>2+</sup> in the organic phase by zinc or iron metal, and the Fe<sup>2+</sup> is easily stripped by dilute sulfuric acid. However, the method is difficult to control and industrialize<sup>[8]</sup>. Another conventional method is that the Fe<sup>3+</sup> is directly stripped by



**Fig. 4** Influence of HCl concentration on iron stripping  
(Phase ratio 1: 1; contact time 5 min)

concentrated hydrochloric acid. The influence of the acidity of hydrochloric acid on  $\text{Fe}^{3+}$  stripping is shown in Fig. 4. It is seen a strong acid solution (6 mol/L) is required to strip  $\text{Fe}^{3+}$  from D2EHPA, at which the  $\text{Fe}^{3+}$  stripping is near 100%.

#### 4 CONCLUSIONS

1) The extraction order of D2EHPA as a function of  $\text{pH}_{0.5}$  is  $\text{Fe}^{3+} > \text{Zn}^{2+} > \text{Ca}^{2+} > \text{Al}^{3+} > \text{Mn}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Mg}^{2+}$ . D2EHPA dissolved in 260# kerosene is used as zinc extractant in solvent extraction of zinc from the leach solution of zinc oxide ore. Increase of extractant content, aqueous pH and O/A ratio will increase the extraction rate of metal.

2) The zinc extraction is low due to the poor cation exchange and the polymerization of the extractant. Using the sodium salt of D2EHPA may increase the extraction rate. However more impurities are likely to be co-extracted because of the increase of equilibrium pH.

3) In the solvent extraction,  $\text{Fe}^{3+}$  is preferentially extracted before the extraction of zinc, and portion of calcium and other impurities are co-extracted or entrained. The co-extraction or entrainment of impurities is successfully removed by scrubbing with zinc sulfate solution, and zinc is

separated from  $\text{Fe}^{3+}$  by selective stripping. The pregnant zinc sulfate solution obtained from leach solution of zinc-oxidized ore by solvent extraction is of low contaminants.

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