



# Germanium recovery by co-precipitation of germanium and iron in conventional zinc metallurgy

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## Synopsis

A modified germanium recovery process in conventional zinc metallurgy, based on the understanding that ferric hydroxide has strong ability to coprecipitate germanium element, was presented. The relaxed lab-scale experiments were conducted to evaluate its technological feasibility. The experimental results obtained show the new process has great competitive advantage over the conventional one.

## Introduction

A considerable fraction of germanium is produced as a by-product in zinc metallurgy. In the conventional roast-leach-electrowin (RLE) process, most of the germanium is incorporated into the neutral leaching residue, which is the main source for germanium recovery. As the largest germanium supplier worldwide, Yunnan Chihong Zinc & Germanium Co., Ltd (Yunnan, China), recover germanium shown in Figure 1. In the process, a great deal of chemical material such as tannic acid is consumed and the germanium concentrate obtained is of very low grade. The reason why a great deal of tannic acid is needed to precipitate germanium is that many types of metal ions can form complexes with it<sup>1-3</sup>.

O.S. Pokrovsky *et al.* found germanium coprecipitate with iron hydroxide<sup>4</sup>. Based on this understanding, a modified process was presented, as in Figure 2. In this paper, the variables influencing the germanium precipitation were investigated

## Experimental

Both of the hot acid leach liquor and fuming dust originated from Yunnan Chihong Zinc & Germanium Co., Ltd. Their chemical composition is listed in Tables I-II, respectively. All other reagents were of analytic grade and used without further purification.

As seen as from Tables I-II, hot acid leach liquor contains a great deal of iron.

Complexation and neutralization experiments were conducted in 500-ml glass

reactors, which were kept temperature constant with a water bath.

In every neutralization experiment run, 250 ml hot acid leach liquor was neutralized by fuming dust with a fixed stirring rate of 5 rps. The pH values were determined with a Beckman F-200 pH meter (Beckman Instruments, Fullerton, CA, USA). After every experiment run, the residue is dried and ground to 98%-180 mesh, and then sent to Yunnan Non-Ferrous Metals & Products Quality Supervision and Analysis Center to analyze the contents of the germanium. The BSE detector used was manufactured by GW Electronics Inc., Atlanta, GA, USA

The values of total germanium precipitation yield were calculated by Equation [1].

$$P_t = \frac{W_p}{W_d} + W_l \quad [1]$$

where,  $P_t$  is the total germanium precipitation yield, %;  $W_p$  is the mass of the precipitated germanium, g;  $W_d$  is the mass of germanium contained in fuming dust, g;  $W_l$  is the mass of precipitation dissolved in the hot acid leach liquor.

## Results and discussion

### Effect of final sulphuric acid concentrations

The relationship between the total germanium precipitation yield and the final solution pH is described in Figure 3.

As expressed in Figure 3, total germanium

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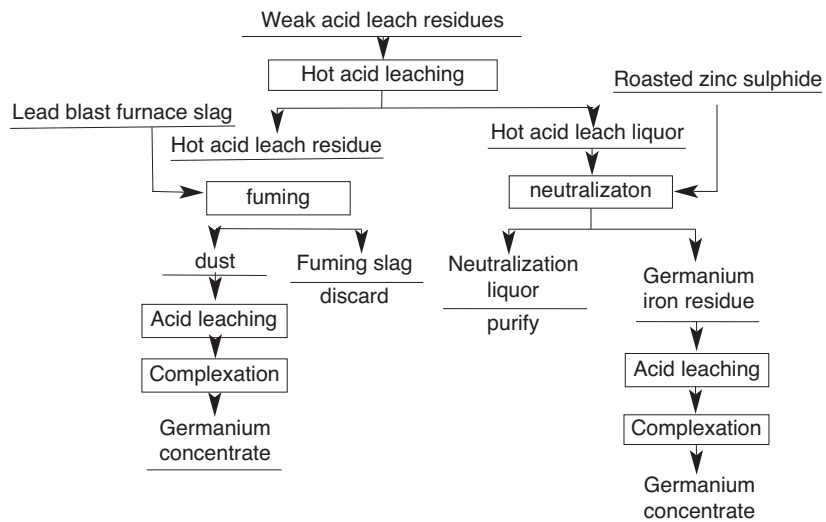


Figure 1 – The routine workflow sheet

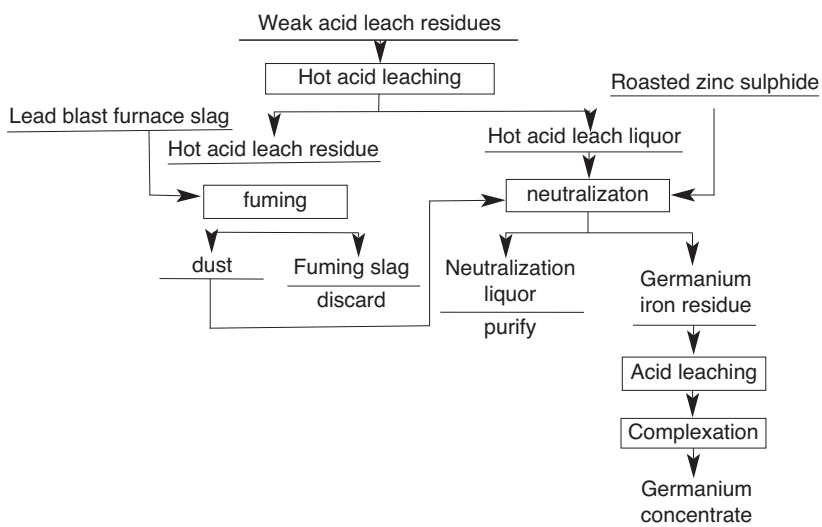


Figure 2 – The recommended workflow sheet

Table I

### The chemical composition of hot acid leach liquor (g·l<sup>-1</sup>)

Element	Zn	Fe <sup>2+</sup>	Fe <sup>3+</sup>	Cu <sup>2+</sup>	Cd <sup>2+</sup>	H <sub>2</sub> SO <sub>4</sub>	Mn	Ge <sup>4+</sup>
Concentration	123.5	8.14	10.15	0.2	0.31	60.70	2.28	0.052

Table II

### The chemical composition of fuming dust (%)

Element	Ge	Zn	Pb	Cd	Fe	S	SiO <sub>2</sub>	Other
Concentration	0.0306	47.04	11.84	0.015	1.83	0.21	3.25	35.78

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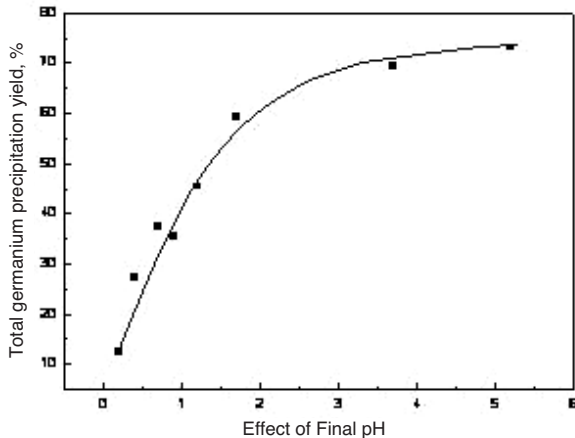
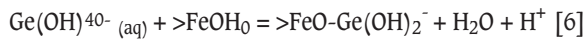
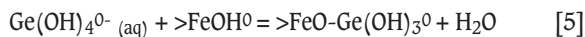
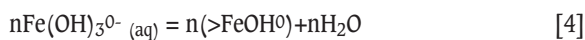
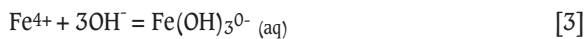
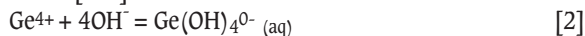


Figure 3—The effect of final pH neutralization conditions: temperature, 353 K; manganese oxide powder, 0 g

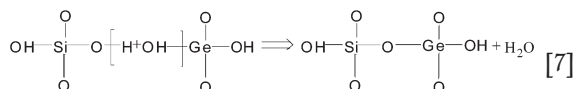
precipitation yield increased rapidly with increasing final solution pH.

O.S. Pokrovsky claimed that germanium hydroxide complexation with ferric hydroxide can be represented by Reactions [2–6].



These reactions indicate that low acidity contributes to the high precipitation kinetics of germanium and iron.

D. D. Harbuck<sup>5</sup> also presented that some germanium ions may become tied up with silicon gel, as in Reaction [7]. In this process, low acidity also helps germanium precipitate.



### Effect of temperature

The relationship between total germanium precipitation yield and neutralization temperature is described in Figure 4.

As expressed in Figure 4, total germanium precipitation yield decreased with increasing neutralization temperature. Reaction equilibrium can be reached at high temperatures, but at such conditions, solubility products of germanium and iron hydroxide become less<sup>6</sup>, which lower germanium precipitation yield.

### Effect of manganese oxide powder usage

The relationship between total germanium precipitation yield and manganese oxide powder usage is described in Figure 5. As seen from it, total germanium precipitation yield increased with increasing manganese oxide powder usage. But when manganese oxide powder usage reached 4 g, total germanium precipitation yield did not increase significantly.

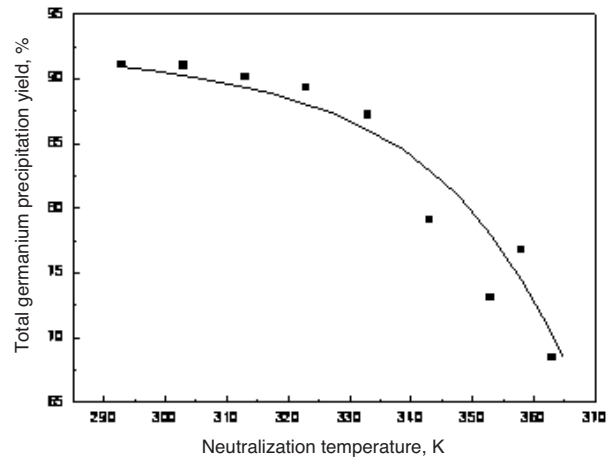


Figure 4—The effect of temperature, final solution pH 5.2; manganese oxide powder, 0 g

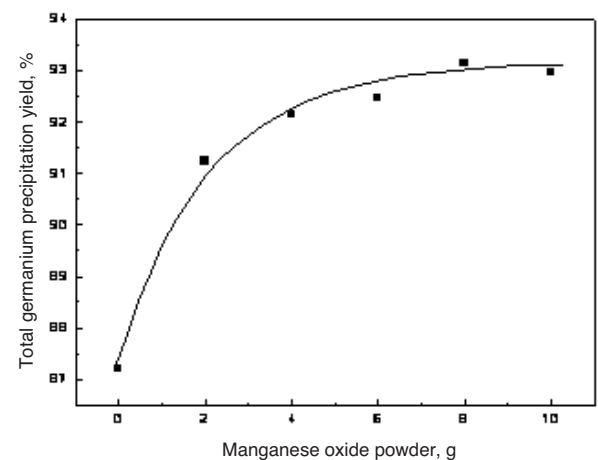
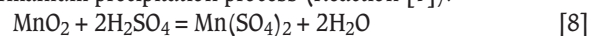
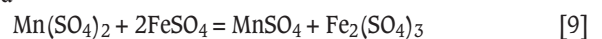


Figure 5—The effect of manganese oxide powder usage, neutralization conditions: final solution pH 5.2; temperature 333 K

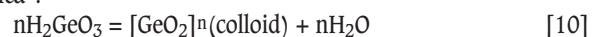
Manganese oxide powder can oxidize the ferrous ions to ferric ones (Reaction [8]), which can accelerate the germanium precipitation process (Reaction [9]).



and



A sample of the germanium-iron residue was polished and carbon-coated for observation with a BSE detector (Figure 6). Germanium's uniform distribution in the iron residue indicates that germanium may polymerized into a colloid by hydrolysis, as given by Reaction [10], behaving similarly to silica<sup>7</sup>.



### Comparisons between the new process and the old one

As mentioned above, iron hydroxide has capability of absorption to germanium. The laboratory-scale the experimental results show that precipitation of germanium by co-precipitation of iron can lead to germanium concentrate with a higher grade, and less tannic acid consumption (Table III), according to the existing technology.

# Germanium recovery by co-precipitation of germanium and iron



Figure 6—BSE image of a sample of germanium-iron residue

## Conclusions

The present study showed that low final solution pH and complexation temperature contribute to higher germanium precipitation yield and less tannic acid consumption.

It is expected that precipitation of germanium by co-precipitation of iron can lead to germanium concentrate with a higher grade, and less tannic acid usage was proved in later scale-up experiments.

## Acknowledgements

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Table III

### Comparison between the old process and the new one

Item	Old process		New process
	dust	liquor	
Consumption of tannic acid (multiple of theory usage)	52.04	27.5	25.4
grade of germanium concentrate (per cent)	9.84	42.5	48.21

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