

# Leaching of Germanium from Zinc Residue in H<sub>2</sub>SO<sub>4</sub>/SO<sub>2</sub> Solutions

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## To cite this article:

Xuelan Wu, Hongming Long, Xin Li, Yanxu Shen, Yangyang Zhang, Zhipeng Li, Yiming Hu. Leaching of Germanium from Zinc Residue in H<sub>2</sub>SO<sub>4</sub>/SO<sub>2</sub> Solutions. *American Journal of Chemical Engineering*. Vol. 6, No. 5, 2018, pp. 86-93. doi: 10.11648/j.ajche.20180605.12

Received: September 12, 2018; Accepted: September 27, 2018; Published: October 26, 2018

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**Abstract:** Zinc residue with high germanium, a waste solid product of hydrometallurgical zinc process is dumped continuously, causing the loss of germanium. Zinc residue was characterized by chemical analysis, X-ray diffraction, and inductively coupled plasma mass spectrometry methods. The results showed that, the mineralogical compositions of the zinc residue used in this research were zinc ferrite, gypsum, hemihydrate gypsum, anglesite, sphalerite and quartz. Approximately 58% and 20% germanium occurred in the ferrite and silicate phases, respectively. Leaching of zinc residue with high germanium was investigated as a process to recover germanium. It was found to be much more effective using sulfur dioxide as a reductant. Batch leaching tests were carried out on zinc residue with high germanium at set pressure in stirred acid solution. The effects of SO<sub>2</sub>, time, sulfuric acid concentration, temperature, liquid-to-solid ratio, and sulphur dioxide partial pressure on the germanium dissolution were studied to optimize the leaching parameters. In the presence of SO<sub>2</sub>, the results showed that the extraction of germanium was maximum of 70% while the extraction of zinc and iron were 90% and 96% under the optimal condition which was determined for 80 g of zinc residue using 56 g/L sulfuric acid, liquid-to-solid ratio of 7 mL/g and sulphur dioxide partial pressure of 200 kPa at 100°C after 120 min. Under optimal conditions, the main minerals of the reduction leaching residue were sodium iron sulfate tetrahydrate, gypsum, hemihydrate gypsum, anglesite, sphalerite and quartz. Zinc ferrite was almost entirely leached.

**Keywords:** Germanium, Acid Leaching, Zinc Residue, Sulphur Dioxide

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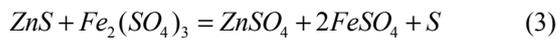
## 1. Introduction

Germanium is an important metal. The small bandgap and high mobility of charge carriers make germanium an attractive material in many application fields, from photovoltaics to microelectronics, from optics to radiation detectors [1]. Germanium's abundance in the Earth's crust is approximately  $1.6 \times 10^{-6}$  [2]. Only a few minerals like argyrodite, briartite, germanite, and renierite contain appreciable amounts of germanium, and none in mineable deposits [3]. Until today germanium is mostly gathered as a coproduct of silver, copper and zinc production or from combustion residues (fly ashes) from certain coals which can contain considerable

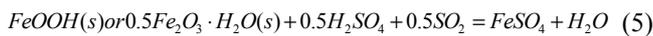
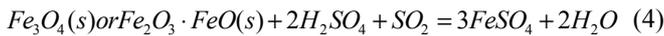
concentrations of germanium [4].

In the process of zinc hydrometallurgy process, improving the rate of zinc recovery and comprehensive utilization of valuable metals in the raw materials are two important problems. Due to the present processing of raw materials of high iron zinc concentrate, it inevitably produces insoluble zinc ferrite (ZnO•Fe<sub>2</sub>O<sub>3</sub>) at the first step in the hydrometallurgical process of Zinc Roasting, the direct leaching rate of zinc is only about 85%, the slag contains about 20% zinc. The researchers found that about 93% or more germanium associated with the material was found in

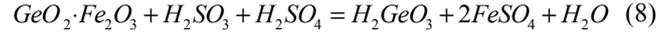
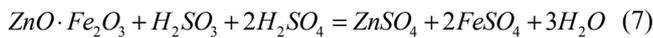
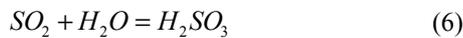
zinc ferrite, most of germanium presents in the form of isomorphism in zinc ferrite and formats Zn(Fe,Ge)<sub>2</sub>O<sub>4</sub> type ferrite solid solution [5-6]. Therefore, the treatment of zinc ferrite is not only the key to improve the recovery rate of zinc, but also the key to recover the scattered metal such as germanium. Because zinc ferrite is difficult to dissolve in low acid, extraction of germanium from zinc residue has a certain degree of difficulty. To recover the zinc and germanium, iron must be into the solution. There are two main ways to make iron into solution. One method is hot acid leaching which needs high temperature and high acid concentration. In the condition of high acidity, zinc ferrite gradually is dissolved. Iron, zinc, and germanium enter the solution together; the iron still exists as Fe<sup>3+</sup>. The recovery of germanium requires the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup>. ZnS in zinc concentrates can reduce Fe<sup>3+</sup> to Fe<sup>2+</sup>. The main reactions are as follows.



The other method is reduction leaching. Thermodynamic analysis shows that it is possible to decompose zinc ferrite into Fe<sub>3</sub>O<sub>4</sub> (or FeO) in a weak reduction atmosphere[6]. Due to the strong reducing nature of Sulfur dioxide (SO<sub>2</sub>), it is an efficient leaching agent for minerals containing oxides of iron, nickel, cobalt and manganese [7-13]. Studies have been reported on SO<sub>2</sub> accelerated leaching of various natural and synthetic iron oxides such as magnetite (Fe<sub>3</sub>O<sub>4</sub>), goethite (α-FeOOH), hematite (Fe<sub>2</sub>O<sub>3</sub>) and nickel/cobalt spiked goethite at atmospheric pressure [8, 12, 14-18]. The main reactions occurred:



Because zinc ferrite (ZnO•Fe<sub>2</sub>O<sub>3</sub>) and Fe<sub>3</sub>O<sub>4</sub> belong to the same category of spinels, SO<sub>2</sub> was used as reducing agent for reducing ZnO•Fe<sub>2</sub>O<sub>3</sub>. The main reactions occurred:



In this work, a typical zinc residue with high germanium content has been used for reduction leaching studies in the presence of gaseous SO<sub>2</sub>. The zinc residue has been characterized by mineralogical analysis and leaching studies have been conducted to understand the effects of various leaching parameters—the effects of SO<sub>2</sub>, time, acid concentration, temperature, liquid-to-solid ratio and sulphur dioxide partial pressure.

## 2. Experimental

### 2.1. Test Materials

The zinc residue with high germanium content used in the present study was kindly supplied by a zinc producer in Guangdong Province of China. The proportions of main chemical elements were 16.23 wt% zinc, 23.12 wt% iron, 8.90 wt% sulphur, 11.2 wt% silica, 3.66 wt% lead, 0.034 wt% germanium, 0.046 wt% sodium, 2.45 wt% calcium, and 0.054 wt% silver (Table 1). X-ray diffraction (XRD, Rigaku D/max-2550VB/PC) analysis showed the zinc residue was mainly composed of zinc ferrite (ZnFe<sub>2</sub>O<sub>4</sub>), sphalerite ((Zn, Fe)S), hemihydrate gypsum (CaSO<sub>4</sub>•0.5H<sub>2</sub>O), gypsum (CaSO<sub>4</sub>•2H<sub>2</sub>O), anglesite (PbSO<sub>4</sub>) and quartz (SiO<sub>2</sub>) as shown in Figure 1. No special germanium bearing minerals were identified. The result of SEM analysis of zinc residue is shown in Figure 2. The shape of zinc ferrite in zinc residue iron is octahedron. The single grain size of zinc ferrite is only about 1µm to 3µm. The phase analysis of zinc in zinc residue is summarized in Table 2, based on the chemical analyses. Zinc ferrite was the main phase and accounted for 71.16%, others were zinc sulfate, zinc sulfide and zinc silicate phase. The germanium present in the different phases of zinc residue is given in Table 3. Approximately 58% and 20% germanium occurred in the ferrite and silicate phases, the content of germanium oxide is about 8%, and it was also found that there were about 11% water soluble germanate in zinc residue. The silicate phase that reported germanate might be mainly the amorphous silica or zinc silicates which were not identified in XRD of the zinc residue (Figure 1). Different particle size fractions were obtained by wet sieving and listed in Table 4. For the present study, the zinc residue with particle size distribution of less than 0.038 mm was used.

**Table 1.** Chemical composition of zinc residue.

Components	Zn	S	Fe	SiO <sub>2</sub>	Pb	Ge	Na	Ca	Ag
Sample/wt.%	16.23	8.90	23.12	11.2	3.66	0.034	0.046	2.45	0.054

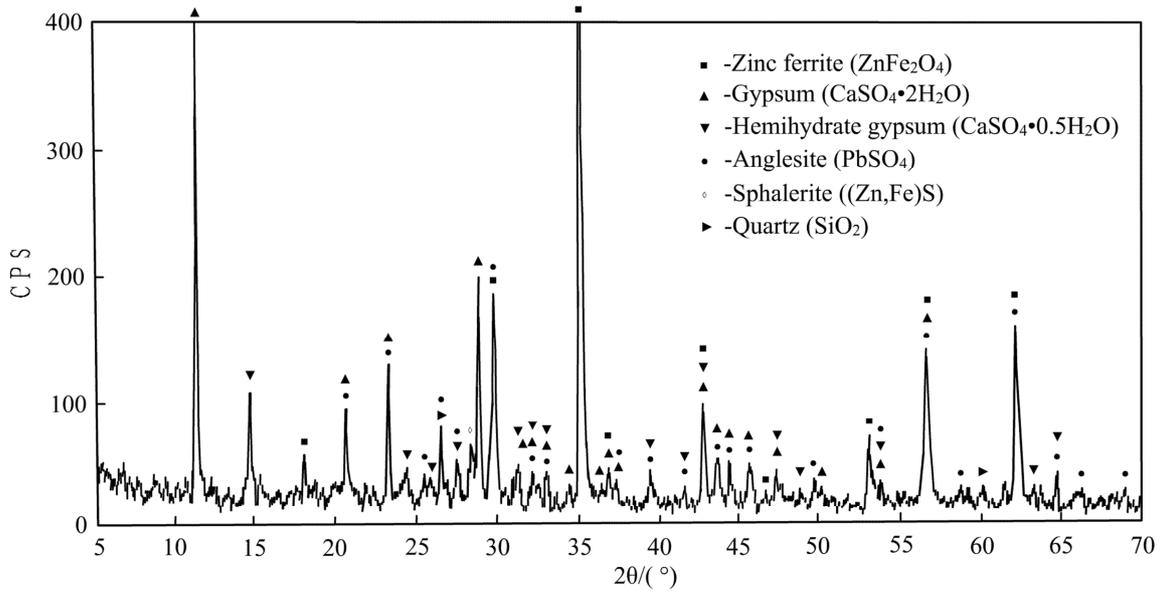


Figure 1. XRD pattern of zinc residue.

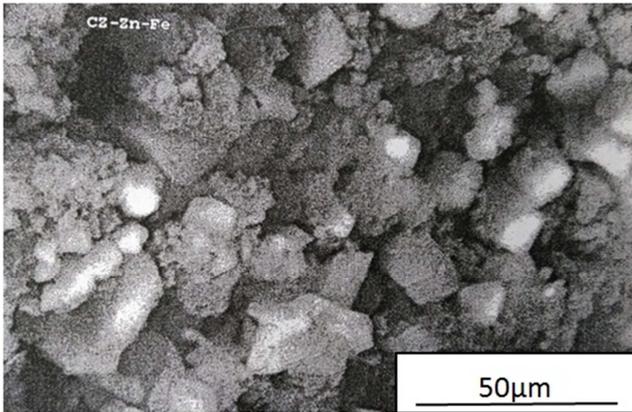


Figure 2. Back scattered electrons image of zinc residue.

Table 2. Phase of zinc in the sample.

Constituent	Zinc sulfate	Zinc sulfide	Zinc silicate	Zinc ferrite	Total
Content/ wt%	2.47	1.83	0.38	11.55	16.23
Distribution/%	15.22	11.28	2.34	71.16	100.00

Table 3. Phase of germanium in the sample.

Constituent	Germanate	Oxide	Silicate	Ferrite	Total
Content/ wt%	0.004	0.003	0.007	0.020	0.034
Distribution/%	11.76	8.82	20.59	58.82	100.00

Table 4. The granularity composition of zinc residue.

Grain size/mm	Weight/g	Proportion/%
>0.25	0	0
0.147~0.25	0.11	0.11
0.104~0.147	0.49	0.49
0.074~0.104	0.68	0.68
0.043~0.074	1.11	1.11
0.038~0.043	1.65	1.65
<0.038	95.96	95.96
Total	100.00	100.00

In all the leaching experiments, the analytical grade sulfuric acid with a mass fraction of 98% and a density of 1.84 g·ml<sup>-1</sup> was used. Sulphur dioxide (g) used was of 99.98% purity. Deionized water and analytical grade chemicals were used in all the experiments.

2.2. Test Equipment and Research Method

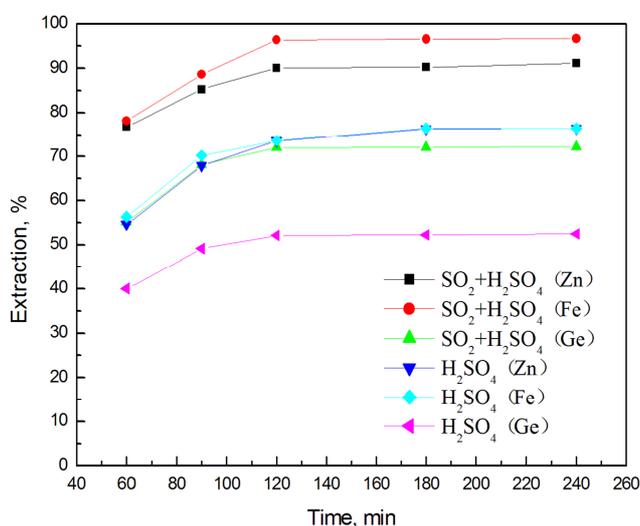
Acid corrosion resistant titanium autoclave was employed in this work. It mainly consists of a heating mantle, a PID temperature controller, a variable speed stirrer and an internally mounted cooling coil. 80 g zinc residue was added to the autoclave. After slurring the residue with sulphuric acid and water in autoclave, and heating the solution to the set temperature of the experiment, the sulphur dioxide was injected and the partial pressure of sulphur dioxide was adjusted to the desired value, which was maintained constant for the duration of the experiment. After the experiment, the sulphur dioxide was shut down, the autoclave was rapidly water-cooled, and the solid residue was then vacuum filtered and dried at 80°C for 24 h. The solid residue and solution were analyzed, and extraction of zinc and iron were calculated from the solids chemical analysis. The germanium concentration during the leaching process was measured by an inductively coupled plasma mass spectrometry (ICP-MS, VG PQEXCELL, Thermo Electron Corporation).

3. Results and Discussion

The effects of SO<sub>2</sub>, leaching time, sulfuric acid concentration, temperature, liquid-to-solid ratio and sulphur dioxide partial pressure were examined to optimise the leaching parameters. The results obtained are discussed below.

### 3.1. Effect of SO<sub>2</sub> and Leaching Time

In the reduction leaching, the majority of the iron (III) present in the leach process is converted to the iron (II) state. Injection of sulfur dioxide into the solution provides a reductant of converting Fe<sup>3+</sup> into Fe<sup>2+</sup>, more than 95% of the iron is reduced by sulphur dioxide into the solution. Figure 3 shows that the leaching of the zinc residue in H<sub>2</sub>SO<sub>4</sub> solution was insignificant giving poor extractions of zinc, iron and germanium; the extractions were 76% zinc, 76% iron and 52% germanium after 240 min. However, in SO<sub>2</sub>-H<sub>2</sub>SO<sub>4</sub> solution, the extractions of zinc, iron and germanium were increased significantly giving 91%, 96% and 72% respectively. Das *et al.* [9] reported a similar effect for the SO<sub>2</sub> in H<sub>2</sub>SO<sub>4</sub> leaching of West Australian limonite ore. The higher extraction of iron from smectite ore in SO<sub>2</sub>-H<sub>2</sub>SO<sub>4</sub> appears to be due to the SO<sub>2</sub>, facilitating the reduction of Fe(III)-sites within the nontronite and at the surface of the iron oxide mineral enabling Fe(II) to dissolve readily, the latter proposed previously by Byerley *et al.* [8]. Figure 3 also presents the effect of leaching time on the leaching of zinc residue. With the increase of leaching time, the leaching efficiencies were improved, especially in the initial periods of 0-120 min. With the leaching time of 120 min, the germanium leaching efficiency reached 72% at 100°C. When the leaching time was above 120 min, there was no significant increase in zinc, iron and germanium extraction. It shows that the leaching has been basically completed in the early stage. Considering the equipment production capacity and production cost, a leaching time of 120 min was chosen in the study.

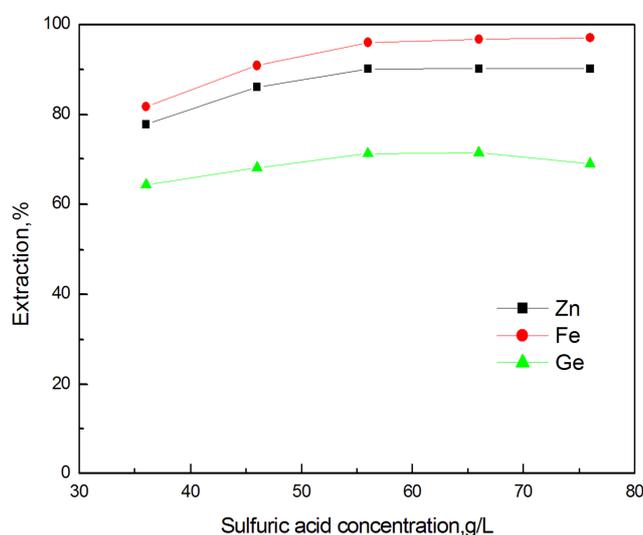


**Figure 3.** Effect of SO<sub>2</sub> on extraction of zinc, iron and germanium from zinc residue. (Temperature: 100°C; 56 g/L H<sub>2</sub>SO<sub>4</sub>; L/S: 7 mL/g; sulphur dioxide partial pressure: 200 kPa).

### 3.2. Effect of Sulfuric Acid Concentration

In the reduction leaching process, the solubility of sulfur dioxide decreases with increasing in sulfuric acid concentration, which is not conducive to the reduction of leaching. So selecting the appropriate concentration of sulfuric acid is necessary. The effect of sulfuric acid

concentration on the leaching of zinc residue was studied in the range 36 g·L<sup>-1</sup> to 76 g·L<sup>-1</sup>. Figure 4 shows the extraction of zinc, iron and germanium as a function of sulfuric acid concentration in the leaching solution. It can be seen from Figure 4 that the curves of leaching efficiencies of zinc, iron and germanium increased faster with the increase in the sulfuric acid concentration from 36 to 56 g·L<sup>-1</sup>, but leaching efficiencies of zinc, iron were slightly improved when the concentration was over 56 g·L<sup>-1</sup>. The leaching efficiencies of zinc, iron and germanium reached 90%, 96% and 71% when sulfuric acid concentration was 56 g·L<sup>-1</sup>. Above 56 g·L<sup>-1</sup> sulfuric acid germanium extraction slight decreased. For increasing the amount of sulfuric acid, the germanium in the solution will be precipitated by GeO<sub>2</sub>. And in the cooling process after the completion of the leaching, the germanium into the solution was absorbed by Si(OH)<sub>4</sub>, which reduced the apparent leaching rate of germanium [19]. It can be seen that the amount of sulfuric acid is a very important factor in the leaching of germanium. Normally, if sulfuric acid concentration is too low, so it can't provide the acidity required for the reduction leaching reaction. The reductant in the solution is not completely impregnated with zinc residue, and then the leaching effect of various metals in zinc residue is affected. If the concentration is too high, other impurity metal ion will dissolve. Moreover, the size of the acidity is also an influence on the subsequent process. Considering the equipment corrosion resistance requirements and reasonable cost requirements, the sulfuric acid concentration of 56 g/L is appropriate, the final solution when the acid concentration was about 2.5 g/L. It is beneficial to the follow-up process.



**Figure 4.** Effect of sulfuric acid concentration on extraction of zinc, iron and germanium from zinc residue. (Temperature: 100°C; L/S: 7 mL/g; sulphur dioxide partial pressure: 200 kPa; 120 min).

### 3.3. Effect of Temperature

The extraction of metals is also affected by leaching temperature. For most reactions, by Van Hove rules:

$$\gamma = \frac{\kappa_{t+10}}{\kappa_t} \quad (9)$$

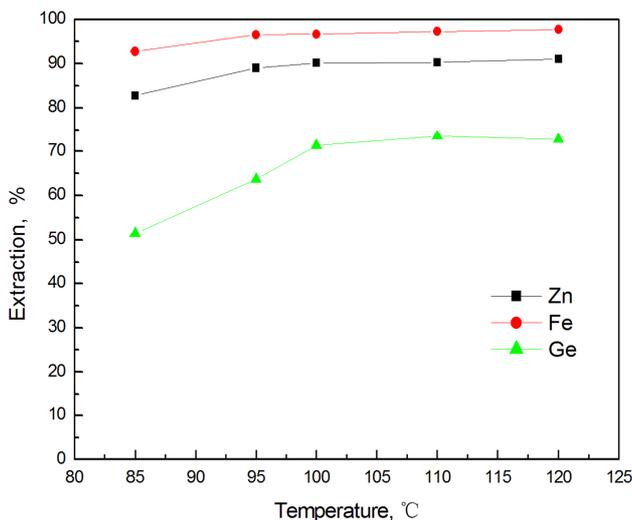
$\kappa_{t+10}$  - rate constant at temperature (t+10)°C;

$\gamma$  - the temperature coefficient of the reaction rate, dimensionless, with a value of about 2-4;

$\kappa_t$  - rate constant at temperature t°C.

The reaction temperature is increased by 10°C, the reaction rate can be increased by 2-4 times, so increasing leaching temperature is beneficial to metal leaching, whilst high temperatures have disadvantages such as higher energy consumption. So in our present study, a medium temperature range from 85°C to 120°C was selected and its affect on metal extraction was studied.

Figure 5 shows the effect of temperature on the leaching of zinc residue. Germanium extraction increased from 51% to 71% when the temperature increased from 85°C to 100°C, but a further increase in temperature to 120°C had no significant affect. Accordingly, the extraction of zinc increased from 82% to 90% while that of iron increased from 92% to 96% when the temperature increased from 85°C to 100°C. And a further increase in temperature to 120°C again had no significant affect. This is mainly related to the solubility of SO<sub>2</sub>. Reduction of SO<sub>2</sub> is mainly generated by dissolving H<sub>2</sub>SO<sub>3</sub> in water, then the redox reaction of H<sub>2</sub>SO<sub>3</sub> and zinc ferrite occurs. SO<sub>2</sub>-H<sub>2</sub>O system E-pH diagram shows that with the increase of temperature the SO<sub>2</sub> stable region increased significantly at 100°C compared with 25°C, which means that the concentration of H<sub>2</sub>SO<sub>3</sub> decreases. The spreading of H<sub>2</sub>SO<sub>3</sub> to the inner mineral becomes the control steps. Therefore the optimum temperature appeared to be 100°C and all further experiments were carried out at this temperature.

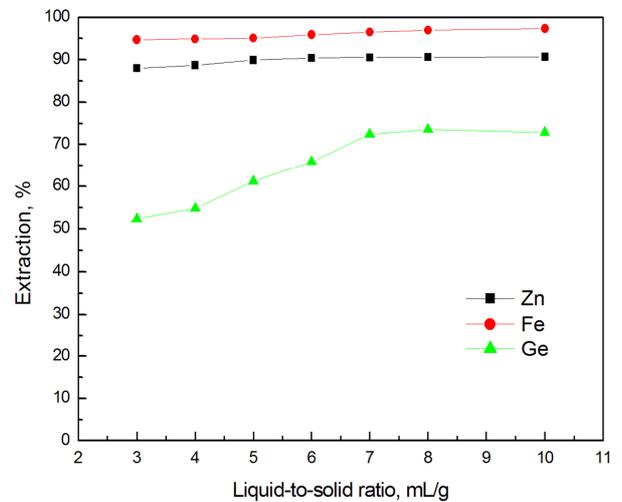


**Figure 5.** Effect of temperature on extraction of zinc, iron and germanium from zinc residue. (56 g/L H<sub>2</sub>SO<sub>4</sub>; L/S: 7 mL/g; sulphur dioxide partial pressure: 200 kPa; 120 min).

### 3.4. Effect of Liquid-to-Solid Ratio

In general, the leaching speed will accelerate with

increasing L/S, this is because the viscosity of the reaction liquid is decreased with increasing L/S, and the diffusion condition can be improved. But the volume of the leaching container needs to be increased and the investment of the equipment will be increased with increasing L/S. Therefore, liquid-to-solid ratio should be chosen according to the specific situation [20]. In the study, under conditions of sulfuric acid concentration: 56 g·L<sup>-1</sup> and sulphur dioxide partial pressure: 200 kPa, zinc residue was leached for 120 min at 100°C. The extractions of zinc, iron and germanium in such conditions are plotted in Figure 6 at different L/S (3-10 mL/g). Results show that germanium extraction increased with increasing L/S. When L/S was greater than or equal to 7 mL/g, the curve changed to be steady. Considering the burden of filtration and energy consumption, thus a liquid-to-solid ratio of 7 mL/g was considered optimal.



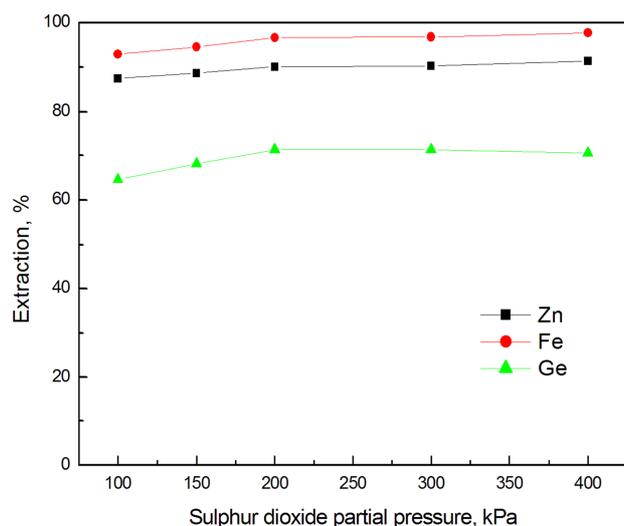
**Figure 6.** Effect of liquid-to-solid ratio (L/S) on extraction of zinc, iron and germanium from zinc residue. (Temperature: 100°C; 56 g/L H<sub>2</sub>SO<sub>4</sub>; sulphur dioxide partial pressure: 200 kPa; 120 min).

### 3.5. Effect of Sulphur Dioxide Partial Pressure

According to Henry's law, increasing the partial pressure of SO<sub>2</sub>, the solubility of SO<sub>2</sub> in solution will be improved. In the same solution, the concentration of SO<sub>2</sub> will increase; SO<sub>2</sub> molecules dissolved in the solution will increase. The contact probability of SO<sub>2</sub> molecule and zinc residue increase, then the rate of chemical reaction will be promoted.

Five tests were carried out at different sulphur dioxide partial pressures ranging from 100 kPa to 400 kPa for liquid-to-solid ratio of 7 mL/g and 56 g·L<sup>-1</sup> sulfuric acid concentration at 100°C for 120 min.

Figure 7 shows the variation in extraction of zinc, iron and germanium as a function of the sulphur dioxide partial pressure. When sulphur dioxide partial pressure was 200 kPa, the extraction of germanium was maximum of 71%. The extraction of zinc and iron were 90% and 96%. However, a further increased in the sulphur dioxide partial pressure from 200 to 400 kPa did not produce a substantial increase in the dissolution rate. So it can be constructed that 200 kPa was the best pressure for leaching of zinc residue.



**Figure 7.** Effect of sulphur dioxide partial pressure on extraction of zinc, iron and germanium from zinc residue. (Temperature: 100°C; 56 g/L H<sub>2</sub>SO<sub>4</sub>; L/S: 7 mL/g; 120 min).

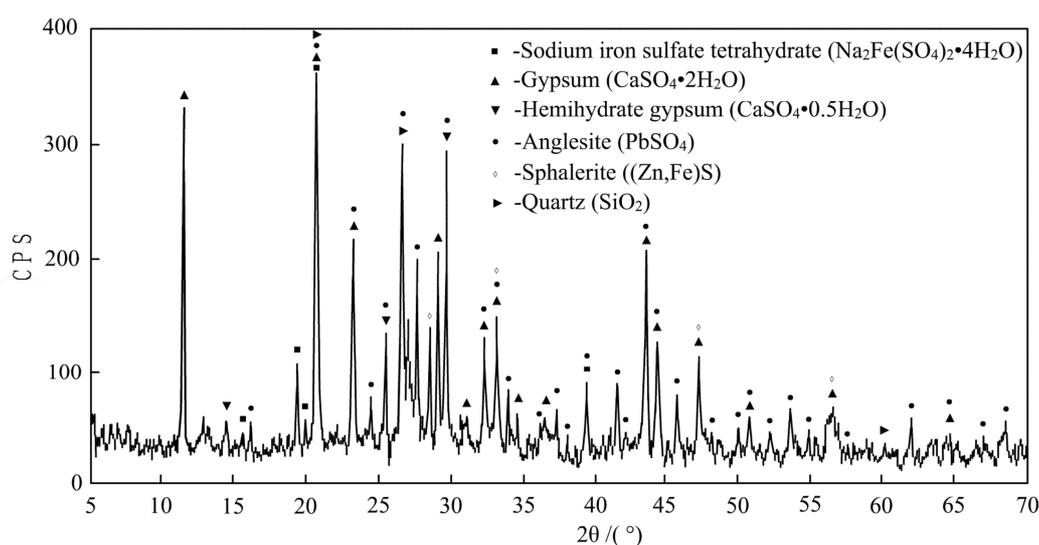
### 3.6. Characterization of the Residues from Reduction Leaching

In order to control the range of error and investigate the stability of the process, it is necessary to carry out the comprehensive condition test under the optimum technological conditions. Based on the above factors and the result analysis, it is concluded that the reasonable technological conditions for SO<sub>2</sub> leaching of zinc residue are as follows: 56 g·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, 200 kPa sulphur dioxide partial pressure, liquid-to-solid ratio of 7 mL/g, at 100°C for 120 min. The test results of comprehensive conditions are shown in table 5. According to table 5, under reasonable technological conditions, the extraction of germanium was maximum of 70% while the extraction of zinc and iron were 90% and 96%. Table 6 is the

main chemical composition of reduction leaching residue. It shows that the reduction leaching residue became a Pb rich material (PbSO<sub>4</sub>) with high SiO<sub>2</sub> containing ~0.2% Ag. There were small amounts of Zn and Fe. Germanium content was very low. Phase analysis of germanium in reduction leaching residue is shown in Table 7. As shown in Table 7, the ferrite has dissolved completely, 66% of germanium in the reduction leaching residue exists in silicate form and it is difficult to dissolve in sulfuric acid system. This is also the main reason for the low leaching rate of germanium. A typical XRD pattern of the reduction leaching is given in Figure 8. It can be seen clearly in Figure 8 that constituent phases of the residue changed as compared to the zinc residue. The main compositions of the residue were sodium iron sulfate tetrahydrate (Na<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O), gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), hemihydrate gypsum (CaSO<sub>4</sub>·0.5H<sub>2</sub>O), anglesite (PbSO<sub>4</sub>), sphalerite ((Zn, Fe)S) and quartz (SiO<sub>2</sub>). Zinc ferrite (ZnFe<sub>2</sub>O<sub>4</sub>) was almost entirely leached. The result of SEM analysis of the reductive leach residue is shown in Figure 9. The surface of the material changed obviously after the leaching. Gypsum (GYP), colloidal silicon (Si) and copper silver sulfide (YZ) is more common. In addition, there is a kind of fine acicular crystal with fine structure(NFS), which has been determined to be sodium iron sulfate tetrahydrate (Na<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O).

**Table 5.** The results of comprehensive condition.

Leachate volume/ml	Terminal acid/(g/L)	Leaching rate/%		
		Zn	Fe	Ge
625	4.26	89.97	96.35	70.98
640	5.03	90.97	95.41	70.54
630	4.66	91.21	95.87	69.58
615	5.42	90.78	96.20	69.47
625	3.89	90.89	95.87	70.55



**Figure 8.** XRD pattern of reduction leaching residue.

**Table 6.** Chemical composition of reduction leaching residue.

Components	Zn	S	Fe	SiO <sub>2</sub>	Pb	Ge	Na	Ca	Ag
Sample/wt.%	1.91	17.98	0.92	32.25	14.66	0.005	0.046	4.63	0.18

**Table 7.** Germanium mineralogical analysis of the reduction leaching residue.

Constituent	Germanate	Oxide	Zinc silicate	Ferrite	Total
Content/ wt%	0.0007	0.0005	0.0033	0.0005	0.005
Distribution/%	14.00	10.00	66.00	10.00	100

**Figure 9.** Secondary electrons image of reductive acid leaching residue.

## 4. Conclusions

- (1) The mineralogical compositions of the zinc residue used in this research were zinc ferrite, gypsum, hemihydrate gypsum, anglesite, sphalerite and quartz. Approximately 58% and 20% germanium occurred in the ferrite and silicate phases, respectively. The silicate phase that reported germanate might be mainly the amorphous silica or zinc silicates which were not identified in XRD of the zinc residue.
- (2) In the presence of SO<sub>2</sub>, the extraction of germanium was maximum of 70% while the extraction of zinc and iron were 90% and 96% under the optimal condition which was determined for 80 g of zinc residues as sulfuric acid concentration of 56 g·L<sup>-1</sup>, sulphur dioxide partial pressure of 200 kPa, liquid-to-solid ratio of 7 mL/g, leaching temperature of 100°C for 120 min.
- (3) Under optimal conditions, the main minerals of the reduction leaching residue were sodium iron sulfate tetrahydrate, gypsum, hemihydrate gypsum, anglesite, sphalerite and quartz. Zinc ferrite was almost entirely leached.

## Acknowledgements

This work was supported by the Natural Science Foundation of China (No. 51504004) and the Education Department of Anhui Province of China (No. KJ2015A118).

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