Research on Leaching Performance of Low Grade Zinc Oxide Ore in the System of (NH₄)₂SO₄-NH₃-H₂O

Kaiwei Song¹,²,a, Jingjie Yuan¹,³,b, Peilun Shen¹,²,c, Jialei Li¹,²,d, Jianmin Li¹,²,e, Dianwen liu¹,²,*

¹Faculty of Land Resource Engineering, Kunming University of Science and Technology, Kunming 650093, Yunnan, China
²State Key Laboratory of Complex Nonferrous Metal Resource Cleaning Utilization, Kunming, Yunnan 650093, China
³Sichuan Metallurgical Geological Exploration Institute, Chengdu 610051, Sichuan, China

*Corresponding author e-mail: ldwkust@126.com, ¹songkaiwei@126.com,
²370131803@qq.com, ³546217044@qq.com, ⁴1332240413@qq.com,
⁵2088523506@qq.com

Abstract. Leaching test on the oxidized zinc ore from Kashi, Xinjiang Autonomous Region is studied in the (NH₄)₂SO₄-NH₃-H₂O system; Systematic studies are made to show the effects of various factors on the leaching rate of zinc. The optimum conditions for leaching is finally confirmed, i.e., the grinding fineness is 80% -74um, concentration of ammonium sulfate is 2mol/L, concentration of ammonia is 4mol/L, reaction temperature is 40°C, the ratio of liquid to solid is 4: 1; stirring rate is 300rpm and leaching time is 3h. Ultimately, the leaching rate of Zn could reach more than 91%.

1. Introduction

As one of the two primary of oxide zinc processing, flotation technology receive the reputation of the central and full-blown method [1]. However it is difficult to select zinc from complicate and low grade zinc oxide ore by flotation and the cost is high. Therefore, leaching becomes the best technology for zinc oxide ore, which is approved by a lot of researchers made both at home and abroad. Particularly, the ammonia leaching and its joint technology is the main development direction concerning the low grade zinc oxide ore [2, 3, 4, 5].

The zinc oxide ore from Kashi, Xinjiang Autonomous Region is a typical low grade one with alkaline gangues and high content of silicon and slime. Ammonia leaching is likely to be the best technology for the treatment of zinc. This passage systematically analyses the main factors and their influence on leaching efficiency of zinc oxide ore.
2. Experiment

2.1. Materials and Apparatus
The ore used in the experiment from Kashi, Xinjiang Autonomous Region of China. After being ground and dry sieved, the ore was analyzed in Kunming Metallurgical Research Institute. Table 1 shows the chemical analysis of the raw ore, and Table 2 shows the mineralogical composition of zinc in the ore, respectively. The tables show that the raw ore contains smithsonite (ZnCO$_3$), wittlite (ZnSiO$_4$) as major minerals, as well as magnesium oxide (MgO), calcium oxide (CaO), and quartz (SiO$_2$) as gangue minerals.

| Table 1. Chemical analysis of raw ore (%wt.) |
|---------------------------------------------|
| Element | Zn | Pb | TFe | S |
| Content (%) | 1.81 | 0.26 | 1.49 | 0.37 |
| element | Al$_2$O$_3$ | MgO | CaO | SiO$_2$ |
| Content (%) | 2.24 | 8.36 | 16.49 | 43.79 |

| Table 2. Mineralogical composition of zinc in the ore (%wt.) |
|----------------------------------------------------------|
| Substance | ZnCO$_3$ | ZnSiO$_4$ | ZnS | ZnFe$_2$O$_4$ and Others | Total zinc |
| content/% | 1.09 | 0.12 | 0.05 | 0.55 | 1.81 |
| Distribution/% | 60.22 | 6.63 | 2.78 | 30.37 | 100.00 |

Reagent grade chemicals were used for all the experiments. The leaching agents used were ammonia and ammonium sulphate which were provided by Tianjin Chemical Reagents Company, and the distilled water was used throughout the leaching process. The grinding using ball mill (XMQ-67 Wuhan Resource Exploration Mechanical Factory, China), Precision force electric Blender (DSX-120 Hangzhou instrument electric machine Ltd., China) was used for agitated leaching.

2.2. Experimental Methods
Firstly, the zinc oxide ore that has been crushed will be ground into different fineness by ball mill according to the requirement of particle size. Then, weighing a 100g’s sample and moving it into three-hole flask which is filled with leaching solution then proceeding agitation leaching in pressure-tight and temperature-constant three-holes flask with backflow condenser placed in one of the holes, in order to reduce the volatility of ammonia and water loss. After that, separating the liquid-solid slurry with suction filter after leaching is completed and washing filter residue three times with distilled water. Finally, the filter residue will be dried in an oven at room temperature in order to forbid the sulfide ore being oxidized into the oxide ore, made samples and sent to the analytical center for further analysis.

2.3. Evaluation Method
Leaching efficiency ($X$) was calculated according to the Eq. (1):

$$X = \frac{M_a - m_b}{M_a} \times 100\%$$

Where $M_a$ = the weight of sample before leaching (g), $m_a$ = the weight of leaching residue (g), a = the zinc grade of raw ore (%), $\beta$ = the zinc grade of leaching residue (%).
3. Results and Discussion

3.1. Single-factor conditional experiments

3.1.1. Effect of grinding fineness. To determine the effect of particle size on leaching efficiency of zinc, leaching conditions were as follows: total ammonia concentration as 8mol/l; ammonia-to-total ammonia molar ratio of 1/2; reaction temperature at 25°C; a liquid-to-solid ratio of 4; leaching time 3h; with a stirring rate of 300rpm. The results are shown in Fig.1. And Fig.1 shows that leaching efficiency will increase as the grinding fineness increases. And at 80%-74um, the zinc extraction reaches 91.19%. After that, increase the fineness continuously, the addition of leaching efficiency is inconspicuous. That’s because when the particle size of the ore is too thin, there will produce the aggregation among leaching slurry and reducing the dispersion of particles. Consequently, there is no obvious addition of zinc extraction and even will go against leaching as the fineness increases continuously. Therefore, at the following tests, selecting the sample with the grinding fineness 80%-74um.

![Figure 1. Effect of grinding fineness on leaching efficiency of zinc](image)

3.1.2. Effect of total ammonia concentration. To investigate the effect of total ammonia concentration on leaching efficiency of zinc, the leaching conditions were as follows: ammonia-to-total ammonia molar ratio of 1/2; reaction temperature at 25°C; a liquid-to-solid ratio of 4; leaching time 3h; with a stirring rate of 300rpm. The results are shown in Fig. 2. It is easily observed that the leaching efficiency of zinc rises up as the concentration of total ammonia increases. And when the total ammonia concentration is in the range of 1-8mol/L, the zinc extraction rate increases quickly. However, in the range of 8-9mol/L the total ammonia concentration will not have a further improving effect on the zinc extraction, and the leaching rate tends to be changeless. So selecting the total ammonia concentration as 8mol/L to carry out the following experiments.
3.1.3. Effect of molar ratio of ammonia/total ammonia. To determine the effect of molar ratio of ammonia/total ammonia on leaching efficiency of zinc, leaching conditions were as follows: total ammonia concentration set as 8mol/L, using various molar ratios (from 0/8 to 8/8); reaction temperature at 25℃; a liquid-to-solid ratio of 4; leaching time 3h; with a stirring rate of 300rpm. The results are shown in Fig.3. The curve in the Fig.3 shows the zinc extraction rises up as the molar ratio increases among the range of 0/8-4/8. And in the range of 4/8-8/8, the leaching efficiency decreases. The data indicates that in the leaching system, using mono ammonia or mono ammonium sulfate as lixiviant will not have the promotion effect on the zinc extraction. And at the ratio of 4/8, the leaching efficiency reaches 91.89%. Therefore, the best molar ratio of ammonia/total ammonia for zinc extraction is 4/8.
3.1.4. Effect of liquid/solid ratio. To confirm the effect of liquid/solid ratio on the zinc extraction using various liquid/solid ratios. The leaching conditions employed were as follows: total ammonia concentration 8mol/L; ammonia-to-total ammonia ratio of 1/2; reaction temperature at 25°C; leaching time 3h; a stirring rate of 300rpm. The results are shown in Fig.4. As can be seen from Fig.4, zinc extraction increases with the increasing of liquid/solid ratio in the range of 2-4. That is because the viscosity of pulp is reducing as the ratio of liquid/solid increases. After the liquid-solid ratio reaches the proportion of 4, the leaching efficiency adds more slowly. But the consumption of reagent increases along with liquid-solid ratio. Considering the leaching rate and cost, setting the ratio of liquid/solid as 4.

![Figure 4. Effect of liquid-solid ratio on leaching efficiency of zinc](image)

3.1.5. Effect of leaching time. To investigate the effect of leaching time on leaching efficiency of zinc, using various leaching time. The leaching conditions applied were as follows: total ammonia concentration 8mol/L; ammonia/total ammonia ratio of 1/2; reaction temperature at 25°C; a ratio of liquid/solid of 4; stirring rate of 300rpm. The results are shown in Fig.5. It shows the leaching efficiency increases with the passage of time from 2h to 3h. When the leaching time is more than 3h, the leaching rate fluctuates. That is due to hardly keeping the total ammonia concentration constant with extending leaching time. Therefore, selecting 3hours as the optimum leaching time.
3.1.6. Effect of reaction temperature. To research the effect of reaction temperature on zinc extraction, varying the temperature. The leaching conditions adopted were as follows: total ammonia concentration 8mol/L; ammonia/total ammonia ratio of 1/2; liquid/solid ratio of 4; stirring rate of 300rpm; leaching time 3h. The results are shown in Fig.6. It is clear that reaction temperature has apparent effect on zinc extraction. At 40°C, the leaching efficiency reaches the highest, 91.60%. That is because with the reaction of temperature rising, the spread of lixiviant molecules in leaching solution speeds up, more easily attacks the mineral grains and the stockpile energy of mineral particles increases, so the ability of damage or weakening of the chemical bonds of mineral enhances, and the number of molecules whose kinetic energy is equal to or greater than activation energy increases. While the reaction temperature increases more than 40°C, the zinc extraction decreases a little. That is because the volatility of ammonia will increase, once the temperature exceeds some point.

Figure 5. Effect of leaching time on leaching efficiency of zinc

Figure 6. Effect of reaction temperature on leaching efficiency of zinc
3.1.7. Effect of stirring rate. To examine the effect of stirring rate on zinc extraction, changing the stirring rate. Leaching conditions were as follows: total ammonia concentration 8mol/L; ammonia/total ammonia ratio of 1/2; reaction temperature at 40°C; liquid/solid ratio of 4; leaching time 3h. The results are shown in Fig.7. The results show that zinc extraction rate increases as the stirring rate rises. Especially, when the stirring rate is in the range of 0-300rpm, it has a significant influence on leaching efficiency. When the stirring speed exceeds 300rpm, the zinc extraction rate tends to be stable. That is because increasing the stirring rate also will increase the relative motion between mineral particles and leaching solution which will impede the leaching process.

![Figure 7. Effect of stirring rate on leaching efficiency of zinc](image)

3.2. Verification test

After systematically examining the influence of various factors on the leaching efficiency of zinc, the optimal technical conditions have been confirmed, viz, the particle size of 80 -0.074mm; concentration of ammonium sulfate 2mol/L, concentration of ammonia 4mol/L; reaction temperature at 40°C; a liquid/solid ratio of 4; leaching time 3h; and with a stirring rate of 300rpm. The results of three tests under the upper conditions are shown in Table 3. It is clear that the optimum leaching conditions of the test have proved the correctness of the result because the leaching efficiency of zinc is more than 91% in the three times of verification experiment. The result is approving.

| Test number | Leaching efficiency of total zinc (%) | Leaching efficiency of leachable zinc (%) |
|-------------|--------------------------------------|------------------------------------------|
| AJ-1        | 33.92                                | 91.63                                    |
| AJ-2        | 34.08                                | 92.06                                    |
| AJ-3        | 33.91                                | 91.59                                    |
| Average     | 33.97                                | 91.76                                    |

4. Conclusions

On the basis of the discussion above, some conclusions can be drawn as follows:

1. The studies of technological mineralogy indicate that the zinc oxide ore has the characters of high calcium and silicon. It belongs to mixed sulphide–oxide zinc ore with alkaline gangue–minerals.
2. The optimum conditions are identified as follow: the grinding fineness is 80% -0.074mm,
concentration of ammonium sulphate is 2 mol/l, concentration of ammonia is 4 mol/l, reaction temperature is 40°C, the ratio of liquid to solid is 4:1; stirring rate is 300rpm and leaching time is 3h.

(3) The leaching test results show that the leaching process technology is feasible to deal with the zinc oxide ore, and the leaching rate is up to 91.76%.

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