Study on separation of low-grade zinc oxide ore with sulfurization-amination flotation

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Abstract: With the continuous depletion of a large number of zinc sulphide ores that are easy to treat, the finely disseminated and refractory low-grade zinc oxide ores has become an important source for the production of zinc minerals. In this paper, a sulfurization-amination flotation process has been proposed for concentrating large amounts of low-grade zinc oxide ore in Lanping, Yunnan Province. Spectrum analysis, chemical analysis and element analysis was performed to provide research basis for process design and operational control. The main influencing factors during the process, including grinding fineness, reagent types and dosage, etc., have been studied through flotation tests. The results showed that the optimum grinding fineness was -0.074 mm accounting for 89.78% for the target run-of-mine ore. Moreover, optimum dosages of sodium carbonate, sodium silicate, sodium hexametaphosphate, sodium sulphide and octadecylamine were determined as 1500 g/t, 500 g/t, 200g/t, 8000 g/t and 500 g/t, respectively. Under these conditions, an open circuit test and a closed circuit test with one stage rougher, two stage scavenger and three stage cleaner flotation were carried out with the run-of-mine ore with a zinc grade of 6.52% and the oxidation ratio of 94.62%. The zinc concentrate can be obtained with zinc grade of 44.09% at a zinc recovery of 66.35% with a 9.70% yield of zinc concentrate yield. The results confirmed the validity and practicability of the proposed process design and experimental operation. This study is of special value as it provides referencing significance for economically exploiting low-grade zinc oxide ore.

Keywords: low-grade zinc oxide ore, sulfurization-amination flotation, grinding fineness

1. Introduction

Zinc oxide ore accounts for 23% of the total known zinc ore reserves in the world, and the proved zinc oxide reserves in China are above 40 million tons (Cao et al, 2013). Yunnan Lanping Zinc Oxide Mine is the largest proven zinc oxide deposit in China where the reserves of zinc metals are up to 14 million tons. However, the zinc minerals in Lanping are highly oxidized and finely disseminated, which brings great difficulty for its separation and beneficiation (Lan et al, 2013). Thus, the mined refractory ore can only be stored or even abandoned, and more than 30 million tons of low-grade raw zinc oxide ore are stockpiled on site which cannot be processed and further utilized (Yang et al, 2011).

The zinc oxide ore, which include smithsonite ($\text{ZnCO}_3$), hemimorphite ($\text{Zn}_n\text{Si}_3\text{O}_9(\text{OH})_2\cdot\text{H}_2\text{O}$), Willemite ($\text{Zn}_n\text{SiO}_4$) and Hydrozincite ($\text{Zn}_n(\text{CO}_3)_3(\text{OH})_6$), is derived from zinc sulphide ore after being interacted with oxygen, carbon dioxide, underground water and bioorganic matter, etc. The gangue minerals in zinc oxide are mainly limestone, dolomite, quartz, clay, etc. Thus, very fine particles and a lot of slime are easily generated during crushing and grinding, which greatly interfere the flotation performance of zinc oxide ore (Pietro et al, 2012).

As a classical separation technique for fine particles, flotation plays an important role in industrial application for recovering zinc oxide ore, such as bulk flotation, heavy medium separation – flotation, and magnetic separation-flotation method, etc. Bulk flotation means all the ore grains go to flotation.
process after grinding. For separation after classification, heavy medium flotation is used to concentrate coarse particles while fine grains go to flotation process. For those containing magnetic minerals, magnetic separation is carried out before particles going to flotation process. (Liang et al., 2013 & Ejtemaei et al., 2014). However, the beneficiation of zinc oxide ore still confronts with technical challenge as there is no major breakthroughs in equipment, process design and effective reagents until so far.

New reagents have been developed for the flotation of oxide minerals (Wu et al., 2018). However, in the case of zinc-oxide ores, sulfurization-xanthate flotation methods are applied. After being conditioned by sodium sulphide, copper sulphate and xanthate are added as activator and collector, respectively. However, for zinc oxide with high content of silicate ore and iron or willemite, there is little chance to obtain satisfactory product using xanthate as collector in flotation. Besides, it requires a strict dosage control for sodium sulphide. Once exceeded, the flotation of zinc oxide would be depressed (Majid et al., 2011). By contrast, the sulfurization-amination flotation method has outstanding merits (Zhang et al., 2017). After being sulfurized by sodium sulphide, the surface of zinc oxide ore is modified, and the surface electronegativity and hydrophobicity are increased, which is similar to sulphide minerals. Thus, the amine collector is more easily adsorbed on the mineral surface and forms a zinc-ammonium complex, which can significantly improve the floatability of the zinc oxide ore without pre-desliming treatment. In view of this principal, the sulfurization-amination flotation method was applied in processing zinc oxide ore in Lanping mine.

2. Materials and methods

2.1. Materials

To quantify the mineralogical composition of the raw ore, element type and contents were semi-quantitatively analysed by spectrometer (ICP-OES, German) as is shown in Table 1. Then atomic absorption spectrophotometer (4530F, China) was employed to quantify the valuable elements and gangue components shown in Table 2. According to the data of element analysis, X-ray diffractometer (XRD, BTX-II, Japan) analysis was performed to determine the mineral composition of the raw ore as is shown in Table 3. The results indicate that the Lanping Zinc Oxide Mine is mainly sandstone type ore and metallic minerals are mainly smithsonite, hemimorphite and cerussite, etc., and the gangue minerals are mainly quartz, followed by clay, calcite and dolomite, etc. To further confirm the zinc mineral type, Zn phase analysis was carried out. Zinc oxide and zinc sulfide contents of the ore were assayed by titration method and content of insoluble zinc was measured by Atomic Absorption Spectrometry (WFX-120, China). The weight fraction of zinc chemical compounds (wB/%) and zinc weight fraction in raw ore (w(Zn)) were presented in Table 4. The results showed that the ore has a low zinc grade of 6.52% and a quite low lead content (0.63%). Additionally, approximately 94.62% of zinc minerals are distributed in carbonates and silicates with a high degree oxidation.

| Table 1. Spectrum Analysis results of raw ore/% |
|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Ba   | As   | Mg   | Sb   | Mn   | Si   | Zn   | Sn   | Fe   | Ca   | Cu   | Pb   |
| 0.12 | >0.1 | <1   | <0.01| 1.2  | >4   | >1   | <0.01| 6    | 3    | <0.1 | >1   |

| Table 2. Multi-element analysis results of ore/% |
|-----------------|-------|-------|-------|-------|-------|-------|
| Zn   | Pb   | S    | Fe   | SiO₂ | CaO  | MgO  | Al₂O₃ |
| 6.52 | 0.63 | 1.48 | 5.62 | 25.78| 22.43| 1.65 | 2.37  |

| Table 3. Mineralogical composition of raw ore /% |
|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| smithsonite    | hemimorphite | sphalerite | cerussite | limonite | calcite | quartz | dolomite | feldspar | Others | Total |
| 6.25 | 7.13 | 0.40 | 1.53 | 9.23 | 37.14 | 22.67 | 9.75 | 3.01 | 2.89 | 100   |

2.2. Methods

To determine the optimum experimental conditions, including the optimal particle size fraction for flotation and the optimum reagents dosages, rougher flotation tests were conducted. The raw ore (300g)
was first milled with a cone ball mill (XMQ-240×90) to different size distribution to determine optimal particle size fraction. Flotation tests were conducted in a single flotation cell (XFD of 0.75 L and 1 L) with adding sodium carbonate (Na₂CO₃) as pH adjuster, sodium sulphide (Na₂S) as sulfurizing reagent, octadecylamine (C₁₈H₃₉N) as collector, pine oil as frother and sodium hexametaphosphate (NaPO₃)₆ and sodium silicate (Na₂SiO₃) as depressants. After confirming the optimum size fraction of the flotation feed, optimal reagents dosages were determined by flotation tests. Finally, the open circuit test and closed circuit test was carried out to examine the feasibility of the process. The pH Value during the flotation was monitored by a precise pH meter (FE20, China).

<table>
<thead>
<tr>
<th>Zinc phase</th>
<th>Carbonate</th>
<th>Silicate</th>
<th>Sulphide</th>
<th>Ferrite &amp; others</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>wB/%</td>
<td>48.47</td>
<td>46.76</td>
<td>2.85</td>
<td>1.92</td>
<td>100</td>
</tr>
<tr>
<td>w(Zn)/%</td>
<td>3.45</td>
<td>2.72</td>
<td>0.27</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>Distribution/%</td>
<td>52.91</td>
<td>41.71</td>
<td>4.11</td>
<td>1.27</td>
<td>100</td>
</tr>
</tbody>
</table>

In the sulfurization – amination flotation method, the zinc oxide ore was sulfurized by sodium sulphide to form a surface similar to sulphide minerals. In weakly alkaline pulp (pH=8~10), a large amount of RNH₂ molecules are generated. The lone pair electron in the nitrogen atom of RNH₂ react with Zn²⁺ and forming complexes on surface of the mineral, while the R group faced outward, enhancing the hydrophobicity and floatability of the minerals (Ejtemaei et al, 2014), as shown in Fig. 1. Other main equipment includes a standard set of sieves and a disc vacuum filter (DL-5C), etc.

![Fig. 1. The reaction between amine and zinc oxide minerals in the alkaline pulp](image)

3. Results and discussion

3.1. Effect of grinding fineness

Grinding fineness is an important factor affecting the flotation efficiency of low-grade zinc oxide ore. Relatively, when the grinding particle size is not fine enough, the ore liberation degree is low, which impede the flotation and lead to a low zinc grade and recovery rate. The finer the grinding particle, the higher dissociation degree of the useful mineral from gangue mineral, which is favourable for improving the recovery rate of metal. On the other hand, when the grinding particle size is too fine, there is not only an increase of grinding energy, but also a serious sliming which negatively affect the recovery of zinc minerals. Therefore, on the premise of ensuring the separation performance, the appropriate grinding fineness should be ensured as much as possible.

Rougher flotation tests were carried out to determine the optimized grinding fineness. Fig. 2 shows

![Fig. 2. The process of condition experiment](image)
the flow chart of the tests. The slurry concentration in grinding was 65%, and the dosage of each agent was 1300 g/t of sodium carbonate, 400 g/t of sodium silicate, 250 g/t of sodium hexametaphosphate, 7000 g/t of sodium sulphide, and 400 g/t of octadecylamine, 10 g/t of pine oil.

Referring to the grinding tests results shown in Table 5, with the increase of the proportion of particles of -0.074mm, the zinc grade and recovery rate increased and then decreased. When -0.074 mm particles accounted for 89.78%, the zinc grade was 17.97%, and recovery rate was 42.94%. Therefore, it is determined that the optimum grinding fineness is -0.074 mm accounting for 89.78%.

Table 5. Results of grinding fineness tests

<table>
<thead>
<tr>
<th>-0.074 proportion/ %</th>
<th>yield/ %</th>
<th>Zn grade/ %</th>
<th>Zn recovery / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>69.97</td>
<td>17.07</td>
<td>14.68</td>
<td>38.43</td>
</tr>
<tr>
<td>80.34</td>
<td>16.91</td>
<td>15.45</td>
<td>40.06</td>
</tr>
<tr>
<td>89.78</td>
<td>15.58</td>
<td>17.97</td>
<td>42.94</td>
</tr>
<tr>
<td>99.02</td>
<td>17.47</td>
<td>15.34</td>
<td>41.12</td>
</tr>
</tbody>
</table>

3.2. Effect of reagents dosage

3.2.1. Sodium carbonate

Zinc oxide ore contains calcium magnesium minerals, and its dissolution and dissociation make the zinc oxide slurry contains a large amount of Ca$^{2+}$ and Mg$^{2+}$ ions, which not only consume a large amount of collector, but also influence the selectivity as it activates the silicates. Sodium carbonate can reduce the influence of Ca$^{2+}$ and Mg$^{2+}$ by precipitation, and adjusting the surface charge property of minerals, thus preventing the agglomeration of fine-grained minerals and slime coating on mineral surfaces, hence, resulting a good particle dispersion (Cheng et al, 2016, Wang et al, 2013 & Shang et al, 2016). The combination use of sodium sulphide and sodium carbonate can improve the flotation selectivity, strengthen the depression of dolomite and stabilize the sulfurization effect of sodium sulphide (Pereira & Peres, 2005).

Sodium carbonate can also act as a pH regulator to keep the pulp in a weak alkaline environment with pH between 8 to 10. The dosage of sodium carbonate used in the test was (500 g/t, pH=8.35), (1000 g/t, pH=9.08), (1500 g/t, pH=9.55), (2000g/t, pH=10.17), (2500g/t, pH=10.72). For the other reagents, it was 50 g/t of sodium silicate, 250 g/t of sodium hexametaphosphate, 7000 g/t of sodium sulphide, 400 g/t of octadecylamine, 10 g/t of pine oil.

![Graph showing the influence of Na$_2$CO$_3$ dosage on Zn rougher flotation](image)

Fig. 3. The influence of Na$_2$CO$_3$ dosage on Zn rougher flotation

As is shown in Fig. 3, with the increase of sodium carbonate dosage, the zinc grade and recovery rate increased up to a certain dosage and then decreased. As an excessive amount of sodium carbonate can impede the sulfurization process of smithsonite by reversely facilitate the following reaction (Wu et al, 2015), thus the flotation recovery is decreased. As for the grade, excessive amount of sodium carbonate can facilitate the electronegativity of not only the mineral surface but also the gangue surfaces, enhancing the adsorption possibility of amine collector and gangue minerals and thus increasing the
3.2.2. Sodium silicate and sodium hexametaphosphate

The high content alkaline gangue in Lanping low-grade zinc oxide ore shows serious sliming. Sodium silicate can hydrolyze to silicic acid. \( \text{H}_2\text{SiO}_3 \) and \( \text{SiO}_3^{2-} \) can easily adsorb on the surface of gangue minerals and enhance its hydrophilicity, thus leading to a stable suspension of gangue minerals in solution. However, when the dosage of sodium silicate increases, silicic acid tends to form micelle and further polymerize and finally precipitate into the solution. So, the effective components \( \text{H}_2\text{SiO}_3 \) and \( \text{SiO}_3^{2-} \) decreases, which weakens the inhibition ability of sodium silicate on gangue minerals, resulting in a decline in the grade and recovery of zinc concentrate accordingly (Gong et al, 1993). Sodium hexametaphosphate can complexate the calcium and magnesium ions in the solution to form a hydrophilic and stable complex, which has a good inhibitory effect on the minerals containing calcium and magnesium (Andreola et al, 2004). The adsorption of sodium hexametaphosphate on the mineral surface can also increase the electronegativity of the surface and separate the mineral from other negatively charged minerals under the electrostatic repulsion forces. Therefore, sodium silicate and sodium hexametaphosphate were used as depressant (for calcite, dolomite, silicate, etc) could enhance the slurry dispersion (Kashani & Rashchi, 2008). While its dosage exceeds modest amount, the complex formed by the reaction will not all remain on the surface of calcite, but also disperse in the pulp. After its adsorption onto the zinc oxide surfaces, it will also cause inhibition, resulting in a decrease in the grade and recovery rate of zinc concentrate.

The test dosages of sodium silicate and sodium hexametaphosphate are A(300 g/t+100 g/t, pH=9.13), B(400 g/t+150 g/t, pH=9.22), C(500 g/t+200 g/t, pH=9.30), D(600 g/t+250 g/t, pH=9.37), E(700 g/t+300 g/t, pH=9.42), respectively. The other conditions are 150 g/t+300 g/t of sodium carbonate, 7000 g/t of sodium sulphide, 400 g/t of octadecylamine and 10 g/t of pine oil. As is shown in Fig. 4, with the increase of the combined dosage of sodium silicate and sodium hexametaphosphate, the zinc grade and recovery rate increased up to a certain point and then started to decrease. Therefore, the combined reagent dosage C (500 g/t+200 g/t) is determined as the grade and recovery of zinc reach the maximum.

Fig. 4. The influence of Na\(_2\)SiO\(_3\) and (NaPO\(_3\))\(_6\) dosage on Zn rougher flotation

3.2.3. Sodium sulphide

Sodium sulphide shows good activation effect for zinc oxide ore within sulfurization-amination flotation (Yang et al, 2014). It can increase the pH value of the slurry and help with stabilizing the alkaline environment. And the thiohydride ions can adsorb on surfaces of zinc oxide minerals, increasing its hydrophobicity (Majid et al, 2011). The amine collector hydrolysis releases RNH\(^3+\) - RNH\(^2\) and OH\(^-\). At pH=9.30, the concentration of amine cation RNH\(^3+\) - RNH\(^2\) reaches its highest. When the sodium sulphide dosage is increased, pH value and concentration of OH\(^-\) is increasing accordingly. However, when pH value is higher than 10, there is RNH\(_2\)(s) precipitating out from the pulp and concentration of action amine decreased, thus leading to a decline of the zinc recovery (Mehdiloo et al,
2012). Besides, based on the chemical solution calculation, the concentration of HS\textsuperscript{-} decreased when pH value is higher than 10, which weakens the sulfurization of zinc oxide ore as is discussed in previous section (Wu et al, 2015).

The dosage range of sodium sulphide used in the test was (4000 g/t, pH=8.44), (6000 g/t, pH=8.95), (8000 g/t, pH=10.3), (10000 g/t, pH=11.10), (12000 g/t, pH=12.24). Other conditions are 1500 g/t of Na\textsubscript{2}CO\textsubscript{3}, 500 g/t of sodium silicate, 200 g/t of sodium hexametaphosphate, 400 g/t of octadecylamine, 10 g/t of pine oil. The results are shown in Fig. 5, 8000 g/t is the best dosage of sodium sulphide with the zinc grade was 18.26% and the recovery was 81.03%. As measured, pH value is about 10 when sodium sulphide at a dosage of 8000 g/t.

![Fig. 5. The influence of Na\textsubscript{2}S dosage on Zn rougher flotation](image1)

3.2.4. Octadecylamine

Octadecylamine is a kind of cationic amphoteric collector. It possesses a non-polar carbon chain group and a polar amine group. The non-polar ends oriented towards the bulk solution to enhance the hydrophobicity of the particle surfaces. Amine collector molecules dissociate cations in water with hydrophobic hydrocarbon groups. Complexation chemical adsorption takes place on mineral surface mainly by amine molecule (RNH\textsubscript{2}) with covalent bond when interacting with ZnCO\textsubscript{3}. For the flotation of zinc oxide ore in alkaline medium, nitrogen atoms in amine molecules can form stable complexes [Zn(C\textsubscript{18}H\textsubscript{37}N\textsubscript{2})\textsubscript{4}]\textsuperscript{2+} by covalent bonding with Zn\textsuperscript{2+} ions on the mineral surface, thus enhancing the hydrophobicity of mineral surfaces (Yang et al, 2013).

It is proverbial that this ionizing collector should be used in small amounts, substantially those necessary to form a monomolecular layer on particles surfaces (starvation level), as increased concentration tends to float other minerals apart from the cost of the targeted mineral thus reducing the selectivity. And an excessive concentration can also have an adverse effect on the recovery of the aimed minerals, due to the development of collector multi-layers on the particles, reducing the proportion of hydrocarbon radicals oriented into the bulk solution and thus decreasing the hydrophobicity (Wills and Finch, 2015). Also, there are many related studies showing this similar trend for amine collectors (Mehdilo et al, 2012).

![Fig. 6. The influence of C\textsubscript{18}H\textsubscript{37}N dosage on Zn roughing](image2)
The dosage range of octadecylamine was between 300-700 g/t. Other reagents dosage was 1500 g/t of sodium carbonate, 200 g/t of sodium hexametaphosphate, 8000 g/t of sodium sulphide and 10 g/t of pine oil. As is shown Fig. 6, zinc recovery reached the peak at an octadecylamine dosage of 500 g/t, while the zinc grade arrived at the turning point at a dosage about 550 g/t. As from our perspective of improving the recovery rate, the dosage of 500 g/t was adopted in the following tests.

3.3. Open-circuit test

Based on the above results with optimum grinding fineness and reagents dosage for rougher flotation, the open circuit tests were performed. The process includes one rougher, three cleaner and two scavenger stages as shown is Fig. 7. Table 6 gives the reagents dosage for the three stages. Table 7 displays the open circuits test results with one concentrate, one tailing and five middlings. The grade of concentrate can reach as high as 45.20% with zinc recovery of 51.00%.

3.4. Closed-circuit test

To better verify the feasibility and rationality of the whole process, closed-circuit test was carried out on the basis of the open-circuit test, the five middling products were returned to roughing stage as shown in Fig. 8. The addition amount of the reagents was same with that in open circuit test (Table 5). The stable closed circuit test results are demonstrated in Table 8 with a satisfactory zinc concentrate yield of 9.70%, Zn grade of 44.09% and Zn recovery rate of 66.35%.
4. Conclusions

This work was targeted to beneficiate the low-grade & refractory zinc oxide ore in Lanping mine. Chemical analysis and Zn phase analysis were conducted to find out the property of raw ore, which laid the foundation of the process design and the reagents selection. Conditional tests were conducted separately in order to determine the optimum grinding fineness and proper dosage for each reagent. After exploring the effect of these factors, open circuit tests and closed circuit tests were performed to verify the feasibility and rationality of the sulfurization-amination flotation method. A decent result was obtained from close circuit test with zinc concentrate yield of 9.70%, Zn grade of 44.09%, and Zn recovery rate of 66.35%. This work not only proves the feasibility of sulfurization-amination method, but also displays an integrated research approach for improving the recovering efficiency of refractory zinc oxide ore. This work is of special value for playing an exemplary role in processing low-grade zinc oxide ore. However, there is possible room to improve the flotation performance. The reagents dosage determination test should consider the interaction effect among the reagents. Also, more surface studies should be conducted in order to achieve a better understanding of the function mechanism of each reagent and their interaction effect. Additionally, the choice of flotation techniques also could make a difference for fine refractory zinc oxide ore. Further research work on beneficiating zinc oxide ore could be implemented in these aspects.

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References


