Influence of polysorbate 80 on the flotation of zinc oxide ores with amines

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Abstract:
In this study, the influence of polysorbate 80 on zinc oxide flotation was investigated with an amine collector. The results indicated that the pretreatment of amines with polysorbate 80 enhanced the Zn grade and recovery obtained using zinc oxide flotation. Desliming prior to flotation is not suggested based on the results of this study. The appropriate temperature for flotation was as low as 8 °C, and this flotation method also could be applied to different types of zinc oxide ores. Under optimum flotation conditions, a concentrate with a Zn grade of 48.34% and a Zn recovery of 95.97% was obtained.

Keywords: polysorbate 80, pretreated amines, zinc oxide, flotation

1. Introduction
Currently, zinc is produced mainly from zinc sulphide ores because they are easy to separate from their gangues and concentrate using conventional flotation techniques. However, these ores have gradually been depleted because of their increased consumption, resulting in rising shortages of zinc sulphide (Zhang et al., 2020b; Xiong et al., 2017).

In China, most zinc sulphide ores contain 1–3% Zn. Flotation reagents cost approximately $9 per ton of ore using current flotation techniques. The lowest flotation reagents cost approximately $4 per ton of ore for some mineral processing plants. However, the zinc content of these ores should not be less than 1.2%. China is historically rich in zinc oxide ores, and zinc reserves of more than 40 million tons have been reported (Zhenhua, 2003). These ores are concentrated in Yunnan, Sichuan, Gansu, Hunan, and other places. Yunnan contains the most abundant zinc oxide ore resources, which represents roughly a quarter of China’s total zinc oxide ores (Yin, 2011). Hunan has more than 3 million tons of zinc oxide ores, and Gansu contains a large amount of zinc oxide ores, which is not less than 0.26 million tons of zinc (Sanjun, 2004; Ailiang et al., 2008). Zinc oxide ores contain approximately 5–35% Zn, which is much higher than the content in sulphide ores. Therefore, the development and utilization of zinc oxide ores have attracted increased attention.

Oxidized zinc ores exist as carbonate and silicate forms such as smithsonite, hydrozincite, zincite, willemite, and hemimorphite (Zhao et al., 2021). Smithsonite is a typical oxide mineral of zinc (Liu et al., 2021). In the case of zinc oxide ores, there is often no selectivity in terms of zinc recovery (Seyed, 2008) because of the similarities in the physico-chemical properties and surface chemistry of the constituent minerals (Irannajad et al., 2009). In the case of smithsonite, the surface activity of the mineral increases in water, and the adsorption of water molecules occurs via chemisorption. This high
activity to water dipoles is one of the main factors for the low natural floatability of smithsonite compared to that of sphalerite (Irannajad et al., 2009).

Oxidized zinc ores are generally found in silicate or carbonate forms in different parts of the world. These minerals are friable and produce a large amount of fines and slimes, leading to both primary slimes and secondary slimes which are created during crushing and grinding processes. Slimes have a marked effect on oxidized zinc flotation and result in excessive reagent consumption with less selectivity (Mehdilo et al., 2012). The major problem in zinc oxide ore flotation is the large volume of fines and slimes associated with increasing reagent consumption, which causes a slime-coating phenomenon that hinders selectivity and renders the process unfeasible in some cases (Majid et al., 2014). Desliming is used to prevent slime coating and to increase the recovery of zinc. However, analyses have shown that fine particles in the sample mostly contain zinc, thus desliming is not suggested (Navidi Kashani and Rashchi, 2008).

In order to enhance the recovery of oxidized minerals, many investigations have been performed. In practice, semisoluble oxide minerals are typically recovered by sulphidation before the flotation process. Based on an analysis of current techniques in the mineral industry, sulphidation is still a competent, applicable option. The most common flotation technique used commercially for treatment of zinc oxide minerals is sulphidation with Na2S, followed by treatment with conventional cationic collectors, namely amines (Ma et al., 2021; Liu et al., 2020; Feng et al., 2019; Wu et al., 2017). But in practice, these processes are not selective enough. The amount of sulphidising reagent and pH of the pulp must be carefully controlled (Hamid and Forsberg, 2006). Amine-type collectors are sensitive to slimes. Hence, slimes need to be removed before flotation, which reduces the zinc recovery (Seyed, 2008). In general, lead is recovered by adopting preferential flotation. After lead flotation, almost all the remaining zinc is in tailings and cannot be recovered by adding different reagents because of its complicated mineralogical structure (Nal et al., 2005).

In China, the present flotation techniques are not applicable for zinc oxide ores because of their high cost and low grade and low recovery of Zn. There are approximately 10 million tons of zinc oxide ores in Lanping and more than 3 million tons in Hunan. However, any mineral processing plant can effectively process these ores. In this study, the influence of collector type, sulphide, depressant, desliming, temperature, and ore type on the separation of zinc oxide ores have been investigated using amine-type collectors with polysorbate 80 (P80), and the optimum values of these parameters are reported.

2. Materials and methods

2.1. Materials

The zinc oxide ore samples were collected from Hunan zinc ores in China. Four kinds of zinc oxide ore samples were used for experiments and were classified as samples 1, 2, 3, and 4. The zinc contents of samples 1, 2, 3, and 4 were 16%, 10.18%, 25%, and 31.25%, respectively. Sample 1 was mainly smithsonite, and the main impurities of Sample 1 were calcite and quartz. Octadecylamine (ODA) and dodecylamine (DDA) (Jinan Chemical Co. Ltd., China) were used as the amine-type collectors. The surfactant P80 was obtained from Dow Chemical Co. (Midland, MI, USA) and used as an emulsifier to pretreat amines, to enhance their dispersion effect, to reduce the interaction between amines and slimes, and to minimize the harmful effects of slimes. Potassium amyl xanthate (PAX) was used as a collector and purchased from Shandong Qixia Flotation Reagent Co. Ltd., (Shandong, China). Sodium sulphide was used as the sulphidising reagent, sodium hexametaphosphate (SH) and sodium silicate (SS) were respectively the dispersant and depressant, NaOH was the pH adjuster, and pine oil was the frother. Tap water was used in all experiments.

2.2. Methods

Fig. 1 shows the experimental procedure which was implemented. The zinc oxide ore samples were crushed, wet ground, and sieved to collect the -74 μm fraction.

In the desliming process, a dispersant at a specific dose was added to the ground pulp with approximately 50% solid content and incubated for 5 min, and then the pulp was incubated for
10 min. Next, the overflow of the approximately -10 μm fraction was discharged. Finally, the -74 + 10 μm fraction was collected for flotation.

Flotation tests were performed using a flotation machine (XFD, China) with a volume of 0.75 L, an impeller speed of 2000 rpm, and an airflow rate of 200 dm³/h. The solid content of the testing mixture was 25%, the temperature was 25 °C, and pH was adjusted to 11–12 using a Na₂S aqueous solution. For each experiment, a 187.5 g zinc oxide ore sample with a particle size of -74 +10 μm (desliming) or -74 μm (no desliming) was incubated for 2 min with depressant. Sodium sulphide (3000–9500 g/Mg) was added to the pulp as a sulphidation reagent, the pH was adjusted to approximately 11.5, and the sample was incubated for 5–10 min. The pulp was also incubated with collectors (100–300 g/Mg) for 5 min. Finally, pine oil was used as a frother (150 g/Mg) for 1 min. The froth was hand-scraped for 3 min to collect the concentrate. The flotation concentrates and tailing pulps were filtered, dried, and weighed to determine the flotation recovery and grade of the mineral being studied.

Before flotation, either DDA or ODA was first mixed with acetic acid in a proportion of 1:1, followed by heating to approximately 80 °C until the solid dissolved completely. The solution was cooled down, and P80 (0–100% Mamine) was added. Finally, the mixture was diluted to 1% with water. The amount of P80 added to the solution was determined to achieve a desired proportion with amine, and the proportion of P80 and amine (P80-amine proportion) was calculated using Eq. (1).

\[
\text{Proportion\%} = \frac{M_{\text{P80}}}{M_{\text{amine}}} \times 100\% \tag{1}
\]

where Proportion\% is the mass proportion of P80 and amine. \(M_{\text{P80}}\) (g) and \(M_{\text{amine}}\) (g) are the masses of P80 and amine, respectively.

3. Results and discussion

3.1. Effect of P80 on amines

According to Fig. 2, the results revealed that the Zn grade and recovery were less than 35% and 70%, respectively, when using the amine ODA or DDA without P80. However, the pretreatment of amines with P80 increased the Zn grade and recovery to more than 40% and 85%, respectively, suggesting that P80 enhanced the performance of amines toward zinc oxide ores.

Fig. 3 shows the effects of different P80-amine proportions on the Zn grade and recovery of zinc ore flotation. The P80-amine proportion is the mass percentage of P80 and amines. The results showed that the Zn grade and recovery increased as the P80-amine proportion increased from 0 to 33.3%. However, these parameters did not change significantly in response to increasing the P80-amine proportion from 33.3% to 100%, indicating that excess P80 had little effect on the grade and recovery of zinc. Therefore, the optimum P80-amine proportion was 33.3%, and a concentrate with a Zn grade of 48.34% and a Zn recovery of 95.97% was obtained. These results were consistent with the guideline.
that the P80-amine proportion should be higher than 30% to obtain a microemulsion of amines which can be uniformly dispersed in an aqueous solution. The amines ODA and DDA are known to be insoluble in water and have foaming properties, resulting in a lot of large, sticky foam and enhancing the entrainment of slime. Meanwhile, P80 is a kind of nonionic surfactants with high surface activity, low surface tension, low critical micelle concentration, strong solubilization, and excellent emulsification and dispersion (SUN et al., 2020; Riquelme et al., 2019). Based on these properties, the combined use of amines and P80 enhanced the adsorption of amines on the mineral surface by promoting the dissolution and dispersion of the amine solution, which reduced the interaction between amines and slime and minimized the harmful effects of fine slimes (Seyed, 2008). Moreover, as an emulsifier, increasing the P80 concentration reduced the particle size of the amines, which further formed a microemulsion, effectively improving the dispersion effect of amines and obtaining better foamability (Kubbutat et al., 2021).

Fig. 2. Zn grade and recovery of ore flotation with amines with and without polysorbate 80 (P80) in the presence of 7500 g/Mg sulphide, 600 g/Mg dispersant, 600 g/Mg depressant, and 150 g/Mg pine oil at 25 °C with a Zn grade of 15.74% in raw ore.

Fig. 3. Zn grade and recovery of ore flotation by amines with different polysorbate 80 (P80)-amine proportions in the presence of 7500 g/Mg sulphide, 600 g/Mg dispersant, 600 g/Mg depressant, and 150 g/Mg pine oil at 25 °C with a Zn grade of 15.74% in raw ore.

Fig. 4 depicts the Zn grade and recovery of ore flotation using various doses of pretreated amines (33.3% P80-amine proportion) in the presence of 7500 g/Mg sulphide, 600 g/Mg dispersant, 600 g/Mg depressant, and 150 g/Mg pine oil at 25 °C with 15.74%-grade Zn in raw ore. The results showed that the Zn grade and recovery increased first and then decreased with increasing pretreated collector concentration. The optimal dose of pretreated amines (total content of DDA and ODA) was 194 g/Mg, resulting in a concentrate with a Zn grade of 48.34% and a Zn recovery of 95.97%. Decreasing the Zn grade and recovery by increasing the pretreated collector concentration to more than 194 g/Mg might be attributed to the flotation of more gangue minerals (Mehdilo et al., 2013) and
formation of a second layer on the surface, which resulted in a more hydrophilic ore (Amir and Fereshteh, 2008). In addition, the optimum amount of pretreated amines was 194 g/Mg, which represented a one quarter decrease in comparison with the traditional amine method (Ejtemaei et al., 2011).

Fig. 4. Zn grade and recovery of ore flotation as a function of pretreated amine (33.3% polysorbate 80 (P80)-amine proportion) concentration in the presence of 7500 g/Mg sulphide, 600 g/Mg dispersant, 600 g/Mg depressant, and 150 g/Mg pine oil at 25 °C with a Zn grade of 15.74% in raw ore

3.2. Effect of desliming

Slime is an important factor directly affecting the Zn grade and recovery, which results in a fragile froth, decreased recovery of coarse zinc minerals, and no selectivity without desliming. Zinc oxide contains large amounts of fine slimes, which increase the reagent consumption, cause the so-called slime coating phenomenon, hinder selectivity, and possibly render the process unfeasible. To preclude this negative result, desliming prior to flotation is necessary.

The results of desliming with 1500 g/Mg dispersant (sodium hexametaphosphate) and 50% solid content are shown in Table 1. The results indicated that the size fraction of -74 + 10 μm had a Zn grade of 16.61% and a Zn recovery of 95%, only losing 5% of the maximum Zn recovery. This result was attributed to the adsorption of the dispersant at the cation sites (Zn$^{2+}$) which conferred a high negative charge on the mineral surface and easily separated fine slimes.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Slime (-10 μm)</th>
<th>-74 +10 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn grade (%)</td>
<td>7.87</td>
<td>16.61</td>
</tr>
<tr>
<td>Zn recovery (%)</td>
<td>5</td>
<td>95</td>
</tr>
</tbody>
</table>

The flotation performance of zinc oxide with and without desliming is shown in Table 2. The results indicated that the flotation of the size fraction -74 +10 μm after desliming obtained a concentrate with a Zn grade of 49.16% and a Zn recovery of 96.01%. In addition, the flotation of the size fraction -74 μm without desliming obtained a concentrate with a Zn grade of 48.34% and a Zn recovery of 95.97%. These results indicated that flotation of zinc oxide with and without desliming both obtained good flotation responses. The obtained results were inconsistent with previous studies of the flotation of smithsonite (Mehdilo et al., 2012; Majid et al., 2014) that reported an increase in Zn recovery and sodium sulphide with desliming compared to those without desliming. The good flotation performance in the present study was obtained without desliming because of the addition of P80, which improved the dispersion effect of the amines, reduced the interaction between amines and slimes, and minimized the harmful effects of fine slimes. However, considering the desliming recovery of 95%, the total recovery for flotation of the desliming zinc oxide was approximately 91.21%, which was less than without desliming. Therefore, desliming is not suggested in the presence of P80 based on this data.
Table 2. The effect of desliming on flotation in the presence of 7500 g/Mg sulphide, 194 g/Mg pretreated amine (33.3% polysorbate 80 (P80)-amine proportion), 600 g/Mg dispersant, 600 g/Mg depressant, and 150 g/Mg pine oil at 25 °C with a Zn grade of 15.74% in raw ore

<table>
<thead>
<tr>
<th>Condition</th>
<th>Without desliming</th>
<th>Desliming</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn grade (%)</td>
<td>48.34</td>
<td>49.16</td>
</tr>
<tr>
<td>Zn recovery (%)</td>
<td>95.97</td>
<td>96.01</td>
</tr>
</tbody>
</table>

3.3. Effect of sulphide dose

The sulphidation process converts the surface of the zinc oxide ore into a sulphidised surface film, improving the surface hydrophobicity and activating the flotation of oxide minerals. This process includes the dissolution of Na$_2$S where HS$^-$ and S$^{2-}$ ions form in an aqueous suspension; HS$^-$ dominates when pH > 7.0, whereas S$^{2-}$ dominates at pH > 13.9 (Wang et al., 1986; Majid et al., 2014). Moreover, the optimum pH of flotation is in the range (10.5–12) where HS$^-$ is the predominant species. Therefore, the adsorption of HS$^-$ ions occurs on mineral surfaces where chemical and/or electrochemical reactions occur to form metal sulphides at these surfaces. Sulphidation reactions are shown in Eqs. (2) to (4) (Ke et al., 2014).

$$
\text{Na}_2\text{S} + \text{H}_2\text{O} \leftrightarrow \text{HS}^- + 2\text{Na}^+ + \text{OH}^- \quad (2)
$$

$$
\text{ZnCO}_3\text{(surf)} + \text{HS}^- \leftrightarrow \text{ZnS}_\text{(surf)} + \text{HCO}_3^- \quad (3)
$$

$$
\text{Zn(OH)}_2\text{(surf)} + \text{HS}^- \leftrightarrow \text{ZnS}_\text{(surf)} + \text{H}_2\text{O} + \text{OH}^- \quad (4)
$$

The influence of sulphide dose on zinc oxide flotation is shown in Fig. 5. The results showed that optimal dose of Na$_2$S in such conditions was up to approximately 7500 g/Mg, which was much less than other studies (12,000 g/Mg) (Mehdilo et al., 2012). In the literature, a dose of Na$_2$S less than 7500 g/Mg is not enough for particle surface sulphidation owing to the large amount of fine slimes on the mineral surface. In addition, excess Na$_2$S did not significantly depress the flotation of zinc oxide. This result was consistent with the results reported by Marabini and Keqing. These authors found that the Zn recovery was not sensitive to the Na$_2$S concentration when the sodium sulphide concentration was high (Marabini et al., 1984; Keqing et al., 2005; Mehdilo et al., 2013). However, an excess Na$_2$S dose increased the reagent cost. Thus, the amount of reagent should be carefully controlled in flotation processes.

3.4. Effect of depressant dose

Quartz and other mineral impurities present in the ore can be simultaneously floated by amine (Li et al., 2017). However, sodium silicate (type N) is a quartz depressant and partially reduces quartz recovery in cationic flotation (Ĕţemaei et al., 2010).

The influence of depressant dose on zinc oxide flotation is shown in Fig. 6. The results showed that the Zn grade remained at approximately 48% as the depressant dose increased from 600 g/Mg to 1000...
g/Mg and then decreased from approximately 48% to less than 44% when the depressant dose exceeded 1000 g/Mg. In addition, the Zn recovery decreased as the depressant dose increased, suggesting that extra depressant influenced the zinc recovery. The reason for this observation was that the depressant mainly depressed the flotation of silicate minerals and other impurities and regulated the pH. However, extra depressant hindered the flotation of zinc containing silicate minerals, resulting in decreased zinc recovery. Moreover, extra depressant made the pulp become viscous and difficult to filter. Therefore, the optimal dose of depressant was 600 g/Mg, and a concentrate with a Zn grade of 48.34% and a Zn recovery of 95.97% was achieved.

Fig. 6. Zinc grade and recovery of ore flotation for various dosage of depressants in the presence of 7500 g/Mg sulphide, 194 g/Mg pretreated amine (33.3% polysorbate 80 (P80)-amine proportion), 600 g/Mg dispersant, 150 g/Mg pine oil at 25 °C with a zinc grade of 15.74% in raw ore

3.5. Effect of temperature

Fig. 7 shows the effect of temperature on the flotation of zinc oxide. The Zn grade and recovery were approximately fixed values as the pulp temperature decreased. This behaviour could be explained by only some amines and P80 directly reacted with zinc oxide on the surface without sulphidation, whereas these compounds readily reacted (Massacci et al., 1984) with the sulphidised zinc oxide. According to these findings, the flotation of zinc oxide using amines and P80 was carried out at temperatures as low as 8 °C, and this flotation temperature was much lower than those previously reported (Keqing et al., 2005; Hosseini and Forssberg, 2006; Ejtemaei et al., 2010; Majid et al., 2014).

Fig. 7. Zinc grade and recovery of ore flotation in concentrate and tailing for various temperatures in the presence of 7500 g/Mg sulphide, 194 g/Mg pretreated amine (33.3% polysorbate 80 (P80)-amine proportion), 600 g/Mg dispersant, 600 g/Mg depressant, and 150 g/Mg pine oil with a zinc grade of 15.74% in raw ore

3.6. Effect of different types of zinc oxide ores

Fig. 8 shows the effect of different types of zinc oxide ores, which had different Zn grades, on the flotation of these ores. The results showed that the Zn grade and recovery exceeded 45% and 90%, respectively, as the Zn grades in the raw ore increased from 10.18% to 31.25% owing to the use of
amines and P80, suggesting that the sulphidation method using amines and P80 also could be applied to different types of zinc oxide ores.

Fig. 8. Zinc grade and recovery of ore flotation in concentrate for different kinds of zinc oxide ore in the presence of 7500 g/Mg sulphide, 194 g/Mg pretreated amine (33.3% polysorbate 80 (P80)-amine proportion), 600 g/Mg dispersant, 600 g/Mg depressant, and 150 g/Mg pine oil with a zinc grade of 15.74% in raw ore at 25 °C

3.7. Energy-dispersive X-ray spectroscopy (EDX) and XRD results

Table 3 and Fig. 9 show the results of EDX for the raw ore and the concentrate. According to the obtained results, the concentrate contained 48.34% Zn, whereas the raw ore contained 15.74% Zn. After using the flotation method, the Zn grade of the concentrate was much higher than that of the raw ore, the contents of Ca, Al, and Si sharply decreased, and the content of Fe increased a small amount. These results indicated that Zn was concentrated in the flotation concentrate, whereas Ca, Al, and Si impurities were concentrated in the tailing.

Fig. 9. The results for chemical analysis using EDX on ore sample (-25μm), left - raw ore; right - concentrate

Table 3. Results of EDX for the raw ore and the concentrate

<table>
<thead>
<tr>
<th>Element</th>
<th>Zn</th>
<th>Pb</th>
<th>Ca</th>
<th>Si</th>
<th>Fe</th>
<th>Al</th>
<th>O</th>
<th>C</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw ore (%)</td>
<td>15.74</td>
<td>0.24</td>
<td>18.99</td>
<td>11.92</td>
<td>6.34</td>
<td>4.62</td>
<td>31.54</td>
<td>6.73</td>
<td>0.77</td>
</tr>
<tr>
<td>Concentrate (%)</td>
<td>48.34</td>
<td>0.33</td>
<td>2.70</td>
<td>6.33</td>
<td>8.82</td>
<td>0.85</td>
<td>23.26</td>
<td>8.15</td>
<td>1.23</td>
</tr>
</tbody>
</table>

Fig. 10 shows the results of XRD for the raw ore and the concentrate. According to the obtained results, the raw ore mainly contained smithsonite (ZnCO₃) and hemimorphite (Zn₄Si₂O₇(OH)₂·H₂O). Quartz (SiO₂), magnesite (MgCO₃), calcite (CaCO₃), siderite (FeCO₃), and aluminosilicate were present as mineral impurities. After flotation, smithsonite and hemimorphite were concentrated in the concentrate, whereas quartz, magnesite, calcite, and other mineral impurities were retained in the tailing. The results further confirmed that the use of amines and P80 with the sulphidation method could be applied to different types of zinc oxide ores.
Fig. 10. XRD results of zinc oxide raw ore and its concentrate, raw ore - ZnCO$_3$, Zn$_4$Si$_2$O$_7$(OH)$_2$·H$_2$O, MgCO$_3$, CaCO$_3$; concentrate - ZnCO$_3$, Zn$_4$Si$_2$O$_7$(OH)$_2$·H$_2$O

4. Conclusions

The pretreatment of amine collectors with P80 enhanced the flotation efficiency of zinc oxide. An amine mixture of DDA and ODA performed better than either amine alone. The highest recovery and grade of zinc in the concentrate were respectively 48.34% and 95.97%, and the conditions which obtained this result were a P80-amine proportion of 33.3%, 7500 g/Mg Na$_2$S, 600 g/Mg dispersant, and 600 g/Mg depressant.

The pretreatment of amine collectors with P80 made the flotation less sensitive to slime, so desliming prior to flotation is not suggested in the future. In addition, the flotation temperature was as low as 8 °C, and the sulphidation method which includes pretreatment of amines with P80 could be applied to different types of zinc oxide ores.

Acknowledgement

This work was supported by the Science, Technology and Innovation Commission of Shenzhen Municipality (No. JCYJ20180503182130795).

References


