Investigation of the causes of low leachability and examination of the solutions to increase leachibility of Mehdi-Abad nonsulfide zinc ore

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Abstract: Extensive mineralogical and metallurgical tests were carried out in order to understand the reasons for low leachability of Mehdi-Abad nonsulfide zinc ore. The characterization study revealed the presence of smithsonite and hemimorphite as the main zinc bearing minerals. Zinc was also detected in iron (oxy) hydroxide minerals, which led to low zinc recovery. The results of agitation leaching tests indicated that approximately 75% of zinc could be dissolved. To find out an effective solution for increasing the dissolution of zinc, a flowsheet was proposed comprising a magnetic separation step to produce a magnetic and a non-magnetic product. Hot and mild acid leaching were carried out on magnetic and non-magnetic fractions, respectively. The result showed the dissolution of zinc was increased by 8.3% and reached to 83.35%.


Keyword: nonsulfide zinc, leaching, characterization study, Mehdi-Abad.

1- Introduction

Nowadays, zinc is obtained mostly from sulfide ores because sulfides are easy to treat by usual flotation procedures. With the depletion of sulfide reserves and development of acid leaching, solvent extraction, and electrowinning process, there has been a renewed economical interest for nonsulfide ores [Espiair et al., 2006]. However there are several zinc bearing mineral but the only important minerals for zinc extraction are: Smithsonite (ZnCO3), Hydrozincite (2ZnCO3, 3Zn (OH) 2), zinct (ZnO), willemite (ZnSiO3), and hemimorphite (Zn2SiO3,H2O) [Boni et al., 2009; Hitzman et al., 2003].

Extensive pyrometallurgical and hydrometallurgical works have been carried out on the treatment of nonsulfide zinc ores [De wet, 2008; Boni et al., 2009; Moradi et al., 2011]. Due to environmental considerations, lower capital and operating costs, and more added incentives, there has been a worldwide upsurge of interest in the hydrometallurgical processes. Leaching is the first step in hydrometallurgical route and the obtained pregnant leach solution (P.L.S) defines the next process steps. A lot of academic and industrial researches have been carried out on the leaching of nonsulfide zinc ores. Frenay leached various nonsulfide zinc ores in different solvents in laboratory tests by agitation leaching and in some cases by percolation leaching [Frenay,1985]. He used sulfuric acid, sulfurous acid, ammonium hydroxide, and sodium hydroxide. The best results were achieved by sulfuric acid and caustic soda. According to his results, Smithsonite completely leaches but hemimorphite is refractory to leaching in any solvent studied. Bodas studied the suitability of sulfuric acid leaching for the silicate ore found in paedang (Thailand) [Bodas, 1996]. At the optimum condition the zinc recovery reached to 95%. Abdel-Aal studied the kinetics of sulfuric acid leaching, and reported that the leaching of nonsulfide zinc is controlled by the diffusion-controlled reactions [Abdel-Aal, 2001]. Hongsheng carried out sulfuric acid leaching of zinc silicate under pressure [Hongsheng, 2010]. The obtained results showed that the acid leaching under pressure is more efficient compared to other process in terms of decreased dissolution of silica and iron and increased zinc extraction.

The Mehdi-Abad Zinc Project is located in central Iran, approximately 120 kilometers south east of the city of Yazd and approximately 550 kilometers directly south east of Tehran. Mehdi-Abad is the world’s largest undeveloped zinc resource. It comprises both sulfide and nonsulfide ores. The samples were obtained from the nonsulfide zone.

2- Materials and Methods

2-1 Characterization study

To understand the operating parameters which affect the leaching of zinc, a comprehensive study was carried out, both on mineralogy and metallurgical characteristics of the ore. The mineralogy was studied by using optical microscopy,
SEM, XRD, and XRF. In addition, a rough evaluation was made by testing the macroscopic sample with zinc zap reactant (a solution of 3% potassium ferricyanide and 0.5% diethylaniline dissolved in 3% oxalic acid). Metallurgical characterization was carried out by a fractionation of the ore. Magnetic fractions were prepared by using a high intensity magnetic separator. Moreover, heavy liquid test was carried out as well in order to well characterize the ore and gangue minerals.

2-2 Agitation leaching

The agitation leaching tests were carried out in a glass reactor. Agitation was provided with a mechanical stirrer which enables adequate dispersion of the materials. Sulfuric acid from Merck was used, with a purity and density of 98% and 1.84 g/cm$^3$, respectively. The temperature of the medium was controlled with an accuracy of ±2°C. Twenty experiments were designed by applying D-optimal methodology. Based on previous studies (several rough tests), three factors were considered to have more influences on the leaching process. The selected control factors, including acid concentration, particle size distribution, and solid: liquid ratios (S/L) with their levels are presented in table 1. The other operational factors including the reaction temperature (60°C), leaching time (90min.), and agitation rate (600 r.p.m.) were kept constant.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Low value</th>
<th>High value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid concentration (v/v) %</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>Particle size (micron) -74</td>
<td>-177</td>
<td></td>
</tr>
<tr>
<td>Solid/liquid (g/ml)</td>
<td>10</td>
<td>30</td>
</tr>
</tbody>
</table>

Analysis of variance (ANOVA) and studies of optimization were carried out by using the “Design Expert (DX7)” software. The optimum condition was defined as a state with the maximum extraction of zinc, the minimum extraction of iron, higher value of particle size and solid: liquid ratio, and lower value of acid concentration.

2-3 Magnetic separation followed by leaching

A high intensity magnetic separator (2T) was employed to produce two magnetic and non-magnetic fractions. Particle size was between +105-177 microns. Hot (90°C) and mild (60°C) acid leaching were carried out on magnetic and non-magnetic fractions, respectively. The other parameters were kept equivalent to the obtained optimum condition of the agitation leaching experiment. After filtration of slurry, to remove the high amount of iron which was dissolved during hot acid leaching, the pH of the P.L.S. was increased to 4. At the end, both P.L.S.s were mixed and the final P.L.S. was formed. The flowsheet is shown in figure 1.

![Figure 1. Magnetic separation followed by leaching](image-url)
3-1 characterization study

The XRD analysis showed that zinc occurs mainly as smithsonite and hemimorphite. Several XRD analyses were carried out on different samples. A number of the XRD analysis indicated the presence of chalcophanite [(Zn,Mn,Fe)Mn\textsubscript{2}O\textsubscript{5}.2H\textsubscript{2}O]. However, chalcophanite was not present in all the XRD patterns which can be attributed to the low quantities of this mineral, but as it will be discussed, optical microscopy and SEM showed some quantity of chalcophanite in all the samples. In addition, the sample contained significant levels of hematite, goethite, calcite, dolomite and quartz. The XRF results revealed that the sample contains 10.1\% ZnO, 13.6\% SiO\textsubscript{2}, 6.4\% CaO, 36.7\% Fe\textsubscript{2}O\textsubscript{3}, 11\% MnO, 2.58\% Al\textsubscript{2}O\textsubscript{3}, 1.57\% MgO, 1.18\% PbO, and 0.57\% K\textsubscript{2}O, and 14.93\% L.O.I.

The main zinc minerals including hemimorphite, smithsonite, and chalcophanite were verified under optical microscopy and SEM. Furthermore, it was observed that Zn and Mn were partially present in iron (oxy)hydroxide minerals (figure 4). SEM-EDX shows approximately 20\% of zinc is adsorbed by Fe-(oxy)hydroxide.

Figure 2. Zinc and manganese present in iron (oxy)hydroxide A) optical microscopy B) back scatter image by SEM. B-1,B-2,B-3) element distribution maps of Zn, Fe, and Mn.

Figure 3. SEM image of leaching residue A)optical microscopy B & C)back scatter image by SEM D,E,E) element distribution maps of Zn, Fe, and Mn
3-2 Agitation leaching

Under the aforementioned conditions in section 2-2, the maximum zinc extraction reached 86.9% but a significant percentage of iron (15%) was dissolved as well. The optimum condition that was proposed by the software was -125 micron, 5%, and 28% for particle size, acid concentration, and solid: liquid ratio, respectively. Under the proposed optimum condition the percentage of zinc and iron extraction were reached to 75.05% and 1.87%, respectively.

The nature of the leaching residue was examined by SEM, and showed the Fe-(oxy)hydroxide and chalcophanite as the main source of untreated zinc bearing minerals (figure 3).

3-3 The magnetic separation followed by leaching

The mass balance of magnetic separation step is shown in table 2.

<table>
<thead>
<tr>
<th>Table 2. The magnetic separation results</th>
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</thead>
<tbody>
<tr>
<td>Weight (g)</td>
</tr>
<tr>
<td>Feed</td>
</tr>
<tr>
<td>Magnetic</td>
</tr>
<tr>
<td>Non-magnetic</td>
</tr>
</tbody>
</table>

Semi-quantitative x-ray diffraction analysis indicated that 35% of the ore was magnetic minerals; however, the presence of chalcophanite as a paramagnetic mineral, and also the imperfect liberation of minerals made the magnetic fraction 45.89%.

The results of hot and mild acid leaching on the magnetic and non-magnetic fractions are shown in table 3. The percentages of zinc extraction in magnetic and non-magnetic fractions were 69.02% and 90%, respectively. Totally, 83.37% and 9.9% of zinc and iron were dissolved in both magnetic and non-magnetic fractions.

<table>
<thead>
<tr>
<th>Table 3. The results of hot and mild acid leaching on the magnetic and non-magnetic fractions</th>
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</thead>
<tbody>
<tr>
<td>P.L.S (ml)</td>
</tr>
<tr>
<td>Magnetic</td>
</tr>
<tr>
<td>Non-magnetic</td>
</tr>
</tbody>
</table>

Using a precipitation step, by neutralization to pH 4, the concentration of iron decreased to 1680 ppm in the P.L.S. of magnetic fraction. Due to environmental consideration, it is highly recommended to use hematite precipitation method for iron removal because the precipitated hematite can be used with the leaching residue in the cement industry and/or as a pigment. Therefore in addition to producing a by-product of hematite, the disposal concerns will be decreased.

At the end, both P.L.S were mixed and analyzed. The final solution had 22860 ppm zinc and 300 ppm iron. By using this scheme, the overall zinc recovery increased by nearly 8.3%, and reached to 83.35%.

4- Conclusion

The complete characterization study revealed that zinc is present in the carbonate, silicate and iron (oxy)hydroxide minerals. Iron (oxy)hydroxides have specifically high surface areas (up to 600 m²g⁻¹) (Lee, 2003). This high surface area, associated with the affinity of ferric iron (oxy)hydroxides to Me (II)-ions, results in a highly effective adsorption of these ions. When nonsulfide zinc rocks form, Cu, Cd, Pb, Zn and As can be adsorbed onto Fe-(oxy)hydroxides (goethite, hematite etc.) and this process of cation-adsorption onto hydrous ferric oxides is highly dependent on the pH level of the aqueous solution (Martinez, 2001).

As observed, in the Mehdi-Abad ore, Fe-(oxy)hydroxides show partly high concentrations of zinc (approximately 20 %, SEM-EDX). The nature of the leaching residue showed that iron hydroxides is the main source of untreated zinc bearing minerals. The results of agitation leaching tests indicated that at the optimum condition about 75% of zinc is dissolved. The low leachability, in addition to a low grade ore, rejected the usual tank leaching process. Therefore, a different scheme was considered to improve the efficiency of the leaching process. To find out an effective solution for increasing the dissolution of zinc, a flowsheet was proposed comprising a magnetic separation step before leaching. Hot and mild acid leaching was carried out on magnetic and non-magnetic fractions,
respectively. The result showed the dissolution of zinc was increased by 8.3% and reached to 83.35%.

5- Reference