Antimony Production from Domestic Stibnite Ores via Niederschlag Process

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Abstract

Niederschlag process is used to produce metallic antimony. This process is a metallothermic reduction method which is based on the reduction of metallic Sb from Sb₂S₃ (stibnite) by using metallic iron as reductant at high temperatures. The low reaction specific heat value makes the use of external heating a necessity apart from other metallothermic processes. During heating, antimony sulfide is decomposed and sulphur combines with iron to form the matte phase. Metallic antimony is collected at the bottom of the crucible. In this study, the parameters of metallic Sb production from Sb₂S₃ concentrate, which is obtained in Etibakir A.Ş. Emirli mine, were investigated by using Niederschlag Process. In the experimental studies, a constant amount of flux materials (borax, sodium carbonate, silica) were mixed with Sb₂S₃ concentrate and the increasing amount of Fe. AAS (atomic absorption spectrometry) and XRD (X-ray diffraction spectrometry) techniques were used for the characterization of the concentrate, metallic nuggets and matte phases. The experiment, with the addition of 100% stoichiometric Fe at 100°C, had the highest Sb recovery rate as 79.25%.

1. Introduction

Antimony is a metalloid with an atomic number of 51. It is found in over 100 mineral species and found in nature mainly as a sulfide mineral stibnite (Sb₂S₃). Antimony is a lustrous grey metal that has a Mohs Scale Hardness of 3. This metalloid exists in two forms; metallic antimony is bright, silvery, hard and brittle, nonmetallic form is a grey powder. Antimony has poor electric and heat conduction. It is not attacked by dilute acid or by alkalis and stable in dry air [1-4].

Several production methods can be used for antimony production such as gasification and reduction method, electrolyte method and Niederschlag Process [1, 5].

Stibnite is totally oxidized at 350-400 °C in reverberatory furnaces as for gasification and reduction method and it takes 10-12 hours approximately with carbon source. Gasification method is a two step production method. The first step is oxidation and the second step is reduction. The main reactions of the process in question are given below [1, 5].

\[
\begin{align*}
2\text{Sb}_2\text{S}_3 + 9\text{O}_2 & \rightarrow 2\text{Sb}_2\text{O}_3 + 6\text{SO}_2 \quad (1) \\
\text{Sb}_2\text{O}_3 + 3\text{C} & \rightarrow 2\text{Sb} + 3\text{CO} \quad (2)
\end{align*}
\]

As electrolyte method; antimonite dissolves in hot sodium sulfide solution and then obtained sodium thio antimonite is electrolyzed with steel anodes and cathodes to produce metallic antimony [1].

In Niederschlag Process, stibnite can be directly reduced with metallic iron and a slight amount of carbon (to soften the bonds) in reverberatory furnaces or blast furnaces. Niederschlag Process is candidate to be the most economic production method for antimony production if the process can be optimized to work with high metallization ratios. In this method antimony can reduced in one step. Sulphur is decomposed from stibnite and interacts with iron then a matte phase, mainly consists of FeS, is obtained over the metallic antimony. The main reaction of Niederschlag Process is shown with Equation (3) and Equation (4) [5].

\[
\begin{align*}
\text{Me}_1\text{X} + \text{Me}_2 & \rightarrow \text{Me}_1 + \text{Me}_2\text{X} \quad (3) \\
\text{Sb}_2\text{S}_3 + 3\text{Fe} & \rightarrow 2\text{Sb} + 3\text{FeS} \quad (4)
\end{align*}
\]

Reduction reaction starts over 1100 °C. Various flux materials can be used for the process, such as silica (SiO₂), sodium borax decahydrate (Na₂B₄O₇·10H₂O), calcium carbonate (CaCO₃), glauber salt or NaHCO₃ to avoid metal losts. System has FeS-Na₂S founded liquid matte phase and a metallic antimony phase is underneath the matte phase [5].

2. Experimental Procedure

In this study the stibnite concentrate (Table 1, Figure 1), which is mined in Ödemiş-Emirli and concentrated via flotation in Etibakir A.Ş. Halikoy Plant was subjected to produce metallic antimony through Niederschlag Process.

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\end{align*}
\]
Table 1. Chemical content of stibnite concentrate (wt.%).

<table>
<thead>
<tr>
<th></th>
<th>Sb</th>
<th>S</th>
<th>Fe</th>
<th>Pb</th>
<th>Sn</th>
<th>Al</th>
<th>As</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>68.67</td>
<td>27.11</td>
<td>1.08</td>
<td>0.14</td>
<td>0.12</td>
<td>0.08</td>
<td>0.08</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Dry concentrate was mixed with borax, sodium carbonate and SiO₂ as flux materials and iron as reductant. Used flux ratios were 10.5% for borax, 20.1% for sodium carbonate and 10.5% for SiO₂ (flux / Sb₂S₃ concentrate, %). Experiments were conducted with various iron reductant ratios and refractory acidity ratios.

Figure 1. XRD pattern of stibnite concentrate.

In the Niederschlag experiments, stibnite concentrate having a Sb₂S₃ content of 68.67% and an average particle size of 60.76 μm was used. For different acidity ratios of refractory, two types of crucibles were used. The first experimental set was completed with the crucible which had 1.4 acidity ratio and the second experimental set completed with the crucible which had 3.2 acidity ratio.

The initial mixtures were prepared from dried powders at various stoichiometric Fe ratios from 75% to 200%. The powder mixtures were charged into cylindrical fireclay pots. At the first experimental set 1.4 acidity ratio crucibles were used. These crucibles had 40 mm thickness, 58 mm inner diameter and 142 mm height. In the second experimental set 3.2 acidity ratio crucibles were used. These crucibles had 23 mm thickness, 42 mm inner diameter and 52 mm height.

The all experiments were conducted in an electrical resistant furnace at 1100 °C for process duration of 60 minutes. Duration and temperature were fixed for all experimental sets. The obtained phases were characterized by using X-rays diffraction spectrometer (XRD, Rigaku Miniflex, Cu Kα X-ray tube - 30 kV; 15 mA), X-rays fluorescence spectrometer (XRF, ThermoScientific, w/ He tube), chemical analysis techniques and atomic absorption spectrometer (AAS, Perkin Elmer AAS 800).

3. Results and Discussion

For the first experimental, the ratio of required stoichiometric reductant amount was investigated for 1.4 crucible acidity ratio. In this study, iron nails were used as reductant. Reductant amount was used from 75% stoichiometric Fe to 200% stoichiometric Fe. The highest metallization ratio was measured as 46.92% for the experiment conducted with 150% stoichiometric amount of Fe (Figure 2).

Figure 2. Sb recovery with increasing Fe stoichiometry for 1.4 crucible acidity ratio.

The second experimental set was conducted to understand the investigation of refractory acidity ratio on the metallization ratios of antimony by using different types of the crucibles. For the second experimental set, we used the crucibles which had an acidity ratio of 3.2.

Figure 3. Sb recovery with increasing Fe stoichiometry for 3.2 crucible acidity ratio.

As a result of the experiments, it was determined that increasing acidity ratio increased the metal recovery. The highest metallization ratio was obtained in the experiment conducted with 100% Fe stoichiometry as 79.25% metallization ratio. It was also the highest metallization ratio during the all experiments (Figure 3, Figure 4, Table 2).

However, it is possible to collect the lost antimony amount (apart from the slight amount solved in the matte phase) in the form of antimony oxide in a dust collector of such a furnace system.
Figure 4. XRD patterns of metallic phases obtained with increasing Fe stoichiometry for 3.2 crucible acidity ratio (wt.%).

Table 2. Sb recovery ratios and the chemical content of metallic phases with the increase in reductant stoichiometry for 3.2 crucible acidity ratio (wt.%).

<table>
<thead>
<tr>
<th>Fe sto., %</th>
<th>Sb Rec., %</th>
<th>Sb</th>
<th>Fe</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>N/A</td>
<td>91.38</td>
<td>4.93</td>
<td>1.65</td>
</tr>
<tr>
<td>100</td>
<td>79.25</td>
<td>91.86</td>
<td>5.14</td>
<td>0.81</td>
</tr>
<tr>
<td>125</td>
<td>70.35</td>
<td>58.04</td>
<td>39.57</td>
<td>4.11</td>
</tr>
<tr>
<td>150</td>
<td>58.46</td>
<td>41.00</td>
<td>57.94</td>
<td>6.35</td>
</tr>
<tr>
<td>175</td>
<td>68.54</td>
<td>38.82</td>
<td>59.45</td>
<td>6.59</td>
</tr>
<tr>
<td>200</td>
<td>77.86</td>
<td>56.66</td>
<td>45.54</td>
<td>4.76</td>
</tr>
</tbody>
</table>

4. Conclusion

In the present study, parameters to produce metallic Sb from Sb$_2$S$_3$ concentrates were investigated by using a one-step production method which is called “Niederschlag Process”. Niederschlag Process is a metallothermic reduction method which is based on the reduction of metallic Sb from Sb$_2$S$_3$ by using metallic iron as reductant at high temperatures. The low reaction specific heat value makes the use of external heating a necessity apart from other metallothermic processes.

In the experimental studies, a constant amount of flux materials (borax, sodium carbonate, silica) were mixed with Sb$_2$S$_3$ concentrate and the increasing amount of Fe. The experiments were conducted in two different crucibles having an acidity ratio of 1.4 and 3.2 respectively.

In the experiment which was conducted in the crucible having acidity rate of 3.2 and with the addition of 100% stoichiometric Fe had the highest metal recovery ratio was calculated as 79.25%. It was also determined that the lost amount of antimony was collected in the dust collector of furnace in the form of Sb$_2$O$_3$ during the experiments.

References