REDUCTIVE-SULFURIZING SMELTING TREATMENT OF SMELTER SLAG FOR COPPER AND COBALT RECOVERY

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Abstract

Recovery of copper and cobalt from smelter slag using reductive-sulfurizing smelting method was performed in this study. The effects of reductive agent (coke), sulfurizing agent (pyrite), slag modifier (CaO) and smelting temperature and duration on the extractive efficiencies of Cu, Co and Fe were discussed. The phase compositions and microstructure of the materials, copper-cobalt matte and cleaned slag were determined. The results showed that copper and cobalt contents in cleaned slag could decrease averagely to 0.18% and 0.071% respectively after cleaning. 91.99% Cu and 92.94% Co and less than 38.73% Fe were recovered from the smelter slag under the optimum conditions: 6 wt.% coke, 20 wt.% pyrite and 6 wt.% CaO addition to the smelter slag, smelting temperature of 1350°C and smelting duration of 3h. The addition of CaO can increase the selectivity of Co recovery. The cleaning products were characterized by XRD and SEM-EDS analysis. The results showed that the main phases of copper-cobalt matte were iron sulfide (FeS), geerite (Cu 8S5), iron cobalt sulfide (Fe 0.92 Co 0.08 S) and Fe-Cu-Co alloy. The cleaned slag mainly comprised fayalite (Fe 2SiO 4), hedenbergite (CaFe(Si 2O 6)) and magnetite (Fe 3O 4).

Keywords: Smelter slag; Reductive-sulfurizing smelting; Slag cleaning; Recovery of cobalt and copper; Copper-cobalt matte; Cleaned slag

1. Introduction

In copper-cobalt sulfide concentrates smelting process, cobalt inevitably followed iron into smelting or converting slags due to their similarities in the oxidative-reductive behaviors [1-3]. As a result, large amount of cobalt lost in the slags and may be disposed as waste material which led to a huge waste of cobalt resource. Furthermore, the similarities in chemical property of cobalt and iron also resulted in difficulties in separating from each other during the subsequent Hydrometallurgical process. To solve these series of problems above, authors had present a new process of low iron smelting of cobalt-bearing copper sulfide concentrates[4, 5], aiming at separating iron prior to the converting step. Cobalt and copper lost in slags were recovered using reductive-sulfurizing smelting method.

More recently, there has been a great deal of interest expressed in the recovery of cobalt (often together with nickel and copper) from a variety of slags because of the obvious economic implication [3]. However, with the increasing of oxygen enrichment during smelting, copper and cobalt in smelter slag increasingly are lost in fayalite and magnetite in form of oxydic dissolution and lattice substitution. Besides, taking mechanical entrainment of copper-cobalt matte and metallic copper-cobalt droplets [6] into account, conventional slag cleaning techniques [7], such as slow cooling of the slag followed by milling and flotation [8], already cannot efficiently recover valuable metals lost in slags [9, 10]. These problems have been studied by some investigators[2, 4, 7, 11 -14]. The research results [15] provided several feasible methods to recover the oxidized metals dissolved in slag. But some alternative routes for treatment of the complex and changeable smelter slag need to be further developed.

The recovery of oxidized metals dissolved in the slag, however, can be easily achieved by adding sulfurizing agent (such as pyrite) to slag-cleaning furnace together with reductant (such as coke) and/or slag modifier (CaO generally), which can efficiently recover valuable metals at relatively lower operating temperature. The oxides of cobalt and copper were reduced to different extent by selective carbothermic reduction because of the presence of carbon [1], while retaining the maximum possible quantity of iron as oxides in the slag. When add pyrite for further process, cobalt and copper will be sulfurized to produce a low grate copper-cobalt matte [3, 16] and then separate from cleaned slag .

Reductant (such as coke) is used in many metallurgical processes to control oxygen potential of
molten slag and recover metals. The roles of coke have been discussed in detail [17-19]. Sulfurizing agent was found to act as a collector phase to promote removal of the valuable metals from the slag, decrease the liquidus temperature of the final cobalt-containing product and provide sufficient volume of matte product to allow separation from slag [18]. Pyrite, as the sulfurizing agent, it ensured the conduction of sulfurization reaction of cobalt and copper oxides. The reaction mechanism can be briefly represented as follows (the square bracket “[ ]” represents materials in matte. The round bracket “( )” represents materials in slag):

\[
\begin{align*}
2\text{FeS}_2 &\rightarrow 2\text{[FeS]} + \text{S}_2(g) \quad \Delta G_T^\circ = -2.87 \times 10^8 + 208.02 \\
2\text{(Cu}_2\text{O)} + \text{S}_2(g) + \text{C} &\rightarrow 2\text{[Cu}_2\text{S]} + \text{CO}_2(g) \quad \Delta G_T^\circ = -0.097 - 342.86 \\
2\text{(CoO)} + \text{S}_2(g) + \text{C} &\rightarrow 2\text{[CoS]} + \text{CO}_2(g) \quad \Delta G_T^\circ = 0.0167 - 240.17 \\
2\text{(Cu}_2\text{O)} + \text{C} &\rightarrow 4\text{[Cu]} + \text{CO}_2(g) \quad \Delta G_T^\circ = -0.157 - 97.2 \\
2\text{(CoO)} + \text{C} &\rightarrow 2\text{[Co]} + \text{CO}_2(g) \quad \Delta G_T^\circ = -0.147 + 34.87 \\
\text{(Cu}_2\text{O)} + \text{[FeS]} &\rightarrow \text{[Cu}_2\text{S]} + \text{(FeO)} \quad \Delta G_T^\circ = -0.0397 - 79.26 \\
\text{(CoO)} + \text{[FeS]} &\rightarrow \text{[CoS]} + \text{(FeO)} \quad \Delta G_T^\circ = 0.0167 - 28.77 \\
\end{align*}
\]

Fig. 1 showed the relationship between \( \Delta G_T^\circ \) and T of Equations (1)-(7). Relative thermodynamic data based on HSC 6.0 Chemistry database (Outokumpu).

![Figure 1. Relationship between Gibbs free energy (\( \Delta G^\circ \)) and temperature (T) of reactions (1)-(7)](image)

<table>
<thead>
<tr>
<th>Materials</th>
<th>Cu</th>
<th>Co</th>
<th>Fe</th>
<th>S</th>
<th>Mg</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smelter slag</td>
<td>1.4</td>
<td>0.7</td>
<td>38.73</td>
<td>0.51</td>
<td>0.41</td>
<td>24.19</td>
<td>5.36</td>
<td>2.41</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.022</td>
<td>0.008</td>
<td>45.43</td>
<td>48.35</td>
<td>0.045</td>
<td>2.31</td>
<td>0.83</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Table 1. Chemical compositions of materials /wt.%

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Industrial analysis</th>
<th>Chemical composition of the ash</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FC₂</td>
<td>V_d</td>
</tr>
<tr>
<td>Smelter slag</td>
<td>81.27</td>
<td>3.3</td>
</tr>
</tbody>
</table>

It illustrated FeS₂ would decompose into FeS and S₂ gas at high temperature, which afterwards react with copper and cobalt oxides respectively. Copper and cobalt oxides are favorably reduced and sulfurized to corresponding sulfide at reductive atmosphere. These decompose and exchange reactions during cleaning formed copper-cobalt matte ultimately. FeO and CaO combined with silica and formed cleaned slag. However, copper oxide was easier to be reduced and sulfurized than cobalt oxide from the point of thermodynamics. That indicated recovery of cobalt is a little more difficult than copper during cleaning process.

Addition of slag modifier to molten slag affects the Fe³⁺/Fe²⁺ ratio, the CaO/ΣSiO₂ ratio (or basicity). It also increases the activity coefficients of iron oxide, silica, even cobalt oxide [17]. Kongoli and Yazawa found that the addition of CaO, at constant Fe/SiO₂ ratio, decreased the liquidus temperature in reductive conditions and improved the separation of the cobalt-containing product from slag [18, 20].

Based on the previous investigations, this study evaluated the influence of reductive agent, sulfurizing agent, slag modifier, smelting temperature and duration on cleaning efficiency of copper-cobalt smelter slag. Furthermore, the phase compositions and microstructure of smelting products were investigated by XRD and SEM-EDS as well.

2. Experimental
2.1 Materials

Copper-cobalt smelter slag used in the experiments obtained from flash smelting slag dump in Yanggu Xiangguang Copper Co., LTD., Shandong, China. Pyrite, the sulfurizing agent, was provided by Shui Kou Shan Nonferrous Metals Group Co., LTD, Hunan, China. The reductant was metallurgical coke. Analytically pure CaO was used as slag modifier. The materials were finely ground and prepared. Table 1 presented the main chemical composition of materials. The particle size distribution results of materials were showed in Fig. 2. It could be known that smelter slag comprised 0.7 wt.% Co and 1.4 wt.% Cu, which attached a significant economic value to recover.

X-ray Diffraction analysis(XRD, Rigaku 3014, Cu-Kα-radiation, λ=1.54Å) and Scanning Electron Microscopy (SEM-EDS, JEOL JSM-6490LV) analysis results of smelter slag were presented in Fig.
It illustrated that the main phases in smelter slag were fayalite (Fe₂SiO₄), magnetite (Fe₃O₄), augite (Ca(Fe,Mg)Si₂O₆) and (Cu₀.₈₆Fe₂.₁₄O₄). Fig. 4 showed some matte droplets of size about 10µm entrained in hedenbergite. In addition, some copper and cobalt dissolved in the magnetite as lattice substitution. A little of cobalt was detected dissolved in the augite. Therefore, the recovery method of these valuable metals must base on recovering both the entrapped matte and the dissolved oxides.

2.2 Methods

The reductive-sulfurizing smelting treatment of copper-cobalt smelter slag was carried out under Ar atmosphere in a vertical MoSi₂ tube furnace. As an experimental procedure, 200g smelter slags were mixed with the given amount of coke and pyrite and/or slag modifier (CaO). Corundum crucible (150 ml, 73 mm outside diameter, 43 mm inside diameter and 67 mm high) was chosen as a container. The effect of alumina dissolution from corundum crucible on the reaction of slag can be ignored because the scale of each experiment. The crucible was placed in the constant temperature zone of tube furnace. The tube furnace temperature was raised to the desired value and hold for preset time.

In all experiments, the matte accumulated at the bottom of the crucible after equilibration. The crucible was naturally cooled to a relatively low temperature and then taken out from the furnace, broken to separate the copper-cobalt matte and cleaned slag for samples. The samples were finely ground after completing the measurements. The chemical compositions of copper-cobalt matte and cleaned slag were analyzed by ICP-AES(IRIS Intrepid II XSP). The metals recoveries were calculated based on the mass balance principle. In addition, the cleaned slag and copper-cobalt matte were characterized by XRD and SEM-EDS.

3. Results and discussion

3.1. Effect of reductive agent

The results of reductive agent experiments were shown in Fig. 5. It was observed that the initial increasing addition of coke(4 wt. % to about 6 wt.%)) evidently increased the recovery of copper and cobalt, peaking at 6 wt.% of coke where about 88.61% Co and 92% Cu and less than 34.42% Fe were recovered. Then metals recovery decreased sharply after a steady recovery from 6 wt.% to 10 wt.% coke addition.

The results suggested that an adequate reductive atmosphere was necessary for the recovery of metals. The presence of “enough” carbon ensured the “complete” of all the reducible oxides in the slag. However, cobalt oxide and iron oxide in smelter slag were associated closely with the fayalite phase. The reduction of metallic iron was evident when copper and cobalt levels in the slag fell below a lower value [18]. This diluted the copper and cobalt levels in the matte and changed the properties of slag and eventually reduced the recovery of copper and cobalt.
3.2. Effect of sulfurizing agent

The effect of various quantities of pyrite on the recovery of cobalt and copper were presented in Fig. 6. It was observed that the initial metals recovery ratio were very low at only 30.11% Cu and 31.11% Co attributed to the deficiency of sufficient pyrite. The recovery tended to increase with increasing pyrite addition from 5 to about 20 wt.%, peaking at Cu 92% and Co 88.61% at 20 wt. % pyrite dosage. After that, the recovery began to remain stable at about 92% and 85% because enough FeS were present to extract “complete” copper and cobalt from the slag to matte, that meant further increase of pyrite had little effect on the recovery of copper, or even led to reduction to a certain degree in cobalt recovery.

As discussed earlier, iron was transferred from slag to matte as iron sulfide during reductive-sulfurizing smelting process. As the ratio of matte to slag increasing, the quantity of iron in matte would also increase, and hence the iron contents in cleaned slag after 2h contact with the matte would decrease. These series of exchange reactions changed the composition of the cleaned slag, and also the matte, which may affect the distribution behaviors [5] of the elements in the system.

3.3. Effect of smelting temperature

Fig. 7 showed the results of smelting temperature on recovery of Cu, Co and Fe at the range of 1200~1400°C. It was clear that the cobalt and copper recovery increased as temperature increasing. At 1300°C, 86.69% Cu and 88.66% Co had been extracted in Cu-Co matte. Smelting temperature continued to increase, the copper and cobalt recovery continually rose slowly. As we know, the viscosity of molten slag decreases with the temperature increasing and the diffusion of species and delamination of cleaned slag and copper-cobalt matte are also improved. At 1400°C, copper and cobalt recoveries reached 94.78% and 93.29% respectively. But consideration must be given to the increased energy consumption.

3.4. Effect of smelting duration

It was observed as shown in Fig. 8 that the recovery of copper and cobalt were 59.46% and 78.43% respectively when smelting lasted for 1h. Prolong the smelting time, the metals recovery were up to a maximum (Cu 93.57%, Co 89.88%) at 3h. Above 3h, the recovery decreased slightly. For the results of 1h and 2h experiments, the initial recovery of copper was low and then increased sharply compared with cobalt. This corroborated the thermodynamic analysis results that the behaviors of cobalt and copper were different. Cobalt and copper
were not present together in the same droplets during settling. It suggested that the copper matte particles perhaps settled slower than cobalt matte.

3.5. Effect of slag modifier CaO

The plot in Fig. 9 showed that the addition of CaO to smelting system increased copper and cobalt recovery, especially cobalt. CaO, to some extent, played a role in selectively recovering cobalt compared with no CaO addition. But CaO addition also tended to increase the levels of undesired iron along with increasing copper and cobalt recovery. This effect is explained by the fact that the addition of CaO replaces the FeO in the silicate leading to an increase in the activity of “free” FeO in the slag, then the “free” FeO may transfer from slag to matte [17]. It is apparent that in cases of CaO addition, an optimum recovery exists and excess CaO may lead to a certain extent decreases in metals’ recovery.

3.6. Comprehensive experiments and characterization of reductive-sulfurizing smelting products

After optimizing smelter slag reductive-sulfurizing smelting conditions: coke dosage of 6 wt.%, addition of pyrite 20 wt.%, adding CaO 6 wt.% to the smelter slag, smelting at 1350°C for 3h, comprehensive expanding experiments of 1000g smelter slag were performed under optimum conditions (W smelter slag : W coke : W pyrite : W CaO = 1000:60:200:60, 1350°C, 3h).

The results presented in Table 2. It revealed that copper and cobalt contents in cleaned slag could decrease averagely to 0.18% and 0.071% respectively.

![Figure 8](image1)

**Figure 8.** The effect of smelting duration on copper, cobalt, iron recovery (coke: 6 wt.%; pyrite: 20 wt.%; no CaO addition; 1350°C)

![Figure 9](image2)

**Figure 9.** The effect of CaO dosage on copper, cobalt, iron recovery (coke: 6 wt.%; pyrite: 20 wt.%; 1350°C; 3h)

![Figure 10](image3)

**Figure 10.** XRD analysis of the cleaned slag and copper-cobalt matte

### Table 2. The results of comprehensive expanding experiments

<table>
<thead>
<tr>
<th>No.</th>
<th>Cu-Co matte</th>
<th>Cleaned slag</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu (%)</td>
<td>Co (%)</td>
<td>Fe (%)</td>
</tr>
<tr>
<td>1</td>
<td>4.67</td>
<td>2.48</td>
<td>61.23</td>
</tr>
<tr>
<td>2</td>
<td>4.46</td>
<td>2.26</td>
<td>60.15</td>
</tr>
<tr>
<td>3</td>
<td>4.59</td>
<td>2.37</td>
<td>61.02</td>
</tr>
<tr>
<td>AVG</td>
<td>4.57</td>
<td>2.37</td>
<td>60.8</td>
</tr>
</tbody>
</table>
91.99% Cu and 92.04% Co were recovered and enriched in Cu-Co matte. That illustrates reductive-sulfurizing smelting treatment was a reliable and high-efficient method to recover valuable metals lost in smelter slag.

The reductive-sulfurizing smelting products, i.e. the cleaned slag and the copper-cobalt matte, were characterized by XRD and SEM-EDS. It was found in Fig. 10 that the main phases of the cleaned slag were fayalite (Fe$_2$SiO$_4$), hedenbergite (CaFeSi$_2$O$_6$) and magnetite (Fe$_3$O$_4$). Cu$_{0.86}$Fe$_{2.14}$O$_4$ phase existed in initial slag disappeared after cleaning. The main phases of copper-cobalt matte were iron sulfide (FeS), geerite (Cu$_8$S$_5$) and iron cobalt sulfide (Fe$_{0.92}$Co$_{0.08}$S). That meant copper and cobalt mainly enriched in matte in form of sulfide together with FeS.

Fig. 11 showed the SEM-EDS image of the copper-cobalt matte. It illustrated that major compositions in point A were Fe, Cu and little S and Co. Point B have more amount of sulfur compared with point A. Combined the results of SEM-EDS with ICP and XRD analysis, it was suggested that the main phases at point A were Fe-Cu-Co alloy and little sulfide. At point B, the main phases were ferrous sulfide (FeS), geerite(Cu$_8$S$_5$), cobalt sulfide (CoS).

4. Conclusions

The laboratory-scale test works developed an alternative and high-efficient route for the treatment of the complex and changeable smelter slags. This study investigated and discussed the effects of reduction agent (coke), sulfurizing agent (pyrite), slag modifier (CaO) and smelting temperature and duration on the recovery efficiencies of copper, cobalt and iron during slag cleaning process. It was found that copper and cobalt can be extracted from the smelter slag into a low grate iron-cobalt-copper matte by reductive-sulfurizing smelting. Under the optimum conditions: coke dosage of 6 wt.%, addition of pyrite 20wt.%, adding CaO 6wt.% respectively to the smelter slag, smelting temperature of 1350°C and smelting time of 3h, 91.99% Cu, 92.94% Co and less than 38.73% Fe were recovered from the smelter slag. To some extent, addition of CaO played a selective role in cobalt recovery. The contents of Cu and Co in cleaned slag decreased to...
0.18% and 0.071% respectively. The main phases of copper-cobalt matte were iron sulfide (FeS), geerite (Cu$_8$S$_5$), iron cobalt sulfide (Fe$_{0.92}$Co$_{0.08}$S) and Fe-Cu-Co alloy. The cleaned slag mainly comprised fayalite (Fe$_2$SiO$_4$), hedenbergite (CaFe(Si$_2$O$_6$)) and magnetite (Fe$_3$O$_4$).

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