UTILIZATION OF IRONMAKING AND STEELMAKING WASTES IN LEAD RECYCLING TECHNOLOGY

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Abstract

The iron and steel metallurgy produces significant quantities of solid, liquid and gaseous wastes. The solid wastes like dusts, sludges and scales have been stored in dumping area due to their chemical composition, mainly by high content of zinc, cadmium, lead or organic compounds contamination. There are some alternatives to waste disposal such as pyrometallurgical and hydrometallurgical processes or their combination for separation of iron and heavy metals. The paper presents the other possibility of utilization of these wastes in non ferrous metallurgy, specifically in lead recycling technology. Investigations were carried out on effective utilization of iron together with non ferrous metals.

Keywords: Dusts, Sludges, Scales, Iron, Utilization.

1. INTRODUCTION

On average the production of 1 tonne of steel results in 200 kg electric arc furnace (EAF) to 400 kg blast furnace (BF)/basic oxygen furnace (BOF) of wastes. These include slags, dusts, sludges and other materials [1].

The outputs from gas cleaning system are gaseous and fine-grained metallurgical wastes in various forms – dust and sludge. The mill scale is produced in hot rolling operations in the iron and steel industry. A considerable amount of literature [2, 3, 4] has focused the chemical and mineralogical composition of waste materials, such as blast furnace dust and sludge, basic oxygen furnace fine and coarse sludge, electric arc furnace dust or mill scale.

These iron-bearing wastes are primarily composed (in wt%) of iron oxide (40-90), and remaining components are oxides of silicon (1-10), calcium (1-10), aluminum (0.1-3), magnesium (0.1-4) and elements such as zinc (0.1-30), lead (0.001-1), cadmium (0.0001-0.01), alkali compounds (0.01-3) also sulfur (0.01-0.5) and carbon (0.1-3) especially. Mill scale moreover contains too much oil [2, 3].

The blast furnace dust and sludge are composed of detrital and sharply angular particles of coke, hematite, magnetite, silica and slag, size of particles are vary from 3 to 60 till 100 μm [4].

The steelmaking dusts and sludges are mainly ideal globular or distinctively rounded particles from 1 to 90 μm, sporadically larger. Predominant parts of sludges are formed of metallic iron and magnetite globules. The dust from electric arc furnace contains essential amount of franklinite [4].

Direct recycling of these wastes in iron and steel metallurgy is limited by their high zinc content. Zinc can be separated using hydrometallurgical, pyrometallurgical processes and/or their combination. The review of relevant zinc separation processes is introduced at literature [5].

Data from several sources [6, 7, 8, 9, 10] have identified the use of only metallic iron in lead secondary production. Ironmaking and steelmaking fine grain wastes or mill scale are not commonly used as source of iron in secondary lead production.

The paper describes experimental utilization of mill scale instead of turnings in lead recycling process. The aim of this work is to study influence on blast furnace process.
2. MATERIAL AND METHOD

2.1 Material

The mill scale used for the experimental studies were obtained from Czech ironmaking plant. Material was sampled for analyzing mineralogical composition by X-ray diffraction (XRD) on performed PANanalytical X’pert diffractometer using CuKα radiation, at 40 kV and 30 mA, over the range 5-89° 2θ a step 0.02° and counting time of 20 s in each step (X’Celerator detector). Mineralogical composition of mill scale is given in Table 1.

Table 1 Mineralogical composition of mill scale

<table>
<thead>
<tr>
<th>Component</th>
<th>[wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO</td>
<td>58</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>22</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>20</td>
</tr>
</tbody>
</table>

The analytical result shows high contents of iron oxides, mainly wüstite. The chemical composition is typically for this kind of material.

2.2. Lead recycling technology description in Kovohute Pribram

The technology of lead-wastes recycling is known. Many plants are using technology of blast furnace; scheme is presented on Fig. 1. Old lead batteries are only simply crushed in order to outlay the sulfuric acid and the next steps are polypropylene separation via original separation technology.

Batteries are afterwards mixed together with other lead wastes, returning slag, coke, lime, quartz – usually crashed TV screen, metallic iron and are charged into the blast furnace at the top. Granulometry of charge materials is between 0.3 and 450 mm. The charge requires ca 8 hours to go down at the hearth. Air blown through tuyeres at the lower part of the blast furnace can be enriched with gaseous oxygen.

The carbon of coke initially burns in air blown into the furnace to give carbon dioxide and the heat, which is necessary for the process. The carbon dioxide then undergoes an endothermic reaction with more carbon to yield carbon monoxide – Boudouard reaction:

\[
    C + O_2 \rightarrow CO_2 \quad \Delta H^\circ_{298} = -400 049 \text{ J} \quad (1)
\]

\[
    C + CO_2 \rightarrow 2 CO \quad \Delta H^\circ_{298} = 166 258 \text{ J} \quad (2)
\]

Lead contained in the charge like PbSO₄ is reduced:

\[
    \text{PbSO}_4 + 4 \text{ CO} \rightarrow \text{PbS} + 4 \text{ CO}_2 \quad \Delta H^\circ_{298} = -293 863 \text{ J} \quad (3)
\]

\[
    \text{PbSO}_4 + 4 \text{ C} \rightarrow \text{PbS} + 4 \text{ CO} \quad \Delta H^\circ_{298} = 379 770 \text{ J} \quad (4)
\]

\[
    \text{PbSO}_4 + \text{PbS} \rightarrow 2 \text{ Pb} + 2\text{SO}_2 \quad \Delta H^\circ_{298} = 441 081 \text{ J} \quad (5)
\]

\[
    \text{Pb} + \text{PbSO}_4 \rightarrow 2 \text{ PbO} + \text{SO}_2 \quad \Delta H^\circ_{298} = 183 950 \text{ J} \quad (6)
\]

Lead oxide is consequently reduced to lead metal:

\[
    \text{PbO} + \text{CO} \rightarrow \text{Pb} + \text{CO}_2 \quad \Delta H^\circ_{298} = -63 765 \text{ J} \quad (7)
\]

\[
    2 \text{ PbO} + \text{PbS} \rightarrow 3 \text{ Pb} + \text{SO}_2 \quad \Delta H^\circ_{298} = 241 020 \text{ J} \quad (8)
\]

In the hearth liquid products of melting are collected. Lead bullion (t\text{tapping} = 900-950 °C) and slag plus matte (t\text{tapping} = 1 000-1 100 °C) are periodically tapping. The top gases with a temperature 150-200 °C leaving the furnace are after-burned in the de-burning chamber and filtered in a bag filter [11].
Lead bullion is an alloy of lead and other chemical elements. The most frequent impurities of lead bullion (in wt%) are Sb (0.2–2), Sn (0.01–0.7), Bi (0.015–0.025), Cu (0.03–0.06), As (0.01–0.05) and Ag (0.002–0.004) [11].

Fig. 1 Scheme of blast furnace for lead recycling, Kovohute Pribram

2.3 Iron in lead recycling process

The charge for lead recycling process usually contains iron in turnings form. The iron is added to capture the sulfur in the form of matte [12]. The sources of sulfur are mainly PbSO₄ and sulfuric acid from lead batteries. The lead in form of PbS is reduced by iron at 1 000-1 200 °C [13]:

\[
PbS + Fe \rightleftharpoons FeS + Pb \quad \Delta H_{298}^0 = -1 257 \text{ J} \quad (9)
\]

Sulfides of iron (FeS), copper (Cu₂S) and lead (PbS) are basic compounds of homogenous alloy so-called matte. The iron content is between 45-65 wt% in matte. The matte contains except iron sulfide also iron fixed to oxygen [14, 15].

Stability of the metal oxides shows the Ellingham diagram. The iron oxides can be reduces by carbon, carbon monoxide and hydrogen. When using coke as a reducing agent, carbon of coke is oxidized into carbon dioxide by reaction (1). At a given temperature will be in equilibrium composition of gaseous phase in blast furnace. The \( p_{\text{CO}/p_{\text{CO}_2}} \) ratio in compliance with equilibrium composition of Boudouard reaction (2), where equilibrium constant, calculated from [11]:

\[
K(2) = \frac{p_{\text{CO}}}{p_{\text{CO}_2}} \cdot a_c \quad (10)
\]

\( p_{\text{CO}/p_{\text{CO}_2}} \) – partial pressure of carbon monoxide and carbon dioxide in gaseous mixture
\( a_c \) – activity of carbon (when is using coke \( a_c = 1 \))

The mill scale contains three iron oxides: primarily Fe₂O₃, FeO and Fe₂O₄. The iron oxide reduction under blast furnace conditions - \( t > 570 \text{ °C} \) - takes place mainly by scheme [16]:

\[
Fe_2O_3 \rightarrow FeO \rightarrow Fe \quad (11)
\]
The following reactions describe indirect reduction of iron oxides [16]:

\[
\begin{align*}
3 \text{Fe}_2\text{O}_3 + \text{CO} &\rightleftharpoons 2 \text{Fe}_3\text{O}_4 + \text{CO}_2 \quad \Delta H^{0\,298} = -52,460 \text{ J} \quad (12) \\
\text{Fe}_3\text{O}_4 + m \text{ CO} &\rightleftharpoons 3\text{FeO} + \text{CO}_2 + (m - 1) \text{ CO} \quad \Delta H^{0\,298} = 26,670 \text{ J} \quad (13) \\
\text{FeO} + n \text{ CO} &\rightleftharpoons \text{Fe} + \text{CO}_2 + (n - 1) \text{ CO} \quad \Delta H^{0\,298} = -13,942 \text{ J} \quad (14)
\end{align*}
\]

To ensure the forward reaction reduction \( \text{Fe}_3\text{O}_4 \) to wüstite and especially wüstite to iron, the concentration CO in gaseous phase has to exceed its stoichiometric value [16].

3. EXPERIMENT

The industrial test on charging mill scale was carried out at shaft furnace of Kovohute Pribram nastupnicka, a.s. Utilization of mill scale instead of proportion turnings was tested experimentally in one campaign in full production scale. Composition of experimental and standard charge is presented in Table 2. The campaign took place in March and April 2013.

Table 2 Composition of charge – Kovohute Pribram

<table>
<thead>
<tr>
<th>Charge</th>
<th>Lead batteries</th>
<th>Returning slag</th>
<th>Silicon dioxide</th>
<th>Turnings</th>
<th>Mill scale</th>
<th>Limestone</th>
<th>Coke</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>18 218</td>
<td>4 421</td>
<td>143</td>
<td>1 877</td>
<td>469</td>
<td>186</td>
<td>1 687</td>
</tr>
<tr>
<td>Standard</td>
<td>17 161</td>
<td>4 406</td>
<td>130</td>
<td>2 179</td>
<td>0</td>
<td>151</td>
<td>1 652</td>
</tr>
</tbody>
</table>

The mill scale was charged along with turnings in the ratio 1:0.25 (103 kg·t\(^{-1}\)Pb batt. turnings and 26 kg·t\(^{-1}\)Pb batt. mill scale).

The important parameters for furnace operation were monitored, mainly amount of air blown, gas pressure, coke consumption, matte production, slag production, dust production, chemical composition of matte, slag and emission \( \text{SO}_2 \). The results were compared with outcomes for standard charge that means without scale.

4. RESULTS AND DISCUSSION

The representative samples of slag and matte were taken at the end of campaign for analyzing the chemical and mineralogical composition. Analytical methods X-ray fluorescence spectrometry (XRF) and X-ray diffraction (XRD), on performed THERMO ARL 9400 XP and PANanalytical X’pert diffractometer, were used to analyzing chemical and mineralogical composition. PANanalytical X’pert diffractometer using CuKα radiation, at 40 kV and 30 mA, over the range 5-89° 2θ a step 0.02° and counting time of 20 s in each step (X’Celerator detector). The pattern was analyzed by using the HighScore plus software and the PDF database was used for the phases. Chemical composition of slag and matte is given in Table 3, 5; mineralogical composition in Table 4, 6.

Table 3 Chemical composition of slag – Kovohute Pribram

<table>
<thead>
<tr>
<th>Charge</th>
<th>Fe</th>
<th>Si</th>
<th>Ca</th>
<th>Pb</th>
<th>S</th>
<th>Al</th>
<th>Na</th>
<th>Mn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experimental</td>
<td>27.9</td>
<td>12.6</td>
<td>5.8</td>
<td>2.8</td>
<td>5.0</td>
<td>2.0</td>
<td>2.0</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>Standard</td>
<td>30.3</td>
<td>14.3</td>
<td>6.7</td>
<td>2.3</td>
<td>3.0</td>
<td>2.6</td>
<td>2.0</td>
<td>1.1</td>
<td>1.2</td>
</tr>
</tbody>
</table>
As shown in Table 3 and 5 iron oxides in mill scale increased sulfur contents in the slag and matte. The concentrations of other analyzing chemical elements are similar.

The mineralogical composition of the slag and matte are listed in Table 4 and 6. The XRD analysis indicated presence of five phases in slag (wüstite, lead, kirchsteinite, magnetite, troilite) and six phases in matte (troilite, wüstite, magnetite, lead, iron). Other phases were not identified regardless of iron source. The kirchsteinite content in the studied slag is higher in slag of charge without mill scale.

The data of furnace operation parameters are summarized in Table 7. Mill scale increasing slag and matte production. Pressure difference of gas was to make scale finesses. The SO$_2$ emission was equivalent for both type of charge that is maximal 800 mg·m$^{-3}$.

**Table 4** Mineralogical composition of slag – Kovohute Pribram

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Wüstite</th>
<th>Lead</th>
<th>Kirchsteinite</th>
<th>Magnetite</th>
<th>Troilite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>FeO</td>
<td>Pb</td>
<td>Ca$<em>{0.54}$Fe$</em>{1.46}$SiO$_4$</td>
<td>Fe$_3$O$_4$</td>
<td>FeS</td>
</tr>
<tr>
<td>Ref. Code</td>
<td>04-004-8989</td>
<td>01-072-6646</td>
<td>00-021-0147</td>
<td>01-075-0449</td>
<td>04-013-1915</td>
</tr>
<tr>
<td>Charge</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experimental</td>
<td>major</td>
<td>major</td>
<td>present</td>
<td>minor</td>
<td>minor</td>
</tr>
<tr>
<td>Standard</td>
<td>major</td>
<td>major</td>
<td>major</td>
<td>minor</td>
<td>minor</td>
</tr>
</tbody>
</table>

**Table 5** Chemical composition of matte – Kovohute Pribram

<table>
<thead>
<tr>
<th>Charge</th>
<th>Pb [wt%]</th>
<th>Cu [wt%]</th>
<th>Fe [wt%]</th>
<th>S [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>5.7</td>
<td>0.3</td>
<td>57.3</td>
<td>21.6</td>
</tr>
<tr>
<td>Standard</td>
<td>6.5</td>
<td>0.3</td>
<td>57.2</td>
<td>20.2</td>
</tr>
</tbody>
</table>

**Table 6** Mineralogical composition of matte – Kovohute Pribram

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Troilite</th>
<th>Wüstite (a=4.33 Å)</th>
<th>Wüstite (a=4.30 Å)</th>
<th>Magnetite</th>
<th>Lead</th>
<th>Iron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>Fe$_{0.985}$S</td>
<td>FeO</td>
<td>FeO</td>
<td>Fe$_3$O$_4$</td>
<td>Pb</td>
<td>Fe</td>
</tr>
<tr>
<td>Ref. Code</td>
<td>04-003-4470</td>
<td>04-004-8989</td>
<td>01-089-0687</td>
<td>04-006-6497</td>
<td>01-072-6646</td>
<td>04-003-3641</td>
</tr>
<tr>
<td>Charge</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experimental</td>
<td>major</td>
<td>major</td>
<td>major</td>
<td>major</td>
<td>present</td>
<td>present</td>
</tr>
<tr>
<td>Standard</td>
<td>major</td>
<td>major</td>
<td>major</td>
<td>major</td>
<td>present</td>
<td>present</td>
</tr>
</tbody>
</table>

As shown in Table 3 and 5 iron oxides in mill scale increased sulfur contents in the slag and matte. The concentrations of other analyzing chemical elements are similar.

The mineralogical composition of the slag and matte are listed in Table 4 and 6. The XRD analysis indicated presence of five phases in slag (wüstite, lead, kirchsteinite, magnetite, troilite) and six phases in matte (troilite, wüstite, magnetite, lead, iron). Other phases were not identified regardless of iron source. The kirchsteinite content in the studied slag is higher in slag of charge without mill scale.

The data of furnace operation parameters are summarized in Table 7. Mill scale increasing slag and matte production. Pressure difference of gas was to make scale finesses. The SO$_2$ emission was equivalent for both type of charge that is maximal 800 mg·m$^{-3}$.

**Table 7** Blast furnace operation parameters – Kovohute Pribram

<table>
<thead>
<tr>
<th>Charge</th>
<th>Amount of air blown [m$^3$·hod$^{-1}$]</th>
<th>Gas pressure [Pa]</th>
<th>Consumption of coke [kg·t$^{-1}$bullionPb]</th>
<th>Production of matte [kg·t$^{-1}$bullionPb]</th>
<th>Production of slag [kg·t$^{-1}$bullionPb]</th>
<th>Production of dust [kg·t$^{-1}$bullionPb]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>3 368</td>
<td>4 200</td>
<td>114</td>
<td>251</td>
<td>392</td>
<td>32</td>
</tr>
<tr>
<td>Standard</td>
<td>3 356</td>
<td>3 100</td>
<td>114</td>
<td>217</td>
<td>317</td>
<td>27</td>
</tr>
</tbody>
</table>
5. CONCLUSION

The experiments were undertaken to ascertain the impact of iron oxides on lead recycling process. Important parameters for blast furnace operation were similar. The final result from trial of utilization iron oxides in mill scale form – iron oxides can partly substitute metallic iron as turnings. Based on the data of this study will be provided next trial of utilization ironmaking and steelmaking wastes. Fine materials have to be agglomerated by pelletizing or briquetting with regard to suitable lumpiness.

LITERATURE


