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 PANanalyical 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

Component	[wt%]
FeO	58
Fe_2O_3	22
Fe_3O_4	20

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:

$$C + O_2 \rightleftharpoons CO_2 \qquad \Delta H^0_{298} = -400\ 049\ J \qquad (1)$$

$$C + CO_2 \rightleftharpoons 2\ CO \qquad \Delta H^0_{298} = 166\ 258\ J \qquad (2)$$

Lead contained in the charge like $PbSO_4$ is reduced:

$$PbSO_4 + 4\ CO \rightleftharpoons PbS + 4\ CO_2 \qquad \Delta H^0_{298} = -293\ 863\ J \qquad (3)$$

$$PbSO_4 + 4\ C \rightleftharpoons PbS + 4\ CO \qquad \Delta H^0_{298} = 379\ 770\ J \qquad (4)$$

$$PbSO_4 + PbS \rightleftharpoons 2\ Pb + 2SO_2 \qquad \Delta H^0_{298} = 441\ 081\ J \qquad (5)$$

$$Pb + PbSO_4 \rightleftharpoons 2\ PbO + SO_2 \qquad \Delta H^0_{298} = 183\ 950\ J \qquad (6)$$

Lead oxide is consequently reduced to lead metal:

$$PbO + CO \rightleftharpoons Pb + CO_2 \qquad \Delta H^0_{298} = -63\ 765\ J \qquad (7)$$

$$2\ PbO + PbS \rightleftharpoons 3\ Pb + SO_2 \qquad \Delta H^0_{298} = 241\ 020\ J \qquad (8)$$

In the hearth liquid products of melting are collected. Lead bullion ($t_{tapping}$ = 900-950 °C) and slag plus matte ($t_{tapping}$ = 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].

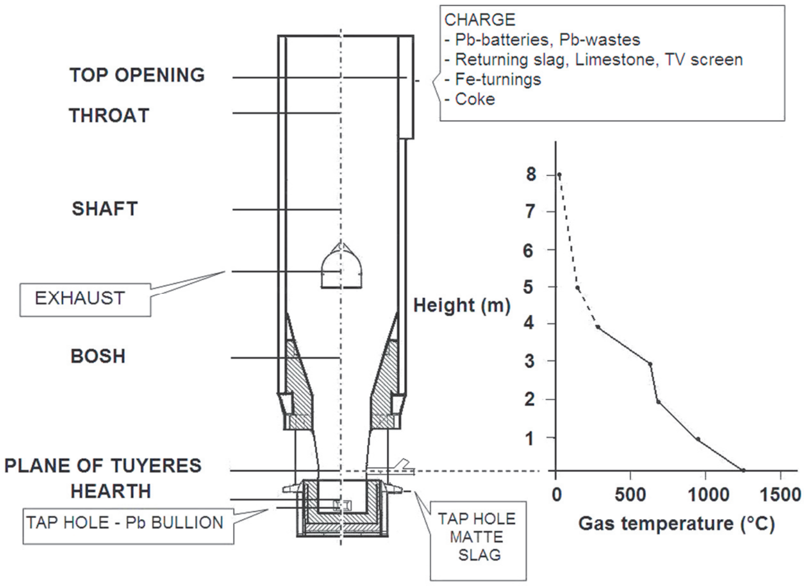

Fig. 1 Scheme of blast furnace for lead recycling, Kovohute Pribram

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 $PbSO_4$ and sulfuric acid from lead batteries.

The lead in form of PbS is reduced by iron at 1 000-1 200 °C [13]:

$$PbS + Fe \rightleftharpoons FeS + Pb \qquad \Delta H^0_{298} = -1\,257 \text{ J} \qquad (9)$$

Sulfides of iron (FeS), copper (Cu_2S) 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_{CO}/p_{CO2} ratio in compliance with equilibrium composition of Boudouard reaction (2), where *K* is the equilibrium constant, calculated from [11]:

$$K_{(2)} = \frac{p_{CO}^2}{p_{CO_2}.a_C} \qquad (10)$$

p_{CO}/p_{CO2} - 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 Fe_2O_3, FeO and Fe_3O_4. The iron oxide reduction under blast furnace conditions - t > 570 °C - takes place mainly by scheme [16]:

$$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe \qquad (11)$$

The following reactions describe indirect reduction of iron oxides [16]:

$3\ Fe_2O_3 + CO \rightleftharpoons 2\ Fe_3O_4 + CO_2$ $\Delta H^0_{298} = -52\ 460$ J (12)

$Fe_3O_4 + m\ CO \rightleftharpoons 3FeO + CO_2 + (m - 1)\ CO$ $\Delta H^0_{298} = 26\ 670$ J (13)

$FeO + n\ CO \rightleftharpoons Fe + CO_2 + (n - 1)\ CO$ $\Delta H^0_{298} = -13\ 942$ J (14)

To ensure the forward reaction reduction Fe_3O_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

Charge	Lead batteries	Returning slag	Silicon dioxide	Turnings	Mill scale	Limestone	Coke
	[kg]						
Experimental	18 218	4 421	143	1 877	469	186	1 687
Standard	17 161	4 406	130	2 179	0	151	1 652

The mill scale was charged along with turnings in the ratio 1:0.25 (103 $kg \cdot t^{-1}_{Pb\ batt.}$ turnings and 26 $kg \cdot t^{-1}_{Pb\ batt.}$ 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 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 PANanalyical X´pert diffractometer, were used to analyzing chemical and mineralogical composition. PANanalyical 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 **Tables 3, 5**; mineralogical composition in **Tables 4, 6**.

Table 3 Chemical composition of slag - Kovohute Pribram

Charge	Fe	Si	Ca	Pb	S	Al	Na	Mn	Zn
	[wt%]								
Experimental	27.9	12.6	5.8	2.8	5.0	2.0	2.0	1.1	1.0
Standard	30.3	14.3	6.7	2.3	3.0	2.6	2.0	1.1	1.2

Table 4 Mineralogical composition of slag - Kovohute Pribram

Compound Name	Wüstite	Lead	Kirchsteinite	Magnetite	Troilite
Formula	FeO	Pb	$Ca_{0,54}Fe_{1,46}SiO_4$	Fe_3O_4	FeS
Ref. Code	04-004-8989	01-072-6646	00-021-0147	01-075-0449	04-013-1915
Charge	Abundance				
Experimental	major	major	present	minor	minor
Standard	major	major	major	minor	minor

Table 5 Chemical composition of matte - Kovohute Pribram

Charge	Pb	Cu	Fe	S
	[wt%]			
Experimental	5.7	0.3	57.3	21.6
Standard	6.5	0.3	57.2	20.2

Table 6 Mineralogical composition of matte - Kovohute Pribram

Compound Name	Troilite	Wüstite (a=4.33 Å)	Wüstite (a=4.30 Å)	Magnetite	Lead	Iron
Formula	$Fe_{0.985}S$	FeO	FeO	Fe_3O_4	Pb	Fe
Ref. Code	04-003-4470	04-004-8989	01-089-0687	04-006-6497	01-072-6646	04-003-3641
Charge	Abundance					
Experimental	major	major	major	major	present	present
Standard	major	major	major	major	present	present

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 $mg \cdot m^{-3}$.

Table 7 Blast furnace operation parameters - Kovohute Pribram

Charge	Amount of air blown [$m^3 \cdot h^{-1}$]	Gas pressure [Pa]	Consumption of coke [$kg \cdot t^{-1}_{bullionPb}$]	Production of matte [$kg \cdot t^{-1}_{bullionPb}$]	Production of slag [$kg \cdot t^{-1}_{bullionPb}$]	Production of dust [$kg \cdot t^{-1}_{bullionPb}$]
Experimental	3 368	4 200	114	251	392	32
Standard	3 356	3 100	114	217	317	27

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.

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