ENERGY BALANCE OF THE REDUCTION PROCESS OF IRON-BEARING WASTE MATERIALS

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Abstract

The metallurgical industry is a trade where large amounts of waste are generated, including mill scale and iron-bearing sludge, which in the reduction process can be a valuable raw material for the production of sponge iron. In this publication the energy balance for such a process has been prepared and it has been shown that the electrical energy flow necessary to carry out reduction of mill scale with a CO + H_2 gas solution is 17.48% of the total energy stream supplied to the process. The highest value of the supplied energy stream is chemical energy brought with a reducing gas of approx. 71.65%. The largest energy losses occur in gaseous products of reduction and constitute 57.15% of the total energy flux of products. Raising the temperature of the reaction gas from 25°C to 300°C reduces the electricity consumption about 14%. The determined energy losses to the environment are strongly dependent on the final design of the reactor for the reduction of iron-bearing materials.

Keywords: Reduction, iron-bearing waste materials, energy balance

1. INTRODUCTION

What proves to be decisive of the choice of waste management technology is not only economy, but also environmental protection aspects. Recyclable waste is distinguished by the considerable content of valuable components, which is comparable to their content in raw materials [1]. Even though material engineering has been developing very dynamically and further new structural materials are being designed, steel has not lost its leading position in terms of industrial production. Steel industry is among the sectors of the economy with the highest market share, as steel and cast steel account for more than 92% of total consumption of metals. This industry generates considerable volumes of waste (including iron-bearing waste), such as: blast furnace and steelmaking slag, mill scale, sintering dust, steelmaking dust from the process of dust removal from electric arc furnaces, dust produced in consequence of cleaning iron and steel casts as well as iron-bearing sludge [1-3]. Iron-bearing waste can be utilised as raw material for production of direct reduced iron (DRI), also referred to as sponge iron. Depending on its chemical composition, including the content of impurities and moisture, the options for using metallurgical waste as secondary raw material are diversified. More and more waste is regularly recycled all around the world, while further new waste utilisation technologies are being designed.

This publication provides a discussion on the energy balance for a technology being currently developed and concerning mill scale reduction in carbon monoxide and hydrogen atmosphere in order to receive direct reduced iron (DRI).

2. ENERGY BALANCE ASSUMPTIONS

The energy balance assumed for the process of reduction of the iron oxides contained in mill scale in carbon monoxide and hydrogen atmosphere was developed with reference to service data of a laboratory-scale rotary furnace as well as experiments performed in the furnace. For the final product assumed, namely metallic iron, and its yield as well as the substrates introduced into the process, the energy balance components for the furnace's steady state were calculated based on the formula (1) and **Figure 1** provides graphical representation of the energy balance in question.

$$\dot{E}_{zw} + \dot{E}_{gr} + \dot{E}_{el} = \dot{E}_{zg} + \dot{E}_{gp} + \dot{Q}_{ot} \ , \qquad (1)$$

where:

$\dot{E}_{zw}$ - energy stream of mill scale (kW)
$\dot{E}_{gr}$ - energy stream of reduction gas (kW)
$\dot{E}_{el}$ - electric energy stream (kW)
$\dot{E}_{zg}$ - energy stream of direct reduced iron (kW)
$\dot{E}_{gp}$ - energy stream of gas following reduction (kW)
$\dot{Q}_{ot}$ - heat released into the environment (kW)

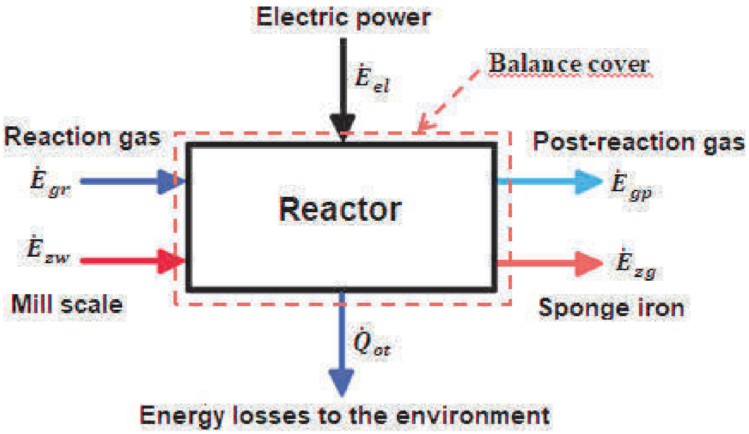

Figure 1 Energy balance for the iron-bearing waste material reduction process

The stream of scale mass was assumed in the balance at $\dot{m}_{zw}$= 33.3 $kg\ h^{-1}$. The $\dot{n}_{gr}$ stream of reduction gas was characterised by molar fractions of $z_{CO} = 0.50$ and $z_{H2} = 0.50$ retrieved from the balance of substance and consistent with the process behaviour. The DRI stream value was $\dot{m}_{zg}$= 27.4 $kg\ h^{-1}$, while the value of the $\dot{n}_{gp}$ gas stream following the scale mill reduction was characterised by the following molar fractions: $z_{CO} = 0.47, z_{H2} = 0.37, z_{CO2} = 0.09\ , z_{H2O} = 0.13$ (balance of substance). **Table 1** provides mass fractions of chemical compounds contained in the scale mill and direct reduced iron.

Table 1 Mass fractions of chemical compounds contained in the scale mill and direct reduced iron

	Chemical compound	**Mark**	**Mass (wt.%)**
Substrates scale mill	Fe	g_{Fe}	0.027
	Fe_2O_3	g_{Fe2O3}	0.279
	FeO	g_{FeO}	0.646
	MnO	g_{MnO}	0.012
	Al_2O_3	g_{Al2O3}	0.004
	CaO	g_{CaO}	0.001
	SiO_2	g_{SiO2}	0.023

Table 1 Continue

	Chemical compound	**Mark**	**Mass (wt.%)**
Substrates scale mill	C	g_C	0.002
	Cr	g_{Cr}	0.001
	Cu	g_{Cu}	0.005
Products direct reduced iron	Fe	g_{Fe}	0.865
	FeO	g_{FeO}	0.077
	MnO	g_{MnO}	0.016
	Al_2O_3	g_{Al2O3}	0.005
	CaO	g_{CaO}	0.001
	SiO_2	g_{SiO2}	0.029
	Cr	g_{Cr}	0.001
	Cu	g_{Cu}	0.006

The temperature of the reduction process substrates (scale mill and reduction gas) came to $T_s = 298.15\ K$ and was assumed as the reference point for physical energy calculations. The temperature of both products (direct reduced iron and post-reduction gas) was $T_p = 1273.15\ K$. The energy of substrates and products was calculated as a sum of chemical energy and physical energy. Specific chemical energy and specific physical energy as well as bulk mass of the balanced substances have been provided in **Table 2** (substrates) and **Table 3** (products) [4-8]. For all the reduction process substrates, the physical energy (at the temperature of *298.15 K*) equalled *0 kJ/mol.*

Table 2 Bulk mass, specific chemical energy and specific physical energy substrates [4-8]

Substrates	**Chemical compound**	**Bulk mass** M	**Specific chemical energy** e_{ch}	**Specific physical energy** (298.15 *K*) e_f
		(kg/kmol)	**(MJ/kmol)**	**(MJ/kmol)**
Scale mill	Fe	55.847	412.12	0
	Fe_2O_3	159.692	0	0
	FeO	71.846	140.16	0
	MnO	70.937	134.81	0
	Al_2O_3	101.961	185.69	0
	CaO	56.080	178.44	0
	SiO_2	60.085	0	0
	C	12.011	393.51	0
	Cr	51.996	569.86	0
	Cu	63.54	201.59	0
Reduction gas	CO	28.011	282.98	0
	H_2	2.016	242.00	0

Table 3 Bulk mass, specific chemical energy and specific physical energy products [4-8]

Products	**Chemical compound**	**Bulk mass** M	**Specific chemical energy** e_{ch}	**Specific physical energy** (1273.15 K) e_f
		(kg/kmol)	**(MJ/kmol)**	**(MJ/kmol)**
Direct reduced iron	Fe	55.847	412.12	33.928
	FeO	71.846	140.16	54.922
	MnO	70.937	134.81	50.645
	Al_2O_3	101.961	185.69	115.470
	CaO	56.080	178.44	49.407
	SiO_2	60.085	0	63.117
	Cr	51.996	569.86	29.113
	Cu	63.54	201.59	32.404
Post-reduction gas	CO_2	44.009	0	48.498
	H_2O	18.015	0	37.515
	CO	28.011	282.98	30.230
	H_2	2.016	242.00	29.580

3. ENERGY STREAM OF SCALE MILL AND REDUCTION GAS

The data used to calculate the energy stream of scale mill were computational data consistent with the balance assumptions made with regard to mass stream, temperature and mass fractions (**Table 1**), as well as specific chemical and physical energy (**Table 2**). The scale mill energy stream is illustrated by the following equation (2):

$$\dot{E}_{zw} = \dot{E}_{zwFe} + \dot{E}_{zwFe2O3} + \dot{E}_{zwFeO} + \dot{E}_{zwMnO} + \dot{E}_{zwAl2O3} + \dot{E}_{zwCaO} + \dot{E}_{zwSiO2} + \dot{E}_{zwC} + \dot{E}_{zwCr} + \dot{E}_{zwCu}, \tag{2}$$

where:

$\dot{E}_{zwFe}$ - energy stream of metallic iron (kW)

$\dot{E}_{zwFe2O3}$ - energy stream of Fe_2O_3 (kW)

$\dot{E}_{zwFeO}$ - energy stream of FeO (kW)

$\dot{E}_{zwFeO}$ - energy stream of FeO (kW)

$\dot{E}_{zwMnO}$ - energy stream of MnO (kW)

$\dot{E}_{zwAl2O3}$ - energy stream of Al_2O_3 (kW)

$\dot{E}_{zwCaO}$ - energy stream of CaO (kW)

$\dot{E}_{zwSiO2}$ - energy stream of SiO_2 (kW)

$\dot{E}_{zwC}$ - energy stream of carbon (kW)

$\dot{E}_{zwCr}$- energy stream of chromium (kW)

$\dot{E}_{zwCu}$ - energy stream of copper (kW)

Once the mass stream, the mass fractions as well as the specific chemical and physical energy have all been taken into consideration, equation (2) assumes the following form:

$$\dot{E}_{zw} = \dot{m}_{zw}\Big[\frac{g_{Fe}}{M_{Fe}}\left(e_{chFe} + e_{fFe}\right) + \frac{g_{Fe2O3}}{M_{Fe2O3}}\left(e_{chFe2O3} + e_{fFe2O3}\right) + \frac{g_{FeO}}{M_{FeO}}\left(e_{chFeO} + e_{fFeO}\right) + \frac{g_{MnO}}{M_{MnO}}\left(e_{chMnO} + e_{fMnO}\right) + \frac{g_{Al2O3}}{M_{Al2O3}}\left(e_{chAl2O3} + e_{fAl2O3}\right) + \frac{g_{CaO}}{M_{CaO}}\left(e_{chCaO} + e_{fCaO}\right) + \frac{g_{SiO2}}{M_{SiO2}}\left(e_{chSiO2} + e_{fSiO2}\right) + \frac{g_{C}}{M_{C}}\left(e_{chC} + e_{fC}\right) + \frac{g_{Cr}}{M_{Cr}}\left(e_{chCr} + e_{fCr}\right) + \frac{g_{Cu}}{M_{Cu}}\left(e_{chCu} + e_{fCu}\right)\Big]\text{lkjkljkljkl} \tag{3}$$

As with the scale mill, so with the reduction gas stream calculation, computational data consistent with the relevant balance assumptions and the data provided in **Tables 1-3** were used, while the energy stream in question was represented as the following relationship:

$$\dot{E}_{gr} = \dot{E}_{grH2} + \dot{E}_{grCO}, \tag{4}$$

where:

$\dot{E}_{grH2}$ - energy stream of hydrogen (kW)

$\dot{E}_{grCO}$ - energy stream of CO (kW)

Following the substitution of the molar stream of substance, the relevant molar fractions as well as the specific chemical and physical energy, equation (4) took the following form:

$$\dot{E}_{gr} = \dot{n}_{gr}\left[z_{H2}\left(e_{chH2} + e_{fH2}\right) + z_{CO}\left(e_{chCO} + e_{fCO}\right)\right] \tag{5}$$

4. ENERGY STREAM OF DIRECT REDUCED IRON

The energy stream of direct reduced iron in reduction products (reduced iron oxides) was determined analogically to that of scale mill and reduction gas, the outcome of which was the following equation (6):

$$\dot{E}_{zg} = \dot{E}_{zgFe} + \dot{E}_{zgFeO} + \dot{E}_{zgMnO} + \dot{E}_{zgAl2O3} + \dot{E}_{zgCaO} + \dot{E}_{zgSiO2} + \dot{E}_{zgCr} + \dot{E}_{zgCu}, \tag{6}$$

where:

$\dot{E}_{zgFe}$ - energy stream of metallic iron (kW)

$\dot{E}_{zgFeO}$ - energy stream of FeO (kW)

$\dot{E}_{zgMnO}$ - energy stream of MnO (kW)

$\dot{E}_{zgAl2O3}$ - energy stream of Al_2O_3 (kW)

$\dot{E}_{zgCaO}$ - energy stream of CaO (kW)

$\dot{E}_{zgSiO2}$ - energy stream of SiO_2 (kW)

$\dot{E}_{zgCr}$ - energy stream of chromium (kW)

$\dot{E}_{zgCu}$ - energy stream of copper (kW)

Once the mass stream, the mass fractions as well as the specific chemical and physical energy (at the temperature of $T_p = 1{,}273.15\ K$) have been taken into consideration, equation (6) assumes the following form:

$$\dot{E}_{zg} = \dot{m}_{zg}\left[\frac{g_{Fe}}{M_{Fe}}\left(e_{chFe} + e_{fFe}\right) + \frac{g_{FeO}}{M_{FeO}}\left(e_{chFeO} + e_{fFeO}\right) + \frac{g_{MnO}}{M_{MnO}}\left(e_{chMnO} + e_{fMnO}\right)\right.$$
$$+ \frac{g_{Al2O3}}{M_{Al2O3}}\left(e_{chAl2O3} + e_{fAl2O3}\right) + \frac{g_{CaO}}{M_{CaO}}\left(e_{chCaO} + e_{fCaO}\right) \tag{7}$$
$$\left. + \frac{g_{SiO2}}{M_{SiO2}}\left(e_{chSiO2} + e_{fSiO2}\right) + \frac{g_{Cr}}{M_{Cr}}\left(e_{chCr} + e_{fCr}\right) + \frac{g_{Cu}}{M_{Cu}}\left(e_{chCu} + e_{fCu}\right)\right]$$

5. ENERGY STREAM OF POST-REDUCTION GAS AND HEAT LOSS INTO THE ENVIRONMENT

For purposes of calculations of the post-reduction gas energy stream, computational data consistent with the balance assumptions and the data provided in **Tables 1-3** were used. The above energy stream was expressed as the following relationship:

$$\dot{E}_{gp} = \dot{E}_{gpH2} + \dot{E}_{gpCO} + \dot{E}_{gpH2O} + \dot{E}_{gpCO2}, \tag{8}$$

where:

$\dot{E}_{gpH2}$ - energy stream of hydrogen (kW)
$\dot{E}_{gpCO}$ - energy stream of CO (kW)
$\dot{E}_{gpH2O}$ - energy stream of steam (kW)
$\dot{E}_{gpCO}$ - energy stream of CO_2 (kW)

Once the molar stream of substance, the molar fractions as well as the specific chemical and physical energy have all been substituted, the stream of energy of gaseous reduction products (equation 8) assumes the following form:

$$\dot{E}_{gp} = \dot{n}_{gp}\left[z_{H2}\left(e_{chH2} + e_{fH2}\right) + z_{CO}\left(e_{chCO} + e_{fCO}\right) + z_{H2O}\left(e_{chH2O} + e_{fH2O}\right)\right.$$
$$\left. + z_{CO2}\left(e_{chCO2} + e_{fCO2}\right)\right] \tag{9}$$

The energy losses into the environment were determined analogically to similar systems. For purposes of the relevant calculations, the mass loading of the reactor core surface was assumed to range between 65 and 105 kg/m^2, while the unit energy stream was assumed at (50 ÷ 75) x 10^3 W/m^2. The low thermal loads of unit surface result from the low thermal conductivity coefficient for the mill scale, which ranges at 1.4 ÷ 2.1 W/(m x K) [6]. The outer reactor wall temperature was assumed to equal 40°C. The total energy stream losses into the environment came to 9.9% of the power applied in electric energy.

What was also added to the energy losses into the environment was other energy losses resulting from the balance arrangements. The calculations of the heat losses into the environment are but approximate due to the preliminary nature of the relevant experiments as well as the general concept behind the reduction reactor design.

6. RESULTS OF THE REDUCTION PROCESS ENERGY BALANCE

Individual items of the rotary furnace energy balance for the assumed temperature of substrates of T_s = *298.15 K*, the temperature of products of T_p = *1,273.15 K* and the mill scale mass stream of $\dot{m}_{zw}$ = *33.3 kg/h* have been collated in **Tables 4** and **5**. The impact of the process temperature changes on energy streams of individual products as well as on the electric energy consumed has been summarised in **Table 6**.

Table 4 Balance for substrates energy stream

Substrates	Mark	Chemical energy stream (kW)	Physical energy stream (kW)	Total energy stream (kW)
Scale mill	$\dot{E}_{zw}$	14.57	0	14.57
Reduction gas	$\dot{E}_{gr}$	96.12	0	96.12
Electric energy	$\dot{E}_{el}$	xxx		23.46
In total				134.15

Table 5 Balance for products energy stream

Products	Mark	Chemical energy stream (kW)	Physical energy stream (kW)	Total energy stream (kW)
Direct reduced iron	$\dot{E}_{zg}$	50.21	4.95	55.16
Post-reduction gas	$\dot{E}_{gp}$	64.08	12.59	76.67
Heat loss	$\dot{Q}_{ot}$	xxx		2.32
In total				134.15

Table 6 Dependence of products energy stream, electric energy and losses to the environment of process temperature for $\dot{m}_{zw}$= 33.3 $kg\ h^{-1}$

Products	Mark	Energy stream for T_p = 950 ^0C (kW)	Energy stream for T_p = 1000 ^0C (kW)	Energy stream for T_p = 1050 ^0C (kW)
Direct reduced iron	$\dot{E}_{zg}$	54.85	55.16	55.47
Post-reduction gas	$\dot{E}_{gp}$	75.96	76.67	77.38
Heat loss	$\dot{Q}_{ot}$	2.21	2.32	2.44
Electric energy	$\dot{E}_{el}$	22.33	23.46	24.59

7. CONCLUSIONS

- The electric energy stream required to run the process corresponds to 17.48% of the total stream of energy fed into the process, while the highest share in the supplied energy stream is attributable to the chemical energy transferred along with the reduction gas, and it comes to ca. 71.65%.
- The highest energy losses are those of the gaseous reduction products, and they correspond to 57.15% of the total stream of energy of products. They are mainly attributable to the stream of chemical enthalpy (H_2 and CO), being five times higher than the stream of physical enthalpy of gas.
- For the sake of energy loss reduction (see conclusion no. 2), it is proposed that the relevant processes should be combined and that post-reaction gases are utilised. An optional solution is also to use a recuperator to pre-heat the reduction gas. It poses more serious technical problems, but in return, in reduces the losses resulting from the operation time mismatch of the combined systems.
- Raising reaction gas temperature from 25°C to 300°C reduces electric energy consumption by 14%.
- The identified energy losses into the environment are heavily dependent on the final design of the reactor to be used for reduction of iron-bearing materials (iron oxides).

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