

## CONTENT OF IRON (II) AND (III) IN SCALE GENERATED BY STEEL MILL

Krzysztof NOWACKI <sup>1</sup>, Teresa LIS <sup>2</sup>, Harald KANIA <sup>3</sup>, Karolina ŁAKOMY <sup>4</sup>

*Silesian University of Technology, Faculty of Materials Engineering and Metallurgy,  
Katowice, Poland, EU*

<sup>1</sup>[krzysztof.nowacki@polsl.pl](mailto:krzysztof.nowacki@polsl.pl), <sup>2</sup>[teresa.lis@polsl.pl](mailto:teresa.lis@polsl.pl), <sup>3</sup>[harald.kania@polsl.pl](mailto:harald.kania@polsl.pl), <sup>4</sup>[karolina.lakomy@polsl.pl](mailto:karolina.lakomy@polsl.pl)

### Abstract

The article presents the results of research of iron content (II) and iron (III) in mill scale. The total content of iron was marked by the absorptive atomic spectroscopy, however the analysis of Fe content (II) and Fe (III) was carried out with the spectroscopy methods. The gained results indicate between 65-85 % of total content of iron in the analysed samples. It was proved that the content of Fe (II) in the analysed samples amounts to 15-32 % while the content of iron (III) 22-40 %.

**Keywords:** Waste, scale, steel industry, iron

### 1. INTRODUCTION

The substances described as „waste” are subject to rigorous regulations which aim is to protect human health and environment. The limitation of waste production and management over already produced waste is a basic principle of rational usage of natural and anthropogenic resources [1,2].

The iron and steel industry (along with mining and energy industries) is a branch that produces the biggest amounts of waste, which the scale is a significant part.

According to the current law regulations, the possessor of waste is first of all obliged to prevent waste creation and then to secure the reuse of waste which creation was impossible to avoid.

The main factors deciding on the choice of waste management technology are not only economical aspects but also the exact knowledge of the chemical composition of the waste products. One of the processes that may be applied is a direct reduction of ferric oxides which results in sponge iron. The possibility of direct reduction application and its results evaluation requires the knowledge of iron (II) and iron (III) content in the substrate [3-5].

### 2. RESEARCH MATERIAL

The research material consisted of five types of scale mill collected in steelworks and foundries located in Poland. The choice of the material was justified by potentially high content of iron, qualifying the waste as useful for further process of iron recycling.

The samples were marked as in the **Table 1**. The average chemical composition in the **Table 2** was presented. The material for each sample was split up and analysed in order to investigate the chemical and phase composition using:

- carbon and sulphur analyser LECO CS844,
- oxyge analyser LECO ONH836,
- scanning mikroscope Hitachi S-3400N equipped with EDS Thermo Scientific Noran System 7 detector and WDS MagnaRay.

**Table 1** Research material

Sample marking	Scale type
A	Scale mill with oil
B	Scale mill from the rolling mill
C	Scale mill from the hardening
D	Scale mill from the rolling mill
E	Scale mill from the steelworks

**Table 2** Average chemical composition, % of mass

Sample	C	O	Al	Si	Ca	Mn	Fe	Mg	Cr	S	Cu	V	Ni
A	0.14	11.8	0.17	10.3	0.57	1.47	83.67	-	0.3	-	0.6	0.07	0.2
B	0.27	12.3	0.4	1.6	1.03	1.73	81.67	0.3	0.27	-	0.33	-	-
C	0.07	15.77	0.27	2.53	0.37	6.37	72.83	0.9	0.77	0.1	-	-	0.17
D	0.1	16.67	0.1	0.77	0.1	0.8	81	-	0.1	-	0.27	-	-
E	2.47	5.45	1.23	2.57	0.1	0.53	87.37	-	0.1	0,3	-	-	-

### 3. FE (II) AND FE (III) CONTENT IN METALLURGICAL SCALE MILLS RESEARCH

Before the research was started, 2 g of each sample was weighted out, poured 2 times with 10 ml of concentrated HCl, heated to boiling, cooled, alternatively filtered to a graduated flask (of 50 ml capacity) and made up with a distilled water.

#### 3.1. Methodology

##### Total content of iron

The total content of iron was determined by means of redox titration consisting of oxidization the reduced iron ions (II) by KMnO<sub>4</sub> solution and calculation of the content volume in the sample, and by the atomic absorption spectrometry (ASA) consisting of arousing the iron atoms in the flame of a burner and the absorbancy measurement according to the Lambert-Beer law.

For the redox titration determination method, 5 ml from a previously prepared sample was collected and added to 40 ml of distilled water. The iron ions (III) were reduced to Fe<sup>2+</sup> by SnCl<sub>2</sub> and later HgCl<sub>2</sub> solutions. The solution was titrated for research with the KMnO<sub>4</sub> oxidizer of 0.0183 molar concentration (the titre was set as for oxalic acid weighed amount) in the environment of Reinhard-Zimmerman mixture (environment stabilizer).



For the atomic absorption spectrometry (ASA) determination method, 1ml from a previously prepared sample was collected in a graduated flask (of 50 ml capacity) and made up with distilled water. Subsequently, 0.5 ml of this solution was poured into the graduated flask (of 25 ml capacity) and made up with distilled water. The samples were measured by the AAS 30 Carl Zeiss (Jena, Germany) which is characterised by the following

parameters: electric current of the lamp for iron 8 mA, clearance 0.30 mm, measurement wavelength Fe - 248.3 nm. The absorbancy was read and the iron content was calculated from the calibration curve.

#### Iron ions determination

The iron ions were determined by means of the spectrophotometric method in reaction with thiocyanate ions - Fe (III) and in reaction with the bathophenanthroline solution - Fe (II).

The iron ions (III) determination was performed in reaction with thiocyanate ions. The method consists of creation the colourful complex between iron ions (III) and thiocyanate ions in a suitable environment and absorbancy measurement at the wavelength of the maximum absorption value of this complex. For determination, 1ml from a previously prepared sample was collected in a graduated flask (of 50 ml capacity) and made up with a distilled water. Subsequently, 0.5 ml of this solution was poured into a graduated flask (of 25 ml capacity), added 5 ml of thiocyanate potassium solution, 5 ml of 2 molar solution of hydrochloric acid and made up to the line with distilled water. The measurement was performed with the HP 8452 A (Hewlett Packard) spectrophotometer at the wavelength of  $\lambda = 476$  nm. The contents were calculated by the absorption calibration curve from iron ions concentration (III) in complex with thiocyanates.

The iron ions (II) determination was performed in reaction with bathophenanthroline solution. The method consists of creation the colourful complex between iron ions (II) and bathophenanthroline solution in a suitable environment and absorbancy measurement at the wavelength of the maximum absorption value of this complex. For determination, 1ml from a previously prepared sample was collected in a graduated flask (of 50 ml capacity) and made up with a distilled water. Subsequently, 1 ml of this solution was poured into a graduated flask (of 25 ml capacity), added 10 ml of bathophenanthroline solution, 5 ml of ethyl alcohol and made up to the line with distilled water. The measurement was performed with the HP 8452 A (Hewlett Packard) spectrophotometer at the wavelength of  $\lambda = 534$  nm. The contents were calculated by the absorption calibration curve from iron ions concentration (II) in complex with bathophenanthroline.

### 3.2. Measurement results

#### Titration

The titration of samples turned out to be problematic. The samplec B, D and E was discoloured (reduced) became instantly grey once the HgCl<sub>2</sub> solution was added which made the further reaction impossible. The remaining samples were titrated and the results are presented in the **Table 3**.

**Table 3** Total content of iron - titration

Number of sample	Titanta (ml)	Content (g)	Content (%)
A	24.3	0.125	57.3
B	-	-	-
C	22.5	0.116	50.4
D	-	-	-
E	-	-	-

#### Total iron content determination by the AAS method

The absorbancy of the samples was measured at the wavelength of  $\lambda = 248.3$  nm and the iron content was calculated by the absorption calibration curve:  $y = ax + b$ , where  $a = 0.0245$ ,  $b = 0.0093$ ,  $r^2 = 0.9958$ . The results are presented in the **Table 4**.

**Table 4** Total content of iron - AAS method

Sample number	Content (µg/ml)	Content (g)	Content in the mass (%)
A	14.79	1.849	<b>85.2</b>
B	12.92	1.615	<b>77.9</b>
C	11.78	1.473	<b>64.3</b>
D	11.14	1.391	<b>68.2</b>
E	13.58	1.698	<b>70.6</b>

Iron (III) ions content determination by the spectrophotometric method

The absorbancy of the samples was measured at the wavelength of  $\lambda = 476$  nm and the iron (III) content was calculated by the absorption calibration curve:  $y = ax + b$ , where  $a = 0.145$ ,  $b = 0.0025$ ,  $r^2 = 0.9998$ . The results are presented in the **Table 5**.

**Table 5** Iron (III) content determination - spectroscopic method - determination with SCN<sup>-</sup> ions

Sample number	Content (µg/ml)	Content (g)	Content in the mass (%)
A	6.45	0.805	<b>37.1</b>
B	4.59	0.574	<b>27.7</b>
C	4.14	0.517	<b>22.6</b>
D	4.31	0.539	<b>26.4</b>
E	7.73	0.966	<b>40.2</b>

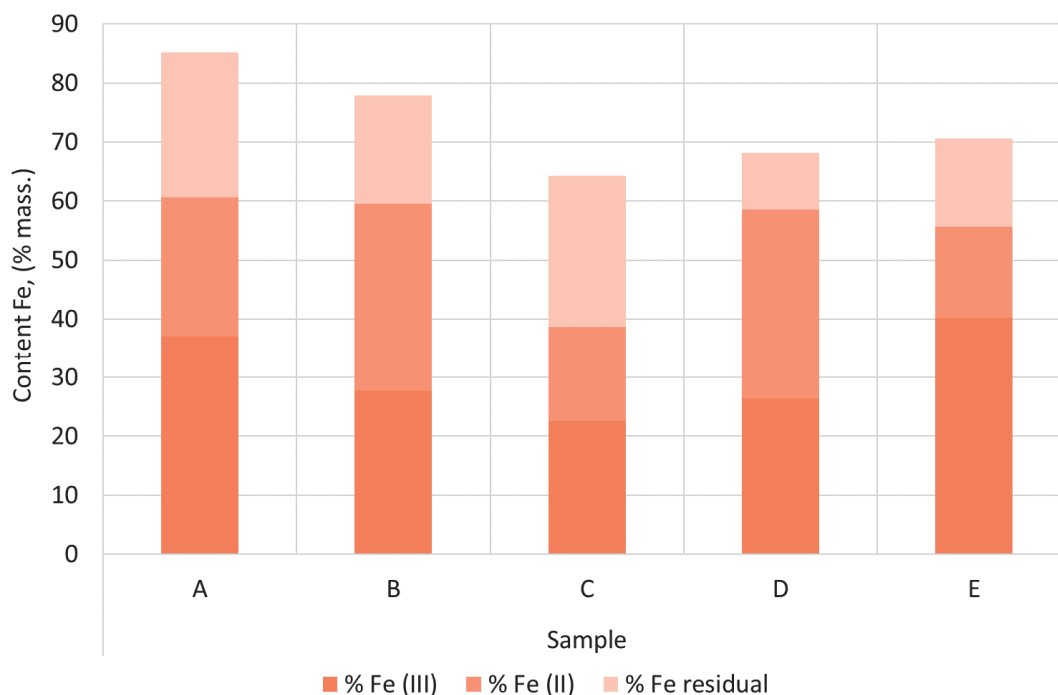
Iron (II) ions content determination by the spectrophotometric method

The absorbancy of the samples was measured at the wavelength of  $\lambda = 534$  nm and the iron (II) content was calculated by the absorption calibration curve:  $y = ax + b$ , where  $a = 0.3499$ ,  $b = 0.1184$ ,  $r^2 = 0.9997$ . The results are presented in the **Table 6**.

**Table 6** Iron (II) content determination - spectroscopic method - determination with bathophenanthroline

Sample number	Content (µg/ml)	Content (g)	Content in the mass (%)
A	0.327	0.510	<b>23.5</b>
B	0.422	0.659	<b>31.8</b>
C	0.236	0.369	<b>16.1</b>
D	0.421	0.658	<b>32.2</b>
E	0.236	0.369	<b>15.4</b>

The % content of iron (III) and iron (II) ions is presented per the mass of a sample used in the analysis and per the total content of iron in the material used for the determination. If we compare the chemical composition obtained by the physical and chemical methods we may conclude that both the total iron, iron (II) and iron (III) ions content may be increased by the iron of zero oxidation state and Fe<sub>3</sub>O<sub>4</sub> which transform into ions during the preparation of the sample - digestion in hydrochloric acid. The aggregate Fe content in the examined scale mills, including the Fe (II) and Fe (III) contents is presented in the **Figure 1**.



**Figure 1** The Fe content in the examined dusts (spectroscopic methods)

#### 4. SUMMARY

The total content of iron was marked by the absorptive atomic spectroscopy, however the analysis of Fe content (II) and Fe (III) was carried out with the spectroscopy methods. The gained results indicate between 65-85 % of total content of iron in the analysed samples. It was proved that the content of Fe (II) in the analysed samples amounts to 15-32 % while the content of iron (III) 22-40 %.

#### REFERENCES

- [1] Directive 2008/98/EC of 19 November 2008 on waste.
- [2] Rozporządzenie Ministra Gospodarki w sprawie dopuszczenia odpadów do składowania na składowiskach (DzU 2015.1277) .
- [3] MRÓZ, Jan, *Procesy redukcji tlenków żelaza w fazach ciekłych*. Wyd. Pol. Częstochowska, Częstochowa, 2010.
- [4] LIS, Teresa, NOWACKI, Krzysztof, ŻELICHOWSKA Monika. Innovation in metallurgical waste management. *Metalurgija*. 2015. vol. 54, no. 1, pp. 283-285.
- [5] SANIUK, Anna., JASIULEWICZ-KACZMAREK, Małgorzata, SAMOLEJOVA, Andrea, SANIUK, Sebastian., LENORT, Radim. Environmental Favourable Foundries Through Maintenance Activities. *Metalurgija*. 2015. vol. 54, no. 4, pp. 725-728.