IMPACT ON THE ENVIRONMENT OF IRON-CONTAINING METALLURGICAL WASTE

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Abstract

Steel has never ceased to be the most important structural material. Steel and cast steel account for more than 92% of total consumption of metals. Unfortunately, this sector generates massive amounts of waste, including iron-bearing types. Substances referred to as *waste* are subject to rigorous legal regulations the purpose of which is to protect human health and natural environment. Restricting waste generation and utilising the waste already produced are the most fundamental principles of rational use of natural and anthropogenic resources. More and more of metallurgical waste is reclaimed, yet part of it is stored. This paper presents the results of research on waste containing iron (dust, mill scale, sludge) in terms of their environmental impact when stored, the results of the assessment of the quality of water extracts in relation to the legal requirements for the introduction of sewage into waters or to land.

Keywords: Metallurgical industry, environment, waste containing iron

1. INTRODUCTION

The increasing environmental pollution is observed along with the world population growth and the development of the industry. The development of cities, business activity and industrial centres results in emission of more and more harmful substances into the environment. The emissions and industrial waste make the greatest contribution to the pollution. The metallurgy industry is a branch (along with mining and power industry) that generates great amounts of waste. Some part of this waste is stored. The article presents the research results of metallurgical waste containing iron (dusts, sludges, mill-scale) from the point of view of their environmental impact if they are being stored.

2. WASTE MANAGEMENT

In line with the European Union requirements, the term waste is used in reference to any substance or object which the holder (producer) discards or intends or is required to discard [1]. In the metallurgical industry, waste is dust, sludge, mill scale, slag and ceramic debris. Steel slags, furnace slags and ceramic debris are used in road construction in the country. The waste like dusts, sludges and mill-scale contain iron which may prove cost-effective to recover if its content is sufficient and the appropriate technology is applied [2]. The metallurgical dusts (EAFDs), for example, may be used in production of clinker, building materials, domestic and decorative glassware. The waste which proves to be uneconomical to recycle is stored - which does not mean that such stored waste is not harmful to the environment. Waste storage is not positive from the point of view of environmental protection.

The waste storage is understood as a temporary storage or accumulation of waste before its transport, recovery or disposal. The storage is time-limited. The time limit of this operation means that the phase of waste management should be transitional, preceding the final waste management (recovery or neutralisation) [1]. The storage may be only performed on the territory which the waste possessor is legally entitled to.

The water extracts research from the point of view of meeting the requirements included in the Regulation of the Minister of Environment of 18 November 2014 regarding the required requirements that have to be met for the sewage disposal into water or ground, and regarding the substances particularly harmful for water enviroment [3] should answer whether the waste storage is safe for the environment, or - out of concern for our health - should we maximally reduce the waste storage time.

3. RESULTS AND DISCUSSION

The research concerned metallurgical sites wastes, containing iron and occurring as dusts, sludges and mill-scale. The research of chemical composition of this waste and water extracts prepared on its base was carried oud.

There were examined three samples of dusts (the dust of the dedusting of electric arc furnace in a steel plant and in a foundry - D1, D2 - and the dust from the moulding compound - D3), three samples of sludge (the sludge from the blast machine - S1, the sludge from the steel mixer - S2 and the sludge from the current production of the converter steelmaking plant - S3) and three samples of mill-scale iron from different steelwork plants - M1-M3. Prior to the examination, the samples were dried.

In order to obtain the accurate results of the chemical composition analysis, three samples of ~0,1 g were collected from the material of each sample, analysed, and subsequently the medium value and the standard deviation of the elements concentration in these samples were determined. Analysis of chemical composition was performed by means of:

- carbon and sulfur analyzer LECO CS 844;
- oxygen analyzer LECO ONH 836;
- a scanning electron microscope Hitachi S-3400N equipped with EDS detector Scientific Thermo Noran System 7, and WDS MagnaRay.

The results of the quantitative analysis of the chemical composition in the examined samples are presented in the **Table 1**, and the water content in the examined samples (before drying) are presented in the **Figure 1**.

Table 1 Results of quantitative analysis of the chemical composition of the examined waste

Element	D1	D2	D3	S1	S2	S3	M1	M2	M3
C	2.42	2.64	14.37	1.18	1.88	3.66	0.27	0.25	0.14
O	17.63	39.17	20.33	37.17	16.80	16.57	12.30	11.30	11.50
Mg	0.80	0.43	1.67	0.67	0.17	0.73	0.30	-	-
Al	0.50	1.63	7.43	6.03	0.77	0.50	0.40	0.20	0.17
Si	1.50	28.33	28.83	17.67	8.90	2.30	1.60	1.10	1.03
S	1.0	-	0.43	0.30	0.50	0.87	-	-	-
Ca	5.20	0.53	17.57	0.33	0.73	4.20	1.03	0.10	0.57
Mn	4.37	0.47	0.23	0.57	0.60	3.90	1.73	1.03	1.47
Fe	44.77	26.40	7.83	24.13	67.57	38.50	81.67	85.10	83.67
Zn	18.63	-	-	-	0.4	22.20	-	-	0.50
Cr	0.37	-	-	10.77	0.23	0.90	0.27	0.13	0.30
Cu	0.30	-	-	-	0.73	0.40	0.33	0.53	0.60
K	2.4	0.13	0.9	0.43	0.1	3.3	-	-	-

The research material was glued to the titanium pads, in result this element was excluded from the results of the quantitative x-ray microanalysis (the area of the excitation is so wide, that apart from the examined material it includes also the pads the material was attached to).

According to the national law, implementing the directives of the European Union, as the hazardous wastes may be classified the wastes containing, among other things; vanadium. chromium, nickel, copper, zinc, arsenic, tin, barium and mercury compounds. Almost all examined materials contain at least one of the listed compounds, which may result in perceiving them as hazardous wastes - except the dust from the cast iron and cast steel foundry and the dust from the moulding compound.

The results of the quantitative analysis of the chemical composition indicate that the wastes like mill-scale iron, due to the over 80% of iron content, should be completely managed as a precious secondary raw material in steel production processes.

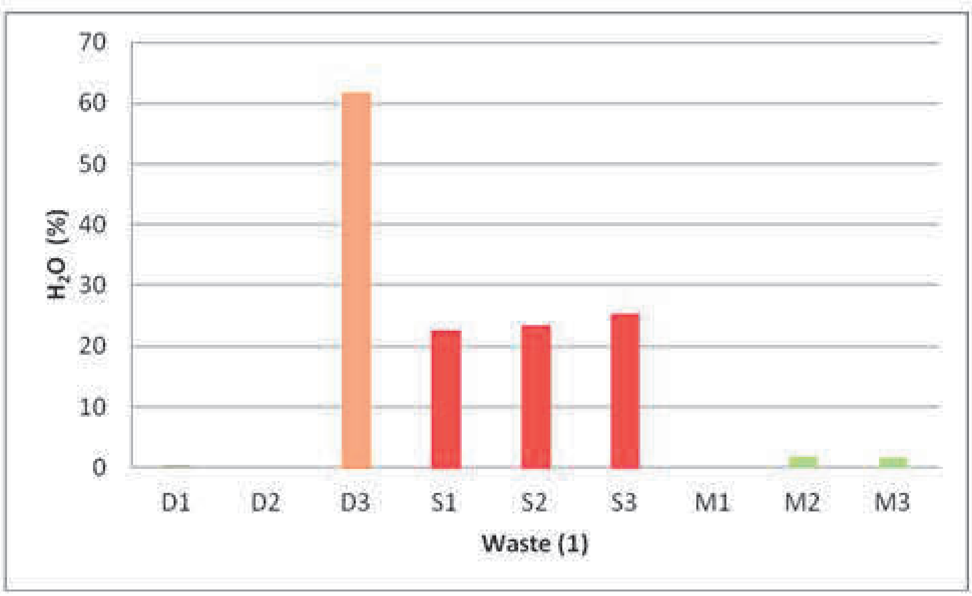

Figure 1 Water content of the iron-containing waste tested

The examined waste materials should be, first of all, recycled [1]. The chosen technology of reprocessing the waste materials should take water content into account.

In many technologies, the first stage is to dry the waste - the higher water content is, the greater costs of reprocessing are. Among the examined waste materials the dust from the moulding compound (D3) is characterised by high content of water (over 60%) and at the same time small content of iron - the basic components of this waste are calcium and silicon oxides. Due to the unprofitability of reprocessing such materials it is possible that they will be stored. In that case, the knowledge about the safety to the natural environment (first of all to the water resources) of this waste is necessary. The assessment of water extracts from the examined materials was carried out from the point of view of meeting the requirements listed in the Regulation of the Minister of Environment of 18 November 2014 regarding the required requirements that have to be met for the sewage disposal into water or ground, and regarding the substances particularly harmful for water enviroment [3] - the permissible value concerning the so-called other types of sewage was adopted. All the waste types subject to testing contained at least one of the foregoing compounds, which may be decisive of their classification as hazardous waste. Water extracts of these waste sorts were tested for determination of arsenic, barium, cadmium, chromium, copper, molybdenum, nickel, lead, antimony, zinc, mercury, selenium, bromide, chloride, fluoride, sulphate, total and dissolved organic carbon, total dissolved solids and alkalinity. The results thus obtained were compared with the highest permissible levels of pollutants which may be discharged into aquatic environment (**Table 2**). Domestic legal regulations are implementing the relevant European Union directives [4]. The relevant tests were conducted at a laboratory certified by the Polish Centre for Accreditation (AB 213) for sampling and testing of waste specimens.

Table 2 Values of contamination ratios for substances classified as particularly harmful to aquatic environment based on tests of water extracts of the waste types studied (values obtained for industrial waste, mg /L)

Pollution	Results									The highest limit
	D1	D2	D3	S1	S2	S3	M1	M2	M3	
Arsenic	0.015	<0.0010	0.0047	<0.0010	**0.12**	<0.0010	0.0021	0.0053	0.0031	0.1
Barium	0.070	0.090	0.0717	0.011	0.107	0.724	0.0127	0.0089	0.0021	2
Cadmium	<0.001	<0.0005	<0.0005	<0.0005	0.006	<0.00050	<0.0005	<0.0005	<0.0005	0.4
Chromium total	0.006	<0.003	<0.003	<0.003	0.0399	**3.34**	0.0077	<0.003	0.0086	0.5
Copper	<0.005	0.0188	0.0244	<0.004	**1.38**	<0.0040	0.184	0.0489	0.0105	0.5
Mercury	<0.0005	<0.0005	<0.0005	<0.0005	0.0006	0.004	<0.0005	0.005	<0.0005	0.06
Molybd.	0.021	0.0238	0.0151	0.146	0.149	**7.84**	0.0233	0.151	0.0459	1
Nickel	0.0071	<0.004	0.0124	0.0047	**0.547**	<0.0040	0.0158	0.0357	0.0339	0.5
Lead	**1.387**	<0.010	0.0176	<0.010	0.0888	**5.71**	0.0101	<0.010	<0.010	0.5
Antimony	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	0.3
Selenium	<0.001	<0.001	<0.001	<0.001	<0.001	0.031	<0.001	<0.001	<0.001	1
Zinc	0.154	0.135	0.102	0.0266	0.625	**6.29**	0.108	0.037	0.0413	2
Chloride	8.7	3.50	12.0	2.6	<2.0	**2360**	<2.0	<2.0	4.2	1000
Fluoride	0.81	0.98	0.51	3.3	0.24	21	0.61	0.17	0.19	25
Sulfate	7.7	4.40	48.0	54.0	44.0	**1480**	3.4	3.5	8.6	500
Dissolved organic carbon	19	16.8	**48.2**	4.29	21.5	**60.1**	9.09	3.21	4.94	30
pH	**12.4**	**9.3**	8.9	7.8	7.8	**12.3**	8.3	7.8	8.0	6.5-9.0

The values which exceed the highest permissible contamination ratios have been marked in bold.

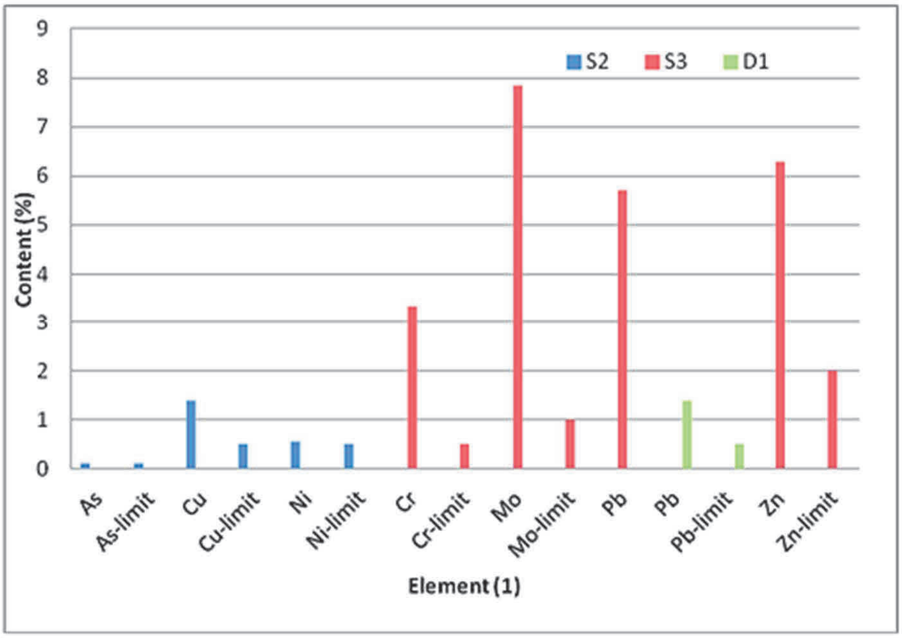

Figure 2 Exceeded limits of the content of elements in the examined waste

In the **Figure 2** the wastes are listed that present the exceedance of the highest permissible contents of elements. In the water extract from the dust of the EAF dedusting of steel plant the permissible lead content was exceeded, in the water extract of sludge from the steel mixer the permissible arsenic, copper and nickel contents were exceeded. In the sludge from the current production of the converter steelmaking plant the permissible contents of chromium, lead and zinc are exceeded.

In accordance with the applicable European Union requirements [4], substances classified as particularly harmful to aquatic environment and causing pollution of waters have been divided into two categories: substances which should be eliminated and substances the generation of which should be restricted. The substances to be eliminated among the water extracts of the waste types analysed are mercury and its compounds. None of the waste materials tested exceeded the permissible content of mercury or its compounds in water extracts.

Based on the contamination ratios obtained from the tests of water extracts of the waste types studied, it was established that (**Table 2**):

- water extracts of all waste types studied did not contain substances considered as particularly harmful to aquatic environment and causing contamination of water, which should be eliminated; the mercury content in the extracts tested was also below the permissible threshold which is 0.06 mg / L;
- in all water extracts of each examined mill-scale and sludge from the blast machine there were noticed no substances particularly harmful to the water environment, causing water pollution that should be limited;
- the permissible value of the contamination ratio for lead, being one of substances classified as particularly harmful to aquatic environment, the generation of which should be restricted, was found to be exceeded in water extract of the EAF dust from steelworks (D1). No contamination ratio was found to be exceeded in the water extract of the EAF dust from the foundry (D2), considering the substances regarded as particularly harmful to aquatic environment. Chemical composition of EAFD depends on the chemical composition of the scrap feedstock used;
- in the water extract of the moulding sand dust (S2) subject to testing, the limit value was exceeded for dissolved organic carbon, being a substance causing contamination of waters, the generation of which should be restricted;
- in the water extract of the steelmaking agitator sludge (S1), the permissible limit values were found to be exceeded for copper and nickel, being substances causing contamination of waters, the generation of which should be restricted.

CONCLUSIONS

The waste generated in production processes provided that they could not be prevented or recycled, must be landfilled in a manner which does not pose a threat to natural environment. What is required in the first instance is defining whether the given waste is hazardous. In this respect, considerable aid is provided by the list of waste types referred to in article 7 of Directive 2008/98/EC [5], since all waste types marked with asterisk (*) in the list are considered hazardous. According to the said list, the hazardous waste generated in the iron and steel industry include:

- solid wastes from gas treatment containing hazardous substances (code 10 02 07*);
- wastes from cooling-water treatment containing oil (code 10 02 11*);
- sludges and filter cakes from gas treatment containing hazardous substances (code 10 02 13*).

Bearing in mind the aforementioned guidelines, among the waste sorts from regular production tested in the study addressed in the paper, the hazardous waste is the electric arc furnace dust (D1 - 10 02 07*), as it contains chromium. Tests of the water extract of this waste imply that it is necessary to restrict the generation of lead and decrease pH, both being factors considered particularly harmful to aquatic environment.

According to the foregoing classification, the remaining regularly produced waste types tested are not classified as hazardous waste, however, on account of their content of zinc (agitator sludge S2 and sludge from the blast furnace S3), chromium (fettling sludge S1, agitator sludge S2 and sludge from the blast furnace S3, scale M1 and M2), nickel (agitator sludge S1), vanadium (fettling sludge S2) and copper (agitator sludge S1, scale M1, M2 and M3), they may be considered hazardous waste.

On account of the iron content exceeding 80%, waste types such as M1 and M2 (scale) should be subject to iron reclamation processes instead of being landfilled.

The examined metallurgical wastes containing iron, except the mill-scale waste, affect the environment negatively, mainly due to the disposal into water or ground the harmful elements or compounds. The activity of the metallurgical industry, besides production, should focus on the technologies of generated waste management.

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REFERENCES

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[4] **Council Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment and Directive** 2010/75/EU of the European Parliament and of the Council of 24th November 2010 on industrial emissions (integrated pollution prevention and control).

[5] Commission Decision of 18 December 2014 amending Decision 2000/532/EC on the list of waste pursuant to Directive 2008/98/EC of the European Parliament and of the Council.