Method for Assessment of Potentially Pollution of Slag from Iron and Steel Industry

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Abstract: The physical and chemical characteristics of slags, after a preliminary preparation, can make possible their use in various industrial sectors, such as cement industry and road construction, according to their properties. Thus, it is necessary to assess theirs environmental impact, especially for the hazardous elements (heavy metals) being present in their content, and the risk of their leacheability into soil and groundwater by help of rainwaters. The most usual laboratory test for this assessment is the leaching test. In this paper are presented the procedure, results and data interpretation.

Keywords: Slag, Leaching test, Environment, Heavy metals, Iron and steel industry.

1. INTRODUCTION

Leachate is the liquid produced when water percolates through any permeable material. It can contain either dissolved or suspended material, or usually both[1].

This liquid is most commonly found in association with landfills, where rain percolates through the waste and reacts with the products of decomposition, chemicals and other materials in the waste to produce the leachate. If the landfill has no leachate collection system, the leachate can enter groundwater, and this can pose environmental or health problems as a result.

In our country, criteria for acceptance of a waste into a landfill are made according to waste characteristics [1]:

- Physical and chemical composition;
- Organic content;
- Biodegrability of organic compounds;
- Hazardous elements content;
- leaching test / prognosis;
- Ecotoxicological properties of the waste and the leachate.

Due to physical and chemical characteristics, wastes from iron and steel industry represent may be used in various industrial sectors.

Now, these types of wastes are partially recovered and they represent 70% from total waste amount. The physical and chemical slag characteristics, after a preliminary preparation, can make possible their use in various industrial sectors. For example, the most current method for slag recovery is their use in cement industry and road construction, according to their properties. Their recycling is an environmental task that can lead to natural resource protection and soil pollution prevention by minimizing areas with slag deposit [2].

In order to establish if the types of slags from different iron and steel areas can be recovered as building materials for roads, it is necessary to assess their environmental impact, beginning with finding the content of the hazardous elements (heavy metals) and the risk of their leacheability into soil and groundwater by help of rainwaters.

This assessment is made with leaching test, which consists from the extraction into a liquid medium, in this case is rainwater, of different hazardous elements from waste, based on theirs solubility in that medium.

In this paper are presented the results obtained after the leaching test applied for slag and dust samples generated in iron and steel industry. The tested wastes are now disposed in dumps, without being reused, and their quantity increases continuously.

2. LEACHING TEST FOR IRON AND STEEL SLAGS

The national standard referring to waste analysis by leaching test is SR EN 12457 - 2003: Waste characterization. Leaching test. Validation test for granular wastes and sludges.

The leaching test standard refers to a liquid / dry solid ratio of 2 l / kg dry solid and 10 l / kg dry solid for 3 types of acid liquid phase: pH about 6

(distillate water), pH about 5 (buffer solution), pH about 3,5 (acetic acid solution).
The optimum stirring time is about 4 hours. The granular sizes are 4 mm and 10 mm for the waste.
After filtration, form liquid phase the specific indicators are analyzed.
This standard has been adopted as national standard according to the Environmental Acquis. At European level, the leaching test is available as requirement in German, Dutch or French standards.
For these laboratory experiments had been followed SR EN 12457 - 2003: Waste characterization. Leaching test. Validation test for granular wastes and sludges.
This standard presents the method for the solubilization of the solid sample, the obtained solution being analyzed by atomic absorption technique.
The method is used for solid and plastics wastes, which can be crushed and is not suitable for those wastes for which the leachate volume (aqueous solution) is less than 2l.
The experiments had been made on basic oxygen furnace (BOF) and electric arc furnace (EAF) slags and (EAF) electric arc furnace dust. Their chemical characterization is presented in table 1.

Table 1. Chemical composition of some wastes from iron and steel industry

Chemical composition, (%)	**Basic oxygen furnace (BOF) slag**	**Electric arc furnace (EAF) slag**	**Electric arc furnace (EAF) dust**
Ca	39,84	33,26	31,9
SiO_2	9,82	14,55	1,60
Al_2O_3	0,90	0	ND
MnO	6,26	7,46	2,4
MgO	1,97	22,71	ND
P_2O_5	2,26	0,48	ND
Fe tot	12,86	12.09	49,13
Fire losses	0,002	5,60	ND

ND-unavailable; the element has not been analyzed.

The test had been made in order to:
- Assessment of the soluble portion from waste samples;
- Assessment of the waste quality;
- Behavior assessment of pollutants from slag during leaching test.

Working procedure had involved the following steps:
- 1. Preparation of the samples for testing;
- 2. The contact between solid sample and aqueous solution;
- 3. Separation of the solid material from liquid medium (leachate);
- 4. Leachate analysis.

1) Preparation of the samples for testing

The procedure refers to the obtaining of the laboratory samples, after checking of the waste state (diameter, solid or slurry aspect, etc).
In the first step, the waste samples had been crushed in order to obtain the solid particles with size less than 4 mm.
According to standard, in case of a size higher than 4 mm, being impossible to reach at this size, the sample will be the subject of an especially analysis and will be establish depending by final objectives. The other recommended size is 10 mm.
By using the ball crusher and sieve set had been possible the obtaining of an adequate size.

2) The contact between solid sample and aqueous solution

This represents the main leaching step. When the waste is brought into the contact with aqueous phase, it takes place the transfer of the soluble compounds from the waste into liquid medium.
The contact time of the solid waste with the solution is an important parameter, the separation efficiency of the soluble compounds being related with this.
The contact time depends on the following factors:
- Material size;
- Composition of tested material and its compounds;
- Stirring frequency.

The optimum contact time, according with the standard SR EN 12457:2003 is about 4 hours under continuous stirring for the two phases, with the help of the magnetic stirrer, at 60 – 80 rot/min.

3) Separation of the solid material from liquid medium (leachate)

The standard recommends as a separation technique the filtration and/or centrifugal hydro extraction in order to obtain a higher efficiency. Filtration was made by a filter paper with pore sizes up to 0,45 μm, after a coarse filtration.
The liquid phase – *the leachate* will be available for chemical characterization in order to analyze *the heavy metal traces*, thus being possible to assess the negative impact of these metals on soil and ground waters.

4) Leachate analysis

The obtained leachate (the liquid medium) was analyzed in order to establish its chemical composition with help of atomic absorption spectrometry, using as apparatus for analysis an atomic absorption spectrometer.

The work procedure was made according to SR EN 12506 – 2004: Wastes characterization. The elute analysis. Determination of: pH, As, Ba, Cd, Cl^-, Co, Cr, Cr^{6+}, Cu, Mo, Ni, NO_2^-, Pb, S total, SO_4^{2-}, V and Zn. The metallic elements are analyzed by help with the atomic absorption method.

An overview of the activities applied during leaching test is presented in figure 1.

The experiments had been made for chemical characterization of the solution obtained by leaching test in static condition.

The chemical composition of the leachates (liquid solution after separation from slag samples) is presented in the table 2.

The maximum admitted values are established in Order no. 867/2002 regarding *classification criteria of the wastes in order to be accepted in national list of the wastes and into different deposits.*

According with this Order, the iron and steel slags are classified into the deposit class of the nonhazardous wastes, 10 08 09 code – the others slags, 10 06 01 code – primary and secondary treatment slags, 01 03 08 code – dust and powder wastes.

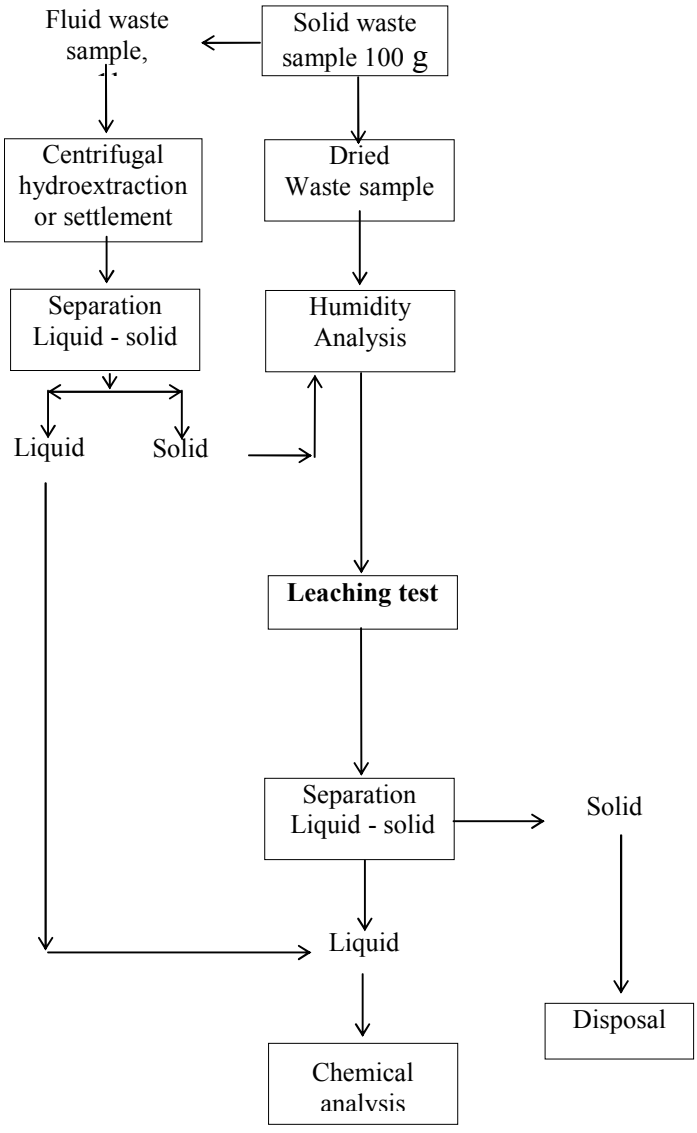

Fig. 1 Leaching test steps

Table 2. Chemical composition of leachate (mg/dm^3)

Indicators	BOF slag	EAF slag	EAF dust	Maximum admitted values, Order 867/2002	Analysis method
Ni	0,0006	0,0013	0	1,0	SR EN 12506 – 2004
Pb	0,021	0,016	0,005	0,5	
Zn	0,006	0,023	0,019	1,0	
Cd	0,003	0,003	0	0,3	
Cr tot	0,02	0,01	0,02	1,5	
Cr^{6+}	0,007	0,002	0,005	0,2	
Cu	0,01	0,014	0,009	0,2	
Ca	11,21	17,98	10,45	100*)	
Fe_{tot}	3	2,4	2,0	0,1*)	
pH	9	7 - 7,5	7,2	6,5 – 7,4*)	

**) the Order no. 867/2002 has not limited the calcium and iron content and also the pH value from leachate and these values were compared with STAS 1342 – 91 standard for potable water quality as reference.*

3. RESULTS

From laboratory tests, it can be observed that some heavy metals ions can be solubilized by demineralized water.

The contact time for these samples was 4 hours. Thus, even if the initial composition of the wastes has not comprised the heavy metals content, which can be appear by accident, it could be observed, that some ions, due to contact between water and crushed samples of slags, were solubilized by demineralised water in small quantities.

Thus, for basic oxygen slag, where pH of the leachate has a basic value (pH=9), the heavy metal ions contents are important due to the impurities and fluxes content during the steel process (the similar effect is for electric arc furnace slag and dust).

In this case, it is expected the presence of some ions as Cd^{2+}, Pb^{2+}, Zn^{2+}.

The iron ions, due to slightly acid (amphoteric feature) characteristic of the ferric oxide Fe_2O_3 and the low water solubility of the ferrous oxide FeO (II), the efficiency values obtained for the total amount of iron are below 1 %.

For the calcium ions, the separation efficiency values are higher for electric arc furnace slag due to calcium oxide amount from initial composition of the wastes (and the CaO has high water solubility).

Thus, for 1 t waste, the maximum iron and calcium quantities, expected to be extracted by about 10 m^3 water from one tone of slag into soil and groundwater are presented in table 3.

Table 3. Iron and calcium quantities extracted by leaching test application

Leachate from 1 t slag:	Ca^{2+}, g	Fe_{tot}, g
- basic oxygen furnace slag	220	60
- electric arc furnace slag	360	48
- electric arc furnace dust	209	40

It is important to observe that the heavy metal ions are not presented in high quantities.
After leachate analysis, it was observed that maximum admitted values are not exceeding, except iron, comparing with values admitted according with water quality standard. However, the iron quantity is expected to be higher having in mind the chemical composition of the waste and the possibility of iron ions to be extracted into liquid medium.

4. CONCLUSIONS

Physical and chemical characterization and study of these types of wastes brought into contact with the water, according to leaching test, offer some information regarding the possible risk on environment of these wastes in case of theirs reuse as road construction materials, especially for analyzed slags.
The leaching test is important for assessment of the soluble portion from wastes samples and the waste quality and also for behavior study of pollutants from wastes during the test.
Three types of wastes were analyzed: BOF and EAF slags and EAF dust.
The samples were prepared according to working steps from the standard SR EN 12457:2003 and were analyzed according to SR EN 12506 – 2004 and Order 867/2002 requirements.
The obtained results show the presence of calcium, silicium and iron oxides, in the large amounts, as a result of used fluxes.
Applying this laboratory test on steel wastes (basic oxygen furnace slags and electric arc furnace slags) it is observed that:
- No one of these heavy metal ions are presented in high quantities in the leachate over the maximum admitted values:
- There are high quantities of some elements from leachate, such as iron and calcium, due to theirs presence in initial composition of the slags; the concentration values of these ions are not exceed the maximum admitted values for potable water (STAS 1342-91);
- The wastes from iron and steel industry are not hazardous wastes on environment, but the risk of some heavy metal ions appearance is possible, this being a reason for time-to-time testing of these waste types, having in mind the influence of these heavy metals on environment and life.

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