CHARACTERISATION AND PRE-TREATMENT OF STEELMAKING DUSTS IN ORDER TO RECOVER VALUABLE PRODUCTS

A. Delalio[1], Z. Bajger[2], P. Balaz[3], F. Castro[4], J. Magalhães[4] and J. Curilla[5]

INTRODUCTION

Steelmaking dusts are frequently classified as hazardous residues, due to their eco-toxicity characteristics. This derives mainly from the presence of heavy metals like zinc, lead and cadmium in their compositions, in forms that are easily leachable by water or slightly acidic or alkaline media. Following the most employed eco-toxicity standard tests, like DIN 38414-S4[1)] from Germany, and TCLP (Toxicity Characteristic Leaching Procedure)[2)] from the United States, steelmaking dusts present a high level of mobility of heavy metals, what is relevant for the evaluation of their environmental impact, when disposed in controlled landfills.

By this work, financed by the European Communities COPERNICUS Programme, a characterisation of the dusts generated in different steelmaking plants has been done. Also, the behaviour of the dusts when washed with cold water has been evaluated, giving some informations on the mobility of metals and on the prospects for pre-treatment of the residues to recover valuable products.

----

[1] Ecometal, s.r.l., Brescia, Italy
[2] Vítkovice, J.S.C., Ostrava-Vítkovice, Czech Republic
[3] Institute of Geotechnics, Kosice, Slovakia
[4] TecMinho, Guimarães, Portugal
[5] VSZ OCEL, Kosice, Slovakia

CHARACTERISATION OF DUSTS

Twelve different dusts have been collected in companies from Slovakia, the Czech Republic and Portugal. They are of the following types:

Basic Oxygen Furnace dusts – Sample 2 from Slovakia and sample 8 from the Czech Republic

Basic Oxygen Furnace sludges – Sample 1, from Slovakia, samples 3, 4 and 7, from the Czech Republic and sample 10 from Portugal.

Basic Oxygen Furnace muds – Samples 5 and 9 from the Czech Republic.

Ladle Furnace sludge – Sample 11 from Portugal.

Electric Arc Furnace dusts – Sample 6 from the Czech Republic and sample 12 from Portugal.

The following tables resume the characterisation that has been done, on a dried basis.

values in %

Sample	Zn	Pb	Fe	Mn	SiO_2	CaO	Cu	Cr
1	2.2	0.6	54	1.1	1.6	6.2	0.03	0.02
2	1.6	0.5	54	0.9	1.4	6.0	0.02	0.02
3	3.6	0.8	62	0.9	1.8	4.6	0.04	0.06
4	0.5	0.05	78	0.6	2.1	5.3	0.04	0.07
5	0.4	0.07	52	0.09	8.0	4.6	0.01	0.01
6	15.1	3.7	28	3.6	2.3	3.7	0.16	0.17
7	4.2	0.5	48	1.0	1.8	11.9	0.03	0.06
8	1.6	1.2	39	0.2	77.5	4.0	0.03	0.01
9	10.0	2.1	54	0.9	1.8	1.4	0.09	0.09
10	2.4	0.6	71	1.1	1.3	6.1	0.03	0.04
11	0.1	0.1	16	10.7	6.2	21.3	0.02	0.03
12	19.5	3.3	29	2.2	1.7	26.5	0.22	0.12

Table 1 – Chemical composition of the collected samples

Sample	Bulk Density ($g.cm^{-3}$)	Volume Magnetic Susceptib. (x 10^3) (SI units)	Specific Surface Area (m^2g^{-1})
1	3.34	162	21.6
2	3.54	451	7.9
3	4.84	145	11.0
4	5.75	448	0.75
5	3.88	104	5.3
6	4.79	310	3.7
7	3.84	87	13.2
8	3.63	87	10.4
9	4.98	326	7.1

Table 2 – Bulk density, volume magnetic susceptibility and specific surface area of some of the samples collected

Sample	< 0.04	0.04-0.063	0.063-0.100	0.100-0.125	0.125-0.250	0.250-0.500	0.500-1.000	> 1.00
1	52.1	4.8	6.0	2.3	5.8	3.9	20.1	5.0
2	72.7	8.3	3.6	1.5	5.3	6.9	1.8	---
3	17.6	2.3	3.3	0.5	4.9	7.0	16.4	48.0
4	2.4	0.7	1.0	0.5	2.1	4.0	9.4	79.9
5	62.8	8.0	9.6	3.5	7.6	4.8	3.7	---
6	85.9	3.2	3.9	1.0	1.9	1.9	2.2	---
7	45.4	7.8	10.5	1.6	3.3	4.2	14.3	12.9
8	22.6	6.8	6.8	3.8	7.8	4.4	7.0	40.8
9	41.1	9.7	6.9	1.5	3.0	2.2	11.7	23.9

grain size in mm, expressed in % of the total weight of the sample

Table 3 – Grain size distribution of some of the collected samples.

Specific surface area has been determined by the low temperature adsorption method in Gemini 2360 sorption apparatus, from Micrometrics. Volume magnetic susceptibility measurements have been achieved on the apparatus Kappabridge KLY-2/Geophysics Brno, Czech Republic, under the following conditions: intensity of magnetic field 920 Am^{-1}, homogeneity of field 0,2%, frequency 920 Hz.

In order to evaluate the dispersion of chemical composition data concerning electric arc furnace dusts, fifteen analysis have been done on samples from the same origin as sample 6. The average results, as well as the respective dispersion are presented bellow.

values in %

	Zn	**Pb**	**FeO**	**Fe_2O_3**
Average	15.1	3.7	4.2	34.7
Stand. Dev.	5.5	1.3	2.2	4.3

Table 4 – Dispersion of chemical analysis of EAF dusts (Sample 6).

The eco-toxicity characterisation of sample 12, by two standardised methods, gave the following results:

Test	DIN 38414-part 4	TCLP
pH	12.7	-----
Zn ($mg.l^{-1}$)	4	4
Pb ($mg.l^{-1}$)	330	320
SO_4^- ($mg.l^{-1}$)	600	500

Table 5 – Results of the eco-toxicity tests applied to sample 12.

Results of both tests implies the classification of this residues as eco-toxic, due to high amount of dissolved lead.

By means of the simultaneous DTA/TGA characterisation of the dust's samples, done at the SDT 2960 equipment from TA Instruments available at the Laboratory of Metallurgy of the University of Minho, Guimarães, Portugal, several features can be highlighted:

- all the samples present a weight loss behaviour, at around 600 ºC;
- some samples (numbers 2, 4, 5 and 12) present also a first weight loss step, at around 400 ºC;
- both weight loss processes are endothermic ones;
- degrees of weight loss are highly variable from sample to sample, reaching, for samples 8 and 12, more than 25 % of the initial weight.

WATER WASHING BEHAVIOUR

Water washing behaviour has been evaluated for sample number 12. Cold distilled water at 25 ± 2 ºC was mixed with dried dust (at 110 ºC for 24 hours) and agitated with a glass stirrer, at a speed of 1100 r.p.m., during 24 hours. The extraction degree has been determined by chemical analysis of the water - by atomic absorption spectrometry - and by the chemical analysis of the dusts - by X-ray fluorescence spectrometry - giving the following results:

values in % of extraction, except for pH

Liquid/solid ratio	pH	Na	K	S	Cl	Ca	Pb
20	12.7	> 99	92	38	97	5	28
10	12.8	> 99	91	36	97	8	25
5	12.9	> 99	92	14	97	< 2	21
3	12.8	> 99	92	14	96	< 2	16

Table 6 – Water leaching results, expressed in terms of pH of the solution after leaching, and of % of dissolution of elements present in dust number 12.

It is evident the high level of elimination of chlorides, what may be of relevance for the further treatment of dusts, in order to recover zinc, ferrites and lead, by pyro- or hydrometallurgical methods. The dissolution of an important part of the lead contained must be considered, taking into account the partial elimination of this heavy metal. However, this obliges to consider the elimination of this metal from the pre-treatment wastewaters, to respect environmental protection rules. The relatively high degree of dissolution of lead in water may be explained by the eventual presence of some lead chloride in the dusts, and also by the high alkalinity of the leachate.

CONCLUSIONS

Steelmaking dusts contain frequently some valuable metals that encourage its treatment in order to add value to the residue. Also, due to their eco-toxicity characteristics, they must be treated prior to disposal. This study has presented some physical and chemical data concerning these residues, that may be relevant for any treatment plant design, be from one pyrometallurgical process or from a hydrometallurgical one. Pre-treatment of dusts by leaching with cold water has proved the high efficiency for the removal of chlorides and the capability for the extraction of lead.

REFERENCES

1) Standard DIN 38414-S4, October 1984
2) U.S. E.P.A. SW 846, method 1311; Title 40-261.24 of the Code of Federal Regulation, in Federal Register, Vol. 51, number 114, June 13, 1986, pages 21648-21693.