Morphology, Structure and Composition of Some Technological Wastes Released from Blast Furnace Operation

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The purpose of this paper attempts the characterization by optical microscopy of the composition, type and structure of some technological powdered wastes generated from a blast furnace in Romania, in terms of identification of pollution source and their potential for recycling. The samples collected mainly from the primary and fine purification stages were petrographically investigated providing complementary information to physico-chemical methods, particularly valuable and unique on the morphology of a mixture of solid dust particles having different sizes and origins (coal, coke, iron ore). The closely dependent relationship between microstructure and anisotropy of different structural types, allows the evaluation of coal particles, coke morphology and mineral matter. The results can indicate the pollution source from an environmental perspective, as well as the proportion of organic and mineral matter in the dust mixture, in case of their recycling.

Keywords: petrography, blast furnace, technological waste dust, sludge, pollution

It is well known the process of iron making which involves chemical reduction of iron oxides with the reducing agents in blast furnace gas (CO₂, H₂) using coke as solid fuel and auxiliary fuels (natural gas and coal dust injected - to reduce the coke specific consumption). Blast furnace technological flow includes, generally, more units, functional and constructive directly connected: furnace itself, cast house, coarse and fine gas cleaning, air heaters, as well as compartment bins and automation. Blast furnace gas is routed to consumers after preliminary treatment of rough and fine dust, in adequate facilities. Rough treatment consists of dust bag and cyclone and related equipment for removing the wet dust up to approx. 70% of the total dust amount. Dust content in the furnace gas is of approx. 15-20 g/m³ resulting an average of 10-15 kg/ton iron. Fine cleaning is done in diameter adjustable Venturi tubes, after which purged gas also contains approx. 5-10 mg dust. Evacuation of dust from dust bag and cyclone is made with high releases into the environment [1].

Pollution with metallurgical industrial wastes was largely investigated by studying their environmental risks a detailed scientific interest being aimed to recover and reuse them after physico-chemical and micro-morphological characterization [2] that the authors also made [3 - 6]. A digital atlas of anthropogenic particles from different sources was elaborated [7] and a monography was published [8] to help identification of waste particles under microscope, giving the possibility to find the type and source of pollution.

The solid wastes represent not only an environmental issue for conserving metals and mineral resources but a technological feature for the metallurgical industry, since they can be used as secondary resources [9, 10]. Therefore, in Romania, powdered waste dusts released from dust bag and cyclone enters the agglomeration circuit materials [1]. Studies carried out on different materials have indicated that most of the valuable products can be recovered by simple physical, chemical and metallurgical beneficiation techniques [11 - 27].

This study is, in our opinion, especially attractive since the residual solid dusts from the blast furnace could be evaluated by optical microscopy to indicate the pollution source from an environmental approach, as well as the proportion of organic and mineral matter in the powder mixture, in case of reusing it in an appropriate manner. Although the amount of powdered wastes is not a currently risk problem, the present prospective study could be useful in terms of accidental pollution.

Experimental part
Materials and methods
Analytical methods
The six samples used in the present study are technological solid dusts generated from the blast furnace located on an industrial platform in South-East of Romania. They are powders collected from the blast furnace burden supply area, but mainly after gas purification steps located on the rough and fine de-dusting flow at the outlet of cyclone, dust bags, Venturi tube and sludge disposal. From each points of interest were collected 4 individual samples during 24 h. From the individual samples average samples of 2 kg each have been made, considered as being representative for our research. According to the standards in force, from the representative average samples were prepared samples for analysis by grinding, milling and sieving operations. The equipment included: mortar, Retsch AS200 sieves shaker with different sizes of metal sieves with square mesh, Sartorius analytical balance to ensure accuracy in weighing 0.0002 g, heating laboratory oven with a precision of 1°C and horizontal electric muffle oven (1000°C) with an accuracy of ± 20°C.

After the samples were prepared for laboratory analyses, general physico-chemical characterization of average representative samples was focused to establish the limits variation of the basic parameters, as: dimensional distribution of particles, moisture content, and bulk density. For the determination of chemical composition was used X-Ray Fluorescence (XRF) method. The XRF analysis was
performed using an Axios-Panalytical device and the corresponding (IQ+) soft allowing qualitative and semiquantitative evaluation of the chemical composition.

Microscopical analysis

In terms of quantitative petrographic composition of the wastes, polished sections of twelve samples were microscopically investigated, using moulds by agglomerating 20 g of average samples of -1 mm grain size, embedded in synthetic resins. The polished blocks were studied using reflected light, the measurements of organic and mineral matter particles recording a minimum of 500 points. Coal and coke particulate population were evaluated on two sizes < 0.1 µm and > 0.1 µm, their repartition being made using the ocular micrometer of a binocular optical microscope IOR MC1 and a point counter of Eltinor type [6].

In terms of qualitative petrographic analysis was used a binocular optical microscope Olympus BX51M with a transmission images camera model CCD-1300QB, reflected light (RL), gliceryn immersion and 500x magnification. The method of preparing coal samples and determining structural composition followed ISO 7404-2 and -5 (1994), respectively [28, 29]. To distinguish between the petrographic textures corresponding to the optical texture (isotropic or anisotropic) and optical type and size (punctiform, mosaic, fiber, ribbon, domain), was used the ASTM D 5061 (1997) method [30].

Results and discussions

Relation between physical-chemical and microscopical characteristics

From the average granulometric analysis one may observe that the blast furnace is an issuing source of pulverulent wastes with a significant percentage of fine fractions of particles. Generally the results from the physical characterization methods showed that size distribution indicates that up to 50% of the particles have a median diameter under 100 µm (table 1). The percents of organic and mineral components of residual solid dusts determined by optical methods led to differentiation between the samples and give valuable information for a possible recycling (table 2). The optical micrographs in figures 1-3 show the structural type and optical appearance of the wastes. The mineral matter determined by point counting petrographical method is consistent with the results given in table 1 and 3 showing the correlation between the ash content and its composition.

The particle size distribution of the technological dusts (table 2) had its maximum of 28.5% for coal particle sizes of < 0.1 µm and of 33-35% for coke particles sizes of > 0.1 µm. This was expected since coal and coke particles are released in significant amounts during rough purification of blast furnace gas.

Mineral matter, mostly as iron oxides, had its maximum of 84-85% for the solid dusts from the burden supply and cast hall, as well as of 70% for those evacuated into the sludge bin. The mineral composition determined microscopically (table 2) correlates satisfactory with Fe2O3 content determined chemically in case of all samples (table 3).

The correlation can be explained either by the fact that the material prepared for microscopical study had a proper size, which allowed the accurate identification of the optical fields studied.

The chemical composition, measured by X-ray fluorescence, depend on the quality and composition of the generating processes. The chemical composition (X-ray fluorescence) shows that, depending on the emitting source, wastes are residues rich in Fe (up to 83 wt.% Fe2O3), Si (up to 35 wt.% SiO2), lime (CaO up to 10.4 wt.%), Mg (MgO 8.2 wt.%), Al (Al2O3 up to 7 wt.%), S (SO3 up to 5.5 wt.%), with minor elements (wt.%): Na (<0.8%), K (<0.9%), P (<0.7%), Mn (<0.8%), Cu (<0.1%), Pb (<0.5%), Zn (<0.5%), Ti (<0.5%), Cr (<0.1%), Sr (<0.1%), Ba (<0.1%). A higher amount of Zn was found in the dust residues from gas fine purification (13 wt.%) and sludge bin (3.7 wt.%).

<table>
<thead>
<tr>
<th>Sample/Waste origin</th>
<th>Grain size distribution (mm) %</th>
<th>Bulk density, g/cm³</th>
<th>A supremacy</th>
<th>V supremacy</th>
<th>C supremacy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;0.08</td>
<td>0.08-0.2</td>
<td>0.2-0.8</td>
<td>0.8-1.25</td>
<td>1.25-2</td>
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<td>DF1 Burden supply</td>
<td>32.94</td>
<td>30.09</td>
<td>23.46</td>
<td>4.74</td>
<td>4.5</td>
</tr>
<tr>
<td>DF2 Cast hall</td>
<td>33.55</td>
<td>36.19</td>
<td>21.38</td>
<td>1.97</td>
<td>2.30</td>
</tr>
<tr>
<td>DF3 Cyclone</td>
<td>17.32</td>
<td>46.73</td>
<td>34.64</td>
<td>0.98</td>
<td>0.33</td>
</tr>
<tr>
<td>DF4 Dust bag/cyclone</td>
<td>49.01</td>
<td>25.71</td>
<td>12.64</td>
<td>2.18</td>
<td>2.40</td>
</tr>
<tr>
<td>DF5 Venturi tube</td>
<td>18.40</td>
<td>28.36</td>
<td>44.77</td>
<td>3.98</td>
<td>2.49</td>
</tr>
<tr>
<td>DF6 Sludge bin</td>
<td>7.78</td>
<td>10.20</td>
<td>20.28</td>
<td>15.56</td>
<td>32.53</td>
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</table>

<table>
<thead>
<tr>
<th>Sample/Waste origin</th>
<th>Grain size</th>
<th>Total organic material</th>
<th>Mineral matter ferrous</th>
<th>Mineral matter other</th>
<th>Total mineral matter</th>
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<tr>
<td></td>
<td>&lt;0.1 µm</td>
<td>&gt; 0.1 µm</td>
<td>Total</td>
<td>Coal</td>
<td>Coke</td>
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<tr>
<td>DF1 Burden supply</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.4</td>
<td>6.6</td>
</tr>
<tr>
<td>DF2 Cast hall</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.9</td>
<td>3.7</td>
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<tr>
<td>DF3 Cyclone</td>
<td>-</td>
<td>-</td>
<td>28.5</td>
<td>2.7</td>
<td>32.6</td>
</tr>
<tr>
<td>DF4 Dust bag/cyclone</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.1</td>
<td>34.9</td>
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<tr>
<td>DF5 Venturi tube</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>DF6 Sludge bin</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
</tbody>
</table>

Table 1
BLAST FURNACE TECHNOLOGICAL DUSTS SIZE DISTRIBUTION AND PHYSICO-CHEMICAL CHARACTERISTICS

Table 2
COMPOSITION AND TYPE OF POWDERED WASTES, BY MICROSCOPICAL ANALYSIS (%)
Optical constituents and textural characteristics

The petrographic analysis shows that the shapes and morphology of the technological solid dusts is a difficult issue because in a metallurgical environment there are many pollution sources. Therefore, the promotion of optical microscopy as a nondestructive method to identify the composition of the wastes that can largely vary, it is of great significance to describe the optical appearance of the carbon/mineral textures and identify the morphological differences [6].

In case of the blast furnace dust samples, a very simple evaluation scheme was used, in which the criteria to distinguish between the petrographic textures representing the structural organization of the organic matter corresponding to different solid carbon particles, considered both the optical texture (isotropic or anisotropic), optical type and size (punctiform, mosaic, fiber, ribbon, domain), origin of the particles and the porosity development.

Table 3
BLAST FURNACE RESIDUAL SOLID DUSTS CHEMICAL COMPOSITION (%)

<table>
<thead>
<tr>
<th>Sample/Waste origin</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>P₂O₅</th>
<th>SO₃</th>
<th>MnO</th>
<th>CaO</th>
<th>PbO</th>
<th>ZnO</th>
<th>TiO₂</th>
<th>Cr₂O₃</th>
<th>SrO</th>
<th>BaO</th>
<th>Cl*</th>
</tr>
</thead>
<tbody>
<tr>
<td>DF1 Burden supply</td>
<td>34.84</td>
<td>5.18</td>
<td>50.10</td>
<td>1.03</td>
<td>5.13</td>
<td>0.73</td>
<td>0.91</td>
<td>0.14</td>
<td>0.62</td>
<td>0.42</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>0.33</td>
<td>0.52</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>0.08</td>
</tr>
<tr>
<td>DF2 Casting hall</td>
<td>8.33</td>
<td>3.70</td>
<td>82.96</td>
<td>0.73</td>
<td>2.36</td>
<td>0.10</td>
<td>0.17</td>
<td>0.13</td>
<td>0.31</td>
<td>0.79</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>0.14</td>
<td>0.23</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>0.06</td>
</tr>
<tr>
<td>DF3 Cyclone</td>
<td>15.52</td>
<td>3.24</td>
<td>63.77</td>
<td>8.21</td>
<td>6.10</td>
<td>0.22</td>
<td>0.76</td>
<td>0.17</td>
<td>0.85</td>
<td>0.5</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>0.27</td>
<td>0.11</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>0.24</td>
</tr>
<tr>
<td>DF4 Dust bag/cyclone</td>
<td>16.28</td>
<td>2.43</td>
<td>69.33</td>
<td>4.11</td>
<td>4.91</td>
<td>0.11</td>
<td>0.32</td>
<td>0.15</td>
<td>0.96</td>
<td>0.29</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>0.50</td>
<td>0.11</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>0.45</td>
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<tr>
<td>DF5 Venturi tube</td>
<td>17.58</td>
<td>6.72</td>
<td>36.35</td>
<td>4.07</td>
<td>10.38</td>
<td>0.82</td>
<td>0.80</td>
<td>0.69</td>
<td>5.59</td>
<td>0.43</td>
<td>&lt;0.10</td>
<td>0.53</td>
<td>13.05</td>
<td>0.19</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>2.85</td>
</tr>
<tr>
<td>DF6 Sludge bin</td>
<td>12.67</td>
<td>4.21</td>
<td>63.10</td>
<td>4.25</td>
<td>6.84</td>
<td>0.20</td>
<td>0.46</td>
<td>0.15</td>
<td>2.19</td>
<td>0.32</td>
<td>&lt;0.10</td>
<td>0.34</td>
<td>3.76</td>
<td>0.09</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>1.43</td>
</tr>
</tbody>
</table>

*Calcination loss

The photomicrographs of figure 1-3 show the typical shape and morphology of the particles identified in different powdered mixtures. The coal particles were investigated either by measuring their random vitrinite reflectance (RmVi). This type of carbon form is typical for low volatile bituminous coals of 0.5-0.7 RmVi% used for the injection into the blast furnace (fig.1 A,B). The size of the particles vary from coarse to very fine and differ also on the wastes sampling point. Depending on the emitting source, they illustrate the presence of organic matter as coal and coke particles which size where smaller to be observed by optical microscopy, but present in aggregates (fig.1 C,D). The coke particles are porous and have mainly anisotropic texture of punctiform, mosaic and flow type. The coke inclusions are of isotropically unmelted coal and inertinite (fig.1 E,F and fig.2 A-F).
Conclusions

This study demonstrates the advantages of using petrographic analysis as a nondestructive and complementary method on investigating the technological powdered wastes released within the blast furnace area, showing satisfactory correlation with the results obtained by physico-chemical methods. It is the single method that can identify the dust particle morphology and the emitting source, if they will rise environmental concerns and, by quantitative assessment can be used to find ways to waste recycle.

The results highlight that type of constituents identified in different proportions in the technological waste samples recovered mainly from purification of blast furnace gas, include: coal dust, coke, iron ore particles and solidified melted metal, and inorganic compounds (as oxides of Fe, Ca, Mg) and other impurities.

Acknowledgments: POSDRU Project /88/1.5/S/61178 support is gratefully acknowledged.

References


16. REHMAT, A., MENSINGER, M., C., Recovery of direct reduced iron from blast furnace dust. In: Second international symposium on extraction and processing for the treatment and minimization of wastes, 1996, p. 27–30


Manuscript received: 22.09.2014