Assessment of heavy metal content and leaching characteristics of ash from a coal-fired power plant in Romania

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Abstract: The study investigates the heavy metal content of ash from one major coal-fired power plant in South-Western Romania. The ashes were analysed for the presence of As, Cu, Pb, Zn, Ni, Cr, Mn, Co, V, Mo, Ba, Cd, Hg. Major, minor and trace element concentrations in solid samples were determined by means of X-Ray Fluorescence (XRF), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

Detectable levels over 100 ppm of some of the minor elements were found in ash recovered from the waste dumps. In this regard, experimental results indicate that toxic trace metals may leach out and contaminate soils as well as surface water and groundwater. This can generate health, environmental and land-use problems. The leachates were analyzed using ICP-MS and ICP-OES. Leaching tests that were performed showed that total solubilised substance (TDS) and heavy metals are below the limits of Romanian Ministry Order (RMO) 2005/95, on waste acceptance criteria for disposal in landfills.

Key-Words: Coal ash, Combustion, Heavy metal, Leaching

1. Introduction

The production of energy by burning fossil fuels is widely considered as one of the major sources of anthropogenic particles in the overall pattern of major polluters of the environment. This refers both to air pollution by releasing large amounts of greenhouse gases and acidifying, particulate matter, and large quantities of waste (ash and slag) deposited on wide areas by landfill [1].

The severe impact on the environment caused by the solid waste generated from industrial processes, include soil pollution (mainly due to the wind which drive the light weight materials from landfills area to cropland or human communities), pollution of surface and groundwater. Residues such as ash and slag are usually contaminated with toxic heavy metals. These metals leach out after contact with water, thus polluting the groundwater and soil.

Because of major implications on the environment and human health, numerous studies and researches on the assessment of heavy metal content and disposal in mostly of the thermal power plants throughout the world have been carried out [2-19]. The studies have been extended to heavy metals leachability [20-24] and their toxic effects due to exposure to ash by skin contact, inhalation of fine dust particles and potable water that could raise population health risks [25-29].

In Romania, one of the coal power plants in Gorj County is Energy Centre Turceni (ECT) with an installed capacity of 2310 MW. It uses as fuel, lignite with significantly contents of xylite, extracted from quarries in the Oltenia coal basin. Coal is typically of Pliocene origin, for burning into the power plant being ground to fineness that 80% passes through a sieve of 74 mm, and 50% through the sieve of 300µm. The physical-chemical composition of ash and slag depends on physical-chemical composition of parent coals and of a series
of particular factors, as are the coalification degree and the petrographic composition [30].

Lignite has high content of minerals (clays, quartz, feldspar, calcite, dolomite, pyrite, etc.), presented both as finely dispersed, bands or nodules of centimetres order. During the combustion process, the mineral matter in coal is partially melted and turned into very fine granules with various shapes, which are driven by combustion gas stream.

From coal combustion for producing electricity results ash and slag that are disposed by land filling, so that were built deposits to store huge quantities of this waste mainly at Ceplea Valley belonging to ECT, located at 3.3 km from ECT. The compartment no.1 of Ceplea Valley deposit affects 52.64 ha, the amount of ash deposited being of 13,034,470 m$^3$ and the compartment no.2 of Ceplea Valley deposit affects 45.40 ha and the amount of ash deposited is of 10,825,795 m$^3$. Ash and slag resulting from lignite burning in ECT power plant are discharged by hydro-mixture (with a dilution of 1:10) to the wastes deposits [31].

Ash and slag are characterized by a very low organic matter when the combustion takes place with good yield. Ash and slag have a high content of heavy metals and other substances that are known to be harmful to health. Potentially toxic trace elements in coal are: arsenic, barium, beryllium, chromium, copper, lead, mercury, molybdenum, nickel, radium, selenium, thorium, uranium, vanadium and zinc. In addition, soluble sulphates are present in variable concentration-dependent on sulphur content of coal. The ash concentration in most trace elements is about 10 times the initial concentration of coal.

In national and international lists of waste, ash and slag are considered inert waste, or no dangerous (e.g. No dangerous waste in the European Waste List - Decision 2001/118/EC, and also forms the „green” side of the list of OECD Decision C (92) 39/Final).

The present study investigates the heavy metal content and leaching characteristics of ash and slag stored in Ceplea Valley dumps of ECT power plant, situated in the South-Western side of Romania.

2. Materials and methods

From the compartment no.2 of Ceplea Valley were chosen 14 points, and 14 elementary samples were taken from equidistant points on a surface of approx. 4 hectares (about 8% of the deposit) and a depth of 0.5 to 0.7 m following basic sampling methodologies in accordance to the national standards of sampling (SR ISO 1988:1996). The ash and slag mixture taken from the dump were light gray to dark grey in colour and mostly regularly shaped. The amount of each elementary sample was of 10 kg. Of the elementary samples were made four cumulative average samples (A, B, C, D) of 30-40 kg which were prepared for laboratory analyses according to SR ISO 5069-1 and 2:1994. Laboratory tests in order to establish the chemical composition and trace elements of the supplied coal ash and slag have been carried out. The methods used were: X-Ray Fluorescence (XRF) using an Axios-Panalitical device and the corresponding (IQ+) soft allowing qualitative and semi quantitative evaluation of chemical composition and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES TELEDYNE) for major heavy metals determination.

In order to assess the potential environmental impact of the ashes from ECT, leaching tests were performed for the four average samples (A, B, C, D). The leaching test was conducted according SR – EN 12457/1-4 (for L/S=10 l/kg), and the limit values are those provided by (RMO) 2005/95. This order transposes Council Decision 2003/33/EC establishing criteria and procedures for accepting waste at landfills as a result of art. 16 and Annex II of Directive 1999/31/EC. For minor elements (under 100ppm) found in the ash and slag leachate, it was used Inductively Coupled Plasma Mass Spectrometry (ICP-MS THERMO X) and for Hg determination the Atomic Absorption Spectrometry Cold Vapours (HYDRA AA). Beside the assessment of heavy metals in leachate, were determined either: pH (by potentiometer method), total dissolved substances (TDS) by conductometry using INOLAB conductometer, fluorine (volumetric method, Hirschman biurette), chlorine (volumetric method, Hirschman biurette), sulphates (gravimetric method).

3. Results and discussion

Factors determining the ash and slag characteristics are: chemical and mineralogical composition of inert material; oven temperature and the duration of stationary combustion; cooling rate; fineness of grinding of coal; the particle size of mineral matter; progressing and control the combustion process; type of deducting installations.

Depending on the coal source, the conditions of coal preparation before burning, and burning technology, the chemistry of the ash and slag varies considerably. The minerals of ash and slag are silicates, carbonates, sulphates, sulphides, oxides of
aluminium, iron, calcium, magnesium, potassium and sodium. In the combustion zone the minerals are dehydrated and lose water of crystallization, carbonate thermally dissociates as CaO and SO$_2$. 

Due to the minerals high speed movement by the high temperatures, outside oxidation and dissociation processes, other reactions do not occur. Sequences of chemical reactions that occur in the boiler include dehydration, decomposition with the formation of the gases CO$_2$, SO$_2$ and SO$_3$ and alkali volatilisation. Ash is driven by exhaust gases to the chimney, its retention occurring in several areas on the gas route. Coarse particles, partially melted, are stored at the bottom of the burning chamber in the form of clusters with dimensions of 0.02...30mm (either size can also have more than 2mm), being the ash and slag. The rest of the remaining particles in the air stream undergo melting and liquid droplets suspended have spherical shape. Quickly driven out of the hot zone to cool them suddenly in a quasi-spherical contour preserving solidification and amorphous structure; some particles that are cooled more slowly may suffer partial recrystallization. The selenium, thorium, uranium, vanadium and zinc.

Table 2 shows the metal concentration of an ash average sample, leaching limits and the leachability of the A, B, C and D samples. Note that all the values are below the limits allowed in RMO 2005/95. Jones has described that As, B, Mo, and Se in coal fly ash are likely to leach out, because those elements tend to form hydrophilic oxides to be dissolved as oxyanion forms [32].

An important indicator for the analysis of the leaching test results is represented by ‘% leaching’. This value was defined as [(leaching amount) / (element concentration in fly ash)]×100. The heavy metals with high values of % leaching is Mo (between 5.6 and 8.3 %), followed by Hg (between 1.8 and 3.2 %), Cu (between 1.7 and 1.9 %) and Se (between 1.7 and 2.9 %). For other heavy metals the % of leaching values are below 1.

Also, all the values for the pH, TDS, F, Cl$^-$ and SO$_4^{2-}$ are below the leaching limits allowed in RMO 2005/95, for all the A, B, C and D ash and slag average samples taken from Ceplea Valley, see Table 3.

### 4. Conclusion

The study investigates the heavy metal content and leaching characteristics of ash and slag on a particular coal-fired thermal power plant in South-

The leaching tests showed that heavy metals, such as As, Ba, Cd, Cu, Hg, Mo, Pb, Se, Zn in ash leached out at below the standard limit. Also, all the values for the pH, TDS, F, Cl$^-$ and SO$_4^{2-}$ are below the leaching limits allowed in RMO 2005/95, for all the investigated ash and slag samples.

### Acknowledgements

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References


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**Annex**

### Table 1. Chemical composition of average ash and slag samples, % wt.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>CaO</th>
<th>MnO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>P₂O₅</th>
<th>SO₃</th>
<th>CL</th>
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<tr>
<td>A</td>
<td>49.7</td>
<td>0.77</td>
<td>20.95</td>
<td>8.96</td>
<td>2.48</td>
<td>9.25</td>
<td>0.08</td>
<td>0.21</td>
<td>1.55</td>
<td>0.2</td>
<td>0.59</td>
<td>5.06</td>
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<td>B</td>
<td>40.8</td>
<td>0.67</td>
<td>15.7</td>
<td>8.4</td>
<td>2.36</td>
<td>13.75</td>
<td>0.08</td>
<td>0.19</td>
<td>1.35</td>
<td>0.21</td>
<td>4.6</td>
<td>11.69</td>
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<tr>
<td>C</td>
<td>45.24</td>
<td>0.76</td>
<td>19.15</td>
<td>8.65</td>
<td>2.35</td>
<td>9.45</td>
<td>0.07</td>
<td>0.2</td>
<td>1.44</td>
<td>0.24</td>
<td>1.52</td>
<td>10.73</td>
</tr>
<tr>
<td>D</td>
<td>46.8</td>
<td>0.68</td>
<td>19.4</td>
<td>8.9</td>
<td>2.42</td>
<td>9.35</td>
<td>0.08</td>
<td>0.25</td>
<td>1.42</td>
<td>0.24</td>
<td>1.38</td>
<td>8.88</td>
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### Table 2. Metal concentrations on ash and slag leachability (mg metal/kg ash)

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Ba</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Hg</th>
<th>Mo</th>
<th>Ni</th>
<th>Pb</th>
<th>Se</th>
<th>Zn</th>
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<tr>
<td>Ash and slag average</td>
<td>101.1</td>
<td>895.4</td>
<td>1.27</td>
<td>102.5</td>
<td>90.9</td>
<td>0.05</td>
<td>5.5</td>
<td>108.5</td>
<td>69.5</td>
<td>4.1</td>
<td>174.1</td>
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<tr>
<td>Leachability limit</td>
<td>2</td>
<td>100</td>
<td>1</td>
<td>10</td>
<td>50</td>
<td>0.2</td>
<td>10</td>
<td>10</td>
<td>0.5</td>
<td>50</td>
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<tr>
<td>Leachability sample A</td>
<td>0.40</td>
<td>0.58</td>
<td>&lt;0.01</td>
<td>0.04</td>
<td>1.80</td>
<td>0.0015</td>
<td>0.43</td>
<td>0.12</td>
<td>0.06</td>
<td>0.07</td>
<td>0.5</td>
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<tr>
<td>Leachability sample B</td>
<td>0.37</td>
<td>0.74</td>
<td>&lt;0.01</td>
<td>0.04</td>
<td>1.59</td>
<td>0.0009</td>
<td>0.41</td>
<td>0.14</td>
<td>0.10</td>
<td>0.09</td>
<td>0.5</td>
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<tr>
<td>Leachability sample C</td>
<td>0.27</td>
<td>0.92</td>
<td>&lt;0.01</td>
<td>0.04</td>
<td>1.56</td>
<td>0.0011</td>
<td>0.31</td>
<td>0.21</td>
<td>0.21</td>
<td>0.06</td>
<td>1.09</td>
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<tr>
<td>Leachability sample D</td>
<td>0.28</td>
<td>0.72</td>
<td>&lt;0.01</td>
<td>0.05</td>
<td>0.67</td>
<td>0.0016</td>
<td>0.46</td>
<td>0.25</td>
<td>0.25</td>
<td>0.08</td>
<td>0.55</td>
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Table 3. The value obtained for pH, TDS, F, Cl and SO$_4^{2-}$ (mg /kg ash)

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>TDS</th>
<th>F</th>
<th>Cl</th>
<th>SO$_4^{2-}$</th>
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<td>Leachability limit</td>
<td>7.5-8.0</td>
<td>60000</td>
<td>150</td>
<td>15000</td>
<td>20000</td>
</tr>
<tr>
<td>Leachability sample A</td>
<td>7.53</td>
<td>526</td>
<td>0.5</td>
<td>&lt;0.50</td>
<td>316.90</td>
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<tr>
<td>Leachability sample B</td>
<td>7.27</td>
<td>1833</td>
<td>2.2</td>
<td>&lt;0.50</td>
<td>1658.50</td>
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<tr>
<td>Leachability sample C</td>
<td>7.67</td>
<td>926</td>
<td>0.6</td>
<td>&lt;0.50</td>
<td>680.00</td>
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<tr>
<td>Leachability sample D</td>
<td>7.56</td>
<td>1491</td>
<td>1.6</td>
<td>&lt;0.50</td>
<td>1243.00</td>
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