REDUCE OF THE THERMAL POWER PLANT IMPACT UPON ENVIRONMENT BY REUSE OF BOTTOM ASH AS A SOURCE OF RAW MATERIALS FOR OTHER INDUSTRY

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ABSTRACT: *Lignite power plants from Oltenia generates yearly important amounts of slag and ash due to the high ash of lignite. Slag and ash storage involves the coverage of large areas of land generating environmental impact by air, water, and soil pollution. The reuse of ash and slag as raw material for other industry represent an economic way to reduce the environmental impact. The paper aims to present some possibilities of ash and slag from thermal power plant use based on physical and chemical composition.*

KEY WORDS: *coal ash, rare metals, rare earth elements.*

1. INTRODUCTION

In Romania, the energy industry generates yearly great amounts of ash and slag which claims a lot of work for transport and storage by landfill. The Oltenia Lignite Basin deposits are located in the Oltenia region (Gorj county, Romania), and the coal is mined in open pits by the Energy Complex Oltenia (CEO), and burned in two of the largest Romanian power plants.

The impact due to lignite burning in the thermal power plants of South-West Oltenia represents a major environmental and economical concern in this region. Currently, large quantities of ash are landfilled causing negative environmental impacts such as leaching of potentially toxic substances (for example heavy metals) into soils and groundwater. The best way to solve the disposal problem of ash is to decrease the quantity for disposal with utilization of ash as raw materials in other industries.

The production of electricity in thermal power plants generates significant amounts of slag and ash, which are characterized by a very low content of organic matter when the combustion process is carried out with good yield and the geotechnical properties are good so that the residues can be used for various purposes in construction field [1].

By the technological process results two kind of ash: fly ash (with a diameter <0,25 mm), which is collected from flue gases through electrostatic precipitators (ESP), and from there it is mixed with water and sent to a pumping station or is collected in silo in order to delivery in cement industry; bottom ash, with a diameter 0.25 – 1 mm and more, which is collected at the furnace bottom (Figure 1).

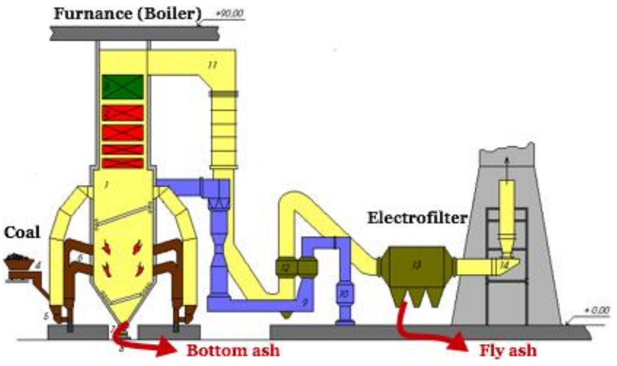

Figure 1. Ash generation in thermal power plant

Both of them - bottom ash and slag (this last one after crushing) and fly ash - are transported in the form of hydro-mixtures (solid/liquid 1:8 and 1:10, respectively) or dense slurry into landfills, generating a strongly impact upon environment [2 - 4].

The physical and chemical composition of ash depends of the coal being burned coal in boiler, coal prepare conditions and the combustion technology. For thermal power plant from Oltenia, the coal quality is characterized by [3]:

- Calorific power: Q=1.740 kcal/kg
- Ash: A=39.5%,
- Moisture: W=41.6%
- Sulfhur S=1.2%.

Due to high ash content of lignite from the Oltenia coal basin (approximately 20-40%), the ash amounts generated yearly by the most important thermal power plants of Romania (Rovinari and Turceni) are very high [3]:

- approximately 3 millions tons/year at Rovinari thermal power plant;,
- approximately 2,3 millions tons/year atTurceni thermal power plant.

The ash landfilled occupied surfaces are as follows:

1. Thermal power Rovinari:

- Deposit Girla: 160 ha, with a storage capacity of approximately 32 millions m^3,
- Deposit Cicani-Beterega: 284.7 ha, with a storage capacity of approximately 74 millions m^3,
- Deposit Balta Uncheasului: 34.2 ha, with a storage capacity of approximately 6 millions m^3

2. Thermal power Turceni:

- Deposit no. 1 Valea Ceplea: 265 ha, with a storage capacity of approximately 42 millions m^3,
- Deposit no. 2: 200 ha, with a storage capacity of approximately 32 millions m^3.

2. BOTTOM ASH – A POTENTIAL SOURCE FOR CRITICAL ELEMENT

Within the project "*Assesment of possible recycling directions of heavy & rare metals recovered from combustion waste products – RAREASH*" (under the scope of the "2nd ERA-MIN Joint Call (2014) on Sustainable Supply of Raw Materials in Europe") landfilled Oltenia lignite (Romania) bottom ash was selected to assess their content in rare earth elements includes metals from the Lanthanide group (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) plus Scandium and Yttrium due to the huge amounts of ash accumulated after decades of landfilling [5]. The information obtained within this project will contribute to the recycling of these bottom ashes. To have a coverage and representativeness of bottom ash in this landfill over the years, and to search rare earth elements plus Ytrium and Scandium (REE+Y) anomalies inside the deposit, five areas were defined, each comprising nine drilling points, placed equidistant (50 m), respectively areas of 2.25 hectares comprising 112,500 m^3 ash per each depth (approx. 130 thousand tons per each drilling area and depth) (Figure 2) [3, 6].
After cumulating 180 individual samples, resulted 20 cumulative average samples (A, B, C, D and E, to shares -5, -10, -15 and -20m depth). Also, using the same scheme, five cumulative average samples were collected at zero level (A, B, C, D, E ground level), in the five selected areas of the deposit. In this study

a total of 25 samples were studied (about 30 kg each) and labelled as follows taking into account the five areas defined and the sampling depth: AM-0 to AM-20; (...); EM-0 to EM-20 [3, 6].

One of the basic principles of industrial waste recycling procedures is that of developing technologies that will not in turn generate other waste that will again represent natural environmental contamination factors.

In the RAREASH project context, this goal require two elements of high specificity:

a. Heavy and Rare metals recovery technology from bottom ash involves a specific chemical processing stage, after that can results some components (specially reactive solutions) that require specific neutralization treatments.

b. In ashes composition, the metallic elements are present in ppm concentrations, which means after their recovery process a sterile will result equivalent to the initial quantities of processed ash in terms of mass ratio [3].

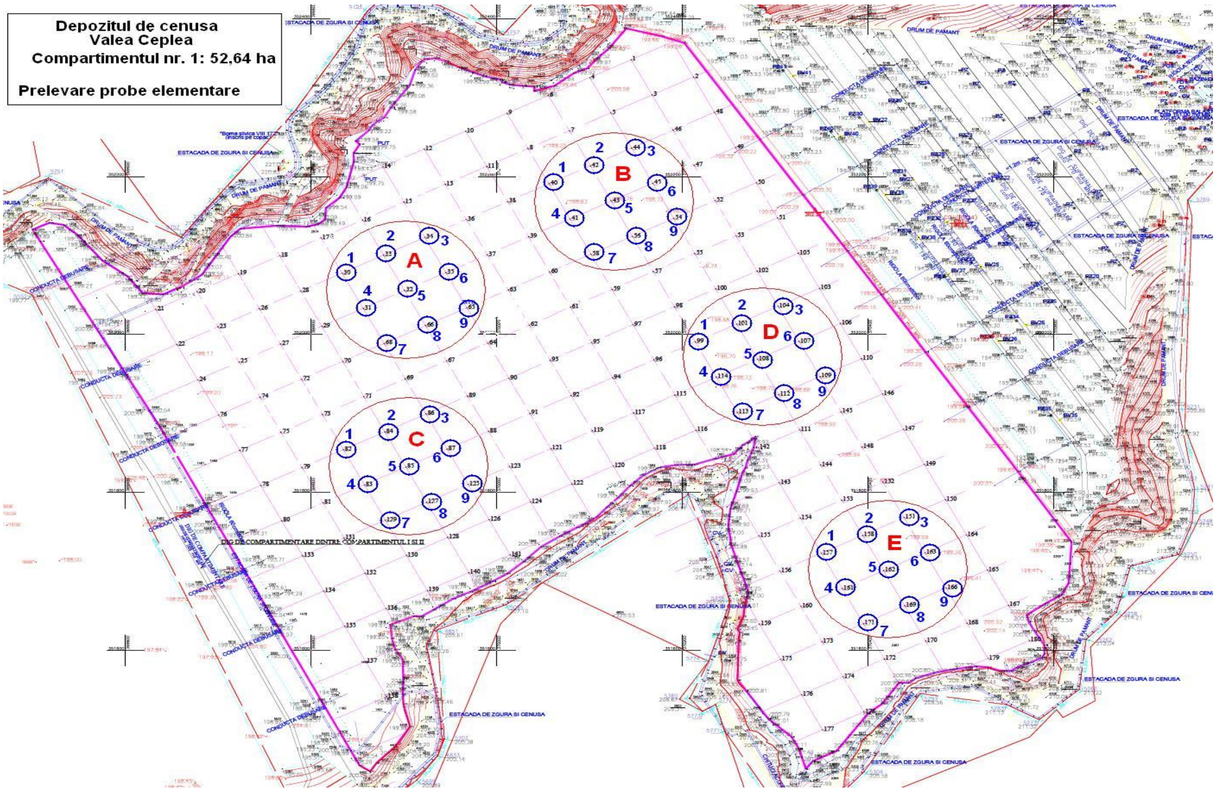

Figure no. 2. Sampling grid areas at Ceplea Valey landfill.

3. MATERIALS AND METHODS

In order to recovery heavy and rare metals from ash, within RAREASH project, the ash samples were chemical treated in acid environment, and then cleaned and dryed. The chemical analysis of the ash major oxide elements was made on average sample before and after specific chemical attack. The results of analyses are presented in Table 1 [3].

Technical analyzes were also made in these ash samples in order to emphasize the variation of parameters regarding organic matter (carbon) content. The results of analyses are presented in Table 2 [3].

Table 1. Chemical analysis of ash before and after chemical atack.

Avarage sample	Chemical analysis before chemical attack (%)							
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O
D10	52.86	0.87	22.08	9.74	2.75	8.42	0.21	1.44
D15	54.70	0.89	21.25	9.10	2.62	8.25	0.59	1.44
Avarage sample	Chemical analysis after chemical attack (%)							
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O
D10	69.79	1.05	16.67	5.96	1.58	2.75	0.50	1.29
D15	71.68	1.03	15.95	5.41	1.43	2.36	0.55	1.28

Table 2. Technical analysis of ash before and after chemical analyses (M - moisture; A – ash; V – Volatile matter)

Average sample	Technical analysis before chemical attack				Technical analysis after chemical attack			
	M %	A %	V %	C_{fix} %	M %	A %	V %	C_{fix} %
D10	2.18	94.05	4.44	0.63	19.19	86.34	12.23	1.43
D15	2.18	93.93	4.93	1.14	16.3	88.73	9.75	1.52

These two result grups of laboratory analyzes offers important information regarding compositional changes of ash after the chemical attack specific procedure in order recover heavy and rare metals from ash.
The samples were sieved to obtain size fractions for REE+Y+Sc analysis in order to find any positive anomaly that may justify a pre-concentration process based on these bottom ashes sieving.

One bottom ash composite sample made from all drilling core samples was air dried and

screened to remove the >4 mm material, which was then crushed to <4 mm. This step was necessary because above 4mm the size of the particles was very variable. The remaining sample was automatically screened using a set of seven sieves of >2 mm, >1 mm, >500 µm, >250 µm, >125 µm, >90 µm, >63 µm (10, 18, 35, 60, 120, 170, and 230 mesh, respectively),

and each fraction weighted. The crushed <4mm was combined with the >2mm sample portion and thoroughly mixed [6].
Two replicates of each bottom ash sample, crushed to <75 µm, were analyzed at the Bureau Veritas analytical laboratories (Vancouver, Canada. Accredited laboratory nº 720 by ISO/IEC 17025:2005, using in house certified reference material or in its absence samples are certified against internationally certified reference materials such as CANMET and USGS standards) for trace elements using ICP-MS. Prior to the ICP-MS analysis, 0,25 g split is digested in HNO_3-$HClO_4$-HF mixed solution, and then taken to dryness. The residue is dissolved in HCl and then is diluted to a constant volume with pure water [6].

Table no. 3. Concentration of REY+Sc in Oltenia lignite bottom ash from Ceplea Valley, and in the Upper Continental Crust (UCC; Rudnick and Gao, 2014 [7])

Analyte	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Unit	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
UCC	14.0	21.0	31.0	63.0	7.1	27.0	4.7	1.0	4.0	0.7	3.9	0.8	2.3	0.3	2.0	0.3
AM-0	11.7	19.8	21.5	53.7	6.2	24.1	4.8	1.0	4.6	0.6	3.7	0.8	2.2	0.4	2.1	0.3
AM-5	12.6	21.3	28.3	67.8	7.7	31.3	5.6	1.2	5.5	0.8	4.4	0.9	2.4	0.3	2.3	0.3
AM-10	12.4	20.5	24.2	57.6	6.8	24.6	5.7	1.1	5.7	0.7	4.3	0.9	2.3	0.3	2.3	0.3
AM-15	12.4	21.5	26.5	64.0	7.5	27.8	5.8	1.2	5.3	0.7	4.7	0.9	2.4	0.4	2.4	0.4
AM-20	12.5	21.7	26.5	62.9	7.1	27.9	5.9	1.2	5.3	0.8	4.8	0.9	2.6	0.4	2.3	0.4
BM-0	11.1	20.4	21.9	52.3	5.9	23.5	5.2	1.1	4.9	0.7	4.3	0.9	2.4	0.3	2.1	0.3
BM-5	12.6	21.7	29.0	67.8	7.4	29.5	5.7	1.2	5.5	0.7	4.8	1.0	2.5	0.3	2.5	0.4
BM-10	11.8	19.3	23.8	56.4	6.5	26.0	5.5	1.1	4.8	0.7	3.7	0.9	2.4	0.4	2.0	0.3
BM-15	12.9	22.2	27.9	65.8	7.5	27.9	5.7	1.2	6.5	0.7	4.4	1.0	2.7	0.4	2.4	0.4
BM-20	12.1	20.6	26.1	63.5	7.4	28.2	5.2	1.2	5.4	0.7	4.3	0.9	2.4	0.3	2.5	0.4
CM-0	12.4	21.8	26.4	62.6	7.0	26.4	5.7	1.4	6.1	0.8	4.3	0.9	2.7	0.4	2.1	0.3
CM-5	12.0	21.9	26.8	63.7	7.6	28.0	5.5	1.2	5.1	0.8	4.2	0.9	2.6	0.4	2.4	0.3
CM-10	11.4	19.9	23.5	57.1	6.6	26.6	5.6	1.1	4.9	0.7	4.3	0.9	2.3	0.4	2.2	0.4
CM-15	12.2	20.6	25.7	60.2	6.7	26.7	5.4	1.2	5.4	0.7	4.7	0.9	2.5	0.3	2.3	0.4
CM-20	11.8	20.8	26.4	61.4	6.7	25.5	5.4	1.2	4.8	0.7	4.3	0.8	2.4	0.3	2.2	0.3
DM-0	11.4	23.2	33.6	75.4	8.5	30.5	6.5	1.3	5.8	0.7	4.6	1.0	2.7	0.3	2.5	0.4
DM-5	11.4	20.4	25.0	58.3	6.7	25.6	5.0	1.2	5.3	0.6	4.2	0.8	2.5	0.4	2.3	0.3
DM-10	10.4	18.6	20.1	49.4	5.6	22.6	4.8	1.1	5.1	0.6	4.1	0.8	2.1	0.3	2.1	0.3
DM-15	11.1	19.0	21.8	52.0	6.0	22.0	4.9	1.0	5.1	0.6	3.7	0.8	2.2	0.4	2.1	0.4
DM-20	11.5	19.0	23.7	56.9	6.5	24.8	5.4	1.2	4.9	0.7	4.0	0.8	2.3	0.4	2.2	0.3
EM-0	10.7	19.2	23.8	56.0	6.4	24.2	5.1	1.0	4.9	0.6	4.2	0.8	2.5	0.3	2.3	0.3
EM-5	12.4	22.6	28.0	66.0	7.5	29.0	6.0	1.1	5.0	0.7	4.3	0.9	2.4	0.3	2.1	0.3
EM-10	12.6	21.3	27.9	65.4	7.5	29.0	5.9	1.1	5.7	0.7	4.5	0.9	2.3	0.3	2.3	0.3
EM-15	11.6	21.3	24.8	58.4	6.8	25.3	5.9	1.2	4.9	0.6	4.0	0.8	2.0	0.4	2.1	0.3
EM-20	11.3	19.0	22.6	55.0	6.2	24.8	5.1	1.0	4.7	0.6	3.4	0.8	2.2	0.3	2.1	0.3
Average	11.9	20.7	25.6	60.5	6.9	26.5	5.5	1.1	5.2	0.7	4.2	0.9	2.4	0.3	2.2	0.3
Depth average																
Surface	11.5	20.9	25.4	60.0	6.8	25.7	5.5	1.2	5.3	0.7	4.2	0.9	2.5	0.3	2.2	0.3
5 meters	12.2	21.6	27.4	64.7	7.4	28.7	5.6	1.2	5.3	0.7	4.4	0.9	2.5	0.3	2.3	0.3
10 meters	11.7	19.9	23.9	57.2	6.6	25.8	5.5	1.1	5.2	0.7	4.2	0.9	2.3	0.3	2.2	0.3
15 meters	12.0	20.9	25.3	60.1	6.9	25.9	5.5	1.2	5.4	0.7	4.3	0.9	2.4	0.4	2.3	0.4
20 meters	11.8	20.2	25.1	59.9	6.8	26.2	5.4	1.2	5.0	0.7	4.2	0.8	2.4	0.3	2.3	0.3

4. RESULTS

The concentrations of the REE+Y+Sc analysis are listed in Table 3 [6]. The concentration of REE+Y+Sc in all the samples studied is similar, which is an indicator that the type of coal, the combustion conditions, and conditions inside the landfill did not change for decades.

ACKNOWLEDGMENT

„This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CCCDI – UEFISCDI, project "*Assesment of possible recycling directions of heavy & rare metals recovered from combustion waste products – RAREASH*" project under the scope of the "2nd ERA-MIN Joint Call (2014) on Sustainable Supply of Raw Materials in Europe", Contract number 28/2015.

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