Strategy for Ecologically Closure of Ash and Slag Deposits Using Energetic Crops

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In the field of renewable energy, national targets imposed by the European Directive on promoting the use of energy from renewable sources is to reach 24% of gross final consumption of energy by 2020. This paper presents a solution for this target and for sustainable management of ash and slag closed deposits by plantation of energetic crops. Process of plantation was assessed by tracking energetic crops by determining the capacity of metals accumulation in wood biomass, correlations between the crops diameter and height, chemical composition of ash. The obtained data were compared with similar data recorded for other intensive crops. Amount of biomass harvested from 5.3 kg/m^2 green table (after 3 years) reveals a good development and production of plantation wood, grown on the surface of ash and slag deposit. Based on obtained experimental data, we propose a model of vegetation with energy plants (Salix sp.) of a deposit of ash and slag after its closure was achieved. By implementing experimental model these surfaces can be reinserted in landscape and economic circuit, being in accordance with the provisions of Order No. 757 of 26/11/2004 for approval the Technical Normative of Waste Storage.

Keywords: energetic crops, renewable sources, sustainable management

Ashes and slag deposits represent a major source of environmental pollution. Ash is a major by-product of coal-fired power plants. Ashes contain amorphous ferro-aluminosilicate minerals (Si, Al, Fe, Na, K Ca, Mg, etc.) with physical-chemical and mineralogical characteristics that depend on the coal's quality, combustion process, duration and storage conditions [1-3].

The ash particles are weakly fixed, they are light and can spread over large distances causing a negative impact upon the environment, flora, fauna and human health, causing soil and groundwater pollution, reduction of photosynthesis capacity by dust deposition on plants and trees, etc. [4-6].

In order to fix and stabilize ash layers within the warehouse and to minimize the phenomenon of deflation, research works in recent years were focused on the vegetation of ash and slag deposits [7-9]. Several studies have shown that deposition vegetation has been effective in reducing pollution caused by wind-induced ash and ash particles, improving habitat quality and aesthetic appearance of deposits [7, 10, 11]

A viable and sustainable strategy for the transformation of ash and slag deposits into economically productive sites would be the selection and use of plants of high economic value.

Stabilization of cultivations should take into account, besides the economic aspects and a viable strategy of environmentally friendly plant cover, with biological requirements, also the economic efficiency [12,13].

The objective of this study was to investigate the potential of energy crops in ash vegetation. Energy crops have a root system and rhizomes that reach up to 1 meter deep in the soil, are known as intensive crops with plant/logging exploitations of approx. 25 years [12,14]. Compared to their ecological qualities (rapid and deep soil fixation, rapid growth, etc.), energy crop species can produce significant amounts of biomass, usable for energy purposes (renewable energy sources) [15]. Obtaining renewable resources is also in line with the European Strategy for smart, sustainable and inclusive growth - Europe 2020 through Objective 3 on Climate Change and Sustainable Use of Energy [16]. To investigate the growth potential of *Salix sp.* on ash and slag deposits, the experiments were carried out in situ on an ash and slag deposit. The growth and development of plants on the ash and slag deposit was compared to that obtained from energy crops grown on a reference soil (nursery). In order to obtain information on plant's adaptation, several physical-chemical parameters of topsoil and *Salix sp.* plants have been investigated after their growth. To evaluate the feasibility of cultivating *Salix sp.* on a large scale agricultural land preparation works were carried out consisting on the fertilization of the upper layers of ash with stabilized sludge resulted from an urban wastewater plant [17,18].

Experimental part

Materials and methods

Presentation of the ash and slag deposit

The experimental studies were carried out in-situ on the Utvin ash and slag deposit located 10 km South of the city of Timisoara. Ash and slag deposited results from burning lignite in the district heating plant. For physical-chemical characterization (table 1) of the upper layers of ash samples were taken from the depth of 20-40 cm.

In table 1 are presented the reference values according to Order No.756/1997 [19] and Order No.344/708/2004 [19] of the Romanian environmental legislation.

The reaction of upper layers is slightly acidic (*p*H = 6.2). Analyzed ash and slag contains a small amount of organic matter, 8%. The total nitrogen content is low (0.201%). The

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Parameter	Measured Units	Values	Normal values / Alert threshold*[18]	Limit values for soil metal concentration [19]
pH	pH units	6.2	-	> 6,5
Humidity	%	49.3	-	-
Volatile matter	%	8.2	-	-
Total N	%	0.201	-	-
Total P	mg/kg d.m.	123	-	-
Cd	mg/kg d.m.	0.34	1 /5	3
Cr	mg/kg d.m.	111	30 / 300	100
Cu	mg/kg d.m.	46.3	20 / 250	100
Ni	mg/kg d.m.	39.7	20 / 200	50
Pb	mg/kg d.m.	167	20 / 250	50
Zn	mg/kg d.m.	135	100 / 700	300
Fe	mg/kg d.m.	2987	-	-
Mn	mg/kg d.m.	269	900 / 2000	-

Notes: d.m. = dry matter
**values for soils with less sensitive use*

Table 1
PHYSICO-CHEMICAL CHARACTERISTICS OF THE UPPER LAYER OF ASH AND SLAG IN THE EXPERIMENTAL LOTS

soil is poorly stocked with small contents of P (123 mg P/ kg d.m.).

It was found that iron content is highest, up to 2.9 g/kg d.m. Slag and ash contain amounts of Cd and Mn below normal values, but Cr, Cu, Pb, Zn and Ni exceed the values for a normal soil, according to Order No.756/1997 of the Romanian environmental legislation [19]. No analyzed metal presented values above the alert threshold for less sensitive soil. The analyzed metals (except Pb) did not exceed the maximum admissible value in accordance with Order No. 344/708/2004 [20].

Characterization of stabilized sludge

To increase the percentage of organic matter and N: P: K the upper layers of ash and slag were fertilized with stabilized sludge generated from a municipal wastewater treatment plant (WWTP sludge). Sludge stabilized on drying beds loses its pathogenic potential. Spread on land and embedding on the same day limited the dispersion of residual pathogenic potential. Protecting access to slag and ash deposits minimized the likelihood of spreading infectious germs [21]. The amount of stabilized sludge used in the experimental study was 2.5 kg/m^2.

The stabilized sludge is predominantly organic - the content of the organic substance is 69.78%. The sludge contains nutrients: 3.8% total nitrogen and 0.95% phosphorus. Also, an important aspect of the experiment was that the sludge contains heavy metals.

The analyzed metals did not exceed the max. admissible value in accordance with Order No. 344/708/ 2004 of the Romanian environmental legislation on the approval of technical norms for the protection of the environment, and in particular the soil, when the sludge from the treatment plants is used in agriculture.

By comparing the content of metals in the sludge with those in ash and slag it was found that Cd, Mn and Zn were in smaller quantities in the deposit than in the sludge. The other analyzed metals Cr, Cu, Fe, Ni, Pb were in larger quantities in the ash and slag deposit.

Determination of metals (Cd, Cu, Cr, Ni, Pb, Zn, Mn) in the upper ash and slag layer, soil and sludge was performed according to ISO 11047-99 [22]. The principle of the method consists in the determination by atomic absorption spectrometry of metals from a soil extract in aqua regia obtained according to ISO 11466-99 [23] using an Avanta Atomic Absorption. In the case of *iron determination,* the ash, soil or sludge sample were prepared according to ISO 11466:1999 and the analysis of the extract were carried using the same equipment [24]. *Determination of metals* (Fe, Cu, Cd, Cr, Ni, Pb, Zn, Mn) *from plants* was performed according to ISO 6869:2002 [25]. The vegetable mass

Parameter	Measured Units	Values	Limit values [19]
pH	pH units	8.2	-
Humidity	%	74.5	-
Volatile matter	%	69.8	-
Total N	%	3.84	-
Total P	mg/kg d.m.	9507	-
Cd	mg/kg d.m.	3.43	10
Cr	mg/kg d.m.	42.6	500
Cu	mg/kg d.m.	39.4	500
Fe	mg/kg d.m.	364	-
Mn	mg/kg d.m.	1248	-
Ni	mg/kg d.m.	42.6	100
Pb	mg/kg d.m.	46.4	300
Zn	mg/kg d.m.	325	2000
K	mg/kg d.m.	3158	-
BTEX	mg/kg d.m.	<0.01	-
PCB	mg/kg d.m.	<0.1	0.8
TOC	%	32.5	-

Table 2
CHARACTERISTICS OF STABILIZED SLUDGE USED FOR FERTILIZATION OF UPPER LAYERS OF ASH AND SLAG

sample, after calcination at 525 ± 25°C, was dissolved with hydrochloric acid. The solution was analyzed by atomic absorption spectrometry using an Avanta Atomic Absorption Spectrophotometer. All experiments data presented in the present paper represent the average of three samples.

The transfer factor (TF) was determined by the ratio between the amount of metal present in the plant stem (Cp) and the amount of metal from soil (Cs) [26]. TF parameter represents the amount of metal that passes from the soil into the plant tissue.

Initiating cultures of Salix sp.

On the experimental lots were planted *Salix sp.* (Energy willow), Inger variety. The planting was done with butchers (18 cm in length). The butchers were buried in the upper layers of ash and slag, fertilized, at a distance of approx. 75 cm.

Results and discussions

Determination of the composition and concentration of heavy metals in treated topsoil

To characterize topsoil (upper layers of ash fertilized with stabilized sludge) from the experimental lots, samples were taken after biogeochemical stabilization (after 22 days from fertilization with stabilized sludge), (table 3). The soil samples were taken from the depth of 20-40 cm.

Table 3

CHARACTERISTICS OF TOPSOIL AFTER BIOGEOCHEMICAL STABILIZATION PERIOD

Parameter	*Measured Units*	*Average determined for experimental lots*
pH	pH units	6.4
Total N	%	0.469
Total P	mg/kg d.m.	311
K	mg/kg d.m.	2281
Cd	mg/kg d.m.	1.6
Cr	mg/kg d.m.	113
Cu	mg/kg d.m.	43.3
Fe	mg/kg d.m.	2551
Mn	mg/kg d.m.	556
Ni	mg/kg d.m.	53.7
Pb	mg/kg d.m.	183
Zn	mg/kg d.m.	248
TOC	%	2.16

The treatment applied to the upper ash layer with stabilized sludge resulted in significant changes in the nitrogen, phosphorus and potassium content of the fertilized topsoil. The *p*H value (6.4) indicates a weak acidic soil, which shows the availability of vital nutrients for plant growth [17].

The total carbon, nitrogen and potassium content were higher in the fertilized topsoil. Compared to the initial ash layer, it was consistent with the growth and maintenance of a long-term culture. These elements play an essential role in plant metabolism.

Regarding the supply of topsoil micronutrients (Zn, Cu, Mn, Fe) it was observed that addition of stabilized sludge led to the increase of their concentrations, with approx. 84% for zinc, approx. 107% for manganese. Iron content drops from 2.98 g/kg d.m. to 2.55 g/kg d.m. By applying the treatments to the experimental lots the characteristics of the upper ash layer were changed and conditions were created for the development of the energy cane roots and fixation of the upper ash layers.

Crops analysis

Observations on plant growth were performed for a period of 4 months after cultivation.

All the willow buds planted on the experimental plots of the ash deposit have risen and developed similar to those planted on a blank soil. The tracking of energy willow crops was achieved by the *average height* indicator (fig. 1) of the plants and the number of bivalves grown on a plant.

From the experimental studies it was found that approx. 50% of the energy willow plants on all the experimental lots have 2-3 shellfish. For reference soil the percentage is 80%.

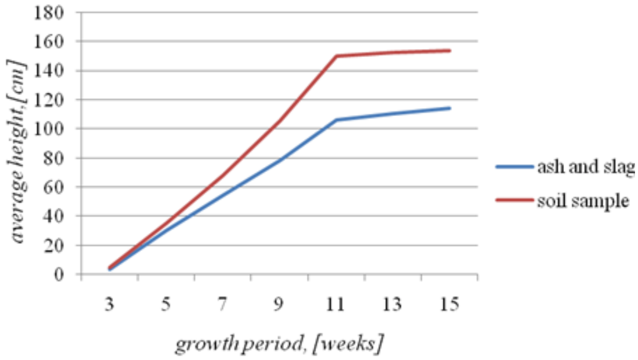

Fig 1. The growth rate of the energy willow over a period of 4 months, depending on the type of soil: ash and slag / soil sample

During the 4 months it was found that the *average height* of the *Salix sp.* is higher for soil sample. Significant differences were observed from the 7th week after cultivation. Growth rate increased for the entire period of time for the energetic willow in the soil sample. This difference was explained by the lower content and availability of nutrients in the ash deposit.

Although *Salix sp.* were smaller and generally have fewer fins than those grown on the sample soil, they are vigorous and have a healthy appearance. There have been no signs of illness of the leaves or willow plants grown on the ash deposit.

Production of biomass

Energetic willow was harvested after a period of 3 years of vegetation. Harvesting was done after leaves' fall.

There was a significant difference in strains both in their length and in their thickness for the culture of *Salix sp.* growned on the ash deposit and those grown on the sample soil. Biomass harvested on the reference soil was 1.4 times higher compared with that harvested on the ash deposit. This increase in biomass was also consistent with the observed differences in the first 4 months of culture (fig. 1). Dry matter in harvested biomass (green mass) was between 35-40% for both crops.

Table 4

ASPECTS ON THE WILLOW CROP FROM THE ASH DEPOSIT VS. SOIL SAMPLE

Culture features	*Ashes Deposit*	*Soil Sample*
Maximum no. of sprouts, pcs	6-15	10-20
Maximum height, m	4.5 (1,8 – 4,5)	7 (5-7)
Max. Diameter, cm	4 (1-4)	8 (3-8)
Biomass harvested*, kg/m²	5.3	7.5

** - biomass is composed of Salix sp. without leaves*

- is the first harvest from cultivation

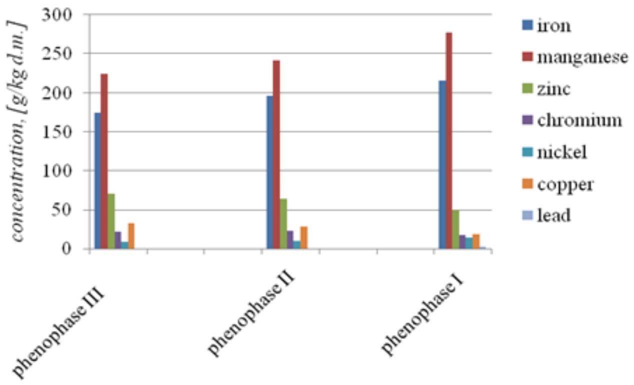

Fig. 2. Quantity of metals in Salix sp. ash

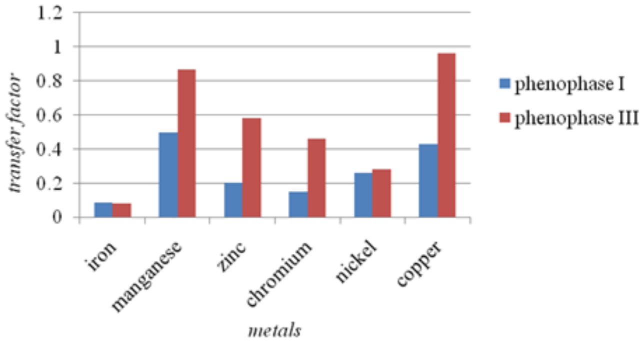

Fig. 3. The degree of transfer of metals from the topsoil of the ash deposit into the Salix sp

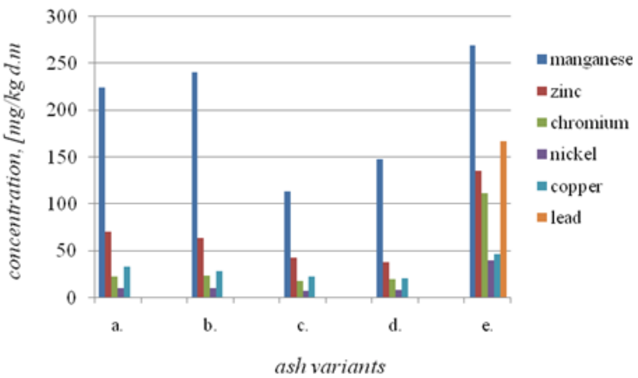

Fig. 4. Quantities of metals in ash resulting from the burning of *Salix sp*. cultivated on the ash storage site (a. phenophase III, b. phenophase II) compared to the one cultivated on the reference soil (c.phenophase III, d. phenophase II) and the content of metals in the ash deposit (e.)

Considering the production of biomass it can be said that *Salix sp.* has adapted to the environmental and substrate conditions of the ash.

Determination of the quantities of metals accumulated in the strain of Salix sp.

The storage capacity of metals in *Salix sp.* biomass was similar to the amount of metals determined in the ash resulted from the wood combustion.

Determination of the quantities of metals was performed during a vegetation period of 3 years (phenophase I - 5 months, phenophase II - 17 months, phenophase III - 29 months) (fig. 2).

During 3 years of vegetation, *Salix sp.* showed a similar accumulation capacity as the trend for the analyzed metals. While the Mn, Fe and Ni decreased with the increase of vegetation period, Zn, Cr and Cu quantities increased in the same vegetation period.

The quantities of metals accumulated in the strain of *Salix sp.* presented high values of above 170 mg/kg in the case of Fe and Mn and below 70 mg/kg for Zn, Cr, Ni, Cu. This distribution may also be influenced by the content of metals in the ash deposit. That is why we introduced a parameter that takes into account these aspects, namely the transfer factor of metals from the ash deposit topsoil of the *Salix sp* [26].

From the graphical representation of the variation of the transfer factors for the analyzed metals (fig. 3) it was found that the highest values (over 0.5) were recorded for Cu, Mn and Zn. This significant increase tends to confirm the hypothesis that *Salix sp.* acts as a bio-accumulator for Cu, Mn and Zn. The increased bioaccumulation capacity of *Salix sp.* for these metals was consistent with the fact that Mn, Cu, Zn and Fe are microelements and have an essential role in the growth and development of living organisms.

Throughout the analyzed period *Salix sp.* does not accumulate Cd and Pb, the concentrations determined in ash being below the detection limit. The amount of Pb in the upper ash fertilized layers was high, of 183 mg/kg d.m. (table 3) and was correlated with a slightly acidic *p*H, Pb mobility was expected to be high, however, *Salix* plants did not accumulate Pb. It is known that Cd and Pb present toxic action on plants. Based on the analyzes (table 3 and fig. 2) it can be said that *Salix sp.* does not have affinity for Pb and Cd, which was also noted by the growth, development and adaptation of plants to ash storage conditions (fig. 1).

Biomass of *Salix sp.* is considered an important source of renewable energy. If used as heat source of heat the ash results as waste. In the ashes there are quantities of metals accumulated by the *Salix sp.* strains. Figure 4 shows the quantities of metals in ash resulting from the burning of *Salix sp.* cultivated on the ash storage site versus the one cultivated on the reference soil. Also, the content of metals in the ash and slag storage were reported.

The ash obtained by burning *Salix sp.* cultivated on the ash deposit contained higher amounts of metals compared to the ash obtained from the burning of *Salix sp.* on the reference soil. The increase was between 29.6% (Ni) and 98% (Mn) in case of phenophase III. It correlates with the fact that in the top soil of the ash deposit there are larger

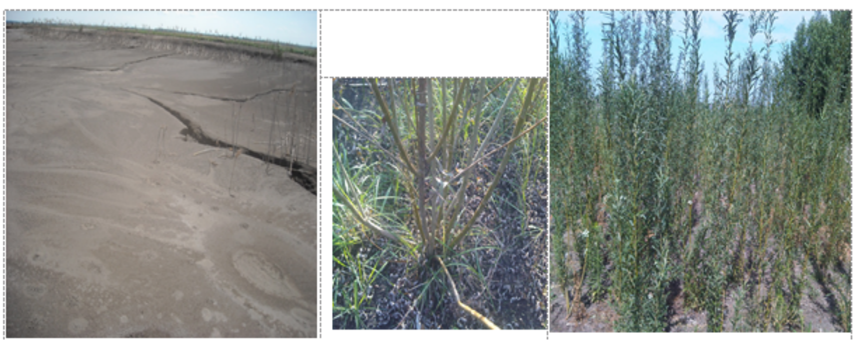

Fig.5. Ash and slag storage: a) initial; b) culture of Salix sp in phenophase II (17 months from cultivation)

amounts of metals than in the reference soil. Therefore these metals were taken up in the large quantities of *Salix sp.* grown on the ash deposit.

Regarding the content of metals in the ash and slag storage, the values recorded in *Salix sp.* cultivated on ash and slag storage were smaller for each of the analyzed metals.

If the biomass of energy plants is used as a source of thermal energy by the operator of the ash and slag deposit or by third parties, the ash resulted from its burning can be eliminated in the current ash and slag.

After a cultivation period of 3 years it can be concluded that the growth and maintenance of the culture of *Salix sp.* demonstrates the ability to adapt and develop at the substrate of the deposit (fig. 5).

Conclusions

In situ experiments on the ash and slag storage showed that the metal accumulated by *Salix sp.* was higher than the *Salix sp.* content on the reference soil. In both cases the amount of metals in the ash *Salix sp.* decreased in the order: *Copper > Manganese > Zinc > Chromium > Nickel > Iron .*

For the ash storage site considered as a land without economic utility it was proposed an approach through which it can be transformed into a land that brings benefits by cultivation and capitalization of *Salix sp.* culture obtained.

Based on the obtained experimental data, it was proposed a phytoremediation model with *Salix sp.* for the ecological closure of ash and slag deposits.

Phases of phytoremediation process with Salix sp. for closing an ash and clay deposit were: soil preparation, elimination of weeds by total herbicide before planting *Salix sp.* (preferably autumn); soil fertilization with a 2.5 kg/m^2 stabilized sludge resulted from the urban waste water treatment plant and its incorporation into the upper layers of the deposit; planting *Salix sp.* after the bio-geochemical stabilization period of 15-20 days after the field fertilization, during March-April. The distance between the slips is 75-80 cm; irrigation during the dry season; herbicide or mechanical work to combat weeds in the first year of culture; fertilization of the land with a dose of 2 kg/m^2 urban sludge in the 2nd year of culture (optional - fertilization of *Salix sp.* crops starting with the second year of culture is done only if productivity growth is desired); harvesting plants after fall of leaves starting with year 3 of culture.

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