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STUDY ON ELEMENTS LEACHING FROM BOTTOM ASH OF ENEL MARITSA EAST 3 THERMAL POWER PLANT IN BULGARIA

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ABSTRACT

Use of lignite in power generation has led to increasing environmental problems associated not only with gaseous emissions but also with the disposal of ash residues. In particular, use of low quality coal with high ash content results in huge quantities of bottom ash to be disposed of. The main problem related to bottom ash disposal is leaching and release of contaminants constitute. Due to the stricter environmental regulations, the leaching characteristics of bottom ash obtained from thermal power plant were studied to assess their safe disposal.

The mobility of metals from bottom ash was tested using acidic leach liquor (H_2SO_4), alkaline leaching solution (NaOH) and distilled water under different conditions (liquid:solid ratio, number of leaching stages and pH) at room temperature. The results obtained were evaluated with a toxicity characteristic leaching procedure according to the Bulgarian regulation leaching test. It was found that the concentration of various metals in leachates depends on their chemical nature, in association with mineral phases of ash. The results showed that the extraction of metals from bottom ash depends on the leaching medium, liquid:solid ratio and number of leaching stages. The results give a possibility for classification of the waste and for assessment the potential use of some components.

Keywords: thermal power plants, bottom ash, leaching.

INTRODUCTION

Extraction of elements from solid wastes is a subject of studies, related to the classification and utilization of wastes [1]. World net electricity generation increases from 18.0 trillion kilowatt hours in 2006 to 23.2 trillion kilowatt hours in 2015 and 31.8 trillion kilowatt hours in 2030. Coal continues to fuel the largest share of worldwide electric power production, by a wide margin. In 2006, coal-fired generation accounted for 41% of world electricity supply; in 2030, its share is projected to be 43%. Sustained high prices for oil and natural gas make coal-fired generation more attractive economically, particularly in nations that are rich in coal resources, which include China, India, and the United States [2]. Combustion of bituminous and sub-bituminous coal and lignite for generation of electricity in thermal power plants produces solid wastes such as fly ash, bottom ash, and flue gas desulphurization (FGD) materials, which are commonly known as coal combustion by-products (CCPs) [3].

In Bulgaria, coal-fired power plants supply more than 40% of the electricity and generate about 5.5 – 6.5 million tons of wastes annually. Less than one quarter of them is being used, mainly in concrete production [4]. The rest is being disposed in landfills creating serious risk of air, soil and ground and surface water which had a strong effect on the deposition cost of such waste. Therefore, it is desirable to recover metals from bottom ash and development of methods for greater utilization and production of high value compounds from such waste. After such a treatment, the content of hazardous components in waste is reduced and it can be used in the building industry and road constructions [5, 6].

Bottom ash from coal-fired thermal power plants are known to contain number of toxic elements, such as Pb, Zn, Cd, Ni and Co, which can leach out from the ash and contaminate soils as well as surface water and groundwater [7, 8].

The powerful method to extract the metals content of bottom ash is using acids, since high concentration of hydrogen ions induce the solubilization of inorganic components. A few compounds are dissolved in caustics, but low pH is generally favorable for metal ion solubilization. Treatment with strong acids followed by filtering and washing of the solid residue, is an effective way to achieve low concentrations of trace elements [9-13]. Quite promising results are obtained during ultrasonic extraction of Al, Fe and Ti [14]

The aim of the present study is to investigate the leaching behavior of bottom ash produced during the combustion of coal in the thermal power plants and in addition to compare the results with the toxicity characteristic leaching procedure according to the Bulgarian regulation leaching test [1]. Investigations were performed using one leaching stage and two leaching stages at different pH and L/S ratios.

EXSPERIMENTAL

In order to develop data that are broadly applicable to the release of metals from bottom ash, the sampling is according to the standard requirements. The experimental procedures followed during the leaching of bottom ash with distilled water, sulfuric acid and sodium hydroxide are described below.

Table 1. Chemical analysis of bottom ash sample.

Oxide	Content (wt /wt %)	Element	Content (mg/kg)
Fe_2O_3	9.44	Cu	112
MnO	0.07	Zn	86
TiO_2	0.76	As	22
CaO	3.42	Ba	1021
K_2O	1.18	Cr	76
P_2O_5	0.09	Mo	14
SiO_2	51.68	Ni	58
Al_2O_3	21.70	Pb	25
MgO	1.75		
Na_2O	0.51		
L.O.I	3.98		

Material

Bottom ash samples are collected from Enel Maritsa East 3 TPP, one of the three large power plants in the Maritza East complex, all of them supplied with locally mined lignite from the Maritza East Mines. Before treatment, samples were dried at 100°C to a constant weight and sieved to obtain fraction below o.63 mm. The chemical composition of the bottom ash, determined by X-ray fluorescence is shown in Table 1. The test results indicate that the bottom ash sample is composed mainly of SiO_2, Al_2O_3 and Fe_2O_3.

The mineral composition and morphology of the bottom ash sample were studied using X-ray diffraction

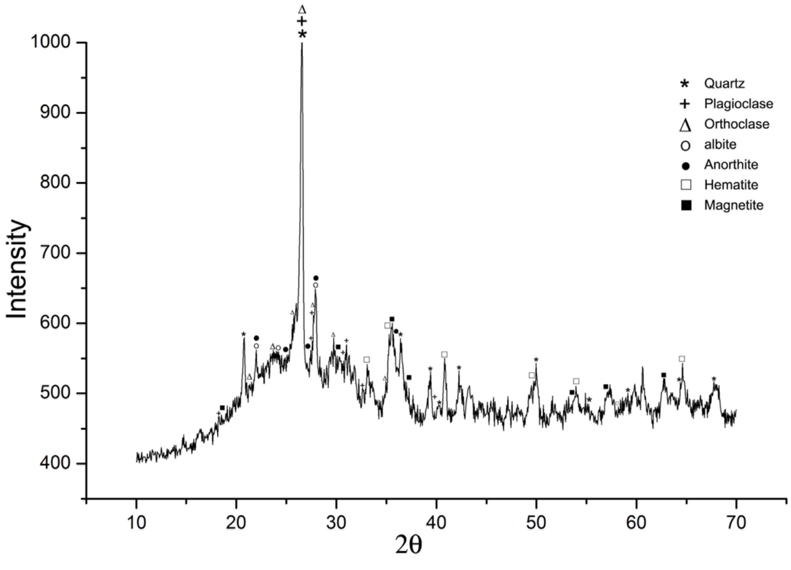

Fig. 1. X-Ray diffraction patterns of bottom ash.

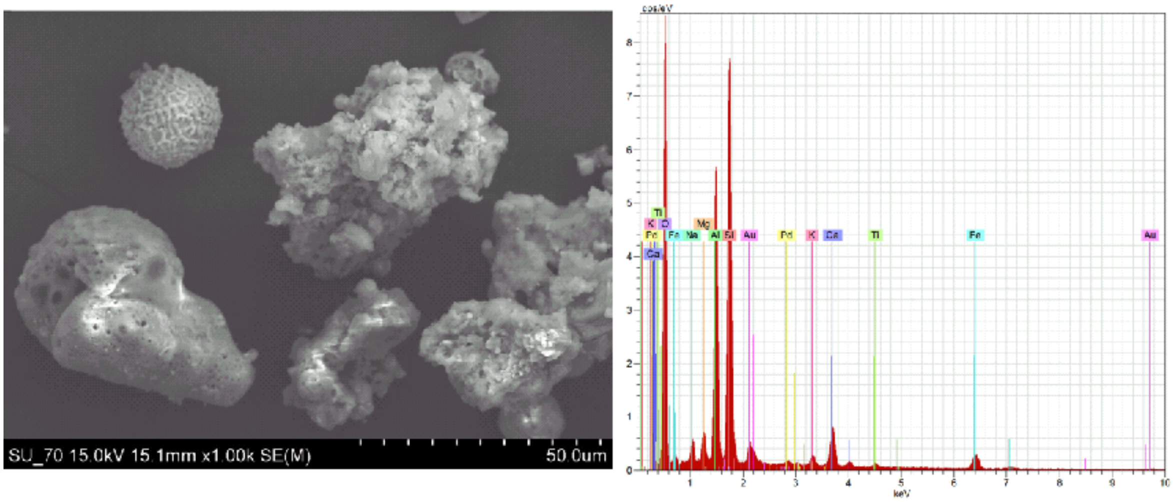

Fig. 2. SEM micrograph with EDX of bottom ash sample.

(XRD) and scanning electronic microscopy (SEM). XRD analysis was performed using a Philips diffractometer with Cu Kα radiation. Step-scanned data were collected from 10 to 70° 2θ, with a fixed time of 3 s per 0.05° 2θ. A scanning electron microscope combined with energy dispersive X-ray (EDX) spectroscopy (Hitachi SU-70, Ultra-High-Resolution Analytical FE-SEM equipped with Bruker's XFlash Silicon Drift Detector) are also used during carried out experiments. The mineral composition and morphology of the bottom ash sample are shown in Figs. 1 and 2. XRD and SEM analyses indicated that the bottom ash is a mixture of fine inorganic compounds, and the detected crystalline phases include minerals such as SiO_2 (quartz), $NaCa_4Al_3Si_5O_{19}$ (plagioclase), $KAlSi_3O_8$ (orthoclase), $NaAlSi_3O_8$ (albite), $CaAl_2Si_2O_8$ (anorthite), Fe_2O_3 (hematite) and Fe_3O_4 (magnetite). A general view of as-received bottom ash is shown in Fig. 2. Different glassy spheres, spheroids and aggregates with improper form predominantly constitute the studied bottom ash.

Leaching procedure

The experiments were done using distilled water with pH = 7, aqueous NaOH solution with pH = 10 and H_2SO_4 solution with pH = 4. The leaching of fly ash is realized in a sequential batch extraction process. Such an extraction process gives an idea about the maximum extraction of elements from a bottom ash sample. The leaching experiments were performed using 1g of the bottom ash sample at 25°C during 24 h and different L/S ratio. The glass flasks were shaken with 200 rpm intensity. Extractions mixtures were separated by filtration and collected leachate were diluted with distilled water to certain volume. During the two leaching stages, the same procedure was repeated for 24 hours with the solid residue. The second leachate was collected and mixed with the leachate obtained from first step, completed with distilled water to certain volume. The content of elements, according to the regulation, was determined by ICP-UV Spectro-Analytical Instruments. The pH and conductivity of leachates were recorded with a digital pH meter and conductivity meter.

RESULTS AND DISCUSSION

Change of pH and conductivity

The experimental results from the leaching of elements from bottom ash under varying conditions are presented in this section. The effects of the leaching medium and the important process parameters such as leaching stages, pH and L/S ratios on the dissolution of elements from bottom ash have been observed. Fig. 3 illustrate the change in pH and conductivity of leachates at different L/S ratios for one leaching stage and two leaching stages. Obvious change of pH is observed when H_2SO_4 and NaOH are used as leachant. For H_2SO_4 leachant, the final pH of the leachate increased while it decreased for NaOH leachant for one stage and two stages leaching at all L/S ratios. When we use extragent with acid value of pH the solutions obtained increase their values from 4 to the range of 6.7 to 7.2 for all experiments. As seen from the data (Fig. 3) the pH of the final solution decreases from initial value of 10 to neutral values for all conditions of the experiments. Obviously under the action of acid and alkaline extragents

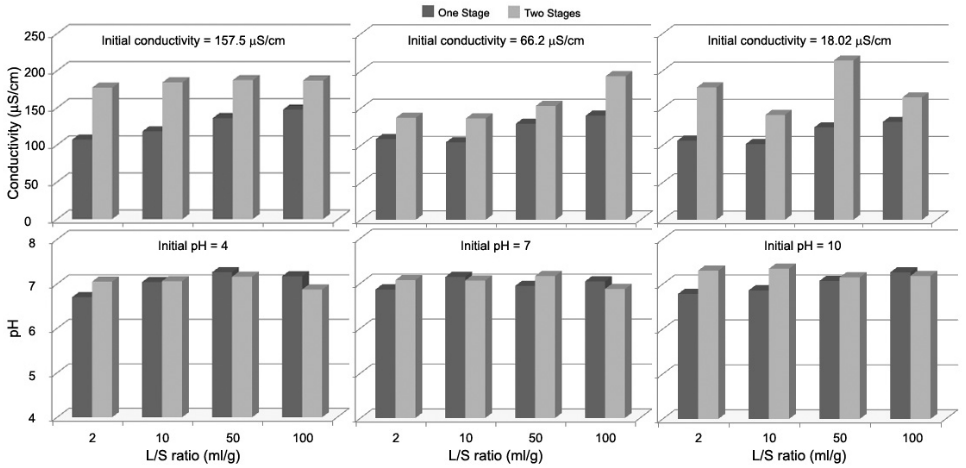

Fig. 3. Change in leachate pH and conductivity as a function of S/L ratio for one leaching stage and two leaching stages.

part of the basic ions remove into solution in the form of soluble compounds. The conductivity values are directly related to the release of metals present in bottom ash [15]. The values of the conductivity of leachates of H_2SO_4 and NaOH leachants increased compared to the initial values of the conductivity of the pure leachates. The change of pH of the leachates may be is mainly governed by the amount as well as mobility of calcium in the ash. From Fig. 3, marginally change in pH is observed when distilled water is used as the leachant indicating low mobility of calcium in the ash. For another leachants more significant change of pH was observed especially for one leaching stage.

Leaching of toxic trace elements

The mobility of toxic trace elements for one and two leaching stages in different leaching medium at L/S ratio 2 and 10 from bottom ash sample is presented in Tables 2 and 3 respectively. It was found that the concentrations of Ba, Cu, Mo, Ni and Zn in leachate vary with the nature of the leaching medium and number of leaching stages. The concentration of Zn in leachate decreases for second stage significantly. In all three leaching solution used the quantity of the As, Pb and Cr removed into solution after treatment preserve constant values independently of the kind of the extragents and L/S ratio.

When the concentrations of toxic trace elements in leachate were compared with the Bulgarian limit values in the regulation at L/S ratio 2 and 10 at pH = 4, 7 and 10 for one and two leaching stages, it was found that bottom ash leachates should be classified as a hazardous.

Leaching of major elements

The mobility of Na, K, Mg, Ca, Mn and Si from bottom ash in leaching liquids at various pH for the

Table 2. Effect of pH and leaching stages on the leaching of metals from bottom ash comparing with the maximum concentration of contaminants according to the Bulgarian regulation leaching test at L/S = 2 mg/kg.

Contaminate	pH = 4		pH = 7		pH = 10		Maximum Conc.*
	One Stage	Two Stages	One Stage	Two Stages	One Stage	Two Stages	
As	<5	<5	<5	<5	<5	<5	0.10
Ba	2.50	7.25	1.50	3.75	2.75	5	7
Cr	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	0.20
Cu	<1.25	<1.25	<1.25	2.75	1.25	3.75	0.90
Mo	5	12.50	2.50	5	2.50	7.5	0.30
Ni	<2.50	7.50	2.50	<2.50	<2.50	<2.50	0.20
Pb	<7.50	<7.50	<7.50	<7.50	<7.50	<7.50	0.20
Zn	15	<1.25	19.25	12.25	21.25	7.75	2

* According to the Bulgarian regulation leaching test

Table 3. Effect of pH and leaching stages on the leaching of metals from bottom ash comparing with the maximum concentration of contaminants according to the Bulgarian regulation leaching test at L/S = 10 mg/kg.

Contaminate	pH = 4		pH = 7		pH = 10		Maximum Conc.*
	One Stage	Two Stages	One Stage	Two Stages	One Stage	Two Stages	
As	<5	<5.00	<5	<5.00	<5	<5.00	0.50
Ba	3.25	7.25	1.75	3.25	2.5	4.25	20
Cr	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	0.50
Cu	2	<1.25	6.25	2.75	1.50	4	2
Mo	5	2.50	2.50	5	2.50	<2.50	0.50
Ni	5	2.50	2.50	2.50	<2.50	<2.50	0.40
Pb	<7.50	<7.50	<7.50	<7.50	<7.50	<7.50	0.50
Zn	12.75	<1.25	12.25	15	22.5	3.75	4

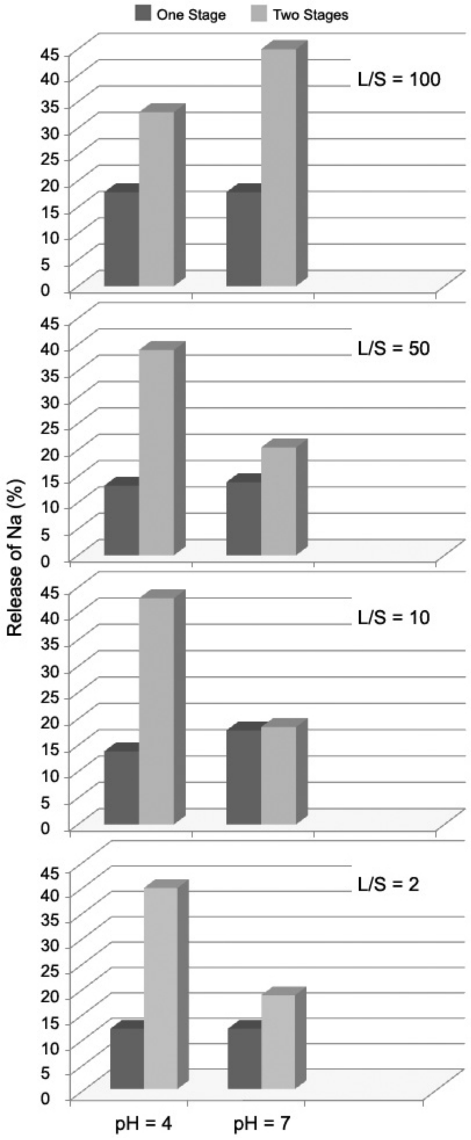

Fig. 4. Effect of leaching stages and pH on the leaching of Na at different L/S ratios.

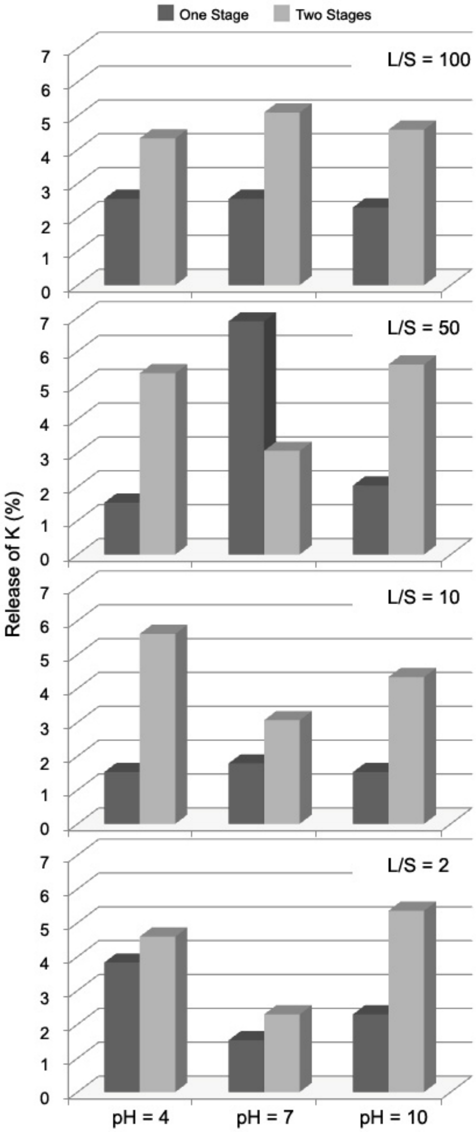

Fig. 5. Effect of leaching stages and pH on the leaching of K at different L/S ratios.

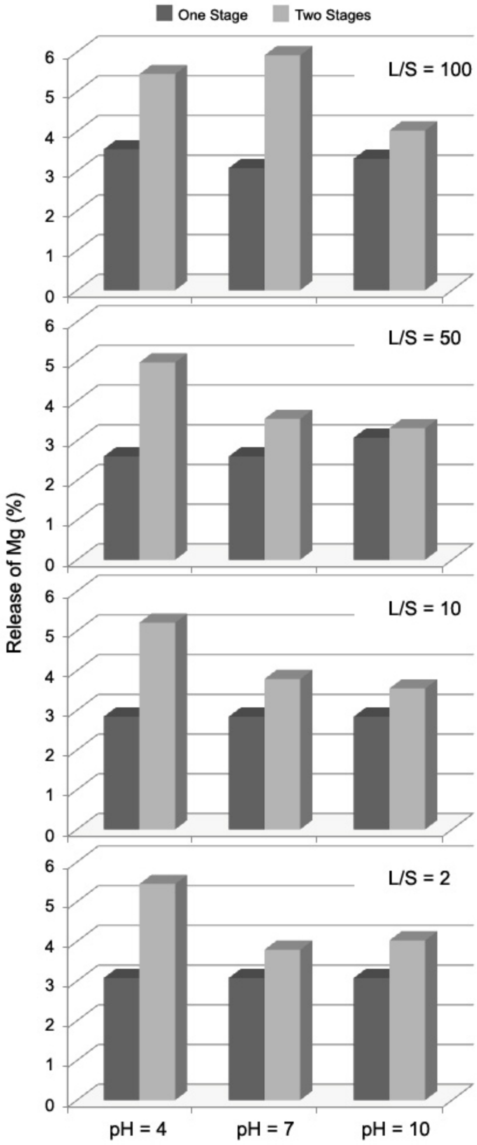

Fig. 6. Effect of leaching stages and pH on the leaching of Mg at different L/S ratios.

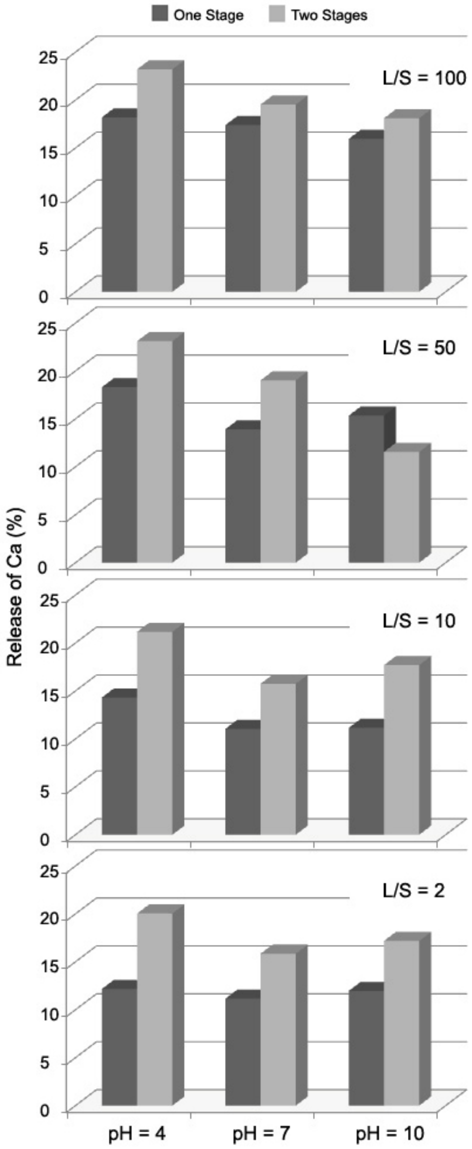

Fig. 7. Effect of leaching stages and pH on the leaching of Ca at different L/S ratios.

first and second leaching stages at different L/S ratios was studied and the results are reported in Figs. 4, 5, 6, 7, 8 and 9 respectively. For a medium of initial pH 4, the concentration of Na in the leachate of two leaching stages is much higher than that of one leaching stage at all L/S ratios (Fig. 4). Sodium is known to be associated with the surface of the bottom ash particles as well as the main components of the aluminosilicate glass fractions [16]. The amount of Na leached from bottom ash in a medium of initial pH=7 in two stages is marginally higher than that in one stage. For two leaching stages, the concentration of Na in the leachate of a medium of initial pH=4 is twice the amount in the leachate of a medium of initial pH=7 at L/S ratio 2, 10 and 50. Contrary at L/S ratio 100, the leachability of Na at pH = 7 is higher than that at pH = 4 for two leaching stages.

Extraction of K in different leaching mediums for one leaching stage and two leaching stages at different L/S ratios are given in Fig. 5. For all leaching mediums, the amount of K released from the bottom ash in two leaching stages is higher than that in one leaching stage for all L/S ratios except for a medium of initial pH=7 at L/S = 50.

For all leaching mediums, the concentrations of both Mg and Ca in the leachates for two stages are higher

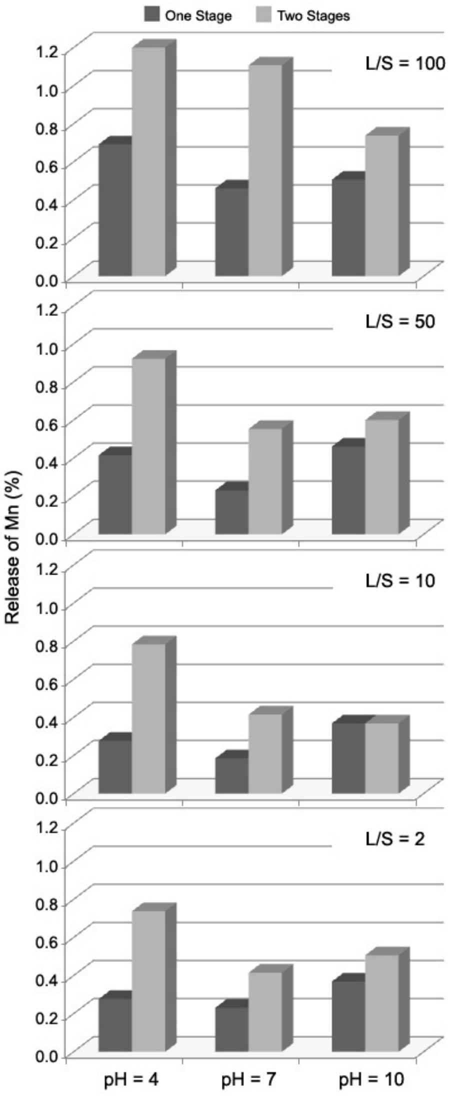

Fig. 8. Effect of leaching stages and pH on the leaching of Mn at different L/S ratios.

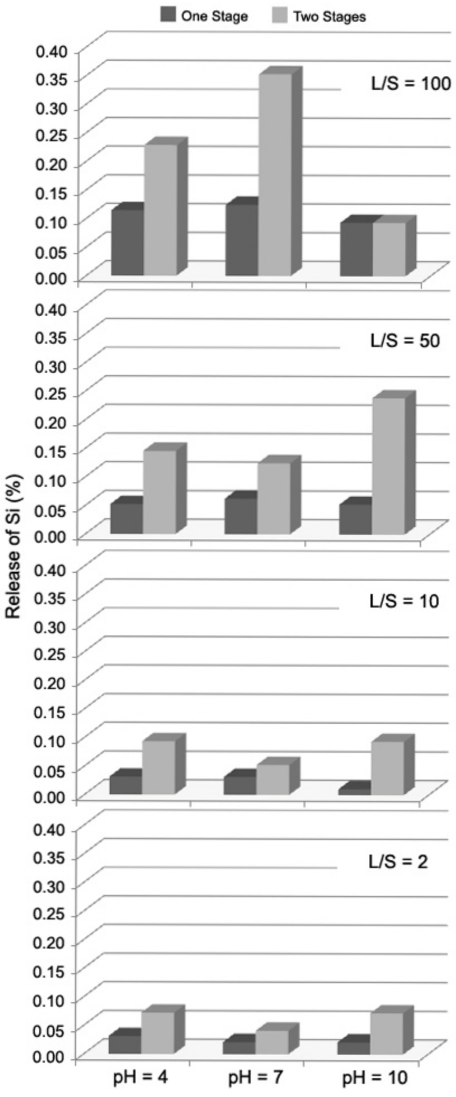

Fig. 9. Effect of leaching stages and pH on the leaching of Si at different L/S ratios.

than that for one stage (Figs. 6 and 7). A comparison with the results for K extraction shows similar extraction degree with those of Mg for all experiments. They vary between 1.5 and 7%. Comparing the results for Mg and Ca extraction degree a conclusion can be made that the mobility of Ca ions is from 3 to 5 times more than the same of Mg. The maximum extraction of Mg and Ca is reached in a medium of initial pH = 4 at L/S ratio = 100 for two leaching stages. The high extraction of Ca was reported before [17].

The concentration of Mn in the leachates has maximum for two leaching stages, pH = 4 at L/S = 100 (Fig. 8). A possible explanation is the formation of a glassy phase during combustion that breaks open at high L/S ratio. For a medium of pH 10, it was found that concentration of Mn at all L/S ratios was very low because of the precipitation of Mn as its hydroxides and oxyhydroxides. The extraction of Si is also very limited even in two leaching stages (Fig. 9). It was found that the concentration of Fe in the leachate of all experiments was below detection limit. The results obtained indicate that pH, L/S ratio and number of leaching stages are important parameters affecting the leaching rate of metals from ash deposits.

CONCLUSIONS

Data and information have been generated in this work on leaching of elements, including some toxic heavy metals from Enel Maritsa East 3 thermal power plant bottom ash sample. Widely varying mobility of heavy metals has been observed in the experiments covering weak acidic to basic pH of the solutions for one stage and two stages in sequential batch leaching. It is found that the concentration of studied elements in leachate of two leaching stages is higher than that of one leaching stage in all leaching medium. The extraction of elements increases in acidic medium rather than basic medium indicating that the extraction results are pH dependent. The leaching rate is less sensitive to L/S ratio. According to the Bulgarian regulation test, the bottom ash sample is classified as hazardous waste. Further studies are required to utilize bottom ash as secondary raw materials for metal productions.

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