**University of Chemical
Technology and
Metallurgy**

University of Chemical Technology and Metallurgy

Faculty of Chemical Technology

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Studies on the Recovery of Elements from Thermal Power Plant Solid Wastes

In partial fulfillment of the requirements for the degree of Doctor of Philosophy

Scientific Specialty: Technology for Utilization and Treatment of Wastes

Code 02. 22. 04

Supervisors

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Sofia, 2010

Дисертационният труд е написан на 184 страници и съдържа 129 фигури и 19 таблици. Цитирани са 239 източника.

Представеният дисертационен труд е обсъден и приет на защита на заседание на разширен научен съвет на научното звено на катедра „Неорганични и електрохимични производства", състояло се на 23.11.2010 г.

Публичната защита на дисертационния труд ще се проведе на 08.06.2011 г. от 15 часа в зала 335, сграда „А" на ХТМУ.

Материалите са на разположение на интересуващите се на интернет страницата на ХТМУ и в отдел „Научни дейности", стая 406, етаж 4, сграда „А" на ХТМУ.

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1. Introduction

As coal is burned in a power plant, its noncombustible mineral content is partitioned into bottom ash, which remains in the furnace, and fly ash, which rises with flue gases. Two other by-products of coal-combustion air-pollution control technologies are flue-gas desulfurization (FGD) wastes and fluidized-bed combustion (FBC) wastes. 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 fly ash and bottom ash to be disposed of. The main problem related to fly ash and bottom ash disposal is leaching and release of contaminants constitute.

Due to the stricter environmental regulations, this work presents a detailed study on leaching as well as the recovery of elements from fly ash and bottom ash samples obtained from Enel Maritsa East 3 thermal power plant. Inductively coupled plasma optical emission spectrometer, X-ray diffraction (XRD), scanning electronic microscopy (SEM), Fourier transformed infrared (FT-IR) spectrometry, differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) were used to characterize fly ash and bottom ash.

Understanding the leaching behavior of elements in fly ash and bottom is important in evaluating the potential environmental impact of the thermal power station wastes. For this purpose three leaching solutions included H_2SO_4 solution of initial pH = 4, distilled water of pH = 7 and NaOH solution of pH = 10 have been used under different conditions, liquid:solid ratio, number of leaching stages and pH, at room temperature to study the mobily of metals from fly ash and bottom ash. The content of elements, according to the Bulgarian regulation, was determined by ICP-UV, Spectro Analytical Instruments.

The recovery of elements from fly ash and bottom was studied. The recovery rate factors are concentration of sulfuric acid (X_1), temperature (X_2), the non-stoichiometric norm (X_3) and time of leaching (X_4). By applying multiple regression analysis on the experimental data, the experimental results of the design were fitted with a second-order polynomial equation. Thus, a mathematical regression models for recovery of seventeen elements from fly ash and bottom fitted in the coded factors are created.

The recovery of elements from fly ash and bottom under hydrothermal autoclave conditions was examined at 100°C, 120°C and 140°C for different times. 20% H_2SO_4 used as extragent in case of fly ash while 25% H_2SO_4 was used for extraction of elements from bottom ash.

2. Summary of Literature Survey

Environmental pollution due to release of smoke, gases, effluents and solid wastes from industries is one of the major issues of global concern. 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.

Combustion of bituminous and sub-bituminous coal and lignite for generation of electricity in thermal power plants produces a complex mixture of pollutants in the atmosphere, even with pollution control devices, including SOx, NOx, CO, acid gases, organic compounds and solid wastes such as fly ash, bottom ash, and flue gas desulphurization (FGD) materials, which are commonly known as coal combustion by-products (CCPs). About 80% of the combustion residue in a pulverized coal-fired power plant appears as coal fly ash.

The conventional method for disposal of TPP solid wastes is landfilling. The increase of landfilling of such waste brings to high land consumption with impacts to the environment. Therefore, it is desirable to recover metals from TPP solid wastes and development of methods for greater utilization and production of high value compounds from such wastes. 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.

A powerful method to extract the metals content of TPP solid wastes includes acids, since high concentration of hydrogen ions induces the solubilization of inorganic components. A few compounds are dissolved in caustics, but low pH is generally favorable for metal ion solubilization. Treatment in strong acids followed by filtering and washing of the solid residue, is an effective way to achieve low concentrations of trace elements. Certain compounds, notably metallo-organic chelates and sulfidic inclusions, are less affected by acid treatment alone [15-16]. Today, acid extraction is optimized by using an ultrasonic field (20 kHz, 80 W) to remove Al, Fe, and Ti.

The utilization of TPP solid wastes in industrial applications, principally construction, across the world is 44.53%. With the depletion of natural resources used in construction and an increasing awareness of the importance of protecting the planet, the need to more effectively employ TPP solid wastes has never been greater.

2.1. Conclusion of Literature Survey

1. The coal fired power plants all over the world generate a large amount of solid wastes from the burning process such as fly ash, bottom ash or boiler slag and gypsum from FGD cleaning process.

2. One of the main problems is related to the solid wastes usually land field and requiring more and more land area and required insulation and water cleaning systems.
3. Due to the implementation of the European Union stricter environmental legislation, the leaching characteristics of solid wastes obtained from TPP must be studied. Different standards are introduced in the EU and other countries for test studies on the way to determine the leaching efficiency of toxic elements from the TPP wastes.
4. The chemical and physical properties of TPP solid wastes changed from plant to another depending on type of coal burned and techniques used for handling and storage. They usually contain a quantity of valuable metals.
5. There are not available systematic investigations on the leaching behavior of bottom ash and fly ash from Enel Maritsa 3 TPP in Bulgaria using leaching procedure according to the Bulgarian regulation leaching test. There are not data for toxicity characteristics of these wastes and their classification on the base of the legal requirements.
6. There are publications and working technologies for utilization of the wastes from TPP as a component for building composites, cement production, glass-based materials, ceramic tableware and art ware, ceramic filters for gas cleaning, mining applications, road structure fills, concrete products, sorbents, soil conditioners and others.
7. Most of the studies are directed to the use of those wastes as secondary raw materials for extraction of different valuable elements. The recovery of all types of materials is related to several critical factors, including specific element solubility and availability or release potential. Solubility can be influenced by pH, formation of complexes with inorganic species or dissolved organic matter and other specific properties.
8. Recovery of metals with mineral acids is the most promising way for treatment of the wastes and transforming them to the secondary raw materials. Main driving parameters are the concentration and the norm of the acid used, but other parameters also have to be taken into account. It is stated that optimal conditions should be determined for each specific waste. Alkaline extraction is also tested and recommended by some other authors in some studies with limited success.
9. Bio- and hydrothermal technologies are proposed as new directions for the recovery of valuable metals from solid wastes.
10. Using best available techniques as mineral processing technologies, hydrometallurgical and bio-hydrometallurgical processes for recovery of metals from solid wastes is an important direction for solving raw materials shortage and achieving sustainable development.

3. Aim of the Work

On the base of the literature survey and the conclusions made the aim of this thesis is focused on the studies of recovery of elements from solid wastes, generated from Enel Maritsa East 3 Thermal Power Plant.

According this aim, the basic tasks for our studies were determined as follows:

1. Study the chemical and physical characteristics of fly ash and bottom ash from Enel Maritsa East 3 Thermal Power Plant.
2. Study the leaching of toxic elements from fly ash and bottom ash of Enel Maritsa East 3 Thermal Power Plant and compare the results with the toxicity characteristics leaching procedure, according the Bulgarian regulation leaching test.
3. Study the leaching of some major and minor elements from fly ash and bottom ash of Enel Maritsa East 3 Thermal Power Plant.
4. Study acid solubilization and the possibility for recovery of elements from fly ash and bottom ash using statistical analysis and the method of experimental design. On the basis of the results, mathematical models of the objective function to be obtained and optimization in searching optimal values of the objective functions to be done.
5. Study the possibility for recovery of elements from fly ash and bottom ash under hydrothermal autoclave conditions. Determination the basic parameters, that affect the solubility of the TPP solid wastes.

4. Investigations on Fly Ash
4.1. Characterization of Fly Ash

Different techniques were used to characterize fly ash such as ICP, XRD, SEM-EDX, IR and DTA-TG.

Table 4.1: The chemical composition of fly ash.

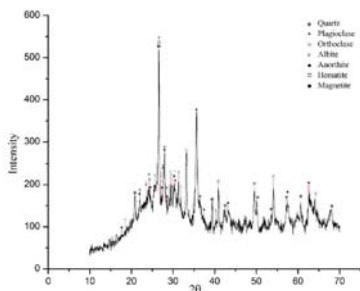| Oxide	Content (wt /wt %)	Element	Content (mg/Kg)
Fe_2O_3	13.13	Cu	112
MnO	0.09	Zn	105
TiO_2	0.78	As	31
CaO	5.80	Ba	1279
K2O	1.07	Cr	80
P_2O_5	0.09	Mo	26
SiO_2	49.47	Ni	75
Al_2O_3	21.58	Pb	35
MgO	2.04	SO_4^{-2}	10297.79
Na_2O	0.55		
L.O.I	1.39		

Fig.4.1: XRD analysis for fly ash sample.
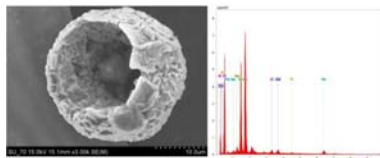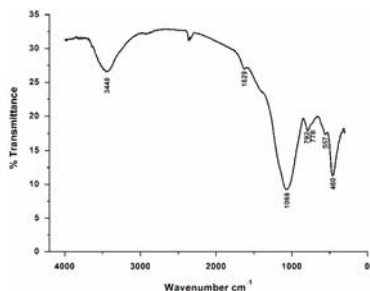

Fig. 4.2: SEM-EDX of fly ash sample.
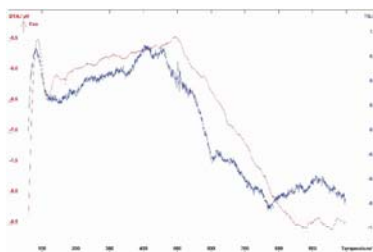

Fig. 4.3: Infrared spectrum of fly ash sample

Fig. 4.4: TG/DTA of fly ash sample

New data on the structure of the fly ash solid waste from Enel Maritsa East 3 thermal power plant have confirmed that the crystal phases are the silicates, iron oxides and aluminum silicates with high thermal stability and very low, less than 1%, volatile components during thermal treatment up to 1000^0C.

The content of Al_2O_3 has a value about 22%, Fe_2O_3 about 13%, alkaline oxides of Ti, Na, K and Mg about 4.5% and those elements could be of practical interest for use as secondary raw materials.

4.2. Leaching Characteristics of Elements from Fly Ash

Leaching of elements from fly ash from Enel Maritza East 3 TPP has been reported. The leaching conditions were selected to evaluate the potential environmental impact of coal fly ash from this TPP and to assess the possibility of contamination of the sites by release of heavy metal ions. The leaching experiments were done using distilled water of pH = 7, aqueous NaOH solution of pH = 10 and H_2SO_4 solution of pH = 4. The leaching of fly ash is realized in a sequential batch extraction process.

4.2.1. Results and Discussion
4.2.1.1. *Change of pH and conductivity*

Figure 4.5 illustrate the change in pH and conductivity of leachates at different L/S ratios for one leaching stage and two leaching stages.
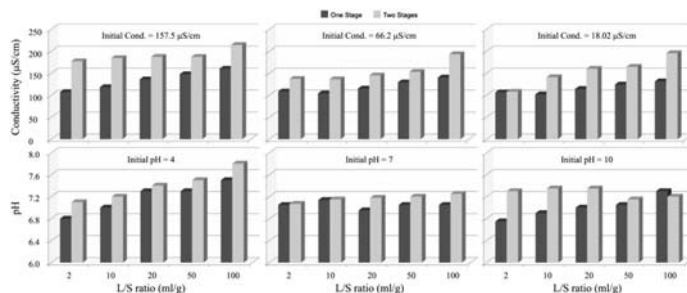

Fig. 4.5: Change in leachate pH and conductivity as a function of S/L ratio for one and two leaching stages.

For all experiments, the pH of leachant with acid value increased from 4 to the range of 6.8 to 7.8 while for NaOH of initial pH 10, the pH of the final solution decreases neutral values at all conditions of the experiments. The conductivity of leachates of H_2SO_4 and NaOH leachants rapid increased from its initial values. The change of pH of the leachates may be is mainly governed by the amount as well as mobility of calcium in the ash. Marginally change in pH is observed when distilled water is used as the leachant indicating low mobility of calcium in the ash.

4.2.1.2. *Leaching of toxic trace elements*

The effect of pH and leaching stages on the mobility of toxic trace elements from fly ash was studied and the results were compared with the maximum conc. of contaminants according to the Bulgarian regulation leaching test.

Table 4.2: The mobility of toxic trace elements at L/S = 2 for different pH.

Contaminate	pH = 4		pH = 7		pH = 10		Max. Conc. (mg/kg)
	Stage		Stage		Stage		
	One	Two	One	Two	One	Two	
As	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	0.10
Ba	26.75	28.25	21.75	21.85	6.00	6.25	7.00
Cr	<1.25	<1.25	<1.25	<1.25	<1.25	<1.50	0.20
Cu	7.00	12.75	5.75	13.00	3.50	10.00	0.90
Mo	<2.50	<2.50	<2.50	<2.50	<2.50	<2.50	0.30
Ni	<2.50	<2.50	<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	20.50	27.25	14.50	16.50	12.35	15.75	2.00

Table 4.3: The mobility of toxic trace elements at L/S = 10 for different pH.

Contaminate	pH = 4		pH = 7		pH = 10		Max. Conc. (mg/kg)
	Stage		Stage		Stage		
	One	Two	One	Two	One	Two	
As	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	0.50
Ba	19.25	13.75	19.50	6.50	11.00	20.25	20.00
Cr	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	0.50
Cu	4.75	10.75	14.00	13.25	4.50	11.00	2.00
Mo	<2.50	<2.50	<2.50	<2.50	<2.50	<2.50	0.50
Ni	<2.50	5.00	<2.50	2.50	<2.50	<2.50	0.40
Pb	15.00	15.00	<7.50	<7.50	<7.50	15.00	0.50
Zn	28.25	35.65	18.5	25.38	14.50	21.50	4.00

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 is found that fly ash should be classified as a hazardous.

4.2.1.3.   Leaching of major and minor elements

The mobility of Na, K, Mg, Ca, Mn and Si from fly ash in leaching liquids at various pH for one and two leaching stages at different L/S ratios was studied.
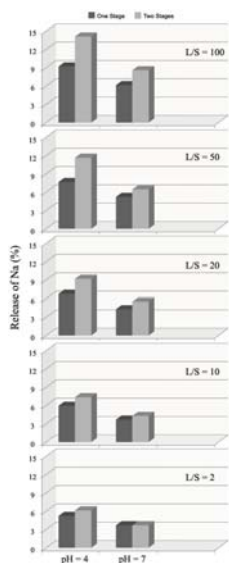

Fig. 4.6: Effect of leaching stages and pH on the leaching of Na at different L/S ratios.
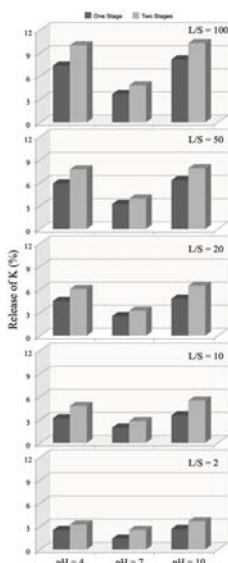
Fig. 4.7: Effect of leaching stages and pH on the leaching of K at different L/S ratios.

Fig. 4.8: Effect of leaching stages and pH on the leaching of Mg at different L/S ratios.

Fig. 4.9: Effect of leaching stages and pH on the leaching of Ca at different L/S ratios.
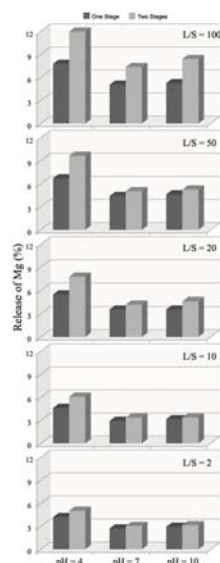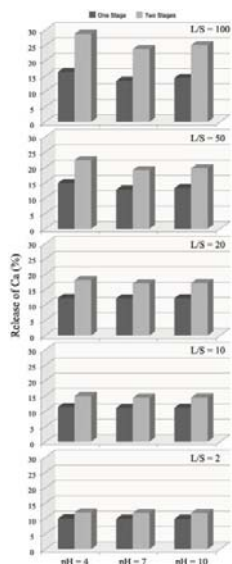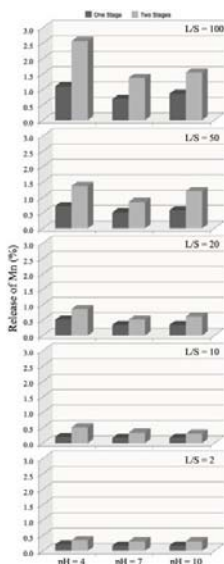
Fig. 4.10: Effect of leaching stages and pH on the leaching of Mn at different L/S ratios.
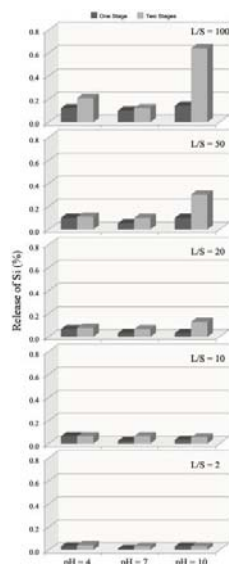
Fig. 4.11: Effect of leaching stages and pH on the leaching of Si at different L/S ratios.

In all leaching mediums, 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. The amount of Na leached from fly ash in a medium of initial pH = 4 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 all L/S ratios. The maximum leaching of Na is 14% at L/S ratio = 100 in a medium of initial pH = 4.

For all leaching mediums, the amount of K released from the fly ash in two leaching stages is higher than that in one leaching stage for all L/S ratios. The degree of release of K in H2SO4 and NaOH leachants is higher than that in water. For all leaching mediums, the concentrations of both Mg and Ca in the leachates for two stages are higher than that for one stage. The concentration of Mn in the leachates has maximum for two leaching stages, pH = 4 at L/S = 100. 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.

4.2.2. Conclusion

1. Widely varying mobility of heavy metals has been observed in the experiments covering weak acidic to basic pH of water for one stage and two stages in sequential batch leaching, but following the Bulgarian standard limits it was found that the studied fly ash has a characteristics close to the inert solid wastes, but for some elements it is classified as hazardous waste.
2. 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, but it is higher with sulfuric acid then with sodium hydroxides water solutions.
3. The extraction of elements like Mn and Si is less than 1%, when for sodium as the most mobile element of the waste it is up to 14%.
4. The extraction rate is sensitive to L/S ratio and it has the highest value when L/S ratio is 100.

4.3. Recovery of Elements from Fly Ash

The process of optimizing systematically and simultaneously a collection of objective functions is called multi-objective optimization. The effects of acid concentration, extraction time, norm and temperature on the solubility of the elements from fly ash were investigated using multi-objective optimization and quantitative data obtained from properly designed experiments. The range and the levels of the variables investigated in this study are given in Table 4.4. Each factor in the design was studied at three different levels (-1, 0, 1). All variables were taken at a central coded value considered as zero. A 24 full factorial central composite design for four independent variables each at three levels with twelve star points and six replicates at the centre points was employed to fit a second order polynomial model in which 30 experiments were required for this procedure.

Table 4.4: Independent variables and limits of the main factors.

Variables	Range and levels		
	-1	0	1
Concentration of H_2SO_4 (wt %)	20	30	40
Temperature (°C) (X_2)	65	75	85
Norm∗ (%) (X_3)	200	300	400
Leaching time (min) (X_4)	60	90	120

The experiments performed using 10 gm fly ash with different amounts of H_2SO_4 solution of different concentration and stirred at a constant velocity for different times and temperatures, Table 4.5. The amounts of H_2SO_4 used are calculated on the basis of chemical content of oxides in the sample. After the desired extraction time for each experiment the solid and liquid phases were separated by filtration. The liquid phase was diluted to known volume. Elements in liquid phase were determined by ICP-OES (Varian Vista-MPX).

Table 4.5: Sample number and experimental conditions for recovery of elements from fly ash.

Sample No.	Conc. of H_2SO_4 (wt	Temp. (°C)	Norm (%)	Leaching time
1	20	85	400	120
2	40	65	200	120
3	40	85	400	60
4	40	65	300	60
5	40	85	200	60
6	20	65	200	60
7	40	65	400	120
8	30	85	200	120
9	20	75	200	120
10	20	65	400	60
11	40	85	300	120
12	20	65	300	120
13	20	85	200	90
14	30	75	300	90
15	20	85	300	60
16	30	65	200	60
17	40	75	200	60
18	40	65	200	90
19	40	65	400	60
20	30	65	400	120
21	40	85	400	90
22	20	75	400	60
23	40	75	400	120
24	30	85	400	60
25	20	65	400	90
26	20	85	400	120
27	20	65	200	120
28	20	85	200	60
29	40	85	200	120
30	30	75	300	90
31	20	85	300	300
32	20	85	400	180
33	20	85	400	240
34	20	85	400	300
35	20	85	500	180
36	20	85	500	300
37	20	85	500	420

An empirical model was developed incorporating interaction effects of all parameters and optimized using response surface methodology. For each extraction of the chemical elements regression equations were built. The optimum values of the selected variables were obtained by solving the regression equation and by analyzing the response surface contour plots.

Later, depending on the results of the regression analysis, the experiments have been extended on a larger scale of extraction time in order to increase the degree of

extraction of elements from fly ash, samples 31-37, at 85°C using 20 wt% H_2SO_4 and different norm.

4.3.1. Results and Discussion

Using statistical analysis and following the method of experiment design, the experimental results for the objective functions ($Y_1 - Y_{17}$) were obtained. The mathematical models are used second degree equations.

By applying multiple regression analysis on the experimental data, the experimental results of the design were fitted with a second-order polynomial equation. Thus, a mathematical regression models for recovery of seventeen elements from fly ash fitted in the coded factors is given, Table 4.6. Y_1, Y_2, Y_3, Y_4, Y_5, Y_6, Y_7, Y_8, Y_9, Y_{10}, Y_{11}, Y_{12}, Y_{13}, Y_{14}, Y_{15}, Y_{16} and Y_{17} are the degree of extraction (wt/wt %) of Na, Mg, Al, Si, P, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Mo and Ba respectively. X_1, X_2, X_3 and X_4 are the independent variables, concentration of H_2SO_4 (wt %), temperature (°C), Norm (%), extraction time (min), respectively. The optimal conditions were obtained using deduced regression equations. The optimum conditions for metals extraction are respectively: X_1 = 20 wt %; X_2 = 80°C; X_3 = 200 and X_4 = 120 min.

Our experimental data confirms the optimum values of the objective parameters after optimization (%): Y_1 = 60.84 %; Y_2 = 44.82 %; Y_3 = 30.03 %; Y_4 = 4.69 %; Y_5 =32.84 %; Y_6 = 25.91 %; Y_7 = 24.70 %; Y_8 = 11.19 %; Y_9 = 29.73 %, Y_{10} = 49.40 %, Y_{11} = 26.25 %, Y_{12} = 43.48 %, Y_{13} = 49.00 %, Y_{14} = 74.53 %, Y_{15} = 72.05 %, Y_{16} = 62.88 % and Y_{17} = 0.11 % . The degree of extraction of seventeen elements from fly ash for different values of the variables can also be predicted from the respective contour plots. Each contour curve represents an infinite number if combinations of two test variables with the other two maintained at their optimal constant value. Figures 4.12 - 4.17 show the contour curve for Al. The contour plots show the relative effects of any two variables when the remaining variables are kept constant at the optimum values. These plots showed the interactive effect of the four variables and demonstrated that the degree of extraction of elements from fly ash is dependent of the concentration of sulfuric acid, temperature, norm and extraction time.

Table 4.6 Mathematical models, coefficient of determination and adjusted R-square for

| Mathematical model	R-sq (%)	R-sq(adj) (%)
$Y_1 = 48.6 - 2.68\,X_1 + 4.52\,X_2 - 5.00\,X_3 + 2.44\,X_4 - 0.048\,X_1X_2 + 0.186\,X_1X_3 - 0.638\,X_3X_4 + 0.151\,X_3X_4 + 0.283\,X_1^2 + 0.173\,X_2^2 - 0.207\,X_3^2$	99.7	99.3
$Y_2 = 37.4 - 2.35\,X_1 + 3.66\,X_2 - 1.35\,X_3 + 2.10\,X_4 + 0.206\,X_2X_4 + 0.234\,X_3X_4$	98.7	98.0
$Y_3 = 23.9 - 0.050\,X_1 + 3.25\,X_2 - 1.55\,X_3 + 2.53\,X_4 + 0.202\,X_2X_3 + 0.292\,X_1^2 + 0.296\,X_3^2$	98.4	97.3
$Y_4 = 2.72 - 2.31\,X_1 - 0.0370\,X_2 - 0.0320\,X_3 + 0.0589\,X_4 + 0.0614\,X_1X_2 - 0.0284\,X_1X_4 + 0.0263\,X_2X_3 - 0.192\,X_2X_4 - 0.088\,X_2^2 - 0.294\,X_3^2\ 0.027\,X_4^2$	99.6	99.2
$Y_5 = 30.2 - 2.08\,X_1 - 0.755\,X_2 - 1.40\,X_4 + 0.184\,X_1X_2 - 0.140\,X_1X_3 - 0.427\,X_2X_4 - 2.43\,X_1^2 + 0.0488\,X_2^2 + 4.56\,X_3^2 - 0.371\,X_4^2$	100	99.9
$Y_6 = 21.0 - 0.527\,X_1 + 3.17\,X_2 - 1.36\,X_3 + 1.57\,X_4 + 0.279\,X_1X_4 - 0.126\,X_3X_4$	99.3	98.9
$Y_7 = 23.7 - 9.17\,X_1 - 5.66\,X_2 + 0.907\,X_3 - 0.140\,X_4 + 6.23\,X_1X_2 - 1.67\,X_2X_3 - 1.28\,X_2X_4 - 2.72\,X_3X_4 - 4.75\,X_1^2 - 1.68\,X_3^2 - 1.25\,X_4^2$	99.9	99.7
$Y_8 = 15.2 + 1.97\,X_1 - 1.90\,X_2 - 1.31\,X_3 - 1.19\,X_4 + 2.24\,X_2X_3 + 0.310\,X_3X_4$	93.6	88.8
$Y_9 = 25.1 + 0.086\,X_1 + 3.65\,X_2 - 0.462\,X_3 + 2.00\,X_4 - 0.251\,X_2X_4 + 0.354\,X_4^2$	92.8	89.8
$Y_{10} = 42.4 - 2.37\,X_1 + 3.52\,X_2 - 1.48\,X_3 + 1.27\,X_4 + 0.45\,X_2^2 - 0.11\,X_3^2$	85.9	80.9
$Y_{11} = 23.3 - 0.770\,X_1 + 3.26\,X_2 - 0.216\,X_3 + 0.912\,X_4 - 0.585\,X_1^2 - 0.055\,X_4^2$	96.5	94.8
$Y_{12} = 38.6 - 1.03\,X_1 + 5.29\,X_2 - 1.30\,X_3 + 0.707\,X_4 - 0.328\,X_2X_3 - 0.97\,X_4^2$	89.0	83.9
$Y_{13} = 39.7 - 1.34\,X_1 + 5.74\,X_2 - 1.78\,X_3 + 3.13\,X_4 + 0.196\,X_1X_3 + 0.095\,X_1X_4$	93.3	90.5
$Y_{14} = 42.8 - 2.81\,X_1 + 17.2\,X_2 - 2.55\,X_3 + 10.9\,X_4 - 4.84\,X_1X_3 + 5.82\,X_2X_4 + 9.92\,X_2X_4 + 6.37\,X_1^2 + 10.1\,X_2^2 - 0.84\,X_{3,2} + 4.28\,X_4^2$	99.8	99.3
$Y_{15} = 66.5 - 8.03\,X_1 - 1.62\,X_2 + 1.68\,X_3 + 1.14\,X_4 - 0.49\,X_1X_2 - 1.08\,X_4^2$	45.4	30.6
$Y_{16} = 54.1 - 6.43\,X_1 - 2.85\,X_2 + 0.632\,X_3 - 0.830\,X_4 + 3.66\,X_1X_4 + 1.17\,X_2X_3 - 0.477\,X_3X_4 + 6.26\,X_2^2 + 2.75\,X_4^2$	99.5	98.8
$Y_{17} = 0.0845 - 0.0233\,X_1 - 0.00115\,X_2 - 0.00819\,X_3 - 0.00034\,X_4 - 0.00003\,X_1X_3 + 0.00014\,X_2^2$	73.8	61.8

14
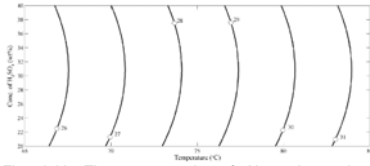
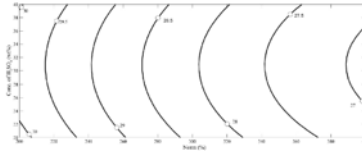Fig. 4.12: The contour plot of Al at the optimal constant value of X_3 = 200 and X_4 = 120 min.

Fig. 4.13: The contour plot of Al at the optimal constant value of X_2 = 80°C and X_4 = 120 min.
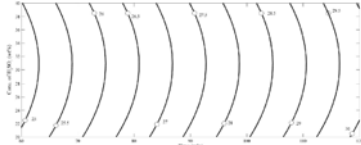

Fig. 4.14: The contour plot of Al at the optimal constant value of X_2 = 80°C and X_3 = 200.
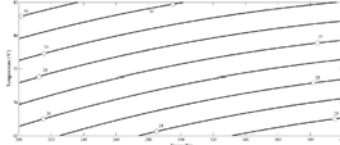

Fig. 4.15: The contour plot of Al at the optimal constant value of X_1 = 20 wt% and X_4 = 120 min.

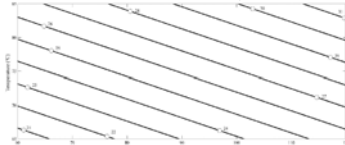

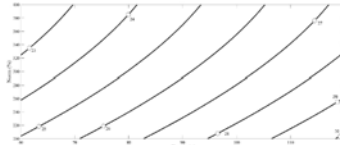Fig. 4.16: The contour plot of Al at the optimal constant value of X_1 = 20 wt% and X_3 = 200.

Fig. 4.17: The contour plot of Al at the optimal constant value of X_1 = 20 wt% and X_2 = 80°C.

The results of extended experiments, Table 4.7, show that the degree of extraction of the elements was significantly increased with time.

Table 4.7: The degree of extraction of elements from fly ash for extended experiments.

Sample No.	Degree of Extraction (wt/wt %)								
	Na	Mg	Al	Si	P	K	Ca	Ti	Cr
31	75.11	57.23	39.51	3.46	33.08	39.42	56.18	9.73	41.87
32	59.06	44.96	29.11	3.36	26.72	28.66	59.90	9.41	34.13
33	60.53	47.56	30.37	3.57	36.90	30.69	66.32	10.16	38.00
34	68.25	54.47	37.17	3.63	39.44	38.12	72.30	9.733	46.75
35	69.84	55.77	34.81	4.27	50.89	34.58	82.20	11.55	46.25
36	78.66	58.29	37.46	3.63	43.26	38.52	81.80	9.63	51.00
37	90.18	59.10	43.22	3.74	45.81	41.90	68.10	10.48	44.75

Sample No.	Degree of Extraction (wt/wt %)						
	Mn	Fe	Ni	Cu	Zn	As	Mo	Ba
31	60.45	35.96	56.67	64.55	100	77.40	53.85	0.21
32	52.20	30.47	55.33	50.53	53.52	45.16	48.07	0.16
33	57.39	34.14	54.67	51.68	87.38	54.84	51.92	0.16
34	65.72	41.69	64.00	57.34	76.86	66.13	53.85	0.19
35	68.46	41.36	73.33	63.69	95.14	77.42	30.77	0.26
36	71.21	46.44	73.33	67.29	99.33	54.84	30.77	0.35
37	63.30	44.19	70.67	88.19	100	83.87	80.77	0.63

4.3.2. Conclusion

1. Using the D-optimal plan for second order model, it was possible to determine the mathematical equations describing the relationship between experimental conditions and the level and rate of elements extractions. The validity of the model was proved by fitting the values of the variables in the second-order polynomial equation and by actually carrying out the experiments at those predicted values for the four independent variables, the concentration of acid, extraction temperature, non-stoichiometric norm and extraction time.

2. Among the four independent variables tested, the concentration of acid, extraction temperature, non-stoichiometric norm and extraction time showed significant influence on the recovery of elements.

3. Interactions between the four independent variables were observed from the contour plots. The data indicated that the lower acid concentration (20 wt %) and non-stoichiometric norm (200) and the higher temperature (80°C) and extraction time (120 min) applicable, the greater is the extraction degrees of the elements. Those are the optimal conditions determined according to the experimental plan.

4. The methodology as a whole proved to be adequate for the design and optimization of the recovery of elements. Therefore, a multi-factorial statistical approach that considers interaction of independent variables provided a basis for the model to search for a non-linear nature of the response in a short term experiment.

5. Extended experiments depending on the results of the D-optimal plan for second order model showed that the degree of extraction for aluminum and iron is up to 44%, when for Na it comes to 90%. The lowest extraction value is for Ti, about 10-11%.

4.4. Hydrothermal Autoclave Recovery of Elements from Fly Ash

Depending on the results of the previous section, the recovery of elements from fly ash under hydrothermal autoclave conditions was examined. The experiments were performed using 1g of the fly ash and 23.5 ml of 20% H_2SO_4 solution. Each sample was autoclaved at 100, 120 and 180°C in a sealed Teflon reactor for different times, Table 4.8.

Table 4.8.: Sample number and experimental conditions for hydrothermal autoclave recovery of elements from fly ash.

Sample	Temperature (°C)	Time (min)
1	100	120
2	100	240
3	100	360
4	100	480
5	120	120
6	120	240
7	120	360
8	120	480
9	140	120
10	140	240
11	140	360
12	140	480

4.4.1. Results and Discussion

Figures 4.18, 4.19, 4.20, 4.21, 4.22, 4.23, 4.24, 4.25 and 4.26 represent the degree of extraction of Mg, Al, K, Ca, Cr, Mn, Fe, Ni and Cu respectively.
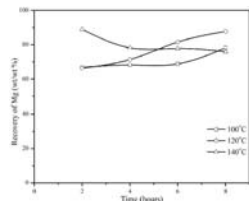

Fig.4.18: The effect of temperature on the degree of extraction of Mg at different times.
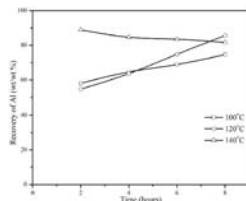
Fig.4.19: The effect of temperature on the degree of extraction of Al at different times.
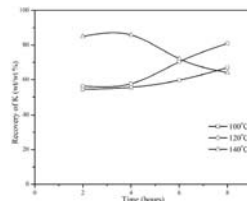
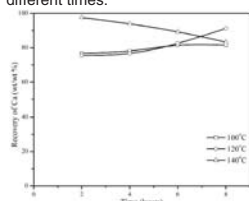Fig.4.20: The effect of temperature on the degree of extraction of K at different times.

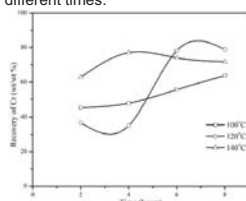Fig.4.21: The effect of temperature on the degree of extraction of Ca at different times.

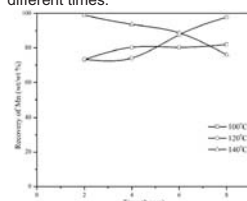Fig.4.22: The effect of temperature on the degree of extraction of Cr at different times.

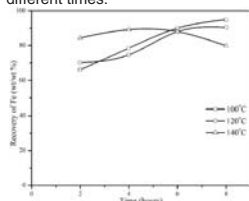Fig.4.23: The effect of temperature on the degree of extraction of Mn at different times.

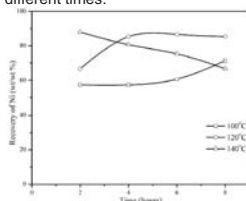Fig.4.24: The effect of temperature on the degree of extraction of Fe at different times.

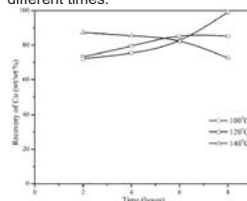Fig.4.25: The effect of temperature on the degree of extraction of Ni at different times.

Fig.4.26: The effect of temperature on the degree of extraction of Cu at different times.

The results of extraction of Mg have revealed that Mg attained high extraction yields, 89%, after 2 hours treatment at 140°C. At 100° and 120°C, the degree of extraction increase with time and reached after 8 hours treatment, 78.27% and 87.8%, respectively.

The increase in temperature of 100–140°C during the autoclave extraction of fly ash with 20 wt% sulfuric acid resulted in a relatively significant improvement in the extraction efficiencies of Al at 2 and 4 hours. However at 6 hours a relatively insignificant extraction is observed. At 100° and 120°C, the degree of extraction of Al increase with time and reached 74.64% and 85.64%, respectively, after 8 hours treatment. On the contrary, the extraction decreases with time at 140°C. Like Mg and Al, the degree of extraction of K is the maximum at 140°C for 2 and 4 hours, 84.92%

and 85.82%. The extraction decreases with time, 64.09% at 8 hours. At 100°C and 120°C, the degree of extraction of K increases with time. The extraction of calcium increased from 76.81% to 97.59% as the temperature increased from 100°C to 140°C at 2 hours. As the curing time increased at 100° and 120°C, the rate of reaction increased and therefore the extraction of calcium increased. However, at 140°C when the curing time was increased from 2 hours to 8 hours, the extraction of calcium decreased by about 14% from 97.59% to 83.27%.

The extraction of chromium decreased as the temperature increased from 100°C to 120°C and increased again at 140°C at 2 hours. As the curing time increased to 4 hours, a significant increase in the extraction observed at 140°C and decreased again when exceeds 6 hours curing. The degree of extraction of chromium obviously observed when the curing time increased from 4 hours to 6 hours at 120°C. 98.95% of Mn extracted at 140°C for 2 hours curing. As the curing time increased at 120°, the extraction of Mn increased, 97.87% after 8 hours curing. However, at 140°C when the curing time was increased from 2 hours to 8 hours, the extraction of Mn decreased by about 22% from 98.95% to 76.03%.

The increase in curing time from 2 to 8 hours during the autoclave extraction of fly ash at 100° and 120°C resulted in a relatively significant improvement in the extraction efficiencies of Fe. However at 140°C a relatively constant extraction is observed. At 100° and 120°C, the degrees of extraction of Fe for 8 hours are 95 % and 90.43 %, respectively. Ni extracted at 140°C for 2 hours curing and obviously decrease observed with time. However, at 120°C the degree of extraction of Ni is increased with time. At 120°C the degree of extraction of Cu is approximately 100% after 8 hours treatment. 87.38% of Cu extracted at 140°C for 2 hours curing and the degree of extraction decreased with time. However, at 100° and 120°C, distinct increase in the extraction is observed.

4.4.2. Conclusion

1. The extraction efficiency of nine elements using 20 wt% H_2SO_4 from fly ash under hydrothermal autoclave conditions is influenced by treatment temperature and time.
2. For most of the studied elements the optimal maximum degree of extraction from fly ash waste is observed at 140°C for 2 hours treatment.
3. Under optimal conditions the extraction efficiency of Mg, Al, K, Ca, Mn, Fe, Ni and Cu are 89%, 88.96%, 85%, 97.59%, 98.95%, 84.50%, 88% and 87.50 respectively. It is obvious that a number of the valuable elements could be extracted very well and it confirms that hydrothermal autoclave treatment is the most effective and promising treatment method for next step studies and development, including innovation and practical application.

5. Investigations on Bottom Ash

5.1. Characterization of Bottom Ash

Different techniques were used to characterize bottom ash such as ICP, XRD, SEM-EDX, IR and DTA-TG.

Table 5.1: The chemical composition of bottom ash.

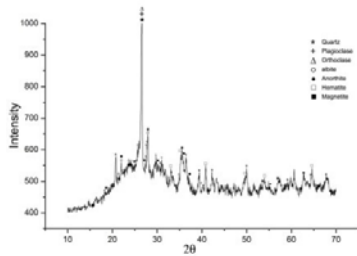| Oxide	Content (wt /wt %)	Element	Content (mg/Kg)
Fe_2O_3	9.44	Cu	112
MnO	0.07	Zn	86
TiO_2	0.76	As	22
CaO	3.42	Ba	1021
K2O	1.18	Cr	76
P_2O_5	0.09	Mo	14
SiO_2	51.68	Ni	58
Al_2O_3	21.70	Pb	25
MgO	1.75		
Na_2O	0.51		
L.O.I	3.98		

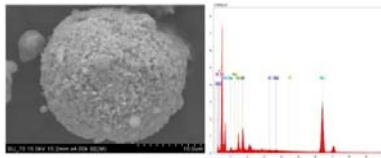Fig.5.1: XRD analysis for bottom ash sample.

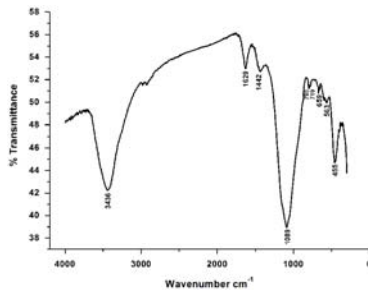Fig. 5.2: SEM-EDX of bottom ash sample.
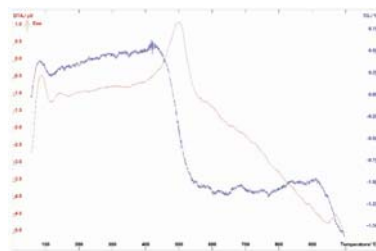

Fig. 5.3: Infrared spectrum of bottom ash sample

Fig. 5.4: TG/DTA of bottom ash sample

It was confirmed that the bottom ash particles from Enel Maritsa East 3 thermal power plant have a crystal structure and the chemical composition is closed to that of fly ash waste.

5.2. Leaching Characteristics of Elements from Bottom Ash

Leaching of elements from bottom ash from Enel Maritza East 3 TPP has been reported. The leaching experiments were done using distilled water of pH = 7, aqueous NaOH solution of pH = 10 and H_2SO_4 solution of pH = 4.

5.2.1. Results and Discussion
5.2.1.1. *Change of pH and conductivity*

Figure 5.5 illustrates the change in pH and conductivity of leachates at different L/S ratios for one leaching stage and two leaching stages.
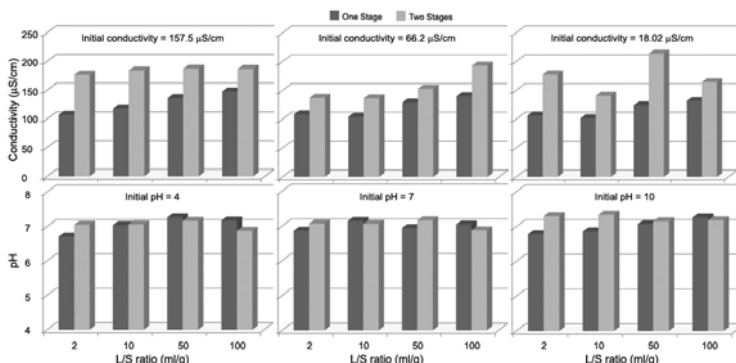

Fig. 5.5: Change in leachate pH and conductivity as a function of S/L ratio for one and two leaching stages.

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. However, for NaOH the pH of the final solution decreases to neutral values for all conditions of the experiments. The conductivity of leachates of H_2SO_4 and NaOH leachants rapid increased from its initial values.

5.2.1.2. *Leaching of toxic trace elements*

The effect of pH and leaching stages on the mobility of toxic trace elements from bottom ash was studied and the results were compared with the maximum conc. of contaminants according to the Bulgarian regulation leaching test. 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 is found that bottom ash should be classified as a hazardous.

Table 5.2: The mobility of toxic trace elements at L/S = 2 for different pH.

Contaminate	pH = 4 Stage One	Two	pH = 7 Stage One	Two	pH = 10 Stage One	Two	Max. Conc. (mg/kg)
As	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	0.10
Ba	2.50	7.25	1.50	3.75	2.75	5.00	7.00
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	5.00	12.50	2.50	5.00	2.50	7.50	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	15.00	<1.25	19.25	12.25	21.25	7.75	2.00

Table 5.3: The mobility of toxic trace elements at L/S = 10 for different pH.

Contaminate	pH = 4 Stage One	Two	pH = 7 Stage One	Two	pH = 10 Stage One	Two	Max. Conc. (mg/kg)
As	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	0.50
Ba	3.25	7.25	1.75	3.25	2.50	4.25	20.00
Cr	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	0.50
Cu	2.00	<1.25	6.25	2.75	1.50	4.00	2.00
Mo	5.00	2.50	2.50	5.00	2.50	<2.50	0.50
Ni	5.00	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	15.00	22.50	3.75	4.00

5.2.1.3. *Leaching of major and minor elements*

The mobility of Na, K, Mg, Ca, Mn and Si from bottom ash in leaching liquids at various pH for one and two leaching stages at different L/S ratios was studied.

For a medium of initial pH 4, the concentration of Na in the leachate of two leaching stages is much higher than of one leaching stage at all L/S ratios. 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.

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 than that for one stage. 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 drawn 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.
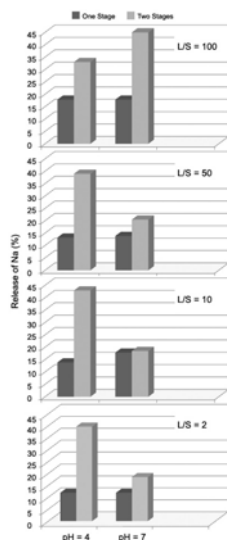
Fig. 5.6: Effect of leaching stages and pH on the leaching of Na at different L/S ratios.
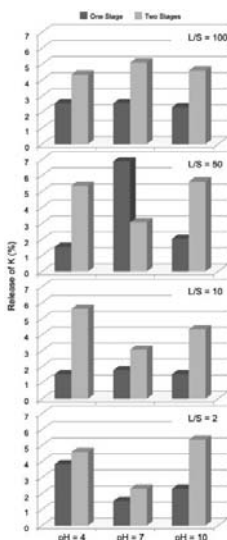
Fig. 5.7: Effect of leaching stages and pH on the leaching of K at different L/S ratios.

Fig. 5.8: Effect of leaching stages and pH on the leaching of Mg at different L/S ratios.

Fig. 5.9: Effect of leaching stages and pH on the leaching of Ca at different L/S ratios.
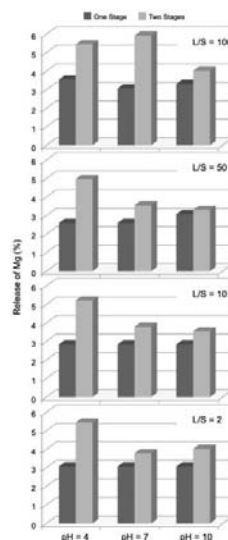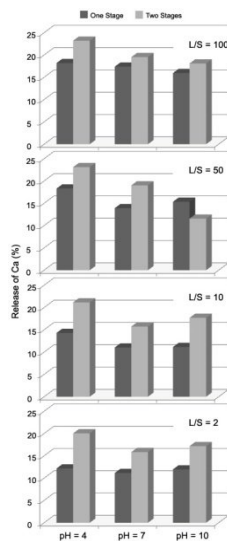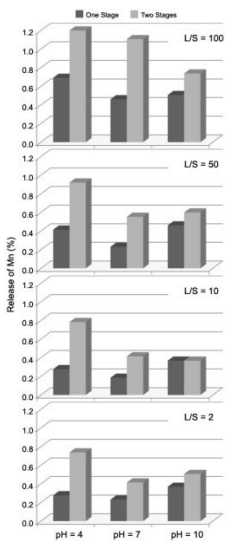
Fig. 5.10: Effect of leaching stages and pH on the leaching of Mn at different L/S ratios.
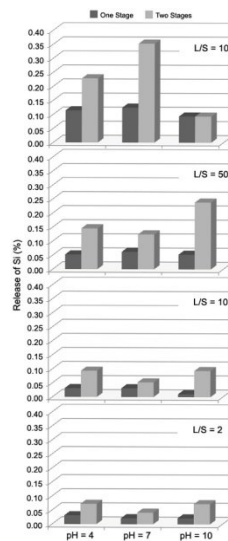
Fig. 5.11: Effect of leaching stages and pH on the leaching of Si at different L/S ratios.

The concentration of Mn in the leachates has maximum for two leaching stages, pH = 4 at L/S = 100. 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. The results obtained indicate that pH, L/S ratio and number of leaching stages are important parameters affecting the leaching degree of metals from ash deposits.

5.2.2. Conclusion

1. Widely varying mobility of heavy metals has been observed in the experiments covering weak acidic to basic pH of water for one stage and two stages in sequential batch leaching. Extracted values are higher for acidic media and very limited in alkaline water solutions.
2. It is confirmed that the concentration of studied elements in the liquate phase for two leaching stages is higher than that of one leaching stage in all leaching medium, but it is in general lower than for fly ash. The rate and level of extraction of the elements is not so sensitive to L/S ratio.
3. Leaching of toxic elements, according to Bulgarian regulation test, have given evidence that the bottom ash sample should be classified as hazardous waste.

5.3. Recovery of Elements from Bottom Ash

The effects of acid concentration, extraction time, norm and temperature on the solubility of the elements from bottom ash were investigated using multi-objective optimization and quantitative data obtained from properly designed experiments. The range and the levels of the variables investigated in this study are given in Table 5.4. Each factor in the design was studied at three different levels (-1, 0, 1). All variables were taken at a central coded value considered as zero. A 2^4 full factorial central composite design for four independent variables each at three levels with twelve star points and six replicates at the centre points was employed to fit a second order polynomial model in which 30 experiments were required for this procedure.

Table 5.4: Independent variables and limits of the main factors.

Variables	Range and levels		
	-1	0	1
Concentration of H_2SO_4 (wt %)	45	55	65
Temperature (°C) (X_2)	60	70	80
Norm∗ (%) (X_3)	600	700	800
Leaching time (min) (X_4)	30	60	90

The experiments performed using 10 gm bottom ash with different amounts of H_2SO_4 solution of different concentration and stirred at a constant velocity for different times and temperatures, Table 5.5. The amounts of H_2SO_4 used are calculated on the basis of chemical content of oxides in the sample. After the desired extraction time for each experiment the solid and liquid phases were separated by filtration. The

liquid phase was diluted to known volume. Elements in liquid phase were determined by ICP-OES (Varian Vista-MPX).

An empirical model was developed incorporating interaction effects of all parameters and optimized using response surface methodology. For each extraction of the chemical elements regression equations were built. The optimum values of the selected variables were obtained by solving the regression equation and by analyzing the response surface contour plots.

Later, depending on the results of the regression analysis, the experiments have been extended on a larger scale of extraction time in order to increase the degree of extraction of elements from bottom ash, samples 31-36.

5.3.1. Results and Discussion

Using statistical analysis and following the method of experiment design, the experimental results for the objective functions ($Y_1 - Y_{17}$) were obtained. The mathematical models are used second degree equations.

By applying multiple regression analysis on the experimental data, the experimental results of the design were fitted with a second-order polynomial equation. Thus, a mathematical regression models for recovery of seventeen elements from bottom ash fitted in the coded factors is given, Table 5.6. Y_1, Y_2, Y_3, Y_4, Y_5, Y_6, Y_7, Y_8, Y_9, Y_{10}, Y_{11}, Y_{12}, Y_{13}, Y_{14}, Y_{15}, Y_{16} and Y_{17} are the degree of extraction of Na, Mg, Al, Si, P, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Mo and Ba respectively. X_1, X_2, X_3 and X_4 are the independent variables, concentration of H_2SO_4 (wt %), temperature (°C), Norm (%), extraction time (min), respectively. The optimal conditions were obtained using deduced regression equations. The optimum conditions for metals extraction are respectively: $X_1 = 45$ wt %; $X_2 = 80$°C; $X_3 = 600$ and $X_4 = 90$ min. Our experimental data confirms the optimum values of the objective parameters after optimization (%): $Y_1 = 34.90$ %; $Y_2 = 30.37$ %; $Y_3 = 16.80$ %; $Y_4 = 0.29$ %; $Y_5 = 25.70$ %; $Y_6 = 13.70$ %; $Y_7 = 14.24$ %; $Y_8 = 7.95$ %; $Y_9 = 18.20$ %, $Y_{10} = 40.21$ %, $Y_{11} = 27.26$ %, $Y_{12} = 36.30$ %, $Y_{13} = 36.26$ %, $Y_{14} = 45.20$ %, $Y_{15} = 18.24$ %, $Y_{16} = 48.51$ % and $Y_{17} = 0.12$ %.

The degree of extraction of seventeen elements from bottom ash for different values of the variables can also be predicted from the respective contour plots. Each contour curve represents an infinite number if combinations of two test variables with the other two maintained at their optimal constant value. Figures 5.12 – 5.17 show the contour curves for Al. These plots demonstrated that the degree of extraction of elements from bottom ash is dependent of the concentration of sulfuric acid, temperature, norm and extraction time.

Table 5.5: Sample number and experimental conditions for recovery of elements from bottom ash.

Sample No.	Conc. of H_2SO_4 (wt	Temp. (°C)	Norm (%)	Leaching time
1	45	80	800	90
2	65	60	600	90
3	65	80	800	30
4	65	60	700	30
5	65	80	600	30
6	45	60	600	30
7	65	60	800	90
8	55	80	600	90
9	45	70	600	90
10	45	60	800	30
11	65	80	700	90
12	45	60	700	90
13	45	80	600	60
14	55	70	700	60
15	45	80	700	30
16	55	60	600	30
17	65	70	600	30
18	65	60	600	60
19	65	60	800	30
20	55	60	800	90
21	65	80	800	60
22	45	70	800	30
23	65	70	800	90
24	55	80	800	30
25	45	60	800	60
26	45	80	800	90
27	45	60	600	90
28	45	80	600	30
29	65	80	600	90
30	55	70	700	60
31	25	80	400	150
32	25	80	400	240
33	25	80	500	150
34	35	80	500	150
35	35	80	500	240
36	25	80	400	360

Table 5.6 Mathematical models, coefficient of determination and adjusted R-square for recovery of

| Mathematical model	R-sq (%)	R-sq(adj) (%)
$Y_1 = 19.1 - 2.40\ X_1 + 3.15\ X_2 - 1.58\ X_3 + 2.40\ X_4 - 0.366\ X_1X_2 - 0.953\ X_1X_4 + 0.740\ X_2X_4 + 2.81\ X_2^2 + 1.72\ X_4^2$	97.0	95.3
$Y_2 = 18.1 - 1.16\ X_1 + 2.45\ X_2 - 1.49\ X_3 + 1.86\ X_4 - 0.615\ X_1X_4 + 0.718\ X_3X_4 + 2.79\ X_2^2 + 1.47\ X_4^2$	97.4	96.1
$Y_3 = 8.41 - 1.17\ X_1 + 2.12\ X_2 - 0.678\ X_3 + 1.56\ X_4 - 0.417\ X_1X_4 + 0.486\ X_2X_4 + 1.46\ X_2^2 + 0.635\ X_4^2$	98.8	98.2
$Y_4 = 0.0836 - 0.186\ X_1 - 0.0300\ X_2 - 0.0465\ X_4 + 0.0171\ X_1X_2 + 0.0289\ X_1X_4 + 0.00804\ X_2X_4 + 0.118\ X_1^2 + 0.0126\ X_2^2 + 0.00744\ X_4^2$	99.9	99.8
$Y_5 = 18.5 - 1.62\ X_1 + 1.39\ X_2 - 0.463\ X_3 + 1.60\ X_4 - 0.548\ X_1X_3 - 0.175\ X_2X_3 + 1.47\ X_2^2 - 0.598\ X_3^2 + 0.458\ X_4^2$	98.6	97.5
$Y_6 = 5.61 - 1.28\ X_1 + 1.95\ X_2 - 0.575\ X_3 + 1.38\ X_4 - 0.257\ X_1X_4 - 0.451\ X_1X_4 - 0.164\ X_2X_3 + 0.510\ X_2X_4 + 1.18\ X_2^2 + 0.460\ X_4^2$	98.8	98.0
$Y_7 = 7.73 - 1.52\ X_1 - 0.743\ X_2 - 1.21\ X_3 - 0.307\ X_4 + 0.526\ X_3X_4 + 1.79\ X_1^2 + 2.72\ X_2^2 + 0.981\ X_4^2$	97.0	95.3
$Y_8 = 9.00 - 3.30\ X1 - 1.95\ X_2 - 2.12\ X_4 + 0.762\ X_1X_4 + 1.05\ X_2X_3 - 0.716\ X_2X_4 + 1.21\ X_3X_4 + 4.46\ X_2^2 - 1.47\ X_4^2$	89.0	81.9
$Y_9 = 10.4 - 0.620\ X_1 + 2.72\ X_2 + 1.91\ X_4 + 2.57\ X_2^2$	93.9	92.6
$Y_{10} = 27.1 - 1.80\ X_1 + 2.89\ X_2 - 1.86\ X_3 + 2.37\ X_4 - 1.20\ X_1X_4 + 0.518\ X_2X_4 + 2.85\ X_2^2$	98.0	96.9
$Y_{11} = 19.1 - 0.434\ X_1 + 2.60\ X_2 - 1.11\ X_3 + 1.52\ X_4 - 0.301\ X_1X_4 + 2.39\ X_2^2$	97.6	96.7
$Y_{12} = 26.2 + 4.23\ X_2 - 1.46\ X_3 + 2.50\ X_4 + 0.770\ X_2X_4 + 2.34\ X_2^2 - 1.47\ X_3^2$	97.3	96.4
$Y_{13} = 25.9 + 3.39\ X_2 - 1.94\ X_3 + 2.32\ X_4 - 0.889\ X_1X_2 + 0.550\ X_2X_4 + 2.33\ X_2^2 - 1.07\ X_3^2$	92.6	89.7
$Y_{14} = 25.0 - 3.72\ X_1 + 5.53\ X_2 - 1.27\ X_3 + 2.24\ X_4 - 2.34\ X_2X_3 - 3.08\ X_1X_4 + 1.42\ X_3^2 + 0.35\ X_4^2$	86.8	80.2
$Y_{15} = 17.0 - 4.55\ X_1 + 0.95\ X_2 + 1.09\ X_3 - 1.47\ X_4 + 1.43\ X_1X_2 + 2.50\ X_1X_3 - 1.82\ X_1X_4 - 4.36\ X_2^2$	58.2	39.7
$Y_{16} = 32.3 + 3.04\ X_2 - 1.92\ X_3 + 1.63\ X_4 + 2.99\ X_1^2 + 4.85\ X_2^2 + 2.17\ X_4^2$	81.3	75.1
$Y_{17} = 0.142 + 0.0354\ X_1 - 0.0232\ X_2 - 0.0150\ X_3 - 0.0150\ X_1X_2 + 0.0150\ X_1X_3 + 0.0128\ X_2^2 - 0.0159\ X_3^2 + 0.0143\ X_4^2$	99.2	98.5

26
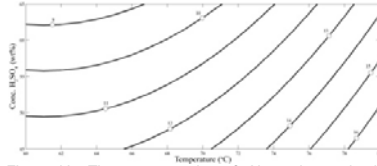
Fig. 5.12: The contour plot of Al at the optimal constant value of $X_3 = 600$ and $X_4 = 90$ min.
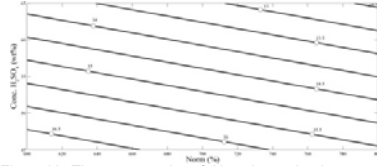

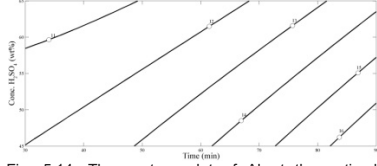Fig. 5.13: The contour plot of Al at the optimal constant value of $X_2 = 80°C$ and $X_4 = 90$ min.

Fig. 5.14: The contour plot of Al at the optimal constant value of $X_2 = 80°C$ and $X_3 = 600$.
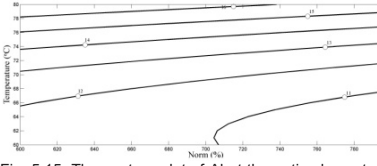

Fig. 5.15: The contour plot of Al at the optimal constant value of $X_1 = 45$ wt% and $X_4 = 90$ min.

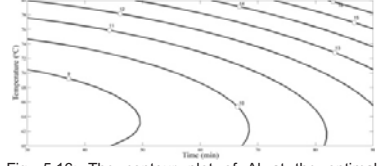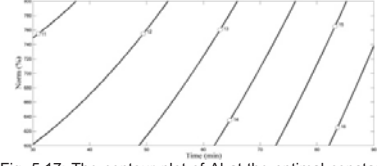Fig. 5.16: The contour plot of Al at the optimal constant value of $X_1 = 45$ wt% and $X_3 = 600$.

Fig. 5.17: The contour plot of Al at the optimal constant value of $X_1 = 45$ wt% and $X_2 = 80°C$.

The results of extended experiments, Table 5.7, show that the degree of extraction of the elements was significantly increased with time.

Table 5.7: The degree of extraction of elements from bottom ash for extended experiments.

Sample No.	Degree of Extraction (wt/wt %)								
	Na	Mg	Al	Si	P	K	Ca	Ti	Cr
31	30.92	26.25	15.74	1.03	20.96	13.37	50.40	3.18	19.80
32	46.25	37.67	22.57	1.27	28.82	21.23	70.66	3.73	29.34
33	38.32	31.98	17.98	1.28	26.20	16.64	59.94	3.84	23.42
34	36.60	31.03	17.47	0.67	27.51	15.77	28.21	1.98	24.47
35	36.07	31.80	18.67	0.54	23.58	17.41	28.76	1.54	25.40
36	52.60	42.45	27.92	1.15	28.82	25.32	60.73	3.29	28.22

Sample No.	Degree of Extraction (wt/wt %)						
	Mn	Fe	Ni	Cu	Zn	As	Mo	Ba
31	38.21	29.84	39.66	33.26	46.45	<4.55	<3.57	0.13
32	54.34	42.95	54.31	45.13	55.47	18.18	<3.57	0.15
33	45.29	34.67	43.10	40.45	49.59	<4.55	<3.57	0.13
34	45.18	34.75	43.97	37.63	43.90	<4.55	<3.57	0.12
35	44.33	35.37	46.55	36.88	57.04	<4.55	<3.57	0.15
36	50.64	39.98	50.86	55.54	63.61	<4.55	53.57	0.40

5.3.2. Conclusion

1. Using the D-optimal plan for second order model, it was possible to determine the optimal conditions for recovery of elements from bottom ash. The optimal conditions for metals extraction are respectively: X_1 = 45 wt %; X_2 = 80°C; X_3 = 600 and X_4 = 90 min.
2. The validity of the model was proved by fitting the values of the variables in the second-order polynomial equations and by actually carrying out the experiments at those predicted values for the four independent variables, the concentration of acid, extraction temperature, non-stoichiometric norm and extraction time.
3. Among the four independent variables tested, the concentration of acid, extraction temperature, non-stoichiometric norm and extraction time showed significant influence on the recovery of elements.
4. Interactions between the four independent variables were observed from the contour plots. The data indicated that 45 wt% acid concentration, 600 non-stoichiometric norm, 80°C temperature and 90 min extraction time are the optimal conditions for greater extraction degrees of the most valuable metals and alkaline elements. Any way the extraction of aluminum and the valuable alkaline elements are lower in comparison with fly ash extraction. Extraction of silica is rather low.
5. The methodology as a whole proved to be adequate for the design and optimization of the recovery of elements. Therefore, a multi-factorial statistical approach that considers interaction of independent variables provided a basis for the model to search for a non-linear nature of the response in a short term experiment.
6. The extended experiments which depend on the results of the D-optimal plan for second order model showed good degree of extraction of the elements from bottom ash, but any way did not contribute too much to the extraction values – the behavior is similar to the fly ash.

5.4. Hydrothermal Autoclave Recovery of Elements from Bottom Ash

Depending on the results of the previous section, the recovery of elements from bottom ash under hydrothermal autoclave conditions was examined. The experiments were performed using 2g of the bottom ash and 25.6 ml of 25% H_2SO_4 solution. Each sample was autoclaved at 100, 120 and 180°C in a sealed Teflon reactor for different times, Table 5.8.

Table 5.8.: Experimental conditions for hydrothermal autoclave recovery of elements from bottom ash.

Sample	Temperature (°C)	Time (min)
1	100	120
2	100	240
3	100	360
4	100	480
5	120	120
6	120	240
7	120	360
8	120	480
9	140	120
10	140	240
11	140	360
12	140	480

5.4.1. Results and Discussion

Figures 5.18, 5.19, 5.20., 5.21, 5.22, 5.23, 5.24, 5.25, 5.26, 5.27, 5.28 and 5.29 represent the degree of extraction of Na, Mg, Al, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn and Mo respectively.
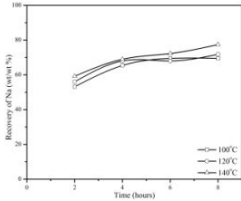

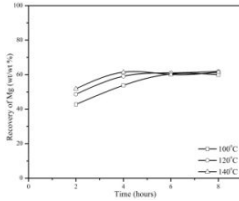Fig.5.18: The effect of temperature on the degree of extraction of Na at different times.

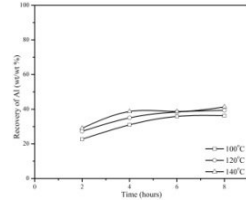Fig.5.19: The effect of temperature on the degree of extraction of Mg at different times.

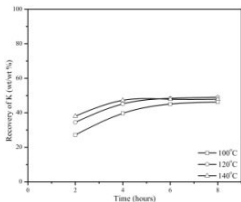Fig.5.20: The effect of temperature on the degree of extraction of Al at different times.

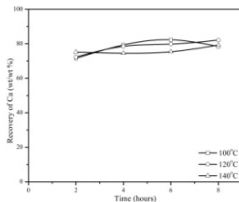Fig.5.21: The effect of temperature on the degree of extraction of K at different times.

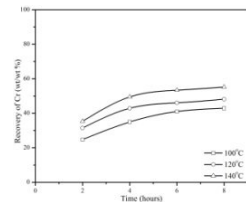Fig.5.22: The effect of temperature on the degree of extraction of Ca at different times.

Fig.5.23: The effect of temperature on the degree of extraction of Cr at different times.

Fig.5.24: The effect of temperature on the degree of extraction of Mn at different times.

Fig.5.25: The effect of temperature on the degree of extraction of Fe at different times.
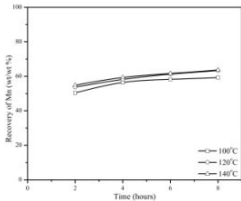
Fig.5.26: The effect of temperature on the degree of extraction of Ni at different times.

Fig.5.27: The effect of temperature on the degree of extraction of Cu at different times.

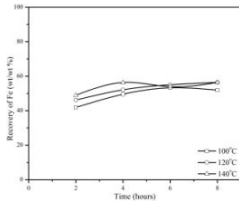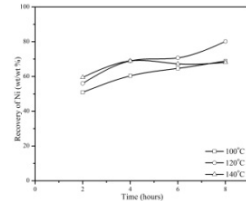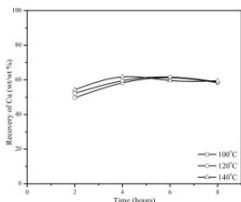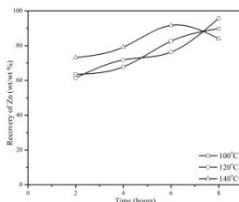Fig.5.28: The effect of temperature on the degree of extraction of Zn at different times.
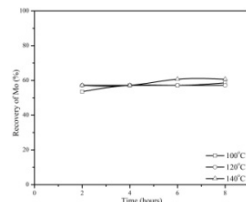
Fig.5.29: The effect of temperature on the degree of extraction of Mo at different times.

77.45% of Na is extracted at 140°C for 8 hours treatment. At 100° and 120°C, the degree of extraction increase with time and reached after 8 hours treatment, 53.16% and 69.47%, respectively. At 2 and 4 hours treatment there was difference in the degree of extraction of magnesium among the treatment temperatures. However at 6 and 8 hours the difference is very small. 61.5% extraction observed at 140°C for 4 hours treatment.

The degree of extraction of aluminum is shown in Figure 5.20. At a reaction temperature of 100°C, extraction of Al is 22.7% after 2 hours and raises to 36.3% after 8 hours. At a reaction temperature of 120°C, the degree of extraction increases with time. The maximum degree of extraction, 41.3%, is observed at 140°C after 8 hours treatment.

The extraction of potassium increased as the temperature increased from 100°C to 140°C for all reaction times. As the curing time increased at 100°C and 120°C, the rate of reaction increased and therefore the extraction of calcium increased. However, at 140°C when the curing time was increased, the extraction of potassium remains constant, about 47.5%. The maximum degree of extraction of calcium, 82%, is observed at reaction temperature 100°C and reaction time 6 hours, also at 120°C for 8 hours. While at 140°C, insignificant effect of reaction time on the degree of extraction of calcium is observed.

Obviously change in the extraction of chromium is observed when the reaction temperature was changed from 100°C to 140°C. At all reaction temperatures, the extraction of chromium increased with reaction time increase. The optimum degree of extraction is observed at reaction temperature 140°C and reaction time 8 hour, 55.2%.

It is clear from Figure 5.24 those at all reaction times unnoticeable change was observed on the degree of extraction of manganese with temperature increase from 120°C to 140°C. 63.7% of manganese was extracted at 140°C after 8 hour treatment.

The autoclave extraction of bottom ash with 25 wt% sulfuric acid resulted in a relatively improvement in the extraction efficiencies of Fe, Figure 5.25. An insignificant change in the degree of extraction of iron with change in reaction temperature at different times. The maximum degree of extraction of iron is approximately 56.5%.

obviously increase in the amount of nickel extracted observed with time at 100°C and 120°C. However, at 140°C the degree of extraction is almost constant. The maximum degree of extraction, 80%, is observed at 120°C after 8 hours curing time.

The change in reaction temperature and time is indistinct effect on the degree of extraction of copper. However the hydrothermal treatment resulted in a relatively significant improvement in the extraction efficiencies of copper. Approximately 60% of copper extracted by hydrothermal treatment. The autoclave treatment of bottom

ash improves the extraction of zinc. Approximately 96 % of zinc extracted at 120°C after 8 hours treatment. , the change in reaction temperature and time is indistinct effect on the degree of extraction of molybdenum. However the hydrothermal treatment resulted in a relatively significant improvement in the extraction efficiencies. Approximately 60.714% of molybdenum extracted at 140°C after 6 hours treatment. In all experiments, recovery of silicon and titanium from bottom ash was poor.

5.4.2. Conclusion

1. The hydrothermal autoclave treatment using 25 wt% H_2SO_4 revealed a significant increasing in the extraction efficiency of twelve studied elements from bottom ash, but the efficiency is not as high as for the fly ash.
2. For Ca, Mn, Fe, Cu and Mo, the higher reaction temperature does not practically effect on the degree of extraction, however for Na, Mg, Al, K, Cr, Ni and Zn this effect is clear.
3. The optimal conditions for high recovery differ from element to element. The highest level of extraction, about 90-95%/ was registered for Zn at temperatures 120-1400C and treatment time 6-8 hours. Quite high level of extraction was achieved also for Ca, about 80-85 % in the studied temperature range. For other group of elements like Mo, Ni, Cu, Na, K, Fe and Ti the maximum extraction is between 55-80% and for Al, Cr and others it is even lower, 30-40%.
4. Different range of extraction of elements from fly ash and bottom ash shows that it would be better to have a separate releasing of both types of solid wastes on the way to find more efficient utilization of fly ash as a secondary raw material for metal productions.

6. General Conclusion

1. Studied wastes, fly ash and bottom ash, from Enel Maritza East 3 TPP were characterized using different techniques. The characterization results of such wastes have confirmed their crystal structure with different particles size. The results indicate that fly ash and bottom ash samples are mainly composed of SiO_2, Al_2O_3 and Fe_2O_3 and are mixtures of 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 (magnetite).

2. It was found that the mobility of metals from such wastes is different for the studied leaching solutions. The results were evaluated by toxicity characteristic leaching procedure according to the EU and Bulgarian legislation were made at the first time. The extraction of the elements increases in acidic medium rather than basic medium indicating that extraction results are pH dependent. It was 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 rate is sensitive to L/S ratio. Based on the results, these solid wastes were classified as hazardous waste. Taking into account shortage of natural resources for production of number of metals and the environmental problems created, because of deposition of solid waste it is obvious that the selected solid wastes from Enel Maritsa East 3 TPP should be considered as potentially secondary raw materials. Using this approach it would be possible to save land area and reduce fresh water use.

3. It is the first time that the recovery of the elements from fly ash and bottom ash was studied using statistical analysis and following of the experimental design. The investigations were performed with H_2SO_4 and the objective factors were concentration of sulfuric acid (X_1), temperature (X_2), the non-stoichiometric norm (X_3) and time of extraction (X_4). Using the D-optimal plan for second order model and on the basis of the experimental results obtained, mathematical regression equations describing the relationship between experimental conditions and the level and extent of element extraction for 17 elements from fly ash and bottom ash were obtained. It was improved that the four independent variables tested, have significant influence on the recovery of valuables elements. The mathematical models will allow a better control of the H_2SO_4 processing of fly and bottom ash.

4. Based on the deduced adequate regression equations obtained, an optimization for the process of acid solubilization using H_2SO_4 of solid wastes in searching a maximum values for the objective function ($Y_1 - Y_{17}$) was made and optimal conditions were done. The data indicated that for fly ash the lower acid concentration (20 wt %) and non-stoichiometric norm (200) and the higher temperature (80°C) and extraction time (120 min) applicable, the greater is the

extraction degrees of the elements. Interactions between the four independent variables were observed from the contour plots.

5. Using the D-optimal plan for second order model, it was possible to determine the optimal conditions for recovery of elements from bottom ash. The optimal conditions for metals extraction are respectively: X_1 = 45 wt %; X_2 = 80°C; X_3 = 600 and X_4 = 90 min. The validity of the model was proved by fitting the values of the variables in the second-order polynomial equations and by actually carrying out the experiments at those predicted values for the four independent variables. Interactions between the four independent variables were observed from the contour plots. Any way the extraction of aluminum and the valuable alkaline elements are lower in comparison with fly ash extraction. Extraction of silica is rather low. The extended experiments which depend on the results of the D-optimal plan for second order model showed good degree of extraction of the elements from bottom ash, but did not contribute to the extraction values, the behavior is similar to the fly ash.

6. On the basis of the results obtained after optimization of the process of the sulphuric acid solubilization of the solid wastes extended experiments were performed. The results showed a higher degree of extraction for more of the studied elements. For investigations with fly ash we reach a degree of extraction over 80% for Na, Cu, Zn, Mo, As and in the intervals of 60 -80% for Mg, Ca, Mn and Ni. For investigations with bottom ash this values are lower.

7. Using the results from investigations on the sulfuric acid solubilization of fly ash and bottom ash with the help of the experimental design a hydrothermal autoclave treatment of the solid wastes was made. The results indicated that a high extent of extraction can be achieved for fly ash as well as for bottom ash. Extraction efficiency of nine elements using 20 wt% H_2SO_4 from fly ash under hydrothermal conditions is influenced by treatment temperature and time. For most of the studied elements the optimal maximum degree of extraction from fly ash waste is observed at 140°C for 2 hours treatment. Under optimal conditions the extraction efficiency of Mg, Al, K, Ca, Mn, Fe, Ni and Cu are 89%, 88.96%, 85%, 97.59%, 98.95%, 84.50%, 88% and 87.50 respectively. It is obvious that a number of the valuable elements could be extracted very well and it confirms that hydrothermal autoclave treatment is the most effective and promising treatment method for next step studies and development, including innovation and practical application.

8. The hydrothermal autoclave treatment using 25 wt% H_2SO_4 revealed a significant increasing in the extraction efficiency of twelve studied elements from bottom ash, but the efficiency is not as high as for the fly ash. For Ca, Mn, Fe, Cu and Mo, the higher reaction temperature does not practically effect on the degree of extraction, however for Na, Mg, Al, K, Cr, Ni and Zn this effect is clear.

9. Optimal conditions for high recovery of the elements obtained using hydrothermal autoclave treatment are different for the studied elements. The

highest level of extraction is about 90-95% for Zn at temperatures 120-140^{0}C and treatment time 6-8 hours. Quite high level of extraction was achieved also for Ca, about 80-85 % in the studied temperature range. For other group of elements like Mo, Ni, Cu, Na, K, Fe and Ti the maximum extraction is between 55-80% and for Al, Cr and others it is even lower 30-40%.

10. Different range of extraction of elements from fly ash and bottom ash shows that it would be better to have a separate releasing of both types of solid wastes on the way to find more efficient utilization of fly ash as a secondary raw material for metal productions. On the base of the results obtained it could be recommended to use hydrothermal treatment of the wastes for extraction of the interested metals and the separation could be realized using suitable membrane method used as the best available techniques for production of some metals in the practice.

Thesis Contribution

1. Different techniques were applied for physico-chemical characterization of fly ash and bottom ash from Enel Maritsa East 3 TPP.

2. Studied wastes, fly ash and bottom ash, were evaluated by toxicity characteristic leaching procedure according to the EU and Bulgarian legislation. Based on the results, these solid wastes were classified as hazardous waste.

3. Using statistical analysis by applying D-optimal plan for second order model to study the recovery of metals from fly ash and bottom ash using H_2SO_4. The mathematical models will allow a better control of the H2SO4 processing of these wastes.

4. Based on the deduced adequate regression equations obtained, an optimization for H_2SO_4 solubilization of fly ash and bottom ash was made and optimal conditions of degree of extraction for the 17 elements were obtained.

5. It is the first time that a hydrothermal autoclave method has been used recover of metals from TPP solid wastes using H_2SO_4. The results showed that this method is most effective and promising treatment method for innovation and practical application. On the base of the results obtained it could be recommended a separate releasing of both types of solid wastes on the way to find more efficient utilization of fly ash as a secondary raw material for metal production.

List of Publications

1. A.S. Meawad, D.Y. Bojinova, Y.G. Pelovski, D.L. Damgaliev, Optimization of leaching metals with sulfuric acid from TPS bottom ash. International Journal of Human Geography and Environmental Studies, 1, 2009, 27-31.

2. A.S. Meawad, D.Y. Bojinova, Y.G. Pelovski, Study on elements leaching from bottom ash of Enel Maritsa East 3thermal power plant, Bulgaria. Journal of the University of Chemical Technology and Metallurgy, 45, 3, 2010, 221-228.

3. A.S. Meawad, D.Y. Bojinova, Y.G. Pelovski, An overview of metals recovery from thermal power plant solid wastes. Waste management, 30, 2010, 2548-2559. (**Impact Factor:** 2.924).

Conferences Attended

International Conference on Sustainability, Human Geography and Environmental Studies, Diano Marina, Italy, 6-8 November 2009