MATERIALS BASED ON ASH FOR ENVIRONMENTAL PROTECTION. I. OBTAINING AND CHARACTERIZATION

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The fly ash produced from the burning of pulverized coal in a coal-fired boiler is a fine-grained, powdery particulate material that is carried off in the flue gas. Approximately 70 to 75 percent of the generated fly ash is still disposed of in landfills or storage lagoons. Much of this ash, however, can be recovered and used. Examples of these applications are: additives for the immobilization of industrial wastewater treatments; Extraction of valuable metals, such as Al, Si, Fe, Ge, Ga, V, Ni, Zn; Land stabilization in mining areas; Sorbents for flue gas desulfurization et all. In order to use the ash for synthesis of zeolites and adsorbents, we proposed to conduct their characterization from a chemical, mineralogical and technological point of view. For this we performed the chemical analysis for the oxidic compounds, the thermogravimetrical and the FTIR analysis. Also, we have run analysis in order to determine their density and their Blaine specific surface. This paper presents the result of the study of ash characterization produced by CET Iasi in order to obtain new adsorbents for wastewater treatment.

***Keywords**: ash, adsorbent, zeolite, waste waters, chemical characterization.*

His mental capacity has always allowed man to be the determining factor in modifying natural systems without considering the possibility of biosphere regeneration; the consequence of this behavior was that the intensive and irrational use of the biosphere has lead to a change in the structure of the ecosystems through modifications of the ratio between advantaged and endangered species to the benefit of those species that man holds important. The fly ash produced from the burning of pulverized coal in a coal-fired boiler is a fine-grained, powdery particulate material that is carried off in the flue gas and is usually collected from the flue gas by means of electrostatic precipitators, baghouses or mechanical collection devices such as cyclones [1-5]. Approximately 70 to 75 percent of the fly ash generated is still disposed of in landfills or storage lagoons. Much of this ash, however, could be recovered and used. In this context it was attempted to reduce the amount of waste by the superior capitalization of the ash in view to obtain new materials with adsorptive properties and different applications Additives for immobilization of industrial and wastewater treatments, extraction of valuable metals, such as Al, Si, Fe, Ge, Ga, V, Ni, Zn, land stabilization in mining areas, sorbents for flue gas desulfurization, fireproof materials, 'Slash'' (fly ash/sludge blend) production for soil amendment, filter material for the production of different products, ceramic applications [5, 10-13].

This paper presents our results regarding the characterization study (chemical, mineralogical and technological characterizations of these oxides compounds, termogravimetry, FTIR) of ash produced by CET Iasi in order to obtain some new adsorbents for wastewater treatment and also some new types of materials based on ash.

MATERIALS AND METHODS

Materials. The studied material was fly ash - a waste product from CET Iasi. In Romania, where the main source of thermal power is the lignite, which contains an average of 30% ash, it is necessary to find some proceedings to allow the capitalization of this waste. The fly ash produced from the burning of pulverized coal in a coal-fired boiler is a fine-grained, powdery particulate material that is carried off in the flue gas. The samples have been numbered according to the month and year when they were collected: sample 1 - taken in October 2006 and sample 2 – in November 2006.

Method. In order to use the ash for the synthesis of zeolites or adsorbents with lime, the ash has to undergo a process of characterization from a chemical, mineralogical and technological point of view. For this we performed the chemical analysis of the oxide compounds, the thermogravimetrical analysis using a MOM Budapest Q-1500 Thermogravimeter, and the FTIR analysis using a DIGILAB FTS 2000 spectrometer. The chemical characterization of the ash has been performed in accordance with the SR EN standard - 450-1:2006 the specific surface has been determined by the Blaine permeabilimeter.

From sample 2 **zeolite material** was obtained by direct alkaline conversion processes in autoclaves at the 393 K, NaOH 2Msolution, at different treatment intervals: 4h, 12h, 24h, and 48h. The fly ash was added to a NaOH solution 10 mL/g ratio. The zeolites obtained were filtered, washed and dried for 4 hours at 373 K. We synthesized an **adsorbent on the base of fly ashes and lime**, at the 353 K in the reactor with magnetic agitation. We used fly ash (sample 2) and lime with 97,68% active CaO. In preparation we took 10 g of fly ash/lime (2/1) and put it in the reactor, in which there were also 90 mL of deionized water at the temperature in question. Reaction time was 1, 2, 3, respectively 4 hours.

RESULTS AND DISCUSSION

Characterization of ash

The possibilities to use the ash in order to obtain new types of materials with adsorptive properties result from their chemical and mineralogical composition and also from their technical properties. The specific gravity of fly ash usually ranges from 2.1 to 3.0, while its specific surface area (measured by the Blaine air permeability method) may range from 170 to 1000 m^2/kg. The color of fly ash can vary from tan to gray to black, depending on the amount of unburned carbon in the ash. The lighter the color, the lower the carbon content.

The chemical properties of fly ash are influenced to a great extent by those of the coal burned and the techniques used for handling and storage. The main components of coal fly ash are silica, alumina, iron oxide and calcium, with varying amounts of carbon, as measured by the loss on ignition (LOI) (*Tab.1*).

Table 1

The characterization of fly ash

Composition, %	**Sample 1**	**Sample 2**
SiO_2	51.198	51.21
Al_2O_3	26.93	25.08
Fe_2O_3	6.98	6.28
CaO	8.31	5.21
MgO	1.075	0.7596
Ignition loss 1200°C – total loss, %	2.42	1.3
Density (kg m^{-3})	2340	2518
Ration SiO_2/Al_2O_3	1.9	2

Based on their chemical composition, these ashes are classified in Class F [8, 9, 10]. The main difference between Class F and Class C of fly ash consists in the amount of calcium and the silica, alumina, and iron content in the ash. In Class F, total calcium typically ranges from 1 to 12 percent [10], mostly in the form of calcium hydroxide, calcium sulfate, and glassy components in combination with silica and alumina. The loss on ignition, which measures the amount of unburned carbon remaining in the fly ash, is one of the most significant chemical properties of fly ash, especially as an indicator of suitability for use as a cement replacement in concrete. Even though the results we got regarding the chemical oxide composition correspond to the ones reported in the reference literature [11, 12].

The results of thermogravimetrical analysis, respectively the TG and DT curves are presented in *Figure 1*.

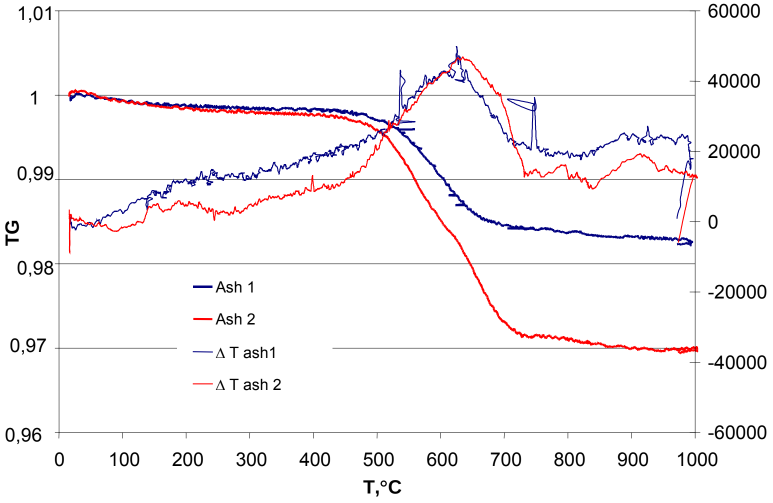

Figure 1. **Thermogravimetric curves for samples 1 and 2**

Figure 1 showed that for samples 1 and 2 the losses are of 2.84% and 1.7% respectively (including humidity), in accordance with ignition loss. The destructive chemical analysis allows the determination of the oxide compounds in the sample without offering any information about „mineralogical” composition of the ash. To get some further information about the way the oxide compounds bond we have performed the IR analysis and the obtained spectrums are presented in *Figure 2*.

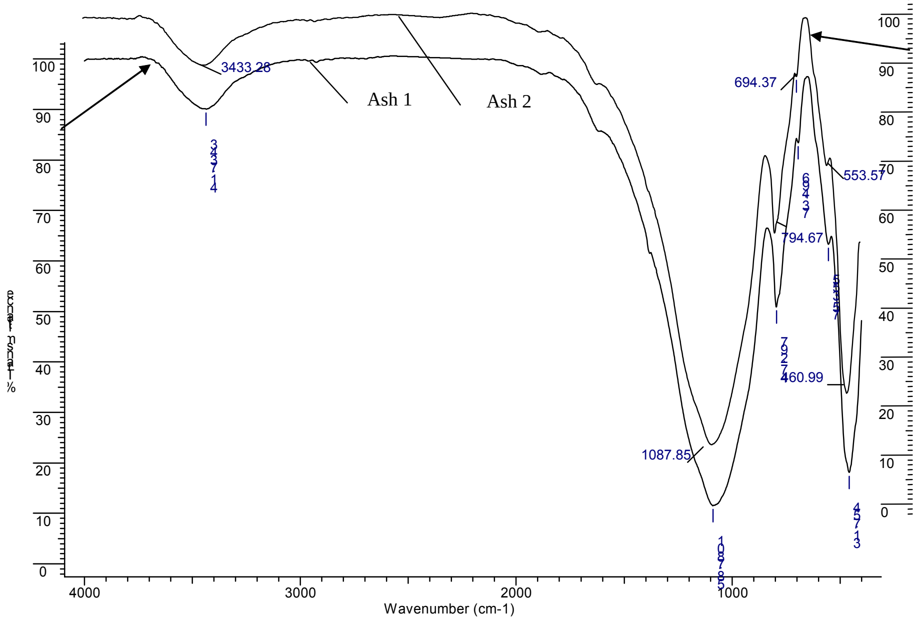

Figure 2. **The IR spectrums for samples 1 and 2**

The analysis of IR spectrums proves that in the ash samples we can find compounds like: hematite, quartz, kaolin, illit, glow, montmorilonite, carbon. Moreover, these are the compounds which can be found in the clayey material, respectively the fuel’s ballast.

Characterization of other adsorbent materials based on ash

The **zeolites** synthesized were IR analysed (*Fig.3*). From *Figure 3* we observed that the zeolitization time modifies the content of free calcium oxides.

Samples of **adsorbents with ash and lime** were dried and analyzed for the determination of the CaO content (complexonometric method). The degree of hydration was calculated in relation to this:

$$\eta_{Ca^{2+}} = 1 - \frac{C_{Ca^{2+}}}{C^0_{Ca^{2+}}} \quad (1)$$

The maximum value for the degree of hydration was 54% for 4 hours. The solids obtained were IR analyzed, and the spectrum for 4 hours of hydration is presented in *Figure 4*.

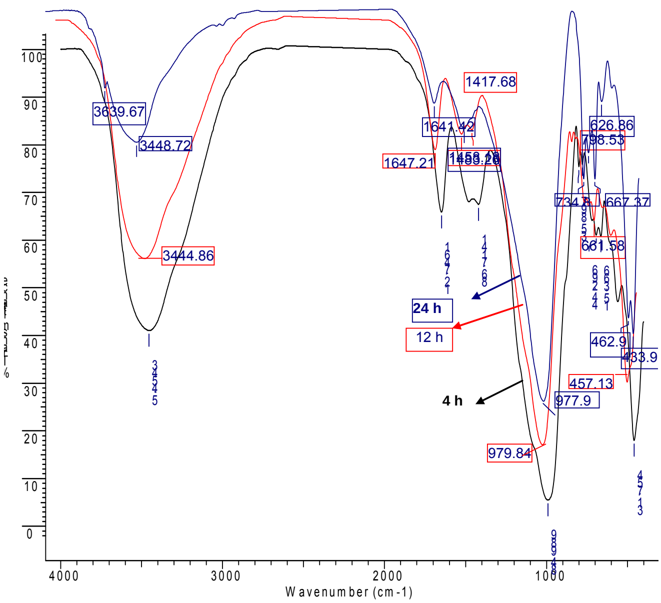

Figure 3. **The IR spectrum of zeolites**

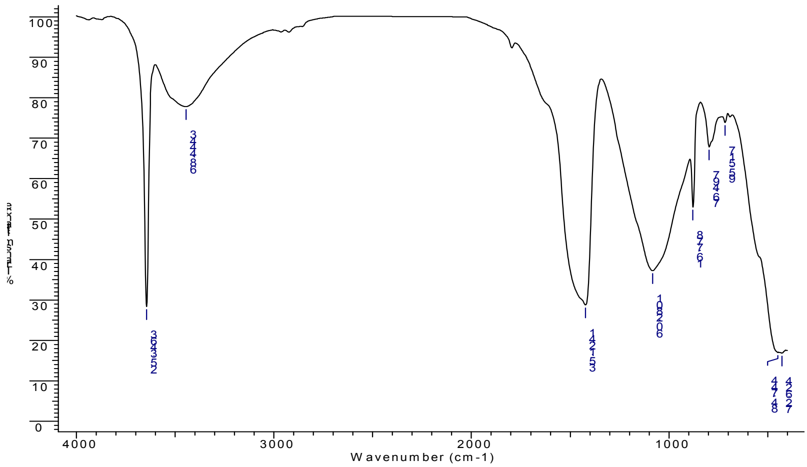

Figure 4. **The IR spectrum of fly ash- lime adsorbant**

CONCLUSIONS

Based on the experimental results we obtained, the analyzed ash belongs to the F class, as it results after the combustion of a bituminous fuel. This type of ash can be used to obtain zeolitic materials for the uptake heavy metals.

The potential industrial application of zeolitic materials varies. Thus, zeolite X has a high CEC (5 meq g^{-1}), while hydroxy-sodalite (2.3 A) accounts for the low potential application for both molecular sieving and ion exchange.

For zeolitization of fly ash the activation time is 12-24 h, the concentration of the activation agents 2.0 M and the fly ash/solution ratio is of 10-20 ml g^{-1}. The temperature may be smaller than < 150 °C for synthesis zeolites with a high CEC.

The conversion efficiencies are dependent on the contents of non-reactive phases and resistant aluminum–silicate phases, such as mullite and quartz and the grain size distribution. For higher aluminum–silicate glass content, shorter activation periods and lower solution/ fly ash rates are needed to reach high zeolites synthesis yields.

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