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Synthesis of New Adsorbents for Desulphurization on the Base of Ash and Lime

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Abstract

The development of new materials with fly ash offers new scientific and technological perspectives due to the specific interesting physical properties of these materials. Adsorbents can be produced from waste materials containing Si and Al and lime. The utilization of adsorbents based on fly ash represents an alternative with ecological and economical implications because of reduction of pollution and the use of wastes. The authors present in this study the results of experimental researches on the adsorbents prepared in laboratory using fly ash produced at CET Holboca Iasi and lime from Bicaz. The conditions of obtaining are established and the characterization of synthesized materials is realized.

Key words: *ash, lime, adsorbent, synthesis*

Introduction

The social economical development is strongly connected to energy production. Because the power plants based on coal fuel greatly affect the environment, the improvement of producing processes of energy by diminishing the ecological impact is welcome [1-3]. Among the adsorbents, the limestone, respectively the lime has the smallest price. Experimentally, it was determined that the basic components contained by the coal, respectively by the ash, determine a higher efficiency in bonding the sulfur dioxide, these acting as additive [4]. The use of adsorbent based on ash as retaining agents of sulfur dioxide from gases also ensures a diminishing of technology impact on the environment by liberation of great soil surfaces which are now used for waste storage [5-8].

Desulphurization was and constitutes also today the object of significant researches which have elaborated a lot of desulphurization methods. Independently of placement and method type, to a desulphurization equipment two conditions are imposed:

- removing the sulfur dioxide from the residual gaze must be done with minimum investment and exploitation costs;

- the obtained product must present a capacity of storage and capitalization.

From the analyze of gaze desulphurization problems it can observe that, both lime and lime derivatives (hydrated lime, milk lime), together with calcium carbonate (limestone, precipitate calcium carbonate, dolomite) can be and are used in coal power plant.

An adsorbent can be used if it has near the chemical composition corresponding surface properties that mean a high specific surface. The assurance of fine granulation needs supplementary energy consumptions with the manufacturing processes [6]. Analyzing the ash composition resulted from the coal burning it was observed that it contains CaO and MgO, and by mixing with lime, in controlled conditions it can synthesize an adsorbent for desulphurization of burned gases [8]. By using the ash for obtaining the adsorbent, the pollution reduction is obtained in two ways [9,10]:

- reduction of sulfur dioxide from the burned gases;

- capitalization of the waste that today is less capitalized and that is storage in large areas that results in soil pollution.

Concerning the contact mode, usually the lime is preliminary hydrated, after which the ash is introduced in reactors with magnetic or mechanic agitation. The reactors ratio varies between 1/2 … 1/6. Liquid-solid ratio usually has values in range 8 - 12. The working temperature is between 50 - 95 °C, and the hydration time is between 1 - 37 h.

On the base of presented data it was chosen the magnetic agitation reactors, working with ratios 1/ 2 – 1/3, temperature of 50 °C and hydration times of 1 - 4 hours.

Experimental part

For adsorbent synthesis it was used lime from Bicaz and ash from power plant Holboca Iaşi. The lime and the ash were characterized from the chemical, mineralogical and technological point of view. The chemical analysis for oxide components, thermo-gravimetrical analysis, FTIR analysis and electronic spectroscopy were realized. Morphology of particles was determined by SEM with Vega Tescan – Analytical Scanning Electron Microscope.

Chemical and mineralogical characterization was realized with following devices:
- Microanalysis of the ashes samples were determined by SEM/EDX. The samples were studied with a QUANTA 3D series AL99/D8229.
- Analysis FT-IR with spectrometer DIGILAB FTS 2000.
- Multi-Parameter Consort C831 (pH, mV, C, Conductivity), measures of pH=0-14.00, electrical conductance 0 - 200 mS.

An adsorbent was synthesized on the base of ash-lime, working at a temperature of 50 °C, in a laboratory installation realized of a reactor with magnetic stirring. The conductivity and pH of suspensions in time were registered. Samples of 10 g were prepared which were introduced in reaction vessel that contained 90 ml distillated water at working temperature. The timing and stirring were started during 1, 2 and 4 hours. The samples were filtered, dried in oven until constant mass and analyzed for determining the content of free CaO by chemical analysis. The synthesis was taken place in conditions presented in Table 1.

Table 1. Adsorbent samples and working conditions

Test number	Time (h)	Temperature (°C)	Lime/ash ratio
A1	1	50	1/3
A2	2	50	1/3
A3	4	50	1/3
A4	1	50	1/3
A5	2	50	3/1
A6	4	50	3/1

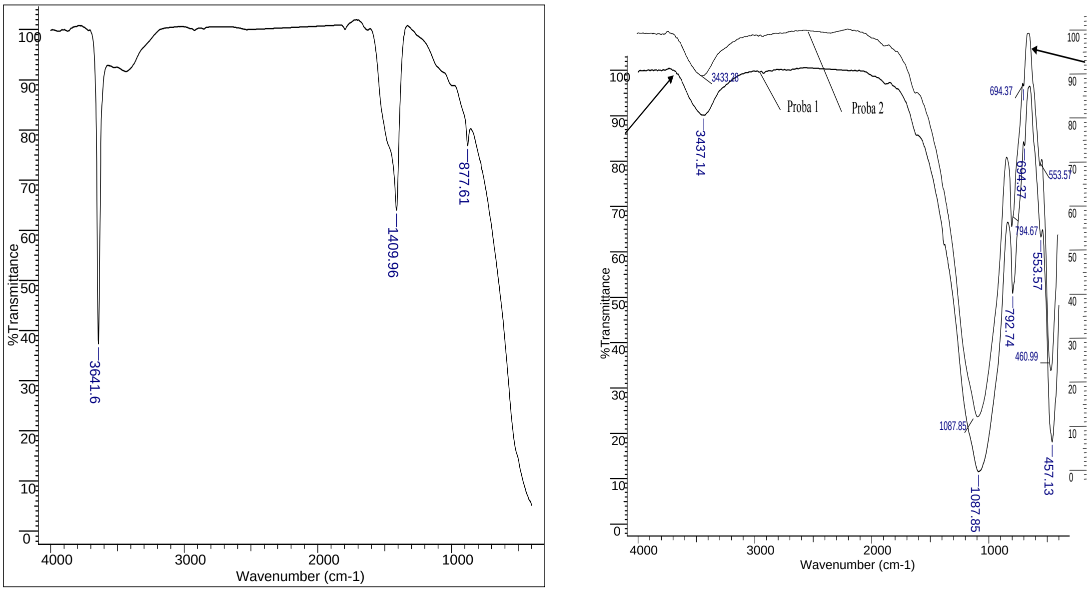
Results and discussion

The principal component of lime is calcium dioxide. Near this the lime contains a series of impurities from the raw material. The chemical composition of lime, in oxide components is presented in Table 2. The coal ash, function the origin, has the oxide components presented in Table 2 [2,11-14].

Table 2. Chemical composition of ash and lime used for preparing the adsorbent

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	MnO	Losses
Ash	48.4	36.64	5.12	2.86	1.02	1.01	0.44	0.43	2.8
Lime	3.64	0.34	0.44	86.4	3.51	1.01	0.048	0.01	4.43

FTIR Spectrum of lime is presented in Fig. 1. For comparison, FTIR spectrum of ash is also presented [15-17].



lime ash

Fig. 1. FTIR spectrum of reaction components

From Fig. 1 it can observe that the principal component of lime is calcium dioxide but there are also some peaks which corresponds to the impurities from the coal, peak from 3641,6 cm^{-1} corresponds to water, that means the lime was partially hydrated. Analyzing data from Fig. 2b, it finds out that in ash samples there are components such as: hematite, quartz, kaolin, illit, rutile, montmorillonite, carbon [18-20], which is found in argillaceous material, ballast fuel respectively. The resulted solids were analyzed and FTIR spectrum obtained for sample A2 is presented in Fig. 2.

From Fig. 2 it founds out the existence of peaks corresponding to hydrated lime, of components which correspond to ash, but also to calcium silicate.

SEM analysis was done for samples A2, A4 and A6 with Vega Tescan analyzer at 30 kV. The results are presented in Fig. 3. By hydration the obtained particles grow on the surface of ash, which results in the increasing of specific surface of adsorbent.

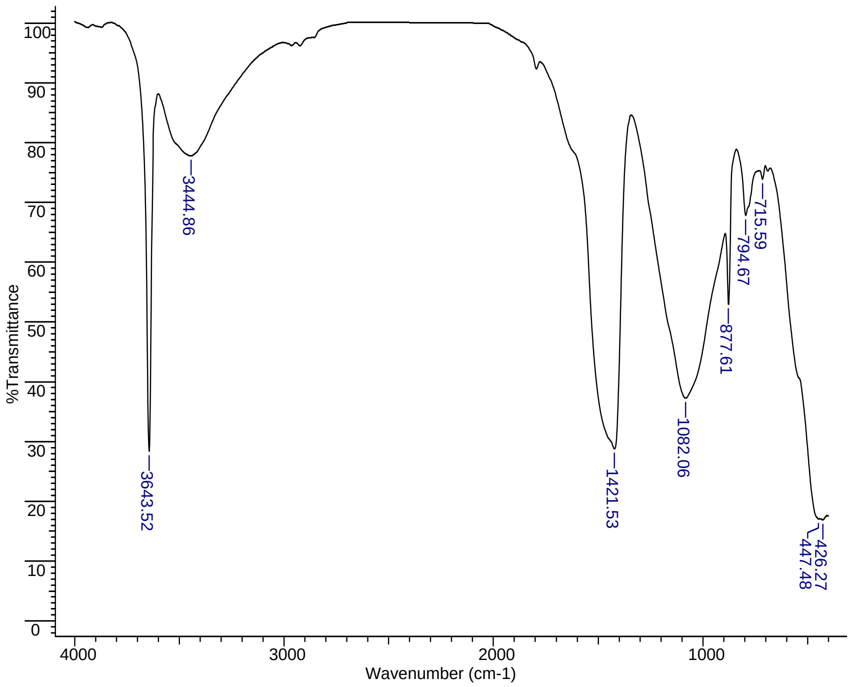


Fig. 2. IR Spectrum for adsorbent ash-lime

Hyaline particles of ash are round and the lime particles have irregular shape. The adsorbent particles are fine due to the re-crystallization of hydrated lime. SEM images to 10 and 5 μm respectively allow the observation of ash particle surface. It can observe differences between the surface morphology. So, on the big particle surface are storage small particles of hydrated lime, which can be called microparticles.

The number of microparticles depends on the ratio ash-lime and hydration time. This phenomenon was mentioned also in other articles. Practically the ash represents the support for increasing the contact surface of adsorbent. In parallel, the ash substances such as Fe, Ti, Mn and other oxides can have catalytic activity for oxidation of sulfur dioxide to sulfur trioxide. From Fig. 3 it results that by increasing the time of reaction, the adhesion of lime particles to the ash is better, for the same ratio lime-ash. The lime particles of irregular shape cover almost entirely the ash particles of round shape.

Lime hydration has as effect the increasing of specific surface and a very good adhesion to ash particles, the number of microparticles depends on the ratio ash-lime and the hydration time. The maximum hydration time that was attained was of 54 % for 4 hours of stirring.

The adhesion phenomenon of microparticles is very important in desulphurization reactors with fluid layer, because lime microparticles will be more rapidly drawn from reactor while the ash particles with sticking lime microparticles can stay more time in the reactor.

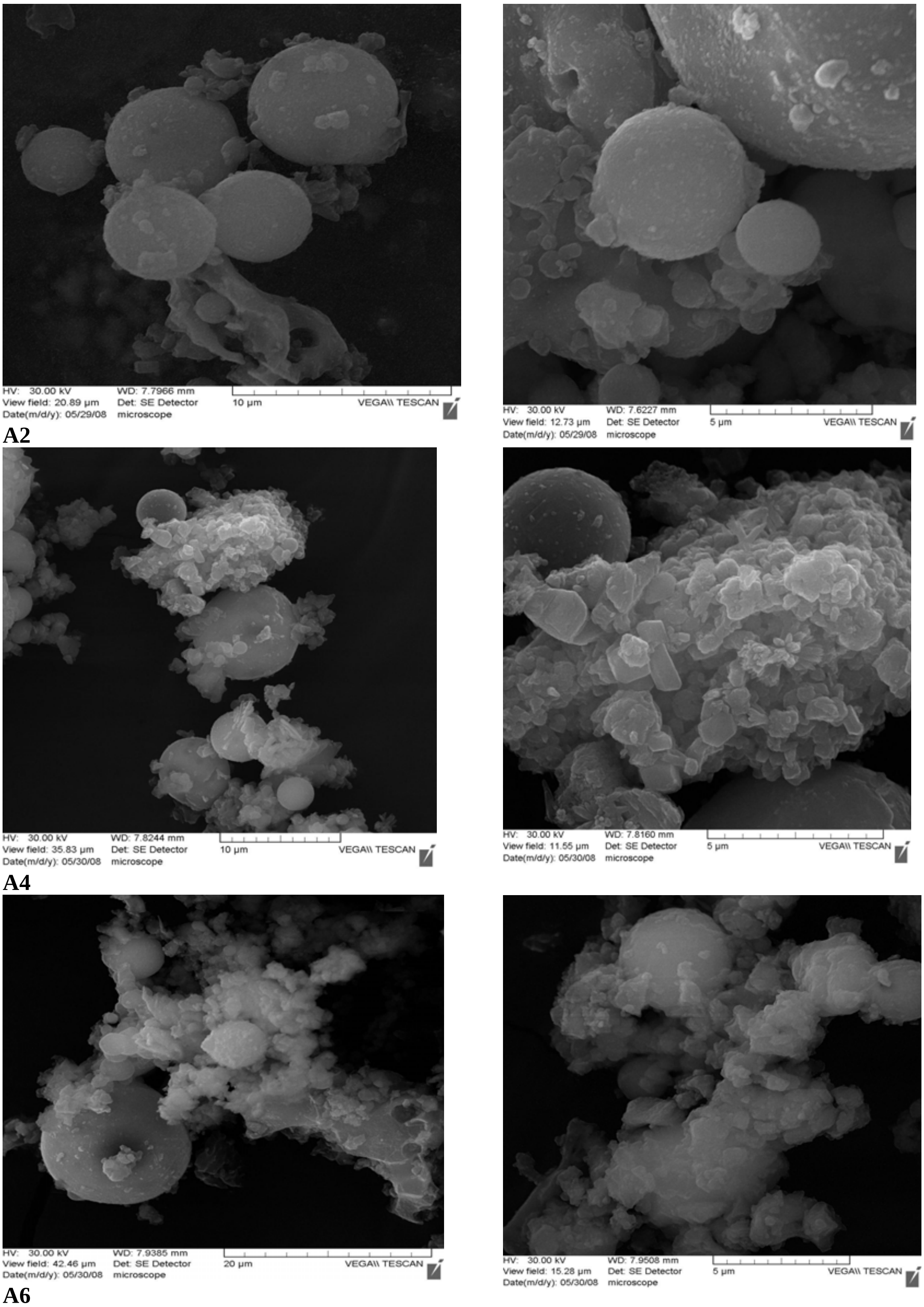


Fig. 3. SEM analysis for samples A2, A4 and A6

Conclusions

Concerning the reduction of dioxide sulfur on the base of critical analysis of scientific literature it is proposed the use of adsorbent ash-lime. The use of ash presents the advantage that this is a waste found in great quantities, and it is a way for its capitalization. The resulted product is easy to separate and can be used in industry of construction materials. On the other hand, the reaction product is not polluted for the environment. The ash by its properties can be used for synthesis of some adsorbents for retaining the gases with green house effect. The maximum hydration grade that was attained was 54 % for 4 hours of stirring. By increasing the reaction time, the adhesion of lime particles to ash is better, for the same ratio lime-ash. The lime particles, of irregular shape, cover almost entirely the ash particles of round shape.

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Sinteza de noi materiale adsorbante pe bază de cenuşă şi var

Rezumat

Utilizarea de noi materiale pe bază de cenuşă oferă noi perspective ştiinţifice şi tehnologice cu privire la proprietăţile acestor materiale. Adsorbanţii pot fi obţinuţi din deşeuri care conţin Si şi Al şi var. Utilizarea adsorbanţilor pe bază de cenuşă reprezintă o alternativă cu implicaţii ecologice, în sensul reducerii poluării şi economice prin folosirea unor materiale reziduale. In această lucrare se prezintă rezultatele cercetărilor experimentale cu referire la sinteza de adsorbanţi pe bază de cenuşă rezultată la CET Holboca Iaşi şi var de Bicaz. Se stabilesc condiţiile de obţinere a noi adsorbanţi şi se realizează caracterizarea materialelor sintetizate.