

Use of Coal Ash in Zeolite Production And Applications in Manganese Adsorption

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ABSTRACT: This study aimed at the reuse of coal ashes produced in Brazil to increase sustainability. Results obtained for zeolite synthesis using Brazilian mineral coal ashes at ambient temperature and pressure are reported. The results indicate that the application of ambient temperature at the evaluated NaOH concentrations and times resulted in the synthesis of a Na-X (type FAU) zeolite from the ash dissolution. This indicates that zeolite formation is influenced by the process variables. An increase in synthesis time, as well as of NaOH concentrations, in the zeolitic phases resulted in an increase in the ion exchange capacity of the final product. In experiments with 6 M NaOH during 30 days of reaction, the beginning of the formation of the mineralogical phase of zeolite X was observed. XRD results indicated the transformation of the ashes into zeolite X with increased reaction time, while SEM micrographs elucidated morphological changes. BET results demonstrate that increases in surface area influence manganese cation adsorption properties.

Keywords: zeolites, coal ash, faujasite.

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I. INTRODUCTION

The consumption of fossil fuels has increased significantly in the last decades, mainly due to the high world energy demand, with 41% of the world's electricity production originated from coal. In Brazil, coal-based thermoelectric plants are located in the south, close to main coal deposits [1]. Approximately 85% of coal is used for power generation in thermoelectric plants, with the largest coal reserves in Brazil distributed between Rio Grande do Sul (89.25%) and Santa Catarina (10.41%) [2]. The Candiotá-RS deposit comprises 38% of the national coal reserves [3].

One of the main environmental problems in coal-fired power plants is waste generation, with coal ashes being the most problematic. The global annual output of coal ash is about 800 million tonnes. However, the current recycling rate of these ashes is low, generating great challenges in waste management [4]. Although this material is reused in road construction, soil reclamation and cement manufacturing, most of their volume is still destined for landfills. Most of the ash generated by coal combustion in thermoelectric plants is disposed of in stabilization ponds and landfills, leading to high environmental impacts due to the contamination of surface and groundwater and soil by toxic elements that leach from this co-product [5].

The light ash produced in thermoelectric plants corresponds to about 70% of the total coal combustion residue generated, while coarse ashes amount to about 30%. Ashes are generally composed of 30-60% SiO₂, 10-30% Al₂O₃, 5-10% Fe₂O₃, 1-5% MgO and 2-4% CaO, among other compounds [6]. Due to this growing environmental problem, the development of new applications for this residue becomes necessary, aiming to minimize its negative impacts when discarded in the soil [7]. The use of coal ash in the synthesis of higher added value products such as zeolites has been indicated to reduce the environmental impact of the disposal of this waste in the environment.

Fly ash is a source of aluminum and silicon, which are the main elements that compose zeolites. Because of this and the fact that they contain high content of ash and fine granulometry reactive phases, fly ash is considered an excellent raw material for zeolite synthesis [8].

Zeolites are porous aluminosilicate minerals with a three-dimensional structure composed of (AlO_4) and (SiO_4) tetrahedra, characterized by a regular system of channels and cavities. This structure confers interesting properties for applications that include ion exchange, molecular sieving, catalysis and adsorption [9].

Most studies regarding the use of zeolites derived from coal ash indicate that one of the main potential applications of these compounds is the assimilation of toxic metallic ions from synthetic pollutant solutions under laboratory conditions[8]. Thus, zeolites can be synthesized from coal ash, which, in addition to being rich in silica and alumina, is abundant and available in several coal-producing countries, due to coal-based energy production. It is possible to synthesize zeolites from coal ash through hydrothermal treatments, i.e. in aqueous solutions, under high pressure and temperature. Several articles have proposed different methods for the hydrothermal activation of coal ash during zeolite synthesis, by varying several synthesis parameters [10,11,8].

The zeolite synthesis process from coal ash generally involves the addition of a caustic agent, usually alkali or alkaline earth metal hydroxides, at high temperatures. All developed synthesis methodologies are based on the dissolution of the ash phases sustained by Si and Al and alkaline solutions and the subsequent precipitation of the zeolitic material[8]. Currently, the literature presents some studies on ash conversion to zeolites by hydrothermal alkaline treatment and their use in metal removal from water. However, some studies on ashes generated in Brazil using open systems at ambient temperature and pressure are available. Brazilian coal displays certain specific characteristics that influence ash properties and their respective zeolites and, consequently, the ion exchange capacity of the adsorber.

In search of a way to reduce costs and significantly simplify the zeolite production process from fly ash from thermoelectric plants located in Southern Brazil, studies were developed herein for zeolite synthesis at ambient temperature and pressure (open system), considered potentially more profitable than other processes. In addition, the determination of zeolite manganese adsorptive potential, a heavy metal originating from the coal production chain, was also evaluated.

II. LITERATURE REVIEW

Toxic species of heavy metals cause serious damage to the ecosystem. Manganese, for example, present in surface waters, originates mainly from acid mine drainage which is generated by chemical and bacterial oxidation processes of sulfide minerals. Therefore, the presence of high concentrations of this ion, in addition to sulphate, iron and other metals dissolved in these effluents is very common. Because of this, an increase in the number of research on treatment effluent processes is observed. Many of these processes are based on the adsorptive or ion exchange properties of materials that immobilize these heavy metal species.

Recently, several materials of natural or synthetic origin, such as sugarcane bagasse, coal ash, shale, carbonates, phosphates and zeolites, have been tested regarding their adsorptive capacity. Many researchers have used coal ash as a low-cost precursor material to obtain zeolites, as they are a source of silica and aluminum and present characteristics similar to certain volcanic materials, the precursors of natural zeolites [12]. Different types of zeolites can be obtained, such as zeolite X, zeolite A, ZSM-5 and hydroxysodalite, using hydrothermal alkali treatments, [13,14] for example.

Zeolite synthesis has gained notoriety as one of the most promising uses for coal ash, adding value to the final product and reducing the disposal of this residue in the environment. Zeolites are commonly used for the adsorption of heavy metals due to their physical and chemical properties (thermal stability, molecular structure and ion exchange capacity). They are widely used in the industrial environment as a sorbent material for removing ions in liquid and gaseous effluents [15], for the removal of mercury in gaseous effluents [16], and as a capture material of CO_2 [16]. These applications make synthetic zeolites a high value-added product compared to coal ash.

Currently, one of the most widely used, non-renewable, energy sources in the world is coal, with a global contribution to energy generation of around 40% [2]. Its high availability, safety and relatively low costs lead to this fuel playing an important role in the world energy matrix[17]. Coal is one of the most abundant fossil fuels in the world, and its reserves are distributed throughout the continent. For this reason, coal is considered a strategic energy source of great importance in a worldwide context[18]. Brazil's largest mineral coal reserves are in the south, with the largest reserves located in the states of Rio Grande do Sul and Santa Catarina. Approximately 85% of the coal in Brazil is used for power generation in thermoelectric plants[2]. Thermoelectric plants that use coal as raw materials for electricity generation are considered one of the factors most responsible for pollution generation, including solid waste pollution, as coal ash, one of the most significant volume-wise in Brazil. The world coal ash production exchanges 750 million tons per year. In Brazil, seven thermoelectric plants in the south were responsible for ash production, produced at a rate of 3 million tons a year, where 65-85% are composed of light ashes and 15-35% of background ashes[19].

In this sense, attention has been paid to ash disposal and utilization methods, which account for about 80% of by-products generated in the thermal conversion of coal, where its reuse has become a global problem[20]. The need to remove ashes from mills at low cost means that disposal practices are adopted in

inappropriate areas and without the adequate protection measures. Only 30% of the heavy ash is deposited in landfills and/or in sedimentation ponds, generating significant environmental impacts[5], whereas most fly ash is used in the production of cement and concrete due to its pozzolan properties[21], as well as in the manufacture of ceramic materials[22] and as small-scale fertilizers. Natural ash leaching causes soil, groundwater and surface waters contamination by toxic substances[23]. One of the ways to reduce the environmental impacts resulting from waste disposal in the environment is to increase its use potential. An alternative to recovery is the conversion of coal ash into low cost adsorbents capable of removing toxic substances from contaminated water.

Mineral coal originating in southern Brazil comprises a high content of inorganic mineral matter compared to the other types of coal used for energetic purposes in thermoelectric power plants around the world, in addition to different nature and properties, which causes the ashes generated after burning to display specific characteristics[24]. To attempt to reduce ash impacts, other application possibilities have been studied. The use of coal ash in the synthesis of higher value-added products such as zeolites, for example, is effective, since the amount of coal residue tends to increase with the operation of new thermoelectric power plants. It is estimated that in the coming years, with the increase in the use of coal as a raw material for energy generation in Brazil, ash production will suffer a two-fold increase, reaching 6 million tons per year[25].

The use of alternative and low cost materials in zeolite synthesis has developed in the last decades due to the fact that processes using conventional aluminum and silicon solutions are extremely expensive[26]. The adsorptive capacity of zeolites synthesized from coal ash is dependent on certain synthesis conditions, such as the concentration of the alkaline solution and the reaction time, as well as the adsorption operations, including temperature and metal cation concentrations in the sorption process solution[27]. In this context, the purpose of this study was to perform the synthesis of zeolite phases in open systems from coal ash with the aim of removing manganese from aqueous solutions by sorption processes.

III. MATERIAL AND METHODS

The raw material for this study consisted of two samples, one of fine fly ash and another of coarse bottom ash, supplied by a thermoelectric plant located in the state of Santa Catarina, Brazil. The chemical compositions of the coal ash samples were determined by the gravimetric method for Si quantification, atomic absorption with a C_2H_2 /air flame for Fe quantification and atomic absorption with a C_2H_2/N_2O /air flame for Al and Ca quantification (model 55B, Agilent).

The morphology of the ash samples and the synthesis products was evaluated using a FEI QUANTA 400 Electronic Scanning Microscope (SEM) at 20 KV. The mineral phases present in the ash samples and in the synthesis products were determined on a Bruker-AXS D4-ray diffractometer with a linear detector sensitive to the lynxEye position with $Co K\alpha$ 40 KV and 40 mA radiation at a 2θ angle ranging from 5 to 80 degrees.

The adsorption and nitrogen desorption isotherms were obtained on a Micromeritics Tristar II 3020 equipment at nitrogen boiling temperature ($-196^\circ C$) during a specific surface area (BET) analysis. Searching for a methodology that simplifies and reduces costs for zeolite production from coal ash, the synthesis experiments were performed at room temperature. The proposal is that these ashes, which are a waste from the coal burning process, may be used as a material to synthesize zeolites that behave as a heavy metal adsorbent material, specifically regarding manganese. One hundred-gram samples of coarse and fine coal ash were treated with NaOH solutions (VETEC) at concentrations ranging from 0.1 to 6 mol/L, at solid-liquid S/L (g/mL) ratios of 1/3 to 2/1 and time ranging from 30 to 300 days, in an experimental design with 76 tests including replicates. The suspensions were stored in polyethylene bottles and shaken occasionally. At the end of the experiment, the solids were separated on pre-weighed filter paper, washed continuously with deionized water until the filtrate reached approximately pH 7, and dried at $60^\circ C$ for 24 hours in an oven. All samples were then characterized and applied in the manganese adsorption tests.

For the manganese adsorption assays, 50 mL volumes of a synthetic Mn(II) sulphate solution (VETEC) at 100 mg/L were placed in erlenmeyers containing about 5 g of ash (modified and unmodified, resulting from the zeolitic tests). These mixtures were subjected to stirring using a shaker-type mechanical stirrer (IKA) at a 300 rpm over 3 hours at room temperature. The pH values of the solutions were adjusted to 7 with 0.05 mol/L H_2SO_4 or 0.1 mol/L NaOH. At the end of the experiment, the equilibrium pH was verified. The test parameters were chosen based on previous tests with the ashes and on information from the literature [28-30].

After the procedures, the reaction mixtures were filtered through a glass funnel and quantitative filter paper. The final solutions, as well as the feed solutions, were analysed by atomic absorption spectroscopy in order to determine the % of Mn adsorption in each sample. The results of manganese adsorption were used to evaluate which synthesis variables directly influence sorption capacity, using the Statistica 12 software package. In addition, information about the surface areas was obtained by the BET methodology of the formed products. The results were compared with the X-ray information to evaluate the formed zeolite phases.

IV. RESULTS AND DISCUSSION

Initially the study consisted in characterizing the coal ash and synthesized zeolites samples. This is important in order to compare the precursor material and the obtained product. The SEM technique was used in to complement the other characterization techniques and to evaluate the shape of the particles present in the coal ash samples.

In general, Brazilian flying ashes are considered heterogenous, because they are composed of particles of varied sizes, both spherical and irregular, due to the different physical states of silica present in coal ash samples [31]. Figures 1 and 2 display the micrographies of the fine and coarse ash samples, respectively, for morphology evaluations prior to the zeolitization process. The results corroborate with the literature, as fine ash samples are comprised of several smooth surface spheres, whereas the coarse ash sample is sphere-shaped with rough surfaces.

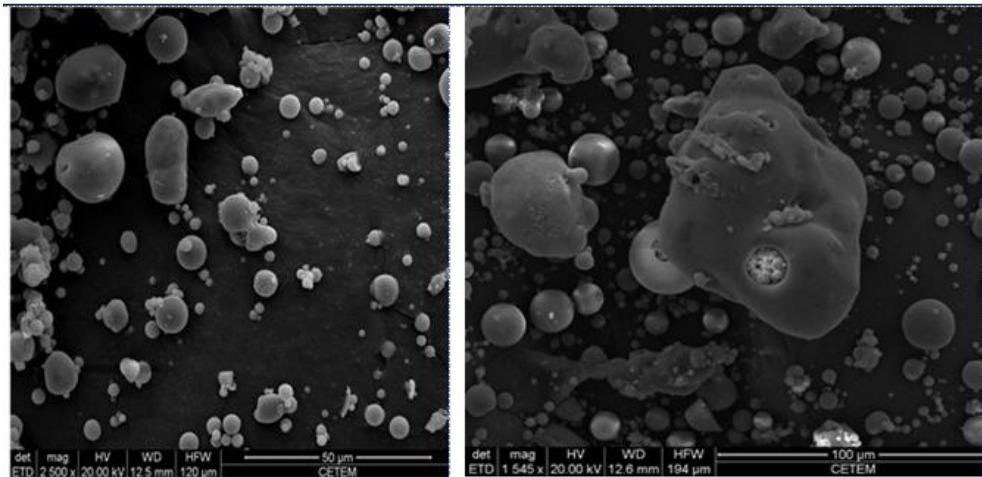


Fig.1- Fine ash sample micrography.

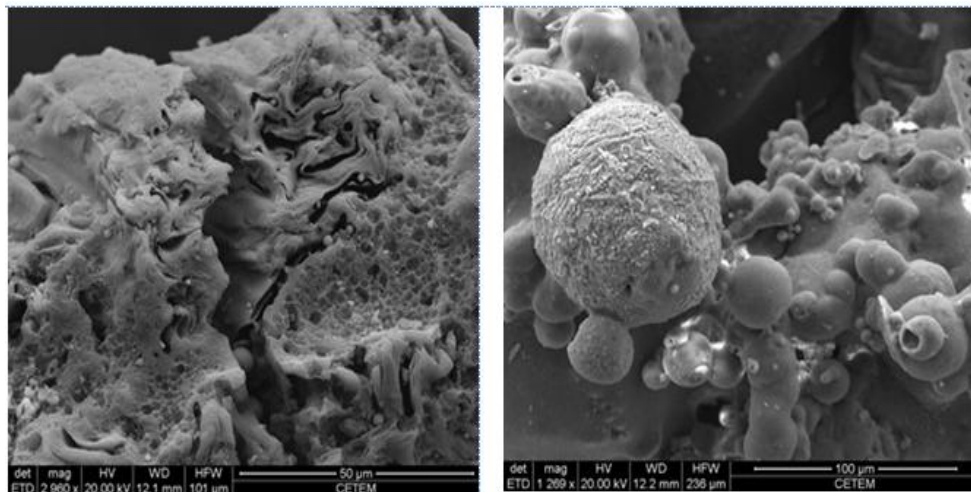


Fig.2- Coarse ash sample micrography.

The spherical particles may be compact and hollow and may be called cenospheres (Figure 2), or may be particles with smaller particles in their interior, then called pleurospheres (Figure 1). Hollow particles are formed due to the expansion of gases such as CO_2 and/or water vapor into the coal when it is being burned[32]. The spongy appearance in the coarse ash sample morphology (Figure 2), is characteristic of ash samples with high unburnt carbon content, due to the type of combustion system used[23]. Many data in the literature show the influence of ash mineral composition on the zeolitization process results[32]. Thus, an X-Ray diffraction analysis was performed in order to estimate the presence of the main mineral phases in the evaluated ashes. In both samples, quartz and mullite phases were present. Magnetite, silimanite, hematite and calcite phases were also present, although the peaks referring to these mineral phases were less intense. In the literature, mullite, quartz and magnetite have also been identified as the main mineral phases in coal ash samples, characteristics necessary for the starting material in zeolite synthesis [27,32].

Quantification of the mineralogical phases was not performed herein. However, the literature reports that the differences between the amounts of the mineral phases between the two types of coal ash can be attributed to the different combustion conditions in thermoelectric plants, since ash formation depends both on temperature and cooling rates [33]. The mullite present in the ashes is the result of the reactions that occur during coal combustion. Quartz, on the other hand, is present in the precursor coal and does not melt under the burning conditions in the plants [24]. The presence of hematite and magnetite in the ashes is due to the oxidation of iron sulphides in the form of pyrite, usually present in the burned coal [34]. The presence of aluminosilicates in the ash as quartz and mullite favors zeolite formation, requiring shorter periods of time for activation and more dilute alkaline solutions [8]. The application potential of coal ash is defined by its chemical composition. The percentages of Fe, Si, Ca and Al in the fine and coarse ash samples were characterized quantitatively according to the aforementioned methods. The results are displayed in Table 1. The main constituent of the coal ash is silicon, followed by aluminum and iron, indicating that coal ash is composed mainly of aluminum and iron silicates or a small fraction of iron oxides.

Table 1. Quantitative analysis of coal ash (%) samples and Si/Al ratios.

Type of ash	Al	Si	Ca	Fe	Si/Al
Fine ash	9.6	29.3	0.72	2.9	3.05
Coarse ash	9.5	26.5	0.93	5.6	2.79

The main compounds forming zeolitic structures are quartz and mullite. The chemical elements Si and Al are derived from these compounds and were present at 29% and 10%, respectively, in fine ash and 26% and 10% in coarse ash. Fe and Ca contents were lower than 6% and 1%, respectively, for both ashes. The phases containing Fe and Ca are detrimental to zeolite formation, since Fe is not reactive during the zeolite synthesis process and calcium can generate phase formation of hydrated calcium silicates [35]. The formation of a particular type of zeolite depends significantly on the Si/Al ratio of the starting material. The Si/Al ratio presented by the coarse ash was 2.79 and of 3.05 in fine ash. According to the literature, the formation of Na-X type zeolites tends to form when the starting material has a Si/Al ratio of about 3.12 [36], the Na-A type zeolite is favored at a Si/Al ratio of 2.53 [37] and the Na-P1 zeolite, at a Si/Al ratio of 2.9 to 2.5 [19]. Therefore, the Si/Al ratio values presented in this study indicate a good possibility for the synthesis of the mentioned zeolite phases.

The parameter time (days), solid-liquid ratio S/L (g/mL) and NaOH concentration (mol/L) were investigated in the synthesis tests. X-ray diffractograms indicate that the main zeolitic phase formed was type X (or faujasite), as well as philipsite. The presence of quartz and mullite residues was also observed in the synthesis products diffractograms. The literature reports that the presence of non-zeolite phases in the conversion products from coal ash limits the ion exchange capacity, making it difficult to apply zeolites as heavy metal adsorbents [38]. However, herein, non-zeolitic phase formations were not limited to the identification of pre-existing mullite and quartz phases, probably characterizing incomplete zeolite conversion. In the X-ray diffractograms of the synthesis samples, the zeolite phase X (faujasite) was detected after 30 days of contact of the coarse ash with concentrated NaOH 3 mol/L and 6 mol/L solutions. However, the best results were obtained when using 6 mol/L NaOH and a longer contact time of 300 days (Figure 3). According to the literature, NaOH concentrations do not affect only the degree of zeolitization, but also the type of zeolite that will be obtained as product. The difference observed in the formed products is related to the increase in supersaturation achieved due to the higher proportion of soluble species with the increase of the NaOH concentration. According to Ostwald's rule of successive transformation, the higher the supersaturation, the better the nucleation conditions of the metastable zeolitic phases, which later redissolve or recrystallize and are transformed into more stable phases [39].

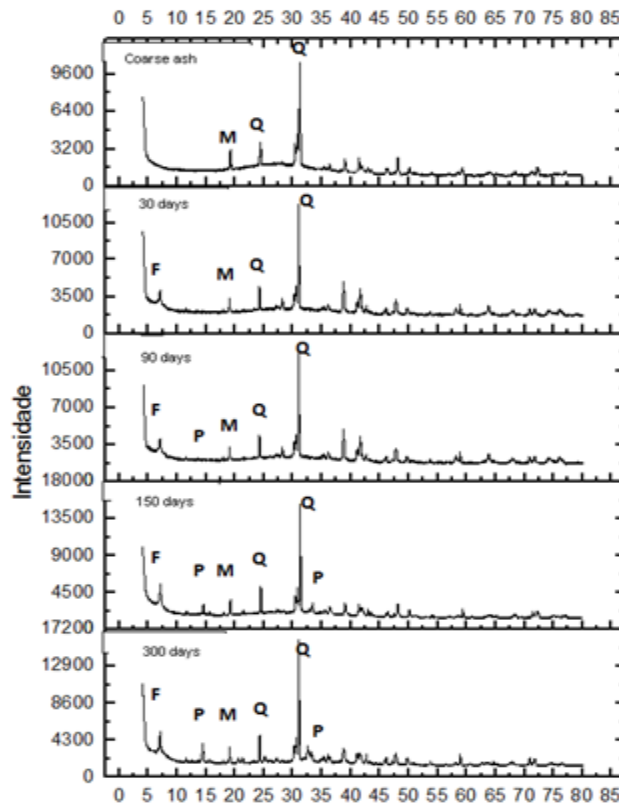
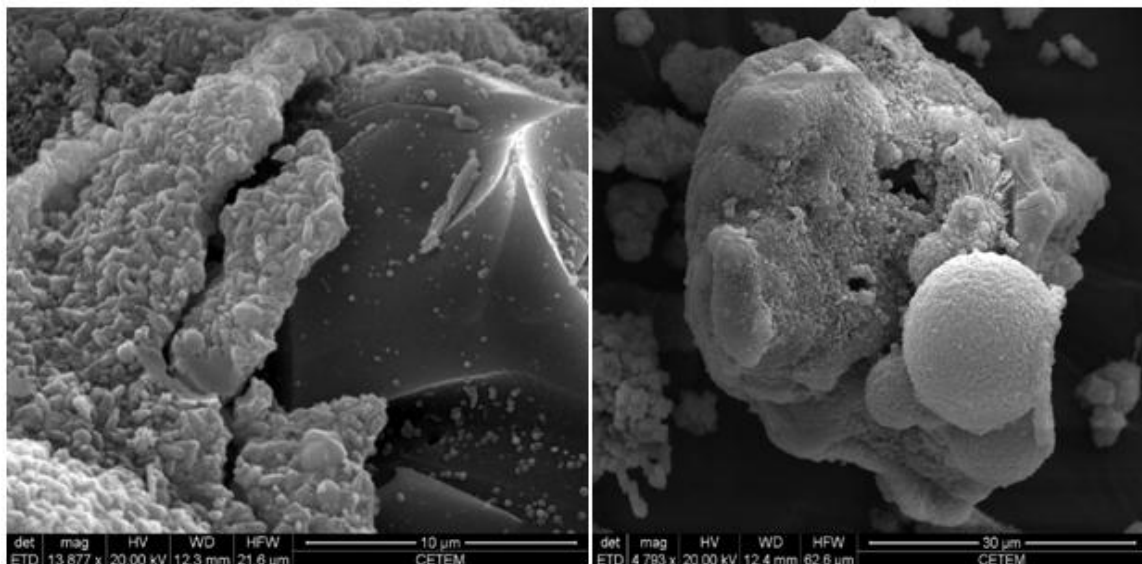


Fig. 3 - X-ray diffractograms of the ash samples at 30, 90, 150 and 300 days with 6 mol/L NaOH

The SEM analysis of the product obtained in tests with coal ash in contact with 6 mol/L NaOH for 150 days is displayed in Figure 4. The beginning of the formation of the faujasite and philipsite crystals with octahedral and prismatic morphologies can be observed. These morphologies have also been observed by other researchers[40].



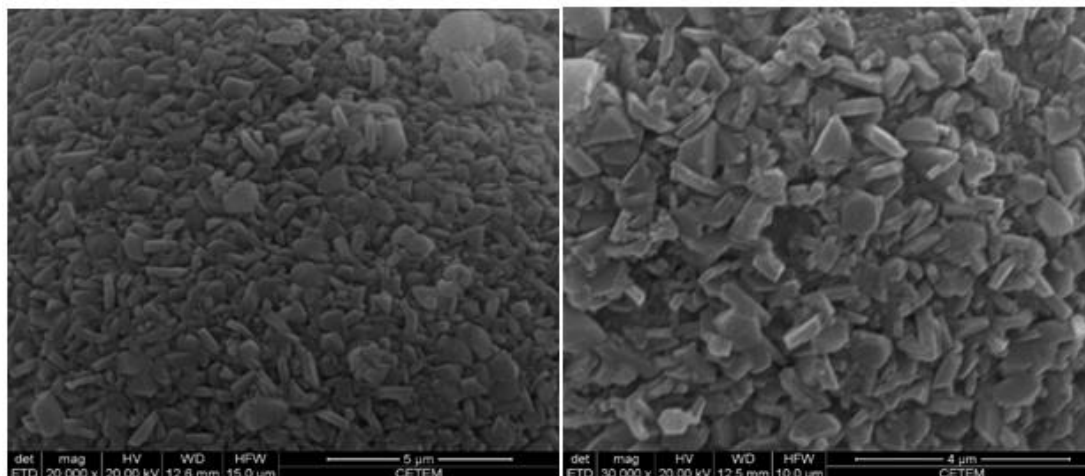


Fig.4- SEM analysis of the post-synthesis product.

Samples of synthetic zeolites exhibit surface area values around 10 times greater than the starting ash, which is another indication of zeolite formation and the improvement of the adsorptive properties of the formed product. Table 2 presents the results obtained in the analysis of surface area (BET) of coarse ash and the synthetic zeolites produced from this material.

Table 2. BET analysis data for coarse ash and respective synthetic zeolites

Sample	Surface area – BET (m ² /g)
Coarse ash	1.91
Synthetic zeolite (150 days)	21.57
Synthetic zeolite (300 days)	29.00

The following adsorption tests prove that the zeolite products obtained after 300 days of synthesis present better results in manganese adsorption, probably due to their greater surface area. Manganese sorption tests were performed and the removal rates ranged from 20 to 99% for the zeolite synthesized from fine ash and 10 and 99% for the zeolite synthesized from coarse ash. The results of manganese extraction rates are displayed in Figure 5. For the samples synthesized from fine ash, the percentages of manganese adsorption reach values close to 80% even at an NaOH concentration 0.5 mol/L (S/L = 1/2 and 300 days). Under these same conditions, the coarse ash, now zeolitized, presents low levels of manganese uptake, slightly above 20%. The same is observed for the other conditions, indicating the ability of the fine ash to adsorb higher amounts of manganese after the synthesis process under milder conditions. Both starting materials reach the maximum uptake of manganese from 3 mol/L NaOH for the other evaluated variable conditions.

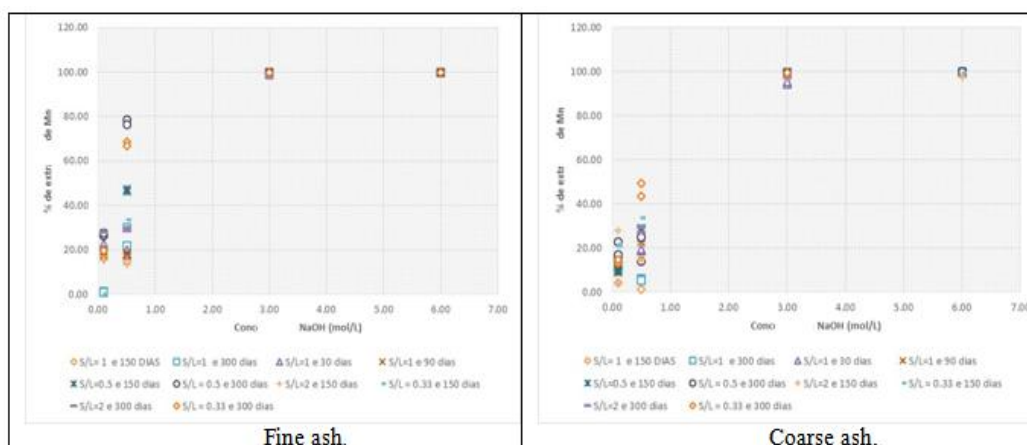


Fig.5- Manganese adsorption as a function of NaOH concentration for zeolites produced from fine and coarse coal ash

A statistical analysis was performed using the Statistica 12 software, with the percentage of manganese extraction as the dependent variable, and S/L ratio, NaOH concentration and time as the independent variables. For the statistical calculations, the maximum, minimum and intermediate values observed for each independent

variable in the experimental plan were used (Figure 6). The NaOH concentration is the most important variable, both in its linear and quadratic effect for the zeolitization experiments from fine ash, yielding a maximum observed curvature, as displayed in the Pareto plot of Figure 6a, at a 95% confidence level. The response surface shown in Figure 6b clearly represents this quadratic dependence of the NaOH concentration and its major importance over time. This, in turn, shows a very discrete curvature in the studied interval. The S/L ratio was not a relevant variable in this process.

For coarse ash, the results of effect variables are similar regarding the effect of NaOH concentration (Figure 6c). This variable is the most important for the synthesis process, even in its quadratic form. On the other hand, the S/L ratio was shown to have a certain some on the zeolitization of coarse ash. The behavior of these two variables versus the % manganese is displayed in Figure 6d.

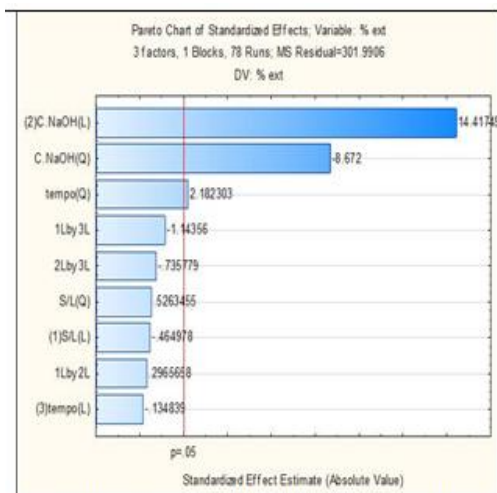


Fig.6a- Pareto plot for the influencing variables in the zeolitization process of fine ash.

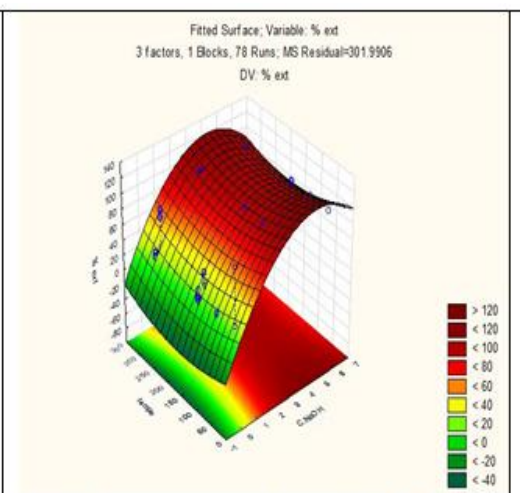


Fig.6b- Response surface for % of sorbed manganese as a function of NaOH concentration and time of zeolitization of fine ash. Synthesis time of 150 days.

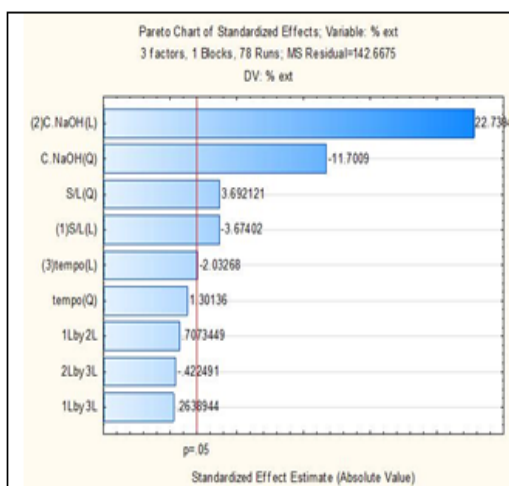


Fig.6c- Pareto plot for the influencing variables in the zeolitization process of coarse ash.

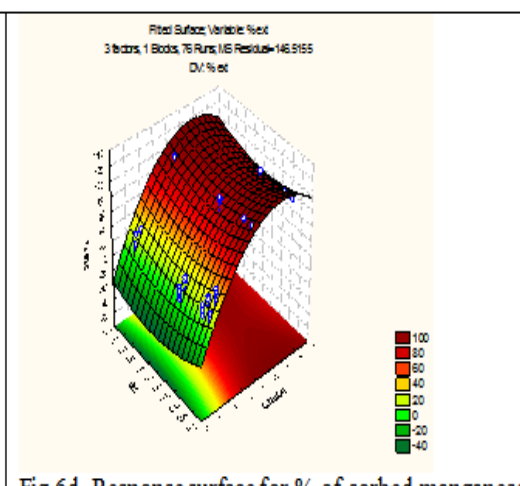


Fig.6d- Response surface for % of sorbed manganese as a function of NaOH concentration and time of zeolitization of coarse ash. Synthesis time of 150 days.

Fig.6- Analysis using the % of manganese extraction as the dependent variable and S/L ratio, NaOH concentration and time as independent variables

When analyzing the zeolite phases obtained in the different zeolitization experiments, the data are completely consonant with the Pareto graph, since the experiments with the highest concentrations of NaOH were those that obtained better results for manganese adsorption, independent of the other applied parameters, arriving close to the maximum extraction, as well as the formation of type X zeolite phases (faujasite) and philipsite. Experiments carried out at higher NaOH concentrations showed a greater influence on zeolite formation, higher surface area values and, consequently, better manganese removal results. The samples in

which the formation of zeolitic phases did not occur, presenting only quartz and mullite as crystalline phases, presented a 20 % removal average.

V. CONCLUSIONS

The study carried out herein indicates that it is possible to synthesize zeolites from top and bottom coal ashes at ambient temperature and pressure. The results of the X-ray diffractograms indicate the formation of zeolite phases faujasite and philipsite. The results of manganese adsorption indicate that the zeolitic products containing these mineral phases would have a better adsorption capacity for this ion. A statistical analysis was performed and the results of effects of the zeolite synthesis independent variables were represented in diagrams as a function of the % of extracted manganese. When fine ash is the starting material, the NaOH concentration is the most important variable in the process, followed by the time of synthesis. In the case of coarse ash, the NaOH concentration is again the most important variable in the zeolitization process, followed by the solid/liquid ratio in manganese sorption.

Thus, the results of this study indicate the technical viability of the production of synthetic zeolites from coal ash under ambient temperature and pressure and their adsorptive potential when compared to the top and bottom ashes for the treatment of solutions containing manganese. It is important to consider that the zeolites used herein as solid adsorbents are obtained using an abundant residue produced in thermoelectric plants, and that much of this residue still does not have an environmentally correct destination. Thus, zeolites synthesized from coal ash may have a high competitive potential compared to other adsorbent materials and other industrially used effluent treatment techniques.

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