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Thermodynamic Study of the Synthesis of Zeolites from Coal Ash and Its Use as Sorbents for Heavy Metals

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1. Introduction

Species of toxic heavy metals cause serious damage to the ecosystem and as a result of this fact there is an increase in research on processes for wastewater treatment. Many of these processes are based on adsorptive properties or ion exchange some of these materials which immobilize the heavy metal species. Recently, various materials of natural or synthetic origin, such as bagasse, coal ash, carbonates, phosphates and zeolites, have been tested for its sorption capacity. Zeolites are commonly used for sorption of heavy metals due to their physical and chemical properties (thermal stability, defined molecular structure and ion exchange capacity).

The synthesis of zeolites from some mineral phases has been investigated by several researchers. It is well established that the coal ash composed mainly of phases such as quartz (SiO_2), mullite ($\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10-x}$), hematite (Fe_2O_3) and magnetite (Fe_3O_4) can produce zeolites from alkaline hydrothermal treatment. But the mechanism of hydrothermal synthesis is still not very detailed. In general, increasing the temperature tends to favor the formation of hydrated aluminosilicate phase.

Zeolites synthesized from the coal ash, its adsorptive capacity are dependent on certain reaction conditions, for example, the concentration of metal cation in solution and the temperature at which sorption occurs. However, temperature and reaction time in the stage of the synthesis zeolite are also considered important variables affecting the behavior of the adsorptive materials such as zeolites of heavy metals in solution.

This chapter presents a study based on the sorption of cations of heavy metals by zeolites synthesized from hydrothermal treatment of coal ashes produced in Brazil.

2. Literature review

2.1. Coal

With the progress of humanity and its new challenges, we started to research the various types of energy production coupled with environmental preservation as a tool for sustainable development. Nowadays, the search for new processes using renewable energy sources is increasing, but the non-renewable energy sources occupy yet a large portion of production[1].

Although the use of coal represents a small share in electricity generation, its use is extremely important because it's the non-renewable energy resource most abundant of the globe.

The main environmental problems related to use of coal in power generation are: changes in vegetation and geomorphology of mining activities, formation of acidic water in the handling of coal due to the presence of pyrite, a large amount of waste in the process of improvement, gaseous emissions after combustion and the generation of potentially toxic waste.

One way to reduce the environmental impacts of disposal of these wastes in the environment involves the expansion of the potential for their use. An alternative use of these residues is the processing of coal ash in an sorbent low cost. The ashes of coal are composed mainly of silica and alumina, and you can convert them into zeolitic material after hydrothermal treatment in alkaline medium. The zeolitic material is characterized by high cation exchange capacity and good sorption allowing numerous potential applications.

The ashes of coal are composed mainly of silica and alumina, and you can convert them into zeolitic material after hydrothermal treatment in alkaline media. The zeolitic material is characterized by high cation exchange capacity and good sorption allowing numerous potential applications [2].

2.2. Coal ashes

Coal ashes are inorganic solid wastes generated after burning coal in power generation processes in power plants worldwide. The formation of ash is achieved by the direct combustion of lignite, which is a solid raw material, consisting of two intimately mixed fractions, an organic (volatile matter more fixed carbon) and a fraction (mineral clay, quartz, pyrite, carbonates, etc.). By the action of heat, generates volatile organic fraction and coke, while the mineral fraction becomes gray with a mineralogy modified in view, the water loss of clays, carbonates and decomposition of sulfide oxidation [3].

The combustion of pulverized coal occurs at high temperatures, between 1200 and 1600° C in an oxidizing gaseous environment and for total or partial melting of matter [4]. Three main wastes are generated from coal combustion in power plants, which are:

- Light Gray or steering wheel: they are extremely fine particle size of less than 0.15 mm, is collected in cyclones mechanical or released into the atmosphere;
- Heavy ash, are coarser particle size, is typically agglomerated at the bottom of the furnace being removed by a water flow;
- Slag or ash thick, coarse grain size and has high content of unburned carbon from 10 to 20%;

The fly ashes are usually composed of 30-60% SiO₂, 10-20% Al₂O₃, 5-10% Fe₂O₃, 5-10% MgO and 2-4% CaO, and other compounds.

In the process of coal combustion, these minerals are partially fused particles form ashes and light in which the crystalline phases such as quartz (SiO₂) and mullite (3 Al₂O₃.2SiO₂) remain in the core, while the aluminosilicate (Al₂O₅ Si) remains the surface [5].

The ash generated from burning coal in power plants in Brazil are comprised 65-80% fly ash and bottom ash of 15-35% [6].

In general, mineral coal ashes are aluminosilicates formed by amorphous and crystalline phases and the pH of ash ranges from 4.5 to 12 depending on the characteristics of the carbon precursor geochemical [7].

From the standpoint of generating electric power, coal ash waste are considered as residues, however, to evaluate its characteristics and possible uses, these can be considered as a resource that can be widely used and exploited [8].

The storage of the dry coal ash has the major advantage that its physicochemical properties of the ash remain unchanged, which constitutes a buffer for further use [9].

Several potential applications of coal ash have been developed or are under development at research centers all over the world. These applications are directed primarily to remove toxic metals present in industrial wastes [10] in the building materials industry [11], and the synthesis of zeolites that have been studied by many researchers [12].

2.3. Zeolites

Zeolites are hydrated aluminosilicates formed by three-dimensional crystal structures of SiO₄ tetrahedra and AlO₄, linked together by four oxygen vertices. In this configuration, the negative charges of AlO₄ tetrahedra are compensated by interstitial cations (Na⁺, K⁺, Ca²⁺ and Ba²⁺) and form an open structure with large channels, where water and other molecules can stay and have considerable freedom of movement, permitting ion exchange and reversible hydration [13].

Zeolites include a wide range of mineral and synthetic products, whose structure has an electrical imbalance, as it has an excess negative charge on each atom of aluminum present. Therefore, atoms of alkali metals and alkaline earth metals cause the balancing of charge, can easily be exchanged for other ions. This transfer of material between the spaces intracrystalinos is limited by the pore diameter that ranges from one to another zeolite.

In nature, are usually found in deposits associated with the activation of alkaline volcanic rocks. As naturally occurring normally have a high content of impurities and / or do not possess the properties required for their use, therefore, be synthesized zeolites started [14] .

Zeolites exhibit features as high selectivity, high stability and high exchange capacity, which together with the properties of sorption and catalysis, provide their technological application in various sectors [15] .

One advantage of synthetic zeolites is to provide uniformity in size and shape of the channel, another is its chemical composition pre-defined in relation to the purposes intended. Considering, however, its high cost, synthetic zeolites are reserved for applications that require features more uniform structure and composition, as in the catalysis of hydrocarbons and in the detergent industry. The zeolites type A, X and Y are the predominant for commercial use as ion exchangers and adsorbers [16] .

Among various uses, natural zeolites can be applied to wastewater treatment for removal of toxic metals, in removing odors in the air purification and in the conditioning of soil [17].

The fly ash are sources of aluminum and silicon, which are the main elements in the composition of the zeolites, because of this, the high content of reactive stages of ash and fine particle size thereof, are considered excellent feedstock for the synthesis of zeolites[12] .

2.4. Hydrothermal synthesis of zeolites

The synthesis of zeolites from some mineral phases has been investigated by several researchers. It is well established that the coal ash composed mainly of phases such as quartz (SiO_2), mullite ($2\text{SiO}_2 \cdot 3\text{Al}_2\text{O}_3$), hematite (Fe_2O_3) and magnetite (Fe_3O_4) can produce zeolites from alkaline hydrothermal treatment. By doing the necessary adjustments in the Al / Si, the ashes can be used for the synthesis of zeolites such as Zeolite Na-A, faujazita, zeolite Na-P and philipsita [18] . [19] report the synthesis of zeolite-type Na from coal ash. The synthesis methodology is focused on so-called "activation" of gray, or was more popularly known as "hydrothermal synthesis" in closed systems for solutions of NaOH or KOH.

Pure zeolites are synthesized from supersaturated solutions of silicates and aluminates under stringent experimental conditions [20] .

It is therefore possible to synthesize zeolite from coal ash by the hydrothermal treatment or in aqueous solution at elevated pressure and temperature [14] .Several articles have proposed various methods for the hydrothermal activation of coal ash in zeolite synthesis, using for this variation of several parameters involved in this synthesis [12,21-24].

The zeolites that have been obtained by hydrothermal treatment of the coal ash with sodium hydroxide (NaOH) are analcime, zeolite A, zeolite P (gismondina), zeolite X and Y (faujasite), sodalite, chabazite, gmelinite and cancrinite .

All methods are developed based on the dissolution of the phases of fly ash supported by Al and Si with alkaline solutions and subsequent precipitation of the zeolitic material [12].

According to [25], the hydrothermal reaction mechanism involves stages of dissolution, condensation or gelation and crystallization.

The dissolution of the ash is between 20-120° C. The amorphous silica, quartz and mullite, which are the phases of Al and Si are present in the ash dissolved. The kinetics is very dependent on the concentration of OH⁻, which is responsible for dissolving the reagents and keeps them in solution, providing its saturation to occur the formation of zeolites.

The next step is the condensation or gelation which is the phase where the reaction occurs between aluminate and silicate ions with the formation of aluminosilicate gel (hydrogel). In the final stage of crystallization the hydrogel is transformed into a zeolite crystal (the reaction speed is dependent on the amount of Na⁺). The crystallization of zeolites generally results in a final product containing 40-60% of zeolite.

The zeolite synthesis from the coal ash is therefore an equilibrium reaction between the alkaline solution and solid phase. By raising the temperature, the solubility of silica and alumina ions increases and condensation reactions for the formation of crystal nuclei are initiated. The crystal growth leads to a complete dissolution of the original material for the formation of amorphous phases zeolite.

Depending on the experimental conditions and the chemical composition of the ash used, one obtains different zeolites. The most important parameters in the processes of zeolitização by hydrothermal process are the chemical composition of ash concentration and type of agent activation, the ratio liquid / solid, temperature, reaction time and intensity of agitation [9].

Each zeolitic material obtained has application in accordance with its characteristics and properties. At least 15 different types of zeolites can be produced from a gray by varying the activation parameters. The activation conditions may be optimized to maximize the adsorptive capacity of the product obtained and the production costs [12].

Most studies on the use of zeolites derived from coal ash describes a major potential applications of this zeolites as the sorption of toxic metal ions from solutions of pollutants under laboratory conditions [12].

2.5. Sorption

The sorption process is the separation of components of a mixture through a mass transfer phenomenon when a component in the mixture which may liquid or gaseous called adsorbate is in contact with a solid called sorbent. When the two phases are in contact, the dilute component in the mixture is transferred the liquid phase to the surface of the sorbent [2]. The sorption process depends on several factors such as nature and concentration of the adsorbate, the characteristics of sorbent and the sorption conditions (pH, temperature, ratio solid \ liquid).

The sorption phenomena are classified into two types: physical sorption and chemisorption. In physical sorption occurring weak interactions like Van der Waals, featuring a reversible process. By not having any sort of change in the nature of the species involved, the physical sorption is a non-specific, and can occur for different adsorbates [26]. In the chemical sorption or chemisorption, the chemical species involved are altered, as there is an effective exchange of electrons between the solid and the adsorbed molecule, resulting in the formation of a monolayer on the solid surface [27].

If the sorption of one or more ionic species is accompanied by simultaneous desorption of an equivalent amount of ionic species, this process is regarded as ion exchange. The shapes of sorption usually encountered in environmental studies are the physical sorption, chemical sorption and ion exchange [2]. Being essentially a phenomenon of sorption surface, that has an sorption capacity of sorbent significant, must have large surface area, which implies a highly porous structure.

The sorbent materials, in turn, are natural substances or synthetic crystalline structure whose inner surface of the pores is accessible by a selective combination between the solid and solution [26].

The sorption isotherms are the main way of studying the capacity to remove toxic metals from different solid sorbents [28].

2.6. Sorption isotherms

To obtain the sorption isotherms is the first step for quantitative evaluation of the sorption mechanisms. The data obtained from the isotherms can be used to project and define the operating conditions of industrial equipment that are based on the principle of sorption [1].

Isotherms relates the concentration of the adsorbate fluid phase and solid phase at a certain temperature and are represented in graphic form, presenting in various ways that reflect the behavior of the mechanism of sorption. In general, the isotherms convex represent usually the solid microporous sorbent. The more complex shapes may be associated with multilayer sorption or the varying sizes of pores of the sorbent material.

We can cite as examples, the isotherms of Henry, Langmuir, Freundlich, BET and Radke-Prausnitz. The Langmuir and Freundlich isotherms are the most commonly used to demonstrate the balance of removing a metal ion sorption, and are the most used models to describe the mechanisms of sorption on zeolites [29].

To provide us with data on the mechanisms of sorption isotherms can be linearized and applied to mathematical models.

3. Materials and methods

The fly ash used in this study originated from a coal thermo power station located in southern Brazil that operates with pulverized Brazilian coal. Ashes and synthetic zeolites

produced by hydrothermal treatment were previously characterized chemically and mineralogically and subsequently used in sorption experiments. These experiments were performed with synthetic solutions of sulphate salts of Pb (II), Cu(II), Zn(II), and Mn(II) prepared with analytical grade reagents in deionized water.

3.1. Zeolite preparation

The coal fly ash was submitted to hydrothermal treatment at different temperatures, reaction times, NaOH concentrations, solid/ liquid ratios (S/L) and aluminum/silicon (Al/Si) ratios as shown in Table 1. A Plackett–Burmann experimental design (25-2 fractional factorial design) was used in order to identify the most important variables in a preliminary analysis [30]. The tests were performed in duplicate. The molar ratio Al/Si was modified by adding analytical grade Al₂O₃ in the reaction media.

The hydrothermal treatment was carried out in a 450 ml reactor PARR-4562, made of Nickel-200 equipped with a turbine impeller and stirred constantly at 300 rpm. The reaction products were filtered and washed with water to remove the excess of sodium hydroxide.

The mineralogical characterization of the zeolites as well as of the ashes was carried out by X-ray diffraction (XRD) in a Bruker – AXS D5005 powder diffractometer with Goebel mirror and CoKa (35 kV/40 mA) radiation.

Tests	Concentration (mol/l) NaOH	Temperature (°C)	Time (h)	Ratio Al/Si	Ratio Solid/Liquid (S/L)
1	2.0	100	0.5	1.00	1\6
2	5.0	100	0.5	0.51	1\8
3	2.0	150	0.5	0.51	1\6
4	5.0	150	0.5	1.00	1\8
5	2.0	100	6.0	1.00	1\8
6	5.0	100	6.0	0.51	1\6
7	2.0	150	6.0	0.51	1\8
8	5.0	150	6.0	1.00	1\6

Table 1. Experimental conditions of the hydrothermal experiments

3.2. Preliminary evaluation of the response variable

The zeolites as well as the coal fly ash were washed up to pH 9 and subsequently dried at 60°C for 24 h before the sorption experiments. The sorption capacity was determined by contacting, 50 ml of Mn and Cu solutions (100 mg/l) with 0.5 g of zeolites in plastic bottles. The solution pH of each test was chosen conveniently, between 4 and 5 to avoid cation precipitation.

The bottles were shaken for 2 h at 180 rpm in a KS501 IKA shaker and the solids were filtered with Whatman filter paper. The concentrations of metal ions of all tests were determined in a Varian Atomic Absorption Spectrometer - model Spectra 50B.

The sorption capacity was defined as a percentage and calculated by the equation (1):

$$\text{Sorption capacity (\%)} = \left(\frac{C_i - C_e}{C_i} \right) \times 100 \quad (1)$$

C_i and C_e are respectively initial and final concentrations of the metal ion in solution.

3.3. Sorption experiments

The sorption experiments for the heavy metals, Cu^{2+} , Pb^{2+} , Zn^{2+} , and Mn^{2+} with synthesized zeolite were carried out using the shaking device and methodology described previously in Section 3.2. A concentration range from 100 to 3000 mg/l was used for each cation. Only the zeolitic material from test 8 (Table 1) was used as sorbent.

The obtained data were plotted and adjusted with isotherm sorption models to analyze the cations sorption onto the sorbents.

3.4. Investigation of temperature effect – Thermodynamic study

Samples of 30 g ash were mixed with 150 ml of a 3 mol/L NaOH solution. This mixture was reacted in an autoclave Parr - 4562, made of nickel alloy 200, equipped with a turbine impeller for 2 hours and 350 rpm agitation and temperatures of 50, 100, 150, 200 and 250 ° C. The product formed after cooling was filtered, washed with 2 liters of distilled water and dried at 60 ° C for 24 hours.

4. Experimental results

4.1. Characterization and preparation

The XRD analysis of the ashes used for zeolite preparation is shown in figure 1. In according to the results of X ray diffraction, the sample ash is mainly formed by mullite phases ($\text{Al}_6\text{Si}_2\text{O}_{13}$) and quartz (SiO_2) with some traces magnetite (Fe_2O_3), shown in Figure 1. Chemical analysis carried content was 56.8% of SiO_2 , 24.5% of Al_2O_3 and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 2.32.

Figure 2 shows the XRD of all products of the hydrothermal treatments. It can be observed that treatments resulted in formation of zeolitic phases as zeolite A, cubic analcime, philipsite, hydroxycancrinite and $\text{Na}_8(\text{AlSiO}_4)_6(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. Table 2 shows the sorption capacity obtained for the zeolitic products. The results show that a hydrothermal treatment can increase 10–25 times the % sorption when comparing with the value of the original ashes. The sorption of Mn^{+2} is higher than 85% and the absorption of Cu^{+2} reaches up to 99%. In the case of a solution with 100 ppm of Mn the sorption increased about 25 times when compared with the results of the test for the same Mn concentration performed with ashes

with no hydrothermal treatment. The increasing was about 16 times for Cu^{+2} . The tests 1 and 2 showed small sorption capacity for cations tested. In figure 2, these tests did not show zeolitic phases.

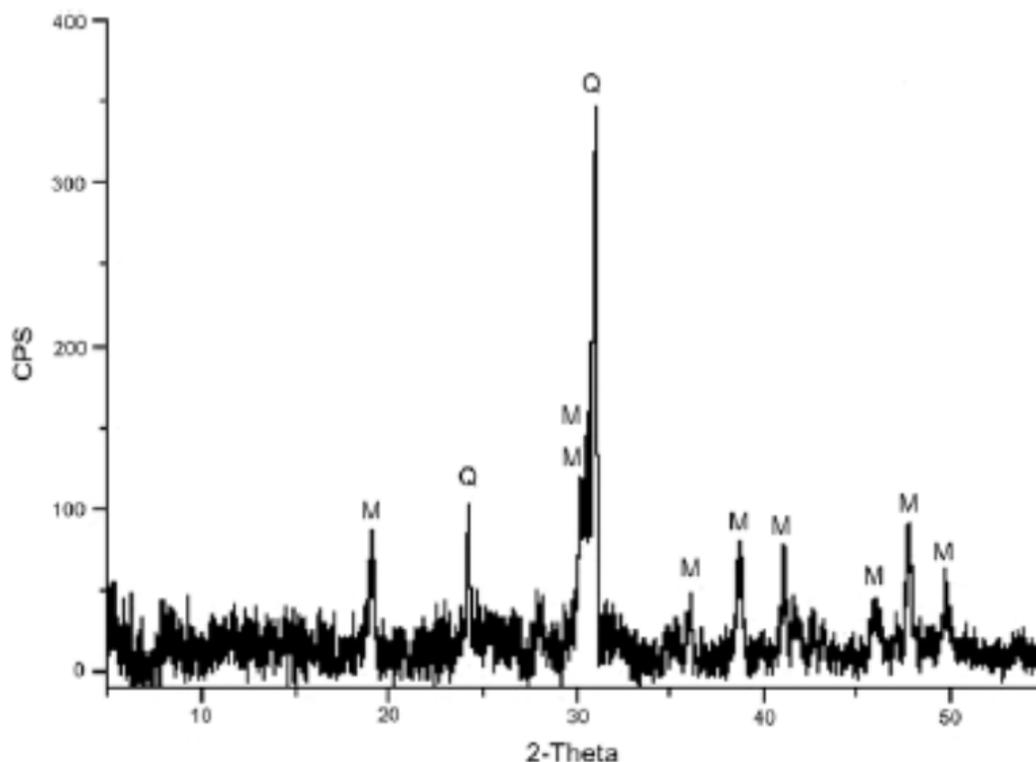


Figure 1. XRD pattern of coal fly ash. Mineral abbreviations: M, mullite; Q, Quartz.

Test	Cu^{+2}		Mn^{+2}	
	C_e (mg/l)	Sorption capacity %	C_e (mg/l)	Sorption capacity %
1	37.43	62.57	42.80	57.20
2	34.36	65.64	66.19	33.81
3	1.66	98.34	15.98	84.02
4	0.37	99.63	26.48	73.52
5	1.11	98.89	24.19	75.81
6	0.02	99.98	21.77	78.23
7	0.11	99.89	15.25	84.75
8	0.22	99.78	14.40	85.60
Coal fly ash	93.95	6.05	96.60	3.40

Table 2. Results of Cu^{+2} and Mn^{+2} sorption

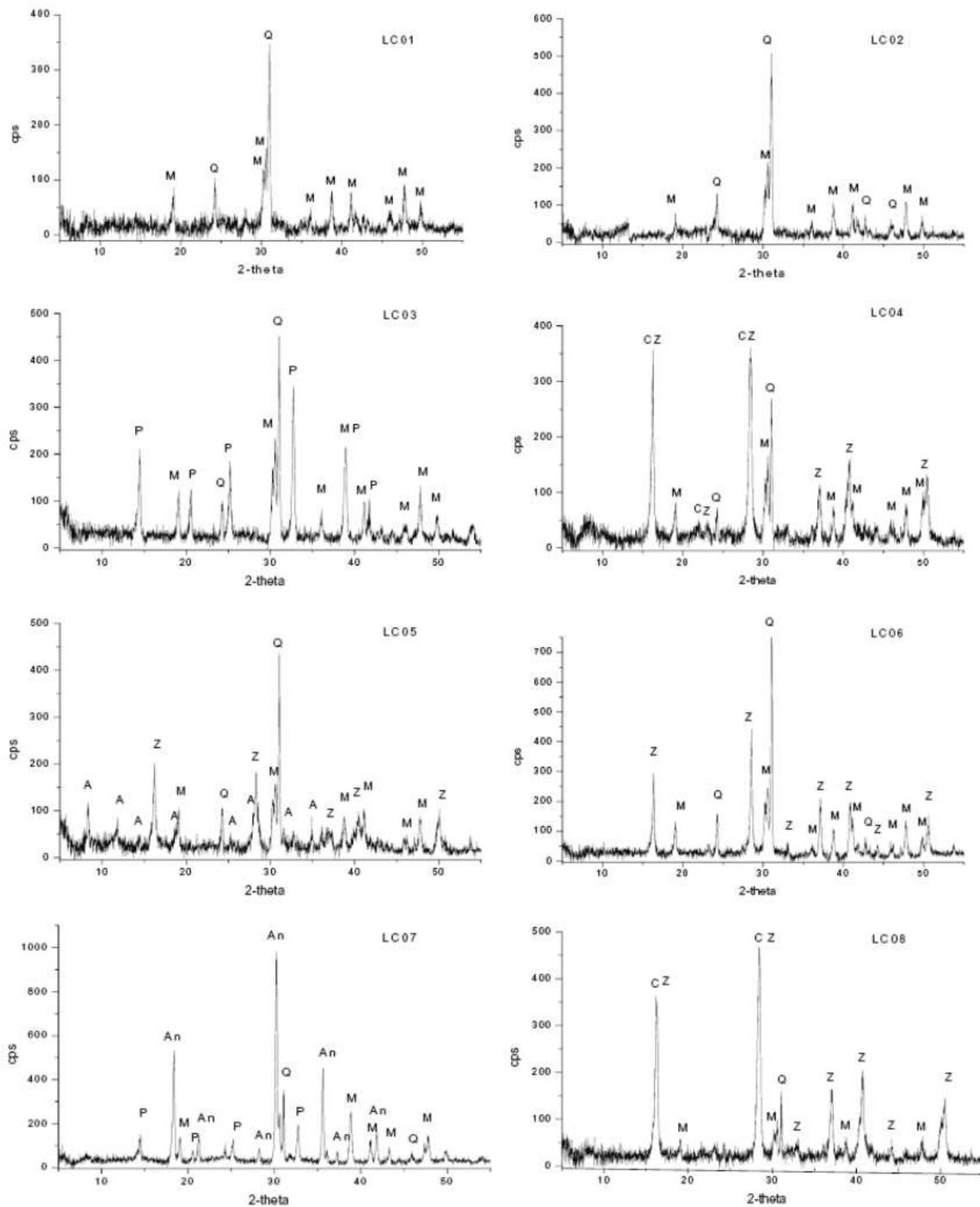


Figure 2. XRD pattern of modified coal fly ash. Phases abbreviations: M, mullite; Q, quartz; Z, zeolite $\text{Na}_8(\text{AlSiO}_4)_6(\text{OH})_2 \cdot 2\text{H}_2\text{O}$; C, hydroxycancrinite; A, zeolite A; An, analcmite; P, zeolite P. the legends LC01 to LC08 are related with tests 1-8 from Table 1.

Figure 3 and 4 show the results of preliminary statistical analysis and the effects of the variables. The *F*-test was used to identify the most significant variables in the hydrothermal process. The significance level (*p*-value) adopted was 0.05. Temperature and time were the most significant variables in the synthesis of the zeolites. An increase of the level of these variables tends to increase the sorption capacity for Mn and Cu.

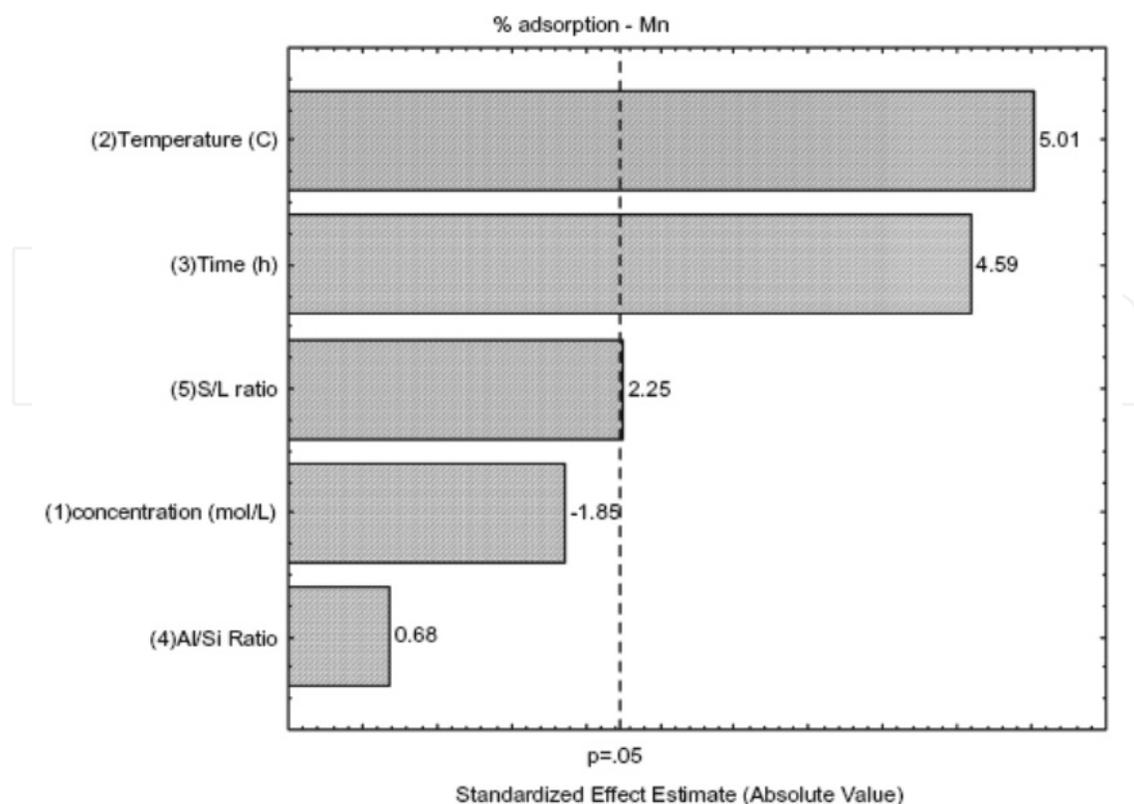


Figure 3. Pareto chart of standardized effects to factorial planning - % Mn sorption (p -level = 0.05)

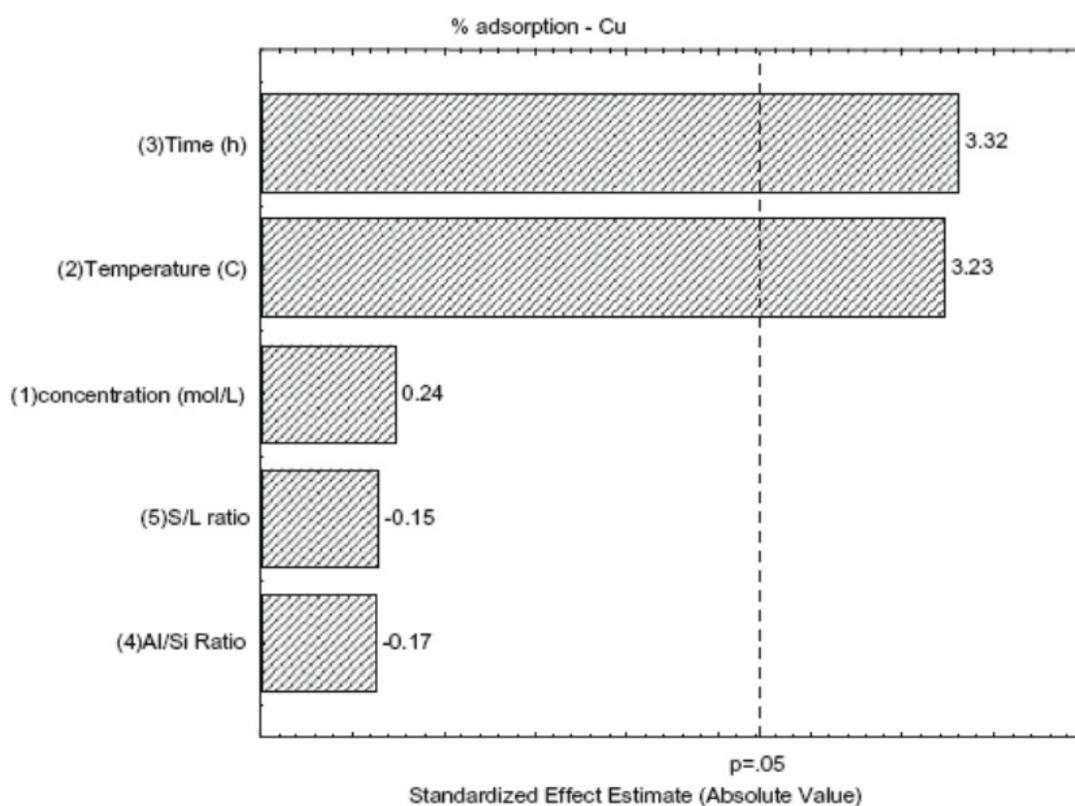


Figure 4. Pareto chart of standardized effects to factorial planning - % Mn sorption (p -level = 0.05)

Several authors suggest that changes in synthesis temperatures lead to different zeolitic phases. The differences among sorption capacities of the various zeolites synthesized may be credited to the different zeolitic phases present in the products of the hydrothermal synthesis [25,31-32]. An increase in the reaction time tends to promote a better crystallization of the phases formed, which it might also explain the increase in the of sorption capacity [33].

4.2. Sorption studies

The sorption of different metal ion concentrations onto synthetic zeolite at 25^o C was studied for Cu⁺², Pb⁺², Zn⁺², and Mn⁺² in the range 100-3000 mg\L keeping all other variables constant. The results are shown in figure 5. The sorption for Cu⁺², Pb⁺², Zn⁺², and Mn⁺² increases with increasing metal concentration in aqueous solutions. These results indicate that energetically less favorable sites become involved when the concentration of metal in solutions increases. The metal uptake can be credited to different mechanisms of both ion-exchange and sorption. During the ion-exchange process, metal ions have to move through the pores of the zeolite, but also through channels of the lattice, and they have to replace exchangeable cations (mainly sodium and calcium). Difusion is faster through the pores and is retarded when ions move through channels of small diameter. In this case the metal ion uptake can mainly be credited to ion- exchange reactions in the porous of the zeolitic samples [34].

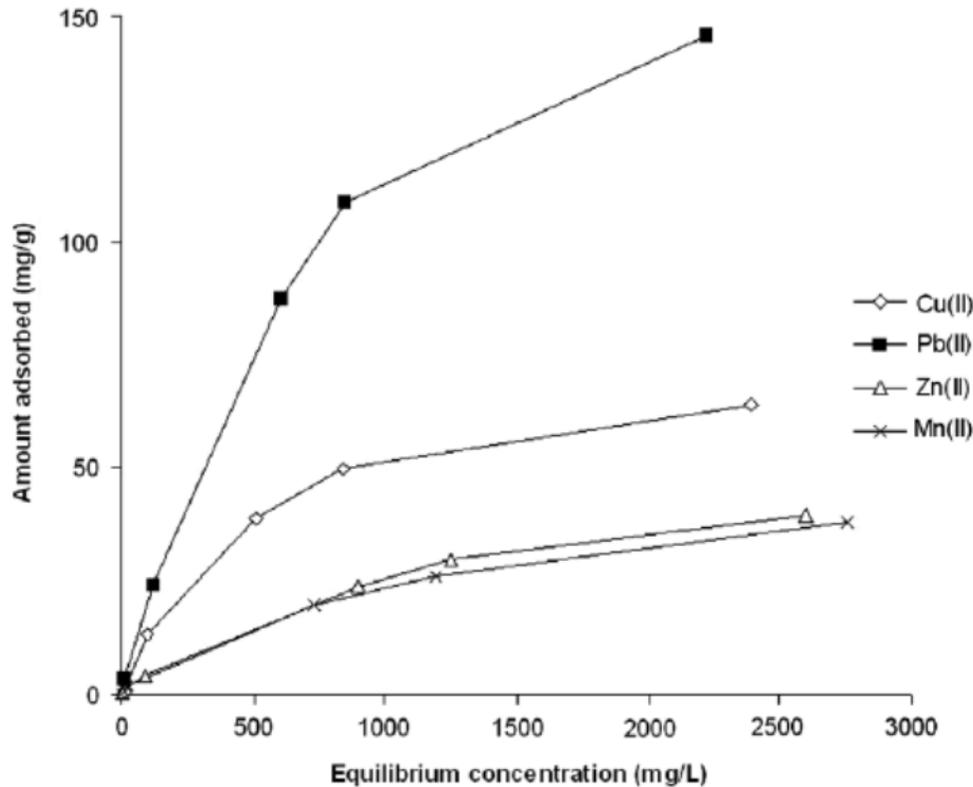


Figure 5. Sorption isotherms of de Mn⁺², Cu⁺², Zn⁺², Pb⁺².

The preferred order observed for sorption was $Pb > Cu > Zn > Mn$. In the literature, similar results were obtained when the sorption capacity of a large variety of zeolite minerals for cadmium, copper and zinc and revealed that zinc had the lowest sorption for all zeolites synthesized [31,35-36]. Zeolites obtained under same conditions as philipsite and chabazite had limited sorption capacity (CA) for zinc as compared to copper [37]. The sorption characteristics of Zn (II) onto pure fly ash showed that the solution pH was the key factor affecting the sorption characteristics [38-39].

4.3. Investigation of temperature results – Thermodynamic study

According to figure 6, near the temperature of 100°C, the X-ray diffraction indicates that no phase transformation occurs. According to literature, the reaction kinetics is highly temperature dependent, and it is believed that in this case, a larger reaction time would be required.

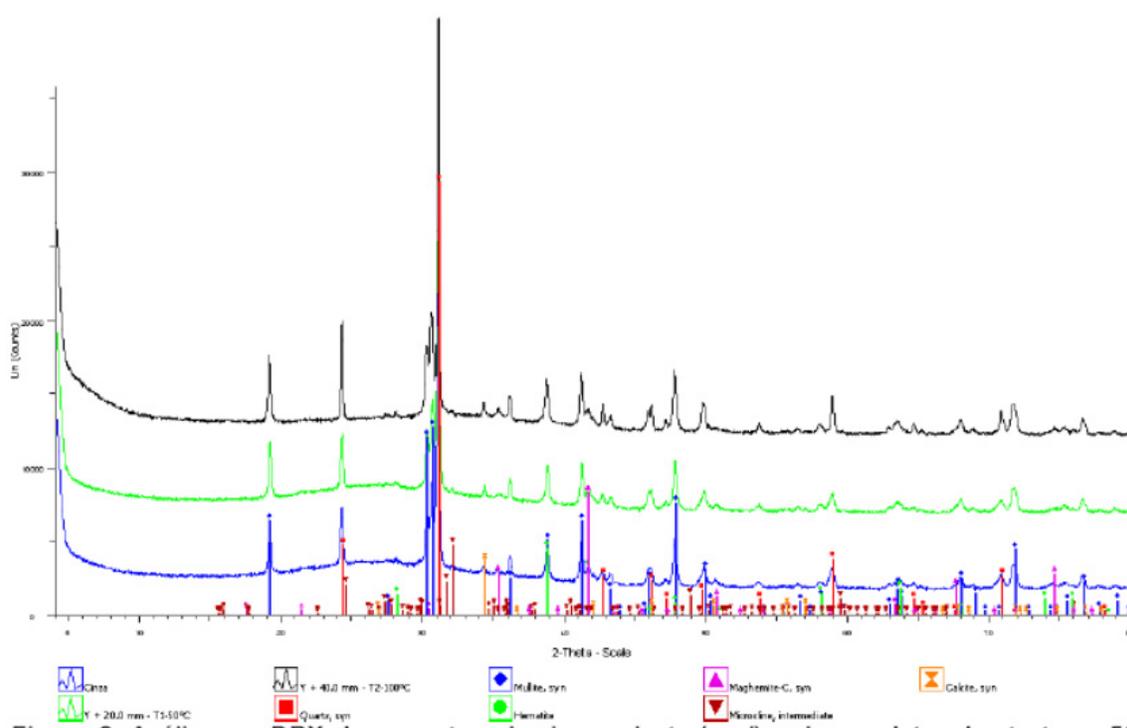


Figure 6. XRD analysis of samples of gray (blue) and the products of the tests at 50 and 100°C (green and black, respectively)

From a temperature of 150°C (Figure 7), zeolite P was identified in the X-ray diffractograms have been replaced by analcime 200°C (Figure 8), which was later replaced by hydroxycantrinite phase at 250°C (figure 9).

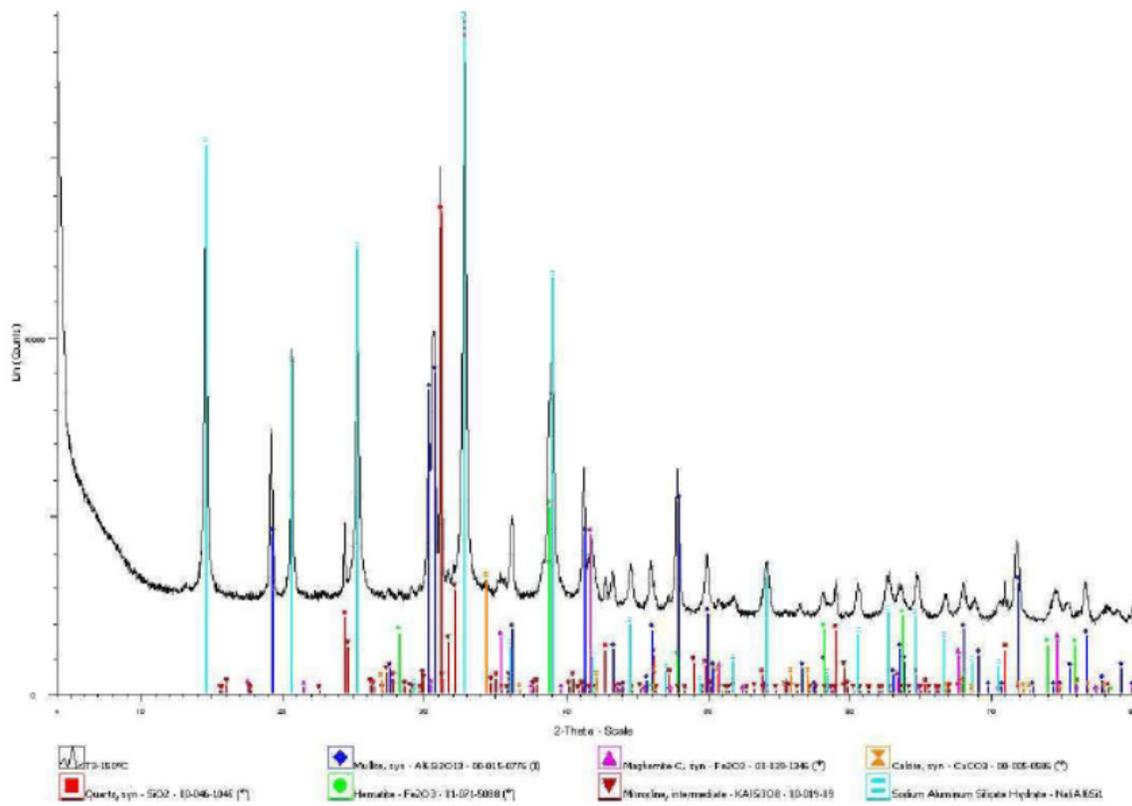


Figure 7. XRD analysis of the product for testing at 150 ° C

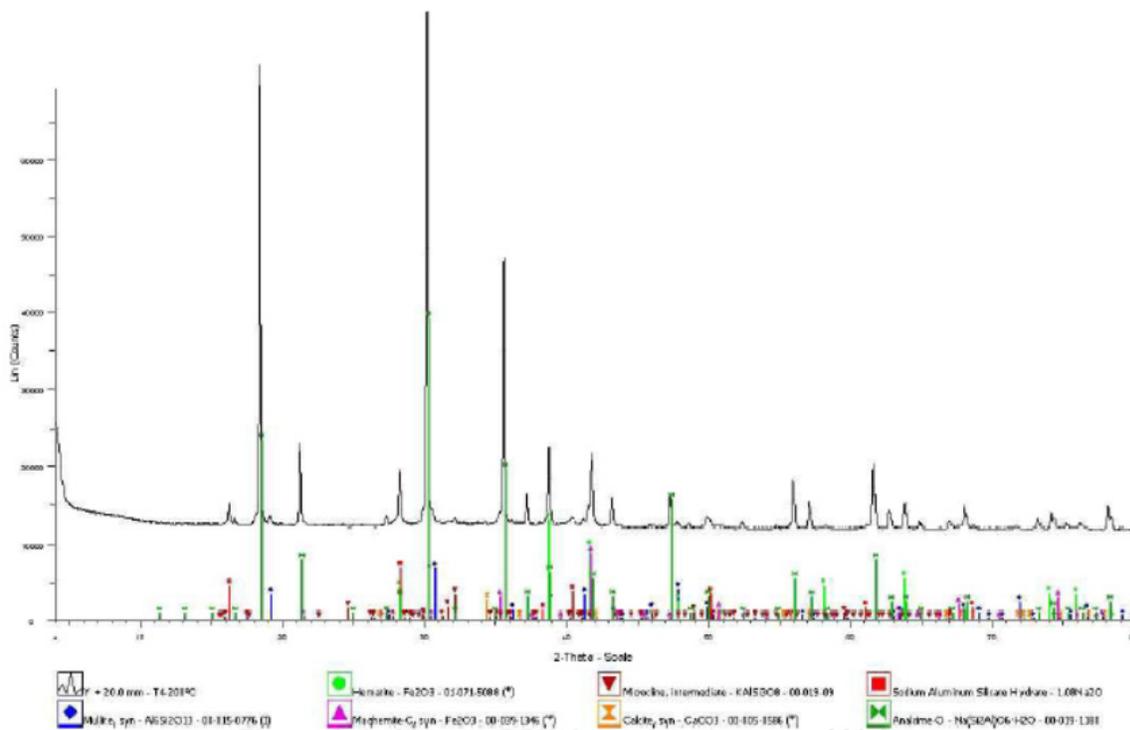


Figure 8. XRD analysis of the test product at 200 ° C

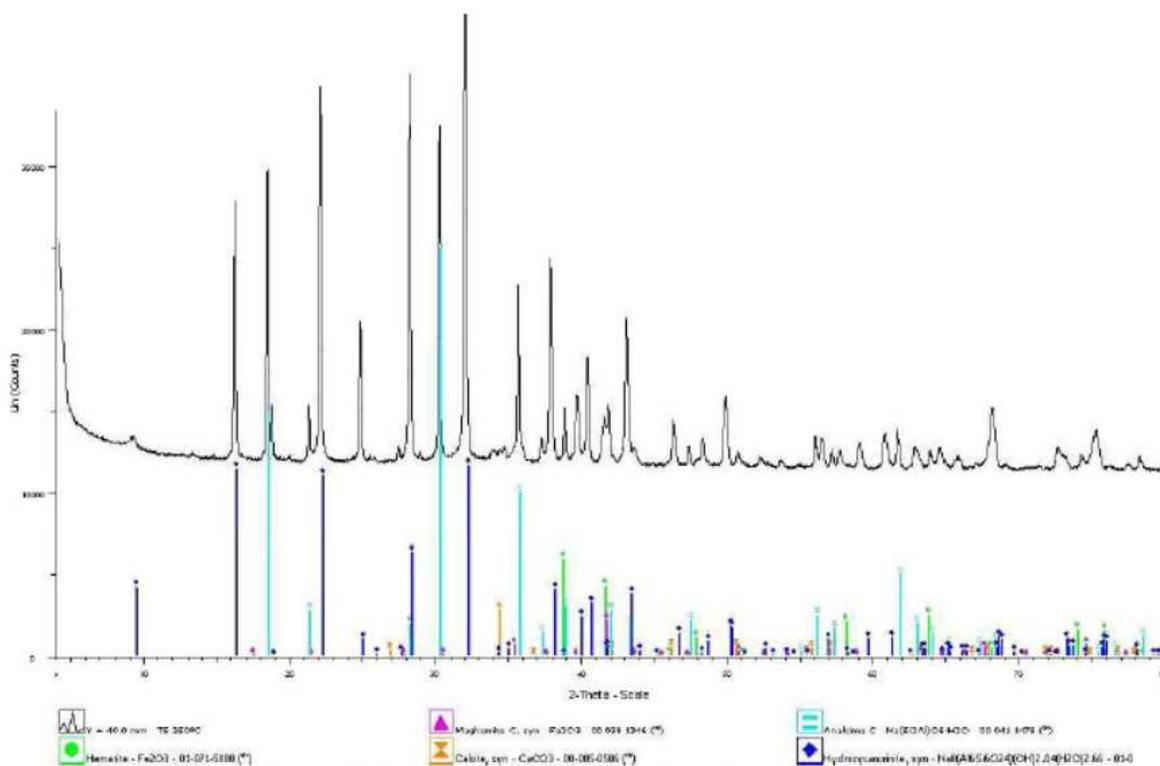


Figure 9. XRD analysis of the product for testing at 250 ° C

From the experimental results, we performed a thermodynamic study, to investigate the effect of temperature on the synthesis of these zeolite phases. For the species treated zeolite in this work, whose thermodynamic properties were not known, estimates have been proposed. Was used for this study a variation of the equation developed by [40] for estimating enthalpies of formation for the species treated in this work, to enable the calculation of free energies at several temperatures.

The proposed equation for calculating the enthalpy of formation of species (kJ/mol) is shown in equation 2, in which β_1 is a parameter calculated by nonlinear regression of data made from enthalpy of known species.

$$\begin{aligned} \Delta H_f^\circ = & n_{\text{Na}} \Delta H_f^\circ [\text{NaOH}] + n_{\text{Al}} \Delta H_f^\circ [\text{Al}(\text{OH})_3] + \\ & + n_{\text{Si}} \Delta H_f^\circ [\text{Si}(\text{OH})_4] - (y - x) \Delta H_f^\circ [\text{H}_2\text{O}] - \beta_1 n_{\text{Na}} R_{\text{Na}} \end{aligned} \quad (2)$$

The magnitudes n_{Na} , n_{Al} , n_{Si} , are the stoichiometric coefficients of the respective Na, Al and Si present in the molecular formula of each species. The quantity y is the coefficient of oxygen stoichiometric, x the stoichiometric coefficient of water incorporated and R_{Na} the radius of sodium ion (0.102 nm). The values of enthalpies of formation (ΔH_f°) and the standard molar entropies (S_f°) species used in the calculations were taken from the database program HSC Chemistry 7.0

The calculation of nonlinear regression allowed us to estimate β_1 equal to 613.231, with a correlation coefficient of 0.999. In Table 3 are the values estimated by the model and the

waste from the values taken from the database. One can observe that the maximum residue was 3.08% for the species andalusite.

Species	ΔH°_f (kJ/mol)	ΔH°_f (model) (kJ/mol)	Residues %	Residues
Cianite	-2581.097	-2604.19	0.894	23.091
Caulinite	-4119.599	-4085.29	0.832	-34.313
Pirofilite	-5637.900	-5618.33	0.347	-19.568
Paragonite	-5944.209	-5901.83	0.712	-42.374
Analcime 1	-3282.348	-3286.31	0.120	3.958
Jadeita	-3032.760	-3011.82	0.690	-20.943
Albita	-3927.659	-3921.25	0.163	-6.404
Analcime 2	-3309.841	-3297.65	0.368	-12.194
Metasilicate de sodium	-1561.511	-1600.57	2.501	39.058
Andalusite	-2686.965	-2604.19	3.080	-82.777

Table 3. First estimation results for the model enthalpy of formation

The estimation of standard molar entropy (S°_f) was performed using a simple regression, taking into account only the stoichiometric coefficients of each species (Equation 3). The best results were achieved with a correlation coefficient of 0.97 for the model.

$$S^{\circ}_f = 27.148 + 46.608 n_{Na} - 11.321n_{Al} + 5.111n_{Si} + 16.147 n_O + 43.487 n_{H_2O} \quad (3)$$

The thermodynamic data used for the calculation and the values estimated by the model S°_f and residues, are shown in Table 4.

Species	Na	Al	Si	O	H ₂ O	S°_f (J/molK)	S°_f (model) (J/molK)	Residues	Residues %
Cianite	0	2	1	5	0	86.680	90.353	-7.667	8.845
Caulinite	0	2	2	7	2	205.016	214.744	-6.993	3.411
Pirofilite	0	2	4	11	1	239.171	246.059	-8.905	3.723
Paragonite	1	3	3	11	1	276.833	276.235	0.379	0.137
Analcime 1	0.96	0.96	2.04	6	1	226.776	211.822	11.577	5.105
Jadeite	1	1	2	6	0	133.499	169.542	-19.060	14.277
Albite	1	1	3	8	0	226.400	206.948	11.397	5.034
Analcime 2	1	1	2	6	1	223.802	213.029	10.129	4.526
Andalusite	0	2	1	5	0	104.600	90.354	-24.169	23.106
Sillimannita	0	2	1	5	0	95.790	90.354	10.778	11.251
Nefeline	1	1	1	4	0	123.000	132.136	2.572	2.091

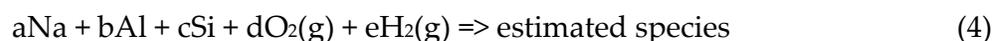
Table 4. Results estimated of S°_f by linear regression model.

To check the validity of the models surveyed, we compared the values of the standard energies of formation (ΔG_f°) of some species sodium zeolite, whose values of ΔG_f° were already known. Using the values of ΔH_f° estimated by the model developed S° of the value at 298 K calculated by linear regression is calculated to ΔG_f° values for each species to be compared (Table 5).

Species	ΔG_f°	ΔG_f° (calculated)	Residues (%)
Analcime 1	-6144.3	-6138.166	0.100
Analcime 2	-6172.2	-6116.414	0.904
Analcime DH1	-5648.3	-5679.663	0.555
Analcime DH2	-5625.2	-5662.739	0.667
Na-clinoptilolite	-10270.1	-10218.262	0.505
Natrolite	-5330.7	-5384.351	1.006
Na-phillipsite	-7444.2	-7693.379	3.347
Zeolite 4A	-5214.3	-5174.898	0.756
Zeolite 13X	-5767.7	-5711.523	0.974

Table 5. Comparison between the values of ΔG_f° at 298K (in kJ/mol) calculated from the models.

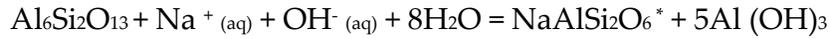
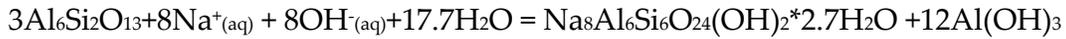
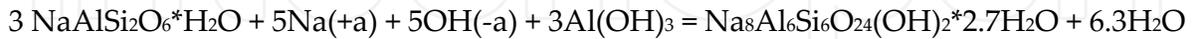
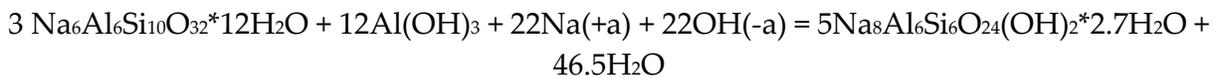
These values of ΔG_f° were estimated using the program HSC Chemistry 7.0, using the values of enthalpy of formation and standard molar entropy of the species included in the required database program, and using the balanced chemical equation as the model reaction represented by Equation 4:



Where a, b, c, d and e are the respective stoichiometric coefficients. The model of the reacting species (more stable forms of each element) were already in the database program HSC Chemistry 7.0. The maximum error obtained was slightly higher than 3%, showing that the estimate used seems appropriate.

4.4. Calculation of equilibrium

Using the estimated values of enthalpies of formation and standard molar entropy of analcime and hydroxycancrinite species, we calculated the values of free energies as a function of temperature reaction for the formation of analcime reactions (reaction A), hydroxycancrinite (reaction B) and zeolite P (reaction C) from the reaction of mullite with sodium hydroxide. Furthermore, it has been provided in the processing of analcime to hydroxycancrinite (reaction D), Zeolite P to hydroxycancrinite (reaction E) and analcime to zeolite P (reaction F). For each of these reactions studied were calculated the values of ΔG reaction and equilibrium constant at each temperature studied.

Reaction A)**Reaction B)****Reaction C)****Reaction D)****Reaction E)****Reaction F)**

It was considered the activities of solid phases equal to 1 and that the activities of Na^+ and OH^- are equal.

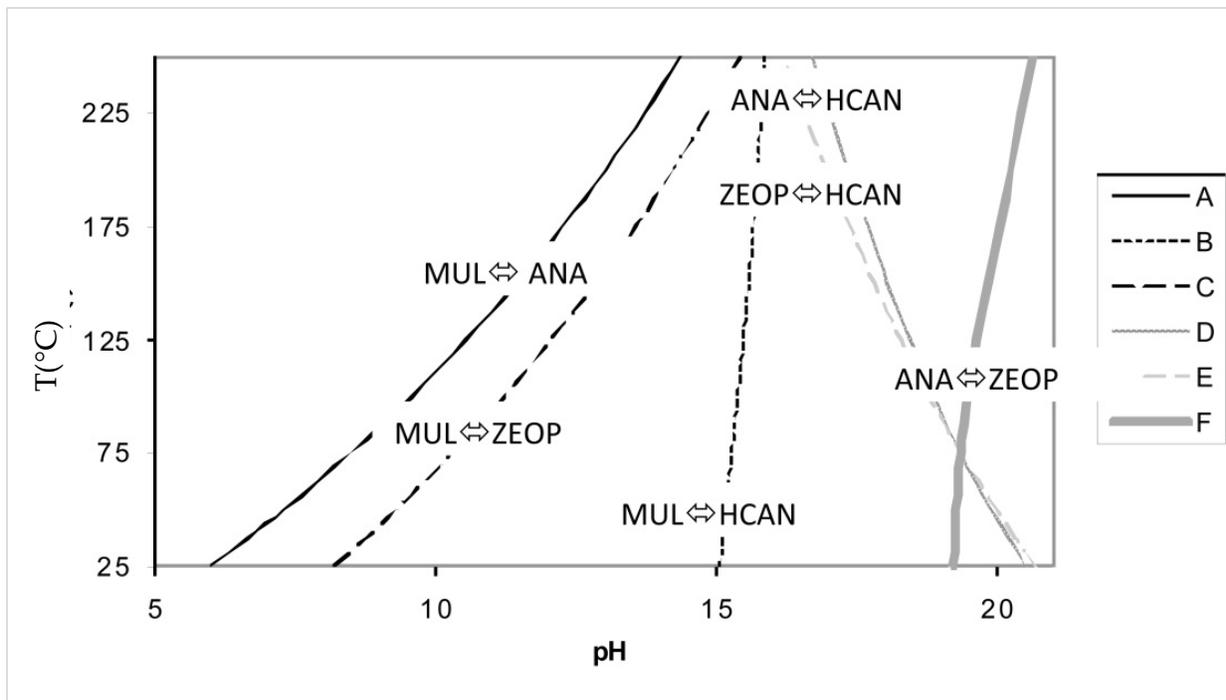


Figure 10. Phase diagram of stability of zeolite formed from the coal ash. (Abbreviations: ANA – Analcime; MUL – Mullite; ZEOP – Zeolite P; HCAN- Hidroxycancrinite)

It was possible to make a survey of pH versus temperature diagram as shown in Figure 10. It is possible to check, at 25 °C, a large region of stability of the zeolite P type, ie the reaction of the mullite forming zeolite P, at pH values between 8 and 15. This region decreases as the

temperature increases. Starting pH 15, the reaction hydroxycancrinite form, rather than zeolite P. The stability region analcime phase (pH between 6 and 8 to 25 ° C) maintains a constant-width around two pH units, but with increasing temperature is shifted to pH also higher. Higher values of pH, therefore higher concentrations of NaOH, promote the transformation of phases formed in hydroxycancrinite. The remaining balance for the reactions D, E and F are present in high pH values, and in all cases the phase stability hydroxycancrinite prevails.

5. Conclusions

The study demonstrates the application of Brazilian fly ash for zeolite synthesis by hydrothermal treatment. Statistical analysis shown that an increase of time and temperature in zeolite synthesis tends to increase the capacity of sorption of ions tested onto products.

The products obtained are effective sorbent for removal of Pb^{2+} , Zn^{2+} , Mn^{2+} and Cu^{2+} ions from aqueous solutions. The performance of sorption increased up to 25 times when compared with the original ashes.

From the results obtained and discussed, it was concluded that the formation of zeolitic phases from coal ash is thermodynamically possible. The thermodynamic values obtained for the models in the literature and the proposed in this study had similar, and allowed the establishment of equilibrium diagrams that define the regions of thermodynamic stability of the species present in the reaction medium.

The analysis of these diagrams shows that the temperature and concentration of alkali present in the medium are the most important factors affecting the stability of species to be formed during the hydrothermal treatment of coal ash with alkaline solution of NaOH. Among the equilibrium reaction studied, we found that the phase hydroxycancrinite phase tends to be more stable zeolite with increasing reaction temperature and the NaOH concentration, rather than formation of zeolite P and analcime phases. Therefore, to obtain phase zeolite P and zeolite such as analcime, are required low reaction temperatures and low concentrations of NaOH.

These results show the existence of a potential reduction of manufacturing costs of these products zeolites which may eventually enable the production of zeolites from an industrial waste such as coal ash.

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