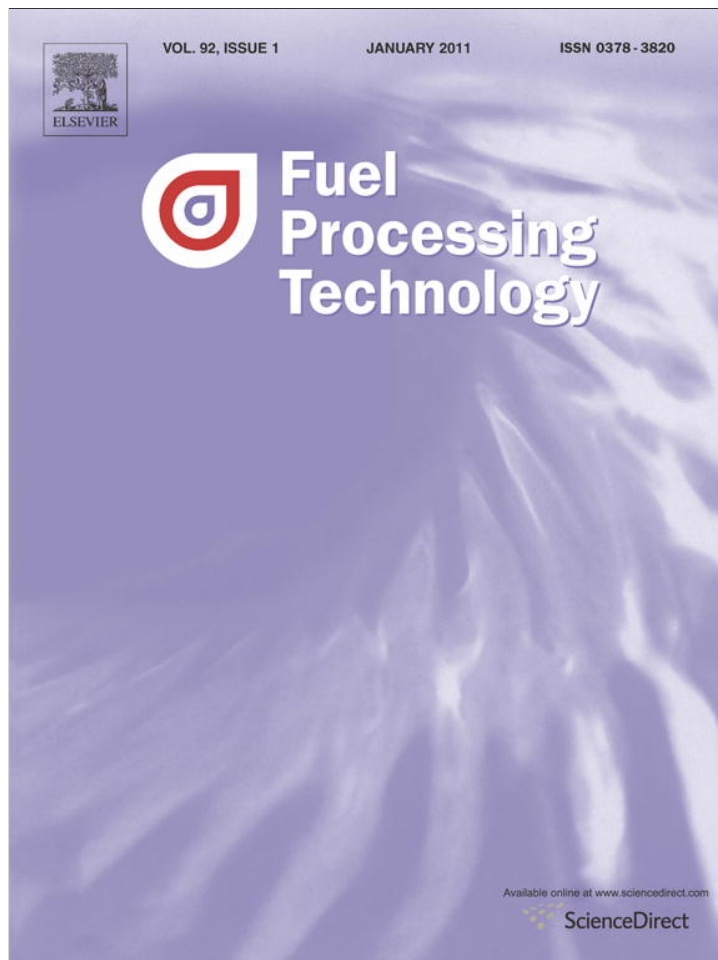


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Characteristics of Brazilian coal fly ashes and their synthesized zeolites

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ABSTRACT

Five different Brazilian fly ashes were used to synthesize zeolites by hydrothermal treatment. Raw fly ash materials and zeolitic products were characterized in terms of pH, conductivity, real density (Helium Pycnometry), specific surface area (BET method), morphological analysis (SEM), chemical composition (XRF), mineralogical composition (XRD) and cation exchange capacity (CEC). Humidity and loss of ignition (LOI) of the fly ashes were also evaluated. Results indicated that the fly ash sample from Figueira power plant (FG) has a high content of Pb. The fly ash from São Jerônimo power plant (SJ) presents a higher content of unburned carbon. Chemical composition analyses indicate that the content of SiO₂ and Al₂O₃ is above 70 wt.% in all fly ashes. After hydrothermal treatment, various zeolites such as hydroxy-sodalite, NaP1 and X zeolites were formed depending on sourced fly ash. Hydroxy-sodalite zeolite was formed in all samples. NaP1 zeolite was formed in fly ashes with high content of Ca while X zeolite was formed from the fly ashes with high content of Al. CEC values of the zeolitic materials are 40 times higher than fly ash samples, potential for use as ion exchangers.

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1. Introduction

Coal is the world's most abundant fossil fuel and its reserves are distributed in all the continents [1]. For these reasons, coal is currently considered as a strategic energy source and has large importance to the context of global energy generation. In Brazil, coal reserves are estimated at 11.1 billion tons [2] and are sufficient for energy production over 500 years at the current consumption rate [1]. After burning of coal, coal-based thermal power plants generate a large amount of inorganic residues: fly ash, bottom ash, slag and flue gas desulfurization by-products [3], which have low value for utilization and several environmental problems associated with their disposition. Fly ash is a more abundant by-product from coal-based thermal power plants and its production is around 4 Mt per year while the annual utilization for incorporation into cement and concrete accounts only for about 30% of total fly ash production. In Brazil, the quantity of fly ash produced corresponds to 80–85 wt.% of total production of ashes [4] and a major industrial application for this inorganic residue lies in the production of concrete and Portland cement [5]. However, the problem is aggravated due to high ash content presented in Brazilian coal compared to other countries [6]. Previously, some Brazilian fly ashes have been investigated [4,6–8], but more studies addressing

the utilization of these materials in the synthesis of products with higher added value are needed because of increase in the quantity of fly ash due to operation of new coal-based thermal power plants.

Fly ashes can be converted into zeolites due to their high contents of silicon and aluminum, which are the structural elements of zeolites [3,9,10]. Other kinds of waste such as rice husk ash, clay and kaolin can also be converted into zeolites [11–15], but the use of coal ash for zeolite conversion is mostly explored due to the significant quantity of the waste generated all over the world. The production of zeolites using coal fly ash as a resource constitutes one important issue of waste management and many techniques have been investigated [9,10,16–21]. The most common method involves a hydrothermal process, whereby the fly ash is mixed with an alkali solution at different conditions of temperature, pressure and reaction time. Such a treatment process can lead to the formation of various types of zeolite. The type of zeolite formed is a function of temperature, pressure, concentration of alkaline reagent, reaction time and solution/fly ash ratio.

Zeolites synthesized from fly ash have higher cation exchange capacity than original fly ash [3]. In addition to applications as a cation exchanger, zeolites can act as molecular sieves, catalysts, and adsorbents [22]. Zeolitic materials have been widely used as low-cost adsorbents for the removal of pollutants from aqueous solution, soil and air [23–33]. The present work is to characterize five fly ashes from different Brazilian thermal power plants, synthesize zeolites from these samples and compare the characteristics of the products and raw materials for their potential application.

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2. Materials and methods

2.1. Materials

The coal fly ash samples used in this study were collected from bag filter, electrostatic precipitators and cyclone filter of five different Brazilian thermal power plants: Figueira Power Plant, located in Paraná State, Jorge Lacerda Power Plant, located in Santa Catarina State, São Jerônimo Power Plant, Charqueadas Power Plant and Presidente Médice Power Plant, located in Rio Grande do Sul State. All the power plants are located in southern Brazil, where it is the main reserve of coal in the country. Raw ash samples from each power plant were used without any pretreatment. The samples were labeled as: FG, JL, SJ, CH and PM. Sodium hydroxide obtained from Merck was used in zeolite synthesis.

2.2. Zeolite synthesis from fly ashes

In zeolite synthesis by a conventionally hydrothermal treatment [10], 0.02 kg of coal fly ash was mixed with $1.6 \times 10^{-4} \text{ m}^3$, 3500 mol m^{-3} NaOH aqueous solution in a $3 \times 10^{-4} \text{ m}^3$ Teflon vessel. This mixture was heated to 373.15 K in an oven for 24 h without stirring. After finishing of the process, the suspension was filtered through a quantitative paper filter (Nalgon 3400, diameter = 0.15 m). The solid was repeatedly washed with deionized water until the pH of filtrate is at ~9 and then the solid was dried at 373.15 K for 24 h. The zeolitic products obtained were labeled as: ZFG, ZJL, ZSJ, ZCH and ZPM, respectively, based on the fly ash sources.

2.3. Characterization of fly ashes and zeolites

2.3.1. pH and conductivity

The samples ($2.5 \times 10^{-4} \text{ kg}$) were placed in $2.5 \times 10^{-5} \text{ m}^3$ of deionized water and the mixture was stirred for 24 h in a shaker at 120 rpm (Ética – Mod 430). After filtration, the pH of the solutions was measured with a pH meter (MSTecnoyon – Mod MPA 210) and the conductivity was measured with a conductivimeter (BEL Engineering – Mod W12D).

2.3.2. Humidity and loss of ignition

The contents of humidity and loss of ignition (LOI) of coal fly ashes in this study were calculated according to the weight loss of the samples subjected to heating at 378.15 K for 24 h in an oven and 1323.15 K for 4 h in a muffle furnace, respectively, and expressed in percentages. The mass of the materials used was $5 \times 10^{-4} \text{ kg}$.

2.3.3. Real density and specific surface area

The real density and the specific surface area of fly ashes and zeolite samples were determined by a helium pycnometer (Micromeritics Instrument Corporation – Accupyc 1330) and by a BET Surface Area Analyser (Quantachrome Nova – 1200), respectively. Prior to determination of the specific surface area, samples were heated at 423.15 K for 12 h to remove volatiles and moisture in a degasser (Nova 1000 Degasser). The BET surface areas were obtained by applying the BET equation to the nitrogen adsorption data.

2.3.4. Morphological analysis and chemical composition

To verify the morphology, samples were covered with a thin layer of gold to make them conductive and examined using a scanning electron microscope (Philips – XL30). The chemical composition of the samples was determined by an X-ray fluorescence equipment (Rigaku – RIX 3000 X-ray Fluorescence Spectrometer).

2.3.5. Mineralogical composition and cation exchange capacity (CEC)

The mineralogical composition of samples was determined by X-ray diffraction (Rigaku – Miniflex II X-ray Diffractometer) using Cu

K α radiation at 30 kV and 15 mA. The scan rate was 0.05°/s and ranged between 5 and 80° (2 θ). Phase identification was made by searching the ICDD powder diffraction file database, with the help of JCPDS (Joint Committee on Powder Diffraction Standards) files for inorganic compounds.

In CEC measurements, the samples were saturated with sodium acetate solution (1000 mol m^{-3}), washed with distilled water ($1 \times 10^{-3} \text{ m}^3$) and then mixed with ammonium acetate solution (1000 mol m^{-3}). The sodium ion concentration of the resulting solution was determined by optical emission spectrometry with inductively coupled plasma – ICP-OES (Spectroflame – M120).

3. Results and discussion

3.1. pH and conductivity

The pH and conductivity obtained from various Brazilian fly ashes and zeolitic products are given in Table 1. The pH values of fly ash suspension were very close and ranged from 7.6 to 8.2. These values are justified by the presence of compounds formed by the cations, K⁺, Na⁺, Ca²⁺ and Mg²⁺ combined with carbonates, oxides or hydroxides which cause the alkalinity of the suspension [34]. For zeolites the pH ranged from 8.3 to 9.3, higher than those of fly ash samples. The pH rose due to the hydrothermal treatment with NaOH solution.

The conductivity values are related to some compounds present in coal fly ashes that can undergo dissolution. The conductivity values of fly ash suspension ranged from 188.8 μS (SJ) to 538.0 μS (FG). The fly ash sample from Figueira power plant (FG) presented a higher value if compared to other samples. This result is in accordance with another study reported the values of conductivity for different Brazilian fly ashes [4]. This is due to the low ash content present in the coal used in Figueira power plant, which enables the solubilization of a higher number of compounds and consequently higher amount of ions present in solution. Conductivity values of the zeolites were higher than the fly ash samples due to the presence of exchangeable cations in the structures of the zeolites formed by the hydrothermal treatment.

3.2. Humidity and loss of ignition

The determination of humidity and loss of ignition is often carried out on coal fly ash samples because they may indicate the performance in the synthesis of zeolites. The loss of ignition for fly ashes is usually due to the presence of unburned carbon (indicating the burning efficiency of a thermoelectric power plant) and mineral phases not stable at high temperatures [35].

As shown in Table 1, all fly ash samples presented less than 3% of humidity. This was because the samples were collected directly by the filters or electrostatic precipitators at high temperature. The values are in accordance with the results obtained from different Spanish and South African fly ashes [35].

Table 1
Characteristics of Brazilian coal fly ashes and their synthesized zeolites.

Sample	pH	C (μS)	% Humidity	% Loss of ignition	R _{density} (g cm^{-3})	S _{BET} ($\text{m}^2 \text{g}^{-1}$)	CEC (meq g^{-1})
FG	8.2	538.0	0.800	9.13	2.40	8.7	0.035
JL	8.0	259.0	1.40	15.1	2.26	9.6	0.026
SJ	7.9	188.8	3.00	15.2	2.46	30.0	0.027
CH	7.8	201.0	0.600	2.60	2.54	3.3	0.026
PM	7.6	203.0	0.600	1.44	2.31	1.4	0.026
ZFG	9.0	495.0			2.00	65.8	1.4
ZJL	8.4	389.0			2.01	134.3	1.3
ZSJ	8.3	318.0			2.24	145.7	1.5
ZCH	9.3	431.0			2.20	56.7	1.9
ZPM	8.9	481.0			2.45	65.8	1.6

For the loss of ignition, SJ and JL fly ashes presented the highest values (15.2% and 15.1%, respectively). FG fly ash presented an intermediate value (9.13%). The CH and PM fly ashes presented the lower values: 2.60% and 1.44%, respectively.

According to the values of loss of ignition, the decreasing burning efficiency of coal-fired power plants in Brazil is as follows: Presidente Médice power plant > Charqueadas power plant > Figueira power plant > Jorge Lacerda power plant > São Jerônimo power plant. Compared with the data of humidity, the samples with higher loss of ignition showed higher humidity. This is due to the presence of unburned carbon which will easily adsorb water.

3.3. Real density and specific surface area

The real density and specific surface area obtained for Brazilian fly ashes and zeolitic products are also given in Table 1. The density values for all samples were very close. In general, zeolites presented

lower values of density than those of the ashes. The average values for fly ashes and zeolites were 2.39 g cm^{-3} and 2.18 g cm^{-3} , respectively. This indicated that the hydrothermal treatment produced a porous and less compact material than the precursor materials.

The specific surface area of fly ash samples ranged from $1.4 \text{ m}^2 \text{ g}^{-1}$ (PM) to $30.0 \text{ m}^2 \text{ g}^{-1}$ (SJ). The higher specific surface area of SJ is ascribed to a large amount of unburned carbon [4]. Higher unburned carbon in the fly ashes particles contributes to higher specific area [36] due to the porous structure.

In general, large surface area will result in higher reactivity with the activating agents during the synthesis of zeolites. The surface areas of fly ashes follow the order: SJ > JL > FG > CH > PM. The specific surface area values of the zeolites were higher than those of their precursor ash, ranged from $56.7 \text{ m}^2 \text{ g}^{-1}$ (ZCH) to $145.7 \text{ m}^2 \text{ g}^{-1}$ (ZSJ). The decreasing order of the specific surface area of zeolites was: ZSJ > ZJL > ZPM > ZCH > ZFG.

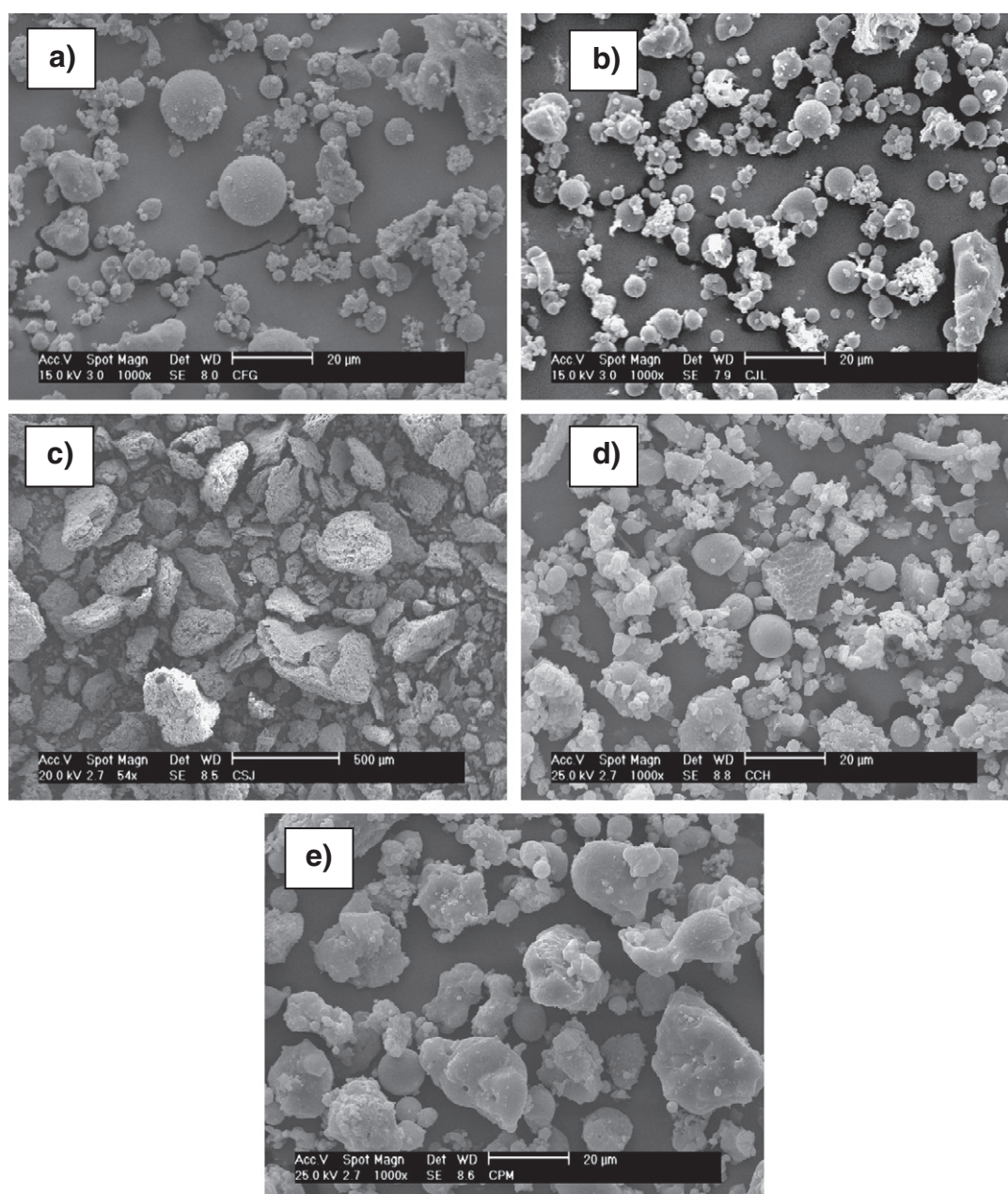


Fig. 1. SEM micrographs of fly ashes from a) Figueira power plant – FG; b) Jorge Lacerda power plant – JL; c) São Jerônimo power plant – SJ; d) Charqueadas power plant – CH; e) Presidente Médice power plant – PM.

3.4. Morphological analysis

The scanning electron micrographs (SEM) of the original fly ashes are shown in Fig. 1. Coal fly ash particles typically had the predominance of spherical shapes at different sizes and smooth surfaces, similar to previous observations in other studies [6,37–40]. Different physical states of silica are responsible for the particles of irregular size [39].

The particles of SJ fly ash presented a different aspect (Fig. 1c). The spongy appearance of this particle is the characteristic of fly ash samples with high content of unburned coal, which contributes to the high values of loss of ignition and surface area found for this sample [35]. This morphology is due to low efficiency of the burning system used in São Jerônimo power plant.

The SEM photos of the synthesized zeolites are shown in Fig. 2. Different from the fly ash microphotographs, the surface of zeolites is rough, indicating that zeolite crystals were deposited on the surface of fly ash particles during the hydrothermal treatment [38,40].

3.5. Chemical composition

Usually, the characteristics of fly ashes varied depending on their sources. Chemical composition of fly ash affects the properties of the end products. The chemical compositions of five fly ash samples (by wt.%) are given in Table 2.

Fly ash is mainly composed of metal oxides derived from inorganic compounds in the coal. It can be observed from Table 2 that the major constituents for all samples of the Brazilian fly ashes are: SiO_2 , Al_2O_3 ,

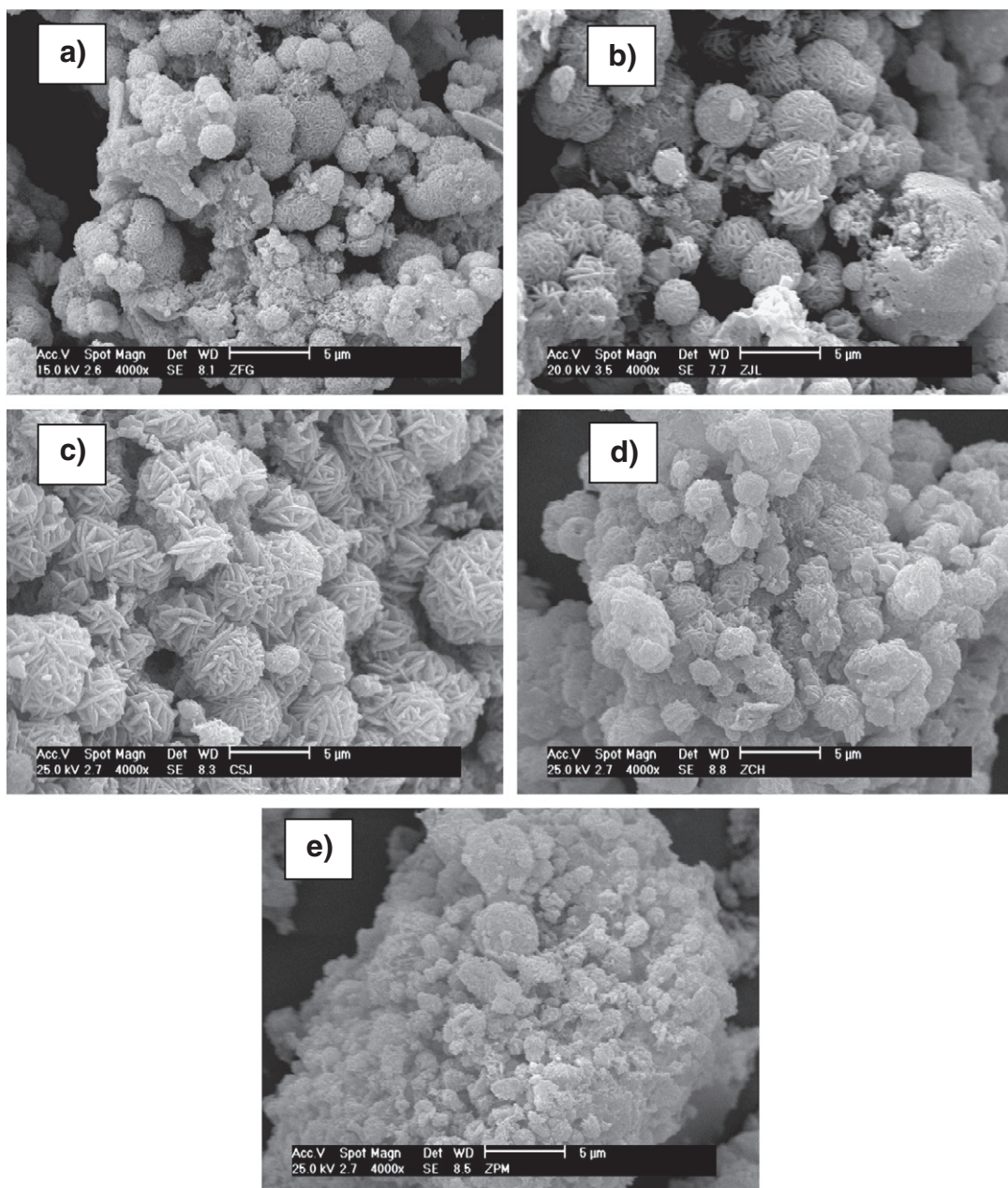


Fig. 2. SEM micrographs of zeolites synthesized using the fly ashes from a) Figueira power plant – ZFG; b) Jorge Lacerda power plant – ZJL; c) São Jerônimo power plant – ZSJ; d) Charqueadas power plant – ZCH; e) Presidente Médice power plant – ZPM.

Table 2
Composition (wt.%) of fly ash obtained from different Brazilian thermal power plants.

Components	FG	JL	SJ	CH	PM
SiO ₂	48.4	50.3	54.5	57.5	62.4
Al ₂ O ₃	23.8	29.8	26.7	32.6	22.9
Fe ₂ O ₃	10.2	6.70	5.00	3.60	4.90
K ₂ O	4.60	5.30	3.00	2.00	3.00
CaO	4.70	2.70	2.80	1.40	2.40
TiO ₂	1.70	2.20	3.80	1.60	1.10
SO ₃	2.10	1.40	2.90	0.40	0.500
MgO	1.70	1.10	1.00	0.70	1.10
Na ₂ O	1.30	–	–	–	1.30
P ₂ O ₅	0.200	0.170	0.110	0.0900	0.0900
ZnO	0.300	0.100	0.0300	0.0200	0.0200
MnO	0.100	0.0700	0.0400	0.0200	0.0300
PbO	0.110	0.0300	–	0.0160	–
SiO ₂ /Al ₂ O ₃	2.03	1.69	2.04	1.76	2.72

and Fe₂O₃. The content of SiO₂ and Al₂O₃ is above 70 wt.% for all samples. Quantities below 5 wt.% of K₂O, CaO, TiO₂, SO₃, and MgO are also observed. The SiO₂/Al₂O₃ ratios were calculated for the fly ashes and the values ranged from 1.69 to 2.72, indicating good source to synthesize zeolites [16].

It is noted that FG sample presented a high content of Pb (0.110 wt.%). Thus, the fly ashes from FGPP should be carefully deposited due to potential leaching of this element and other toxic elements [4].

The chemical compositions of zeolitic products (by wt.%) are shown in Table 3. The chemical composition of zeolitic materials synthesized from fly ash is mainly silica, alumina, iron oxide and sodium oxide. A significant amount of Na element is incorporated in the final product due to hydrothermal treatment with NaOH solution. Due to dissolution of SiO₂ by the hydrothermal treatment, the content of this compound in the zeolitic products decreased for all samples.

The SiO₂/Al₂O₃ ratio for zeolites is associated to the cation exchange capacity and the values ranged from 0.96 (ZJL) to 1.34 (ZFG). In general, if a zeolite has a low SiO₂/Al₂O₃ ratio, it will have higher cation exchange capacity due to the substitution of Si (IV) by Al (III) in the zeolite framework that results in a negative charge [3]. The SiO₂/Al₂O₃ ratios for the zeolites are lower than the values of raw fly ashes, indicating that the hydrothermal treatment contributed to the increase in the cation exchange capacity of these materials.

3.6. Mineralogical composition

Fig. 3 shows X-ray diffraction patterns of different Brazilian coal fly ashes. According to Fig. 3, the Brazilian fly ashes used in this study are very similar and are composed mainly of mullite and quartz and some amounts of hematite and magnetite, which are also confirmed from their chemical compositions (Table 2).

Table 3
Composition (wt.%) of zeolites obtained from Brazilian fly ashes.

Components	ZFG	ZJL	ZSJ	ZCH	ZPM
SiO ₂	36.5	36.6	43.6	41.5	42.4
Al ₂ O ₃	27.3	38.0	32.9	37.2	34.9
Fe ₂ O ₃	12.8	8.30	5.40	5.60	7.80
Na ₂ O	9.20	6.90	9.10	9.80	6.70
CaO	6.10	3.60	3.70	2.10	3.50
TiO ₂	2.00	2.70	2.30	2.20	1.50
MgO	2.00	1.40	0.700	0.700	1.80
SO ₃	1.90	1.30	1.00	0.300	0.600
K ₂ O	1.00	0.800	1.00	0.500	0.700
ZnO	0.300	0.0900	0.0400	0.0300	0.0300
MnO	0.200	0.100	0.0400	0.0300	0.0600
PbO	0.100	0.0300	–	0.0110	0.0150
P ₂ O ₅	0.0600	0.0600	0.0700	0.0600	0.0500
SiO ₂ /Al ₂ O ₃	1.34	0.96	1.32	1.12	1.21

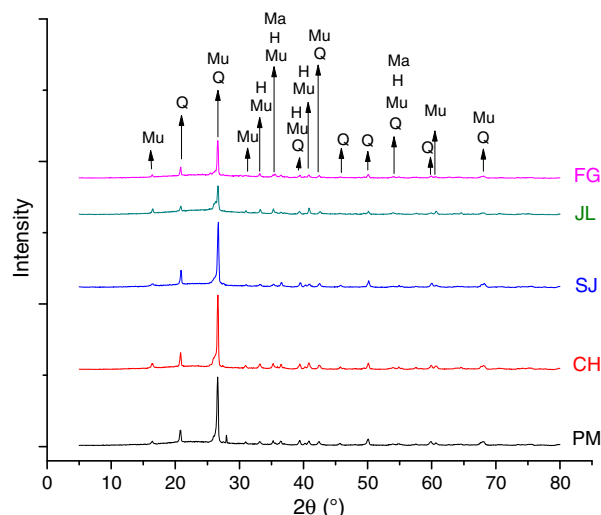


Fig. 3. XRD Patterns of Brazilian fly ashes (Q = Quartz – JCPDS 85-0796, M = Mullite – JCPDS 74-4143, H = Hematite – JCPDS 33-0664 and Ma = Magnetite – JCPDS 71-6336).

Fig. 4 shows X-ray diffraction patterns for the zeolitic materials obtained from fly ashes. Table 4 shows the crystalline phases identified for each zeolite sample.

According to Fig. 4, quartz and mullite could not be completely dissolved during the hydrothermal treatment and remained in all samples after the synthesis. Thus, the compounds responsible for the formation of zeolites were mainly amorphous SiO₂ and Al₂O₃. Although all the fly ashes presented similar SiO₂ and Al₂O₃ mass percentage, the amount of these amorphous compounds were different and were responsible for the formation of zeolites of different types and quantities. As shown in Fig. 4, hydroxy-sodalite zeolite (S1) was formed in all samples. This type of zeolite has high stability under variations of temperature and can occur during the synthesis of zeolites using coal fly ash as raw material crystallized between 353.15 K and 413.15 K [41]. It can be noticed that ZFG zeolite presented only one kind of zeolite (S1), due to high content of the elements which inhibit the formation of zeolites, such as iron and calcium. On the other hand, the fly ash which presented the lowest content of iron and calcium (CH), gave rise to the products of three kinds of zeolite (S1, P1 and X zeolite). The formation of three zeolites in ZCH sample can also be related to the large amount of aluminum present in the precursor fly ash (CH) (32.6%, Table 2). As previously mentioned, aluminum is a structural element of zeolites and its quantity influences the formation of these materials. The formation of NaP1 zeolite (presented in ZCH and ZPM products) was only possible using fly ashes with low content of iron and calcium. X zeolites could be synthesized using the fly ashes with high content of aluminum, like JL, SJ and CH fly ashes (Table 2).

3.7. Cation exchange capacity

The CEC values of fly ashes and zeolites are shown in Table 1. The CEC values of the ashes are much low, ranged from 0.026 to 0.035 meq g⁻¹ and are similar to the values reported in the literature [34]. CEC values of the zeolitic materials ranged from 1.3 to 1.9 meq g⁻¹ and were 40 times higher than fly ash samples due to formation of zeolites. Variations in the CEC values may be attributed to factors such as the type and extent of zeolite formation [42].

The CEC value for ZCH sample presented the highest value due to formation of three zeolites, NaP1, hydroxy-sodalite and X-type zeolites. NaP1-type zeolites generally have higher CEC values for NH₄⁺ cations than do hydroxy-sodalite zeolites, which have a smaller pore size [43]. Therefore, the synthesized zeolites can be used as good

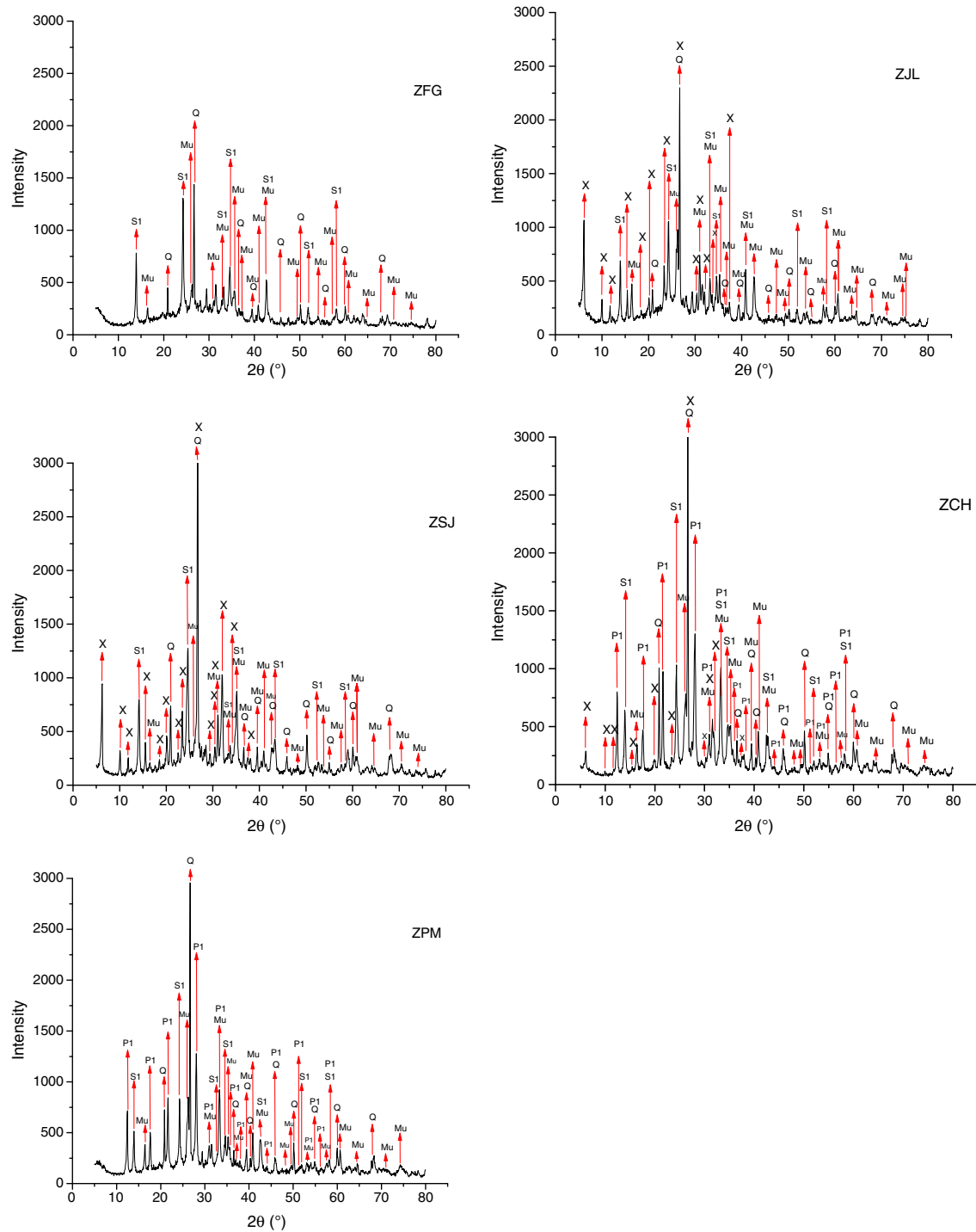


Fig. 4. XRD Patterns of zeolitic materials synthesized by hydrothermal reaction at 373.15 K for 24 h, NaOH 3500 mol m⁻³, S/L ratio = 125 kg m⁻³ (Q = Quartz – JCPDS 85-0796, M = Mullite – JCPDS 74-4143, P1 = NaP1 Zeolite – JCPDS 39-0219, S1 = Hydroxy-sodalite zeolite – JCPDS 31-1271, X = X zeolite – JCPDS 38-0237).

cation exchangers. A preliminary test showed that ZCH presented high adsorption capacities for Zn²⁺ and Cd²⁺ [44].

4. Conclusion

1. Fly ash sample from Figueira Power Plant (FG) was considered to be more hazardous for deposition due to high content of Pb. The fly ash from São Jerônimo Power Plant (SJ) presented higher unburned carbon content and specific surface area.

2. Five coal fly ashes from Brazil coal-fired power plants showed the content of SiO₂ and Al₂O₃ above 70 wt%. Hydroxy-sodalite, NaP1 and X zeolites were formed after hydrothermal treatment. The kind of zeolite varied depending on the chemical composition of fly ash. The products presented different morphology and higher specific surface area values than precursor ashes.

3. NaP1 zeolite was formed only using fly ashes samples with low content of iron and calcium. X zeolites were synthesized using fly ashes with high content of aluminum.

Table 4
Crystalline phases of zeolites from Brazilian fly ashes.

Sample	Crystalline phase
ZFG	Q, S1, Mu
ZJL	Q, X, S1, Mu
ZSJ	Q, S1, X, Mu
ZCH	Q, P1, S1, Mu, X
ZPM	Q, P1, S1, Mu

Quartz (Q): SiO₂, Mullite (Mu): Al_{4,44}Si_{1,56}O_{9,78}, Hydroxy-sodalite (S1): 1.08Na₂OAl₂O₃1.68SiO₂1.8H₂O, X-type zeolite (X): Na₂Al₂Si_{2,5}O_{9,6}2H₂O, NaP1 (P1): Na₆Al₆Si₁₀O₃₂12H₂O.

4. CEC values for the zeolitic materials were 40 times higher than those of fly ash and can be used as ion exchangers.

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