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## Potassic zeolites from Brazilian coal ash for use as a fertilizer in agriculture

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### ABSTRACT

Brazilian coal has an ash content ranging from 30 to 50% by weight. Consequently, its use in coal-fired thermoelectric for power production generates a lot of waste. The construction sector is the largest consumer of coal ash, but it cannot absorb the entire amount generated. Thus, other applications for coal ash should be studied in aim to optimize the use of this industrial waste. This research had as focus to synthesize potassic zeolite from the coal ash into on potassium fertilizer for the grown wheat plant. In this work, it was used a subbituminous coal from Mina do Leão (RS, Brazil) presenting 48.7% ash content on a dry basis. Concerning the synthesis of potassic zeolite, it was adopted the conventional method of hydrothermal treatment with potassium hydroxide. A schedule of experiments was conducted in order to define the optimum condition of zeolite synthesis that was then used an alkaline solution of 5 M KOH with a reaction time of 24 h at 150 °C. According to this procedure, it was obtained a zeolite with a single crystalline phase, identified through X-ray diffraction as Merlinoite. Subsequently, it was performed a set of tests using potassic zeolite as a fertilizer for plants in a greenhouse. The synthesized potassic zeolite showed a good potential for its use as fertilizer in agriculture.

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### 1. Introduction

In terms of volume, the thermoelectric plants for energy production, generate a significant amount of solid waste known as ash from the burning of coal (Kahlreuth and Levandowski, 2009). According to the Thermal Generation of Electric Power Company, CGTEE (2010), 1.0 kg of raw material produces 1 kWh of energy and 0.5 kg of ash in the case of coal from the Mine of Candiota (Brazil, RS). This coproduct is formed by unburned particles and non-combustible material present in the coal (Pozzobon, 1999).

The main applications of ashes are: manufacture and incorporation into the cement and ceramics, stabilizing soils, landscape recultivation, geopolymers production, fertilizers materials, among others (Ahmaruzzaman, 2010; Rhim et al., 2006; Egger et al., 2009; Lee et al., 2011; Bessa et al., 2015; Berekaa, 2015; Li, 2003; Bernardi et al., 2010a; Bernardi et al., 2010b; Li et al., 2014; Bernardi et al., 2015). However, this still occurs on a small scale when compared to the amount of ash generated (Derkowski

et al., 2006). Therefore, there is the need to search for more ways to take advantage and add value to this coproduct.

In this context, a promising application for ash is its conversion into zeolitic material by hydrothermal treatment with potassium or sodium hydroxide (Henmi, 1987; Querol et al., 1997a, 1997b; Poole et al., 2000; Rayalu et al., 2006; Kolay et al., 2001; Murayama et al., 2002; Fukasawa et al., 2017a). Zeolites are minerals consisting of aluminum, silicon and hydrous alkali or alkaline earth metals (typically Na, K, Mg and Ca) (Fukasawa et al., 2017b; Lee et al., 2017). Since the coal ash is composed in average of 85% alumina and silica (Fukasawa et al., 2017b; Missengue et al., 2017), this solid waste is a good precursor for zeolite synthesis.

Zeolite has microporous structure organized in three-dimensional crystal lattices (Böer, 2013). This gives it great power of adsorption and ion exchange capacity (Luz, 1994), features that are suitable for a wide range of processes like catalysts supports. Therefore, transforming coal fly ash into zeolite adds value to this coproduct. Using ash as raw material minimizes the impacts to the environment and eliminates, in part, the volume of ash for disposal (Holler and Wirsging, 1985).

The synthesis of zeolites from coal ash is directly influenced by the following parameters: type and composition of the ash, type

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**Table 1**  
Experimental conditions for the synthesis of zeolites.

Test	KOH concentration (mol L <sup>-1</sup> )	Coal fly ash mass (g)	KOH mass (g)	Water volume (mL)	Temperature (°C)	Time (h)
1	3	10.0	10.0	60.0	100	24
2	3	10.0	10.0	60.0	150	24
3	3	10.0	10.0	60.0	100	72
4	3	10.0	10.0	60.0	150	72
5	5	25.0	14.0	50.0	100	24
6	5	25.0	14.0	50.0	150	24
7	5	25.0	14.0	50.0	100	72
8	5	25.0	14.0	50.0	150	72

and concentration of alkaline solution, pressure, temperature, reaction time, ratio of volume of alkaline solution and mass of ash, and the use of promoters (Siddique, 2004). It is then important to characterize the synthesized zeolites in order to understand the interference of the factors above. Thus, the identification of properties such as chemical composition, crystallinity, ion exchange capacity and morphology, can be made from analytical techniques such as X-ray diffraction (XRD), X-ray fluorescence (XRF), cation exchange capacity (CEC) and scanning electronic microscopy (SEM). Therefore, the objective of this study was to obtain potassic zeolites from Brazilian coal ash for use as a fertilizer in agriculture.

## 2. Material and methods

### 2.1. Synthesis of zeolites

Coal fly ash samples obtained in a pilot fluidized bed combustor using coal from Mina do Leão (RS, Brazil) were used for the zeolite synthesis. An amount of 4 kg of ash was packed in plastic bags without pretreatment according to Brazilian Standard (NBR 5736, 1991). For its conversion into zeolites, the conventional methodology of hydrothermal treatment was adopted. Following this procedure it was prepared an alkaline solution with potassium hydroxide in concentrations of 3 and 5 M using distilled water. A mixture of coal fly ash and alkaline solution (2 and 6 mL g<sup>-1</sup>) was inserted into a cylindrical carbon steel reactor with an internal teflon container.

Subsequently, the reactor was placed in an oven in order to achieve the synthesis temperature. It was used the reaction temperatures at 100 and 150 °C during reaction periods of 24 and 48 h. After this time, the mixture that remained in the reactor was filtered and the solid (i.e. zeolitic mixture) was washed with distilled water. The solid was further dried in an oven at 100 °C for 24 h. The experimental conditions for the zeolite synthesis are presented in Table 1.

### 2.2. Characterization of zeolites

The chemical composition of ash and zeolite were determined by X-ray fluorescence (XRF) according to the ASTM method D4326-04 (2003). The analysis was carried out under molten tablet and using standard coal fly ash (SRM 2689, 2690 and 2691 NIST 1994) for equipment calibration (Rigaku Dengui WD-XRF, model 3100). Beyond this, it was possible to obtain the loss on ignition (LI) of each sample. This technique is determined with base in Brazilian standard NBR NM 18:2004. The methodology consists on heating a sample at 900–1000 °C temperature and then cooling until at room temperature and to weight samples. Thus the mass lost after heating is determined before heating and after cooling.

The crystalline phases present in the zeolites were detected by X-ray diffraction (XRD). This analysis was performed in a XRD equipment (Rigaku Dengui D-Max, model 2000) with Cu K $\alpha$  radiation generated at 30 kV and 15 mA. To assist in the detection, it

was used the software Jade Plus 9 2010 and JCPDS diffraction pattern database.

The cation exchange capacity (CEC) of the coal ash based zeolites was determined by the simple exchange method. In this case, it was placed 0.5 g of the produced zeolite in contact with 50 ml of a 0.1 M solution of ammonium acetate for 24 h with stirring. Then the mixture was filtered and the NH<sub>4</sub><sup>+</sup> ion concentration was determined by ion chromatography through the methodology described by ASTM D7503-10.

To compare the obtained zeolites, the CEC was calculated according to Eq. (1).

$$CEC = \frac{(C_0 - C_f)V_{sol}}{m_{zeolite}} \quad (1)$$

where  $C_0$  is the initial concentration (mg L<sup>-1</sup>),  $C_f$  is the final concentration (mg L<sup>-1</sup>),  $V$  is the solution volume (L) and  $m_{zeolite}$  is the mass of zeolite (g).

Using the technique of scanning electron microscopy (SEM) in an equipment Zeiss (model EVO50), it was possible to observe the morphology of the synthesized product. The samples were placed on aluminum brackets with carbon scotch tape and metalized with a gold coat. The images were generated by secondary electrons with voltages of 15 kV.

### 2.3. Zeolite application in the green house

The zeolite produced in the Test 6, after a careful study, was chosen for application in the green house, it had around 15% of K<sub>2</sub>O. For comparison means, it was used the commercial fertilizer potassium chloride (KCl) which contains about 60% of K<sub>2</sub>O.

#### 2.3.1. Cultivation in the green house

The wheat culture (*Triticum aestivum* L) was seed using only one type of soil for the cultivation experiments. The soil used was collected in Bagé (RS, Brazil). It is a typical Luvisol Haplic Orthic, shallow, imperfectly drained and B horizon. It has a naturally good fertility, high CEC and high basis saturation (Table 2).

A sample of this soil was subjected to complete chemical analysis in the Laboratory of Soil Science at UFRGS. Table 2 shows the

**Table 2**  
Soil used for the wheat cultivation characterization.

	Content
pH (H <sub>2</sub> O)	5.9
OM (%) <sup>a</sup>	3.0
Al + H (cmol <sub>c</sub> dm <sup>-3</sup> )	3.5
CEC (cmol <sub>c</sub> dm <sup>-3</sup> )	12.6
%Saturation CEC <sup>b</sup>	72
Clay (%)	18
P (mg dm <sup>-3</sup> )	12.0
K (mg dm <sup>-3</sup> )	126.0

<sup>a</sup> OM is the organic matter.

<sup>b</sup> Sat of CEC is the saturation of cations.

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