

ZEOLIFICATION OF ASHES OBTAINED FROM THE COMBUSTION OF SOUTHERN'S BRAZIL CANDIOTA COAL

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Abstract

This work aims at the presentation of the results obtained as part of a joint research on the use of ashes for the production of zeolites. The ashes are produced in large scale in a 440MW coal-fired power plant located in Candiota, southern Brazil (at Rio Grande do Sul State).

Brazilian coals are characterized, amongst other things, for very high ash content ranging between 45 and 60%. This represents an annual production 1.7×10^6 tons of fly ash (80%) and bottom ash (20%). Despite the fact that a small quantity of the ashes produced are commercialized, the remaining amount is returned to exhausted mine pits. This practice, despite the care taken during handling and disposal, has contributed to the contamination of both surface and ground waters. A pioneer study on the production of zeolites from this abundant resource was started in 1997.

The ashes studied were generated from the combustion of the Candiota Mine coal by two different processes: i) pulverized-bed high temperature combustion on a large scale unit (power-plant) and, ii) fluidized-bed low temperature (800 °C) combustion on a pilot plant (CIENTEC's experimental unit).

The zeolification tests were carried out at three temperature levels and a single NaOH concentration, without agitation. Reaction time ranged between 1 and 10 days. The samples – ashes and by-products - were afterwards analyzed through X-ray diffraction. The results confirmed the zeolification of the materials and the zeolites obtained were found to be compatible with some of those reported in the literature such as Faujasite, Hydroxysodalite and -P-type zeolite.

Introduction

Due to the enormous worldwide production of coal ashes ⁽¹⁾, they are presently treated as a mineral resource and no longer as a residue. The Candiota Mine is Brazil's largest coal reserve and the power generation unit located in the region contributes with approximately 50% of the total amount of ashes (fly and bottom) produced in the country. The annual production of coal ashes in Brazil ranges around 1.7×10^6 tons, but this figure might reach 4.0×10^6 tons by year 2005. Since just 30% of that total are commercialized for the production of building materials (bricks, blocks, cement), it is then necessary to search for new alternative uses.

Fly ashes are composed, mainly, by quartz, mullite and amorphous materials which contain silicate glass and aluminium compounds. When subjected to hydrothermal alkaline treatment, the amorphous materials present in the ashes are almost entirely dissolved whereas the quartz fraction might show a pattern of partially-to-totally dissolved. In any case, changes in the operating conditions play an important role.

The mullite fraction, however, is practically not affected by the alkaline treatment at atmospheric pressure. Mullite present in fly ash is known to be very stable because it is formed by the transformation of phyllosilicates, kaolinite, chlorite and montmorillonite present in the coal, particularly when this material is subjected at high temperatures – around 1200°C – during pulverized bed combustion. Mullite, however, is not formed during fluidized bed combustion due to the lower temperatures adopted with the latter process – $800\text{-}900^{\circ}\text{C}$.

It has been suggested, as a consequence, that the formation of zeolite from fly ash is due mainly to the dissolution of materials such as quartz, silicate glass and aluminum compounds.

Based on these findings it was decided that one should work both types of ashes, i.e., those generated by pulverized-bed and fluidized-bed combustion.

Although the hydrothermal alkaline treatment for fly ashes is a common practice worldwide⁽³⁻¹⁴⁾, the work underway in Brazil is pioneering.

Experimental procedure

Materials

Two ash samples obtained after the combustion of Candiota ROM Coal (about 50% of ashes) were used in the tests which involved hydrothermal treatment with NaOH: *i*)ashes obtained at CIENTEC'S fluidized-bed pilot plant (FB samples), and *ii*)ashes produced after combustion on a large scale (160MW) pulverized-bed power generation unit (CL samples). *Table 1* presents the chemical composition of the ashes obtained after burning in a muffle at 750°C ⁽²⁾ (called ASTM ash).

Table 1 - Candiota ROM Coal Chemical composition of ASTM ashes, wt %.

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	K ₂ O	MgO	CaO	Others
65.7	20.3	4.6	0.10	1.12	0.46	0.37	7,35

Analysis

Powder Diffraction Files – PDF – were used for the identification of crystalline structures in X-ray diffraction (XDR) patterns obtained through the use a equipment make SIEMENS, model D5000.

Hydrothermal Treatment

Both FB and CL samples were activated by means of a NaOH (3.5N) solution in a opened system. The zeolite conversion was studied as a function of changes in temperature (at 40, 60 and 100°C) and reaction time(1, 3, 6, 7 and 10 days). The activation was performed using a sample concentration of 0.125g/mL (s/l). The tests were performed in a laboratory furnace fitted with a temperature controller. When the activation time was reached, the sample was centrifuged, filtered and washed with deionized water, dried at 105°C for a 24-hour period and finally analyzed by X-ray diffraction. Six series of tests were performed, three with which kind of ash.

Results and Discussion

Figure 1 shows the diffractograms for CL series at 100°C. For 1 and 3 days reaction time (CL2 and CL4 samples) **chabazite** and **faujasite** were formed. For longer periods (6-7 days), however, (CL6 and CL8 samples) **chabazite** was found to be the most important crystalline structure formed; hydroxysodalite appeared only after 6-days reaction time, whereas traces of **faujasite** were observed in both. Quartz and **mullite** phases were also present.

For the maximum reaction time period adopted in this work – 10 days reaction time – (CL10 sample) it was observed that the quartz present was entirely dissolved whereas **mullite** remained insoluble. Catalfamo⁽³⁾ had also reported on the the stability of **mullite** during hydrothermal alkaline treatment of fly ashes. In this case, for a maximum reaction time for CL sample, at 100°C, **hydroxysodalite** was the most important crystalline structure formed, with traces of transformed **chabazite**.

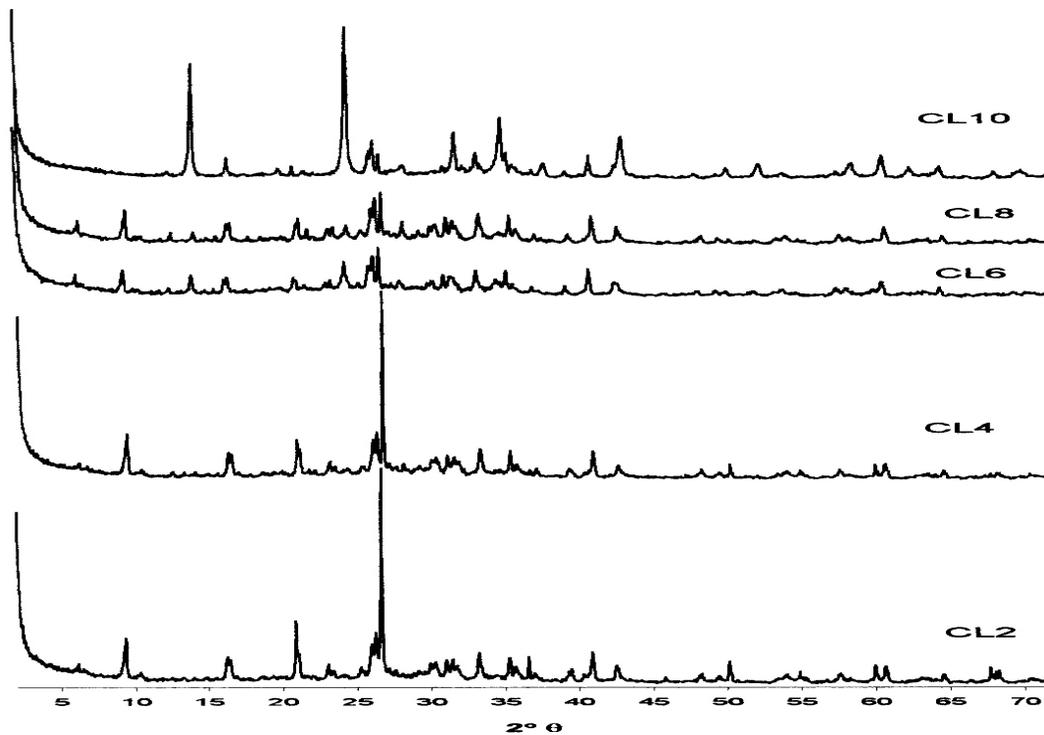


Figure 1 – XDR patterns of CL ash samples, hydrothermal treatment with NaOH (3.5N) solution, at 100°C. Index 2: 1-day, 4: 3-day, 6: 6-day, 8: 7-day and 10: 10-day reaction times.

Table 2 shows that the sole crystalline structure formed at 60°C, for CL ashes, was **faujasite**. For the maximum reaction time period (10 days) the **quartz** and **mullite** intensities observed were bigger than that shown for **faujasite**. This demonstrates, for the sample tested, the poor conversion of quartz to a zeolite form.

Table 2 - CL ash, at 60°C, hydrothermal treatment with NaOH (3.5 N) solution.

Sample	Reaction time (day)	Crystalline structure in XRD, by intensity order
CL2	1	Qz, Mu,
CL4	3	Qz, Mu, He
CL6	6	Qz, Mu, Fa, He
CL8	7	Qz, Mu, Fa, He
CL10	10	Qz, Mu, Fa, He

Where: Qz = quartz; Mu = mullite; He = hematite and Fa = faujasite

For FB sample series at 60°C (FB2, FB4, FB6, FB8 and FB10) the XRD patterns (*figure 2*) revealed three crystalline structures at all reaction times: **quartz**, **faujasite** and **hematite**, in this order of intensity. For this set of tests, **quartz** fraction suffered poor dissolution. The pattern observed here is similar to that found for the CL sample series, for the same temperature.

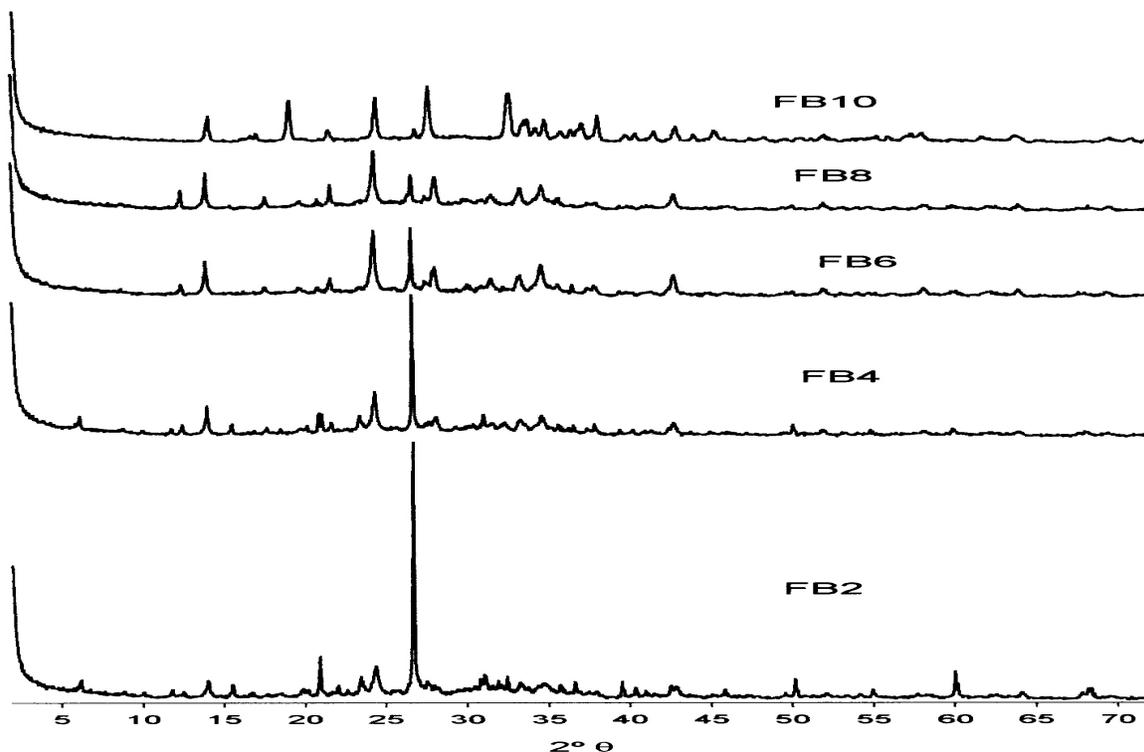


Figure 2 – XDR patterns of FB ash samples, after hydrothermal treatment with NaOH (3.5N) solution, at 100°C. Index 2: 1-day, 4: 3-day, 6: 6-day, 8: 7-day and 10: 10-day reaction time periods.

Figure 2 evidenciates the crystalline structure of the FB sample series, (FB2, FB4, FB6, FB8 and FB10 samples), at 100°C. In this case, for 1 and 3 days reaction times (FB2 and FB3 samples), it was observed a mixture of **hydroxysodalite**, **faujasite** and **P-type zeolite**. When the reaction time was extended to 6 days (FB6 sample) the analyses revealed a mixture of **hydroxysodalite** and **P-type zeolite**. For a 7-day reaction time (FB8 sample), however, **hydroxysodalite** was the most important structure formed, with traces of **P-type zeolite**. For this series - FB samples, at 100°C and 10-day reaction time, particularly FB10 sample, **quartz** was entirely dissolved. These results matches those observed for CL10 sample at 100°C, where **cancrinite**, followed by **hydroxysodalite** were the zeolite structures observed.

Finally, it was observed that at 40°C temperature reaction, and for both kinds of ashes tested (FB and CL), no evidence zeolite formation.

Conclusions

Under the experimental conditions adopted in this work, for the two kinds of Candiota Coal ashes tested, five zeolites were identified: **faujasite**, **hydroxysodalite**, **P-type zeolite**, **cancrinite** and **chabazite**.

After hydrothermal treatment, only FB ash samples (low temperature combustion) produced **P-type zeolite** and **cancrinite**, whereas the CL ash samples (high temperature combustion) formed **chabazite**. Both FB and CL samples, however, produced **hydroxysodalite** and **faujasite**, for the operating conditions tested throughout the work.

As expected, low temperature produced ashes (FB samples) appeared to be more reactive than the high temperature produced ashes (CL samples). Reaction in the former case started at low temperatures and after short periods of time. CL samples obtained at the maximum temperature (100°C) and reaction time (10-day period) showed better crystallinity.

Under the conditions of 100°C and 10-day reaction time, the fly ashes obtained after pulverized-bed combustion produced **hydroxysodalite** as the main crystalline structure, whereas the fly ashes obtained after fluidized-bed combustion produced **cancrinite** as the main crystalline structure.

The Candiota Coal fly ashes, after hydrothermal treatment with NaOH (3.5N) solution, formed **faujasite** within the whole 1-10 day reaction period, for temperatures equal to 60°C and upwards, ratio fly ash/NaOH solution equal to 0.125. Shih,⁽⁵⁾ has reported that the formation of **faujasite** could occur at 38°C with the use of a NaOH (2.8N) solution, after a 3-day reaction time, and for a ratio fly ash/NaOH solution equal to 0.4.

According to the literature⁽⁴⁾ both types of ashes showed residual coal that favors the formation of **P-type zeolite**. That is way a both types of ashes were expected to form **P-type zeolite**. However, only CL samples, which has **mullite**, are, according to the literature⁽³⁾, insoluble at temperatures up to 100°C and retêm 70-90% of the aluminium present in the ashes. That is, possibly, the answer way only FB samples produced **P-type zeolite**.

The present study demonstrates the potencial application of fly ash from Candiota ROM Coal for zeolite synthesis. Now, we intend to study products resulting from this hydrothermal treatment of fly ash as cation exchange to remove toxic elements from waste water at power station.

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