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Crystaline Microstructure Modification of Brazilian Coal Ash with Alcaline Solution

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ABSTRACT

Past studies carried out on chemical and mineralogical composition of ashes generated as a result of the combustion of Brazilian coals, have shown that these materials are similar to mineral clays, due to the fact that their composition are aluminium-silicate based. Brazilian coals are used, almost exclusively, for power generation purposes. Coal consumption is around 3,7 x 10^6 t/year, whereas the amount of ashes produced are around 1,7 x 10^6 t/year. The ashes produced are, as a rule, deposited in exhausted mine pits, practice that has somehow contributed to the deterioration of the surrounding environment. The present work, sheds some light into the search for noble uses for this aboundant residues. The ashes similarity to mineral clays has allowed the synthesis of zeolites by modifying their crystaline microstructure with a consequent change of its the chemical properties. The tests were carried out with samples collected through the combustion of coals from the minefields of Recreio and Butiá, southern Brazil. Samples were, afterwards, treated at varied temperature levels and with an NaOH solution and the addition of Al_2O_3. The samples obtained were finally analyzed by X-ray Diffraction, X-ray Fluorescence, Scanning Eletron Microscopic and Thermal Gravimetric Analysis at the Industrial Research Center of Shiga Prefecture laboratories. The results obtained confirmed the production of P- and H-type zeolites.

INTRODUCTION

The combustion of high ash content coals promotes a serious enviromental problem in southern Brazil. It is in the south, in the States of Rio Grande do Sul – RS and Santa Catarina – SC, that the coal mines coal-fired power plants are located. The amount of coal burned ranges around 3,7x 10^6 tons/year, with the consequent production of approximately 1,7x 10^6 tons/year of ashes (fly+bottom). Most of these ashes are deposited randomly in landfills (DNPM, 1994).

The States of RS and SC shown areas which are already environmentally degraded with the resulting contamination of both surface and ground waters (Binotto et al, 1996; Teixeira & Sánchez, 1998). The growing ash production is, consequently, a constant concern even though one takes into account that a small amount (30%) of the ashes produced are used in the cement and civil construction industries. Out of remaining 66% of ashes produced, another huge amount is returned to exausted mine pits.

Data published in 1996 (Zwonok; Chies; Silva 1996), estimate that the figure presented earlier might reach 4,0 x 10^6 tons/year of ashes produced by the year 2005, as a result of the installation of new power stations. No new strategy, however, has been put forward on how to manage these huge amounts of residues. In environmental terms, ashes are considered solid wastes and are supposed to be handled, studied and managed as such.

Worldwide, a huge number of projects are underway in order to find proper uses for the coal ashes generated. In Brazil, particularly at CIENTEC, time and resources have been spent over the last 20 years on the development of projects which use coal ashes as raw material for the production of civil construction artefacts such as bricks and blocks as well as in mixtures for cement and paving materials.

The Brazilian coal ashes have already been the object of exhausted studies leading to its proper characterization. It consists, basically, of a aluminium silicate with high silicon and aluminium oxide contents. Depending on its origin, the iron oxide contents can vary over a wide range.

Since the ashes are composed of 1A Group (Na, K) and 2A Group (Ca, Mg) aluminium silicates, and also due to a low ratio SiO_2/Al_2O_3 = 2,1, they can be treated through chemical methods in order to alter their crystaline structure and be turned into zeolites (Shih, Wei-Heng), (Höller, H. and W. 1985), Amrhein, Ch. Et al. 1990).

Zeolites are 1A and 2A hydrated aluminium silicates, structured around tridimensional crystaline clusters composed of TO_4-type tetrahedrons (T = Si, Al, b, Fe, P....) linked by oxigen atoms (luz, A. B.1995). The zeolite crystaline structure presents properties of high industrial interest such as high hydration level, low density and large void volume when dehydrated, high stability when dehydrated, as wells as cation-exchange, electrical conductivity, gases and vapours adsorption and catalyst properties.

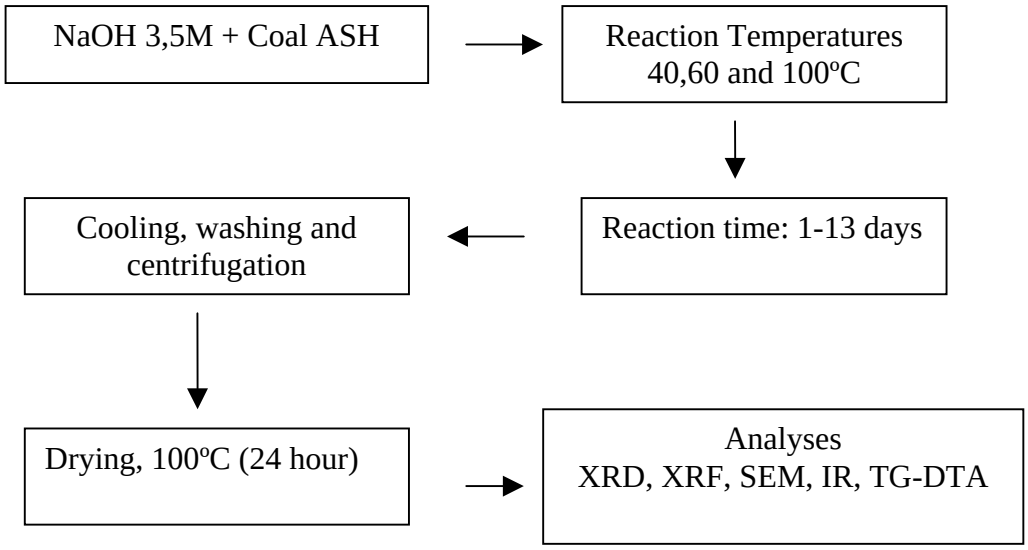
The present work aims at the publication of the first results obtained after ash treatment with alkaline solution under controlled conditions of temperature and reaction time. It has been developed as a joint project with the Industrial Research Center of Shiga Prefecture, Japan.

EXPERIMENTAL PROCEDURE

The work was carried out with ashes produced after its burning of Leão Minefield coal, owned by COPELMI. The coal presents ash content of 29% and Gross Calorific Value is 5.200 kcal/kg. The ashes were generated at 1.380 ^oC (samples identified as **"R"**) at RIOCELL's private owned power plant. RIOCELL is one of the country's largest cellulose and cellulose pulp producers. In order to allow for comparisons, the same coal was burned at 750 ^oC according ASTM D 3174

(samples identified as **"C"** using a small scale furnace). For this to reason, two types of ashes from the same coal were used to study the effects of the treatment with alkaline solutions upon the crystaline structure.
The activation tests were developed on both types of ashes, using a NaOH (3.5N) solution, at 40, 60 and 100 ^{o}C temperatures, whilst the reaction time ranged between 1 and 13 days.

The following steps were taken:



60 ash samples activated with NaOH solution were obtained following the above procedure. Later on, a total of 42 samples were sent to the laboratories of the Industrial Research Center of Shiga Prefecture for necessary characterization analyses. The tests carried out were: XR Difraction (equipment used: make Rigaku Denki, models RAD-RB and RINT 2500 VHF), XR Fluorescence (equipment used: make Shimadzu, model XRF 1700), FE Scanning Electronic Microscope (equipment used: make Hitachi, model S4200), Fourier Transformed Infrared (equipment used: make Shimadzu, model FTIR 4200), TG-DTA (equipment used: make Rigaku Denki, model TAS 100). The remaining analyses were carried by XRD at the Universidade Federal do RS (Federal University of the State of RS) (equipment used: make Siemens, model D 5000).

RESULTS AND DISCUSSION

The comments which follow will be based solely on results obtained through XRD na SEM techiniques, even though the materials were also analyzed by FTIR, TG-DTA and XRF.

The composition of the samples ash "C" and "R" are:

Coal Ash	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O
R	60,5	28,0	2,1	1,2	2,1	0,4	1,2	0,2
C	63,3	26,9	2,8	1,2	1,2	0,5	1,0	0,4

The **“C”**-type samples, submitted at reaction with NaOH, at 40 ^{o}C, for a 1-3-day period showed no modification according to the diffractograms obtained. Ash samples submitted to the same conditions for a 7-10-day period, however, showed typical Faujasite-type characteristic peak difractograms.
The same type samples when submitted at 60 ^{o}C, however, presented difractograms with lesser peaks of equal intensity which correspond the Hidroxisodalite (HS)- and Phillipsite (P)-type zeolites, and regardless of the reaction time.

The **“C”**-type samples, submitted at 100 ^{o}C, showed peak difractograms typical of the Hidroxisodalite-type zeolite. It was observed that at lower reactions times the peaks obtained correspond to the Phillipsite (P)-type zeolite, which was transformed after some time into Hidroxisodalite (HS), (Figure 01). Some of the results reported here, find support in the work of Singer et al, who tested Colombian coals. It was also observed through SEM images that at the maximum reaction time,the amount of quartz found initially was totally converted (Figures: 02, 03 and 04).

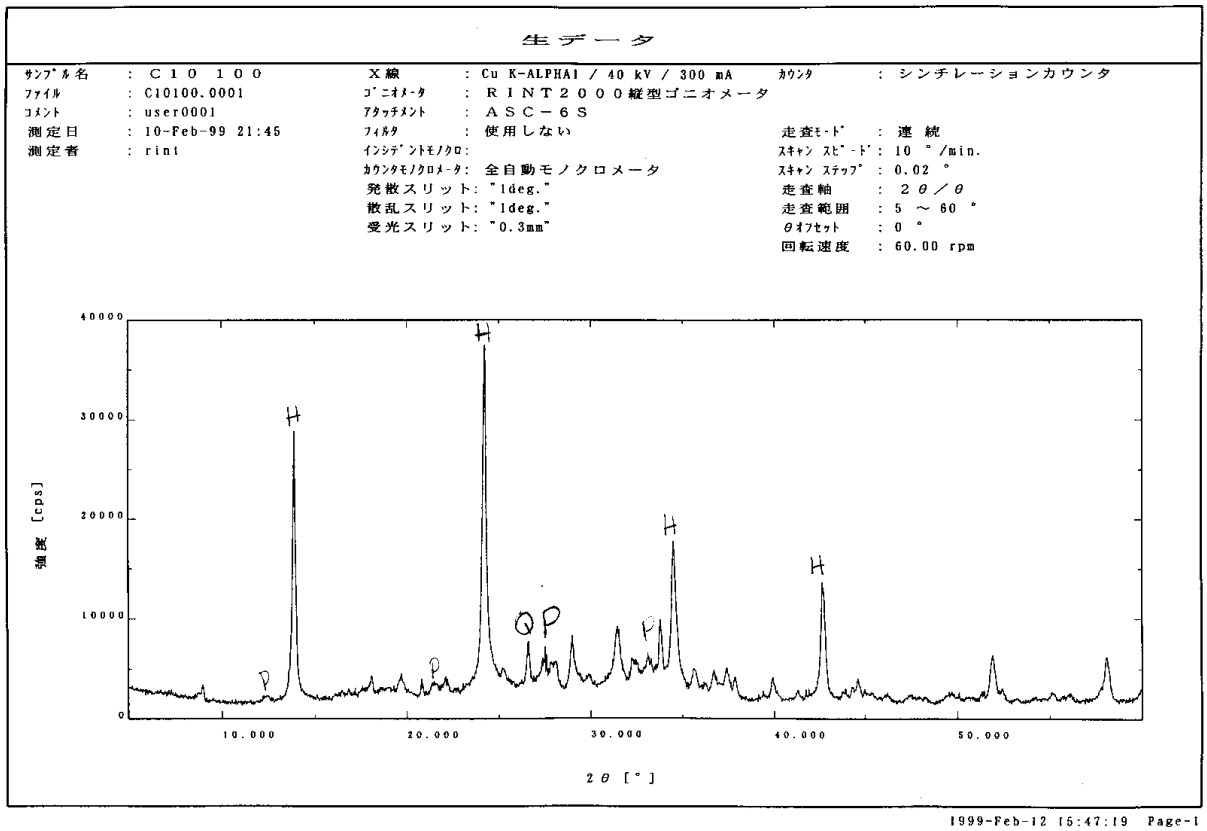


Fig: 01: X-ray Diffraction of "C" ash treated with NaOH at 100°C for 12 days.

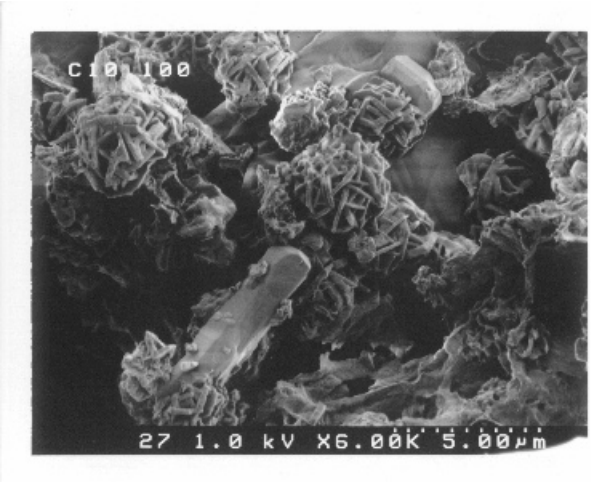


Fig.:02: Scanning Electron Micrograph of "C" ash treated with NaOH at 100ºC for 3 days

Fig. 03: Scanning Electron Micrograph of "C" ash treated with NaOH at 100ºC for 5 days

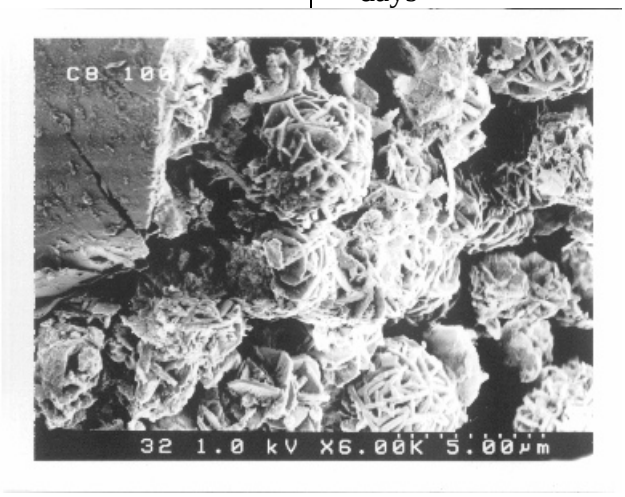


Fig. 04: Scanning Electron Micrograph of "C" ash treated with NaOH at 100ºC for 10 days

The “R” type samples treated at 40 ^{o}C showed no modification in their structures. The “R” type samples treated at 60 ^{o}C, on the other hand, presented diffractograms with peak traces corresponding to the Hidroxisodalite (H)- and Phillipsite (P)-type zeolites, for the same intensity (Figures: 05, 06).

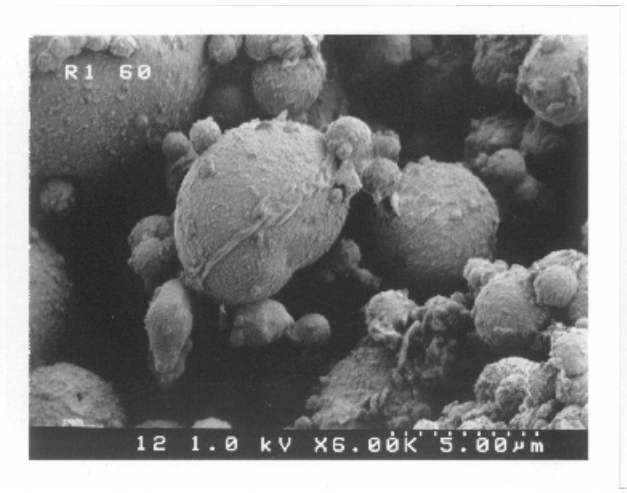


Fig 05: Scanning Electron Micrograph of "R" ash treated with NaOH at 60ºC for 1 days

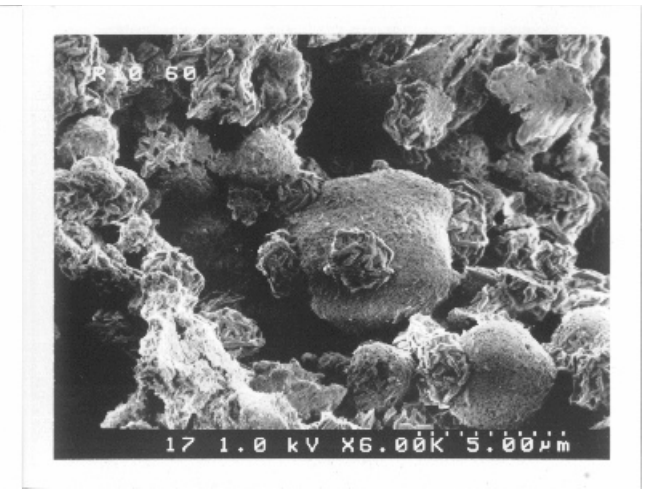


Fig 06: Scanning Electron Micrograph of "R" ash treated with NaOH at 60ºC for 12 days

The “R”samples ash type samples treated to 100 ^{o}C presented the following peaks:

-R1,2 (1-day reaction time): Qz + Mu + P + HS;
-R3,4 (3-days reaction time): Qz + Mu + P + HS;
-R5,6 (6-days reaction time): P + Qz + Mu + HS;
-R7,8 (7-days reaction time): P + Mu + Qz + HS;
-R9,10 (12-days reaction time): P + Mu + HS + Qz,

where: Qz = quartz; Mu = mullite; P = zeolite P-type (Phillipsite); HS = hydroxisodalite-type zeolite.

At the maximum reaction time the whole amount of quartz was consumed.

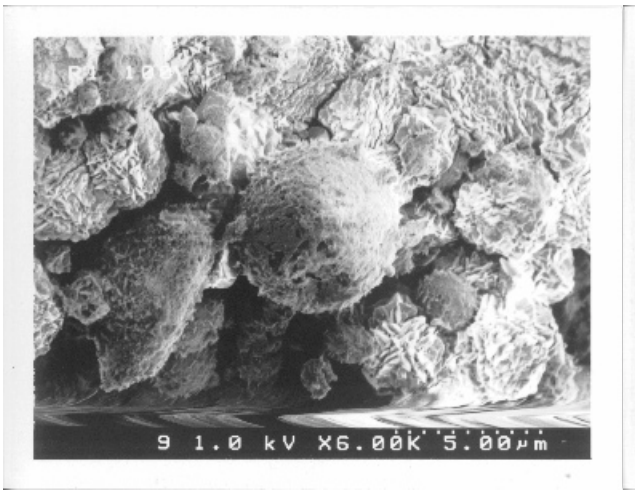


Fig 07: Scanning Electron Micrograph of "R" ash treated with NaOH at 100ºC for 1 day

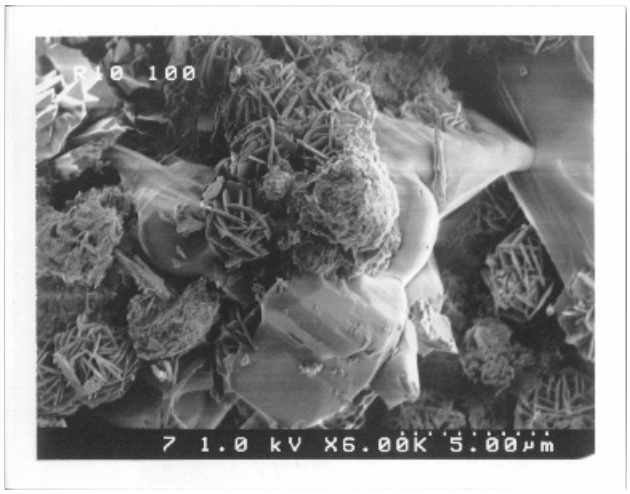


Fig 08: Scanning Electron Micrograph of "R" ash treated with NaOH at 100ºC for 10 days

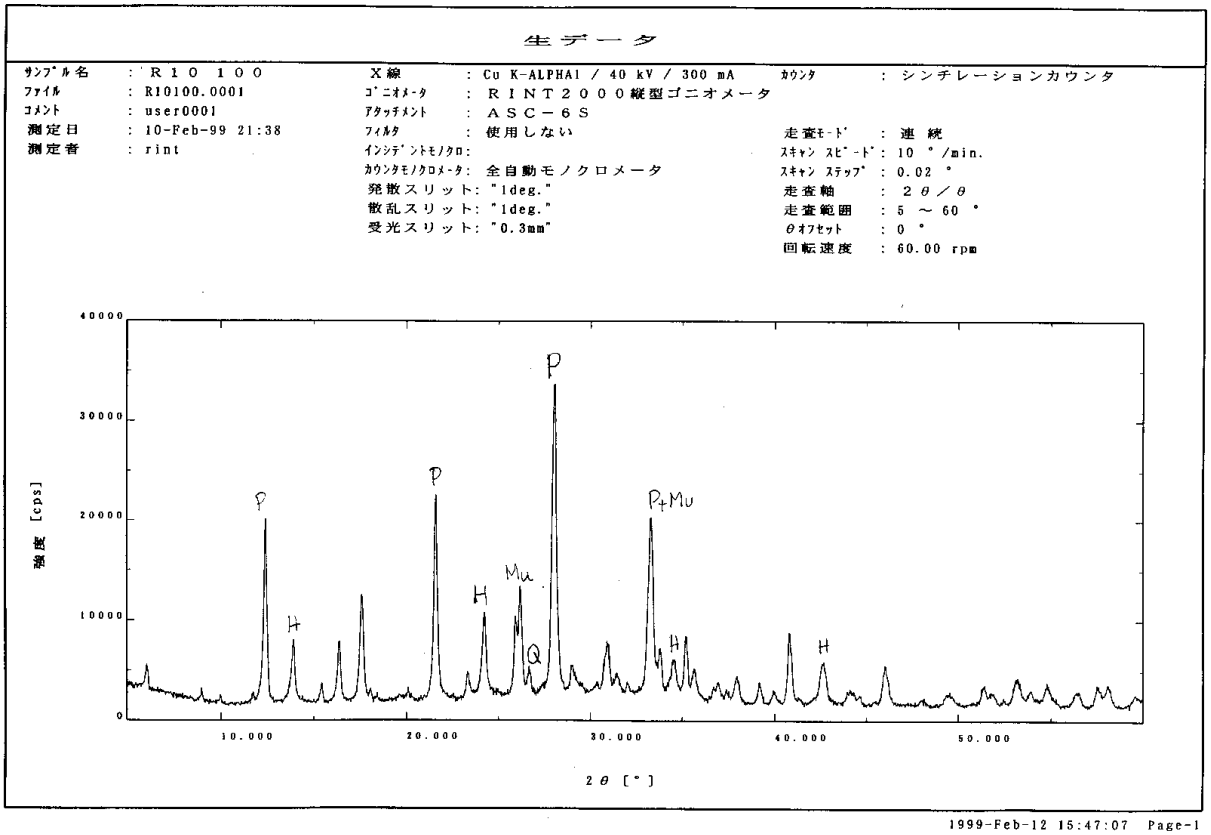


Fig 09: X-ray Diffracion of "R" ash treated with NaOH at 100ºC for 12 days.

The results found so far, suggest that a different approach for alkaline treatment should be tested. Testes with alkaline solutions of lower concentrations and defined shorter of time are underway. The results obtained through XRF revealed high sodium content, indicates a possible contamination which is expected be eliminate before one carries on with the analyses. Another procedure has been tested consists on the addition of alumina (Al_2O_3) as a means to reduce the ratio SiO_2/Al_2O_3 and increase, as a consequence, the processe's yield.

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