New method for the synthesis of zeolite NaA from coal fly ash and its application in Warm Mix Asphalt

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ABSTRACT

The development of new materials for modification of asphalt cements (AC) is an alternative to improve the quality of pavements. Warm mix asphalt (WMA) technology promises to reduce the application temperature by 20-40°C compared to hot mixtures (150-170°C). The use of zeolite – a hydrated aluminosilicate – has proved to enhance workability by the action of water releasing. In this work, we present a new synthesis route for zeolite A (named FA-S-Z), having coal fly ash (FA) as the starting material. Research on FA is attractive given the significant amounts of waste generated in different parts of the world (500 million tons per year). Due to the low Si/Al ratio, the investigated zeolite has relatively high amounts of water in its crystalline structure, an interesting property that may be useful for WMA. The zeolites synthesis was confirmed by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM). The AC was modified with 1% w/w of zeolite (FA-S-Z). The rheological properties of the pure and the modified AC were assessed by a rotational viscometer (Brookfield®) and a dynamical shear rheometer (DSR) AR 2000. The analyses of the viscosity variation over time, under constant temperature (120°C), show promising results with respect to the microfoaming process. The results showed that coal fly ash was successfully used in the proposed synthesis, and the zeolite showed encouraging potential as an additive for WMA.

Keywords: Zeolite NaA, WMA, Coal fly ash, Industrial waste.

1. INTRODUCTION

The development of new materials for improving the quality of paved roads, making them safer and more resistant, has been a constant concern both because of growing traffic and environmental aspects related to pollutant emissions released during the paving process [1]. Global awareness on safety, health and environment has resulted in efforts to develop cleaner technologies and new materials that provide longer life for pavements. In this context, WMA is presented as an alternative to reduce pollutant emissions, by demanding less energy and reducing environmental and harmful health impact caused by the Hot Mix Asphalt (HMA) application, without affecting performance [2]. HMA is generally used in the pavement industry, but the high temperatures necessary to a suitable viscosity to coat the mineral aggregates and then compact the mixture (150-170°C) give rise to problems such as early aging of the binder and increase of pollutant emissions [2]. WMA are considered those in which the mixing and compaction temperatures are typically 100-140°C. Compared to temperatures employed for conventional mixtures (HMA), 150-170°C, this represents a considerable reduction in the amount of fuel used in asphalt plants, also reducing emissions that contribute to mitigate greenhouse effect [3].

Recent research has been conducted in the field of WMA using as additives waxes, vegetable oils and zeolites [4]. One of the most efficient processes utilizes synthetic zeolite in

the asphalt mix. Currently, the two technologies are Aspha-min® developed in Germany (Eurovia) and Advera® developed in the United States. Both methods reduce the spreading and compaction temperatures of mixes without affecting their workability. Zeolites have the property of retaining water in its structure due to a complex porous structure. The retained water is released as steam when the zeolite is subjected to temperatures above the water boiling point [5].

In this work, we present a synthesis procedure for a Zeolite NaA containing 18-21% of water, from coal fly ash, an industrial waste from thermoelectric power plants. There is a demand for the use of these ashes because the amount of 500 million tons per year presents a serious environmental problem [6]. The production of zeolite A using a coal ash as the source of silicon and aluminum is presented as a useful way to synthesize zeolite at low cost with useful applications for WMA technologies.

2. EXPERIMENTAL

2.1 Materials

Fly ash (FA) was provided by the thermoelectric power plant from the ENEVA/EDP group located on Pecém, Ceará (Brazil), and it was used as a source of silicon and aluminum for the zeolites synthesis. Sodium hydroxide and sodium aluminate used in the hydrothermal zeolite synthesis were obtained from Merck. The asphalt binder with 50/70 penetration grade was provided from Campo Fazenda Alegre (FA) in the state of Espírito Santo, and refined by Petrobras/Lubnor in Fortaleza, Ceará.

2.2 Zeolite synthesis

The synthesis of FA-S-Z was carried out via the hydrothermal route. The FA sample was submitted to a pretreatment for the solubilization of silicon and aluminum oxides, becoming suitable for the zeolite growth by the hydrothermal synthesis. The synthesis method comprises the following steps:

(i) FA is mixed with a NaOH solution, in a proper concentration, for 1h at 100°C, then the product is centrifuged and the supernatant is separated for the hydrothermal synthesis.
(ii) The supernatant is mixed with sodium aluminate, aiming to match the Si/Al ratio equal to one.
(iii) The resulting mixture is added to a Teflon-lined stainless-steel reactor and then heated at 90°C for 4h.
(iv) The final product was washed with distilled water until reach pH ~ 9, then dried at 70°C in an oven.

2.3 Test methods

2.2.1 FA and FA-S-Z characterization

The samples FA and FA-S-Z were fully characterized by the following techniques: X-ray diffraction (XRD) (diffractometer Panalytical Xpert Pro MPD, Co Kα radiation with λ: 1.79026 Å); Scanning electron microscopy (SEM) in a Quanta 450 FEG - FEI microscope with the secondary electrons detector (SE); Energy Dispersive spectroscopy detector (EDS).

2.2.2 Modification of the asphalt binder

For the modification of the AC, it was used a mixer IKA®, model RW20 equipped with an electronic thermometer, a mechanical stirrer and a propeller. The AC was modified by the addition of 1% FA-S-Z (AC-FA-S-Z). FA-S-Z was slowly added to the binder under stirrer for two hours at 90 ± 5°C and 1500 rpm (propeller speed).

2.2.3 Characterization of AC and AC-FA-S-Z.

The rotational viscosity was determined using a Brookfield viscometer model DVII+, in accordance with the standard ASTM D4402. The viscosity was measured at 135, 150 and 177°C. The variation of viscosity with time at 120°C was also determined. Rheological parameters were determined using a dynamic shear rheometer (DSR) model AR2000®, following ASTM D7175.

3. RESULTS AND DISCUSSION

3.1 FA and FA-S-Z characterization

3.1.1 XRD

According to the XRD patterns (Fig. 1), the three main crystalline phases are: quartz, hematite and iron oxide. The quartz present in ash, confirmed by the diffractogram, is the major source of silicon used in the synthesis of the zeolites. The presence of both hematite and iron oxide are worrying, because they interfere in the hydrothermal synthesis process, since iron oxide precipitate in the form of $Fe(OH)_3$ [7].

The proposed synthesis method was successful in the formation of zeolite NaA as confirmed by its diffractogram (Fig. 2). The coincidence of the diffraction peaks with the zeolite A pattern (ISCD 24901) shows that the FA was converted in the zeolite NaA phase, which is a zeolite with high amount of water, and can be utilized in the WMA technology.

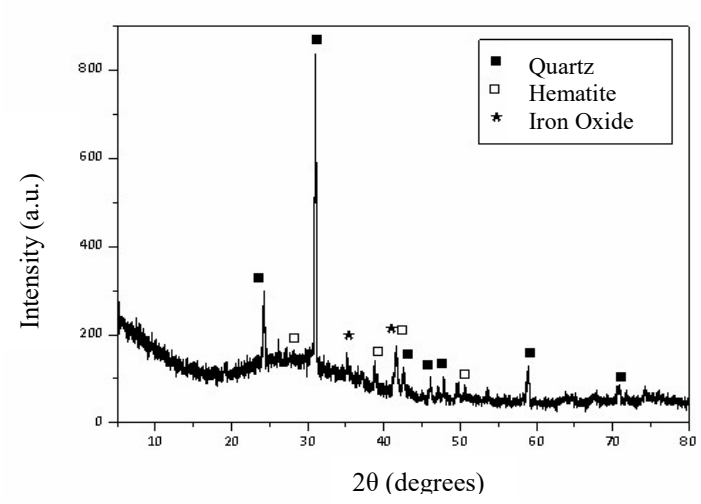

FIGURE 1: X-ray diffraction of FA sample.

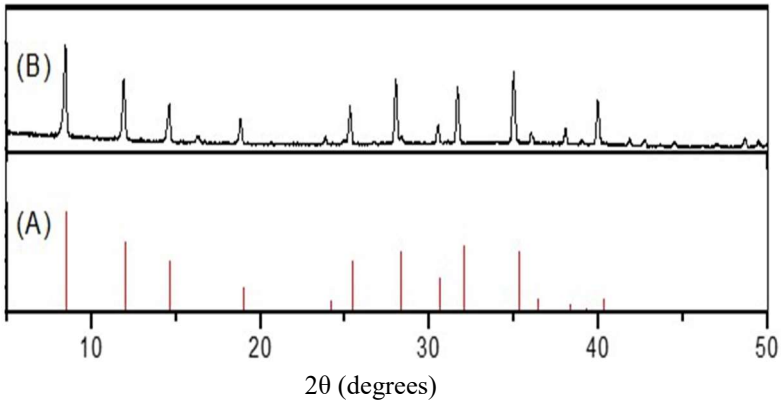

FIGURE 2: X-ray diffraction of A) zeolite A pattern and B) FA-S-Z.

3.1.2 SEM characterization

The SEM micrographs (Fig. 3) show the morphology of the FA sample, with a characteristic spherical shape, formed as a result of the expansion of the combustion gases during the burning of the coal (cenospheres) [8]. Figure 3 also shows the morphology of the FA-S-Z sample, which is composed of cubic crystals with well-defined edges (characteristic of zeolite type A), without the presence of secondary phases [9,10].

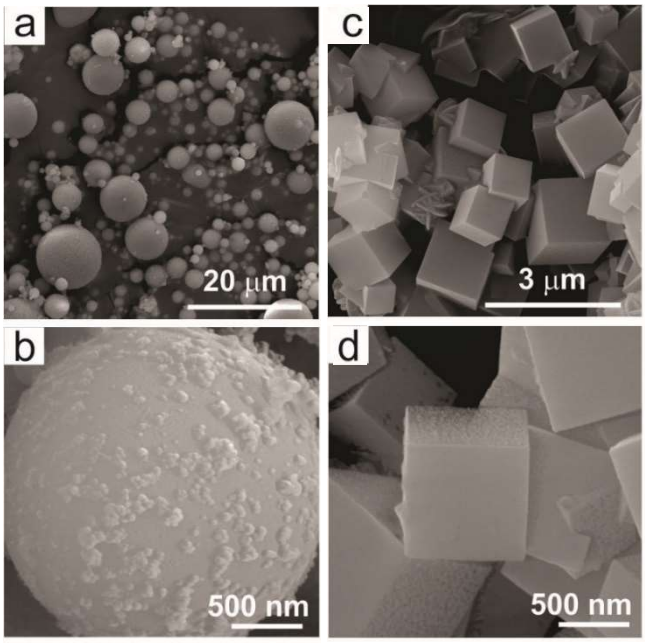

FIGURE 3: SEM images of: a-b (FA) and c-d (FA-S-Z).

3.2 AC and AC-FA-S-Z characterization

3.2.1 Rotational viscosity

The graphic of viscosity over temperature (Fig. 4) shows that the viscosity of the AC-FA-S-Z sample is a little higher than the viscosity of the pure AC. The higher viscosity of the AC-FA-S-Z sample goes against the objective, which is to synthetize a WMA additive. This must occur because the water responsible for the microfoam process is released during the viscosity test. The test, as performed, cannot be used to determine mixing and compaction

temperatures [11]. A new test was then developed, where the variation of viscosity over time is evaluated at 120°C. Fig. 5 shows that the viscosity of the AC-FA-S-Z sample decreases in the first ten minutes, what does not happen with the pure AC sample. This may indicate that the release of water steam by the additive promotes the reduction of the viscosity by the expansion of the binder, enhancing workability [12].

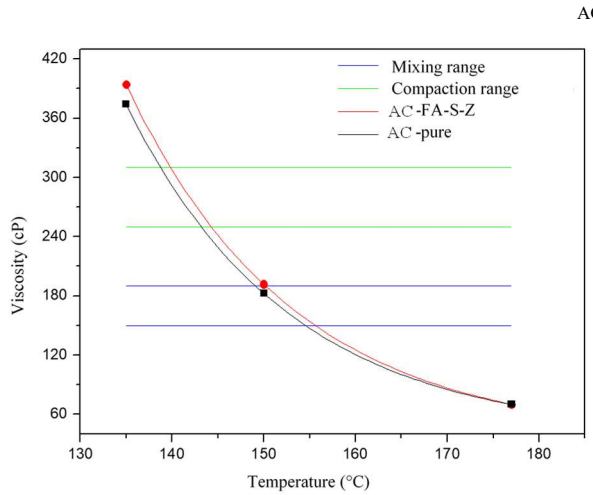

FIGURE 4: Viscosity as a function of temperature.

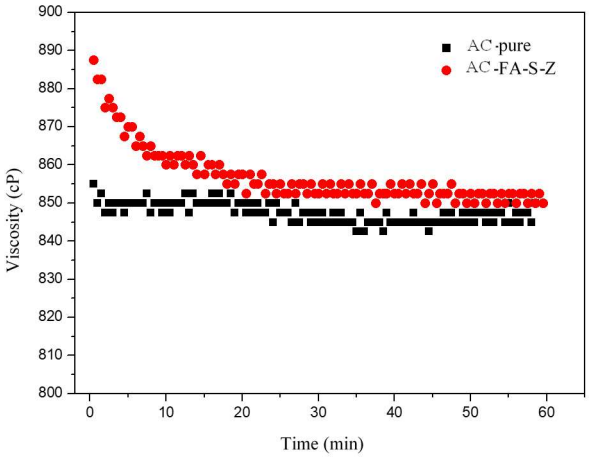

FIGURE 5: Viscosity as a function of time.

3.2.2 Rheological parameters

Complex modulus (G*) and phase angle (δ) were determined using frequency sweep master curves at different temperatures. Both G* (Fig. 6) and δ (Fig.7) did not show significant variation with the use of the FA-S-Z additive. This result shows that the binder modified with the synthetized zeolite maintains the same rheological properties of the pure AC. Other studies present similar results when the master curve is analyzed [13]. The non-variation of the rheological parameters may be associated to the small amount of zeolite (1% w/w) added to the binder [12].

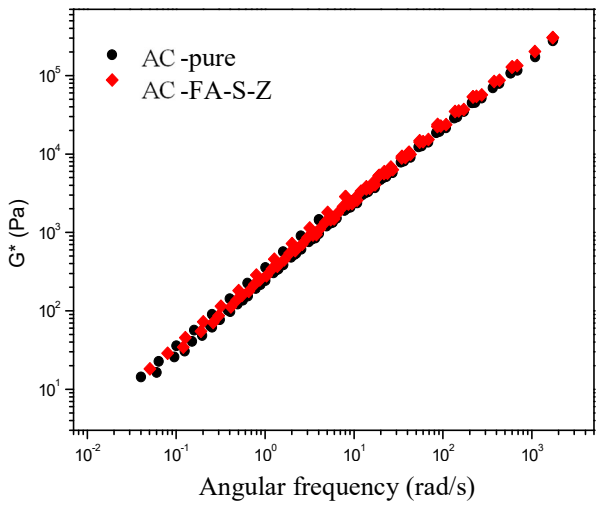

FIGURE 6: G* as a function of frequency.

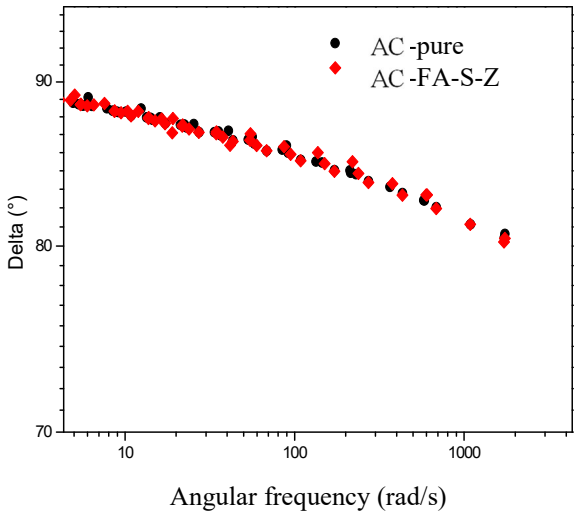

FIGURE 7: δ as a function of frequency.

4. CONCLUSIONS

Zeolite NaA, with cubic crystals and well-defined edges, was successfully synthesized by a new route using fly ash, whose silicon and aluminum oxide were extracted in alkali conditions. The use of the synthetized zeolite as a WMA additive showed that it does not permanently act to reduce the viscosity of the binder. The reduction of viscosity as a function of the additive occurs in a timely and temporary manner, precisely at the moment when the water steam is released from the zeolite, where the microfoaming process occurs. The synthetized zeolite NaA seems to be potentially useful as a WMA additive given the fact that its composition and characteristics are similar to those of commercial zeolites.

5. REFERENCES

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