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EPI-type zeolite synthesis from Greek sulphocalcic fly ashes promoted by H_2O_2 solutions

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Abstract

EPI-type zeolite was synthesised from Greek sulphocalcic lignite fly ashes. They consist mainly of SiO_2, CaO and Al_2O_3, while the SiO_2/Al_2O_3 ratio was found to be 2.74. The activation was performed by 30% H_2O_2 in an open system. Zeolite formation was observed only when activated products aged at 95 °C. The resulting materials were characterised by means of PXRD, FT-IR and SEM-EDS. PXRD and FT-IR results are in good agreement, confirming the zeolite formation. The role of H_2O_2 as a dominant factor in the zeolite synthesis is attributed to the oxidation of Fe(II) to Fe(III) and to the oxidative action on the unburned organic mater of the fly ash to prevent the reduction of Fe(III) to Fe(II). Fe(III) is proposed to participate in the reaction with Si–OH and HO–Al groups in the preliminary steps, resulting to the formation of an intermediate group [Fe–(H^+)O(O–Si)–Al] which then gives Si–O–Al groups and Si–O–Fe groups to a lesser extent, both of which lead to a zeolite structure. Formation of the latter group explains the presence of Fe(III) in the zeolite crystal structure.

Keywords: Zeolite synthesis; Fe(III) effect; Sulphocalcic fly ash; Epistilbite; Greece

1. Introduction

The production of electricity in Greece is heavily dependent (more than 73%) on the steam electric power stations of the Public Power Corporation S.A., which use domestic lignite as combustion material. These stations produce nearly 13 million tones of fly ash annually. Most of the fly ash is landfilled at the mine sites or disposed of, in specific mounds [1,2]. Due to their large quantities, as well as their open-air deposition, the Greek fly ashes can be characterised as semi-geological type deposits with enhanced geochemical and environmental interest.

Silicates, carbonates, clays, sulphates and oxides dominate the mineral matter in coals [3–5]. During combustion the mineral matter of coal undergoes a series of physical and chemical changes [5,6]. The major mineral phases detected in fly ash samples from LCWM were anhydrite, lime, calcite, quartz and feldspars. Micas, clays, portlandite, melilites, ettringite and hematite were also found as minor or trace phases. Minerals contained in the fly ash were either initial constituents of the mined lignite, products of lignite combustion, or the result of soaking the fly ash during its transportation by conveyor belt, from the Power Plants to ash disposal areas [5,7,8].

Several potential applications of fly ashes have been proposed, e.g. as an additive in cement production and in the biological cleaning process of sewage effluents [9], for the extraction of metals (Ni, Cr, Cu, Pb) from industrial liquid wastes [10], and as a source of rare elements such as germanium [11]. However, only 10–20% of the fly ash produced in Greece is used in cement factories and in large-scale constructions such as dams [1]. Zeolite synthesis from coal fly ash by treatment with basic solutions of NaOH or KOH, usually performed in autoclave systems at elevated temperature, has already been reported, e.g. [12–30]. The chemical and mineralogical composition of the aforementioned fly ashes, were considerably different from the fly ash

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of the LCWM, which in particular exhibits an increased calcium concentration and the existence of calcite, anhydrite and lime, in addition to low SiO_2 and Al_2O_3 percentages.

In the present study, we report the role of 30% H_2O_2 in zeolite synthesis under moderate conditions using sulphocalcic fly ash of high iron content and we try to correlate the formation of the crystal structure of the zeolite with the Fe(III) species existing in the mixtures during the experimental process.

2. Experimental

2.1. Materials and methods

A carefully chosen sample of fly ash from Agios Dimitrios Power Plant of the LCWM was used as starting material. The experiments were performed as follows: 10 g of the used fly ash were placed in each of four tubes and 30, 60, 90, or 120 mL volumes of 30% H_2O_2 were added at room temperature with continuous stirring (the experiments were marked as FA30, FA60, FA90 and FA120, respectively) thus creating the basic chemical environment, by the presence of basic oxides, necessary for zeolite synthesis and the oxidative environment to prevent the reduction of Fe(III) to Fe(II). The temperature was gradually raised to 80 °C. The synthesis was performed in an open system on an oil bath equipped with a thermostat to adjust the temperature to 80 ± 2 °C, with continuous stirring for 180 min. At the end of the treatment the slurry mixture was filtered and the solid experimental products were placed into a porcelain-evaporating basin and aged in an oven for 7–15 h at 95 °C. Two further sets of experiments were performed: the first was under the same conditions but the solid experimental products were air-dried at room temperature to constant weight and in the second distilled water instead of 30% H_2O_2 and the filtrate dried at 95 °C.

2.2. Physical measurements

The pH of sample FA120 was measured using a Jenway 3045 pH/ion meter until the solid experimental product was dry. Chemical analysis of the starting material was carried out using atomic absorption spectrometry (Perkin–Elmer 5000 with graphite furnace).

Powder X-ray Diffraction (PXRD) was performed on the starting fly ash and the treated samples using a Philips (PW1710) diffractometer with Ni-filtered CuK_α radiation. The samples were scanned over the 3–53° 2θ interval at a scanning speed of 1.2°/min. A semi-quantitative estimation of the abundance of the mineral phases was derived from the PXRD data, using the intensity of a certain reflections and external standard mixtures of the minerals. An estimation of the percentage of amorphous material in the studied samples was achieved by comparing the area of each broad background hump representing the amorphous material in each sample with the analogous area in PXRD patterns of standard mixtures of minerals and different contents of natural amorphous material [31,32] scanned under the same conditions. The PXRD method is an effective and useful tool for the semi-quantitative determination of the amorphous material contained in natural or synthetic samples, with a standard deviation of ±2 wt% [32].

The FT-IR measurements were performed on KBr pellets prepared by adding 1.8 mg of the sample to 250 mg KBr. The transmission FT-IR spectra of the pellets were recorded using a Bruker IFS113v spectrometer working under vacuum in the MIR region (4500–400 cm^{-1}) with a resolution 2 cm^{-1}.

The solid experimental products were also studied by scanning electron microscopy (SEM) using a Jeol JSM-840 scanning electron microprobe, equipped with a LINK 10,000 AN Energy Dispersion Analyser. Corrections were made using the ZAF-4/FLS software provided by LINK.

3. Results

The chemical composition of the starting fly ash is given in Table 1 and can be characterised as sulphocalcic. Despite the low total content in SiO_2 and Al_2O_3, which are the main components for the zeolite synthesis (52.20 wt% in total), the SiO_2/Al_2O_3 ratio of 2.74 (Si/Al ratio 2.42) is considered suitable for zeolitization [27,33–35]. On the other hand, the sum of the CaO and MgO percentages was found to be high (29.80 wt% in total).

The semi-quantitative mineralogical composition of the starting fly ash and the resulting products are listed in Table 2 and Fig. 1. The fly ash mainly consists of amorphous material (21 wt%), lime (28 wt%) and anhydrite (24 wt%), while quartz (6 wt%), calcite (5 wt%), gehlenite (5 wt%), portlandite (4 wt%), hematite (3 wt%), feldspars (2 wt%) and micas + clays (2 wt%) were found in minor amounts. Calcite, quartz, feldspars and micas + clays were initial constituents of the mined lignite, however lime, anhydrite, gehlenite, portlandite, and hematite were formed during lignite combustion [5,7,8]. The amorphous material (identified as a broad background hump from about 9 to 22° 2θ, Fig. 1) in the starting fly ash may be amorphous inorganic material formed during the combustion of

Table 1
Chemical composition (wt%) of the fly ash from the Agios Dimitrios Power Plant, Lignite Center of Western Macedonia

SiO_2	38.24	Na_2O	0.68
TiO_2	0.12	K_2O	0.96
Al_2O_3	13.96	P_2O_5	0.23
Fe_2O_{3T}	4.88	SO_3	4.26
MnO	0.14	L.O.I.	6.54
MgO	4.34	Total	99.81
CaO	25.46	SiO_2/Al_2O_3	2.74