



A comprehensive evaluation of sedimentary zeolites from Turkey as pozzolanic addition of cement- and lime-based binders



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HIGHLIGHTS

- The specific surface area affects zeolite reactivity in the initial stages.
- Si/Al ratio controls the pozzolanic activity at longer hydration times.
- Among the exchanged forms, K⁺-clinoptilolite has the highest lime fixation capacity.
- Ability of lime fixation does not always lead to a better mechanical behavior.
- XRD is a more sensitive technique to detect reaction products than FTIR.

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ABSTRACT

The pozzolanic action played by five natural zeolite-rich materials (three clinoptilolite- and one each mordenite- and analcime-bearing rocks) coming from Turkey, has been examined, evaluating also the influence of various chemical–physical parameters, such as grain size of the zeolitic materials and nature of the cation present as extra-framework component of the structure. Pozzolan activity has been estimated by the official test of the European Standards and by thermogravimetry, finding a good accordance between the two procedures. Clinoptilolite-rich rocks gave the best results, but performance turned out to depend on the specific surface area and pre-enrichment in a potassium form. Experimental data analysis demonstrated that the pozzolanic reaction is kinetically controlled by the diffusion of reactants through a layer of dense reaction products. Experimental blended cements with the five zeolite-rich rocks were also prepared and the compressive strengths measured as a function of the curing time. The effectiveness of the pozzolanic action was monitored by XRD and FTIR analyses. An accurate microstructural study of the hardened pastes was also carried out and point analysis performed, pointing out that the zeolite–lime interaction is characterized by two stages: initially zeolite subtracts calcium from the environment by cation exchange, then it acts as a true pozzolan as soon as its structure breaks down.

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1. Introduction

According to ASTM C125 definition [1], pozzolan is intended as “a siliceous and aluminous material which, in itself, possesses little or no cementitious value but which will, in finely divided form in the presence of moisture, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties”.

Pozzolans can be (1) naturally occurring products, such as volcanic ash and pumice, zeolitic tuff and zeolites, (2) heat treated natural resources, e.g., metakaolin and rice husk ash, or (3) industrial by-products having different origins, such as silica fume and fly ash. All these products are widely used in manufacturing blended cements, due to their ability to fix portlandite, i.e., the detrimental free lime, Ca(OH)₂, coming from the hydration reaction of Portland clinker. The partial replacement of clinker with pozzolan is gaining an increasing significance, because of its beneficial effect on (i) the reduction of CO₂ emission, (ii) energy-saving and (iii) enhancement of several technical features of the hardened

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mortars [2]. In fact, pozzolans are known (a) to reduce the amount and rate of heat evolution and thermal expansion, (b) to favor the workability of the mortars, (c) to improve the durability of the concrete structures, (d) to decrease the risk of alkali-silica reaction and finally (e) to improve the resistance to chemical attack [3]. Adversely, a negative effect of pozzolan addition is the slowdown of the pozzolanic reaction, resulting in a deceleration of the hardening process and a delay in the achievement of the optimal strengths [4,5].

Natural zeolites are a family of hydrated aluminosilicates with high contents of reactive silica and alumina [6]. They proved to be interesting pozzolanic materials, in spite of the larger amount of mixing water required for manufacturing the relevant mortars, compared to other pozzolans [5,7–10]. Due to their excellent pozzolanic activity, their parent rocks (zeolitic tuffs) have frequently been used since Roman times as admixtures in cement for any type of construction. The reactivity of natural zeolites arises from (a) their highly porous structure and the related large external surface area, (b) metastability, (c) ion exchange ability, all of three parameters favoring interaction with lime. Accordingly, zeolite crystals are easily dissolved in the alkaline contact solution, giving rise to precipitation of hydrated calcium silicates and aluminates (C-S-H and A-S-H), having cementitious properties [11–15].

Many investigations have been carried out to test the pozzolanic activity of materials and several methods have been proposed for its direct or indirect evaluation. Relevant procedures are based on (a) X-ray diffraction (XRD), (b) chemical analysis (c) thermogravimetry (TGA), (b) mechanical properties of mortars (e.g., compressive strength), (c) electrical conductivity, (d) conduction calorimetry, (e) pore-size distribution of pastes and (f) microstructural properties of zeolite-blended cements [16–19]. Additional studies are however needed, to better understand the relationship between the ability to fix lime and the field performance of the materials.

The aim of this study is therefore to upgrade our knowledge on the action played by zeolites as pozzolanic materials, testing different types of natural zeolites.

More in detail, this study deals with the mineralogical, physical and chemical characterization of different zeolites, coming from the main tuff deposits in western Turkey, and the evaluation of their reactivity as pozzolanic additions in lime pastes. Among the various procedures to evaluate the pozzolanic activity, the method recommended by the European Standards, namely the Fratini's test [20], has been selected, but also thermal analysis, one of the most effective techniques [16], has been tested, with the aim to compare the results of both methods. Another purpose of this study is the evaluation of the pozzolanic activity of cation-exchanged tuff samples in order to further investigate on the relationship between cation nature and content of zeolites and their ability to fix calcium. The last intent of this investigation is monitoring the development of the mechanical properties of tuff/Portland cement mortars with the progress of the pozzolanic reaction and studying the relevant disappearing and appearing phases with help of the Wavelength-Dispersive X-ray Spectroscopy (WDS).

2. Experimental

2.1. Materials and their characterization

Five zeolite-rich tuffs, collected in the main zeolite deposits in the western Turkey, were investigated. Three of these, coming from Gördes (Manisa), Aliğa (İzmir) and Bigadiç (Balıkesir), here referred to as CLI-G, CLI-A and CLI-B, respectively, were clinoptilolite-rich tuffs. One sample of mordenite-bearing tuff (MOR) was from Foça (İzmir) and one of analcime-bearing tuff (ANA) was from Ayvacık (Çanakkale) region. In all these occurrences, zeolites formed in Neogene basins by diagenetic alteration [21].

The five rock samples were crushed in coarse fragments and then ground, making use of a ball mill (MG 171 automatic swing mill) for 20 min. The particle size distribution of the powdered materials was determined with a particle size analyser (Malvern Mastersizer 2000). Blaine fineness was also measured in accordance with the ASTM C204 standard method [22].

Tuff samples were ignited until definitive loss of volatiles and then subjected to chemical analysis by ICP optical emission spectrophotometry (ICP-OES, Perkin Elmer Optima 2100 DV) after digestion, under microwave-induced heating (Perkin Elmer Multiwave 3000 oven), in a standard solution.

The cation exchange capacity (CEC) of the zeolitic materials was measured with the batch exchange method (BEM) [23]. Accordingly, the original extra-framework cations in zeolites, i.e., Na⁺, K⁺, Mg²⁺ and Ca²⁺, were exhaustively displaced from the solid through percolation of a 1 M solution of NH₄Cl. Cations released were analyzed in the collected liquors by ICP-OES. CEC was calculated from their concentration and expressed in meq/g.

Specific surface area was measured by N₂ adsorption, using the Brunauer–Emmett–Teller (BET) method (Micromeritics Gemini 2360 apparatus) after tuff samples activation under vacuum at 150 °C for 5 h.

Quantitative electron microprobe analysis in wavelength dispersive mode (EPMA-WDS) was performed on polished sections of zeolite tuffs coated with carbon, using a JEOL JXA 8200 electron microprobe. In order to reduce the crystal dehydration due to the electron bombardment, the system was operated using a defocused electron beam (diameter: 5 ÷ 10 nm), an accelerating voltage of 15 kV, a beam current of 10 nA measured by a Faraday cup and counting times of 20 s on the peaks and 5 s on the backgrounds. Crystals of natural K-feldspar (for Si, K, Al), ilmenite (for Ti), forsterite (for Mg), fayalite (for Fe), wollastonite (for Ca), barite (for Ba), celestine (for Sr), and omphacite (for Na), were used as standards. The results were corrected for matrix effects using a conventional ZAF routine in the JEOL suite of programs.

Qualitative and quantitative phase analysis was performed by means of X-ray powder diffraction (XRPD) using a Panalytical X'Pert Pro diffractometer equipped with a RTMS detector (X'Celerator) and a X'Pert High Score Plus 3.0 software. Operating conditions were: CuK α radiation, 40 kV, 40 mA, 2 θ range from 3° to 80°, equivalent step size 0.0179° 2 θ , equivalent counting time 120 s per step. Data sets were analyzed using RIR/Rietveld method [24] with internal standard and a TOPAS 4.2 software (BRUKER AXS Company). Powders with grain size <10 μ m were obtained using a McCrone micronizing mill (agate cylinders and wet grinding time of 15 min). An α -Al₂O₃ internal standard (1 μ m, Buehler Micropolish) was added to each sample at a rate of 20 wt.%. Atomic starting coordinates for identified phases were taken from literature (ICSD, International Crystal Structure Database, 2012), according to the following specific references: clinoptilolite [25], quartz [26], cristobalite [27], biotite [28], and sanidine [29]. PO (preferred orientation) was treated, whenever required, for each phases with spherical harmonics approach.

The morphology of zeolites was observed by optical microscopy. Thin sections of tuff samples were examined under a Nikon polarizing microscope in order to identify the mineralogy and to observe the relevant petrographic and textural features. Scanning electron microscope (SEM) analyses were also performed on tuff samples previously coated with Au. A QUANTA 400F device, equipped with energy-dispersive X-ray (EDX), was accordingly used.

Cation-exchanged samples of the clinoptilolite-rich CLI-B tuff were also prepared. Accordingly, weighted amounts (around 10 g) of powdered tuff were converted into Na⁺-, K⁺- or Ca²⁺-rich forms, contacting them, under continuous stirring, with 1 litre of 0.5 M NaCl, KNO₃ and Ca(NO₃)₂ solutions, respectively. The spent solution was replaced several times for a fresh one until the concentration of the outgoing cations from the tuff samples, evaluated by ICP-OES, turned out to be \leq 1 mg/l.

Reagent grade Ca(OH)₂ (Carlo Erba RPE-ACS) was used to prepare lime-zeolitic tuff pastes.

A commercial Portland cement, classified as CEM I 52.5 R in compliance with the European Standard EN 197-1 and supplied by Cementerie Aldo Barbetti S.p.A. (Gubbio, Italy), was used to manufacture cement-zeolitic tuff mortars; its main chemical and physical features are summarized in Table 1 (data made available by the producer company).

2.2. Experiments and measures on lime-tuff pastes

Several samples of lime-tuff mixtures, containing equal amounts of the two components, were prepared. Suitable amount of water was added to the blends (liquid-to-solid ratio equal to 0.5) to obtain a good workability. After a careful mixing, the obtained pastes were cured in sealed polyethylene containers at room temperature. The hardened compacts were collected after time intervals of 3, 7, 28, 56, 90, and 180 days, ground, treated with acetone to stop further hydration, and stored in sealed containers until analysis.

The pozzolanic activity of zeolitic tuffs was estimated by TG analysis (Netzsch STA409 PCLuxx apparatus), using alumina crucibles, N₂ gas flow and a heating rate of 10 °C/min in the temperature range 25–1000 °C. The weight loss of pastes in the range 400–500 °C, due to the dehydroxylation of unreacted Ca(OH)₂, was regarded as an indirect measure of the advancement of pozzolanic reaction.

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