The effect of acid treatment on the reactivity of natural zeolites used as supplementary cementitious materials

Lisa E. Burris *, Maria C.G. Juenger

Department of Civil, Architectural and Environmental Engineering, University of Texas at Austin, 301 E. Dean Keeton St., Austin, TX 78712, USA

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ABSTRACT

This work investigated the use of acid treatment as a method for increasing the reactivity of natural zeolite used as a supplementary cementitious material. The effects of treating a natural clinoptilolite zeolite with nine acid solutions, 0.1 M, 0.5 M, or 1 M hydrochloric or nitric acid or 0.1 M, 0.5 M, or 0.87 M acetic acid, were measured using x-ray diffraction, particle size analysis, pore size distribution and surface area analysis. The zeolite pozzolanic reactivity was determined by measuring the quantity of portlandite in hydrated zeolite-cement paste after 28 and 90 days. Results showed that acid treatment increased zeolite surface area, resulting in increased zeolite pozzolanic reactivity, independent of the solution concentration used. Cement hydration was also increased, evidenced by greater rates of heat evolution from cement-zeolite pastes. Additionally, although reductions of portlandite occurred most quickly in pastes with zeolites treated with strong acids, by 90 days the zeolites treated with acetic acid solutions showed comparable portlandite reductions.

1. Introduction

Natural zeolites are aluminosilicate minerals prevalent throughout the world. Prior research has shown natural zeolites to be feasible for use as supplementary cementitious materials (SCMs), replacing a portion of the cement in concrete while still generating similar or improved concrete properties [1–4]. Natural zeolites have also been shown to be pozzolanic, reacting with portlandite (calcium hydroxide) and water in cementitious systems to create more C-S-H [2,5]. Zeolites improve many concrete properties when included as part of the cementitious binder including resistance to alkali silica reaction, sulfate attack, and penetration by chlorides [3,4]. However, several disadvantages are associated with the use of natural zeolites in cementitious mixtures; properties generated by cementitious mixtures using natural zeolites can vary greatly depending on zeolite source [6], and mixtures using natural zeolites have been shown to produce lower concrete compressive strengths, especially at early ages [1,3], than several other commonly used SCMs.

It is possible that the performance of zeolites as SCMs could be improved through acid pretreatment, which has been shown to effectively increase the reactivity of various other SCMs such as fly ash and rice husk ash [7–9]. However, no work has been published on the effect of acid pretreatment on the pozzolanic reactivity of zeolites. Previous studies have shown that acid treatment changes natural clinoptilolite zeolite properties that can be linked to better SCM performance, including increases in the SiO_2/Al_2O_3 ratio [10–12,17], reductions in zeolite

crystallinity [10,11,13,14], removal of system impurities [15] and increases in specific surface area [10,11,16,17]. Similar results have been demonstrated for clays [18,19], including smectite minerals [20], which can be present as impurities in natural zeolite samples.

However, none of the studies in the literature examining acid treatment on natural zeolites actually tested treated zeolites in cementitious systems. Therefore, the study presented in this paper examined the effects of acid treatment on the physical and chemical properties of a natural zeolite sample and investigated the correlation between these properties and hydrated zeolite-cement paste composition to determine whether acid treatment could be an effective process for increasing the reactivity of natural zeolite samples used as SCMs.

2. Materials and experimental methods

2.1. Zeolite sample preparation

Clinoptilolite zeolite, mined from Tilden, Texas, was used in this study. The natural zeolite sample was classified by the supplier as #30 mesh (0.595 mm) size and was not treated or washed by the supplier before delivery. Prior to treatment and testing, the as-received sample was ground to pass a 0.149 mm (#100 sieve) and dried for at least 24 h in a low vacuum desiccator. This ground sample is referred to hereafter as 'untreated zeolite.' The chemical composition, determined using x-ray fluorescence (XRF),[1] is shown in Table 1.

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* Corresponding author. Tel.: +1 913 306 4286.
  E-mail address: lisaelanna@gmail.com (L.E. Burris).

[1] Testing conducted at the Texas Department of Transportation Concrete Materials Laboratory in Austin, TX.

Material	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	SO$_3$	Na$_2$O	K$_2$O
Zeolite	62.23	11.88	1.12	2.21	0.64	-	1.00	1.68
OPC	19.36	5.13	2.53	63.17	1.03	3.22	0.09	0.88

An ASTM C150 [21] Type I/II cement (Texas Lehigh Cement Co., Buda, Texas), referred to hereafter as 'ordinary portland cement' (OPC), was used for all pastes in this work. The chemical and physical properties of the cement are shown in Table 1. A quartz filler (Old Hickory, Clay World) was used to help differentiate between improvements due to filler effects [22] and those occurring as a result of the pozzolanic reaction. The particle size distributions of the OPC, untreated zeolite, and quartz filler are shown in Fig. 1.

Three treatment solutions were chosen to test the effect of acid treatment on zeolite reactivity: hydrochloric acid (HCl), nitric acid (HNO$_3$), and acetic acid (HAc). ACS-grade HCl was initially used to match treatments in prior studies [10,23–27], and then the matrix was expanded to include nitric and acetic acid. ACS grade nitric acid was chosen as an alternative strong acid to HCl, in order to avoid using an acid that could potentially leave behind chloride ions, which can contribute to corrosion of reinforcing steel in concrete [28–30]. A household grade acetic acid, "All Natural Distilled White Vinegar" (H. J. Heinz Co., Pittsburgh, PA, USA), was used to determine if a weak acid could obtain similar effects as strong acids. The use of household vinegar was chosen because this acid would pose far fewer environmental and worker safety concerns than would the use of the other two strong acids, and if all three successfully increased zeolite reactivity, would be preferable and easier to use industrially.

Each acid treatment solution was prepared with three concentrations in order to determine the effect of acid strength on natural zeolite sample properties: 0.1 M, 0.5 M, and 1 M for the HCl and HNO$_3$ solution and 0.1 M, 0.5 M and 0.87 M (molarity of the stock solution) for the acetic acid solution. The solutions for each acid were prepared from stock acid solutions (12.1 M HCl, 15.8 M HNO$_3$, and 50 grain (0.87 M) HAc) using ultrapure water (resistivity of 18 MΩ-cm) for dilution. Exact concentrations of each solution may have varied slightly from intended values due to impurities in the stock acid solutions, but for the purposes of this research variations were assumed to be negligible.

To prepare acid-treated samples, 15 g of natural zeolite was ground to pass a 0.149 mm (#100) sieve and dried for at least 24 h in a low vacuum desiccator. The natural zeolite was then added to a 0.1 M, 0.5 M or 1 M solution of hydrochloric, nitric or acetic acid with 1 g natural zeolite to 25 mL of solution. The samples were continuously mixed on a rotary mill (U.S. Stoneware, East Palestine, Ohio) for 24 h. At 24 h from sample-solution contact time the samples were centrifuged (Beckman Coulter Avanti J-E) at 7500 rpm for 5 min. The liquid was decanted and saved for analysis. Each sample was washed with deionized water, centrifuged and decanted four additional times in order to remove the acids'
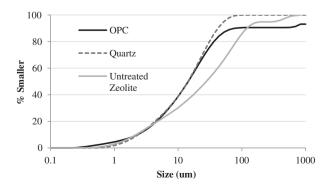
conjugate base ions and prevent their interference in future test results. The natural zeolites were dried for 24 h at 60 °C and then lightly ground to return the sample to powder form. This procedure was performed in independent duplicates for each sample.

2.2. Zeolite physical and chemical characterization testing

Characterization testing was completed in order to track the physical and chemical properties of the natural zeolites that were affected by acid treatment in order to link those changes with natural zeolite reactivity in cementitious systems. All testing was performed in duplicate from independently prepared samples. Testing tracked changes from acid treatment in the phases present in the natural zeolite samples, as well as particle size, surface area and pore sizes.

Inductively coupled plasma spectrometry (ICP) was used to measure aluminum remaining in the acid solutions after treatment of the natural zeolite in order to help gauge the effectiveness of acid at removing aluminum from the natural zeolite structure. Element concentrations present in the decant solutions reserved from natural zeolite acid treatment were analyzed using a Varian 710-ES Inductively Coupled Plasma-Optical Emission Spectrometer.

X-ray diffraction (XRD) was used to determine what phases were present in each sample and to gauge the effectiveness of reducing crystallinity and impurities by acid treatment. X-ray diffraction scans were performed using a Siemens D500 x-ray diffractometer, using a copper x-ray source producing Ni-filtered CuKα radiation. The diffractometer was operated at 40 kV and 30 mA with scans taken from 5–70° 2θ with a step size of 0.2° 2θ and a 2 s dwell time. The diffractometer was configured with 4° soller slits and 1° anti-scatter slits on both the beam and detector sides, a 1° divergence slit on the beam side and a 0.15 mm receiving slit and 0.6 mm detector slit on the detector side. Cu K-β radiation was removed before reaching the detector by a graphite monochromator. Crystalline phases present in each natural zeolite sample were determined using files from the inorganic crystal structure database [31], Jade MDI software package [32], and a report on zeolite diffraction patterns published by the IZA structure commission [33]. Relative crystallinity was qualitatively gauged according to the reduction of the peak heights of each phase compared to other phases present in the material. In general, lower peak heights correlate with lower sample crystalline content [34].

Specific surface area was measured on natural zeolite samples before and after acid treatment by nitrogen sorption using a Micromeritics ASAP 2020 Surface Area and Porosimetry Analyzer. In order to determine the degassing requirements the natural zeolite samples were degassed at a pressure of 500 μmHg or less for 12 h at 100 °C, 6 h at 300 °C, or 6 h as 400 °C. Specific surface area results were similar for 100 °C and 300 °C samples, but were reduced for the 400 °C sample, signaling the occurrence of structural degradation with 400 °C heating. Thus all further untreated and pretreated samples were degassed for 6 h at 300 °C and a pressure of 500 μmHg or less. Surface area was determined using the BET model [35] and pore size distribution with the BJH model [36]. For this study, nitrogen-available internal surface area (hereafter, internal surface area) of each sample was calculated as the difference between the total nitrogen-available surface area determined by BET and the external surface area calculated using a t-plot [37]. Internal surface area, in this work, represents micropore- (0.5–2.5 μm) and gel-sized (2.5-10 μm) pores, and does not assess changes to pore openings of the clinoptilolite lattice opening size.

Due to the large internal surface area inherent in the natural zeolite crystal structure, surface area and particle size were assumed to be independent of each other for the purposes of this work. Particle size distributions of the natural zeolite samples were measured before and after milling using a Malvern 2000 Laser Particle Size Analyzer. Enough sample was added to 1 L of distilled water to generate 5-15% obscuration and was ultrasonicated for 60 s in order to reduce particle agglomeration. The instrument default optical parameters were used for all

Fig. 1. Particle size distributions of OPC, untreated zeolite, and quartz filler.