1 THE EFFECT OF ACID TREATMENT ON THE REACTIVITY OF NATURAL
2 ZEOLITES USED AS SUPPLEMENTARY CEMENTITIOUS MATERIALS

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10
11 **ABSTRACT**

12
13 This work investigated the use of acid treatment as a method for increasing the reactivity
14 of natural zeolite used as a supplementary cementitious material. The effects of treating a
15 natural clinoptilolite zeolite with nine acid solutions, 0.1 M, 0.5 M, or 1 M hydrochloric
16 or nitric acid or 0.1 M, 0.5 M, or 0.87 M acetic acid, were measured using x-ray
17 diffraction, particle size analysis, pore size distribution and surface area analysis. The
18 zeolite pozzolanic reactivity was determined by measuring the quantity of portlandite in
19 hydrated zeolite-cement paste after 28 and 90 days. Results showed that acid treatment
20 increased zeolite surface area, resulting in increased zeolite pozzolanic reactivity,
21 independent of the solution concentration used. Cement hydration was also increased,
22 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 of the 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio [10–12], reductions in zeolite crystallinity [10,11,13,14], removal of system impurities [15] and increases in specific surface area [10,11,16]. 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 hours 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.

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 Figure 1.

Three treatment solutions were chosen to test the effect of acid treatment on zeolite reactivity: hydrochloric acid (HCl), nitric acid (HNO₃), 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

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

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, Pennsylvania, 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 HNO₃ 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 HNO₃, 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. The calculated pH of each solution prior to addition of the natural zeolite is shown in Table 2.

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 hours 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 hours. At 24 hours from sample-solution contact time the samples were centrifuged (Beckman Coulter Avanti J-E) at 7500 rpm for 5 minutes. 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 hours 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 $\text{CuK}\alpha$ radiation. The diffractometer was operated at 40 kV and 30 mA with scans taken from $5\text{--}70^\circ 2\theta$ with a step size of $0.2^\circ 2\theta$ and a 2 second 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 hours at 100°C, 6 hours at 300°C, or 6 hours 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 hours 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 seconds in order to reduce particle agglomeration. The instrument default optical parameters were used for all materials, with a refractive index of 1.5026 and 1.33 used for the natural zeolite sample and water, respectively.

Measurements were taken in triplicate over 10 seconds using both a HeNe red gas laser and a LED blue light in a reverse Fourier convergent beam lens arrangement. The laser light scattering measurements were analyzed by the Malvern software using Mie Scattering Theory and Fraunhofer Diffraction Theory in order to generate particle size distribution data for each sample.

2.3 Acid Treatment Testing Methods: Reactivity Testing

Changes to natural zeolite sample pozzolanic reactivity after acid treatment were tracked using the portlandite content of hydrated zeolite-cement pastes. The portlandite content of hydrated cement-zeolite pastes was determined for pastes using untreated natural zeolites and natural zeolites treated with 0.1 M, 0.5 M, or 1 M HCl, 0.1 M, 0.5 M, or 1 M HNO₃ or 0.1 M, 0.5 M or 0.87 M HAc, with a w/cm of 0.4, and a 20% replacement of cement with natural zeolite. Before the addition of water, the cement and natural zeolite sample were mixed together by hand for 30 seconds. The cement, natural zeolite and water samples were then mixed by hand for two minutes and each 14 g sample was sealed in an individual plastic cup and cured at 23°C. At 28 or 90 days after mixing, the sample was removed from the cup, the edges of each sample were removed, the remaining sample mass was recorded and the sample was crushed to pass the No. 8 (2.36 mm) sieve. The sample was dried under vacuum for seven days to stop hydration. After seven days the sample was reweighed to determine the mass loss of water in the system and then ground to pass the No. 100 (149 µm) sieve. Each sample was then heated to 1000°C at a

temperature ramp rate of 20°C/min in a nitrogen environment in a Mettler Toledo Thermogravimetric Analyzer.

The amount of portlandite present in the sample was calculated from the amount of mass lost from approximately 450°C to 550°C, which corresponds to the dehydration of portlandite. It was assumed that one mole of portlandite was present for each mole of water lost in this range. The dehydration temperatures used were tailored to each specific sample using the inflection points on the differential thermogravimetric analysis curves to determine the start and end of dehydration for each sample. The quantity of portlandite present in the paste was normalized by the anhydrous cement content of the paste, determined by accounting for free water lost on drying.

2.4 Testing to Determine the Influence of Acid-Treated Zeolite on Cement Hydration

Isothermal calorimetry was used to examine the effects of acid-treated natural zeolites on cement hydration kinetics. Testing was done on cement pastes with 0% or 20% natural zeolite replacement for natural zeolite samples treated with 0.1 M, 0.5 M, or 1 M HCl, 0.1 M, 0.5 M, or 1 M HNO₃ or 0.1M, 0.5 M or 0.87 M HAc. Heat evolution was measured in a TAM AIR (Thermometric) calorimeter for 10g paste samples prepared with a w/cm of 0.4, and a 20% replacement of cement with natural zeolite over 72 hours.

Samples were hand-mixed for two minutes and placed into vials according to ASTM C1679 [38].

Several parameters were investigated using isothermal calorimetry in order to understand how the incorporation of raw or acid-treated natural zeolites affected cement hydration. These parameters include: 1) the slope of the rate of heat evolution versus time during the acceleration period, referred to in this work as the rate of reaction during the acceleratory period; 2) the time required for the mixture to enter the acceleration period (i.e. the length of the induction period); 3) the time required for the mixture to reach its peak rate of heat release (for the presumed alite peak); and 4) the magnitude of the rate of heat evolution at the peak. The time of the start of the acceleration period was determined for all mixtures in this study as the point at which the minimum rate of heat evolution occurred following the initial dissolution peak. The time of the maximum rate of heat evolution was determined for all mixtures in this study as the time to the first maximum occurring after the start of the acceleration period. In cases where the alite and aluminate peaks overlapped and the maximum rate of heat evolution for the alite peak could not be definitively determined, the time the peak occurred was visually estimated. In this study, since the acceleration period isn't completely linear, the slope of the acceleration period was standardized by using the slope at the time halfway between the time at which the acceleration period began and the time the maximum rate of heat evolution occurred.

3 RESULTS AND DISCUSSION

3.1 Physical and Chemical Characterization

Previous research suggested that acid treatment could reduce the crystallinity of natural zeolite samples [10,11,13] and reduce system impurities such as dolomite, quartz and feldspar phases, which are inert with respect to the hydration reactions occurring in cementitious systems [15]. However, this was not evident from the XRD phase analysis results performed for this study, shown in Figures 2 to 4. The XRD patterns did not reveal any changes in the phases present in the natural zeolite samples after treatment with acid, nor were shifts in the lattice parameters evident after acid-treatment of the zeolites. However, although reductions in crystallinity were not apparent from XRD measurements, increased quantities of aluminum in solution after treatment, shown in Figure 5, and discussed further later, may indicate the occurrence of dealumination of the material.

The aluminum concentrations present in the acid treatment decant solutions were reserved, measured, and used to calculate the percent decrease in natural zeolite aluminum content for the blank (DI water), 1M HCl, 1M HNO₃, and 0.87M HAc samples and are shown in Figure 5. Significantly greater decreases in aluminum content occurred for the HCl, HNO₃ and HAc solutions compared to the blank sample. The quantity of aluminum present in the decant solutions from all acid samples (1M HCl, 1M HNO₃, and

0.87HAc) was very similar, indicating that acid strength contributes more significantly to zeolite dealumination than does anion type. It is unclear whether the aluminum in solution was a result of dealumination or of sample dissolution, however it is evident that acid treatment resulted in a change in the zeolite that did not also occur in the blank sample. However, the lack of changes observed in XRD patterns before and after acid treatment suggest that dissolution was not the mechanism controlling the release of aluminum into the treatment solutions.

Changes to the natural zeolite sample particle size after acid treatment are shown in Table 2. Treatment with all acid types and concentrations considerably reduced the coarsest fraction, the d_{90} , of the natural zeolite sample. Some of this reduction could be an artifact of the light regrinding used after acid treatment. However, as the length and force employed were only enough to break up aggregated chunks of the dried zeolite, it is not likely that this procedure affected more than the largest particles remaining in the sample. Also apparent from Table 2 is that, in addition to the effect of the acids on the coarsest material fraction, the nitric acid and acetic acid also reduced the mean particle size, the d_{50} , of the natural zeolite sample by about 50%. Acid concentration, however, did not seem to have a significant effect on the natural zeolite sample's particle size after treatment with any of the acids.

The changes to the nitrogen available specific surface area (henceforth, surface area) and pore sizes, of the natural zeolites after acid treatment are shown in Figures 6 to 8. Acid

treatment was generally successful at increasing the nitrogen-available specific surface area, similar to the results in literature [10,13,15]. Changes in natural zeolite surface area are likely primarily effects of cation exchange and structural dealumination, a conclusion which is supported by the increases in internal surface area versus external surface area of the natural zeolite with acid treatment. However, the response of the natural zeolite differed with acid type and concentration.

Figure 6a shows the effect of hydrochloric acid on the natural zeolite surface area. Treatment with 0.1 M, 0.5 M and 1 M HCl resulted in increases in the surface area relative to the surface area of the untreated natural zeolite. The surface area was increased considerably more for the 0.1 M and 0.5 M concentrations compared to the 1M HCl treatment. Figure 6a also shows that the increase in surface area was primarily a result of increased internal surface area, as external surface areas remained constant regardless of the concentration of the acid treatment solution. Some of the increases in surface area could be due to differences resulting from the exchange of larger cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+) for H^+ , affecting the local electric field of the zeolite and resulting in changes in N_2 adsorption depending on the number and type of cations present in the zeolite structure [39–41]. Although changes in surface area measurements resulting from ionic changes do not represent true changes in surface area, larger ionic potential may still correlate with greater reactivity, through increased attraction of molecules, such as calcium hydroxide, in the cement paste. Other changes may be a result of increasing porosity and structural dealumination. The pore size distribution data shown in Figure 5b suggest that treatment

with 0.5 M HCl resulted in an increase in the volume of ~2-7 nm pores, which may be a result of the removal of aluminum from the structure [10,13,15,27]. The subsequent decrease in surface area after treatment with 1 M HCl could be a result of structural collapse from further structural dealumination, as observed by Rivera et al. [42] and Salvestrini et al. [16]. The slight increase in particle size after treatment with 1 M HCl compared to the 0.5 M HCl-treated sample, shown in Table 2, seems to support this theory.

Treatment of the natural zeolite sample with nitric acid was the most successful of the acid treatments investigated in this study, resulting in increases to surface area proportional to the concentration of acid used, as shown in Figure 7a. Treatment with 0.1 M HNO₃ more than doubled the surface area of the natural zeolite sample, and after treatment with 1 M HNO₃, the surface area was nearly triple the surface area of the untreated sample. Similar to the hydrochloric acid treated samples, surface area increases appear to be a result of increases in the total volume of ~2-7 nm pores after treatment with 0.5 M and 1 M HNO₃, shown in Figure 7b. Therefore, it is again likely that increases in surface area occurred as a result of cation exchange and dealumination. The increase in surface area after treatment with 1 M HNO₃ could be a result of continued cation exchange, slightly increased porosity, reduced particle size and further structural dealumination that did not, in this case, result in structural collapse. However, experimental verification of this theory was outside the scope of this work.

Overall, treatment with acetic acid, shown in Figure 8, was less successful at increasing the surface area of the natural zeolite than were the nitric and hydrochloric acid solutions. However treatment with the acetic acid solutions did still increase the natural zeolite specific surface area compared to the control. Reduced improvements to surface area relative to the other acids are likely a result of the strength of the acid, with the stronger acids able to exchange greater quantities of cations for protons in the interior of the zeolite crystal structure. Additionally, use of acetic acid resulted in less structural dealumination, shown by considerably lower amount of aluminum in solution in the ion analysis results in Figure 5. Further, treatment with acetic acid resulted in very little change in pore size distribution of the natural zeolite sample, although it was still effective at reducing natural zeolite sample particle size.

3.2 Pozzolanic Reactivity

The portlandite contents of pastes containing untreated natural zeolite and natural zeolite treated with hydrochloric, nitric or acetic acid are shown in Figures 9 to 11. Acid treatment using hydrochloric or nitric acid was effective in improving the performance of the natural zeolite as an SCM, with the portlandite content of all pastes using acid-treated zeolites reduced compared to the cement-only and quartz-cement samples as well as the untreated zeolite-cement pastes at both 28 and 90 days. The portlandite content of acetic acid-treated zeolite-cement paste, shown in Figure 11, was approximately equal to the untreated zeolite-cement paste at 28 days, but was significantly lower at 90 days.

Treatment with the strong acids, hydrochloric and nitric, seemed to be more effective at increasing the early portlandite consumption ability of the natural zeolite sample, with pastes using strong-acid-treated-zeolites yielding lower portlandite contents at 28 days. However, use of the stronger acids seemed only to have increased the pozzolanic reaction rate, as the amount of portlandite in the acid-treated zeolite-cement pastes was similar for all three types of acid shown in Figures 9 to 11 after 90 days. Acid concentration had very little effect on the magnitude of the portlandite reduction.

Interestingly, acid treatment seemed to extend the duration and increase the extent of the pozzolanic reaction for all acid types, as the portlandite contents of the 90-day pastes were lower than in the 28-day pastes regardless of acid type. For the pastes using untreated natural zeolite sample, the pozzolanic reaction appeared to have been finished before 28 days, evidenced by the similar or greater quantities of portlandite present in pastes at 90 days compared to 28 days. However, using acid-treated natural zeolite samples, the portlandite content of all of the pastes was reduced at 90 days from the 28-day level by around 3-4% of the total paste content. This effect is likely a result of the dealumination occurring in the sample during acid treatment, increasing the amount of silica available to participate in the pozzolanic reaction and affecting natural zeolite long-term pozzolanicity. This effect is supported by the findings of Snellings et al. [43], who showed that zeolites with higher Si/Al have higher reactivity.

3.3 Influence of Acid Treated Zeolite on Cement Hydration

The effects of acid-treated natural zeolites on cement hydration, measured through isothermal calorimetry, are shown in Figures 12 to 14 and Table 3. The rate of reaction during the acceleratory period and the maximum rate of heat release, shown in Table 3, were increased for all acid-treated zeolite-cement pastes. The slopes in the acceleration period for hydrochloric and nitric acid-treated zeolite-cement pastes were considerably higher than for the cement-only, quartz filler and untreated natural zeolite pastes, whereas for the acetic acid-treated zeolite the slope was increased much less.

Differences in the maximum rate of heat evolution for each of the zeolite-cement pastes are shown in Table 3. Using acid-treated natural zeolites generally resulted in increases to the maximum heat of hydration of zeolite-cement pastes relative to the cement-only, quartz filler and untreated zeolite-cement pastes for all types and concentrations of acid treatments tested. The maximum rate of heat evolution can be used to compare the amount of growth in each sample occurring during hydration in the acceleration period. Thomas et al. [44] demonstrated that when heat releases are normalized by the quantity of cement, an inert filler material generated a greater maximum rate of heat release because the filler had nucleated a greater quantity of growth regions than what would have developed in a cement-only paste [44]. Therefore, in this study, heat evolution rates greater than those generated by the cement-only paste indicated that the acid treated natural zeolite samples increased nucleation sites and total quantity of alite dissolved and

hydrated. The increases in surface area with acid treatment, discussed previously, are likely responsible for the increased reaction rates as higher surface area materials have been shown by other researchers to generally correlate with greater nucleation and rates of reaction during the acceleratory period [45,46].

4 CONCLUSIONS

Natural zeolite samples were treated for 24 hours with one of three types of acid, hydrochloric, nitric, or acetic, at three different concentration levels, 0.1 M, 0.5 M or 1 M for hydrochloric and nitric acid samples, or 0.1 M, 0.5 M or 0.87 M for acetic acid samples. The physical and chemical characteristics of the materials were then determined using XRD, nitrogen adsorption, laser particle size analysis, and ICP in order to determine what changes the material underwent with acid treatment. These results were compared to the portlandite contents of pastes using untreated and acid-treated natural zeolites. The effect of acid-treated natural zeolites on early age hydration of cement was also tested using isothermal calorimetry.

Acid treatment was found to improve the pozzolanicity of natural zeolites through removal of aluminum from the zeolite crystal structure, and increases in the nitrogen available specific surface area of the zeolite. Overall, acid treatment appeared to be successful at improving the performance of natural zeolite samples used as SCMs. Additionally, improvements gained by treatment of natural zeolite samples with strong,

highly concentrated acids were equivalent to those gained by natural zeolite samples treated with a low concentration of household acetic acid at 90 days. This suggests that the benefits of acid treatment of zeolites may be possible to obtain using lower risk solutions.

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REFERENCES

- [1] V. Lilkov, I. Rostovsky, O. Petrov, Physical and mechanical characteristics of cement mortars and concretes with addition of clinoptilolite from Beli Plast deposit (Bulgaria), silica fume and fly ash, *Clay Miner.* 46 (2011) 213–223.
- [2] T. Perraki, E. Kontori, S. Tsivilis, G. Kakali, The effect of zeolite on the properties and hydration of blended cements, *Cem. Concr. Compos.* 32 (2010) 128–133.
- [3] B. Ahmadi, M. Shekarchi, Use of natural zeolite as a supplementary cementitious material, *Cem. Concr. Compos.* 32 (2010) 134–141.

- 436 [4] I. Janotka, L. Krajči, Sulphate resistance and passivation ability of the mortar made
437 from pozzolan cement with zeolite, *J. Therm. Anal. Calorim.* 94 (2008) 7–14.
- 438 [5] V. Lilkov, O. Petrov, V. Petkova, N. Petrova, Y. Tzvetanova, Study of the
439 pozzolanic activity and hydration products of cement pastes with addition of
440 natural zeolites, *Clay Miner.* 46 (2011) 241–250.
- 441 [6] M. Ackley, Application of natural zeolites in the purification and separation of
442 gases, *Microporous Mesoporous Mater.* 61 (2003) 25–42.
- 443 [7] K.M. Alexander, Activation of pozzolans by treatment with acid, *Aust. J. Appl.*
444 *Sci.* 6 (1955) 327–333.
- 445 [8] R.T. Hemmings, E.E. Berry, B.J. Cornelius, D.M. Golden, Evaluation of acid-
446 leached fly ash as a pozzolan, in: *Mater. Res. Soc. Symp. Proc.*, 1989: pp. 141–
447 160.
- 448 [9] Q. Feng, H. Yamamichi, M. Shoya, S. Sugita, Study on the pozzolanic properties
449 of rice husk ash by hydrochloric acid pretreatment, *Cem. Concr. Res.* 34 (2004)
450 521–526.
- 451 [10] K. Elaiopoulos, T. Perraki, E. Grigoropoulou, Monitoring the effect of
452 hydrothermal treatments on the structure of a natural zeolite through a combined
453 XRD, FTIR, XRF, SEM and N₂-porosimetry analysis, *Microporous Mesoporous*
454 *Mater.* 134 (2010) 29–43.
- 455 [11] E. Unveren, G. Gunduz, F. Cakicioglu-Ozkan, Isomerization of Alpha-Pinene
456 Over Acid Treated Natural Zeolite, *Chem. Eng. Commun.* 192 (2005) 386–404.
- 457 [12] S. Wang, Y. Peng, Natural zeolites as effective adsorbents in water and wastewater
458 treatment, *Chem. Eng. J.* 156 (2010) 11–24.
- 459 [13] F. Cakicioglu-Ozkan, S. Ulku, The effect of HCl treatment on water vapor
460 adsorption characteristics of clinoptilolite rich natural zeolite, *Microporous*
461 *Mesoporous Mater.* 77 (2005) 47–53.
- 462 [14] N. a. Hernández-Beltrán, M.T. Olguín, a. Rosas-Aburto, Effect of acid phosphate
463 media on the stability of clinoptilolite-rich tuff, *J. Incl. Phenom. Macrocycl. Chem.*
464 61 (2008) 93–100.
- 465 [15] A. Ates, C. Hardacre, The effect of various treatment conditions on natural
466 zeolites: ion exchange, acidic, thermal and steam treatments., *J. Colloid Interface*
467 *Sci.* 372 (2012) 130–40.

- 468 [16] S. Salvestrini, P. Sagliano, P. Iovino, S. Capasso, C. Colella, Atrazine adsorption
469 by acid-activated zeolite-rich tuffs, *Appl. Clay Sci.* 49 (2010) 330–335.
- 470 [17] H. Kurama, a. Zimmer, W. Reschetilowski, Chemical Modification Effect on the
471 Sorption Capacities of Natural Clinoptilolite, *Chem. Eng. Technol.* 25 (2002) 301–
472 305.
- 473 [18] A.K. Panda, B.G. Mishra, D.K. Mishra, R.K. Singh, Effect of sulphuric acid
474 treatment on the physico-chemical characteristics of kaolin clay, *Colloids Surfaces*
475 *A Physicochem. Eng. Asp.* 363 (2010) 98–104.
- 476 [19] M. Hassan, H. El-Shall, Texture and Microstructure of Thermally-treated Acid-
477 leached Kaolinitic Clays, *Adsorpt. Sci. Technol.* 27 (2009) 671–684.
- 478 [20] J. Madejová, J. Bujdák, M. Janek, P. Komadel, Comparative FT-IR study of
479 structural modifications during acid treatment of dioctahedral smectites and
480 hectorite, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 54 (1998) 1397–
481 1406.
- 482 [21] ASTM C150: Standard Specification for Portland Cement, *Am. Soc. Test. Mater.*
483 (2012) 1–9.
- 484 [22] B. Lothenbach, K. Scrivener, R.D. Hooton, Supplementary cementitious materials,
485 *Cem. Concr. Res.* 41 (2011) 1244–1256.
- 486 [23] S.J. Allen, E. Ivanova, B. Koumanova, Adsorption of sulfur dioxide on chemically
487 modified natural clinoptilolite. Acid modification, *Chem. Eng. J.* 152 (2009) 389–
488 395.
- 489 [24] K. Belkassa, F. Bessaha, K. Marouf-Khelifa, I. Batonneau-Gener, J. Comparot, A.
490 Khelifa, Physicochemical and adsorptive properties of a heat-treated and acid-
491 leached Algerian halloysite, *Colloids Surfaces A Physicochem. Eng. Asp.* 421
492 (2013) 26–33.
- 493 [25] M. Valášková, K. Barabaszová, M. Hundáková, M. Ritz, E. Plevová, Effects of
494 brief milling and acid treatment on two ordered and disordered kaolinite structures,
495 *Appl. Clay Sci.* 54 (2011) 70–76.
- 496 [26] M.J. Hey, A. Nock, R. Rudham, I.P. Appleyard, G. a. J. Haines, R.K. Harris, The
497 effect of acid treatment on the properties of dealuminated Y zeolite, *J. Chem. Soc.*
498 *Faraday Trans. 1 Phys. Chem. Condens. Phases.* 82 (1986) 2817.

- 499 [27] A.E.W. Beers, J.A. van Bokhoven, K.M. de Lathouder, F. Kapteijn, J.A. Moulijn,
500 Optimization of zeolite Beta by steaming and acid leaching for the acylation of
501 anisole with octanoic acid: a structure–activity relation, *J. Catal.* 218 (2003) 239–
502 248.
- 503 [28] G.K. Glass, N.R. Buenfeld, The presentation of the chloride threshold level for
504 corrosion of steel in concrete, *Corros. Sci.* 39 (1997) 1001–1013.
- 505 [29] K.Y. Ann, H.-W. Song, Chloride threshold level for corrosion of steel in concrete,
506 *Corros. Sci.* 49 (2007) 4113–4133.
- 507 [30] S.E. Hussain, Rasheeduzzafar, A. Al-Musallam, A.S. Al-Gahtani, Factors
508 Affecting Threshold Chloride for Reinforcement Corrosion in Concrete, *Cem.*
509 *Concr. Res.* 25 (1995) 1543–1555.
- 510 [31] G. Bergerhoff, I.D. Brown, *Crystallographic Databases*, Int. Union Crystallogr.
511 F.H. Allen (1987).
- 512 [32] R.T. Downs, M. Hall-Wallace, The American Mineralogist crystal structure
513 database, *Am. Mineral.* 88 (2003) 247–250.
- 514 [33] M.M.J. Treacy, J.B. Higgins, *Collection of simulated XRD powder patterns for*
515 *zeolites*, 4th ed., Elsevier, Amsterdam, 2001.
- 516 [34] G.J. McCarthy, D.M. Johansen, S.J. Steinward, A. Thedchanamoorthy, X-ray
517 diffraction analysis of fly ash, *Adv. X-Ray Anal.* (1988) 331–342.
- 518 [35] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of Gases in Multimolecular
519 Layers, *J. Am. Chem. Soc.* 60 (1938) 309–319.
- 520 [36] E.P. Barrett, L.G. Joyner, P.P. Halenda, The determination of pore volume and
521 area distributions in porous substances. I. Computations from nitrogen isotherms,
522 *J. Am. Chem. Soc.* 73 (1951) 373–380.
- 523 [37] G. Quercia, a. Lazaro, J.W. Geus, H.J.H. Brouwers, Characterization of
524 morphology and texture of several amorphous nano-silica particles used in
525 concrete, *Cem. Concr. Compos.* 44 (2013) 77–92.
- 526 [38] ASTM C1679: Standard Practice for Measuring Hydration Kinetics of Hydraulic
527 Cementitious Mixtures Using Isothermal Calorimetry, *Am. Soc. Test. Mater.*
528 (2009) 1–14.

- 529 [39] S.-T. Yang, J. Kim, W.-S. Ahn, CO₂ adsorption over ion-exchanged zeolite beta
530 with alkali and alkaline earth metal ions, *Microporous Mesoporous Mater.* 135
531 (2010) 90–94.
- 532 [40] O. Talu, S.Y. Zhang, D.T. Hayhurstt, Effect of Cations on Methane Adsorption by
533 NaY, MgY, CaY, SrY, and BaY Zeolites, *J. Phys. Chem.* 97 (1993) 12894–12898.
- 534 [41] K.S. Walton, M.B. Abney, M. Douglas LeVan, CO₂ adsorption in Y and X
535 zeolites modified by alkali metal cation exchange, *Microporous Mesoporous*
536 *Mater.* 91 (2006) 78–84.
- 537 [42] A. Rivera, G. Rodriguez-Fuentes, E. Altshuler, Time evolution of a natural
538 clinoptilolite in aqueous medium : conductivity and pH experiments, *Microporous*
539 *Mesoporous Mater.* 40 (2000) 173–179.
- 540 [43] R. Snellings, G. Mertens, Ö. Cizer, J. Elsen, Early age hydration and pozzolanic
541 reaction in natural zeolite blended cements: Reaction kinetics and products by in
542 situ synchrotron X-ray powder diffraction, *Cem. Concr. Res.* 40 (2010) 1704–
543 1713.
- 544 [44] J.J. Thomas, H.M. Jennings, J.J. Chen, S. Quentin, V. Falla, Influence of
545 Nucleation Seeding on the Hydration Mechanisms of Tricalcium Silicate and
546 Cement, *J. Phys. Chem. C.* 113 (2009) 4327–4334.
- 547 [45] J.W. Bullard, H.M. Jennings, R. a. Livingston, A. Nonat, G.W. Scherer, J.S.
548 Schweitzer, et al., Mechanisms of cement hydration, *Cem. Concr. Res.* 41 (2011)
549 1208–1223.
- 550 [46] J. Cheung, a. Jeknavorian, L. Roberts, D. Silva, Impact of admixtures on the
551 hydration kinetics of Portland cement, *Cem. Concr. Res.* 41 (2011) 1289–1309.

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Table 1 - Oxide compositions (%) of the natural zeolite and cement determined using XRF.

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

Table 2 - Summary of zeolite particle size distributions before and after treatment with hydrochloric, nitric, or acetic acid.

Acid Treatment	Particle Sizes (μm)		
	d ₁₀	d ₅₀	d ₉₀
Untreated	2.62	33.29	142.29
0.1M HCl	4.02	31.72	100.96
0.5M HCl	3.80	29.46	100.90
1M HCl	3.91	32.20	105.83
0.1M HNO ₃	3.38	23.19	95.48
0.5M HNO ₃	3.13	22.55	90.80
1M HNO ₃	3.19	20.75	80.09
0.1M HAc	2.27	16.72	86.88
0.5M HAc	2.83	23.40	97.31
1M HAc	2.72	18.45	93.42

Table 3 - Acceleration period slope in isothermal calorimetry (23°C) of pastes with 80-100% cement and 0-20% untreated or hydrochloric, nitric, or acetic acid-treated zeolite or quartz filler (w/c = 0.4).

SCM/filler	Acceleration Period Slope (mW/g/hr)	Maximum Rate of Heat Evolution (mW/g cement)
None	0.66±0.05	3.71±0.09
Quartz	0.64±0.03	3.79±0.01
Untreated zeolite	0.61±0.11	3.43±0.31
0.1M HCl treated zeolite	0.89±0.01	4.26±0.20
0.5M HCl treated zeolite	0.87±0.05	4.10±0.19
1M HCl treated zeolite	0.87±0.05	4.07±0.69
0.1M HNO ₃ treated zeolite	0.90±0.04	4.05±0.07
0.5M HNO ₃ treated zeolite	0.82±0.02	4.05±0.02
1M HNO ₃ treated zeolite	0.85±0.01	4.14±0.00
0.1M HAc treated zeolite	0.70±0.01	3.99±0.01
0.5M HAc treated zeolite	0.71±0.02	3.94±0.04
1M HAc treated zeolite	0.70±0.01	3.90±0.07

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

Figure 2 - Phases present in the zeolite sample before and after treatment with hydrochloric acid. B = biotite, C = clinoptilolite, Cr = cristobalite, M = montmorillonite, Q = quartz. Numbers in parenthesis indicate the d-spacing of the reflection.

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Figure 5 – Untreated and hydrochloric acid treated zeolites’ (a) nitrogen-available specific surface area, and (b) pore size distribution.

(a)

(b)

Figure 6 – Untreated and nitric acid treated zeolites' (a) nitrogen-available specific surface area, and (b) pore size distribution.

(a)

(b)

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