1 **Milling as a Pretreatment Method for Increasing the Reactivity of Natural**
2 **Zeolites for Use as Supplementary Cementitious Materials**

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1 ABSTRACT

This work examined the effects of milling using a gravity ball mill on the reactivity of natural zeolites used as supplementary cementitious materials (SCMs). Six different particle size distributions of zeolites, created by milling the as-received zeolite in a ball mill for a specified amount of time, were characterized using x-ray fluorescence, quantitative x-ray diffraction, particle size analysis, pore size distribution and surface area analysis. Following material characterization, the pozzolanic reactivity of the zeolites was determined by measuring the quantity of calcium hydroxide in paste after 28 or 90 days and by tracking the compressive strength of zeolite-cement mortars. Results showed that a critical milling time exists, corresponding to a d_{50} of 7-9 μm , after which reductions in particle size can no longer be achieved and zeolite performance can no longer be improved through ball milling.

Keywords: zeolite, particle size, milling, pozzolanic reactivity, supplementary cementitious materials, clinoptilolite

2 INTRODUCTION

Milling, the process of reducing a material's particle size, is a common process in the manufacture of cement and has also been used to prepare other materials, such as ground granulated blast furnace slag, for use as supplementary cementitious materials (SCMs) [1–3]. Many studies have shown that milling can improve the performance of SCMs [2–6], therefore it is hypothesized that milling will also be successful in improving the performance of zeolites as SCMs. Several studies have explored the idea of increasing zeolite reactivity through milling. However, these studies primarily employed high-

energy ball mills operating at speeds in excess of 500 rpm [7–10], conditions that are not feasible for use with the large quantities used in the construction industry. Large-scale milling operations in the construction industry typically consist of large rotary ball mills operating at relatively slow rotational speeds [11,12]. This work explores whether conditions similar to those found in industrial cement mills can generate improvements in zeolite performance similar to those seen with the use of high-energy planetary mills.

The influence of particle size on the performance of zeolites used as SCMs has not been comprehensively characterized, although several studies' findings point towards increased reactivity of zeolites after a reduction in particle size [8,9,13–16]. Charkhi et al. [8] noted that reduction of particle size increases the quantity of external surface area available for interaction and results in shorter diffusion path lengths for sorption applications and also enhancing selectivity. Snellings et al. [16] showed that in paste mixtures of clinoptilolite zeolites and calcium hydroxide in a 1:1 ratio, smaller grain size and higher external surface area increased both the early heat evolution and the rate of heat release during the pozzolanic reaction. In addition, in the zeolite-calcium hydroxide pastes, more calcium hydroxide was consumed by the finer-zeolite mixtures when tested at 6, 24, and 72 hours. Similarly, using 20 mm cubes made of a hydrated clinoptilolite zeolite and calcium hydroxide, Ortega et al. [15] demonstrated that unconfined compressive strength and zeolite particle size are almost inversely linearly related, with lower particle sizes yielding higher compressive strengths.

Interestingly, the researchers that have investigated the effect of zeolite milling have found that milling can not only decrease zeolite particle size, but that long milling time and high rotational speed result in a reduction of crystallinity and increase in the

73 quantity of amorphous material [8,9,13,17,18]. Kosanovic et al. [13] milled a 1g zeolite
74 sample using 10 mm Wolfram carbide balls in a planetary ball mill operated at 3000 rpm.
75 During the first 15-20 minutes of milling they found that 75% of the crystalline phase
76 was converted to amorphous material in addition to reduced particle sizes [13]. Zielinski
77 et al. [9] saw similar results after milling six types of artificially-synthesized zeolites in a
78 high-energy ball mill using a set of three 9.5 mm diameter steel balls and a speed of 1010
79 rpm. The crystallinity of all six types of zeolite was significantly reduced after only ten
80 minutes of milling and eliminated in nearly all of the samples by 60 minutes. Charkhi et
81 al. [8] also saw nearly complete elimination of clinoptilolite zeolite crystallinity after
82 milling for only 20 minutes at 600 rpm using 20 mm zirconium oxide balls and a high-
83 energy planetary ball mill. Similarly, Xie and Kaliaguine [10] found that KNaX zeolite (a
84 type of synthetic zeolite created from a kaolin precursor) milled at 1010 rpm became
85 amorphous after 120 minutes of milling. The de-crystallization of zeolite crystals with
86 milling was suggested by several researchers to occur as a result of breakage of the Si-O-
87 Si and Si-O-Al bonds on the external surface of the zeolite leading to structural collapse
88 [8,13].

89 In addition to reductions in particle size and crystallinity, other researchers
90 observed changes in the zeolite pore structure and surface area after milling. Xie and
91 Kaliaguine [10] found that milling their KNaX zeolite at 1010 rpm progressively reduced
92 the surface area and micropore volume with increasing milling time. The work of
93 Zielinski et al. [9] suggested that ball milling initially opened macropores. However,
94 additional milling time caused these pores to gradually disappear. They linked the rate of

surface area loss resulting from the destruction of the macropores to the $\text{SiO}_2/\text{AlO}_3$ content of the zeolites, with high silica materials decomposing more slowly.

The results of studies examining the effects of ball milling on zeolite properties suggest that milling can increase zeolite amorphous content, decrease particle size, and increase accessible porosity. Such changes should produce increased pozzolanic reactivity of the zeolite and improve the performance of zeolite-cement mixtures using milled zeolites [19–22]. However none of the studies in the literature examining milled zeolites actually tested milled zeolites in cementitious systems. Therefore, this study examined the effects of ball milling on zeolite properties, including external surface area, particle size, and crystallinity, and investigated the correlation between these properties and zeolite-cement mixture performance using milling techniques closer to those currently in use by the construction industry.

3 MATERIALS AND EXPERIMENTAL METHODS

3.1 Materials

Clinoptilolite zeolite, mined from Tilden, Texas, was used throughout this study. The zeolite was classified by the supplier as #30 (0.595 mm) mesh size, and was not treated or washed before delivery. The chemical composition, determined using x-ray fluorescence (XRF) is shown in Table 1.

An ASTM C150 [23] Type I/II Texas Lehigh cement, referred to hereafter as ‘ordinary portland cement’ (OPC), was used for all pastes and mortars 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 throughout this work to help differentiate between

improvements due to filler effect and those occurring as a result of the pozzolanic reaction. The particle size distributions of the OPC and quartz filler are shown in Figure 1. The particle size of the quartz filler was similar to the average particle size of the milled zeolite samples investigated in this study. An ASTM C109 [24] graded Ottawa sand, certified to meet the ASTM C778 [25] standard, was used for all mortars in this work.

3.2 Milling

Although several literature studies investigated the effect of milling on zeolites milled in high energy planetary mills, a simple rotational mill was chosen to mimic the conditions present in mills currently used to grind cement clinker or other SCMs such as metakaolin, since this type of milling would be more feasible to industrially implement. A low powder load of 30%, corresponding to a formal interstitial filling of the void spaces of the ball bed, was chosen to mimic the conditions present in industrial cement grinding mills [11]. Prior to milling, samples were dried at 105°C for 12 hours in a ceramic crucible. The mill was operated at 85 rpm, or 75% of the critical speed, similar to industrial cement ball mills. The zeolite was then milled for 1, 2, 4, 6, or 8 hours. In preliminary testing it was noticed that samples ground for longer than 2 hours became caked against the sides of the mill. This was believed to be a result of moisture released from the zeolite as particle size was reduced, so samples ground for longer than 2 hours were stopped at 2 hours of milling and dried for an additional 8 hours at 105°C to remove excess moisture from the system, then returned to the ball mill to continue milling.

3.3 Zeolite Physical and Chemical Characterization Testing

The zeolite physical and chemical properties were characterized in order to determine the changes resulting from milling and which of these factors contributed to changes in zeolite reactivity in cementitious systems. Characterization testing tracked changes in particle size, surface area and crystalline phases present in the zeolites.

X-ray diffraction (XRD) was used to determine what phases were present in each sample and to gauge the effectiveness of reducing crystallinity by milling. XRD samples were prepared by grinding the treated sample to a powder passing the No. 325 (44 μm) sieve using an agate mortar. Each specimen was then pressed into plastic XRD sample holders using a glass plate such that the plane of the specimen surface was even with the edge of the sample holder in order to create a specimen face in the focusing circle of the powder diffractometer [26]. 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 5-70° 2 θ with a step size of 0.2° 2 θ 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 0.15mm receiving slit and 0.6mm 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 zeolite were determined using files from the inorganic crystal structure database [27] and Jade MDI software package [28]. 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 [29].

Specific surface area was measured on zeolite samples before and after milling by nitrogen sorption using a Micromeritics ASAP 2020 Surface Area and Porosimetry Analyzer. Prior to measurement, zeolite samples and the sample tubes were individually weighed to microgram precision. The raw zeolite samples were then degassed for 12 hours at 100°C and a pressure of 500 μ mHg or less. Pretreated samples were degassed for 6 hours at 300°C and a pressure of 500 μ mHg or less. Samples were heated individually during degassing using a heating mantle with a Type K thermocouple controlled by the nitrogen adsorption testing software program. After degassing, samples were reweighed, and this value was used as the sample mass for analysis. Nitrogen adsorption was tracked using high purity nitrogen as the adsorbate with liquid nitrogen used as the coolant. All the values of the adsorbed volume reported at the isotherm are equal to the equivalent gas volume in standard pressure and temperature (273K, 1 atm). The surface area and pore size distribution were calculated from N₂ adsorption-desorption isotherms recorded at the temperature of liquid nitrogen (77K). Surface area was determined using the BET model [30] and pore size distribution with the BJH model [31]. 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. Due to the large internal surface area inherent in the zeolite crystal structure, surface area and particle size were assumed to be independent of each other for the purposes of this work.

Changes to material particle sizes were tracked in order to determine the effect of pretreatments on the particle size distribution of the zeolite, as well as the role particle size plays in the generation of zeolite-cement system properties. Particle size distributions

of the zeolites were measured before and after milling using a Malvern 2000 Laser Particle Size Analyzer. Enough sample was added to 1L 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 zeolites 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 an average particle size distribution data for each sample.

3.4 Zeolite Reactivity Testing

In this study two methods were used to track changes to zeolite pozzolanic reactivity after milling: 1) measurement of calcium hydroxide content of hydrated zeolite-cement pastes and 2) compressive strength development in zeolite-cement mortars. All pastes and mortar mixtures used a 20% replacement by mass of cement with zeolite.

The calcium hydroxide content of hydrated zeolite-cement pastes was determined for pastes using unmilled zeolite and zeolite milled for 0, 2, 4, 6 or 8 hours. The calcium hydroxide (also called portlandite) content of hydrated zeolite-cement pastes was determined for pastes using unmilled and milled zeolites, with a water to cementitious materials ratio (w/cm) of 0.4, and a 20% replacement by mass of cement with zeolite. Before the addition of water, the cement and zeolite were mixed together by hand for 30 seconds. The cement, 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 calcium hydroxide 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 calcium hydroxide (Ca(OH)₂) according to Equation 1 [32]:

It was assumed that one mole of calcium hydroxide was present for each mole of H₂O 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 calcium hydroxide present in the paste was normalized by the anhydrous cement content of the paste.

The influence of milling on compressive strength was tested on mortars of cement and either unmilled zeolite or zeolites milled for 0, 2 or 8 hours. All zeolite-cement mortars used a 20% substitution by mass of zeolite for cement. Mortars using a 20% substitution by mass of cement with a finely ground quartz were used to understand whether differences between zeolite-containing mortars and cement-only control mortars

were occurring due to a filler effect or from contributions of the zeolite [33]. 50 mm (2-in.) mortar cubes, mixed in accordance with ASTM C305 [34], were cast at a w/cm of 0.51, in order to provide adequate workability for the high water demand zeolite mixtures. The cubes were removed from the molds after 24 hours and stored in limewater at 23°C until tested. Compressive strengths were obtained 1, 3, 7, 28 and 90 days after mixing following the procedures of ASTM C109 [24].

3.5 Testing to Determine the Effects of Zeolite on Cement Hydration

Isothermal calorimetry was used to examine the effects of the milled zeolites on cement hydration kinetics. Testing was done on cement pastes with 0% or 20% zeolite mass replacement of cement for zeolite milled for 0, 2, 4, 6, or 8 hours. Heat evolution was tracked per gram of cement in a TAM AIR (Thermometric) calorimeter for 10g paste samples prepared with a w/cm of 0.4, and a 20% mass replacement of cement with zeolite. Samples were hand-mixed for two minutes and placed into vials according to ASTM C1679 [35]. Heat evolution was tracked for 72 hours.

Several parameters were investigated using isothermal calorimetry in order to understand how the incorporation of unmilled or milled zeolites affected cement hydration. These parameters include: 1) the slope of the rate of heat evolution versus time curve during the acceleration period, referred to in this work as the rate of reaction in the acceleration 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); 4) the magnitude of the rate of heat evolution at the peak; and 5) the cumulative heat released over 72 hours. In this

study, since the acceleration period was not 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. 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 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. The cumulative heat produced was calculated for each mixture using the heat release measured every three minutes by isothermal calorimetry and applying the trapezoidal rule. If milling improves zeolite interactions with cement hydration, increases in the rate of reaction during the acceleration period [36–38], decreases in the time to the start of the acceleration period and time to the maximum rate of heat release [37], an increased maximum rate of heat release [37] and greater cumulative heat evolved than for a comparable quartz-cement paste can be expected [39].

4 RESULTS

4.1 Physical and Chemical Characterization Testing Results

The crystalline phases present in the zeolite before and after milling are shown in Figure 2. Even after 8 hours of milling, crystalline phases in the zeolite appear unchanged.

Zeolite particle size distributions before and after milling are shown in Table 2 and Figure 3. Particle sizes were reduced progressively over 8 hours of milling with the most significant reduction taking place in the first 4 hours. From Figure 3 it can be seen that milling completely eliminated the coarsest fraction of the original zeolite material ($>500\text{ }\mu\text{m}$) and increased the proportion of material in the 2 nm and 20 nm diameter size fractions. Although particle sizes continued to decline slightly from 4 to 8 hours of milling, overall the particle size distribution stabilized after 4 hours of milling, with only slight increases in the volume of fines present in the system after 4 hours of milling.

The effect of milling on the nitrogen-accessible surface area of the zeolite is shown in Figure 4 and the materials' pore size distributions are shown in Figure 5. It is evident from Figure 4 that the surface area of the material is inversely correlated with particle size, as it trends upward until 2 hours of milling, at which time there are no further increases in surface area. Figure 5 confirms this hypothesis, as milling had little effect on the pore size distribution of the material.

4.2 Zeolite Reactivity Characterization Results

The pozzolanic reaction occurs when the silica present in a supplementary cementitious material (i.e. a pozzolan, and in this case, a zeolite) reacts with calcium

hydroxide, one of the primary products of cement hydration, to form additional C-S-H. Therefore, differences between the amount of calcium hydroxide present in the paste of a SCM-cement paste and an OPC cement paste can give quantifiable information on the ability of SCMs to react pozzolanically [39–41]. The reaction of calcium hydroxide to form C-S-H can also result in decreases in porosity and corresponding increases in strength [41]. Therefore, in this study, two methods were used to track changes to zeolite pozzolanic reactivity after milling: 1) measurement of calcium hydroxide content of hydrated zeolite-cement pastes and 2) compressive strength development in cement-zeolite mortars. The calcium hydroxide contents of hydrated pastes containing unmilled and milled zeolite are shown in Figure 6. The pastes containing unmilled zeolite showed evidence of the pozzolanic reaction, with the unmilled zeolite-cement pastes having lower calcium hydroxide contents than both the sample using inert quartz filler and the cement-only paste. Antoni et al. [42] showed that a quartz filler increased the amount of calcium hydroxide produced compared to a cement-only paste because it allows more space for hydration product growth. The same effect is shown in Figure 6 for the quartz-cement paste sample. The reduction in calcium hydroxide content compared to the quartz filler sample is due to the pozzolanic reaction of the added zeolite. The greater increase in calcium hydroxide content from 28 to 90 days in the zeolite-cement pastes compared to the cement-only paste indicates that the pozzolanic contribution of the zeolite has either been completed, or at least considerably slowed, prior to 90 days.

As far as the relationship between mill time and pozzolanicity of the zeolite is concerned, milling the zeolite for 1 hour did not change the zeolite pozzolanicity relative to the unmilled zeolite. The zeolite milled for 1 hour showed the same

magnitude of reduction of calcium hydroxide as the unmilled sample. Milling times greater than 1 hour were successful in improving the calcium hydroxide consumption of the zeolite, with calcium hydroxide contents of the 28-day samples lower than for the paste with unmilled zeolite. Milling for 4 hours further increased the calcium hydroxide consumption, however further improvements were not seen with mill times greater than 4 hours, as expected since the particle size was not changed with extended milling.

The effect of milling on the compressive strengths of the zeolite-cement mortars is shown in Figure 7. Milling the zeolite increased the compressive strengths of the mortars at all ages compared to the unmilled zeolite mortar. However, the zeolite milled for 8 hours generated significantly more compressive strength in a mortar than the zeolite milled for 2 hours. Strengths of the zeolite-cement mortars were initially lower than or equal to strengths generated by mortars containing a similar replacement level of a quartz filler, however the strengths of the unmilled zeolite-cement mortars exceeded that of the quartz filler mortars after 28 days, while the strengths of the milled zeolite-cement mortars exceeded the quartz filler mortars after only 7 days.

4.3 Influence of Milled Zeolites on Cement Hydration Testing Results

The effects of milled zeolite on cement hydration kinetics are shown in Figure 8 to 11. Both the unmilled and milled zeolites decreased the time to the start of the acceleration period and also decreased the time to the maximum rate of heat release compared to the cement-only paste (Figure 9), likely through contribution of C-S-H nucleation sites. It is apparent, however, from Figure 11 that the zeolites do not behave at early ages merely as inert fillers, as their influence on the rate of and quantity of heat

released is significantly greater than the quartz filler-cement paste regardless of the particle size of the zeolite. Other researchers have suggested that this effect is due to increased adsorption of Ca^{2+} on zeolite surfaces, resulting in more rapid dissolution of C_3S and growth of C-S-H [43].

Despite increasing the rate of nucleation of cement hydration products, overall the unmilled zeolite may have hindered the total extent of cement hydration, evidenced by the lower maximum rate of heat released by the cement compared to the cement-only paste (Figure 10), and lower rate of reaction in the acceleration period (Table 3). In contrast, the pastes using milled zeolites generated greater rates of heat release per gram of cement than the cement-only paste, the quartz filler paste and the unmilled zeolite-cement paste. Longer milling times correlated with greater reductions in times to the end of the induction period and the time to peak rate of heat release. Milled zeolites also increased the rate of reaction during the acceleration period compared to the cement-only, quartz and unmilled zeolite-cement pastes (Table 3). Similar to the results seen with the calcium hydroxide testing, initial milling for one and two hours resulted in increases in the rate of reaction during the acceleration period. Additional milling, for 4 hours, further increased the slope of the acceleration period but the rates of reaction during the acceleration period of the 4, 6 and 8 hour milled zeolite-cement pastes were equivalent, as expected from their similar particle size distributions. Time of milling did not seem to make a significant difference in the magnitude of the maximum rate of heat release, shown in Figure 8 and Figure 10, as all milled samples had similar maximum rates. Similarly, Figure 11 shows that, except for the paste using zeolite milled for 8 hours, all milled zeolite-cement pastes produced similar amounts of heat over 72 hours.

5 DISCUSSION OF THE EFFECTS OF MILLING ON ZEOLITE POZZOLANIC REACTIVITY

The goal of the ball milling was to improve the properties of the zeolite to allow it to react faster or more completely as a pozzolan, resulting in improved performance in cementitious systems. It was hypothesized that milling would result in reduced particle sizes, increased porosity, and a loss of zeolite crystallinity, creating a more reactive material. The literature suggests that milling substantially reduces zeolite crystallinity with very short durations of milling [8,9,11,13,17,18]. However, nearly all of the studies of milled zeolites to date employed planetary ball mills capable of much greater forces than cylindrical ball mills with only a single axis of rotation, such as the mill used in this work and by the cement industry. It is evident from the XRD results shown in Figure 2 that the forces imposed on the zeolites in a horizontal rotary ball mill were not high enough to cause a reduction in zeolite crystallinity as in the studies using high energy planetary ball mills.

Although milling did not reduce the zeolite crystallinity, it did significantly reduce particle size, leading to increased surface area of the zeolite, as shown in Table 2 and Figure 3 and 4. Contrary to previous work that showed that milling increased porosity through the creation of macropores [9], very little change occurred in the pore sizes of the material, shown in Figure 5, and it can be assumed that the increases in surface area in this work occurred only as a result of the reductions in particle size.

Performance tests on the milled zeolite showed that the pozzolanicity of the zeolite was increased by milling, with milling for four hours corresponding to an average particle size (d_{50}) of 9 μm or less, resulting in the greatest gains in reactivity. Shown in

Figure 6, zeolite milled for 2 hours or more reduced paste calcium hydroxide content relative to unmilled zeolite. However, milling for greater than 4 hours generated no additional calcium hydroxide reduction. This is as expected, as pastes using the zeolites milled for 4, 6 and 8 hours had similar particle size distributions. In addition to the effect from reduced particle sizes, surface area increases were also found to correlate with decreased calcium hydroxide content of the zeolite-cement pastes. However, as increases in surface area were deemed to occur as a result of reductions in particle size, surface area is not believed to itself be the primary driver of calcium hydroxide content reductions.

Evidence of increased pozzolanic reactivity with milling was also shown in the increased compressive strengths of the zeolite-cement mortars. Milled zeolite-cement mortars, shown in Figure 7, yielded significant increases in compressive strengths compared to the unmilled zeolite, as early as 7 days after casting. Similar to the calcium hydroxide testing results, milling for 8 hours did not increase the long term pozzolanic reactivity of the zeolite (as demonstrated by compressive strength) compared to milling for 2 hours, as the 90 day compressive strengths of the mortars containing zeolite milled for 2 or 8 hours were not significantly different. Therefore, particle size seems to play a large role in determining the extent of the pozzolanic reactivity of the milled zeolites.

However, particle size and filler effects [42] do not entirely explain zeolite performance as increased milling time did increase the rate of strength development despite the similar particle size distributions of the two samples. Other researchers have concluded that milling can result in breakage of the surface Si-O-Si and Si-O-Al bonds of the zeolite structure [8,13] and this may have played a role in increasing the initial

strength development rate of the zeolite-cement mortars. Longer milling times may have generated greater quantities of broken Si-O and Al-O bonds, enabling the zeolite crystal structure to more easily dissolve and react than with unmilled zeolites and zeolites milled for shorter times which may lack, or have fewer, broken chemical bonds. However, testing the surface characteristics of the zeolites after milling is beyond the scope of the work presented here.

In addition to increased pozzolanic reactivity, milled zeolites also contributed an accelerating effect to cement hydration reactions, decreasing both the time to the start of the acceleration period as well as the time of the maximum alite reaction peak, shown in Figures 8 to 10. These times decreased corresponding to the particle size, with the largest reductions in time seen in the 8 hour milled zeolite. The rates of nucleation and growth, expressed by the slope of the acceleration period and peak rate of heat release values shown in Table 3 and Figure 10, were also increased for all milled zeolites relative to both the cement-only, quartz filler and the unmilled zeolite-cement pastes. Both of these effects are similar to effects seen in the literature with the use of very fine inert quartz fillers [44,45], finer than the one used in this study. However, the length of the hydration reactions during the deceleration period was much shorter for the milled-zeolite pastes compared to the quartz filler-paste. This may indicate that the zeolite particles initially act as nucleating agents, speeding up the timing and rate of reactions, but are not contributing to the dilution effect often seen with fillers which tend to extend the magnitude of hydration during the first 72 hours [39].

6 CONCLUSIONS

Natural zeolite was milled using a ball mill in order to mimic a pretreatment that could be implemented in the field using existing industrial SCM and cement clinker ball mills [11,52]. Zeolite was milled for 1, 2, 4, 6, or 8 hours and characterized to determine the changes with ball milling to zeolite crystallinity, particle size, surface area, and porosity. Performance was determined by measuring the calcium consumption in a calcium hydroxide solution, tracking reductions in calcium hydroxide in zeolite-cement pastes due to the pozzolanic reaction, and testing the compressive strengths of zeolite-cement mortars. The effect of milling on early age cement hydration was also investigated.

Ball milling of zeolites significantly improved the performance of the zeolite used in cementitious mixtures, increasing the pozzolanic reactivity of the zeolites as well as increasing compressive strengths of mortars containing milled zeolites. Milled zeolites also accelerated cement hydration reactions, seen in isothermal calorimetry, and increased the maximum rate of heat release of the milled zeolite-cement mixtures. Milling zeolites for four hours or longer, corresponding to an average particle size (d_{50}) of 9 μm or less, yielded the greatest gains in reactivity. These improvements were primarily due to decreased particle sizes with milling, but undetected chemical changes to the zeolites with increased mill times may have also contributed to the enhanced performance seen in ball milled zeolite-cement mixtures.

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Black and white figures for printed paper version.

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

Figure 2 - Crystalline phases in the zeolite sample before and after milling. C = clinoptilolite zeolite $[(Na,K,Ca)_{2-3}Al_3(Al,Si)_2Si_{13}O_{12} \cdot 12H_2O]$, Cr = cristobalite (SiO_2), M = montmorillonite $[(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O]$ Q = quartz (SiO_2). Numbers in parenthesis indicate the d-spacing of the reflection.

Figure 3 - Volumetric particle size distribution of unmilled and milled zeolite.

Figure 4 - Nitrogen available surface area of the unmilled and milled zeolite.

Figure 5 - Pore size distribution of unmilled and milled zeolite.

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615 **Figure 6 - Calcium hydroxide (CH) content by weight of hydrated cement pastes containing 80-100%**
 616 **OPC and 0-20% unmilled or milled zeolite or quartz filler (w/cm = 0.4).**

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618 **Figure 7 - Compressive strengths of cement mortars containing 80-100% cement and 0-20% of unmilled**
 619 **zeolite, milled zeolite, or a quartz filler (w/cm = 0.51).**

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Figure 8 - Isothermal calorimetry (23°C) results of pastes with 80-100% cement and 0-20% unmilled zeolite, milled zeolite, or quartz filler (w/cm = 0.4).

Figure 9 - Time to the end of the induction period and time to the maximum value of heat flow in isothermal calorimetry (23°C) of pastes with 80-100% cement and 0-20% unmilled or milled zeolite (w/cm = 0.4).

Figure 10 - Value of the maximum heat flow in isothermal calorimetry (23°C) of pastes with 80-100% cement and 0-20% unmilled or milled zeolite (w/cm = 0.4).

Figure 11 - Cumulative heat over 72 hours during isothermal calorimetry (23°C) of 80-100% cement and 0-20% unmilled zeolite, milled zeolite, or quartz filler pastes (w/cm = 0.4).

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

Oxide	Zeolite	OPC
SiO ₂	62.23	19.36
Al ₂ O ₃	11.88	5.13
Fe ₂ O ₃	1.12	2.53
CaO	2.21	63.17
MgO	0.64	1.03
SO ₃	-	3.22
Na ₂ O	1.00	0.09
K ₂ O	1.68	0.88

Table 2 - Summary of zeolite particle size distributions before and after milling

Mill Time (hrs)	Particle Sizes (µm)		
	d ₁₀	d ₅₀	d ₉₀
Unmilled	12.8	77.4	408.6
1	2.6	25.1	111.7
2	2.0	13.9	42.3
4	1.7	9.0	29.5
6	1.7	7.8	25.7
8	1.6	6.9	24.3

Table 3 - Acceleration period slope in isothermal calorimetry (23°C) of pastes with 80-100% cement and 0-20% unmilled zeolite, milled zeolite, or quartz filler (w/cm = 0.4).

SCM/filler	Acceleration Period Slope (mW/g/hr)
None	0.66±0.05
Quartz	0.64±0.03
Unmilled zeolite	0.60±0.11
Milled 1 hr zeolite	0.76±0.06
Milled 2 hrs zeolite	0.77±0.10
Milled 4 hrs zeolite	0.83±0.08
Milled 6 hrs zeolite	0.85±0.12
Milled 8 hrs zeolite	0.83±0.07