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Properties of alkali-activated clinoptilolite

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Abstract

Materials made by hydrating the natural zeolite clinoptilolite with calcium hydroxide ($Ca(OH)_2$) have been characterised and compared to other alkali-activated waste-derived and naturally occurring pozzolana. Compressive strength is dependent on the $Ca(OH)_2$ content, clinoptilolite particle size, and curing conditions. Optimising each of these factors has produced compacted materials containing 20 wt.% $Ca(OH)_2$ with average compressive strengths of 38.7 MPa. Capillary rise tests have been used to determine sorptivity coefficients of dry samples that range from 0.027 to 0.087 cm $min^{-1/2}$ depending on the alkali addition and the clinoptilolite particle size. Sorptivity depends on the $Ca(OH)_2$ content and reducing the clinoptilolite particle size reduces sorptivity but increases the level of water accessible porosity. X-ray diffraction (XRD) confirms that $Ca(OH)_2$ is consumed during curing and that it is not present in high strength, fully cured materials. Scanning electron microscopy combined with energy dispersive X-ray (SEM–EDX) analysis indicates the formation of hydration products with Ca/Si ratio in the range 0.8–1.2 and that a significant amount of unreacted clinoptilolite remains in optimised materials. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Pozzolanas react with lime and water to form insoluble hydration products and consist predominantly of silica and alumina [1]. They may also undergo pozzolanic reactions when mixed with materials that release lime during hydration such as ordinary Portland cement (OPC) [2]. Partial replacement of OPC by pozzolana in concrete can decrease porosity and sorptivity, resulting in improved long-term durability and the use of pozzolana in concrete mixes is increasing [3]. Natural and artificial pozzolana are also being increasingly considered for use in environmental protection applications, such as in barriers to contaminant migration and as binders in waste solidification systems. This is because they are often readily available in regions where the use of more conventional materials such as OPC may not be economically viable [4,5].

Zeolites are crystalline aluminosilicates with a three-dimensional framework structure based on repeated units of silicon–oxygen (SiO_4) and aluminium–oxygen (AlO_4) tetrahedra. They contain exchangeable alkaline and alkaline earth metal cations such as Na^+, K^+, Ca^{2+}, and Mg^{2+} that maintain charge neutrality. The microporous crystalline structure of zeolites is able to adsorb species that have diameters that fit through surface entry channels, while larger species are excluded, giving rise to molecular sieving properties that are exploited in a wide range of commercial applications. These include the use of natural zeolites in water and air filtration, pollution, and odour control, animal hygiene, aqua-culture, pond filtration, soil amendment, and as an industrial filler and dietary supplement in animal feeds [6].

Clinoptilolite is a naturally occurring zeolitic pozzolana. Its use as a mineral admixture in concrete has been reported in China, Greece, and Bulgaria [7–9]. It has also found application in the recovery of Cs from radioactive wastewater and ammonia from municipal wastewater [10]. The use of natural zeolites in the treatment of metal contaminated effluents has recently been reviewed [11]. Previous investigations on clinopti-

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Table 1
Chemical composition (oxide percent) of the clinoptilolite used in this investigation and other pozzolanic materials (from Massazza [3])

	Clinoptilolite	Natural pozzolanas range	Siliceous fly ashes range	Calcareous fly ashes range	Blast furnace slags range
SiO_2	67.9	50–75	47–54	18–25	30–40
Al_2O_3	11.9	10–20	28–35	12–15	5–17
Fe_2O_3	1.2	3–9	4–12	6–8	0.2–1.0
MgO	1.1	2–9	1–4	43–49	0.3–1.0
CaO	3.8	1–6	1–2.5	2–3	35–48
Na_2O	0.4	1–3	0.2–2	2.5	
K_2O	1.5	2–7	1–6	2.5	

lolite have reported particularly effective removal of lead, cadmium, thorium, and ammonia from effluents [12–14].

This work reports on the properties of materials made by alkali activation of clinoptilolite using calcium hydroxide ($Ca(OH)_2$). It forms part of a wider study aiming to develop alternative solidification binder systems for treating industrial wastes in Mediterranean countries. Clinoptilolite was identified as a potential solidification binder as it is readily available in some parts of Greece, where OPC is generally considered to be prohibitively expensive for use in this type of waste treatment process. The effects of the amount of $Ca(OH)_2$ added, clinoptilolite particle size and curing time and temperature on compressive strengths and microstructure are reported, as these are considered to be the main processing parameters likely to control the properties of natural zeolite cement pastes [15]. In addition, cured samples have been subjected to capillary rise tests, as moisture transport in porous media is important in many processes of environmental and technological concern. These allow sorptivity coefficients to be determined and have also been used to indicate the amount of water-accessible porosity [16,17]. The effects of the addition of real and synthetic metal containing wastes to alkali-activated clinoptilolite is the subject of further research.

2. Experimental

2.1. Materials and sample preparation

The clinoptilolite used throughout this work was obtained from natural deposits in Greece. The chemical composition was determined by acid digestion followed by analysis using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The total content of SiO_2, Al_2O_3, and Fe_2O_3 in the clinoptilolite was found to be approximately 81%, and this is typical of some other pozzolanic materials such as fly ash and blast furnace slag, as shown in Table 1.

Alkali-activated samples were prepared by mixing clinoptilolite and reagent grade $Ca(OH)_2$ (Fisher Scientific) with sufficient distilled water to produce an initial water:solids (w/s) ratio of 0.3. Cylindrical samples, 20 mm high and 20 mm in diameter were produced by compacting the damp powder at 16 MPa, as this greatly reduced variability in compressive strength and sorptivity data, allowing trends in the properties to be clearly identified. Compaction caused some water loss from samples and this varied slightly with clinoptilolite particle size (Table 2). The pressed samples were wrapped in a double layer of cling film and parafilm to minimise exposure to CO_2 and water loss through evaporation and were cured in a temperature-controlled chamber.

2.2. Methods

Unconfined compressive strengths (UCS) was measured using an Amsler test machine at a loading rate of 0.06 k Ns^{-1}. Results are presented as the mean and standard error of replicate samples (*n* as indicated). The statistical significance was determined using analysis of variance and Tukey's honestly significant difference (THSD) test with significance determined at the 5% level.

Samples for capillary rise tests were dried overnight at 105°C, weighed, and placed on a stack of filter papers (Whatman No.1) that were saturated with distilled water, as shown schematically in Fig. 1. The increase in sample

Table 2
Sorptivity, water accessible porosity, and strength data for alkali-activated clinoptilolite compacted at 16 MPa and cured for 28 days at 50°C (initial w/s = 0.3)

Clinoptilolite particle size range (μm)	$Ca(OH)_2$ content (%)	Final w/s ratio	Sorptivity (cm min$^{-1/2}$)	Water accessible porosity (%)	As-pressed density (g cm^{-3})	Average compressive strength (MPa)
< 150	5	0.23	0.084	39.7	1.36	18.8
< 150	10	0.24	0.054	40.6	1.36	37.1
< 150	20	0.25	0.040	41.5	1.35	38.7
< 150	30	0.26	0.039	44.0	1.36	36.9
< 150	50	0.26	0.030	42.7	1.37	33.0
500–1000	20	0.20	0.087	34.7	1.44	3.6
250–500	20	0.23	0.041	36.2	1.40	7.8
150–250	20	0.24	0.032	37.0	1.36	10.6
45–75	20	0.25	0.027	39.5	1.32	13.8
OPC compacted at 16 MPa, w/c = 0.3			0.021	24.1	2.09	81.2
OPC paste (not compacted), w/c = 0.3			0.029	28.8	1.60	48.5

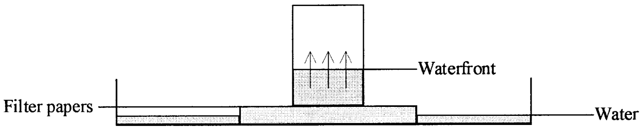

Fig. 1. Schematic diagram of capillary rise test.

weight due to water absorption was recorded over periods up to 24 h. Sorptivity coefficients, S, were then calculated from:

$$\Delta W/A = St^{1/2} + S_o \quad (1)$$

where ΔW is the increase in sample weight due to absorbed water, A is the surface area of the sample exposed to water, t is time, and S_o is a correction term that accounts for surface effects when the specimen is initially placed in contact with the water. S is therefore the slope of the $\Delta W/A$ vs. $t^{1/2}$ graph and was determined using least squares analysis. The maximum water uptake, $\Delta W_{\max}$, at the end of capillary rise tests was used to indicate the volume of 'water-accessible' porosity. Tests were generally run at least in duplicate and were found to give highly reproducible results.

Samples for X-ray diffraction (XRD) were dried overnight at 105°C, ground to less than 70 μm, and analysed using a Phillips PW 1710 diffractometer with Cu anode, between angles of 5° and 100° 2θ, at a rate of 2.4° min^{-1}. Peak intensities were compared to give qualitative information on the relative amounts of clinoptilolite and $Ca(OH)_2$.

Scanning electron microscopy combined with energy dispersive X-ray (SEM–EDX) analysis used a JEOL JSM 35-CF scanning microscope with a Princeton Gamma-Tech Prism digital spectrometer with PGT IMIX software. Samples were embedded in epoxy resin, polished, and coated with carbon. Back-scattered electron (BSE) images covering approximately 3.76 mm^2 of sample surface were thresholded to provide approximate area data for clinoptilolite, $Ca(OH)_2$, and hydration products.

2.3. Effect of $Ca(OH)_2$ addition

Clinoptilolite with particle size of <150 μm was mixed with $Ca(OH)_2$ additions between 0% and 50% (w/w). Compacted samples were cured at 50°C for 28 days and tested for UCS and identically prepared samples were also used for capillary rise testing. Crystalline phases were analysed by XRD and samples were examined using SEM–EDX).

2.4. Effect of curing time and temperature

The effect of curing time and temperature on UCS was investigated on 20% $Ca(OH)_2$ mixes that were cured at 13°C, 25°C, and 50°C for periods up to 180 days.

2.5. Clinoptilolite particle size

The as-received clinoptilolite was ground to produce powders with different particle size fractions. These were mixed with 20% w/w $Ca(OH)_2$ at an initial w/s ratio of 0.3, compacted at 16 MPa and cured at 50°C for 28 days prior to UCS and capillary rise testing. Water loss during compaction was recorded to determine the final w/s ratio in the cured samples.

3. Results

Table 2 shows sorptivity, water accessible porosity and compressive strength data for samples containing different $Ca(OH)_2$ contents and different clinoptilolite particle size fractions. Data for compacted and non-compacted cement pastes tested under the same conditions is also included for comparison.

3.1. Compressive strength data

The effect of $Ca(OH)_2$ content on the compressive strengths of clinoptilolite with particle size <150 μm, cured at 50°C for 28 days is shown in Fig. 2. Increasing the $Ca(OH)_2$ from 5% to 10% increased the average UCS from 18.8 to 37.1 MPa. The highest mean UCS value of 38.7 MPa was achieved at 20% $Ca(OH)_2$, although this was not significantly different from the strengths of the 10%, 30%, and 50% samples. These compressive strengths are comparable to those reported for other alkali-activated pozzolana systems such as lime–slag and fly ash, calcined kaolinitic clays, and lime–sugar cane straw ash [18–21]. It is recognised that compressive strength depends on sample preparation method and that this can make it difficult to directly compare strength data from studies using different alkali-activated pozzolana. However, the results do indicate that strength forming pozzolanic reactions occur when clinoptilolite is hydrated with $Ca(OH)_2$ and that significant strengths can be achieved.

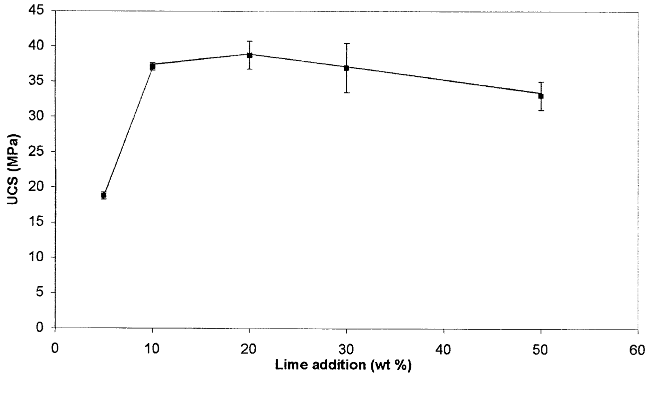

Fig. 2. Effect of $Ca(OH)_2$ addition on UCS of clinoptilolite samples cured at 50°C for 28 days.

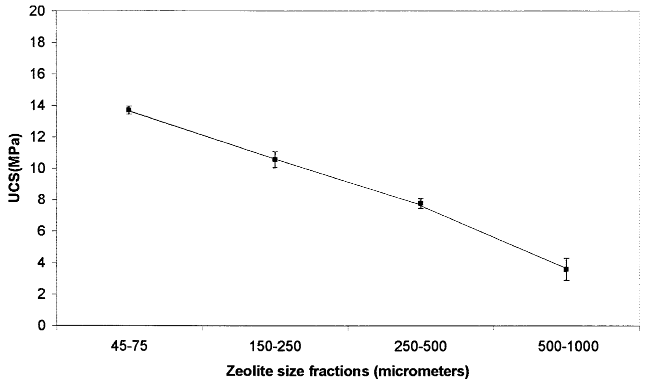

Fig. 3. Effect of particle size on 28 day UCS of clinoptilolite samples containing 20% (w/w) $Ca(OH)_2$ cured at 50°C.

The effect of clinoptilolite particle size on UCS is shown in Fig. 3 and Table 2. Maximum strengths of 13.8 MPa were obtained for clinoptilolite samples with particle size between 45 and 75 μm. This was significantly lower than obtained for samples ground to <150 μm and this difference is assumed to result from the improved particle packing in the <150 μm sample. This is reflected in the high density of the as-pressed <150 μm samples, although the coarse zeolite samples were also characterised by high density but low strength, as seen in Table 2.

The effect on UCS of curing time and temperature is shown in Fig. 4. Mixes cured at 50°C for 7 days were approximately five times as strong as those cured at 13°C and were significantly stronger than those cured at 25°C. After longer curing times the strength differences between the 50°C- and 13°C-cured mixes remained, but after 90 days there was no significant difference between mixes cured at 25°C and 50°C. Improved rates of strength development due to thermal activation of this type are reported to be a characteristic of pozzolana [22].

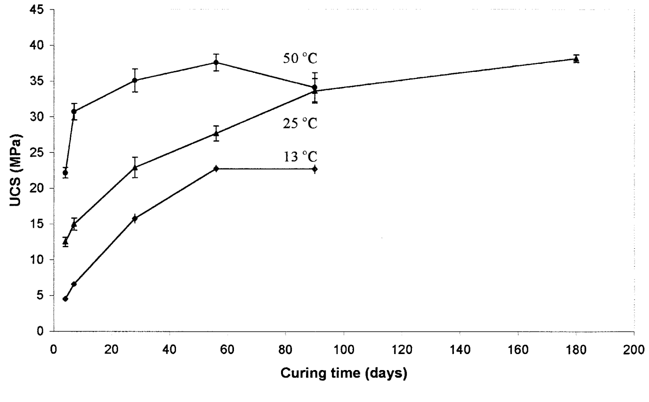

Fig. 4. Effect of curing time and temperature on the UCS of clinoptilolite, 20% (w/w) $Ca(OH)_2$ samples compacted at 16 MPa.

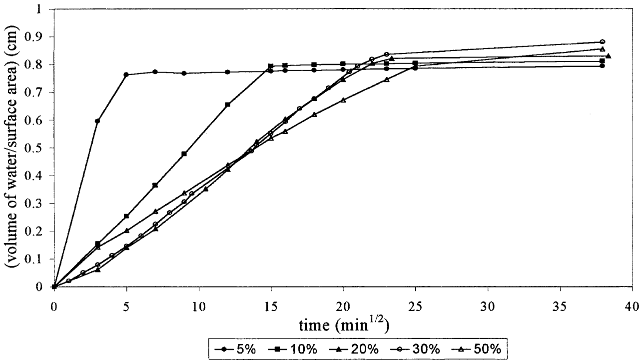

Fig. 5. Capillary rise test data for clinoptilolite (<15 μm) samples containing different $Ca(OH)_2$ contents. Samples were cured at 50°C for 28 days.

3.2. Capillary rise data

Capillary rise test data for mixes containing different $Ca(OH)_2$ content samples is given in Fig. 5 and shows an initial approximately linear relationship between water uptake per unit area (W/A) and $t^{1/2}$. Sorptivity coefficients calculated using Eq. (1), are given in Table 2 that also contains comparative sorptivity data obtained from identical tests completed on compacted and non-compacted OPC pastes with a 0.3 w/c ratio.

The sorptivity of alkali-activated clinoptilolite decreased with increasing $Ca(OH)_2$, indicating a reduction in average pore radii and increased pore tortuosity as hydration products form. Sorptivities ranged from approximately 0.03 to 0.084 cm $min^{-1/2}$ and were significantly higher than the values obtained for the compacted and non-compacted OPC pastes of 0.021 and 0.029 cm $min^{-1/2}$, respectively.

The effect of changing the clinoptilolite particle size is shown in Fig. 6 and Table 2. Reduction in particle size is associated with reduced sorptivity, increased strength but

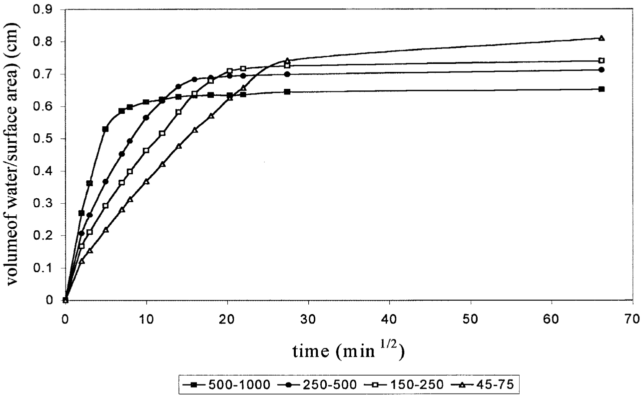

Fig. 6. Capillary rise test data for clinoptilolite samples containing different particles size range (μm). All samples contained 20% $Ca(OH)_2$ and were cured at 50°C for 28 days.

increased levels of water accessible porosity. Sorptivity is reported to be proportional to the square root of the capillary pore radius [23]. Therefore, the effective capillary pore radius in these samples is believed to fall by a factor of approximately 10 on reducing the clinoptilolite particle size from 500–1000 to 45–75 μm. The level of water accessible porosity is determined by the total capillary porosity. This includes a significant contribution from very fine water accessible porosity associated with the pozzolana hydration products. The sorptivity results indicate that the level of this fine porosity and therefore the amount of hydration increases with decreasing particle size, and this may be a result of the changing water content in these samples.

3.3. Microstructural analysis

A typical SEM micrograph of a region of a 20% $Ca(OH)_2$-activated clinoptilolite sample cured for 28 days at 50°C is shown in Fig. 7. Significant amounts of unreacted clinoptilolite remain surrounded by what appear to be relatively dense hydration products. SEM–EDX analysis confirms that the Al/Si mole ratio in the unreacted clinoptilolite grains were similar to the values of 0.2 derived from bulk analysis. However, the Ca/Si mole ratios ranged from 0.07 to 0.14, and this indicates elevated Ca content compared to the as-received zeolite. The Ca/Si ratio in the surrounding hydration products ranged between 0.77 and 1.22, with Ca concentrations tending to increase with distance away from the unhydrated zeolite. This ratio is significantly lower than normally found in OPC where values are typically around 1.7 [24]. Low Ca/Si ratios suggest that the equilibrium hydration products are likely to be C-S-H and SiO_2 gel and these phases are reported to produce a more acid resistant materials [25]. Analysis of BSE images of polished surfaces confirmed that unreacted clinoptilolite represented an area fraction of approximately 60–70%, compared to 23–40% for hydration products. No significant levels of $Ca(OH)_2$ were detected.

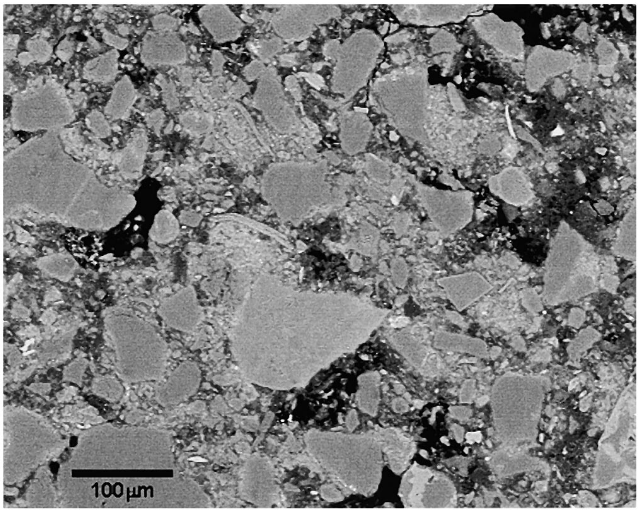

Fig. 7. SEM micrograph of 80% clinoptilolite, 20% $Ca(OH)_2$ (w/w) hydrated for 28 days at 50°C.

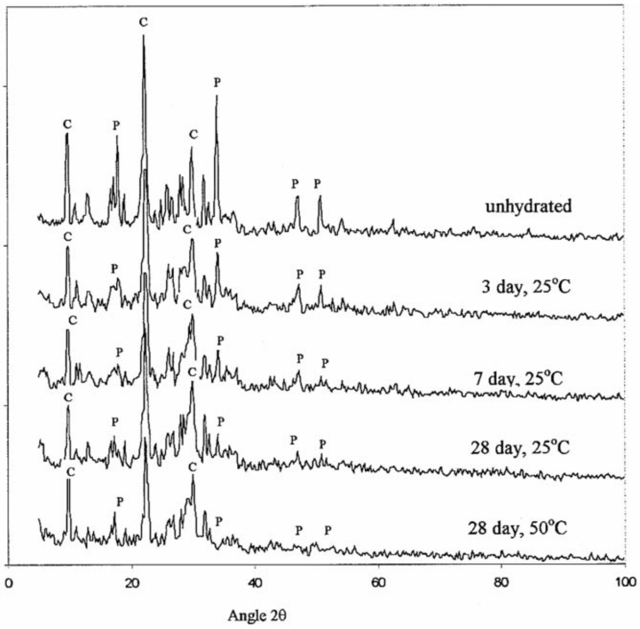

Fig. 8. XRD traces of 80:20 (%w/w) unhydrated clinoptilolite and $Ca(OH)_2$ (top), and hydrated samples cured for 3, 7, and 28 days at 25°C and 28 days at 50°C. The main peaks of clinoptilolite, C, and $Ca(OH)_2$, P, are shown.

XRD data of an unhydrated 80:20 mix of clinoptilolite and $Ca(OH)_2$ is compared to samples with the same composition that had been cured for 3, 7, and 28 days at 25°C in Fig. 8. Hydration is clearly associated with consumption of $Ca(OH)_2$ and reduction in the relative intensity of clinoptilolite peaks. Fig. 8 also presents data for the same composition cured for 28 days at 50°C and this shows that under these curing conditions the $Ca(OH)_2$ peaks are significantly reduced.

The observation that clinoptilolite is surrounded by low Ca/Si ratio hydration products in a relatively high sorptivity matrix suggests that alkali-activated clinoptilolite may form suitable materials for use where selective uptake of migrating heavy metal ions is required. Although it is known that natural zeolites are added to some proprietary cement-based waste solidification binder systems, their use as binder materials for waste containment has not been reported. The development of appropriate waste solidification/stabilisation systems based on the use of natural zeolites is the subject of ongoing research.

4. Conclusions

Alkali activation of the natural zeolite clinoptilolite can produce materials with high compressive strengths. The physical properties depend on sample preparation method, curing conditions, clinoptilolite particle size, and level of alkali addition. High strength samples contain unhydrated clinoptilolite particles surrounded by a low Ca/Si ratio matrix. The potential for using these materials in a range of environmental protection applications is currently being investigated.

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