



# Early age hydration and pozzolanic reaction in natural zeolite blended cements: Reaction kinetics and products by *in situ* synchrotron X-ray powder diffraction

R. Snellings<sup>a,\*</sup>, G. Mertens<sup>a</sup>, Ö. Cizer<sup>b</sup>, J. Elsen<sup>a</sup>

<sup>a</sup> Department of Earth and Environmental Sciences, Katholieke Universiteit Leuven, Celestijnenlaan 200E, B-3001 Heverlee, Belgium

<sup>b</sup> Department of Civil Engineering, Katholieke Universiteit Leuven, Kasteelpark Arenberg 40, B-3001 Heverlee, Belgium

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## ABSTRACT

The *in situ* early-age hydration and pozzolanic reaction in cements blended with natural zeolites were investigated by time-resolved synchrotron X-ray powder diffraction with Rietveld quantitative phase analysis. Chabazite and Na-, K-, and Ca-exchanged clinoptilolite materials were mixed with Portland cement in a 3:7 weight ratio and hydrated *in situ* at 40 °C.

The evolution of phase contents showed that the addition of natural zeolites accelerates the onset of C<sub>3</sub>S hydration and precipitation of CH and Aft. Kinetic analysis of the consumption of C<sub>3</sub>S indicates that the enveloping C–S–H layer is thinner and/or less dense in the presence of alkali-exchanged clinoptilolite pozzolans. The zeolite pozzolanic activity is interpreted to depend on the zeolite exchangeable cation content and on the crystallinity. The addition of natural zeolites alters the structural evolution of the C–S–H product. Longer silicate chains and a lower C/S ratio are deduced from the evolution of the C–S–H *b*-cell parameter.

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## 1. Introduction

The contemporary cement industry has faced with the challenge of producing more sustainable, less energy intensive and more durable products without sacrificing the mechanical properties of the end product. One of the most widespread developments with limited interference in the conventional production process is the blending of supplementary cementitious materials or pozzolans with Ordinary Portland Cement (OPC) [1]. The replacement of a specific amount of cement clinker with pozzolans results in a proportional decrease in the economic and environmental cost of the end product. Moreover, the use of pozzolans in blended cement and concrete applications has been observed to significantly improve the cement durability, especially the vulnerability to chemical attack or alkali-aggregate reaction can be mitigated [2].

The broad group of pozzolanic materials consists mainly of (alumino-)silicate materials which share the ability to combine with portlandite (Ca(OH)<sub>2</sub>) in the presence of water to form reaction products with binding properties in a process designated as the pozzolanic reaction [3]. Among these materials are industrial by-products such as slags, fly-ashes and microsilica, but also naturally occurring materials such as vitreous pumice, diatomite earths and zeolitised tuffs [2]. Zeolite tuffs are the diagenetically altered counterparts of vitreous pumice and occur in abundant quantities in areas of recent or ancient volcanism. As the deposited volcano-sedimentary sequences have frequently experi-

enced diagenetic zeolitisation, zeolite tuffs represent probably one of the most abundant natural sources of pozzolanic material [4]. Zeolites belong to the tectosilicate mineral group and are build up by a framework of corner-sharing (alumino-)silicate tetrahedra. The framework is arranged as such to form a microporous structure with large cages (diameters of less than 2 nm) connected into channels. The resulting voids are occupied by water molecules and metal cations to compensate for the substitution of Si<sup>4+</sup> by Al<sup>3+</sup> in the framework. The extra-framework species are weakly bound to the framework and are exchangeable. The zeolite crystals occurring in diagenetically altered tuffs are generally very fine-grained (crystal size typically 10–100 μm) and show important concentrations of crystal defects. In contrary, hydrothermally precipitated zeolite crystals occurring in vugs and geodes can grow up to cm-sizes and possess few defects.

The reactivity of pozzolans or pozzolan activity is generally conceived as the rate of the pozzolanic reaction and is usually measured in terms of the evolution of the portlandite weight fraction or of the Ca<sup>2+</sup> concentration in the pore solution over time [3,5]. Natural zeolite tuffs have shown to be more reactive than chemically similar unaltered vitreous pumice or tephra [6]. Moreover, zeolite tuffs presented a superior pozzolanic activity over many widely used industrial by-products such as fly-ashes and blast-furnace slags [7–9]. Especially the higher specific surface area available for reaction and the open zeolite structure have been suggested to contribute increased reactivity [6,10,11]. In addition to these factors, the absolute zeolite content of the pozzolanic material and the zeolite crystal chemistry, i.e. the framework Si/Al ratio and the exchangeable cation content, were observed to influence both long and short-term reactivity, respectively. Zeolites with an elevated Si/Al ratio showed higher long-term pozzolan

\* Corresponding author. Tel.: +32 16 327593; fax: +32 16 326401.  
E-mail address: [ruben.snellings@ees.kuleuven.be](mailto:ruben.snellings@ees.kuleuven.be) (R. Snellings).

activities and better mechanical properties compared to low silica zeolites [11–13]. Zeolite tuffs containing exchangeable alkali cations changed the cement pore solution chemistry and increased the rate of pozzolanic reaction with respect to zeolite tuffs having predominantly  $\text{Ca}^{2+}$  as exchangeable cation [11,14–16]. A first *in situ* synchrotron radiation X-ray powder diffraction (SR-XRPD) study on the pozzolanic reaction between zeolite tuffs and portlandite [14] has pointed out that the reaction kinetics and the structural evolution of the main C–S–H reaction product (cement chemistry notation: C = CaO, S = SiO<sub>2</sub>, H = H<sub>2</sub>O, A = Al<sub>2</sub>O<sub>3</sub>; F = Fe<sub>2</sub>O<sub>3</sub>, and  $\hat{\text{S}}$  = SO<sub>3</sub>) were influenced by the exchangeable cation content.

In contrast to the limited number of SR-XRPD studies on the pozzolanic reaction *in se*, the advantages of SR-XRPD have been exploited more frequently to study the *in situ* hydration processes of single or mixtures of cement components [17–19], in Portland cements [19–22] and in belite cement systems [23,24] with or without additives or at various temperatures. The superior intensities and resolution of synchrotron radiation compared to laboratory X-ray sources in combination with the advent of powerful new detector systems allow to follow *in situ* reactions with an increased time resolution. Rietveld quantitative phase analysis of the recorded patterns allows to quantitatively analyse the consumption of starting materials and formation of crystalline reaction products. In addition, crystal structural parameters evolving during the reaction can be followed [14,18].

In this paper, the hydration of natural zeolite blended cements at 40 °C was investigated by means of *in situ* SR-XRPD. The combined action of the Portland cement hydration reactions and the pozzolanic reaction of the added natural zeolites was quantitatively determined by kinetic analysis of the Rietveld quantitative phase analysis results. To examine the influence of zeolite type on the cement hydration kinetics, two different types of zeolite materials were used: a well-crystallized hydrothermal Ca-rich chabazite (general structure formula  $\text{Ca}_2\text{Al}_4\text{Si}_8\text{O}_{24} \cdot 12\text{H}_2\text{O}$ ; Si/Al = 2), representing natural zeolites of high crystallinity with low Si/Al ratio, and a diagenetically zeolitised tuff predominantly composed of clinoptilolite (general structure formula  $(\text{Na},\text{K},\text{Ca}_{0.5})_7\text{Al}_7\text{Si}_{29}\text{O}_{72} \cdot 22\text{H}_2\text{O}$ ; Si/Al = 4.1), representing more siliceous zeolites of typically lower crystallinity. In order to assess the impact of zeolite crystal chemistry on the hydration processes, the clinoptilolite tuff was exchanged to its Na-, K-, and Ca-forms, each added as supplementary cementitious material.

## 2. Experimental

### 2.1. Material preparation and characterization

The OPC used was a commercial cement classified as CEM I 52.5R. Zeolite blended cements were prepared with a 3:7 zeolite:cement

weight ratio. This ratio allows to investigate the consumption and structural evolution of the pozzolan more easily than lower replacement ratios. In practice optimal cement replacement ratios around 10–20 wt.% are more frequently reported [25–28], but higher replacement ratios from 30 up to 55 wt.% have also been found suitable for application [29–31]. The selected clinoptilolite tuff originated from Buckhorn, New Mexico (USA), and the chosen chabazite sample was a well-crystallized specimen from Wasson's Bluff, Nova Scotia (Canada). The samples were hand ground in an agate mortar to pass a 250 μm sieve and were subsequently wet milled in a McCrone Micronising Mill® with methanol. Wet grinding has been shown to result in a narrow Gaussian grain size distribution. After wet milling the granulometry was determined by laser diffractometry on a Malvern Mastersizer S Long Bed with a 300RF optical lens. Final mean grain size diameters ( $d_{50}$ ) were 7.4 and 9.1 μm for the clinoptilolite and the chabazite material respectively. Cation exchange of the ground clinoptilolite tuff was performed by immersing the samples in nearly saturated NaCl, KCl and CaCl<sub>2</sub> solutions. The solutions were stored in closed containers at 60 °C to enhance the exchange process. After 1, 3, 5, and 10 days the solutions were renewed. The cation concentrations in the outcoming solutions were monitored by Atomic Absorption Spectroscopy (AAS) to determine the rate of cation exchange. After 14 days, the cation exchange was considered to be complete and the samples were separated from the solution by centrifugation and triply washed with distilled water to remove remainders of soluble salts.

The bulk chemical composition of the starting materials was analysed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), and an anhydrous lithium metaborate fusion flux was used to dissolve the samples. SO<sub>3</sub> content was indirectly derived from the Rietveld quantification results of gypsum and anhydrite. Loss on ignition (LOI) was determined by heating the samples for 2 h at 1050 °C.

The mineralogical phase composition of the starting materials was analysed by SR-XRPD using Rietveld analysis. A 10 wt.% ZnO spike was thoroughly intermixed with the samples to allow the calculation of the amorphous phase content. The samples were subsequently loaded into 2 mm capillaries and SR-XRPD patterns were collected at the BM01b beam line of the European Synchrotron Radiation Facility in Grenoble (France). The wavelength used was 0.50199 Å, calibrated to the NIST SRM 640b Si standard. The measurements were recorded in transmission geometry over an angular range of 1–26.5° 2θ, with a step size of 0.003° 2θ and a scan time of 200 ms per step. The phase quantification procedure initiated with the identification of major and minor mineral phases by the DiffracPlus EVA software (Bruker) and proceeded with full-profile Rietveld quantitative phase analysis (QPA) using the Topas Academic v4.1 software [32]. Peak profiles were fitted using the fundamental parameters approach [33]. The initial crystal structure information of the identified phases was adopted from the

**Table 1**

Chemical and mineralogical phase composition of the cement and zeolite starting materials. The designation 'other' comprises mainly X-ray amorphous phases and possibly some crystalline phases present in minor or trace amounts.

Portland cement (CEMI52.5R)				Clinoptilolite tuff				Ca-chabazite					
Chemistry	wt.%	Mineralogy	wt.%	Chemistry	Ca-clinoptilolite	K-clinoptilolite	Na-clinoptilolite	Mineralogy	wt.%	Chemistry	wt.%	Mineralogy	wt.%
					wt.%	wt.%	wt.%						
SiO <sub>2</sub>	20.58	C3S [34]	65.7	SiO <sub>2</sub>	63.74	62.73	63.29	Clinoptilolite [14]	90	SiO <sub>2</sub>	52.55	Chabazite [43]	91.6
Al <sub>2</sub> O <sub>3</sub>	4.67	β-C2S [35]	6.5	Al <sub>2</sub> O <sub>3</sub>	12.03	11.79	11.94	Quartz [41]	1	Al <sub>2</sub> O <sub>3</sub>	15.7	Quartz [41]	7.9
Na <sub>2</sub> O	0.44	α'-L-C2S [36]	0.5	Na <sub>2</sub> O	0.41	0.34	6.57	Plagioclase [42]	1.6	Na <sub>2</sub> O	0.81		
CaO	63.01	C3A [37]	5.7	CaO	5.41	0.1	0.13			CaO	7.47		
K <sub>2</sub> O	0.62	C4AF [38]	8.2	K <sub>2</sub> O	0.91	10.36	0.86			K <sub>2</sub> O	0.68		
MgO	1.85	CŠ [39]	2.7	MgO	1.14	0.59	0.65			MgO	0.08		
TiO <sub>2</sub>	0.45	CŠH2 [40]	0.6	TiO <sub>2</sub>	0.16	0.16	0.16			TiO <sub>2</sub>	0.01		
Fe <sub>2</sub> O <sub>3</sub>	3.79	Quartz [41]	0.1	Fe <sub>2</sub> O <sub>3</sub>	1.45	1.42	1.36			Fe <sub>2</sub> O <sub>3</sub>	0.05		
P <sub>2</sub> O <sub>5</sub>	0.76			P <sub>2</sub> O <sub>5</sub>	0.17	0.17	0.03			P <sub>2</sub> O <sub>5</sub>	0.16		
SO <sub>3</sub>	2.12												
LOI	1.31	SUM	89.9	LOI	14.96	12.55	13.65	SUM	92.6	LOI	20.85	SUM	99.5
SUM	99.6	Other	10.1	SUM	100.37	100.21	98.63	Other	7.4	SUM	98.35	Other	0.5

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