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Pozzolanic reactions of common natural zeolites with lime and parameters affecting their reactivity

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ABSTRACT

The pozzolanic reaction between portlandite and different types of nearly pure natural zeolites was studied. Analcime, phillipsite, chabazite, erionite, mordenite and clinoptilolite-rich tuffs were mixed with portlandite and water (1:1:2 by weight), and the progress of the pozzolanic reaction was quantitatively determined by thermogravimetrical analyses from 3 to 180 days.

A thorough characterization of the raw materials was performed by quantitative XRD, XRF, SEM-EDX, BET specific surface area measurements, grain-size analyses, FTIR and Cation Exchange Capacity measurements. The difference in reactivity of the samples containing zeolites with varying Si/Al ratios, as well as between clinoptilolite-rich samples exchanged with different cations or ground to different grain sizes was assessed.

The results indicate that the external surface area only influences the short-term reactivity, whereas the cation content has an effect on both the long- and short-term reactivity. The early reactivity of the unexchanged samples can be explained by these two parameters, but their long-term reactivity is mainly related to the Si/Al ratio of the zeolites. Samples with zeolites rich in Si react faster then their Al-rich counterparts.

1. Introduction

One of the most promising types of natural high-quality pozzolans is the group of natural zeolites [1]. Pozzolans are materials that consist predominantly of silica and alumina [2] and are able to combine with portlandite in the presence of water to produce new reaction products exhibiting a binding character [3,4]. Therefore, they are widely used as an additive in cement in which portlandite is a major hydration product. Their widespread use can be explained both by their beneficial effect on the properties of concrete [5,6] as well as by the economic and ecologic advantage of their use [7].

Pozzolans are known to increase the durability [2,5,8–10], lower the heat of hydration [5,9,11], increase the resistance to sulphate attack [2,11,12] and reduce the energy cost per cement unit [9]. However, their influence on the early and final strength development of the cement is not straightforward [13–17] and seems to depend on a number of parameters, unarguably including their reactivity. This 'pozzolanic activity' encompasses the maximum amount of portlandite that a pozzolan can combine as well as the rate at which such combination occurs [14]. However, the parameters influencing the reactivity of the pozzolans and the mechanisms controlling their interaction with portlandite are not fully understood [2].

Several types of natural and artificial pozzolans have been studied so far. The addition to cement or portlandite of industrial by-products such as ground blast-furnace slags, fly ashes and silica fume has been investigated extensively [9,18,19] and their use is generally accepted. In the case of natural pozzolans, most studies relate to the reactivity of metakaolin [8,10,20–24] or other types of thermally activated clay minerals [25,26]. More recently, increased interest is shown for tuff or zeolite deposits [6,7,15,27,28]. However, since most studies consist of separate case studies of single and specific deposits or minerals, it is difficult to draw general conclusions or to predict the reactivity of a potential pozzolan. In the case of clay minerals, only a few systematic studies [29–31] have been conducted in order to predict the influence of the mineralogy and the temperature of the heat treatment on the pozzolanic activity. For zeolite minerals, these systematic studies [32,33] are even scarcer. Therefore, the main aim of this study is to gain a better understanding of the parameters affecting the reactivity of these nearly pure zeolite minerals. Moreover, it is aimed to provide a more fundamental insight into the reaction mechanisms underlying the pozzolanic activity.

Natural zeolites are hydrated alumino-silicates that occur mainly in altered volcanic tuffs. Because of their origin, they can be associated with substantial amounts of clays, feldspars or glass. Zeolites consist of an open silica framework, for which alumina can substitute in variable proportions, whereas exchangeable alkaline and alkaline-earth metals compensate for the resulting charge deficit. Together with variable amounts of water, these cations are more or less loosely bound to framework oxygens in the open channels in which they occur. The main differences between the selected zeolite samples are related to a different organisation of the zeolite framework (structural), varying Al

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substitution (different Si/Al ratio), different amounts and types of exchangeable cations (different CEC: Cation Exchange Capacity) and the nature and amount of mineral impurities. Since many variables can affect the samples' reactivity, a first and important step in our study is to conduct a thorough characterisation of the ground mineral samples.

In previous studies, several methods were applied to estimate the pozzolanic activity of a material. Several authors [6,15] use mechanical properties, as the compressive strength of a cement-pozzolan blend mortar, as a measure for pozzolanic reaction, whereas others [21,26,34] have tried to determine the pozzolanicity by chemical means. The latter test methods are based on measuring the Si or Al concentration or the conductivity of the solutions obtained from samples treated with acid or base. The Chapelle and Fratini methods consist in measuring the portlandite concentration of pozzolan–portlandite and pozzolan–cement mixtures [35,36]. Other methods, rely on measuring the amount of material reacted in a lime-pozzolan paste. A summary of these methods can be found in [2]. However, a fast and reliable method has not yet been found.

In the current study, two methods have been used to determine the pozzolanicity of the samples. The first method determines the remaining portlandite content by thermal analysis in lime-pozzolan mixtures after several curing intervals as in a number of previous studies [8,16,18,20,23,37,38]. The second method used is the EN 196-5 standard test method for determining the pozzolanicity of pozzolanic cements [39] even though this method was solely conceived to differentiate an inert addition from an active one [40]. To be able to place the results in a more general context, silica fume (Elkem Microsilica 983U) has been added to the group of studied samples. It is used as a reference material.

2. Materials and methods

2.1. Characterization

Some authors [41] have related the pozzolanic activity of a material to the amount of the amorphous fraction or to the formation of an amorphous layer covering the surfaces of the mineral grains during milling [42]. Since the main objective of this study is to measure the reactivity of the true minerals, the effect of grinding was minimised by wet milling the samples with hexane in a Mc Crone Micronising Mill® in order to reduce the grain size of the samples to a similar level.

Furthermore, two mineral samples were ground to three different grain sizes; Very Fine (VF), Fine (F) and Coarse (C)—to examine the influence of the grain size on the reactivity. After milling, the raw materials were physically, mineralogically and chemically characterised and their pozzolanic reactivity was determined. Correlations between the reactivity of the samples and their characteristics are subsequently discussed.

2.1.1. Physical characterisation

The grain size of all the samples after wet milling was determined in an aqueous suspension by laser diffraction using a Malvern Mastersizer S Long Bed with a 300RF optical lens for grain sizes between 0.05 and 880 µm.

The Brunauer–Emmet–Teller or BET method was used to obtain the total surface area of the samples. The sample preparation consisted of 12 h heating at 250 °C with a heating rate of 5 °C per minute and a continuous N_2 gas flow. Measurements were performed with N_2 as an adsorbate, in liquid N_2 using a Micrometics Tristar 3000. The external surface area was obtained from the *t*-plot, using the Harkins–Jura Thickness model in the data range from 0.67 to 0.90 nm.

2.1.2. Mineralogical characterisation

Prior to quantitative X-ray diffraction (QXRD) measurements, part of all bulk samples were finely ground and mixed with an internal standard (10 wt.% ZnO) with hexane as a milling agent in a McCrone Micronising Mill® to obtain mean grain sizes of ±10 µm. After air-drying, samples were side-loaded into aluminum holders and equilibrated for at least 24 h in an atmosphere of ±56% relative humidity. XRD spectra were then recorded on a Philips PW1830 instrument with Bragg–Brentano geometry from 5 to 70 °2θ using CuKα radiation generated with an acceleration voltage of 45 kV and a current of 30 mA. Step size was 0.02 °2θ with a counting time of 2 s.

Identification of major and minor mineral phases was carried out with the DiffracPlus EVA software (Bruker). Subsequent Rietveld analysis was performed using the Topas Academic software [43]. Quantitative phase analysis was achieved by full Rietveld structure refinement of the major phases. Structure models of minor compounds were taken from the literature. In Topas Academic, the fundamental parameters approach was used to differentiate instrumental and sample inherent contributions to the diffraction pattern [44]. The first stages of the Rietveld analysis included introducing the identified phases into the model and refining of global parameters such as specimen displacement and zero error. The background was fitted with a cosine Chebyshev polynomial, initially using less than 5 terms, gradually increasing the number of terms, if necessary, during progressive refinement stages. Structure refinement started for all identified phases from literature models; scale factors, lattice parameters and sample inherent profile parameters. The later stages of the structure refinements of the main zeolite component involved the refinement of atomic coordinates of extra-framework cations and/or water molecules in all cycles. While atomic coordinates of the zeolite framework were restrained, isotropic atomic displacement parameters and site occupancies for extra-framework positions were allowed to vary in alternate cycles. Site occupancies were restrained to the average zeolite chemical compositions obtained by SEM-EDX.

Fourier Transform Infra Red (FTIR) analyses were performed on all ground samples, mainly to check the results of the Scanning Electron Microscopy/Energy Dispersive X-ray (SEM-EDX) analyses, after mixing with KBr (0.5–5 wt.% of sample), in a Nicolet Magna 860 using the Diffuse Reflectance Infrared Transmission (DRIFT) mode in a range from 4000 to 500 cm^{-1}. Measurements consisted of 128 scans with a data spacing of 1.928 cm^{-1}. Each sample was mixed and measured 3 times.

2.1.3. Chemical characterisation

Loss on Ignition (LOI) was determined from the weight loss after heating the samples to 1050 °C for 2 h. The subsequent bulk chemical analysis of the samples was measured by X-ray Fluorescence (XRF) with a Bruker SRS3400 on glass beads made from 3 g of sample and 8 g of flux (Li-tetraborate/metaborate) and fused at 1100 °C and after cooling.

Since the samples contain mineral impurities, the bulk chemical analysis does not give accurate information on the true Si/Al content of the reactive zeolites. This ratio is important, since it could be related to the nature of the reaction products formed during the pozzolanic reaction but also to its reactivity more in general. Therefore, Si/Al ratios of the zeolites were determined using polished samples by semi-quantitative SEM-EDX analyses, measured on a FEG XL30 (FEI) instrument, using a low acceleration voltage (10 kV) to restrict beam damage. Spectra were collected during 60 s at a working distance of 10 mm. The Oxford software (Inca platform) was used to analyse the spectra in a semi-quantitative manner (ZAF correction).

Beside the Si/Al ratio, the cation content of the zeolites is another important parameter that potentially influences the pozzolanic behaviour. The applied methodology for the determination of the Cation Exchange Capacity (CEC) was based on the method described by Kitsopoulos [45]. To study the influence of the cation content on the pozzolanic activity, two samples were portioned in three equal parts that were respectively exchanged to three different cations; Potassium (K^+), Sodium (Na^+) and Calcium (Ca^{2+})—by immersing them in a nearly saturated solution of the corresponding acetate. The samples were stored in sealed containers in an oven at 60 °C to promote the exchange and the solutions were renewed periodically at 1, 4 and 10 days. The exchange was considered as completed after 20 days.

2.2. Pozzolanic activity

The European Norm EN 196-5:2005 [39] was used to estimate the pozzolanic character of all materials. The test was applied to a blend of

30 wt.% of pozzolan and 70 wt.% of CEMI (52.5R) mixed in a Turbula® mixer.

The pozzolanic activity of the samples was studied more in detail by preparing lime-pozzolan mixtures. All the pozzolans were equilibrated in a 56% relative humidity environment before mixing. The mixtures of 1:1 wt. proportion of ground pozzolans and CL90 commercial hydrated lime were blended with a Turbula® mixer. Afterwards, distilled water was added to achieve a water/solid ratio of 1. The pastes were thoroughly blended and stored in sealed polyethylene containers in an oven at 40 °C. After time intervals of 3, 7, 14, 28, 56, 90 and 180 days, the hardened pastes were unmoulded, ground and vacuum dried for 2 h to stop further hydration by removing non-crystalline water. Later, the samples were stored in sealed containers in a desiccator until analysis.

The samples were analysed by combined TG/DSC in a temperature range from 25 to 1000 °C. The equipment used for this purpose was a Netzsch STA 409 PC *Luxx*®. Measurements were done in alumina crucibles in an inert N_2 gas flow of 60 ml/min at a heating rate of 10 °C/min. The TG analyses were used to quantify the amount of portlandite, by determining the weight loss at 430 °C by linearly extrapolating the data from 335 °C to 370 °C and from 490 °C to 525 °C (Fig. 1). This method, proposed by Taylor [46] subtracts the amount of water released from the dehydration of other compounds. It results in a background-corrected weight loss from which the amount of remaining portlandite can be calculated.

Another set of pastes containing lime and ground pozzolans (1:1 weight proportion and 1:1 water/solid ratio) were prepared to find evidence for either a dissolution or a diffusion controlled reaction mechanism by SEM (Scanning Electron Microscopy). The pastes were prepared using coarser zeolite powders (average d_{50} of 100 µm) to visualise the reaction products more easily. After curing in sealed polyethylene containers in an oven at 40 °C for 56 days, the samples were placed in a low vacuum ($\pm 10^{-4}$ atm.) overnight and impregnated with an ultra low viscosity epoxy (Spurr's low viscosity embedding media). The impregnated samples where cured at 60 °C in an N_2-filled vacuum oven for at least 3 days. Afterwards, samples were ground manually with dry sandpaper, systematically decreasing the paper roughness from Grit 80 to Grit 12000. BSE (Backscattered Secondary Electron) images of the carbon-coated samples were taken at 10 kV using an XL30 FEG (FEI) scanning electron microscope at a working distance (WD) of 10 mm.

3. Results

3.1. Characterization

The bulk chemical composition of the samples (non-exchanged) is listed in Table 1, together with the bulk Si/Al ratio. For most samples, this ratio deviates from the Si/Al ratio of the zeolites determined from SEM-EDX analyses, because of the presence of mineral impurities.

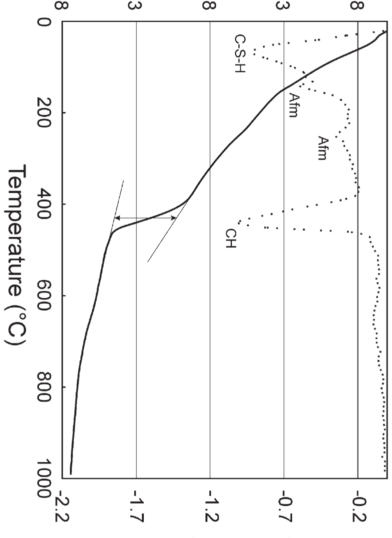

Fig. 1. Determination of the weight loss on decomposition of portlandite (Sample 'Ana' after 28 days). Both TG (full line) and DTG (dotted line) curves are plotted with indication of the reaction products at their peak of disintegration (C–S–H: calcium silicate hydrate; AFm: Monosulfoaluminate; CH: portlandite).

Table 1

Main sample characteristics including their origin, bulk chemical composition, the atomic Si/Al ratio of the zeolites (determined by SEM-EDX), the sample's strongest Si–O absorption band in FTIR spectra and physical parameters as the d_{50}, the *t*-plot external and total BET surface areas of the powder

Sample name	Main mineral	Sample origin	Grain size	Chemistry												SEM-EDX	t-plot	BET	FTIR
			d_{50} (µm)	LOI	SiO_2	Al_2O_3	Na_2O	CaO	K_2O	MgO	TiO_2	Fe_2O_3	SUM	Bulk atomic Si / Al		Atomic Si / Al zeolites	External surface area (m^2/g)	Total BET surface area (m^2/g)	Si–O strongest absorption band (cm^{-1})
Ana	Analcime	Unknown	9.35	7.67	62.90	15.81	8.82	0.63	1.10	0.17	0.10	1.26	98.46	3.5		2.6	4.5	4.5	1034
Phi	Phillipsite	Tuffo Giallo Napolitano (Italy)	6.29	11.28	54.43	16.00	2.71	2.39	7.67	0.21	0.39	3.15	98.23	3.0		2.8	12.9	33.8	1034
Cha	Chabazite	Christmas Arizona (USA)	5.17	20.12	52.11	13.45	3.47	2.03	1.42	0.46	0.31	1.91	95.28	3.4		3.2	34.9	400.0	1039
Eri	Erionite	Pine Valley Nevada (USA)	4.86	16.54	57.90	13.64	5.36	0.39	3.47	0.15	0.06	1.15	98.66	3.7		3.7	9.0	397.0	1039
Mor	Mordenite	Mangatarem (Philippines)	6.01	15.15	65.88	10.56	1.89	3.36	0.54	0.14	0.39	1.42	99.32	5.5		5.4	30.4	120.0	1055
Cli_1	Clinoptilolite	Cayo Formation (Manabí, Equador)		15.85	58.48	15.52	0.96	3.71	2.07	0.32	0.46	2.24	96.60	4.1		4.6			n / a
Cli_1_Na			8.20														17.2	25.9	
Cli_1_Ca			8.20														17.0	22.1	
Cli_1_K			8.20														19.9	26.9	
Cli_2	Clinoptilolite	Simav Graben (Turkey)		14.02	62.09	12.35	1.18	1.88	4.17	0.21	0.21	1.15	97.26	4.4		4.7			1055
Cli_2_VF			3.97														18.5	26.6	
Cli_2_F			8.45														14.7	21.8	
Cli_2_C			20.97														4.9	7.6	
Cli_3	Clinoptilolite	Zlatokop (Serbia)		14.49	64.14	11.26	1.01	3.37	1.01	0.22	0.16	0.97	96.62	5.0		4.6			1066
Cli_3_Na			6.10														20.4	25.4	
Cli_3_Ca			6.10														25.8	31.8	
Cli_3_K			6.10														31.2	36.1	
Cli_3_VF			2.53														24.4	31.1	
Cli_3_C			28.48														16.5	23.3	
SF	Silica Fume	Elkem Microsilica 983U	*0.2*	0.75	98.25	0.29	0.07	0.19	0.20	0.02	0.00	0.04	99.81	±300		n / a	10.1	17.7	1128

(n/a: not applicable, LOI: Loss on Ignition).

The nature and quantity of these impurities and the amount of zeolites in each sample determined by QXRD are summarised in Table 2. The erionite- ('Eri') and the three clinoptilolite-containing ('Cli') samples are very pure, with zeolite contents from about 84% to nearly 100%. The 'Mor', 'Cha' and 'Ana' samples have zeolite contents around 70%. The 'Phi' sample has the lowest purity, with a zeolite content around 50%. Most common impurities are quartz and various types of feldspars. In samples 'Mor' and 'Cha', a considerable amount of non-identified phases remain. Part of this fraction could be volcanic glass or poorly crystalline opal-CT. These reactive phases will inevitably participate in the pozzolanic reaction. In the QXRD pattern of Silica Fume ('SF') no peaks other than those of the internal standard were observed, indicating that the sample is amorphous to X-rays. The R_{wp} and gof (goodness of fit) parameters give an indication of the quality of the fit between the measured and the calculated XRD pattern. Fits are good for low R_{wp} and gof values.

The grain size distributions determined after wet milling, are shown in Fig. 2A. Fig. 2B shows the grain size distributions of the samples ground to three different finesses. These are mineralogically identical samples ground to different finesses in order to investigate the influence of the grain size on the pozzolanic reactivity, keeping all other parameters constant. The d_{50} of all the samples is shown in Table 1. This value corresponds to the grain size below which 50% of the total volume fraction is situated. The d_{50} ranges from 4.86 µm for 'Eri' to 9.35 µm for 'Ana'. The samples that were ground to very fine grain sizes; 'Cli_2_VF' and 'Cli_3_VF'—have a d_{50} of 3.97 µm and 2.53 µm respectively. The coarsely ground samples 'Cli_2_C' and 'Cli_3_C' have a d_{50} of 21 µm and 28 µm respectively. The d_{50} of 'SF' (0.2 µm) is an estimate obtained from measurements on SEM images.

The cation content of the zeolites is derived from the CEC data, shown in Fig. 3. The markedly dominant cation in samples 'Ana' and 'Eri' is Na^+, whereas other samples do not contain a single dominant cation. K^+ is the main cation in the 'Phi' and 'Cli_2' samples, whereas it is present only in subordinate amounts in most of the other samples.

The external and total specific surface areas as determined by N_2 adsorption, are included in Table 1.

The position of the main Si–O stretching band in the FTIR spectra of zeolites is dependent on their Si/Al ratio [47,48]. The strongest absorption band for each sample is shown in Table 1. These FTIR data are in agreement with the SEM-EDX measurements and give at least a qualitative support to the relative Si/Al ratios determined from the SEM-EDX spectra. It is indeed clear from these data that samples with zeolites having a low Si/Al ratio, also have maxima at lower wavenumbers. The correlation between both parameters is good (R value of 0.87) but not perfect, probably because of the influence of silicate mineral impurities and the rather large data spacing in the spectra.

To study the influence of the cations, Cli_1 and Cli_3 were exchanged with K^+, Na^+ and Ca^{2+} before evaluating their pozzolanic activity. Beside this compositional difference, all other parameters were considered to be equal. However, since a change in the type of extra-framework cation influences the quantity of adsorbed water, TGA analyses were used to determine this amount. The samples exchanged with Na^+ appeared to contain more water (16–17%) than the other samples (13–15% for K^+ and 15.5–16% for Ca^{2+}).

3.2. Pozzolanic activity

The European Standard Pozzolanicity test for pozzolanic cements EN 196-5:2005 [39] was followed to ascertain that the tuff–cement

Table 2
Quantitative mineralogical composition of all the samples as determined by QXRD

Sample	Ana	Phi	Cha	Eri	Mor	Cli_1	Cli_2	Cli_3
Analcime	**73.3**	7.6						
Phillipsite		**31.6**						
Chabazite		9.4	**67.6**	6.4				
Erionite				**90.0**				
Mordenite					**64.4**			
Clinoptilolite					7.2	**98.9**	**84.5**	**83.8**
Quartz	16.4		2.4	0.7		1.1	0.7	3.8
Cristobalite							1.5	
Oligoclase	0.7							
Andesine								6.5
Anorthite			1.7					
Anorthoclase		14.2	3.1	2.2			5.5	
K-feldspar	7.4	29.0					4.2	
Augite		3.7						0.4
Muscovite			5.6				3.6	2.6
Calcite	0.9							2.8
Jarosite				0.7				
Gypsum				1.1				
Total zeolite content	73,3	48,6	67,6	96,4	71,6	98,9	84,5	83,8
Sum	98.6	95.5	80.4	101.1	71.7	100.1	99.9	99.9
Unidentified	1.4	4.5	19.6		28.3			
R_{wp}	12.9	19.0	11.6	14.8	12.9	11.3	15.2	9.8
Gof	2.0	1.4	1.8	2.3	2.0	1.3	1.2	1.4

The data in bold are aimed to highlight the most important figures of the table, i.e. the true purity of each sample on which the further discussion is built.

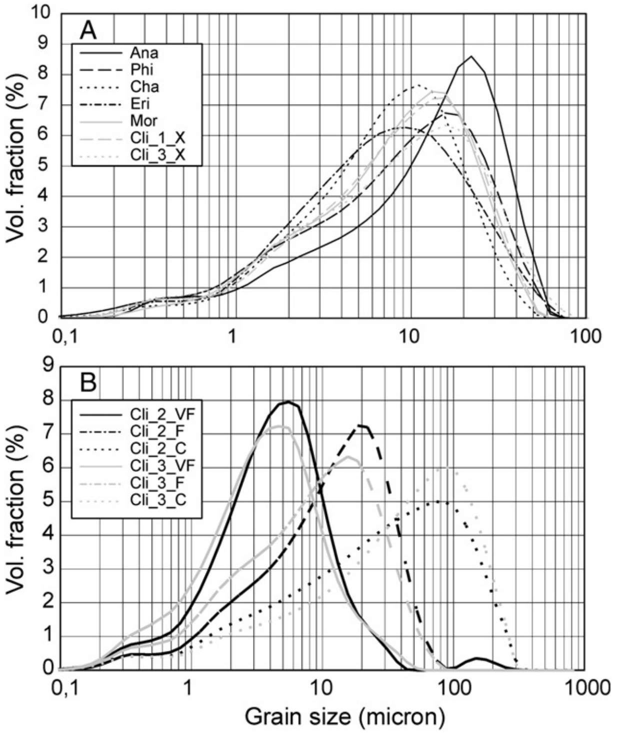

Fig. 2. (A) Grain size distribution of the samples (B) Grain size distrution of the "Cli_2" and "Cli_3" samples ground to different finesses (different scale).

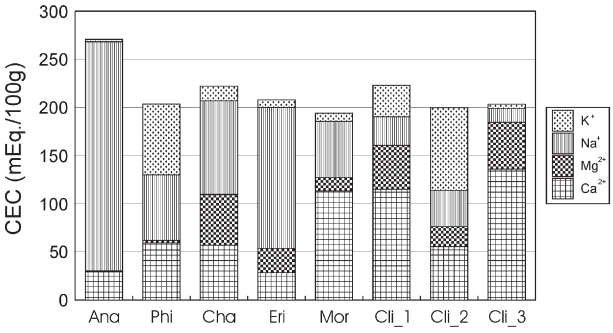

Fig. 3. Cation Exchange Capacity (CEC) of the samples determined according to the method described by Kitsopoulos [45] for K^+, Na^+, Mg^{2+} and Ca^{2+}.

mixtures satisfy the Fratini criterion. The alkalinity and CaO contents in the cement contact solution at 3, 7 and 28 days of curing are presented in Fig. 4. From 7 days on, all tuff–cement samples give a positive Fratini test, indicating that the cement is pozzolanic. Through time it is observed that the CaO content is decreasing to a larger extent than the solution alkalinity.

Based on the amount of portlandite remaining in the reacted tuff–portlandite mixtures after successive reaction times, its consumption compared to the initial amount was calculated. This reacted amount was taken as the degree of reaction (α) in the modified Jander's equation [49] for three-dimensional diffusion processes:

$$\left(1-\sqrt[3]{1-\alpha}\right)^{N}=Kt \tag{1}$$

The equation allows classifying reaction processes [50] based on the exponent of reaction N. If $N\le1$; the reaction is believed to be controlled by dissolution/precipitation processes, or by the immediate reaction at the surface of the grains. If $N>1$; the reaction is believed to be controlled by the diffusion of reactants through a layer of reaction products. This layer is porous if $N\le2$ and dense if $N>2$. Other parameters in the equation are the reaction constant K and the reaction time t.

The equation has been plotted on a semi log-scale in Fig. 5 for all zeolites samples. The slope of the curves represents the exponent of reaction N. The values of N are included in Table 3. Based on repeated measurements of identical samples, an average standard deviation of 0.16 could be calculated for the amount of portlandite reacted in terms of percentages. Standard deviations on the N-values calculated from repeated measurements are in the order of 0.06.

4. Discussion

All samples gave positive results in the pozzolanicity test (Fig. 4); all contact solutions were found to be unsaturated in portlandite. The CaO and alkalinity content decreased progressively over the 28 day testing period. This indicates that the pozzolanic reaction is progressively consuming excess lime from the pore solution. This conclusion, solely based on the pozzolanicity test would be premature because the increased alkali content released from the hydrating cement constituents and the zeolite phases lowers the solubility of portlandite significantly through the common ion effect [51].

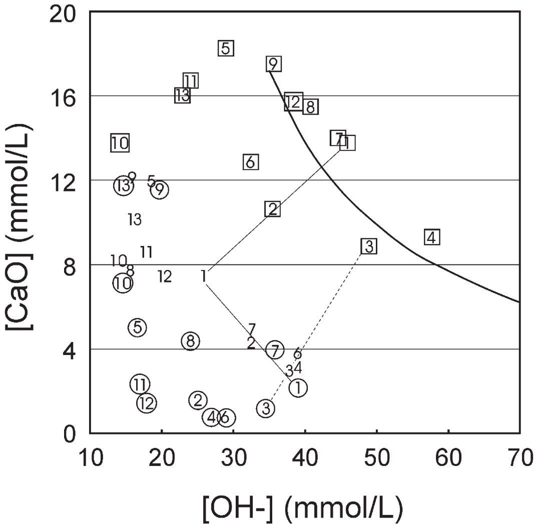

Fig. 4. Saturation line of Portlandite with position of samples after 3 days (numbers in squares), 7 days (free numbers) and 28 days (encircled numbers). The lines show the evolution of samples 1 and 3 (see text for discussion). 1—Ana; 2—Cha; 3—Eri; 4—Cli_1_Na; 5—Cli_1_Ca; 6—Cli_1_K; 7—Phi; 8—Cli_2_F; 9—Cli_3_C; 10—Cli_3_VF; 11—Cli_3_F; 12—Mor; 13—SF.

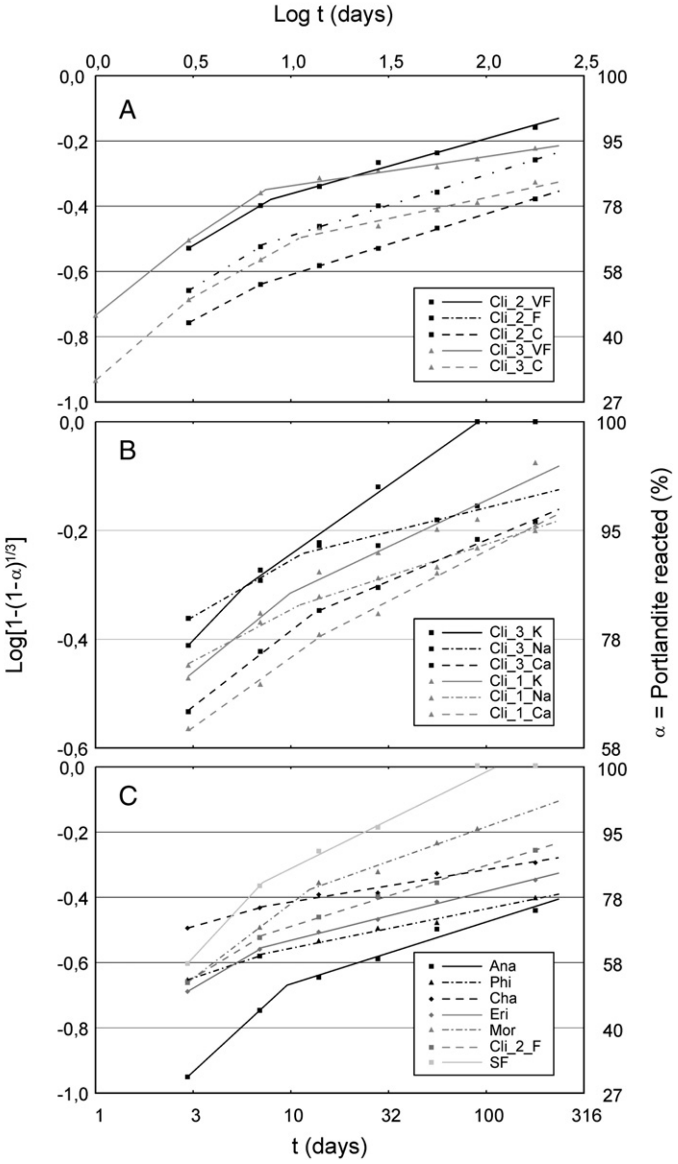

Fig. 5. Pozzolanic reaction kinetics in lime-pozzolan pastes after different time intervals for (A) samples Cli_2 and Cli_3 ground to different grain sizes, (B) samples Cli_1 and Cli_3 exchanged with different cations (different vertical scale) and (C) samples with different Si/Al ratios.

Several authors (e.g. [36]) have linked the low CaO content to the zeolite's base exchange capacity. However, all zeolites described here, except analcime, show pronounced exchange selectivity for K^+ [52]. It is expected and described [53] that zeolites would take up K^+ released from the hydrating cement minerals. Zeolite exchangeable cation content has therefore a strong influence on the alkali concentration of the solution [28,53] whereby zeolite type and composition could possibly corrupt the results of the standard pozzolanicity test.

The data in Fig. 5 and Table 3 give a more profound indication of the pozzolanic activity of each sample in the lime/pozzolan mixtures. Fig. 5A shows the reaction curves for samples Cli_2 and Cli_3 ground to different grain sizes. From these curves it is evident that the reaction has progressed considerably in the first three days, before the first set of analyses. After three days, the reaction progresses in two distinct steps. A steeply inclined curve can be fitted between the two first data points, corresponding to 3 and 7 days of reaction. From about 7 days on, the data points fit to a less steeply inclined curve. In terms of reaction exponents, this two-step evolution could correspond to a condensation of the layer covering the outer part of the grains. Evidence for such

Table 3
N-values obtained from Jander's equation

	1–3 days	3–7/14 days	7/14–180 days
Ana	n.a.	1,8	5,3
Phi	n.a.	5,0	8,3
Cha	n.a.	6,0	10,1
Eri	n.a.	2,9	6,7
Mor	n.a.	2,2	4,7
Cli_1			
Cli_1_Na	n.a.	5,3	8,5
Cli_1_Ca	n.a.	3,9	5,4
Cli_1_K	n.a.	3,4	5,9
Cli_2			
Cli_2_VF	n.a.	2,8	5,9
Cli_2_F	n.a.	2,7	5,4
Cli_2_C	n.a.	3,1	5,3
Cli_3			
Cli_3_Na	n.a.	4,8	11,1
Cli_3_Ca	n.a.	3,6	6,6
Cli_3_K	n.a.	2,7	3,9
Cli_3_VF	2,1	2,5	11,2
Cli_3_C	1,9	3,0	7,8
SF	n.a.	1,5	3,4

(n.a.: not analysed).

a layer of hydrates covering the zeolite grains was found in the BSE images taken from the polished samples. Fig. 6 shows a layer of reaction products covering a grain of a clinoptilolite-rich sample (Cli_3) after 56 days of reaction. In this BSE image, the rim has a larger average density—thus brighter colour, compared to the grain, mainly due to the calcium present in the reaction products. According to the theory, which suggests that higher values of *N* correspond to denser reaction rims [49,50], the layer of reaction products through which the diffusion process proceeds, must become denser at about 7 to 10 days. As a result, the value of *N* for Cli_2 increases from about 3 to about 5.5 for all three samples, pointing towards a diffusion reaction through a dense layer of reaction products. Remarkably, the three samples show a similar evolution from the beginning of the analyses at three days until the end at 180 days, even though the amount of portlandite reacted at three days is very different. From these observations, it is deduced that the grain size determines the early reaction, whereas it has no influence on the progress afterwards, at least not in the range of the grain size distributions under consideration. From these data, it is not possible to determine the exact moment at which the samples start to behave similarly. However, by inspecting the evolution of samples Cli_3_VF and Cli_3_C for which measurements of the portlandite content started at 1 day, it appears that the grain size has no influence on the reaction beyond the first day as both the coarsely and the very finely ground samples behave in a similar way. Between 1 and 3 days, the exponent of reaction is about 2 for both samples. According to Kondo et al. [50] this value is indicative for a diffusion-controlled reaction through a layer of porous reaction products. Afterwards, the exponent increases first to about 3 and later to about 10. Both Cli_3 samples (C and VF) show a similar trend, even though the parallelism is less pronounced than for sample Cli_2. By considering the complete set of data for the two samples Cli_2 and Cli_3, it appears that the external surface area (Table 1) correlates well with the amount of portlandite reacted after three days.

The results for the samples exchanged with different cations are given in Fig. 5B. In the first 3 days the ‘Cli_1’ samples have reacted less than the corresponding ‘Cli_3’ samples, probably because of the slightly higher external surface area and smaller grain size of the latter. However, the general trend for the samples exchanged with the same cation is very similar. The K^+-forms have low reaction exponents compared to the other samples. The Na^+-exchanged samples have the highest exponents of reaction, even though the amount of lime reacted after 3 days is higher than for the K^+-exchanged samples. The Ca^{2+}-containing zeolites have reaction exponents in between the two other samples. The higher amount of lime combined after 3 days in the samples exchanged with K^+ and Na^+ could be explained by a higher pH of the pore solution. Idorn [54] noticed that, for cement pastes, Na^+ and K^+ suppress the concentration of Ca^{2+} and increase the pH. In the pozzolanicity tests (Fig. 4), higher OH^- concentrations have indeed been observed for ‘Cli_1_Na’ and ‘Cli_1_K’ (4 and 6 in Fig. 4). A higher pH brings about an increased solubility of silica [54–56], enhancing the formation of C–S–H, thus promoting the pozzolanic reaction. It is likely that the increase in pH of pore solutions rich in K^+ and Na^+ also applies to the lime–pozzolan mixtures. The concentration of Na^+ or K^+ in the solution is dependent on how readily the zeolites exchange these cations. The ion-exchange behavior of zeolites is indeed influenced by several factors as the channel configuration and dimension, the ion size, the concentration of the electrolyte solution, etc. [52]. The clinoptilolite framework contains three sets of intersecting channels with relatively large apertures (3.0×7.6 Å; 3.3×4.6 Å; 2.6×4.7 Å) and can therefore easily exchange cations. Since the ions are readily exchanged, the pH increases accordingly and strongly influences the early reactivity. Channel apertures for other zeolites can be found in Armbuster and Gunter [57].

Even though the parallelism between samples with identical cation contents is clear, the reason for the differences in the exponents of reaction between samples containing different cations after 3 days is not obvious. The difference in the early reactivity (<3 days) is probably related to the size of the cations and the way in which they are bound to the framework. Na^+ that has a smaller ionic radius is more loosely bound to the framework and is more readily exchanged compared to K^+. The slower release of K^+ will therefore result in a slower reaction during the first 3 days.

Fig. 5C shows the data for the samples containing different zeolites that were ground to nearly similar grain sizes (Fig. 2). Also for these samples, the reaction has progressed considerably in the three days before the first analyses. The differences in these early reactivities can be partially accounted for the different external surface areas. The ‘Ana’ sample, with an external surface area of 4.5 m^2/g has reacted least after three days, whereas sample ‘Cha’ with an external surface area of 34.9 m^2/g has reacted the most. The latter sample has combined even more portlandite than the reference ‘SF’ sample after 3 days, which has an external surface area of only 10.1 m^2/g. The correlation is however not

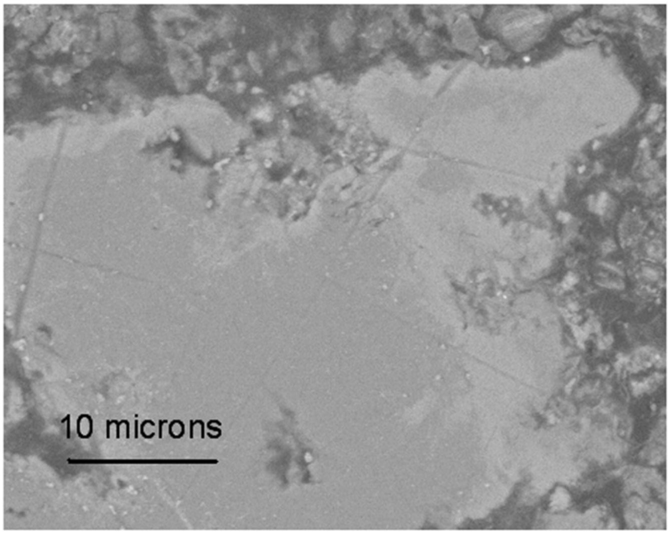

Fig. 6. BSE image of a polished section showing a reaction rim around a grain of clinoptilolite (sample Cli_3) after 56 days of reaction with lime (FEI FEG-SEM, 10 kV, WD 10 mm).

perfect, since samples 'Phi', 'Eri', 'Mor' and 'Cli_2_F' all have reacted with approximately 50% of the available lime after three days, whereas their external surface areas range from 9 to 30 m^2/g. The reason is that the cation content of these samples is different. 'Eri' with a small external surface area of 9 m^2/g contains a very high amount of Na^+ (Fig. 3) that is easily exchanged through its large channels (3 channels with apertures of 3.6×5.2 Å). The increase of Na^+ in the solution causes an increase in the pH. This is confirmed by the pozzolanicity test (Fig. 4) where 'Eri' (3 in Fig. 4) reaches rapidly high pH values. The 'Phi' (7 in Fig. 4) and 'Cli_2_F' (8 in Fig. 4) samples with comparable external surface areas of 12.9 and 14.7 m^2/g have reacted with an identical amount of portlandite compared to the 'Eri' sample after 3 days. 'Phi' and 'Cli_2_F' are rich in K^+ (Fig. 3). For the exchanged samples in Fig. 5B it can be observed that K^+-exchanged samples have combined less lime than Na^+-exchanged samples after 3 days. The higher external surface areas of the two samples compensate for this and yield a similar reactivity after 3 days compared to 'Eri'. Finally, there is the 'Mor' sample with a high external surface area of 30.4 m^2/g but a cation content of mainly Ca^{2+}. The Ca-exchanged samples in Fig. 5B have combined clearly less lime than their K^+- and Na^+-homologues. The pH of the solution in these Ca-rich samples (5-9-10-11-12 in Fig. 4) is indeed lower, leading to a comparatively lower reactivity, expressed in the lower amount of reacted lime.

Generally, the trend of the curves in Fig. 5C is very similar to that in Fig. 5A and B, with a more steeply inclined part from 3 to about 7–14 days, and a less steeply inclined curve afterwards. The interpretation is therefore analogous; the layer through which the diffusion proceeds is becoming less porous at the inflection of the curve and remains constant afterwards. The exponent of the reaction after the inflection point is no longer related to the external surface area or to another physical parameter, but seems to be governed by the composition of the samples. Samples with zeolites richer in silica are reacting faster than others. The 'Cha' sample, that combined a high amount of portlandite after 3 days, reacts slowly from 7 days on, whereas the 'Mor' and 'Cli_2_F' samples are reacting much faster comparatively. An exception to this is sample 'Ana'. Although this sample is composed of zeolites with a low Si/Al ratio, the rate at which it combines with lime after 7 days is high. Even though 'Ana' has a high Na^+-content (Fig. 3), the exchange is believed to be limited due to its dense structure and the absence of intersecting channels and cavities [52]. Moreover, the existing channels have small apertures (1.6×4.0 Å). Therefore, the release of Na^+ and the corresponding increase in pH is retarded and related to the dissolution of the framework. The pore solution of 'Ana' (1 in Fig. 4) in the pozzolanicity test has indeed the highest pH of all tuff–cement mixtures after 28 days compared to a low pH during the first days of the reaction. Even though reasonable correlations are obtained, it must be noted that the reactivity of the samples 'Mor' and 'Cha' could also be affected by the presence of other reactive phases beside the main zeolite minerals present in these samples.

The general evolution for all the samples is the noticeable increase in the reaction exponent from 7–14 days on. The theory suggests that a higher exponent of reaction corresponds to the formation of a denser layer of the reaction products [49,50]. The higher exponent of the samples with zeolites rich in Al could also have other reasons. It is known that tetrahedral Al centres are relatively inert to hydroxide attack due to the associated negative charge [58]. The slowing down of the reaction will therefore be due to a relative enrichment in Al of the network at the surface of the grains, where mainly Si is dissolved. The attack will slow down when less Si becomes available for dissolution at the surface of the grains.

Based on these reaction exponents, it can be concluded that the reaction in a lime pozzolan-mixture after 3 days is probably diffusion controlled, whereby the permeability of the reaction rim surrounding the grains determines the progress of the reaction. Držaj et al. [59] and Takemoto and Uchikawa [3] already suggested that the pozzolanic reaction was topochemical and mainly diffusion controlled. In situ measurements of portlandite/zeolite concentrations immediately after mixing should be done to determine the early reaction exponent and identify the mechanisms controlling the initial mixtures. These data could add to the knowledge and give a more complete view of the pozzolanic reaction as a whole. It can indeed only be inferred indirectly from the present data that the reaction before 3 days is probably based on dissolution and precipitation, rather than on diffusion. Sersale [4] and Dron [60] have suggested this reaction mechanism previously, but it seems likely that these processes prevail during the first hours after mixing.

5. Conclusions

By mixing lime with tuffs consisting mainly of natural zeolites with variable Si/Al ratios or ground to different grain sizes and exchanged to different cations, the pozzolanic reaction has been studied from 3 days on, based on the consumption of portlandite measured by TGA after vacuum-drying.

The thickening of the reaction rim at 7–14 days marks the general evolution of the reaction from three days on. The subsequent evolution follows the behaviour predicted by the Jander's equation for three dimensional diffusion processes through a layer of constant permeability.

The results in this study confirm the previous findings [4–14] that finer grain sizes or higher specific surface areas of pozzolans yield a higher short-term pozzolanic activity. It appears from the results that mainly the external surface area is important for zeolites. This parameter has however no influence on the reaction after 1 day.

In addition to the surface area available for reaction, the results of this study show that the short-term reactivity is also affected to a significant extent by the cation content of the zeolites and the ease with which these cations are exchanged. For the two clinoptilolite samples exchanged with K^+, Ca^{2+} and Na^+, consistent data were obtained and a clear difference in the amount of lime combined before and after 3 days of reaction was observed. The Na^+-exchanged samples had reacted with more lime during the first three days, but they combined lime more slowly afterwards when compared to the samples exchanged with Ca^{2+} and K^+. The K^+-exchanged zeolites react very fast after 3 days. The Ca^{2+}-clinoptilolites had reaction exponents between the K^+- and Na^+-exchanged samples after three days. The difference in reactivity can be related to the influence of the cations on the pH of the pore solution.

Massazza [14] suggested that at longer ages, the pozzolanic reaction is controlled by other factors such as the silica and alumina active contents. These findings are confirmed by the present data. The exponents of reaction succeeding the first three days can indeed be explained by the zeolite Si/Al ratios. Samples with zeolites having higher Si/Al ratios have lower reaction exponent, thus reacted faster. Only the analcime-rich sample ('Ana') showed a deviant behavior, which is probably governed by its slow release of Na^+, leading to a retarded increase of Na^+ in the pore solution with a retarded increase in pH as a consequence.

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