The Effect of Natural Zeolites on the Composition of Cement Pore Fluids at Early Ages

K. Luke[1]

Halliburton, Duncan OK, USA

Abstract

Recent studies have shown that substituting a percentage of Portland cement with natural zeolite can benefit concrete durability due in part to the pozzolanic reaction. Natural zeolite can also influence the early age performance, and factors involved have not been well characterized or previously reported. The pore fluid composition of two different ordinary Portland cements, one finely ground, the other coarsely ground, were investigated with and without 30% replacement of cement by zeolite up to 8 hours at 25, 50 and 65°C. Not all zeolites behave the same and the modifying effects of three natural zeolites having different mineral composition were compared. Analyses covered Na, K, Ca, SO_4, Al, Si, Fe, Mg, as well as pH. Addition of zeolite was observed to reduce the time at which the Ca ion concentration depleted with a resultant acceleration on the onset of setting. Alkali contribution to the pore solution increased with zeolite and values differed dependant on mineral composition of zeolite used. SO_4 contents typically follow those of the Ca ions, but in the present study were observed to remain high even on setting, indicating an effect of zeolite on the AFt/AFm reaction. Si and Al contents remained low in all pore solutions. Higher cure temperatures accelerate the reaction apparently in the same direction as at 25°C. These data were assessed with a view to explaining the early performance characteristics observed with zeolite blended cements.

1. Introduction

Zeolites are aluminosilicates having unique cage structures that are of importance in chemical engineering in relation to ion exchange, desiccants and solid acid catalysts. They are, in most cases, also pozzolanic in nature and react with lime to form a cementitious material having a composition similar to that formed on hydration of cement [1]. Zeolites are either naturally occurring or can be synthesized. Natural zeolites are of volcanic origin and form on weathering and cementation by diagenetic or other natural processes on unconsolidated deposits of minute loose and heterogeneous particles of ash from eruptive explosions. Over 40 natural zeolites have been identified and differ in relation to chemical composition, type of framework, cavity-and-channel structure and the exchangeable alkaline and alkaline earth metals that are required to maintain charge neutrality [2]. Synthetic zeolites are readily formed on mixing solutions of

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[1] K. Luke, formerly with Halliburton, is now with Trican Well Services.

appropriate stoichiometric compositions and maintaining the resulting gel under mild hydrothermal conditions, typically around 150°C at suitable pressure and aging period.

Zeolites are crystalline and have a three-dimensional framework structure based on repeated units of silicon-oxygen (SiO_4) and aluminum-oxygen (AlO_4) tetrahedral. The anionic Al-O-Si framework encloses cavities linked by channels. Substitution of Si^{4+} with nAl^{3+} in what would otherwise be SiO_2 requires a counter-ion M^{n+} to maintain charge neutrality. The M^{n+} ions tend to be exchangeable Na^+, K^+, Ca^{2+} and Mg^{2+} ions and occupy the cavity channel system and along with the water molecules are easily replaceable with other cations such as the $Ca(OH)_2$ formed on hydration of cement. Zeolites are represented by $M_{a/n}[(AlO_2)_aSiO_2)_b]\cdot xH_2O$ where $1 \leq b/a \leq 5$ and with x ranging from 1 to 700 [3].

Natural zeolites that have been used in partial substitution for cement include analcime, leucite, clinoptilolite, mordenite, philipsite and chabazite. Such zeolites have been used as a cement blending material in Greece and China for many years [4-7]. Although crystalline in nature, natural zeolites have similar or better technical properties to that of amorphous or glassy aluminosilicates such as fly ash, blast furnace slag and natural pozzolanic tuffs when used in partial substitution of cement [5, 8-11]. It is generally considered that zeolite contributes to compressive strength through the pozzolanic reaction with $Ca(OH)_2$ like other pozzolanic materials. Studies, however, indicate somewhat contrary effects on compressive strength development with natural zeolite blended cements. This in part can be attributed to the different chemical composition of the zeolites used, the fineness of the zeolite, the reactivity of the zeolite to $Ca(OH)_2$ and the percentage of the zeolite present in the zeolitic deposit. The amount of $Ca(OH)_2$ taken up is much greater than explained by cationic exchange, and although this may be the initial process, the main reaction is likely destruction of the aluminosilicate framework and formation of C-S-H and hydrated aluminate phases or C-A-S-H [12].

The resultant effect of zeolites on compressive strength is therefore variable. Chabazite and philipsite, at up to 40% by weight additions, improved strength development in terms of higher reactivity in comparison to pozzolanic glass [9]. Mordenite is reported to give higher compressive strength than clinoptilolite, even though both have similar chemical composition [6]. Compressive strengths similar to that of a control were achieved with clinoptilolite, at 15 and 25% weight replacements and at a water to blend ratio of 0.25 cured for 7 days or longer [5]. Increasing the water to blend ratio to 0.30 gave lower compressive strengths, achieving values at only 93% of the corresponding control. Compressive strength was also slightly lower than a control after 3 years water immersion at 20ºC at 10% by weight addition, and significantly lower at 15% by weight addition [13]. At 268 days, the compressive strength of 10% replacement of cement by zeolite was reported to have increased by 10 to 15% [10]. At less than 10% addition, compressive strength was observed to increase with fineness of the cement zeolite blend and decreasing gypsum content. Cements containing less than 8% zeolite give the best combinations of tensile strength and surface hardness. However, it is also noted that high surface hardness can be achieved by addition of silica fume and super-plasticizers.

The microstructure of hardened cement paste is improved by addition of zeolite, and the content of large pores is reduced, making the paste more impervious [14]. The porosity, however, seems to be dependent on the percentage of zeolite replacement, with a reduction in porosity at 15% replacement and increase in porosity at 25% replacement [5]. Alkali-activation of clinoptilolite indicates that the level of water-accessible porosity increases as the particle size of the clinoptilolite decreases [7].

Literature clearly shows that the effect of the composition, fineness and the percentage replacement of zeolite have a significant effect on properties of cured pastes. The effect of temperature on the reactivity and performance of zeolites has also been observed to affect the performance of oilwell cements and has not previously been reported. The purpose of the present work was to determine the effect of natural zeolites on the early age aqueous chemistry at 30% cement replacement by weight and at temperatures of 25, 50 and 65°C in an attempt to understand the effects of natural zeolites on performance. In addition, some solid phase studies using ESEM were also made of pastes made from natural zeolite with pure C_3S or C_3A phases at 30°C and 85°C to elucidate further on the phenomena observed.

2. Experimental

The two ordinary Portland cements used in this study were commercial Class H and Class C oil well cements conforming to API Specification 10A/ISO 10246-1 specifications. The Class H cement, comparable to a coarse-grind ASTM Type V, was obtained from Lafarge Cement, Ohio, USA and the Class C cement, comparable to ASTM Type III, was obtained from Mitsubishi Cement, California, USA. Specific Wagner fineness for the Class H and Class C were 1400 and 2800 cm^2/g respectively. Zeolites were natural minerals mined in the USA and were determined by XRD to be consistent with chabazite, ferrierite and mordenite. Chabazite, $(Na_2Ca)_6(Al_{12}Si_{24}O_{14})\cdot 40H_2O$, mined in Arizona USA was supplied by C2C Zeolite Corporation, BC, Canada. Ferrierite, $(Na,K)_2Mg(Si,Al)_{18}O_{36}\cdot 9H_2O$, and mordenite, $(Ca,Na_2,K_2)Al_2Si_{10}O_{24}\cdot 7H_2O$, were mined in Wyoming and supplied by Agrilite Industries LLC, Wasilla, Alaska. The mean particle size was determined using a Malvern Mastersizer S particle size analyzer and was determined as 4.75 µm for the chabazite, 3.28 μm for the ferrierite and 3.34 μm for the mordenite. The cage structures for these zeolites are presented in Fig. 1 and the cell dimensions and physical properties in Table 1.

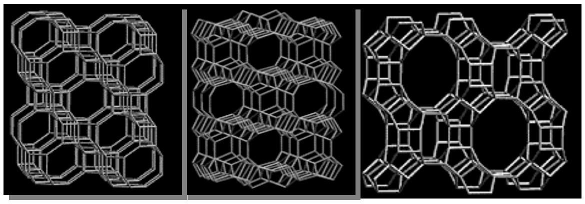
Chabazite Ferrierite Mordenite

Figure 1. Cage structure of zeolites: chabazite, ferrierite and mordenite [2].

Table 1. Cell Dimensions and Physical Properties of Zeolites

	Chabazite	Ferrierite	Mordenite
Framework Type	CHA	FER	MOR
Space Group	Rhombohedral R-3m	Orthorhombic Immm	Orthorhombic Cmcm
Cell Parameters			
a	9.42 Å	19.156 Å	18.1 Å
b	9.42 Å	14.127 Å	20.5 Å
c	9.42 Å	7.489 Å	7.5 Å
α	94.47°	90°	90°
β	94.47°	90°	90°
γ	94.47°	90°	90°
Volume (Å^3)	835.90	2026.65	2782.88
Framework Density	14.5 T/1000 Å^3	17.8 T/1000 Å^3	17.2 T/1000 Å^3
Specific Gravity	2.200	2.257	2.304

Zeolite blends were prepared in the proportion of 70% cement/30% zeolite by weight and mixed with water in a Waring blender according to API Specification 10B/ISO 10246-2. Approximately 100 mL of slurry was placed into each of 10 plastic containers and placed in a water bath at the required temperature. At hourly intervals, a plastic container was removed and the slurry filtered under suction through a Whatman No. 40 filter paper. The volume of solution extracted initially was around 40 mL and decreased to about 2.5 mL with curing time as the slurry started to set. The pH was determined immediately after extraction using a Russell electrode pH meter. Na, K, Ca, Si, Al and Fe were determined using a Thermo Elemental, Iris Intrepid, ICP. Sulfate was measured using a turbimetric method read at 425 μm with a Spectronic 21D spectrophotometer.

Solid phase studies on the hydration of zeolites hydrated with the pure phases, namely C_3S and C_3A, were also investigated. Pastes were prepared by mixing a dry blend of C_3S or C_3A phase with natural zeolite in a ratio based on an equivalent 70:30 weight ratio of cement to zeolite at water to cement ratio of 0.5 and cured for periods of 1, 3 and 7 days at 30 and 85°C as previously discussed [15]. Electron microscopic analysis of the reaction products was made using a Philips XL 30 ESEM on selected samples coated with Au using an Anatech Ltd. sputtering system for high-resolution images.

3. Results

3.1 Class H cement

Table 2 shows the solution data for the Class H cement with and without 30% replacement by chabazite at 25°C and water to solid ratio of 0.5. Values are also given for the Class H cement slurry assuming 30% replacement by an inert material. Al and Si values were low in both the neat Class H and the Class H with 30% replacement of chabazite. Fe was below detectable limits in all slurries. Ca values remained relatively constant up to 6 hours in the neat Class H slurry, whereas with 30% replacement by chabazite, Ca values decreased from 12.0 to 1.4 mM in 4 hours. Ca concentration is a good indication of the early hydration reaction and onset of renewed hydration after the induction period.

Table 2. Aqueous Phase Data on Class H Cement*

Sample	Time (Hr)	Al	Ca	K	Na	Si	SO_4
		(mM)					
Class H	1	<0.002 (<0.001)	20.2 (14.2)	133.4 (93.4)	29.0 (20.3)	0.100 (0.071)	67.7 (47.4)
	2	<0.002 (<0.001)	20.8 (14.5)	129.0 (90.6)	27.8 (19.5)	0.068 (0.046)	59.4 (41.6)
	3	0.03 (0.02)	20.8 (14.6)	130.9 (91.7)	28.0 (19.6)	0.167 (0.114)	58.3 (40.8)
	4	0.011 (0.007)	19.9 (13.9)	127.6 (89.3)	27.0 (18.9)	0.071 (0.050)	56.3 (39.4)
	5	0.007 (0.003)	19.9 (13.9)	128.5 (89.9)	27.3 (19.1)	0.071 (0.050)	55.2 (38.6)
	6	<0.002 (<0.001)	19.2 (13.4)	132.6 (92.8)	28.7 (20.1)	0.050 (0.036)	56.3 (39.4)
70/30 Class H /Chabazite	1	<0.002	12.0	3.8	261.3	<0.002	100.0
	2	<0.002	4.7	3.4	279.9	<0.002	89.6
	3	0.030	2.8	3.6	292.1	<0.002	86.5
	4	0.052	1.4	3.8	287.3	0.104	80.2

*Values in () relate to the dilution expected if 30% inert material were used.

A decrease in Ca concentration typically corresponds to precipitation of calcium hydroxide and the end of the induction period [16, 17]. The lower values of Ca in the chabazite slurry, 12.0 mM compared to 14.2 mM for an equivalent Class H slurry with inert material, suggests that the chabazite acts as an accelerator to cement hydration even within the first hour. Acceleration of hydration is also confirmed by the fact that the neat Class H cement was still fluid at 6 hours, whereas the 70/30 Class H/chabazite slurry had already become viscous and showed signs of setting at 4-5 hours. K and Na ion concentrations in the aqueous phase were constant over the time period investigated for both the neat Class H slurry and the 70/30 Class H/chabazite slurry. Differences in K and Na values between the two slurries were notable. K concentrations were typically around 90.0 mM in the Class H slurry making allowance for 30% replacement by inert material in comparison to a value of about 3.6 mM for the Class H slurry with 30% chabazite. Na concentrations showed the converse to the K ion concentration, with low values obtained in the Class H slurry at around 20 mM allowing for 30% replacement by inert material compared to around 280 mM with chabazite. The hydration products, particularly the C-S-H typically do not incorporate significant amounts of alkalis. Difference in the Na and K concentrations between the Class H and the 70/30 Class H/chabazite slurries is more readily explained by the ion exchange capacity of the chabazite with Na being replaced by K. Na ion concentrations in the 70/30 Class H/chabazite slurries are however significantly higher than would be expected on the basis of a one to one direct ion exchange with K ions from the Class H cement. The additional Na ions along with the almost two-fold increase in SO_4 values in the 70/30 Class H/chabazite slurry suggest that there is Na_2SO_4 present in the mineral chabazite deposit. Dissolution of the natural chabazite in water showed about 10% of soluble material that on analysis consisted of 8.75 mM Ca, 0.41 mM K, 120.8 mM Na and 64.6 mM SO_4 ions. XRD confirmed the presence of thernadite (Na_2SO_4) as a component in the natural chabazite. The slight decrease in SO_4 with time suggests it is being used up in hydration of the C_3A with formation of either AFm or AFt phases. The pH was determined for all extracted solutions and was found to be typically around 12.2 with no distinct difference over time or on replacing 30% Class H cement with chabazite.

3.2 Class C cement

The solution data for the Class C cement with and without 30% replacement by chabazite at 25°C are shown in Table 3. A water to cement ratio of 0.93 was used for the Class C slurries and related to increased water demand and hydration kinetics attributed to the fineness of both the cement and chabazite. Values for the aqueous phase composition are also given for the Class C cement slurry, assuming 30% replacement by an inert material. Although the absolute values differ from those obtained with the Class H cement, due to the difference in cement composition and water to solid ratio, the trends are the same. Al, Si and Fe contents are low and typically below detectable limits of the test method and are normal for cement. Ca is initially high and after attaining supersaturation, tends to fall off rapidly with precipitation of $Ca(OH)_2$. This rapid decrease in Ca concentration relates to setting of cement, and again, it can be seen that the chabazite accelerates the hydration of cement, with concentrations starting to decrease at 4 hours and reaching a value of 1.2 mM at 6 hours, compared to the neat cement which started to show a decrease in Ca at 6 hours and with values still high at 12 mM equivalent at 10 hours. K and Na concentrations in neat cement slurry at early ages are dependent on the soluble alkali sulfates [18]. K content is significantly higher in the neat cement by comparison to the Na content, with values of K around 50 mM and Na at about 6.5 mM. K and Na contents notably increase with time and are assumed to result from K and Na ions that are incorporated into the cement phases, in particular the C_3A, being released on hydration of these phases. This increase is consistent with additional hydration and complements the decrease in Ca ions [17].

Table 3. Aqueous Phase Data on Class C Cement*

Sample	Time (Hr)	Al	Ca	K	Na	Si	SO_4
		(mM)					
Class C	1	<0.002 (<0.001)	35.6 (25.0)	76.5 (53.6)	8.8 (6.2)	<0.028 (<0.002)	28.5 (20.7)
	2	0.05 (0.03)	34.9 (24.5)	80.0 (56.0)	14.8 (10.3)	<0.002 (<0.002)	30.8 (21.5)
	3	0.111 (0.078)	33.8 (23.6)	82.4 (57.7)	15.2 (10.6)	<0.002 (<0.002)	30.8 (21.5)
	4	0.926 (0.067)	31.8 (22.3)	83.0 (58.1)	18.4 (12.9)	<0.002 (<0.002)	34.3 (24.0)
	5	0.222 (0.156)	31.0 (21.7)	83.9 (58.8)	17.4 (12.2)	0.025 (0.018)	30.8 (21.5)
	6	0.030 (0.022)	26.1 (18.3)	90.0 (62.8)	27.4 (19.2)	<0.002 (<0.002)	36.7 (25.7)
	8	0.089 (0.063)	21.8 (15.3)	96.1 (67.3)	14.1 (9.9)	<0.002 (<0.002)	36.7 (25.7)
	9	0.100 (0.070)	24.1 (16.8)	95.4 (66.8)	13.6 (9.5)	<0.002 (<0.002)	34.3 (24.0)
	10	0.219 (0.152)	16.5 (11.5)	126.6 (88.6)	19.7 (13.8)	<0.002 (<0.002)	41.4 (28.8)
70/30 Class C /Chabazite	1	<0.002	19.4	3.2	177.8	<0.002	58.3
	2	<0.002	21.6	3.7	207	<0.002	58.3
	3	<0.002	19.6	4.9	217	<0.002	58.3
	4	0.133	12.5	6.90	221	<0.002	60.4
	5	<0.002	4.1	9.67	224	<0.002	63.5
	6	0.200	1	17.2	225	<0.002	67.7

*Values in () relate to the dilution expected if 30% inert material were used.

K and Na content in the 70/30 Class C/chabazite slurry again shows the inverse to that of the neat Class C slurry, with K content around 3.2 mM and Na at 173.9 mM and is again indicative of ion exchange capacity of the zeolite whereby Na is replaced by K. Interestingly, the K content increases with time, showing a 5-fold increase over 6 hours compared to 1.5-fold increase over 10 hours for the neat cement. This suggests that in the 70/30 Class C/chabazite slurry both the cement and zeolites are hydrating and that breakdown of the structures releases K into the aqueous phase. Na content of the 70/30 Class C/chabazite comes predominantly from ion exchange with the chabazite as well as from Na_2SO_4. Increase over time as seen in both the neat Class C cement and the 70/30 Class C/chabazite slurry is undoubtedly due to cement hydration and release of Na from the C_3A. In the 70/30 Class C/chabazite slurry, the greater increase in Na, 178 to 225 mM, along with the increase in sulfate ion from 58.0 to 67.7 mM over the 6 hour hydration period, suggests that some of the Na_2SO_4 may be trapped in the chabazite cage structure and is released into solution as the chabazite structure is destroyed by dissolution during hydration. K and Na are not typically taken up by the hydration products and concentrations increase over time as hydration continues.

3.3 Temperature effects

Solution data for Class C cement and 70/30 Class C/chabazite, water to solids ratio 0.93 and cured at temperatures of 25, 50 and 65°C are given in Figs. 2-5. The values for the neat Class C slurries were normalized assuming the addition of 30% by weight inert material. At 25°C, the Ca content shows a gradual decrease from about 17.5 to 12.5 mM at a curing time of 7 to 9 hours (Fig. 2). Ca content decreases more rapidly with increasing temperature and decreases from around 17.5 to 0 mM in 3 to 7 hours at 50°C and 3 to 5 hours at 60°C. That is to say that it takes more than 8 hours for the neat Class C cement to set at 25°C, 7 hours for it to set at 50°C, and only 5 hours at 65°C. The 70/30 Class C/chabazite blends show similar trends with setting accelerated by approximately 3 hours in comparison to the neat Class C cement at all temperatures. Data points are limited with the 70/30 Class C/chabazite slurries, as they had started to set after a few hours and could not be filtered, again confirming the accelerated setting due to the chabazite. K and Na, Figs. 3 and 4, follow the same ion exchange trends at higher temperatures as they do at 25°C with high K and low Na values in neat Class C slurries and high Na and low K in the 70/30 Class C/chabazite slurries. The K values in the neat Class C slurries increase both with increasing temperature and time, indicating more complete hydration whereby the additional K is released on dissolution of the cement phases, particularly the C_3A. The K content although low in the 70/30 Class C/chabazite also shows a slight increase with temperature and time and suggests increased reaction/dissolution of the chabazite. The Na content in the neat Class C cement is relatively constant over time and shows only minimal increase with temperature. In the case of the 70/30 Class C/chabazite, the Na content complements that of the K with high Na values that increase with time at the higher temperatures. The SO_4 content, Fig. 5, in the neat Class C cement is constant as a function of both the temperature and time. Values are again higher in the 70/30 Class C/chabazite slurries and show only a slight increase with time, 57.3 to 67.7 mM, and temperature. This again is consistent with the presence of Na_2SO_4 in the chabazite.

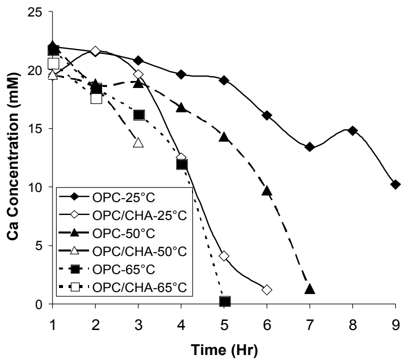

Figure 2. Effect of temperature on Ca content of Class C/chabazite (OPC/CHA) slurries.

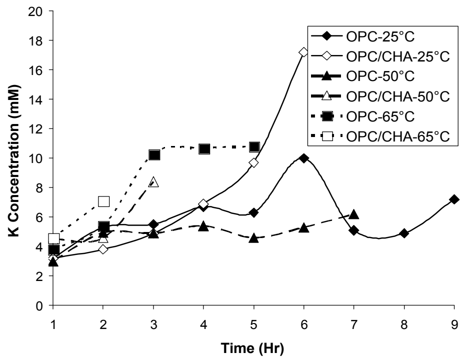

Figure 3. Effect of temperature on K content of Class C/chabazite (OPC/CHA) slurries.

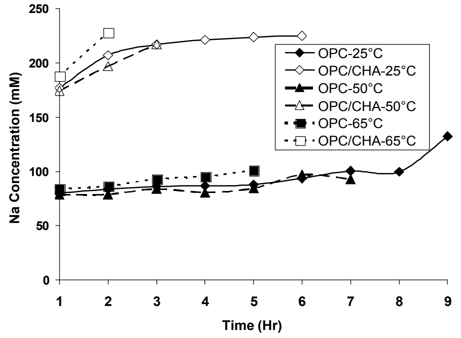

Figure 4. Effect of temperature on Na content of Class C/chabazite (OPC/CHA) slurries.

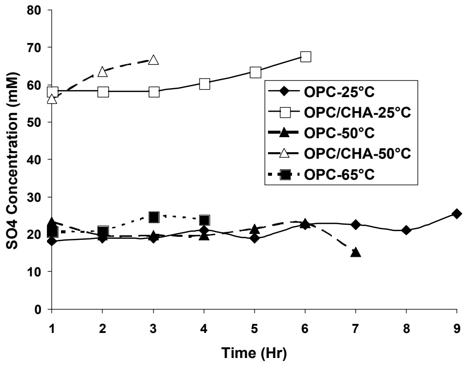

Figure 5. Effect of temperature on SO_4 content of Class C/chabazite (OPC/CHA) slurries.

3.4 Comparison of natural zeolites on hydration

The aqueous composition and hydration of Class C cement with the zeolites, chabazite, ferrierite and mordenite at 25°C and water to solid ratio of 0.93 is shown in Figs. 6 -9. Chabazite, ferrierite and mordenite differ significantly in chemical composition, crystal structure, type of cage structure and exchangeable alkali ions or alkaline earth metals and also in their reactivity with Class C cement. Ca content, Fig. 6, clearly shows the differences in hydration rate of the Class C cement with the different zeolites. The ferrierite gives the highest Ca content, 36 mM, but shows only a small decrease over time, indicating minimal reaction and no onset of hydration, which was consistent with the fact that the slurry was still fluid after 6 hours. Mordenite showed a somewhat greater degree of hydration with a rapid decrease in Ca concentration from 32.5 mM at 2 hr to 10.4 mM at 6 hr. Chabazite, although having the lowest degree in supersaturation, appeared to have the greatest degree of reaction with only 1.2 mM Ca at 6 hours, indicating almost complete precipitation of $Ca(OH)_2$ and onset of C_3S hydration. Fig. 7 shows the Na content. Values differ considerably and range from around 30 mM for ferrierite and 220 mM for chabazite. Variations in the Na concentrations complement that of the Ca such that the higher the Na, the more the Ca is depressed. Na content although variable remains relatively constant over time, indicating that the Na remains in solution and is neither absorbed by the zeolite nor cement hydration product [19]. K, Fig. 8, shows somewhat different trends occurring with the different zeolites. The constant K content over time in the Class C/mordenite is what would typically be expected and results more or less from dissolution of soluble sulfates in cement. Increased K over time with the Class C/chabazite is considered to be due to hydration and breakdown of the chabazite structure. The decrease in K during the initial 2 hr in the Class C/ferrierite slurry is less easily explained and may be due to K from the cement being taken up in the zeolite cage structure. SO_4 content, Fig. 9, again complements the Na content indicative of the presence of Na_2SO_4 in association with chabazite though not with ferrierite and mordenite.

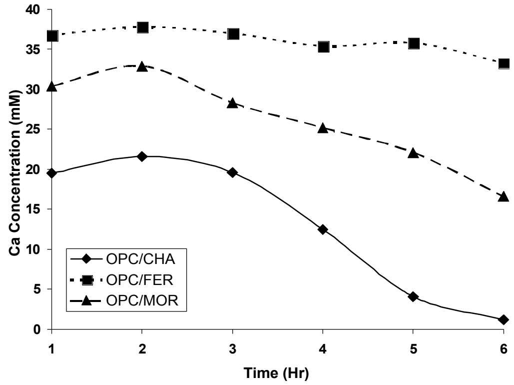

Figure 6. Effect of zeolite on Ca content of Class C cement slurry.

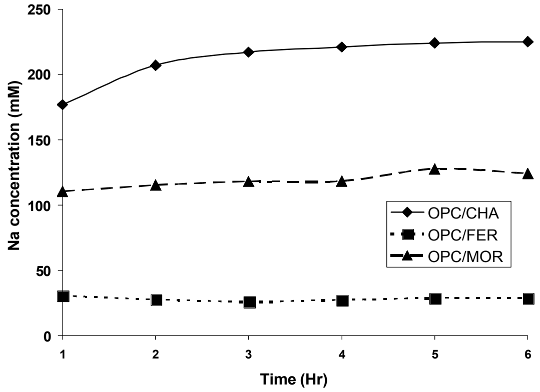

Figure 7. Effect of zeolite on Na content of Class C cement slurry.

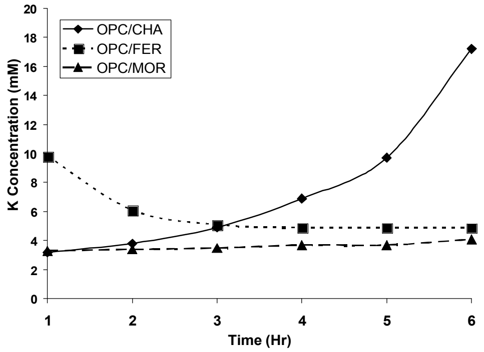

Figure 8. Effect of zeolite on K content of Class C cement slurry.

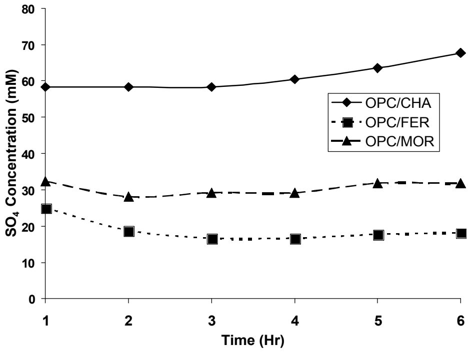

Figure 9. Effect of zeolite on SO_4 content of Class C cement slurry.

3.5 Comparison of natural zeolites on C_3S and C_3A

Hydration of C_3S with chabazite at 30°C and 1 day shows a considerable abundance of C-S-H though no evidence of $Ca(OH)_2$ (Fig. 10). Angular particles of chabazite, sparsely coated with hydration product, indicate that pozzolanic reaction is occurring even at this early age.

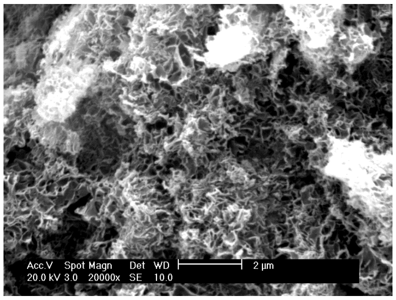

Figure 10. Micrograph of C_3S and chabazite at 30°C for 1 day.

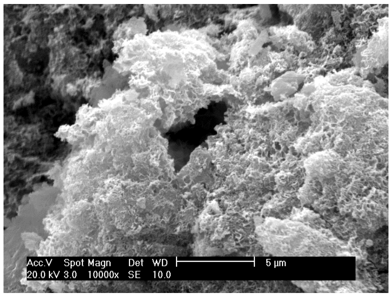

Figure 11. Micrograph of C_3S and chabazite at 30°C for 7 days.

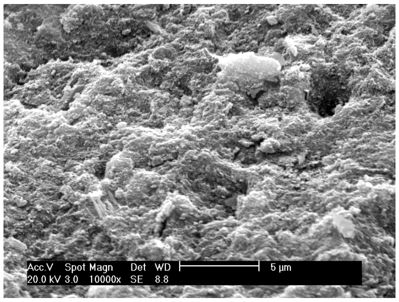

Figure 12. Micrograph of C_3S and chabazite at 85°C for 7 days.

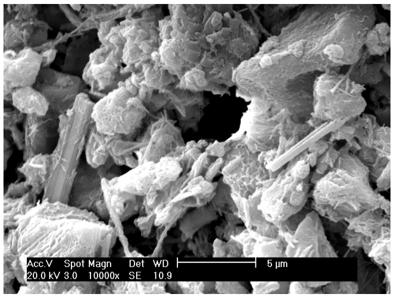

Figure 13. Micrograph of C_3S and mordenite at 30°C for 1 day.

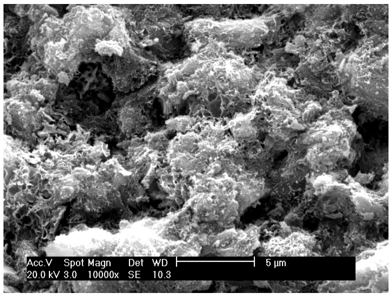

Figure 14. Micrograph of C_3S and mordenite at 85°C for 7 days.

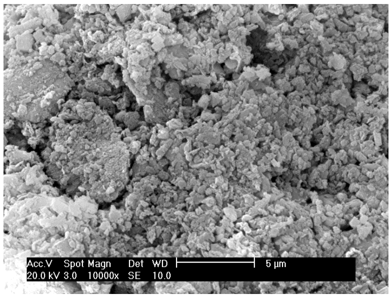

Figure 15. Micrograph of C_3A and chabazite at 30°C for 7 days.

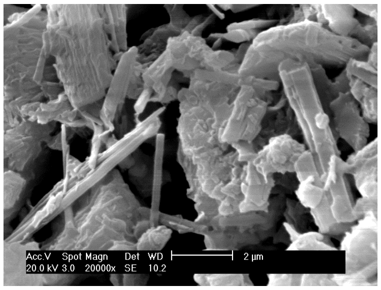

Figure 16. Micrograph of C_3A and mordenite at 30°C for 1 day.

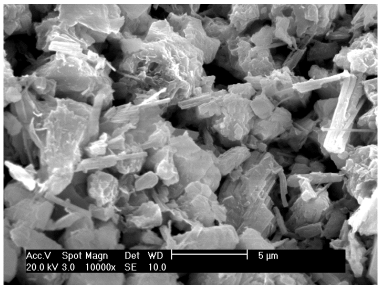

Figure 17. Micrograph of C_3A and mordenite at 85°C for 7 days.

Continued reaction, Fig. 11, gives a more compact C-S-H with time and there are also indications of C-A-S-H hydration product having an almost non-descript morphology. Reaction at 85°C shows an even greater degree of reaction with formation of Type III C-S-H (Fig. 12). Reaction products from hydration of C_3S with mordenite show a completely different morphology compared to chabazite. Morphology at 1 and 7 days and 30°C is similar with no indication of C-S-H or $Ca(OH)_2$, only mordenite with some surface coating of hydration product and a mesh of fibrous material that appears to give some bonding structure to the matrix (Fig. 13). Reaction at 85°C, Fig. 14, was similar to that of chabazite with formation of a non-descript C-S-H or C-A-S-H and absence of $Ca(OH)_2$ indicative of the pozzolanic reaction of mordenite. Results suggest that chabazite accelerates hydration whereas mordenite tends to retard the hydration at 30°C.

Hydration of C_3A with either chabazite or mordenite was retarded by comparison to neat C_3A paste, and even at 7 days and 85°C was still a pliable paste. The morphological characteristics, however, showed some significant differences. At 30°C there was no indication of hydration product with the chabazite, Fig. 15, whereas with mordenite, irregular crystals with and without surface coatings were observed inter-dispersed with well defined needles (Fig. 16). There was no indication of typical reaction products from the C_3A. Particles showed no signs of cohesion consistent with the lack of strength. At 85°C, mordenite reaction with C_3A was similar to 30°C, whereas the chabazite showed significant reaction showing a honeycomb structure of C-A-S-H and well defined crystalline products of calcium aluminosilicates (Fig. 17).

4. Discussion

Pore solution composition is controlled by a balance of a number of competitive processes and in simplistic terms can be considered as resulting from an increase in solution concentration arising from dissolution or removal of ions from solution. Dissolution of ions occurs from hydration of cement and/or zeolite and gives an increase in concentration, whereas removal of ions from solution is a consequence of incorporation of ions into the solid hydration products. These processes occur at different rates and can markedly affect the overall performance of the zeolite blended cements.

The rate of hydration and dissolution of ions of the cement itself can have a considerable influence on pore solution composition and is a function not only of the chemical composition of the cement but also its fineness. Ca content typically relates to the hydration of the cement phase assemblage and initially increases on dissolution of these phases until super saturation is attained after which it decreases rapidly as $Ca(OH)_2$

precipitates. This decrease is also associated with renewed cement hydration and setting of cement and thus gives an indication on cement reactivity. Alkali, Na and K, are another feature of the cement and contents vary considerably from one cement to another. Alkalis tend not to be incorporated in the solid hydration products and remain in the pore solution and are obtained initially from soluble alkali sulfates and later from the hydration of the cement phase assemblage particularly the C_3A, which tends to have a higher degree of alkali substitution.

Addition of zeolite modifies the pore solution to an extent that is dependent on the zeolite used. The most notable effect is the significant decrease in K content. This decrease is balanced by an increase in either Na or Ca or both and relates to the zeolite used and is consistent with the ion exchange capacity of the zeolite. In the case of the zeolite, chabazite, K exchanges with Na. Total Na content, however, far exceeds that of the K in terms of a mass balance, and solution analysis indicates that some of the Na is also attributed to a high percentage of Na_2SO_4 present probably as an “impurity” in the mined zeolite material. Ca content of the chabazite blend is lower and is most likely attributed to the additional Na and the common ion effect, although reaction of chabazite with Ca to form C-A-S-H in the pozzolanic reaction cannot be neglected even at this early age. Pozzolanic reaction at 1 day was clearly evidenced on reaction with C_3S, though C_3A was retarded. This source of chabazite was found to clearly accelerate the hydration of the cement. Mordenite increased both Na and Ca contents in respect to exchange with K, and the slightly higher SO_4 content over that of the neat cement again indicated the presence of some Na_2SO_4 in the zeolite source. The hydration products of mordenite indicate more of a retardation effect although at 1 day there was some slight indication of the pozzolanic reaction occurring. Ferrierite on the other hand clearly retarded the setting of cement and showed only ion exchange between Na and Ca. Interestingly SO_4 content did not show a rapid decrease with time corresponding to that of the Ca content either for the neat cements or the zeolite blended cements [17]. It appears the zeolite inhibits the growth of aluminate phases, though the reason for this is not clear. Increase in temperature increased the rate of reaction as expected and did not elucidate further on mechanism of reactions.

The pore solution data gives some indication on how and why the zeolites show different performance characteristics. The chabazite for example shows acceleration of set that can also be associated with increased early strength development by comparison to the mordenite and ferrierite and is consistent with such differences noted in the literature [6,9]. The variations in pore solution attributed to the zeolites and the alkali ion exchange capacity can also explain the differences in strength related to water to cement blend ratio, percentage addition of zeolite and effect of zeolite fineness [5,10,13]. The influence of the alkali content, particularly the high

Na content in the chabazite may also be of concern in relation to alkali-silica reaction, though zeolites are typically reported to have beneficial effects [20,21].

5. Conclusions

Zeolites are pozzolanic in nature. The degree at which the pozzolanic reaction occurs differs depending on the composition and source of the zeolite. In the present study, the difference in pore solution chemistry and morphology of zeolite blends was clearly illustrated. Notably the zeolite reduced pore solution K and increased the content of Na or Ca or both depending on the zeolite used. This was considered to be a result of the cation exchange capacity of the zeolite. The zeolite chabazite accelerated the hydration of cement, whereas the mordenite and ferrierite appeared to retard the hydration. Acceleration in hydration was considered to result from the presence of Na_2SO_4 in the mined chabazite material though the chabazite itself may also have an effect as seen by the formation of hydration products and lack of $Ca(OH)_2$ on hydration of C_3S at 1 day. Mordenite showed some reaction at 1 day but with formation of different reaction products. Chabazite and mordenite both appeared to retard hydration of C_3A. Clearly, a more fundamental study in understanding the chemistry of the reactions between the various zeolites and cement needs to be undertaken.

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