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Cement & Concrete Composites 30 (2008) 455–462

Cement & Concrete Composites

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# Some advances in understanding the pozzolanic activity of zeolites: The effect of zeolite structure

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Received 2 November 2006; received in revised form 26 July 2007; accepted 6 August 2007

## Abstract

To investigate the pozzolanic activity of zeolites, experimental blended cements prepared by mixing together ordinary Portland clinker, isochemical sodium zeolites type A [LTA] or X [FAU], and gypsum, were subjected to the Fratini's test, i.e., the official test recognized in the European Standards. The same mixtures without gypsum were used to prepare cement pastes with deionized water, which, after curing for 3–28 days, were subjected to mechanical strength measurements. Both zeolites proved to be effective as pozzolanic materials. Their action involved various steps, including (1) cation exchange, (2) dissolution and/or breakdown of the zeolitic structure, (3) possible formation of transient gel phases, and (4) precipitation of hydrated calcium silicates and aluminates. Pozzolanic activity was demonstrated to depend on zeolite structure. Zeolite A reacted, in fact, more readily than zeolite X. Zeolite X, on its turn, being slightly more siliceous than zeolite A, contributed to a greater extent to the development of the mechanical resistances of the cement pastes at short curing times.

*Keywords:* Blended cement; Cement paste; Compressive strength; Pozzolanic activity; Synthetic zeolite

## 1. Introduction

Pozzolanic cements are a class of composite cements [1], in which the basic Portland clinker is partly substituted by mineral additions which are said to possess a "pozzolanic activity". Pozzolanic activity is the ability of some silica- and alumina-rich materials to react with lime forming hydraulic compounds, i.e., hydrated calcium silicates (e.g., tobermorites) and aluminates, and harden in both aerial and aqueous environments [1]. This property is typical of pozzolan, an unconsolidated, mostly glassy, rock of volcanic origin, widespread especially in Central-Southern Italy, which has been used since ancient times, in mixture with lime to prepare hydraulic mortars. Other materials having the same property are: fly ash (pulverized fuel ash), microsilica (condensed silica fume) and heat treated clay (even crushed bricks or tiles), among the artificial materials, and zeolitized tuffs, diatomaceous earth, pumice, and some vitreous rhyolites, among the natural materials [1,2].

The production and use of pozzolanic cements, introduced in the first decades of the twentieth century, give several advantages: (a) the pozzolanic material, reacting with lime formed during the hydration of Portland cement gives rise to cementitious products behaving therefore like a hydraulic binder [3]; (b) the reduction of free $Ca(OH)_2$ (portlandite) in the hardened concrete improves the durability of the material, in that the concrete becomes more resistant to lime leaching by flowing waters and to expansion due to sulfate attack [3]; (c) the reduction of the overall energy required in manufacturing the cement is beneficial for the cost but also for environmental reasons; (d) the slowing down and decrease of heat evolution during the cement hydration is beneficial in the setting-up of structures of large dimensions [3].

Natural, zeolite-rich volcanic tuffs [4] have been proposed and frequently used as pozzolans, in several

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doi:10.1016/j.cemconcomp.2007.08.004

countries, such as Bulgaria, China, Cuba, Germany, Greece, Italy, Jordan, Russia, Turkey, the United States, and Serbia–Montenegro (formerly Yugoslavia) [5].

In recent years, much research has been carried out into the utilization of zeolite-bearing tuffs in place of true pozzolans for manufacturing blended cements (see, e.g., [6–10]). Zeolite types that have been tested so far are those most common in the sedimentary zeolite (tuff) deposits widespread all over the world, namely, clinoptilolite, mordenite, phillipsite and chabazite [11]. It has been ascertained that: (a) natural zeolites are excellent pozzolanic materials, which often behave better than pozzolan itself [3] or a glass of identical composition [12]; zeolite reactivity is related to its large external specific surface and metastability, which favor its dissolution into the saturated lime solution and the successive precipitation of CSH (hydrated calcium silicate) and CAH (hydrated calcium aluminate) phases [13]; (b) the replacement of Portland clinker by zeolitic tuff reduces workability [4] and increases water demand [14], but this effect may be overcome by using a superplasticizer [15]; (c) the replacement of Portland clinker by zeolitic tuff reduces the alkali level of the blend minimizing the risk of alkali-silica reaction, which would result in undesired expansion and cracking of concrete [4,16].

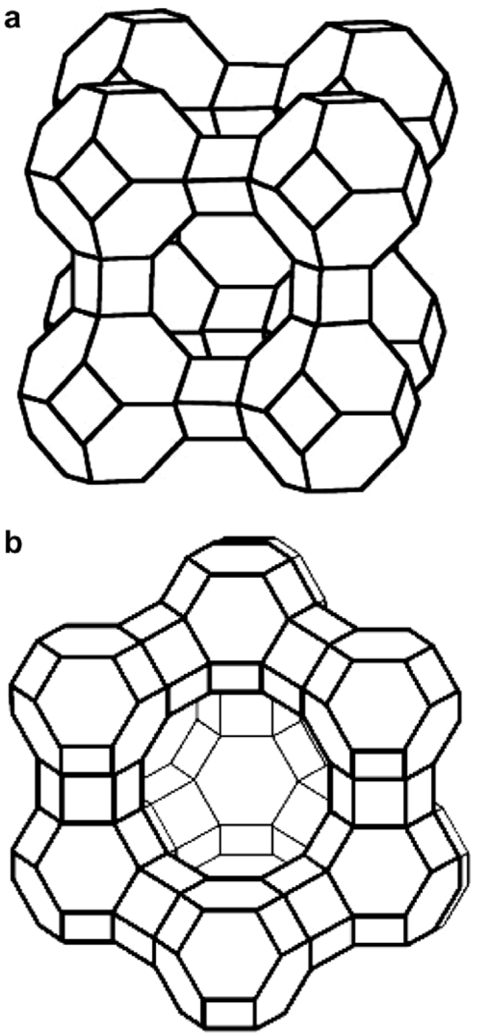

Fig. 1. Zeolite A (a) and zeolite X (b) structures [17], based on different arrangements of the same polyhedral building unit (the truncated octahedron, usually called β-cage or sodalite-cage).

Despite the large number of papers available in the literature on this subject (see Refs. [4–14] and the papers quoted therein), limited efforts have been made to date to investigate both the action mechanism of zeolite as pozzolanic addition to Portland clinker and, particularly, the role played by the nature and composition of the zeolite. This is due to the difficulty to study complex systems, such as zeolitized tuffs, in which many components normally co-exist, some having pozzolanic behavior (e.g., zeolites – having different structure and chemical composition, clay minerals, glass, slags, pumice, gel-like phases, etc.), and other being largely inert (e.g., crystalline silica, feldspars, pyroxene, biotite, etc.).

To examine the zeolite behavior as pozzolanic material in detail, the addition to Portland cement of pure, commercially available, synthetic zeolites has been investigated. To restrict the number of variables mainly to structure, two synthetic, aluminous, sodium zeolites, types A [LTA] and X [FAU], having close Si/Al ratios and sharing the same polyhedral building unit have been selected (Fig. 1) [17]. The study focused on the pozzolanic activity exhibited by these two zeolites in blend with ordinary Portland cement (OPC) and on the mechanical properties of the corresponding hardened pastes. The results obtained have only comparative value because no attempt was made to optimize the chemical or mechanical properties of the studied blends and to compare their performances to those of ordinary pozzolanic cements.

## 2. Experimental

### 2.1. Materials and blends

The synthetic sodium zeolites A and X, marketed with the trade names of Molecular Sieves 4A and 13X, respectively, were provided by Carlo Erba AnalytiCals (Italy). The grain size of both samples is reported to be 0.5–5 μm.

The chemistry of zeolite type A is invariable, as regards either the Si/Al ratio, equal to 1, or the water content, equal to 22.2%, as measured by thermogravimetry (Stanton STA-780 thermoanalyzer). Its formula is therefore $NaAlSiO_4 \cdot 2.25H_2O$. Unlike the type A, the chemical formula of the zeolite type X is variable in a wide range [17]. It was obtained indirectly, measuring the water content (= 22.7%) and estimating the Si/Al ratio from the measured unit cell size [18]. The unit cell size, estimated with the aid of a suitable computer program from the X-ray diffraction pattern using $Pb(NO_3)_2$ as internal standard, turned out to be 25.027 Å, which gave a Si/Al ratio of 1.20 [18]. The calculated formula was, therefore, $NaAlSi_{1.2}O_{4.4} \cdot 2.5H_2O$. All the other chemicals used were reagent grade Carlo Erba. The ordinary Portland clinker utilized was supplied by the company Cementi della Lucania S.p.A. from Avigliano (PZ), Italy. Its chemical and mineralogical compositions, provided by the supplier, are reported in Table 1. The fineness of the clinker sample is mostly <180 μm.

The experimental blended cements were prepared by gently mixing together in a mortar, with the help of a pestle, samples of the clinker with appropriate quantities of the above described zeolites and finely ground gypsum ($CaSO_4 \cdot 2H_2O$), in such a way that the zeolite was 5–25% by weight of the total amount of the actual and potential binding components (clinker + zeolite), and gypsum (retarder of setting) was constantly 5% of the total mixture. An experimental OPC, made by mixing together 95% Portland clinker and 5% gypsum, was used as reference. Table 2 reports the actual compositions of the blends examined, referred to as A/X-5/25. It is to be observed that the industrial practice to grind all the cement components together to obtain a blend of a given Blaine specific surface was disregarded in this study, because, as already pointed out by Fragoulis et al. [14], this would have produced blends with different finenesses and therefore introduced an undesired new variable.

Clinker–zeolite mixtures in the same proportions as in the above blended cements, but without gypsum, were also utilized to obtain pastes for the mechanical measurements. Accordingly, blends referred to as a/x-5/25 in Table 2 and ordinary Portland clinker (OPCl), used as reference, were mixed with deionized water to give a blend/water ratio of 0.36 (w/w), which is very close to that used in real conditions, thereby ensuring a good workability.

Table 1
Chemical and mineralogical composition of the clinker sample utilized

| Compounds | % | Minerals (Bogue) | % |
|---|---|---|---|
| $SiO_2$ | 20.44 | $2CaO\ SiO_2$ | 14 |
| CaO (total) | 63.60 | $3CaO\ SiO_2$ | 59 |
| CaO (free) | 0.64 | $3CaO\ Al_2O_3$ | 10 |
| $Al_2O_3$ | 5.58 | $4CaO\ Al_2O_3\ Fe_2O_3$ | 9 |
| $Fe_2O_3$ | 3.02 | Other | 8 |
| MgO | 2.54 | | |
| $Na_2O$ | 0.48 | | |
| $K_2O$ | 0.99 | | |
| Loss on ignition | 0.78 | | |

Some minor components have not been analyzed.

## 2.2. Methods

The prepared cement pastes were used to check the zeolite ability to act as pozzolanic material. This was performed: (1) directly through the evaluation of the pozzolanic activity of both zeolites and (2) indirectly through the evaluation of the mechanical performances of the hardened cement pastes at different curing times.

Among the various chemical methods proposed to evaluate the pozzolanic activity [19] Fratini's test, which is still recognized in the European Standards [20] although it was devised more than fifty years ago [21,22], was selected. In this test the amount of $Ca(OH)_2$ leached from a blended cement put into contact with deionized water is estimated. Accordingly, 20 g of each experimental blend (Table 2) were mixed with 100 ml of deionized water, and the mixture was kept at 40 °C for 8 days. The $Ca^{2+}$ and $OH^-$ concentrations were then estimated in the resulted solution by standard methods of volumetric analysis, namely complexometric titration with EDTA and acid–base titration, respectively. Experimental results (average values of runs performed in triplicate) were projected in a plot reporting the solubility curve of $Ca(OH)_2$, as a function of $Ca^{2+}$ and $OH^-$ concentrations in solution. Points above the curve and on the curve are representative of over-saturated and saturated solutions, respectively, and prove the lack of pozzolanic activity. On the contrary, points under the curve represent under-saturated solutions and therefore prove the existence of definite pozzolanic action shown by the specific mineral addition to the OPC. Reference tests similar to those above described but at very short reaction times (2–8 h) were also performed, in order to examine the early stages of the clinker–zeolite interaction.

Mechanical performances of the experimental clinker–zeolite blends were estimated by measuring the compressive strength of the hardened cement pastes, described in the previous section, at different degrees of curing. Pastes were put into cylindrical moulds (diameter = height = 30 mm) and cured for 3, 7, 14 or 28 days at 25 °C and 100% humidity. The hardened compacts obtained in this way were subjected to compressive strength measurements by Instron 4301 apparatus. All runs were performed in triplicate and the relative results averaged.

The solid fragments recovered from the two above-mentioned experiments (evaluation of the pozzolanic activity and mechanical evaluation) were subjected, after suitable

Table 2
Components and relative contents of the blended cements and clinker–zeolite blends

| Component | Blends | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | OPC[a] | A/X-5 | AX-10 | A/X-25 | OPCl [b] | a/x-5 | a/x-10 | a/x-25 |
| Portland clinker | 95.00 | 90.25 | 85.50 | 71.25 | 100.00 | 95.00 | 90.00 | 75.00 |
| Zeolite A/X | – | 4.75 | 9.50 | 23.75 | – | 5.00 | 10.00 | 25.00 |
| Gypsum | 5.00 | 5.00 | 5.00 | 5.00 | – | – | – | – |

[a] Ordinary Portland Cement.

[b] Ordinary Portland clinker.

grinding, to X-ray diffraction (XRD) analysis, made with a Philips PW 1710 apparatus, in order to estimate the presence of residual zeolite and/or unreacted $Ca(OH)_2$. Semi-quantitative estimations were made by comparing peak intensity of the examined cement samples and the reference materials. The peaks considered were the most intense for each phase: $2\theta = 18.1°$ (1 0 1) for portlandite, 7.2° (2 0 0) for zeolite A, and 6.9° (1 1 1) for zeolite X.

## 3. Results

### 3.1. Pozzolanic behavior of the cement–zeolite blends

Fig. 2 shows the results of the test for estimating the reactivity of types A and X zeolites as pozzolanic materials. The points representative of the OPC and of the blends A-5, A-10, X-5 and X-10 (see Table 2) are above the solubility curve of $Ca(OH)_2$, i.e., the contact solution of these blends is over-saturated in portlandite, possibly due to insufficient amount of the pozzolanic materials utilized in relation to its composition. On the contrary, the blends with higher zeolite content (A-25 and X-25 in Table 2) gave rise to conditions of $Ca(OH)_2$ under-saturation. Increasing the zeolite addition caused a progressive decrease of $Ca^{2+}$ and raising of $OH^-$ concentrations in solution. Fig. 3 gives the results of reference tests on the blends A-25 and X-25, analogous to those described above in Fig. 2, but performed at very short reaction times. Comparing the experimental points in Fig. 3 (open symbols) with those relative to Fratini's test, taken from Fig. 2 and reported as reference (solid simbols), makes evident the effectiveness of both zeolites to act as pozzolanic addition from the early stages of the reaction, with a progressive shifts of the relevant points rightwards and downwards at increasing times.

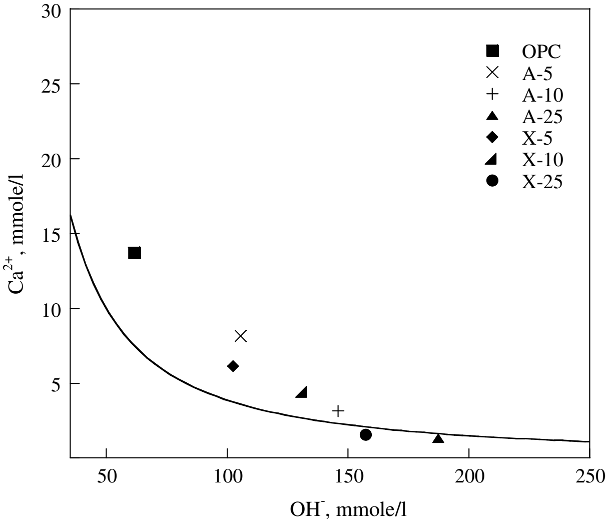

Fig. 2. Results of Fratini's test [21,22] for evaluating the ability of the zeolites A and X to act as pozzolanic addition. Solid line: $Ca(OH)_2$ solubility curve; sample abbreviations: see Table 2.

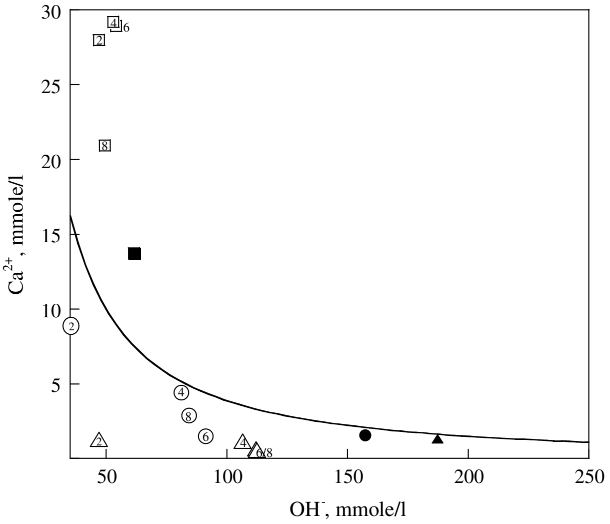

Fig. 3. Results of tests analogous to those of Fig. 2, but carried out at shorter and variable reaction times. Square: OPC; triangle: blend A-25; circle: blend X-25 (Table 2). Reaction times in hours are indicated within the open symbols. Solid symbols as in Fig. 2.

A solid phase analysis of the hardened cement pastes at various reaction stages may help give further light on the evolution of the clinker–zeolite–water system in course of time. Fig. 4a and b shows the XRD patterns of a selection of solids relative to Figs. 2 and 3 (blends A-25 and X-25 at various curing stages), comparing them with the patterns of the zeolites (top XRD patterns in both sequences) and original unreacted blends (the immediately subsequent XRD patterns in both sequences). To make the diffractograms of the blends comparable with those of the pure zeolites, the peak intensity of the zeolites patterns was reduced to 25% of their original value. Inspecting Fig. 4a and b points out the progressive peak lowering of the zeolite XRD patterns, which ends with a substantial disappearing of zeolite peaks in the diffractograms relative to the final solids of Fratini's test (FT). It should be noted that also the clinker constituents deplete as cement hydration proceeds (the main XRD peaks can be recognized by comparing the diffractograms of the dry blends to those of the relevant zeolites).

It is worth observing, in addition, that Fratini's test helps check if a material is able to reduce the amount of dissolved $Ca(OH)_2$ in a solution in contact with the blended cement, but does not give any information on the possible presence of portlandite in the hardened pastes. The diffractograms of the hydrated blends in Fig. 4a and b show, in fact, the presence of portlandite (P), which is particularly evident in the bottom patterns relative to Fratini's test.

### 3.2. Mechanical performance of the hardened pastes

Fig. 5 compares the values of the compressive strength of the compacts obtained from the experimental blends a/x-5/25 in Table 2, at different curing times, to those of

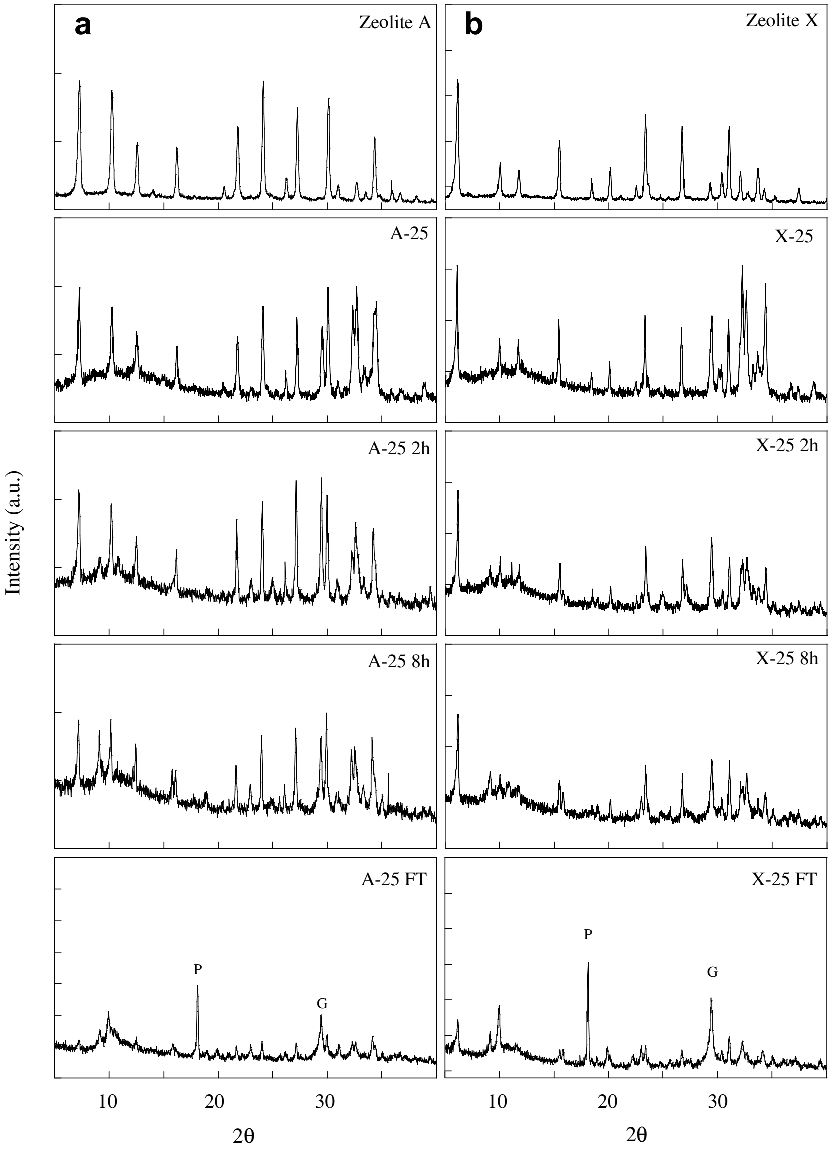

Fig. 4. XRD patterns of the hardened A-25 (a) and X-25 blends (b) (Table 2) at various curing times. Reaction time in hours (h); FT = product of Fratini's test (P = portlandite; G = gypsum). Reference components of the blends are in the first two top diffractograms of each set (peak intensity of zeolite A and zeolite X diffractograms was reduced to 25% of the original).

the corresponding compact formed with only OPCl. As expected, the compressive strength increased with time for all the hardened blends as the hydration reactions proceeded. Calcium aluminates and alumino-ferrites are the first cement components to give rise to hydration (phase of setting), followed at medium and long reaction times by calcium silicates, the hydration of which is substantially responsible for hardening [1].

All the blends gave compressive strengths lower than the corresponding reference values (relative to the OPCl). However, as known from the literature [2], at longer reaction times (e.g., a few months or more) the mechanical resistance of the hardened blends may become comparable or even higher than those of the hardened OPCl, depending on the nature and quantity of the pozzolanic material added. Replacing Portland clinker by zeolite involves, in

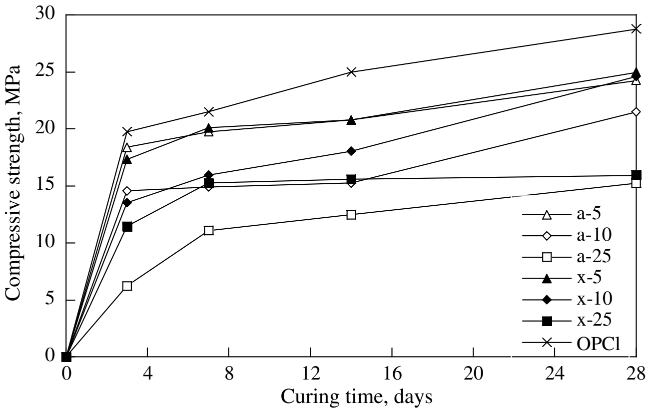

Fig. 5. Compressive strength of the compacts of hardened clinker–zeolite pastes at different curing times. Sample abbreviations: see Table 2.

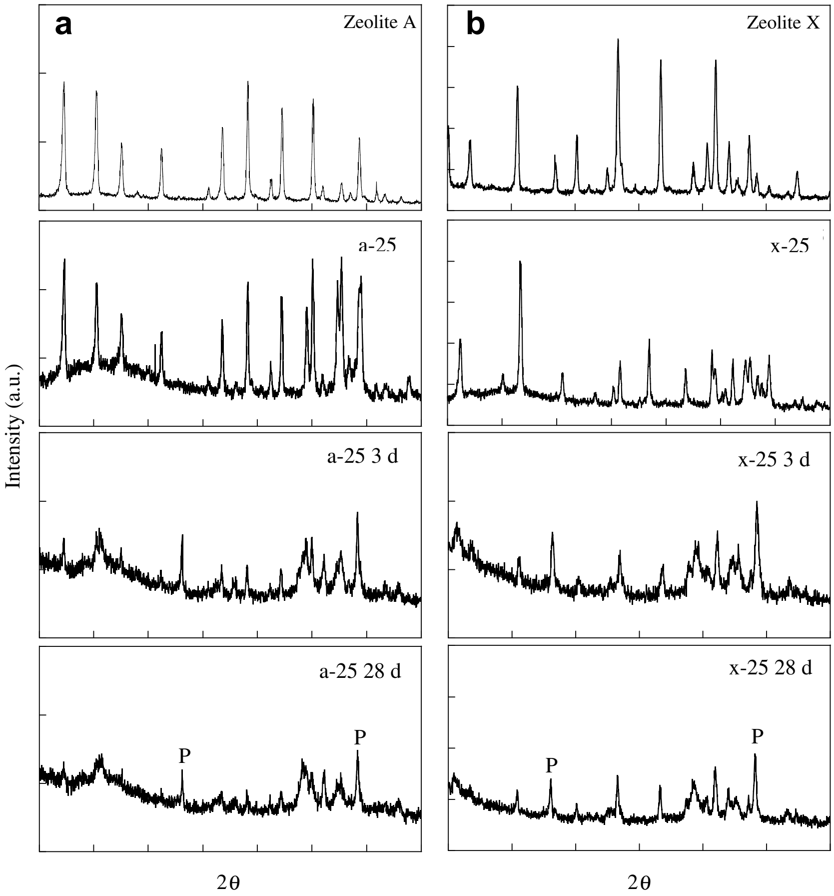

Fig. 6. XRD patterns of the a-25 (a) and x-25 blends (b) (Table 2), after curing for different times (in days). Symbols as in Fig. 4.

fact, a slowdown of the hardening process, as zeolite, contrary to clinker which is a real binder, exhibits a hydraulic behavior only when reacted with $Ca(OH)_2$.

Inspecting Fig. 5 points out that:

(a) *ceteris paribus*, the higher the zeolite content, the lower the mechanical resistance;
(b) the two zeolites gave rise to comparable resistances at low loadings (A-5 and X-5), whereas, at higher zeolite contents, compacts made with zeolite X presented higher resistances than the corresponding compacts based on zeolite A.

The results of the XRD analysis of the hardened clinker–zeolite pastes after curing, shown in Fig. 6, substantially agree with those concerning Fratini's test (Fig. 4), i.e., either zeolite A or zeolite X rapidly disappeared from the diffractograms and were practically absent after three days curing. Portlandite, which was present in the compacts from the first stages of hydration, showed a decreasing trend starting from three days reaction onwards.

## 4. Discussion

Some noteworthy results arose from this investigation allowing a better understanding of the role played by zeolite as pozzolanic addition in blended cements in terms of: (1) effectiveness of $Ca(OH)_2$ abatement in the solid/liquid reaction environment, and (2) contribution to the development of the mechanical resistances of the hardened pastes.

(1) The data in Figs. 2 and 3 show that sodium zeolites A and X modify the chemistry of the contact solution decreasing the $Ca^{2+}$ concentration and increasing alkalinity. This is likely the result of variuos simultaneous reactions and equilibria, such as:
  (a) hydration of the Portland clinker constituents with formation of solid $Ca(OH)_2$;
  (b) dissolution of $Ca(OH)_2$ and related dissociation equilibria:

$$Ca(OH)_{2(s)} \rightarrow Ca(OH)^+_{(l)} + OH^-_{(l)},$$
$$Ca(OH)^+_{(l)} \leftrightarrows Ca^{2+}_{(l)} + OH^-_{(l)}$$

where subscripts s and l refer to solid and liquid (solution), respectively;
  (c) ion-exchange equilibria involving $Ca^{2+}$ and $Ca(OH)^+$ in solution and $Na^+$ in zeolite:

$$2Na^+_{(z)} + Ca(OH)^+_{(l)} \leftrightarrows Ca^{2+}_{(z)} + 2Na^+_{(l)} + OH^-_{(l)},$$
$$2Na^+_{(z)} + Ca^{2+}_{(l)} \leftrightarrows 2Na^+_{(l)} + Ca^{2+}_{(z)},$$

where subscript z refers to zeolite phase;

(d) dissolution, breakdown and/or conversion into amorphous material of the zeolite in alkaline solution followed by the formation of hydrated calcium aluminates and hydrated calcium silicates. The alkaline alumino-silicate magmas, rich in $Ca^{2+}$, are, in fact, prone to form silicates and aluminates more than aluminum-silicates (framework silicates) [23]. A close inspection of Fig. 3 points out that, although both zeolites are effective in removing $Ca^{2+}$ from the solution (the experimental points are under the curve from the very early stages of the reaction), zeolite A appears to be more effective and/or more prompt in the control of $Ca^{2+}$ concentration, as the relevant points are practically on a straight line all over the reaction time and are constantly lower than the corresponding points relative to zeolite X. The fact that the (slightly) less siliceous zeolite A appears to be a better pozzolanic material than the more siliceous zeolite X can be explained on the base of different structure and related reactivity. In fact, the higher zeolite A reactivity may depend on:

(i) its higher exchange selectivity for $Ca^{2+}$, i.e., its major propensity to exchange its extraframework cation, $Na^+$, for $Ca^{2+}$ present in solution ($\Delta G^0_{298}$ for $Na^+ \rightarrow 1/2\,Ca^{2+}$ exchange, at a total cation concentration of 0.1 N, is equal to −733 cal/g equiv and −320 cal/g equiv for zeolites A and X, respectively [24]);

(ii) its more rapid hydrolysis and dissolution, because of the more extensive, external surface area (*S*) exposed to solution attack (*S* amounts to 4.6 $m^2/g$ and 0.8–0.9 $m^2/g$ for zeolites A and X, respectively [25]).

(2) Data in Fig. 5 point out that, in addition to grain size (and related specific surface), not examined in the present study, the development of the mechanical resistances of the clinker–zeolite blends depends, among other physical and chemical parameters, on the reactivity of the pozzolanic material and its content in the blend. The reason why zeolite X behaves better than zeolite A in terms of development of compressive strengths, is not conflicting with its previously discussed lower reactivity. In fact, its Si/Al ratio, which is slightly higher than that of zeolite A, ensures the formation of a higher amount of hydrated calcium silicates, which are mostly responsible for the mechanical resistance of the hardened pastes.

It is worth mentioning that the increasing trend of the curves in Fig. 5 indicates that the pozzolanic character of the blends is preserved after the zeolite XRD reflections have disappeared in the XRD traces of the cement pastes (seven days, see Section 3.2). This suggests that the action of the alkaline environment involves the transformation of zeolites into amorphous materials (presumably alumino-silicate gels), which are able to play a pozzolanic activity. The formation of gels as transient phases on the way of the formation of new crystalline compounds has already been reported in literature (see, e.g. [26]).

## 5. Summary and conclusions

The results obtained and the related discussion allow to conclude that: (1) aluminous zeolites, such as synthetic Na-zeolites A and X, having a Si/Al ratio equal to 1–1.2, are effective in reducing the concentration of calcium hydroxide in the solution in contact with the cement–zeolite blend; nevertheless, some solid free portlandite continues to be present in the hardened cement pastes; (2) the pozzolanic action of both zeolites involved presumably the following steps: (a) cation exchange, (b) dissolution and/or breakdown, (c) possible formation of a transient alumino-silicate gel, and (d) precipitation of hydrated calcium silicates and aluminates from solution; (3) the transient gel and/or some unknown non crystalline material continues to play a pozzolanic action also after the zeolite breakdown; (4) zeolite A reacts more readily than zeolite X, but zeolite X, being slightly more siliceous, contributes to a greater extent to the development of the mechanical resistances of the cement pastes at short curing times.

In conclusion, this study, while pointing out the critical role played by zeolite structure in determining pozzolanic ability, indicates, in addition, that pozzolanic action and development of mechanical resistance of hardened pastes may be conflictual requirements. The former seems, in fact, to be preferentially played by less siliceous zeolites, whereas the latter would request more siliceous zeolites.

Therefore, future work should examine in detail the behavior of more siliceous zeolites and the specific action played by the nature and amount of their extraframework cations (e.g, $Na^+$ or $Ca^{2+}$) in blended cements. Investigation on the leaching properties of the resulted hardened cement pastes, as a function of the above cations, would also be timely.

## Acknowledgement

Thanks are due to the company Cementi della Lucania S.p.A. (Avigliano, PZ) for supplying us with a sample of Portland clinker and the related analytical data.

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