318 Brouwers and Chen

<u>SP-221-18</u>

Evaluation of Zeolite-Bearing Tuffs as Pozzolanic Addition for Blended Cements

by B. Liguori, D. Caputo, M. Marroccoli, and C. Colella

Synopsis:

Four of the most widespread sedimentary zeolitic tuffs were tested to evaluate their pozzolanic character. The zeolitic tuffs were: a chabazite-phillipsite-rich tuff from Tufino (Naples, Italy), a phillipsite-rich tuff from Marano (Naples, Italy), a clinoptilolite-rich tuff from Eskişehir (Anatolia, Turkey) and an erionite-rich tuff from Agua Prieta (Sonora, Mexico). Suitable tuff-lime mixtures were cured at room temperature and the reactivity data were collected in form of kinetic curves. All the tuffs showed a pozzolanic activity better than that reported for a typical pozzolan from Campi Flegrei (Naples), i.e., the volcanic glassy material precursor of the Neapolitan tuffs. Tuff reactivity was tentatively related to the microporosity of the zeolite components of the single tuffaceous materials. Zeolitic materials were also evaluated, investigating the behavior of blended cements prepared by mixing portland clinker, tuffs and gypsum. The pozzolanic behavior of the blended cements was estimated according to the European Standards, using the so-called Fratini's test, that allows to evaluate whether the material under investigation, regardless of its nature and the mixture ratio, is able to combine with Ca(OH)₂ produced by hydration of portland clinker. Although this test was positive for most prepared blends, X-ray diffraction analysis demonstrated that the hardened pastes still contained residual amounts of Ca(OH)2 confined in the inner part of the manufacts.

<u>Keywords</u>: Fratini's test; pozzolanic behavior; pozzolanic cements; pozzolanic materials; zeolitic tuffs

Barbara Liguori, 29, is a researcher of Material Science and Technology at the Department of Materials and Production Engineering, Federico II University of Naples, Italy. Her main research interest is zeolite synthesis and natural zeolite characterization and application in various fields of environmental and industrial relevance, including cement industry.

Domenico Caputo, 38, is Associate Professor of Materials Science and Technology at the Engineering Faculty of the Federico II University of Naples, Italy. Research interests are in the broad field of microporous materials, either synthetic or natural, with particular emphasis in applications connected with their extensive surface.

Milena Marroccoli, 43, is Associate Professor of Materials Science and Technology at the Engineering Faculty of the University of Basilicata, Potenza, Italy. Her research interests concentrate on cement chemistry and technology, especially in the field of recycle of natural and industrial by-products as rough materials for cement manufacture.

Carmine Colella, 62, is Full Professor of Materials Science and Technology at the Engineering Faculty of the Federico II University of Naples, Italy. Research interests range over the broad field of ceramics, *lato sensu*. Special relevance is given to the exploitation of natural materials for technological purposes and for the manufacture of ceramic materials.

INTRODUCTION

Pozzolana, a mostly glassy, natural product, occurring in a volcanic areas around the world, but widespread especially in central-southern Italy, was used since ancient times as addition to lime to obtain hydraulic mortars (1). Starting roughly from the beginning of the twentieth century, pozzolana has being used to manufacture blended cements, i.e., pozzolanic cements, in which the function of the volcanic material is to react with portlandite, formed by hydration of portland clinker, by producing additional C-S-H and hence improving the performances of the hardened concretes (2).

Other materials having the ability of pozzolana have been discovered in the course of the last century, namely, fly ash, silica fumed and calcined clay (in form of metacaolin or even crushed bricks), among the artificial materials, and

zeolitized tuffs, diatomaceous earth and some vitreous rhyolites, among the natural materials (2,3).

In the last years much research has been carried out on zeolite-bearing tuffs as pozzolanic materials. Zeolite types that have been tested so far are those more frequently found in the sedimentary zeolite (tuff) deposits widespread all over the world, i.e., clinoptilolite, mordenite, phillipsite and chabazite (1). Despite the large number of papers appeared on this subject (see, e.g., 4-10), research is still needed on the zeolite reactivity related to its nature and composition.

A simplified approach to this problem has recently been made, investigating some experimental blended cements, manufactured with portland clinker, gypsum and commercial synthetic zeolites (11).

The aim of this paper is to extend the previous study, analyzing and comparing the "pozzolanic character" of different natural zeolitic materials, investigating their reactivity with $Ca(OH)_2$ and evaluating their performances in combination with portland cement. The latter evaluation has been made using an official test, proposed by Fratini at the end of the 1940's (12,13), and more recently accepted by the European Standards (14). The Fratini's test is based on a standardized hydrothermal treatment of experimental clinker-pozzolana-gypsum pastes. The final Ca^{2+} and OH⁻ concentration in the contact solution is assumed as an indicator of the presence/absence of portlandite in the paste and therefore of the effectiveness of the pozzolanic action. Additional aim of this study is to analyze more in depth the efficacy of this test, as previous findings suggested it is unable, even when positive, to ensure the absence of portlandite in the hardened pastes (11).

EXPERIMENTAL

Materials

Four different zeolitic tuffs, representative of the most common materials in worldwide deposits, were selected as pozzolanic materials: (a) phillipsite-rich tuff (PHT) from Marano (Naples, Italy), belonging to the huge formation of the so-called *Neapolitan yellow tuff* (15); (b) phillipsite- and chabazite-rich tuff (CHT) from Tufino (Naples, Italy), belonging to the enormous formation of the *Campanian Ignimbrite* (15); (c) clinoptilolite-rich tuff (CLT) from Eskişehir (Anatolia, Turkey); (d) erionite-rich tuff (ERT) from Agua Prieta (Sonora, Mexico). The structural features of the above mentioned zeolites are reported in the Atlas of Zeolite Framework Types (16), whereas

their idealized chemical compositions can be found in the recent Recommended Nomenclature for Zeolite Minerals (17).

The chemical and mineralogical composition of the portland clinker used for manufacturing blended cements is shown in Table 1. The particle size distribution of the four zeolitic tuff samples and of the portland clinker utilized is reported in Table 2. The chemical compositions of the four tuff samples on anhydrous basis are shown in Table 3.

Reagent grade $Ca(OH)_2$ used in some experiments, and $CaSO_4 \cdot 2H_2O$, used as set regulator, were supplied by Carlo Erba Analyticals.

Methods

Qualitative and quantitative X-ray diffraction analyses (XRD) were performed. The mineral composition, limited to the estimation of zeolite content, was determined using the Reference Intensity Ratio (RIR) procedure (18), which is an improved version of the well known XRD technique based on the use of the internal standard [19]. These are the results obtained:

- PHT: phillipsite 46%; chabazite 5%; analcime 9% (to be noticed is the smectite content of 10%);
- CHT: phillipsite 31%; chabazite 27% (smectite 4%);
- CLT: clinoptilolite 91%.

Zeolite phases present in the ERT sample were: erionite and clinoptilolite. Data on quantitative mineral composition of the ERT sample are not available for lacking of an erionite standard. A semi-quantitative estimation, based XRD and thermogravimetry analyses, gave a rough erionite content close to 60%, whereas clinoptilolite was around 10%.

The reactivity of the zeolitic materials towards lime was evaluated at 25°C by continuous stirring of 5 g of zeolitic material with different amounts of Ca(OH)₂ suspended in 500 ml of deionized water (20). For each tuff sample, three series of lime-tuff mixtures with weight ratios of 0.2, 0.3 and 0.4 were prepared. These mixtures will be denoted hereafter as L20, L30 and L40, respectively. Concentrations of Ca²⁺ and OH⁻ in solutions were analyzed at given times (from 3 hours to 50 days) until all lime was combined and the solution became under-saturated in Ca(OH)₂. This condition was evaluated with the help of the Fratini's plot (see below).

The Fratini's test (14) was carried out on tuff-clinker-gypsum blends prepared according to the following percent proportions: 10:85:5, 20:75:5 and 40:55:5, denoted hereafter as F10, F20 and F40, respectively. In agreement with

the prescribed procedure, 20 g of each sample were mixed with 100 ml of deionized water and kept at 40°C for 8 days or 15 days (if the test was negative after 8 days). Concentrations of Ca^{2+} and OH^- were estimated in the mother liquor at the end of the experiment through the ordinary methods of volumetric analysis. Results (average values of runs performed in triplicate) were evaluated projecting them in a plot, that shows the solubility curve of $Ca(OH)_2$ as a function of Ca^{2+} and OH^- concentrations in solution. In this plot, points over the curve or on the curve are representative of over-saturated or saturated solutions (absence or deficiency of pozzolanic activity); on the contrary, points under the curve are representative of under-saturated solutions (presence of pozzolanic activity).

The solids recovered at the end of each of the above runs (without clinker and with clinker) were subjected, after suitable grinding, to XRD analysis, in order to check the presence of unreacted $Ca(OH)_2$, i.e., residual portlandite. Pure $Ca(OH)_2$ was utilized as reference material.

RESULTS AND DISCUSSION

Tuff-Ca(OH)₂ Reactivity Test

Figure 1 summarizes the results of the reactivity test of the four tuff samples with $Ca(OH)_2$. Data are presented in form of kinetics plots, reporting the amount of lime fixed by 100 g of tuff as a function of the reaction time.

Points in Fig. 1 represent the maximum capability of the four zeolitic tuffs to fix lime in each examined mixture (L20, L30, L40) in the conditions of validity of the Fratini's test, i.e., when the contact solution becomes under saturated in Ca(OH)₂ (see Experimental). Inspecting the kinetic curves in Fig. 1 points out that:

(a) all the tuffs denote a remarkable reactivity for $Ca(OH)_2$, as they can fix more than 30 g of lime per 100 g of tuff within a few days. This reactivity is, of course, theoretical, because it has been measured in conditions very far from reality;

(b) the fastest kinetics is presented by the ERT tuff, as can be deduced from the initial slope of the curves. The ERT tuff is able to fix in 15 hours the same amount of lime fixed by chabazite/phillipsite-, phillipsite- or clinoptilolite-rich tuffs in 3 days. The reaction rates of the CHT, CLT and PHT are similar for short times, whereas for longer times the rates become different, following the order CHT >CLT >PHT.

The reactivity of the four tuffs is comparable or even higher of the same pozzolan. Although this statement can not be generalized, it is interesting to note that tests on a glassy material, called *pozzolana flegrea*, which has been proved to be the genetic precursor of Neapolitan yellow tuff (see Experimental) (21), demonstrated that the fixation of Ca(OH)₂ in the analogous conditions as the L30 run, lasted about 90 days (20).

Figure 2 shows the X-ray patterns of the various solids collected at the end of the experiments. Vertical lines refer to the main peaks of lime, that are associated to the (001) and (101) planes. It is evident the absence of $Ca(OH)_2$ and this confirms that lime has been completely fixed by the zeolitic tuffs.

A detailed interpretation of the above results is difficult. Tuff reactivity is, in fact, a function of a number of variables such as: (a) zeolite structure and composition, namely, "acidity" (the specific Si/Al ratio (17)) and extraframework cation population; (b) zeolite amount in the tuff; (c) nature and amount of other phases (clay, hydrated amorphous materials, such as glass, alumino-silicate gel and others). It seems undeniable, however, from the results of Fig. 1, that zeolites with "open" structures, such as chabazite and, partly, erionite, behave better than zeolites characterized by higher compactness (especially clinoptilolite), possibly because of their more extensive surface exposed to lime action.

Fratini's Test

The results of the Fratini's test are presented in Fig. 3 in three different plots, one for each of the compositions examined. Inspection of the figure lets to point out immediately that the test was positive (i.e., the added materials succeeded to act as pozzolan) for all the prepared blends, except for the F10 blend, concerning PHT. Note that for the F10 blends, relative to CHT and CLT, the test was negative after 8 days, but positive after 15 days. In summary, according to this test, the presence of at least 10% of tuff in the blends, was sufficient, except one case, to fix portlandite formed by clinker hydration. These results are in substantial agreement with the results of the above mentioned reactivity test, in that the phillipsite-rich tuff demonstrated a reduced reactivity compared to the other tuffs, the most reactive of which turned out to be the erionite-rich tuff. It has to be remarked, however, that the use of erionitic tuffs is at present questionable, because of the proved risk that the fibrous crystals of erionite are responsible of the genesis of mesothelioma (22).

Notwithstanding the satisfactory results of the Fratini's test, the XRD analysis of the hardened pastes showed constantly the presence of portlandite. A close inspection of the pastes at the end of the test gave the possibility to explain the reason for this unexpected behavior. The pastes appeared clearly stratified

with a change of color from the top (in contact with supernatant water), pale gray, to the bottom, gray, suggesting a possible segregation. A XRD analysis of samples taken from various layers confirmed this suspect. Figure 4 compares the X-ray patterns of an average sample of the F10 hardened blend, relative to ERT (Fig. 4a) with three samples taken from three layers of the same sample: top layer (roughly 2 mm of 17 mm) (Fig. 4b), middle layer (roughly 10 mm of 17 mm) (Fig. 4c), bottom layer (roughly 5 mm of 17 mm) (Fig. 4d). XRD pattern (a) evidences the presence of Ca(OH)₂, CaCO₃ and residual ERT; (b) is pure Ca(OH)₂ and CaCO₃; (d) lastly, is pure Ca(OH)₂. It is therefore evident the satisfactory fixation of portlandite in the top layers (apart some minor surface carbonation), whereas the unreacted fraction in the bottom layers points out a downward segregation of portlandite, likely prevented from reacting for lack of water due to the progressive pore obstruction with hardening.

In summary, the Fratini's test, even when positive, does not necessarily ensure the absence of hydrolysis lime in the hardened paste, which should be checked by XRD. This emphasizes the necessity of a preventive careful evaluation of the amount of pozzolanic material to be added to clinker, to avoid excess, which would be detrimental for the mechanical strength of the concretes, and defect, which would make further difficult the fixation of portlandite.

CONCLUSIONS

The results of this investigation have demonstrated that all tested tuffs (erionite-, chabasite/phillisite-, clinoptilolite- and phillipsite-rich tuffs) perform as good pozzolanic materials. Their reactivity, in fact, is comparable with and may exceed that of the pozzolan itself. Although a strict relation between reactivity and type of zeolitic components of the tuffs is difficult to find, because of the remarkable number of variables that affect the tuffs performances, it is undeniable a faster reaction kinetics of the materials characterized by the presence of more "open" zeolites (erionite-rich and chabazite-rich tuffs) compared to more compact zeolite such as clinoptilolite.

It has also ascertained that the test adopted by the European Standards to evaluate the pozzolanic behavior of a material, i.e. the so-called Fratini's test, does not give completely reliable results. The XRD analysis of the hardened pastes proved, in fact, that the absence of portlandite in solution does not ensure its absence also in the solid phase, even if the presence of $Ca(OH)_2$ is confined to the inner part of the manufacts.

ACKNOWLEDGMENT

The Authors are grateful to the company I.Z.-Italiana Zeoliti (Pigneto di Frignano, Modena, Italy) for supplying the tuff sample samples labeled as PHT and CHT. Thanks are also due to the company Cementi della Lucania S.p.A. (Avigliano, Potenza, Italy) for providing the portland clinker sample.

REFERENCES

1. Colella, C., de' Gennaro, M. and Aiello, R., "Use of zeolitic tuff in the building industry", "Natural Zeolites: Mineralogy, Occurrence, Properties, Applications", D.L. Bish and D.W. Ming Eds., Reviews in Mineralogy & Geochemistry, Mineralogical Society of America, Vol. 45, Washington, D.C., 2001, pp. 551-587.

2. Taylor, H.F.W., "Cement Chemistry", Academic Press, London, 1990, pp. 277-315.

3. Massazza, F., "Pozzolanic Cement"; Cement & Concrete Composites, 15, 1993, pp. 185-214.

4. Nai-Qian, F., Hsia-Ming, Y. and Li-Hong, Z., "The strength effect of mineral admixture on cement concrete"; Cem. Concr. Res. 18, 1988, pp. 464-472.

5. Huizhen, L., "Effect of structure and composition on reactivity of zeolitetuff used as blending material of Portland cement"; "Proceedings of the 9th Int. Congr. on Chemistry of Cement", Nat. Council for Cement and Building Materials, New Delhi, India, 1992, Vol. 3, pp. 128-134.

6. Sersale, R., "Zeolite tuff as pozzolanic addition in the manufacture of blended cements", "Natural Zeolites '93", D.W. Ming and F.A. Mumpton Eds., International Committee on Natural Zeolites, Brockport, New York, 1995, pp. 603-612.

7. Kitsopoulos, K.P. and Dunham, A.C., "Heulandite and mordenite-rich tuffs from Greece: a potential source for pozzolanic materials"; Mineral. Deposita, 31, 1996, pp. 576-583.

8. Fagroulis, D., Chaniotakis, E. and Stamatakis, M., "Zeolitic tuffs of Kimolos island, Aegean Sea, Greece, and their industrial potential", Cem. Concr. Res. 27, 1997, pp. 889-905.

9. Alcantara Ortega, E., Cheeseman, C., Knight, J. and Loizidou, M., "Properties of alkali-activated clinoptilolite"; Cem. Concr. Res. 30, 2000, pp. 1641-1646.

10. Türkmenoğlu, A.G. and Tankut, A., "Use of tuffs from central Turkey as admixture in pozzolanic cements. Assessment of their petrographical properties", Cem. Concr. Res. 32, 2002, pp. 629-637.

11. Caputo, D., Liguori, B. and Colella, C., "Some advances in understanding the pozzolanic activity of zeolites"; "Proceedings of EUROMAT 2001" (CD Rom), Associazione Italiana di Metallurgia, Milano, 2001 (Abstract in "Conference Abstracts", p. 353).

12. Fratini, N., "Researches on hydrolysis lime in cement pastes. - Part I." (in Italian); Annali di Chimica (Rome), 39, 1949, pp. 41-49.

13. Fratini, N., "Researches on hydrolysis lime in cement pastes. – Part II: Proposal of a test for chemical evaluation of pozzolanic cements" (in Italian); Annali di Chimica (Rome), 40, 1950, pp. 461-469.

14. Anonymous, Methods of testing cement: Pozzolanicity test for pozzolanic cement, EN 196-5, European Committee for Standardization, Bruxelles, Belgium, 1994, 10 pp.

15 de' Gennaro, M. and Langella, A., "Italian zeolitized rocks of technological interest", Mineral. Deposita, 31, 1996, pp. 452-472.

16. Baerlocher, Ch., Meier, W.M. and Olson, D.H., Atlas of Zeolite Framework Types, Elsevier, Amsterdam, 2001, p. 96-97, 126-127, 146-147, 220-221.

17. Coombs, D.S., et al., "Recommended nomenclature for zeolite minerals: Report of the Subcommittee on Zeolites of the International Mineralogical Association, Commission on New Minerals and Mineral Names"; Can. Mineral., 35, 1997, pp. 1571-1606.

18. Chipera, S.J. and Bish, D.L., "Multireflection RIR and intensity normalizations for quantitative analysis: applications to feldspar and zeolite"; Powder Diffr. 10, 1995, pp. 47-55.

19. Chung, F.H., "Quantitative interpretation of X-ray diffraction patterns of mixtures. I. Matrix-flushing method for quantitative multicomponente analysis"; J. Appl. Cryst. 7, 1974, pp.519-525.

20. Sersale, R. and Sabatelli, V., "On the pozzolanic activity of zeolites. Part I: Reactivity of hershelite with calcium hydroxide solutions." (in Italian); Rend. Accad. Sci. Fis. Mat. (Naples), 27, 1950, pp. 263-282.