Utilization of zeolite-rich tuff for the manufacture of building materials based on calcium silicate and trisulphoaluminate hydrates

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Abstract

Hydration of the system tuff–lime–gypsum with and without small addition of Portland cement has been studied in the range 25–85°C and up to 28 days curing. The simultaneous formation of calcium silicate and trisulphoaluminate hydrates makes cured products suitable for manufacturing pre-formed building elements, provided that curing temperature is at least 40°C. Portland cement acts as a true catalyst as its addition enhances the formation of both the hydration products. Among other sources of reactive silica and alumina, such as granulated blast furnace slag and coal fly ash, tuff has proved to be the most reactive material. The process studied in this paper offers an opportunity for optimally employing tuff by recycling quarry dust. © 1997 Elsevier Science B.V.

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1. Introduction

The occurrence of zeolitic tuffs is particularly widespread in Southern–Central Italy. From a mineralogical point of view, these materials have the common characteristic that, independent of the genesis and location of the deposit, only chabazite and phillipsite are found as zeolitic phases [1].

Since the Roman age, zeolitic tuffs have been widely employed. Small cube-shaped tuff stones were cemented by means of lime–pozzolana mixture in a typical diagonal pattern called opus reticulatum. In recent years, in addition to this ancient utilization, zeolitic tuffs have found a number of other applica-tions, such as admixture of Portland cement clinker, general purpose adsorbent, ionic exchanger and additive for animal feeding [2,3]. Furthermore, the wide availability of these low-cost materials can also favour the exploitation of their chemical properties in new applications.

As the range of tuff uses widens, the production of quarry dust increases, especially from the cutting of dimension stones. Tuff quarry dust is considered a true solid residue by the Italian environmental regulation, and should be properly disposed of, unless some utilization in a productive process is found. Then, the search for useful ways to consume large amount of tuff quarry dust should be given high priority to satisfy requirements from the economical and environmental point of view, that is, for optimum exploitation of natural resources.

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In the last few years, materials containing reactive alumina and silica have been studied for the manufacture of building materials whose properties rely on the formation of calcium trisulphoaluminate and silicate hydrates [4–8]. The chemical nature of zeolitic tuffs suggests that these materials could be advantageously employed in the above application. To this scope, the chemical behaviour of zeolitic tuffs must be studied in the presence of calcium hydroxide (lime) and sulphate (gypsum), as these reactants are required to convert the alumina present in the tuff into calcium trisulphoaluminate hydrate (ettringite). This conversion takes place in addition to the well-known pozzolanic reaction which converts lime and silica into calcium silicate hydrate (C-S-H).

In this paper, the hydration kinetics of mixtures containing a powdered zeolitic tuff, lime, gypsum and small amount of Portland cement have been studied from 25 to 85°C and up to 28 days ageing. The hydration products have been characterized by differential thermal analysis (DTA) and evaluation of chemically bonded water and mechanical properties. The results have been compared to those obtained with the system gypsum (or phosphogypsum)–granulated blast furnace slag [4] and the system gypsum (or phosphogypsum)–lime–fly ash [5–7], that is, other two systems in which the simultaneous formation of C-S-H and ettringite takes place.

Table 1
Chemical composition of tuff

Component	wt%
Loss on ignition	9.80
SiO_2	53.00
Al_2O_3	17.30
CaO	3.54
MgO	1.44
Fe_2O_3	3.71
MnO_2	0.13
K_2O	7.26
Na_2O	2.97
SO_3	0.13
Total	99.28

Table 2
Particle size distribution of tuff

Size range, μm	wt%
>180	9.7
150–180	5.6
125–150	36.6
106–125	31.3
90–106	9.8
75–90	3.1
63–75	2.4
53–63	0.2
45–53	1.1
<45	0.2

2. Experimental

The zeolitic tuff employed in this work comes from a quarry located in the Neapolitan area (Licola, Italy). Its chemical composition and particle size distribution are reported in Tables 1 and 2, respectively. Chemical analysis was carried out according to ASTM C311 standard method, while particle size distribution was determined by sieving. Furthermore, the mineralogical nature of the crystalline phases was found by X-ray diffraction analysis, whose results are reported in Fig. 1. It is seen that chabazite, phillipsite and K-feldspar are the main mineralogical phases present.

The quantitative composition of the system tuff–lime–gypsum (system T) was designed on the basis of theoretic conversion of 35% silica into C-S-H and 70% alumina into ettringite. This composition is tuff 45%, lime 28% and gypsum 27%. It was inferred that the yield of hydration products could grant the desired properties to the manufacts while keeping the amounts of the more expensive components to reasonable levels. Lime and gypsum were analytical grade $Ca(OH)_2$ and $CaSO_4 \cdot 2H_2O$, respectively.

System TC was obtained adding Portland cement to system T. Three levels of addition were tested equal to 4.1, 8.2 and 12.3%. It was judged that the addition of small amount of Portland cement could improve the performances of the products with limited effect on the process economics. The complete set of compositions of systems T and TC is reported in Table 3.

Hydration was carried out at 25 and 40°C, 100% R.H. for 1, 3, 7, 14 and 28 days and at 70 and 85°C, 100% R.H. for two days. In any case the water/solid ratio was 0.53. At any pre-fixed hydration time, samples were taken, ground under acetone and rinsed with diethyl ether to stop the reaction. Specimens of the samples were then analysed for the amount of
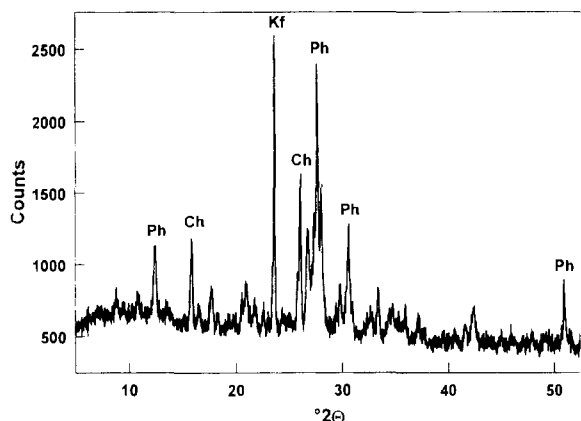
Fig. 1. X-ray diffraction pattern of zeolitic tuff showing the main peaks of chabazite (Ch), phillipsite (Ph) and K-feldspar (Kf).

Fig. 2. Effect of Portland cement addition on the degree of hydration at different curing times.

chemically bonded water by means of loss of ignition at 1000°C for 2 h. The consumption of reactants and the formation of products with hydration time were monitored carrying out DTA by means of a Netzsch STA 409 apparatus.

Cubic samples 4×4×4 cm³ aged 28 days at 25 and 40°C and two days at 85°C were tested for unconfined compressive strength using an Instron 8100 apparatus.

3. Results and discussion

Fig. 2 shows the amount of chemically bonded water for systems T and TC. In the latter case, the results are relative to the three compositions containing 4.1, 8.2 and 12.3% Portland cement. The figure shows the effect of Portland cement content on the hydration kinetics when tested at different times. It is clearly seen that the addition of 8.2% Portland cement
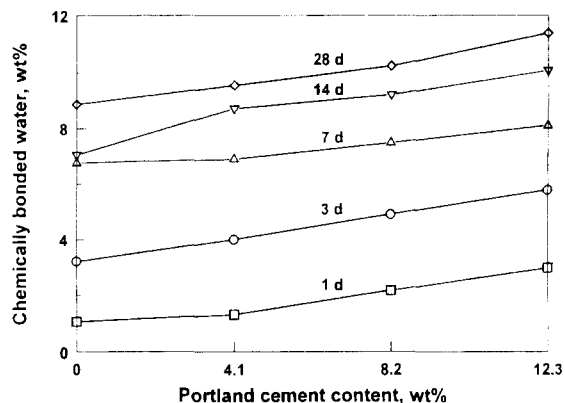
Table 3
Composition of the systems investigated, wt%

Component	System			
	T	TC		
		1	2	3
Tuff	45.0	43.2	41.3	39.5
Ca(OH)₂	28.0	26.8	25.7	24.5
CaSO₄·2H₂O	27.0	25.9	24.8	23.7
Portland cement	—	4.1	8.2	12.3

makes the amount of chemically bonded water significantly increase in respect to system T as early as after 1 day hydration. This effect is present up to 28 days. Although the highest addition of Portland cement further improves the hydration kinetics, it was judged that 8.2% addition could be optimum to get good performance and low raw materials cost. This level of addition was used in the subsequent part of the work.

Previous work carried out on systems containing granulated blast furnace slag [4] and six different coal fly ash samples [5–7] instead of tuff as sources of reactive silica and alumina had shown that the main factor that affects reactivity in systems of the type studied is particle size distribution. The samples of slag and fly ashes used in the work referred above had the fraction of size less than 75 μm equal to 42.7% (slag) and in the range 63.7–92.4% (fly ashes). When they were used under test conditions similar to those employed in this paper, values of chemically bonded water were found comparable to those observed in this work with the tuff *as received*. As the fraction of size less than 75 μm is about 4% for the tuff (see Table 2), it was inferred that a reduction of particle size could be advantageous to get better performance. Then, the tuff was ground to pass completely a 75 μm sieve.

Mixtures of systems T and TC containing the tuff after grinding were hydrated up to 28 days at 25 and 40°C to check not only the effect of size reduction, but also that of temperature.

The kinetics of hydration of systems T and TC at 25 and 40 C is shown in Fig. 3 in terms of chemically
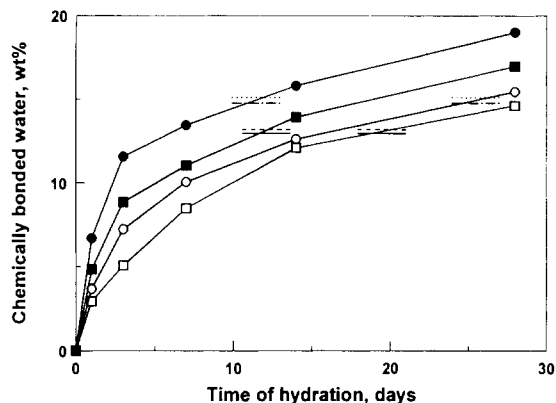
Fig. 3. Effect of time and temperature on hydration of systems T (squares) and TC (circles). Open symbols: 25 C; closed symbols: 40°C. Lines show chemically bonded water of system T at 70 (solid) and 85°C (dashed) and system TC at 70 (dash-dotted) and 85°C (dotted).

bonded water versus time of hydration. It clearly shows the increase in reactivity gained after grinding. In fact, the values of chemically bonded water reached at 25°C after 28 days hydration by both systems T and TC containing the tuff *as received* are very similar to those observed after seven days when the systems contain the tuff after grinding. From the results of Fig. 3, it is also seen that temperature has quite a large effect, as the values of chemically bonded water at 40°C are well above those observed at the lower temperature at any hydration time. In particular, after 28 days hydration the increase in chemically bonded water is 16% for system T and 23% for system TC, proving that the favourable effect of the addition of Portland cement is enhanced by temperature. Finally, the comparison of the present data with those obtained in the previous work carried out with blast furnace slag [4] and coal fly ashes [5–7] shows that tuff is more reactive than both slag and fly ash in systems designed to produce manufacts from the simultaneous synthesis of C-S-H and ettringite.

The consumption of reactants and formation of products are seen in Figs. 4 and 5 that show the results of DTA carried out on selected samples of systems T and TC hydrated at 25 and 40°C, respectively. The thermograms in these figures, as well as in subsequent Fig. 6, show endotherms relative to dehydration of C-S-H (80 ± 10°C), ettringite (127 ± 7°C), gypsum
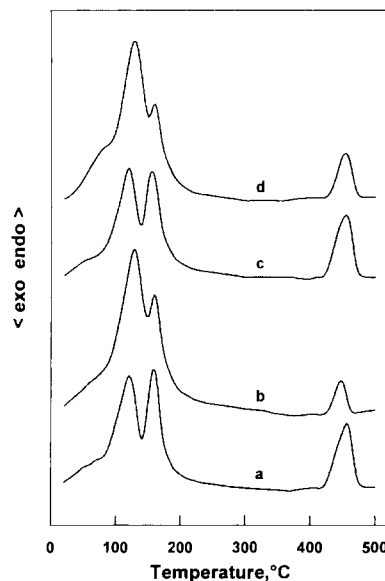

Fig. 4. Thermograms of samples of systems T (a,b) and TC (c,d) hydrated for seven days (a,c) and 28 days (b,d) at 25°C.

(157 ± 3°C), calcium monosulphoaluminate hydrate (192°C) and lime (451 ± 5°C) [9,10].

The examination of the results, shown in Figs. 4 and 5, provides us with number of conclusions. First of all,
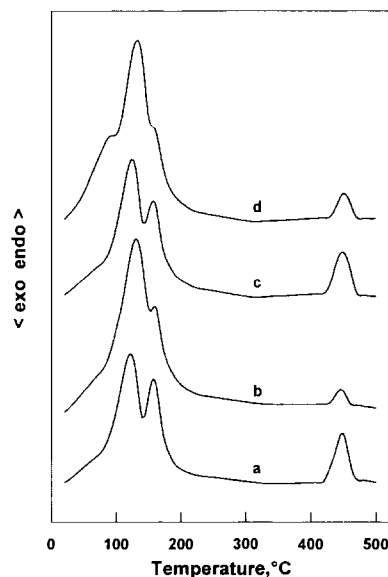

Fig. 5. Thermograms of samples of systems T (a,b) and TC (c,d) hydrated for seven days (a,c) and 28 days (b,d) at 40°C.
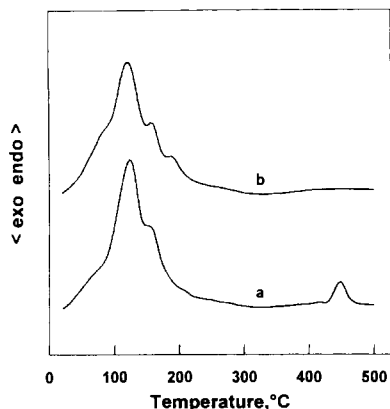
Fig. 6. Thermograms of samples of system TC hydrated for two days at 70 (a) and 85°C (b).

it is confirmed that the hydration products are C-S-H and ettringite, whose formation is enhanced by the temperature. In addition, it is clearly seen that the addition of Portland cement not only makes C-S-H to be produced in larger amount, but also catalyses the formation of ettringite at both temperatures. Finally, Figs. 4 and 5 give information about the degree of conversion of the reactants which is seen to be particularly high for both systems after 28 days hydration at 40°C.

Table 4 shows the quantitative data of chemically bonded water for systems T and TC hydrated for two days at 70 and 85°C. It is seen that, for any system, the values of chemically bonded water are very similar at the two temperatures, being about 13% for system T and about 15% for system TC. The values of Table 4 are also reported as horizontal lines in Fig. 3, and this allows a direct comparison with the times at which the same hydration degrees are reached at 25 and 40°C for each system. Specifically, times between 14 and 28 days are required at 25°C and between 7 and 14 days at 40°C.

Although the quantitative date of Table 4 are nearly the same for each system at both the temperatures, the

Table 4
Chemically bonded water after two day hydration, wt%

System	Hydration temperature	
	70°C	85°C
T	12.96	13.20
TC	14.76	15.10

qualitative behaviour is quite different, depending on the hydration temperature. This is shown in Fig. 6 where the results of DTA relative to system TC are reported. In respect to 70°C, hydration at 85°C causes: (a) the complete conversion of lime; (b) higher yield of C-S-H; (c) the formation of calcium monosulphoaluminate hydrate beside C-S-H and ettringite and, consequently, (d) higher amount of unreacted gypsum.

Mechanical testing was limited to system TC that appears of higher applicative interest in the light of the results of the hydration study. The values of unconfined compressive strength after 28 days hydration at 25 and 40°C are 6.0 and 13.1 MPa, respectively, showing a 118% increase with temperature which is much higher than that expected simply on the basis of the effect of temperature on the hydration degree (23% increase). The comparison between the results of DTA relative to the samples of system TC hydrated 28 days at 25°C (Fig. 4) and 40°C (Fig. 5) shows that the qualitative composition of the hydrated samples is entirely different in these two cases, especially in terms of C-S-H content which is quite higher at the higher temperature. Then, it can be concluded that in these systems C-S-H is primarily responsible for the development of mechanical strength.

The unconfined compressive strength was found to be 8.8 MPa after hydration for two days at 85°C. This value, when compared to the value of 13.1 MPa found after 28 days at 40°C, confirms the strong effect of C-S-H on the development of mechanical strength, as observed before. In fact, the comparison between thermograms of Fig. 5(d) and Fig. 6(b) shows that C-S-H forms in quite larger amount in the former case. On the other hand, the comparison with the value of 6.0 MPa observed after 28 days at 25°C shows that the better mechanical behaviour of the sample hydrated two days at 85°C can be due to the higher yield of sulphoaluminate hydrate phases. Thermograms of Fig. 4(d) and Fig. 6(b) show, when compared to each other, that reactants are almost completely consumed in the latter case and this implies that the total amount of sulphoaluminate hydrate phases is higher, as the amount of C-S-H formed in the two cases is almost the same.

According to previous findings on systems containing blast furnace slag and coal fly ash [8], the results of mechanical testing indicate that processes suitable for the manufacture of pre-formed building materials

based on system TC require at least 40°C hydration temperature.

4. Conclusions

It has been verified that zeolitic tuffs can be advantageously employed in mixtures containing lime, gypsum and small amount of Portland cement able to generate calcium silicate and trisulphoaluminate hydrates for the manufacture of building materials.

In comparison to other sources of reactive silica and alumina such as granulated blast furnace slag and coal fly ash, tuff has shown to be the most reactive material.

Portland cement has a very favourable effect on the hydration kinetics because it enhances the formation of both calcium silicate and trisulphoaluminate hydrates.

The mechanical properties of the hydrated mixtures containing Portland cement are such that the system is suitable for the production of pre-formed building elements, provided that curing temperature is at least 40°C. At room temperature, it does not seem that compressive strength reaches values high enough within 28 days.

From the environmental point of view, the process studied in this paper is useful for recycling large amount of tuff quarry dust. According to Italian law, this is a true residue and then this study offers an opportunity to optimally exploit tuff, a cheap and widely occurring natural resource.

Acknowledgements

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