USE OF THERMAL ANALYSIS FOR THE EVALUATION OF ZEOLITE CONTENT IN MIXTURES OF HYDRATED PHASES

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ABSTRACT

A method, based on water vapour desorption, for the estimation of zeolite content in mixtures of hydrated phases is presented. The accuracy and reliability of the method and the ease of its application are demonstrated through an evaluation of the chabazite and phillipsite contents of Italian tuffs. The method is suitable for more general use provided that the pure phases of the mixture under investigation are available and their thermal features are known.

INTRODUCTION

Thermal analysis techniques can be used to evaluate the amount of hydrated compounds contained in natural or artificial mixtures. A necessary condition for this is that the thermal behaviours of the various phases are sufficiently different, from either a thermodynamic or a kinetic point of view, that the contribution of each hydrated phase to the total water loss can be estimated. The phase content in the mixture can then be deduced.

A problem of great practical interest which can be solved by this type of analysis is the evaluation of zeolite content in mixtures containing zeolitic and non-zeolitic hydrated phases, e.g. volcanic rocks, such as zeolitic tuff, or zeolitic crystallization products of amorphous alumino–silicate magmas.

Limiting our attention to tuff, a widespread rock in many recent and ancient volcanic districts [1,2] which is gaining a pre-eminent position in many industrial, agricultural and civil applications [3–5], recent papers [6–9] have pointed out the advantages of estimating zeolite content through measurement of water loss/gain in dehydration/rehydration cycles.

The purpose of the present work is to rationalize all the previous work on this subject and present a general method, applied in this case to Italian tuffs but easily extensible, with appropriate changes, to other rocks of the same type, even rocks containing different zeolites.

ITALIAN TUFFS: OCCURRENCE AND CONSTITUTION

Zeolitic tuff is a rock formed as a result of a complex cementing process of volcanic material which was originally predominantly X-ray amorphous. Water is involved in this process, regardless of the temperature at which it is accomplished [10–14]. Glass dissolution and the possible intermediate precipitation of a gel-like alumino–silicate phase leads to the formation of a zeolite, which is primarily responsible for the consolidation of the material [15,16].

There are many enormous tuff deposits in Italy, spread over large areas of the Central–Southern part of the peninsula [17], some of which contain increased amounts of interesting zeolites. Even when they have originated through distinct mechanisms, the various types of Italian tuff are of similar constitution, as the chemical character of the original material was almost identical. Tuff may be defined as a volcanic conglomerate consisting of pumice, lithic and scoriaceous lapilli, and occasional crystals of sanidine, pyroxene and biotite, cemented together by finely crystalline zeolites, such as chabazite (CHA), phillipsite (PHI) and analcime (ANA).

The interesting potential applications of chabazite and phillipsite allow it to be foreseen that industrial and commercial exploitation of Italian tuffs may be possible, and this has been confirmed at the level of laboratory tests [18–20]. The usefulness of an easy and accurate method for the rapid evaluation of zeolite content in tuff is therefore evident.

CHEMICAL AND THERMAL FEATURES OF HYDRATED TUFF CONSTITUENTS

As well as the zeolite types described above, tuff contains other hydrated constituents: glassy products (GL) such as pumice, glass fragments, scoriae, etc., and amorphous compounds (AM), namely gel-like alumino–silicate phases and hydrated ferric oxide, both of which are formed in the early stages of the alteration of the volcanic material. While the non-crystalline products are always present in the tuff, albeit in variable amounts, zeolite types can sometimes be found as single phases, often in association with one another. As far as is known at present, the only associations to be found in Italian tuffs are as follows.

(i)   CHA + PHI + GL + AM.
(ii) CHA + GL + AM.
(iii) PHI + ANA + GL + AM.
(iv) PHI + GL + AM.

The most common assemblages are those with four components, as are present, for instance, in so-called Neapolitan yellow tuff (i, iii) [9,18], and in the zeolitic facies of Campanian tuff (i) [19].

TABLE 1

Chemical analysis of tuff constituents [a]

Constituents	NP tuff				GS tuff			
	PHI [b]	ANA	GL [b]	AM	PHI [c]	CHA [c]	GL [c]	AM
SiO_2	51.80	52.50	57.89	42.49	51.29	48.20	56.94	44.51
Al_2O_3	18.60	24.10	17.46	15.49	19.20	18.70	20.42	16.20
Fe_2O_3	0.25	0.10	4.37	15.82	0.17	0.10	4.38	14.50
MgO	0.45	0.27	1.03	0.21	0.68	0.29	1.35	0.30
CaO	2.12	3.53	3.04	0.31	0.98	5.95	2.59	0.50
SrO	–	–	–	–	0.13	0.10	–	–
BaO	–	–	–	–	0.25	–	–	–
K_2O	7.91	4.75	8.26	7.47	6.62	5.60	6.93	8.50
Na_2O	2.83	8.97	4.06	3.95	4.82	1.09	3.91	2.14
H_2O [d]	15.50	5.54	3.70	13.77	15.48	20.05	3.36	12.90

[a] Samples were stored for a week in an environment at 50% relative humidity. Values are given as percentages.
[b] From ref. 6.
[c] From ref. 7.
[d] Ignition loss.

Table 1 reports the results of chemical analysis of the hydrated constituents of samples of Neapolitan yellow tuff collected at two different sites (the deposits of Nuovo Policlinico (NP), Naples, and Grotta del Sole (GS), Quarto), both of which belong to the extended tuff outcrops present in Phlegraean Fields [18]. To obtain the products referred to in Table 1 the tuff samples were subjected to enrichment processes based on the different friabilities and densities of the various tuff constituents [21]. A remarkable similarity can be seen between the chemical compositions of corresponding phases from the two tuff samples. This similarity is also apparent in the thermal behaviour of the samples, as can be seen from the thermodifferential and thermogravimetric profiles shown in Fig. 1. For this reason, only the phases constituting GS tuff were considered for further research, except for analcime which is present only in NP tuff.

Detailed study of the TG traces for the hydrated tuff constituents at various temperatures has revealed three key temperatures [6–9].

(a) 240°C — At this temperature the non-crystalline phases of the tuff and analcime lose water irreversibly, while chabazite and phillipsite undergo a partial reversible dehydration. This is indicated in Fig. 2, which shows the kinetics of isothermal dehydration at 240°C and rehydration on cooling of the various hydrated phases.

(b) 350°C — At this temperature phillipsite breaks down during dehydration, so that it does not readsorb water, while chabazite undergoes reversible dehydration. Figure 3 shows this behaviour clearly.

(c) 900°C — At this temperature the tuff sample is definitely ignited, with no more chance that water vapour will be taken up.
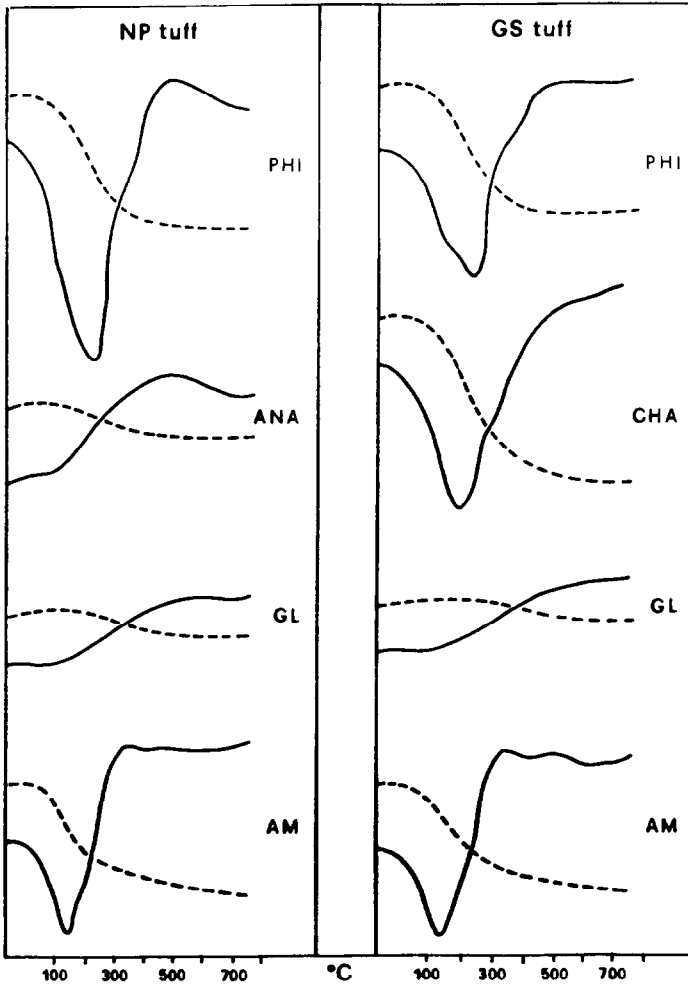
Fig. 1. DTA and TG (dashed lines) curves for hydrated tuff constituents. Sample weights, 100 mg; heating rate, $10\,^{\circ}C\ min^{-1}$; atmosphere, air.

Table 2 summarizes water loss data for the various hydrated tuff phases at these three temperatures, as deduced from TG curves.

EVALUATION OF ZEOLITE CONTENT

Knowledge of the thermal behaviour of the various hydrated constituents of the tuff allows the development of a method for the evaluation of zeolite content, as this is proportional to the amount of water released during dehydration or readsorbed during rehydration. In order to distinguish the contributions of each hydrated phase, it is necessary to subject a tuff sample to suitable thermal cycles, according to the thermal features of its con-
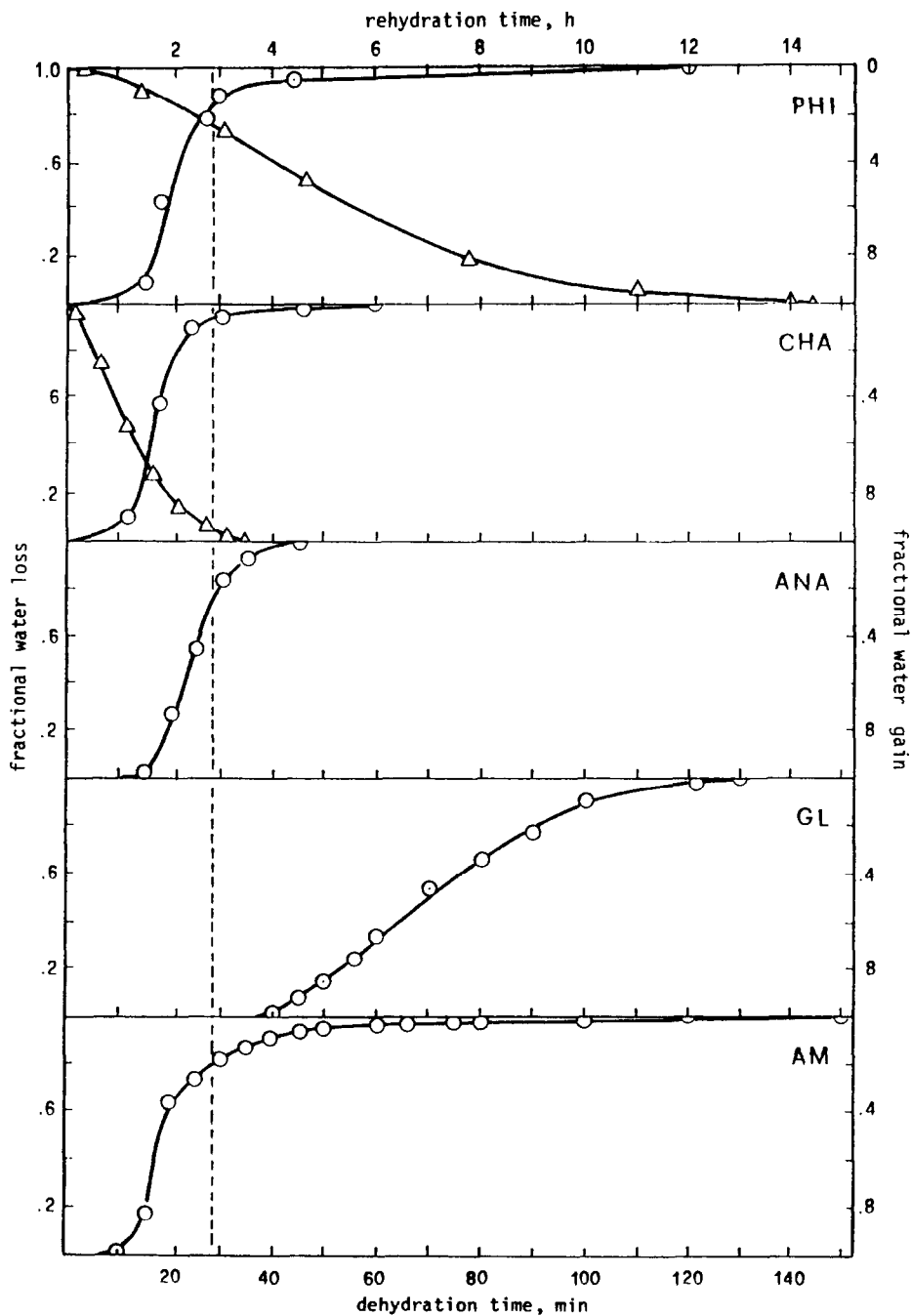
Fig. 2. Kinetics of isothermal dehydration at 240 ° C (⊙) and of rehydration on cooling to room temperature (△). The vertical dashed lines refer to the beginning of the isothermal stage of heating.
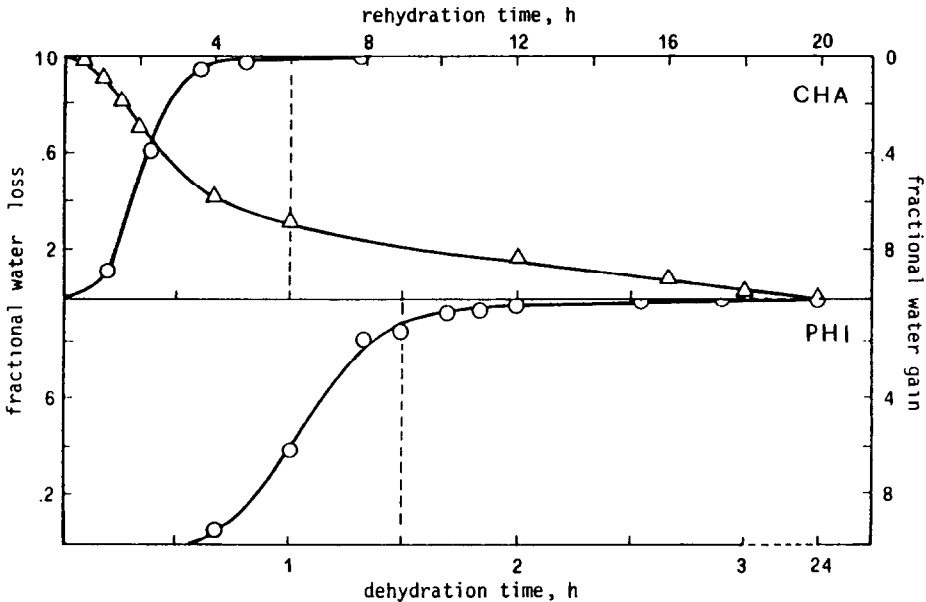
Fig. 3. Kinetics of isothermal dehydration at 350°C (⊙) and of rehydration on cooling until room temperature (△). The vertical dashed lines refer to the beginning of the isothermal stage of heating.

stituents, so that at the end of each cycle the amount of water measured is due to a single phase. Figure 4 shows a flowsheet summarizing the steps necessary for the evaluation of phillipsite and chabazite content, both in the case that one or other is present separately, and in the case that they are jointly present. The length of each operation is deduced from the data of Figs. 2 and 3.

The thermal cycles referred to in Fig. 4 were performed using a thermo-balance (Netzsch STA 409) equipped with an apparatus which assures a continuous air flow at constant humidity (40 ± 5%) and temperature (25 ±

TABLE 2

Amounts of isothermal water loss for hydrated tuff phases at various temperatures [a]

Phase	Water content [b]	Water loss at 240°C	Water loss at 350°C	Water loss at 900°C
CHA	20.05	17.48	20.34	20.34
PHI	15.48	11.89	15.56	–
ANA	5.54	5.50	–	–
GL	3.36	3.34	–	–
AM	12.90	12.84	–	–

[a] Values are given as percentages.
[b] Values from Table 1.

Sample

W_1

ISOTHERMAL
HEATING
240°C, 2h

COOLING
R.T.,~15h

W_2 ①

ISOTHERMAL
HEATING
350°C, 24h

W_2 ②

IGNITION
900°C,~2h

W_3

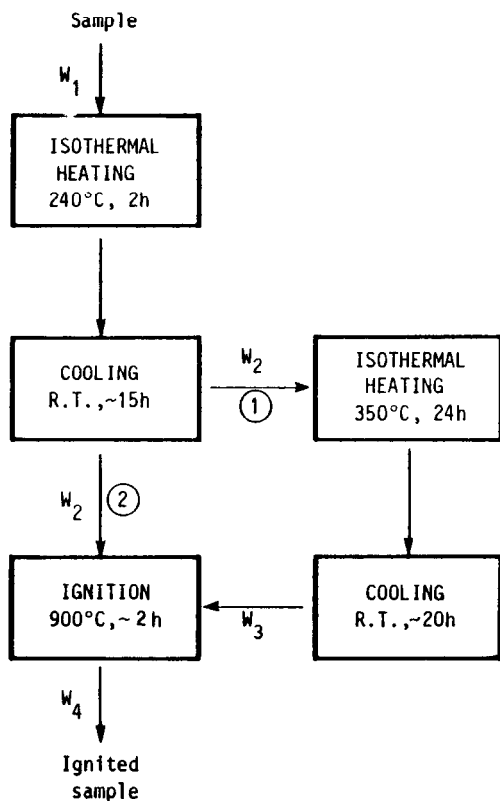COOLING
R.T.,~20h

W_4

Ignited
sample

Fig. 4. Flowsheet summarizing the methodology for hydrated tuff constituent evaluation by thermogravimetry: (1) route to be chosen in the case of joint presence of PHI–CHA; (2) route to be chosen otherwise. W_1–W_4: sample weights at the various steps of the evaluation.

1°C), either on heating or on cooling [8]. The complete TG trace recorded at the end of the two or three thermal cycles [8] allows measurement of the sample weights W_1–W_4 shown in Fig. 4 and, taking into account the water content of the pure phases, calculation of the zeolite content of the tuff. The relevant equations are

$$\text{ZEO\%} = \frac{100(W_2 - W_4)}{W_1 w_{\text{ZEO}}}$$

(where w_{ZEO} represents percentage of water in the pure zeolite) in the case that only phillipsite or chabazite is present, and

$$\text{PHI\%} = \frac{100(W_2 - W_4)}{W_1 w_{\text{PHI}}}$$

$$\text{CHA\%} = \frac{100(W_3 - W_4)}{W_1 w_{\text{CHA}}}$$

(where w_{PHI} and w_{CHA} represent percentage of water in phillipsite and

TABLE 3

Comparison of theoretical and measured compositions of zeolite mixtures

N	Theoretical composition					Measured composition	
	PHI	CHA	ANA	GL	AM	PHI	CHA
1	70			20	10	73	
2	50			30	20	50	
3		70		20	10		70
4		60		30	10		58
5	60		30	10		65	
6	80		10	10		84	
7	60	20		20		60	20
8	40	40		20		39	40
9	40	30		20	10	37	33
10	30	40		20	10	28	38

chabazite, respectively) in the case that both chabazite and phillipsite are present.

RESULTS AND CONCLUSIONS

Table 3 reports the results of application of the above method to standard mixtures obtained from weighed amounts of the pure hydrated phases. It can be seen that agreement between the actual values and the experimental results is good. The average percent deviation is around 3%, which is reasonable given the difficulty of analysing mineral mixtures. So the method proposed shows the qualifications of accuracy and reliability, besides ease of application, and appears to be advisable for use in routine estimations of zeolite in natural or artificial mixtures, provided it is adapted to suit the thermal features of the particular hydrated phases present in the mixture under investigation.

ACKNOWLEDGEMENTS

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