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ESTIMATION OF ZEOLITE CONTENT IN NEAPOLITAN YELLOW TUFF.
II. PHILLIPSITE AND CHABAZITE IN TYPICAL PHLEGRAEAN DEPOSITS

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ABSTRACT. — Following previous researches on phillipsite estimation in practically monozeolitic samples of Neapolitan yellow tuff, a method based on water vapour desorption is proposed for quantitative evaluation of both phillipsite and chabazite in more typical occurrences of the tuff. The method, which appears simple, reliable and accurate for routine estimations, contemplates a thermal cycle including three heating steps (240, 350 and 800° C) alternating with two rehydrations. It has been shown that the water loss at each temperature is related to non zeolitic phases, phillipsite and chabazite, respectively. Finally it is emphasized that the method is applicable to almost all the Italian tuffs.

RIASSUNTO. — Facendo seguito a precedenti ricerche sulla valutazione del tenore di phillipsite in campioni praticamente monozeolitici di tufo giallo napoletano, viene proposto un metodo, basato sul desorbimento di vapore d'acqua, per la valutazione di phillipsite e cabasite nelle giaciture più frequenti dello stesso tufo. Il metodo, che appare semplice, affidabile e accurato per determinazioni rutinarie, prevede un ciclo termico di riscaldamento in tre stadi (240, 350, 800° C), alternati con due reidratazioni. È stato mostrato che la perdita d'acqua a ciascuna delle dette temperature è relazionabile a fasi non zeolitiche, phillipsite e cabasite, rispettivamente. Viene infine messo in evidenza che il metodo proposto è applicabile a quasi tutti i tufi italiani.

Introduction

The most common occurrence of Italian tuffs of commercial interest (SERSALE, 1978; GOTTARDI and OBRADOVIC, 1978), particularly of Neapolitan yellow tuff (DE' GENNARO et al., 1983), is characterized by the joint presence of phillipsite and chabazite. The possibility of the quantitative evaluation of both zeolites in these tuffs is of remarkable interest, in consideration of their potential industrial applications, the most promising of which appear at present to be the purification of wastewaters, *e.g.* ammonium removal from tertiary sewages (COLELLA et al., 1983), and the preparation of pozzolanic cements (SERSALE and FRIGIONE, 1983).

In a previous paper (COLELLA et al., 1982-83) two methods based on ion exchange and water vapour desorption techniques have been reported for the estimation of zeolite content in practically monozeolitic (phillipsitic) Neapolitan tuffs. The use of the above methods for the estimation of phillipsite and chabazite in more typical tuff occurrences, processing the experimental data through the use of simultaneous equations, does not give reliable results. The two zeolites, in fact, do not have sufficiently distinct ion-exchange capacities (they differ from each other by a few unites percent), if compared with the error connected with the analytical determination ($\geqslant 1$ %).

The aim of this paper is to test a new estimation method of phillipsite and chabazite content in Neapolitan yellow tuff, which,

Fig. 1. — General view of Neapolitan yellow tuff quarries at Grotta del Sole (Quarto, Napoli).

taking advantage of phillipsite thermolability (Colella et al., 1982-83), contemplates a suitable thermal pre-treatment, causing phillipsite breakdown, and making it possible to bring the analytical problem back to the quantitative evaluation of one zeolite at a time.

Experimental

The samples of Neapolitan yellow tuff come from five of the seven quarries, operating the large outcrop of Grotta del Sole (GS, Quarto, Napoli) (fig. 1). Table 1 reports the listing of the samples examined and the description of the position in every quarry — quarries have been numbered from 1 (West) to 7 (East) — from which they were collected.

X-ray powder diffraction patterns show that all the samples of table 1 consist essentially of phillipsite and chabazite, with lesser amounts of K-feldspar, augite, and biotite. *Non*-crystalline fractions (small pumices and unzeolitized glass) are also present, as evidenced by microscope observations.

Table 2 reports the chemical analyses of a samples of GS tuff (table 1, N. 2) and of pure phillipsite, chabazite and glass, obtained from the tuff, following suitable enrichment processes described elsewhere (Colella et al., 1982-83). Table 3 summarizes the main chemical and physical parameters of the two zeolitic phases. The calculated ion exchange capacities on the basis of the chemical formulas are 3.70 meq/g for phillipsite and 3.82 meq/g for chabazite, both values in good agreement with those measured for the two zeolites (table 3). Phillipsite, chabazite and glass were used for the preparation of binary of ternary mixtures to be tested for quantitative determinations. For this purpose weighed amounts of the two zeolites, with or without added glass, were carefully wet-mixed in presence of acetone. The mixtures were then dried at 80° C for several hours and stored at 25° C in environment at *R.H.* = 50 %.

Ion exchange and water vapour desorption measurements were carried out according to techniques already reported (Colella et al., 1982-83).

Table 1

Localization of the tuff samples

N°	Quarry number	Description
1	3	South wall:15 meters downwards from the top
2	3	South wall:30 meters downwards from the top
3	4	NE wall: 7 meters downwards from the top
4	4	NE wall:28 meters downwards from the top
5	5	North wall:18 meters downwards from the top
6	6	SW wall:10 meters downwards from the top
7	6	SW wall:20 meters downwards from the top
8	7	East wall:25 meters downwards from the top

Thermal treatments of the samples were performed in oven at the programmed temperature. Rehydration tests were carried out storing the heat-activated samples at 25° C in environment at *R.H.* = 50 % until constant weight.

Results and discussion

THERMAL BEHAVIOUR OF PHILLIPSITE, CHABAZITE AND GLASS

Phillipsite has been shown to be a bad heat-resistant zeolite; the maximum treatment temperature, without any detectable breakdown being recorded turned out to be 240° C (Colella et al., 1982-83). Figure 2, reporting only a selection of the collected data, shows the residual crystallinity of phillipsite, measured from the intensity decrease of the main reflections of the X-ray

TABLE 2
Chemical analysis◇ *of GS tuff, phillipsite, chabazite, and glass*

	tuff	phillipsite	chabazite	glass
SiO_2	54.76	51.29	48.20	56.94
Al_2O_3	18.05	19.20	18.70	20.42
Fe_2O_3	3.04	0.17	0.10	4.38
MgO	0.19	0.68	0.29	1.35
CaO	1.46	0.98	5.95	2.59
SrO	-	0.13	0.10	-
BaO	-	0.25	-	-
K_2O	7.45	6.62	5.60	6.93
Na_2O	3.85	4.82	1.09	3.91
H_2O*	11.68	15.48	20.05	3.36
	100.48	99.62	100.08	99.88

* Ignition loss. ◇ Samples stored for a week in environment at 50 % relative humidity (*R.H.*).

TABLE 3
Chemical and physical parameters of GS phillipsite and chabazite

	phillipsite	chabazite
Ion exchange capacity, meq/g	3.65	3.89
Density, g/cm^3	2.13	2.07
Mean refractive index	1.48	1.47

Chemical formulas

$PHI(Na_{2.02}K_{1.83})(Ca_{0.23}Mg_{0.22})\left[Al_{4.89}Si_{11.10}O_{32}\right]\cdot 11.18H_2O$

$CHA(Na_{0.36}K_{1.22})(Ca_{1.08}Mg_{0.07})\left[Al_{3.75}Si_{8.20}O_{32}\right]\cdot 11.39H_2O$

diffraction patterns, after treatment at temperatures ranging between 300 and 350° C for various times. Phillipsite appears to be completely destroyed as a results of a 24 hours treatment at 350° C. This is confirmed by the data of fig. 3, referring to rehydration processes after 3 (△), 12 (□) and 24 hours (○) of thermal treatment at 350° C, showing that phillipsite does not readsorb water any more, when treated at that temperature for one day.

Chabazite turns out to be more heat-resistant than phillipsite. Figure 4, reporting the residual crystallinity of the zeolite after 2 hours of thermal treatment, as a function of temperature, shows that the framework is stable up to about 400° C. This is confirmed by the data of fig. 5, where the water vapour readsorption capacity of chabazite is tested after 2 hours of thermal treatment at tem-

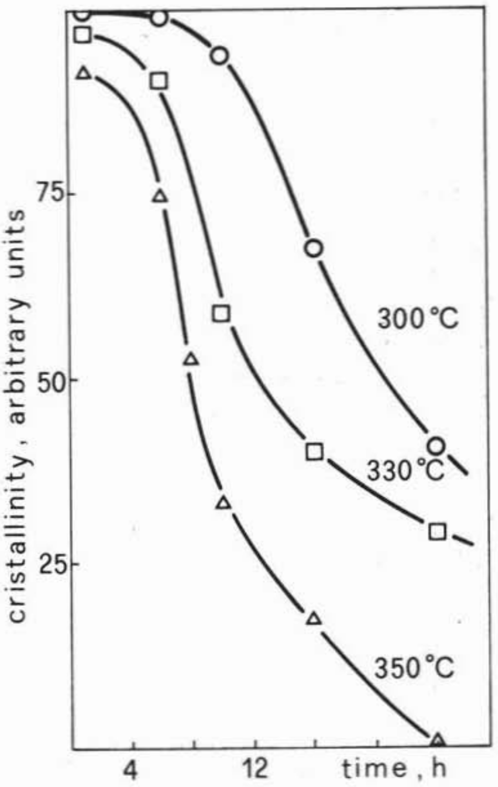

Fig. 2. — Residual crystallinity of phillipsite as a result of thermal treatments at different temperatures, as a function of time.

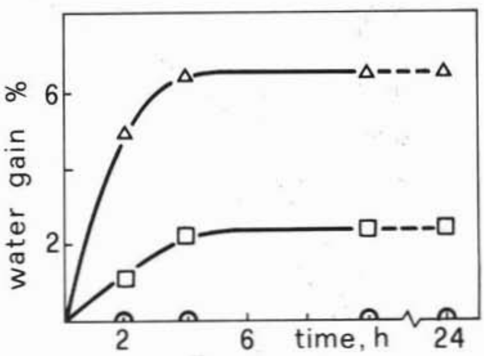

Fig. 3. — Water vapour uptake of phillipsite at room temperature, as a function of time, after treatment at 350° C for 3 (△), 12 (□) or 24 hours (○).

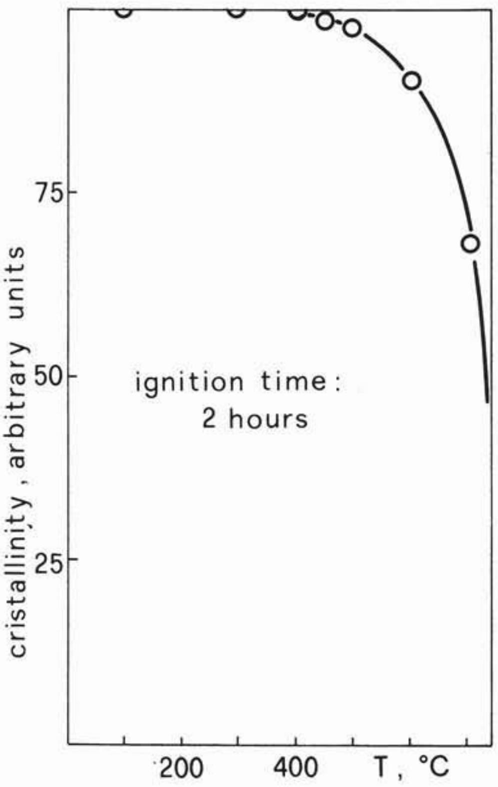

Fig. 4. — Residual crystallinity of chabazite, as a function of the treatment temperature.

peratures ranging between 300 and 450° C. Chabazite readsorbs in a few hours all the lost water (dotted lines), when heat-treated up to 400° C.

On the contrary thermal treatment at 450° C for 2 hours causes breakdown of zeolite and therefore cuts down its capacity for sorbing water by about 25 %. Referring to the above conditions causing a complete breakdown of phillipsite, fig. 6 shows, on the contrary, that chabazite framework remains perfectly undamaged. A chabazite sample which loses at 350° C its water in 14 hours, regains its original weight through reydration in about the same time.

Glass, obtained from GS tuff, shows a thermal behaviour analogous to that of the glass obtained from the phillipsite tuff previously studied (COLELLA et al., 1982-83). Fig. 7 shows that glass, heat-treated for 2 hours at 240° C, loses almost all its water content in about 2 hours. Rehydration tests lasting up to about 10 days show that water is definitely not readsorbable.

Note that the above temperature should be sufficiently elevated to assure the irreversible dehydration of hydrated ferric oxides (MACKENZIE, 1957). Thermal tests on a light fraction, coming from the zeolite enrichment

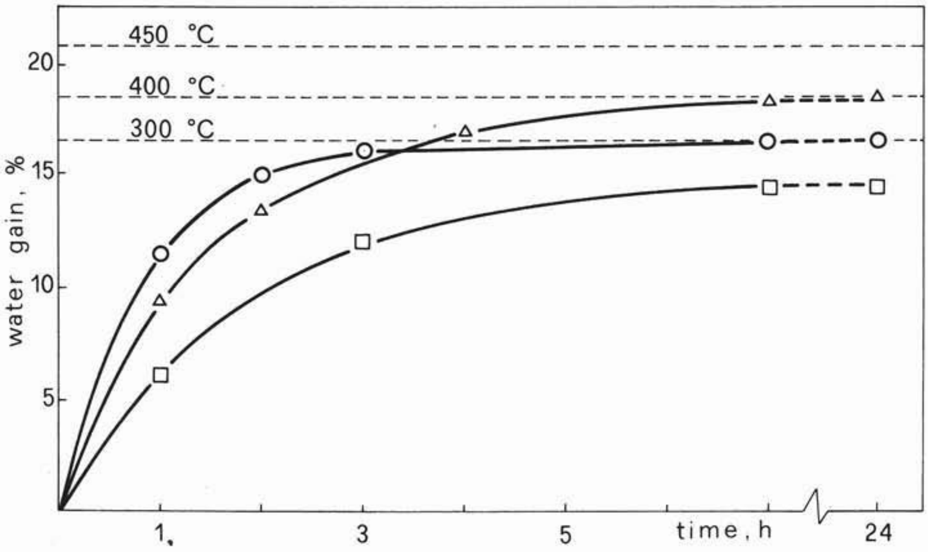

Fig. 5. — Rehydration curves at room temperature of chabazite, activated by heating at 300 (○), 400 (△) or 450° C (□). Dotted lines refer to water lost during the activation.

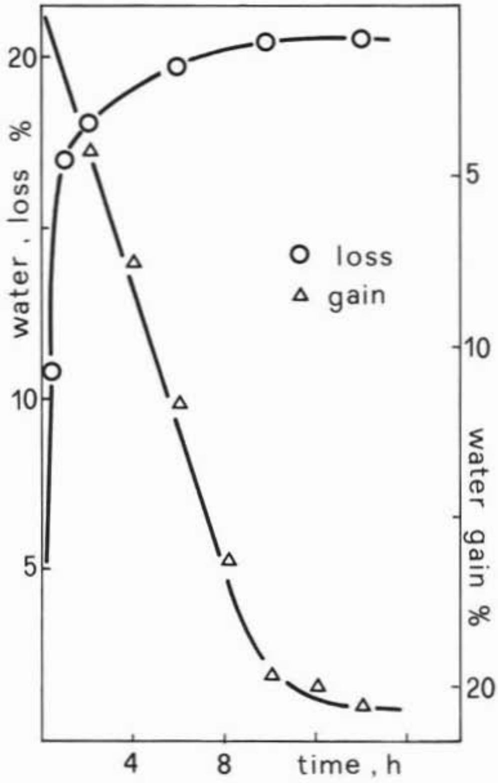

Fig. 6. — Dehydration (at 350° C) and rehydration (at room temperature) curves of chabazite.

processes of the tuff and constituted mostly by hydrated ferric oxides, show that the treatment at 240° C for 2 hours determines an irreversible weight loss equal to 95 % of the ignition loss at 800° C. The little water amount saved at 240° C has to be considered insignificant for the successive evaluations.

TESTS OF ZEOLITE ESTIMATION ON ARTIFICIAL MIXTURES

Quantitative evaluation of phillipsite and chabazite was tested on artificial binary and ternary (including glass) mixtures. On the basis of thermal data reported in the preceding section, the following method is proposed for zeolite estimation:

I) the sample (initial weight: W_1) is heat-treated in oven at 240° C for 2 hours; this causes the definitive dehydration of glass (if present) and a partial water vapour desorption by zeolites, the frameworks of which remain however perfectly undamaged;

II) the sample is stored at 25° C in an environment at *R.H.* = 50 % until constant weight (W_2) (mean lenght of time: 14 hours); this allows a complete rehydration of both zeolites;

III) the sample is heat-treated in oven at 350° C for 24 hours; this causes the breakdown of phillipsite and a partial water vapour desorption of chabazite, the framework of which remains perfectly undamaged;

IV) the sample is stored at 25° C in an environment at *R.H.* = 50 % until constant weight (W_3); this allows a complete rehydration of chabazite;

V) finally the sample is heat-treated in oven up to 800° C (final weight: W_4); this allows the complete dehydration and breakdown of chabazite.

The total percent water is thus divided in

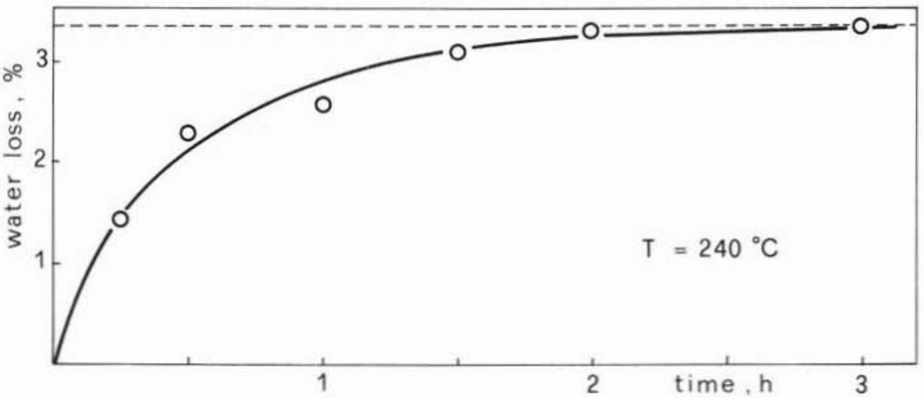

Fig. 7. — Water loss curve of the glass fraction of the tuff, as a function of time. Dotted line refers to the water content of the glass (see chemical analysis in table 2).

TABLE 4
Zeolite content in standard mixtures

Mixture composition %			W_p %	W_c %	W_g %	Measured phillipsite %	Measured chabazite %
PHI	CHA	GL					
75	25	-	11.39	5.12	-	74	26
60	40	-	9.48	8.10	-	61	40
40	60	-	6.06	12.44	-	39	62
25	75	-	4.10	14.97	-	26	75
60	20	20	9.25	4.02	0.71	60	20
50	30	20	7.80	5.92	0.70	50	29
40	40	20	6.05	7.97	0.73	39	40

three parts: W_g, related to non zeolitic phases (mainly glass and hydrated ferric oxides), W_p and W_c, directly proportional to phillipsite and chabazite contents, respectively.

W_p, W_c and W_g are easily calculated in the following way:

$$W_p = \frac{W_2 - W_3}{W_1} \cdot 100;$$

$$W_c = \frac{W_3 - W_4}{W_1} \cdot 100;$$

$$W_g = \frac{W_1 - W_2}{W_1} \cdot 100.$$

The phillipsite and chabazite amounts in the mixtures are then calculated, correlating W_p and W_c to the water content of pure zeolites (see table 2). Table 4 reports the tests of zeolite estimation on artificial mixtures.

The values of measured phillipsite and chabazite show a good agreement with the theoretical ones, evidencing the reliability and the accuracy of the proposed method.

TABLE 5
Phillipsite and chabazite content in GS tuff samples

Tuff samples (Table 1)	W_p %	W_c %	W_g %	Measured phillipsite %	Measured chabazite %
1	3.30	5.59	1.25	21	28
2	5.63	4.60	1.45	36	23
3	4.34	7.76	1.30	28	39
4	4.16	4.70	1.00	27	23
5	4.59	5.90	1.45	30	29
6	5.00	4.85	1.81	32	24
7	5.65	6.68	1.65	36	33
8	5.68	6.10	1.20	37	30

ESTIMATION OF PHILLIPSITE AND CHABAZITE IN TUFF SAMPLES

Table 5 reports the results of quantitative zeolite evaluations in the tuff samples of table 1, according to the method described in the preceding section.

Apart from the different distribution of the two zeolites in the examined tuff samples, it is interesting to note in most samples the substantial constancy of zeolite content, ranging around 60 %.

Conclusion

The results of both this and the previous research (COLELLA et al., 1982-83) show that methods based on water vapour desorption may be advantageously employed for the quantitative evaluation of the zeolite (phillipsite and chabazite) content in the Neapolitan yellow tuff. The proposed method appears easy in the execution, reliable and sufficiently accurate for routine estimations.

The method is practically applicable to almost all the Italian tuffs, owing to the already mentioned constancy of zeolite types occurring in them.

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REFERENCES

COLELLA C., DE' GENNARO M., FRANCO E., AIELLO R. (1982-83) - *Estimation of zeolite content in Neapolitan yellow tuff. I. Phillipsite in nearly monozeolitic deposits.* Rend. SIMP, 38, 1423-1427.

COLELLA C., NASTRO A., AIELLO R. (1983) - *Impiego di tufi zeolitici per la rimozione di ammonio da acque reflue.* In: « I Materiali per l'Ingegneria », Atti del 1° Convegno ASMI, Eds. F. Sandrolini and A. Motori, Pitagora Editrice, Bologna, 193-198.

DE' GENNARO M., COLELLA C., FRANCO E., AIELLO R. (1983) - *Italian Zeolites 1. Mineralogical and technical features of Neapolitan yellow tuff.* Industrial Minerals, n. 186, 47-53.

GOTTARDI G., OBRADOVIC J. (1978) - *Sedimentary zeolites in Europe.* Fortschr. Miner., 56, 316-366.

MACKENZIE R.C. (1957) - *The differential thermal investigation of clays.* Mineralogical Society, London, 307-311.

SERSALE R. (1978) - *Occurrences and uses of zeolites in Italy.* In « Natural Zeolites. Occurrence, properties, use », Eds. L.B. Sand and F.A. Mumpton, Pergamon Press, Oxford, 285-302.

SERSALE R., FRIGIONE G. (1983) - *Utilisation of quarry dust of the Neapolitan yellow tuff for the manufacture of blended cements.* Chimica e Industria, 65, 479-481.