

ESTIMATION OF ZEOLITE CONTENT IN NEAPOLITAN YELLOW TUFF. I. PHILLIPSITE IN NEARLY MONOZEOLITIC DEPOSITS

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ABSTRACT. — Two methods, based on ion exchange and water vapour desorption, for the estimation of phillipsite content in nearly monozeolitic samples of the Neapolitan yellow tuff are presented. The accuracy and the reliability of the methods and their applicability for routine evaluations, through tests on standard phillipsite-calcined glass mixtures, are proved. The methods are applied for estimation of zeolite content in several samples of Neapolitan yellow tuff and the use of that based on desorption is suggested at last because of its execution rapidity.

RIASSUNTO. — Vengono presentati due metodi, basati sullo scambio cationico e sul desorbimento di vapore d'acqua, per la valutazione del contenuto di phillipsite in campioni di tufo giallo napoletano praticamente monozeolitici. L'accuratezza e l'affidabilità dei metodi e la loro possibile applicazione per valutazioni di routine è messa in evidenza mediante prove su miscele standard di phillipsite e vetro calcinato. I metodi vengono applicati alla valutazione del contenuto zeolitico in alcuni campioni di tufo giallo napoletano e quello basato sul desorbimento del vapore d'acqua viene giudicato più conveniente, data la sua maggiore rapidità di esecuzione.

Introduction

The quantitative determination of zeolite content in synthesized *omo*-zeolitic products is usually accomplished by XRD (SAND et al., 1971; CULFAZ and SAND, 1973), ion exchange (SUBOTIĆ and ŠMIT, 1980) or water vapour adsorption (MEISE and SCHWOWCHOW, 1973) methods, although the use of X-ray quantitative analysis is not considered universally correct (JOHNSON, 1978). As far as the natural zeolites are concerned very

little has been done either for the minor interest they have aroused until now, or for the remarkable difficulty in analyzing the systems in which they are included. Several methods of estimation of zeolite content in natural products have indeed been proposed, based on the evaluation of ion exchange or adsorption capacities and of adsorption heat (see for example VALYON et al., 1981 and CIAMBELLI et al., 1980), but, even if accurate, they are neither easy nor rapid.

The growing interest in the use of sedimentary zeolites in processes of relevant technological value, on the other hand, makes it necessary to have available a method of estimation of zeolite content, which may conveniently be used in routine operations. Among the various Italian natural zeolites, *Neapolitan yellow tuff* (DE' GENNARO et al., 1983) has most recently shown interesting perspectives of use in the field of ammonium removal from wastewaters of different origin (NASTRO and COLELLA, 1983; COLELLA et al., 1983; CIAMBELLI et al., 1983). This application depends mainly on the massive presence of phillipsite, which is in this tuff constantly prevailing on chabazite. The known variability of zeolite content in tuff samples occurring in the same formation, makes it necessary a frequent evaluation of their zeolite content.

The aim of this research is to investigate the suitability and reliability of processes

such as water vapour desorption and ion exchange for routine estimations of zeolite content in Neapolitan yellow tuff. The results here presented refer to materials, in which the total zeolite amount is practically coincident with phillipsite, the total content of chabazite being very low.

Experimental

The samples of Neapolitan yellow tuff come from the large quarry of Nuovo Policlinico (NP, Napoli) (fig. 1). Table 1 reports the denomination of the samples examined and the description of the position in the quarry from which they were collected. The last two samples of table 1 come from the

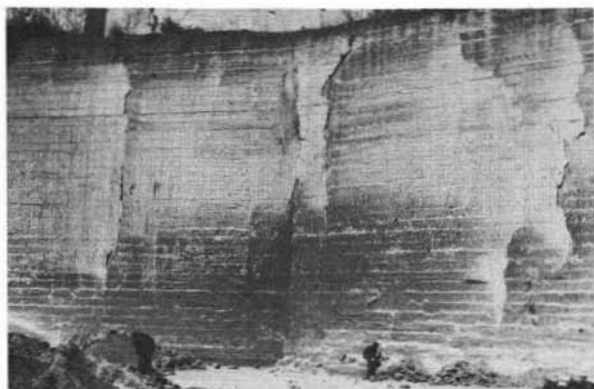


Fig. 1. — Quarry of Neapolitan yellow tuff. Locality Nuovo Policlinico (Napoli).

bug dust of the cutting operations for the production, directly in the quarry, of dimension stones for building purposes. This material, the grain size distribution of which appears in fig. 2, has been considered because of the notable interest presented by its potential industrial utilization. It, in fact, couples particularly low cost with very large availability (several thousands tons *per* year).

X-ray powder diffraction patterns indicate that all the samples of table 1 consist essentially of phillipsite, with lesser amounts of chabazite (few units percent), K-feldspar, augite, and biotite. Microscope observations evidence the presence of *non*-crystalline fractions, constituted by small pumices and unzeolitized glass. A chemical analysis of the tuff is listed in the first column of table 2

TABLE 1
Localization of the tuff samples

N.	Denomination	Description
1	t _A	West wall: 30 meters down wards from the top
2	t _B	West wall: 27 meters down wards from the top
3	t _C	West wall: at the top
4	t _D	East wall: 25 meters down wards from the top
5	t _E	East wall: at the top
6	bd ₁	Bug dust, grain size fraction 30 x 50 mesh
7	bd ₂	Bug dust, grain size fraction >100 mesh

TABLE 2
Chemical analysis of NP tuff, phillipsite and glass

	tuff	phill.	glass
SiO ₂	52.08	51.80	57.89
Al ₂ O ₃	16.52	18.60	17.46
Fe ₂ O ₃	3.50	0.25	4.37
MgO	1.02	0.45	1.03
CaO	2.71	2.12	3.04
SrO	0.01	-	-
BaO	0.05	-	-
K ₂ O	8.67	7.91	8.26
Na ₂ O	2.06	2.83	4.06
H ₂ O [*]	13.72	15.50	3.70
	100.34	99.46	99.87

* Ignition loss.

TABLE 3
Chemical and physical parameters of NP phillipsite

Chemical formula	
(Na _{1.19} K _{2.19})(Ca _{0.49} Mg _{0.15})[Al _{4.76} Si _{11.24} O ₃₂] · 11.23H ₂ O	
Ion exchange capacity, meq/g	3.46
Density, g/cm ³	2.14
Mean refractive index	1.48(2)

and appears to be typical of such material (SCHERILLO, 1955).

Pure phillipsite was obtained from a tuff sample following enrichment processes (DE' GENNARO and FRANCO, 1979), based on the greater friability and the lower density of the zeolite, compared to the other tuff constituents. The chemical analysis of NP phillipsite appears in the second column of table 2. Table 3 reports the chemical formula and the main chemical and physical parameters characterizing this phase.

Pure glass fraction of NP tuff was obtained by treating the residue of the previous separa-

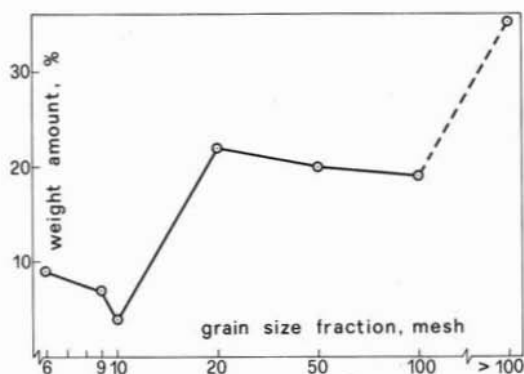


Fig. 2. — Grain size distribution of bug dust, coming from the cutting operations of NP tuff.

ration with heavy liquids of known densities and submitting the resultant suspensions to repeated centrifugations. XRD analysis excluded the presence of crystalline phases in the glass.

Water content in the glass fraction turns out to be 3.70 % (see table 2). Rehydration tests of the length of 10 days show that water is definitely not reabsorbable. Glass shows a mean ion exchange capacity of 0.40 meq/g. Ion exchange kinetics is however so low, in comparison with phillipsite, that the presence of glass in a sample negligibly affects the determination of its ion exchange capacity.

NP phillipsite and calcinated glass were used for the preparation of standard mixtures to be tested for quantitative determinations. For this purpose weighed amounts of the two phases were carefully wet mixed in presence of acetone. The mixtures were then dried at 80° C for several hours and stored at 20° C in environment at 50 % relative humidity.

Zeolite estimations were performed correlating ion exchange and water vapour desorption capacities of the samples with those of pure zeolite. The evaluation of the ion exchange capacity has been made in column on 1-gram samples. These were previously Na- (or K-) exchanged, percolating them, at 60° C, with 0.5M NaCl (or KCl) solution, till when no further potassium (or sodium), calcium and magnesium were detectable in the eluate. The samples made mono-cationic were then K- (or Na-) exchanged in analogous way and the eluates collected and analyzed

for sodium (or potassium). The mean ion exchange capacity was at last calculated from the averages of Na and K contents in the eluates.

The water vapour desorption measurements were carried out, according to the method described in the next section, heat treating at the programmed temperature in thermobalance or in oven until constant weight standard mixtures (see below) or tuff samples, stored beforehand at controlled temperature and humidity (see above). Thermogravimetry (TG) and differential thermal analysis (DTA) were performed employing a Netzsch mod. 409 Thermoanalyzer.

Results and discussion

Table 4 reports the results of the phillipsite quantitative evaluations in standard phillipsite-calcined glass mixtures. The values of measured phillipsite, calculated as said above (see Experimental) either from ion exchange or from water desorption data, show a good agreement with the theoretical ones, evidencing the sufficient reliability of both methods.

TABLE 4
Phillipsite content in standard mixtures

Mixture composition (phill., %)	Ion exchange capacity (meq/g)	Measured phillipsite (%)	Water loss at 800° C (%)	Measured phillipsite (%)
80	2.55	74	12.0	78
50	1.75	51	7.4	48
30	1.12	32	4.3	28

The application of these methods to the estimation of phillipsite content in tuff samples requires some preliminary considerations on the accessory phases present in the rock. While, in fact, minerals such as K-feldspar, augite and biotite do not possess any ion exchange and adsorption properties and may be considered inert, chabazite can affect, in an unnegligible way, the ion exchange and water vapour desorption determinations. The approximation made in the present work is that chabazite, due to its limited content in the tuff considered, and also due to the values of ion exchange and water vapour desorption capacities not very far from those of phillipsite, may be evaluated as phillipsite.

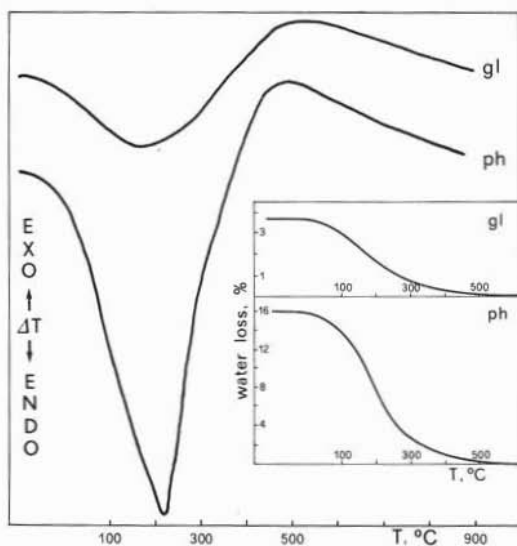


Fig. 3. — DTA and TG curves for NP glass fraction (*gl*) and phillipsite (*pb*). Weight of the samples: 100 mg; heating rate: 10° C/min.; atmosphere: air.

With reference to the desorption method, a source of error, particularly considerable in samples with low zeolite content, is the presence in the tuff of hydrated glass (water content: 3.70 %, see table 2). This water is lost approximately in the same temperature range as phillipsite (fig. 3), although it is definitely not reabsorbable (see Experimental). The possibility of its removal, following a preliminary partial dehydration of the tuff sample, must be examined in the light of the known thermolability of phillipsite. The data of fig. 4, where the residual crystallinity of phillipsite after two hours of thermal treatment, measured from the intensity decrease of the main reflections of the X-ray diffraction patterns, is reported as a function of the treatment temperature, show that phillipsite cannot be heat treated over 240° C without at least some partial structural breakdown. Desorption tests at 240° C on pure glass fraction, obtained from the tuff, show on the other hand that within two hours glass loses almost all its water content (fig. 5).

On the ground of these introductory data, phillipsite estimation, based on the desorption method, was performed as follows:

- I) the weighed tuff sample (W_1) was thermally treated in oven at 240° C for two hours;

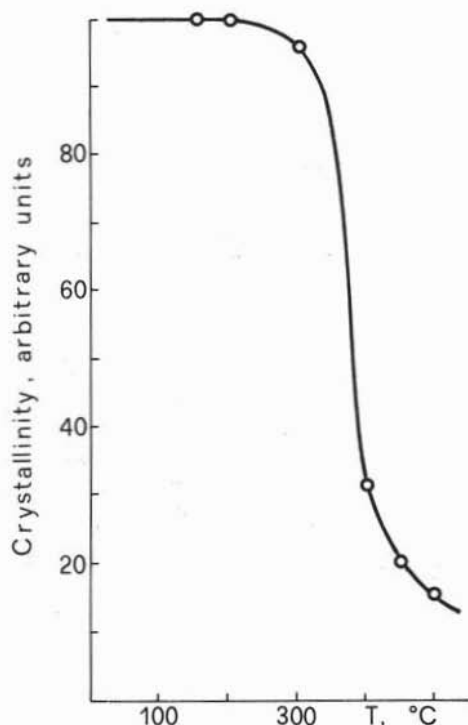


Fig. 4. — Residual crystallinity of NP phillipsite as a function of the treatment temperature.

- II) it was then stored at 25° C in an environment at 50 % relative humidity until constant weight (W_2) (mean length of time: 14 hours);
- III) finally the sample was thermally treated in thermobalance up to 800° C (final weight: W_3).

The total percent water content was thus

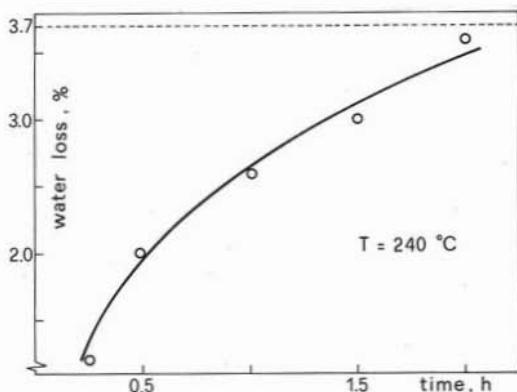


Fig. 5. — Water loss curve of NP glass fraction at 240° C as a function of the treatment time.

divided in « zeolitic » (W_z), directly proportional to zeolite content, and « non zeolitic » (W_g), associated mostly to glass fraction. W_z and W_g were easily calculated in the following way:

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

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

TABLE 5
Phillipsite content in tuff samples

Tuff samples	Ion exchange capacity (meq/g)	Measured phillipsite (%)	Water loss (%)		Measured phillipsite (%)
(Table 1)			W_g	W_z	
t _A	1.19	34	1.6	5.7	37
t _B	2.20	63	1.3	9.0	58
t _C	2.79	80	0.2	11.4	73
t _D	2.75	79	0.4	12.4	80
t _E	2.73	79	1.2	12.4	80
bd ₁	1.71	49	0.8	7.2	46
bd ₂	2.16	62	1.6	9.2	59

The phillipsite amount in the tuff was then calculated, as already said, correlating W_z to

the water content of the phillipsite (15.50%, see table 2). Table 5 reports the results of the quantitative estimations of phillipsite in the tuff samples described in table 1. The data show a good agreement between the values determined according to the two techniques, which accounts indirectly for their accuracy and reliability. It is interesting to observe the remarkable constancy of zeolite content (near to 80 %) in tuff samples from central levels of the formation.

Conclusion

The results of the present research show that methods based on ion exchange or water vapour desorption may be used for routine evaluation of phillipsite content in nearly monozeolitic samples of Neapolitan yellow tuff. Both methods appear sufficiently accurate and reliable. The desorption method is perhaps preferable for its execution rapidity; the complete cycle, as described in the above section, is usually accomplished, in one day.

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