C. COLELLA, R. AIELLO, R. SERSALE

GENESIS, OCCURRENCE AND PROPERTIES
OF ZEOLITIC TUFF

SUMMARY. — The results of an experimental research devoted to evaluate the possible utilizations of volcanic tuffs, owing to the zeolitic nature of their matrix, have been reported.

After a short discussion on the genesis, occurrence and potentiality of zeolitic tuff deposits, the evaluation of the adsorption and cationic exchange properties of a typical chabazite tuff, chosen as a simple model, has been done.

The interesting properties as dessiccant of the tuff, competitive, in particular conditions, with silica gel and even better at higher than room temperature and low humidities, have been pointed out.

Its possible utilization also in the field of water softening has been, at last, indicated, on the basis of its very low cost, its easy supply and of the eventual reutilization of the exhausted product in other industrial sectors.

RIASSUNTO. — Gli Autori riportano i più significativi risultati di una ricerca sperimentale, rivolta ad approfondire la genesi dei tufi vulcanici a matrice zeolitica ed a proporre loro vantaggiose utilizzazioni industriali.

Dopo puntualizzazione sulla distribuzione e sulla potenzialità di tali tufi zeolitici, con particolare riferimento a quelli del distretto eruttivo campano, viene affrontato il problema della genesi, definito sulla base di esperienze di laboratorio.

Si passa successivamente alla valutazione delle proprietà di adsorbimento e di scambio cationico, scegliendo come modello un campione di tufo contenente soltanto cabasite, quale minerale zeolitico costituente la massa di fondo cementante.

Sulla base di risultanze sperimentali, vengono poste in luce le interessanti proprietà disidratanti di tale tufo, competitive od addirittura superiori, in particolari condizioni chimico-fisiche, a quelle dei prodotti disidratanti tradizionali.

Sulla base dei dati acquisiti, viene infine fatto il punto sulla possibile utilizzazione dei tufi zeolitici nel campo del raddolcimento delle acque, stante il loro interesse, a seguito del basso costo, del facile approvvigionamento e della possibile reutilizzazione del prodotto esaurito in altri settori industriali.

Introduction.

Tuff is a pyroclastic rock, widely found in central and southern Italy. Its origin is to be connected with alteration phenomena, which took place on the amorphous fraction of unwelded materials, deposited, in different ways, after volcanic explosions. This alteration led to the *neo*-formation of aluminosilicate phases, *i.e.* zeolites or feldspars, responsible for the cementation of the parent materials. The most welded tuffs appear stone-like, showing compressive strengths (100-300 Kg/cm^2) (1), close to those shown by bricks, and therefore have been used since ancient times as building materials.

By considering the enormous potentiality of zeolite-bearing tuffs and their very low cost, possibilities of application are to be considered interesting.

The aim of this research is, therefore, the evaluation of some peculiar properties (*i.e.* adsorption and ion-exchange) of zeolitic tuffs, with a view to their possible industrial application, and, at the same time, to contribute to the explanation of their genesis mechanism.

Occurrence.

The greatest tuff deposits of central and southern Italy belong to the *Latian, Campanian* and Vulture volcanic districts. Referring particularly to Campania it is possible to distinguish at least two principal kinds of tuff: the first, more ancient, locally named *Campanian tuff* (1), extending over the whole Campanian Region, the second, more recent, locally named *Neapolitan yellow tuff* (2), covering the Phlegraean Fields, including the Naples area. The potentiality of these tuffs runs into milliards of tons.

The upper part of the Campanian tuff formation is often zeolitized, the lower is sometimes sanidinized (*i.e.* « piperno »). Neapolitan yellow tuff is normally zeolitic; sometimes on top of it can be found an amorphous product (« pozzolana »), representing the original unwelded material. The transition from pozzolana into completely zeolitized yellow tuff is continuous. Both these tuffs, showing a similar chemical composition, contain chabazite and phillipsite in different amounts, the former zeolite being generally predominant in Cam-

panian tuff, the latter in Neapolitan. Apart from analcite, appearing in a few cases, no other zeolites have been found in the Italian tuffs examined (3). Besides, similar zeolites constitute the matrix of the Rhenish « trass » (4, 5) and the Great Canary Island yellow tuff (6).
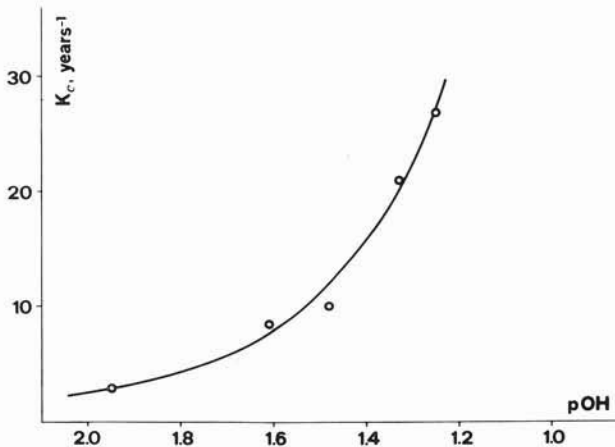

Fig. 1. — Kinetic constants of chabazite crystallization from pumices, as a function of pOH in the contact solution, at 100°C.

In other countries, however, tuffs containing typical sodic zeolites have been reported by the literature, but the *neo*-formation of these zeolites, especially clinoptilolite (7), seems to be normally related to the presence of sea water during the zeolitization process.

Genesis.

According to the literature, the pyroclastic materials, whose alteration led to the formation of the Campanian and Neapolitan yellow tuffs, were deposited with different mechanisms. In the former case deposition would have taken place through a pyroclastic flow, as a result of a fissure activity (8), in the second it would be due to a typical volcanic explosion (9).

The alteration process of these unwelded materials was, in any case, hydrothermal, under the action of natural waters, while the

variable distribution of chabazite and phillipsite in both considered tuffs is certainly related to the influence of at least three factors: water alkalinity, solid/liquid (tuff/water) ratio by weight, and temperature.

The role of these factors on the zeolitization process can be defined on the ground of a series of laboratory experiments, carried out by numerous Authors on different materials. Such studies, even if performed in physico-chemical conditions quite different from the natural ones, allow to draw out some informations about the trend of the system to evolve into a certain zeolite.

In particular, referring to the zeolites normally present in our tuffs (*i.e.* chabazite and phillipsite) a series of hydrothermal syntheses, starting from gels (10), metakaolinite + amorphous silica (11), natural glasses (12, 13) and carried out in an eminently potassic environment, has shown that, *ceteris paribus*:

— increasing values of water alkalinity favour chabazite,
— increasing values of solid/liquid ratio favour phillipsite,
— increasing values of temperature favour phillipsite ([1]).

By considering that the zeolitization process of both tuffs happened in presumably similar conditions of water alkalinity and solid/liquid ratio, we can deduce that temperature is the determining factor for the growth of chabazite or phillipsite into the tuff.

The interpretation of the tuff genesis can not leave out of account kinetic considerations. In fact the above mentioned factors strongly affect the kinetics of zeolite crystallization. In figure 1, for example, are reported, as a function of pOH of the contact solution, the kinetic constants, calculated assuming a first order kinetics (14), of the chabazite formation, starting from an amorphous material, pumices, taken from a sample of chabazite Campanian tuff. The experimental conditions were: temperature 100°C, solid/liquid ratio 1/10, $0.1 \div 0.5\%$ KOH in the contact solution. It can be seen that the kinetics of the zeolitization process becomes enormously slow, when the alkalinity tends towards the normal values of a natural water.

([1]) Quite high temperatures (300°C or more) seem to favour the growth of anidrous phases (for example felspars).

By means of ^{238}U decay measurements (15) it has in fact been demonstrated that the zeolitization process of Neapolitan yellow tuff lasted not less than $4000 \div 5000$ years.

Tuff characterization.

The experimentation has been carried out on a sample of chabazite Campanian tuff, phillipsite free. The reason for this choice is that it represents a simple and proper model for the study of adsorption and cation exchange properties of zeolitic tuffs. The sample has been collected near Mercogliano (Avellino).

The chemical composition of the tuff, stored for a week over saturated $Ca(NO_3)_2$ solution at 25°C, is reported in Table I.

TABLE I. — *Chemical composition of Mercogliano tuff.*

SiO_2	50.62%
Al_2O_3	16.05
Fe_2O_3	3.75
FeO	0.35
TiO_2	0.46
MnO	0.11
P_2O_5	0.15
CaO	4.29
MgO	1.33
Na_2O	2.55
K_2O	7.02
H_2O	13.60
	100.28

X-ray diffraction investigation showed a chabazite dominant pattern, together with weak reflections attributed to sanidine and biotite. The microscope examination in thin section showed the material to be constituted by an isotropic matrix (chabazite) surrounding crystalline fragments (sanidine, biotite and, secondarily, pyroxene and plagioclase) together with pumices and slags.

The results of the electron microprobe analysis (^{2}), performed on a polished section of the sample, previously exchanged with Ag^+, are reported in figure 2. The image shows a sanidine crystal, surrounded
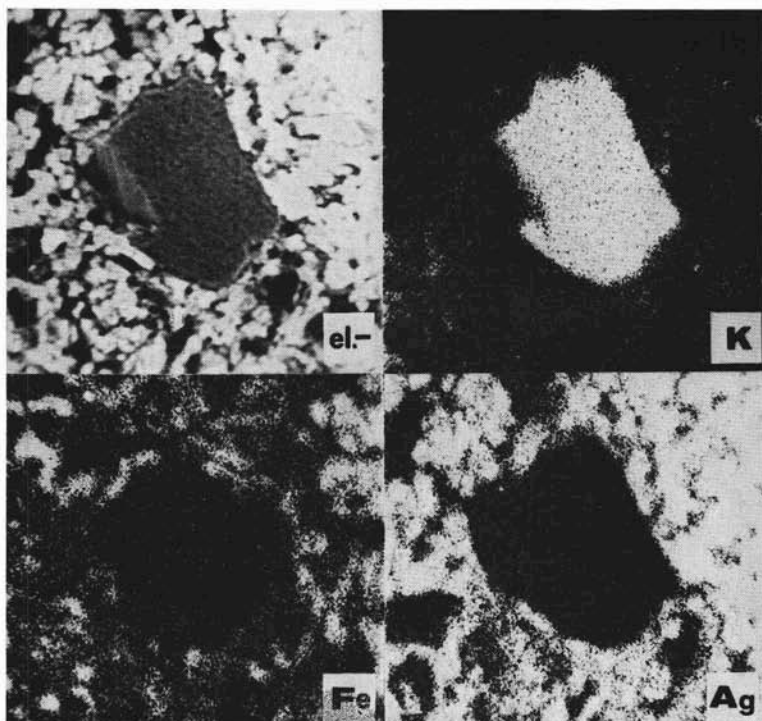

Fig. 2. — Scanning micrographs. Investigated area: $4 \times 10^4 \mu^2$; el-: negative electronic image.

by a *crypto*-crystalline zeolitic matrix. It can be noticed that, unlike K^+ ion, belonging to the zeolite, completely exchanged by Ag^+, iron is not exchangeable, so that we may assume this element to be present as hydrated oxide, spread in the tuff matrix.

The evaluation of chabazite percentage in the tuff has been per-

(^{2}) It has to be remembered that the concentration of the investigated elements is proportional, within the limits of a single image, to the density of the white spots.

formed by means of water vapour adsorption, using, as a reference, a sample of chabazite mineral from Dessiè (Ethiopia), both previously exchanged into Na$^+$ form; chabazite resulted at about 65%.
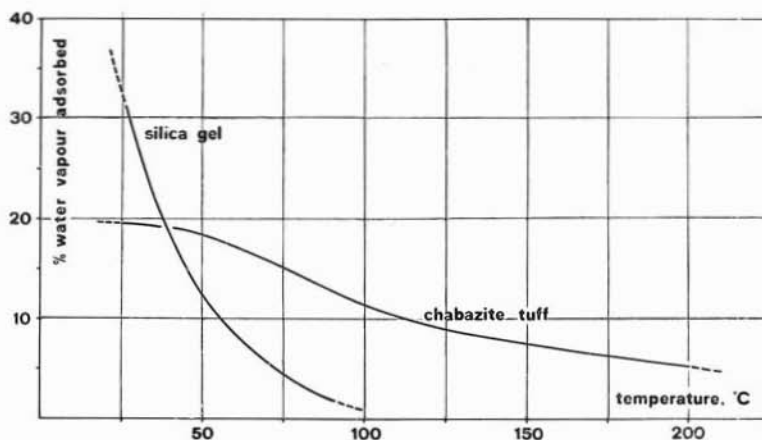

Fig. 3. — Water adsorption isobars at atmospheric pressure and 75% R.H.

Given the heterogenity of the material and particularly the variable hardness of its constituents, it has been possible to obtain a zeolite enrichment of the tuff (16). Being the zeolitic fraction the most friable, only one minute of grinding, using a Fritsch Pulverisette Mortar-Grinder, is needed to give 40% powder passing at 256 mesh sieve and bearing more than 85% chabazite.

Samples of tuff, enriched in this way, have been employed for adsorption and ion exchange measurements.

Tuff as adsorbent.

The evaluation of the adsorption properties of the Mercogliano tuff has been preceded by the study of the water vapour adsoption kinetics, in order to compare the behaviour of the tuff with that of chabazite, both exchanged in Na$^+$ form.

The results showed that the attainment of equilibrium is slightly slower for the tuff than for the zeolite. This could mean water dif-

fusion is slowed down in the tuff, because of the heterogenity of the material or, as previously reported by us (16), because of the presence into the zeolite framework of either structural faults, or occlusions, constituted, for instance, by hydrated ferric oxide (^{3}).

Preliminary test on the adsorption properties of Mercogliano tuff with different gases and vapours seemed to indicate that water vapour adsorption offers the highest possibilities of practical utilization. The study has been carried out using silica gel as reference. Even if si-
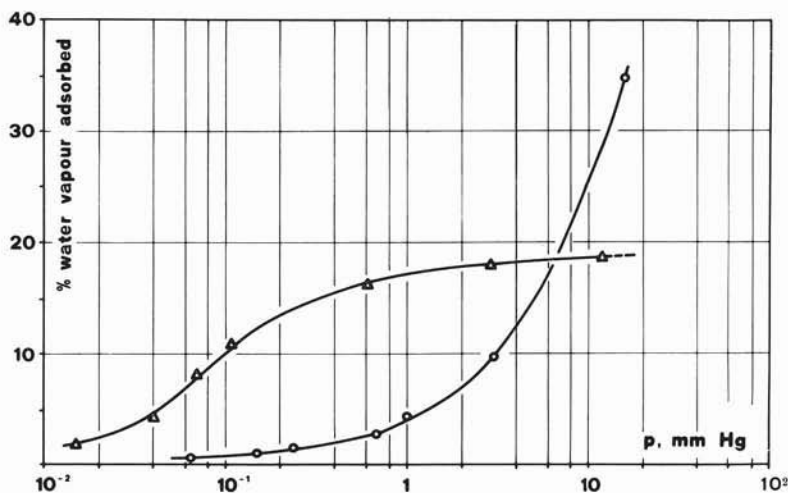

Fig. 4. — Water adsorption isotherms at 25°C for silica gel ($\bigcirc$) and chabazite tuff ($\triangle$).

lica gel, at room temperature and humidity, shows water vapour adsorption capacities about 50% higher than chabazite tuff, this tendency is inverted, when temperature rises and water vapour pressure decreases.

In figure 3 are reported the water vapour adsorption isobars from a humidified nitrogen flow (R.H. 75%), and in figure 4 appear the adsorption isotherms at 25°C for silica gel and Mercogliano tuff.

(^{3}) The possibility that zeolites include some hydrated ferric oxide has been discussed in a previous paper (17).

The utilization of zeolitic tuffs as dessicant appears, therefore, particularly advisable in conditions of low humidity or higher than room temperatures. In these conditions, in fact, silica gel can no longer be employed.

Tuff as cation exchanger.

The utilization of zeolites as cation exchangers is limited by their moderate exchange kinetics. However the employement of zeolitic tuff has been proposed in the field of the decontamination of radioactive waste waters (18).

In spite of the low selectivity of Mercogliano tuff for Ca^{++} and Mg^{++}, we thought it interesting, because of its low cost and, therefore, the possibility of using it in massive amounts, to study its behaviour as water softener.

To this end a series of eight « model waters » with different hardnesses was prepared. In these waters the normalities $[Na^+] = [HCO_3^-] = 1 \times 10^{-3} N$ and $[Ca^{++}]/[Mg^{++}] = 4$, $[Cl^-]/[SO_4^=] = [Cl^-]/[NO_3^-] = 3$ were kept constant. As an example, in Table II is reported the composition of a model water with 250 ppm $CaCO_3$ hardness.

TABLE II. — *Typical composition of a « model water »*
(hardness equal to 250 ppm $CaCO_3$).

Cations	eq/l	Anions	eq/l
Ca^{++}	4×10^{-3}	Cl^-	3×10^{-3}
Mg^{++}	1×10^{-3}	NO_3^-	1×10^{-3}
Na^+	1×10^{-3}	SO_4^-	1×10^{-3}
		HCO_3^-	1×10^{-3}

The water softening experiments were carried out by allowing water to pass through 5 g powder, constituting a cylindrical bed with diameter/height ratio equal to about 4. The flow rate was varied by regulating the depression under the tuff bed.

Preliminary tests showed that there were no detectable differences in the water hardness decrease, working with flow rates ranging between 3 and 1 ml/min. That is why all the experiments have been performed keeping the water flow rate constant and equal to 3 ml/min.

In figure 5 is reported the hardness decrease as a function of the amount of the effluent water for three waters with different
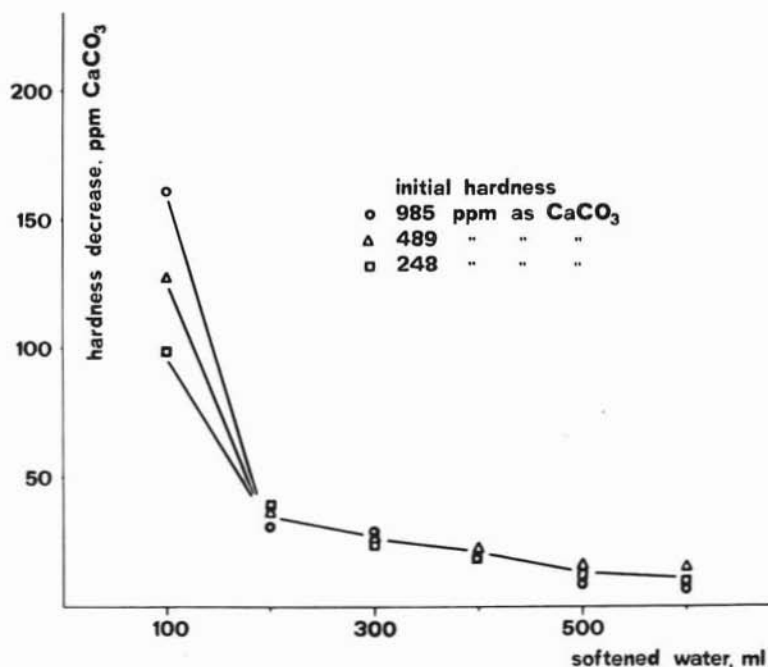

Fig. 5. — Water hardness decrease as a function of the amount of softened water.

initial hardness. It can be seen that the greatest hardness decrease is reached in correspondence with the first 100 ml of softened water; after that the decrease is almost independent of the initial hardness, because of the already mentioned low selectivity of the zeolite for Ca^{++} [4] and the *quasi*-saturation of the tuff under these particular

---

[4] Controls of Ca^{++} and Mg^{++} concentrations in the softened waters showed tuff to posses negligible tendency to exchange magnesium.

dynamic exchange conditions. Figure 6 refers to the hardness decrease of 100 ml water volumes as a function of the initial hardness. It is interesting to notice that the highest percentages of hardness decrease are reached in correspondence with the lowest values of initial hardness.
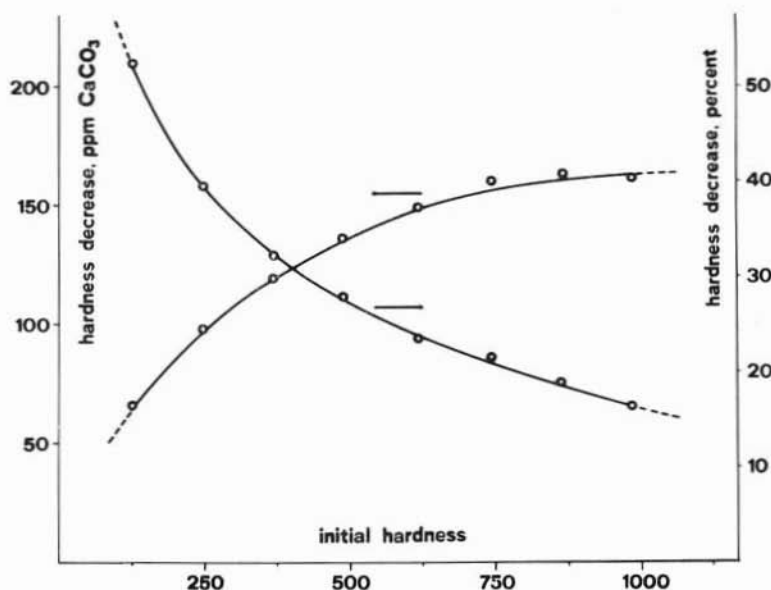

Fig. 6. — Water hardness decrease of 100 ml water volumes as a function of the initial hardness.

The results obtained indicate that the employment of zeolitic tuff as water softener could be advisable in *multi*-stage processes, when the request for softened water is not high. A further advantage is that the exhausted charges of powdered tuff need not be reused as cation exchanger, because of their low cost. On the other hand this exhausted tuff could be utilized as addition to Portland cement clinker, because its « pozzolanic » activity is higher than that of pozzolana itself (19).

Experimental.

Synthesis. For the evaluation of kinetic constants of chabazite crystallization from pumices, a series of 1 gr samples of powder was allowed to react, in polypropilene bottles, at 100°C (air thermostated oven), with solutions of variable alkalinities (0.1 ÷ 0.5% KOH) and with solid/liquid ratio 1/10. In correspondence of each value of alkalinity, differently prolonged experiments (7 ÷ 30 days) were arranged and the relative amounts of chabazite crystallized were determined by means of water vapour adsorption and quantitative X-ray analysis.

Microscopy. The electron microprobe analysis has been performed utilizing a CAMECA microanalyser mod. MS 46, equipped for the determination of all the elements with atomic weight higher than 5. The surfaces of the specimens to be analized were metallized by deposition under vacuum of a copper film having a thickness of about 100 Å. Each scanning has been performed with an accelerating voltage of 20 kV and a beam current of 50 nA, employing the K and Fe $K\alpha_1$ radiation and the Ag $L\alpha_1$.

Adsorption. A « Stanton Massflow » type MF-H 5/20 thermobalance, suitably adapted, has been employed for all the adsorption measurements.

In order to obtain the water vapour adsorption isotherms, the activation of tuff samples was carried out at 500°C in a final vacuum higher than 10^{-3} mmHg. Silica gel was activated at 100°C. For the quantitative evaluation of the adsorption capacity as a function of the time and of the temperature, in conditions of constant humidity, the samples were previously activated at the above mentioned temperatures, under a dry nitrogen flow. Nitrogen was then made to gurgle in a washbottle containing distilled water, and pass through the thermobalance chamber, with flow rate constant and equal to 1.44 l/min. The value of the relative humidity, measured in equilibrium conditions by a Regnault hygrometer, was near to 75%.

Exchange. Model waters for exchange experiments were prepared by using reagent grade $NaHCO_3$, $MgSO_4 \cdot 7H_2O$, $CaCl_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$. Hardness controls by EDTA on the prepared solutions, gave the following values: 126; 248; 369; 489; 617; 742; 862; 985 ppm as $CaCO_3$.

Softening experiments were performed, by putting tuff powder in a gooch filter and allowing waters to pass through under depressions produced by a water pump.

Further details òn the experimental part have been reported previously (20).

Istituto di Chimica Applicata, Facoltà d'Ingegneria, Università di Napoli.

LITERATURE CITED

(1) DI GIROLAMO P. (1968) - *Rend. Accad. Sc. Fis. Mat.*, Napoli, [4], 35, 329.

(2) SCHERILLO A. (1955) - *Rend. Accad. Sc. Fis. Mat.*, Napoli, [4], 22, 345.

(3) SERSALE R. (1972) - *Atti Accad. Sc. Fis. Mat.*, Napoli, [3], 8, 1.

(4) SERSALE R., AIELLO R. (1965) - *Silicates Ind.*, 30, 13.

(5) SERSALE R., AIELLO R., VERO E. (1965) - *Ind. Ital. Cemento*, 35, 513.

(6) SERSALE R. (1959) - *Rend. Accad. Sc. Fis. Mat.*, Napoli, [4], 26, 441.

(7) IIJIMA A. (1971) - *Advan. Chem. Ser.*, 101, 334.

(8) DI GIROLAMO P. (1970) - *Rend. Soc. It. Min. Petr.*, 26, 547.

(9) RITTMANN A., VIGHI L., FALINI F., VENTRIGLIA U., NICOTERA P. (1950) - *Boll. Soc. Geol. It.*, 69, 117.

(10) BARRER R. M., BAYNHAM J. W. (1956) - *J. Chem. Soc.*, 2282.

(11) BARRER R. M., MAINWARING D. E. (1972) - *J. Chem. Soc.*, 562.

(12) COLELLA C., AIELLO R. (1971) - *Rend. Accad. Sc. Fis. Mat.*, Napoli, [4], 38, 243.

(13) SERSALE R. (1958) - *Rend. Accad. Sc. Fis. Mat.*, [4], 25, 181.

(14) KERR G. T. (1966) - *J. Phys. Chem.*, 70, 1047.

(15) CAPALDI G., CIVETTA L., GASPARINI P. (1971) - *Geochim. Cosmochim. Acta*, 35, 1067.

(16) AIELLO R., COLELLA C. (1972) - *Chim. Ind.*, Milano, 54, 303.

(17) AIELLO R., COLELLA C. (1971) - *Ann. Chim.*, Roma, 61, 122.

(18) BOENZI D., BRANCA G. (1965) - *Energia Nucleare*, 12, 413.

(19) SERSALE R. (1960) - *Silicates Ind.*, 25, 499.

(20) COLELLA C., AIELLO R. (1970) - *Ann. Chim.*, Roma, 60, 587.