Hydrothermal treatment at low temperature of Sardinian clinoptilolitebearing ignimbrites for increasing cation exchange capacity

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AbstrAct. — Two clinoptilolite-bearing ignimbrites belonging to Tertiary Sardinian volcanism and outcropping in different localities were treated with 2M NaOH, 3M NaOH and 2M NaOH + Al(OH)₃ at 100, 80 and 70 °C in order to enhance their cation exchange capacity. Bronze Teflon-lined autoclaves and a reactor equipped with magnetic stirrer were used for hydrothermal interactions, with interaction times ranging from 30 minutes to 36 hours. In all experimental cycles, clinoptilolite dissolution was followed by Na-P1 zeolite crystallization. The newlyformed zeolite changes from typical ball-shaped morphology to star-shaped grains with interaction increasing. The best interacting solution was 2M NaOH+Al(OH)₃. The cation exchange capacities (CEC) of the reacted products were higher than those of the raw materials (up to 2.5 times, i.e., from 88 to 268 meg/100 g). The use of a reactor equipped with magnetic stirrer strongly reduces interaction times for complete clinoptilolite dissolution and Na-P1 crystallization. (e.g. < 6 hours at 80 °C).

riAssunto. — Al fine di aumentarne la capacità di scambio cationico (CEC), due campioni di ignimbriti

Terziarie pomiceo-cineritiche della Sardegna, il cui vetro era stato trasformato in clinoptilolite, sono state fatte interagire con soluzioni 2M NaOH, 3M NaOH and 2M NaOH + Al(OH), a 100, 80 and 70 °C. Per le interazioni idrotermali sono state utilizzate autoclavi rivestite in Teflon ed un reattore con agitatore magnetico con tempi di interazione compresi tra 30 minuti e 36 ore. In tutti i cicli sperimentali alla dissoluzione della clinoptilolite è seguita la cristallizzazione di una nuova zeolite ascrivibile alla Na-P1. La zeolite di neoformazione si presenta inizialmente in piccole sfere che, all'aumentare dei tempi di interazione, si trasformano in individui con una morfologia stellata. La migliore soluzione interagente e risultata essere la 2M NaOH+Al(OH)₂. La capacità di scambio cationico nei prodotti sintetici è aumentata anche di due volte e mezzo rispetto a quella del materiale naturale (da 88 a 268 meq/100 g). E' importante sottolineare che, utilizzando il reattore con agitatore magnetico, la completa dissoluzione della clinoptilolite e cristallizzazione della Na-P1 si realizza in meno di sei ore a 80 °C.

Key Words: Ignimbrite, clinoptilolite, cation exchange capacity, hydrothermal synthesis, Na-P1 zeolite.

introduction

The poorly welded ignimbrites and related deposits (e.g., epiclastites and base surges) belonging to Sardinian Tertiary volcanism (Lecca et al., 1997) underwent postdepositional alteration processes, leading to more or less severe changes in the glassy components (e.g. pumice, shards and ash) which are often replaced by a mosaic of authigenic minerals (Ghiara et al., 1997, 1999, 2000; Langella et al., 1998; Morbidelli et al., 1999, 2001; Cerri et al., 2001, 2002). In the central to northern Sardinian ignimbrites, essential authigenic minerals, in order of decreasing abundance, are: clinoptilolite, smectite, opale-CT and quartz; mordenite, analcime, erionite, calcite, glauconite, chalcedony and adularia are also locally observed. Clinoptilolite is a natural zeolite currently mined all over the world and used in the fields of agriculture, industry and pollution control (Mumpton, 1984; Pansini, 1996; Kazantseva et al., 1997).

Textural evidence indicates that the authigenic clinoptilolite of the Sardinian ignimbrites grows on glassy components (ash, shard) or fills vugs and tubular to subspherical vesicles (Morbidelli *et al.*, 1999). According to Morbidelli *et al.*, (1999) and Cerri *et al.*, (2001), alteration processes are driven by circulating mineralized hydrothermal fluids.

The amount of clinoptilolite in the poorly welded ignimbrites from central-northern Sardinia varies greatly, from 32-81 wt. %, with many samples in the range 45-69 wt. % (Cerri et al., 2002). Notably, in several ignimbritic flows, there is evidence of sudden variations in clinoptilolite content, even within a single cooling unit (Morbidelli et al., 2001). For instance, in the Case Oddorai ignimbritic sequence (70 m thick), the clinoptilolite content progressively increases from the lower (~30 wt. %) to the intermediate portions (~ 60 wt. %), and than decreases to a few wt. % toward the upper portion (Morbidelli et al., 2001). This is a major problem for mining purposes. In spite of this, some thick deposits from the Bonorva and Romana areas have high clinoptilolite content suitable for largescale mining.

According to the cross exchange method the clinoptilolite-bearing pyroclastic flows from central-northern Sardinia have a cation exchange capacity (CEC) in the range 0.35-1.20 meq/g with

many samples in the range 0.87-1.20 meq/g (Cerri *et al.*, 2002). If compared with other deposits mined in the world, the Sardinian zeolitites from the central-northern Sardinia have on average a low cation exchange capacity.

It is well-known that high-power zeolites can be synthesized through hydrothermal treatment with strongly alkaline solutions (e.g., 2-3 M NaOH) starting from various natural materials, including clinoptilolite-bearing ignimbrites. As an example, three Korean acidic tuffs containing differing amounts of clinoptilolite and mordenite, treated with a 2M NaOH solution at 103 °C for times ranging from 1 to 16 hours, experienced clinoptilolite and mordenite complete dissolution, forming zeolite Na-P aggregates (Kang and Egashira, 1997). The CEC of the synthesized products were higher by more than 2 times than those of the starting materials and ranged from 175 to 418, 129 to 286 and 108 to 271 meq/100g respectively. Therefore, hydrothermal processes able to enhance the exchange capacity of natural zeolite-bearing rocks in northern Sardinia must be considered.

In this work, the hydrothermal treatment at low temperature (*i.e.*, 70, 80 and 100 °C) with NaOH and NaOH + Al(OH)₃ solutions of two different clinoptilolite-bearingignimbrites (samples 1-2a and PON 16) outcropping near the villages of Bonorva and Romana (northern Sardinia) respectively was investigated. The aims of this study were to identify the newly-formed minerals and to define the exchange capacity of synthetic products, in order to highlight the potential use of Sardinian natural clinoptilolite-bearing ignimbrites.

exPeriMentA1 Methods And MAteriA1s

Samples

As raw materials two poorly welded ignimbrite blocks sized 25x25x25 cm were sampled near Case Oddorai (sample 1-2A I GMI F. 480 sez.II Foresta Burgos) and Romana village (sample PON16 -I GMI F. 479 sez. II Mara). Both pyroclastic rocks have a eutaxitic texture and a porphyritic index variable from 5 to 30 wt. %. The phenocrystic assemblage is dominated by plagioclase, quartz, biotite, rare K-feldspar, and minor clinopyroxene grains. The main lithic clasts (~5wt. %) are

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represented by angular or fragments of "andesitic" rocks and welded ignimbrites. A mosaic of clinoptilolite grains almost replaces cuspate shards and the ashy matrix; euhedral crystals also occur within vugs and tubular or subspherical vesicles. Lastly, smectite on glassy components and chlorite on biotite laths may be observed as newly formed phases; CT opal lepispheres, minor newly-formed hematite grains and late fibres of mordenite occur locally. Quantitative diffractometric analyses carried out on 1-2A sample using the combined Rietveld-RIR (Reference Intensity Ratio) method (for major details see Morbidelli et al., 2001 and references therein) indicated a clinoptilolite content of 53±3 wt. % and lower amounts of CT opal (~4 wt. %), glassy components (~8 wt. %) and clay minerals (~2 wt. %). A higher clinoptilolite content (~62 \pm 2 wt. %) with minor amounts of glass (~6 wt. %) and mordenite (~5 wt. %) occurs in the PON 16 sample.

The chemical formula, determinated by electron microprobe analysis, of clinoptilolite from sample 1-2A is: $(Na_{0.43}K_{2.41}Ca_{0.90}Mg_{0.73})$ $(Si_{29.72}Al_{16.16}O_{72})$ 16.66 H₂O.

Blocks 1-2A and PON16 were crushed and reduced to particles with grain size between 5-0.7 mm and 3-0.5 mm, respectively. Only for the 1-2A sample the fraction passing through a 0.25-mm sieve was also collected. Since the present study is part of a research project for agricultural applications of Sardinian zeolitites (PON Project n. 12701), only the former grain sizes (*i.e.*, 5-0.7 and 3-0.5) were used in hydrothermal experiments carried out in a 4560 Parr reactor (see below).

Mineralogical and chemical analyses

Rock mineralogy and newly-formed phases in the synthesized products were investigated by X-ray powder diffraction in the 5°-75° 2 θ range (SEIFERT PAD 4 diffractometer equipped with a pyrolitic graphite analyzer crystal) using the following operative conditions: unfiltered CuKa radiation, 40 KV, 30 mA, step size = 0.02°, counting time 18 s for each step, 0.5° divergence slit, 0.1 mm receiving slit, 0.5° antiscatter slit. Side loading was used for all samples in order to minimize preferred orientation effects.

Newly-formed phase morphology in the synthesized products was observed by scanning

electron microscopy (SEM LEO EVO 50VP, Oxford Instruments, Progemisa S.p.A. Laboratory, Cagliari).

Al concentrations in the filtered interacting solutions was determined by inductively coupled plasma optical emission spectrometry (ICP-OES Perkin Elmer Optima 2100 DV). Detection limit for Al was: 0.20 mg/l.

CEC analyses

Bulk-rock cation exchange capacity was determined in the Progemisa S.p.A. Laboratory following the recommendations of Minato *et al.*, (1997).

Synthesis

Two experimental apparatus were employed: a) bronze Teflon-lined autoclaves, and b) a 4560 Parr reactor equipped with magnetic stirrer. As for a) 5.00 g of raw material were put into the autoclaves and dispersed in 50 ml of the following interacting solutions: 2M NaOH, 3M NaOH and 2M NaOH + Al(OH)₃. The Al(OH) ₃ concentration in the latter solution was 10 wt. %. Unstirred hydrothermal experiments in the autoclaves was carried out at 80 ± 3 °C and 100 ± 3 °C for various times up to 39 hours (Table 1). In the first six hours, the reacted products were analysed hourly and than every three hours. As regards the b) hydrothermal apparatus, 15.00 g of raw material with the coarser grain size were put into the reactor and dispersed in 150 ml of 2M NaOH + Al(OH)₃ solution. As expected the hydrothermal reactions is much faster in the stirred experiments with interaction times ranging from $\frac{1}{2}$ to 6 hours (Table 2). The hydrothermal experiments was carried out at 70 ± 3 °C, 80 ± 3 °C and 100 ± 3 °C and the reacted products were analysed at 1/2 hour and then hourly. After hydrothermal interaction, the vessel was quenched to room temperature and the solid product was filtered, washed three times with deionized water, dried at room temperature, and stored in a polyethylene bottle.

results And discussion

The overall data-set of hydrothermal experiments performed with bronze Teflon-lined autoclaves and 2-3M NaOH solutions showed that clinoptilolite

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Sample	Temperature	Sample weight	Interacting solution	Grain size	Interaction times	Exp.
			50 ml			number
1-2A	100 ±3 °C	5 g	2M NaOH	5-0.7mm	from 1h to 24 h	1
1-2A	80 ±3 °C	5 g	2M NaOH	5-0.7mm	from 1h to 39 h	2
1-2A	100 ±3 °C	5 g	2M NaOH	$< 0.25 \ \text{mm}$	from 1h to 29 h	3
1-2A	80 ±3 °C	5 g	2M NaOH	$< 0.25 \ \text{mm}$	from 1h to 27 h	4
1-2A	100 ±3 °C	5 g	3M NaOH	5–0.7mm	from 1h to 24 h	5
1-2A	80 ±3 °C	5 g	3M NaOH	5-0.7mm	from 1h to 24 h	6
1-2A	100 ±3 °C	5 g	3M NaOH	$< 0.25 \ \text{mm}$	from 1h to 28 h	7
1-2A	80 ±3 °C	5 g	3M NaOH	$< 0.25 \ \text{mm}$	from 1h to 27 h	8
1-2A	100 ±3 °C	5 g	2M NaOH+Al(OH) ₃	5-0.7mm	from 1h to 24 h	9
PON16	100 ±3 °C	5 g	2M NaOH	3-0.5mm	from 1h to 24 h	10
PON16	100 ±3 °C	5 g	3M NaOH	3-0.5mm	from 1h to 24 h	11
PON16	100 ±3 °C	5 g	2M NaOH+Al(OH) ₃	3-0.5mm	from 1h to 24 h	12

table 1	
Bronze Teflon-lined autoclaves#experimental co	onditions

tAble 2 4560 Parr reactor#experimental conditions

Sample	Temperature	Sample	Interacting solution	Grain size	Interaction times	Exp.
		weight	150 ml			number
1-2A	100 ±2 °C	15 g	2M NaOH+Al(OH) ₃	5-0.7mm	from ½ h to 6h	13
1-2A	80 ±2 °C	15 g	2M NaOH+Al(OH) ₃	5-0.7mm	from ½ h to 6h	14
1-2A	70 ±2 °C	15 g	2M NaOH+Al(OH) ₃	5-0.7mm	from ½ h to 6h	15
PON16	100 ±2 °C	15 g	2M NaOH+Al(OH) ₃	3–0.5mm	from ½ h to 6h	16
PON16	80 ±2 °C	15 g	2M NaOH+Al(OH) ₃	3–0.5mm	from ½ h to 6h	17
PON16	70 ±2 °C	15 g	2M NaOH+Al(OH) ₃	3–0.5mm	from ½ h to 6h	18

progressively dissolves and that a new zeolite starts to crystallize at higher interaction times. The most intense peaks of this newly formed zeolite were at 3.17, 7.10, 4.10, 2.68 and 5.01 Å, corresponding to the Na-P1 zeolite (Breck 1974), a high capacity cation exchanger. The interaction times for the appearance of Na-P1 zeolite and disappearance of clinoptilolite are listed in Table 3. They are mainly related to the temperature of hydrothermal system and to the grain size of the starting material, but are irrespective of NaOH concentration.

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Times of clinoptilolite disappearance and Na-P1 appearance in the Teflon-lined bronze autoclaves. Interacting solutions#2M NaOH and 3M NaOH

Sample	Grain size	Interacting	T °C	Na-P1	Clinoptilolite	Exp.
		solution		appearance	disappearance	number
1-2A	5-0.7 mm	2M NaOH	100 ±3 °C	6 h	12 h	1
1-2A	5-0.7 mm	2M NaOH	80 ±3 °C	15 h	39 h	2
1-2A	< 0.25 mm	2M NaOH	100 ±3 °C	4 h	6 h	3
1-2A	< 0.25 mm	2M NaOH	80 ±3 °C	9 h	21 h	4
1-2A	5-0.7 mm	3M NaOH	100 ±3 °C	6 h	9 h	5
1-2A	5-0.7 mm	3M NaOH	80 ±3 °C	24 h	27 h	6
1-2A	< 0.25 mm	3M NaOH	100 ±3 °C	4 h	6 h	7
1-2A	< 0.25 mm	3M NaOH	80 ±3 °C	9 h	21 h	8
PON 16	3–0.5 mm	2M NaOH	100 ±3 °C	6 h	10 h	10
PON 16	3–0.5 mm	3M NaOH	100 ±3 °C	6 h	10 h	11

As expected, early crystallization of Na-P1 zeolite occurs in the raw natural material with lower grain size (i.e., <0.25mm).

The XRD patterns of the synthesized products in experiment number 1 (Table 1) revealed the following aspects:

1) the characteristic peaks of clinoptilolite progressively decrease in their intensities whereas those of Na-P1 zeolite progressively increase with increasing interaction;

2) No relevant reduction in the peak intensity, at 3.33–3.34 Å for quartz and at 3.21 Å for feldspars, has been observed;

3) after 21 h of reaction the characteristic peaks of Na-P1 tend to decrease in intensity.

It should be noted that SEM observations of the reacted products from experimental run 3 after 29 h of interaction show few analcime crystals.

As regards points 1) and 2), similar behaviour is shown by the XRD patterns of all the synthesized products in the other experiments.

SEM observations of the starting materials (Fig. 1*a*) and reacted products from various runs of experiment number 1 show an early dissolution of the glassy component. The alteration of clinoptilolite starts from the outer surface (Fig. 1*b*) of the crystals, forming small cavities which progressively increase in size with increasing

interaction times. As the clinoptilolite begins to dissolve, small amounts of Na-P1 zeolite with typical ball-shaped morphology appear (Fig. 1*b*). At higher interaction times (6-8 h), many Na-P1 zeolite spherules of less than 2μ m and only a few clinoptilolite relicts occur (Fig. 1*c*). After 15 h of interaction, the Na-P1 zeolite gradually turns into bladed rosettes (Fig. 2*a*) and then into star-shaped grains (Fig. 2*b*), with no change in the XRD patterns.

As clinoptilolite and Na-P1 zeolite have different Si/Al ratios, in order to better define the processes of clinoptilolite dissolution and Na-P1 crystallization, the behaviour of Al in the interacting solutions was studied. The concentrations of Al in the interacting solutions first increase, mainly due to clinoptilolite dissolution (Fig. 3). As Na-P1 zeolite starts to crystallize, the Al concentration suddenly decreases. This geochemical behaviour is due to high Al consumption during Na-P1 crystallization, since Al contents are higher with respect to those released by the dissolution of clinoptilolite. This geochemical scenario suggests the use of interacting solutions containing 10 wt. % of Al in order to favour Na-P1 crystallization. The experimental hydrothermal cycles with autoclaves and 2M NaOH + Al(OH)₃ solutions gave slightly different results with respect to those discussed

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Fig. 1 – Experimental run 1. Scanning electron micrograph of: a) clinoptilolite crystals and opal-CT lepispheres in the starting material; b) large cavities in the clinoptilolite crystals after 5h of interaction and Na-P1 spherules; c) clinoptilolite relicts and clusters of ball-shaped Na-P1 zeolite at 6 h of interaction.

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Fig. 2 – Experimental run 1. Scanning electron micrograph of: a) cluster of bladed rosettes of Na-P1 zeolite after 15 h of interaction; b) clusters of star-shaped Na-P1 zeolite after 16 h of interaction.

above (Table 4). As expected, the appearance of Na-P1 and disappearance of clinoptilolite in sample 1-2A shift slightly toward lower and higher times of interaction, respectively. In sample PON16 no differences were observed with respect to the experimental cycle carried out using Na(OH) solution.

The XRD patterns, including progressive changes in peak intensities and SEM micrographs of the reacted products, are very similar to those described above for experimental cycles with 2M Na(OH) solutions. Hydrothermal experiments in a 4560 Parr reactor equipped with magnetic stirrer and 2M NaOH+Al(OH)₃ solutions show a sharp fall in interaction times for both Na-P1 appearance and clinoptilolite dissolution (Table 5). Note that Na-P1 zeolite also forms at relatively low temperatures (*e.g.*, 80 °C) and low interaction times (*e.g.*, 2 h). In addition, with increasing interaction at 100 °C analcime starts to crystallize and Na-P1 tends to be consumed. Either in these experimental runs, quartz and feldspars are not altered.

The XRD patterns of clinoptilolite show a sharp decrease in peak intensity until the first times of

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LADLE 4Times of clinoptilolite disappearance and Na-P1 appearance in the Teflon-lined bronze autoclaves.Interacting solutions#2M NaOH + $Al(OH)_3$

Sample	Grain size	Interacting solution	Т	Na-P1	Clinoptilolite	Exp.
				appearance	disappearance	number
1-2A	5–0.7mm	2M NaOH+Al(OH) ₃	100 ±3 °C	5 h	18 h	9
PON16	3–0.5mm	2M NaOH+Al(OH) ₃	100 ±3 °C	6 h	10 h	12

tAble 5

Times of clinoptilolite disappearance and Na-P1 appearance in the 4560 Parr reactor. Interacting solutions # 2M NaOH + Al(OH)₃

Sample	Grain size	Interacting solution	T °C	Na-P1	Clinoptilolite	Exp.
				appearance	disappearance	number
1-2A	5-0.7mm	2M NaOH+Al(OH) ₃	100 ±2 °C	¹∕2 h	3 h	13
1-2A	5-0.7mm	2M NaOH+Al(OH) ₃	80 ±2 °C	1 h	4 h	14
1-2A	5-0.7mm	2M NaOH+Al(OH) ₃	70 ±2 °C	2 h	>6 h	15
PON16	3-0.5mm	2M NaOH+Al(OH) ₃	100 ±2 °C	¹∕2 h	2 h	16
PON16	3-0.5mm	2M NaOH+Al(OH) ₃	80 ±2 °C	1 h	3 h	17
PON16	3–0.5mm	2M NaOH+Al(OH) ₃	70 ±2 °C	2 h	>6 h	18

hydrothermal interaction, whereas a very good settlement of those of Na-P1 zeolite already occurs after 1 h of interaction, even at 80 °C.

SEM observations on synthesized products from experimental cycle 13 show early Na-P1 spherules

after $\frac{1}{2}$ h of interaction. Note that, in experimental cycles 14, many Na-P1 spherules of less than 2μ m (Fig. 4*a*) already appear after 1 h of hydrothermal interaction. Also in the later experimental cycles, Na-P1 zeolite progressively changes its

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Fig. 4 – Experimental run 13. Scanning electron micrograph of: *a*) clusters of ball-shaped Na-P1 zeolite at 1h of interaction; note the strongly corroded relict of clinoptilolite; *b*) clusters of bladed rosettes of Na-P1 zeolite at 2 h of interaction; *c*) clusters of star-shaped Na-P1 zeolite at 6 h of interaction. Analcime start to crystallize.

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morphology, from spherical aggregates to starshaped Na-P1 zeolite with increasing interaction without any changes in the XRD patterns (Figs. 4b-c). The appearance of a few analcime crystals at higher interaction times in experimental cycle 13 is clearly revealed by SEM studies (Fig. 4c).

Cation Exchange Capacity (CEC)

In order to evaluate the cation exchange capacity (CEC) of the synthesized products, several samples with high interaction times and containing bladed or star-shaped Na-P aggregates were analysed following the technique described by Minato (1997). As regards products synthesized in autoclaves (Table 6), the CEC values are often more than twice as high as those of the respective starting materials. In particular, the CEC value of reacted products of samples 1-2A and PON16 are in the range 183-217 meq/100g and 189-267 meq/100g respectively after 15 h of interaction. The high CEC values of sample PON16 are due to the higher clinoptilolite amounts in the starting materials.

On the basis of the theoretical CEC (460 meq/ 100 g) of pure zeolite Na–P1, the maximum content of zeolite Na–P1 after the alkaline treatment of Sardinian clinoptilolite-bearing ignimbrites is estimated to be about 60%.

Note that higher CEC values are obtained using 2M NaOH+Al(OH)₃ interacting solutions.

The products synthesized in the Parr reactor (Table 7) clearly show that their CEC progressively increases with interaction time (Table 7). These reacted products reach very high exchange capacity in a short time.

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Exchange capacity (meq/100g) of synthesized products with the Teflon-lined by	ronze autoclaves.

Sample	Interacting solution	Times	Т	CEC	Exp.
				meq/100gr	number
1-2A Starting material				88	
1-2 A	2M NAOH	21h	100 ±3 °C	183	1
1-2 A	3M NaOH	20h	100 ±3 °C	201	7
1-2 A	3M NaOH	22h	100 ±3 °C	197	7
1-2 A	2M NAOH+Al(OH) ₃	18h	100 ±3 °C	212	9
1-2 A	2M NAOH+Al(OH) ₃	20h	100 ±3 °C	217	9
PON 16 Starting material				127	
PON 16	2M NAOH	24h	100 ±3 °C	189	10
PON 16	3M NAOH	21h	100 ±3 °C	211	11
PON 16	2M NAOH+Al(OH) ₃	15h	100 ±3 °C	260	12
PON 16	2M NAOH+Al(OH) ₃	18h	100 ±3 °C	267	12

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Exchange capacity (meq/100g) of synthesized products in the in the 4560 Parr reactor.

Sample	Interacting solution	Times	Т	C.E.C. meq/100g	Exp.
					number
1-2A Starting material				88	
1-2A	2M NAOH+Al(OH) ₃	1 h	100 ±2 °C	157	13
1-2A	2M NAOH+Al(OH) ₃	2 h	100 ±2 °C	228	13
1-2A	2M NAOH+Al(OH) ₃	6 h	100 ±2 °C	268	13
1-2A	2M NAOH+Al(OH) ₃	1 h	80 ± 2 °C	184	14
1-2A	2M NAOH+Al(OH) ₃	2 h	80 ± 2 °C	218	14
1-2A	2M NAOH+Al(OH) ₃	6 h	80 ± 2 °C	210	14
1-2A	2M NAOH+Al(OH) ₃	1 h	70 ± 2 °C	140	15
1-2A	2M NAOH+Al(OH) ₃	2 h	70 ± 2 °C	192	15
1-2A	2M NAOH+Al(OH) ₃	6 h	70 ± 2 °C	227	15
PON 16 Starting Material				127	
PON 16	2M NAOH+Al(OH) ₃	1 h	100 ±2 °C	211	16
PON 16	2M NAOH+Al(OH) ₃	2 h	100 ±2 °C	223	16
PON 16	2M NAOH+Al(OH) ₃	6 h	100 ±2 °C	238	16
PON 16	2M NAOH+Al(OH) ₃	1 h	80 ± 2 °C	183	17
PON 16	2M NAOH+Al(OH) ₃	2 h	80 ± 2 °C	277	17
PON 16	2M NAOH+Al(OH) ₃	6 h	80 ± 2 °C	266	17
PON 16	2M NAOH+Al(OH) ₃	2 h	70 ± 2 °C	169	18
PON 16	2M NAOH+Al(OH) ₃	3 h	70 ±2 °C	214	18
PON 16	2M NAOH+Al(OH) ₃	6 h	70 ±2 °C	214	18

conclusiVe reMArKs

Zeolites belonging to the Na-P group were synthesized with hydrothermal treatment starting from various materials, including sodium aluminosilicate gels, kaolinite and halloysite, illite-smectite, fly ash, volcanic glass and natural zeolitites (Mondragom *et al.*, 1990; Amrhein *et al.*, 1996; Berkgaut and Singer, 1996; Baccouche *et al.*, 1998; Kang *et al.*, 1998; Faghihiam and Kazemian, 2000; Gualtieri, 2001; Mimura *et al.*, 2001; Moreno *et al.*, 2001 *a, b;* Querol *et al.*, 1997, 2001, 2002; Juan *et al.*, 2002).

The overall data-set of hydrothermal treatment at low temperatures (<100 °C) of two clinoptilolite-

bearing ignimbrites belonging to Tertiary Sardinian volcanism clearly indicate that:

• Under alkali hydrothermal conditions (2 and 3M NaOH solutions) clinoptilolite laths dissolve and afterwards a zeolite Na-P1 starts to crystallize;

• the best interacting solution was 2M NaOH+Al(OH)₃, probably due to the different Si/ Al ratios of clinoptilolite and Na-P1 zeolite;

• during the hydrothermal treatment, quartz and feldspars are not dissolved;

• lower interaction times (<6 h) occur in autoclaves equipped with magnetic stirrers;

• in the later hydrothermal experiments total clinoptilolite dissolution, followed by extensive Na-P1 zeolite crystallization, occurs at relatively

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low temperatures (~70°C); this was the main result of the present research;

• the cation exchange capacity of the synthesized products is by far higher than that of the starting materials (up to 2.5 times). It is important to note that, in the hydrothermal experiments carried out at 80 °C using a reactor equipped with magnetic stirrers, the cation exchange capacity of 1-2A sample increases from 88 to 268 meq/100 g after 6 h of interaction.

Our essential results fit those obtained by Kang. and Esagashira (1997) on Korean natural zeolitebearing rocks.

In conclusion, and taking into account the aims of the present work, hydrothermal treatment with

alkaline solutions allows to produce high-power zeolites, starting from clinoptilolite-bearing

ignimbrites outcropping in central-northern Sardinia and often forming wide plateaux. As a consequence, the potential applications for various cation-exchange processes of Sardinian poorlywelded ignimbritic rocks should be carefully reconsidered.

AcKnoWledGeMents.

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