

BENEFICIATION OF ZEOLITE-RICH VOLCANICLASTIC MATERIALS

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ABSTRACT

Clinoptilolites have extensively replaced the vitric matrix of the Akrotiri pyroclastics (Santorini island, Greece), forming a relatively rich zeolitized deposit. However, the *grade* of even rich zeolitized deposits is still considered to be lower than the *grade* of other mineral commodities. By using zeolitized material from Akrotiri (mean starting *grade* 48.6 %), and applying some very simple sample preparation and mineral processing techniques, such as crushing and dry sieving, it was found that clinoptilolites tend to concentrate in the finer fractions (< 0.125mm) produced. The *grade* of these finer fractions ranges from 61.4 to 91.2 %.

KEY WORDS: Clinoptilolite, beneficiation, *grade*, crushing, dry sieving, zeolites, Santorini, Greece.

1. INTRODUCTION

It is known that natural zeolites have not found so far a successful way to the markets. Their market penetration and the relevant commercial success is slow and yet to be seen. The *grade* of even rich in zeolite minerals deposits is still considered to be lower than the *grade* of other mineral commodities, such as limestone, glass sand, kaolin, bentonite (Eyde 1993). However, he suggested that zeolitized materials can be upgraded by using mineral processing techniques. Eyde (1993) suggested that more financial resources need to be allocated by the zeolite industry, to the production of high *grade* end-products. These products could be proved to be competitive with the synthetic analogues of natural zeolites in terms of price and performance. The fact, though, is that there is a considerable lack of research on how natural zeolitized materials can be beneficiated by low cost processing techniques. Some studies of processing natural zeolites have been carried out in USA by Mondale et al. (1978) and Mondale et al. (1988) who used standard wet beneficiation techniques such as hydrocycloning, gravity separation (wet tabling) and froth flotation. Ibrahim and Inglethorpe (1996) applied magnetic and gravity separation techniques to improve the purity of natural zeolites from the Aritayn Formation (Jordan) which consist of phillipsite, faujasite and chabazite. In any case, though, it is obvious that the efficiency and effectiveness of any ore processing technique should be coupled with a credible quantitative determination of the content of zeolite minerals in the initial zeolitized ore and the final products.

A number of methods based on the evaluation of gas and water vapour adsorption, adsorption heat, and ion exchange properties of natural zeolites have been used to estimate their content in volcanoclastics and soils (Negishi 1972, Ciambelli et al. 1980, Noda 1980, Valyon et al. 1981, Ming and Dixon 1987). However, the applicability of these techniques and the accuracy of determinations have long suffered by the presence of clays and usually of more than one zeolite minerals (Nakamura et al. 1992). X-ray

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diffraction (XRD) is another technique which has been widely exploited in quantifying zeolitized materials (Petrov 1984, Nakamura et al. 1992, Ibrahim and Inglethorpe 1996). The quantification by using XRD is certainly more time consuming, but no serious problems have been reported during its use.

The main scope of this study was to investigate the application of a series of sample preparation and mineral processing techniques in an attempt to upgrade the concentration of zeolite minerals in processed products. For that purpose, we processed deeply zeolites-rich pyroclastics from Santorini island (Greece) which mainly contain clinoptilolite minerals. The mineral industry usually considers as fine powders those with a size distribution of less than 0.125mm. In this direction, some very simple methods of sample preparation were used, such as crushing by fly press and then passing through a roll mill, to examine the crushing behaviour of the zeolitized materials. In addition, a relatively low cost mineral processing technique, such as dry sieving, was applied in order to investigate whether the content of clinoptilolite minerals in various fractions produced can be upgraded. The entire investigation was based on a preliminary but careful investigation of the mineralogical composition, the texture, the density, and the particle size of the minerals present in the zeolitized materials. The success of concentrating the clinoptilolite minerals in the different fractions was evaluated by using XRD analysis.

2. Materials

2.1. Geological Setting

Deeply zeolitized pyroclastic materials from the Santorini island (Akrotiri peninsula) of the South Aegean Sea Volcanic Arc, Greece (Fig. 1), were used in this study. Five bulk samples of 5 Kg each were taken from five different exposures of the Akrotiri zeolitized pyroclastics.

The islands of Thera (Santorini), Therasia and Aspronisi are the remnants of the Santorini stratocone, while the Old and New Kameni are the products of a later volcanism (Fig. 2). A calc-alkaline, high-alumina, basalt-andesite-dacite type of volcanism was expressed in Santorini from eight centres. It began in Akrotiri peninsula, where the tuffs, which later on were altered to zeolites, were the initial products. The volcanic sequence in the area contains the tuffs, which are described as acidic pyroclastic rocks with some minor flows or breccias of hornblende dacite, and some more basic rocks such as small domes and flows of andesites and basalts. The white to pale green tuffs originally consisted of ash and/or lapilli, which were vitric and crystalline in composition. Agglomerate bands consist of grey to green dacitic cognate xenoliths up to 15 cm in dimension, forming tuff-breccia.

2.2. Authigenic mineralogy and mineral chemistry

Heulandite group of minerals and illite/smectite have replaced the vitric matrix of the Akrotiri tuffs, forming characteristic pseudomorphs after the inner parts of glass shards. The heulandite group of minerals show typical tabular, platy and sometimes coffin-shape habit with a characteristic monoclinic symmetry.

The composition of the heulandite group of minerals ranges from $(\text{Na}_{2.12}\text{K}_{2.56}\text{Ca}_{0.40}\text{Mg}_{0.19})(\text{Si}_{29.97}\text{Al}_{6.08}\text{O}_{72}) \cdot 24\text{H}_2\text{O}$ and $(\text{Na}_{2.60}\text{K}_{2.28}\text{Ca}_{0.48}\text{Mg}_{0.27})(\text{Si}_{29.71}\text{Al}_{6.20}\text{O}_{72}) \cdot 24\text{H}_2\text{O}$ with a monovalent to divalent ratio of 6.5-7.9 to $(\text{Na}_{1.56}\text{K}_{1.26}\text{Ca}_{1.19}\text{Mg}_{0.58})(\text{Si}_{29.35}\text{Al}_{6.71}\text{O}_{72}) \cdot 24\text{H}_2\text{O}$ and a monovalent to divalent ratio of 1.6 (Kitsopoulos, 1994, 1995a, 1995b). By using thermal tests as proposed by Boles (1972) and Alietti (1972), following the suggestions made by Boles and Surdam (1979), and plotting the microprobe analyses on the compositional triangle proposed by Alietti et al. (1977), the heulandite group of minerals were classified in all cases as heulandites 3, i.e. clinoptilolites. The heulanditic phases which are richer in Na and Ca do show a lower thermal stability than the K-rich members, but the fact still does not justify their classification as heulandite 2.

According to Tsohis-Katagas and Katagas (1989) the pyroclastics were in a region of active heat flow during and after their emplacement. The formation of authigenic silicates may have led to the sealing of open spaces and fractures, and being the main responsible for the original open system into

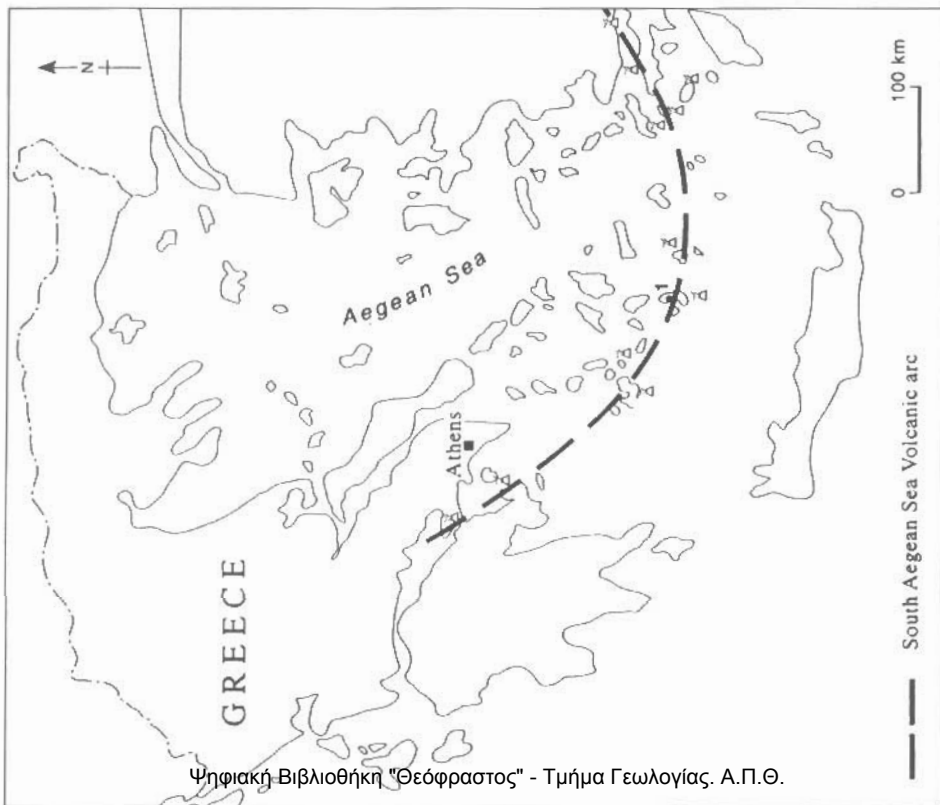


Fig. 1: South Aegean Sea Volcanic Arc
I. Santorini.

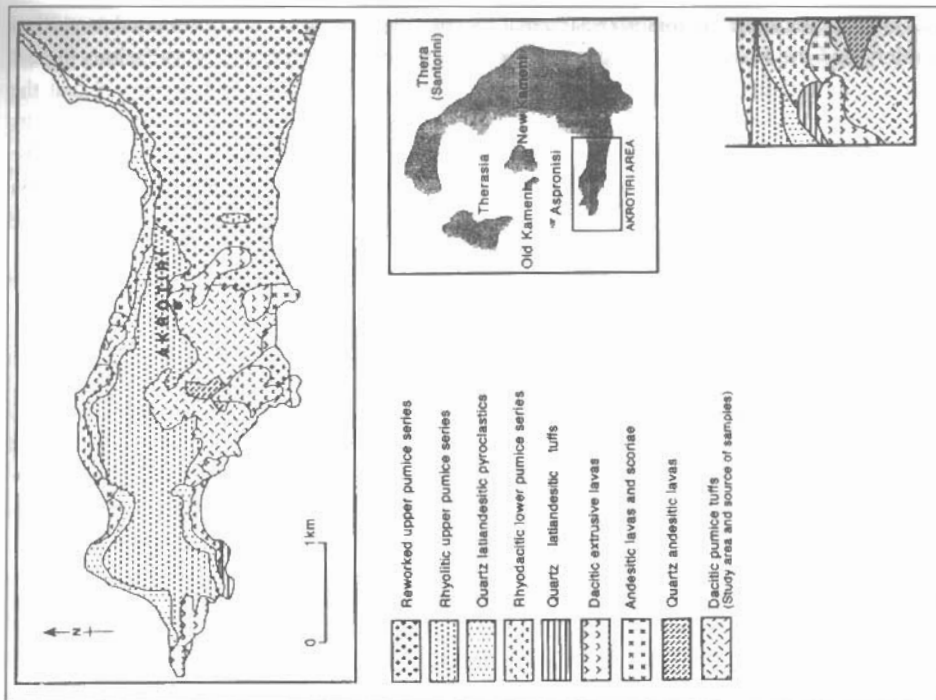


Fig. 2: Geological map and stratigraphic column
of the Akrotiri area of Santorini island
(IGME 1980; Geological sheet "Thera")

smaller closed systems. The same authors suggested that the alteration minerals are not related to vertical or lateral zonation, and the irregular distribution of their assemblages is attributed to variations in heat flow, ionic activity in interstitial waters and permeability. Kitsopoulos (1996, 1997) suggested that the formation of heulandite type of minerals involved a number of reactions. The reactions and their results were often controlled in small closed sub-systems, even within the area of individual glass particles. The formation of the heulandite type of minerals did not proceed through a form of complete glass dissolution or just solid state reaction, but through a continuous two end-member equilibrium reaction between the solid and the fluid components of numerous closed subdomains.

3. METHODS

3.1 Qualitative X-ray diffraction analysis

During the qualitative XRD analysis, the five bulk *head* starting samples and the fractions produced by each of them after sieving were used to prepare micronized powders. The powders were then packed into Al-holders and scanned from 2° to 65° at a speed of 1°/min using CuK α radiation from a Philips PW 1729 Diffractometer.

3.2. Quantitative X-ray diffraction analysis

During the quantitative XRD analysis the percentage of the clinoptilolite minerals was measured for the five bulk *head* starting samples and the fractions produced by each of them after sieving. For that purpose, standard mixtures of known concentration of clinoptilolite minerals were previously analysed by XRD. From the XRD data a standard calibration curve of clinoptilolite minerals content (wt %) vs intensity was constructed. The correlation coefficient was 0.986. The precision of the calibration was estimated by carrying out six repeat XRD runs. The repeatability for clinoptilolite quantification was ± 2.6 %.

3.3. Sample preparation and mineral processing

In this part of the investigation, the overall technical requirements, i.e. the type of equipment used, and the cost were kept at the lowest possible level. Natural zeolites have to compete with high *grade*, relatively inexpensive, synthetic zeolite products. Therefore, if any attempt to upgrade natural zeolitized materials is planned, it has to be made without any extended and/or expensive treatment which can add to the final cost.

The specific terminology which is often used in the area of mineral processing (Wills 1992) is also followed. Any ore material (known as the *head*), which is processed during mineral processing, consists of two major parts: the *gangue* and the *target*. The *gangue* is defined as the sum of all unwanted components of the ore, and the *target* as the component/mineral of the ore that we want to concentrate. The overall scope of the mineral processing is to eliminate the presence of the *gangue* and increase the concentration of the *target*. The *grade* is the wt % of the *target* in end-products, and the *recovery* is the amount of the *target* in the different final concentrates expressed as a percentage of the total amount of the *target* in the original *head*. It is obvious that in all cases the *grade* must be accompanied by an economically acceptable value of *recovery*. In this study, we can consider the Akrotiri zeolitized tuffs as the *head* ore, the clinoptilolite minerals as our *target* and the rest of the minerals found within the tuffs, for example clays, feldspars, amphiboles, Fe-Ti oxides and quartz, as the *gangue*.

The five bulk zeolitized samples were crushed down in smaller pieces by mean of a fly press and then passed through a roll mill. The material obtained from the roll mill was dry sieved, using a series of 200mm diameter standard BS 410 sieves; 1mm, 0.500mm, 0.250mm, 0.125mm, 0.075mm, 0.053mm, 0.045mm and a base. Thus, eight fractions of zeolitized materials from each bulk *head* sample were produced in total. The plus (+) symbol is used to denote "greater than" and the minus (-) denotes "less than". Therefore, the fraction for example which was retained on the 0.500mm sieve and contains particles of between 1mm and 0.500mm in size, is written as - 1 + 0.500mm. The weight of each residue fraction was measured and it was

expressed as percentage (%) of the initial *head* sample. The cumulative amounts of the material retained on and passing through each sieve, also expressed as percentage (%) of the initial *head* sample, were also calculated. Following the sieving procedure, each fraction was qualitatively examined by XRD to give a first indication for the relative abundance of clinoptilolite minerals in each fraction. The fractions were then quantitatively examined by XRD. In this case, the actual *grade* and the *recovery* of each fraction were also estimated.

4. RESULTS AND DISCUSSION

For all fractions produced, the residue of each sieve, the cumulative amount of the material retained on and the cumulative amount of the material passing through each sieve, expressed as percentages (%), are given in Table 1. The values of the residue, the *grade*, and the *recovery*, which are given in Table 1, are the mean values from all five bulk head starting samples. From the results (47.4 % cumulative passing the 0.125mm sieve) it is clear that almost 50 % of the *head* material passed through the 0.125mm sieve producing relatively fine-sized powders.

The standard deviation data which is given for the residue values indicates that all five clinoptilolite-rich bulk head samples finally exhibited a very similar size distribution after crushing and sieving. By examining their size distribution it can, therefore, be suggested that the zeolitized samples showed a similar crushing behaviour. It seems that any differences in the texture, the mineralogical composition, and the *grade* which existed between the head samples, did not result in a different crushing behaviour. Therefore, it can be suggested that the sample preparation and mineral processing means, which were applied to process (crushing and sieving) the zeolitized materials, probably played the most important role in the production of end products of a similar nature and size distribution.

Representative XRD graphs of a typical starting head bulk sample and two representative fractions from the same sample are given in Fig. 3. The qualitative examination of the XRD graphs allowed us to conclude that clinoptilolite minerals clearly tend to concentrate in fine-sized fractions. By examining the 020 main diffraction peak of the clinoptilolite minerals it seemed that our target (clinoptilolite) was relatively much more abundant in the fractions retained on the base, the 0.045mm, 0.053mm and the 0.075mm sieves. This preferable concentration in specific fractions is closely related to the size of the crystals of the clinoptilolites. In general, zeolite minerals, within zeolitized pyroclastics, are usually fine grained. In Santorini, there were no clinoptilolite minerals found to exceed 0.100mm in size. Their sizes were generally smaller than 0.100mm, as little as 0.010mm. Thus, by crushing the Akrotiri zeolitized tuffs and producing a series of fractions which consist of particles of sizes less than 0.125mm, a large number of clinoptilolite minerals was finally liberated in the relevant fine-sized powders (Fig. 3, XRD of the - 0.053 + 0.045mm fraction). Because of the same reason - the size of the clinoptilolite minerals - there is no significant enrichment observed in the coarser fractions. When the zeolitized materials were crushed and the coarser fractions consisting of particles of sizes greater than 0.100mm were produced, the greater number of the clinoptilolite minerals was not liberated, but they remained "clogged" within the particles of these fractions. On the other hand, feldspars are clearly enriched on the 0.125mm and the 0.250mm sieves (Fig. 3, XRD graph of the -0.500 +0.250mm fraction). This was due to the fact that the size of the crystals of the feldspars were usually well over 0.100mm, sometimes reaching even 0.500mm. Therefore, by crushing the Santorini zeolitized materials and producing fractions which consist of particles of sizes greater than 0.100mm, the greater part of the feldspars is liberated and the minerals finally concentrate in the - 0.250 + 0.125mm and - 0.500 + 0.250mm fractions.

Table 1. Residue, cumulative retained, cumulative passing, grade and recovery values of fractions of zeolitized pyroclastics (Santorini island, Greece), after crushing and dry sieving. XRD was used to measure the *grade*. The residue, grade and recovery values given are the mean of five head samples. The cumulative retained and cumulative passing values were calculated by using the mean residue values of the first column. s.d.: standard deviation.

Bulk Head Samples	Residue	Cumulative retained	Cumulative passing	Grade	Recovery	
	%	s.d.	%	%	%	%
Bulk Head Samples				48.6		
Size fraction (mm)						
+ 1.000	2.7	0.15	2.7	97.3	49.4	2.7
- 1.000 + 0.500	20.0	1.20	22.7	77.3	31.2	12.8
- 0.500 + 0.250	13.9	0.76	36.6	63.4	24.6	7.0
- 0.250 + 0.125	16.0	0.65	52.6	47.4	27.0	8.9
- 0.125 + 0.075	11.7	0.34	64.3	35.7	62.6	15.1
- 0.075 + 0.053	8.6	0.12	72.9	27.1	61.4	10.9
- 0.053 + 0.045	6.8	0.32	79.7	20.3	91.2	12.8
- 0.045	20.3	0.48	100.0	0.0	71.3	29.8

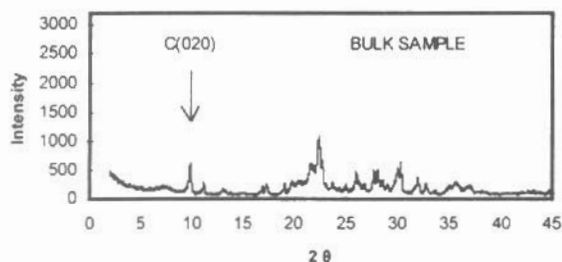
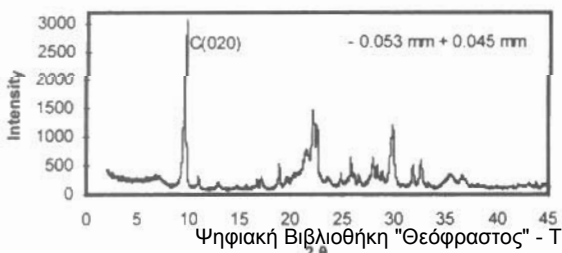
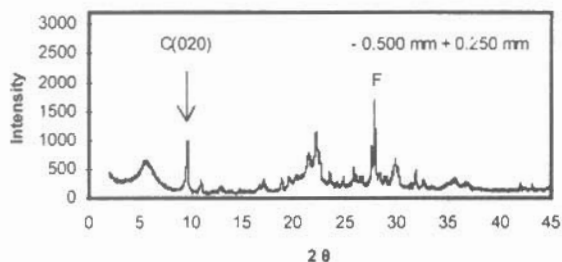


Fig. 3: Representative XRD graphs of a bulk head sample and two fractions of zeolitized pyroclastics (Santorini island, Greece) after crushing and dry sieving. C(020): 020 main diffraction peak of clinoptilolite, F: feldspar.



It is obvious that the successful enrichment of the target (clinoptilolites) in the finer-sized fractions (- 0.125mm) after crushing and sieving was not the result of the application of expensive or complicated or time consuming procedures. It was the result of some simple mineralogical observations, e.g. by XRD and electron microscopy, and the exploitation of a very simple aspect, such as the relative size of the crystals of the minerals forming the head zeolitized ore. However, this enrichment would not have any meaning for the mining industry if some quantitative data and economic parameters were not provided. This is the reason why the enrichment was also quantitatively confirmed by measuring the grade and the recovery. The starting mean

at 48.6 % (Table 1). From the same table it is clear that the grade of the finer-sized (< 0.125 mm) fractions has greatly improved. The *grade* of these fractions ranges from 61.4 to 91.2 %, exhibiting an improvement of up to 42.6 %. This means that some simple sample preparation and mineral processing techniques can vastly improve the *grade* of zeolitized end products. It is quite important to note that the improvement of the starting *grade* was coupled with an economically accepted (Ibrahim and Inglethorpe 1996) *recovery*. The four finer fractions concentrated in total the 68.6 % of the zeolite minerals contained in the *head* zeolitized ore.

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