



Ingeniería y Competitividad

ISSN: 0123-3033

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Universidad del Valle

Colombia

Ríos, Carlos A.; Williams, Craig D.; Castellanos, Oscar M.  
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Ingeniería y Competitividad, vol. 13, núm. 1, 2011, pp. 131-138  
Universidad del Valle  
Cali, Colombia

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## Tratamiento hidrotermal a baja temperatura de una toba rica en clinoptilolita en soluciones de NaOH, KOH y Ca (OH)<sub>2</sub>

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(Recibido: Agosto 19 de 2009 - Aceptado: Junio 1 de 2011)

### Resumen

Una toba rica en clinoptilolita natural del área volcánica del Mioceno de las Montañas Tokay de Hungría fue convertida en productos sintéticos de mayor valor agregado bajo condiciones hidrotérmicas. La clinoptilolita fue activada hidrotérmicamente con NaOH, KOH y Ca(OH)<sub>2</sub> como agentes activantes para sintetizar productos de alta pureza, los cuales incluyen zeolita Na-P1 (GIS), zeolita K-F (EDI) e hidróxidos y silicatos de calcio. Los productos sintéticos se caracterizaron por técnicas de difracción de rayos X, microscopía electrónica de barrido, espectroscopía infrarroja por transformada de Fourier y termogravimetría. Los resultados obtenidos en este estudio son importantes tanto para evaluar la influencia del agente activante sobre la formación de nuevas fases zeolíticas como para simular las condiciones geológicas de formación de zeolitas y otras fases minerales.

**Palabras Claves:** Clinoptilolita, Zeolitas, Montañas Tokay, Condiciones hidrotérmicas, Sintetizar

## Hydrothermal treatment at low temperature of a clinoptilolite-rich tuff in NaOH, KOH and Ca(OH)<sub>2</sub> solutions

### Abstract

A natural clinoptilolite-rich tuff from Miocene volcanic area of Tokay Mountains of Hungary was converted to higher value-added synthetic products under hydrothermal conditions. Clinoptilolite was hydrothermally activated with NaOH, KOH and Ca(OH)<sub>2</sub> as activating agents to synthesize high purity products, which include zeolite Na-P1 (GIS), zeolite K-F (EDI) and calcium hydroxides and silicates. The synthesis products were characterized by X-ray diffraction, scanning electron microscopy, Fourier transformed infrared spectroscopy and thermogravimetry techniques. Results obtained in this study are important both to evaluate the influence of the activating agent on the formation of new zeolitic phases and to simulate the geological conditions of formation of zeolites and other mineral phases.

**Keywords:** Clinoptilolite-rich tuff, Zeolites, Tokay mountains, Hydrothermal conditions, Synthesize

## 1. Introduction

Zeolites are a well-defined class of hydrated microporous crystalline aluminosilicates having an infinite, open and rigid three dimensional structures with high-internal-surface-area arising from frameworks of  $[\text{SiO}_4]^{4-}$  and  $[\text{AlO}_4]^{5-}$  units linked together to form cages connected by pore openings (Szostak, 1989; Davis & Zones, 1997; Yan & Wang, 2003; Chrétien, 2007). There are 40 naturally occurring zeolite species recorded and more than 150 species have been synthesized (Virta, 2004). According to the U.S. Geological Survey, it has worldwide reported the occurrence of natural zeolites in the United States, Japan, Korea, Bulgaria, Czechoslovakia, Romania, Hungary, Russia, Yugoslavia, South Africa, Italy, Germany, Turkey and China, the latter with the greatest World production of zeolite material.

In Latin America deposits are reported in Spain, Mexico, Cuba, Chile and Ecuador, with Cuba standing out with the higher production. The most common natural zeolites are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite. Clinoptilolite, with the ideal formula of  $(\text{Na,K})_6\text{Si}_{30}\text{Al}_6\text{O}_{72}\cdot n\text{H}_2\text{O}$ , is the most abundant natural zeolite found mainly in sedimentary rocks of volcanic origin. It is currently mined all over the world and used in the fields of agriculture, industry and pollution control (Mumpton, 1984). On the other hand, the most common types of synthetic zeolites are types A, X, Y and ZSM-5. Due to their exceptional properties, both natural and synthetic zeolites are used commercially because of their unique adsorption, ion-exchange, molecular sieve and catalytic properties (Breck, 1974).

Different research groups give particular attention to the properties of zeolites, which have been driven by environmental concerns or play significant roles in preserving and improving the environment. Synthetic zeolites hold some key advantages over their natural analogs (Ibrahim, 2007). The synthetics can, of course, be manufactured in a uniform, phase-pure state. It is also possible to manufacture desirable zeolite structures which do not appear in nature. Finally, zeolite manufacturing processes engineered by

man require significantly less time than the 50 to 50,000 years prescribed by nature. Disadvantages include the inability to create crystals with dimensions of a comparable size to their natural counterparts. Although natural zeolites are abundant and inexpensive, these attributes may not offset the effects of impurities and inconsistency of properties relative to the more uniform synthetic zeolites (Ackley et al., 2003). Natural zeolites need greater advantages than low initial cost and abundance if they are to compete with their synthetic counterparts in several applications.

The present study examines the role of NaOH, KOH and  $\text{Ca}(\text{OH})_2$  solutions in the transformation of clinoptilolite occurring in the zeolitically altered rhyolitic tuffs at the Tokay Mountains (Hungary). Previous studies reveal that powdered natural clinoptilolite-rich volcanic rocks can be converted into several zeolitic materials using hydrothermal processes (Faghihian et al., 2000; De Fazio, 2008; Kamali et al., 2009; Kazemian et al., 2003, 2009). However, why transform a natural zeolite in a synthetic counterpart? There are several zeolites which are not directly usable in their original form and, therefore, they can be modified by hydrothermal conditions to improve the effectiveness in a specific application. On the other hand, during the hydrothermal transformation of the natural clinoptilolite to other zeolites it is possible to evaluate the influence of the activating agent on the possibility of the formation of new zeolitic phases. Finally, the experiments on transformation of clinoptilolite as a starting material allow simulating the geological natural formation processes of zeolites and other mineral phases.

## 2. Experimental methods and materials

### 2.1 Starting material

Natural zeolites obtained from different areas of the mining site can also vary in chemical composition. The natural zeolite used in this study was a clinoptilolite-rich tuff from the Miocene volcanic area of Tokay Mountains of Hungary, which contain 65-95% clinoptilolite (Gottardi & Obradovic, 1978). This type of zeolite can be contaminated to varying degrees by other

minerals such as  $\text{Fe}^{2+}$ , quartz,  $\text{SO}_4^{2-}$ , other zeolites and amorphous glass. The presence of these impurities in natural zeolites does not favor their performance compared to the more-favored synthetic zeolites (Ackley et al., 2003). This is very important taking into account that impurities such as soluble silicates can inhibit aggregation of natural zeolites and removing such impurities can be economically prohibitive. The aluminosilicate source was prepared prior to the synthesis process as follows. Powder preparation techniques included both a SpectroMill Ball Pestle Impact grinder and a mortar and pestle. After grinding, the raw material was sieved under dry conditions and the size fraction of 200 mesh collected and particles of  $< 75 \mu\text{m}$  selected for hydrothermal synthesis.

The reagents used to activate the raw material were sodium hydroxide, NaOH, as pellets (99.99%, from Aldrich Chemical Company, Inc.), potassium hydroxide, KOH, as pellets ( $>85\%$ , from Aldrich Chemical Company, Inc.),  $\text{Ca}(\text{OH})_2$  (98%, from BDH Laboratory Supplies) and distilled water using standard purification methods (NSF/ANSI, 2007).

## 2.2 Hydrothermal synthesis

The synthesis conditions for transformation of the clinoptilolite-rich tuff using NaOH, KOH and  $\text{Ca}(\text{OH})_2$  as activating agents are summarized in Table 1 and were selected from previous studies done by Ríos and co-workers (Ríos, 2008; Ríos & Williams, 2008; Sandoval et al., 2009; Ríos et al.,

2009a, 2009b, 2010; Ríos & Williams, 2010) using several starting materials under similar experimental conditions. The raw material was added, with stirring, to NaOH, KOH and  $\text{Ca}(\text{OH})_2$  solutions, which were prepared by dissolving the activating agent in distilled water in reaction plastic beakers (150-250 ml). Calculated amounts of clinoptilolite-rich tuff was added to the activating solutions and stirred until the reagents were dissolved and for homogenization of the reaction mixture. Then, pH of the reaction gels was measured with a pH 211 Auto-calibration bench pH/mV meter (Hanna instruments) the “Standard Methods for the Examination of Water and Wastewater” (APHA, AWWA, WEF, 2005). The crystallization was carried out by hydrothermal synthesis under static conditions in PTFE (polytetrafluoroethylene = Teflon) bottles (Cowie Technology Ltd) of 65 ml for preparations heated at  $100^\circ\text{C}$ , which were previously weighted for preparations heated in an oven. The reactors were removed from the oven at the scheduled times and were quenched in cold water for product identification. Then, pH of the reaction mixtures was measured. After hydrothermal treatment, the reaction mixtures were filtered, washed with distilled water, and the products were dried in an oven at  $80^\circ\text{C}$ . The dried samples were weighted and kept in plastic bags for analysis.

## 2.3 Characterization techniques

The mineral phases in the starting clinoptilolite-rich tuff and as-synthesized products were studied by X-ray diffraction (Philips PW1710

Table 1. Synthesis conditions for hydrothermal treatment of clinoptilolite-rich tuff in NaOH, KOH and  $\text{Ca}(\text{OH})_2$  solutions.

Sample	$\text{H}_2\text{O}$ (ml)	NaOH (g)	KOH (g)	$\text{Ca}(\text{OH})_2$ (g)	CLI (g)	L/S ratio (ml/g)	Hydrothermal treatment		Recognized synthesis products	Residual phases
							T ( $^\circ\text{C}$ )	t (h)		
CLI1	18.00	2.87			3.10	6.73	100	48	GIS	CLI
CLI2	18.00	2.87			3.10	6.73	100	72	GIS	CLI
CLI3	18.00	2.87			3.10	6.73	100	96	GIS	---
CLI4	18.00		4.03		3.10	7.11	100	72	*EDI	CLI
CLI5	18.00		4.03		3.10	7.11	100	120	EDI	CLI
CLI6	18.00		4.03		3.10	7.11	100	168	EDI	CLI
CLI7	18.00			5.32	3.10	7.52	100	72	CH, $\text{C}_3\text{S}/\text{C}_2\text{S}$	---
CLI8	18.00			5.32	3.10	7.52	100	120	CH, $\text{C}_3\text{S}/\text{C}_2\text{S}$	---
CLI9	18.00			5.32	3.10	7.52	100	168	CH, $\text{C}_3\text{S}/\text{C}_2\text{S}$	---

CLI, clinoptilolite; GIS, zeolite Na-P1; EDI, zeolite K-F; CH, calcium hydroxydes;  $\text{C}_3\text{S}/\text{C}_2\text{S}$ , calcium silicates; L/S, alkaline solution/solid ratio.

\* en trazas

diffractometer operating in Bragg-Brentano geometry with Cu-K $\alpha$  radiation (40 kV and 40 mA) and secondary monochromation. Data collection was carried out in the  $2\theta$  range 3-50°, with a step size of 0.02°. Phase identification was made by searching the ICDD powder diffraction file database, with the help of JCPDS (Joint Committee on Powder Diffraction Standards) files for inorganic compounds. The morphology of the starting material and as-synthesized products was studied with a ZEISS EVO50 scanning electron microscope, under the following analytical conditions: I probe 1 nA, EHT = 20.00 kV, beam current 100  $\mu$ A, Signal A = SE1, WD = 8.0 mm. Fourier transform infrared (FT-IR) spectroscopy was carried out by using a Mattson Genesis II FT-IR spectrometer in the 4000-400  $\text{cm}^{-1}$  region.

However, it is discussed only the 1200-400  $\text{cm}^{-1}$  region, because it is where the spectra showed remarkable changes. Thermogravimetric and differential thermal analyses were performed on a Mettler Toledo TG 50 thermobalance. Samples of 15-20 mg were heated under nitrogen gas flow (20ml/min) between 25-700°C at a rate of 20°C/min.

### 3. Results and discussion

#### 3.1 X-ray diffraction analysis

Figure 1 illustrates the XRD pattern of the starting clinoptilolite (background), which is quite similar to that reported for this framework type available for on the internet site of the IZA (<http://www.iza-online.org>) or in the atlas of zeolite framework types (Baerlocher et al., 2001). The XRD patterns (Figure 1) show the progressive dissolution of the starting clinoptilolite-rich tuff with reaction time, which was accompanied by the precipitation of different synthesis products, including zeolite Na-P1 (a member of the gismondine group), zeolite K-F (a member of the edingtonite group), calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) and calcium silicates ( $\text{C}_2\text{S}/\text{C}_3\text{S}$ ). In general, these reaction products show a very constant grade of crystallinity with reaction time. Similar phases were obtained by Ríos and co-workers after hydrothermal transformation of natural clinker (Ríos, 2008;

Ríos & Williams, 2008; Ríos et al., 2009a), kaolinite (Ríos, 2008; Ríos & Williams, 2010), and kaolinite and metakaolinite (Ríos, 2008; Ríos et al., 2009b), using NaOH, KOH and CaO as activation agents, respectively.

Figure 1a reveals that zeolite Na-P1 was the dominant synthesized type, using NaOH as activating agent. The diffraction intensities of the clinoptilolite-rich tuff showed a progressive decrease with reaction time, accompanied by increasing intensity of the reflection peaks of the zeolitic product. In Figure 1b is illustrated the progressive crystallization of zeolite K-F with reaction time after activation of the starting material. It is clear that NaOH acts as a strong mineralizing agent, which forces the reactants into solution, showing more effectiveness as activating mineralizer with regards to KOH, taking into account that longer reaction times were required when potassium hydroxide was used as alkali source for natural zeolite activation. Figure 1c shows evidence of a quick disappearance of the characteristic diffraction peaks of the clinoptilolite-rich tuff, compared with the evolution of the starting materials in NaOH (Figure 1a) and KOH (Figure 1b) solutions, in which a slow dissolution of the natural zeolite is accompanied by the appearance of zeolites Na-P1 and K-F, respectively.

#### 3.2 Scanning electron microscopy

SEM images (Figure 2) shows interesting morphologies that provide new clues on the phase transformation history after the hydrothermal reaction of clinoptilolite-rich tuff in solutions of NaOH, KOH and  $\text{Ca}(\text{OH})_2$  at 100 °C. There was a change in morphology of the original surface of the natural zeolite particles, which can be explained by the dissolution of the clinoptilolite and the crystallization of several synthesis products. Clusters of radiating tetragonal prisms of zeolite Na-P1 are observed in Figures 2a-2b. The morphology of this zeolite ranges from spherical to star-shaped aggregates. Figures 2c-2d reveals the presence of neoformed crystals of K-F zeolite, showing petal flower morphology. As shown in Figures 2e-2f, calcium hydroxide,  $\text{Ca}(\text{OH})_2$ , has a distinguishing hexagonal shape, accompanied by needle-like aggregates that

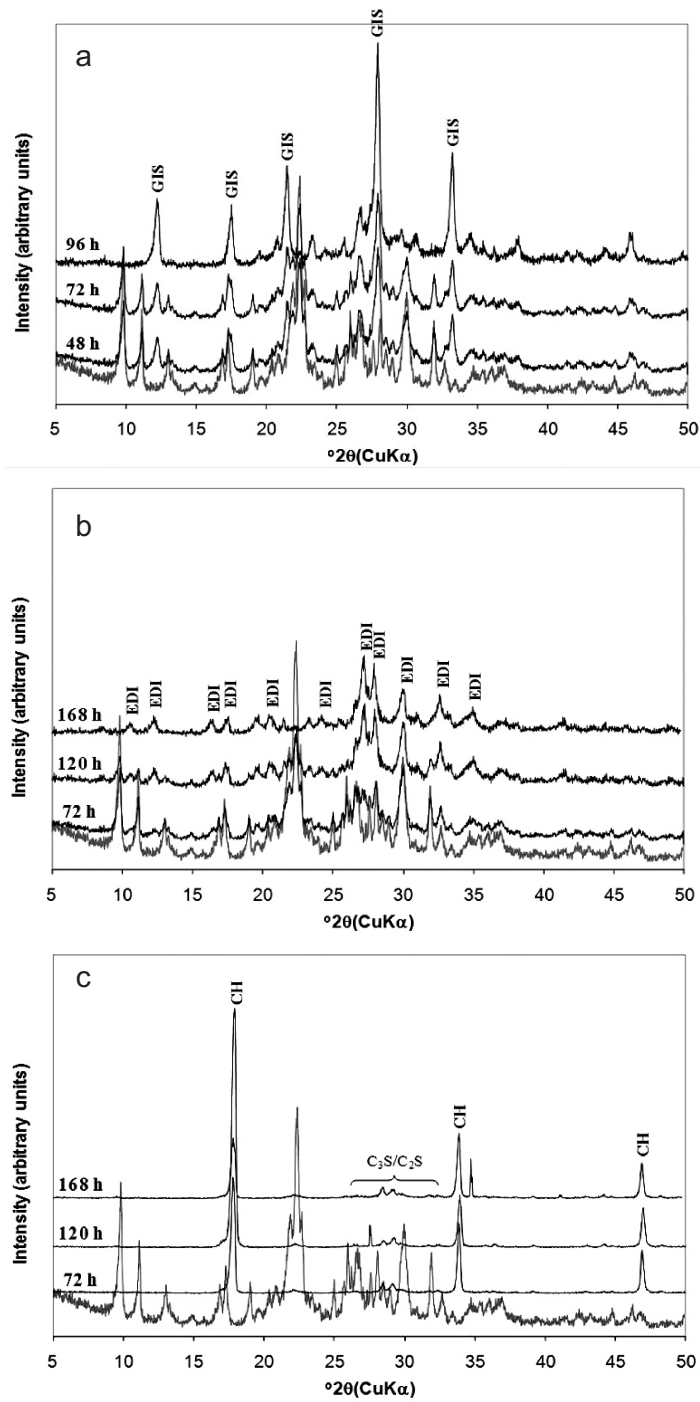


Figure 1. XRD patterns of the unreacted (background) clinoptilolite-rich tuff and representative as-synthesized products obtained after their hydrothermal reaction at  $100^\circ\text{C}$  in solutions of (a) NaOH, (b) KOH and (c)  $\text{Ca}(\text{OH})_2$ . GIS, zeolite Na-P1; EDI, zeolite K-F; CH,  $\text{Ca}(\text{OH})_2$ ;  $\text{C}_2\text{S}/\text{C}_3\text{S}$ , calcium silicates.



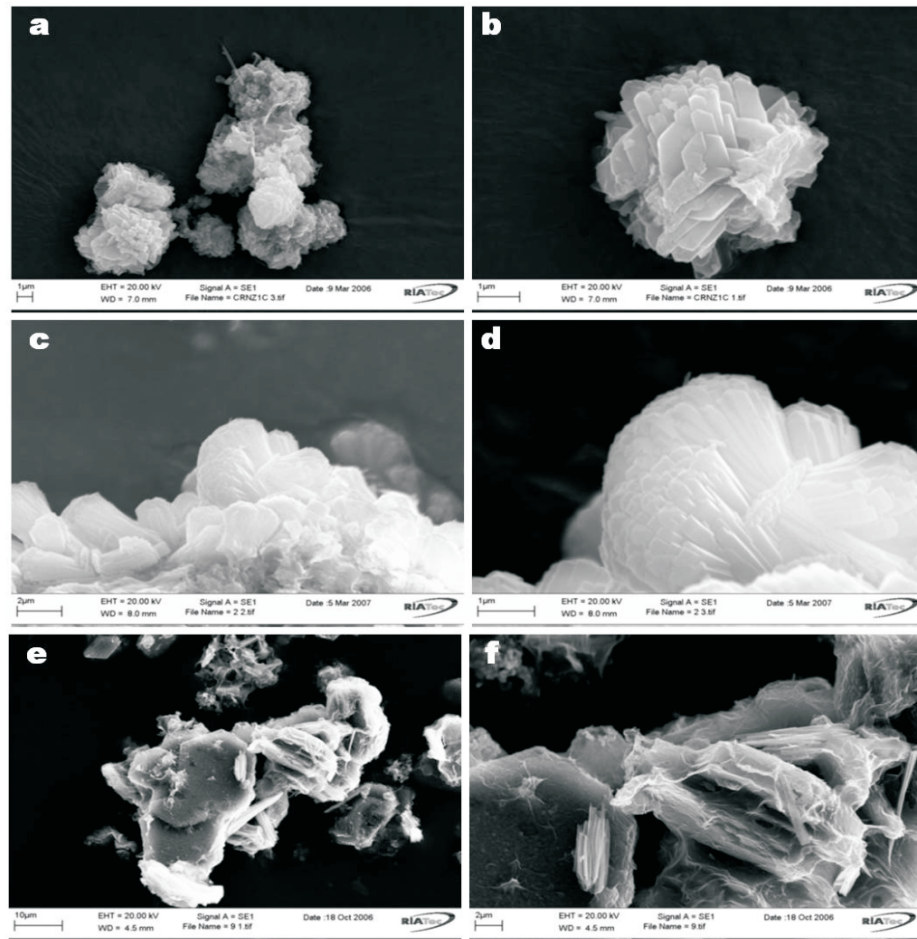


Figure 2. SEM images showing the occurrence of representative synthesis products obtained via hydrothermal treatment of clinoptilolite-rich tuff in solutions of (a-b) NaOH, (c-d) KOH and (e-f)  $\text{Ca}(\text{OH})_2$  at  $100^\circ\text{C}$ .

probably correspond to the occurrence of ettringite (not detected by XRD analysis) growing on preexisting  $\text{Ca}(\text{OH})_2$ . Similar morphologies were obtained by Ríos and co-workers using natural clinker, kaolinite and metakaolinite as starting materials (Ríos, 2008; Ríos & Williams, 2008; Ríos et al., 2009a, 2009b; Ríos & Williams, 2010), in the chemical systems evaluated in this study.

As for potential industrial applications, the most interesting zeolitic product is zeolite Na-P1, due to its high ionic exchange capacity as reported by Querol et al., 2001). Ríos (2008) reported the efficient application of this zeotype in the removal of heavy metals and ammonium.

### 3.3 Fourier transform infrared spectroscopy

Figure 3 shows, the FT-IR spectra of the clinoptilolite-rich tuff and as-synthesized products obtained after its hydrothermal treatment at  $100^\circ\text{C}$  in NaOH solutions, whereas the assignment of their spectral frequencies are given in Table 2. The characteristic peaks of the clinoptilolite-rich tuff disappeared after reacting with NaOH. However, the IR vibration bands reveal the appearance of new vibration bands corresponding to the formation of zeolite Na-P1. IR spectra corresponding to this zeolite show clearly the disappearance of the characteristic vibration bands of the starting material. Absorption spectra are in total accordance with the

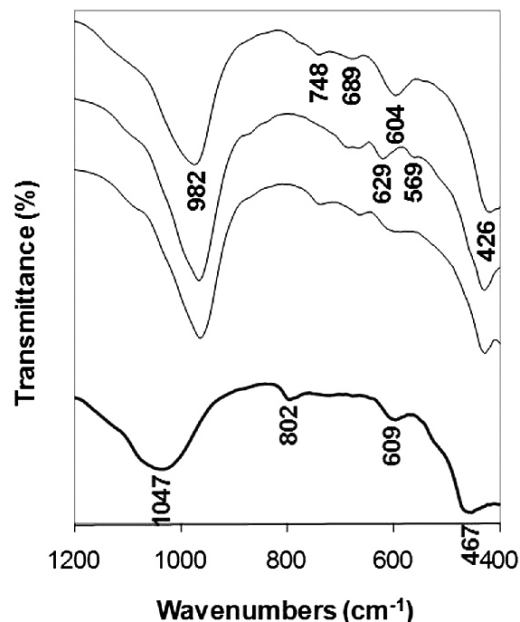


Figure 3. FT-IR spectra of the unreacted (background) natural zeolite and representative as-synthesized products obtained after its hydrothermal reaction at 100 °C in NaOH solutions.

Table 2. Fourier transform infrared assignments of the starting clinoptilolite and the as-synthesized zeolite Na-P1.

Assignment	Band positions (cm <sup>-1</sup> )	
	CLI	GIS
Asymmetric T-O stretching vibrations	1047	982
Symmetric T-O stretching vibrations	802	748-689
4- or 6-membered double rings	609	604
Bending vibrations of T-O	467	426

CLI, clinoptilolite; GIS, zeolite Na-P1.

different absorption peaks given by Breck (1974), with peaks situated respectively at 982, 748, 689, 604 and 426 cm<sup>-1</sup> for the Na-P1 zeolite. The absorption spectra corresponding to the synthetic zeolite obtained after hydrothermal transformation of clinoptilolite are similar to those obtained by Ríos (2008).

### 3.4 Thermogravimetric analyses

Figure 4 illustrates the TG/DTG curves obtained for the raw clinoptilolite-rich tuff and as-synthesized zeolite Na-P1 obtained after the hydrothermal reaction of the starting material at 100 °C in NaOH solutions. The starting material showed major and rapid mass loss between 25 and 200 °C, with slower and less significant mass loss at higher temperatures (Figure 4a). On the other hand, the as-synthesized synthesis product (zeolite Na-P1) shows up to four dehydration steps, which could be explained as a consequence of water molecules dehydrated at lower temperatures that could re-enter the zeolite with or without affecting its framework linkages (Figure 4b).

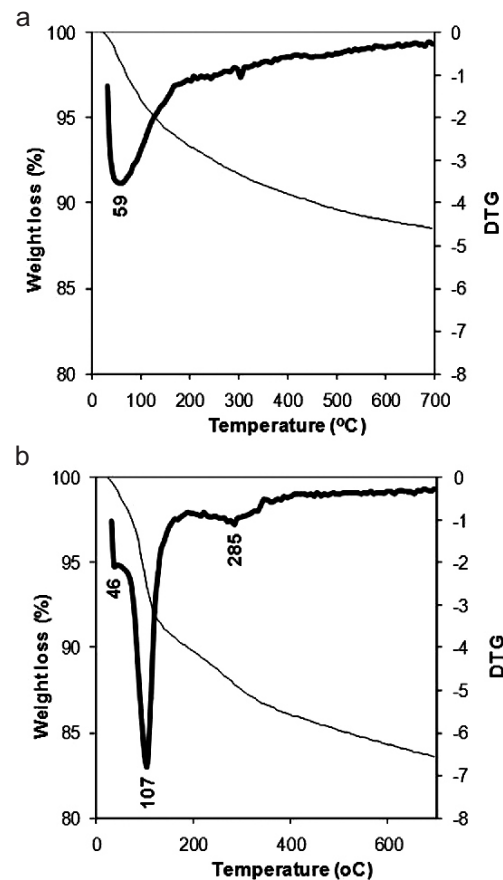


Figure 4. TG/DTG curves between 25-700 °C of the (a) clinoptilolite-rich tuff and (b) representative synthesis products obtained after its alkaline activation at 100 °C in NaOH solutions.



#### 4. Conclusions

Comparing results of the hydrothermal transformation of clinoptilolite-rich tuff provided valuable information to elucidate the mode of crystallization of the synthesis products. Clinoptilolite-rich tuff dissolution was followed by crystallization of different nearly pure synthesis products, namely zeolite Na-P1, zeolite K-F and  $\text{Ca}(\text{OH})_2$ , which were successfully synthesized from the starting material by its hydrothermal reaction at 100 °C, using solutions of NaOH, KOH and  $\text{Ca}(\text{OH})_2$ , respectively.

Synthesis yields were not estimated, taking in consideration that no comparing of their cation exchange capacity with pure commercial products was done. The results obtained in this study prove that further studies should be carried out under well-optimized experimental conditions to successfully prepare highly crystalline zeolites with potential application in the purification of industrial wastewater. The transformation of a natural zeolite such as clinoptilolite in a synthetic counterpart can be done, taking into account that there are several zeolites which are not directly usable in their original form and, therefore, they can be modified by hydrothermal conditions to improve the effectiveness in a specific application. This study is very important not only to evaluate the hydrothermal transformation of the natural clinoptilolite to other zeolites and the influence of the activating agent on the possibility of the formation of new zeolitic phases but also to simulate the geological natural formation processes of zeolites and other mineral phases.

#### 5. Acknowledgments

This work was supported by the Programme Alban, the European Union Programme of High Level Scholarships for Latin America, Scholarship No. E05D060429CO, and the Universidad Industrial de Santander (a remunerated commission) for funding C. Ríos. Special thanks to School of Applied Sciences at University of Wolverhampton for allowing the use of the research facilities.

#### 6. References

- Ackley, M.W., Rege, S.U., & Saxena, H. (2003). Application of natural zeolites in the purification and separation of gases. *Microporous and Mesoporous Materials* 61, 25-42.
- American Public Health Association (APHA), American Water Works Association (AWWA), & Water Environment Federation (WEF). (2005). *Standard Methods for the Examination of Water and Wastewater*. A.D. Eaton, L.S. Clesceri, E.W. Rice, A.E. Greenberg and M.A.H. Franson (Eds.), 21st Ed., 1368p.
- Baerlocher, C., Meier, W.M., & Olson, D.H. (2001). *Atlas of zeolite framework types*. 5th ed. Amsterdam: Elsevier.
- Breck, D.W. (1974). *Zeolite Molecular Sieves: Structure, Chemistry and Use*. New York: John Wiley.
- Chrétien, M.N. (2007). Supramolecular photochemistry in zeolites: From catalysts to sunscreens. *Pure and Applied Chemistry* 79, 1-20.
- Davis, M.E., & Zones, S.I. (1997). *A perspective on zeolite synthesis: How do you know what you'll get?* In: *Synthesis of Porous Materials: Zeolites, Clays and Nanostructures*, M.L. Occelli and H. Kessler (Eds.), Marcel Dekker, Inc., New York, 1-34.
- De Fazio, A., Brotzu, P., Ghiara, M.R., Fercia, M.L., Lonis, R., & Sau, A. (2008). Hydrothermal treatment at low temperature of Sardinian clinoptilolite-bearing ignimbrites for increasing cation exchange capacity. *Periodico di Mineralogia* 77, 79-91.
- Gottardi, G., & Obradovic, J. (1978). Sedimentary zeolites in Europe. *Fortschritte der Mineralogie* 56, 316-366.
- Faghihian, H., & Kazemian, H. (2000). Zeolite-P synthesized from clinoptilolite rich-tuffs as a potential material for removal of  $\text{Cs}^{+1}$ ,  $\text{Sr}^{+2}$ ,  $\text{Ba}^{+2}$  and  $\text{Ca}^{+2}$  from liquid radioactive waste. *Nuclear Science Journal* 37, 180-187.

- Ibrahim, S.A. (2007). *Synthesis and characterization of zeolites from sodium aluminosilicate solution*. MSc thesis, University Sains Malaysia, Penang, Malaysia.
- International Zeolite Association. Available on <http://www.iza-online.org>.
- Kamali, M., Vaezifar, S., Kolahdüzan, H., Malekpour, A., & Reza, M. (2009). Synthesis of nanozeolite A from natural clinoptilolite and aluminum sulfate; Optimization of the method. *Powder Technology* 189, 52-56.
- Kazemian, H., Modarres, H., & Ghasemi, H. (2003). Evaluating the performance of an Iranian natural clinoptilolite and its synthetic zeolite P for removal of Cerium and Thorium from nuclear wastewaters. *Journal of Radioanalytical and Nuclear Chemistry* 258, 551-556.
- Kazemian, H., Modarres, H., Kazemi, M., & Farhadi, F. (2009). Synthesis of submicron zeolite LTA particles from natural clinoptilolite and industrial grade chemicals using one stage procedure. *Powder Technology*, doi:10.1016/j.powtec.2009.06.017
- Mumpton, F.A. (1984). The role of natural zeolites in agriculture and aquaculture. Zeo-Agriculture. In W.G. Pond and F.A. Mumpton (editors), *Use of Natural Zeolites in Agriculture and Aquaculture*, Boulder: Westview Press.
- NSF/ANSI Standard 62 (2007). *Drinking Water Distillation Systems*. NSF International.
- Querol, X., Umaña, J.C., Plana, F., Alastuey, A., Lopez-Soler, A., Medinaceli, A., Valero, A., Domingo, M.J., & Gracia-Rojo, E. (2001). Synthesis of Na zeolites from fly ash in a pilot plant scale: Examples of potential environmental applications. *Fuel* 80, 857-865.
- Ríos, C.A. (2008). *Synthesis of zeolites from geological materials and industrial wastes for potential application in environmental problems*. PhD Thesis, University of Wolverhampton, Wolverhampton, England.
- Ríos, C.A., & Williams, C.D. (2008). Synthesis of zeolitic materials from natural clinker: A new alternative for recycling coal combustion by-products. *Fuel* 87, 2482-2492.
- Ríos, C.A., Williams, C.D., & Fullen, M.A. (2009a). Nucleation and growth history of zeolite LTA as-synthesized from kaolinite by two different methods. *Applied Clay Science* 42, 446-454.
- Ríos, C.A., Williams, C.D., & Fullen, M.A. (2009b). Hydrothermal synthesis of hydrogarnet and tobermorite at 175 °C from kaolinite and metakaolinite in the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system: A comparative study. *Applied Clay Science* 43, 228-237.
- Ríos, C.A., Williams C.D., & Castellanos, O.M. (2010). Synthesis of zeolite LTA from thermally treated kaolinite. *Revista Facultad de Ingeniería (Universidad de Antioquia)* 53, 30-41.
- Ríos, C.A., & Williams C.D. (2010). Hydrothermal transformation of kaolinite in the system K<sub>2</sub>O-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O. *Dyna (Universidad Nacional de Colombia Medellín)* 77, 55-63.
- Sandoval, M.V., Henao, J.A., Ríos, C.A., Williams C.D., & Apperley, D.C. (2009). Synthesis and characterization of zeotype ANA framework by hydrothermal reaction of natural clinker. *Fuel* 88, 272-281.
- Szostak, R. (1998). *Molecular sieves*. London: Blackie Academic and Professional.
- Virta, R.L. (2004). *Zeolites*. In: United States Geological Survey Minerals Yearbook: Vol. 1 (Metals and Minerals), 84.1-84.4.
- Yan, Y., & Wang, H. (2003). *Encyclopedia of Nanoscience and Nanotechnology*. California: American Scientific Publishers.