Natural zeolites, fields of application in sectors of Colombian economy

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Abstract. In the present work, an analysis of the potential of natural zeolites for use in several economic sectors of Colombian territory has been made. Initially, the role played by this mineral in the economies of countries that have zeolite deposits is described. Subsequently the applications of this mineral in fields such as agriculture, animal feed, environmental remediation, chemical synthesis, gas separation, ceramic materials, among many others are reviewed. Based on that review, certain sectors of the Colombian economy were selected. The basis of the selection was the benefits that the use of zeolites could bring to them. The analysis carried out established that relevant environmental benefits in the air, soil, and water components can be obtained by using natural zeolites in sectors such as the mining and textile industries, and companies that use high temperature combustion processes (higher risk of generating nitrogen, NOx). On the other hand, the implementation of the use of natural zeolites could favourably affect the agricultural sector by generating savings in fertilizers, improvements in animal health, and a faster weight gain in poultry, swine, and cattle for meat.

1. Introduction
Zeolites are a group of minerals that are part of the group of the tectosilicates according to the mineralogical classification of Strunz [1]. Chemically, they are aluminosilicates of alkaline and alkaline earth elements of hydrated character [2]. These minerals can be found in igneous, metamorphic and sedimentary environments. However, it is in this latter geological environment that the deposits with the highest concentration of zeolite minerals have been found [2]. 67 types of natural zeolite families have been recognized by the International Zeolite Association (IZA). Heulandite, clinoptilolite, mordenite, analcime, and chabazite phases are the most recognized natural zeolites in the literature [3-5].

Physically, zeolites can be considered as microporous materials, which, due to their particular structure, possess properties that make them a strategic material for today's societal development. These properties allow zeolites to act as adsorbents and as filters, exchange cations, and even serve as catalysts in important chemical reactions like oil cracking [3-4].

Although zeolites have been known for more than 100 years, their technological potential hardly spread until the 1930s, due to their cation exchange properties and their hydrophilic character [6]. Nowadays there is a great variety of applications of this mineral and its homologous synthetic zeolites. Zeolite have been able to achieve high commercial values according to their field of application and the level of treatment received [7]. The monitoring carried out by the bibliographical tool, ‘Scopus’ shows that countries such as Cuba, Japan, Bulgaria, Mexico, Iran, Italy, the United States, China, and Turkey
have carried out important technological developments regarding for the use of this mineral that is available in their territory.

Although zeolites are not as abundant as other groups of aluminosilicate minerals around the world, it has been shown that in many of the "Andean" countries (territories where the Andes mountain range is located) that have presented historical phenomena of volcanism, there is evidence of the presence of zeolite minerals. Countries such as Argentina, Chile, Ecuador, and Mexico have reported the existence of this mineral in their territory and are currently taking advantage of it [2], [8-10]. In the Colombian case, there was no knowledge of the presence of natural zeolites until a few years ago. Recent studies have shown that the region between the central and western mountain range has the potential to find this type of mineral deposit [11].

Following this last event, it is interesting to inform the community about the benefits that the use of this type of material would bring in many of the processes that are carried out day by day throughout the Colombian territory, so that it contributes to massify the use of the mineral in the country.

2. Methodological aspects
For the initial analysis performed, a number of publications associated with the application of natural zeolites were reviewed. This included publications from different databases, libraries, institutional documents of Colombian entities and bibliographic managers such as Scopus, Science direct, Springer, Schoolar, Web of Science, Latindex and Scielo. After this process was carried out, the authors proceeded to choose those cases that could be applied any of the existing representative economic sectors in the Colombian territory. For each selected application, there was a discussion about the advantages of its implementation.

3. Results and discussion

3.1. Zeolites: A strategic mineral for the development of territories
Natural zeolites are crystalline aluminosilicate materials formed by the three-dimensional combination of tetrahedra of the TO$_4$ form (where T in most cases is aluminum or silicon) [11]. The generic mineralogical formula for the ore is M$^{m+n/n}n Si_{1-n}Al_nO_{2n} nH_2O$, where M represents the type of compensation cation that in most cases is Na$^+$, K$^+$, Mg$^{2+}$ y Ca$^{2+}$ [11]. Since Mc Bain discovered in 1932 that dehydrated zeolites have the capacity to selectively absorb certain types of compounds [12], the study and development of applications of this class of materials has increased significantly as evidenced by publication trends (consult in Scopus, June 2018) presented in Figure 1.

![Figure 1. Evolution of scientific research in the field of zeolites.](image)

Figure 1 shows how interest in the study of this class of materials has increased. There has been a notoriously significant increase, since the 1950s, in the number of publications that have been generated,
from no more than 3 publications per year before the 1950s to nearly 2000 publications in the years after 2010. This highlights the relevance of the study of these materials for the present day society. Complementary to this, the bibliographic manager Scopus allows us to know the evolution of the patents associated to the particular subject, enabling us to understand important data. For example, for the decade of 1920 there was only an average of 24 patents per year and at present this number is close to 14000 patents per year.

The main countries that lead the research in this area (according to the Scopus tool) are China, the United States, Japan, Germany, France, Russia, the United Kingdom, Spain, and South Korea. It can be seen that all these countries are among the most developed economies in the world [13]. The main fields of study of zeolites are associated with the chemistry sector and chemical engineering, materials engineering, environment, and energy production, that is to say in work areas that generate products of great added value. The industries with the highest number of patents are associated with the chemical and petrochemical industry with recognized organizations such as Mobil Oil Corporation, BASF Corporation, Chevron Corporation, and Union Carbide Corporation in accordance with the revision made in the Patents domain.

Regarding market issues, it is divided into four groups: detergents, adsorbents, catalysts and others [14]. Flaningen [15] highlights that synthetic zeolites dominate the market due to their application in detergents, catalysts, and adsorbents while in the case of natural zeolites their applications are very varied, but it stands out in the production of cements and fertilizers, China being the main producer of this group of minerals. The prices of zeolites are varied and they depend on the application and the treatment received. Synthetic zeolites are by far the most expensive. Applications in catalysis can cost between 3.0 to 20.0 USD per kilogram; in the case of applications such as adsorbents between 5.0 and 9.0 USD per kilogram, and about 2.0 USD for applications such as cation exchangers in detergents. In the case of natural zeolites, their price can vary depending on the degree of purity of the mineral, the type of phase present, and the treatments received. The price per kilogram can vary between 0.05 and 3.5 USD [7, 16]. If the lowest reported level is taken as a comparison point, it could be affirmed that a ton of low quality natural zeolite with little treatment has the same commercial value as a ton of mineral coal in the Colombian market, with the advantage that, unlike the price of mineral coal, the price of the zeolite is not influenced by the international price of petroleum. Now in the case of having a material enriched in zeolite and with interesting technological properties of use, its commercial price could reach 5 times or more the commercial value of a ton of mineral coal. This last aspect highlights the importance of conducting geological / mining studies in order to find mineral deposits that can be exploited in the Colombian territory.

3.2. Possible applications of natural zeolites in Colombian economic sectors

The literature consulted has shown a large number of studies that reveal the potential of mineral in engineering applications [11]. Separation of gases from their properties of molecular sieve and absorption, drying of gases from the hydrophilic character of the zeolites, removal of dyes from their adsorbent capacity; chemical treatments due to their catalytic potential highlighting the catalytic reduction of nitrogen oxides, cracking of plastic waste, catalytic pyrolysis of biomass to obtain added value chemical products, elimination of dye by advanced oxidation processes in liquid medium; use of cation exchange properties for capturing polluting ions in aqueous media (mining, industry, domestic water) such as NH₄⁺, Pb²⁺, Cu⁺², Fe⁺³, Cr⁺³, Co⁺²⁺ Cu⁺²⁺, Zn⁺², Ni⁺²⁺, Hg⁺²⁺, Cd⁺²⁺ and for the softening of hard waters. Due to its pozzolanic activity, the natural zeolite has shown applicability in the cement industry. Likewise for its high content of alkaline elements (Na and K), it has played an important role in the ceramic industry as these elements allow to reduce the cooking temperatures. Thanks to the combination of adsorbent properties and cation exchange, the material has made very significant advances in agriculture. Its application in fertilizers has increased the yield and quality of crops; similarly, its use in the feeding of cattle, swine, poultry, and aquaculture has shown significant improvements in the growth and fattening of these species [11].
Advanced applications that include the functionalization of the mineral (addition of reactive functional groups and ions to the structure of the zeolite) has led to the application of zeolites in the field of human and animal health, highlighting their viability as antidiarrheals, antacids, antibacterial, their use in water filters and as carriers-releasers of active phases. Similarly, they have been useful in the manufacture of vapor and explosive sensors, the production of carbon nanotubes on its surface, or the production of nanoparticles inside the ore channels [11].

Due to this wide range of possibilities of the use of natural zeolites, specific economic sectors which could be impacted by their use, have been analysed in this document.

3.2.1. Agriculture. This sector plays an important role in Colombian economy [17]. It is the main source of income for the rural population, a source of foreign exchange through exports of products such as coffee, flowers, and bananas, and it also plays an important role in terms of food security through the production of rice, potatoes, corn, oilseeds, sugar, and panela cane [18]. Although there are different varieties of soil for cultivation in the Colombian territory, many of them require conditioning to be used in agriculture [19]. For example, soil type 7, which is the most prevalent in the country (36.1%), is very vulnerable to degradation either by slope or because a high risk of erosion in present; a fact that brings limitations for the development of agriculture. In the same way soils type 4 that are of low fertility, occupy 12.7% of the territory and predominates in the departments of Magdalena, Sucre and Córdoba, and require intervention to be able to serve for agricultural activity. In addition, the effects of climate change play an important role in the cultivation processes, excessive rains or droughts can significantly affect crop yields. Agricultural management practices are necessary to counteract these situations. This is where natural zeolites come into play. Due to the properties of water retention by adsorption, high surface area, selective cation exchange and controlled release of previously adsorbed aqueous phase nutrients natural zeolite is a suitable material to be used in agriculture along with traditional fertilizers. Different studies in rice, tomato and corn crops have demonstrated the potential of zeolites to improve crop yields or to reduce fertilizer consumption [20-22]. The greater retention of ammonium and potassium ions, as well as their capacity to act as a reservoir of humidity, are the most outstanding aspects of these investigations regarding cultivation. On the other hand, there is the environmental factor that comes into play. The zeolite through its retention capacity, its use in crops on slope as the Colombian case would lead to the reduction of pollution by the use of synthetic fertilizers such as urea and diammonium phosphate (DAP), especially in rainy seasons.

3.2.2. Animal production. Raising cattle is an essential part of Colombian economy, cattle breeding, pigs, poultry, and aquaculture are notorious throughout the territory. Different studies reported in the literature have shown that the addition of natural zeolite can improve the growth process, livestock fattening, animal health and reduction of odors generated by excrement [23-26]. In the case of the poultry sector, the regions of Cundinamarca, Valle, Antioquia, Santander, and Norte de Santander stand out for the existence of farms dedicated to the fattening and production of eggs. The use of natural zeolite could bring important benefits for producers. The most important one of these benefits, according to the studies carried out is associated with savings in the consumption of the concentrate used as fodder, since with the addition of natural zeolite it is possible to retain a greater amount of nutrients within the organism of the animal. Thanks to the adsorption properties of ore, these nutrients seem to be released in a controlled manner improving the growth and fattening process of poultry. Although there are contradictory results, the literature also emphasizes that the addition of natural zeolite can favor the quality of the eggshell, bringing with it minor losses at the time of transportation to the final consumer. On the other hand, there is the application of zeolite in beds or soils of the shed (chicken coop). Studies have shown that its use aids in reducing odors and soil moisture, bringing with it a healthier environment for poultry production. In relation to the pork sector whose production excels in Antioquia and the region of the “Eje Cafetero”, the use of natural zeolite could bring improvements in weight gain thanks to the adsorptive capacity already described, but studies have also shown that its use in the food diet leads to reduce health problems in pigs, especially the respiratory problems that usually appear in this type of
livestock. Regarding cattle, the results found in the literature show improvements in weight gain; this fact could be of interest to those producers who are dedicated to raising cattle for meat.

3.2.3. Mining sector. The mining industry represents a significant fraction of Colombia's GDP [17]. Many of the mining processes bring with them the formation of "acid waters" and tailings rich in trace elements of a contaminating nature such as cadmium, lead, chromium, zinc, copper, nickel, barium, among others. The coal mines throughout the country are generating acid waters due to the presence of pyrite inside the coal deposits. The obtaining of metals such as nickel in Córdoba region and iron in Boyacá region, despite being technician, leave some waste and discarding material which is usually disposed in landfills for this purpose, where it may be possible to drag traces of pollutants as a result of rains. In gold and silver mining (Antioquia, Caldas, Chocó and Santander regions) the tailings of the process may contain contaminants (lead, copper and zinc) that are not treated in the treatment plants established by the mining companies due to their low concentration. The copper extraction in Carmen de Atrato (Chocó) and zinc in Junín (Cundinamarca region) could also present a similar behavior. In the field of non-metallic minerals, the exploitation of barite (barium sulphate) in the department of Norte de Santander and Santander could be an opportunity for the use of zeolite in order to control the concentration of barium in the leaches that are formed during its extraction. These polluting elements present in aqueous medium can be eliminated using natural zeolites of high cation exchange capacity. Different works [27-28] have demonstrated the effectiveness of the material to remove ions in solution, although it is important to clarify that in order to achieve efficiency and durability of the materials in the process, it is necessary to study each body of water in order to design the work system, especially in those shedders with high turbidity as those appreciated in some gold processing plants.

3.2.4. Textile industry and clothing. This sector has been relevant for the Colombian economy, although it has gone through ups and downs in recent years. The centers of attention within the value chain in this work are the companies which carry out cloth dyeing activities including industrial laundries. These companies are characterized by the generation of aqueous waste with a high dye load that must be eliminated before being poured into the sewer system. Although companies use different systems to capture dye waste, these are usually selective for some types of dyes or very expensive to implement. The literature consulted shows that the implementation of capture systems from zeolites can become a viable option for these companies [29-30]. Dyes such as orange and violet methyl, methylene blue, azo yellow dye 125, acid red azoic 114 and rhodamine have been some of the compounds that have been removed or degraded to less polluting phases from the adsorption and catalytic properties of the natural zeolite. As in the mining sector, a detailed study of the effluents is necessary for the design of the disposal system.

3.2.5. Combustion processes in fixed sources. The combustion gases emissions from anthropic processes have been identified as those responsible for the greenhouse effect and the production of other negative effects such as the formation of acid rain, photochemical smog and respiratory diseases [31]. Among the gases that are emitted into the atmosphere in combustion processes, nitrogen oxides stand out for its ability to form photochemical smog and acid rain. Therefore, it requires to be controlled by the environmental authorities. In Colombian territory, resolution 909 of 2008 established rigorous standards that obligate companies to reduce the concentration of these types of pollutants in their atmospheric emissions. The use of mineral coal rich in heteroatoms (especially nitrogen and sulfur), old technology in the combustion chambers, and the requirement of high temperature in the manufacturing process mean that compliance with these permissible emission limits through preventive methods is unlikely. Cases such as the brick industry (especially in Norte de Santander), glassmaking, cement, coking, foundries and incinerators can present legal problems with entities that are concerned with environmental control. Post-combustion mitigation activities could solve the problem of nitrogen oxides in these companies. The catalytic processes are one of the possible alternatives to achieve the reduction of nitrogen oxides at a moderate cost. However, it has been shown that many of the available alternatives
(commercial catalysts) are only effective at temperatures of combustion gases lower than 350 °C, with low levels of humidity and sulfur compounds. Under this somewhat dark picture, natural zeolites appear as a viable alternative for companies that have gaseous emissions above 300 °C as some brickmaking companies. This material can tolerate some degree of humidity and presence of sulfur compounds without significant decrease of the catalytic conversion. The review of the literature shows that zeolitic phases such as mordenite, chabazite and clinoptilolite, which have the presence of iron or copper in their composition, have shown high performance results for the abatement of NO, NO₂ and N₂O [31]. As with the other applications it is necessary to perform detailed studies to undertake their implementation. For example, it is important to recognize the presence of other gaseous phases and/or particulate matter that could deactivate the catalyst or the need for some additional reducing agent such as urea, ammonia or hydrocarbons.

4. Conclusion
In the present work, the objective was to document the importance of zeolites as a strategic material for the development of the territories. We have highlighted the versatility of applications, the scientific interest in their study and the commercial value that this kind of material can have compared to other mining resources. The ultimate goal is to awaken the interest of the academic and business community towards the use of these materials in Colombian territory. From the range of possibilities described, a discussion was held on some economic sectors in Colombia where the use of natural zeolites could solve some of their problems, generate savings in supplies and time, as well as possibly increases in production levels in the agricultural sector.

Acknowledgment
The authors appreciate the support given by Universidad Libre for the development of this work. J F Gelves thanks the Administrative Department of Science, Technology and Innovation of Colombia "Colciencias" for the financial support granted during their doctoral training.

References
[1] Strunz H and Nickel E 2001 Strunz mineralogical tables: Chemical-structural mineral classification system (Stuttgart: Schweizerbart)
[2] Tchernich R 1992 Zeolites of the world (Phoenix: Geoscience Press, Inc)
[3] Sersale R 1985 Studies in Surface Science and Catalysis 24 503-512
[4] Colella C 2005 Studies in Surface Science and Catalysis 157 13-40
[5] Iijima A 1980 Pure and Applied Chemistry 52 2115—2130
[6] Vizzanio B 1998 Identificación y caracterización de la zeolita natural tipo clinoptilolita (Monterrey: Universidad Autónoma de Nuevo León)
[7] Kulpratipanana S 2010 Zeolites in industrial separation and catalysis (Weinheim:John Wiley & Sons)
[8] Ostrooumov M, Cappelletti P and Gennaro R 2012 Applied Clay Science 55 27–35
[9] Rodriguez Fuentes G and Rodriguez Iznaga I 2009 Revista Cubana de Física 26 55-60
[10] Vattuone M E, Leal P R, Crosta S, Berbeglia Y, Gallegos E and Martinez Dopico C 2008 Revista mexicana de ciencias geológicas 25 483-493
[11] Gelves J. F 2017 Zeolitas naturales colombianas de la formación Cobia, municipio de La Pintada: mineralogía, caracterización y aplicaciones (Medellín: Universidad Nacional de Colombia Sede Medellín)
[12] Calderón M 2004 Mineralogia, petrografía y química de las rocas volcánicas zeolitizadas del estado de Oaxaca: Implicación económica (México D.F: Instituto Politécnico Nacional)
[13] Dabat Latrubesse, A and Leaf Villegas, P. H 2013 El cotidiano 177 17-28
[14] Transparency market research 2014 Synthetic zeolite market for detergents, adsorbents, catalysts and catalysts and other applications-Global industry analysis, size, share, growth, trends and forecast 2014–2020 (New York: Transparency market research)
[15] Flanigen E, Broach R, and Wilson S 2010 Zeolites in industrial separation and catalysis (Weinheim: Wiley-VCH)
[16] Davis S and Inoguchi Y 2009 CEH marketing research report: zeolites (Menlo Park: SRI Consulting)
[17] Cárdenas S, B 2011 Sociedad y Economía 20 99-124
[18] Machado A and Montañés G 2002 Desarrollo rural y seguridad alimentaria un reto para Colombia
Bogotá: Universidad Nacional de Colombia

[19] Instituto Geográfico Agustín Codazzi IGAC 2017 Las 8 clases de suelos que tiene Colombia y para qué sirven Consulted on: https://noticias.igac.gov.co/en/contenido/colombia-un-pais-con-una-diversidad-de-suelos-ignorada-y-desperdiciada

[20] De Campos Bernardi A, Olivera P, De Melo Monte M and Souza F 2013 Microporous and Mesoporous Materials 167 16–21

[21] Quilambaqui M, Morante F and Bajaña D 2006 Uso de las zeolitas naturales del bloque tecnológico experimental de la zeolita (BTEZ) de la espol y su efecto en el rendimiento de cultivo de maíz X congreso ecuatoriano de la ciencia del suelo

[22] Villarreal J, Barahona L and Castillo O 2015 Agron. Mesoam. 26 315-321

[23] Karamanlis X, Portomaris P, Arsenos G and Kamarianos A 2008 Asian-Aust. J. Anim. Sci. 21 1642–1650

[24] Arguello B, Trujillo R, Elizondo R, Garcia E and Martínez F 2011 Agraria Nueva Época 8 25-30

[25] Öztürk E, Erener G and Sarica M 1998 Tr. J. of Agriculture and Forestry 22 623-628

[26] Pulido R G and Fehring A 2004 Arch. Med. Vet. 36 197-201

[27] Erdem E, Karapinar N and Dona R 2004 J. Colloid Interface Sci. 280 309–314

[28] Panagiotis Misaelides 2011 Microporous Mesoporous Mater. 144 15–18

[29] Valdés H, Tardon R and Zaror C 2009 Ingeniare Revista chilena de ingeniería 17 360-364

[30] Galicia G 2011 Remoción de un colorante de los efluentes de la industria textil mediante adsorción en una zeolita natural (Mexico D.F :Universidad Autónoma metropolitana U. Iztapalapa)

[31] Roy S, Hegde M S and Madras G 2009 Applied Energy 86 2283-2297