

A Synopsis of the Polyvalent Qualities of Zeolite-Clinoptilolite and the Proposed Uses Within the Namibian Medical, Pharmaceutical, Industrial and Economical Sectors: A Proposal for an Integrated Research.

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Abstract

Zeolites are crystalline hydrated aluminosilicates of the alkaline and alkaline-earth-metals with unique properties in cation exchange, adsorption and catalysis. Due to these properties they have been increasingly used in a wide range of applications in industry, environmental protection, agriculture, animal production, veterinary- and human medicine. Their increasing integration in the health sector worldwide with recognized efficacy based on scientific researches, clinical trials and personnel experience of many therapists encouraged the author to write this review. Clinoptilolite, one of the natural zeolites, offers a variety of well documented appliances as medical drug for internal and external use in addition to its utilization as growth promoter in animal feed, potent binder of heavy metals and radionuclides along with ammonium exploited in industries, and the use in filter systems for waste water clearance and building and construction material. Since Namibia provides the climate and geological conditions for deposits containing abundant zeolite, it is worth to look at the options for an efficient exploitation. This could open new markets for the national as well as the international trade.

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The utilization of zeolites within the fields described in this article would offer inexpensive alternatives to cover some shortfalls in the domains of agriculture, building and construction, environment protection and public health. One objective of this literature study is to explore interdisciplinary cooperative efforts to integrate various available information and reports regarding this multipurpose zeolite material in the activities of Namibian educational and research institutions. Several starting points are addressed particularly in the fields of agriculture, animal sciences, pharmacy and human medicine, how natural zeolites could be incorporated into or combined with existing concepts respectively would contribute to develop new strategies, emphasizing the health sector.

Keywords: Clinoptilolite, applications, resource, health sector, Namibia, zeolite

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1 Introduction

Zeolites are natural crystalline aluminosilicates, deriving from altered volcanic ash in lake and/or salt water. The distribution of zeolitic rocks is usually closely located to the site of volcanism (Iijima 1980). Zeolite minerals were first identified by the Swedish mineralogist Fredrik Cronstedt in 1756, who observed the boiling and frothing of zeolites when heated before the blowpipe. Therefore he named the mineral from the Greek words 'zeolites' meaning 'boiling stones'.

But it was only in the 1950's that their broad potential for multiple uses in industry and agriculture was discovered and exploited (Diale 2011). Clinoptilolite being a natural zeolite is composed of a microporous, corner-sharing arrangement of hydrated silica and alumina tetrahedra [SiO_4 and AlO_3], joined into three-dimensional frameworks conferring a cage-like structure to the mineral. This crystal lattice forms canals of an average diameter of 0.4 nm, filled with ions and crystal water.

The zeolite configuration stems from volcanic lava and ash expelled during eruptions millions of years ago and falling into the sea or lakes, then amalgamating with the colloidal, boiling [sea]water. Zeolite is assumed to contain in traces most of the elements of the periodic table from which at least 34 minerals have yet been detected (Hecht and Hecht-Savoley 2005, 2007).

Inside the solid silicon and aluminum tetrahedra network-like lattices, cations like calcium, magnesium, potassium, sodium and others are bound, together with crystal water [no free H_2O] (Hecht 2005, 2007; Polat 2004). In zeolite structures some of the quadrivalent silicon is replaced by trivalent aluminum, giving rise to a deficiency of positive charge. The resulting negative charge is balanced by weakly bonded alkali and alkaline earth ions. Al-

kali elements are those classed in the first group of the periodic system whereas alkaline earth elements are grouped under the second one. The elements of the first group have one electron only in their outer shell that is readily given up in order to obtain noble gas configuration. The elements of the second group possess two electrons in the outer shell, which make them react a tiny bit slower. The electrons of the outer shell of these elements can easily be removed and exchanged by other cations from the environment (Mumpton 1977). This property is called 'cation-exchange capacity' [CEC] and is widely utilized for industrial and medical purposes (Mumpton 1999). Zeolite ion exchange capability is for example exploited in the development of portable, regenerable haemodialysis apparatus' systems for the dialysate regeneration, since ammonia removal from a recirculating dialysate stream is a major challenge (Patzer et al. 1995). In addition the mineral is used in some anaesthesia devices for the adsorption of the most applied anaesthetic gases (sevoflurane, isoflurane and desflurane) (Lass-Seyoum et al. without year). By using a zeolite reflector integrated within an anaesthesia circle system, isoflurane consumption can be significantly reduced (Perhag et al. 2000). Zeolites can also be administered efficiently as an oral contrast agent for magnetic resonance imaging (Young et al. 1995).

Other paramount characteristics are attractive adsorption, dehydration-rehydration, molecular sieve and catalysis function in industries. The adsorption quality is chiefly attributed to the silica. Since natural zeolites are very rich on SiO_4 , they present an average distribution of aluminum to silica of 1:4 to 1:8, hence a fairly high adsorptive potential (Hecht and Hecht-Savoley 2005, 2007). Adsorption potential e.g. is used in industry, agriculture and medicine to bind harmful positively charged molecules, gases and toxins.

The capacity to lose and gain water reversibly plays a role for drying systems and water removal in the industry. The molecular sieve function is due to the lattice-structure and the high internal surface [up to several hundred square meters per gram] allowing only a certain range of molecules to pass. This and the related catalyst qualities are exploited e.g. for petroleum refining in petrochemical industry (Virta 2001).

All these properties are utilized in many different ways in the above mentioned fields as well as in construction, environmental protection, veterinary medicine, animal production and increasingly in human medicine. Globally naturally occurring zeolites for example are used for applications like the removal of caesium [Cs] and strontium [Sr] from nuclear waste and fallout, water and waste water treatment, soil amendment and water retention in arid zones, animal nutrition, animal-waste treatment and aquaculture (Mumpton 1999). The literature about the properties and utilization of natural and synthetic zeolites is abundant and easily to access. This review however intends to make some suggestions for an approach to this topic and the introduction of this interesting and promising natural material in Namibian economic and health concepts. Namibia's varied geology encompasses sedimentary and volcanic rocks all over the country and chances are that this potential of exploitation has not

yet been fully studied and taken in account.

2 Methods

To conduct this exploratory literature review, a number of research engines were used including: Pubmed, Science Direct, and Google Scholar. These web sites were searched between May 2013 and June 2013, however the range of the search went back to the 1977 when the qualities of this mineral became more evident and the scope of exploitation was broadened. Since the existing literature spans a vast range of research relating to zeolite, search terms were limited in order to provide the basic information about the mineral, mention examples of its utilization, describe scientific studies done in different disciplines, seek for applicability to Namibia and to conclude with some ideas for an integrated research in Namibia. Search terms used were: zeolite, clinoptilolite, Namibia. Limitations were then specified, for example, "in medicine". Articles or links from journals, magazines and periodicals of relevance were located. Literature that has already been gathered by the researcher was also included in the review as well as articles identified from the reference lists of relevant articles.

3 Results

3.1 Zeolites in industry and water/waste-water treatment

The use of zeolites in these domains is the topic of innumerable articles, reports and research. For instance, combining the key word 'zeolite' (scholar.google.com) with the following search terms, produced high quantities of articles: waste-water: 19,000; catalyst: 310,000; gas separation: 131,000; removal of heavy metals: 42,600; water treatment: 301,000. Examples of the application of zeolites include their use as catalysts promoting a diverse range of chemical reactions, including acid-base reactions, gas separation due to their porous molecular structure, collection of gases or to control odours, and the use as detergents and soap. Additional examples are the defluorination of industrial waste, removal of heavy metals such as mercury and lead from waste, ammonium removal and copper recovery as well as the neutralization of acid waste and clean-up of sewerage (Polat 2004; Virta 2001).

Large-scale cation-exchanging zeolite-systems are used in water and wastewater treatment, extracting from municipal, industrial and agricultural waste streams for example am-

monium [NH₄⁺], arsenic, heavy and radioactive metals as well as phenols from dyes of textile and leather industries and pesticides plus several other harmful organic molecules. Because of its high selectivity for ammonium ion, some heavy metals and radionuclides, Clinoptilolite has become the major natural zeolite used in [waste] water purification practice (Shoumkova 2011).

Nitrification of sludge can be accelerated by addition of zeolite-clinoptilolite, which selectively exchanges NH₄⁺ from waste water and provides an ideal growth medium for nitrifying bacteria, which then oxidize NH₄⁺ to nitrate. That way treated sludge can be used as fertilizer (Mumpton 1999).

In the rural areas of Namibia where the issues of clean water supply and waste water treatment are often difficultly to solve, the applicability of simple zeolite techniques might be worth exploring (Shoumkova 2011).

3.2 Zeolites as building and construction material

Examples of use of zeolites in building and construction include cement and brick production, light-weight building materials and the use of zeolite buffer qualities. The high silica content neutralizes excess lime produced by setting concrete, as such contributing to a higher stability and durability. The porous structure helps to moderate water content, allowing for slower drying and improvement of break strength (Dipayan 2007). Zeolites have been used as light-weight dimension stones for 2000 years because of their low bulk density, high porosity and close-knit structure. They are easily sawn or cut into inexpensive building blocks. This building material does not crumble in arid climates (Mumpton 1999; Virta 2001). Natural and synthetic zeolites are also used as an additive in the production process of asphalt concrete, lowering the temperature during manufacture (Dipayan 2007).

It has been reported that generally in countries mining large tonnages of zeolites, the ready availability of this mineral at low cost and a shortage of competing minerals may lead to a large scale use of zeolite as substitution for other materials. It is also assumed that a significant percentage of the material sold in some countries as zeolite might be more realistically ground or sawn volcanic tuff containing only a small amount of zeolites (Virta 2001). Obviously the material used suffices for the purpose of building, road construction and soil conditioning. It might be concluded that even a less pure quality of zeolite or volcanic mineral could meet the basic needs of construction. Into the context of Namibia, this could suggest that a potential mine does not need to deliver an absolute pure composition of a natural zeolite intended for building and construction. Thus it seems advisable to look at the geological conditions of the volcanic regions under the aspect of mineable zeolites.

3.3 Geological conditions for zeolites in Namibia

Zeolitic rocks are found all over the world. Volcanism and semi-arid climate create the geological situations of the alkaline, saline lake deposits containing abundant zeolite (Iijima 1980). The Rift Valley in South Africa is one example as well as regions in China, Japan, Russia, Turkey, Hungary, Bulgaria, Slovakia, Greece, Australia, New Zealand, Canada, North- and South America, Cuba (Virta 2001). Zeolite formation is observed at or near to the earth's surface allowing open pit mining. Deep-sea sediments are also exploited by drilling projects in some countries (Iijima 1980).

Sedimentary and volcanic rocks occur all over Namibia, for example, in the Aranos, Huab and Waterberg Basins [the southeastern and northwestern parts of the country], the volcanic Orange River Group in the south, the volcano-sedimentary Khoabendus Group and Rehoboth Sequence in the center of Namibia (Regional Geoscience Division-Ministry of Mines and Energy 2006). Therefore the geological requirements for the development of zeolite deposits over millions of years appear to be distinctly favorable.

No reports however have been found about exploitation and mining of zeolite minerals in Namibia. Most reports merely mention zeolites and/or clinoptilolite in the context of other research objectives, for instance stating that in a certain mineral analysis the presence of zeolites attests to strong deviations from the average pH range towards more alkaline conditions (Dill et al., 2013), or that within the calcrete layers of the Kalahari released silica precipitated under saline conditions to clinoptilolite (Watts 1980).

Within the technical cooperation project "Groundwater for the North of Namibia" clinoptilolite material were found in one explorative drilling at the depth of 105m (Dill et al. 2012). This only being a by-result of another study, but indicating the ready availability of this mineral.

Under the light of these findings further studies could be carried out with the goal to identify mineable zeolite-clinoptilolite deposits and to determine their quality and composition (Zeolite Data Sheet, without year; Material Safety Data Sheet, without year). This topic could be for example proposed to the Department of Geology of UNAM.

3.4 Production and health risks

The mineral is judged to be easily mineable, conventionally by open pit mining techniques (Virta 2001). It is considered to be safe in terms of contamination of the environment and health impairment. The single health hazards indicated are airborne particles, irritating to the

respiratory tract and the eyes. Clinoptilolite with a particle size in the respirable range was tested for carcinogenicity in rats, however no significant increase in incidence of tumors was found (Material Safety Data Sheet, without year). Valid control measures are the wearing of dust respirators [masks] and safety glasses, optionally protective gloves. Neither dangerous decomposition nor hazardous polymerization will occur (Zeolite Data Sheet, without year; Material Safety Data Sheet, without year).

3.5 Use of zeolites as radionuclide binder

The selectivity of zeolites for radionuclides such as caesium and strontium is exploited in the atomic industries. After the clearance of low-level waste streams of nuclear reactors and leaking repositories from ¹³⁷caesium and ⁹⁰strontium, the saturated zeolite is then transformed into concrete, glass or ceramic bodies and stored (Dyer and Keir 1984).

Zeolite processes are utilized to counteract the water contamination and fallout from nuclear test and accidents (Mumpton, 1999; Natural Cellular Defense Overview 2005-1012). Addition of zeolites to soils may reduce the uptake of ¹³⁷caesium by plants up to a factor of 8, as demonstrated by Swedish researchers (Shenbar and Johanson 1992). Other Swedish scientists showed that a zeolite supplemented diet fed to reindeers reduced the accumulation as well as increased the excretion of ¹³⁷caesium ingested with contaminated lichen by Chernobyl fallout (Ahman et al. 1990). It has also been shown conclusively that zeolites can reduce both the uptake and the body burden of radio-caesium by goats and lambs (Forberg et al. 1989).

The effect of a natural clinoptilolite modified by hexacyanoferrate [Radekont[®]] on ¹³⁷caesium uptake into broiler meat was tested when the animals were fed on wheat contaminated by the Chernobyl fallout. The outcome illustrated an enhanced clearance of body tissue and a decrease of biological half-life of ¹³⁷caesium to less than one day (Poeschl and Balas 1999). A German study carried out on mice proved successfully the efficiency in acceleration of excretion and decrease of body burden of caesium chloride [CsCl] by a medical product based on modified clinoptilolite [froximun[®]toxaprevent pure] (Fuetterungsstudie an Maeusen mit froximun toxaprevent pure 2012).

To date, Namibia has not been exposed to the extreme repercussions of Ukrainian [1986] or more recently [2010] Japanese nuclear disasters. Nonetheless there are the imminent issues of uranium mining and milling with the resulting negative impacts of environmental contamination and health hazards for mine workers and close-by inhabitants (The impact of uranium mining in Africa 2013).

Although uranium is a naturally occurring element on our planet [about 40 times as abun-

dant as silver], its derivatives and decay products are recognized as being harmful. Uranium itself is relatively weakly radioactive, but yet a toxic heavy metal ('uranium', Columbia Electronic Encyclopedia, 2013). However the daughter products such as radon, a radioactive inert gas, and uranyl ions are released to the atmosphere and in the water in small quantities when the ore is mined and crushed (Uranium Institute of The Chamber of Mines of Namibia 2012). These substances can cause serious health risks since they are easily inhaled respectively ingested. Under standard environmental conditions uranium typically occurs as the aqueous uranyl cation (UO₂)²⁺ being attracted by and adsorbed to the negatively charged zeolite (Matijasevic et al. 2006). Accordingly the adsorptive and CEC qualities, zeolites have been proved to effectively balance some of the harmful effects on human and animal health.

Study results from State University at New York and the Center for Nuclear Waste Regulatory Analysis, Texas demonstrated an important pH dependant sorption of uranyl ions on the zeolites montmorillonite and clinoptilolite (Reeder et al. 2001). Comparable findings were brought by Serbian researchers who saw efficient uranyl ion sorption on modified zeolites (Matijasevic et al. 2006). A similar pH and concentration dependent uranium(VI) adsorption on a natural zeolite was observed during an investigation of groundwater in New Mexico (Camacho et al. 2010).

In a Swedish study researchers could prove that radon gas was captured and retained by silver exchanged zeolites. The zeolites could be regenerated by heating and their radon capture ability restored (Hedstroem et al. 2012). As several medicine products based on activated clinoptilolite are already available on the international market (Natural Cellular Defense Overview 2005-2012; Poeschl and Balas 1999; Fuetterungsstudie an Maeusen mit froximun toxaprevent pure 2012), it should be considered to provide Namibian pharmacies and health institutions with some of these to prevent productively health damage caused by uranium mining practices. Since the University of Namibia includes a fully operating School of Pharmacy, research on this matter could be undertaken, be it with natural zeolites exploited in Namibia or imported ones for example from South Africa.

A 'Standard of Good Practice for Health, Environment and Radiation Safety and Security' (HERSS Standards), is published by the Chamber of Mines Uranium Institute. It claims to provide 'a practical basis for uranium exploitation or mining companies in Namibia to address Health, Environment and Radiation Safety and Security issues from a business perspective' (Uranium Institute of The Chamber of Mines of Namibia 2012). The proposed 'Occupational Health Programme' includes chiefly the components of health examination, surveillance of hygiene, supervision of working conditions and education (Uranium Institute of The Chamber of Mines of Namibia 2012).

It is one of the objectives of this review to add the health- and welfare perspective for

the 'human resources' to this programme by showing a few simple and inexpensive options for the prevention of greater health damage, for example by providing mine workers at time with zeolite medicine products.

The stakeholders could be approached in this question, given that the Uranium Institute states on its website that "the uranium industry has at its heart a simple but enduring principle, namely that those who create risk are best placed to control that risk, whether they are employers, contractors or managers" (Uranium Institute of The Chamber of Mines of Namibia 2012; <http://aeofnamibia.org./pdf/uranium-institute>, 2012). The University of Namibia could be included in this programme, offering research facilities and imparting expertise, notably the Schools of Medicine and Pharmacy.

3.6 Utilization of zeolites in agriculture

The first reported activities in zeo-agriculture meaning the use and application of zeolites for agricultural purposes-activities had been undertaken for fifty years in Japan where farmers used zeolite tuff from local deposits to sprinkle on farmyards and manure to control odor and moisture content and to increase the pH of acidic soils (Mumpton and Fishman 1977). The growing awareness of the abundance and availability of this inexpensive natural material all over the world opened a broad field for research, experimentations, applications and eventually new markets.

In agronomy zeolites are used as amendments for sandy, clay-poor soils as well as for sandy loams, leading to significant increases of crop yields (Mumpton 1999; Polat et al. 2004). Zeolite treated soil increases its activity for retention of main nutritional elements of mineral fertilizers such as NH_4^+ and K^+ . The selectivity for NH_4^+ and K^+ is exploited in the use of zeolites as slow-release fertilizers. Georgian studies demonstrated that under the impact of natural zeolites soil acidity decreases and an oxidation-reduction potential is established (Andronikashvili et al. 2007).

The same researchers described in 2007 the feasibility of restoring the fertility of overused, acid and depleted soils by the application of natural zeolites in compound with organic fertilizers. It could be a project for the UNAM Faculty of Agriculture to find out whether these methods are applicable to the overgrazed, dry and sandy areas of Namibia with the goal to regenerate and recover pasture land.

An in-depth investigation from 2002 about the availability of agrominerals in sub-Saharan Africa concludes that the best use of locally available and effective agrominerals for Namibia's crop production sector is limited to guano, which is rich in phosphates. The study advises the exploration to find nitrate resources in the coastal zones of the country (Straaten, Peter

van 2002). Instead of going so far, the exploitation of NH_4^+ saturated zeolites could offer a rather inexpensive alternative as described above for waste water purification and below the use of zeolites for animal waste handling.

Several methods for animal excrement treatment have been developed to inhibit the enzymatic and bacterial decomposition of droppings in order to gain an odorless, organic fertilizer rich on minerals and NH_4^+ . The gas adsorption capacity is used in malodor and moisture control of animal waste, especially in poultry houses and horse stables. This removes ammonia from the droppings and improves the general atmosphere, protecting the upper airways of the animals and preventing them from unnecessary irritation (Mumpton and Fishman 1977; Polat et al. 2004).

The technical feasibility and practicability of these proposals could be investigated and analyzed by projects of the Polytechnic of Namibia and the correspondent faculties of the University.

3.7 Application in animal nutrition and production

Experiments on the use of natural zeolites as dietary supplements for small and large livestock have been in progress for about fifty years. Significant increases in the gain of body weight and general health have been described, when $\leq 10\%$ clinoptilolite and mordenite were added to the normal diet of swine and poultry. The average daily gain (of weight) could be enhanced and also the feed conversion ratio markedly improved (Mumpton and Fishman 1977; Suchy et al. 2002; Papaioannou et al. 2006).

Apart from the improved performance traits, the excrements were less odiferous, the number and severity of intestinal diseases decreased (Mumpton 1999; Mumpton and Fishman 1977). The animals were better protected against mycotoxins since clinoptilolite and other zeolites have capacities to bind feed contaminating aflatoxins.

The positive effects of zeolite mineral are attributed to its ability to bind ammonium, toxins of lower molecular weight, the adsorption and inactivation of *Escherichia coli* enterotoxin (Ramu et al. 1997), the regulation of excess water through effects on osmotic pressure, the exchange of the constituent alkali and alkaline-earth cations with harmful metals without major change of their structure and generally the buffering qualities (Norouzian et al. 2010). All this allowed a higher and more efficient utilization of nutrients, protecting the intestinal lining and providing appropriate living conditions to the necessary intestinal microbial flora. A study conducted over one year with pigs showed that the number of gastric ulcers, pneumonia and heart dilation dropped significantly (Papaioannou et al. 2004). Similar results were found in a study carried out with broiler chickens, where apart from the weight

gain none of the zeolite-fed birds died, different to the control groups of normally fed and antibiotic supplemented chickens (Mumpton and Fishman 1977).

The mortality of zeolite supplemented animals decreased in practically all experiments compared to their control groups. Natural zeolites and particularly clinoptilolite have been proven successful in the upgrading of feeding parameters in animal production in addition to an overall enhancement of animal health conditions. In the post-antibiotic era of antibiotic resistance and the overuse of antibiotics as growth promoters the application of natural zeolites should be considered as a valid alternative. This imperative matter could be surveyed for example by the Namibian School of Pharmacy in cooperation with the Faculty of Agriculture, Department Animal Sciences. Besides the above mentioned outcomes much more effects of zeolite-clinoptilolite in animal sciences have been explored in plentiful experiments carried out all over the world and described by numerous researchers. Iranian researchers looked at the effects of clinoptilolite supplemented diet on the performance and health of newborn lambs and found a significantly higher daily gain of weight and reduced incidence, severity and duration of diarrhea (Norouzian et al. 2010). Greek scientists saw significantly lower cases of clinical ketosis during the first month after calving and a higher total milk yield in cows fed on a ration supplemented with 2.5% clinoptilolite (Katsoulos et al. 2006).

A German Inaugural Dissertation from 2010 (Grabherr 2010) dealing with the influence of zeolite A (a synthetic zeolite) on the feed intake, mineral and energy metabolism of dairy cows during the periparturient period, came to the result that the supplementation of this material had a stabilizing effect on the calcium serum concentration around calving. The observed reduction of hypocalcemia incidence leading to what is commonly known as 'milk fever' came to 76% on the day of calving. The author concluded that the feeding of zeolite A as a calcium binder in the last two weeks of pregnancy could be a new strategy to prevent parturient hypocalcemia.

Romanian scientists (Zarcu et al. 2010) conducted an experiment on newborn calves fed on colostrum supplemented with clinoptilolite and stated an increased intestinal immunoglobulin absorption. Consequently the experimental groups showed reduced occurrence of diarrhea. (Calves are born agammaglobulinemic due to the ruminant's specific type of placenta. The transfer of passive immunity is achieved through colostrum in the first 24–36 hours post partum.) The animals fed on clinoptilolite supplemented colostrum presented an improved body mass up to three months after parturition.

A further Greek research study (Pourliotis et al. 2012) analyzed the influence of clinoptilolite on the absorption of antibodies against *Escherichia coli* and the incidence of diarrhea in dairy calves if the mineral was added to colostrum and milk administered to them. Enterotoxic strains of *E. coli* (ETEC) are one of the causative agents of diarrhea in newborn

calves. Prevention on dairy farms normally relies on immunization of mother cows during late pregnancy. The Greek study was focused on finding methods to increase the absorption of colostral immunoglobulins. The results indicated higher antibody levels in blood serum of calves fed on clinoptilolite supplemented colostrums and reduced incidence and duration of diarrhea. However the exact mechanisms of antibody absorption enhancement remained undetermined.

In a study carried out on hens during the first three months of the laying period Iranian scientists observed a superior laying performance reflected by an increase in egg mass, weight and egg shell quality when the animals were fed on zeolite supplemented diet. A better intake and utilization of calcium and more advantageous calcium: phosphorus ratio were also stated (Moghaddam et al. 2008).

Zeolites are even applied in aquaculture, their ammonium binding capacity being used for the removal of this toxic substance. NH_4^+ is produced by decomposition of excrements and unused food and one of the leading causes of disease and mortality in fish (Mumpton and Fishman 1977). Devices based on the zeolite ion-exchange mechanism have the advantages of low cost and high tolerance to changing environmental conditions opposite to the more expensive bio-filtration systems. However these methods have been shown more efficient in fresh than in salt water.

The Panel on Additives and Products or Substances used in Animal Feed (FEEDAP) was asked in 2012 to deliver a scientific opinion on safety and efficacy of natural zeolite clinoptilolite as a technological additive and functional group binder in animal feed. The panel concluded that 10g clinoptilolite per kg complete feed could be considered to be safe for all animal species, since the material is essentially not absorbed but excreted with the feces. No evidence was found that clinoptilolite will be degraded during its passage through the gastrointestinal tract of target animals. Consequently no risk is given for the consumer. Neither the use of this zeolite in animal nutrition poses a danger for the environment (EFSA Journal 2013).

Thus particularly in the light of meeting the goals of Vision 2030, a broad range of applications to look at is offered to the UNAM Faculty of Agriculture and Natural Resources. One question can be for example how zeolite material could be integrated into existing animal feeding concepts and to examine the Namibian animal feed market (Feedmaster, www.feedmaster.com.na). Own tests could be carried out on farm animals with regard to specific animal health problems occurring in Namibia. The improvement of overused soil by zeolite based fertilizer and the animal waste treatment are further issues. The replacement of antibiotics as growth promoters by clinoptilolite has already been mentioned and is worth investigation.

3.8 Zeolites in medicine

The best known positive effect of natural zeolites in human medicine is its action in diarrhea treatment (Mumpton 1999; Mumpton and Fishman 1977; Papaioannou et al. 2004). Since zeolites are recognized to reduce the incidence of diarrheal diseases and subsequent death in animals, scientists from University Habana, Cuba conducted a comprehensive study based on natural clinoptilolite as active material in the therapy of diarrheal diseases in humans. The zeolite material was submitted to rigorous quality tests in order to meet the requirements of the United States Pharmacopoeia (USP) XIII.

The results lead to the approval of the antidiarrheal drug Enterex[®] for use in humans in the form of tablets (Rodriguez-Fuentes et al. 1997). In a test of compatibility with and influence on antibiotic drug activity the investigators experienced no interference with the two most recommended antibiotics in cholera therapy. This result is considered as significant in as much as the use of traditional adsorbent anti-diarrheic drugs is obsolete in cholera therapy due to interference with the antibiotics.

On the other hand no bactericide activity of the clinoptilolite was identified, for instance no retention of enteropathogenic *E coli* was stated (Rodriguez-Fuentes et al. 1997). This does not contradict the findings of the in vitro study of other scientists (Ramu et al. 1997) about the adsorption and inactivation of *Escherichia coli* enterotoxin by various zeolites. There the adsorbents were successfully tested for their ability to bind the enterotoxic molecules produced by *E coli* and *Vibrio cholerae* and not the organisms themselves.

Further approved utilizations of zeolites in the domain of human medicine include the use in filtration systems for anesthesia, kidney dialysis and contrast materials in medical imaging (Mumpton 1999; Perhag et al. 2000; Lass-Seyoum et al. without year; Patzer et al. 1995; Young et al. 1995).

The adsorptive properties proven in dialysis gave rise to a Californian clinical study examining the application of activated clinoptilolite suspension as an agent to increase urinary excretion of toxic heavy metals in patients (Flowers et al. 2009). Although acute heavy metal intoxications occur rather sparsely, chronic disorders due to the long-term accumulation of elements like mercury, lead, arsenic, cadmium and others are increasingly gaining ground. The experiment demonstrated that the intake of the study substance represented a potentially safe and effective way to remove toxic heavy metals from the body without shifting the balance of vital electrolytes into the clinically detrimental range (Flowers et al. 2009). These conclusions are in accord with the results of an in vitro adsorption study carried out by a German laboratory on the instructions of a company that manufactures activated clinoptilolite (Fuetterungsstudie an Maeusen mit froximun toxaprevent pure 2012; Wolfener Analytik GmbH 2004). The outcome showed good adsorptive qualities of the medical prod-

uct for lead and mercury within the gastrointestinal tract and for ammonium in the small intestine whereas the essential trace mineral zinc remained untouched (Wolfener Analytik GmbH 2004).

The ammonium binding capacity of the same modified and activated clinoptilolite product was utilized in the oral therapy of acute and chronic liver disorders. Two different German internists reported their experiences in clinical cases of hepatitis and attributed the therapeutic successes chiefly to the removal of ammonium. Due to the restraint capacity of ammonia metabolism of the dysfunctional liver the metabolite overload constitutes in severe cases the limiting survival factor. Under treatment with activated clinoptilolite an important improvement of laboratory tests for liver enzymes was seen (Stanton 2005; Scheler 2006). It would be an interesting facet to investigate whether the side effects of anti-tuberculosis drugs on the liver of patients suffering from tuberculosis can be moderated by simultaneous application of clinoptilolite. The same applies for patients suffering from hepatitis due to alcohol abuse. Both themes tuberculosis and alcohol abuse are of major concern for Namibia.

The binding properties of activated clinoptilolite for histamine have been analyzed by use of the identical product. In severe cases of leaky gut syndrome this biogenic amine crosses the damaged intestinal barrier and passes from the intestinal lumen into the bloodstream, leading to allergic responses and asthma. The tested medical product showed an affinity to histamine comparable to this one to ammonium, acting in the analogue way of substituting the molecule by ion exchange (Steimecke 2006).

The biological activities of clinoptilolite have also been tested successfully in adjuvant cancer therapy. Scientists reported in 2001 positive results of experiments by application of finely ground clinoptilolite in cancerous tissue cell cultures, laboratory animal models and clinical animal trials. The *in vitro* studies showed that the used material was capable of inducing the expression of tumor suppressor protein and inhibiting cell growth in several cancer cell lines. The clinical treatment of diseased dogs by orally administered clinoptilolite showed a reduction of tumor size and improvement of overall health status in 63% of cases. The best results were obtained in the treatment of skin cancers (Pavelic et al. 2001). The mechanism of action discussed by these authors refers to the hypothesis by other researchers, that silica and silicates might act as nonspecific immune-stimulators, comparable to protein superantigens produced by microorganisms (Ueki et al. 1994; Ueki et al. 1997). It should be mentioned that the experiments of these scientists had been carried out with chrysotile which is asbestos and a fibrous magnesium silicate.

An open and controlled parallel-group study was carried out in Germany to investigate the effects of activated clinoptilolite on the cellular immune systems of patients undergoing treatment for immunodeficiency disorders. The patients were given a daily dietary supple-

mentation of 3.6.g clinoptilolite, the primary medical therapy remained unchanged. The results after six weeks showed significantly increased lymphocyte counts, however the authors recommend that future studies should include a longer period of several months with repeated measurements. No adverse reactions to the treatment were observed (Ivkovic et al. 2004).

It should be noted at this point, that all the above mentioned varieties of medical application are based on a technically modified, purified and qualitatively enhanced natural clinoptilolite (Rodriguez-Fuentes et al. 1997; Pavelic et al. 2001; Ivkovic et al. 2004). A key point of the so called activation is the tribomechanical micronization, a milling technique process developed sixty years ago in Russia (Herceg et al. 2004). The gained particle size differs following the producers, varying from e.g. 6-9 μm : the modified activated clinoptilolite in froximun[®] products (Fuetterungsstudie an Maeusen mit froximun toxaprevent pure, 2012; Wolfener Analytik GmbH 2004; Stanton 2005; Scheler 2006; Steimecke 2006; Europaeische Patentschrift 2007) to 1.5-3 μm : the finely ground clinoptilolite material MZ used in the anticancer therapy study (Pavelic et al. 2001) to only 0.39-0.5 μm in the liquid product of Waiora Natural Cellular Defense NCD (Natural Cellular Defense Overview 2005-2012). The latter ranges within the scope of virus size, expressed in nanometer nm. The average virus diameter comes to 300 nm equal to 0.3 μm . This suggesting that different pharmacokinetics and - dynamics may be involved, since these molecules pass the intestinal mucosa, while products of larger proportions will be excreted structurally unchanged with the feces. Generally a decline of bioavailability is seen in molecules above a molecular mass of 400 Dalton which corresponds to approximately 6.64 μg (El-Kattan and Varma without year).

The external application of zeolite-clinoptilolite powder is efficient in wound treatment and surgical incisions, binding excess moisture, providing that way a more favorable microclimate and leading to a decrease of healing time. No systematic studies have been made yet, but several reports point out the successful use of zeolite powder for example as common practice to dust wounds of livestock animals (Mumpton 1999). These findings are supported by anecdotal reports from German veterinarians who have experienced comparable good results in the wound treatment of animals over years in their own veterinary practices. From this point of view this powder can be recommended to hold on stock in Namibian pharmacies in order to provide the numerous livestock keepers with an inexpensive, simple first aid product in cases of injuries. An additional proposal would be a survey in how far the clinoptilolite powder could be integrated in the treatment of puff adder bites.

This venomous snake is very common in Namibia and its tissue venom causes severe and difficultly treatable injuries. The venom contains proteases, cytotoxic enzymes that destroy the subcutaneous tissue, undermining the connective tissue and eventually leading to expanded necroses. Applied by time the adsorptive capacities of zeolite powder could

possibly remove a part of the detrimental toxins and serve as an adjuvant therapy, though there is no evidence for it yet. The Schools of Medicine and Pharmacy can be requested to undertake a study, including the teaching hospitals.

4 Conclusion

This review gives a cross-section of what has been explored and achieved in the vast field of natural zeolite research and application. Several options if not gaps have been addressed where zeolite mineral could be integrated or introduced in existing concepts in this country. Some proposals were made for the participation of Namibian educational institutions to contribute to research, exploration and exploitation of this topic. They are all invited to give their input.

A first practical step may be to get in contact with international producers and manufacturers of natural zeolite products under the aspect of imports or to get permission for a licensed manufacture particularly of medicinal products. The incorporation of these preparations into routine treatments might be considered, as well as their potential of radioactivity adsorption making them to promising preventive drugs for mine workers. The utilization in animal feed to avoid the overuse of antibiotics as growth promoters is a further facet worth to be looked at. Investigations for the usage of zeolite for soil amelioration and water retention in the semi-arid climate of Namibia could be undertaken. The exploitation of the mineral as a multi-purpose construction material would be a further option. And finally the own natural geological resources should be revised and explored for mineable zeolite deposits.

At the University of Namibia with its numerous centers of excellence, the Polytechnic, and within Namibia there is a substantive resource to address and explore the opportunities described in this article. However, it is pertinent to bring these relevant stakeholders together to best utilize their strengths in an action plan (Figure 1).

1. International producers and manufacturers of natural zeolite (medicine) products
 - (a) discuss feasibility of imports
 - (b) discuss permission for a licensed manufacture
2. Faculty of Health Sciences: Clinical research into the integration of zeolite based medicine products in treatments
3. Faculty of Agriculture for research cooperation:

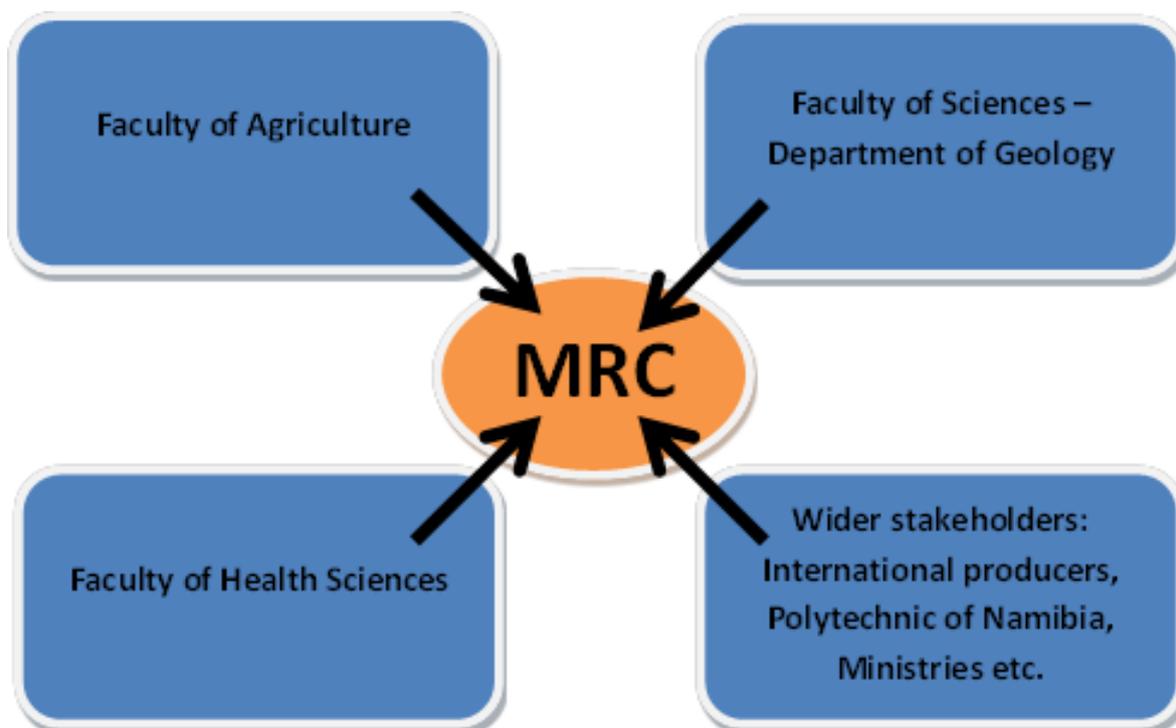


Figure 1: Collaborative approach to investigating the use of zeolites in Namibia

- (a) Department of Animal Science
- (b) Department of Crop Science (Ongongo)
- (c) Department of Fisheries and Aquatic Sciences

4. Faculty of Sciences Department of Geology:

- (a) seek for zeolite deposits in Namibia inclusion in modules 'field geology studies'
- (b) include laboratory work of the module 'crystallography and mineral chemistry'
- (c) include knowledge of the module 'industrial minerals and gemstones'
- (d) include knowledge of the module 'sedimentology and paleontology'

5. Multidisciplinary Research Center (MRC) of UNAM for cooperation

6. NGO's operating within Namibia for funding

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