Manufactured Clinoptilolite Zeolite in a Colloidal Suspension

About the White Paper

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What is a Zeolite?

Commercial grade zeolite.

Zeolites are naturally found, lightweight, porous minerals found in the earth where volcanic rocks and ash reacted with alkaline, or high pH, groundwater, millions of years ago. The microscopic structure of zeolites has millions of regularly arranged holes, or pores that give the material the ability to absorb large amounts of water along with a wide variety of ions, toxins, heavy metals, radioactive particles and gases.

Most of us are familiar with the zeolites used in water softener systems. The zeolite core of the water softener absorbs large amounts of metals like calcium and magnesium from the water. Periodically, the zeolite in your water softener is flushed with highly concentrated saltwater to flush out the metal ions and regenerate the zeolite for more absorption. The most common forms of zeolites used in water softeners are the natural aluminosilicates, gluconites (i.e. greensand), and synthetic permutite.

The strong attraction of zeolites for toxins is the result of the way the elements oxygen, silicon, aluminum, and alkali metals (e.g. lithium, sodium, potassium) are arranged inside the material. The Silicon-Oxygen and Aluminum-Oxygen bonds that create the nanometers-sized hollow cages inside the zeolite are bulky and rigid. The strong bonds between these elements leave the interior space within the cage with a negative electrical charge, and elements and molecular fragments with positive charge are strongly adhered, sometimes by multiple connections, making it very difficult for the captured species to escape.

Natural vs. Synthetic Zeolites

Of the 245 unique zeolite frameworks that have been identified by the International Zeolite Association Structure Commission, over 40 are naturally occurring. Naturally occurring zeolites are rarely pure and are contaminated to varying degrees by other minerals, metals, quartz, or other zeolites. Some of these impurities are simply absorbed inside the zeolite’s pores, while others are an integral part of the structure.

Acid treatments at high temperatures can remove many of these impurities, but as more structural atoms are extracted, the integrity of the zeolite framework becomes compromised, and the important toxin-binding cages begin to collapse. At this point, the zeolite becomes increasingly less effective as regions inside the structure become blocked. In other words, increasing purity is balanced by decreasing function, and it is difficult to completely purify a naturally occurring zeolite from all its impurities and still retain full potency.

Clinoptilolite

Clinoptilolite is a naturally occurring hydrated alkali aluminosilicate that is one of the most abundant minerals in the zeolite family. Its structure consists of an outer framework of silica and alumina tetrahedra, within which water molecules migrate freely and exchangeable cations (e.g., calcium, potassium, sodium) gather inside. Although clinoptilolite's chemical formula varies with composition, a typical representation is given by $(Na_2, K_2, Ca)_3Al_6Si_{30}O_{72}\cdot 24H_2O$. The crystal structure of clinoptilolite has large 12-ring pores, the effective pore size of the zeolite excludes molecules larger than ~0.4 nm (1).

Because of its wide use in agriculture and industry Clinoptilolite has been named the mineral of the 21st century by The International Mineralogical Association. Clinoptilolite has been used with success in animal feed at less than 2% by weight and for the purpose of an anti-caking flow agent.

To produce pure, synthetic clinoptilolite, silica, alumina, and alkali sources with initial Si/Al ratio from 3.0 to 5.0 are heated in an autoclave for 1–10 days at a temperature range from 120 to 195 °C. The Clinoptilolite begins to assemble in tiny crystals, whose crystallization rate and crystallinity is controlled by seeding and manipulation of the reaction conditions (2). Instead of direct heat, microwave, ultrasound and high pressure may be used (3).

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(3) Ng TYS, Chew TL, Yeong YF, Jawad ZA, Ho CD. Zeolite RHO Synthesis Accelerated by Ultrasonic Irradiation Treatment Sci Rep (2019) 9:15062; Gordina NE, Prokof'ev VY, Kul'pina YN, Petuhova NV, Gazahova SI, Hmylova OE. Effect of ultrasound on the synthesis of low-modulus zeolites from a metakaolin. Ultrasonics Sonochemistry. (2016) 33: 210-219; Effects of ultrasound on the synthesis of zeolites: A review. Journal of Porous Materials. (2013) 20: 285–302; Jin H, Ansari MB, Park SE. Mesoporous MFI zeolites by microwave induced assembly between sulfonic acid functionalized MFI zeolite nanoparticles and alkyltrimethylammonium cationic surfactants. Chem Commun (2011) 14;47(26):7482-4; Panzarella B, Tompsett GA, Yngvesson KS, Conner WC, Microwave Synthesis of Zeolites. 2. Effect of Vessel Size, Precursor Volume, and Irradiation Method. J. Phys. Chem. B (2007), 111, 44, 12657-12667; Conner WC, Tompsett G, Lee KH, Yngvesson KS. Microwave Synthesis of Zeolites: 1. Reactor Engineering. J. Phys. Chem. B (2004), 108, 37: 13913-13920.

Modified natural clinoptilolites are commonly produced by treating naturally mined clinoptilolite with acids and organic agents such as cationic surfactants, polymers, or amines (4). The modification intensely changes the surface properties, allowing clinoptilolite to absorb anions or nonpolar molecules, for which the unmodified surface has a little affinity.

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Zeolites in the Diet

The main structural parts of clinoptilolite include the chemically stable/inert silica, or silicon dioxide, and alumina, or aluminum oxide. Humans have been inadvertently and intentionally eating these materials in their diets for centuries (5). For example, the human diet gets significant amounts silicon dioxide from skins of foods like potatoes, peanuts, and beets, and in the bran of whole grains. During ancient times, aluminum oxide clays were used in hide tanning, first aid, fabric dying and fireproofing. Aluminum oxide, occurs in nature as various minerals, has many uses in pharmaceutical and industrial manufacturing processes as an adsorbent, desiccating agent, catalyst, dental cements, toothpaste abrasive, cosmetics, sunscreens, and also as a dispersing agent food additive. Given the long history of human use of these minerals, they are generally considered to be safe.

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Silicon dioxide, also known as silica, is a natural compound made of two of the earth's most abundant materials: silicon (Si) and oxygen (O). Silicon dioxide is found naturally in water, plants (e.g. leafy green vegetables, beets, bell peppers, barley, brown rice, oats, alfalfa), animals, and the earth (5). The earth's crust is 59 percent silica. It makes up more than 95 percent of known rocks on the planet and is even found naturally in the tissues of the human body. Silicon dioxide is inert to most reagents, in particular hydrochloric acid (as found in the stomach). It is attacked by strong alkalis such as caustic soda, and hydrofluoric acid, but these are not found in your gut.

Aluminum oxide, also known as alumina, is a major constituent of the Earth's crust, comprising up to about 8% of the Earth's surface. Aluminum is the third most abundant element in the Earth's crust with oxygen and silicon being the first and second. Aluminum oxide is insoluble in water, practically insoluble in non-polar organic solvents, slowly soluble in aqueous alkaline solutions. It is not a form of aluminum that is significantly bioavailable. In a healthy adult only approximately 15µg of the average daily dietary alumina intake of 3-5mg is absorbed (5). The intestinal absorption of alumina is sometimes enhanced by citrate (which is found frequently in effervescent drug formulations) but this is compensated for by the presence of silica in the formula (5). Aluminum ion leaching (a much more bioavailable form) from Aluminum utensils is more serious and can leach more Al than will advanced TRS (5).

Clinoptillolite, a specific form of zeolite that is a composite of silicon dioxide and aluminun oxide, has been widely used in animal husbandry, resulting in increasing feed efficiency, improving production rates, controlling microbial activity, reducing ammonia levels, reducing need for antibiotics and veterinary medicines, and decreasing mortality rates (6). Animal studies have demonstrated that clinoptilolite exerts immuno-stimulatory effects, modulates anti- and pro-inflammatory mechanisms via super antigens, and might have a use in anticancer therapy (7). Use of micronized natural zeolites like clinoptilolite is a new, exciting area in dietary supplements. Clinically safe, Clinoptilolite can adsorb glucose, can stop diarrhea, and is a potent antioxidant (8). Clinoptilolite may be helpful in combating "leaky gut" that results from over exertion and absorption of pathogens/toxins into tissue and blood stream, and improving neurological function via the "Gut-Brain Axis" (9).

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What is nano?

In a dictionary you can find the following definition for Nano:

Nano: definition, a combining form with the meaning "very small, minute," used in the formation of compound words (nanoplankton); in the names of units of measure it has the specific sense "one billionth" (10^{-9}): nanomole; nanosecond.

Nano, as the definition above indicates, refers to the size of something. Nano is not a thing or creature by itself, and just because something happens to be nano-sized, does not make it necessarily bad or good, dangerous or safe. Nano is just a way to describe the size of a measurable portion of a material that can be detected with the right laboratory tools. Any material can be made into a nano-size with a little work. What size it becomes exactly, and how long it lasts that way, depends on the molecules used, and the surroundings it is placed in. Sometimes things are nano-sized only for a short time, others for centuries. Nano is, in fact, natural, that is, nano-sized objects can be found in the environment everywhere in the world. Microbes, plants and trees produce nano-sized byproducts when they grow. The human cell is a bag containing thousands of nano-sized organelles that do specific things to keep the cell, and the organism it belongs to, alive. Nano has been part of the human world right from the beginning of our existence.

Nano materials vary by size, shape, charge, hardness, elemental composition. Size generally determines the bioavailability of the material (i.e. the ability for the material to participate in the body's metabolic processes). Most materials come in a range of sizes and each grouping of size can be active in different parts of the body. As a rule of thumb, object bigger than about 100 nm are mainly processed in the digestive system, objects between 30-100nm can penetrate the mucous membranes of the mouth, and materials smaller than 30 nm are capable of uncontrolled passive diffusion through the cracks between cells in your tissues and in some cases, depending on the material through the blood brain barrier. Depending on the intended function of the nanomaterial, materials in all these size groups might be desirable.

Size is not everything. Other features of nanomaterials can influence the bioavailability of a material as well. Nano materials, even of the same material can be spherical, oval, triangular, rod-shaped, hard, flexible, fuzzy and smooth. Each of these shapes influence how cells will interact with these materials and where they will go in the body. The electrical charge of the particles further determines whether a suspension of Nano will clump together (less charge=more clumping and aggregation, even in the bottle), and what kind of things will be attracted to it, like toxins (opposing charges attract) or proteins and fats. Hard materials, like metal oxides found in advanced TRS in which all the atoms are strongly bonded to each other, usually pass through the body without metabolizing (i.e. breaking down), while softer materials with weaker bonds made from carbon, hydrogen oxygen and nitrogen tend to be degraded by enzymes during metabolism.

Nano-clinoptilolite

Nano-zeolite found in Advanced TRS is the same safe clinoptilolite material used in micronized zeolite formulas-only smaller to increase active area and accessibility of the toxin-absorbing pores inside the material. On a weight per weight basis, Advanced TRS nano-zeolite has 1000's of times more active area for the capture of toxins, and relatively little wasted space. In larger particles, the toxins have to move quite a distance from the outside of the particle to the inside, and depending on the amount, and types of toxins to remove, this can cause bottlenecks to occur in the particles, leaving large parts of the material unused. Nano-clinoptilolite can be made one of two ways, either from the bottom-up, stopping the laboratory crystallization process when the particles reach the right size, or from top-down by breaking down larger particles into smaller ones (10).

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Nano-safety

There is much misinformation about the nature of nano and its safety for human health. The official definition of a nanoparticle is a particle with diameters less than 100 nanometer in size (less than 100 billionths of a meter). This definition was picked because it was observed that some pure metallic materials below this size started changing their physical properties from being electrically conduction to electrical insulating and began to show unusual chemical reactivity at their surfaces. But the exact size where these changes took place depend on the metal involved, its purity, the presence of oxide, or other counter atoms that stabilize the metal, and keep it from floating away in the fluid. This rather arbitrary definition has led to a lot of unneeded fear of objects with sizes in this range. Because of the confusion, the EU, out of an abundance of caution has limited the size of nanoparticles in ingestibles and topical products to be larger than 100 nm. Even at a relatively large size of 100 nanometers, a particle is still 1000 times smaller than the size of single human cell.

How do scientists know which nano are safe? Scientists do in vitro cell culture testing to show that the ingredient used alone or in combination with other things has no adverse effect on the growth of cells. For some products, animal studies are performed. Coseva's scientific team is currently actively pursuing these advanced studies for Advanced TRS to support all of it historical data already accumulated regarding product safety.

The size of the active cages in Advanced TRS is less than one nanometer, but a single 100 nm particle contains over 4 million cages with up to ½ million just at the surface alone. This makes the nanoparticles in Advanced TRS very effective at capturing their toxin targets. Most importantly these active cages are structurally and chemically stable, as each cage is arranged in such a way that it reinforces its neighboring cages and prevents any changes in electrical or chemical reactivity like some of the other pure-element nanoparticles. In other words, nano-clinoptilolite is a smaller version of micronized clinoptilolite, with stable chemical and physical characteristics with its main advantage coming from its tremendously higher pore accessibility and ability to penetrate more uniformly wherever toxins are found. Clinical studies reported to date do not dispute that nano-clinoptilolite is a safe and effective product.