

AO

AO

ALPHA-OMEGA

**ORGANIC FILTRATION FOR
PROBIOTICS AND WATER
PURIFICATION**

ALPHA OMEGA ECOLOGICAL SOLUTIONS

Head Office: Athinios Port- Santorini

P.O. BOX 2154 Pyrgos-Santorini

Athens Office: 8, R. Garibaldi & Sofroniskou str.

Tel. +30.210.9228225

Web Page: <http://www.alpha-omega.com.gr>

Email: info@alpha-omega.com.gr

SKYPE PHONE: ALPHA OMEGA ECOLOGICAL SOLUTIONS

Direct Phones: +30.697.42 28 012 & +30.698.26 60 768

PAGE 1 OF 17

Head Office: Athinios Port- Santorini

P.O. BOX 2154 Pyrgos-Santorini

Web Page: <http://www.alpha-omega.com.gr>

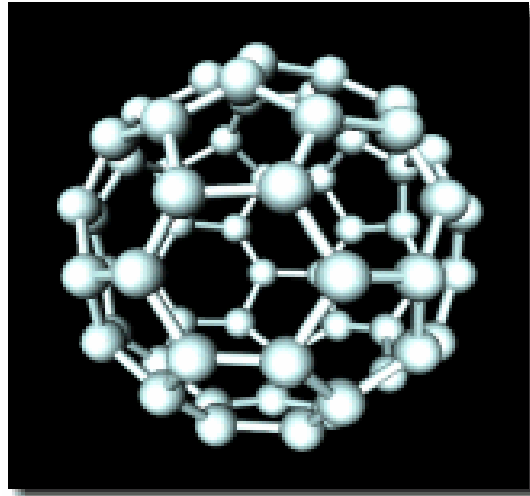
Email: alphaomega.eu@gmail.com

Skype Phone : Alpha Omega Ecological SOLUTIONS

Direct Phones: +30.697.42 28 012 & +30.698.26 60 768



ZEOLITES AND THEIR ROLE IN PROBIOTICS AND WATER PURIFICATION



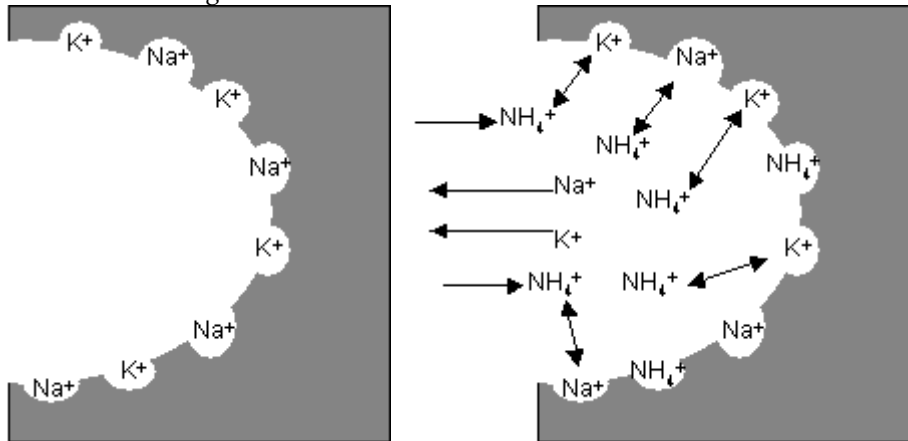


1. INTRODUCTION TO ZEOLITES

Let's start with the basics and ask the question, "What actually is a Zeolite?" Zeolites are minerals, and consist mostly of silica and aluminium, plus other elements like Sodium, Potassium, Iron, and Manganese. The most interesting feature of Zeolites is their crystal structure. You can think of Zeolites as a sponge with holes of different sizes. The small holes are the size of single molecules, about one billionth of a meter. The size of these holes depends on the chemical composition of the mineral. There are hundreds of different Zeolites known in nature, and also many different synthetic Zeolites.

What makes these minerals so special is their ability to absorb specific compounds. Depending on their composition, they preferentially absorb different compounds. This means that they are more likely to absorb one compound more than the other if both are available. For many industrially-used Zeolites, their absorption preferences have been determined. However, thinking of Zeolites just as "absorbers" is a bit oversimplified.

They are actually ion-exchangers. The holes to which a compound binds are not empty, but rather filled with sodium or potassium. As soon as a preferred compound is available, another compound, usually--sodium or potassium, is given off, and the compound will be absorbed. This reaction, the replacement of one ion for another ion, is called *ion-exchange*.



The diagram on the left represents fresh Zeolite. Sodium (Na) and Potassium (K) ions are ready to be exchanged with other positively charged ions. The diagram on the right represents the release of Sodium and Potassium in exchange for Ammonium ions.

It is possible to produce synthetic Zeolites with very specific ion-exchange capabilities that can be "pre-loaded" with specific ions which will then be exchanged against other ions. In a marine environment, the liberation of sodium or potassium is most probably negligible, as they are major constituents of seawater anyways.



Why did so many earlier trials with Zeolites in seawater end unsuccessfully, even though they worked perfectly in freshwater? The answer is easy: The Zeolites commonly used in freshwater adsorb ammonium, which is a desirable function in fresh, AND seawater. However, Zeolites do prefer calcium. Now, you can imagine what happens in seawater! There is usually little to no calcium in normal freshwater, so the Zeolites absorb ammonium. Because there is a lot of calcium in seawater and because these specific Zeolites prefer calcium, the calcium values drop instantly, with sometimes catastrophic results. In the earlier days, when marine zoologists experimented with freshwater Zeolites, they ended up with very low calcium concentrations of less than 200 mg/l.

The Zeolites now used for seawater preferentially absorb ammonium, but this is just one half of the story. The other half is where the biology comes in. As already mentioned, Zeolites have a very porous structure. Under the microscope, they look almost like a sponge. The larger holes are MUCH bigger than the smaller ones, about a thousand times bigger. This porous structure creates a large surface area for bacteria to settle. As the ammonium is adsorbed by the crystal structure, the bacteria living on the Zeolite get their food delivered to their doorstep. To enhance the filtration capacity, a carbon source is added.

Therefore, by adding a carbon source, all bacteria in the marine system receive some additional food. But as those bacteria that sit on the Zeolite get the ammonia much easier and in much greater quantity than others in the tank, they can make much better "profit" from the carbon addition.

Now that we have discussed the basic principles of what happens on the Zeolite, we should take a look inside each grain. Due to the porous structure of the material and the bacterial films coating the surface of each grain, oxygen will rapidly be depleted inside the Zeolite. At the very surface, where oxygen is still available, the ammonium is either oxidized by autotrophic bacteria to nitrate, and then immediately reduced to nitrogen gas by heterotrophic bacteria, or the ammonium may be reduced to nitrogen directly.

The latter process (anaerobic ammonium oxidation, anamox) is known to occur in sewage treatment plants, and has only recently been identified in nature for the first time. Proof of whether or not this process is occurring in a Zeolite filter would be highly difficult, if not impossible. This shouldn't bother the users of these filters; the net reaction is the same: ammonium is removed from the water and transferred to nitrogen gas, which goes off into the atmosphere. All these reactions can only take place when a carbon source is added. Without a carbon source, the filter would first only absorb ammonium and nothing else. It would be a simple ion-exchanger. After a few days to weeks, chemoautotrophic bacteria would settle on the ammonium-loaded Zeolite and oxidize it to nitrate, as indicated in the following reaction:



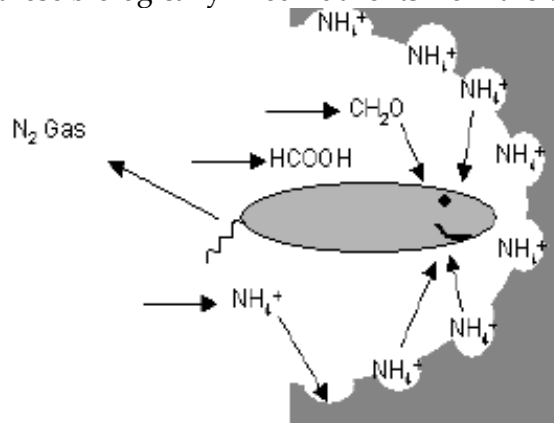
Therefore, such a filter would actually produce nitrate, and its use for a marine application would be rather limited!

Previously mentioned was that the ion-exchange process itself is not of much importance in the marine environment, I may have been a bit too simplistic. In new ponds, a little powerhead with a cartridge full of Zeolite can have a very positive effect on the stability of the pond. As ammonium is oxidized to nitrite, a reduction of ammonium levels reduces the nitrite peak in the start-up phase considerably. As the excess ammonium is taken out of the system before it is oxidized and starts causing problems, the Zeolite filter acts as a buffer which stabilizes the nitrogen cycle in the tank. In such a case, the Zeolites have to be changed every few days and no carbon source is added.

In the "normal" Zeolite filters with the addition of a carbon source, these filters can run for extended periods of time because ammonium is constantly removed from the minerals by the combined efforts of autotrophic and heterotrophic bacteria. After a while, the Zeolite is exhausted and needs to be replaced.

But if the bacteria remove the ammonium from the minerals why doesn't the filter run forever? First of all, the bacterial films will slowly clog up the pores, thereby reducing the adsorbing capacity; secondly other ions will also be adsorbed onto the Zeolite. As the bacteria do not remove these ions (at least not preferentially), they will slowly become enriched and therefore reduce the number of places available for adsorbing ammonium.

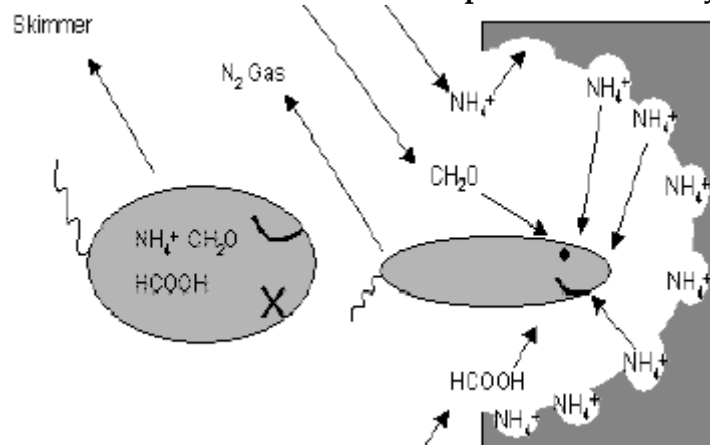
In industrial applications Zeolites are often recycled. There is also another method of nutrient removal working in Zeolite filters. As the bacterial biofilms build up, a lot of nitrogen compounds are actually fixed in the biomass and thereby removed from the water. When the biofilms become too thick and rip off, the skimmer may catch them and thereby remove these biologically fixed nutrients from the water.



The diagram on the top represents bacteria taking advantage of the locally high concentration of Ammonium trapped in the Zeolite and breaking it down to



Nitrogen gas. The diagram on the bottom represents well fed, nutrient rich bacteria that have reached the end of their lives drifting from the Zeolites, destined to be skimmed out of the pond mechanically.



Since these filters entered the market, they have been proven to keep nutrient concentrations at levels usually found in the central Pacific, one of the most nutrient depleted waters on Earth. The major advantage of these filters is also their major danger: They remove ammonium very rapidly and extremely efficiently. Although ammonium concentrations are never high (at least they should not be), it is a very important component in the nitrogen cycle. Don't forget that Zeolites are the most effective ammonium absorbers available.

2. Viral and Bacterial Removal of the Aquatic Environment By Zeolites

Zeolites possess a negative surface charge, which limits their natural ability to attract viruses. In order to reverse this charge, the scientists treated Zeolites with a chemical, abbreviated HDTMA (hexadecyltrimethylammonium), which is found in hair conditioner and mouthwash. They then conducted laboratory and field studies to compare the performance of treated Zeolite as a suitable virus barrier with that of untreated Zeolite and of iron-oxide coated sand.

The researchers found that in both laboratory and field tests, untreated Zeolite failed to remove viruses from the water. Iron-oxide coated sand was effective in removing viruses from water in the laboratory, but largely failed to do so in the field. **Treated Zeolite was an effective barrier in both situations. In the field, treated Zeolite removed at least 99 percent of viruses from the water and 100 percent of E. coli.**

The scientists believe that the results of their study, along with the relatively low cost of treated Zeolite, suggest that a filter pack composed of treated Zeolite could be an effective and practical means for controlling the spread of diseases through the marine aquaculture environment.



In the work conducted by **Castor Pollux Biofuels and Biotechnologies** the Zeolites having been pretreated with an organic acid demonstrated a higher capacity to remove viruses than HDTMA does, and the effective life of the Zeolite was extended up to 35% longer.

3. What are Activated Zeolites?

Natural Activated Zeolites are robust, insoluble and chemically stable aluminum silicate minerals that were formed from the glass component of volcanic ash millions of years ago. They have a unique atomic structure with a well-defined internal porosity of cavities and channels that host cations, water and other molecules.

The large, reactive three dimensional framework of Activated Zeolite is electrically charged (-). This electric field attracts and binds cations (e.g., NH_4^+ , K^+) and, after modification, anions (-). This enables Activated Zeolites to attract and absorb (Very High Cation Exchange Capacity) materials such as Plant Nutrients (slowly released), Odors, Ammonium (e.g. Aquaculture) and Heavy Metals (e.g. Filtration, Pb^{2+} , Ag^+ , Cd^{2+}). The rigid, open structural framework of Activated Zeolite has a large surface area (up to $450\text{m}^2/\text{g}$) and high porosity (up to 45%).

4. Benefits of Activated Zeolite

Natural Activated Zeolites can perform a variety of functions due to their high ion exchange capacity, adsorption-desorption energies, propensity for modification, potential for regeneration and recycling. Frequently Activated Zeolites can reduce production costs and increase yields whilst reducing environmental pollution. Activated Zeolites have significant and substantial applications in:

Horticulture and Agriculture they retain and slowly release (due to their high cation exchange capacity) nutrients in the root zone resulting in savings in water and fertilizer. Further, they help prevent soluble fertilizer leaching and polluting ground and surface waters.

5. WATER & FILTRATION WITH ZEOLITES

Water filtration, apart from the removal of solids and colloids, increasingly demands the efficient removal contaminants including heavy metals and other toxic substances, bacteria and other parasites. Conventional sand filter systems do not remove all contaminants.

The filtering abilities of Activated Zeolites (natural and modified forms) offer a versatile and environmentally friendly option to capture most contaminants found in water systems. Natural Activated Zeolites can perform these functions due to their high ion exchange capacity, adsorption-desorption energies and ability to



modification. Activated Zeolites have an open, regular crystalline framework that generates an electric field that interacts, attracts and binds various cations and, after modification, anions.

Activated Zeolites can remove ammonium (NH_4^+) and metal cations Pb, Cu, Cd, Zn, Co, Cr, Mn and Fe from solutions with the recovery of ammonium and some metals (Pb, CU) as high as 97%

Filtration

Activated Zeolites can be used to filter and purify town water supplies, sewerage effluent, biological wetlands, industrial and mining waste-water, aquaculture ponds and swimming pools.

Water filtration, apart from the removal of solids and colloids, increasingly demands the efficient removal contaminants including heavy metals and other toxic substances, bacteria and other parasites. Conventional sand filter systems do not remove all contaminants and therefore alternative or additional systems are required so that the water quality meets compliance regulations.

The filtering abilities of Activated Zeolites (natural and modified forms) offer a versatile and environmentally friendly option to capture most contaminants found in water systems. Natural Activated Zeolites can perform these functions due to their high ion exchange capacity, adsorption-desorption energies and ability to modification. Activated Zeolites have an open, regular crystalline framework that generates an electric field that interacts, attracts and binds various cations and, after modification, anions.

Activated Zeolites have a particularly high selectivity for ammonium (NH_4^+) and can reduce the ammonium content in waste-water by up to 97%. NH_4^+ has serious environmental consequences because of its toxicity to aquatic life, contribution to algal eutrophication, reduction in dissolved oxygen and detrimental effects on disinfection of water.

Modifications such as charge change from (-) to (+) provides Activated Zeolite with the flexibility to absorb anions as well as cations and also some non-polar organics such as benzene, toluene and xylene.

Activated Zeolite can be charged with 'antibiotic' cations of one of Ag, Cu, Zn to provide antimicrobial properties. Activated Zeolite filter beds can remove contaminants to purify air (Ammonia NH_3 , H_2S , CO_2 , CO, SO_2).

The hard, durable nature of Activated Zeolites enables them to perform a range of filter functions to produce improved water quality more efficiently than both the



conventional slow or rapid sand filter systems. Robust, insoluble Activated Zeolites have improved attrition qualities and are adaptable to re-use through regeneration and recycling.

Benefits of Activated Zeolite/Silica Sand Beds Over Traditional Silica Sand Systems Conventional Slow Sand Filter Systems (Andrews, 1993)

The top 20cm of a 1 metre thick bed of finely graded silica sand (0.5mm to 0.6mm) was replaced with Activated Zeolite. The Benefits Are:

Higher throughput rate up to 0.75m³/hr/m² versus 0.15m³/hr/m², while still maintaining water quality (measured in turbidity).

Longer runs, up to 50%, even at higher loadings.

Up to 3 to 5 times more water processed between maintenance scrapings.

Curing time is less, due to the rapid development of the schmutzdecke or biofilm.

6. Conventional Rapid Sand Filtration

Burtica et al., 1997 found:

The optimum height of the Activated Zeolite filtering layer is 35% of the height of quartz sand. The effluent obtained with Activated Zeolite was better than the results obtained with sand filters.

Activated Zeolite reduced turbidity and, organic charge (2nd filtering cycle) by 30% as opposed to 10% with sand.

7. Sewerage/Waste-water Treatment

Activated Zeolite significantly improves the plant capacity, process efficiency and effluent discharge quality from activated sludge sewerage treatment plants. It is also markedly improves nitrification and reduces odors to negligible levels. The Activated Zeolite particles act as seeds to boost bacterial flocs by attracting and increasing bacterial action per unit volume.

8. Filtration Removal of Heavy Metals

Activated Zeolites are low cost ion-exchangers for the removal and recovery of heavy metals cations (Pb, Cu, Cd, Zn, Co, Cr, Mn and Fe; Pb, Cu as high as 97%) from drinking and waste-waters.



Activated Zeolite rotary hoed (to a depth of 30cm - 40cm; 6.67 mg Activated Zeolite/kg spoil) into a tailings dump with high levels of Cu and Zn sulphide contamination reduced

Cu and Zn levels in waste-water discharge by 95% and 92% respectively.

9. Aquaculture

The natural generation of toxic levels of ammonia by increased densities of fish/crustaceans can be a limiting factor in aquaculture production. Ammonia can affect fish tissue, growth rates, oxygen utilization, and disease resistance and can cause mass mortality.

Activated Zeolites can reduce ammonium and hydrogen sulphide levels in fish/prawn ponds, resulting in increased fish/prawn growth rates and population densities. It also reduces ammonium content in discharge waters to meet environmental requirements. Piper and Smith (1982) suggested that a water recycling system with a Activated Zeolite filter system can allow up to a 10 fold increase in fish density.

Activated Zeolite has a high selectivity for ammonium. When used as an ion-exchange filter medium the Activated Zeolite can reduce ammonium content of circulating freshwater from aquaculture systems by as much as 97%.

The hardness and durability of Activated Zeolite increases their attrition resistance and extends (compared to many overseas varieties) the life of the filter bed. They can also be regenerated, by backwashing with brine or nitrification, for repeat cycles. Brown trout show stress levels at 0.7mg NH₄⁺/L. Trials with brown trout in Victoria found that a Activated Zeolite filter reduced effluent feed to the filter of 0.6 to 0.7mg NH₄⁺-N/L to levels below 2mg (Cooney and Booker, 1996).

Sand filter systems, charged with Activated Zeolite, can remove 1.10 to 2.5 grams of ammonium per kilogram of Activated Zeolite. Activated Zeolite broadcast over the surface of a pond, without filters, is also effective in reducing ammonium. The pond-bed sludge can be recovered and used as a nutrient enriched slow release fertilizer.

Activated Zeolite reduces ammonium build-up during the transport of live fish and can allow a greater density of fish to be transported per litre of water. The addition of 40 grams of clinoptilolite per litre of water reduced ammonia content by 93% in polyethylene bags with fish densities of 22 to 44 grams per litre.

Over the past 50 years, advances in granular filter media water filtration have been achieved by using smaller mesh size sand combined with garnet or garnet/antracite (multimedia) to achieve a nominal 12 to 15µ rating and to improve bed design and



fluidics. High purity Zeolite media is now available that achieves a <5μ nominal rating.

10. Structure and properties

Mineralogical, there are about 40 known types of natural zeolites (hydrated silicates) of which clinoptilolite is the most common.

Clinoptilolite is classified as a crystalline, aluminum, silicon, oxide mineral (Berkhout 2002; Rempel, 1996). This report describes a high purity 14 x 40 mesh, approximately 55 lb/cu. ft. bulk weight, clinoptilolite (zeolite) from the western US that has a high porosity, high surface area, a micro-crystal structure, and is abrasion resistant.

This zeolite media is classified under 21CFR Part 182.2729 and under 40 CFR Part 180 as GRAS (Generally Recognized As Safe). It is also listed under NSF Standard 61.

11. Performance and advantages

Since the mid-1970s, lab and field test data reports in the US have indicated that zeolite filtration media has consistently outperformed sand, sand/anthracite and multimedia in both pressure vessels and gravity filtration tests (e.g., Foreman:1985; Johnson & Petersen, 2001 Hansen, 1997.; Johnson et al, 1997; Fuger, 2003).

Generally, the zeolite filter beds have 1.7 to 1.9 times the solids loading capacity/ft³ and superior filtration performance versus multimedia.

Based on more than 100 lab and field tests (2/3 using pressure vessels and 1/3 using gravity beds) since the mid-1990s representing commercial, residential and industrial water filtration projects, it has been concluded that high purity zeolite media is superior to conventional granular media.

Our test results using pressure vessels indicate:

For solids loading capacity, high purity zeolite surpassed multimedia, sand/anthracite and sand; Zeolite more effectively removes fine particles in the 0.5μ to 10μ range that escape conventional media (see Table I).

Table I. Summary of performance test data for pressure vessels.		
Filter media	Filter rating (nominal)	Solids loading capacity
Sand (20 x 40 mesh)	~20μ	1X
Sand/Anthracite (20 x 40 mesh & Anthracite)	~15μ	~1.4X
Multimedia	~12μ	~1.6X
Zeolite (14 x 40 mesh)	<5μ	~2.6X



Similar results were observed for gravity beds. Some representative examples of high purity zeolite filter performance are provided below.

12. River water turbidity:

Zeolite versus multimedia media filtration tests were conducted for fine particle (turbidity) removal from river water. Pressure vessels (18" diameter) were operated with a service flow rate of 15 gpm/ft² of bed area for six consecutive days and turbidity (NTU) was measured in the feed and filtrate water.

The zeolite filtrate (product water) average NTU was approximately 1/3 of the multimedia filtrate (see Figure 1), indicating superior fine particle removal by the zeolite.

13. Prefilter for GAC:

Municipal water supplied to a restaurant contained elevated iron and other fine particles. Cartridge (5 μ) filters rapidly loaded and caused reduced water flow to the GAC beds and chiller.

A backwashing zeolite filter (10" diameter vessel with a 24" bed depth) was installed and tested by an independent engineer and technical consultant.

The feedwater had 0.1 μ to 10 μ particles (average SDI or silt density index = 4.3). The zeolite bed effectively removed the iron particles. The product water particles were in the 0.1 μ to 2.3 μ range, with an average SDI = 0.

14. RO prefilter:

An electric utility installed a 1,500 gpm water treatment facility with two multimedia filters and RO equipment to produce boiler make-up water. The RO units could not be operated due to filter vessel pressure loss problems and an elevated SDI in the filtrate.

The two multimedia beds were replaced with equivalent bed volumes of 14 x 40 mesh high purity zeolite media and the strict design specifications for the RO feed water have been consistently met for over two years.

15. Bottled water plant:

A bottled water plant pumped groundwater to four 48" diameter pressure vessels that feed two RO units. The multimedia reduced the well water SDI by an average 5 percent compared to 45 to 50 percent SDI reduction for the zeolite media.

16. Cooling tower makeup water:



A major chemical plant facility in South Texas had turbidity problems with river make-up water being used for a cooling tower, The sand/garnet gravity filter inadequately removed turbid particles after rain events. The sand/garnet was replaced with an equal volume (545.5 ft³) of 14 x 40 mesh zeolite. The zeolite, when operated at the same flow rate (2.5 gpm/ft²), removed greater than 98 percent of the turbidity versus approximately 20 percent for the sand/garnet. The zeolite has provided superior filtration for two years.

17. Produced water filtration:

A US oil company wanted to convert unusable oil production water into reusable irrigation water. The production water was processed for oil/water separation: chemical flocculation; clarification; and ozone oxidation. It was then filtered using two pressure vessels (72" diameter) with high purity zeolite media operating at approximately 12 gpm/ft². The filtrate was used directly as feedwater for an RO unit and the product water was recycled as agricultural irrigation water.

18. Flow rates, backwashing guidelines

For pressure vessels, a 36" bed depth is generally used with undergravel, plus approximately 50 percent freeboard, similar to multimedia beds.

The optimum service flow rate for pressure vessels ranges from 12 to greater than 20 gpm/ft² of bed area, depending on the water filtration application.

For example, use 12 gpm/ft² for RO and GAC pre-filtration; use 15 gpm/ft² to achieve low turbidity well water, surface water and for industrial projects; and 18 to 20 gpm/ft² rate to get high water volume for projects with lower filtration requirements.

Since virgin zeolite has "fines" from mine production, it is important to backwash it prior to placing in service. The backwash rule-of-thumb is to achieve 35 percent bed expansion using a backwash rate of 20 gpm/ft² until the water is clear for new zeolite, and for six minutes for routine operational backwash cycles.

Alternatively, air scour can be used with water to reduce backwash water usage.

Tod S. Johnson, Ph.D is president of Filter Flow Technology, Inc., League City, TX.

George A. Desborough, PhD, was senior research geologist, Mineral Resources Program, US Geological Survey, and is now retired.



References

- **Berkhout, Stijn**, 2002. Instazeoliter Photochemistry and Photophysics. Report Summary-Internet www.stijnb@science.uva.nl.
- **Desborough, G.A.**, 1996, Some chemical and physical properties of clinoptilolite-rich rocks, US Geological Survey Open-File Report 96-265.
- **Foreman, G.P.** 1985. "Slow Rate Sand Filtration With and Without Clinoptilolite: A Comparison of Water Quality and Filtration Economics." Masters Thesis, Utah State University, Logan, Utah.
- **Fuger** 2003. Alternative Filter Media: A Step Above The Rest". Aqua: Feb Issue, pp 65-70.
- **Gilbert, J.S., O'Meara, P.M., Crock, J.G., Wildeman, T.R., and Desborough, G.A.**, 1999, Adsorption Capabilities of Selected Clinoptilolite-Rich Rocks As It Relates To Mine Drainage Remediation. US Geological Survey Open-Filte Report 99-17.
- **Hansen** 1997. Engineering Depart-ment, Comparison of Sand and Zeolite Filter Media: Head Loss for Gravity Beds. New Mexico State University, La Cruces, NM. Personnel communication.
- **Johnson, T.S., Peterson, S., and David, J.** (1999). Sorption Removal of Surface Water Turbid Particles As A Filtration Pre-Treatment Method. Filtration '99 Conference, Nov. 2-4, Chicago, IL.
- **McNair, D.R., R.C. Simms, D.L. Sorensen and M. Hulbert**, 1987. "Schmutzdecke Characterization of Clinoptilolite-Amended Slow Sand Filtration. AWWA 79 (12); p 74-81.
- **Pough, F.H.** A Field Guide to Rock and Minerals. 4th Edition, Houghton Mifflin Co., Boston, MA 1983.
- **Rempel, Siefried**, 1996. Zeolite Molecular Traps and Their Use In Preventive Conservation. WAAC Newsletter 18: Number 1, 1-12.
- **Virta, R.L.**, 2002, Zeolites, in US Geological Survey Minerals Yearbook-2002, p. 84.1-84.4.

- **Adams, J. B., Rockett, Angus, Kieffer, John, Wei, Xu, Nomura, Miki, Kilian, Karland A., Richards, David F., and Ramprasad, R.**, "Atomic-level Computer Simulation," *Journal of Nuclear Materials*, Volume 216, pp 265-274, Elsevier: 1994.
- **Adams, K.M., Cavatajo, J.V., Hammerle, R.H.**, *Applied Catalysis B*, 10 (1996) 157-181.
- **B.R. Goodman, W.F. Schneider, K.C. Hass, and J.B. Adams**, "Theoretical Analysis of Oxygen-bridged Cu pairs in Cu-exchanged Zeolites," *Catalysis Letter* 56(4), (1998) 183-188.
- **Chemical Week**, *Shell Develops Open-Pore Zeolite Sheets*. Volume 160, #43, November 11, 1998, page 23.



- **Goodman, B. R., Hass, K. C., Schneider, W.F., and Adams, J.B.**, "Cluster Model Studies of Oxygen-Bridged Cu Pairs in Cu-ZSM-5 Catalysts," Submission to the *Journal of Physical Chemistry B*, pp 1-26, 1999.
- **Hass, K.C., and Schneider, W. F.**, "Density Functional Studies of Adsorbates in Cu-Exchanged Zeolites: Model Comparisons and SO_x Binding," submission to *Journal of Chemical Society, Faraday Transaction*, pp 1-30, 1999.
- **Hayward, D. O., B. M. W. Trapnell, Chemisorption, Butterworths** (1964).
- **Heimrich**, Society of Automotive Engineers, Paper no. 970755 (1997).
- **Hoelderich, W.F. and Heinz, D.**, 1998, Research and Development of Zeolite Catalysis in the 80s and in the 90s as well as Forthcoming Trends: Research on Chemical Intermediates, v. 24, no. 3, March, p. 337-345.
- **Iwamoto, M.; Hamada, H.** *Catal. Today* **1991**, *10*, 57.
- **Iwamoto, Masakazum**, "Copper Ion-exchanges Zeolites as Active Catalysts for Direct Decomposition of Nitrogen Monoxide," *Chemistry of Microporous Crystals*, Proceeding of the International Symposium on Chemistry of Microporous Crystals, Tokyo, Studies in Surface Science and Catalysis, B. Delmon and J. T. Yates, Volume 60, pp 327-334, Elsevier, New York, pp 327-334, 1991.
- **Klimisch, R. L., Larson, J. G., Eds.**; *The Catalytic Chemistry of Nitrogen Oxides*; Plenum: New York, 1975.
- **Mascetta, Joseph**, *Barron's Chemistry*, Barrons, 1998.
- **Masel, Richard**, *Principles of Adsorption and Reaction on Solid Surfaces*, John Wiley and Sons: 1996.
- **Ramprasad, R., Hass, K.C., Schneider, W.F., and Adams, J.B.**, "Cu-Dinitrosyl Species in Zeolites: A Density Functional Molecular Cluster Study," *Journal of Physical Chemistry B*, Volume 101, Number 35, pp 6903-6913, 1997.
- **Ramprasad, R., Schneider, W. F., Hass, K. C., and Adams, J.B.**, "Theoretical Study of CO and NO Vibrational Frequencies in Cu-Water Clusters and Implications for Cu-Exchanged Zeolites," *Journal of Physical Chemistry B*, Volume 101, Number 11, pp 1940-1949, 1997.
- **Robert L Virta**, *Zeolites in Sedimentary Rocks*, United States Mineral Resources, U.S. Geological Survey Professional Paper #820, 1998.
- **Schneider, W. F., Hass, K.C, Ramprasad, R., Adams, J.B.**; *Density Functional Theory Study of Transformations of Nitrogen Oxides Catalyzed by Cu-Exchanged Zeolites*; *Journal of Physical Chemistry B*, Vol. 102, Num. 19, pp 3692 – 3705.
- **Schneider, W.F., Hass, K. C., Ramprasad, R., and Adams, J. B.**, "Cluster Models of Cu Binding and CO and NO Adsorption in Cu-Exchanged Zeolites," *Journal of Physical Chemistry*, Volume 100, Number 15, pp 6032-6046, 1996.
- **Schneider, W.F., Hass, K. C., Ramprasad, R., and Adams, J. B.**, "First-Principles Analysis of Elementary Steps in the Catalytic Decomposition of NO by Cu-Exchanged Zeolites," *Journal of Physical Chemistry B*, Volume 101, Number 22, pp 4353-4357, 1997.



- **Sengupta, D., Adams, J. B., Schneider, W. F., and Hass, K. C.**, "Theoretical Analysis of N₂O to N₂ Conversion During the Catalytic Decomposition of NO by Cu-zeolites," to be published, pp 1-15, 1999.
- **Sengupta, D., Schneider, W. F., Hass, K. C., and Adams, J.B.**, "CO Oxidation Catalyzed by Cu-exchanged Zeolites: A Density Functional Theory Study," *Catalysis Letters*, pp 1-16, 1999.
- **Shelef, M.** *Chem. Rev.* **1995**, 95, 209.
- **Wilber, Ronald A., Boehman, André L.**, "Numerical Modeling of the Reduction of Nitric Oxide by Ethylene Over Cu-ZSM-5 Under Lean Conditions," *Catalysis Today*, Volume 50, pp 125-132, 1999.
- **Marcus, Bonnie K. and Cormier, William E.**, "Going Green with Zeolites", Chemical Engineering Progress, June 1999 SRI Consulting's website, "Process Economics Program"