Clinoptilolite

Dr. Timothy A. Hovanec

Clinoptilolite is a commonly used material for removing ammonia from aquarium water. Clinoptilolite is pronounced clin-op-til-o-lite and usually shortened to just clino. Clino is a type of zeolite and is a naturally occurring clay compound that is also widely used as cat litter and an oil adsorbent. It has a relatively high affinity for ammonia and other cations (ions with a positive charge) as well as certain gases. Clinoptilolite is mined in various parts of the United States, graded into size ranges, de-dusted and then sold in bulk to the aquarium industry. There is no real processing as with activated carbon. The technical name for clinoptilolite is "sodium aluminosilicate" which gives you an idea as to its chemical composition.

Clino removes the cations from the water by ion exchange. Ion exchange is just what it sounds like; one ion is exchanged for another. In the case of clino, however, not all clinos are the same. Some exchange the cation sodium (Na^+) for the cations in the water while others exchange the cation potassium (K^+). In a typical application, the clinoptilolite will exchange the sodium or potassium for another cation such as ammonium ($NH4^+$), calcium (Ca^{2+}), or magnesium (Mg^{2+}) in the aquarium water. Therefore, using clino may slightly increase the sodium or potassium level in the aquarium.

While at first thought it may seem that one could use clino instead of a biological filter for ammonia control, this is not the case because clino is quickly exhausted and rendered ineffective. Under perfect water conditions an ounce of clino will remove about 1 gram of ammonia. Perfect water conditions for maximum ammonia adsorbance by clino would be water with no other cations (so very soft water), no sodium (so no salt), and no dissolved organics or particulate material. Obviously, perfect water conditions for clino are never encountered in an aquarium, so the actual amount of ammonia removed will be less. Also, tests show that the ammonia bonded to the clino is still

available to the nitrifying bacteria which convert it to nitrite. Since clino cannot remove nitrite from the water, without a completely functioning biofilter the nitrite will build-up to toxic concentrations harming the fish. Thus a functioning biological filter is required to convert the toxic nitrite to harmless nitrate. Therefore, clino is used before the biofilter becomes established or when there are transient high ammonia concentrations.

Clino does not solely adsorb just ammonia. It will adsorb many cations. A few, in order of decreasing preference, are: potassium, ammonium, sodium, strontium, copper, calcium, magnesium and iron. The relative concentrations of the adsorbents and their valence determine, to a great extent, which will be removed from the water quicker. The amount of ammonia removed is also negatively affected by increasing levels of dissolved organic compounds and particulate material. Thus, activated carbon and good mechanical filtration should precede the clinoptilolite. The ammonia-removal efficiency of clinoptilolite also decreases with increasing quantities of salt in the water because clino will adsorb sodium from the water. As more salt is added to the water, the sodium concentration becomes much greater than the ammonia concentration and the sodium ion is adsorbed over ammonia. It doesn't take much salt to have such an effect. Studies have shown that a salinity of 5 ppt (seawater, for comparison, is about 33 ppt) will decrease the ammonia adsorption capacity of clino 10 times. As the salt concentration approaches that of seawater, less and less ammonia is removed by the clino. The amount of ammonia adsorbed will also be less in a fresh water aquarium with high concentrations of calcium and/or magnesium (*e.g.,* an African Rift Lake Cichlid tank in which a special salt mix having high calcium and magnesium, to increase hardness, has been added) than in soft water such as one might find in an aquarium with Discus or South American Tetras.

Clinoptilolite can be re-charged and re-used several times but the process is messy and time consuming. Unless you are using a lot of clino it is probably not worth the headaches to recharge the clino. Regeneration must take place outside of the aquarium and its filtration system. The re-charging process is usually done with a brine solution of sodium chloride. A solution of 20 g NaCl per liter adjusted to a pH of 12 is prepared. This solution should be recirculated through the clino for a total of 150 to 200 bed volumes (one bed volume equals the volume of the clinoptilolite). The clino should

then be rinsed with very soft water (deionized or reverse osmosis water is best) for several hours before being used again in the aquarium filtration system. Rinsing with hard water is counter productive as the exchange sites will bind the calcium and magnesium in the rinse water, resulting in fewer sites for ammonia removal. After recharging, the brine solution will contain ammonia and should be disposed of properly - don't use it in an aquarium. Another way to recharge the clino is to heat it at 500°C (932 °F) but this is not practical for most hobbyists. After each re-charging, the amount of ammonia that can be re-adsorbed by the clino will decrease because of the loss of material and the irreversible fouling of the bonding sites. Eventually the clinoptilolite will have to be replaced (it can be used as a garden soil additive instead of being tossed in the trash).

Clinoptilolite can be used where “excess ammonia” needs to be removed or in cases where there is not a functioning biological filter. “Excess ammonia” is that ammonia which is not removed by the biological filter. The biological filter will generally increase in capacity to remove the increased ammonia in the aquarium after a few days in response to the extra ammonia resulting from adding fish or increasing the feed. However, using clinoptilolite will help remove some ammonia and decrease the stress on your fish. Other situations which can produce excess ammonia include: cleaning an undergravel filter after many months and stirring up a lot of brown grunge - in this case, grunge may still be biodegradable and when it is mineralized ammonia will be produced. This can happen very quickly and causes your tank water to turn a light milky white several hours after disturbing the gravel.

Other situations are when changing all, or a large amount, of the media in a canister filter which has not been cleaned in months, adding a lot of new fish to an established aquarium, the start-up of a new aquarium or transporting fish a long distance. A water change should be done in most of these situations, but the use of clinoptilolite can help keep reduce ammonia levels.

However, clinoptilolite should not be counted on as the major ammonia remover in the aquarium filtration system. It is too inefficient and slow to keep up with the ammonia production in an average fish tank. Instead, use it for emergency or special situations.

