A Brief History of Prime - Part 1



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An abbreviated history of dechlorinators and detoxifiers and their evolution

A BIG THANK YOU to Kerry Tolva and Sharon Hollars, DVM for this concept, for the editing of this article and for reviewing it for accuracy and errors! - Mark Porzilli

Discussions on whether dechlorination and detoxification chemicals like <u>Seachem Prime</u>[®] actually work, be they anecdotal or chemical equations, are not hard to find. As the ingredients are largely kept secret, most discussions are laden with speculative chemistry which usually results in more speculation, *often contentious speculation*.

Rather than just adding to the mountains of speculation on what might be in Prime[®] or other commercial products, I thought it may prove more revealing to present examples of similar works that have been performed, tested, and documented by many world-class institutions over the course of nearly a century.

To that end, I've collected a small sampling of *actual test results* on the detoxification of water for aquatics, performed by a variety of authoritative entities from around the world into a chronology, and I've compiled them here.

Please find below a brief, partial review of the chemicals and techniques that have been used by laboratories and universities, as well as *several of the pivotal patents* awarded for well-known dechlorinator/detoxifiers, including the use of specific types of UV lighting. This information may shine some light on what dechlorinators can and cannot do, and perhaps, through their history, we may see how they evolved into the products we currently use.

Virtually all dechlorination chemicals that claim to neutralize *ammonia* are sulfur based. If the dechlorinator claims the additional detoxification of nitrites and nitrates, formaldehyde is also likely present. You can easily smell the **sulfur** and the **formaldehyde** in many of them.

"Contains Complexed Hydrosulfite Salts"

On the <u>Seachem Prime[®]</u> bottle, you'll find only the above statement and little else about what it contains.

The most likely suspect in that vague description is **Sodium Dithionite**, <u>a chemical designed in 1904 by BASF</u>. This same chemical is also known as **Sodium Hydrosulfite** *and* **Sodium Bisulfite**.

It is largely used as a 'reducing agent' which simply means it 'reduces' a target chemical(s) from a stable form (resisting change) to an unstable one that degrades into something that is easily dissolved, dissipated (like a gas), precipitated, or converted to something innocuous.

To that end, Sodium Dithionite *and several related variant chemicals* are logical suspects to be in Prime[®]. As described in a 1991 study; "Selecting a Dechlorinating Chemical for a Wastewater Treatment Plant in Georgia, 1991", they cite that Sodium Dithionate in water will often decay into one or more of the chemicals or variants thereof listed below:

Chemical	Form	Purity %	Application Factor	Chemical Dosage Ib/d/mgd	Chemical Required Ib/d
Sulfur dioxide	gas/liquid	100.0	1.000	12.51	125.1
Sodium metabisulfite	anhydrous	95.0	1.340	17.65	176.5
Sodium sulfite	crystal	96.5	1.775	23.01	230.1
Sodium thiosulfate	pentahydrate	98.0	3.493	44.59	445.9
Sodium metabisulfite	38% solution	34.7	1.340	48.31	483.1
Sodium sulfite	15% solution	15.0	1.775	148.04	1,480.4
Sodium thiosulfate	30% solution	30.0	2.225	92.78	927.8

TABLE 1. Chemical Required to Remove 1.5 mg/l Total Chlorine Residual in 10 mgd Flow

Note: Reprinted from <u>Selecting a Dechlorinating Chemical for a Wastewater</u> <u>Treatment Plant in Georgia, 1991, Dipak Bagchi and Roy Thomas Kelley,</u> <u>Jr.</u>, Georgia Water Resources Conference and the Institute of Natural Resources at The University of Georgia

As mentioned above, the first chemical listed is of particular interest, **sulfur dioxide**. This gas is a natural product of the decay of Sodium Dithionite as well as several other chemicals used for dechlorination. You can easily smell the sulfur dioxide when you open the Prime[®] bottle. In water, it creates sulfurous acids and as you'll see below in **Prime Time**, sulfur dioxide and 'sulfurous acids' have been used effectively to remove chlorine, ammonia, nitrite and nitrate from wastewater--and later for aquatics--<u>for decades</u>.

Prime Beefs

It is not uncommon to read arguments suggesting that chemicals like Prime[®] do NOT detoxify ammonia and nitrites. I have read multiple exclamations that *'this is only true for chlorine and not ammonia, nitrite nor nitrate,'* assertions that it *'totally removes the oxygen from the water,'* even that detoxification of ammonia and nitrite is *'an outright fraudulent claim by the manufacturers.'*

In fact, in most dialogues I've read, there seems to be an incentive to disprove the manufacturers' claims rather than explain them.

However, you'll see below, <u>these chemicals were **first** employed to detoxify</u> <u>ammonia and nitrite</u>, <u>almost a century ago</u>, even before chlorination was in widespread use.



Prime Time

This science is **far** from new. Long before dechlorination in aquatics was a concern, compounds related to modern dechlorinators were first used for detoxifying *ammonia*, NOT chlorine.

In 1932, a study was performed by the *Bowne Hall of Chemistry at Syracuse University* on converting toxic ammonia to far less toxic ammonium through the use of hydrogen sulfide (H2S):

<u>A Phase Study of the System Ammonia-Hydrogen Sulfide, Leopold</u> Scheflan and C.R. McCrosky, American Chemical Society, 1932

This study focuses largely on how certain plant life forms use ammonia, nitrite, and nitrate, with and without the use of a sulfurous additive. This study *and its precursors from <u>several 1929 studies</u> are considered to be the pioneering events that birthed the modern dechlorination and detoxification chemicals in use today.*

But this was just the beginning. <u>By 1935</u>, these techniques were already being modified for use as protection for a variety of *aquatic life forms* from toxic *ammonia* levels by the conversion of ammonia to ammonium salts.

Performed by the *Scripps Institution of Oceanography, University of California, La Jolla, California*, this 1935 study may be the first published instance of using sulfur-based chemicals to detoxify ammonia, nitrite *and* nitrate to protect (microbial) various aquatic life forms:

TABLE 2

OPTIMUM AND INHIBITORY CONCENTRATIONS OF AMMONIUM, NITRITE AND NITRATE FOR THE MULTIPLICATION OF N. closterium and the Concentration of These Ions Reported Found in the Sea

FORM OF	MILL	IMOLS	MILLIMOLS IN S	SEA WATER
NITROGEN	OPTIMUM	INHIBITORY	AVERAGE	RANGE
Ammonium	0.01-0.05	4	0.001-0.005	0 - 0.02
Nitrite	0.05-5.00	25	0.000,1	0-0.001
Nitrate	0.10-40.0	300	0.002-0.01	0-0.05

Note: Reprinted from <u>The Assimilation of Ammonium Nitrogen by Nitzchia</u> <u>Closterium and Other Marine Phytoplankton</u>

A substantial leap in the cognizance of how these reactions occur (from the standpoint of chemistry) took place in 1949. Although it was well known that free ammonia could be neutralized and converted to ammonium salts with sulfurbased acids, this was first described in the study below, performed by the U. S. Department of Commerce, National Bureau of Standards, "Acidic Dissociation Constant of Ammonium Ion at 0* to 50* C, and the Base Strength of Ammonia."

Although this study is quantified in units of the *energy generated* during the reduction of ammonia and nitrites (so the table axes are in temperatures and mols), as opposed to being dedicated to how this affects aquatic life forms, *it clearly documents to great success the reduction (detoxification) of chlorine, ammonia, and nitrites with sulfurous acids.*

In addition, the 1949 study below is possibly the first published instance where a discussion on nitrates *and reducing nitrates* appears (as well as perhaps being the first detailing of the ammonia/ammonium equilibrium relationship):

Acidic Dissociation Constant of Ammonium Ion at 0, by Roger G. Bates and Gladys D. Pinching, U. S. Department of Commerce National Bureau of Standards Research Paper RP 1982, Volume 42, May 1949

At first, ammonia was largely the culprit they sought to reduce. Much later, as The Nitrogen Cycle was becoming more widely understood, more works were performed to examine removal or negation of other toxins, primarily with respect to *nitrites,* as their toxicity towards aquatic life was not well quantified yet.

What was found is that the very mechanisms that detoxify chlorine and chloramine will also detoxify ammonia, nitrates and nitrites, just not in the same time frame.

Prime Examples

While The Nitrogen Cycle has been understood in varying degrees for decades, the pivotal document that brought it to the fore in modern aquaria was published in 1986 and was known as "Anammox". Anammox (*"anaerobic ammonia-oxidizing bacteria that are able to oxidize ammonia and reduce nitrite to produce N2 gas"*) is an acronym for the first observation of ammonia- and nitrite-reducing bacteria, and is well described here:

Frontiers | Biogeography of anaerobic ammonia-oxidizing (anammox) bacteria

An excerpt from the above study focusing on the history of The Nitrogen Cycle can be read here:

A chronology of human understanding of the nitrogen cycle† | Philosophical Transactions of the Royal Society B: Biological Sciences

This excerpt highlights the 1986 work as the pivotal shift in awareness of The Nitrogen Cycle from the scientific community to the global aquatics' community. The study contains a fantastic timeline chart, '*A Timeline of Human Awareness of The Nitrogen Cycle,*' which is reproduced at the end of this article. *

Skipping a decade or two, we find another excerpt from papers published in 1997 and 2009 *that focus entirely on detoxifying nitrites,* again with sulfur-based compounds. An oceanic research article on the conversion of nitrites to nitrogen gas with sulfur-based acids was hidden away in an optical physics publication; Rapid <u>Communications in Mass Spectrometry</u> in 2009:

Removal of nitrite with sulfamic acid for nitrate N and O isotope analysis with the denitrifier method - 2009 - Rapid Communications in Mass Spectrometry

This article employed data from what are now historically pivotal nitrite reduction tests that were <u>first</u> published in *Deep Sea Research—Oceanographic Research Papers in 1997*. In this work, they found the addition of sulfurous acids and sulfur dioxide gas (a gas often released when some of the bisulfite salts mentioned above react with these chemicals and water) could convert nitrites to harmless salts and simple *nitrogen gas*.

<u>Additionally</u>, in a recent edition of the 1955 publication "*Methods in Enzymology*", we find detailed references to nitrite and nitrate reduction using sodium dithionate in studies performed in 1971 and 1976 respectively:

Methods in Enzymology (1955): Methods in Enzymology

Nitrite reduction using Sodium Dithionate (1971): <u>Nitrite reductase -</u> <u>ScienceDirect</u>

Nitrate reduction using Sodium Dithionate (1976): <u>Minimization of a sodium</u> <u>dithionite-derived interference in nitrate reductase-methyl viologen</u> <u>reactions</u>

(Above from the Department of Chemistry, University of Georgia, Athens, Georgia, Analytical Chemistry Division, and the Oak Ridge National Laboratory, Oak Ridge, Tennessee)

Prime Cuts

ARG: AquaScience Research Group (Amquel[®], ChlorAm-X[®] 🔗

"Method and product for removal of chloramines, chlorine and ammonia from aquaculture water-1987"

It was a variant of the BASF's original <u>Sodium Dithionate with added</u> formaldehyde known as **Sodium Formaldehyde Hydrosulfite** or **"SFB"** that would ultimately prove to be the game changer for aquatics use. Although you'll see numerous arguments as to what chemicals are used and what they can actually do, there is little argument over what singular paper contributed the most to the art of dechlorination and detoxification for modern aquaria.

A phenomenal work done by renowned chemist John Farrell Kuhns, "Method and product for removal of chloramines, chlorine and ammonia from aquaculture water" was published in 1987 and was the first quantified analysis of how "Complexed Hydrosulfite Salts," specifically a formaldehyde variant of these--SFB--reduced chlorine, chloramine, and ammonia and was even tested with live, aquatic animals.

He was awarded US and European patents for this work and his formula ultimately became the products **Amquel**[®] and **ChlorAm-X**[®] amongst others. Here is a link to the original European patent:

Method and product for removal of chloramines, chlorine and ammonia from aquaculture water - European Patent Office - EP 0203741 B1 (storage.googleapis.com)

Despite the mass of data dating from 1929, and despite all of the prior research, these techniques would not reach the general aquatic community until the 1987 Kuhns work. Therefore, it would be difficult to argue against the historical significance of the Kuhns patent. It not only demonstrated that water could be detoxified to safe levels for aquatic life, but it also quantified the results and even the *time* required for specific toxin reduction. As such, this singular document paved the way for virtually every dechlorinator and ammonia detoxifier made since.

Cardinal Tetra

Tetra Werke: "Agent for the elimination of active chlorine compounds from water"-1988

The Kuhns patent was quickly followed by another dechlorinator patent for **Tetra in 1988,** invented by Ritter Gunter.

Tetra's patent also used a related variant of Sodium Dithionate with formaldehyde, sodium hydroxymethylsulfonate, and was focused on chlorine, chloramine but *especially* ammonia.

<u>Tetra published the most formulae of all the dechlorination patents as well as extensive results from tests on the effects of zeolites on ammonia:</u>

US Patent for Agent for the elimination of active chlorine compounds from water (Patent # 4,786,434)

Chlor/Amine

Tetra's findings were historically pivotal in that they described and rectified the chloramine problem of ammonia being released from chloramine when removing the chlorine portion.

Many of us may remember using *Sodium Thiosulfate* to remove chlorine years ago. When chloramine became the dominant chemical to negate, Sodium Thiosulfate fell short because in negating the chlorine portion of chloramine, *it released the ammonia in chloramine, creating a secondary issue.*

Tetra's patent delves deeply into this original problem and details the addition of formaldehyde and zeolites to negate ammonia.

Tetra demonstrated that they could reach a 95%-100% reduction of ammonia by adding formaldehyde and zeolites to Sodium Dithionite.

The Tetra patent is in some ways the most interesting in that it supplies the most documentation and supporting formulae of all the dechlorination/detoxification patents.

Yet *Kuhns himself* doubted these chemicals would have a meaningful effect on nitrites and nitrates. It would take another variant and almost two decades for that to be realized.

On the Fritz...

"Process for Treating Water", Fritz Industries, Inc. 2004

It was a third invention by Tiffani Furlough and Kevin Senkevech that saw a US patent awarded to **Fritz Industries in 2004**, where the addition of formaldehydes to Sodium Dithionate (and other chemicals) created a variant known as **Sodium Formaldehydesulfoxylate** or "**SFS**." In this patent it was demonstrated that

SFS not only reduced chlorine, chloramine and ammonia, but also nitrites and nitrates significantly *in just minutes*.

With these findings, the ability to chemically reduce chlorine, chloramine, ammonia, nitrite and nitrate was not only demonstrated, *but it was also quantified* (see some charts from their findings below).

US Patent for Process for treating water Patent (Patent # 7,097,773 issued August 29, 2006)

Less Nitrates, Less Headaches



Although it was referring to water purification for agriculture rather than aquatics, even the pharmaceutical giant **Bayer AG** got into the action with a 2004 patent awarded where <u>they actually achieved 100% removal of nitrates</u> using sulfur dioxide gas:

Process for the Reduction of Concentration of Nitrates and/or Nitrogen-Containing Compounds by Means of SO2

Prime Numbers

From the 2006 Fritz Aquatics US Patent (0-10 minutes-performed at a pH of 8.1):



Below, the nitrates were removed from the graph shown above for improved resolution:



Note 1: The concentration of pollutants in the test sample was determined by methods described in Hach Water Analysis Handbook, 2nd Edition, 1992. Free and total chlorine, P.761; Ammonia, Salicylate Method, P. 781; Nitrite, Diazotization Method, P784; Nitrate, Cadmium Reduction Method (High Range), P. 783.

From the 1987 Amquel US Patent (with varying pH values indicated):





In the first graph, the chlorine degrades very quickly to 0% in under an hour. However, on the second graph for *chloramine*, notice when the initial chlorine is removed, the resultant ammonia actually RISES temporarily (from the chloramine being split apart into chlorine and ammonia).

This is because the time for ammonia reduction is longer than chlorine.

But ultimately, they **both** drop precipitously (Note: The pH significantly affects the reduction):









As explained in **Prime Cuts**, a *dechlorinator-only* product is probably just Sodium Dithionite alone.

However, a dechlorinator that detoxifies ammonia, nitrite and nitrate is most likely a combination of Sodium Dithionite and Formaldehyde.

Prima Facie

Although far from exhaustive, what follows are some informal tests which strongly suggest that <u>Seachem Prime</u>[®] seems to contain <u>Sodium</u> Dithionite and Formaldehyde.

As mentioned above, Sodium Dithionite was originally developed in 1904 as an agent for dyeing and *rust removal* as it proved to be quite effective in removing stains and preparing fabrics and paper for dyeing. As such, it 'reduces' the iron in rust (ferric) to a water-soluble iron (ferrous) that dissolves.^[1]

[1] Sodium Dithionate reduces stable iron to an unstable form. The unstable form is water soluble. <u>It is also bioavailable for plants</u>. This suggests a dose of Prime[®] will temporarily convert all of the iron in the water volume to bioavailable iron.



Left: 40mg of Rust Powder (Fe₂O₃) in 25ml of Water (pH=8), Right: 40mg of Rust Powder has nearly dissolved in 25ml of **Prime**[®] (T=5 min.)



A Standard Chemistry Flame Color Test Indicates that **Prime**[®] Tests Positive for **Sodium** Compounds



Prime[®] Tests Positive for **Formaldehyde** (T=30m)



Prime® Tests Positive for Sulfur Dioxide (SO2) (T=15s)

The earliest dechlorinators (circa 1930) contained Hydrogen Sulfide (H2S) or infused this gas into water. Sodium Dithionite decays into SO2, however H2S smells very similar to Sulfur Dioxide (SO2) such that we needed to verify that Prime[®] did NOT contain H2S:

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Prime® Tests NEGATIVE for Hydrogen Sulfide (H2S) (T=15s)

What a Difference a Day Makes

An important feature of Prime[®] that many of us have relied upon is the ability to detoxify ammonia, nitrite and nitrate for approximately 24-48 hours. This time frame is approximate and is subject to the concentration and the pH of the water.

A little clarity on what's taking place is in order at this point. The sulfur/formaldehyde-based chemicals used in most dechlorinators/detoxifiers do not convert ammonia to ammonium but instead, they actually "bind" elements from Sodium Dithionite (and formaldehyde) to ammonia, nitrite and nitrate and convert them into non-toxic, stable salts rendering them harmless.

To illustrate this using ammonia as an example, in the **ClorAm-X**[®] data sheet, they demonstrated how free ammonia combines with the sulfur/formaldehydebased chemicals used to form a non-toxic salt, aminomethanesulfonate or <u>AMS</u>:

AquaScience Research Group, Inc (hikariusa.com)

In fact, AMS is not only non-toxic; it is a known food source for specific aerobic bacteria, and it has actually been used to treat neurological disorders in schooling (zebra) fish:

Aminomethanesulfonic acid illuminates the boundary between full and partial agonists of the pentameric glycine receptor

 Department of Neuroscience, Physiology and Pharmacology, Division of Biosciences, University College London, United Kingdom; 2. Vollum Institute, Oregon Health and Science University, United States; 3. Laboratory of Soft Matter Physics, Institute of Physics, Chinese Academy of Sciences, China;
Howard Hughes Medical Institute, Oregon Health & Science University, United States

And a supporting quote from "<u>KoiNet</u>, Koi Show Water Management (South Africa)" on AMS:

"...(the) end of the molecule reacts with ammonia to form

aminomethanesulfonate (AMS), a non-toxic, stable water-soluble substance, which can be acted upon by the nitrifying bacteria in biological filtration if needed. On the other hand, the sulfonate-side of the molecule declorinates the water of any hypochlorite, the so called "chlorine". And a further trick in its box: it will

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detoxify all three species of chloramine by the combined action of both ends of the molecule. How versatile can you be if both hands are useful?"

Although not identical in species, the use of AMS as a food source for 'good' bacteria is well known:

Isolation and characterization of two new *methanesulfonic acid-degrading bacterial* isolates from a Portuguese soil sample

While secondary to detoxification, it is a no less remarkable engineering feat, that AMS is usable to the nitrifying bacteria (*particularly the 'nitrite eaters'*) <u>so cycling continues.</u>

Seachem implies there's an expiration of its detoxification via 'reversion back to ammonia' after the 24–48-hour period has expired; however literal *reversion* of AMS to ammonia is almost impossible. The free ammonia is now part of a stable compound that will not even begin to release the ammonia without a great rise in pH (>9.3) or without additional chemical or electronic energy (such as electrolysis) being applied.



FIG. 4. Oxidation of bisulfite (\bigcirc) and of hydroxymethanesulfonic acid (formaldehyde-bisulfite) (\triangle) by Fraction IV and autoxidation of sulfite (\blacksquare) as a function of pH. (Fraction IV and Autoxidation of Sulfite not shown for clarity)

From the Department of Biochemistry and Nutrition, Duke University School of Medicine, Durham, NC-1953

In fact, in some instances such as with nitrite and nitrate reversion is now literally impossible as portions of the negated nitrite and nitrate were dissociated and released as N2 gas (see "Anammox" study above).

In reality the "reversion" is most likely a summation referring to new ammonia, nitrate and nitrite being created unabated, representing new toxin buildup over the 24–48-hour period.

However, *over time* the detoxification chemicals, Sodium Dithionite and Formaldehyde themselves do break down into sulfur dioxide and formaldehyde and other gasses which eventually dissipate. To that end, perhaps the best metric of *how long the protection lasts* might be the actual decay times of sulfur dioxide and formaldehyde in free air:

Table 2. Summary of estimated decay distances and decay times of S and N oxides in air and precipitation

(Distances and Precipitation were removed for clarity, * Equal to Residence Times)	Decay time
Species	(h)
In air	
SO ₂	14*
SO [±]	58
$T-S(SO_2 + SO_4^{=})$	24*
$T-NO_{3}$ (HNO ₃ + p-NO ₃)	16



Top:: Atmospheric decay distances and times for sulphur and nitrogen oxides estimated from air and precipitation monitoring in eastern Canada-1989---Bottom:: Formaldehyde Vapor Characteristics in Varied Decontamination Environments-2021

Above values are in half-lives. In both instances, we see an over 50% loss in sulfur dioxide and formaldehyde within the first 14-16 hours with 24-40 hours being essentially the point at which most has dissipated.

These decay times would suggest that Prime[®] needs be dosed daily for adequate protection.

There's Nothing New, Especially Under the Sun

Ultraviolet light is often employed for the use of deliberate decomposition of chemicals. UV light is classified into three categories, UVA, UVB, and UVC, with UVC being the shortest wavelength of UV light and is highly destructive to microorganisms. It is UVC light that is employed in aquarium UV sterilizers.

UVC is also destructive to many chemicals, and as such, is often employed to effect chemical-free breakdown of chlorine and chloramine, but especially for chloramine. As shown in the graph below, UVC can also completely break down chlorine *and all three forms of chloramine* in just hours.

The circles represent the knee of the curves when chlorine has been exhausted and when chloramine destruction dominates in the graph:





The above graph is from <u>Bad Gas - General Discussion - C.A.R.E.</u> (aquariumcoop.com)

Removal of chlorine products, however, is not always desirable. The ability of UVC light from the sun to destroy chlorine and chloramine is a serious concern in water treatment facilities. Without some form of protection, using a swimming

pool as an example, chlorine and chloramine can be nearly stripped of all disinfection properties by the sun's UVC output *within a day.*

As a result, there are three types of chloramines (mono-, di- and tri-chloramines) employed, as each decay at different rates and under different 'colors' of UV sunlight as the day progresses. This, and chemical additives (like cyanuric acid), are just some attempts to protect chlorine and chloramine from breakdown under UV light.

But--what has been postulated and speculated about in the world of aquatics-is *how UVC affects ammonia*, if at all. <u>It is true that UV light also disassociates</u> <u>ammonia</u>, yet it's been noted that a typical UVC light for aquarium disinfection fails to reduce ammonia levels. This is because UVC light is very inefficient for removing ammonia, such that chemical methods have proven more popular.

However, as mentioned above, UV light literally comes in several 'colors.' *The type of UV light that DOES destroy ammonia, however, is not UVC, <u>but UVA</u>.*

UVA is the longest wavelength UV light and is most well known as the common "blacklight." UVA affords almost no disinfection properties *but can remove ammonia, even directly out of the air.*

Blacklights and Ammonia

A 2020 study was performed jointly by the Department of Animal Biosystems Sciences, Chungnam National University (Korea), the Department of Agricultural and Biosystems Engineering, Iowa State University and the Department of Chemistry, Iowa State University with the goal to reduce ammonia gas in swine farms and poultry barns. They found that ammonia may be partially reduced by the use of blacklight or UVA. However, *it's inefficient and requires a great deal of power* as well as being highly affected by relative humidity (RH) and ambient light. As such, results were far from exhaustive, as even their best efforts resulted in *less than 19% reduction of ammonia and as low as under 3% reduction.*

This is an excerpt from that study, summarizing their findings:

"5. Conclusion The results of the study provide evidence that photocatalysis with TiO2 coating and UV-A light can reduce gas concentrations of NH3. The particular % reduction depends on the presence of photocatalyst, RH, light type (intensity), treatment time, and dust accumulation on the photocatalyst surface.

In the case of NH3, the % reduction varied from 2.6– 18.7% and was affected by RH and light intensity. The % reduction of NH3 was the highest at 12% RH and increased with treatment time and light intensity. The results warrant scaling up to pilot-scale where the technology could be evaluated with economic analyses. It is necessary to investigate the practical applicability to the real system through large scale studies."

From Effects of UV-A Light Treatment on Ammonia in Lab-Scale

Prime Rates

Yet, we've only scratched the surface here for evidence. There are literally hundreds of experiments and studies from around the world that suggest the chemicals SFB and SFS and related compounds, probably in use in Prime[®], do in fact detoxify ammonia, nitrite, nitrate, chlorine and chloramine, *and have done so for decades,* with the reduction of ammonia dating from 1929, the reduction of nitrite dating back to 1935 and the reduction of nitrate in 1949.



In fact, the only common detriment repeatedly cited in using these chemicals is the *depletion of oxygen* along with the reduction of the toxins, as this is concurrent with reduction of the toxins. There is a fundamental difference, however. The oxygen is quickly replaced with simple aeration, whereas chlorine, chloramine, nitrite, and nitrate are predictably reduced until the water volume has been changed in some manner. The graph below displays oxygen depletion from a variety of popular aquarium medications and Prime[®]. This was measured in a 29-gallon tank that had one small air stone for O2 replenishment. Notice how quickly the oxygen is restored by simple aeration. A normal dose of Prime[®] reduces O2 by about 0.5 PPM yet returns to full oxygen saturation in only 15 minutes (or a full 4 hours with Prime[®]'s 5X Emergency Dose):



From LOW O2 - Diseases - C.A.R.E. (aquariumcoop.com)

Primarily...

My input here has been little more here than converting the tedious data tables from the patents into more readable graphs. In the beginning of this article and in the "**Prime Beefs**" section, I mentioned that it takes little effort to find detractors making absolute assertions that the manufacturers are making fraudulent claims.

I've read that "the test procedures (Hach et al) were flawed", that "the formulae are wrong", "the manufacturers are frauds", even that "the patent examiners were corrupt!".

That was, in part, why <u>I decided to present the documented work of others</u>, rather than add my speculation or enter into speculative discussions.

As seen above, many such works have been performed by highly authoritative sources. The detoxification of chlorine, chloramine, ammonia, nitrite and nitrate in varying degrees has been known science for nearly a century. I've cited a mere handful from a plethora of findings indicating documented, quantified, successful outcomes from universities, laboratories, and studies from around the world as well as U.S. and European patents, in the hope that their powerful evidence for these claims sheds some light on what the end user may feel confident about.

From a Hach Industries US Patent:

Stain and rust removing composition US3183191A United States Inventor Clifford C Hach Current Assignee Hach Co

"...the reaction the sodium hydrosulfite is effective to reduce the insoluble rust (ferric iron oxide) to a lower iron oxide which then reacts with the bisulfite and is changed to the more soluble form of ferrous sulfite. The metabisulfites are similar in action to the bisulfites and have been regarded as the hydrate of bisulfites, and the reaction given above would be the same when a metabisulfite is employed."

Download PDF Here: <u>Stain and rust removing composition</u> - Hach Chemical Co, 1965

*A chronology of human understanding of the nitrogen cycle[†] James N. Galloway Allison M. Leach Albert Bleeker and Jan Willem Erisman, Published: 05 July 2013https://doi.org/10.1098/rstb.2013.0120

(See next page)

Table 1. Major event	ts in the history of nitrogen.		
Year	Event		
10 000-8000 BC	Domestication of plants and animals began		
1563	Bernard Palissy advocated for the use of fertilizers		
1675	John Evelyn noted that rainwater contained 'celestial nitre'		
1699	John Woodward proved that what is dissolved in water is essential for plant growth		
1772	Daniel Rutherford discovered nitrogen; he receives credit because he published first		
1772	Carl Scheele, Henry Cavendish, Joseph Priestley, and others concurrently		
	and independently discovered nitrogen		
1774	Joseph Priestley discovered nitrous oxide and ammonia		
1785	C. L. Berthollet determined that ammonia is made up of nitrogen and hydroger	า	
1785	Henry Cavendish discovered HNO ₃		
1787	William Austin was one of the first to try to synthesize ammonia		
1790	Jean Antoine Claude Chaptal officially named nitrogen		
1823	Johann Wolfgang Döbereiner produced ammonia using a platinum catalyst		
1824	Joseph Fourier was one of the first to describe the greenhouse effect		
1836	Jean-Baptiste Boussingault identified nitrogen as a nutrient for plants		
1838	Jean-Baptiste Boussingault determined legumes could fix their own		
	nitrogen, but he did not know how		
1840	Justus von Liebig advocated the addition of certain nutrients to the soil for		
	plant growth, making him the founder of the artificial fertilizer industry		
1843	John Bennet Lawes and Joseph Henry Gilbert confirmed that nitrogen		
	helps plants grow and that nitrogen comes from sources other than		
	precipitation		
1845	M. Ducros determined that hail contained nitric acid, and called it 'pluie		
	acide' or acid rain		
1852	Robert Angus Smith connected the presence of acid rain with human activities	j	
1856	Jules Reiset recognized that decaying matter releases nitrogen, providing		
	the basis for the nitrogen cycle		
1877	Theophile Schloesing and Achille Muntz discover the process of nitrification		
1880	Herman Hellriegel and Hermann Wilfarth discovered the process of		
4000	biological hitrogen fixation		
1886	Ulysse Gayon and Gabriel Dupetit discovered the process of denitrification		
1896	the greenhouse effect was more fully quantified by Svante Arrhenius		
1909	Fitz Haber synthesized animonia from hitrogen and hydrogen gas		
1913	Lit was reported that many lakes in the US and Europe were undergoing		
1947	It was reported that many lakes in the US and Europe were undergoing		
10500	Through the mid 1050s. N additions to coostal approximations were incorrectly		
19508	considered a benefit to productivity		
1950s	Concern about coastal eutrophication was first noted in Moriches Bay, New Yo	ork	
19503	Haagen-Smit et al were some of the first to document ground-level ozone		
1555	formation and the role of NO_{ν} in its formation		
1960s	there existed 9 reported 'dead zones' in coastal areas		
1968	Svante Oden was the first to link NO_x emissions from one country (the LIK) to		
1000	freshwater acidification in another country (Sweden)		
1970s	on a global scale, the rate of N_r creation by the Haber–Bosch process surpass	ed	
	natural N fixation		
1970	Paul Crutzen quantified the role of nitrogen oxides in ozone depletion		
1972	Sweden made a presentation to the UN Conference on the Human Environme	ent,	
	which started efforts to better understand acidification		
1972	Likens et al. demonstrated that nitric acid formed from fossil fuel combustion		
	leads to acid rain		
1985	The greenhouse effect was further quantified by Ramanathan et al., including	the	
	contributions of N2O		
1985	Stratospheric ozone depletion was discovered by scientists from the British		
	Antarctic Survey		
1986	Anammox (anaerobic ammonium oxidation) was first observed in a Dutch		
	wastewater treatment facility		

1989	John Aber <i>et al.</i> demonstrated that excess N deposition to forests not only causes damage to the forest, but it can also make forests a net source of N	
2003	The concept of the nitrogen cascade was proposed	
2009	Ravishankara <i>et al.</i> discovered that N ₂ O emissions are currently the most important ozone-depleting substance	
2011	There are 540 reported dead zones on a global basis	
	The European Nitrogen Assessment provides the first integrated and comprehensive look at N use in Europe	