QUALICHEM
Water Treatment

THINGS TO CONSIDER WHEN USING SODIUM NITRITE IN CLOSED LOOP SYSTEMS

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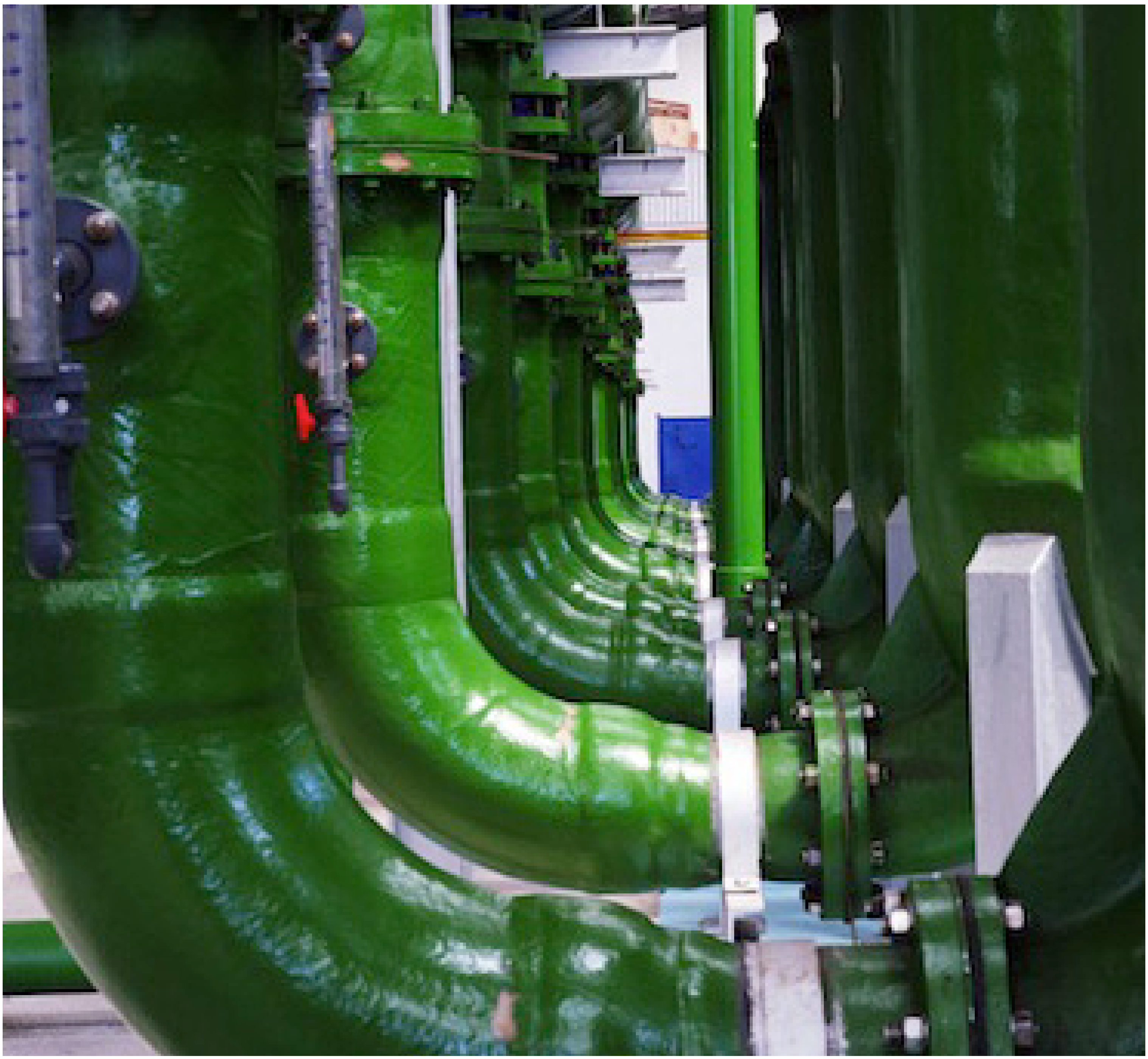
Table of Contents

Introduction

When considering chemical treatment programs for closed loop systems, sodium nitrite can be an economical and effective treatment option. In this informational article, we will provide what you need to know about sodium nitrite for closed loop treatment programs. You will learn how sodium nitrite acts as a corrosion inhibitor, concerns associated with the system, biological phenomenon that can occur, and how to combat problems.



About Sodium Nitrite

Sodium Nitrite has been used as a corrosion inhibitor for closed loop water systems for many years. Sodium Nitrite functions as an anodic corrosion inhibitor. Nitrite works to form a protective gamma iron oxide film on a metal surface. This layer is formed by the reaction of nitrite and dissolved oxygen and then kept in repair by the nitrite alone. Nitrite is not consumed to any practical extent since little is needed to form this film. It is this film that protects the metal surface from corrosive attack.

Sodium Nitrite offers excellent corrosion protection for ferrous metals. Nitrite functions best when used in the pH range 9.5 - 10.5 and formulations for closed systems often make use of borate buffers. In addition to buffering the pH into the desired range, borates promote passivation by facilitating the absorption of oxygen, and also provide some microbiological control. The concentration of nitrite required for inhibition increase with temperature.

Sodium Nitrite is not considered a good corrosion inhibitor for copper or copper alloys.

Concerns With Nitrite

Nitrite converts to nitrate when exposed to oxygen. It is also susceptible to microbiological attack. It is not recommended for open systems or where exposure to air is present (open tanks or sumps and cold storage systems).

Compatibility Concerns

Sodium Nitrite is an oxidizing agent and is not compatible with reducing agents such as sodium sulfite. It also has reduced effectiveness when chlorides and sulfides are present in the water, unless the dosage of nitrite is increased. In general, maintain no less than 500 ppm of sodium nitrite (preferably 1000 ppm), keeping levels of at least 350 ppm above the total concentration of chloride and sublet present in the closed loop system.

Biological Concerns

The reactions that affect nitrite are controlled by varying forms of bacteria. Some fungi and other forms of microorganisms have the ability to react with other forms of Nitrogen. The nitrite ion (NO_2^-) is included either as a primary food source or as an intermediate food source in a number of autotrophic reactions. Within the context of the Nitrogen Cycle there are three microbiological processes that are relevant to the use of Sodium Nitrite as a corrosion inhibitor in closed recirculating water systems.

Nitrogen Cycle

Understanding the nitrogen cycle and how it can impact nitrite based programs, or why your nitrite residuals keep disappearing, will help you learn how to effectively implement a nitrate closed loop water treatment program.

To review so far, the reactions that affect nitrite are controlled by varying forms of bacteria that use nitrite as food. Some fungi and other forms of microorganisms have the ability to react with other forms of Nitrogen. The nitrite ion (NO_2^-) is included either as a primary food source or as an intermediate food source in a number of autotrophic reactions. Within the context of the Nitrogen Cycle there are three microbiological processes that are relevant to the use of Sodium Nitrite as a corrosion inhibitor closed recirculating water systems.

Nitrification

Nitrification is a term used to describe a two-step process involving the nitrite ion. Step 1 involves the oxidation of ammonia ions to nitrite in the following manner:

$$NH_3 + OH^- + 3/2O_2 \rightarrow NO_2^- + 2H_2O$$

This step of the nitrification process usually occurs only when at least 100 pm of NH_3 is present. Because ammonia is not generally found in such high concentrations, this step of the nitrification process is generally found only in systems with process ammonia contamination.

Step two of the nitrification process involves the oxidation of nitrite to nitrate. This reaction proceeds as follows:

$$NO_2^- + 1/2O_2 \rightarrow NO_3^-$$

This reaction occurs naturally when nitrite ions are in the presence of oxygen. Certain bacteria, the most common of which come from the genera Nitrobacter, are able to use enzymes to catalyze this oxidation reaction. The energy produced is then used within the cells to assimilate carbon dioxide.

Each step of the nitrification process is carried out by separate microbial populations. Nitrifying bacteria are most commonly found in soil where they are an important part of the earth's natural fertilizing system. The nitrification process is aerobic and will not proceed under anaerobic conditions.

Denitrification

Denitrification refers to a process whereby nitrite ions are converted into molecular nitrogen (N_2). Denitrification proceeds through nitrite to the formation of nitric oxide, nitrous oxide and, finally, molecular nitrogen.

$$NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

Denitrification is a facultative anaerobic process. In this instance, facultative means denitrification can occur under conditions of no oxygen or conditions of extremely low oxygen concentration. Denitrifying bacteria are generally found in stagnant water. Low flow or no flow areas within a closed recirculating water system, such as dead legs and occasionally used piping, would be ideal areas for denitrifying bacteria to flourish.

Molecular nitrogen can be converted to ammonium ions through a process called Nitrogen Fixation. In nitrogen fixation, the ammonium ions are used to assimilate amino acids and proteins. Nitrogen fixation is an aerobic process. However, aerobic nitrogen-fixing bacteria can withstand extremely low levels of oxygen.

Nitrite Ammonification

Nitrite ammonification refers to the process where nitrite ions are converted to ammonium ions via hydroxylamine (NH_2OH) in a reduction reaction:

$$NO_2^- \rightarrow NH_2OH \rightarrow NH_4^+$$

Ammonium production from this reaction occurs at a relatively high rate. The enzyme responsible for facilitating this reaction is inhibited by the presence of oxygen, making this a strictly anaerobic process. Again, areas such as dead legs and occasionally used piping are ideal areas for this to occur.

As a troubleshooting tool, keep these processes in mind when you start to see nitrite residuals dropping with no apparent water losses and a possible increase in biological activity. While this may be the in-depth technical explanation as to why and how your nitrite residuals keep disappearing, the bottom line is that bugs may be out of control in your closed loop.

Consequences

Now that you understand the function of nitrite closed loop treatment programs, the nitrogen cycle and how biological problems emerge, it is important to discover the consequences of an out-of-control system and how can you remedy the situation.

The use of Sodium Nitrite is a closed system as a corrosion inhibitor at levels 800 - 1500 ppm of nitrite offers an excellent source of nutrition for the three processes described above. Most closed recirculating water systems will have areas of anaerobic and aerobic conditions. Therefore, it is possible to have more than one process operating within the same system. At the present time, there are no field tests available to determine either qualitatively or quantitatively if these processes are occurring.

Therefore, a system experiencing a drop in nitrite levels should be investigated with particular attention given to:

1. Corresponding increase in nitrate levels
2. Corresponding increase in ammonia levels
3. Microbiological activity increase
4. Corresponding loss of alkalinity
5. Addition of make-up water (decrease in conductivity)

If it is suspected that one or more of the microbiological processes described here is operating within the system, it is imperative that the condition be addressed immediately. The loss of inhibitor levels can lead to excessive corrosion within the system. In addition, low levels of ammonia in the presence of low levels of oxygen have been shown to cause severe corrosion cracking. Copper corrosion is accelerated by the presence of ammonia.

Corrective Actions

There are corrective actions you can take when these situations occur.

- **Clean the system** - if cleaning and purging the system is an option, it is highly recommended that the water circuit, including all dead legs and isolated piping, be purged and sanitized with peroxide or chlorine dioxide. The system should then be retreated with a nitrite-free corrosion inhibitor and occasional doses of an appropriate biocide.

- **Filtration** - Side stream filtration is highly recommended for most closed systems and is considered a best practice. Besides removing corrosion byproducts and debris that will cause under deposit corrosion and growth sites for microbes, filtration helps to remove the dead microbiological matter, which will eliminate a source of nutrients for these processes.

- **Biocide selection** - Glutaraldehyde and isothiazolinone biocides are typically recommended, but have been shown to be marginally effective to control these types of microorganisms. For this reason, the occasional addition of these biocides may not arrest the problem.

Here is a summary of the pitfalls related to the various biocidal options that may typically be used for treatment in a closed system.

- Glutaraldehyde is readily biodegradable and can add nutrients for biological activity. It reacts with ammonia and the rate of killing is slowed.
- Isothiazolinone presents handling and skin sensitizing concerns. Copper versions will increase bulk water copper concentration over time.
- The use of biodispersants and the microbicide TTPC has been shown to be extremely effective treatment regime to mitigate the results of denitrification and ammonification.
- Oxidizing biocides are not recommended for closed systems for routine biological control. These include sodium hypochlorite, stabilized bromine/chlorine and chlorine dioxide. As referenced above, some oxidizers may be used to clean up a system for a one-time treatment.

It is worth mentioning that when a water treatment manager is presented with ongoing biological problems with a nitrite program that are not easily resolved, one of the most common ways to combat the issue is to remove the problem altogether. They can do this by, after a proper cleanup, converting to an alternative chemical such as molybdate. Molybdate based programs do not pose the risk of biological problems that nitrite programs do. They may, however, be a bit more costly.

While the use of sodium nitrite in closed water systems has merit as an inexpensive and very effective corrosion inhibitor, very careful consideration should be given to the proper application of the program to avoid the potential downsides discussed in this paper.