The Microbiological Aspects of Sodium Nitrite

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Sodium Nitrite has been used as a corrosion inhibitor for closed water systems for many years. Sodium Nitrite functions as an anodic corrosion inhibitor in much the same manner as chromate and molybdate. As an anodic corrosion inhibitor nitrite induces the metal surface to form an impervious gamma iron oxide film. It is this film that protects the metal surface from corrosive attack.

Sodium Nitrite offers excellent corrosion protection for tin, aluminum and ferrous metals. Nitrite functions best when used in the pH range 9.0-10.5. Because of this pH restriction borate buffers are often used in nitrite formulations. In addition to buffering the pH into the desired range borate also promotes passivation by facilitating the adsorption of oxygen. Sodium Nitrite is not considered a good corrosion inhibitor for copper or copper alloys. It is generally recommended that a specific copper inhibitor be used or that system conditions be kept such that the self protection copper film is not removed.

Certain of the earth's basic elements (Carbon, Oxygen, Nitrogen and Hydrogen) are cycled through the earth's biological system.

These cycles involve physical and chemical reactions. The cycling of the element Nitrogen is highly dependent upon the activities of a wide variety of microorganisms. Microorganisms that are capable of using inorganic matter to produce energy are termed "autotrophic". These autotrophic microorganisms use the energy produced from the reactions with inorganic material to produce ATP (adenosine triphosphate). ATP is converted to ADP (Adenosine diphosphate) in a reaction the yields large quantities of energy.

The energy produced in the reaction is utilized within the cell to allow other, energy requiring reactions to occur.

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. 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.

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.

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:

$$\mathbf{NH_3 + OH^- + 3/2\ O_2 > NO_2^- + 2H_2O}$$

This step of the nitrification process usually occurs only when at least 100 ppm of NH_3 is present. Because ammonia is not generally found naturally 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:

$$\mathbf{NO_2^- + 1/2\ O_2 > NO_3^-}$$

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 where by 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.

$$NO_2^- > NO^- > N_2O^- > N_2$$

Denitrification is a flaculative anaerobic process. It 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 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 a 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:

$$NO_2^- > NH_2OH -> NH_4^+$$

Ammonium production from this reaction occurs at a relatively high rate. The enzyme (dissimilatory nitrate reductase) responsible for facilitating this reaction is inhibited by the presence of oxygen making this a strictly anaerobic process.

The use of Sodium Nitrite as a corrosion inhibitor at levels of 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 the following:

1. Corresponding increase in nitrate levels.
2. Corresponding increase in ammonia levels.
3. Corresponding loss of alkalinity.
4. Addition of make-up water.

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.

Quaternary ammonium/tin biocides have been shown to control these types of microorganisms. However, the use of these products may lead to foaming problems unless an antifoam is incorporated along with them. Certain of these processes are likely to be found in low or no flow areas. For this reason the occasional addition of a biocide may not arrest the problem. In these situations it may be advisable to purge the system and sanitize with a chlorine biocide. The system may then be retreated with nitrite and occasional doses of an appropriate biocide. In larger systems where purging and sanitizing may not be economically feasible, it may be advisable to switch treatment programs in order to eliminate the source of nutrients thus eliminating the microbiological processes.