CORROSION INHIBITORS

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CORROSION INHIBITORS

Understanding how various corrosion inhibitors work is directly related to understanding the corrosion process. In the previous section we discussed in detail the corrosion process and the various forms in which it can appear. However, we can recap this discussion by reiterating that for corrosion to take place we need: an anode, a cathode, a circuit through the metal for electrons to flow, and our "wire" to complete the circuit, the cooling water. I

f any of these items are missing, corrosion will not take place. Once we understand these basics of the corrosion process, it becomes obvious that the formation of a chemical inhibition film at either the anode, cathode, or both of these sights will ultimately minimize the corrosion process. Therefore, corrosion inhibitors are classified as anodic, cathodic, or both, depending upon the corrosion reaction each controls.

Corrosion inhibition usually results from one or more of three general mechanisms. In the first, the inhibitor molecule is adsorbed on the metal surface by the process of chemisorption, forming a thin protective film either by itself or in conjunction with metallic Ions. Some inhibitors, however, merely cause a metal to form its own protective film of metal oxides, thereby increasing its resistance; this constitutes the second mechanism. In the third, the inhibitor reacts with a potentially corrosive substance in the water.

Choice of the proper inhibitor is determined by the cooling system design parameters and water composition. The type of metals in the system, stress conditions, cleanliness and designed water velocity all affect inhibitor selection. In addition, other factors to be considered include treatment levels required, pH, dissolved oxygen content and, salt and suspended matter composition.

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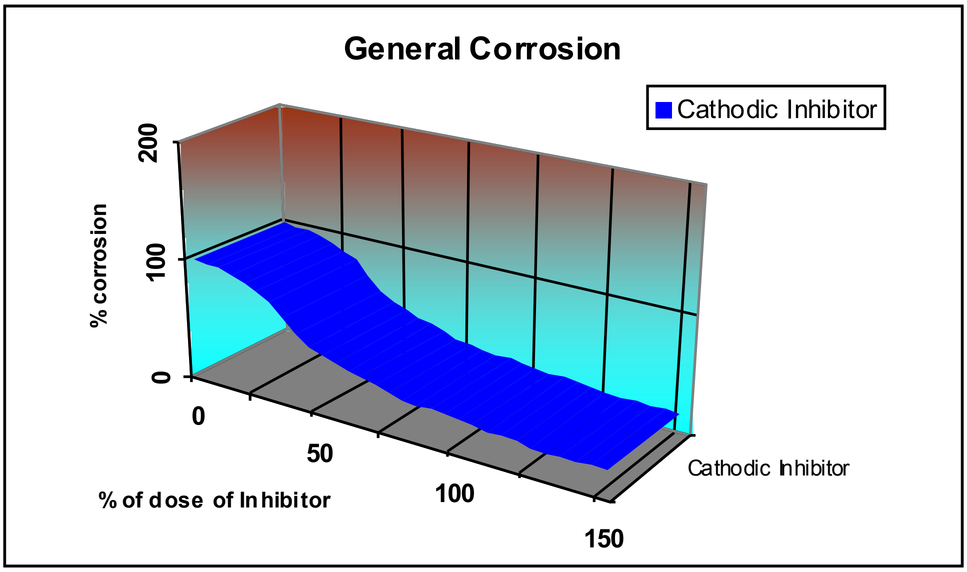
Cathodic inhibitors

Cathodic inhibitors are generally less effective than the anodic type. In contrast, they often form a visible film along the cathode surface, which polarizes the metal by restricting the access of dissolved oxygen to the metal substrate. The film also acts to block hydrogen evolution sites and prevent the resultant depolarizing effect.



The activity of a cathodic inhibitor can be illustrated to the left. Starting at a zero inhibitor concentration, the system performs a corrosion rate of 100%, the untreated and unprotected corrosion level.

As we started to feed the cathodic inhibitor, as the concentration remains at lo9w level, no significant effect in the general corrosion rate will be monitored. This is because the metal dissolution is taking place in the anodes, and the anodic reactions remain unchanged, having sufficient cathodic half cells potential, to combine with.

Of course as the concentration of the inhibitor increases, the cathodic sites are deactivated, and after a certain dose, the available cathodic potential becomes insufficient to cover the anodes requirements. So anodes start to "starve", their activity drops, and the overall general corrosion rate is dropped, to a minimum value, which is related to the specific corrosion inhibitor and to the system's characteristics.

When we start to lower the inhibitors concentration, as it is presented in the right video, after a delay, necessary for the reactivation of the cathodic sites, the general corrosion rate increases again to reach the value of the corrosion rate of the untreated system.

Under the same conditions, if we examined the pitting tendency as a function of the inhibitor concentration, we obtain a similar graph.

The activity of the differential aeration cells (under deposit attack), follows the same way, because the area under the deposit is the anode, while the surrounding free metal area became the cathode.

So the cathode remains available to the cathodic inhibitor to act, and being deactivated, the under the deposit existing anode is deactivated due to the cathodic potential unavailability to combine with it.

Cathodic inhibitors:

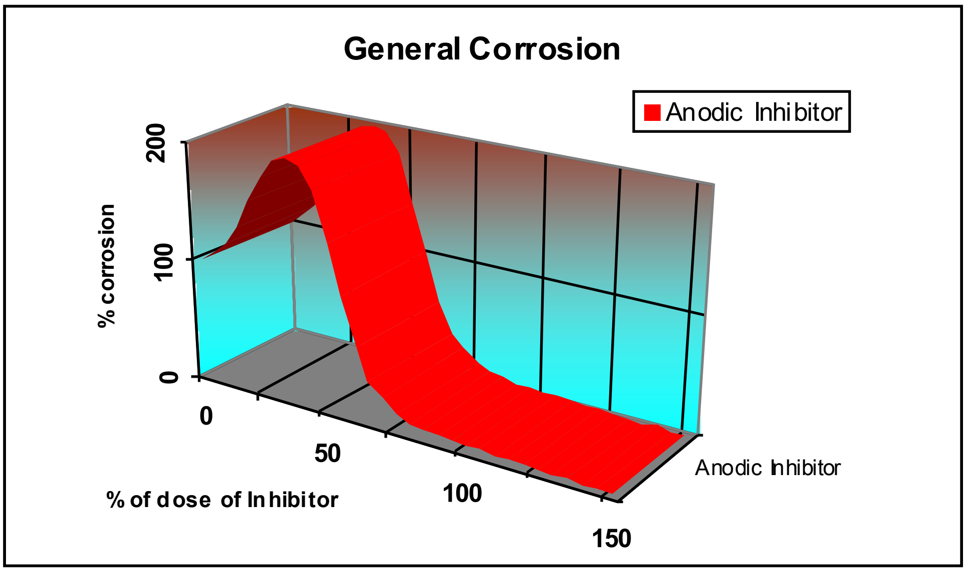
- Zinc hydroxide
- Zinc phosphate
- Calcium carbonate
- Calcium phosphate

Anodic inhibitors

Anodic inhibitors build a thin protective film along the anode, increasing the potential at the anode and slowing the corrosion reaction. The film is initiated at the anode although it may eventually cover the entire metal surface. Because the film is not visible to the naked eye, the appearance of the metal will be left unchanged.

As long as the inhibition is taking place at their anodes, where metal dissolution takes place, the expected corrosion rates as a function of the inhibitor concentration differs in anodic inhibitors than the cathodic ones.

Especially, when we started to feed the inhibitor, at the beginning the corrosivity increases, as it is presented in the following graph.



As the concentration increases, the corrosivity increases, reaches a maximum limit, and afterwards starts to decrease.

This maximum value can be even a hundred times higher than the value of the untreated one.

As the concentration increases, the corrosivity continue to drop, coming asymptotically to the minimum equilibrium value, related to the corrosion inhibitor type and the system's characteristics.

The explanation of the phenomenon is that a corrosion inhibitor is blocking the anodic sites, where corrosion takes place. The concentration of the inhibitor is below the required levels, and the protective films are not yet established, then the inhibitor start to block weak anodes first. as the stronger (and more active anodes resist to the blockage).

As the cathodic potential remains constant and the majority of the strong anodes remains active the blocking of the weak anodes liberates excessive potential to the strong anodes to corrode.

Of course as the concentration increases, then the inhibitor can react with the strong anodes, and blocking them the corrosivity is decreased.

The final value is finally the one tenth of the value that a typical cathodic inhibitor can yield.

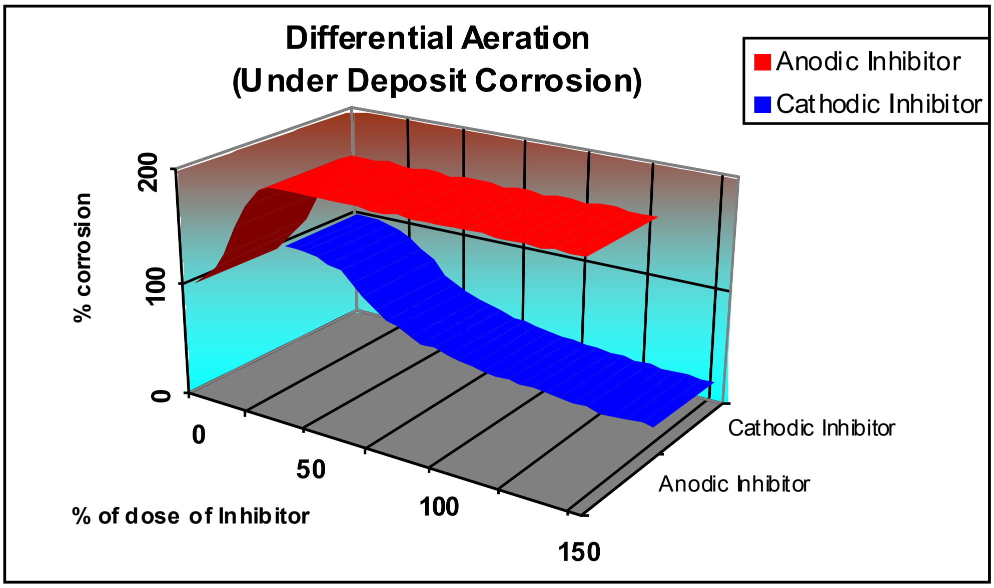
If we are trying to distort the equilibrium, by lowering the inhibitor concentration, as it is presented in the video to the right, at the begining no significant increase of the corrosivity is taking place.

As the decrease continious, start to increase the corrosivity, reaches a maximum limit (much higher than the maximum limit achieved when we where increasing the concentration, and then drops sharply to the untreated system's value.

Due to this characteristic performance anodic inhibitors are characterized as "UNSAFE" and care has to be taken as to:

- Start the application with an initial concentration, normally three to four times the maintenance level as to obtain rapid film formation and to avoid overcorrosivity of the system.
- Observe the inhibitor concentration, especially if the system is leaking to avoid drop of the concentration which will result in excessive acceleration of the corrosion process.

As long as the anodic inhibitor is acting at the anodes, the presence of differential aeration cells creates big problems to the system. A differential aeration cell being protected from inhibitors access due to the porous deposit over it, cannot be reached by the inhibitor.



So the differential aeration cells remain not only untouched, but they are combined to the entire cathodes of the system collecting the sum of the corrosion potential. Their activity is highly accelerated, controlled only from the diffusion of the corrosion products through the porous deposit.

As final conclusion, anodic inhibitors are giving an excellent protection to the system, but care should be taken as :

- Make an initialization treatment in higher dosages for rapid film formation.
- Avoid the drop of the concentration under the required minimum level, because this will accelerate corrosion.
- Never use anodic inhibitors alone in a dirty system.
- This will accelerate differential aeration cells and excessive localized corrosion will take place.
- Preclean the system, or use them in combination with strong cathodic ones

Typical Anodic inhibitors:

- Chromate, molybdate, and nitrite -- catalyze the reaction between the metal and oxygen to form a passivating film. They also become a part of the gamma iron oxide film. Chromate and nitrite are the only anodic inhibitors that function in the absence of oxygen.
- Orthophosphate -- also catalyzes the reaction between steel and oxygen to form a passivating gamma iron oxide film. Oxygen must be present in water for orthophosphate to function as an anodic inhibitor.
- Polyphosphate -- exhibits some anodic properties but functions primarily as a cathodic inhibitor.

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