Ask!Marine Care;

Passivation of carbon steel systems

How to clean and passivate systems with a variety of alloys

Introduction

Corrosion (or rust) in carbon steel systems can occur due to various reasons and is in most cases an unwanted phenomenon. There are many forms of corrosion, depending on the source and the mechanism or processes that initiated the corrosion. For deeper insight in corrosion (engineering) literature is given in the end, as the subject is too broad to describe here. This paper is limited to general iron oxide corrosion or rust on the inside of closed steel systems (for instance closed loop cooling/heater systems, Low/Medium pressure steam boilers and heat exchangers) or systems that might contain other alloys (like copper or stainless steel) besides carbon steel. Combinations of alloys in a system is challenging to remove rust from the steel surface with general acidic cleaners. Not all acids are suitable to use on all alloys or combinations thereof and certain acids will cause galvanic corrosion or plating.

General protection of steel

Unprotected (plain) carbon steel will corrode in a watery environment. And with elevated temperatures, like cooling water and steam boiler systems, the rate of corrosion is increased. In cooling and boiler water systems the steel surface is protected by addition of chemicals to the water. The chemicals have multiple functions, depending on the type of system. These are;

- Raising alkalinity / pH value to prevent general acidic corrosion
- Preventing lime scale precipitation by addition of scale inhibitors or complexing agents
- Addition of inhibitor to protect the steel surface against (high temperature) corrosion
- Removal of dissolved oxygen gas with oxygen scavengers
- Passivation/protection of the steel surface with oxidizers or phosphates

The chemicals will be consumed over time and it is important to monitor the water quality to prevent precipitation of scales or starting the corrosion process.

Besides the dosing of water treatment chemicals, to prevent scales which initiates corrosion in these water systems, it is important that the source of the water is of certain quality and does not introduce contaminants. For instance, well water can contain high concentration of dissolved iron, that could induce corrosion processes. Water with high value of hardness (dissolved calcium carbonate) can cause lime scales. And chlorides are particular corrosive to steel, even at low concentrations. The best type of water to be used for cooling and boiler systems is Reversed Osmose / Demineralized (RO/DI) water. All dissolved solids (salts with ions like chlorides and calcium) and organics (total dissolved organics) are removed by the RO/DI process.

Why it is necessary to remove rust

Any scale, including corrosion products like rust, can cause several issues on the inside of closed loop heating or cooling systems.

1. Scale changes the heat transfer rate of the pipe. Heat transfer will become less with more scale present. With the effect that temperature will rise in the scale contaminated areas.
2. Scale tend to influence the flow inside pipes, and this can cause deposition of more scale (scale build up).
3. Scale prevents the steel surface to react with water treatment chemicals.
4. Scale can induce other corrosion forms, like under deposit corrosion and biological induced corrosion.

Furthermore, corrosion products (iron oxides) themselves can act as a propagator for corrosion, especially in combination (with the presence) of chlorides. Iron oxides or rust has a very porous structure that can adhere dissolved ions like chloride. Chlorides are part of a corrosion process that can induce pitting corrosion, which is an autocatalytic process. An autocatalytic process, once started, will continue and not stop. In the case of pitting corrosion by chloride, this process shall continuously corrode the steel.

Rust removal and passivation/protection of steel surfaces

The removal of rust (iron oxides) is generally performed with an acidic cleaner. The acid will react with the iron oxide and dissolve the iron in the solution. Acids are corrosive to steel so a corrosion inhibitor, specific for the type of acid, should be present. A corrosion inhibitor reduces the corrosion rate of the acid. The rise of iron in the solution, during a cleaning, is a perfect parameter to monitor the progress of the removal of iron oxides from a system. Continuous measurement of dissolved iron will show a stabilization of the iron concentration which indicates a cleaning is finalized.

After an acid cleaning the steel surface is highly active and will react with oxygen from the air forming so called flash rust. Therefore, it is in most cases required to passivate the steel surface prior to commissioning the system. Passivation can be performed in multiple ways, but in all cases requires additional chemicals to the acid

cleaner. Most common passivation treatments of steel systems are based on ammonia citrate or phosphates. Both methods are compatible with the water treatment chemicals used for protecting the system during operation.

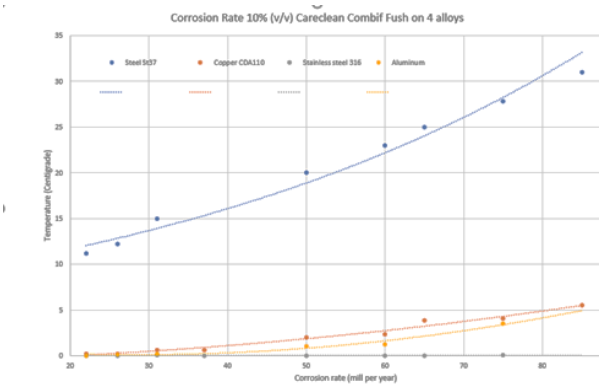
Issues using acid solutions in multiple alloyed system

Steel systems may contain components that consists of other alloys, for example copper coolers or stainless-steel valves. Other alloys than steel have different corrosion potential and this potential difference will show in an acidic environment. Most commonly known phenomena is copper plating on carbon steel surfaces, due to acidic solution in a system with copper and carbon steel alloy. The acid will dissolve both copper (oxides) and iron oxides but copper is more noble than steel and precipitates on the steel surface. Copper plating on steel surfaces are unwanted as the heat transfer will be affected. This chemical reaction of different alloys in an acidic medium is called galvanic corrosion. Second, not all materials and alloys are resistant to all types of acids. For instance, hydrochloric acid is highly corrosive to stainless steel but inhibited hydrochloric acid can be used safely in carbon steel systems. Prior to a cleaning of a system with an acid, it is important to know exactly all the materials present that come in contact with the cleaning solution. To prevent (galvanic) corrosion parts that consists of other alloys than steel should be isolated or temporary removed from the circuit, a highly laborious and in some cases impossible, job.

Careclean Combi-Flush

Marine Care has developed a cleaning product, Careclean Combi-Flush, which solves (most) issues encountered by acid cleaning. Instead of using the strength of an acid to remove iron oxides, highly effective iron complexing agents are used. These complexing agents are even effective in a pH neutral solution and thus limiting the corrosion on steel surfaces and most common alloys. Galvanic corrosion will not occur using Careclean Combi-Flush making it safe to use the product in systems that contain various other alloys next to carbon steel alloys, for the removal of iron oxides. The corrosion rate of a 10% (v/v) Careclean Combi-Flush on various alloys have been monitored (see graph 1) at various temperatures. Careclean Combi-Flush is safe to use on carbon steel, stainless steel, copper alloys, aluminum alloys and in combinations of these alloys in one system. There is some corrosion rate on steel alloys, which makes sense as the product removes iron oxides from the steel surfaces. Careclean Combi-flush has a very low corrosion rate on the other alloys.

The second feature of Careclean Combi-Flush is the fact the product will create a passive film on the carbon steel surface after removal of the iron oxides. This film will (temporary) protect the steel surface to form flash rust and the passive film is compatible with water treatment chemicals that are used in the operational phase of the system.



Con's and pro's for Careclean Combi Flush

Careclean Combi-Flush is used in a 5-10% (volume) solution preferably at a temperature of 45 oC. To monitor the cleaning with Careclean Combi-Flush we advise to measure the iron concentration every hour. The maximum capacity uptake of iron in a 10% Careclean Combi-Flush solution is 6-7 g/l Fe. When iron concentrations reach this value, the solution is saturated and should be refreshed to ensure an optimal cleaning result. The cleaning is finalized once the iron concentration stabilizes. When the cleaning finalizes the solution is not cooled but drained directly. This higher temperature will ensure a better formation of the passivation film on the steel surface and the surface will dry directly, preventing moisture on the steel surface.

Careclean Combi-Flush removes iron oxides and passivates the carbon steel surface in one step, compared to acidic based cleaning procedures to remove iron oxides that involves flushing and separate passivation steps to achieve the same result, Careclean Combi-Flush method reduces the use of water and creation of waste water 2-3 fold.

In case debris is found in the system after draining Careclean Combi-Flush, it is safe to rinse the system with ammoniated demineralized water (pH value around 10).

One of the main advantages of Careclean Combi-Flush is the pH Value of the product making it safe to use for personnel, environment, and equipment. All constituents of Careclean Combi-Flush.

- pH neutral solution
- rust removal and passivation in one step
- less creation of wastewater
- not corrosive to alloys or combinations of alloys

There are limitations in the use of Careclean Combi-Flush. As the product is not acid based, it does not remove scales like lime scale (calcium carbonate) or marine growth. Certain types of hard to remove iron oxides formed under special conditions like magnetite

(high pressure steam boilers) or mill scale (milling and annealing process) are generally hard to remove with most common and relative mild acids, and in most cases hydrofluoric acid is required for the removal of these type of iron oxides.

Comparison Careclean Combi Flush versus common rust removers

Below is a comparison table of Careclean Combi-flush and three most used acid cleaning solutions for the removal of iron oxides in carbon steel boiler and cooling water systems.

Table: Comparison Careclean Combi-Flush with acidic rust removers.

	Careclean Combi Flush	Hydrochloric acid based	Citric acid based	Phosphoric acid based
pH Value 3-10% sol.	Neutral pH	< 1 Strong acid	2-3 Weak acid	< 1 Strong acid
Dilution for rust removal carbon steel	5-10% (v/v)	4-7% (w/w)	4-5% (w/w)	5-10% (w/w)
Performance temperature	>45 °C	>25 °C	>65 °C	>45 °C
Labeling	None	Corrosive	Irritant	Corrosive
Corrosion rate on Carbon steel based on inhibited solution	20-25 mpy at 50 °C	25-50 mpy at 50 °C	20-40 mpy at 50 °C	20-40 mpy at 50 °C
Suitable on (in combination with stainless steel) -Stainless steel -Copper -Aluminum	 Y Y Y	 N N N	 Y N N	 Y N/Y N
Removal of -Mill Scales -Rust -Lime scale	 N Y N	 Y Y Y	 N Y Y	 N/Y Y Limited
Passivation of carbon steel surface	Y	N	Y (additives needed)	Y (depending on procedure)
Flushing after cleaning	Y/N 1 volume	Y 2-3 volumes	Y 2 volumes	Y/N 1-2 volumes
Waste water process	$FeCl_3$ and lime/caustic	Lime/caustic	$FeCl_3$ and lime/caustic	$FeCl_3$ lime/caustic
Raise COD value in effluent	Slight	No	Yes	No

Marine Care product information:

Careclean Combi-flush

[1] Montana, *Corrosion Engineering,* Mcgraw Hill