

NEW TECHNOLOGY FOR SECONDARY HEAT TRANSFER FLUIDS

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The subject of this text is the novel inhibitor technology for use in glycols, water and salt based brines reduces corrosion, sludge, gelling, scaling, developed for industrial use by ChevronTexaco. The new technology offers to the engineer, next to the direct technical advantages also a wider range of material choice for the installation. This long life inhibitor results in long lasting protection and keeps heat transfer capability of the system optimal.

Introduction

One of the first steps a design engineer should take when selecting a heat transfer fluid in a new or existing secondary refrigeration system, is to compare physical properties of secondary heat transfer fluids. This will guide him in selecting the right fluid from a thermophysical point of view. Indeed, it is quite important to select a fluid on the basis of its freeze point, boiling point, viscosity, specific heat, density and thermal conductivity. The correct selection will give a guarantee that in the final realization the system will be able to deal with the thermal load to which it has been designed. Apart from the physical properties also other factors will play a role, depending upon the installation at hand. Factors like toxicity, environment impact and flammability will impact the way a fluid is handled in the daily operation.

Furthermore, the design engineer wants a fluid which is capable of protecting all vital parts for as long as possible. Such vital parts include the heat exchanger(s), pump(s), valves, sensors ...

Keeping the vital parts in good condition will assure a permanent good overall system performance and a constant capacity.

The perception is that during the design phase little or no attention is paid towards the total cost of ownership and the corresponding cost of operation. Solely focusing on initial investment cost is of course much easier, because it is directly visible. Even for small parts of the total investment, like for the heat transfer fluid, only the initial cost is considered. Yet from field experience it can be concluded that many systems have lost their cooling capabilities showing a maintenance costs that could have been avoided or reduced by selecting the correct heat transfer fluid in the first place.

Corrosion and consequences

Corrosion of metal parts and the degradation of plastics can have severe consequences when they occur, especially when the fluid that is inside has an environmental or toxicological impact. Breach, cracks, perforations and the associated leaks today are very much real and they cause, apart from noise, also sometimes the long shut down times of systems. Costs associated to it are generally high and typically exceeding the investment of the heat transfer fluid. Once such a leak occurred, they can trigger more incidents. A few examples of these are: leaks cause an augmented air intake leading to increasing corrosion kinetics in the whole system, whilst also causing corrosion of external surfaces on which the liquid is leaking. The effects can also include, especially in the food industry, the contamination of consumer products. In the best case, the contamination is discovered timely and product can be recalled and destroyed before it is consumed. But the sad reality is that such recalls happen. All this is actually completely unacceptable and the best way to deal with it is to prevent it in the first place.

Furthermore, the industry knew a large growth in systems using heat transfer fluids during the last 15 years. Nowadays, it is known that there is quite a large number of glycol and brine systems, that are 8 years old or older, who are ready for partial renewal, in dramatic cases even complete revamping.

Luckily, for most systems today, the initial effects are not always dramatic. Yet if the internal corrosion and degradation is not stopped, dramatic consequences will become likely.

Process of Corrosion

In short, the process of corrosion needs four factors present in order to proceed:

1. Presence of a material where reduction can take place
2. Presence of a metal that can corrode
3. Presence of an electrolyte (a liquid that conducts electricity)
4. A closed electrical circuit (...-anode – electrolyte – cathode – bulk metal – anode -...)

The presence of oxygen and temperature will have an important impact on the speed of corrosion.

If one of these factors is not present, then no corrosion can occur.

What happens when corrosion starts, is that at a moment in time, galvanic cells start to exist on the metal surface. These galvanic cells are often created by the imperfect metallurgical character of common engineering alloys, but can also be caused by the connection of dissimilar metals or even differences in the chemical environment to which different parts of the metal pieces are exposed. While at the anodic side, metal ions are generated, at the cathodic side the surplus of electrons are transferred to an electron acceptor, in most common cases dissolved oxygen

adhering to the metal surfaces. The presence of the dissolved metal ions can be used as a monitoring tool for the condition of the installation. However, metal ion monitoring is only a blunt tool as often the metal ions formed will hydrolyze or precipitate with various anions present. The presence of deposit, sludge or even more subtle signs as the fading of a dye should not be disregarded as possible signs of active corrosion.

CORROSION MECHANISM

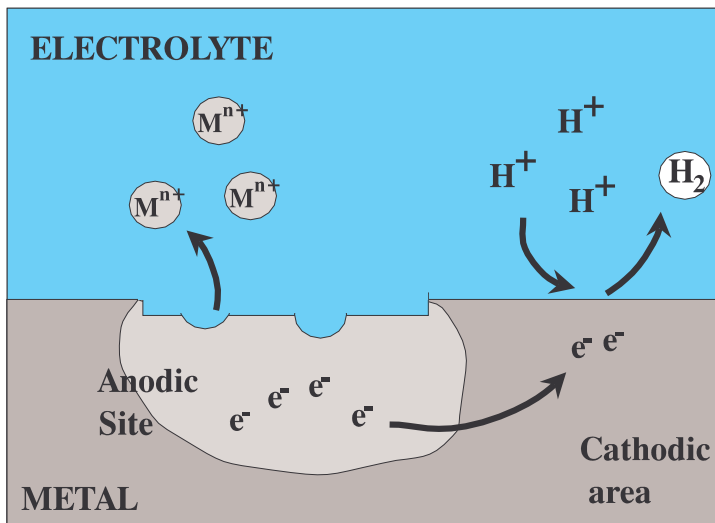


Fig. 1 - Corrosion Process

Traditional inhibition strategy

Different strategies exist to minimize the corrosion rates in secondary refrigeration systems.

Traditional inhibitors often use their isolating nature as their major property to reduce corrosion. The reasoning behind their use is quite simple: if one can achieve an electrically isolating layer, the exchange of ions and electrons can be stopped and the micro-electrical circuit is broken.

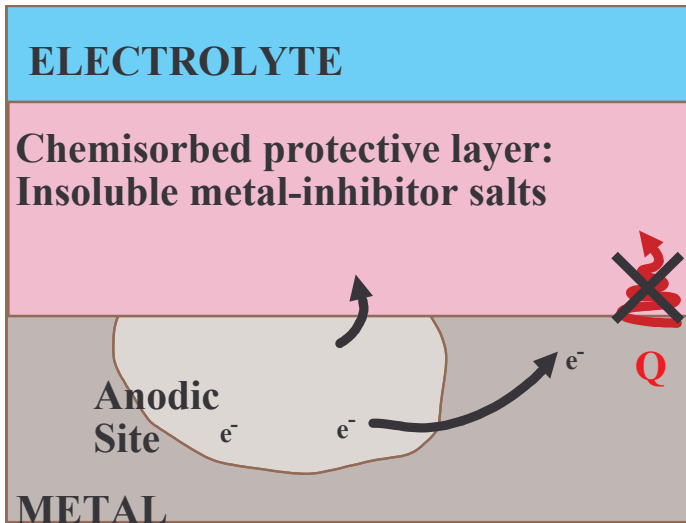


Fig. 2 : Traditional Inhibitor Technology

The inhibitor elements in traditional heat transfer fluids create these layers.

If these inhibitors would be able to cover all the installation on the inside, an efficient corrosion protection will be obtained. But this positive action is exactly often the origin of problems. The precipitation of inhibitors to form a layer is hard to predict; they drop out in various places inside the installation, more or less depending on the local conditions (temperature, pressure) of the environment. In reality important scales are found in large quantities inside heat exchangers. In these heat exchangers usually the thin tubing or canals are used to maximise heat transfer.

Since conductivities of such scales or layers usually lie 100 to 400x lower than the materials used in such heat exchangers. This means a significant loss in efficiency is generated. This is a fact that stands in great contrast to the tremendous amount of effort that is put into the optimisation of today's hi-tech heat exchangers!

To compensate for these losses, pump speeds need to be turned up. This is done to circulate more fluid per time unit, and thus to enable the system to 'transport' the same amount of heat as before. This then in return, increases energy consumption. Increased pump speed creates wear on the pump, in many cases also pump cavitation is detected.

System failures and causes when using traditional inhibition

Instable traditional inhibitors are actually often a cause of corrosion, degradation, and its consequences. They form insoluble, erosive and sludge-generating components generated in the heat transfer fluid itself.

Such contaminations are transported by the fluid and are left behind in areas with reduced flow – such as in a heat exchanger – or they damage by cavitation and erosion the pumps that circulate the fluid. The traditional heat transfer fluid is also a

possible origin of the gelling and sludge causing substances that obstruct pipes and heat exchanger tubes/canals. Because of these obstructing contaminations the effective heat exchanging area is reduced and turbulent flow behavior may be reduced to inefficient laminar flow conditions. In the end the system performance is substantially reduced. These deductions usually are not made since they all are invisible to the eye most of the time; yet it is observed that in industry extra costs are induced by system extensions which are needed to be able to achieve the original performance again. Sometimes brines are introduced in glycol systems in order to try to have the same performance as before, yet without asking oneself what the reason for the decreased performance might be. Also pump and even heat exchanger replacements seem to be considered accepted today. In this way, a seemingly harmless heat transfer fluid may be the cause of greater problems. Even worse, most of the time the heat transfer fluid stays in the system and is not questioned!

Innovative inhibition technology – mechanism and benefits

OAT technology is a totally different approach to corrosion protection, compared to traditional inhibition. Made up of carboxylate molecules, the inhibitors are polar and thus are attracted to the galvanic area that is formed. They attach only to the positive, or anodic site and will become attached to it. In this way they will isolate the area from the electrolyte. In doing this, they create a monomolecular layer. This means that heat transfer on that area is practically not influenced. Because of their action, the OAT inhibitors today are commonly called “selective molecules” since they do not work on surfaces where corrosion is not started. Contrary to traditional technology this means that no layer is formed and thus heat transfer on those areas is not affected - meaning the process can go on without reduction of efficiency. Since all scaling effects are prevented, dissolved eroding particles in the heat transfer fluid, which are made up of complex molecules of traditional inhibitors with metal oxides, are not observed coming from the OAT type inhibitors.

By the character of these molecules and the way they act, it is clear that these inhibitors will need some corrosion to be initiated before they come into action. Nevertheless, the corrosion is immediately stopped by this monomolecular layer since it then electrically isolates the anodic site to the electrolyte. A balance is created in the interchange of electrons, thereby stopping the corrosion process. Since these microscopic anodic areas displace themselves quite rapidly, under the influence of the free electron movement in metals that occurs, these galvanic areas “displace” themselves quite fast. When the anodic area is displaced, the molecules of the inhibitors detach to be taken up by the heat transfer fluid, and will act elsewhere. This is translated into the so called “long life effect” of these heat transfer fluids. It means that practically no depletion is observed.

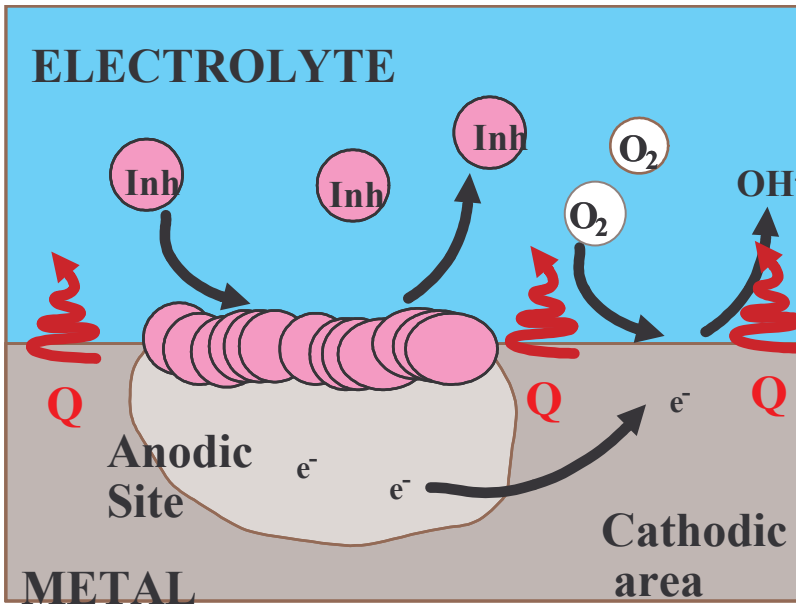


Fig. 3 - New Zitrec OAT Technology

Traditional vs new technology additives

With the Zitrec technology, Artec (a joint-venture of ChevronTexaco and Total) introduced a new class of corrosion- and degradation inhibitor technology for heat transfer fluids, initially developed by ChevronTexaco.

The inhibitors of this new range of heat transfer fluids are based on the synergistical effect of carboxylate acids (OAT) and a well-known yellow metal corrosion inhibitor. More traditional heat transfer fluids on the other hand are based on classical technologies, i.e. complex combinations of rapidly depleting (see fig. 5), less efficient and instable inorganic inhibitors such as nitrates, phosphates, carbonates, nitrites, molybdates, silicates and borates. Although these inhibitors can be quite efficient on one or two metals, they never achieve optimal performance on all materials used in a modern cooling/refrigeration system.

Depending on the type of product different weaknesses are known with the different types of traditional inhibition.

- Phosphate and carbonates are known to be highly unstable in combination with hard water, which is used commonly in Europe to make dilutions. This means by diluting a glycol with hard water, already these inhibitors lose part of their performance before it ever reaches the installation.
- Nitrate becomes aggressive toward solder.
- Nitrite, a classical ferrous metal inhibitor may well become aggressive toward classical steel and also toward Fe containing metals such as cast iron, at the moment that its concentration drops below the minimum dosage. This happens relatively easily as nitrite is oxidation sensitive and is reduced through consumption inside the system. Furthermore, nitrite has been associated with increased aluminum corrosion.

- Silicates, are multipurpose inhibitors. Silicates have the problem that they are intrinsically rather unstable, and have a gelling effect. They can lead to the formation of a hard layer of dehydrated silica combined with corrosion products. When these particles detach from this layer they will circulate through heat exchanger and pumps. There they cause obstructions and mechanical damage through their highly erosive character and damage pump seals.

On top of that, traditional inhibition technology has one more disadvantage. Phosphates and carbonates are known to be highly unstable in combination with hard water, which is commonly used in Europe to make dilutions. This means by diluting the inhibited glycol, these inhibitors already loose part of their performance before they ever reach the installation.

The Zitrec OAT technology on the contrary offers excellent stability toward hard water thanks to a special additive. European municipal water contains high levels of magnesium and calcium, which are kept into solution by using special additives.

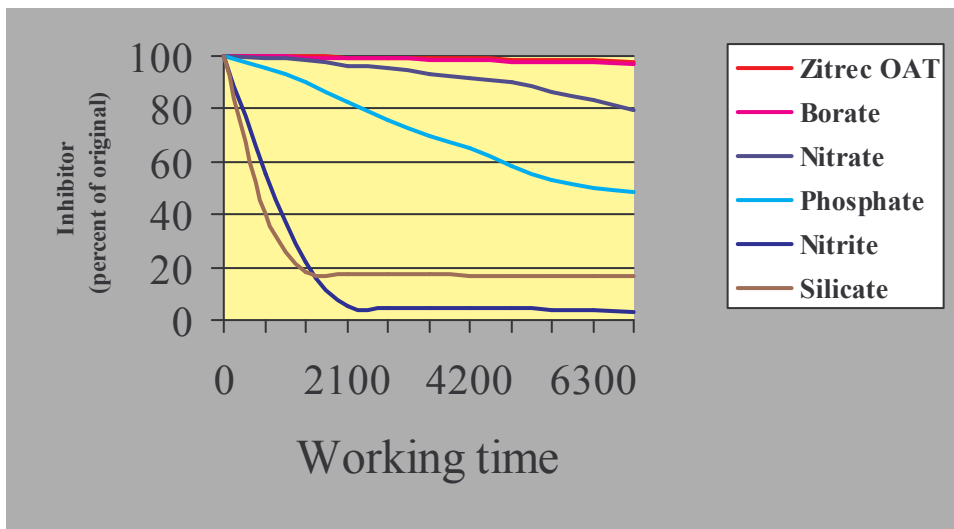


Fig. 4 : Inhibitor depletion rate for traditional corrosion inhibitors

New possibilities in selecting construction material

The OAT Zitrec technology does not only offer excellent corrosion protection and a long life protection effect, it also offers new design possibilities.

Thanks to the improved protection of aluminium, it becomes possible to use this material. Aluminium is much lighter and has significantly better conductivity than stainless steel (SS 316L: 18.5 W/m.K, Alu 237 W/m.K) resulting in an increased interest to use this material in secondary cooling systems.

Next to the protection of newer materials the new technology also offers the possibility to use cast iron pumps at elevated temperatures (+20°C) and even

higher without the risk of having excessive wear on softer materials like seals and heat exchanger.

Conclusion

It is clear that the use of OAT Zitrec technology in heat transfer fluids reduces the maintenance time and problems related to corrosion. Problems of this kind usually are only detected after some time, and it is rarely concluded that the real cause is the heat transfer fluid that is in use. The OAT technology ensures optimal corrosion protection during an extended life period with improved energy efficiency, thereby reducing cost of ownership drastically, and offering new possibilities to the use of alternative materials.

OAT Technology is a patented technology by ChevronTexaco.
For more information : www.zitrec.com