

GALVANIC CORROSION IN COOLING WATER ENVIRONMENTS

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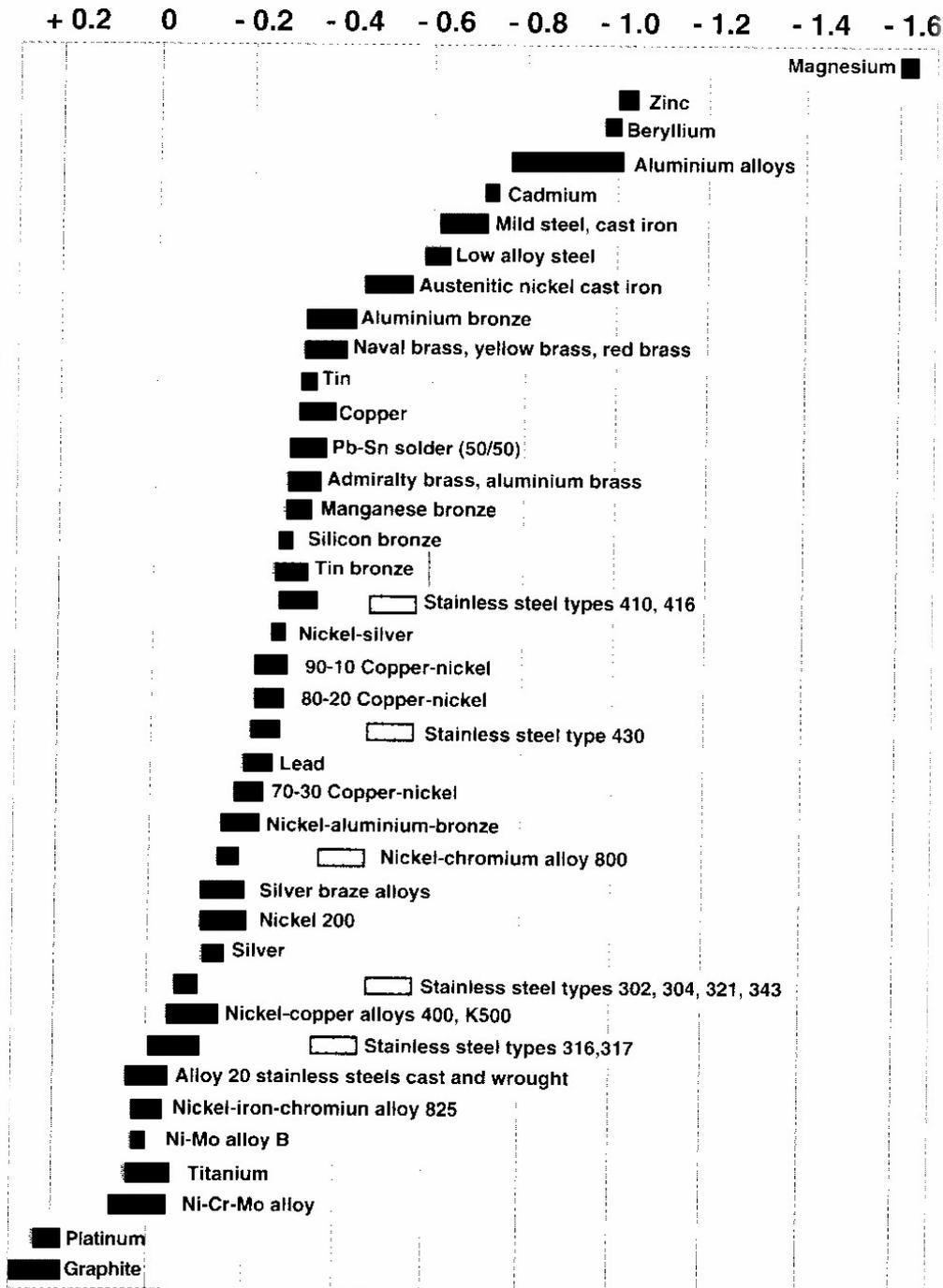
ABSTRACT: Severe galvanic corrosion problems have been identified mainly in heat exchangers used in several industrial cooling systems from chemical plants, refineries, power plants. The causes of heat exchangers failure and the modalities to avoid it in the future are discussed, emphasizing mainly the role of design, operation, maintenance and reparation of this type of equipment.

KEYWORDS: *corrosion, galvanic corrosion, cooling water, heat exchangers, stainless steel, water treatment, corrosion inhibitors.*

INTRODUCTION

Cooling water systems are confronted with three major interrelated problems: scaling, fouling and corrosion [1 - 3]. Many corrosion problems will arise if potential cooling water effects are not considered. Corrosion by water is entirely caused, at cooling water temperatures, by dissolved gases (i.e. oxygen, carbon dioxide) and salts (e.g. sodium and other chlorides, bicarbonates, sulfates) [4].

Volts: saturated calomel half-cell reference electrode



Alloys are listed in the order of the corrosion potential they exhibit in flowing sea water (2.5-4m/sec, 10-27°C)

Alloys indicated by in the chart may become active and exhibit a potential near -0.5volts in low-velocity or poorly aerated water, and in shielded areas

Fig. 1. Galvanic series in seawater [5]

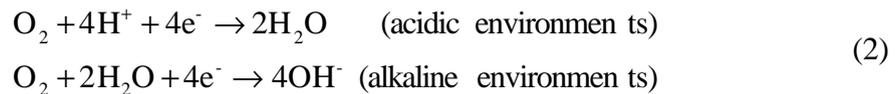
Galvanic corrosion can be defined as the corrosion associated with the current associated from an electrical coupling of dissimilar metals in an electrolyte. This results in the preferential attack of the more active (less noble, anodic) metal, while the corrosion of the other metal (more noble, cathodic) slows down or stops completely. The driving force of the galvanic corrosion is the potential difference between the two dissimilar metals in a certain conductive (electrolyte) environment. Galvanic corrosion potential is a measure of how dissimilar metals will corrode when placed against each other in an assembly. Metals close to one another on the chart (Fig. 1) generally do not have a strong effect on one another, but the farther apart any two metals are separated, the stronger the corroding effect on the one higher in the list. This list represents the potential available to promote a corrosive reaction, however the actual corrosion in each application is difficult to predict. Typically, the presence of an electrolyte (eg. water) is necessary to promote galvanic corrosion.

The oxidation (corrosion) which occurs at the anode could be described by the equation:



where M may be Fe, Cu, Ni, Cr etc.

In the vast majority of situations, the cathodic reaction occurring in galvanic corrosion is oxygen reduction:



hydrogen evolution:



or both.

In oxygen containing waters at near neutral pH the oxygen reduction is of primary importance. The corrosion's extend is frequently controlled by the cathodic area and the rate at which oxygen can reach its surface (mass transfer) [6].

According to Uhlig [7], corrosion rate of the anodic metal is expressed as:

$$r_{cor} = r_0 \cdot \left(1 + \frac{S_C}{S_A} \right) \quad (4)$$

The amount of dissolved oxygen available at the cathode, and the relative sizes of the anodic and cathodic areas are extremely important in galvanic corrosion. The corrosion is caused by a current flow from the anode (more active metal) to the cathode (noble or less active metal). Large cathode and a small anode means high current densities at the anode and, hence, high corrosion rates. Such area ratio (large cathode / small anode) is therefore highly unfavorable. In practical circumstances, corrosion of the anode may be 100 or 1000 times more than if the two areas were the same. The lack of dissolved oxygen, as in deaerated solutions, will limit the reduction reaction to the formation of hydrogen which tends to be absorbed on the cathodic surface thus reducing the cathodic area.

GALVANIC COUPLES ENCOUNTERED IN COOLING SYSTEMS

Cooling systems are often equipped with mixed metallurgy shell-and-tube heat exchangers. This type of heat exchangers were introduced in cooling systems for three main reasons [3]:

1. **Corrosivity of process fluids.** If process fluids are corrosive, parts of heat exchanger with thin walls, i.e. tubes, are made of more resistant materials (i.e. various stainless steels); other parts, with important thickness, i.e. tube sheets, shells, baffles, rods, are made of less resistant mild steel, lower corrosion resistance being counterbalanced by increased thickness.
2. **Aggressiveness of cooling water.** Many cooling systems have been equipped with standard mild steel heat exchangers, without a proper previous analyse of cooling water chemistry. After a short period of time, mild steel tubes failed massively and were replaced with more resistant stainless steel tubes.
3. **Lowering the costs.** A mild steel heat exchanger equipped with stainless steel tubes is less costly than a heat exchanger made entirely in stainless.

Besides mild steel - stainless steel heat exchangers encountered in chemical plants and refineries, many steam turbines are equipped with mild steel surface condensers having tubes made in copper alloys [8].

The most frequent galvanic couples formed in cooling systems are listed in Table 1.

Table 1. Galvanic couples formed in industrial water cooling systems

Galvanic couple			Examples
Cathode	Anode	Δe [V]	
Mild steel	Brass	-0,32	Valves
	Copper	-0,35	Lube oil coolers in FCC units
	Admiralty	-0,39	Turbine steam condensers
	70-30 Cu-Ni	-0,44	Diesel fuel coolers in FCC units
	304 SS	-0,55	Shell-and-tube heat exchangers in refineries, chemical plants
	316, 317 SS	-0,60	
	Graphite	-0,85	Graphitized asbestos seals

Supplemental, galvanic cells may appear in all areas where the metal shows different potentials in a conductive environment. Plating of noble ions (i.e. Cu^{2+}) on more active metal parts (aluminum, mild steel, even stainless steel) leads to local galvanic cells that induce a severe pitting in the less noble metal [9, 10]. Galvanic corrosion also occurs at stainless steel weld if sensitization has taken place or if welding has produced unfavorable dissimilar phases. Homogeneous galvanic corrosion may occur in gray and nodular cast irons (graphitic corrosion), on the surface of steel components partially covered with mill scale or iron sulfide corrosion products, or on the same component if sufficient different temperatures between sites exists (e.g. heat exchangers, refrigeration equipment) [10].

The more conductive the cooling water is, the greater the probability of galvanic corrosion.

Some galvanic corrosion case histories are presented in the followings.

GALVANIC CORROSION OF MIXED METALLURGY SHELL-AND-TUBE HEAT EXCHANGERS IN COOLING WATERS

Case History #1

In an oil refinery, the mild steel fraction C₃ cooler of the gas plant (Fig. 2) was retubed with AISI 304 SS (EN 1.4301) tubes to avoid the frequent shutdowns caused by the tubes' failure. The SS tubes were more resistant, but at the next annual shutdown severe galvanic attack was reported on the tube sheet, the separating walls from the inlet water boxes, and the reinforcing bars between the walls (Fig. 3). Due to the advanced corrosion, most of the separating walls have to be replaced.

The cooling water was chemically treated with a controlled pH stabilized phosphate - molybdate program that kept the general corrosion of mild steel parts below 0.1 mm/year [11].

The causes that led to this severe attack were:

- a high level of dissolved salts in the recirculated cooling water, which exhibited an average TDS content of 1,600 mg/L and a conductivity in the range of 1,000 - 4,000 $\mu\text{S}/\text{cm}$;
- a reduced flowing rate of the cooling water (specially during cold seasons, when operating personnel strangles the cooling water exit from the heat exchanger, in order to maintain the prescribed temperature of the cooled gases).

For remediation, zinc sacrificial anodes were mounted on the separating walls of the inlet water boxes.

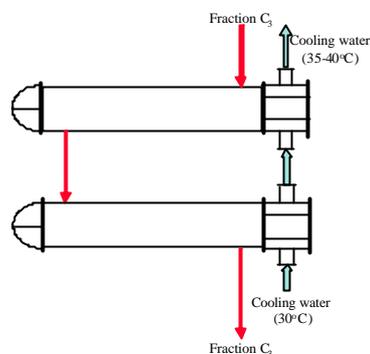


Fig. 2. Fraction C₃ cooler from a gas plant associated with a FCC unit



Fig. 3. Galvanic attack at the inlet water box of the fraction C₃ cooler

Case History #2

In a sulphur unit recovery plant from an oil refinery, as an amine stripper condenser a four way, water-in-tubes, horizontal shell-and-tubes heat exchanger was used. Due to the aggressiveness of the process fluid, tube bundle and tube sheets were made in AISI 321 SS (EN 1.4505). After six months of operation, a leakage was detected; at the hydraulic test 12 tubes were found damaged and the decision to plug them was taken. At each end of the leaking tubes carbon steel plugs were beaten, and the exchanger was reintroduced in circuit. Within a couple of months, at a scheduled inspection, an advanced corrosion of the plugs has been reported (Figures 4 and 5).

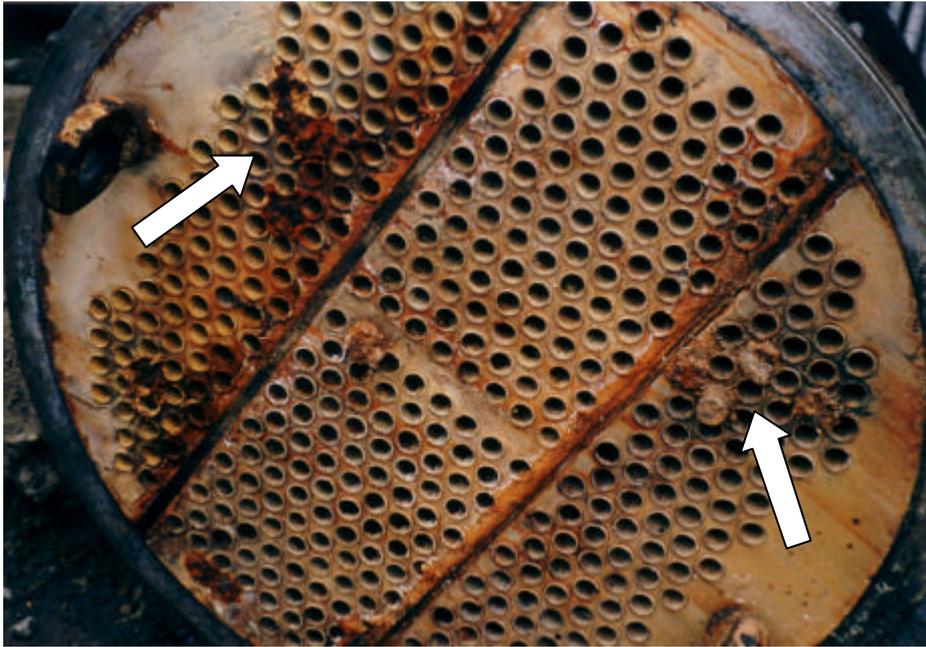


Fig. 4. Water inlet tube sheet of the amine stripper condenser

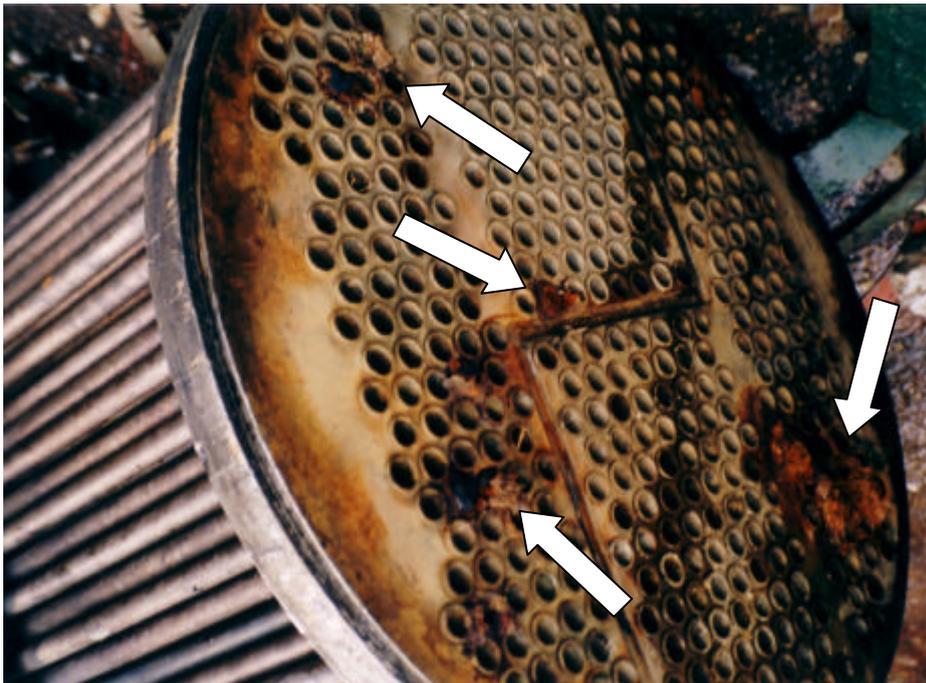


Fig. 5. Water outlet tube sheet of the amine stripper condenser

A galvanic cell with chemically treated cooling water as electrolyte, carbon steel plugs as cathodes, and SS tube sheet as anode was formed. The high area ratio between the noble anode (SS tubes and tube sheets) and the active cathode (mild steel plugs) favoured and accelerated the process.

For remediation, carbon steel plugs have been removed and replaced with AISI 321 SS plugs welded on the tube sheets. There were no more corrosion problems on the cooling water side.

Similar situations have been reported in the same refinery, at the C₄ fraction cooler and at the C₃-C₄ fraction cooler located in the gas plant of the FCC unit (Figures 6 and 7). Both heat exchangers were equipped with AISI 304 SS (EN 1.4301) tubes, but due to the fact that tube sheets were made in mild steel, galvanic corrosion of carbon steel plugs developed slower, a smaller anode - cathode area ratio being achieved.



Fig. 6. Water inlet tube sheet of the C₄ fraction cooler



Fig. 7. Water inlet tube sheet of the C₃ - C₄ fraction cooler

Case History #3

A cooler for diluted ammonia carbamate solutions from a urea plant (Figure 8) has the features presented in Table 2.

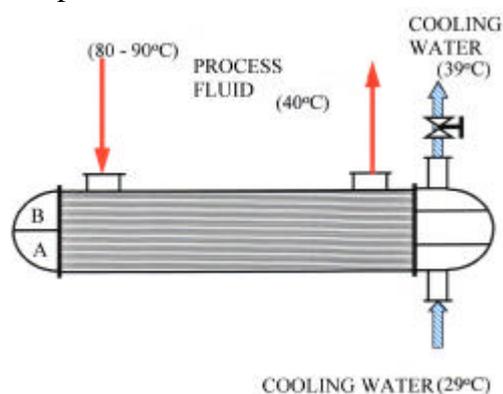


Table 2. Ammonia carbamate solution cooler characteristics

Characteristic	Tube side	Shell side
Number of passes	4	1
Metallurgy	304L	MS
Number of tubes	228	-
Cooling water velocity, m/s	0.85	-
Cooling water flow, m ³ /h	86	-
Capacity, m ³	0.742	0.991
Maximal pressure, MPa	0.5	1.8
Tube OD x thickness, mm	25 x 1.6	
Tube length, mm	7890	

Fig. 8. Ammonia carbamate solution cooler

At a yearly shutdown, large amounts of tubercles (main component iron oxide) and mud have been found in the “A” area of the water turning end of the exchanger. The separating wall from that end being in contact with the tube sheet (also made in AISI 304L SS = EN 1.4306) has been severely corroded, its thickness being reduced from 5 to only 2 mm (Figure 9).

No repair was made to the wall, but an insulating asbestos gasket was fitted between the water turning and the tube sheet. After another year of operating in inhibited cooling water (128 mg/L chlorides, 228 mg/L sulfates, 1,500 μ S/cm conductivity, pH = 7.0 - 7.9), the corrosion of the separation wall has been accentuated. Low flow rates (process fluid temperature control was done by closing the cooling water outlet valve) allowed the suspended solids accumulation in the lid (Figure 10). The galvanic cell formed by the noble tube sheet and the reactive wall was active, leading to the final damage of the wall (Figure 11), that was replaced with a new one, made in mild steel also.

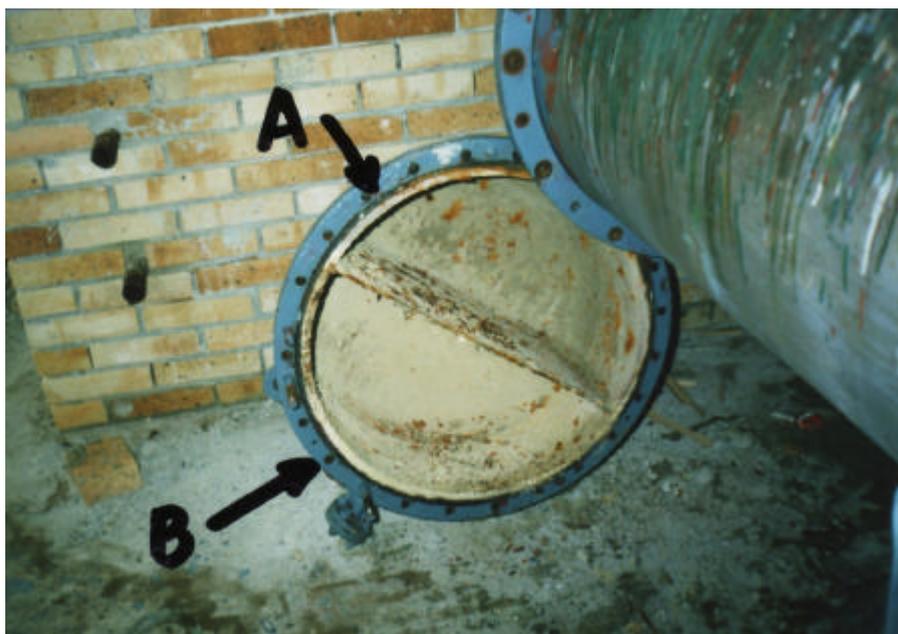


Fig. 9. Ammonia carbamate solution cooler - water turning end



Fig. 10. Ammonia carbamate solution cooler: water turning end prior to washing



Fig. 11. Ammonia carbamate solution cooler: water turning end after washing

It is a typical case where the galvanic couple is “helped” by collateral factors:

**low flow → deposits → differential concentration → under deposits
corrosion → corrosion products → galvanic cell**

The same phenomenon was encountered to the inlet water box too (Figure 12).



Fig. 12. Ammonia carbamate solution cooler: water inlet head box after washing

Case History #4

In a natural gas based ammonia plant (Kellogg licence), for the CO₂ removal from the synthesis gas, an activated potassium carbonate - bicarbonate solution (Carsol®) was used as absorbent. At the time of commissioning (1980), Carsol® and CO₂ coolers were made entirely in mild steel. The main features of the heat exchangers are summarized in Table 3.

Table 3. Main characteristics of carbon dioxide and Carsol® solution coolers

	Spent Carsol® cooler		Carbon dioxide cooler	
	Tube side	Shell side	Tube side	Shell side
Fluid	Carsol®	CW	Wet CO ₂	CW
Mass flow, kg/h	308,000	1,471,000	31,084	182,000
Inlet temperature, °C	119	32.5	60	29
Outlet temperature, °C	70	40	35	35
Pressure, MPa	0.35	0.28	0.02	0.36
Number of passes	2	2	1	1
Heat transfer area, m ²	176.83		271	
Tubes OD x thickness, mm	20 x 2.5		20 x 1.8	
Tubes length, mm	5842		3535	
Number of tubes	482		1222	
Shell ID, mm	820		1128	

After only three years of normal operation, with untreated cooling water, the spent Carsol® cooler, exhibited advanced corrosion (mainly tuberculation) outside the tubes (Figure 13). Also, due to the aggressiveness of wet CO₂ frequent tubes damage were

reported at the carbon dioxide cooler, so the decision to replace mild steel tubes with more resistant AISI 316 SS (EN 1.4401) was taken. In the last case, tube sheets and water boxes were also plated in 316 SS.

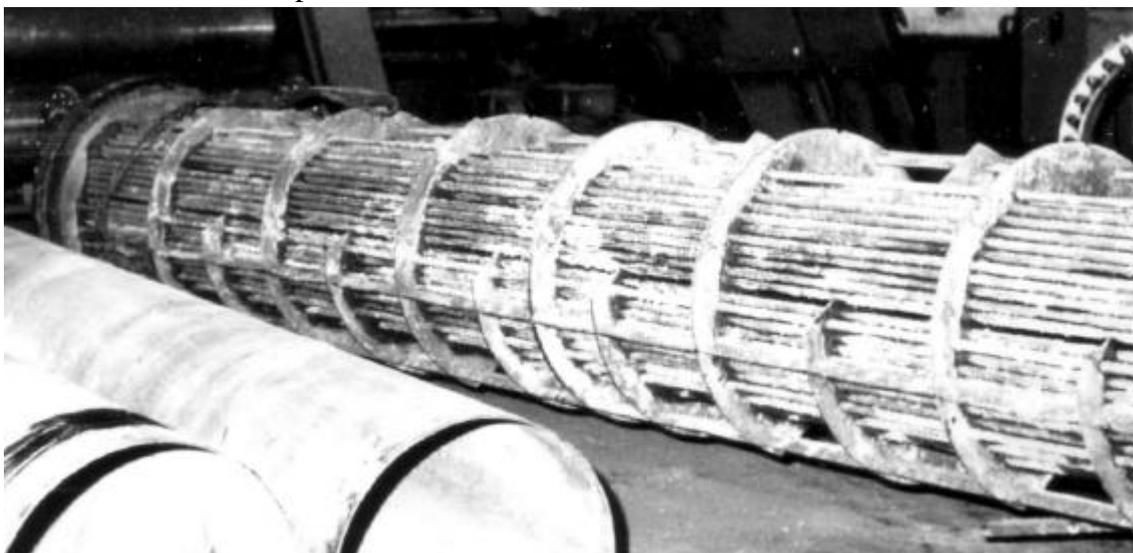


Fig. 13. Mild steel tube bundle of the Carsol[®] cooler after 3 years of operation in untreated cooling water

The replacement of tubes, without taking in consideration of what will happen when noble SS tubes will be in contact with mild steel baffles and rods, in a conductive environment (150 mg/L chlorides, 150 mg/L sulfates, 1,000 mg/L TDS, 1,250 $\mu\text{S}/\text{cm}$ conductivity) was unhappy. Due to the large anode (SS tube bundle) / cathode (MS baffles and rods) area ratio, the baffles and rods were severe corroded within months (Figures 14 and 15). There were no more leaks from the process side, but the cooling process worsened due to the water hydrodynamics unfavorable changes.



Fig. 14. Tube bundle of a wet CO₂ cooler right after dismantling

To avoid baffles destruction, these should be made in the same 316 SS or, at least, in 304 SS. In this case, as it was seen at several CO₂ coolers from a urea plant using very similar cooling water, there will be no more damage to the flow profile of the cooling water on the shell side. Nevertheless, the mild steel heat exchanger shell will be attacked in the contact area with the SS baffles. The galvanic attack will be however reduced, the anode / cathode area ratio being less favorable to the corrosive attack (Figure 16).

Case History #5

Severe galvanic corrosion has been reported at the tube sheets of the relative small lubricating oil coolers of rotating machines like compressors and turbines. Usually, these heat exchangers have copper, brass or stainless steel tubes for cooling water circulation. Parts in contact with oil are made in mild steel.



Fig. 15. Severe galvanic attack of mild steel baffles and rods in contact with the 316 SS tube bundle



Fig. 16. Mild galvanic attack of the carbon steel shell of a CO₂ cooler (urea plant), due to the contact with 304 SS baffles

Figures 17 and 18 present the respectively the galvanic corrosion encountered in a copper tubes oil cooler from a refinery, and a SS tubes oil cooler from a fertilizer plant.

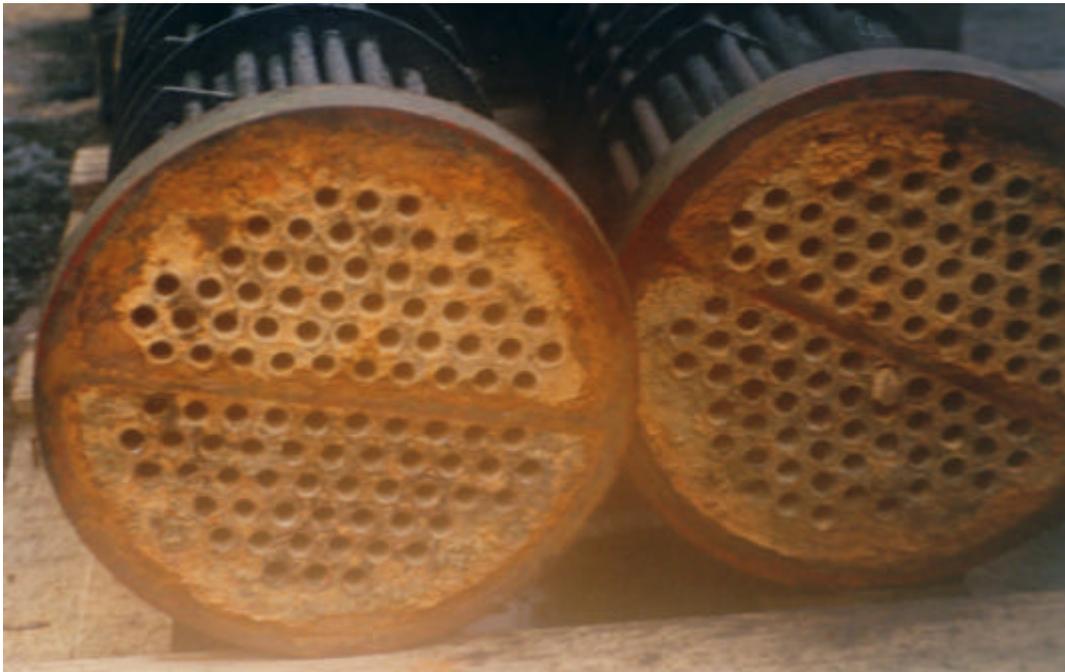


Figure 17. Tube sheets of the oil coolers equipped with copper tubes

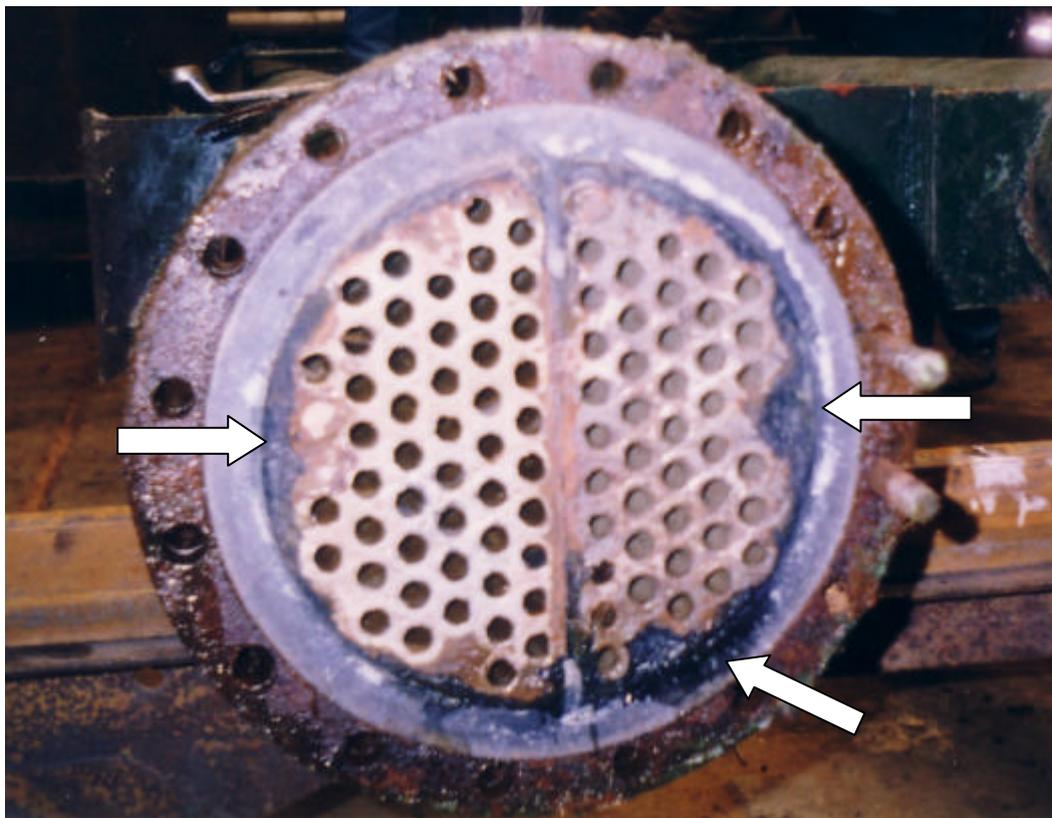


Figure 18. Tube sheets of an oil cooler equipped with stainless steel tubes

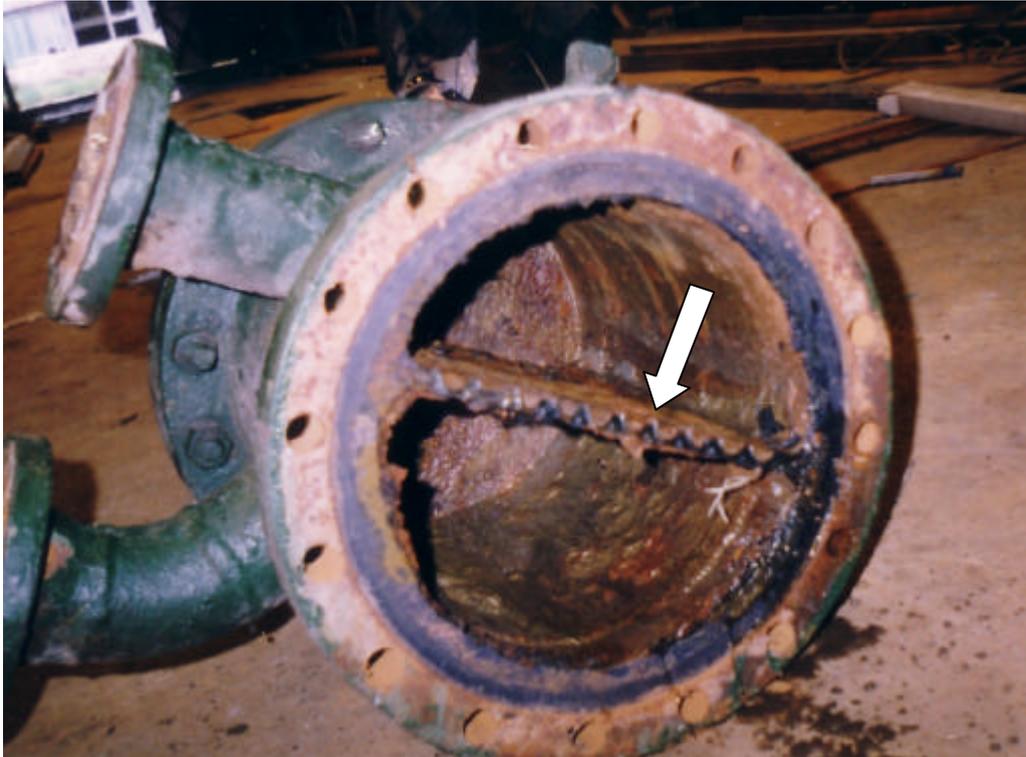


Figure 19. Water box of the oil cooler equipped with stainless steel tubes

In the oil cooler presented in Fig. 18, several leaking tubes were plugged with SS plugs. The corrosion is more accentuated in that areas, the depth of the attack being of 3 - 4 mm, instead of 1 - 2 mm in the rest of the tube sheet. This may be explained by the increase of cathodic area, thus the anode/cathode area ratio being modified disadvantaging the mild steel tube sheet.

Fig. 19 presents the inlet/outlet water box of the same heat exchanger. An interesting corrosion pattern may be observed at the edge of the separating wall of the water passes. At a previous dismantling, the water box has been wrong positioned (rotated with 180°). Due to the imperfect symmetry of the tube sheet, the separating wall was in contact not with the mild steel tube sheet but with the ends of a SS tubes row, thus generating a very active galvanic cell.

In order to avoid in the future the encountered problems, the tube sheets were sand blasted and filled by welding with stainless steel filler. This will eliminate the galvanic corrosion of the tube sheet, but the attack on the separating wall from the water box will persist, unless it won't be properly insulated (e.g. rubber gasket between tube sheet and wall).

CONCLUSIONS

Despite the fact that galvanic corrosion is a topic frequently discussed among the industry people, most of the problems appear again and again from time to time. It looks like there is a "corrosion cycle" that includes four phases [11]:

Phase 1 - Neglect: Corrosion control is ignored; this may be "tempting" to (poor) management as corrosion problems may not show up immediately. It is easy to be lulled into a false sense of security.

Phase 2 - Panic: The previously hidden corrosion danger becomes apparent, possibly with disastrous financial consequences and safety hazards. It is not easy to combat corrosion rationally and effectively in a state of panic.

Phase 3 - Learning Curve: In dealing with the serious corrosion problems, effective corrosion control measures are eventually introduced and failure rates are reduced to manageable levels. Considerable effort may be required before effective solutions are found.

Phase 4 - Unlearning Curve: Once the initial crisis is over, there is a risk that corrosion control will be neglected again and that hard lessons learnt in the past will be forgotten. This is when the corrosion cycle starts all over again, with the neglect stage re-establishing itself.

Several general advices must be reiterated, despite the fact that - at least theoretically - they are well known:

1. Avoid, from the design phase, the creation of equipment containing dissimilar metals in contact, especially if they have very different corrosion potentials;
2. If advice 1 can not be followed, avoid contacting large area of noble metals with small area of less noble metals;
3. Wherever there is a dismantling junction of two dissimilar metals, use insulating gaskets, preferable rubber gaskets. Do not use graphitized gaskets!;
4. In heat exchangers try to avoid "dead areas" and poor circulation. Ensure a flow rate of at least 1 m/s;
5. Use corrosion inhibitors: even they won't protect you from galvanic corrosion, they may decrease the rate of processes that lead to galvanic attack (i.e. azoles will inhibit copper corrosion; thus Cu^{2+} ions won't be carried by cooling water and plated to less noble mild steel, in order to form very active galvanic cells);
6. Use sacrificial anodes (Zn or Mg) placed in the water boxes of the mild steel shell-and-tube heat exchangers equipped with tubes made in stainless steel, copper or copper alloys.

SYMBOLS

- r_0 - corrosion rate of less noble metal in absence of galvanic couple;
 r_{cor} - corrosion rate of the less noble metal;
 S_A - anodic surface, m^2 ;
 S_C - cathodic surface, m^2 ;
 Δe - potential difference, V;

ABBREVIATIONS

- AISI - American Iron and Steel Institute
CW - Cooling Water;
EN - European Norm;
FCC - fluid catalytic cracking;

ID - inner diameter;
MS - mild steel;
OD - outer diameter;
SS - stainless steel;
TDS - total dissolved solids;

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