

## **CORROSION IN MULTI-STAGE FLASH EVAPORATION DISTILLERS**

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## Summary

The various forms of corrosion likely to be encountered in MSF distillers, namely general-, galvanic-, crevice-, pitting-, cracking-, intergranular-, selective leaching- and flow-induced corrosion are reviewed in short. With the material of construction into consideration, the corrosion of the distiller's shell, water boxes, tube-plates, tubes, tube-supports, demisters, flash chambers, distillate troughs and condenser vapor side corrosion are presented in detail. In each case the nature and features of attack, its cause and means of remedy are outlined at some length.

The operation of an MSF distiller involves the execution of a number of processes aiming to overcome a running difficulty or to improve production efficiency. These operations can beneficially or adversely affect material performance. The roles of seawater chlorination, ferrous sulfate dosing, alkaline scale formation, sponge ball cycling, acid cleaning and distiller outage in the corrosion of the various components of an MSF distiller are listed.

## 1. Introduction

A multistage flash (MSF) evaporation unit is a mammoth metallic structure, operating on seawater at temperatures between the ambient and 100 to 110°C. An MSF distiller incorporates a variety of components, each designed to perform a definite task in the overall process of desalination. Distillers are seldom made of the same class of material (Tusel et al. 1993). The various distiller components are normally manufactured from different alloys (Al-Radif et al. 1993). The choice of materials is decided based on their mechanical properties, thermal characteristics, resistance to attack by flowing hot brines, and/or cost considerations. The prices of suitable construction materials differ widely (Sato 1982; Canetta and Valota 1985).

Because of the diversity of materials encountered in MSF distillers, and the presence of high temperature, flow, and brine composition gradients in the unit, corrosion is liable to occur even when the most stringent measures are taken.

This paper is an extended and updated version of a manual produced by the author in 1985 for the Water and Electricity Department of the Emirate of Abu Dhabi (Shams El Din 1985). The material presented herein is largely based on case studies carried out at the Umm Al Nar Power and Desalination Plant in Abu Dhabi. The paper is intended to serve a wide spectrum of people: For the distiller supervisor, with little or no experience in corrosion, it is an introduction to the subject. For the operation engineer it evokes awareness and interest in material performance. For the corrosion specialist it describes the fine features of material failure, and lists alternatives for counter-measures. No attempt is made to present the theory of metal corrosion. Literature citation is adequate but by no means thorough.

## 2. Forms of Corrosion

Corrosion is defined as the deterioration of the properties of a metallic object by the surrounding environment to the extent that it no longer has any value (Fontana and Greene 1972; Shreir 1979). In aqueous solutions corrosion occurs by the flow of electric current through a conducting solution between areas of different potentials on the metal surface. Metal failure however, acquires a variety of forms depending on the relative areas of anodes and cathodes, nature of metal and solution, stagnant or flowing solutions, etc. Recognizing corrosion and understanding its cause is essential in preventing or reducing attack. The forms of corrosion most likely to be encountered in MSF units are the following.

### 2.1. General (Uniform) Corrosion

This form of corrosion results from a homogeneous chemical or electrochemical attack on the entire metal surface exposed to the aggressive environment. The metal becomes thinner with time and eventually fails completely. Examples of general corrosion are the attack on mild steel by seawater and rusting in humid atmospheres. Although general corrosion affects the whole surface, it is considered the least harmful since its rate can be easily measured and the service life of the article predicted with a high degree of reliability.

### 2.2. Galvanic (Bimetallic) Corrosion

Galvanic corrosion develops when two dissimilar metals, differing in their corrosion potentials, are brought into contact in a conducting solution containing a reducible substance (depolarizer). The metal with negative potential corrodes faster than if it were not coupled, while the attack on the other (noble) metal is greatly reduced or completely prevented.

Tables are available listing the corrosion potentials of single metals and alloys in seawater (see Table 1). At the top of the table come the noble metals and alloys which act as the cathode of the galvanic couple. At the bottom of the list are the active or anode metals. The wider the difference between the potentials of the two dissimilar metals, the higher is the risk of galvanic corrosion.

A difference in potential of 20 to 25 mV is considered to be the upper limit for safety, although smaller values can still be harmful over longer exposure times.

The tables of galvanic series usually cite two values for both stainless steels and nickel, depending upon whether they are in the passive or the active states. In practice, care must be taken to ensure the presence of these materials in the passive condition to prevent unpredictable corrosion behavior manifested in potential reversal and/or alternation between the passive and active states. Similarly, the intensity of attack depends greatly on the anode/cathode area ratio. When contact between two dissimilar metals is inevitable, a combination of large anode and small cathode is recommended.

↑	Platinum
	Gold
	Graphite
Noble or cathodic	Titanium
	Silver
	Chlorimet 3 (62 Ni, 18 Cr, 18 Mo)
	Hastelloy C (62 Ni, 17 Cr, 15 Mo)
	18-8 Mo stainless steel (passive)
	18-8 stainless steel (passive)
	Chromium stainless steel 11 to 30% Cr (passive)
	Inconel (passive) (80 Ni, 13 Cr, 7 Fe)
	Nickel (passive)
	Silver solder
	Monel (70 Ni, 30 Cu)
	Cupronickels (60-90 Cu, 40-10 Ni)
	Bronzes (Cu-Sn)
	Copper
	Brasses (Cu-Zn)
	Chlorimet 2 (66 Ni, 32 Mo, 1 Fe)
	Hastelloy B (60 Ni, 30 Mo, 6 Fe, 1 Mn)
	Inconel (active)
	Nickel (active)
	Tin
	Lead
	Lead-tin solders
	18-8 Mo stainless steel (active)
	18-8 stainless steel (active)
	Ni-resist (high Ni cast iron)
	Chromium stainless steel, 13% Cr (active)
	Cast iron
	Steel or iron
	2024 Aluminum (4.5 Cu, 1.5 Mg, 0.6 Mn)
Active or anodic	Cadmium
	Commercially pure aluminum (1100)
	Zinc
↓	Magnesium and magnesium alloys

Table 1. Galvanic series of some commercial metals and alloys in seawater (Fontana and Greene 1972).

### 2.3. Crevice Corrosion

Crevice corrosion is one form of localized attack frequently encountered in practice. It develops on those parts of the metal surface covered by gaskets, deposits, lap joints, washers, etc. For this reason crevice corrosion is also known as gasket- and deposit corrosion. Underneath the cover a thin, stagnant layer of the solution is trapped.

Crevice corrosion develops as a result of the creation of an oxygen concentration cell in which the covered part of the surface acts as the anode while the free surface functions as cathode. Attack on the anodic site is further intensified by the enclosed solution becoming acidic due to hydrolysis of the corrosion products.

In this (and other) respects crevice corrosion simulates pitting attack and some authorities consider both corrosion forms to be identical, but differing in scale (Szkłarska-Smiałowska 1986).

## 2.4. Pitting Corrosion

Pitting is a second form of localized attack which ultimately leads to the perforation of the metallic article. Pits vary in dimension from a fraction of a millimeter to few centimeters. Pits generally grow downwards in the direction of gravity. Some pits start laterally on vertical surfaces, but very rarely upwards from the bottom of a container. Pits grow on defective sites of passivating oxides. The passive surface acts as a cathode and the pit as an anode of the corrosion cell. Pit morphology involves initiation and propagation. Pit initiation occurs after an induction period spanning hours, days, months, or years.

Initiation in the case of iron and stainless steels also requires the presence of a chloride ion as pitting corrosion agent. The induction period decreases with an increase in Cl<sup>-</sup> concentration and/or a rise in temperature. Once it has started, pit propagation occurs rapidly as a result of the high anodic current density sustained by the large cathode/small anode area ratio. Pit propagation is autocatalytic in nature; the hydrolysis of the dissolving metal ions accelerates attack. Pitting occurs more readily in stagnant solutions and is greatly reduced or completely eliminated in flowing solutions.

## 2.5. Corrosion Cracking

Certain ductile metals and alloys undergo localized attack under conditions which cause minimal uniform corrosion. The attack takes the form of a fracture that perpendicularly traverses the metal. Pitting corrosion, and corrosion cracking constitute the two most dangerous forms of metal deterioration. The attack goes on insidiously until a pit or a crack puts an end to the use of the whole structure.

Three distinct but related types of corrosion cracking are recognized. They are as follows.

### 2.5.1. Stress Corrosion Cracking (SCC)

This type of failure develops in alloys carrying a passive surface film subjected to a static tensile stress in a medium containing a specific SCC agent. The nature of the agent depends on the alloy type. For example, stainless steels, coppers/brasses and carbon steel crack in hot solutions containing chloride, ammonia and nitrate respectively. The seriousness of SCC lies in the fact that it develops at stresses within the range of typical design values of the alloys which, in the absence of the corrosive environment, should be completely safe. SCC occurs along two phases, viz., crack initiation and crack propagation. Propagation is usually much faster than initiation. Cracking generally proceeds perpendicular to the applied stress and is either intergranular, progressing along grain boundaries, or transgranular, advancing along grain boundaries as well as through the grains themselves. In both cases the crack has a sharp tip.

### 2.5.2. Hydrogen Induced Cracking (HIC)

This type of cracking is caused by atomic hydrogen diffusing into the metal lattice. Atomic hydrogen results from the cathodic reactions  $H^+ + e^- = H$  and  $H_2O + e^-$

=  $H + OH^-$  occurring during corrosion in acid and natural environments respectively, or during surface cleaning or cathodic protection. A hydrogen induced crack is similar in appearance to one produced under stress, but with lesser or no branching. Also, whereas HIC is accelerated by cathodic polarization, SCC and corrosion fatigue cracking are suppressed by it. The HIC is commonly found in carbon and low-alloy steels, stainless steels, and aluminum- and titanium alloys.

### **2.5.3. Corrosion Fatigue Cracking (CFC)**

Fatigue cracking is a type of mechanical failure that develops under cyclic stress. The susceptibility of pure metals and alloys to this type of damage, as well as its rate, increases greatly in aggressive environments. In contrast to SCC and HIC, corrosion fatigue is characterized by unbranched blunt-tip cracks. The corrosion products are usually present in the crack, which exhibit beach marks and/or striations. These are due to the accumulation of corrosion products during the discontinuous propagation of the crack front.

### **2.6. Intergranular Corrosion (IGC)**

Intergranular corrosion occurs when the grain boundaries are slightly more reactive than grain centers. This state of affairs results when reactive impurities segregate, or when a passivating element is depleted at the boundaries. In a corrosive environment, attack at boundaries proceeds much faster than at the matrix with the result that the grains are physically detached from the alloy surface. One particular form of IGC is that of austenitic stainless steel heated from 425 to 815°C and cooled rapidly. The process is termed sensitization. The carbon of the steel depletes the chromium at grain boundaries by forming the carbide  $Cr_{23}C_6$ . In aggressive solutions the carbide is not attacked, but the chromium-depleted zone corrodes at a rate higher than that of the matrix. Sensitization occurs readily when the steel is welded and cooled rapidly. The effect extends beyond the weld to the heat-affected zone (HAZ). Metallurgically, the weld might appear perfect, but together with the HAZ it represents a location highly susceptible to attack by pitting and cracking.

### **2.7. Dealloying or Selective Leaching**

Selective leaching is noted with some homogeneous, binary or multicomponent alloys in which one element is distinctly more active (electrochemically more negative) than the main alloy constituent(s) (Szklańska-Smiałowska 1986). In corrosive media the active metal is preferentially dissolved, leaving behind an altered residual structure with inferior mechanical properties. The commonly cited example of dealloying is the dezincification of  $\alpha$ -brasses, which occurs in two forms. In uniform or layer type dezincification, the zinc is removed from the whole surface. In plug-type dezincification, on the other hand, dealloying is localized.

Other examples of dealloying are the graphitic corrosion of gray cast iron, the dealuminification of Al-brasses, and the denickelification of cupro-nickels (ASM International 1987).

## 2.8. Flow-Induced Corrosion

The flow of liquid past a metal can affect its rate of corrosion in two distinct ways. When corrosion depends on the bulk concentration of a reducible substance (i.e. cathodically controlled) flow enhances corrosion as a result of increasing depolarizer mass transfer to the metal surface. The rate of mass transfer changes with the flow velocity raised to the power of  $\sim 0.5$  or  $\sim 0.9$ , depending on whether laminar or turbulent flow is operative. Disturbed flow is characterized by an exponent larger than 0.5, but smaller than 0.9 (Sydberger and Lotz 1982). Similarly, the presence of a second phase in the liquid (e.g. solid particles or entrained gas bubbles) also raises the rate of mass transfer.

Flow affects corrosion in another manner. In stagnant or slow-flowing solutions, the metal is usually covered by a film of corrosion products which offers some protection. High flow velocities cause mechanical wear of the film and expose the reactive metal to accelerated attack. This phenomenon is known as erosion-corrosion. Turbulent flow causes more damage than laminar flow. Erosion-corrosion is given specific names, depending on prevailing conditions (Sydberger 1987). If the solution entrains gas bubbles that impinge against certain locations of the surface, attack is termed impingement corrosion. A similar effect may be produced by fine suspended particles, whereby the phenomenon is designated as abrasion-corrosion. Cavitation-corrosion is another type of erosion resulting from the collapse of vapor cavities or bubbles at the metal's surface. Fretting corrosion develops in the vapor phase due to repeated vibrations between the metal and a contacting solid under load. Vibrations abrade the metal's protective films and continuously produce a reactive surface.

## 2.9. Corrosion in MSF Distiller

Pure metals are never used in the construction of MSF distillers. Four classes of alloys are employed instead. These are mild and C-steels, stainless steels, copper alloys and titanium alloys. It is beyond the scope of the present article to list members of these materials useful for application in marine environments, or to describe their corrosion properties. This has been adequately covered in previous publications (Rogers 1968; Laque 1975; Pecker and Bernstein 1977; INCO 1981; European Federation of Corrosion Publications 1989 and 1993; Nickel Development Institute 1987, 1988; Todd 1986; Dawson and Todd 1987; Shams El Din 1991, 1993; Hodgkiess 1993; Carew et al. 1994; IMI 1988). The corrosion of various parts of an MSF plant and the corrective measures to be applied will now be described.

## 3. Corrosion of Distiller Shell

Due to its excellent mechanical properties and its low cost, C-steel is commonly used as the material of construction for distiller stills. In an unprotected state, C-steel suffers uniform corrosion in seawater at a rate of 0.1 to 0.6 mm  $y^{-1}$ . The rate of attack greatly increases when the steel is coupled to other nobler alloys and/or at flow velocities larger than ca. 1 m  $s^{-1}$ . Normal steel is also susceptible to corrosion fatigue. Distiller shells are protected from the outside by appropriate coatings. On the inside the steel is commonly clad below the demister level by either Cu-Ni or stainless steel. The parts above the

demisters are covered with epoxy coat. Both materials to a great extent resist the action of brine on the cladding and water vapor in the gas phase. Erosion-corrosion might, however, develop at the turbulent interface of the flashing water, and blistering and peeling of the coat are frequently noted in the painted area. During shutdowns the chamber walls should be inspected for defects, and corrective measures in the form of cleaning corroded areas filling/repainting by epoxy coating should be made.

A once-through, 39-stage MSF distiller constructed completely from stainless steel was built in Sirte (Libya) more than a decade ago. The shell materials were 65 mm thick, types BOHLER A963 and 1.4439 (X 2 Cr Ni Mo N 17 13 5) stainless steels. Operation is fully computerized, and the unit is reported to be running perfectly with minimum maintenance (Tusel et al. 1993).

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