# Flow-Accelerated Corrosion in Fossil and Combined Cycle/HRSG Plants

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## ABSTRACT

Flow-accelerated corrosion (FAC) has been researched for over 40 years at many locations around the world, and scientifically all the major influences are well recognized. However, the application of this science and understanding to fossil and combined cycle/HRSG plants has not been entirely satisfactory. Major failures are still occurring and the locations involved are basically the same as they were in the 1980s and 1990s. This paper reviews the mechanism of FAC with particular emphasis on fossil and combined cycle/HRSG plants. It includes discussion on a) typical locations of FAC, b) the single- and two-phase variants by describing their typical appearances in plant, c) oxides which grow in the areas of interest, d) the cycle chemistry alternatives and particularly the effect of potential (ORP) on the oxide forms, and e) the major influences on FAC of turbulence, geometry, mass transfer, and materials. Different approaches are needed within fossil and HRSG plants and these are delineated. The important differences between all-ferrous and mixed-metallurgy feedwater systems are emphasized. Overall, organizations should consolidate their inspection, predictive, and chemistry approaches into a company-wide, coordinated, multi-disciplinary FAC program.

# **INTRODUCTION**

Although there had been a number of early references, it was thought that by the mid 1980s sufficient understanding of flow-accelerated corrosion (FAC) had been developed. Confidence was growing in the industry around the world that the parallel research work conducted in Germany, France and the UK throughout the 1970s for different facets of the nuclear and steam turbine industries had addressed the major concerns.

By the early 1960s, FAC, then called erosion-corrosion, had already been theoretically investigated by researchers [1,2]. It was demonstrated that the fundamental conditions for the development of FAC were processes occurring in the laminar boundary layer on the surface of the metal. The anodic iron dissolution in water results in the formation of Fe<sup>2+</sup> ions and electrons reacting with a respective cathodic reaction. Normally iron dissolution was considered as a self-inhibiting process where the pH in the laminar boundary layer increases and, finally, Fe(OH)<sub>2</sub> precipitates after reaching its solubility limit. In this way, the iron dissolution is markedly impeded. Although a ferrous hydroxide layer already inhibits the iron dissolution to some extent, the optimum conditions are reached only after this layer is converted to a magnetite cover layer in a series of condensation reactions.

By the early 1980s there was thought to be consensus on the understanding of FAC along the following lines [3-8]. Magnetite is the oxide which grows on carbon steel surfaces in the feedwater up to about 280 to 300 °C (536 to 572 °F) under low oxygen (now defined as reducing) conditions. Under most operating scenarios with laminar flow (thicker fluid flow boundary layer) the oxide is protective where its growth is usually exactly balanced by its dissolution of mainly ferrous ions into the flowing water or steam/ water mixture. Depending on the temperature its thickness may reach 15-25 µm but at temperatures below about 150 °C (302 °F) it can be very thin. Magnetite growth is controlled by the local cycle chemistries, which at that time were not defined as clearly as today. Wherever turbulent flow conditions exist as a result of local geometries, the dissolved ferrous ions are more rapidly removed from the surface. This process is balanced by an exact growth of more magnetite on the carbon steel surface. This faster oxide removal equates to a faster overall corrosion process (FAC) and thinner remaining magnetite on the surface (can be as thin as a few ångström, or equivalent to an interference film). FAC only occurs in water and water/ steam mixtures and not in dry steam, and there is no mechanical damage to the metal as in liquid droplet erosion and cavitation. By the early 1980s the influences of the following factors on FAC had already been identified and, in some cases, quantified: pH, dissolved oxygen, reducing agent (earlier called oxygen scavenger), temperature, mass transfer, and alloying element composition.

Certainly this research had also identified a number of deficiencies in the state of knowledge, and it became clear that further research was needed into quantifying the effect of alloying elements and the influences of specific cycle chemistries with a concentration on the oxidizing environments, referred to then as the "oxygen effect". No serious damage had been reported during the 1970s, and perhaps the seriousness of the first major case of singlephase FAC at the Navajo fossil plant in Arizona in 1982 had not been identified or recognized.

This level of confidence was removed in 1986 when four workers were killed at the Surry nuclear plant. This event led to a coordinated effort to ensure that FAC was indeed understood at the power plant level, and to a large amount of research and organizational work to develop a coordinated approach of inspection and non-destructive evaluation (NDE). This eventually led to the development of a number of sophisticated FAC codes or models.

Unfortunately this increased research effort did not lead to a reduced amount of FAC being found in the nuclear and fossil industries. Once again the seriousness and complexity of FAC in high energy systems was not fully appreciated. Since 1986, there have been three more incidents where plant workers have unfortunately been killed as a result of single-phase FAC: Pleasant Prairie (1995), Mihama (2004) and most recently at latan (2007). Numerous incidents of two-phase FAC have also taken place.

During this time period a new generating source, the combined cycle/heat recovery steam generator (HRSG), has emerged into the generating industry in enormous numbers all around the world. Very quickly FAC became the number one availability problem in the HRSG with large numbers of single- and two-phase FAC failures occurring.

In a water constrained world an increasing number of both types of plant have been built with air-cooled condensers (ACC), which have experienced FAC and the associated generation of large amounts of corrosion products.

The primary purpose of this review is to indicate that the science of FAC is now much better understood and not a random situation or a mystery, and that this science can and should be easily applicable to all steam/electric generating plants. The paper deals primarily with FAC in conventional fossil plant feedwater systems, combined cycle/HRSG feedwater and evaporator systems, and aircooled condensers. It will mention only briefly a few statistics from the nuclear industry where these can embellish or paint the same picture as in the conventional and combined cycle plants.

## A Few Unofficial Statistics on FAC

No official FAC statistics are kept worldwide for fossil and combined cycle plants. However, EPRI has surveyed the attendees at cycle chemistry and boiler tube failure international conferences for the last 20 years [9,10]. A number of other organizations, such as the HRSG Users Groups, have paralleled these efforts [11]. About 70 % of fossil organizations report some recognition of FAC. The typical systems susceptible to FAC in fossil plants are shown in Table 1. Those occurring generally in single-phase flow areas are marked with an "S"; those in two-phase areas with a "T". Some of these general locations of course can have both.

Individual organizations have also reported similar compilations for many years [12,13]. These overall compilations such as in Table 1 are important to help determine the priorities for comprehensive inspection programs, discussed later.

In combined cycle plants, FAC has been the leading cause of HRSG tube failures (HTF) over the last 10 years and represents about 35–40 % of all HTFs. Both single- and twophase FAC can occur in low pressure (LP) evaporator and economizer tubing but again there are no decent statistics which separate the two. Two-phase FAC has also been a problem in LP evaporator drum steam separation equipment [14].

Feedwater heater drains (S, T). Most prevalent area where about 60 % of organizations record problems
Piping around the boiler feed pump (S). Includes desuperheating supply piping
Piping to economizer inlet headers (S). Especially associated/near valves and supply Tees
Economizer inlet header tubes (S). Most frequent are usually those nearest to header supply
High pressure (HP) feedwater heater tube sheets fabricated in carbon steel (S)
Low pressure (LP) feedwater heater shells (T). Especially near cascading drain entries
Deaerator shells (T) near to fluid entry (HP cascading drains) piping
Reducers on either side of valves
Locations near to thermowells in piping
Turbine exhaust diffuser (T)
Air-cooled condenser (T)

#### Table 1:

Locations of FAC in conventional fossil plants.

Table 2 shows a listing of the major incidents of FAC, which were all single-phase. Although there were no fatalities, the initial major failure at the Navajo plant is included here for comparison. It is worth studying this table in detail because there are some very important commonalities across these plants which should help in the initial screening of conventional fossil plants in the future, and when designing/specifying new plants. First, it should be recognized that all of these failures, with the exception of Mihama, have occurred in systems where the feedwater heaters (LP and high pressure (HP)) are fabricated in stainless steel (usually 304) and that the oxygen levels were extremely low (typically less than 1  $\mu$ g · kg<sup>-1</sup> (ppb)) either because the air in-leakage into the condensate was under very good control or because the location of failure was after a deaerator. In each case a reducing agent (most often hydrazine) was injected at the start of the feedwater system. The low oxygen and the reducing agent ensured that the location of failure was under severe reducing potential conditions. It is also most significant that the pH control range for the feedwater was in the range from 8.75 to 9.3, with the actual most often operated value being 9.1 or less. The temperature range at the failure location has varied widely from 142 to 232 °C (287 to 450 °F), as has the pressure from 0.93 MPa to 20 MPa (134 to 2 900 psi). It is also interesting that most of the single-phase FAC failures at the economizer inlet header tubes (Table 1) were also in systems where the feedwater heaters were all stainless and the feedwater was running under severe reducing conditions as described above for the major incidents [15-17].

# TYPICAL APPEARANCE AND LOCATIONS OF FAC

The last section provides some details on the locations of FAC in conventional and combined cycle/HRSG plants. Despite FAC having been well established by the early 1980s, there is still much confusion in the industry worldwide about the typical appearances of FAC in many of these locations. The reader is referenced to a number of key documents for a comprehensive coverage [24,25]. The selection made here by the author has concentrated on the most prevalent and on the major areas of uncertainty as ascertained by frequently asked questions (Appendix B) during FAC workshops, telephone enquiries and personal contacts at international meetings and conferences.

# Single-Phase FAC in Conventional Plants

Photographs showing the most typical appearance of single-phase FAC are provided in Figures 1 and 2.

Figure 1 shows an FAC failure in a carbon steel economizer inlet header tube. The nipple weld is shown, and the damage starts between 2.5-5 cm (1-2 in) from the header bore. The surface looks like an orange peel, which is the typical appearance of single-phase FAC. There is no evidence of any mechanical (erosive) damage and the loss of wall thickness is purely a chemical dissolution phenomenon. In some areas where the FAC rate is not as fast, there is the appearance of distinct pit like features, but upon further investigation it is clear that these features have some directionality. Figure 1 also shows a reducer associated

		Navajo 2 [18]	Surry 2 [19]	Pleasant Prairie 1 [20,21]	Mihama 3 [22]	latan 1 [23]
Date (Fatalities)		11/1982 (0)	12/1986 (4)	2/1995 (2)	8/2004 (5)	5/2007 (2)
Location		90° bend between booster pump and HP BFP	90° bend following a Tee off main feedwater suction header	Feedwater pipe between isolation valve and economizer inlet	Feedwater piping between LP heaters and deaerator	Superheater attemperation line from discharge of BFP
Temperature	°C (°F)	195 (382)	190 (374)	232 (450)	142 (287)	171 (340)
Pressure	MPa (psi)	4.14 (600)	2.55 (370)	13.8 (2 000)	0.93 (134)	20 (2 900)
Max fluid velocity n	n · s <sup>−1</sup> (ft/s)	7.3 (24)	5.3 (17.6)	6.1 (20)	2.2 (7.2)	
Range of pH (typical)		8.8–9.6 (9.0)	8.9–9.0	Average 8.75	8.6–9.3	8.9–9.1
Oxygen	µg∙kg <sup>-1</sup>	< 1	4	< 1	< 5	< 5
N <sub>2</sub> H <sub>4</sub>		Yes	Yes	Yes	Yes	Carbohydrazide
Material		A105	A106 Gr B	A106 Gr C	JIS G3103 SB42	A106 Gr C
Feedwater Heaters		Stainless		Stainless	Copper containing alloys HP and LP	Stainless

Table 2:

Major single-phase FAC incidents in fossil and nuclear plants.



Figure 1:

Two examples of single-phase FAC.

Left: FAC failure in an economizer inlet header carbon steel tube (Source: T. Gilchrist, 1991).

Right: FAC in a reducer associated with a level control valve in an HP drain system (Source: T. Gilchrist, 2008).

Figure 2:

Two views of the visual surface appearance of single-phase FAC.

A is a further detail from the economizer inlet header tube shown in Figure 1 (Source: T. Gilchrist, 1991).

Example B is a similar view from the FAC surface of an HRSG LP evaporator tube. In both cases the horseshoes or chevrons point in the direction of flow (bottom to top).

Two-Phase FAC in Conventional Plants

tures. Figure 2 shows a detail of the visual appearance of FAC. Where the FAC is slower and very little wall loss has occurred (towards the lower right of Figure 2A) a series or "strings" of these "pit-like" features are clearly evident on the surface. These have been described variously to have a "chevron" or "horseshoe" appearance with the tip pointing in the direction of flow. These chevrons are due to the vectors of turbulent flow touching the surface of the component or surface oxide causing increased dissolution of the oxide at that point because the increased mass transfer assists the removal of the magnetite. As FAC becomes more severe (towards the middle of Figure 2A) then these chevrons overlap until, where the FAC is most severe (towards the top of Figure 2A), the surface takes on the continuous scalloped or orange peel appearance. In these areas there is very little oxide (magnetite) remaining on the surface and if a metallurgical cross-section is prepared, then the oxide is usually very thin (can be a few µm). Figure 2B shows almost exactly the same features of singlephase FAC on the surface of a low pressure (LP) HRSG evaporator tube to illustrate that the key features will be visible wherever single-phase FAC is occurring. Under higher magnification using a scanning microscope the typical scalloped appearance of FAC is always visible (an example is shown later in Figure 5D from an HRSG LP evaporator tube).

with a level control valve which shows all the same fea-

Some of the locations of two-phase FAC have been indicated in Table 1. There are two most predominant appearances of two-phase FAC. The first occurs in deaerators, where most of the surface is subjected to single-phase flow and is generally not subjected to FAC. For units operating under reducing feedwater conditions (AVT(R)), the protection is provided by magnetite and the surface will be mostly grey. For units operating with oxidizing feedwater (either AVT(O) or OT) the protection will be afforded by FeOOH and the surfaces will be mostly red. Two-phase FAC in deaerator vessels is primarily located near to piping which carries fluids into the deaerator. These might be the high pressure (HP) cascading drains for example. At each of these locations, there is a difference in temperature/ pressure between the entering fluid and the bulk fluid in the deaerator, and thus the fluid flashes upon entry into the deaerator. This provides a local two-phase (turbulent) media which "sprays" against the deaerator surface. Figure 3 shows two typical areas adjacent to HP cascading drain entry points. The two-phase FAC is delineated by a surface which is usually black and shiny or even enamellike. It often contains pit-like markings, which sometimes have the chevron/horseshoe directional appearance as seen with single-phase FAC. Two-phase FAC with these characteristics can be found in deaerators of units operat-



ing under either oxidizing or reducing conditions; however, they are much more visible with units on oxidizing cycles, as the two-phase FAC appears as black or shiny black discontinuities immediately adjacent to the red surface protection, as shown particularly well in Figure 3B. The twophase FAC areas are always black (very thin magnetite) because there is no oxidizing power in the two-phase media as it sprays against the surface because of the partitioning of any oxygen to the steam phase.

Both parts of Figure 3 show a typical weld overlay repair, which usually has been conducted with carbon steel material.

The second location is on the shells of low pressure feedwater heaters, usually the lowest LP heater. Figure 4A shows a nice example of two-phase FAC on a LP heater shell. The red areas (FeOOH) define the single-phase flow locations and indicate that the surface is protected from FAC. The black shiny areas define where the two-phase media is striking the surface as a result of flashing of a cascading LP heater drain entry into the vessel. No protection can be afforded in these areas because there is no oxidizing power of the liquid in the two-phase media, despite the unit operating with about 150  $\mu g \cdot kg^{-1}$  of oxygen on OT. Actually the grey magnetite can also be seen beneath the red FeOOH.

There is a very sharp boundary between the protected (single-phase) and the unprotected (two-phase) areas in

## Figure 3:

Examples of severe two-phase FAC in deaerators. Example A is located adjacent to an HP cascading drain entry (shown) into a deaerator.

Example B is directly in the path of the flashing steam from another drain entry. In both cases the two-phase FAC areas are easily seen by a black/ shiny (enamel-like) appearance. In some very severe areas there are "pit-like" indications. Some of the areas have already been weld-overlaid with carbon steel material. The red coloration indicates where there is single-phase fluid because this is protected by the FeOOH covering.

this region. In Figure 4A it is highlighted because of the red/black boundary, but it can also be seen in units operating with reducing treatments where the two-phase media can be equally as severe for FAC. Figure 4B shows the boundary area in a unit operating on AVT(R), where in this case there is also some heavy deposition in the single-phase area.

# Single- and Two-Phase FAC in Combined Cycle/HRSG Plants

In HRSGs there is one variant of single-phase FAC and a number of distinct variants of two-phase FAC depending on the level and type of turbulence, and on how the twophase media "hits" the surface. FAC occurs equally in horizontal and vertical gas path units (HGP and VGP units) and is also common in LP drums. Overall some of the regions of concern are: a) economizer/preheater tubes at inlet headers, b) vertical LP evaporator tubes on HGP units, especially in the bends near the outlet headers, c) LP evaporator transition headers, d) IP evaporator tubes on triple-pressure units which are operated at reduced pressure, e) LP drum internals, and f) horizontal LP evaporator tubes on VGP units especially at tight hairpin bends [26].

Most of the LP evaporators in triple-pressure HRSGs operate at low pressures (0.4–0.5 MPa, 60–80 psi). Both singleand two-phase FAC can occur in these LP evaporator circuits and it is important to recognize exactly which type is occurring because the solutions are different for each type



#### Figure 4:

Two examples of two-phase FAC on the shell side of the lowest LP heater.

Example A is on a unit operating on OT, where the red coloration delineates single-phase flow and is protected by the red FeOOH. The shiny black area is where two-phase FAC is taking place as a result of flashing of a cascaded drain entering the heater (Source: R. Brooker and D. Swainsbury 2002).

Example B shows the sharp demarcation between the area where two-phase FAC is taking place (right) and an area of heavy deposition in the singlephase area (left). This unit was operating on AVT(R). [27]. <u>Figure 5A</u> is a common example of single-phase FAC in the bend of a vertical LP evaporator tube close to the upper outlet header of an HGP HRSG. <u>Figure 5B</u> is an example of two-phase FAC in a similar location. <u>Figure 5C</u> shows an example of two-phase FAC in a horizontal LP evaporator tube tight hairpin bend of a VGP HRSG.

In the cases of single-phase FAC, the damaged surface typically exhibits the same orange peel appearance with the chevron or horseshoes towards the extremities of the damage (slower FAC areas) (Figure 5A) as is seen in single-phase FAC in conventional plant feedwater systems (Figures 1 and 2). In cases where two-phase flow is turbulent the appearance of FAC depends on how the vectors of the flow touch the surface. Figure 5B seems to indicate a "swirly" turbulence created by the tube bend as it approaches the outlet header (to the right). Here the FAC is scalloped or wavy-like. Sometimes both types of FAC occur in the same tube region.

In the hairpin bends of LP evaporator tubing of VGP HRSGs the two-phase media is centrifugally forced to the outside of the bend and results in a smoother black/shiny FAC appearance. Such an example is shown in Figure 5C. This is very similar to the two-phase FAC in deaerators (Figure 3) and LP heater shells (Figure 4) of conventional plants. In all three cases of FAC in HRSGs the typical scalloped appearance of FAC is seen if these surfaces are viewed under the higher magnification of a scanning electron microscope (Figure 5D).

## FAC in Air-Cooled Condensers

Air-cooled condensers (ACC) are becoming more common on fossil and combined cycle plants. As the two-phase mixture of water/steam of around 6–9 % moisture exits the steam turbine it is directed by a series of ducts into the aircooled condenser. Measurements of the water droplets in this mixture have shown that the vast majority of them are less than 0.1  $\mu$ m while a small number are up to 100  $\mu$ m [28-30]. Many operators have recorded large amounts of corrosion products at the condensate pump discharge, sometimes over 100  $\mu$ g · kg<sup>-1</sup> of iron. High levels of iron in the condensate have increased pressure drop and fouled ion exchange resin in units equipped with condensate polishers, and can lead to deposition problems in boilers of conventional plants and evaporators of HRSGs. The problem is thought to be FAC in the ACC, but this area is only just starting to be addressed comprehensively [31,32]. Figure 6 provides a selection of photographs documenting the current understanding. Figure 6A shows a general view of a transfer duct and the entry into the A-frames running along the bottom of the ducting. This particular ducting is red colored because the unit is operating on oxygenated treatment (OT), however grey ducting has also been seen on units running with reducing treatments, AVT(R). Figure 6B shows a clearer detail of the entry into the A-frame tubes. Three distinct regions are usually visible: a) the red colored areas (FeOOH) represent generally protected surfaces, b) black/grey oxide which encompasses the whole entry area into the tubes, where there is turbulence as the two-phase media turns through 90° into the tubes, and c) white appearing areas, which are actually shiny metal. These white areas show up more clearly in Figure 6C together with the adjacent black areas, which are regions of heavy deposition of magnetite particles.

# MECHANISM OF FAC IN FOSSIL AND COMBINED CYCLE/HRSG PLANTS

Since the early work in the 1970/80s much further work has been conducted on FAC worldwide. This together with the development of (unofficial) data bases of failures and damage in both types of plant has led to a much more comprehensive understanding of FAC, which is directly applicable to these fossil and combined cycle plants [10,15,16,33]. The basic process/mechanism remains as



#### Figure 5:

Three examples of FAC in HRSG LP evaporator tubing.

A) shows single-phase FAC in a vertical tube (HGP),B) shows an example of two-phase FAC in a vertical tube (HGP),

C) shows two-phase FAC in a tight hairpin bend of a horizontal tube (VGP), and

D) shows the surface of FAC damage on an HRSG LP evaporator taken with a scanning electron microscope showing the typical scalloped appearance always seen of FAC. (Source: A and B are from Dooley et al. [27])



outlined in the opening section of this paper, where the normally semi-protective magnetite (Fe<sub>3</sub>O<sub>4</sub>) layer on carbon steel "dissolves" in a turbulent stream of flowing water (single-phase) or wet steam (two-phase). This process reduces the oxide layer thickness and leads to a rapid decrease in thickness of the base material until the pipe, tube or pressure vessel bursts. The FAC process can be very rapid and wall thinning rates higher than 3 mm per year (0.120 inch per year) have been measured [10,15]. The rate of metal loss depends in a very complex way on three main factors: the local cycle chemistry, the material composition, and the fluid hydrodynamics. The FAC mechanism is discussed here and first includes a description of the electrochemistry of the basic water chemistries which can be used in these plants, and then describes the formation and properties of the different oxides (Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub> and FeOOH) that can exist on the material surfaces as a function of the oxidizing-reducing potential (ORP). This then leads to how the chemistry, oxides, materials and hydrodynamic factors influence FAC.

## **Feedwater Chemistries**

The feedwater chemistry is critical to overall corrosion, FAC and reliability of fossil and HRSG plants. Over the last 20 years three distinctly different feedwater treatments have been gradually consolidated [34–39]. These, based on the potential of the water, now form a critical part of providing optimized cycle chemistries for the complete cycle in fossil and combined cycle plants [40]:

 Reducing all-volatile treatment, AVT(R), which uses ammonia and a reducing agent in water where the oxygen level is < 10 µg · kg<sup>-1</sup>. Here the oxidizing-reducing potential, ORP, should be in the range –300 to –350 mV [Ag/AgCl/sat, KCl]. It should be noted that this range of ORP is not always achieved, because ORP is a careful balance between the levels of oxygen and reducing agent, and because ORP is a function of pH, temperature, materials, and the sensor characteristics [41].

# Figure 6:

FAC in air-cooled condensers.

A shows the general arrangement of the last section of transfer ducting from the steam turbine and the entry to the A-frame tubes running along the bottom of the duct.

B shows the entry to a set of A-frame tubes.

C shows a detail of the surface appearance near the top of an A-frame tube.

Sometimes a reducing ORP can be as high as -80 to -100 mV.

- Oxidizing all-volatile treatment, AVT(O), where the reducing agent has been eliminated. No oxygen is added. The oxidizing power relies on the level of air inleakage, which should be optimized to give oxygen < 10  $\mu$ g  $\cdot$  kg<sup>-1</sup> at the condensate pump discharge. Here the ORP will be around 0 mV but could be slightly positive or negative.
- Oxygenated treatment (OT), where oxygen and ammonia are added to the feedwater. Here the ORP can be as high as +100 to +150 mV.

# Growth of Oxides in the Feedwater of Plants and in the LP HRSG Evaporator

In the feedwater system of conventional and HRSG plants, the fluid is essentially single-phase water. Here the overriding influence for corrosion and FAC is the feedwater oxidizing-reducing potential (ORP) or redox potential. For the carbon steel materials operating under reducing chemistry the reduced form of iron oxide, magnetite (Fe<sub>3</sub>O<sub>4</sub>), is formed, and its solubility is strongly controlled by the level of the reducing potential. Changing the treatment to oxidizing by eliminating the reducing agent and/or adding oxygen results in the formation of ferric oxide hydrate (FeOOH) [36]; the rate of the conversion depends on the oxidizing power. The formation of this cover oxide reduces the solubility of the surface oxide by at least two orders of magnitude in the temperature range up to just below 300 °C (572 °F). Thus the surface oxide has an enormous effect on both normal corrosion and FAC. However, as can be inferred from frequently asked questions (Appendix B), despite a vast amount of work by tens of researchers over the last 40 years, there is still a lack of understanding of how these oxides grow and the associated electrochemical processes. This section contains a short overview prior to discussion of the FAC mechanism. A full treatment in relation to FAC is provided in [24].

Under reducing feedwater conditions (AVT(R)), the protective oxide which forms on carbon steels in systems up to temperatures just below 300 °C (572 °F) consists almost exclusively of magnetite:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \tag{1}$$

This reaction is considered the sum of two coupled processes. The first process really consists of three simultaneous reactions: a) a direct reaction (oxidation) occurs between iron and the reducing water to form soluble ferrous species and hydroxides, b) the ferrous species diffuse through the porous oxide, and c) the ferrous species dissolve by a reductive process that is promoted by the presence of hydrogen. In power plant terminology, reducing water is considered to contain less than 10  $\mu$ g · kg<sup>-1</sup> oxygen with a reducing agent being added [40,41]; this will give an ORP in the reducing range as defined above.

At the anodic site (carbon steel suface), an oxidation process occurs:

$$Fe \rightarrow Fe^{2+}$$
 (solution) + 2e<sup>-</sup> (2)

At the cathodic site, a reduction process occurs (hydrogen evolution):

$$2H^+$$
 (solution) +  $2e^- \rightarrow H_2$  (evolved from the surface) (3)

In reducing alkalized water, the cathodic reaction:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \tag{4}$$

Combining the anodic and cathodic reactions:

$$Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2 \tag{5}$$

Both ferrous ions and ferrous hydroxide can be obtained according to an equilibrium reaction:

$$Fe^{2+} + 2OH^- \leftrightarrow Fe(OH)_2$$
 (6)

In the second process magnetite forms through the Schikorr reaction:

$$3Fe(OH)_2 \rightarrow Fe_3O_4 + H_2 + 2H_2O \tag{7}$$

A schematic showing the growth mechanism and morphology of  $Fe_3O_4$  under AVT(R) conditions is shown in <u>Figure 7</u> (top right). In single-phase flow at low velocities and/or in straight sections of pipe or tubing, the flow is laminar and essentially parallel to the surface of the metal. In this case the velocity varies from essentially zero in the fluid boundary layer near to the oxide/water surface to a



#### Figure 7:

Illustrating how the growth of oxides on carbon steel surfaces is controlled by the potential (ORP). The figure on the left shows how the amount of iron at the economizer inlet changes as a function of the ORP when the reducing agent is gradually eliminated to zero (Source: Platt, Vinnicombe [43]). The two drawings on the right illustrate schematically under laminar flow conditions (with a slow moving boundary layer or liquid) the growth of magnetite (top) under reducing conditions and the growth of a cover layer of FeOOH (bottom) on the magnetite under oxidizing conditions of AVT(O) or OT (Source: Dooley [36,44]).

maximum at the centerline of the pressure vessel/tube. Under such laminar flow conditions, the second process involves the transfer of the ferrous ions into the bulk water across a boundary layer. In two-phase laminar flow there is a slow moving layer of liquid along the surface of the oxide. The semi-protective magnetite which forms under either of these laminar flow conditions reaches an equilibrium condition where the oxide doesn't continue to increase in thickness and is usually limited to a thickness of no more than about < 20 µm depending on temperature. This is because the layer has lots of oxide hydrates and loose (non-protective) magnetite particles in the outer layers, and there are essentially equal amounts of dissolution of ferrous compounds into the flow and oxidation of iron at the metal/oxide interface. At temperatures below about 150 °C (302 °F), the magnetite formation is very slow [42]: in some cases it is difficult to detect a magnetite layer even after a hundred thousand hours of operation.

The formation of magnetite (Eq. (7)) is inhibited by increasing pH, which causes a reduction of the  $Fe^{2+}$  and  $Fe(OH)^+$ ion concentrations corresponding to the solubility products of  $Fe(OH)_2$ . There have been many studies of the solubility of magnetite. Figure 8 shows one typical profile [45], which increases with increasing temperature to about



Figure 8:

Solubility of magnetite as a function of temperature at various ammonia concentrations (Source: Sturla [45]).

150 °C (302 °F), then decreases with a steep drop to 300 °C (572 °F), which can result in undesired magnetite deposits in this temperature range. To maintain the solubility of ferrous hydroxide (Fe(OH)<sub>2</sub>) in the feedwater below or equal to that of magnetite at around 250 °C (482 °F) and to exclude the possibility of oversaturation, a minimum pH of at least 9.6 should be maintained [46]. A pH of 10 would be even better, but is limited in the cycle if the unit has a copper tubed condenser or condensate polisher operating in the hydrogen cycle. Here it is important to note that the growth of magnetite and FAC are directly related to the pH at the hot operating temperature, not the cold pH as usually measured in fossil and combined cycle plants following sample conditioning.

The growth and dissolution of magnetite into reducing feedwater is also a strong function of potential. As shown in Figure 7 (left), decreasing the ORP (more reducing) will lead to increasing amounts of iron in the water [43]. The cases where this iron is flushed away by the local turbulence is, of course, the reason why a semi-protective situation changes into single-phase FAC and the reason why all-ferrous feedwater systems should be operated on AVT(O) (no reducing agent) or OT to prevent the solubilization of the magnetite surface layers.

Elimination of a reducing agent (AVT(O)) and/or addition of oxygen (OT) raises the free corrosion potential of the steel by several hundred millivolts and the ORP of the fluid into the oxidizing regime. Under these conditions the protective cover layer pores in the magnetite become plugged with ferric oxide hydrate (FeOOH) or ferric oxide (Fe<sub>2</sub>O<sub>3</sub>) (see Figure 7 lower right) [15,36,47]. As a result, the  $Fe^{2+}$ ion diffusion from the steel surface through the pores of the protective magnetite cover layer to the oxide/water phase boundary is strongly inhibited. The few ferrous ions leaving the steel are oxidized either in the layer pores or right at the protective layer/water boundary. For this reason, the ferrous ion concentration in the feedwater should be very low (around 1  $\mu$ g · kg<sup>-1</sup>) under AVT(O) conditions and below 1  $\mu$ g  $\cdot$  kg<sup>-1</sup> for OT conditions. This has been confirmed on almost every unit on AVT(O) and/or OT; the conversion front from magnetite to FeOOH gradually progresses in the direction of flow as the local reducing conditions change to oxidizing. Additionally, the ferric ion concentration becomes almost undetectable [48]. Very few studies have been conducted on the solubility of ferric oxide/hydroxides. Sturla [49] conducted a theoretical study which is shown in Figure 9 and includes the calculated solubility of ferric oxide  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, ferric oxide-hydrate  $\gamma$ -FeOOH, and ferric hydroxide. This figure also shows the solubility field of magnetite replotted from Figure 8 on the axis of Figure 9 so that a qualitative comparison can be made. This shows two features: first it illustrates at least two orders of magnitude lower solubility for the ferric



Figure 9:

Solubility of ferric hydrate-oxides at 0.5 ppm  $NH_4OH$  (data extracted from Sturla [49]). The  $Fe_3O_4$  solubility curve has been replotted from Figure 8 to allow a qualitative comparison of the effects of changing the potential or pH.

oxide hydrates that form with oxidizing treatments (AVT(O) and OT) compared to magnetite at 150  $^{\circ}$ C (302  $^{\circ}$ F), and secondly it also shows the powerfulness of potential compared to changing the pH from 8.7 to 9.6.

The cover layer morphology is determined by the one or both of the reactions [50]:

$$2Fe_{3}O_{4} + H_{2}O = 3Fe_{2}O_{3} + 2H^{+} + 2e^{-}$$
(8)

and

$$Fe_3O_4 + 2H_2O = 3FeOOH + H^+ + e^-$$
 (9)

The formation of FeOOH is known to occur at elevated temperature (up to just below 300 °C, 572 °F), because the red FeOOH is found on economizer tubing just past the inlet header of conventional plants, but is not found on economizer outlet or water wall tubes which operate above 300 °C (572 °F). Also the use of oxidizing environments switches off active FAC of economizer inlet header tubes.

In summary, under the conditions where the ORP is oxidizing, FeOOH will form on magnetite and reduce the solubility of the surface oxide layers (Figure 9) by at least two orders of magnitude. Thus the oxidizing treatments (AVT(O) and OT) have the ability to reduce and even stop the active single-phase FAC mechanism up to just below 300 °C (572 °F) under exactly the same hydrodynamic (turbulent) conditions that existed previously with AVT(R) chemistry.

## **Flow-Accelerated Corrosion**

The previous section has outlined the normal growth of  $Fe_3O_4$  under laminar flow with reducing chemistry conditions, and how this growth is a balance between the cathodic hydrogen evolution reaction and the anodic dissolution of ferrous ions. FAC is simply an extension of this semi-protective process where the dissolution is accelerated by an increasing flow turbulence of water or water/steam mixture (decreasing boundary layer thickness) which causes an increased rate of ferrous species to become incorporated into the flow (increased mass transport). The FAC mechanism under reducing conditions is illustrated in Figure 10 and shows how some flow disturbance (bend, elbow, nozzle, valve, tee, reducer, etc.) introduces turbulence into the flow, which develops flow vectors against the oxide surface as suggested by the arrows.



Figure 10: Schematic of the mechanism of FAC. This causes a reduction or removal (under severe conditions) of the slow moving boundary layer in single-phase flow and the liquid film in two-phase flow. In this case the anodic oxidation and growth of Fe<sub>3</sub>O<sub>4</sub> cannot match the flow-accelerated dissolution or removal of the oxide (Fe<sub>3</sub>O<sub>4</sub>). At temperatures below about 150 °C (302 °F) with very thin magnetite layers and a thin laminar boundary layer due to the local flow conditions (turbulence), the ferrous ions are increasingly transported into the bulk flow; the solubility product of ferrous hydroxide cannot be reached and FAC occurs. This is probably the mechanism within an air-cooled condenser and on the LP heater shells. At higher temperatures, magnetite is formed markedly faster [42]. For this reason, the thin porous magnetite layers are found on the surface. This layer is not adequately resistant and cannot avoid the transport of ferrous ions into the bulk flow. With very high FAC rates the oxide can be as thin as an interference film and often is black/shiny or even has other colorations (green, yellow). The ultimate situation is that the corrosion (FAC) rate increases and the carbon steel component becomes locally thinner.

In these cases, the levels of iron oxide (particulate) measured in fossil plant and HRSG feedwater systems and in HRSG evaporator circuits can be extremely high (above 15–80  $\mu$ g · kg<sup>-1</sup>), which is interesting because the mechanism of FAC relates to increased levels of "dissolution" of Fe<sub>3</sub>O<sub>4</sub> from the surface of the oxide layer under turbulent flow reducing conditions. The level of dissolved Fe<sub>3</sub>O<sub>4</sub> measured in the water of either type of plant, under severe FAC conditions, is always low (<< 5 % of the total iron) and not high enough to explain the rate based solely on dissolution. So under turbulent conditions with a vector of flow towards the oxide surface, "particles" of oxide must be removed from the surface by some assisted "exfoliation" or "spallation" mechanism. A similar mechanism has been discussed to explain FAC in a CANDU nuclear plant [51]. Other mechanisms have also been discussed which involve only dissolution of the ferrous ions from the magnetite on the surface and some saturation phenomena [48]. Clearly this level of fine tuning of the FAC mechanism still needs attention.

## Influences on Single-Phase FAC

The mechanism of single-phase FAC is complex and influenced by three main factors: cycle chemistry, flow hydrodynamics and the material composition.

**Cycle Chemistry** All serious cases of FAC (Table 2) have been observed in systems with low oxygen levels  $(\sim 1 \ \mu g \cdot kg^{-1})$  and where a reducing agent has been added to the cycle. However, it has been found practically that it is not possible to assess the likelihood of FAC by separately monitoring the oxygen and/or the reducing agent.

The oxidizing-reducing potential (ORP) has been found to provide this indicator and is now recognized as the most important influence on single-phase FAC. It is important to note that in fossil and HRSG plants, the ORP is usually reported as a voltage versus that of a Ag/AgCl (sat. KCl) reference electrode. ORP reflects the balance between various conjugate redox systems and must not be confused with the corrosion potential [41]. However, it does provide a useful indicator of the corrosivity of the flowing water. ORP is sensitive to the materials of construction and to the temperature because of the effects of temperature on the redox reactions. ORP also changes with pH, partial pressure of oxygen in the flowing water, mass transport properties and flow rates; thus ORP cannot be compared from unit to unit.

As discussed above, not only does ORP control the surface oxide that forms in feedwater or evaporator water, AVT(R) or AVT(O) (or OT), but as the ORP becomes more reducing the greater is the possibility for FAC (Figure 7). Changing to AVT(O), by eliminating the reducing agent and/or adding oxygen (OT), essentially reduces the possibility of dissolution into the flowing water to very low values, even in areas where there was severe turbulence and FAC under AVT(R). With laminar flow the oxygen will diffuse across the boundary layer. But more importantly for FAC, under turbulent conditions the diffusion of oxygen to the surface will be faster [6] and thus the conversion of Fe<sub>3</sub>O<sub>4</sub> to FeOOH will also occur faster. In most of the early research results [5] it was reported that oxygen inhibited FAC, but there has been much uncertainty in applying this information to fossil and combined cycle plants because the ORP was rarely measured or known in the early laboratory experiments. Simply eliminating the reducing agent will change the potential to oxidizing (AVT(O)) even with very low levels of oxygen (~1  $\mu$ g · kg<sup>-1</sup>) and this will convert the surface layers to red FeOOH and reduce the dissolution of ferrous ions. This is in agreement with a number of the early studies even though the ORP was not measured [5,7]. Operating with higher levels of oxygen will speed up the conversion and protection afforded. It should also be reported that oxidizing conditions will exist even in systems with reducing agent additions if the oxygen levels are above about 10 µg · kg<sup>-1</sup>. Berge suggested that FAC was proportional to the hydrazine content to the one sixth power above about 60  $\mu$ g  $\cdot$  kg<sup>-1</sup> but did not report on the oxygen levels or the ORP [52]. The basic message is that in both conventional and HRSG plants with all-ferrous feedwater systems the optimum cycle chemistry for FAC control is oxidizing (i.e., no addition of a reducing agent).

**The pH** is the second most important chemistry influence on FAC. Although it is the at-temperature pH that is important, it is very rarely measured in fossil and HRSG plants. At 204 °C (400 °F) Fe<sub>3</sub>O<sub>4</sub> is about 10 times more soluble in reducing water at a pH of 8.7 compared to 9.6 (Figure 8) [17,53], and Figure 9 shows how much more powerful changing the potential to oxidizing is compared to changing the pH. Bates et al. found that there was a linear dependence of FAC on pH between 9.0 and 9.7 due primarily to the solubility change [7]. The pH locally at the site of active FAC will decrease as FAC proceeds [54]. **Flow Hydrodynamics** Clearly while FAC is controlled by the cycle chemistry, it is located by the complex interactions of the flow hydrodynamics, and specifically by the geometrical features which create turbulence in the flow and increase mass transport of the soluble ferrous species from the surface. It has not been found practical or economic however to change the flow hydrodynamic factors including the temperature of operation.

**Flow Velocity** FAC is not directly dependent on flow velocity, and recent computational analyses confirmed that the mean flow rate is not a good indicator of the FAC process [55]. Generally FAC shows a rather weak dependence on bulk velocity: Chexal [53] predicted only about a three times increase of the FAC rate when the flow rate is increased from 1.5 to  $9 \text{ m} \cdot \text{s}^{-1}$  (5 to 30 ft/s), and Lister [51] suggested an exponent of about 1.5 for a CANDU outlet feeder coolant case. Also there isn't a threshold or critical velocity above which FAC begins to accelerate. Gabrielli [14] similarly discussed FAC failures in HRSG economizer tubing which had rather slow water flow (0.3 to  $0.9 \text{ m} \cdot \text{s}^{-1}$  or 1 to 3 ft/s), but showed that the turbulence

increased by a factor of two associated with a  $17^{\circ}$  bend compared to straight tubing. The turbulence was even greater for a tube with a  $45^{\circ}$  bend.

**Temperature** Some of the original experimental FAC studies by Keller [8] illustrated a strong dependence on temperature with a peak at about 140 °C (284 °F) for single-phase FAC. Numerous subsequent studies have generally shown similar peaks and temperature profiles. Two examples are shown in Figure 11, where the maximum in FAC rate is between 130 and 150 °C (266 and 302 °F) [4,56]. The temperature of the maximum FAC rate appears to increase with increasing flow rate or mass transfer. The observation of high FAC rates above 140-150 °C (284–302 °F) is consistent with the numerous examples of FAC in fossil plant feedwater systems (economizer inlet header piping and tubing). The lower FAC rates at temperatures above 200 °C (392 °F) reflect that temperature affects changes in other physical and chemical parameters which influence mass transfer (fluid density, viscosity, etc.). It will be noted in Table 2 that serious incidents of FAC have occurred across the temperature range from 142 to



#### Figure 11:

Two examples of the temperature dependence of single-phase FAC under different flow and chemistry conditions. (Sources: A, Bignold and Woolsey [4], B, Heitman and Kastner [56]).

232 °C (287 to 450 °F) so changing the temperature does not appear to be a viable solution, and thus prioritization for inspections/NDE for FAC should also include the complete temperature range.

**Geometry, Turbulence and Mass Transfer** Geometries other than straight pipes or tubing affect mass transfer due to changes in local flow turbulence. FAC does not often occur in straight pipes or tubes, but is most often encountered at points of hydrodynamic disturbance. These include elbows, tight bends, reducer tees, locations downstream of flow control orifices and valves, and even fabrication discontinuities. The geometric enhancement of these features increases turbulence and mass transfer. Mass transfer has been expressed in terms of the correlation:

$$Sh = aRe^{x}Sc^{y}$$
(10)

where the Sherwood number, Sh=Kd/D, the Reynolds number, Re=Vd/ $\gamma$ , the Schmidt number, Sc= $\gamma$ /D, K is the mass transfer coefficient, D is the diffusion coefficient of the relevant species, d the characteristic dimension of the geometry, V is the flow velocity, and  $\gamma$  the kinematic viscosity [53,57]. Various workers over the last 30–40 years have investigated the effects of mass transfer on FAC. Laboratory studies were conducted. Bates [7] for instance showed a cubic relation at 150 °C (302 °F) between FAC of carbon steel and the mass transfer coefficient in PWR type water at a pH of 9.05 over a wide range of flow rates. Further studies [58] showed that the exponent was temperature dependent and decreased to around 1.0 at about 90 °C (194 °F).

There is extensive literature on the geometric factors as they are needed to prioritize inspection locations and for the various analytical models. The earliest work was conducted by Keller [8] for two-phase FAC in steam turbines, but it was quickly determined that these geometrical factors were not applicable to single-phase FAC [53]. This led to the generation of the factors in laboratory studies [57]. Chexal shows a very comprehensive set of geometric parameters which have been used within the Chec series of FAC codes [53]. A comparison of factors from five other authors has also been provided [24]. Usually everything is compared to a geometric factor for a straight section of piping being 1 (one). Larger values denote a greater propensity for flow disturbance and thus turbulence, which increases the mass transfer coefficients: 90° pipe elbows vary depending on the author but are usually around 3.5 to 4, reducers (similar to the one in Figure 1) vary from about 2 at the smaller end to about 2.5 at the larger, orifices and tees are around 5.

It is now possible to use computational fluid dynamics [14,55] to calculate increases in turbulence by geometrical factors as has already been mentioned.

Like with many of the factors which influence FAC, the geometrical factors and mass transfer do not provide unique suggestions for the locations of FAC. As an example, as FAC proceeds the surface becomes roughened (scalloped or orange peel appearance, Figures 1 and 2) and this surface will by itself increase the rate of mass transfer and thus FAC. So while such factors mentioned above provide a nice comparison of geometries, they may not be applicable as FAC progresses. Poulson [57] indeed found that the roughened surface becomes much more important than the original geometry. Bouchacourt's research [59,60] supported this and showed nicely how the surface roughness was caused by and increased FAC. This has a practical side when FAC in pressure vessels (deaerators or LP heater shells) is repaired by weld overlay with carbon steel instead of a 1.25 % Cr alloy. The roughness of the surface can actually make FAC return quicker.

**Materials** There are two distinct issues with respect to materials. The first relates to the plants that have mixed-metallurgy feedwater systems. The second addresses the material composition of the tube, pipe, or pressure vessel which is the subject of FAC.

Mixed-Metallurgy Feedwater Systems. The discussion to date in this review has concentrated on all-ferrous feedwater systems and has illustrated: a) that feedwater systems containing all stainless steel tubing are the most susceptible to FAC under reducing conditions, AVT(R), b) that optimization of the corrosion processes demands oxidizing conditions (AVT(O) or OT), and c) that these treatments have the ability to switch off FAC even in areas of turbulence. Mixed-metallurgy systems, where either all or some of the HP or LP feedwater tubing contains copper alloys, can only use AVT(R) feedwater chemistry with an optimum pH range of 9.1 to 9.3 [40,61]. This maintains a reducing environment under all operating regimes to protect the copper-based tubing (oxygen < 10  $\mu$ g · kg<sup>-1</sup> plus reducing agent). This means that the carbon steel interconnecting piping and the economizer inlet header tubing will also be exposed to the same reducing environment. Knowledge of the worldwide situation with FAC which collates into Tables 1 and 2 indicates that no serious FAC failures have occurred in fossil plants with mixed-metallurgy systems but that failures and wall loss due to FAC have occurred in these plants. This is thought to be because the copper alloys and oxides act as a catalyst for the reducing agent (hydrazine)/dissolved oxygen reaction in the feedwater. Because serious failures have occurred in nuclear plants with mixed-metallurgy systems (Table 2), the carbon steel components in mixed-metallurgy feedwater systems must be assessed within the same corporate FAC programs as used for the all-ferrous systems (Appendix A). Another aspect of copper-based feedwater heaters is that as they become old and fail they are gradually being replaced by materials other than copper. In many cases the feedwater system gradually changes from mixed-metallurgy to an allferrous system, and if the tubing has been changed to

stainless then this system now becomes very prone to FAC as mentioned above and shown by Table 2. Thus it is very important that as this change is made, the cycle chemistry is optimized in two areas to ensure that there is maximum protection against FAC. First the potential should be changed to oxidizing and secondly the pH should be raised into the range for all-ferrous systems (9.2–9.6) [40]. These changes may require that the feedwater system is chemically cleaned to remove any traces of copper that will have deposited throughout the feedwater system during the mixed-metallurgy reducing chemistry days.

Material Composition. Very extensive worldwide research over 25-30 years has shown that small additions of chromium to carbon steel will markedly reduce any FAC. Up to about 25 times improvement in FAC rates can be achieved by using 1.0 or 1.25 % chromium alloys. Similar results have been researched at many places. One of the clearest presentations of the effect is from work conducted by Ducreux in the early 1980s (Figure 12) at 180 °C (356 °F) in single-phase fluid at pH 9.0 under reducing conditions (NH<sub>3</sub> and N<sub>2</sub>H<sub>4</sub>) [62]. Work of Huijbregts [63] showed similar results of about a 50 % reduction in FAC with about 0.1 % Cr addition. Bouchacourt [60] showed that in compiling the data for different conditions in single- and twophase FAC the improvements in FAC rates start at chromium levels above 0.04 %. In all discussions, the improved performance has usually been related to the presence of chromium building up gradually in the oxide film, which should reduce the solubility of the oxide. However, actual solubility data on oxides of this type is scarce, and it also needs to be recognized that the morphology of the oxide which forms on a ferritic steel containing chromium is different than the oxide which grows on carbon steel. On the former there is usually an inner layer of an iron/chromium spinel oxide. Many investigations of fossil plant FAC have also shown that FAC often doesn't occur in identical plant components when the chromium levels are slightly (maybe as small as 0.1 %)



Figure 12:

The effect of chromium on the rate of single-phase FAC. (Source: J. Ducreux [62]).

higher [12,20,21]. This of course has a major effect on the ability to rank components for inspection/NDE. The standard in the fossil and HRSG plants should be to make all materials replacements or repairs with at least 1.25 % Cr alloy. It is always better to make straight replacements with this alloy than to change the geometry, or to weld overlay an active FAC surface with a chromium containing alloy than use carbon steel, where the changes in surface roughness will increase the FAC rate.

## Influences on Two-Phase FAC

As indicated in Tables 1 and 2, two-phase FAC occurs in both conventional plants (deaerators, LP heater shells, and heater drain lines), in HRSGs (LP evaporators and economizers, and LP evaporator drums), and in air-cooled condensers. Two-phase FAC occurs wherever the turbulent steam/water flow interfaces with the carbon steel surface (Figure 10). The slower moving layer of liquid along the surface under laminar two-phase conditions is broken up by the turbulence created by the local geometry in the same way as described for single-phase media. There are various appearances of two-phase FAC which are dependent on how the liquid droplets interface with the surface. Three obvious variants are: a) turbulent/swirling flow such as in a vertical HRSG LP evaporator tube (HGP) near an upper header (Figure 5B), where there are a series of gouges reflecting the swirling flow, b) a continuous stream of droplets being "forced" centrifugally to the outside of a tight (hairpin) bend in a horizontal HRSG LP evaporator tube (VGP) (Figure 5C), and c) areas where fluid flashes on entering pressure vessels operating at different temperature and pressure such as in deaerators (Figure 3) and LP heater shells (Figure 4). The first is similar to the "tiger striping" reported in nuclear plant two-phase areas [24]. The second two generally produce the same appearance, which in its most severe form is black and shiny. The twophase FAC mechanism is controlled by the solubility of the reduced oxide (magnetite) and its mass transfer from the surface. Here there is also the thought that the final removal of particulate magnetite from the surface must relate to similar spalling reactions as discussed for singlephase FAC.

With regards to the temperature dependence of two-phase FAC, the bell-shaped profile is similar to that shown for single-phase FAC (Figure 11), but the peak is generally seen at higher temperatures of 175 to 180 °C (347 to 356 °F) [8,64].

With regards to the chemistry influences for two-phase FAC, the options are much narrower than for single-phase. Increasing the potential (ORP) or oxidizing power (AVT(O) or OT) cannot be adopted as a solution as with single-phase FAC because of the high partitioning of oxygen to the steam phase. It is clear that two-phase FAC occurs even in units operating with OT (Figures 3 and 4). To reduce two-phase FAC chemically, one option is to increase the pH locally at the FAC site. Ammonia used in

fossil and HRSG plant feedwater does not perform well in these two-phase environments as its basicity decreases markedly with temperature and it partitions to steam, resulting in lower pH in the water adjacent to the surface. So basically in fossil plants, increasing the pH of the feedwater to address two-phase FAC will be limited by other factors in the plant (maybe condensate polishing, copper condensers, etc.) and thus solutions are usually materials related, with material or overlay containing at least 1.25 % Cr. For air-cooled condensers the current approach is to operate with higher pH in the range 9.6 to 9.8 [31]. Amines have better distribution properties and higher at-temperature pH for use in air-cooled condensers [32], but are usually not acceptable in fossil and combined cycle plants because of the thermal degradation, breakdown products and increased cation conductivity levels experienced in steam [65].

For HRSG LP evaporator circuits, the best option appears to be the use of a solid alkali, such as tri-sodium phosphate or NaOH, providing the HRSG circuitry and attemperation systems allow [26]. Worldwide, NaOH appears to provide the better protection. Chromium containing alloys can be used at "known" FAC sites again using at least 1.25 % Cr alloys, but it must be recognized that this only addresses FAC locally and not the root cause of the problem.

# SUMMARIES AND SOLUTION APPROACHES FOR FAC

It should be clear that only a few of the various influences on FAC discussed in the last sections can realistically be changed to control/reduce FAC rates. The most important of these are: a) the optimum cycle chemistry for the particular plant and materials within the plant, and b) the materials of the tube, pipe, or pressure vessel that contain the turbulent flow. Both of these approaches ultimately reduce the solubility of the reduced form of iron oxide (magnetite) on the surface. New conventional and HRSG plants should be designed with the optimum chemistry and with materials resistant to FAC in the known locations.

Eluid Elow

Flow Regime	A. Laminar Flow	B. Turbulent Flow	C. Laminar Flow		
Location and Conditions	Boundary layer or slow moving liquid on the surface of the oxide.	Vector of flow against the surface, which reduces the slow moving liquid layer on surface	Returns to A.		
<ol> <li>Areas with single-phase flow in units with reducing chemistries</li> </ol>	Normal magnetite growth on surface. Semi-protective grey oxide dependent on the temperature. Small dissolution of Fe <sup>++</sup> into flow	Increased dissolution of Fe <sup>++</sup> and mass transfer. Chevron markings. With severe turbulence the surface becomes scalloped and black/shiny. FAC. Thinner magnetite.	Reestablishes conditions under 1A.		
2. Areas with two-phase flow in units with reducing chemistries	As 1A.	Areas become black/shiny with some pits (maybe chevrons within black areas). FAC.	Reestablishes conditions under A. HRSG tubing and air-cooled condensers have deposition very close to FAC		
3. Areas with single-phase flow in units with oxidizing chemistries	Surfaces become red. FeOOH forms on top of magnetite.	Surfaces become red. FeOOH forms on top of magnetite even in areas where FAC occurred under AVT(R).	Reestablishes conditions under 3A.		
4. Areas with two-phase flow in units with oxidizing chemistries	Not many such locations (Straight sections of LP evaporator tubing and air- cooled condensers). Both can be red due to FeOOH	Areas will always be grey or black/shiny if turbulence is severe. FAC.	Reestablishes conditions under 4A.		

Table 3:

Summary of FAC in conventional fossil and combined cycle plants.

## Summary of the FAC Mechanism

The frequently asked questions (Appendix B) indicate that there remains some uncertainty about the various indicators of FAC, whether FAC is active or whether it has been slowed down or stopped by a change of chemistry, and what the various surface colors indicate. <u>Table 3</u> provides an overview of the various flow regimes and the possible chemistries as a function of potential. The following two sections then summarize the key approaches for conventional fossil and combined cycle plants.

### **Summary for Conventional Fossil Plants**

Based on the current understanding of the FAC mechanism, the various examples of FAC and reviews of hundreds of organizations' FAC programs around the world, the following conclusions can be drawn for control of FAC in fossil plants:

- Single-phase FAC can be controlled by the potential (ORP) of feedwater chemistry. FAC occurs under reducing conditions (low oxygen and a reducing agent) at locations where turbulence is generated by the system geometry.
- In all-ferrous feedwater systems (copper alloys may be in the condenser), an oxidizing feedwater treatment (AVT(O) or OT) will minimize corrosion, FAC and thus the transport of corrosion products to the boiler. The optimum pH range is 9.2 to 9.6.
- In mixed-metallurgy feedwater systems (copper alloys in the feedwater heaters and maybe also in the condenser) a reducing feedwater treatment (AVT(R)) will provide protection to the copper alloys. The interconnecting carbon steel components and pipework will also be operating under reducing conditions and may be subjected to FAC. Operating in the pH range of 9.1 to 9.3 will provide optimum protection for the copper alloys and will help to prevent dissolution of magnetite from the carbon steel components.
- It is important to change the feedwater chemistry when a change of feedwater heater tube material has been made. Probably the most common example is the change out of copper alloy tubed heaters to stainless. If this change (eventually) encompasses all the LP and HP heaters, then this markedly increases the risk of FAC and mandates an immediate change/optimization of the chemistry to oxidizing and an increase of the pH above that used in the mixed-metallurgy situation.
- For all types of feedwater systems, monitoring the iron (and copper) levels will indicate whether the feedwater chemistry is optimized and FAC is under control. For all-ferrous systems the iron levels should be approaching  $2 \ \mu g \cdot kg^{-1}$ , and for those systems on OT it has been shown consistently worldwide that the iron can be less than  $1 \ \mu g \cdot kg^{-1}$ . For mixed-metallurgy systems the copper levels should be approaching  $2 \ \mu g \cdot kg^{-1}$ .

- Two-phase FAC regions (deaerators, LP heater shells) in the feedwater system generally require a materials solution using a 1.25 % Cr or higher alloy. This is applicable to rebuilding thickness with weld material or equipment replacement. Weld overlaying with carbon steel material will introduce surface roughness which has no better FAC resistance than the original pressure vessel material. Also it is always preferable to replace a component or part of a component in kind than to try to introduce a "better" flow hydrodynamic situation: the experience is also that these can have higher FAC rates than the original.
- FAC is most frequent in drain lines. Thinned or failed sections should always be replaced with at least a 1.25 % Cr alloy. The iron levels in the cascading HP and LP drain lines often provide a good indicator of the extent and activity of FAC.
- Air-cooled condensers are a special case within the fossil plant FAC envelope. Monitoring of the iron levels at the condensate pump discharge provides an important indicator of the extent and activity of FAC in the A-frame tubes. Worldwide experience indicates that initially the pH level around the cycle should be higher than the 9.2 to 9.6 range normally adequate for allferrous systems. Usually a pH of around 9.8 or higher will be required.
- All the activities of a comprehensive FAC program (Appendix A) involving prediction, inspection and a combination of Levels One and Two NDE techniques will also be required.

### Summary for Combined Cycle/HRSG Plants

Based on the current understanding of the FAC mechanism, the various examples of FAC, and reviews of hundreds of organizations' FAC programs around the world, the following conclusions can be drawn for control of FAC in Combined Cycle/HRSG plants:

- The locations of single-phase FAC can be controlled by feedwater and evaporator chemistry. Multi-pressure HRSGs should operate only on an oxidizing cycle (AVT(O)) without any reducing agents. This decision should preferably be made during the specification/ design stages of an HRSG, but if this stage has been missed, then the change should be made as early in the life of an HRSG as possible.
- Two-phase FAC of LP evaporator tubing can be addressed by LP evaporator chemistry by adding either tri-sodium phosphate or NaOH to the LP drum provided that the LP drum doesn't provide feed for upper pressure circuits or attemperation.
- Thus some two-phase FAC will need to be addressed by a materials solution. If obvious susceptible tube locations can be identified, then these should be replaced by a 1.25 % Cr or higher alloy. Steam separat-

ing equipment in the LP drum can also be designed or replaced with at least a 1.25 % Cr steel.

- Monitoring of iron in the feedwater and LP drum will identify whether FAC is active. Satisfying the "rule of 2 and 5", where the iron level is consistently less than  $2 \ \mu g \cdot kg^{-1}$  in the feedwater and less than  $5 \ \mu g \cdot kg^{-1}$  in each drum, will not only provide an indication that FAC is not active, but will also prevent excessive deposition of corrosion products in the HP evaporator tubing.
- Air-cooled condensers are a special case within the combined cycle/HRSG plant FAC envelope. Monitoring of the iron levels at the condensate pump discharge provides an important indicator of the extent and activity of FAC in the A-frame tubes. Worldwide experience indicates that initially the pH level around the cycle should be higher than the 9.2 to 9.6 normally adequate for all-ferrous systems. Usually a pH of around 9.8 or higher will be required.
- All the activities of a comprehensive FAC program (Appendix A) involving prediction, inspection and a combination of Levels One and Two NDE techniques will also be required.

# **CONCLUDING REMARKS**

Flow-accelerated corrosion (FAC) has been researched for over 40 years, and scientifically all the major influences are well recognized. However, the application of this science and understanding to fossil and combined cycle/HRSG plants has not been entirely satisfactory. Major failures are still occurring and the locations involved are basically the same as they were in the 1980s and 1990s. This paper has attempted to delineate the different approaches needed within fossil and combined cycle plants for single- and two-phase FAC, and for cycle chemistries across the potential range from reducing to oxidizing. Because of the importance of FAC failures and the increased levels of corrosion products when the cycle chemistry is not optimized, it appears of paramount importance for organizations to consolidate their inspection, predictive, and chemistry approaches into a company-wide coordinated FAC program in the same way as many do for boiler tube failure reduction. Unfortunately such FAC programs are not too common across these industries. This becomes even more important if changes are made to a unit such as material components (feedwater heaters), piping, valves, tees, reducers and cycle chemistry. Each apparently small change can make a marked difference to FAC locally.

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# APPENDIX A – OVERALL PROGRAMS FOR FAC

The complex interactions of the cycle chemistry and flow hydrodynamics control and locate FAC respectively. An overall comprehensive approach to identify and control FAC is required in steam generating plants. This Appendix provides a very brief overview of the parts required, and the two road maps for conventional (Figure A1) and combined cycle/HRSG plants (Figure A2) illustrate the process.

These road maps should make it crystal clear that optimizing the cycle chemistry and conducting NDE/inspections should never be separated. Only identifying the locations of FAC and addressing them (disposition and reassessment, repair, welding, weld overlay) does not address the root cause of the problem, which in most cases relates to the cycle chemistry. Only optimizing the cycle chemistry leaves possible FAC sites with reduced wall thickness. The following steps are briefly outlined, some are common to both plants, whereas some are unique.

#### Step 1

Development of a Corporate Mandate for FAC which is signed at the highest level in an organization. Such documents have been found in conventional plants to provide the ruggedness to a program and the support that the technical staff needs to conduct the whole program. They have yet to be applied to HRSGs. The overall approach must include an on-going

benchmarking process so that feedback to the executive branch can be provided on how well the organization's FAC program is approaching world class.

## Steps 2 and 3

Experience has shown that the cycle chemistry and the NDE/inspection need to be addressed in parallel chains of activities to comprehensively and safely address FAC.

#### Steps 4, 5 and 6

Identifying and prioritizing the locations of possible FAC damage is one of the critical processes and generally occurs slightly differently in the two types of plant. In conventional plants the prioritization can be accomplished by experience, walkdown and assessment of the heat balance diagram and drawings, or by the use of a predictive code. In combined cycle plants there are currently no specific predictive codes, and the prioritization is accomplished by the experience base in the industry and by the operating chemistry. The internal color (red or black) of the feedwater and LP evaporator pressure containment (Step



#### Figure A1:

Comprehensive FAC program for fossil plants (air-cooled condensers can be included).

NDE nondestructive evaluation

UT ultrasonic testing

 $1 \text{ ppb} = 1 \mu \text{g} \cdot \text{kg}^{-1}$ 

5 for HRSGs) also will play an important part in the process.

#### Step 7

Use of Level One NDE tools to locate damaged areas. In conventional plants this is often performed with pulsed eddy current, fiber optics or radiography. The guided wave ultrasonic testing technology is just emerging as a useful tool and may be able to fill an important Level One gap for the feedwater systems in fossil plants. In HRSGs there doesn't appear to be sufficient tubing and space to apply guided waves to tubing, but fiber optics and electromagnetic acoustic wave transducers (EMAT) appear useful Level One approaches in conjunction with the chemistry indicators ("Rule of 2 and 5").

#### Step 8

Once FAC damage has been located in Step 7, Level Two NDE is required to measure the wall loss and FAC rate. For conventional plants this involves UT with standardized protocols for grid layout and collection of the data at intersecting grid points or by recording the minimum values by scanning the grid. In HRSGs it usually involves UT scanning on tubes and headers.

### <u>Step 9</u>

Analysis to determine reinspection intervals and disposition is required once the FAC rate is known. All repair aspects (weld overlay, replacement of equipment with similar geometry) should involve the use of 1.25 % Cr alloys. Any changes to the unit such as materials in feedwater heaters, piping/components, new equipment, or changes in cycle chemistry will need reassessment.

### Step 10

Cycle Chemistry Optimization of All-Ferrous Feedwater Systems in Both Conventional and Combined Cycle/HRSG Plants This is accomplished by monitoring pH, dissolved oxygen, reducing agent and total iron. All-ferrous systems should not be treated with reducing all-volatile treatment (AVT(R)), which uses chemical reducing agents. Feedwater treatment of all-ferrous feedwater systems should use either oxidizing AVT (AVT (O)) or, where applicable in conventional plants, oxygenated treatment (OT). Total iron transport monitoring provides an overall indication of the activity of both single- and two-phase FAC. In conventional and combined cycle plants with allferrous feedwater systems, employing a properly selected and optimized feedwater treatment, it should be possible to attain iron concentrations consistently  $< 2 \mu g \cdot kg^{-1}$  in the final feedwater as measured at the economizer inlet or comparable sample point location.

#### Step 11

Cycle Chemistry Optimization of Mixed-Metallurgy Feedwater Systems in Conventional Fossil Plants

The monitoring in this step should add total copper to the parameters delineated in Step 10. This step is needed when the feedwater part of the plant contains copper alloys. In these cases it is necessary for the plant to use reducing agents and to operate with AVT(R). Monitoring of total iron will provide an indication of any FAC activity. The goal should be to attain < 5  $\mu$ g · kg<sup>-1</sup> (< 2  $\mu$ g · kg<sup>-1</sup> is preferred).

#### Step 12

Cycle Chemistry Optimization for Combined Cycle Plants This step should ensure that both the feedwater and LP drum evaporator chemical treatments are optimized for



#### Figure A2:

Comprehensive FAC program for combined cycle/HRSG plants (air-cooled condensers can be included).

- NDE nondestructive evaluation
- UT ultrasonic testing
- ACC air-cooled condensers

FAC control. Further reductions in feedwater iron may be accomplished by increasing the pH control range above the normal range of 9.2-9.6. This will be particularly important if the combined cycle plant has an air-cooled condenser and will have a positive effect on the LP drum corrosion and FAC. If however the LP drum iron levels do not reach  $< 5 \ \mu g \cdot kg^{-1}$  by adjusting the feedwater pH, then consideration should be given to the addition of tri-sodium phosphate or NaOH to the LP drum if the LP drum does not provide feed for any upper pressure circuits or steam attemperation. The metric used to assess effective optimization of the feedwater and evaporator water is referred to as "The Rule of 2 and 5" with the final feedwater total iron  $<2\,\mu g\cdot kg^{-1}$  and all the drum evaporator circuits  $<5 \ \mu g \cdot kg^{-1}$ . In cycles that are unable to comply with this rule, despite successful optimization of the chemistry, it should be assumed that there is ongoing two-phase FAC that could not be arrested by any changes in the evaporator chemistry. This means that further action to evaluate and apply non-chemical solutions is needed (Steps 7-9).

# **APPENDIX B – FREQUENTLY ASKED QUESTIONS**

During the second half of 2007 the author received many questions about FAC and its appearance, optimization of cycle chemistry in relation to FAC, prioritization of locations for inspection/NDE, and about developing comprehensive corporate-supported FAC programs. This appendix delineates the most frequently asked questions in no prioritized way. It was thought that these questions would stimulate others to develop optimum approaches and perhaps to prevent an FAC failure.

- What is the difference between single- and two-phase FAC?
- Do both types have chevrons (horseshoes)? Do they always point in the direction of flow?
- What does it mean if the chevrons are red colored, or if FAC damage is red colored?
- · We only dose hydrazine. Is this OK?
- Is there a difference between FAC control in a mixedmetallurgy system and an all-ferrous system?
- What is the difference between having copper in the HP heaters as compared to the LP heaters?
- Is it necessary to change the feedwater chemistry from AVT(R) when initially/finally changing out copper feedwater heaters?
- What should we do on units where there are <u>now</u> no copper heaters?
- What is the optimum pH range for all-ferrous and mixed-metallurgy feedwater systems to control FAC?
- What should we do on "identical" units? Should we inspect the same areas?
- What is the critical level of chromium in a component above which we don't need to inspect?
- Should we concentrate our inspections at temperatures around 150 °C (300 °F)?
- We predict high FAC rates before and after the deaerator. Should we inspect both locations or put a higher priority on one location?
- We don't have time to inspect all the predicted highest priority areas. How do we choose which to inspect?
- The management has given us a small budget for inspection. How do we choose which areas to inspect?
- We have severe FAC which is red. Is this OK?
- We have severe FAC which has areas which look black, green, or yellow. Is this OK?
- Is there a critical fluid velocity we should look for?
- Which conventional fossil boiler components should we include in our FAC program?
- What does a management-supported FAC program look like?

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Barry Dooley is the author or coauthor of over 240 papers and the editor of 14 international conference proceedings, primarily in the areas of metallurgy, power generation, boiler and HRSG tube failures, FAC, cycle chemistry, and life extension and assessment of fossil plants. He is the coauthor of a three volume book on boiler tube failures, a two volume book on steam turbine damage mechanisms, and a book on flow-accelerated corrosion in power plants. Barry Dooley is the Executive Secretary of the International Association for the Properties of Water and Steam (IAPWS). In September 2006, he was made an Honorary Fellow of IAPWS.

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