Design considerations for carbon steel pipes materials' selection applied in fossil powered plants subjected to wet-steam flowaccelerated-corrosion

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Abstract - FAC has only been recognized in the past three to four decades as a corrosion mechanism and has not been greatly understood until recently. There are a wide range of factors that affect the rate of FAC including chemistry, geometry and physical conditions inside the pipe. It is interesting to comprehend all of the factors of FAC within a steam pipe with two-phase flow to see how the temperature makes a difference to the corrosion rates. There are certain unique aspects of steam piping for fossil plants due to its fluid dynamics and control. The analysis of FAC will bring together different aspects using calculated examples and describe how they occur in detail, it gives awareness of the factors and how to calculate their effects. Safety and the integrity of the pipe have been carefully considered and methodologies of reducing FAC have been defined.

Keywords: two-phase steam, magnetite, corrosion allowance, wall thinning, Reynolds number

1.0 Introduction

1.1 The problem

Carbon steel pipes are often used for the transportation of steam in power generation plants. The fossil fuel is burnt in the boiler furnace and the energy released is used heat water, in pipes inside the boiler, and turn it into steam. Steam has been widely used as a means of transporting energy and was especially prevalent in the Victorian era. In power generation this steam is used to rotate a turbine which then turns a magnet inside a coil or vice versa to generate electricity.

Today power plants alter the amount of electricity they produce by predicting the demand. Meaning that not all power plants generators will be working at 100% all of the time. Usually power stations use dry superheated steam as it is much more energy efficient, but due to changes in demand the temperature of the steam can drop into the wet-steam region, wet steam is also known as two-phase steam or flow, additionally a liquid is known as single-phase (flow). Superheated steam does not cause corrosion as it has no water as the water in superheated steam has been further heated above the evaporating temperature where water cannot exist [17]. The main advantage of this is that this steam can contain more energy. Wet-steam causes a much greater rate of corrosion in the pipe than superheated steam. The corroded material gets carried away in the flow of steam causing an uneven surface of the inside wall and the material entrained in the flow can damage the turbines. The uneven surface of the pipe wall causes turbulence and eddies in the flow and this accelerates the rate of corrosion in the pipe, this is process is described as flow-accelerated-corrosion (FAC). The issue with FAC is

that it causes the walls of the pipe to thin at an increasing rate. Eventually the walls of the pipe get so thin that the pressure of the steam causes the pipe to fail by cracking, even small cracks and low levels of corrosion can affect the efficiency of the pipeline. The spontaneous failure can lead to down time for repairs of the pipe and potentially damages surrounding assets and the repairs and down time cost money.

There are several case studies of steam a pipe rupturing due to FAC and below is a table of a selection of those cases;

| Troubles on Large Diameter Pipes | | | | |
|----------------------------------|------------------|----------|---------------------------------|-----------------|
| Year | Unit /Company | Location | Pipe Diameter | Consequence |
| 1986 | Surry unit 2 | USA | 18" Pipe | Rupture |
| 1987 | Doel | Beligium | (large dia) | Rupture |
| 1990 | Loviisa WER 1 | Finland | 12" pipe | Rupture |
| 1990 | Millstone Unit 3 | USA | 6" pipe | Rupture |
| 1990 | Millstone Unit 2 | USA | 8" pipe | Rupture |
| 1993 | Loviisa WER 2 | Finland | 12" pipe | Rupture |
| 1993 | Sequioyah Unit 2 | USA | 10" pipe | Rupture |
| 1996 | Maanshan Unit 2 | Taiwan | 12" pipe | Rupture |
| 1997 | Fort Calhoun | USA | 12" pipe | Rupture |
| 1999 | Point Beach 1 | USA | 4" Vessel | Rupture |
| 1999 | PWR | Korea | 16" pipe | Severe Thinning |
| 2001 | Callaway Unit 1 | USA | Vessel Nozzle | Severe Thinning |
| 2001 | Unknown | USA | 16" pipe | 70% thinning |
| 2004 | Ooi Unit 1 | Japan | 16" pipe | 42% thinning |
| 2004 | Mihama Unit 3 | Japan | 22" pipe | Rupture |

Table 1 – FAC cases, [3]

1.2 Contributions to knowledge

There are many different factors that affect the carbon steel pipes as well as the corrosion issue, such as the pressure of the steam and effects of stress and strain. In this paper we describe the correct design methodologies for steam pipes in fossil power plants so that the steam pipes have the desired design life and do not fail prematurely, causing down time and potential damage to other plant assets.

- We will explain clearly what FAC is and how it can occur. We will also outline the various forms of corrosion that can occur internally on the steam pipeline.
- We will describe in detail the effects of FAC and relate them to the steam temperature and the time the pipe is subjected to that temperature.
- Material choices for the pipes will be outlined such as different alloys and the corrosion allowances that need to be calculated for certain features and situations.
- Stress and strain calculations are key to ensure the structural rigidity and safety of the pipeline system, so not only will the pipeline be considered, suggestions to the positioning of other features such as pipeline supports will be included in the report.

2.0 Corrosion Deposit Removal Issues

2.1 FAC and EC

The issue is when water is present in the pipes, various forms of corrosion or erosion can take place on the carbon steel. Erosion-corrosion (EC) is very similar to FAC, however FAC is the correlation between increasing flow and increasing corrosion, also the oxide layer is dissolved or prevented from forming and EC is the mechanical removal of corrosion deposits or oxide layer by shear stress from the flow of the fluid, EC is also has impingement and turbulence corrosion under its definition and leaves grooves and pits in which the local flow conditions can be seen. The two are very closely interlinked and are dependent on each other and they have very similar variables between them. These variables include: the temperature of the fluid, fluid's velocity, pipe's geometry, steel alloying elements, fluid's pH. We will be referring to FAC however it may technically be EC since they have such similar factors that affect them.

As a general rule the corrosion rate increases as the velocity increases and the type of corrosion changes from general or uniform corrosion to EC and finally cavitation [24]. Increasing temperature causes an increase in corrosion rates as corrosion is an electrochemical process and increasing temperature gives more energy into the process allowing molecules to move with greater momentum.

2.1 Electrochemistry of FAC

When water droplets sit on the steels surface the metal has a tendency to release metal ions into the water until there is equilibrium of ion concentration. The release of metal ions causes loss of material (dissolution) of the metal. Eventually there is a build-up of electrons in the metal and positive ions in the electrolyte at this stage the potential difference between the metal and the liquid is equal to the equilibrium potential (just enough voltage to allow same rate of transfer both ways of ions) rate at the ion concentration obtained in the liquid. [24]

The reaction rate in each direction can be expressed by the rate of electric charges, i.e. by current or current density called the exchange current (density). In equilibrium where there is no net transfer of ions, the exchange current is zero. The exchange current depends on electrode reaction, electrode material and electrolyte. Temperature and concentrations also affect the exchange current significantly. Increasing temperature, conditions steam pipes are subjected to, relates to an increasing current this is because the viscosity of the liquid reduces so the boundary layer is thinner and this leads to increased diffusion [13].

Iron in steel gives up its ions to the solution as iron has good ability to dissolve as it is quite active / not noble. To balance this loss of ions the metal has to be charged relatively negative this means steel has a negative equilibrium potential. The larger the activity of ions in the solution the more ions are released into the solution to balance this higher rate of ion release a positive pressure is needed in the steel, thus with increasing ion release activity the equilibrium potential increases. [2]

When the potential is moved away from the equilibrium potential it is said that the electrode is polarized, the measure of the polarization is the overvoltage or over- potential (i.e. a net current in one direction). There are two ways that polarization can occur activation polarization where there is a resistance at the electrode interface that acts against the current (overvoltage is needed to cope with this resistance) and is caused by the resistance

against the reaction. Concentration polarization is where there is either a shortage of reactants or an accumulation of reaction products. [24]

If a metal is in equilibrium with its ions in the solution and then made more positive by external measures or by polarization (potential is more +ve than the equilibrium potential) an oxidisation reaction (dissolution) of the metal occurs as it tries to balance with the solution again. Resulting in greater metal losses. [11]

Destruction of the passive films in EC occurs mainly due to mechanical breakdown whereas in FAC the breakdown is either due to chemical or electrochemical destruction. In *chemical destruction* the film is dissolved as even the oxide layer has a degree of solubility. By changing the pH, temperature or concentration of aggressive species (destructive species e.g. acids) the solubility is so high that even the passive films can disappear. *Electrochemical destruction* occurs because by potential changes. Lowering the potential from the passive region to the active region (this is illustrated in Pourbaix diagrams) or increasing it into the transpassive region, in these regions the exchange current is increasing positively greater than the equilibrium potential leading to activation. (E.g. for Fe in moderately alkaline environment a passive oxide can be reduced to other oxides or to the metallic state). If there is an opening in the film under these conditions the substrate metal corrodes rapidly and the film may be undercut with newer corrosion products. [2]

This is a case study of research done by General Electric into one failure they encountered from FAC corrosion deposits this illustrates the issues that can occur due to the process described. "Superheated steam turbines are particularly prone to damage by carryover. Sticking of governor and stop valves due to corrosion deposits can cause turbine over-speed and catastrophic damage. Solid particles in steam can erode turbine parts, while deposition on turbine blades can reduce efficiency and capacity. Losses of 5% in turbine efficiency and 20% in turbine capacity have occurred due to deposition. When large slugs of boiler water carry over with steam, the resulting thermal and mechanical shock can cause severe damage." [7]

3.0 Influences to FAC

3.1 Corrosion Deposits

Knowing the process of corrosion and why it happens allows for the detailed explanation of FAC corrosion process. Water droplets can form in the superheated steam when the pressure or temperature drops, it is calculated so that this doesn't happen on the way to the turbine as the droplets can damage the blades and off balance the turbine causing damage to the whole turbine and rotor. This temperature drop can be caused by various reasons and the conditions can be calculated from the ideal gas equation;

$$PV = nRT$$
 (1)

Superheated steam has very little or no oxygen in it due to the control of dissolved oxygen in the water [14]. So when steel is exposed to the oxygen-free water the following reaction occurs;

$$Fe + 2H_2O \Rightarrow Fe^{2+} + 2OH + H_2 \Leftrightarrow Fe(OH)_2 + H_2$$

Due to the anaerobic conditions there is no oxygen that normally causes $Fe(OH)_2$ or Fe(III) to form the oxide layer. Instead magnetite (Fe_3O_4 or Fe(II,III)) forms the protective layer. This is shown in the 'Schikorr' reaction;

$$3Fe(OH)_2 \Rightarrow Fe_3O_4 + 2H_2O + H_2$$

The magnetite inhibits further oxidisation of the steel however magnetite is soluble in demineralized neutral water or slightly alkaline (pH range of 7 - 9.2) and low dissolved oxygen water. In these conditions a protective layer of magnetite may not form[16]. Ammonia (pH=11) is sometimes added to the water to increase the pH above the region where magnetite is soluble. [9,14]



Figure 1- Wear rates and temperature, [3]

If the flow velocity is high enough the Fe^{2+} ions generated get carried away from the steel surface before they can create a magnetite layer. Turbulence in the flow from changes in path geometry increase the likelihood of FAC and the entrainment of Fe^{2+} is greatly enhanced and or the dissolution of the magnetite oxide film occurs more rapidly [9].

In two-phase flow the maximum rate of FAC at the temperature range of 150° C which is around 2000 μ g/cm² hr this can be seen in Figure 1. This is due to the magnetite layer being porous and irregular [13].

Even in normal or maximum operating conditions water can still exist in the pipes due to carryover where water (and other solids and vapour contaminates) get entrained into the flow of the steam from the boiler. This can cause both FAC and EC [8].

3.2 Pipe Lifetime

The pipe thickness is calculated using;

$$t = \frac{(PD')}{2(SE + Py)} + A \tag{2}$$

Where: *P* is the max. internal service pressure, *D*' is the outer diameter of the pipe, *SE* is the max. allowable stress in material caused by internal pressure at the design temperature, *y* is a coefficient (0.4 below 428°C) and *A* is an allowance for corrosion and mechanical strength [19].

Calculating the estimated life of a pipe 10mm thickness at the maximum corrosion rate temperature to estimate the time before the pipe is deemed unacceptable. Given the corrosion allowance is 0.165mm for pipes of 3.2mm or greater thickness [19] so this allowance is added to the 10mm thickness and the pipe is manufactured to 10.165mm thickness. EU regulations dictate that if the thickness of the pipeline falls below 85% [11] of its original thickness then it is unsafe and needs replacing. Which in this example would be a thickness of 8.64mm a change of 1.525mm material loss in a 1cm² element. This would be a mass loss of 1.188x10⁻³kg and this would take 595 hours of service. This seems very rapid however the pipes don't always operate at these conditions. They operate at higher temperatures where corrosion rate is lower. It is also not surprising as wall thinning rates of over 3mm per year have been observed [5].

3.2 Stress Calculations



Figure 2- Stress and strain pipes, [25]

Knowing the elastic limit of low carbon steel is around 300MPa [18] and an internal diameter of 1m and the optimum radial pressure of steam pipes is around 30 bar or 3MPa [15]. The minimum thickness of the pipe needs to be found:

$$t = \frac{qR}{\sigma_2} \tag{3}$$

$$t = \frac{(3x10^6)(0.5)}{(300x10^6)} = 5x10^{-3} = 5mm$$
(4)

This has not taken into account any allowances for corrosion, joints or allowable stresses. Using pressure rating tables and finding the closest values the maximum allowable stress is 13.2MPa [12]. Using this stress in equation 3 gives a thickness of 11.4 mm. If we use equation 2 to find the thickness and ignore the sources recommended corrosion and mechanical allowance and compare it later.

$$t = \frac{(3x10^{6})(1)}{2(13.2x10^{6} + (3x10^{6})(0.4))} + A$$
(5)
= 10.87mm + A (6)

If we add their recommended 0.165mm we get 11.035 mm. This is only 3.3% difference to the thickness we calculated using equation 3. It is also lower than the 11.4mm calculated before showing that their recommended allowance is too small.

Knowing that the maximum FAC corrosion rate is $2000 \ \mu g/cm^2$ hr, and the method outlined before where we used this to calculate the estimated lifetime for a pipe of 10mm thickness, combining this with equation 4 we can accurately calculate a thickness for the pipeline for the desired number of service years using the following derived equation:

$$t = \frac{qR}{\sigma_A} + (yrs \ x \ 87600) 2000 x 10^{-9} \frac{1}{(7800 x 10000)}$$
(7)
$$t = \frac{qR}{\sigma_A} + (yrs \ x \ (2.246 x 10^{-9}))$$
(8)

 σ_2 has changed to σ_A as the maximum allowable stress found from pressure rating tables. *Yrs* is the number of years of service and t is measured in meters. It is worth noting that this formula is only for FAC in pipes and that it is only an estimation as other factors and types of corrosion discussed before can affect the rates.

3.4 Shear

Velocity of the fluid is much lower near to the pipes inner surface this is due to friction between the fluid and pipe. This friction causes the shear stresses. The faster the velocity of the fluid the larger the shear stress will be. Due to the no-slip condition in fluid dynamics where fluid particles at the boundary are at a complete stop this affects adjacent layers to slow down the fluid in the centre has to speed up to keep the mass flow rate constant. Figure 3 shows the shear stress in a laminar flow. Steam at around 150° C has a very low dynamic viscosity of 14 x10⁻⁶ Pa s [17] the Reynolds number of a steam pipe needs to be calculated as the higher the Reynolds number the more turbulence and a higher rate of FAC will occur. It is worth noting that the surface roughness of the pipe also affects the turbulence. For laminar regions there is minimal momentum transfer but for turbulent flow there are high speed particles that rush in after slower particles near to the surface redirect towards the mid region of the flow [22] that can penetrate the metal and can cause plastic deformation that can lead to pitting.



Figure 3 –Shear stress caused by flow, [4]

Today it is not uncommon to see velocities of around 800m/s in steam [23]. Using the example of conditions used previously we can calculate the Reynolds number it. Given that the density of steam at 3 bar is 1.651 kg/m^3

$$R_e = \frac{\rho u D}{\mu} \tag{9}$$

Where ρ is the density, *u* is the mean velocity in the pipe, *D* is the internal diameter and μ is the dynamic viscosity.

$$R_e = \frac{(1.651)(800)(1)}{(14x10^{-6})} = 94.34x10^6 \quad (10)$$

This is well within the turbulent flow region ($R_e > 10\ 000$) and high rates of FAC and impingement will occur causing a rougher surface on the pipe and greater turbulence and shear stresses in a cyclic process. Figure 4 shows the how shear stress and Reynolds number are related.

Wall shear stresses occur due to the fluid flow and also the stresses in the pipe. The pipe considered throughout this report was programmed into MD Solids and a shear stress of 6.60MPa was given.



Figure 5 - Mohr's circle of considered pipeline.

In figure 5 the maximum principal stress is 15.9MPa which is higher than the allowable stress of 13.2MPa. It would be inside the elastic limit at that temperature. The y-direction stresses have been omitted as they would correlate to the weight of the pipeline above the considered element, there would also be a pressure drop ascending the pipeline.



Figure 4- Magnetite solubility and pH, [5]

3.5 Geometry

It is far more likely to have greater amounts of FAC corrosion at locations where flow disturbances occur, they are most likely to occur at "elbows, tight bends, reducer tees, locations downstream of flow control orifices and valves and fabrication discontinuities [5]." Computational fluid dynamics (CFD) software has allowed

different geometries and flow patterns to be analysed with respect to FAC and it has been shown that rates of corrosion exceed the design corrosion allowance [20]. It is not possible to completely estimate the locations of FAC however locations where FAC is likely are frequently ultrasonically tested, these locations can also be accurately guessed using CFD analysis. These locations where FAC has initiated are the areas that need the most attention as FAC roughens the surface to an orange peel or scallop appearance which induces greater FAC rates. [5]

4.0 FAC Reduction

4.1 Material choice

Small amounts of *chromium* added to the steel have dramatic effects on reducing FAC. It has been reported that rates have been reduced by a factor of 25, this has been achieved by adding 1 to 1.25% chromium to the steel alloys, although a reduction in FAC has been observed in alloys as low as 0.04% Cr [5]. Chromium addition increases the hardness of the steel and also the strength, this addition of hardness is induced during the processing of the steel as the alloys increase the response to the heat treatment. The alloys increase the amount of hard carbides inside the martensite matrix. It has been noted that chromium builds up in the oxide film and this reduces its solubility [21].

Molybdenum alloys with Cr-Ni have a reducing effect on FAC rates as they reduce the amount of pitting corrosion from chlorides and sulphur elements that can get into the steam via the feed water or from cracks in the boiler tubes. Molybdenum improves the hardness and strength of steel at high temperatures [1]. Pitting corrosion is often initiated by small surface defects and in steam pipes the cause of these defects could likely be form momentum transfer of particles in turbulent flow.

4.2 Level of pH

As discussed in section 3.1 the addition of ammonia increases the pH of the steam and this reduces the solubility of the magnetite layer, thus reduces the wall thinning rates as magnetite forms from the steel pipe, a graph of this is shown in figure 6. The temperature and pH in a solution are often associated together in a water-ammonia solution as the temperature rises the pH decreases this is due to the increase in dissociation of water, releasing more H^+ ions. The level of pH and the wear rates can be determined from regions in the Pourbaix diagrams. It is not yet currently known if other alkalizing agents have the same effect as ammonia [10].

4.3 Temperature

As stated before the maximum FAC rates occur at around 150°C however these rates drop as the temperature increases. Referring to figure 1 for carbon steel an increase in steam temperature to 250°C reduces FAC rates by approximately 100 times. Increasing the temperature and pressure to the point where the steam becomes superheated so there is no water formed on the pipe walls this reduces other form of corrosion such as pitting.

4.4 Velocity and Turbulence

In recent computational analyses it has been shown that the velocity is not directly related to FAC rates and that average flow rates are not a good guide to determine FAC. It has also been shown that there is not a critical velocity where after FAC rates accelerate. It has been shown that bends in pipes cause turbulence and this turbulence causes an increase in FAC. The turbulence can be controlled through pipe geometry changes however it is impractical to change the velocities, temperatures and pressures as this greatly reduces the efficiency of the plant.

4.5 Pipe Wall Thickness

The most basic way to reduce the effects of FAC and reduce the chance of rupturing is to have piping with a larger wall thickness. The greater thickness allows for corrosion and wear rates whilst not compromising on the structural integrity of the system, although the pipes will be heavier and support structures may have to be reinforced this method may be cheaper than redesigning the pipeline system or changing the steel alloy to NiCr as it is 10 to 16 times more expensive [18]. The change may mean that a higher pressure steam could be used increasing the output of the plant.

5.0 Conclusion

FAC has many contributing factors and areas of pipeline are more susceptible than others. FAC once initiated causes a positive feedback cycle and it is these areas that need to be predicted and frequently tested. There are methods to reduce FAC however they can be costly or cause greater overall inefficiency. The easiest way to reduce FAC is to control calculate the pH at temperature of the steam and adjust for this and add it into the feed water, reducing the loss of magnetite. The formula that has been made to be able to calculate the thickness of pipe needed for the desired years of service has proven that the corrosion allowance estimated is insufficient. The reason why FAC gives the magnetite corrosion product in steam pipes has been described and why it causes high rates of wall thickness reduction due to the environment within the pipe. We have identified the conditions where FAC is highest and the need to monitor those locations.

6.0 Future Work

Other factors that affect FAC could be further looked into with testing equipment, such as looking at various temperature and velocity differences on certain grades of steel. If CFD is known then the physical variables of the steam flow can be changed and different pipe geometries can be looked at and areas where high FAC may be located and investigated. Boiler tube materials could be looked into and the effects of cracking in them affect the steam. Detailed stress and strain for various pressures could be looked into and material suggestions could be given. Research could be done into other alkalizing agents that are put into feed water to see if they have similar or better corrosion reducing effects than ammonia.

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