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Flow Assisted Corrosion (FAC) and Flow Induced Localized Corrosion: Comparison and Discussion

Summary

- The computer model Checworks, used to manage aging of hot high pressure water and steam carbon steel lines was designed for Flow Assisted Corrosion (FAC) phenomena. Erosion Corrosion, Impingement and Cavitation are expressly excluded as unrelated to FAC. It is shown that the latter three corrosion phenomena are extensions of FAC as the local flow intensity due to turbulence increases. The transition from one to the others is continuous and difficult to identify. FAC therefore is only one manifestation of Flow Induced Localized Corrosion (FILC).

- The localized corrosion rate under the umbrella of FAC varies, per definition, almost linearly with fluid velocity; however, this linear relationship transitions into an exponential one as the local turbulence becomes such that erosional features become manifest. Whether such transition actually occurs following a power upgrade (PU) must be determined experimentally. It cannot be estimated from within Checworks.

- It has been stated that "the algorithms used to predict the FAC wear rate are based on extensive laboratory and plant data. This assures that the FAC wear rates predicted by Checworks are accurate." This accuracy is said to be within +/- 50%. However, this statement is based on an erroneous interpretation of the graphic representation of predicted vs. measured wear. Actually, the accuracy is within a factor 2. The measured wear ranges from twice the predicted to half the prediction.

- Partial review of the result from the pipe inspections using Checworks in 2003 and 2006 shows significant unexplained discrepancies.

I. Introduction

The direct testimony by Dr. Jeffrey S. Horowitz and Dr. James C. Fitzpatrick[1)] with regards to NEC Contention 4 – Flow Accelerated Corrosion has raised a number of questions, which are being discussed below:

1) Joint Declaration of Jeffrey S. Horowitz and James C. Fitzpatrick on NEC Contention 4 – Flow-Accelerated Corrosion, May 12, 2008.

- Is the model called Checworks based on sufficiently broad scientific understanding of all pertinent corrosion phenomena?
- Is the model called Checworks broad enough to capture all flow-assisted corrosion phenomena, or more broadly Flow Induced Localized Corrosion (FILC) in general?
- Is the model called Checworks suitable to manage aging of the hot water and steam piping system at the Vermont Yankee Power Plant?
- Is the predictive power of the model called Checworks within a probability range to prevent unforeseen catastrophic failure?
- Does the model called Checworks require extensive recalibration?

In order to tackle some of these questions I shall discuss some of the pertinent background and try to unravel the conundrum of language, which has, it seems to me, caused some misunderstandings if not outright confusion.

II. Background

1. The Chemical Nature of the Passive Steel Surface

It is well established that under certain conditions corrosion occurs in carbon steel hot water pipes in nuclear (and fossil) power generation plants. The chemical nature of this phenomenon is straightforward: iron reacts with water to form iron ions and hydrogen. The reaction is thermodynamically favored.[2)]

However, the physicochemical nature of the processes occurring in conjunction with the oxidation of iron, is infinitely more complex and, although investigated in great detail,[3)] generally not easily understood.

Ferrous (Fe^{+2}) or ferric (Fe^{+3}) ions are not stable by themselves at the prevailing temperatures (~300 ^{O}F) at a neutral or slightly alkaline pH. Either ion will react with water and form hydroxides, oxy-hydroxides, or oxides. The reaction occurs on the surface of the metal where an oxide layer forms, which slows the corrosion reaction or prevents it from occurring altogether. The phenomenon is called passivation and makes it possible for iron, steels, or stainless steels to be used as industrial materials to begin with. At the temperatures in question the passive layer is a thin crystalline "coating" of magnetite on the surface of the steel, Fe_3O_4, a mineral also found in nature. Fe_3O_4 is a combination compound formed from FeO and Fe_2O_3, generically called a Spinell. Because of the nature of the Spinell-type oxide combining in essence a two-valent iron with a three-valent iron ion, magnetite is electrically conductive and

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2) NEC-RH_03: R. H. Hausler, Discussion of the Empirical Modeling of Flow-Induced Localized Corrosion of Steel under High Shear Stress, April 25, 2008, pg 3.

3) See ACS Symposium Series Vol. 89 (1982), Editors: G.R. Brubaker, and P.B. Phipps, Chapters by Maurice Cohen, Vlasta Brusic, and J.E. Draly.

forms a contiguous thin, non-porous albeit crystalline layer on the surface of the metal.

2. The Physical Nature of the Passive Magnetite Layer

Steel in the passive state will not corrode or only at extremely slow rates (10^{-3} to 10^{-2} mpy). The question then is: What makes iron in the passive state corrode? Why do hot water or steam pipes in nuclear power generating units fail due to corrosion? Why are the failures predominantly local while the rest of the structure remains intact and passive for many years?

Any phenomenon that can destroy the protectiveness of the passive layer or assist in removing the passive layer will cause the steel to corrode at rates 10^3 to 10^4 times faster, i.e. at corrosion rates observed in the power plants.

What are these phenomena? In order to better understand this one needs to understand that magnetite is an electronic conductor. It can pass electrons from the metal side to the water-side where they can be consumed by an electrochemical reaction. Magnetite, however, cannot conduct ions. Neither iron ions nor oxide ions are mobile in magnetite.[4)] The phenomena that destroy the protectiveness of the passive layer are essentially chemical in nature, but may, however, be assisted by physical effects. For instance, chlorides in the water will convert magnetite to iron-oxy-hydroxy-chlorides, (various modifications thereof), which are much more soluble than magnetite and also can conduct ions. The result is that the passivity has been lost.[5)] This is the mechanism that prevails in the crevices of the steam generators of PWR's and is the primary cause of denting.

Magnetite has a finite, albeit very small, solubility in hot water. The dissolution of minerals in water is aided by agitation, i.e. forced convection. Salt (sodium chloride), e.g., will not dissolve in stagnant water, but will readily go into solution when the solution is agitated. The dissolution process will stop when the solution is saturated with the salt. This is in essence how the corrosion process of steel in hot water has to be visualized. I have tried to sketch the physical reality as simplified as reasonably permissible in Figure 1.[6)] The water layer close to the magnetite surface is saturated with iron oxide in equilibrium with the magnetite layer. The iron concentration in the bulk water phase is practically zero. Therefore a concentration gradient develops from

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[4)] Because of the physical nature of magnetite iron, it is also called a valve-metal (in analogy to aluminum). However, the magnetite layer is distinctly different from such corrosion product layers as iron sulfide or iron carbonate. Iron sulfide, for instance, is a p-type conductor based on iron ion vacancy mobility. This layer therefore can grow from the solution side, a process not possible with magnetite, because magnetite cannot conduct iron or oxide ions.

[5)] The phenomenon is well known in the nuclear industry since it is the primary cause of "denting" observed in stream generators of PWRs.

[6)] Note that this Figure and the mechanism derived therefrom essentially mirror Dr. Hopenfeld's explanations: NEC_JH_36 at pg 3 and Fig. 1.

the magnetite surface across the stagnant boundary layer. The solubility of iron (from magnetite) is very, very low. Hence, the mass transfer of iron ions across the stagnant water layer near the magnetite surface, which occurs by diffusion and is controlled by the concentration gradient, is very low as well. The thickness of the stagnant layer, which is infinite if there is no flow, is reduced as flow over the surface increases. Therefore, as the flow [rate] over the surface increases, the stagnant layer (also called the laminar boundary layer or the diffusion layer) is reduced in thickness, the diffusion rate increases, and hence the dissolution rate of the passive layer. The thickness of the passive layer (which is very small to begin with) becomes a steady state value when its formation rate (the corrosion rate) equals the removal rate (dissolution and mass transfer rate). The latter is controlled by the flow rate. **Therefore, this type of corrosion has been termed Flow Assisted Corrosion (FAC).** However, as we will see below, the fact that the creators of Checworks have decided that the main characteristic of FAC is its proportionality to the flow rate is entirely arbitrary.

3. The various forms of FAC

If the flow (laminar or turbulent[7)]) is strictly uniform over the entire surface area of interest then the entire area will corrode uniformly and wall thickness loss is uniform.

However, at the prevailing flow rates (24 ft/sec in many cases) the flow pattern is not uniform because of the non-uniformity of the cross sections of the flow channels. **In particular, where flow upsets are built into the system, such as orifice plates, flanges, etc., localized turbulences occur which are much more intensive than are normally described by general flow equations**. The engineering approach is to characterize the flow at such flow disturbances by means of differential pressure drop and an average shear stress occurring at the disturbance. However, the difficulty is that the localized shear stress within the turbulence cannot be captured in this manner and is in general orders of magnitude higher than the average numbers[8)] would indicate.

The different paradigms can perhaps be explained by means of Figure 2 (below). Any geometric feature in a flow channel (pipe for instance) that reduces or expands the [hydraulic]-diameter, or changes the direction of flow, creates a flow disturbance (including sensors inserted into the pipe for temperature, pressure or other parameters). This means that the flow regime, which in the straight sections of the pipe may be fully developed laminar or turbulent flow changes to one, that also incorporates local turbulences (eddies). This leads to locally enhanced shear stress and hence enhanced mass transfer and therefore locally increased corrosion.

Just as flow in a pipe can be characterized by the pressure gradient, flow upsets, such as are shown in Figure 1, can be characterized by an average pressure drop (and

[7)] For definition of turbulence in the general sense see Figure 2 Ref. 2.

[8)] c.f. for instance Figures 4 and 5 of Ref. 2

hence an increased average shear stress. Engineering practice has done this for a large number of flow features (elbows, orifices, t's, etc.) of varying diameter for the purpose of being able to calculate the pressure drop along complex piping systems.

Checworks now uses these flow features (56 of them) to record and classify observed and measured corrosion rates in a data base along with a host of environmental parameters (pressure, temperature, water chemistry, etc), physical parameters (flow rates, metallurgical features, and many more), as well as boundary conditions such as minimum critical wall thickness etc. Once the database has been established, statistical routines, such as multiple linear correlation, can be applied in order to extract explicitly and quantitatively the dependence of corrosion rate within the parameter space. The resulting correlations can then be used to predict corrosion rates for individual situations, which can be characterized well enough to be accommodated in the database (one of the 56 features). Certain theoretical concepts are combined with the multiple correlation, in particular the notion that corrosion increases proportionately with velocity.[9)]

Therefore, there are two major principles imbedded in Checworks:

- Flow features have been standardized in traditional engineering fashion (an elbow is always an elbow, an orifice is always an orifice, etc.). However, for certain features that could not be done: a weld is not always a weld, and a flange is not always a flange (see discussion below).

- A linear (or near linear) relationship between flow rate and mass transfer, i.e. corrosion rate, has been built into Checworks. It is for this reason that Dr. Horowitz indicates that certain failures, which had been identified as being caused by erosion or impingement could not have been predicted by Checworks, but that this lack of prediction does not invalidate the predictive value of Checworks.

It has been shown theoretically that the shear stress governs the mass transfer. Accepting this one can readily understand that at locations of high shear stress the magnetite dissolution is high and therefore the corrosion rate is high as well. This has led to the notion of flow induced *localized* corrosion (FILC). Clearly the phenomenon is "flow assisted" but it is localized. By that one does not mean pitting; rather, one refers to areas of some extension, which corrode faster than the adjoining metal. Much has been made of the extent of the areas subject to FILC (or FAC) because the risk associated with the resulting failure will be governed by the extent of corrosion.[10)]

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9) See Ref. 1 Horowitz at A 49.

10) Understandably, the damage from a half-inch to one-inch "pinhole" may be considerably limited versus the damage from a pipe that splits open the length of several feet.

If only a small area corrodes due to enhanced local turbulence a small pit and eventually a small hole may result with only minor consequences. If on the other hand FILC (FAC) occurs over a larger area, the pipe may split open (as has indeed happened) with potentially disastrous consequences.

One can now reasonably ask the question as to what happens if the flow intensity exceeds that which has been empirically correlated in Checworks. In other words, if a certain localized enhanced corrosion rate has been observed over a period of years in the past and all of a sudden the flow rate (and hence the flow intensity) is increased, (EPU, power upgrade), will the local corrosion rates simply increase proportionately in accordance with the established laws relating average shear stress to mass transfer, or will the local corrosion rates increase exponentially as has been suggested earlier? In the first instance Checworks would predict the new corrosion rate, in the second instance Checworks would have to be recalibrated, or even fundamentally modified to accommodate the new relationships. **This is the fundamental question that must be answered before Checworks can be accepted as the basic tool to manage aging of these pipes.**

Indeed additional phenomena related to high flow rates, high shear stress, have been documented with failure rates in excess of those attributed to FAC. These phenomena are described as erosion corrosion,[11)] impingement corrosion,[12)] and finally cavitation.[13)] All three phenomena result in a much more severe attack than what has broadly been called FAC, and which is at the basis of Checworks (see definitions below).

It is important to highlight this since the phenomena covered by Checworks do not include the most severe corrosion, which can occur particularly after a power upgrade. In fact Dr. Horowitz dismissed as irrelevant with respect to Checworks actual catastrophic failures attributed to erosion corrosion or impingement corrosion and therefore outside the scope of Checworks. This is a serious shortcoming of the

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[11)] This is actually a misnomer in this context since erosion corrosion generally involves solids carried in the fluid stream. However, it is recognized that the terminology is not used consistently. Erosion corrosion, which I prefer to characterize as FILC, starts at some unevenness on the surface (inclusion, scratch, etc.). The high flow rate causes local eddies, which leads to higher removal rate of corrosion product than over the surrounding areas. As the area of enhanced corrosion grows, the flow disturbance grows in intensity. Consequently the rate of penetration is not constant with time.

[12)] Impingement is caused by liquid droplets carried in the gas to hit the surface. This can occur from any angle depending on the direction of the flow vector. When a droplet approaches the surface the liquid between the droplet and the surface has to be displaced. It turns out that the velocity of the liquid parallel to the surface increases exponentially as the droplet approaches values many times higher than the estimated average velocity of the bulk liquid relative to the surface.

[13)] Cavitation occurs when the liquid flows relative to the surface (or the surface moves relative to the liquid) with oscillations such that at one point in time a vacuum is generated and a bubble is created, while right afterwards the pressure increases such that the bubble collapses. This causes enormously high oscillating fluid velocities parallel to the surface and tremendously increased mass transfer and very likely mechanical damage to the corrosion product layer (the passive layer) as well.

model and its application, because if the model forms the basis of aging management of the steam and hot water pipes it must, absolutely must, include the occurrence of all corrosion phenomena including those that lead to the most severe corrosion damage, not be restricted to just the average corrosion. But herein lies the rub as follows:

Checworks fully recognizes the fact that the severity of flow induced corrosion depends on geometric factors as described previously. Checworks, it appears, specifies in excess of 56 different geometric features. However there are things that cannot be specified. For example, the internal residual weld bead from the root pass may in one case be 1/8 inch high, in another ¼ inch. The upstream and downstream turbulence surrounding the weld bead are obviously much more severe in the latter case, and a power upgrade may disproportionately affect the flow over the larger bead.

While an increase in flow rate will affect the mass transfer rate (and hence the corrosion rate) proportionately under conditions of well defined (turbulent) flow, the flow intensity in local turbulences, such as eddies upstream and downstream of mechanical (geometric) flow disturbances are increased exponentially (see earlier). And here exactly is the uncertainty highlighted by Dr. Hopenfeld and denied by Dr. Horowitz. As I have also documented, industry consensus is that the flow intensity in local turbulences is increased to a much larger extent due to a power upgrade than the flow intensity in well-developed turbulent flow.

There are however additional phenomena, which have to be taken into account. Protective corrosion product layers can be destroyed not only through dissolution but by mechanical forces with turbulent areas. The fracture strength of corrosion product layers, such as iron sulfide and iron carbonate (highly protective formations), is extremely high (of the order of many hundreds of mega Pascals). Generally the compressive forces within turbulences are not that high.[14] It has been observed, however, that isolated events occur within the turbulences that match the fracture strength of the corrosion product scale. These events have led to the definition of a critical shear stress (or critical flow intensity) beyond which the protectiveness of the layer is lost. I am not suggesting that this absolutely happens. I am however postulating that past experience as built into Checworks cannot account for such occurrences. Therefore, the aging management process has to be revised or Checworks calibrated accordingly.

III. Discussion of Specific Experiences Involving Checworks

1. The Reliability of the Predictions

It has been said that Checworks can predict the "wear" [cumulative corrosion] within +/- 50 percent. If this were the case the modeling program would indeed be outstanding. However, the notion of predicted rates being with +/- 50% of the

[14]) This discussion relates to the "freak waves" alluded to earlier (see ref. 2).

measured ones is derived from a representation of the data as shown in Figure 3 below. It is true that when the measured wear data are plotted against the predicted ones most of the data points lie between two lines that are plotted +/- 50% off the 45 degree equivalency lines. This interpretation is totally misleading and scientifically dishonest.

First, one sees that there is no correlation between the predictions and the actual measurements. Second, one also sees that measurements which we are made to believe are within 50% of the predicted value are really twice as large or larger; similarly, on the other side one sees that measured values are half or less of the predicted ones, again a factor of 2 different.

Conclusion: **The accuracy of Checworks is such that the measured values are within a factor of +/- two [+/- 2] of the predicted values rather than +/- 50% as claimed.**

A factor-of-two difference between measured and predicted corrosion [or corrosion rate] can be quite significant with respect to selecting a particular item (line) for inspection during a given refueling outage. Indeed the report of the "EPRI Checworks Wear Rate Analysis Results for Cycle 22B"[15] shows that the time predicted to reach the critical minimum wall thickness in a majority of cases is many years *negative*. This means that the item should have failed a long time ago. Similarly, the remaining time to failure may be grossly overestimated. But one will never know unless the proper inspections are performed and the computer model recalibrated, a process Dr. Horowitz and Entergy seem to find irrelevant.[16]

Examination of the data from March 2003 (RFO 23) showed average and measured corrosion rates of the order of 28 and 21 mpy, respectively, for the outlet "P-1-1A" on line 001-16-FDW-01. In May of 2006 these same rates have come down to 7.524 and 5.712 mpy, respectively.[17] It is hard to see how this could have happened. There is in the program something called "Line Correction Factor." This factor has been defined by Dr. Horowitz as the relationship between predicted and measured corrosion rate (see below[18]). However in 2003 this factor was 0.649 and by 2006 it had become 0.175. It is amazing to observe that fudge factors are built into the program which

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15) Exhibit E-4-29.

16) Joint Declaration of Jeffrey S. Horowitz and James C. Fitzpatrick on NEC Contention 4-Flow-Accelerated Corrosion: A 34.

17) Exhibit E-4-30.

18) HOROWITZ'S TESTIMONY STATES THE FOLLOWING ABOUT THE ABOVE-MENTIONED "CORRECTION FACTOR" AT A28: "A Pass 2 Analysis compares the measured inspection results to the calculated wear rates and adjusts the FAC rate calculations to account for the inspection results. The program does this by comparing the predicted amount of degradation with the measured degradation for each of the inspected components. Using statistical methods, a correction factor is determined which is applied to all components in a given pipe line – whether or not they were inspected."

allow the operator to manipulate the data such that they meet certain criteria. (In the particular case mentioned above apparently negative times to failure were quite inconvenient).

Further examination of the data reveal that for the same line the corrosion rate on "Outlet P-1-1C" is exactly the same within 4 digits (+/- ~0.01 percent). Under the circumstances, it is very hard to gain confidence in Checworks and the manner in which it is apparently handled.

Finally it should be mentioned that with all the work that has been done, theoretical and empirical, around the problem of Flow Induced Localized Corrosion the matter is still not understood. In discussing the failure which occurred in April 2004 at the Kewaunee plant, Dr. Horowitz states that the line in question is not FAC-susceptible because apparently it is part of the "raw water system." Therefore it was not analyzed with Checworks and is not covered by NSAC-202L.

This is obviously a very unfortunate approach to the problem of corrosion in its entirety.

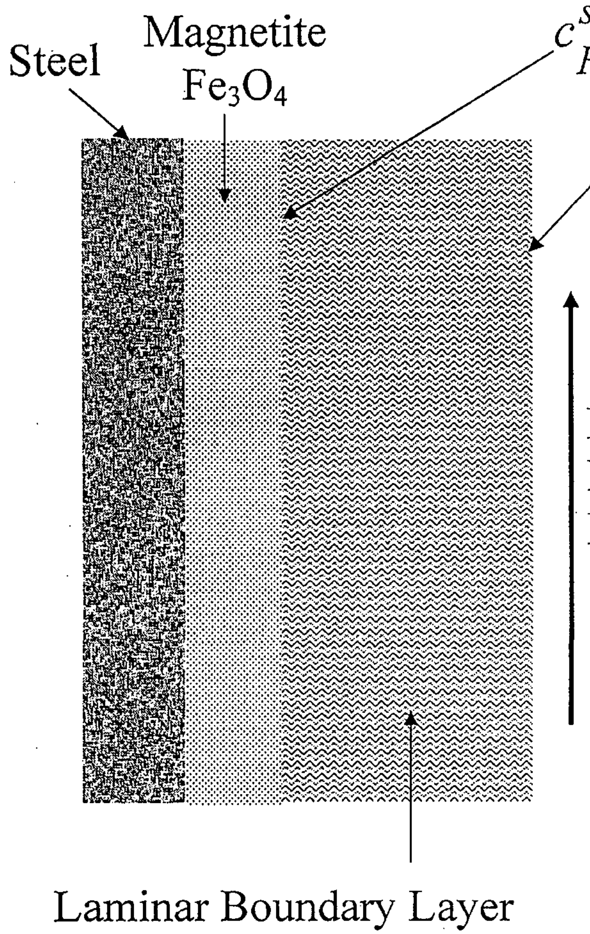
Whenever corrosion is dependent on transfer of corrosion products away from the surface, or transfer of corrodents to the surface, the corrosion rates are mass transfer dependent and hence flow dependent.

In the case of raw water, the oxygen content in the water is responsible for the observed corrosion. The corrosion rate is dependent on the oxygen concentration as well as on the flow rate. Flow rate dependence of corrosion is almost universally true except in a very few cases which are not relevant in this context.

Figure 1

The Concept of Flow Assisted Corrosion

$$c_{Fe^{n+}}^{sat} - c_{Fe^{n+}}^{bulk} = \Delta c \qquad Q = A \cdot \frac{\Delta c}{d}$$



Q = Rate of iron diffusion across laminar boundary sub-layer
A = diffusion coefficient for iron
d = boundary layer thickness

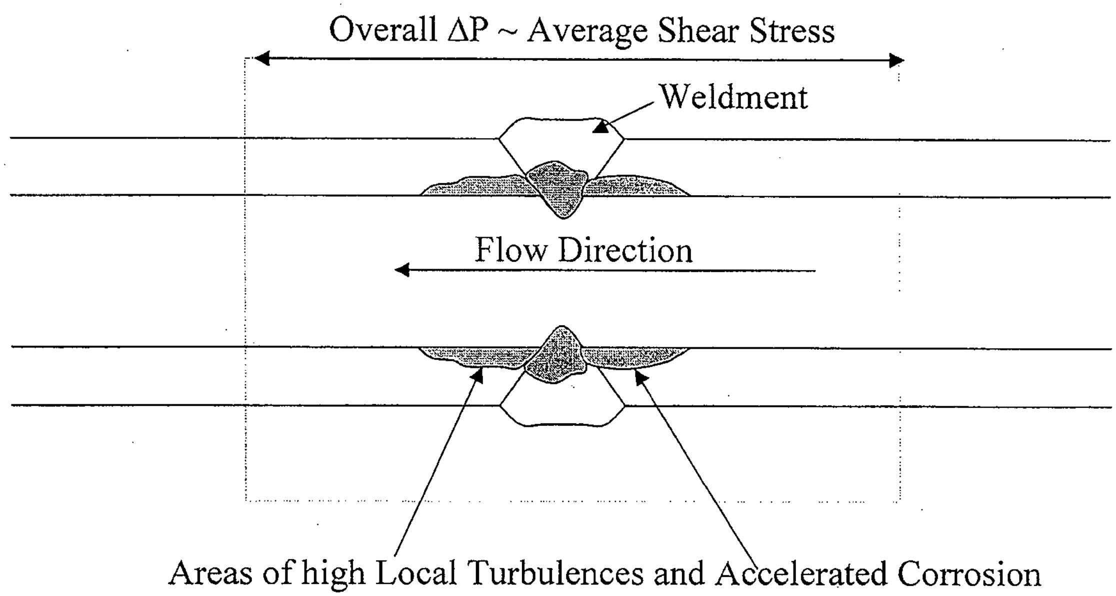
Bulk of solution; Direction of flow
Flow regime likely turbulent in the traditional sense
Re>>2000-3000

As the fluid velocity increases the thickness of the laminar layer decreases hence the mass transfer increases: removal Rate of iron oxide increases hence corrosion Rate increases.

Figure 2

Visualization of Average and Local Shear Stress

Straight Pipe with Weldment



The local shear stress is in no explicit relationship to the average shear stress
And can be orders of magnitude higher depending on geometric factors

Figure 3

Comparison of Wear Predictions