

DOCKETED
USNRC

RAS M-238

August 12, 2008 (11:00am)

NEC-RH_03

OFFICE OF SECRETARY
RULEMAKINGS AND
ADJUDICATIONS STAFF

Discussion of the Empirical Modeling of Flow-Induced
Localized Corrosion of Steel under High Shear Stress

U.S. NUCLEAR REGULATORY COMMISSION

In the Matter of Emerging Nuclear Vermont Yankee LLC
Docket No. 50-271 Official Exhibit No. NEC-RH-03
OFFERED by: Applicant/Licensee Intervenor NEI
NRC Staff _____ Other _____
IDENTIFIED on 7/23/08 Witness/Panel Hausler
Action Taken: ADMITTED REJECTED WITHDRAWN
Reported/Clerk MAC

Dr. Rudolf Hausler
Corro-Consulta
8081 Diane Dr.
Kaufman, TX 75142

April 25, 2008

Template Secy-028

DS-03

TABLE OF CONTENTS

Introduction and Objective.....	1
Definitions of Flow Regimes.....	2
Corrosion Mechanism.....	3
The Nature of the Passive Layer.....	4
The Effects of Mass Transfer.....	5
Further Investigations into the Removal Mechanisms of Corrosion Product Layers.....	7
Figure 1.....	10
Figure 2.....	10
Figure 3.....	11
Figure 4.....	11
Figure 5.....	12
APPENDIX A.....	13
I. The Problem.....	13
II. Determination of Confidence Limits of Corrosion Rate Estimation.....	14
III. Conclusion.....	14
Table 1.....	16
Figure 1.....	17
Figure 2.....	18

Discussion of the Empirical Modeling of Flow-Induced Localized Corrosion of Steel under High Shear Stress

Introduction and Objective

Multiple failures of carbon steel pipes, apparently due to the high velocities of the high-temperature water and steam they carry, have been observed in the past in nuclear power plants. Dr. Joram Hopenfeld has listed a small sample of apparently random, not predicted failures.¹ As a consequence, the industry has attempted to collect these multiple occurrences in a database, called "CHECWORKS," on the basis of which multiple correlations could be established for the purpose of predicting failures.²

Since CHECWORKS (or related computer codes) is based on the experiences from a variety of power plants, its application to an individual facility requires plant-specific input. The process of inputting plant-specific data has been termed "recalibration." Recalibration essentially consists of assessing the prevailing metallurgy, accurately describing the environmental conditions, and determining the prevailing corrosion rates at specific locations deemed most likely to be susceptible to rapid deterioration and failure.³

Of particular concern are the effects of a recent power upgrade ("EPU") and the concomitant effects on Flow-Induced Localized Corrosion ("FILC").

Since the Utility intends to use a recalibrated CHECWORKS for Aging Management of pipes, which are subject to high flow rates, it is the objective of this discussion to:

- a) Review the reliability of empirical modeling in view of modern understanding of Flow-Induced Localized Corrosion (FILC), and
- b) Assess the time requirements for recalibration from a statistical point of view.

To evaluate the corrosion of iron at elevated temperature, one must begin by considering the inherent corrosion processes. Iron will react with water under all environmental conditions (i.e. over the entire pH range).

The rate of reaction depends on the state of the interphase⁴, which controls the rate of reaction (i.e. the corrosion kinetics). The hydrodynamic conditions (including geometry)

¹ Joram Hopenfeld, "Review of License Renewal Application for Vermont Yankee Nuclear Power Station: Program for Management of Flow-Accelerated Corrosion, April 24, 2008, Exhibit NEC-JH_36 at 9-11.

² The CHECWORKS computer code is treated as proprietary.

³ The description represents our understanding of recalibration without detailed knowledge of the software's proprietary code.

⁴ The interphase is defined as the three-dimensional space between the base metal and the bulk of the solution, which is different from either in all its properties. The interphase in general presents a complex structure, which involves a solid phase (corrosion product), an interface between the corrosion product and

are the next relevant aspects of corrosion. One must specifically consider the flow field at locations most likely to be subject to high shear stress, which defines all prevailing mass transfer processes, and the nature of the flow (single phase or multiphase).

When one superimposes the hydrodynamic conditions on the corrosion processes a complex interdisciplinary problem emerges which involves:

- Metallurgy
- Inorganic chemistry
- Electrochemistry
- Solid state chemistry and transport processes
- Hydrodynamics and associated liquid transport processes.

In light of these complexities, it cannot be the goal of this discussion to produce a detailed understanding of the corrosion mechanisms and kinetics of iron in water/steam at high temperatures. Rather we will attempt to produce an overview of the parameter field, which needs to be considered and controlled if one is attempting to model iron corrosion for the purpose of predicting failure under certain defined conditions. We will also attempt to summarize the major correlations, which have been shown to govern the kinetics of iron oxide dissolution/erosion, i.e. what has been called “Flow Assisted Corrosion” (FAC) and what more appropriately should be termed “Flow Induced Localized Corrosion” (FILC). FILC emphasizes the fact that in disturbed turbulent flow the incurred corrosion damage is always highly localized.

Definitions of Flow Regimes

The terminology “Flow-Induced Localized Corrosion” was introduced in the late 1980s, and has now been widely adopted in many parts of the world.⁵ The concept of FILC embraces all phenomena that involve the localized effects of flow on corrosion processes.

For clarification, Figure 1 shows the four main types of flow-induced or flow-assisted corrosion.

The simplest case is that of simple mass transfer controlled corrosion. Here the corrodent (for instance oxygen, hydrogen ion, etc. dissolved in the water) is transported to the metal surface by convective mass transport. This phenomenon, while flow-assisted, generally leads to uniform corrosion and is kinetically controlled by either pure mass transfer, or both mass transfer and metal dissolution kinetics (mixed kinetic control).

the metal, an interface between the corrosion product and the liquid, and an interphase between the solid and the liquid made up of a various property gradients (including mass transfer gradients).

⁵ See for instance *Flow Induced Corrosion: Fundamental Studies and Industry Experience*, K.J. Kennelley, R. H. Hausler and D. C. Silverman, NACE publication 1991, Chapters 15, 16 and 17 by Hausler, Stegmann, Cruz, et. al

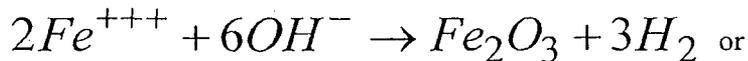
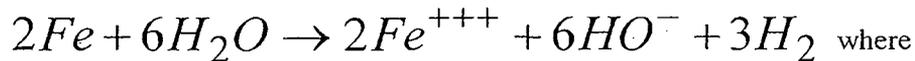
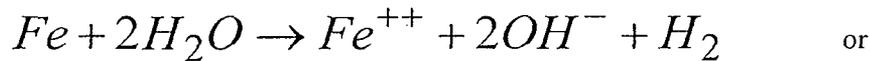
The next phenomenon, which is another case of FAC, occurs when the aggressive phase (for instance water) is carried in a gas stream. This case is central to the flow and corrosion phenomena in wet steam transport.

The third phenomenon in Figure 1 is customarily identified as Erosion Corrosion. However, there are two subcategories to the flow effects occasioned by geometric phenomena. The first is linked to increased turbulence in single-phase flow caused by a change of the geometry in the flow channel (disturbed turbulent flow). The second is attributed to solids carried in the fluid, but does not necessitate a geometric change. For this reason, the term "erosion corrosion" is now being reserved for the situation of solids carried in the fluids, while the term Flow-Induced Localized Corrosion (FILC) refers to single-phase flow associated with a geometric change.

Finally, there is the case in which gas bubbles are carried in the fluids (most often generated by an abrupt pressure drop at a flow disturbance) and collapse under a sudden pressure increase causing extremely high shear stresses locally.

Corrosion Mechanism

Iron (steel) will react with water across the entire pH range.⁶ The reactions



are all thermodynamically favored. The last reaction leads to the well-known magnetite. Under the conditions generally encountered in the industry, a protective magnetite layer forms on the surface of the metal and reduces the progress of further corrosion reactions to essentially nil. It is precisely this passivation phenomenon that renders iron or steel such a useful and pervasive material of construction.

However, passivation is not an absolute phenomenon in the sense that it invariably leads to minimal corrosion. Rather, it is subject to breakdown or removal under certain circumstances. Consequently, the study of iron corrosion must focus on the stability or

⁶ See also: *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Marcel Pourbaix, Cebelcor/NACE 1974, pg. 307

breakdown of the passivation layer. There are a number of mechanisms that can lead to breakdown of passivity or at least increased corrosion by removal of the magnetite layer. These will be briefly discussed around a more detailed description of the nature of the protective oxide layer.

The Nature of the Passive Layer

As indicated above, passivity comes about because of the formation of a magnetite layer on the surface of the metal. Many studies have focused on the formation of this layer as well as on its properties and protectiveness.⁷ By means of electrochemical studies, it has been established and is well accepted that the iron oxide (magnetite) is an ionic composite with a cubic structure, grown epitaxially on the surface of the metal. Magnetite is electrically conductive, but presents a barrier to both iron ion and oxide ion diffusion. Therefore, iron can be electrochemically polarized to high positive potential without the corrosion product layer growing beyond a certain thickness due to any of the above equations, until at about +1.2 V (vs H_2/H^+), in the so-called transpassive region, oxygen evolution takes place.

It is important to understand that under ideal steel/water/temperature conditions, the oxide layer is almost totally protective of iron corrosion. The layer cannot grow significantly either from the metal/oxide interface, nor from the oxide solution interface, because the first case would require oxide ion diffusion to the metal, while the second case requires iron ion diffusion to the water side, and neither can take place at any appreciable rate.

Nevertheless, there are conditions where the passivity can either break down or be removed. Passivity can break down because of certain chemical effects. Chlorides, for instance, will react with the magnetite resulting in a series of iron-oxy-chlorides that are no longer protective.

Of more immediate interest, however, are the phenomena that lead to removal of the passive layer, or at least to temporary removal thereof. Iron oxides (magnetite and mixed hematite/magnetite oxides) have a finite, albeit extremely low, solubility in water above pH 7. These oxides are therefore subject to dissolution, a process that is mass transfer controlled and therefore flow-dependent. Hence, purely phenomenologically, the faster the flow over the surface, the greater the dissolution rate and hence the corrosion rate, because passivity will tend to be reestablished. A steady state develops between dissolution and formation or between the corrosion rate (i.e. formation rate) and the flow rate. Therefore, one must study the mass transfer dependent dissolution rate of the oxide layer.

⁷ See also Maurice Cohen (Dissolution of Iron); Vlasta Brusic (Ferrous Passivation), J.E. Draly (Corrosion of Valve Metals), published in Corrosion Chemistry, ACS Symposium Series, Vol 89, (1982) Lecture Series organized by R.H. Hausler and edited by G. R. Brubaker and P.B. Phipps.

The Effects of Mass Transfer

It is important to note that only in the case of convective mass transport has it been possible to describe the effect of flow on the metal dissolution rate from first principle. For example, in laminar flow the pressure losses due to flow are described by the Hagen Poiseuille equation:

$$\Delta P = \frac{8\mu L}{R^2} \cdot U$$

where: ΔP = pressure drop along the length of the pipe
U = linear velocity
R = diameter of pipe
L = length of pipe
 μ = absolute viscosity of fluid

Since the shear stress is proportional to the pressure drop, which is proportional to linear velocity,

$$\tau \approx \Delta P \approx U$$

a linear relationship between shear stress and linear velocity is obtained, and in fact an additional relationship between the mass transfer rate and the flow rate is established.⁸ If the corrosion rate is dependent on the dissolution rate of the passive film, then the corrosion rate does in fact become proportional to the flow rate for laminar flow.

In turbulent flow, the pressure drop ceases to be proportional to the first power of the average velocity and becomes approximately proportional to the second power of linear velocity. Various formulations have in the past been presented for the case of turbulent flow in circular pipes. All of them involve empirical correlations with dimensionless parameters (like the Reynolds number) and therefore cannot be said to be derived from first principle, but relate to specific cases.

In the majority of cases a relationship between the corrosion rate, w , and the flow rate, U , can be approximated with an exponential relation of the form:

$$w \approx U^\alpha$$

For the trivial case of corrosion which is not flow dependent, $\alpha=0$.

⁸ See E. Heitz in Ref. 5, chapter 1, Chemo-Mechanical Effects of Flow on Corrosion

The relationship for transport-dependent processes is well known in the form of the power law:

$$Sh \approx Re^m$$

where: Sh = the Sherwood number (nondimensional)
Re = Reynolds number (nondimensional)

The exponents in this case are in the range of $0.3 < a < 1$, with the small values relating to laminar flow and larger values relating to turbulent flow conditions.

For corrosion types that involve a mechanical removal of the surface layers (intermittent increase in transport rate) and/or of the basic material, on the other hand, exponents of $\alpha > 1$ are usually found.⁹

Where the surface layer is broken down by shear stress the following estimate can be made for pipe flow:

The pressure loss in circular pipe flow has a linear relationship to the shear stress:

$$\tau_w \approx \Delta P = \lambda \frac{1}{D_0} \frac{\rho}{2} \cdot u_m^2$$

Using the Blasius theorem, one can arrive at:

$$\tau_w = u_m^{-0.25} \cdot u_m^2 = u_m^{1.75}$$

If the breakdown of the surface layer is proportional to the shear stress, relationships for smooth pipe of the form

$$w \approx u^{1.75}$$

and

$$w \approx u^2$$

for rough pipe flow are obtained.

⁹ U. Lotz, E. Heitz, Flow-Dependent Corrosion. I. Current Understanding of the Mechanisms Involved, Werkstoffe und Korrosion, 34. 454-461 (1983)

Since the failures described by J. Hopenfeld¹⁰ point in the direction of Flow-Induced Localized Corrosion, one can safely assume that these localized occurrences are due to the destruction of the protective magnetite layers. This raises doubts at least as to whether the rates of FILC [or FAC] are less than proportional to the flow rate and suggests that the proportionality is of a higher order.

From all of the above reasoning, it should be clear that the corrosive forces following the EPU are much larger than anticipated and not necessarily predictable. Hence the extreme necessity for calibration.

The reason why predictions are so very difficult is again phenomenological and is depicted in additional figures:

Figure 2 shows that in the case of a flow channel diameter change backflow occurs with very high local turbulences. The point of reattachment of the flow is very much dependent on the geometry and will migrate up and down the pipe with flow rate changes.

Figure 3 illustrates the momentum transfer for various flow regimes by way of pictorial explanation. In particular, the pressure impact, which leads to localized corrosion (also often designated as erosion), will need to be discussed in greater detail below.

Figure 4 shows the corrosion mechanism occurring on flow disturbances for copper and ferrous materials. It is important to note that pitting can occur in stagnant (or relatively stagnant) areas while the areas of high flow become cathodic. This is counterintuitive and another reason why it is so very difficult to predict a) where the localized corrosion will occur, b) how fast it will take place, and c) where it will be moved to as the flow rate changes.¹¹ Finally, in Figure 5 one can see that a flow channel restriction can lead to FILC upstream of the restriction as well as downstream.

Further Investigations into the Removal Mechanisms of Corrosion Product Layers

More recently, questions have been asked with respect to the stability and strength of corrosion product layers and the shear forces one might need to actually destroy these layers such that the corrosion rate would no longer be controlled by the kinetics of dissolution of these layers.

G. Schmitt dealt extensively with these questions over the years.¹² He concluded that extrinsic stresses like wall shear stresses (as conventionally calculated) in flowing media are generally too small to contribute much to the destruction of corrosion product layers.

¹⁰ Exhibit NEC-JH_36 at 9-11.

¹¹ Pitting is particularly prevalent under conditions where the passivity can be impaired, as for instance in the presence of chlorides.

¹² G. Schmitt, T. Gude, E. Strobel-Effertz, *Fracture Mechanical Properties of CO₂ Corrosion Product Scales and Their Relation to Localized Corrosion*, NACE CORROSION/96, paper 9

FILC is initiated at sites of local spalling if critical flow intensities prevent re-formation of protective scales.

Subsequently it was shown that fracture stresses for iron sulfide, iron carbonate, and iron oxide layers were in the range of 10^6 to 10^8 Pa (N/m^2).¹³ Shear forces of this order of magnitude cannot be accounted for by conventional hydrodynamic modeling. Since it was clear, however, that in practice many situations are known where apparently flow effects are capable of destroying corrosion product layers, Schmitt set about to measure the shear forces in highly turbulent areas with micro-electrodes and an electrochemical methodology based on the determination of limiting diffusion currents. The methodology is exceedingly complex and only some relevant results can be listed here. In systems of high turbulence it is clear that the limiting diffusion current would be “noisy.” Algorithms were developed to extract from the electrochemical noise the appropriate maximum diffusion currents and convert these to shear stress signals.

It was found that local shear stresses in small areas of 50 to 100 μ diameter were of the order of 10^6 to 10^7 Pa, but not enough to actually greatly damage the corrosion product scales. However, single events of much greater shear stress (10^9 Pa) were observed. These events were attributed to micro “freak waves.” The phenomenon is well known on a macro scale on the oceans, and has recently been reproduced again on a semi-macro scale in the laboratory.

It was visualized that these freak waves act as a continuous barrage of pinpricks, highly localized in areas of highest turbulence. What is not known is the frequency of the phenomenon or the degree of randomness. Additionally, the rate of re-passivation, which in the case of magnetite formation is certainly very high, is also not known.

Nevertheless, the importance of this work can be seen in the fact that it has been possible to measure shear stress phenomena in highly turbulent areas of a magnitude surpassing anything that has been known so far, or modeled with conventional theoretical approaches.

Schmitt defined a critical shear stress as follows:

$$\tau_{w,crit} = \frac{K_v}{n} \cdot \frac{1}{K_{SAC}} \cdot \sigma_y$$

where: K_v = turbulence coefficient that can be calculated from hydrodynamic correlations

n = number of impacts from near-wall turbulence elements

K_{SAC} = accounts for the effects of surface active components that might be present in the system

¹³ R.H. Hausler, G. Schmitt, *Hydrodynamic and Flow Effects on Corrosion Inhibition* NACE CORROSION/2004, paper #402.

σ_y = fracture stress of the protective scale.

This approach visualizes a fatiguing mechanism in the sense that micro turbulences of sufficient strength keep hammering onto the corrosion product layer until fracture occurs.

The importance of these studies and observations is that it is virtually impossible to predict where and to what extent such micro turbulences of sufficient strength might occur, nor exactly when the critical wall shear stress might be reached.

Phenomenologically, however, one can certainly pinpoint general locations subject to high turbulence where these events might occur; how they might be shifted as the velocity vectors change must still be determined by observation.

It would therefore be erroneous for the utility to continue to rely on grids established prior to EPU since these grids may not specifically capture the FILC phenomena observed at the lesser velocities. One might, for instance, refer to Figure 4 and readily understand that the point of reattachment of the flow would move up and down the pipe with changes in the linear flow rate.

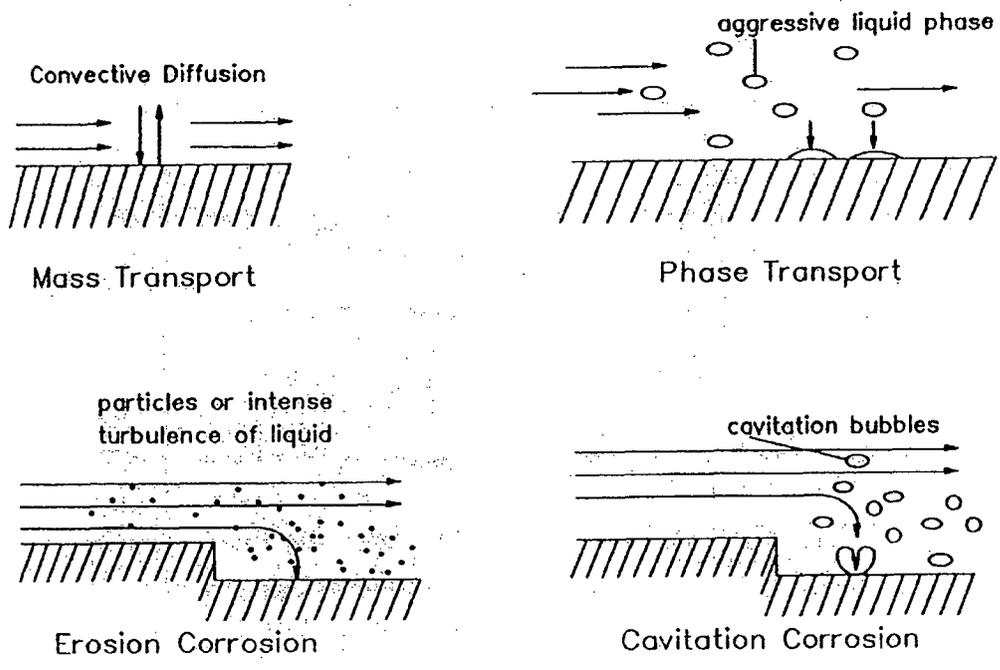


Figure 1: Schematic representation of the four main types of Flow-Induced Localized Corrosion

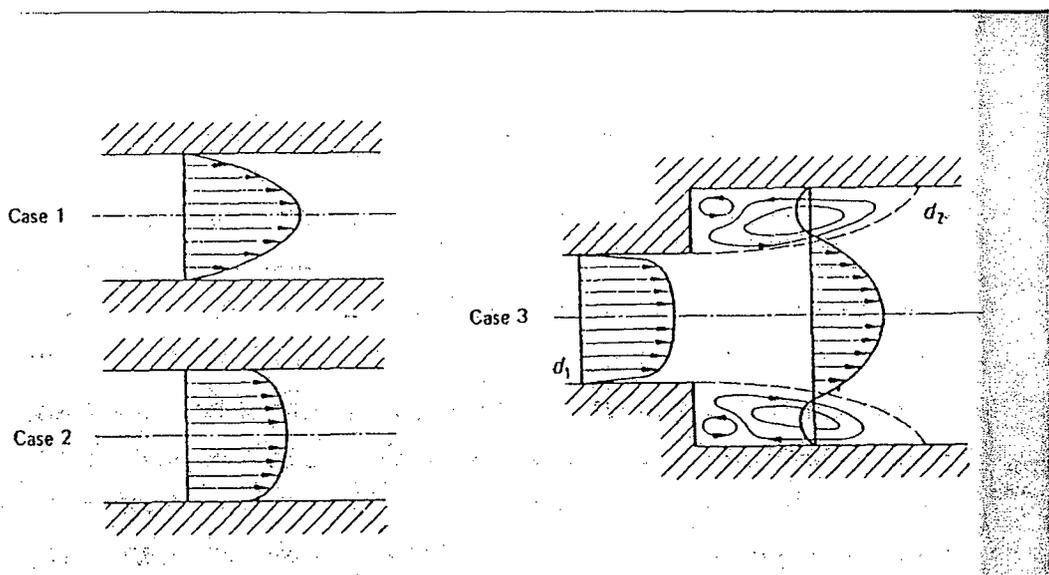


Figure 2: Velocity Profiles in Pipe flow: 1) established laminar pipe flow; 2) turbulent flow with logarithmic velocity profile; 3) turbulent flow with separation; complex velocity field with reverse flow.

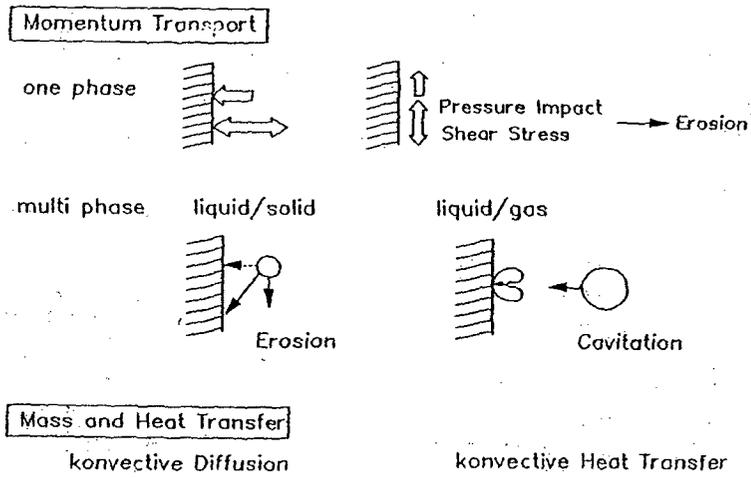


Figure 3: Interaction of liquid flow with a solid boundary (wall of the flow system)

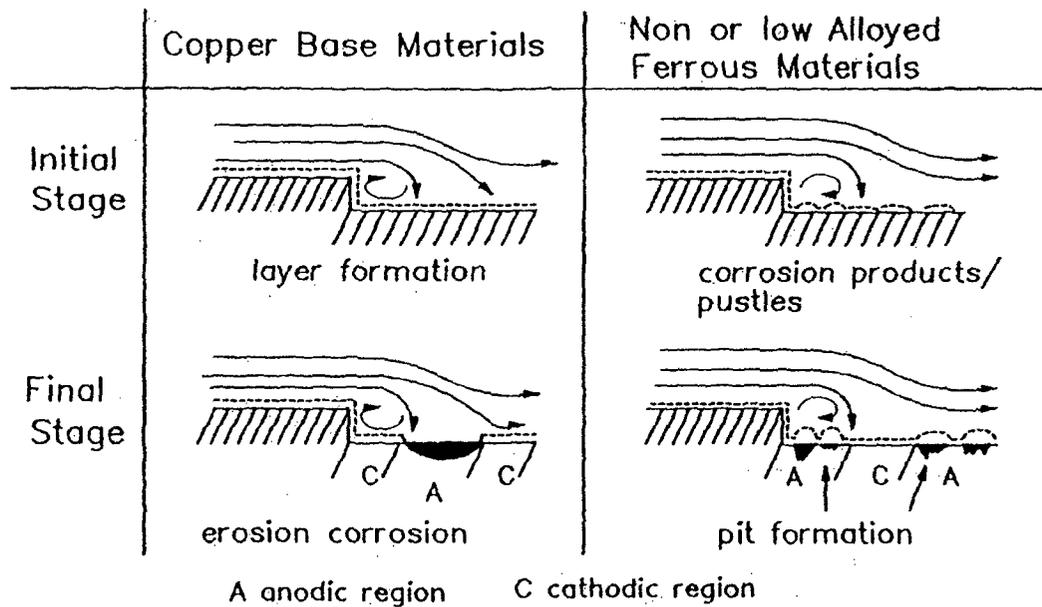


Figure 4: Flow-induced macro cell formation on copper and iron materials in disturbed turbulent flow

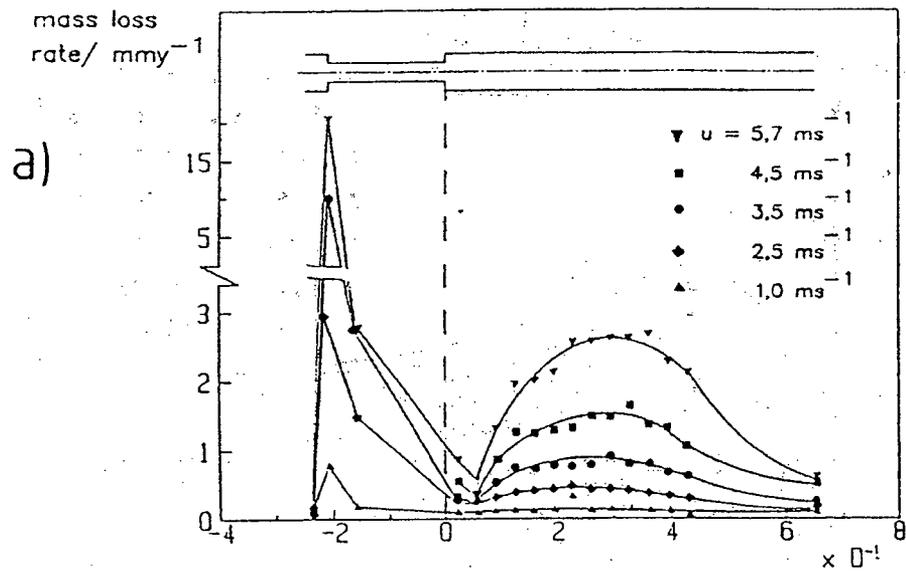


Figure 5: Mass loss rates of 13 % Cr steel in formation water containing sand, measured in a pipe with a constriction; abscissa: normalized pipe length (x/D)

Appendix A

Considerations Regarding the Frequency of Monitoring Based on Statistics and Required Confidence

I. The Problem

Aging management essentially consists of making multiple measurements over time for the purpose of:

- Assessing the integrity of a structure, and
- Estimating the rate of deterioration in order to predict time to failure and consequently taking timely action to prevent such failure.

It therefore stands to reason that at least two measurements are needed to determine the rate of deterioration. However, from two measurements one cannot determine the confidence limit of the resulting slope (rate). Therefore, a minimum of three measurements is required in order to assess confidence limits. However, since with three data points there remains only one degree of freedom for the assessment of the confidence limits, clearly even in the best of cases these assessments would remain wide and predictions uncertain.

When applied to aging management of pipe subject to high flow rates, this phenomenon suggests the following:

If a new thickness measurement is made sometime after the EPU, and if prior to the EPU the rate of deterioration at that particular location had somehow been established, a new rate will likely emerge.¹⁴ The newly calculated rate is afflicted with all the uncertainties inherent in the methodology of measurement.

The uncertainties arise from two factors:

- The inherent variability of the instrument with which the measurements are being made. Handheld ultrasonic thickness (“UT”) measurements have a 95% confidence limit, or about +/- 1% to 2% of wall thickness.
- The inherent difficulty of placing the handheld UT probe at exactly the same location for repeat measurements one-and-a-half to two years apart. This problem applies even to the case where a defined grid may have been used.

In order to develop the most simplified methodology VYNPU should pursue, the following hypothetical example will be discussed.

¹⁴ This scenario presumes that because of the higher flow rate the point of maximum turbulence has not been shifted to a new location – an assumption which cannot be made in good conscience.

II. Determination of Confidence Limits of Corrosion Rate Estimation

In order to perform the necessary calculations, the well-known software from the SAS Institute, JMP, has been used¹⁵.

Table 1 below lists nine UT thickness measurements, which hypothetically have been made over the past nine years, and includes the original thickness.

Figure 1 shows a linear correlation of the first four measurements, including the origin. One can see that the hypothetical data fit the hypothesis of a linear correlation with a correlation factor (R^2) of nearly 0.98, generally considered excellent. The figure shows the 95% confidence limits for the fit (inner boundaries) and the 95% confidence limits for individual measurements (outer boundaries). The slope of the linear correlation is 28.2 mpy with a standard deviation of 2.3 mpy. Hence the slope can vary between 30.5 mpy and 25.9 mpy. These confidence limits for the slope, therefore, are much larger than would be required for the customary 95% acceptance criteria.

Figure 2 shows the correlation for all nine measurements including the origin. It can be seen that the 95 % confidence limits for the fit ($R^2 = 0.98$) are much closer together. This change is essentially because of the increased degree of freedom for the estimate; the data themselves have not become more accurate. However, the slope now is 24 mpy with a standard deviation of 1.3, and 95% confidence limits of +/- 2.6 mpy, or from 21.4 to 26.6 mpy.

The result in Figure 2 is much more accurate than the prediction made on the basis of four years of experience, but still not accurate enough to fulfill the customary NRC requirement of at least 95% accuracy.

III. CONCLUSION

The preceding example refers to a single location where FILC [FAC] can be expected. Basically, the argument shows that the absolute minimum number of thickness measurements required for reasonably accurate prediction of failure is three, if an assessment of the confidence limits of the resulting trend is to be made. This is in agreement with Dr. Joram Hopfenfeld's statements in his report titled "Review of License Renewal Application for Vermont Yankee Nuclear Power Station: Program for Management of Flow-Accelerated Corrosion," (April 24, 2008).¹⁶

¹⁵ SAS: Statistical Analysis Software from SAS Institute Inc. SAS Campus Drive, Cary, NC 27513, Ver. 3.1 of JMP

¹⁶ Exhibit NEC-JH_36 at 16.

This also means that a rate prediction (establishing the new trend) could not be made before two regular outages following the EPU, and that upper and lower limits of this rate prediction would likely be very wide. It is entirely possible, however, that more than three measurements might be required because of how the results may turn out. In other words, one cannot prejudge the accuracy to be expected. In practical terms, this may mean the following: If at a particular location identified by pre-EPU operation or by information imbedded in CHECWORKS, the higher confidence limit of the observed corrosion rate [trend] were such as to predict failure beyond the anticipated service life, then this location would be classified as low risk and would not be monitored as frequently as others. If on the other hand the extrapolation of the upper trend were to show failure within the time interval scheduled for the next inspection of this location, the location would have to be monitored more frequently.

However, the assumption that the locations of highest FILC rates before the EPU should be the same as after is not likely to stand up to scrutiny. It may very well be found that the grids have to be extended or that new grids have to be developed. In this case inspections may extend over originally anticipated time spans.

Since, furthermore, it cannot be assumed that overall operations will be steady state, but that rather power fluctuations will result in flow rate variations, good rate predictions will be difficult. Therefore any risk assessment based on measured trends must take into consideration statistical probabilities. In this light, we think that Dr. Hopenfeld's assessment of the time necessary to recalibrate CHECWORKS, may be reasonable and perhaps even overly optimistic.¹⁷

¹⁷ See, Id.

Table 1
Hypothetical Wall Thickness Measurements over Time

Elapsed Time [years]	Measured Wall Thickness [mils]	Cumulative Wall Thickness Loss [mils]	Corrosion Rate [mpy]
0	375	0	
1	355	20	20.0
2	328	47	23.5
3	303	72	24.0
4	260	115	28.8
5	250	125	25.0
6	210	165	27.5
7	200	175	25.0
8	187	188	23.5
9	160	215	23.9

Figure 1
 Statistical Evaluation of Corrosion Rate Using Data
 From First Four Years

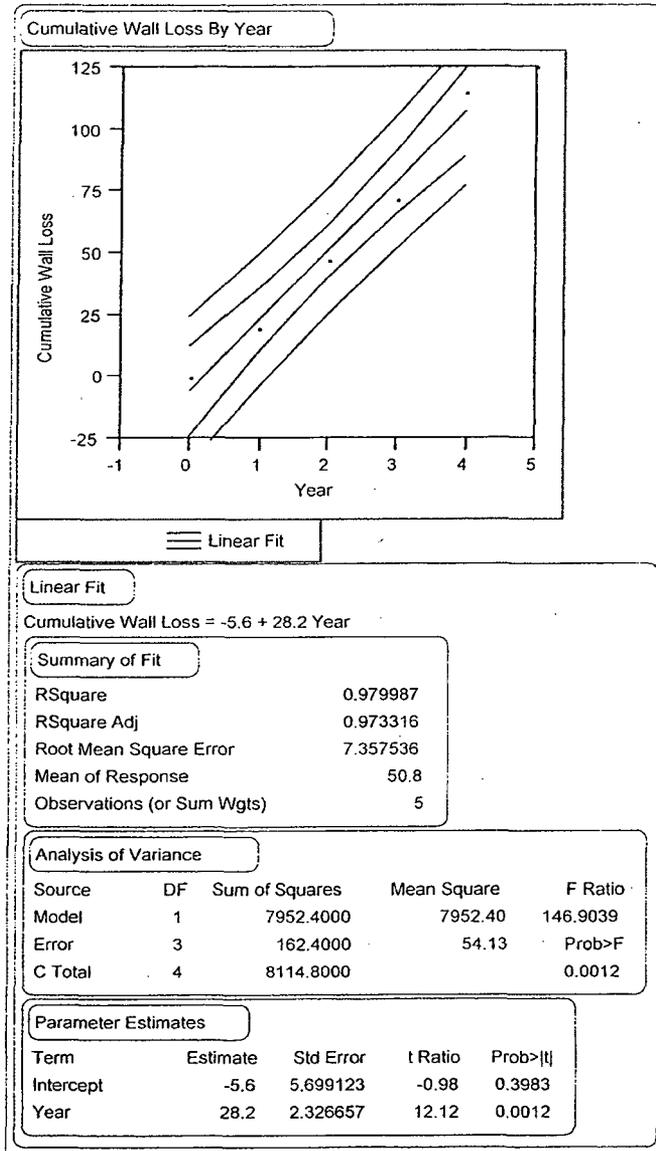


Figure 2
 Statistical Evaluation of All Corrosion Rate Data
 For All Nine Years of Measurements

