Flow-Accelerated Corrosion under Feed-Water Conditions

by

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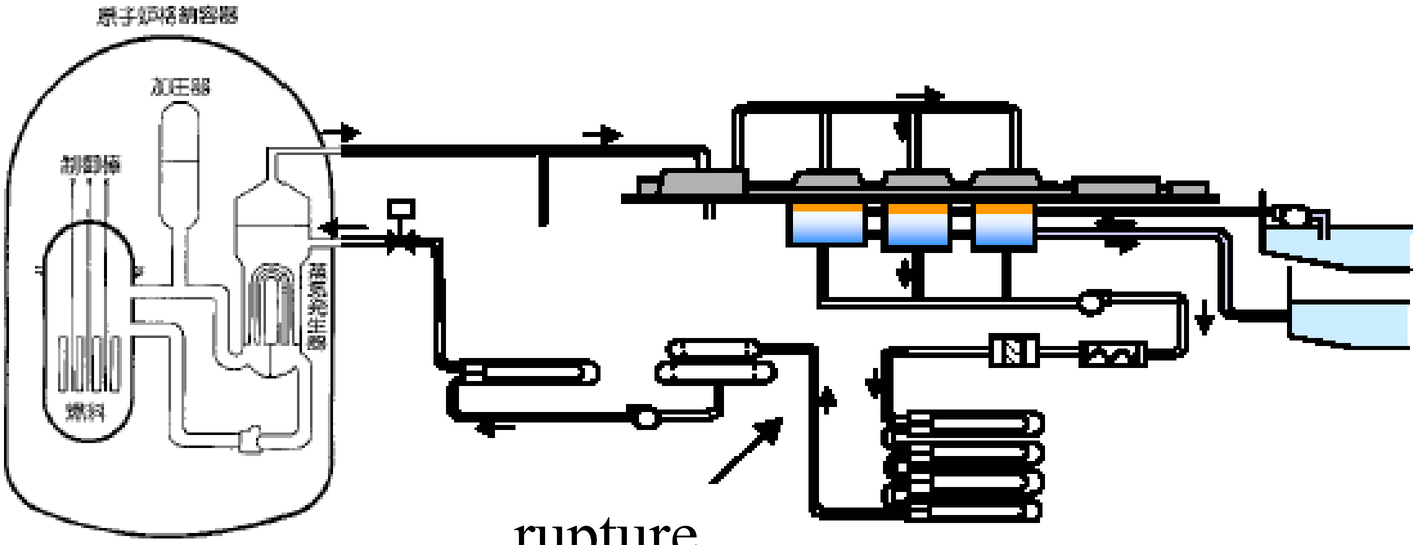
Background

Flow-accelerated corrosion (FAC) of carbon steel (CS) in feedwater systems is a pervasive problem.

It has caused accidents with serious injury or death in several steam-raising plants, including fossil-fired as well as nuclear power plants.

The latest serious nuclear FAC incident was the catastrophic rupture of a feedwater line at the Mihama-3 PWR in 2004.

Summary of Mihama-3 Accident



rupture

Reactor Type : PWR
Licensed output : 82.6 x 10^4 kW
Operation time : 185,700 h

Between LP-heater and deaerator
Material : Carbon steel
Outer diameter : 558.8 mm
Wall thickness : 10 mm
Temperature : 140 ^{o}C
Flow velocity : 2.2 m/s
DO : < 5 ppb
Water chemistry : AVT (pH8.5-9.7)

Ruptured Pipe at Mihama-3

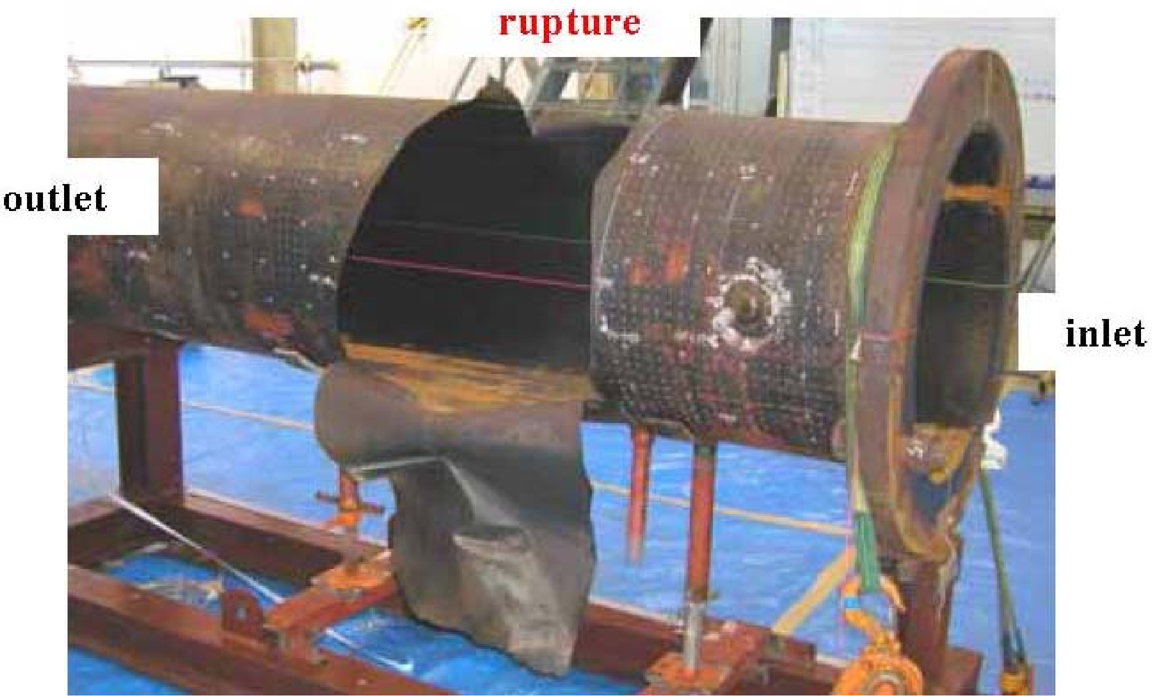
Condensate line between the low-pressure heater and the deaerator ruptured.

Eleven killed or injured.

Cause was identified as flow-accelerated corrosion (FAC) downstream of orifice.

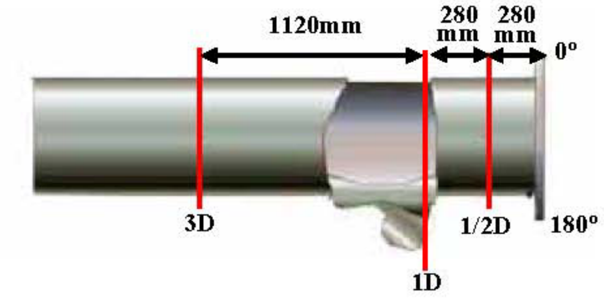
Ruptured point missed for pipe inspection since the plant was in service (1976).

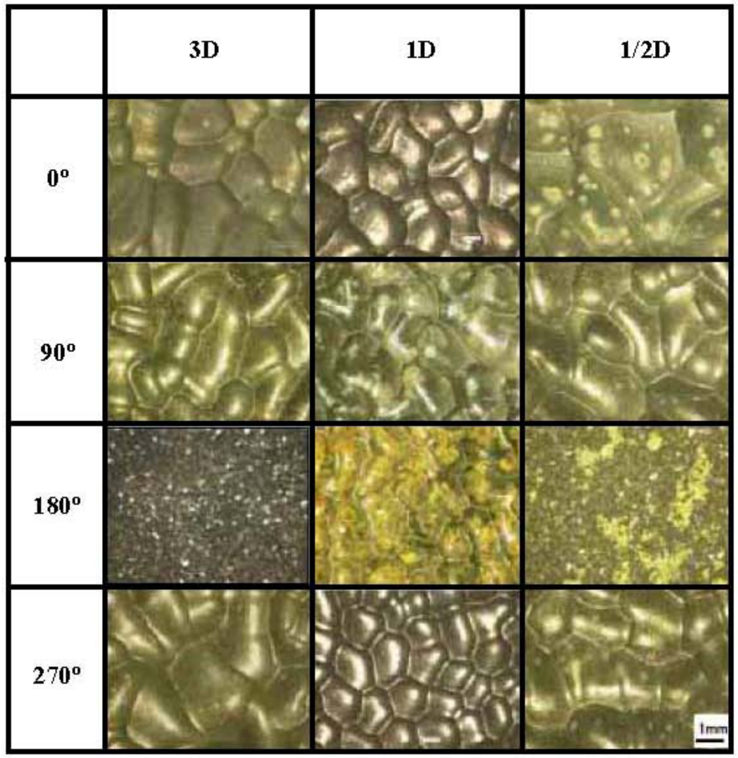
Rupture



Surface Appearance

Scalloped surfaces characteristic of FAC - chemical dissolution of surface oxide and metal, accelerated by flow and flow impingement.





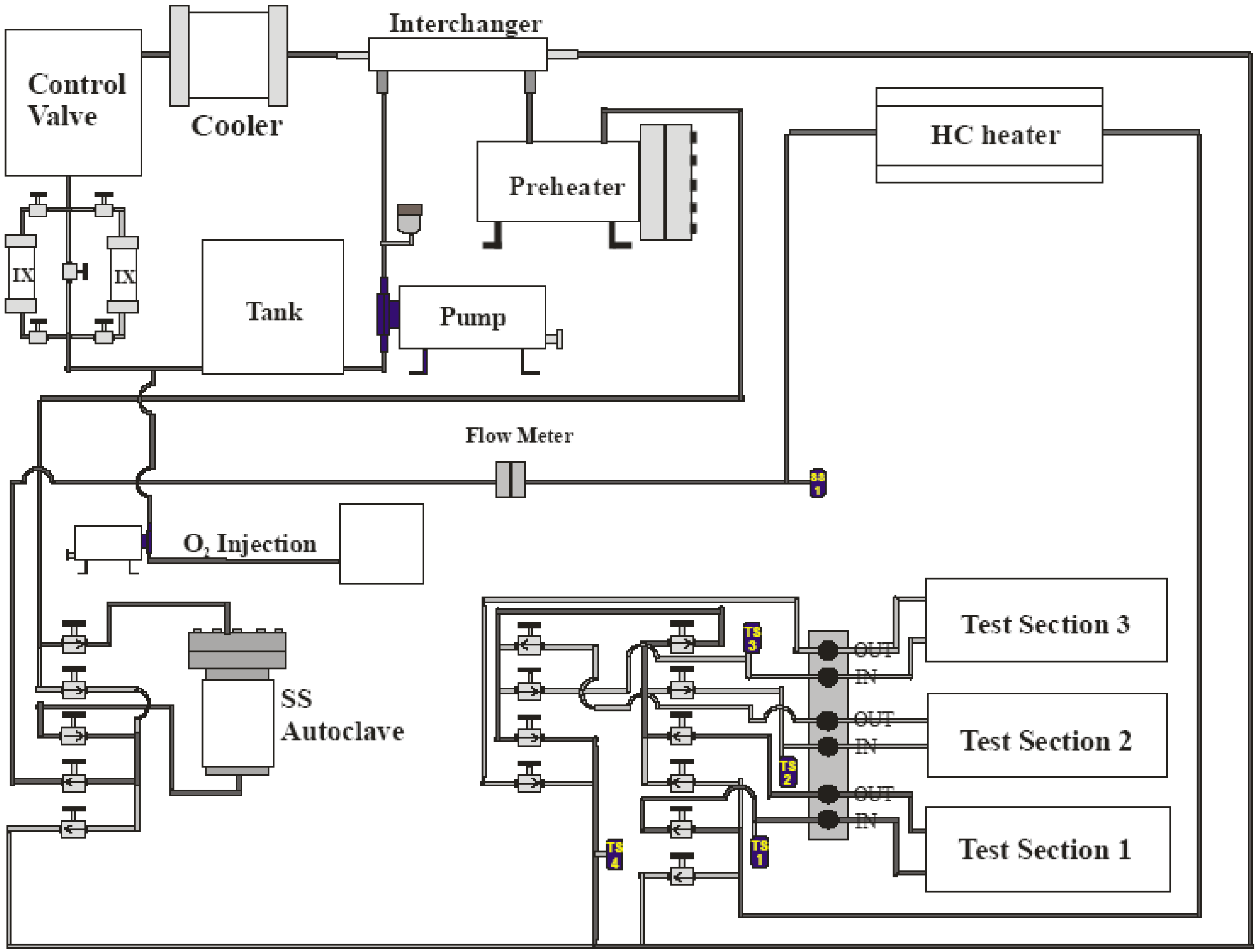
After the Mihama-3 accident, Canada and Japan collaborated on research program to:

- *improve basic understanding of FAC;*
- *develop predictive capability;*
- *formulate optimum chemistry for mitigation.*

Experiments performed at UNB, Canada; surface analyses done at CRIEPI (Central Research Institute of Electric Power Industry), Japan and at UNB; results assessed by whole team.

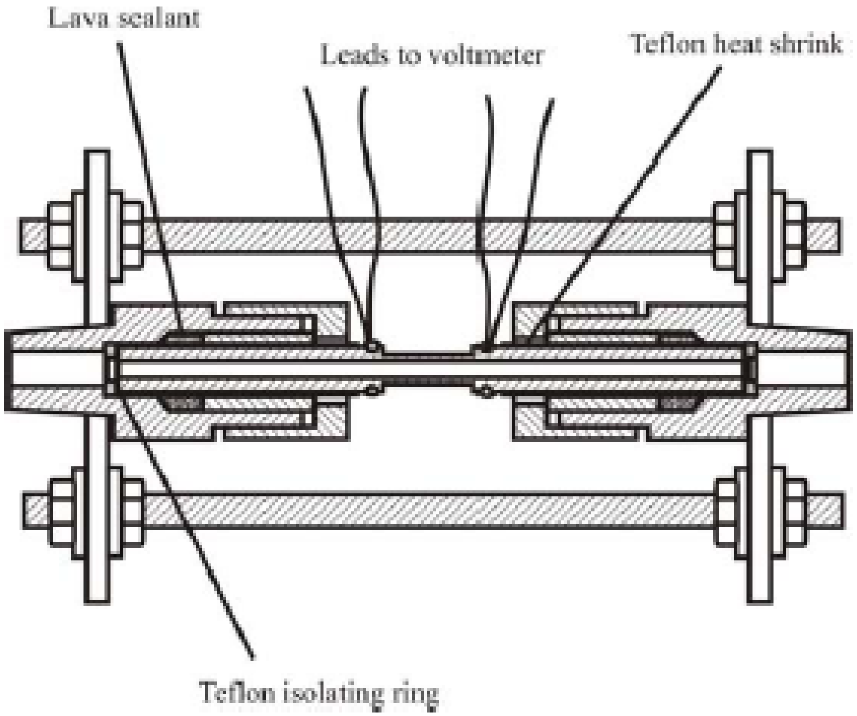
Experiments

On-line probes of CS exposed in high-temperature loop:



Experiments (cont.)

Continuous measurement of FAC via resistance probes:



Two carbon steels studied: SA-106 Grade B (0.019% Cr)

STPT 480 (0.001% Cr).

Measurements

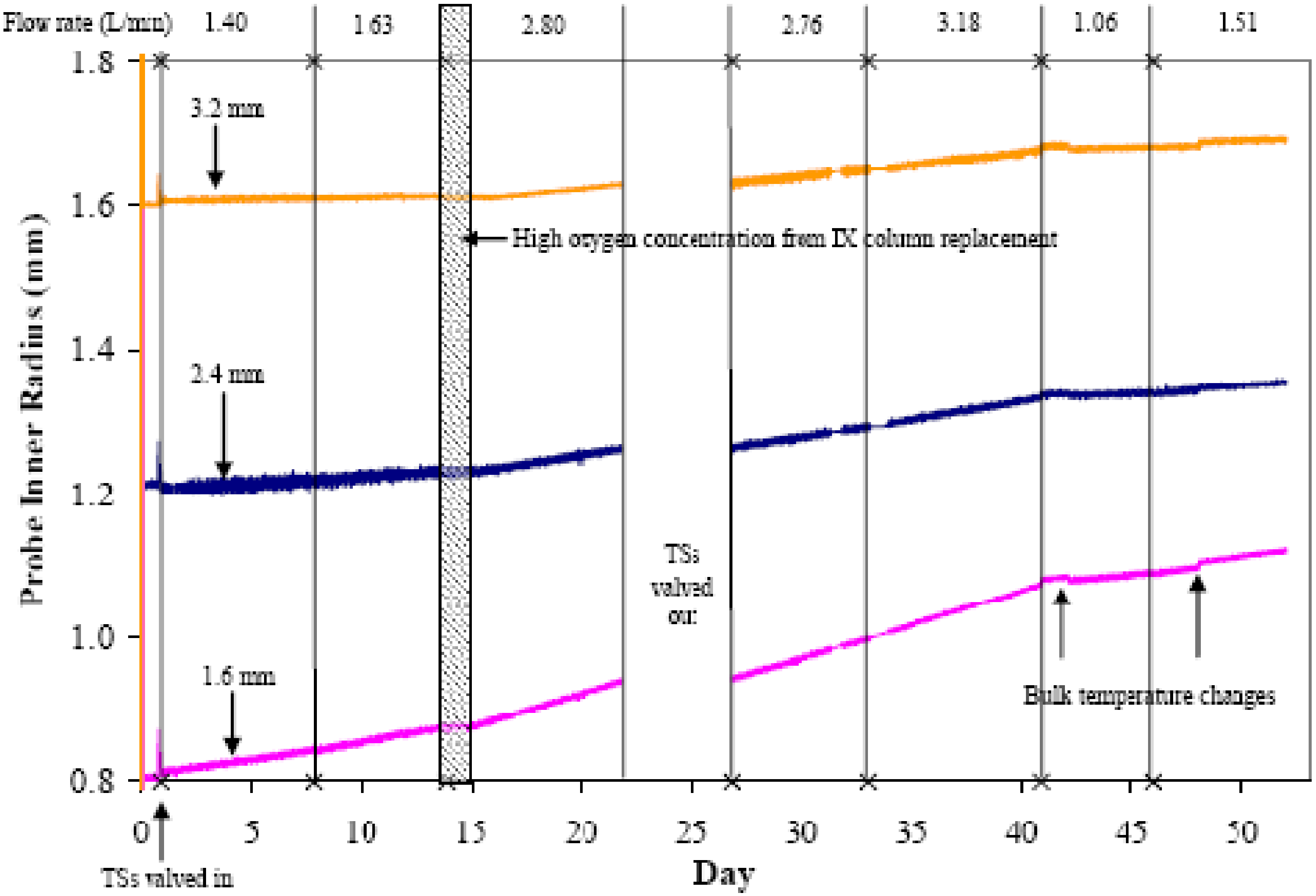
Inner radius of tube plotted against time;

slope gives FAC rate.

Tubes of several internal diameters and measurements at different pumping rates indicate effects of flow (Re, etc.).

After exposure, resistance probes and similar "surface analysis" probes sectioned for examination with SEM, laser-Raman microscopy, etc.

Typical Increase of Probe Radius with Time



Experiments (cont.)

All runs to date at 140^{o}C (temperature of feedwater line at Mihama-3).

Effect of pH studied (runs in neutral water and ammoniated water at pH 9.2).

Concentration of dissolved O_2 required to stifle FAC evaluated.

Results – Neutral Water

Mass transfer seems to control:

Traditional theory is that protective magnetite forms at metal-oxide interface, dissolves at oxide-solution interface, carried to bulk coolant by turbulent diffusion.

FAC rate - - - -
$$R = \frac{\Delta C}{\frac{0.5}{k_d} + \frac{1}{h}}$$

where $\Delta C =$ *undersaturation in [Fe],* $k_d =$ *oxide dissolution rate constant,*

$h =$ *mass transfer coefficient.*

Results – Neutral Water (cont.)

For mass transfer control:

$$R = h\Delta C$$

and differences in FAC rate from different materials are presumably reflected by different oxide solubilities within ΔC (as long as $k_d >> h$).

But: R did not correlate directly with Reynolds Number (Re) very well – as it should for mass transfer:

found $R \;\alpha\; Re^{1.2}$ with correlation coefficient = 0.83

(expect exponent 0.6-0.9).

Results – Neutral Water (cont.)

Assuming $R\ \alpha\ mtc$ and applying Reynolds analogy:

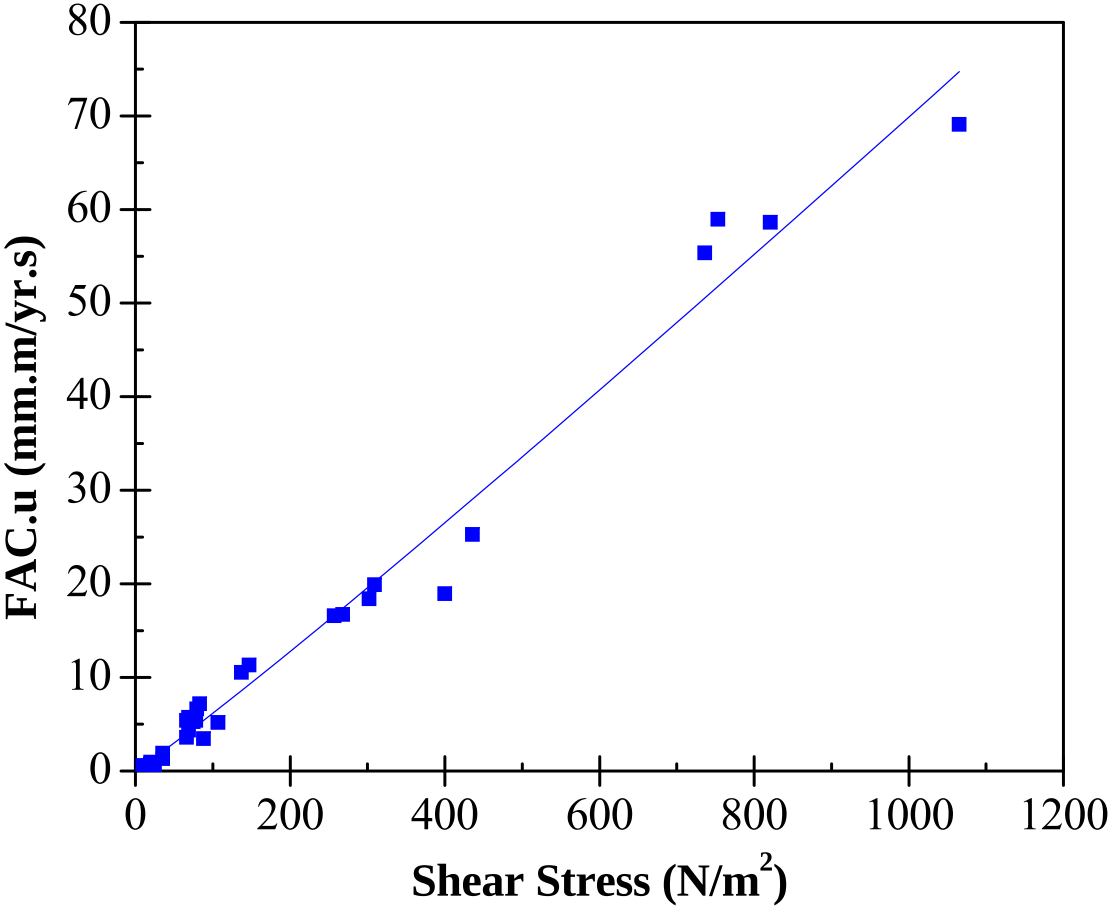
$$St\ (= Sh/Re/Sc) = f\ (= \tau/\rho u^2)$$

where St = Stanton Number, Sh = Sherwood Number, Sc = Schmidt Number, f = friction factor, τ = fluid shear stress at pipe wall, ρ = fluid density, u = fluid velocity.

We derive:

$$R.u\ \ \alpha\ \ \tau$$

Correlation: FAC in Neutral Water



Variation of (FAC rate) x (coolant velocity) with shear stress

Results – Neutral Water (cont.)

Excellent correlations in neutral water:

$R.u = 0.07\tau$ for 0.019% Cr steel; corr. coeff. = 0.98

where R in mm/a, u in m/s, τ in N/m^2;

$R.u = 0.18\tau$ for 0.001% Cr steel; corr. coeff. = 1.0

Lower-Cr steel corroded ~2.4 x faster than higher-Cr steel ***throughout*** 50-day exposures.

Results – Neutral Water (cont.)

Oxide films on both high- and low-Cr steel 0.5-1.0 μm thick.

Cr concentrated in oxide films by factor:

~10 on higher-Cr steel;

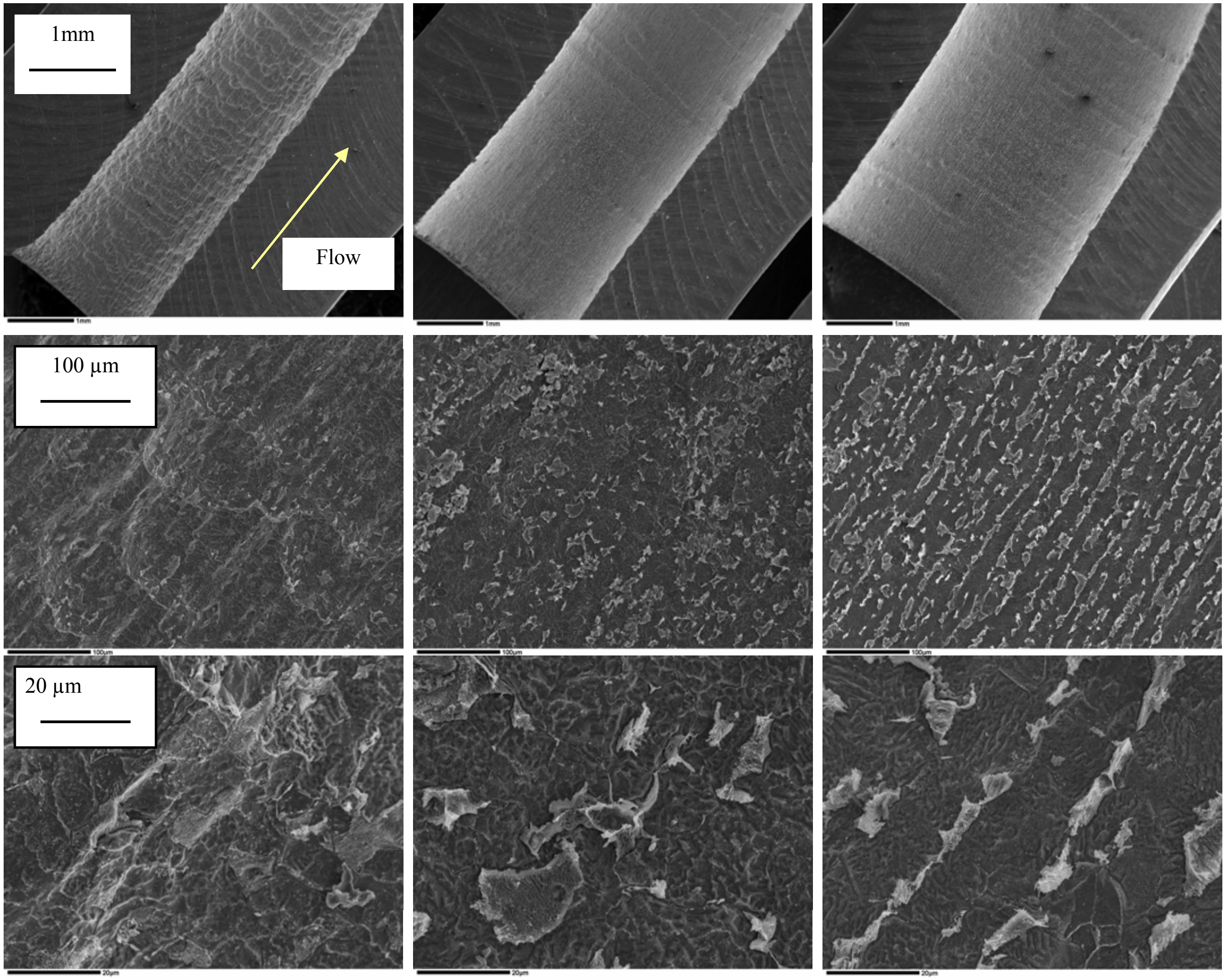
~200 on lower-Cr steel (to final level similar to that on higher-Cr steel) in spite of oxygen injections.

Since FAC rate of low-Cr steel <u>consistently</u> higher than that of high-Cr steel (even though average Cr content in oxides attained similar level by end of experiment), <u>average</u> Cr content of oxide cannot control.

Since FAC rate virtually constant with time for given condition, Cr concentration in oxide at O-S cannot control, even though Fe preferentially leached there.

Suggests oxide modification by Cr at M-O controls – consistent with past observation that soluble Cr added to reactor coolant reduces FAC at 310°C only temporarily.

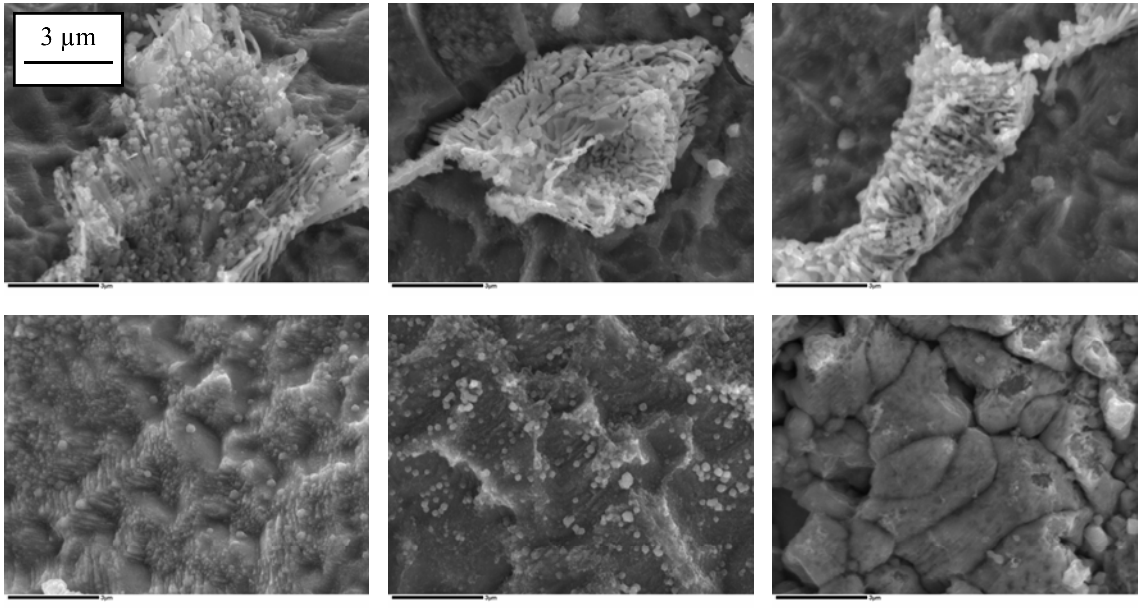
Scallop Development - FAC in Neutral Water



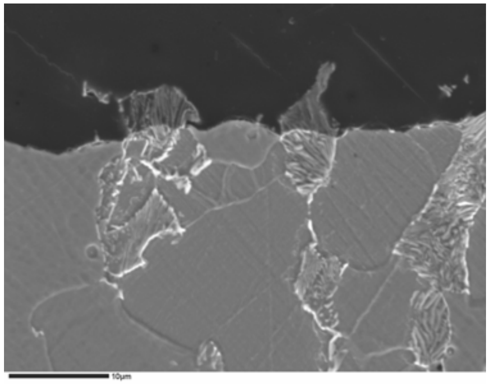
D = 1.6 mm D = 2.4 mm D = 3.2 mm

Probe Surfaces at Higher Magnification

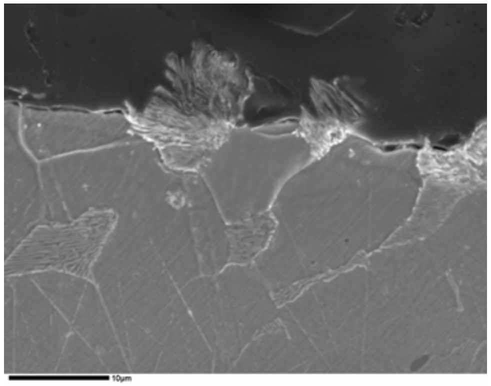
- Scallop development influenced by oxide on pearlite grains



D= 1.6 mm D= 2.4 mm D= 3.2 mm



D= 2.4 mm

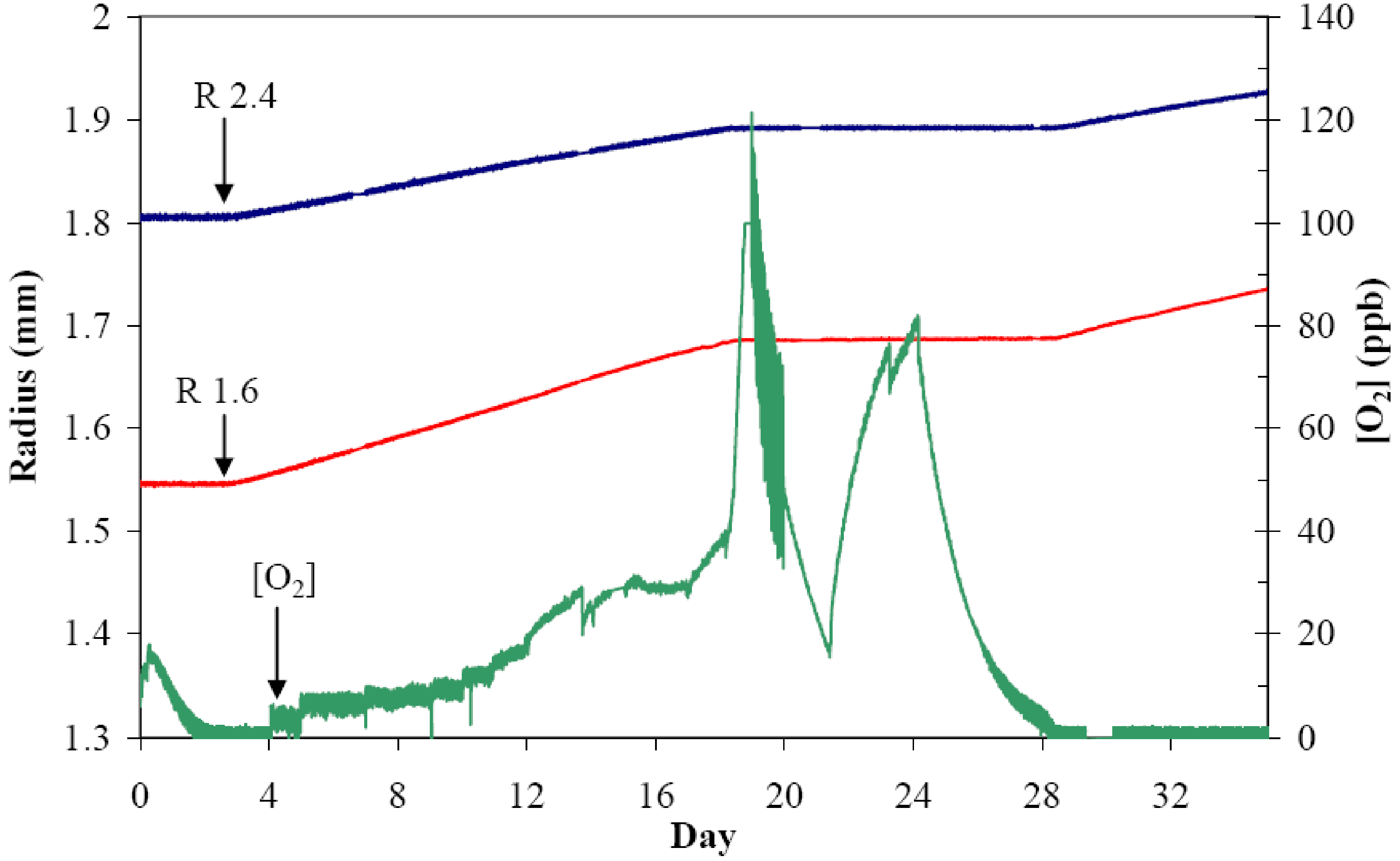


D= 3.2 mm

Results – Neutral Water (cont.)

FAC stifled by ~40 ppb oxygen.

Neutral Water - Effect of $[O_2]$



Variation of probe radius and oxygen concentration with time (neutral pH)

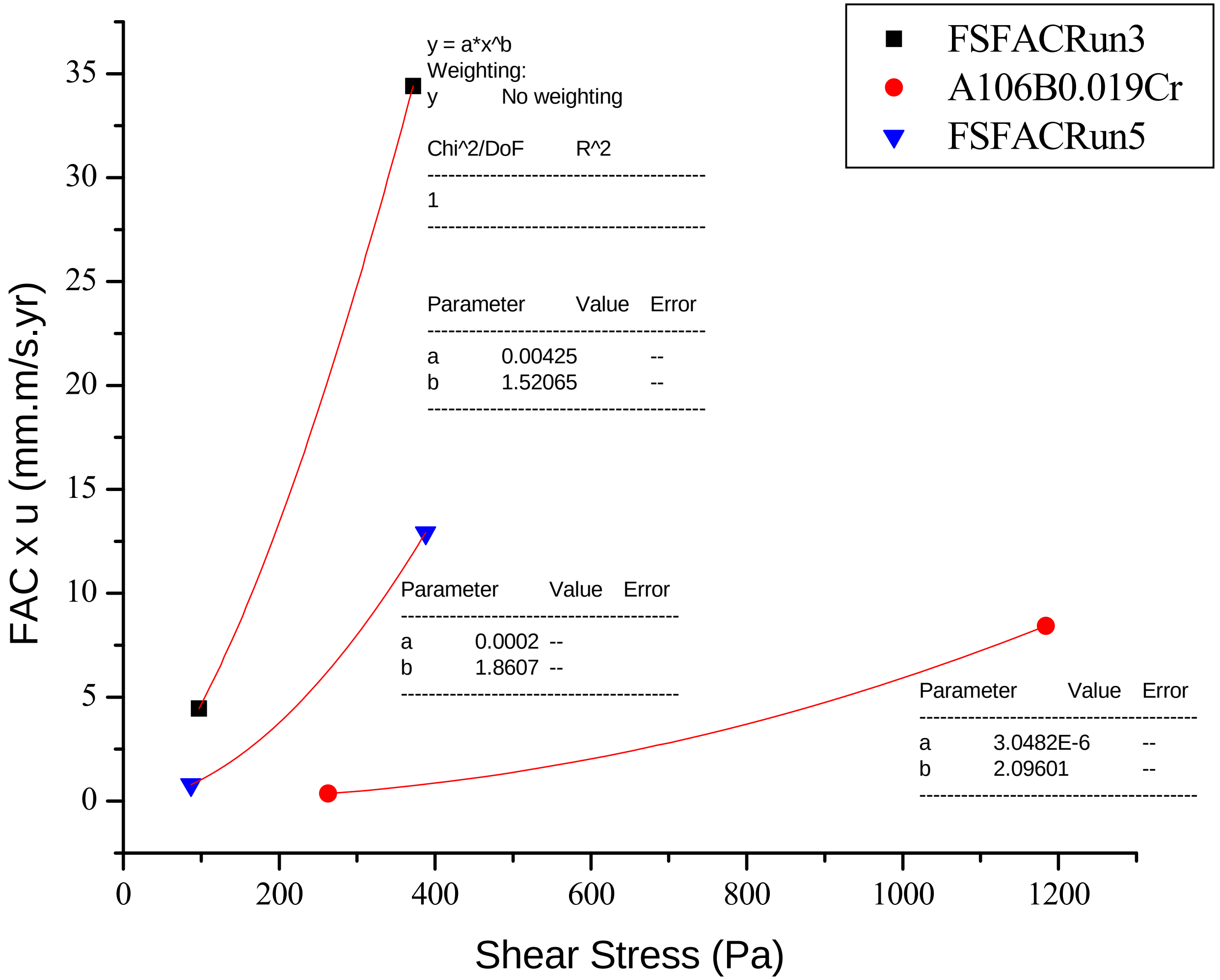
Results – pH 9.2 (NH_3)

Initial indications are that, unlike in neutral water, in high-pH water simple mass-transfer/shear-stress correlations do not apply (this is consistent with observations of FAC at 310°C). Suggests that oxide dissolution may be involved.

Hydrazine (N_2H_4) ***lowers*** FAC rate (pH effect from hydrazine at surface?).

From parallel experiments at pH 9.2 with N_2H_4, FAC rate of low-Cr (0.001%) steel ***much*** higher than that of higher-Cr (0.019%) steel (in neutral water it was a factor of only ~2.4 higher).

Effects of N_2H_4 in Coolant and Cr in Metal on FAC at pH 9.2



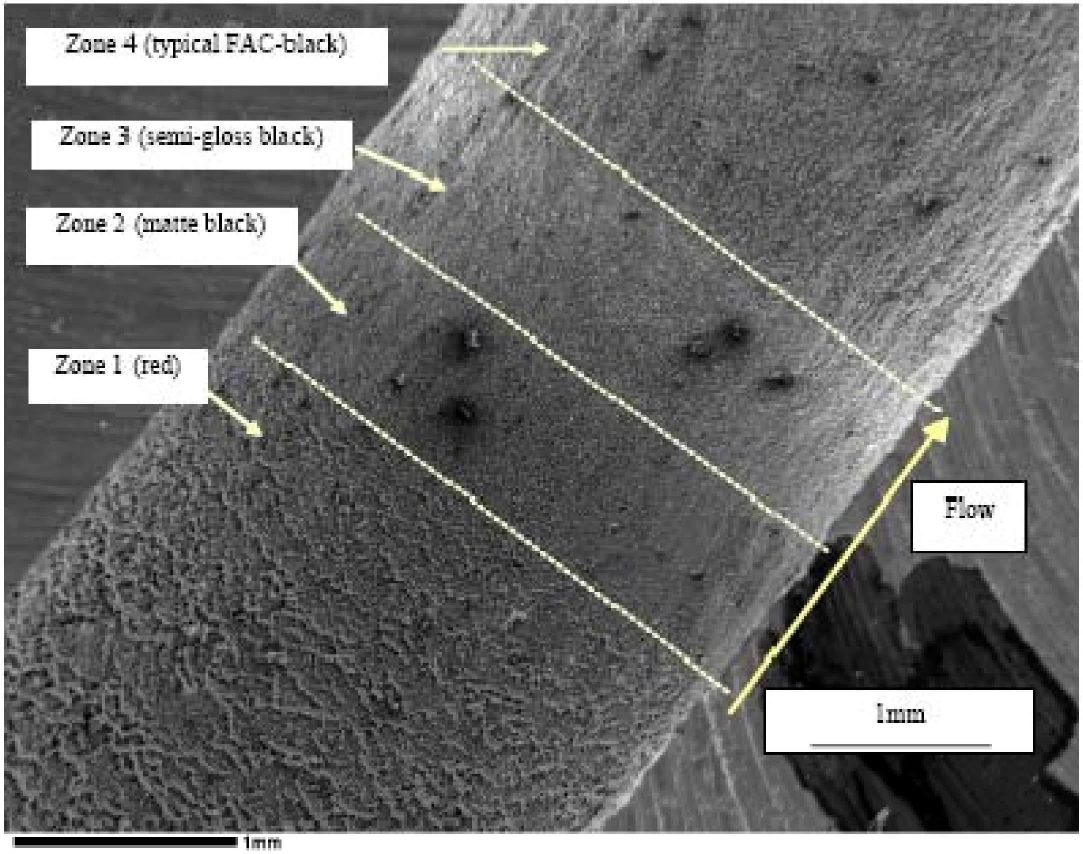
Effects of Oxygen at High pH

Oxygen concentration required to stifle FAC at pH 9.2 without N_2H_4 was ~1 ppb (µg/kg).

Stifling occurred along with a “front” of oxidised film apparently moving downstream.

Oxide Transition Zone on Probe at pH 9.2

Oxidised Front Moving Downstream



Raises possibility of passivating a channel by injecting O_2 at inlet so that ~zero survives at outlet.

Conclusions

NEUTRAL WATER AT 140°C

- FAC controlled by mass transfer – rate correlated well by fluid shear stress;
- 0.001% Cr steel corrodes ~2.4 x faster than 0.019% Cr steel;
- Cr apparently affects FAC by processes at M-O;
- FAC stifled by ~40 ppb oxygen.

Conclusions (cont.)

AMMONIATED WATER AT pH 9.2 AND 140°C

- Without hydrazine (N_2H_4), FAC rate about half that in neutral water;
- Without N_2H_4, FAC stifled by ~1 ppb oxygen; stifling occurs with a front of oxidised magnetite moving downstream (useful for plant applications…?);
- Hydrazine unexpectedly ***lowers*** FAC rate (local pH effect?);
- With N_2H_4, lower-Cr steel has ***much*** higher FAC rate than higher-Cr steel (Cr effect enhanced by AVT).

Acknowledgement

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