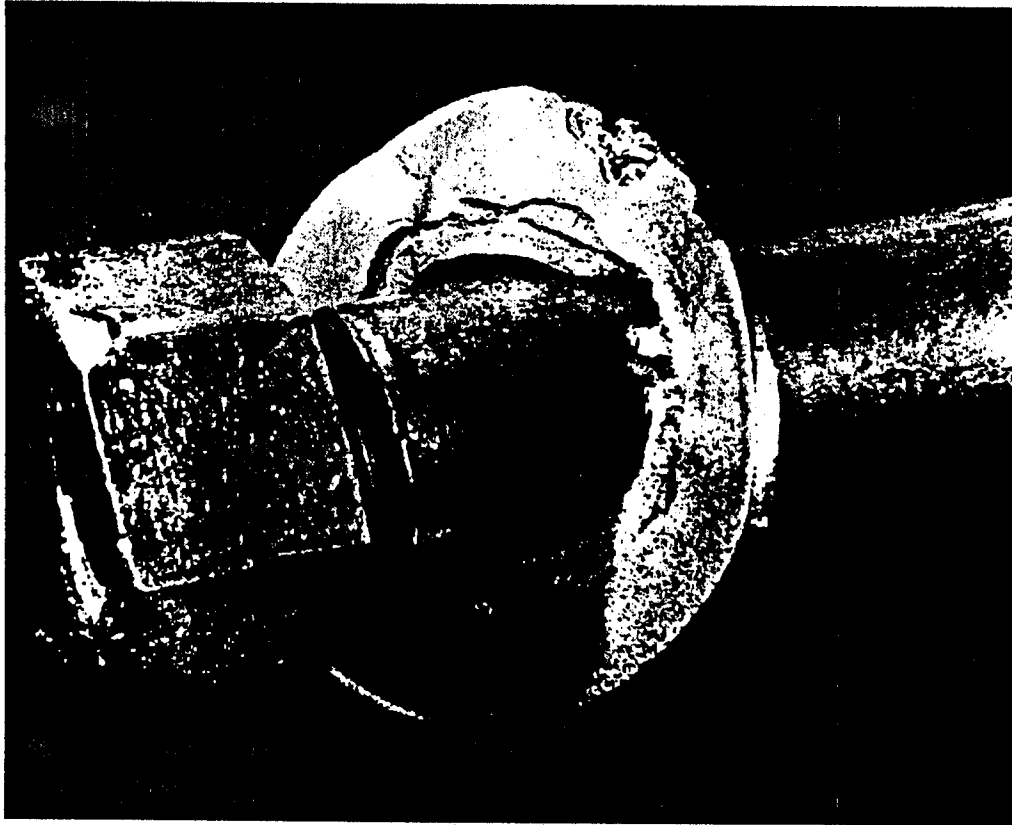


CREVICE CORROSION

Narrow openings, gaps, spaces, pores etc. between metal-metal components or metal-non-metal components may provoke localized corrosion.

NOTE: unintentional crevices (seams, cracks etc.) can also act in the same way
Passive alloys (especially stainless steels) are more vulnerable than more active alloys.

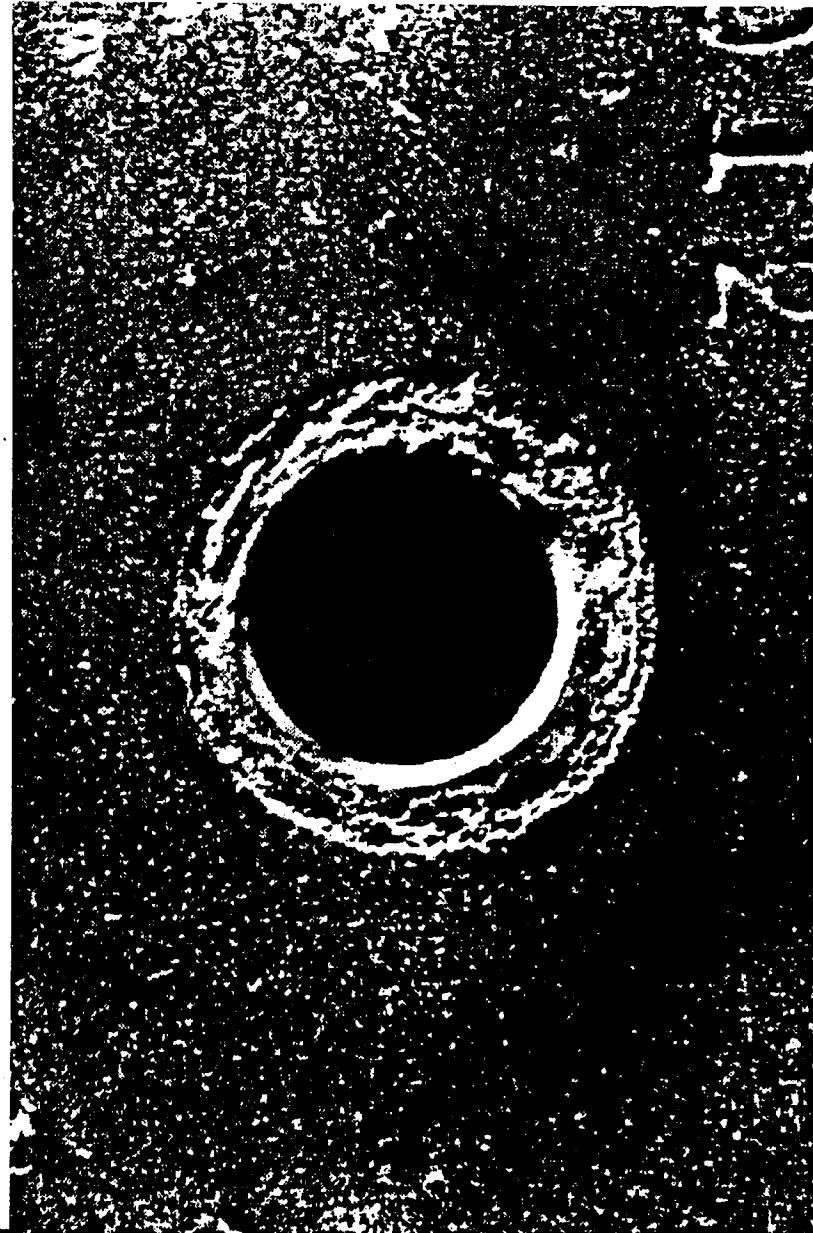


Crevice corrosion at a metal-to-metal crevice site formed between components of type 304 stainless steel fastener in seawater

Crevice Corrosion occurring on a Test specimen of Type 316 SS (Stainless Steel) in Acid Condensate Zone of a Model SO₂ Scrubber.

Crevice corrosion caused by the existence of small volumes of stagnant (corrosive) solution. Small holes, gasket surfaces, lap joints, bolt, rivet heads, nuts, washers, surface deposits; all can cause C.C. (Crevice Corrosion).

Type 304 SS sheet can be cut by stretching a rubber band around it, immersing it in seawater (Fontana). The crevice between the rubber and the metal acts as the “cutting zone”.

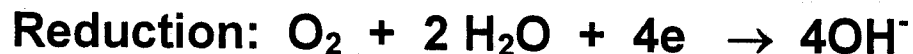


MECHANISM

Consider riveted metal section,
immersed in aerated seawater (pH 7)
e.g., stainless steel

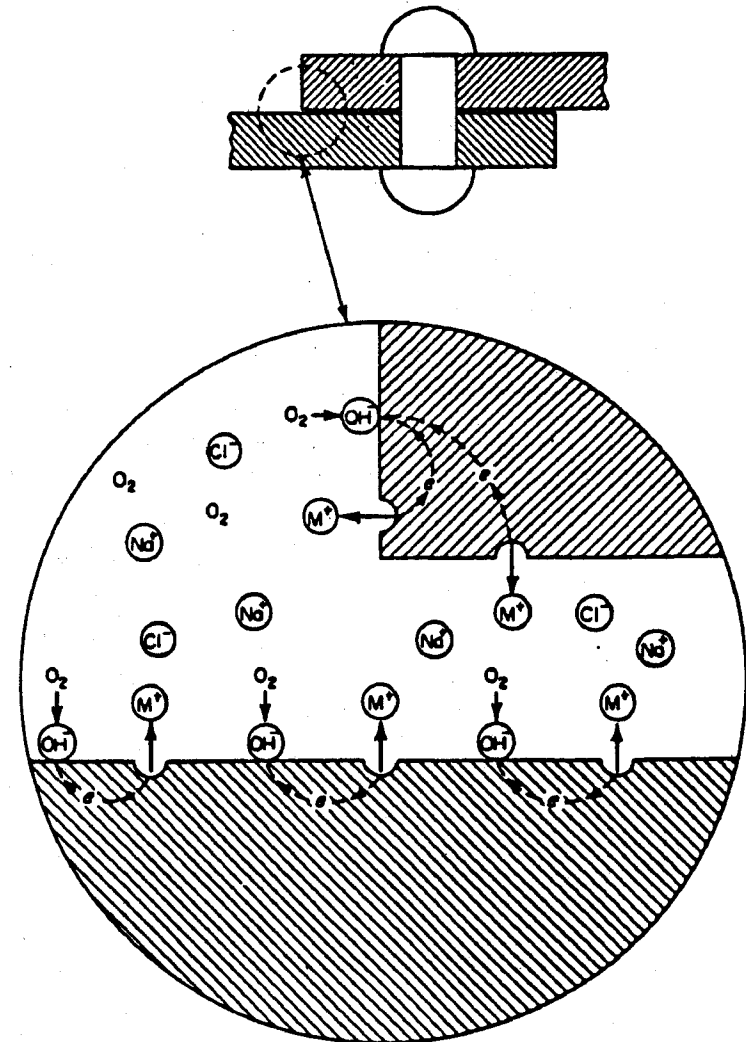
Though O_2 within crevice rapidly used up,
corrosion continues, controlled by overall
cathodic reaction outside crevice.

Tendency to build up M^+ within the crevice
must be balanced by -ve charge diffusing in.
Some OH^- diffuses in, lot of Cl^- diffuses in
(OH^- more mobile, c.f. FONTANA* . . less of it).

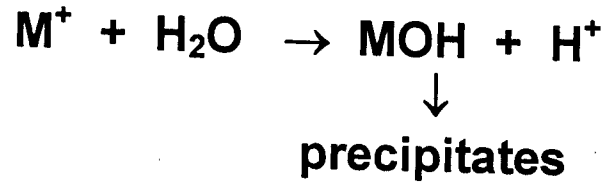


*FONTANA says Cl^- more mobile . . this is wrong.

Initial stages



Most metal ions (except alkali metals)
hydrolyze:

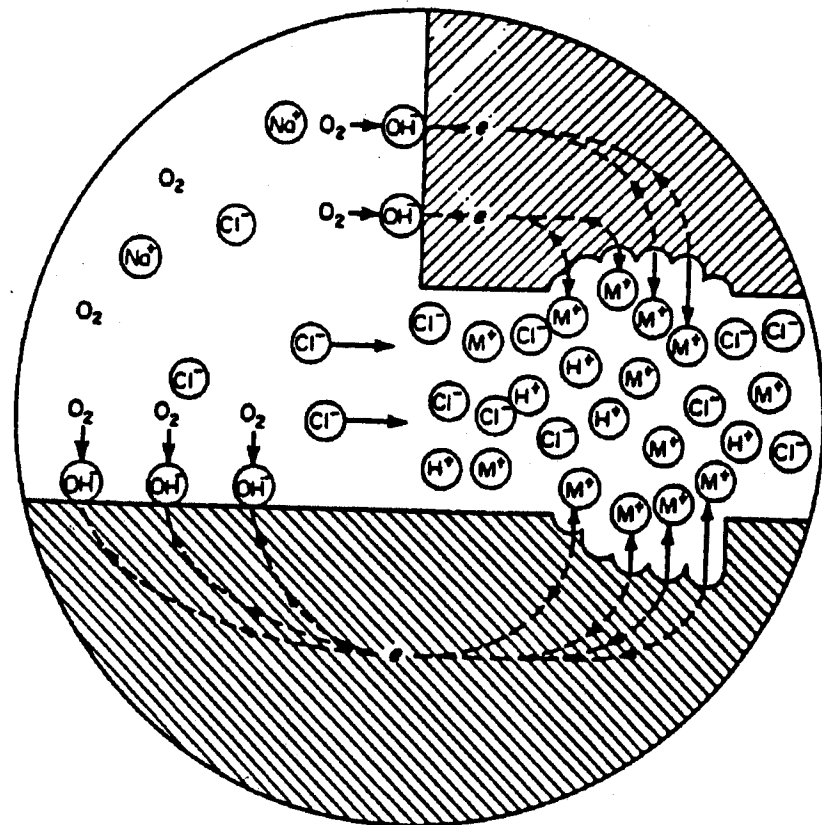


Both Cl^- and H^+ accelerate metal
dissolution (Cl^- breaks down oxide, also
 H^+ partly responsible).

NOTE: there is now the possibility for H_2
evolution within the crevice maybe!

NOTE: solution within crevices exposed
to neutral dilute NaCl has been seen
to have 3-10x $[Cl^-]$ in bulk, pH of 2-3.

Later stages



Factors that can affect the crevice corrosion resistance of stainless steels

Geometrical

Type of crevice:

metal to metal

nonmetal to metal

Crevice gap (tightness)

Crevice depth

Exterior to interior surface area ratio

Electrochemical reactions

Metal dissolution

O₂ reduction

H₂ evolution

Environmental

Bulk solution:

O₂ content

pH

chloride level

temperature

agitation

Mass transport, migration

Diffusion and convection

Crevice solution: hydrolysis equilibria

Biological influences

Metallurgical

Alloy composition:

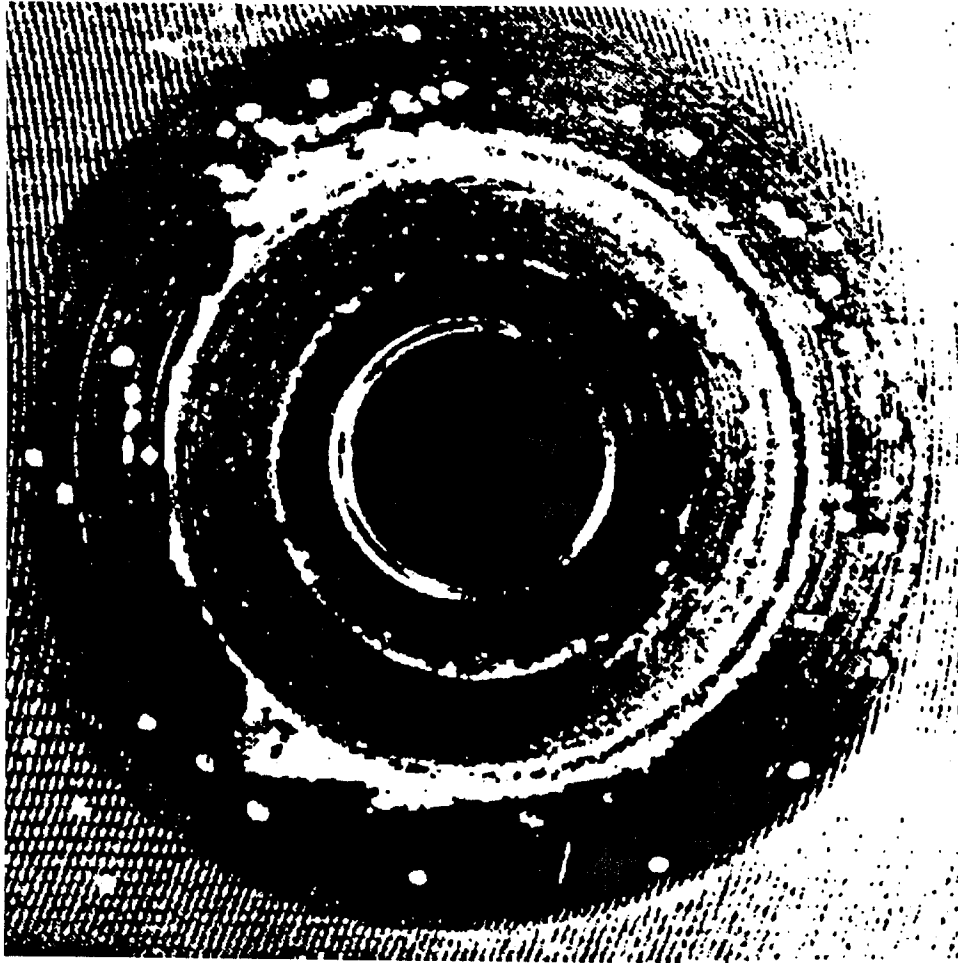
major elements

minor elements

impurities

Passive film characteristics

CREVICE CORROSION OF CU ALLOYS different from that of SS; attack occurs OUTSIDE the crevice.



**“Crevice corrosion” of Alloy 400
(70 Ni - 30 Cu) after 45 Days in
Natural Seawater**

Cathodic conditions inside crevices of Cu alloy have been inferred from observations of deposited Cu metal (where?).

“Differential metal-ion concentration” has been invoked as the mechanism; greater concentration inside the crevice raises the potential and makes it more noble than the outside.

Also, variant of the oxygen depletion mechanism has been invoked. Clearly the situation is complex.

NOTE:

ALL MATERIALS ARE SUSCEPTIBLE TO C.C. (CREVICE CORROSION).

GIVEN NARROW CREVICES, POSSIBILITY OF CONCENTRATING IONS, DIFFERENTIAL AERATION CELLS, DIFFERENTIAL METAL CONCENTRATION CELLS, ETC.

COMBATING CREVICE CORROSION (after Fontana)

Methods and procedures for combating or minimizing crevice corrosion are as follows:

- 1. Use welded butt joints instead of riveted or bolted joints in new equipment. Sound welds and complete penetration are necessary to avoid porosity and crevices on the inside (if welded only from one side).**
- 2. Close crevices in existing lap joints by continuous welding, caulking, or soldering.**
- 3. Design vessels for complete drainage; avoid sharp corners and stagnant areas. Complete draining facilitates washing and cleaning and tends to prevent solids from settling on the bottom of the vessel.**
- 4. Inspect equipment and remove deposits frequently.**
- 5. Remove solids in suspension early in the process, if possible.**
- 6. Remove wet packing materials during long shutdowns.**
- 7. Provide uniform environments, if possible, as in the case of backfilling a pipeline trench.**
- 8. Use "solid," nonabsorbent gaskets, such as Teflon, wherever possible.**
- 9. Weld instead of rolling in tubes in tube sheets.**



A lacquered steel can lid exhibiting filiform corrosion showing both large and small filaments partially oriented in the rolling direction of the steel sheet. Without this 10 x magnification by a light microscope, the filiforms look like fine striations or minute tentacles; (often mistaken for biologically - induced).

Attack usually occurs when relative humidity between 65 and 90%; has been seen at lower R.H. (Relative Humidity).

Average filament width ~ 0.05 - 3 mm .. depending on coating (thickness, porosity, etc.), R.H., and corrosiveness of environment (presence of SO₂, H₂S, etc.).

Filament height ~ 20 μm. Growth rates observed between 0.01 mm/d and 0.85 mm/d.

Filaments are like minute tunnels, full of corrosion products.

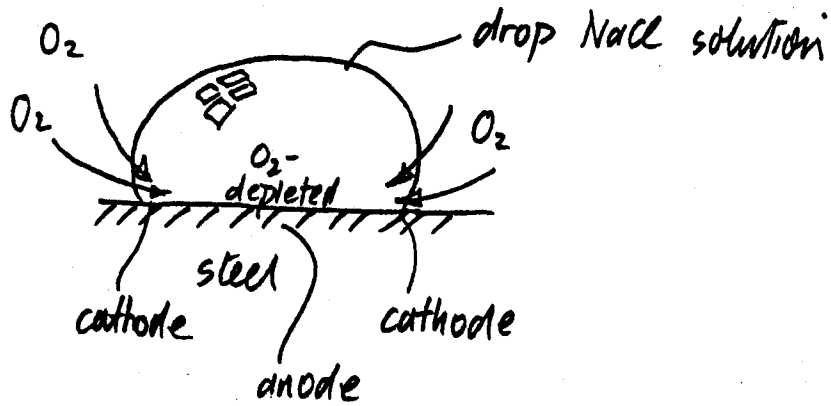
Liquid in “head” is typically acidic. . . . pH 1- 4.

IN ALL CASES.... O₂ (or air) and water are needed to sustain filiform corrosion.. indicates a form of DIFFERENTIAL AERATION CELL.

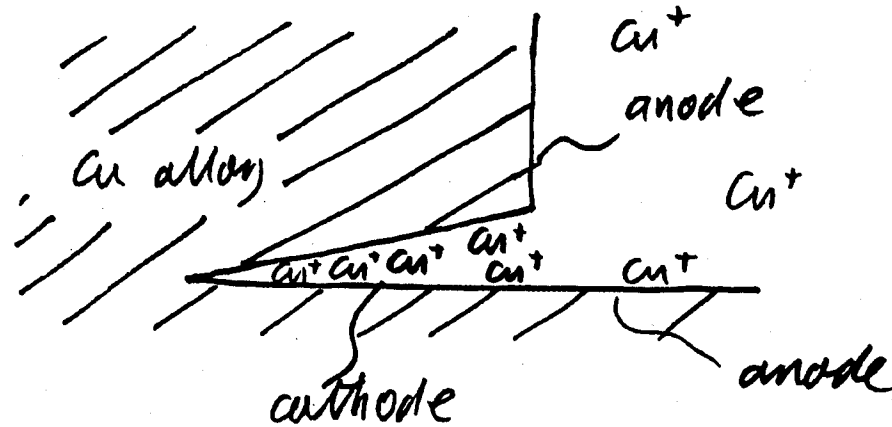
Discuss:

- differential aeration cell
- concentration cell.

An aside on differential aeration . .
remember example:



(differential) concentration cell
remember Cu - alloy crevice:



(potential $\propto \log [a]$)

Attack usually begins at imperfections in coating e.g., cuts, knicks, pores, etc.

CO₂ can stimulate process by dissolving in water → carbonic acid.

Chlorides, SO₄²⁻, S²⁻ which can dissolve in condensing atmospheric moisture also increase attack.

Optimum temperature for attack between 20 & 35°C.

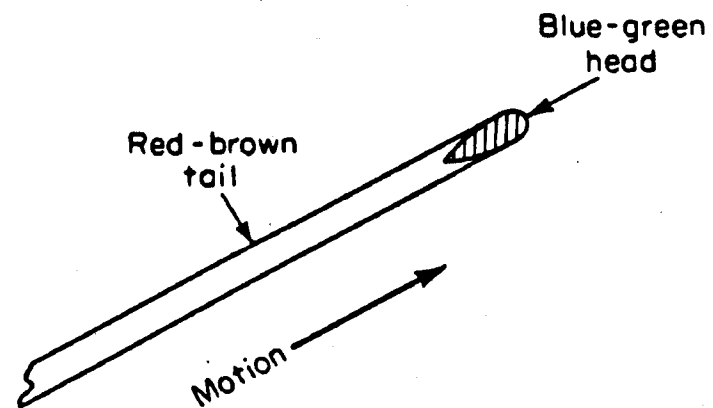
Effect of humidity on filiform corrosion of enameled steel

Relative humidity, %	Appearance
0-65	No corrosion
65-80	Very thin filaments
80-90	Wide corrosion filaments
93	Very wide filaments
95	Mostly blisters, scattered filiform
100	Blisters

Source: M. Van Loo, D. D. Laiderman, and R. R. Bruhn, *Corrosion*, 9:2 (1953).

Appearance:

Schematic diagram of a corrosion filament growing on an iron surface (magnified).



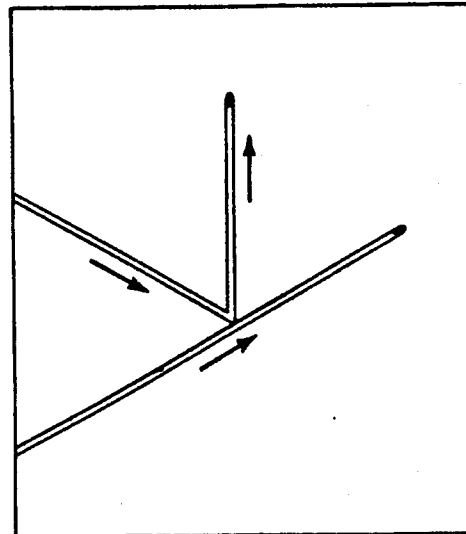
Schematic diagrams illustrating the interaction between corrosion filaments:

(a) Reflection of a corrosion filament;

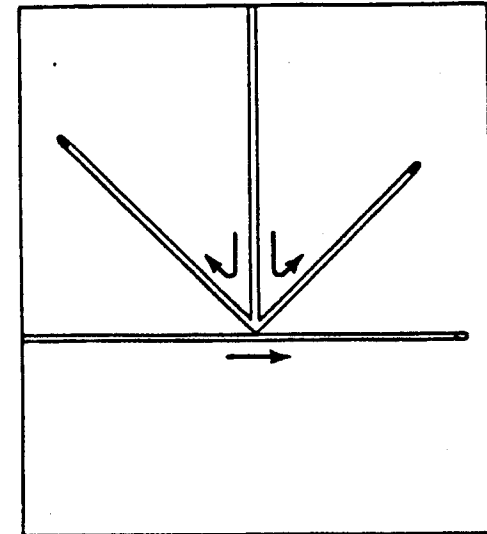
(b) splitting of a corrosion filament;

(c) joining of corrosion filaments;

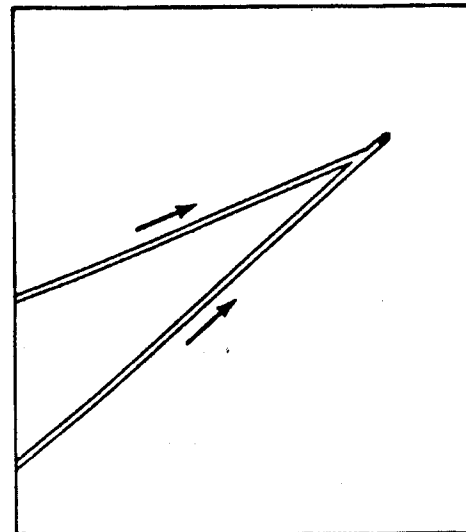
(d) "death trap".



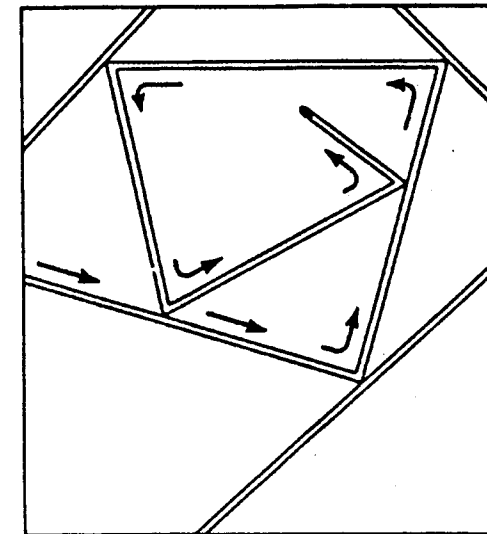
(a)



(b)



(c)



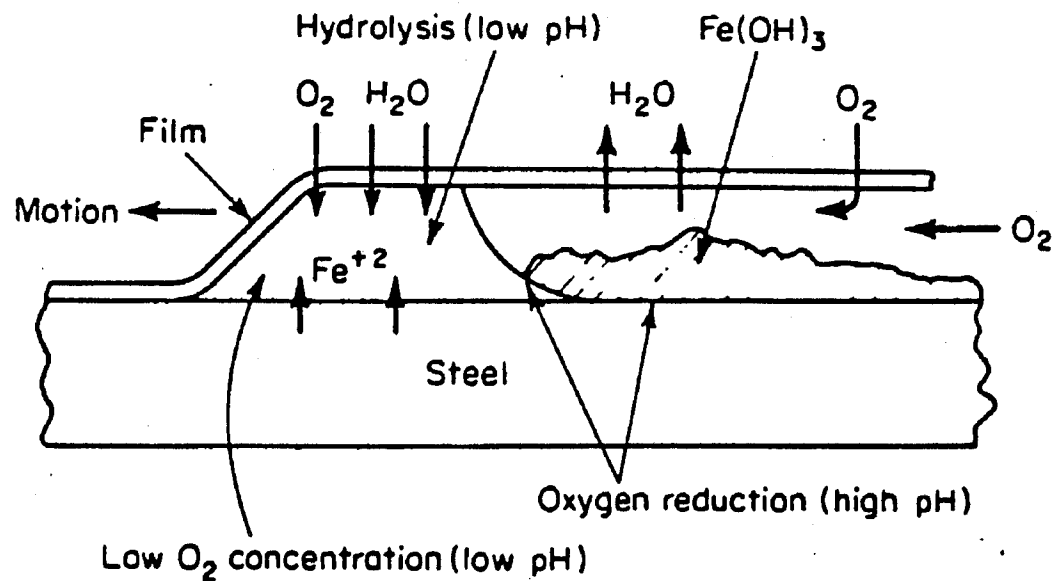
(d)

Mechanism

“Head” supplied with H_2O by osmosis (high concentration of Fe^{2+} inside) through coating and from precipitated hydroxide/oxide. Oxygen reduction creates hydroxide; precipitation creates corrosion product “tail”. . . . further oxidation to Fe^{3+} oxide etc. Hydrolysis of salts in head creates acidic conditions.

Details of mechanism not understood.

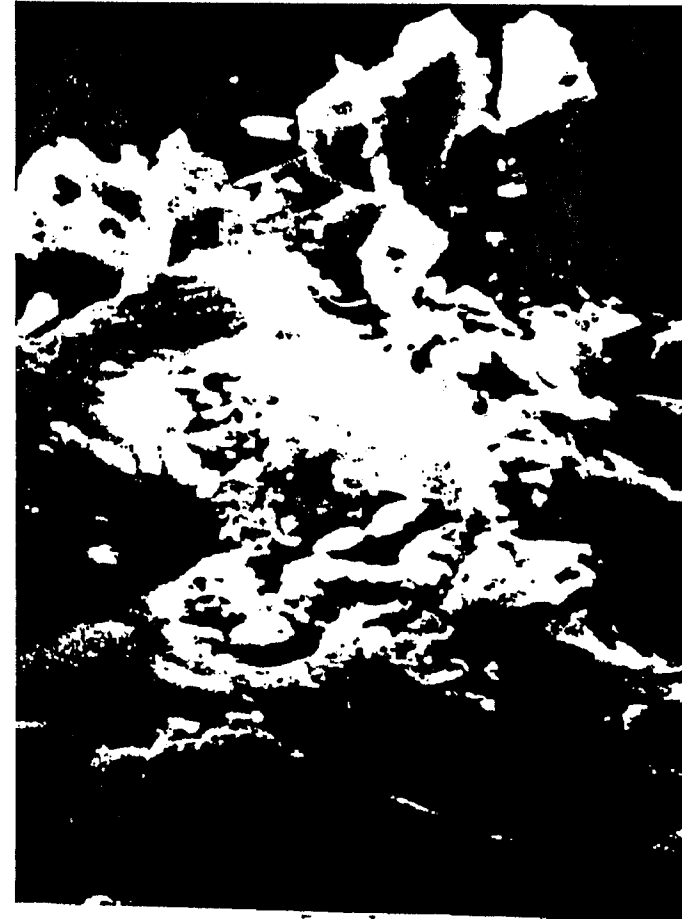
e.g., why do filaments “reflect” off other filaments? etc.



Filiform Corrosion on PVC coated Al Tail



Advancing head and cracked tail
of a filiform cell.
Scale: \longleftrightarrow 0.125 mm



Gelatinous corrosion products
oozing out of porous tail section.
Scale: \longleftrightarrow 1.25 μm

Close-up of the advancing head shown in adjacent figure. Minute cracks can be seen at the head/tail interface of a filiform corrosion cell. These cracks are entry points for water and air to provide a source of hydroxyl ions and an electrolyte. Intermediate corrosion products are just beginning to form in the head, and they undergo further reaction to form an expanded tail. The tail region is a progressive reaction zone that ultimately forms spent corrosion products. Between the head and porous end, ions gradually react with water and oxygen and are slowly transported in the direction of the tail to form final corrosion products.

Scale: \longleftrightarrow 15 μm



Prevention NOT EASY....

- **store coated metals in dry air;**
- **use more brittle films . . . crack at head and destroy differential aeration;**
- **use impermeable coatings.**