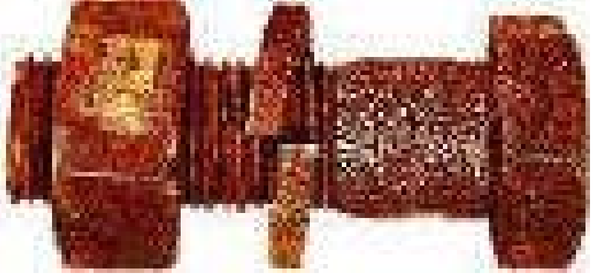

Environmental Degradation of Micro- & Nano-Composites

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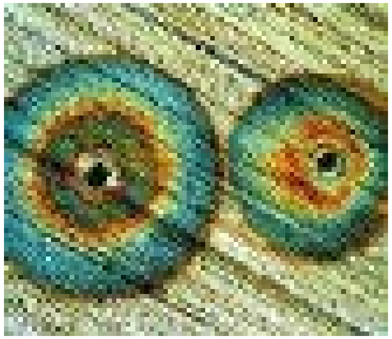


- **Corrosion**
  - Deterioration of materials (generally metals or alloys) resulting from electrochemical attack by its environment (usually aqueous).
  - It is usually a low temperature phenomenon.
- **Degradation**
  - Non-metallic materials such as ceramics & polymers do not suffer electrochemical attack but can be deteriorated by direct chemical attack.

Corrosion rate expressions

- Weight loss per unit area per unit time
  - e.g. mdd (milligram per square decimeter per day)
- The rate of thinning OR rate of penetration
  - can directly be used to predict its life.
  - Expressions:
    - ipy (inches penetration per year)
    - mpy (mils penetration per year), etc.
- Corrosion rate of practically useful and technical materials varies approximately between 1 and 200 mpy.

Comparison of corrosion rates

Corrosion rate	*Grade*
< 5 mpy	Good
5 to 50 mpy	Fair
> 50 mpy	Unsatisfactory

EXAMPLES

Zn placed in air-free dilute HCl

$Zn \rightarrow Zn^{+} + 2e^{-}$ (anodic reaction)

$2H^{+} + 2e \rightarrow H_2$ (cathodic reaction)

Rusting of Fe

$Fe \rightarrow Fe^{2+} + 2e^{-}$ (anodic reaction)

$O_2 + 2H_2O + 4e \rightarrow 4OH^{-}$ (cathodic reaction)

$2Fe + 2H_2O + O_2 \rightarrow 2Fe^{2+} + 4OH^{-} \rightarrow 2Fe(OH)_2$ (ppt)

$2Fe(OH)_2 + H_2O + \frac{1}{2}O_2 \rightarrow 2Fe(OH)_3 \downarrow$ (Rust)

Aqueous Corrosion ; An Electrochemical Phenomenon

Four necessary parameters for corrosion

1) An anode
2) A cathode
3) An electrolyte
4) An electrical contact between anode and cathode

If any of these parameters is absent, corrosion cannot take place

Corrosion Rate in terms of Weight Loss

The corrosion rate mpy can be calculated as

$$mpy = \frac{534W}{DAT}$$

- W = weight loss in mg
- D = density of the metal in g/cc
- A = area in in^2
- T = exposure time in hours

Corrosion Rate in terms of Current Density

$$\text{Corrosion rate (mpy)} = 0.129 \frac{i\,.\,a}{n\,F}$$

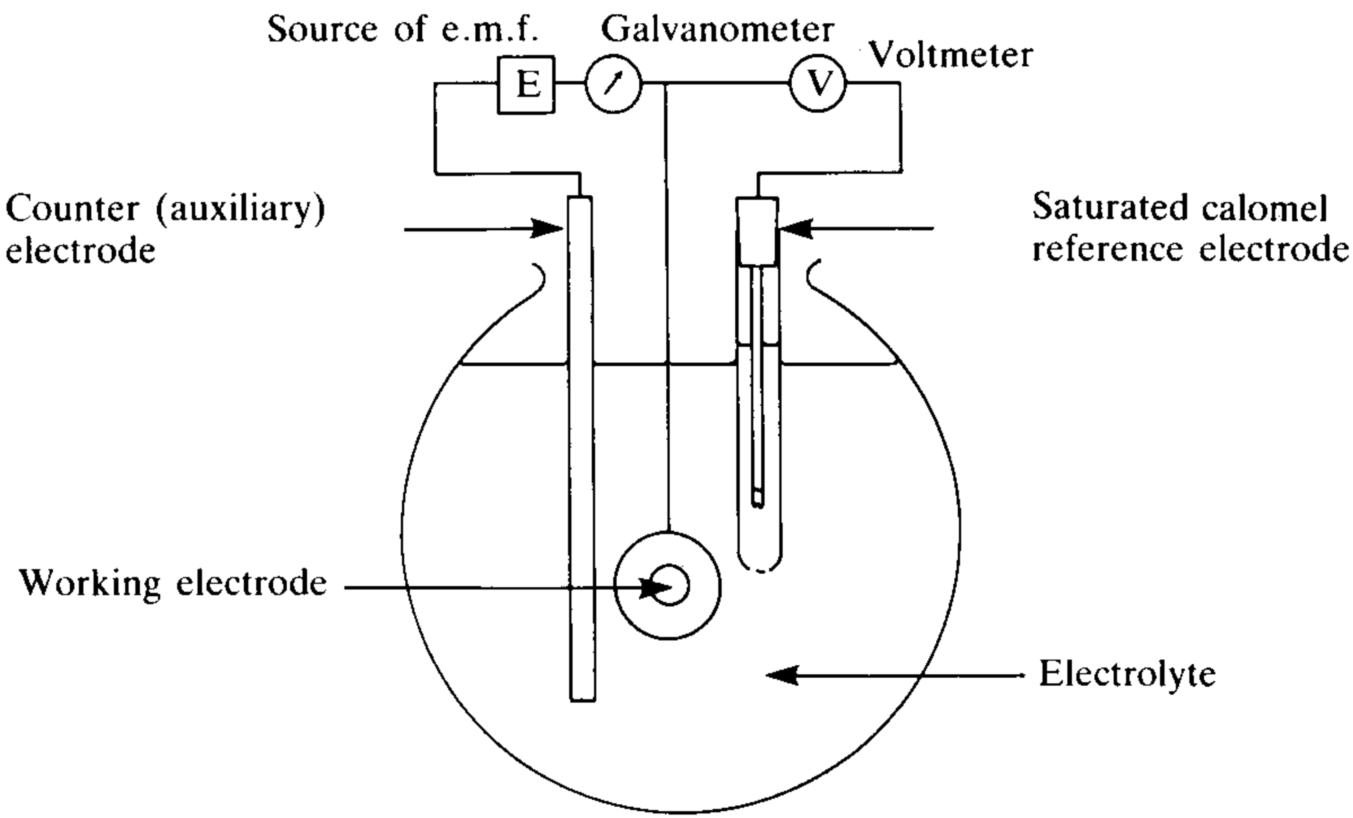
Where i = current density (A/cm^2)

a = atomic mass of metal

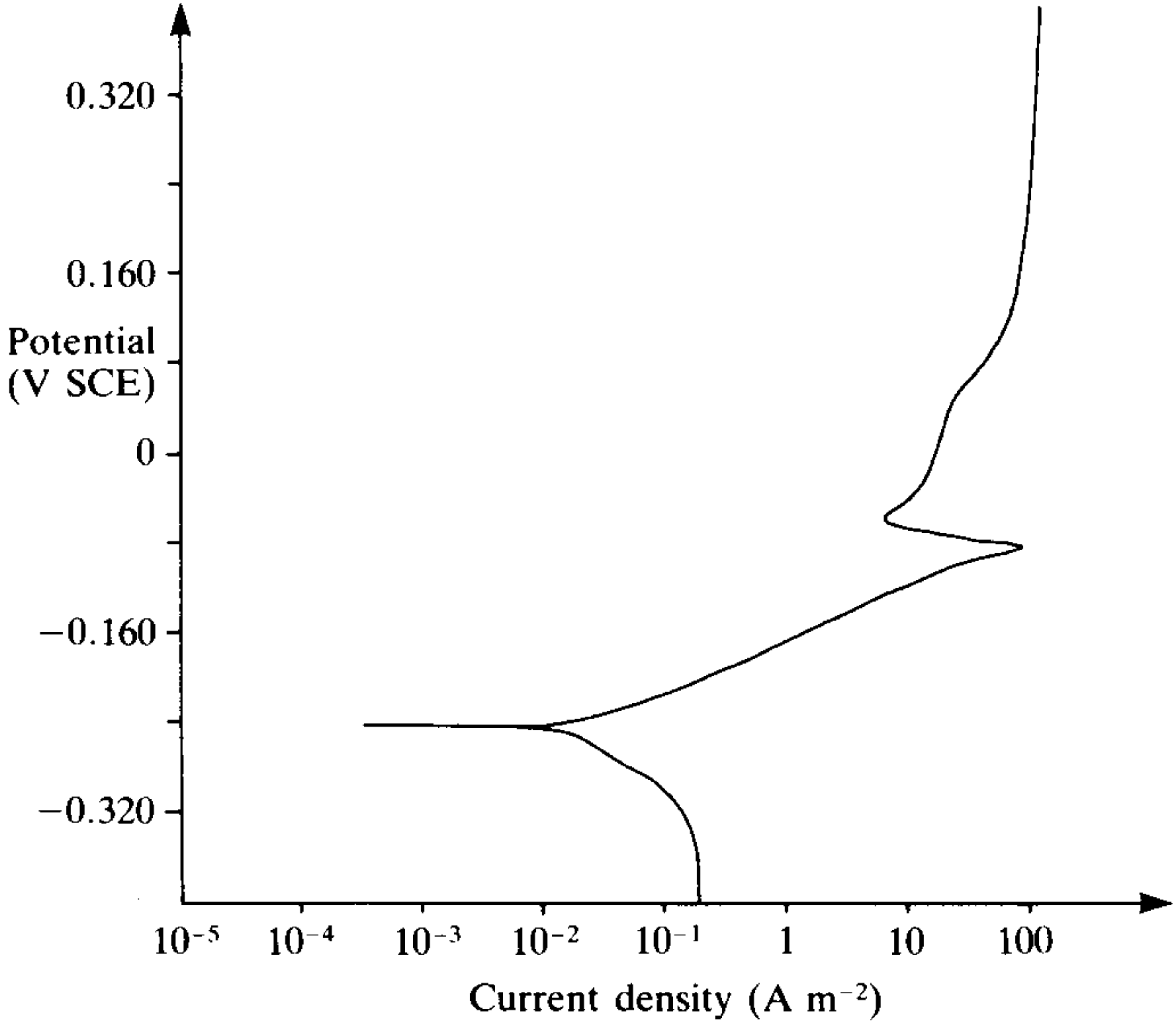
n = no. of electrons released

F = Faraday's constant = 96,490 C/mol.

Laboratory setup for determining corrosion current



The three-electrode cell.



Potentiodynamic scan for copper in 3.5% sodium chloride solution.

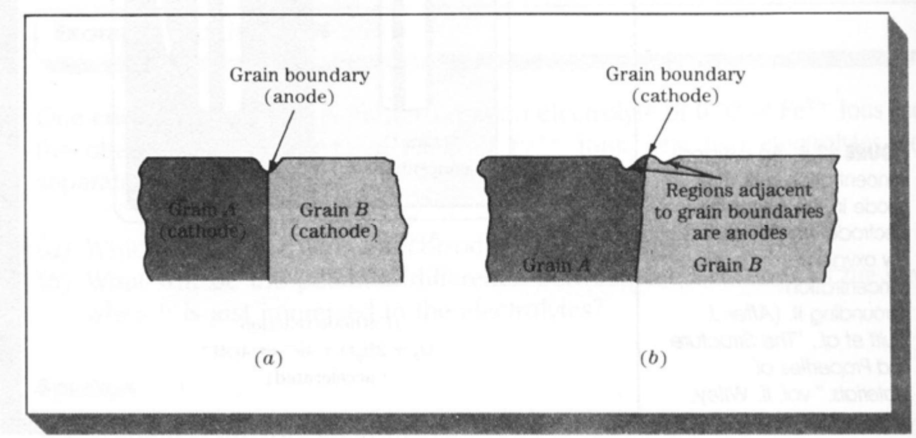
Sources of Galvanic Cells

Galvanic cells are generated by differences in Composition, Structure, and Stress.

1. Grain vs. grain-boundary galvanic cells
2. Multiple-phase galvanic cells
3. Impurity galvanic cells

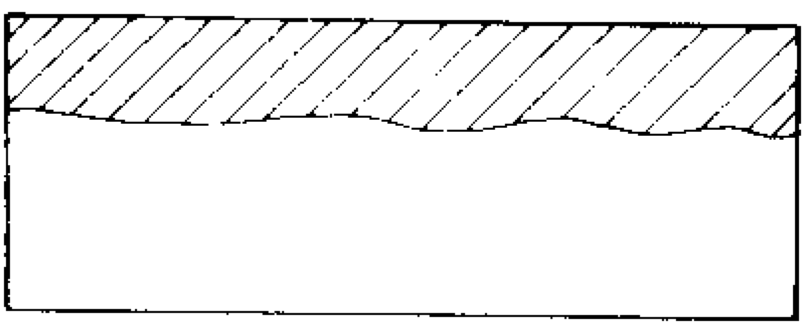
A composite has similar features:

An interface between matrix and reinforcement



Forms of corrosion

1) General Corrosion or Uniform Corrosion



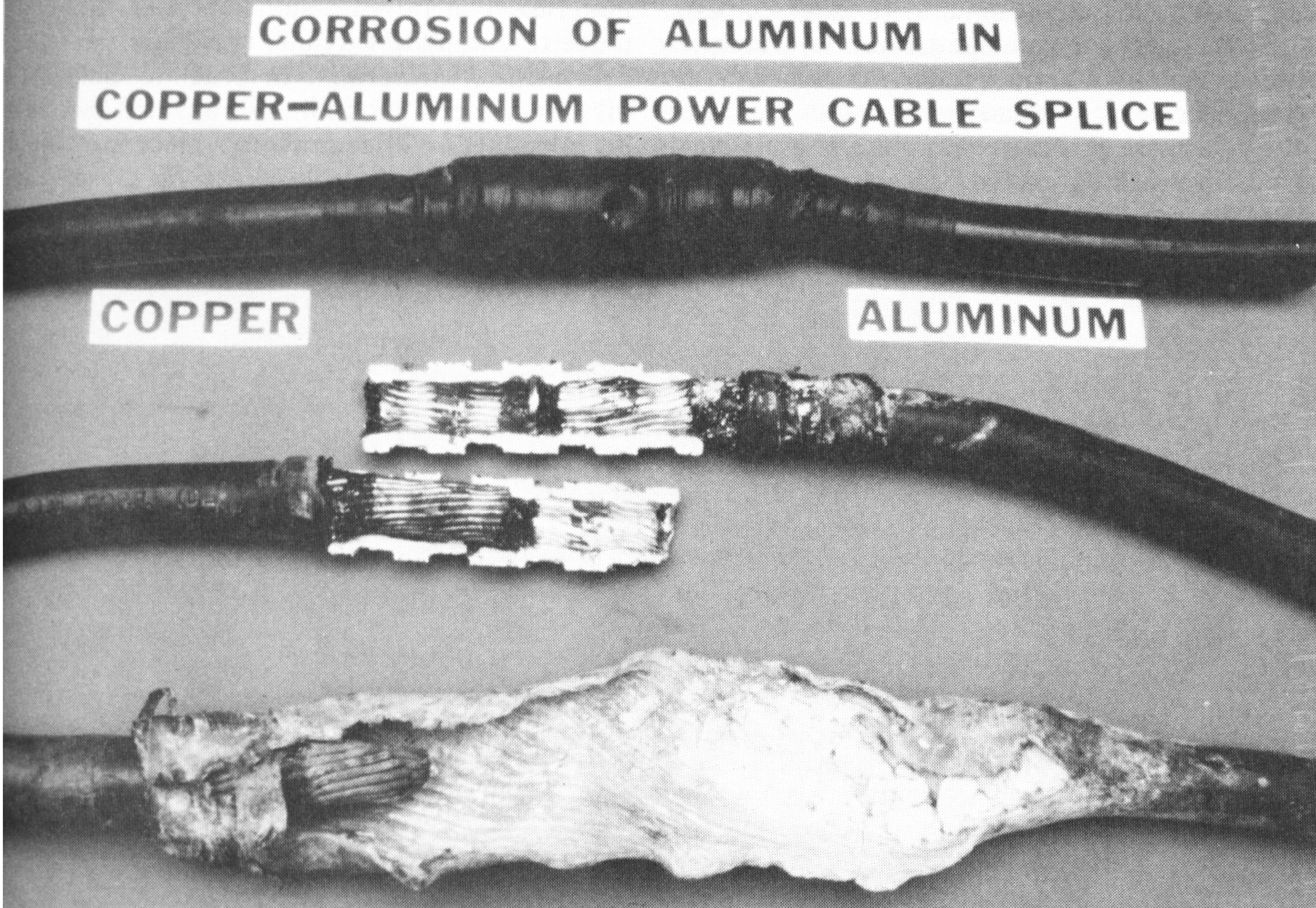
General attack

2) Atmospheric corrosion

3) Galvanic corrosion

Rust staining of the Statue of Liberty torch due to galvanic corrosion of the iron armature in contact with the copper skin.

Moisture that collected on the inside of the Statue of Liberty caused galvanic corrosion of
armature in contact with the copper skin. The copper skin on the nose was ruptured due to me
forces of the resulting corrosion products.

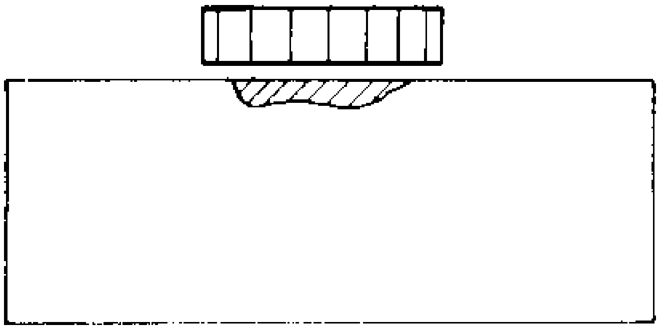


Galvanic corrosion of aluminum in buried power cable splice (copper to aluminum).

Galvanic corrosion of painted steel auto body panel in contact with stainless steel wheel opening molding.

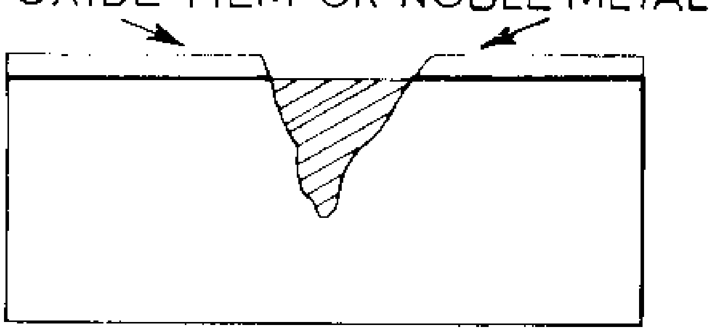
Localized Corrosion

4) Crevice corrosion

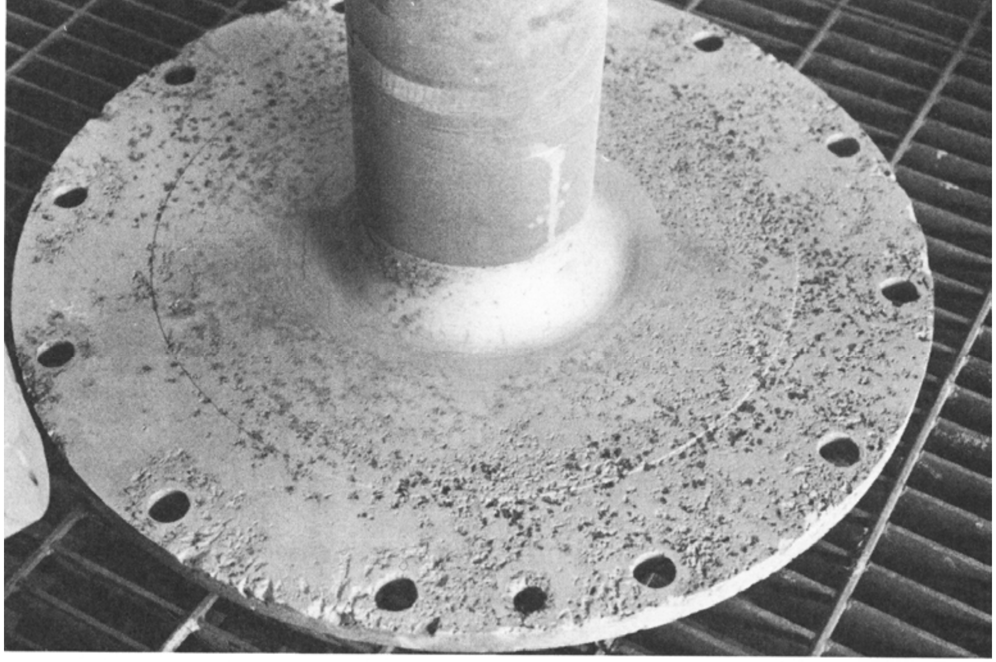


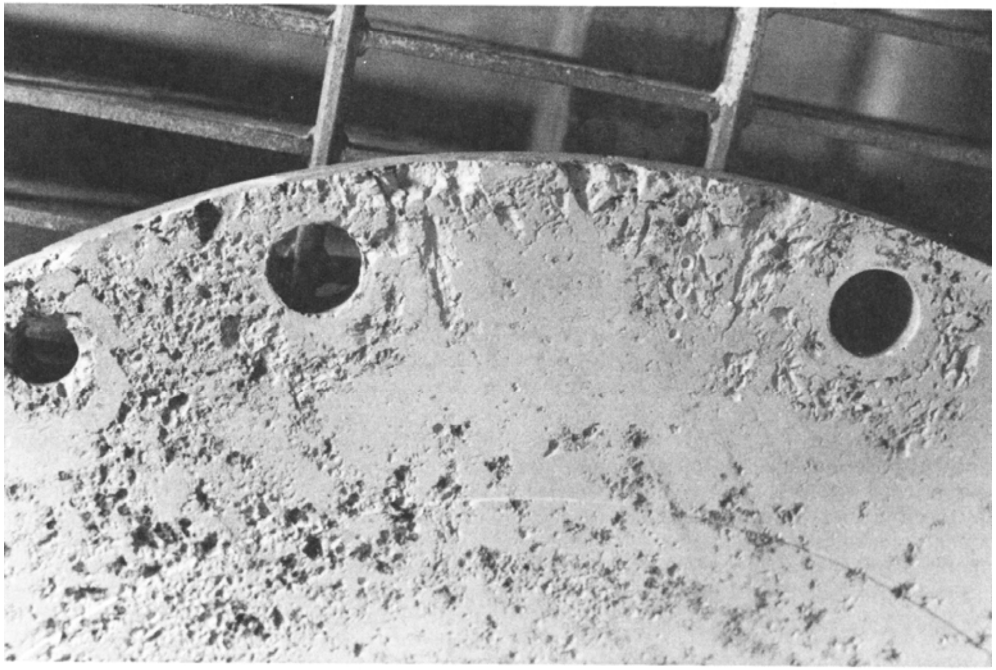
Crevice corrosion

5) Pitting



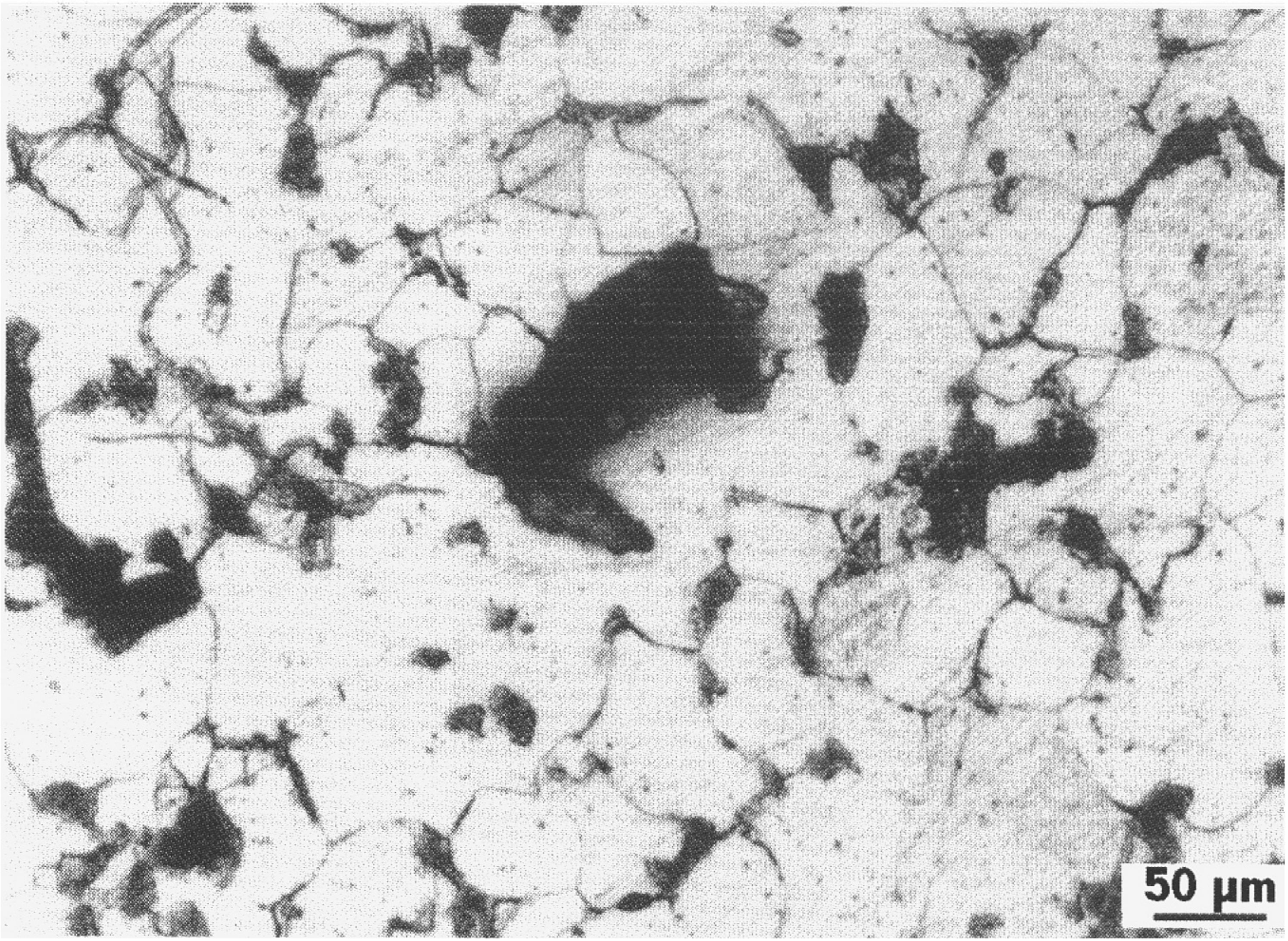
Pitting



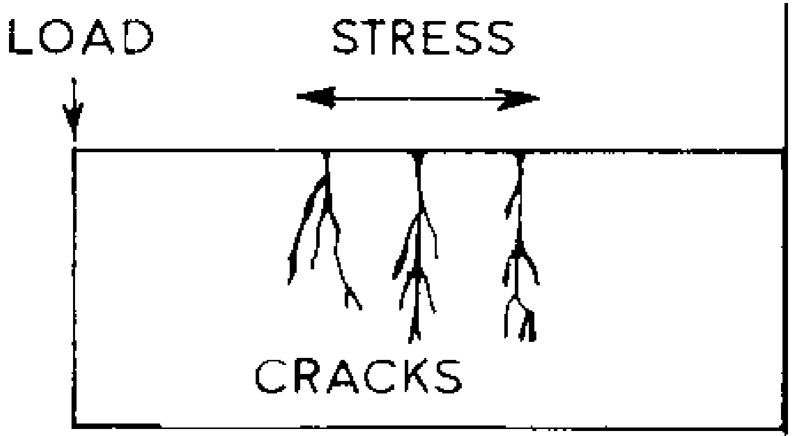


Two views of deep pits in a type 316 stainless steel centrifuge head due to exposure to $CaCl_2$ solution.

6) Intergranular corrosion

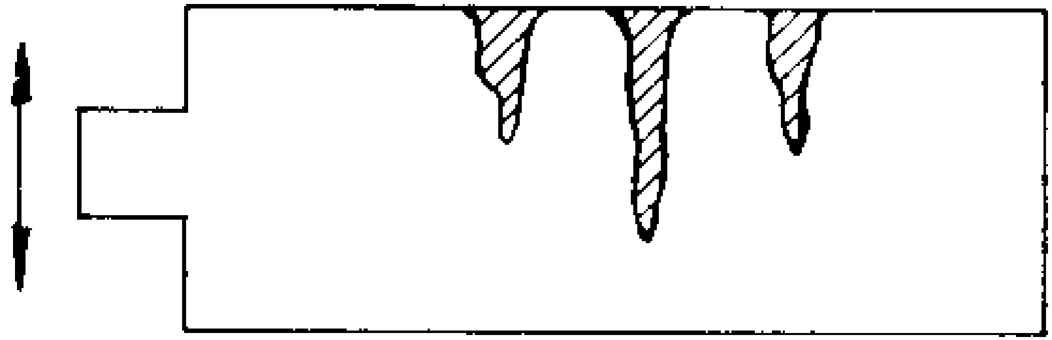


7) Stress Corrosion Cracking



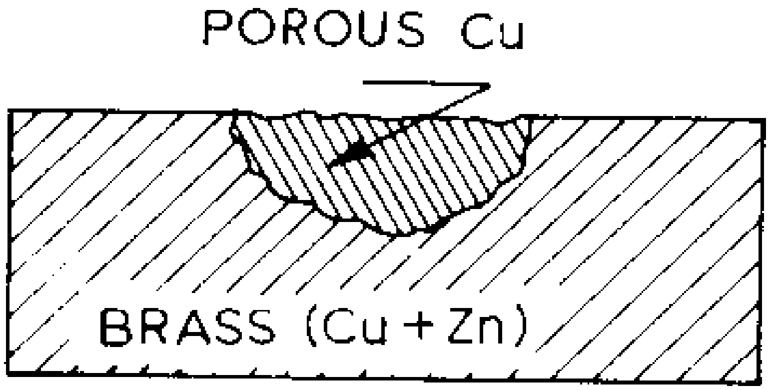
Stress corrosion cracking (SCC)

8) Corrosion fatigue

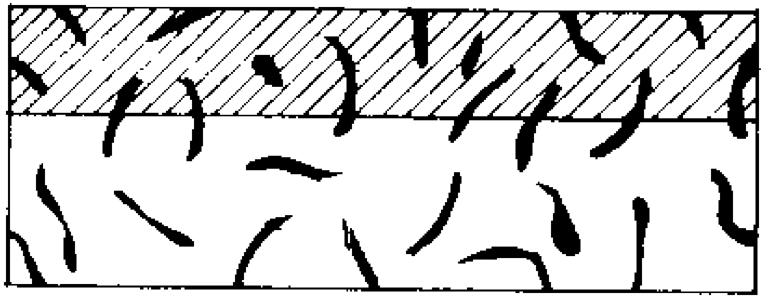


Corrosion fatigue

9) Selective leaching



Selective corrosion



Graphitic corrosion

10) Microbiological corrosion

11) Erosion corrosion

12) Stray current corrosion

13) Cavitation & Impingement

14) High temperature corrosion

- High temperature oxidation
- Hot corrosion
- Hot ash corrosion

Factors accelerating corrosion

- Humidity
- Temperature
- pH
- Aggressive ions
- Oxygen
- Thermal & Mech. Stresses
- Velocity of fluid
- Pressure

CORROSION CONTROL TECHNIQUES

Control by Design

- Avoid bimetallic coupling
  - Use galvanic series for the particular electrolyte
- Avoid crevices
- Avoid sharp bends and corners
- Avoid deposit on the surface
- Stress relieving
- Optimum fluid velocity
- **Avoid Stray Current**

Control by Environmental Change

- Control water chemistry
- Use Inhibitors
  - Anodic inhibitors
  - Cathodic inhibitors
  - Mixed Inhibitors
- Oxygen removal
  - Oxygen scavengers should be used with care
    - E.g. Hydrazine (liberates Ammonia on dissociation)—corrosive to copper and Cu-alloys

Control by Coatings

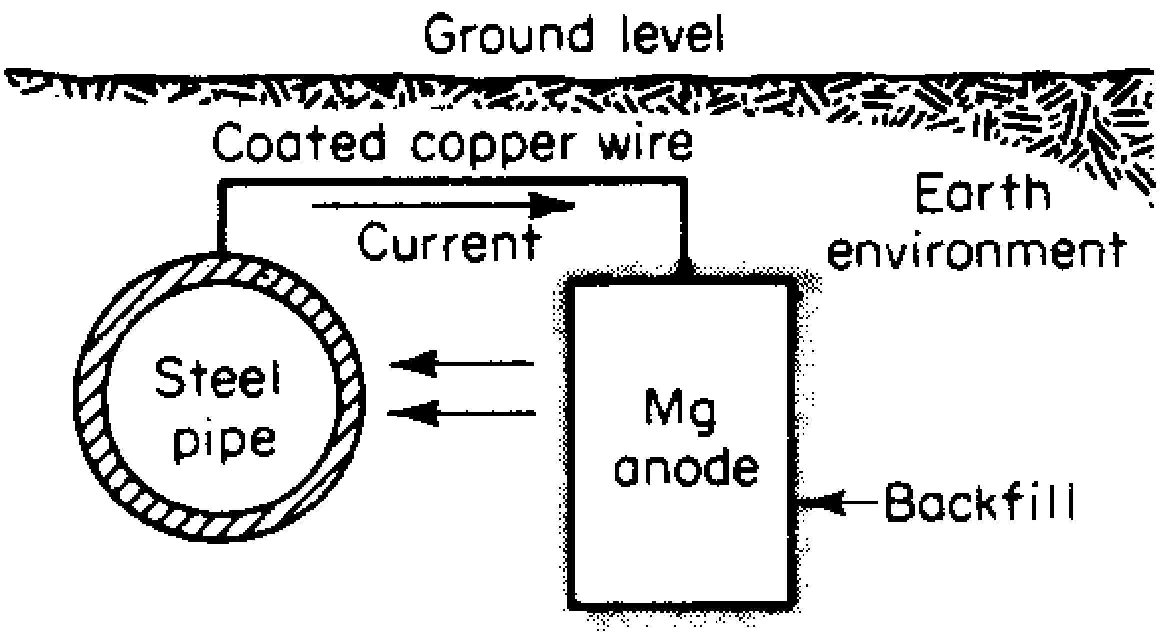
- Epoxies
- Polyurethanes
- Vinyls
- Plastics
- Nylon
- Rubber
- Metals
- PTFE (Teflon)

Cathodic Protection (CP)

Two Types:

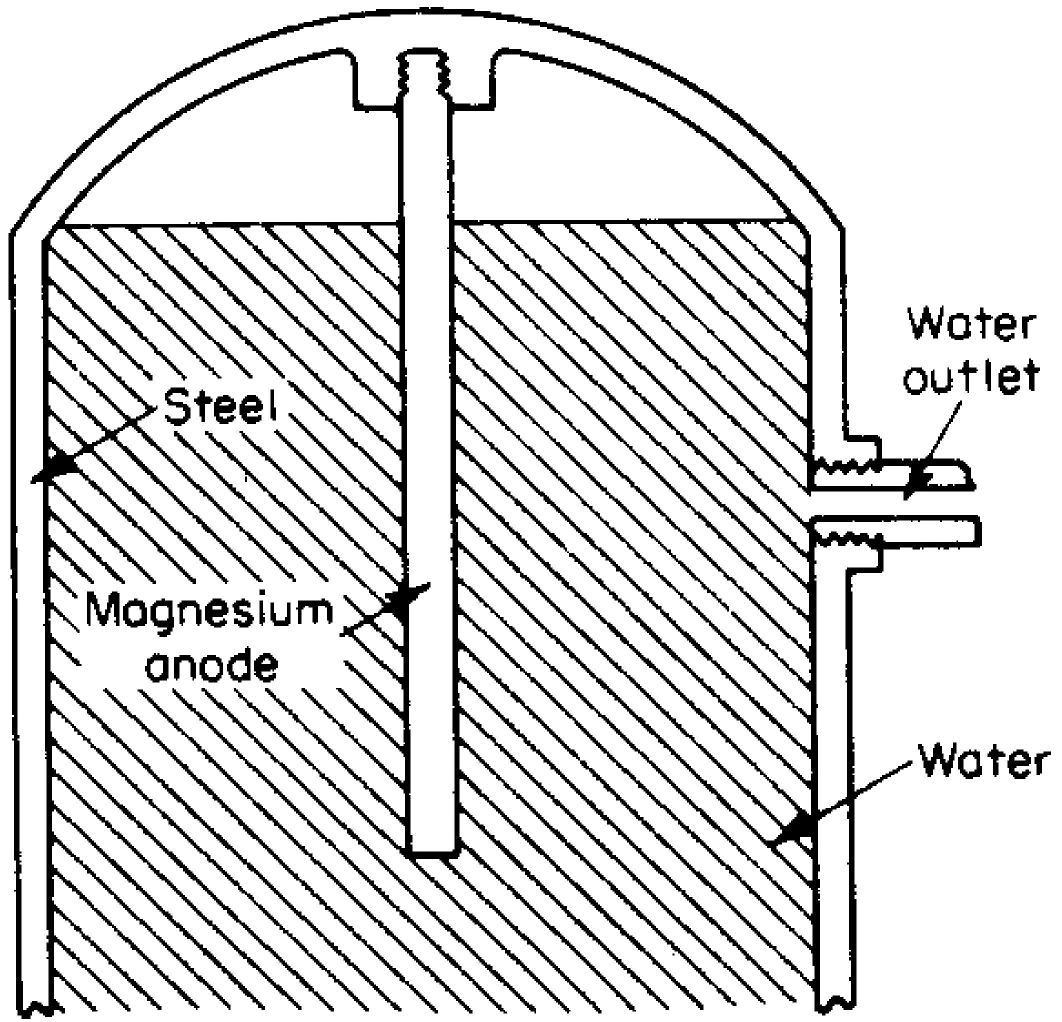
1) Sacrificial anode CP
2) Impressed current CP

Sacrificial anode; Principle;



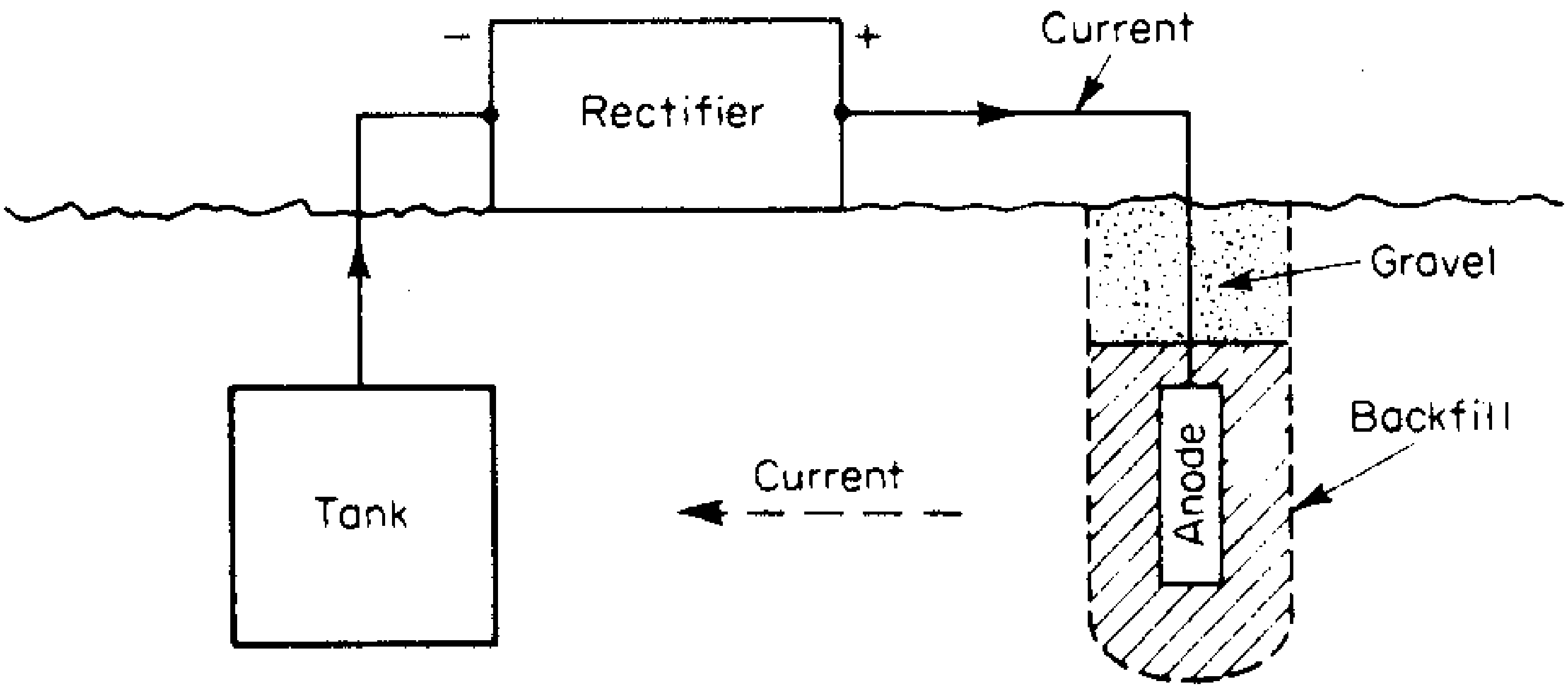
Cathodic Protection (CP)

CP of a domestic water geyser using a sacrificial anode

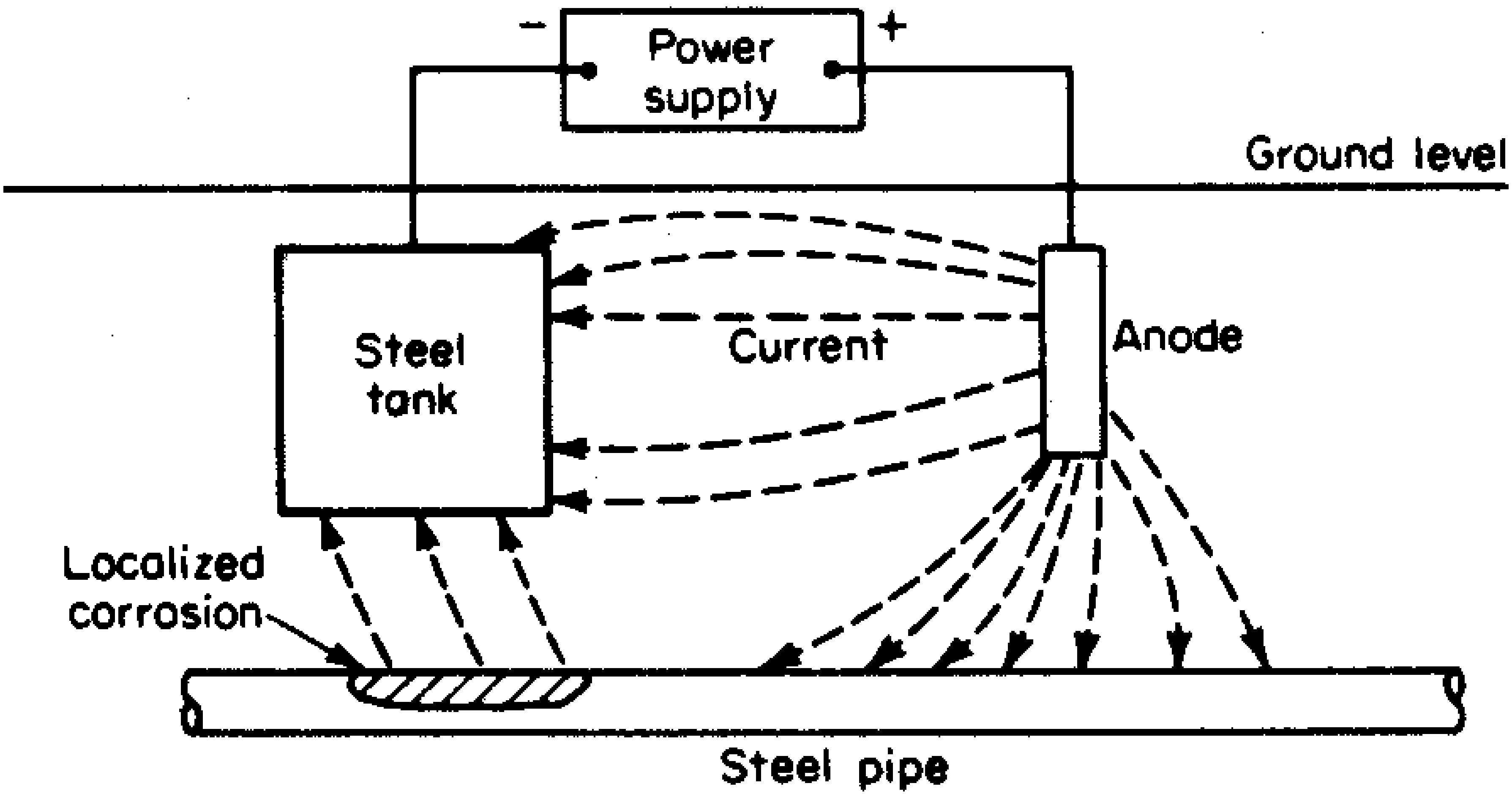


Cathodic Protection (CP)

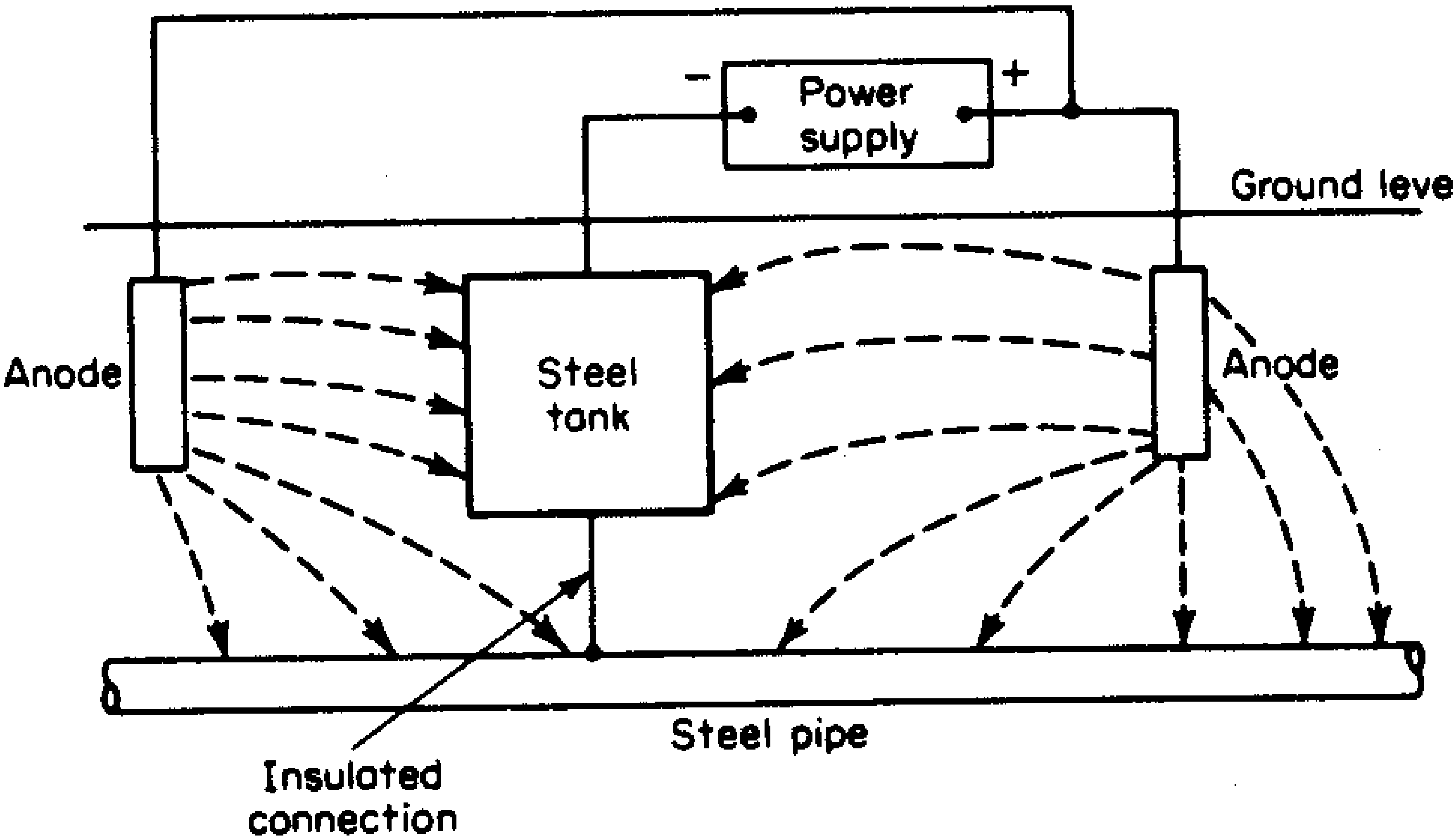
Impressed current;   Principle



Stray current corrosion



Stray current corrosion—Solution



Corrosion in MMCs

- Metal Matrix Composites
  - Sources for cell generation:
    - Interface between matrix and reinforcement
    - The interface acts as anodic site and the reinforcement serves as cathode.
    - Anodes dissolves; the reinforcement loses strength and falls out
    - Corrosion propagates inside through the interface.

Most important MMC systems:

- Aluminum matrix
  - Continuous fibers: boron, silicon carbide, alumina, graphite
  - Discontinuous fibers: alumina, alumina-silica
  - Whiskers: silicon carbide
  - Particulates: silicon carbide, boron carbide
- Magnesium matrix
  - Continuous fibers: graphite, alumina
  - Whiskers: silicon carbide
  - Particulates: silicon carbide, boron carbide
- Titanium matrix
  - Continuous fibers: silicon carbide, coated boron
  - Particulates: titanium carbide
- Copper matrix
  - Continuous fibers: graphite, silicon carbide
  - Wires: niobium-titanium, niobium-tin
  - Particulates: silicon carbide, boron carbide, titanium carbide.
- Superalloy matrices
  - Wires: tungsten

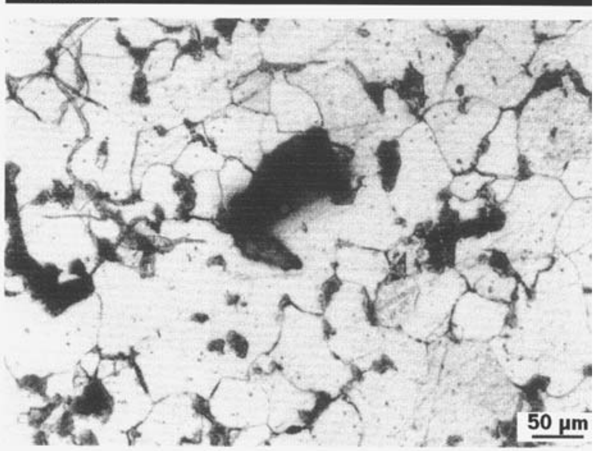
Failure analysis in a Benzene Anhydride HX

- Piping material : AISI 1020 (Mild steel)
- Environment : Benzene Anhydride
- Cooling medium : Water
- Temperature : 165 – 180^{o}C
- Pressure : 0.5 MPa
- Piping size: ID = 75 mm
- Wall thickness = 4 mm

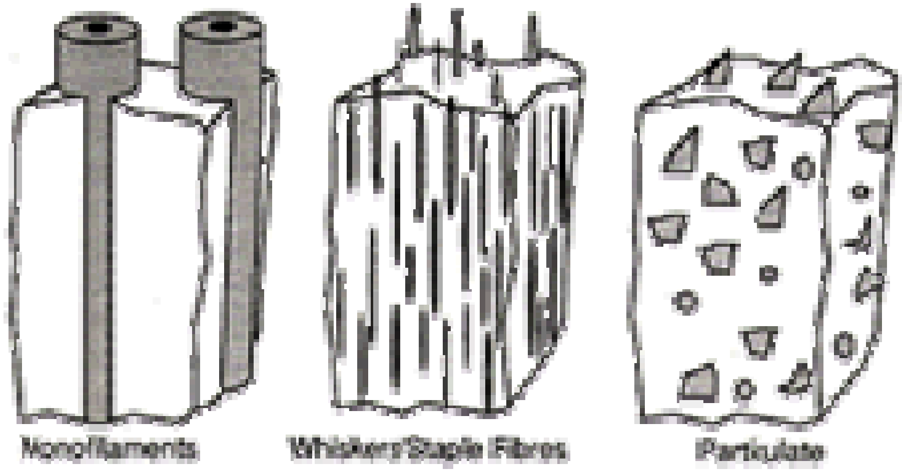
Ref. *Materials Performance*, Aug.2005, p.46

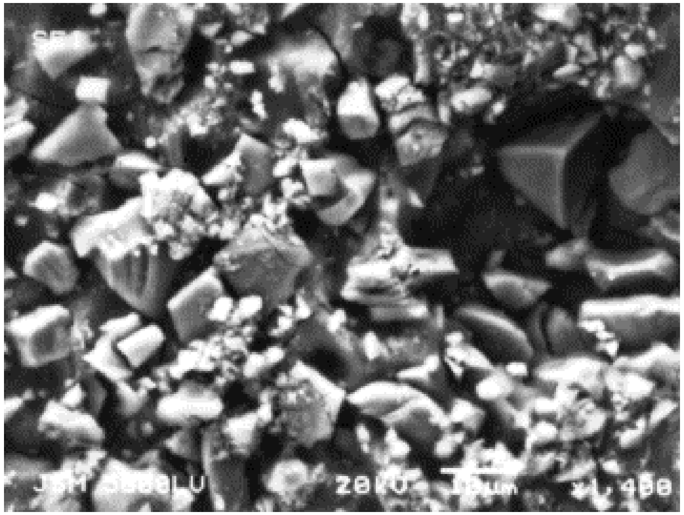
- Corrosion type
  - Grain boundary corrosion
  - Pitting
    - Both lead to Stress Corrosion Cracking
- Source of corrosion
  - S & Cl was found at g.b.
- Suggestions for remedy:
  - Material replacement
    - SS 316 or SS316L
  - Impurities of Cl & S to be reduced.

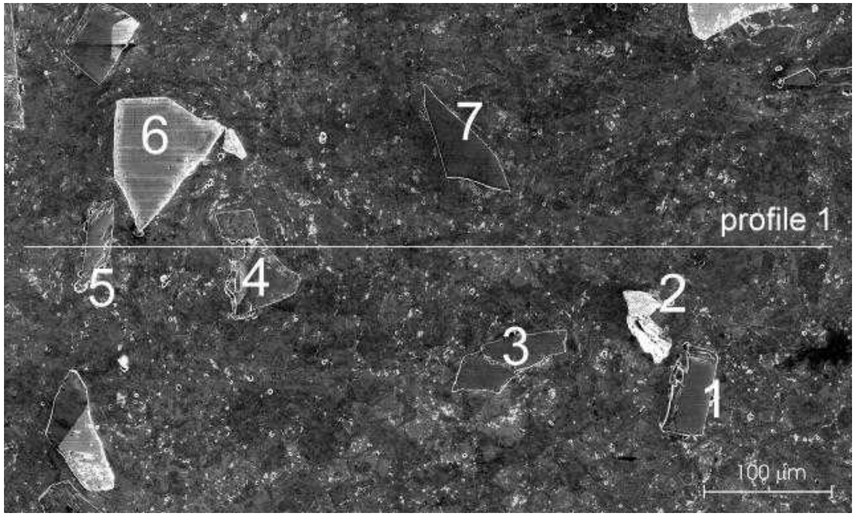
FIGURE 2



Optical micrograph of the piping.


Monofilaments
Whiskers/Staple Fibres
Particulate



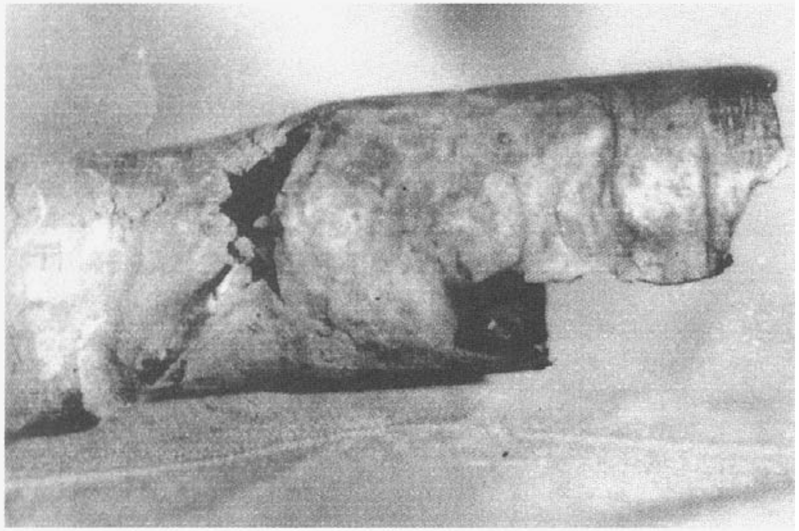

7
6
profile 1
4
5
2
3
1
100 µm

Ni200 HX tubing failed in a Chlorine & Alkali factory

- HX tubing material : Ni200
- Transported material contained:
  - Propylene ($CH_3CH{=}CH_2$)
  - Nitrogen
  - Hydrogen
  - Chlorine
  - Water
- Piping dia.=50.8 mm
- Wall thickness = 2 mm

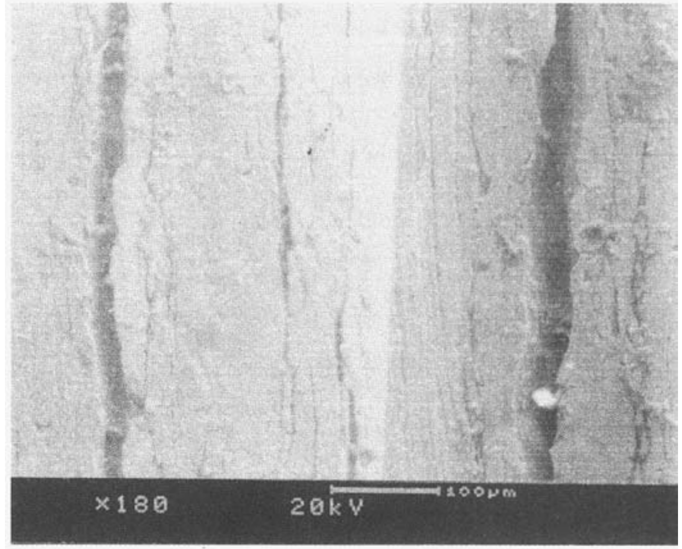
Ref. *Materials Performance*, Aug.2003, p.52

FIGURE 1



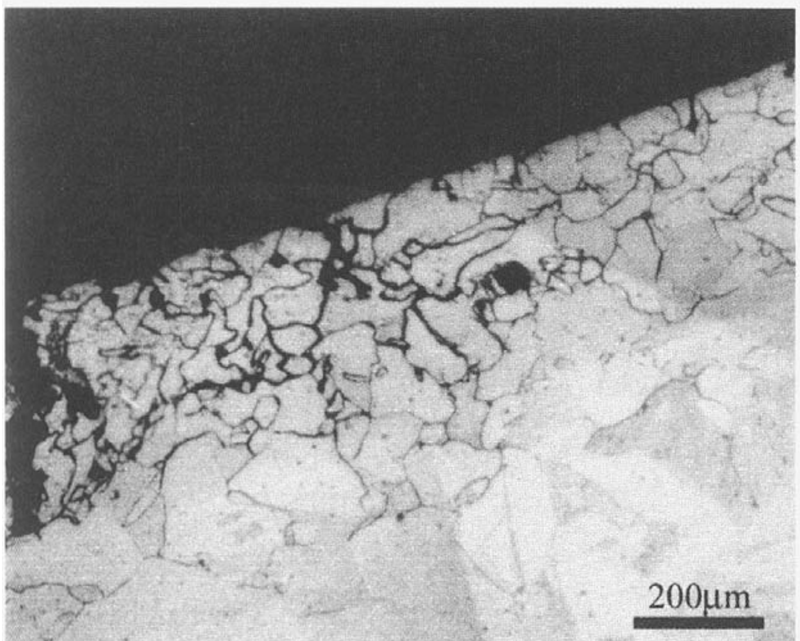
Macroscopic photograph of the corroded pipe.

FIGURE 2



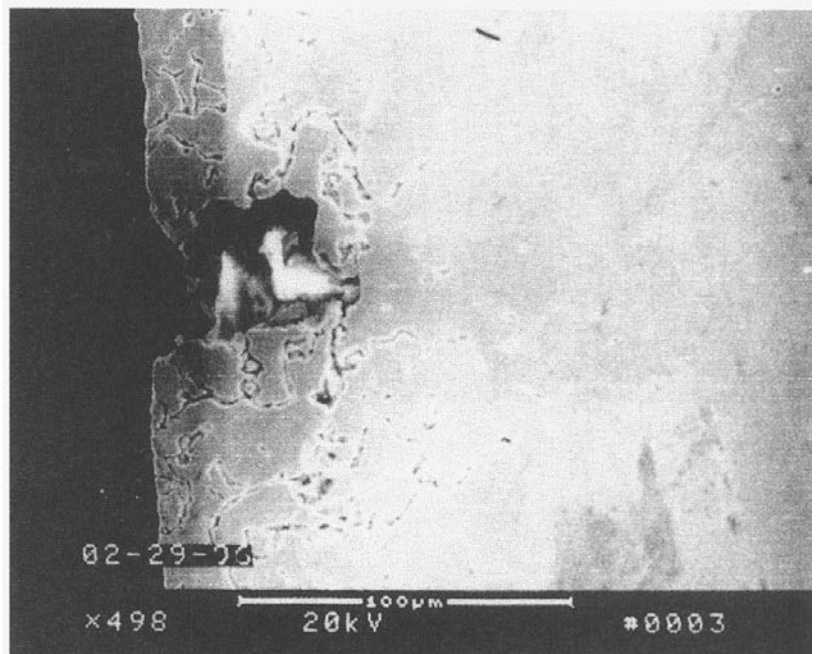
SEM micrograph of the inner surface of the pipe.

FIGURE 3



Optical micrograph of the corroded area.

FIGURE 4



SEM micrograph of the corroded area.

Failure mode

- Intergranular corrosion
- Caused decrease in thickness
- Later on Plastic deformation occurred
- Leading to SCC

Degradation of Glasses, Ceramics & CMCs

Glasses, Ceramics & CMCs

- These materials are:
  - Oxides, fluorides, borates, phosphates, etc.
    - Ceramics—crystalline:
    - Glasses—non-crystalline or amorphous
  - Electrically insulating and contain few carriers, hence,
    - Chemical attack mainly by acid-base type of reactions rather than electrochemical redox reactions.
    - Glasses & ceramics of similar composition—often have quite different corrosion behavior—structure at atomic scale plays an important role.
  - Literature on corrosion of ceramics is sparse since these are not affected under normal aqueous environment.

- Several chemical mechanisms of corrosion of crystalline ceramics and glassy materials:

a) Congruent dissolution of by simple dissolution

- E.g. hot-pressed monophase solid MgF_2—used as optical window material for visible and near-IR region—dissolves in water (independent of pH)

$$MgF_2 \Leftrightarrow Mg^{+2} + 2F^-$$

b) Congruent dissolution by chemical reaction with solvent—dissolution is by acid-base or hydrolysis reaction—no solid reaction product.

- MgO refractories in acidic solution:
  - $MgO + 2H^+ \leftrightarrow Mg^{2+} + H_2O$
  - $MgO + H_2O \leftrightarrow Mg(OH)_2$ Another competing reaction
  - $Mg(OH)_2 + 2H^+ \leftrightarrow Mg^{2+} + H_2O$

c) Incongruent dissolution with formation of crystalline reaction product.

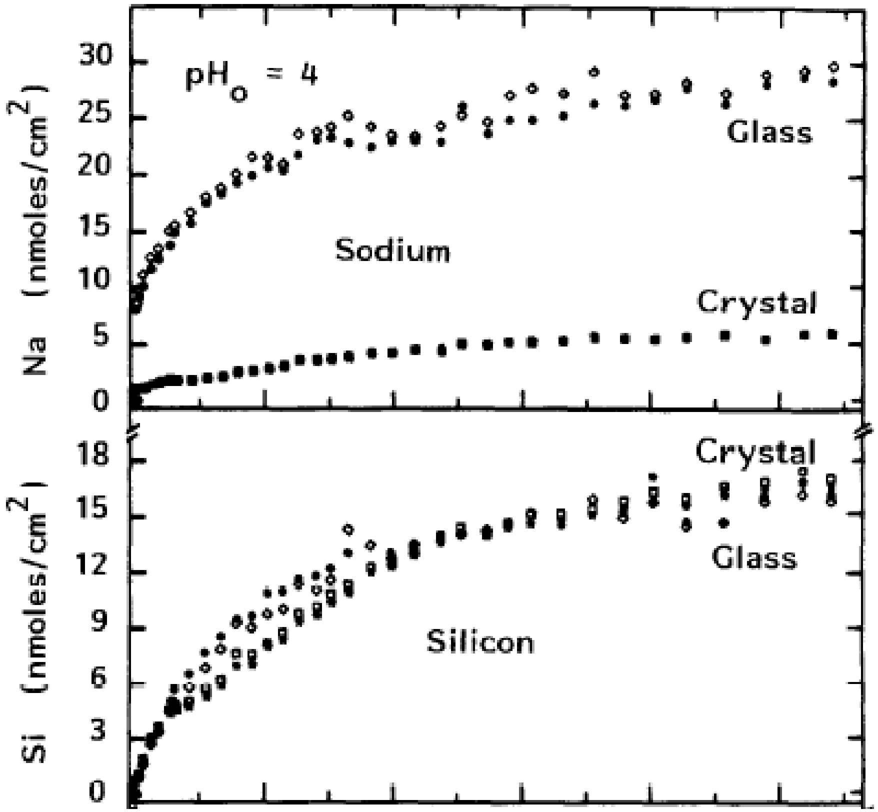
- $SrTiO_3 + 2H^+ \leftrightarrow Sr^{2+} + TiO_2$

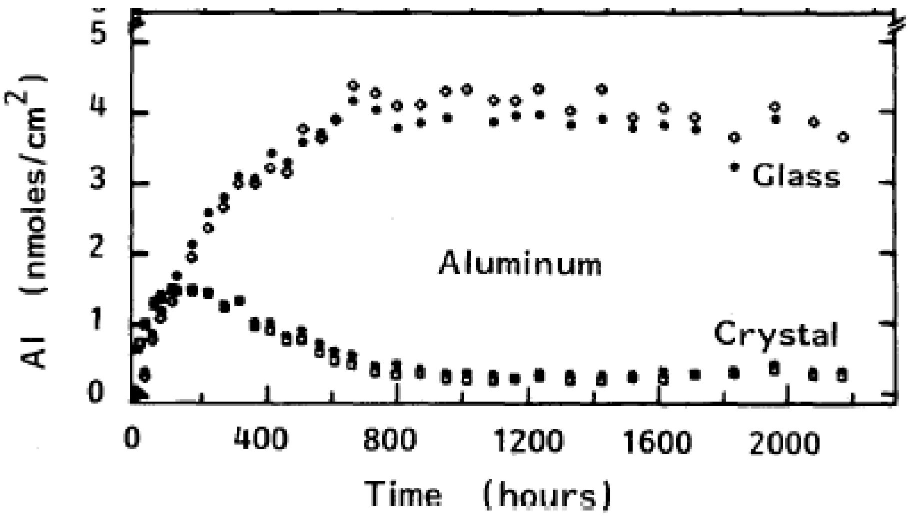
d) Incongruent dissolution with formation of non-crystalline reaction layers.

$$\underset{\text{(Bulk)}}{NaAlSi_3O_8} + H^+ \Leftrightarrow Na^+ + \underset{\text{(Surface)}}{Al_2Si_2O_5(OH)_4} + H_4SiO_4$$

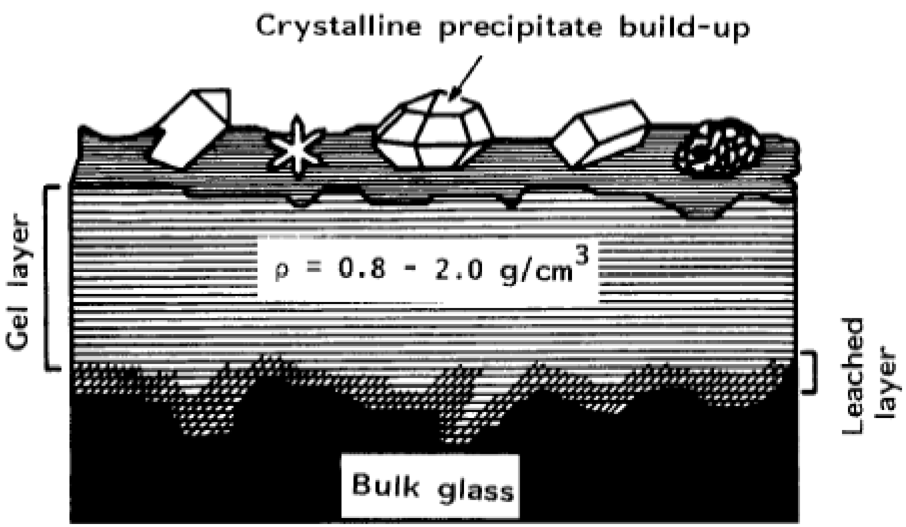
e) Ion-Exchange

$$\underset{\text{(Bulk)}}{NaAlSi_3O_8} + H_3O^+ \Leftrightarrow \underset{\text{(Surface)}}{(H_3O)AlSi_3O_8} + Na^+$$





Comparison of uptake of ions by dissolution of similar compositions of crystalline and glassy $NaAlSi_3O_8$.



Sketch showing a corroded glass surface with ion-depleted leach layer; overlying ppts or “gel” ultimately recrystallizes into reaction product.

Qualitative Ranking of Glasses Into Four Categories

TYPE	PRINCIPAL USE	WEATHERING	WATER	ACID
Soda Lime-1	Lamp Bulbs	3	2	2
Borosilicate-1	General	1	1	1
Borosilicate-2	Pharmaceutical	1	1	1
96% Silica-1	High Temp	1	1	1
Fused Silica-2	Optical	1	1	1
Glass Ceramic-1	Nose Cones	-	1	4
Glass Ceramic-2	Cooking Ware	-	1	2

Durability Key: 1 = excellent; 2 = good;
3 = fair; 4 = poor

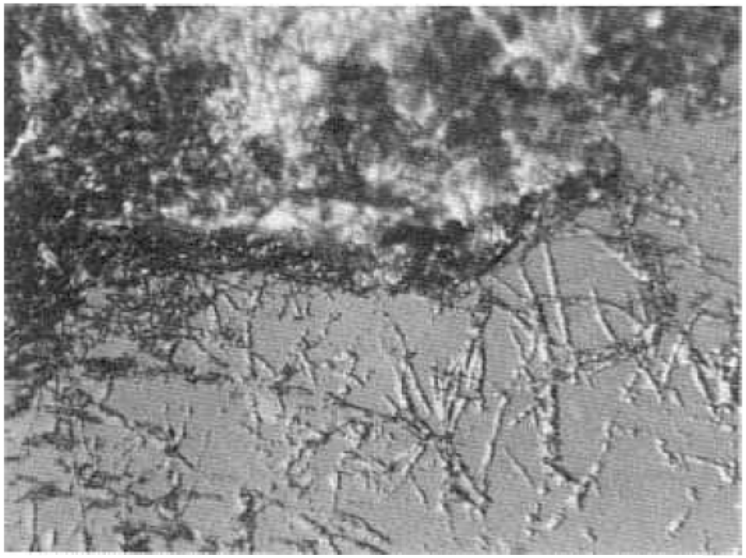
Estimations of the Upper Limits of Elements Extractable from Glass Bottles After 1 Year at 25°C.

(ppm in Solution)

GLASS TYPE	ELEMENT EXTRACTED	INTO STRONG ALKALI	INTO ACID OR WATER
Soda Lime-1	Si	10,000	10E+2
	Na	1,000	10E+2
	Fe	10	10E-1
Soda Lime-2	Si	1,000	10E 0
	Na	100	10E+1
	Fe	1	10E-2
Borosilicate-1	Si	1,000	10E 0
	Na	100	10E 0
	Fe	1	10E-3
Borosilicate-2	Si	1,000	10E-1
	Na	100	10E 0
	Fe	1	10E-3
High silica-1	Si	1,000	10E-1
	Na	1	10E-3
	Fe	1	10E-3
High silica-2	Si	1,000	10E-1
	Na	0.01	10E-5
	Fe	0.1	10E-3

LENS

FUNGUS



Aspergillus penicilloides on spectacle lens.

Etched surface of spectacle lens after removal of fungus.

PLASTER

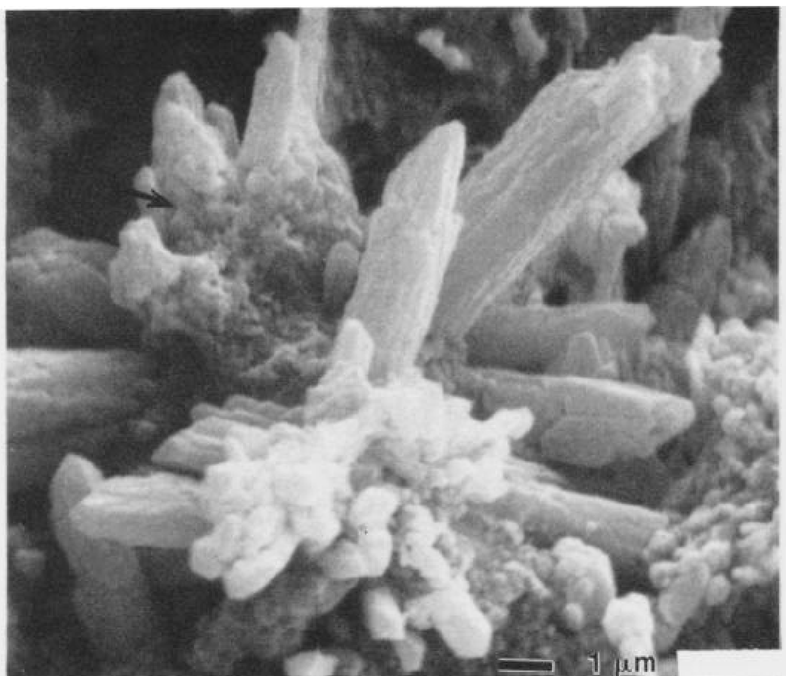


Figure 13-3. Weathered and corroded mixture of gypsum and montmorillonite clay plaster (clay at arrow).

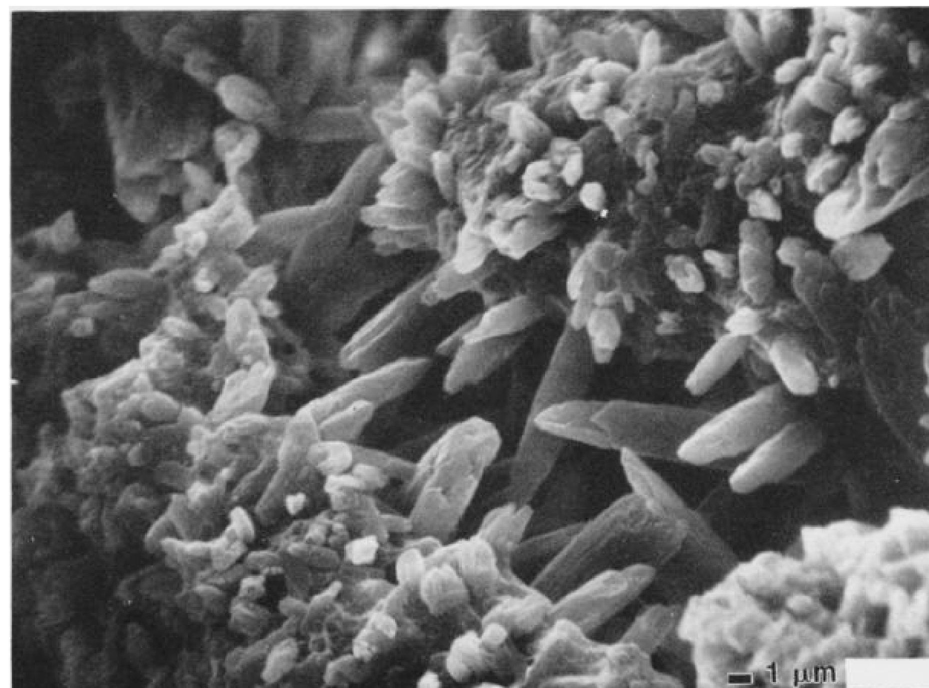


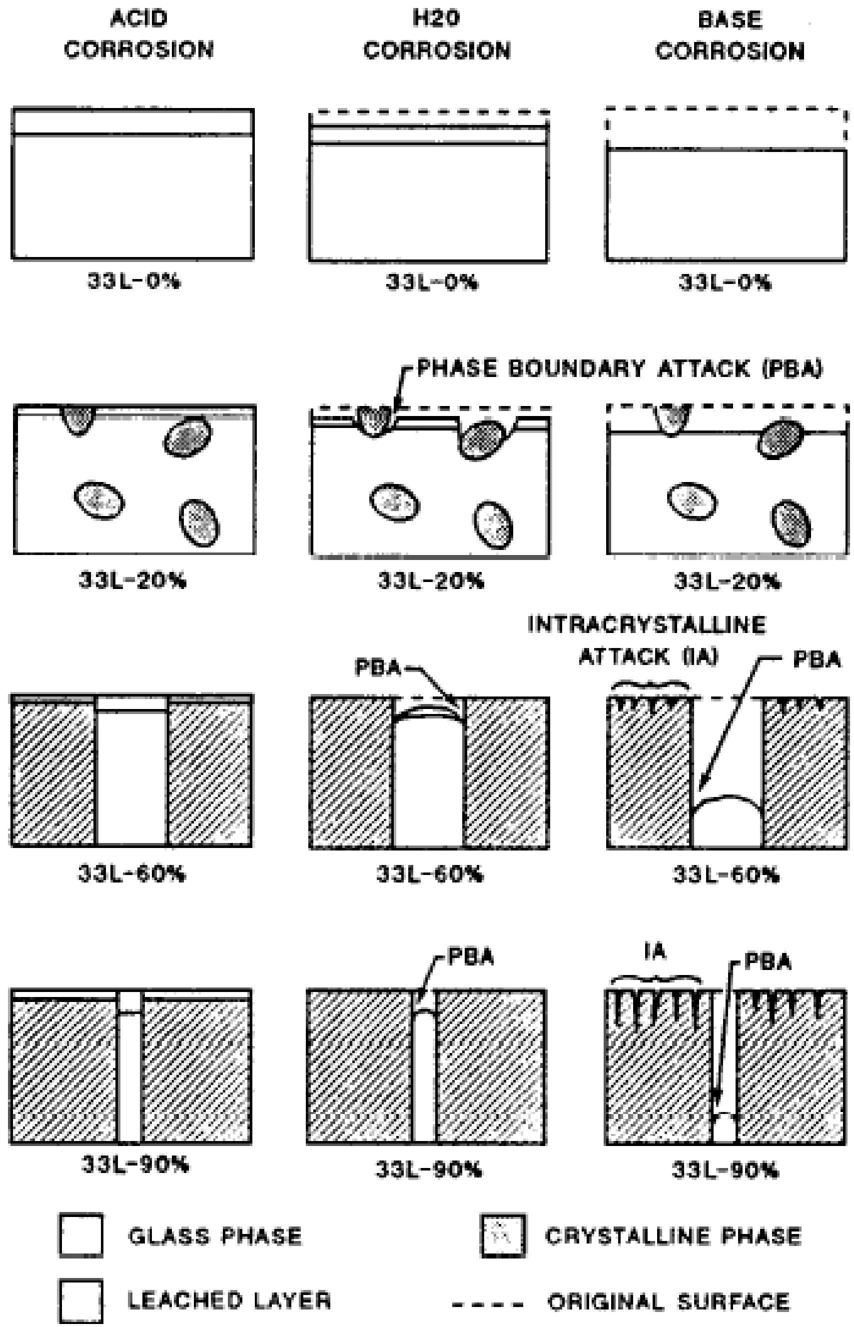
Figure 13-4. Secondary gypsum precipitated in an expanding crack in gypsum plaster.

Degradation of glass ceramics

Some Technical Uses of Glass-Ceramics

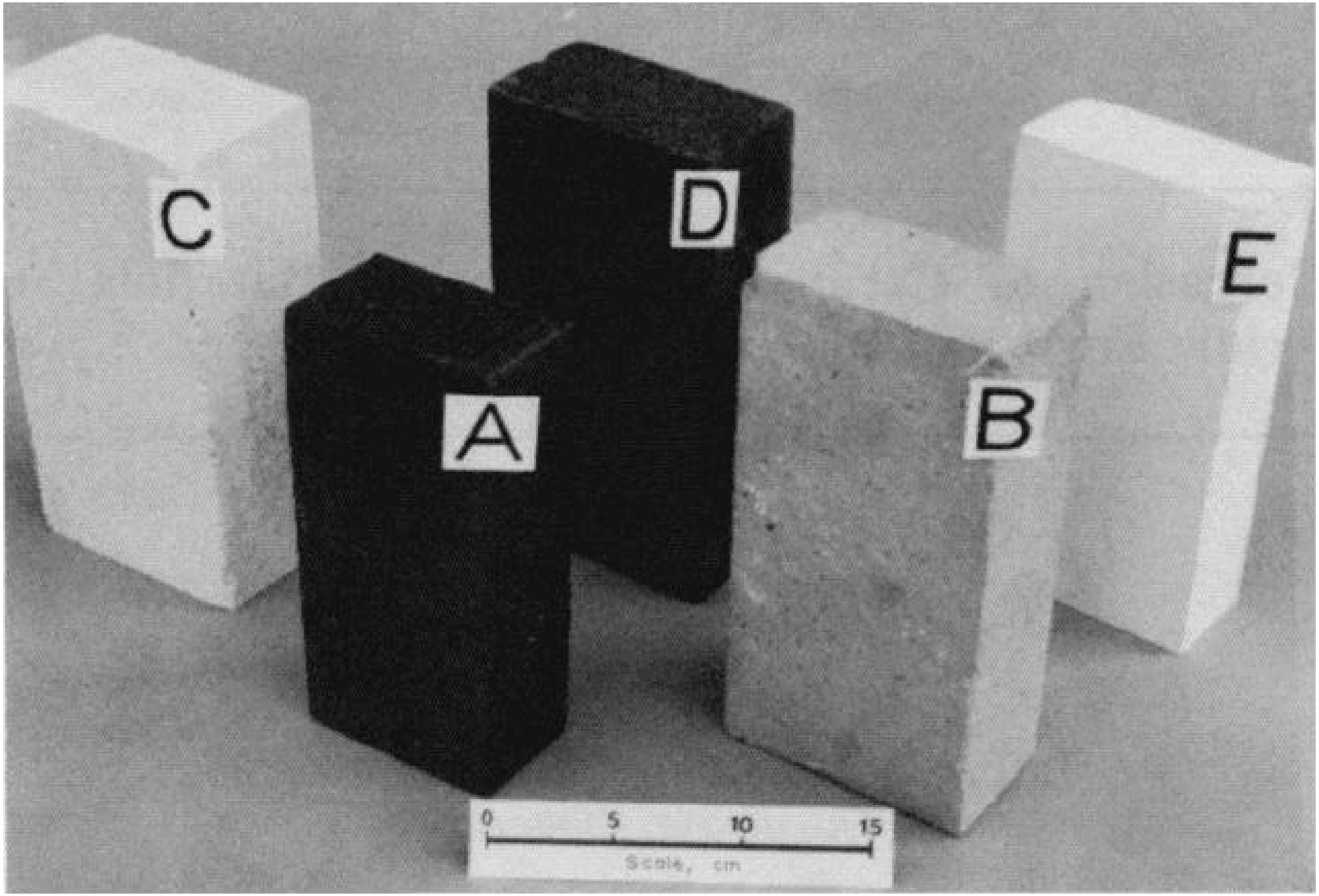
Applications	Compositions
Electronics	
photomachinable circuit boards	Li_2O-Al_2O_2-SiO_2
capacitors	Li_2O-ZnO-PbO-SiO_2
Insulators	Li_2O-$2SiO_2$
Military	
radomes	MgO-Al_2O_3-TiO_2-SiO_2
ceramic seal for bomb triggers	Li_2O-Al_2O_3-SiO_2
Vacuum Technology	
glass to metal seals for CRT	ZnO-B_2O_3-SiO_2
Domestic	
cooking ware	Na_2O-Al_2O_3-SiO_2
tableware	Li_2O-Al_2O_3-SiO_2
heating surfaces	MgO-Al_2O_3-SiO_2
Industrial	
corrosion resistant tubing	Li_2O-CaO-Al_2O_3-SiO_2
pump impellor	Li_2O-MgO-Al_2O_3-TiO_2
telescope mirror blanks	Li_2O-Al_2O_3-SiO_2
Biological	
implants and implant coatings	Na_2O-CaO_2-P_2O_5-SiO_2
dental materials	Li_2O-CaO-Al_2O_3-SiO_2

EFFECT OF CRYSTALLINITY ON CORROSION BEHAVIOR OF GLASS.

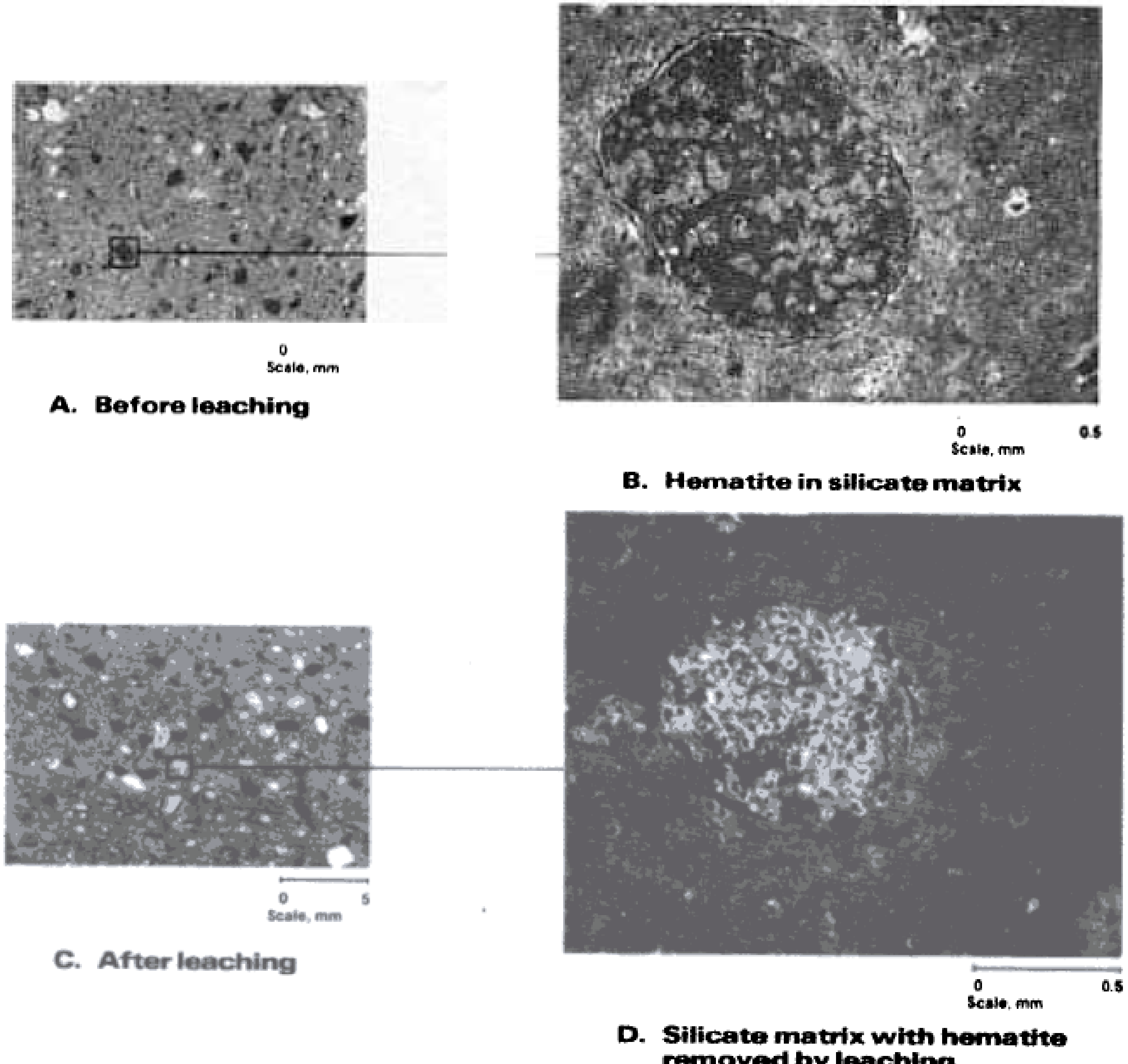


Various modes of glass-ceramic corrosion for 33L glass-ceramics.

Degradation of construction material



Chemical-resistant brick. A) red shale; B) fireclay; C) silica; D) SiC (silicate bonded); and E) high alumina.



Red shale material before and after exposure to 20 wt% HCl at 80°C for 110 days.

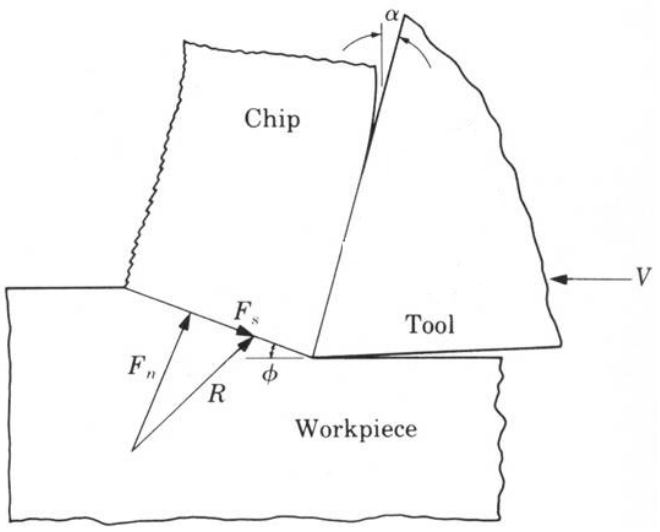
Degradation of Ceramic Cutting Tools

CERAMIC CUTTING TOOL MATERIALS

Tungsten Carbide/Cobalt Composites

Aluminum-Oxide-Based Composites

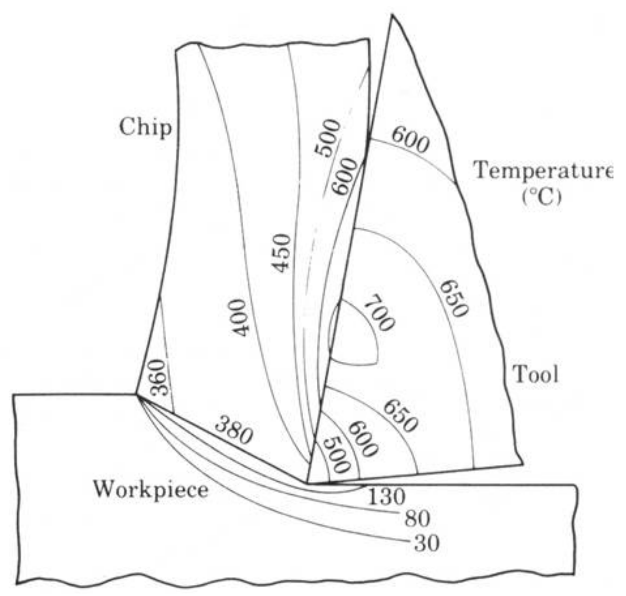
Silicon-Nitride-Based Composites



Forces acting on a cutting tool in two-dimensional cutting.

Degradation mechanisms:

1. Abrasive wear
2. Plastic deformation
3. Fracture
4. Chemical degradation



Typical temperature distribution in the cutting zone. Note the steep temperature gradients within the tool and the chip. *Source:* G. Vieregge.

Some examples of chemical interaction between tool materials are as follows:

Aluminum oxide reacts with iron to form a solid solution according to the equation

$$Al_2O_3\ (s)\ (\text{tool}) + FeO(s)\ (\text{work piece}) \rightarrow FeAl_2O_4\ (s)$$

(Note: Iron always contains some oxide)

Silicon carbide reacts with iron according to the equation

$$SiC\ (s)\ (\text{tool}) + 4Fe\ (\text{work piece}) \rightarrow FeSi + Fe3C$$

$$Si_3N_4 + 2Fe + 3O_2(\text{air}) \rightarrow 3SiO_2 + 2Fe_2N + N_2$$

Such reactions are detrimental to tool performance.

Degradation of TZP Ceramics in Humid Atmosphere

- TZP: Tetragonal Zirconia Polycrystal
  - Has thermodynamically unstable phase
  - $ZrO_2+Y_2O_3$, ZrO_2+CeO_2, $ZrO_2+Y_2O_3+CeO_2$
  - ~10-200nm
- PSZ: Partially Stabilized Zirconia
- FSZ: Fully Stabilized Zirconia
- Stabilizing materials:
  - MgO, CaO, Y_2O_3

Important features of degradation:

1) The degradation occurs significantly in a specific temperature region, at 200 to 300°C in air.
2) The degradation proceeds from the surface to the interior of the specimen.
3) Micro- and macrocracking occur because of the spontaneous phase transformation from t-ZrO_2 to m-ZrO_2.
4) The presence of water accelerates the transformation and the degradation.
5) The degradation can be prevented by increasing the amounts of stabilizing oxides or by reducing grain size.

Degradation of Polymer Matrix Nano-composites

Polymer Matrix Nano-Composites

- Thermal stability
  - In general, nanocomposites of all polymers showed higher thermal stability with dispersion of clay under inert as well as oxygen atmosphere.
- Biodegradability
  - There is no confirmation about the mechanisms of bioconsumption in the presence of clay.
- UV light
  - The degradability under UV light is a serious problem, which may limit the applicability of these materials.

- PE & PP / Clay nanocomposites
  - Nano composites of these polymers exhibited less stability than neat polymers.
  - One may get highly improved material properties by filling the polymer matrix with layered silicates, but the durability in outdoor application is still a challenge.
  - The best way would be to develop nanocomposites by modification in clay rather than functionalisation of thermoplastics to increase the outdoor durability.
- PLA (Polylactide) nanocomposite
  - In preparation of PLA composites thermal degradation has been observed even in the presence of thermal stabilizers which lead the deterioration of properties in the resulting products.
- Polyurethane nanocomposite
  - Durability of few industrially useful polymeric nanocomposites like polyurethane has not been evaluated in any environment.

- Biodegradable nanocomposites
  - Nanocomposites especially biodegradable nanocomposites are an emerging new class of materials.
  - These nanocomposites are the wave of the future and considered as the material of next generation.
  - The moisture sensitivity is still a problem in the starch nanocomposites.
- Overall there is essential requirement to investigate the durability of these nanocomposites in different environmental conditions to extend the applicability of these hybrid materials.

Q & A