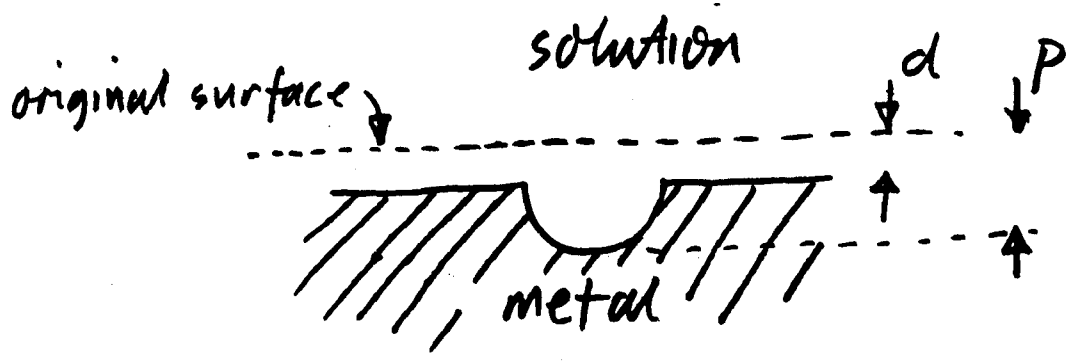
PITTING: Extreme localized attack, may perforate metal sheet/plate . . . etc.

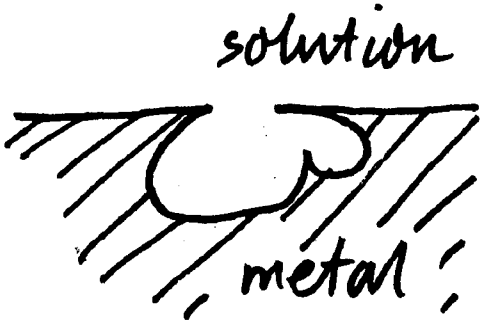


"Pitting factor" = p / d

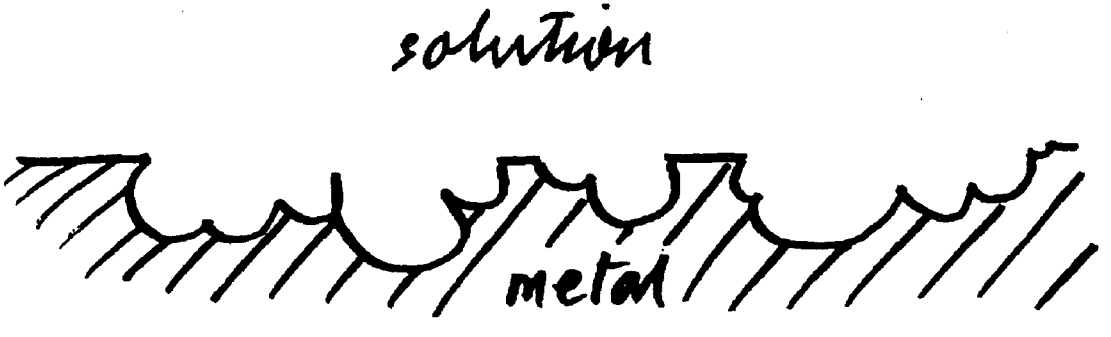
(d = average penetration from weight loss;

p = deepest penetration)

"Undercutting"



pit opening usually < 1 mm.



Pits may overlap to give the appearance of rough, general "wastage".

Pitting is an insidious and destructive form of corrosion:

- **difficult to detect (pits may be small on surface, but extensive below surface from undercutting; may be covered with deposit);**
- **can cause equipment to fail (by perforation) with very little weight loss;**
- **difficult to measure as pit depth and distribution vary widely under (nominally) identical conditions;**
- **"incubation" period may be months or year.**

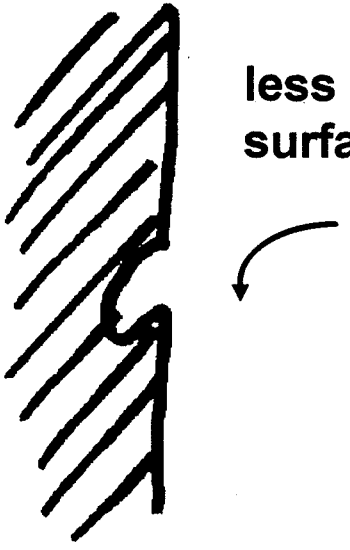
Pitting of 18-8 stainless stel by acid-chloride solution.

Pitting of stainless steel condenser tube.

Pits usually occur an upward-facing horizontal surfaces, and grow downwards:

pit growth

less frequently on vertical surfaces;



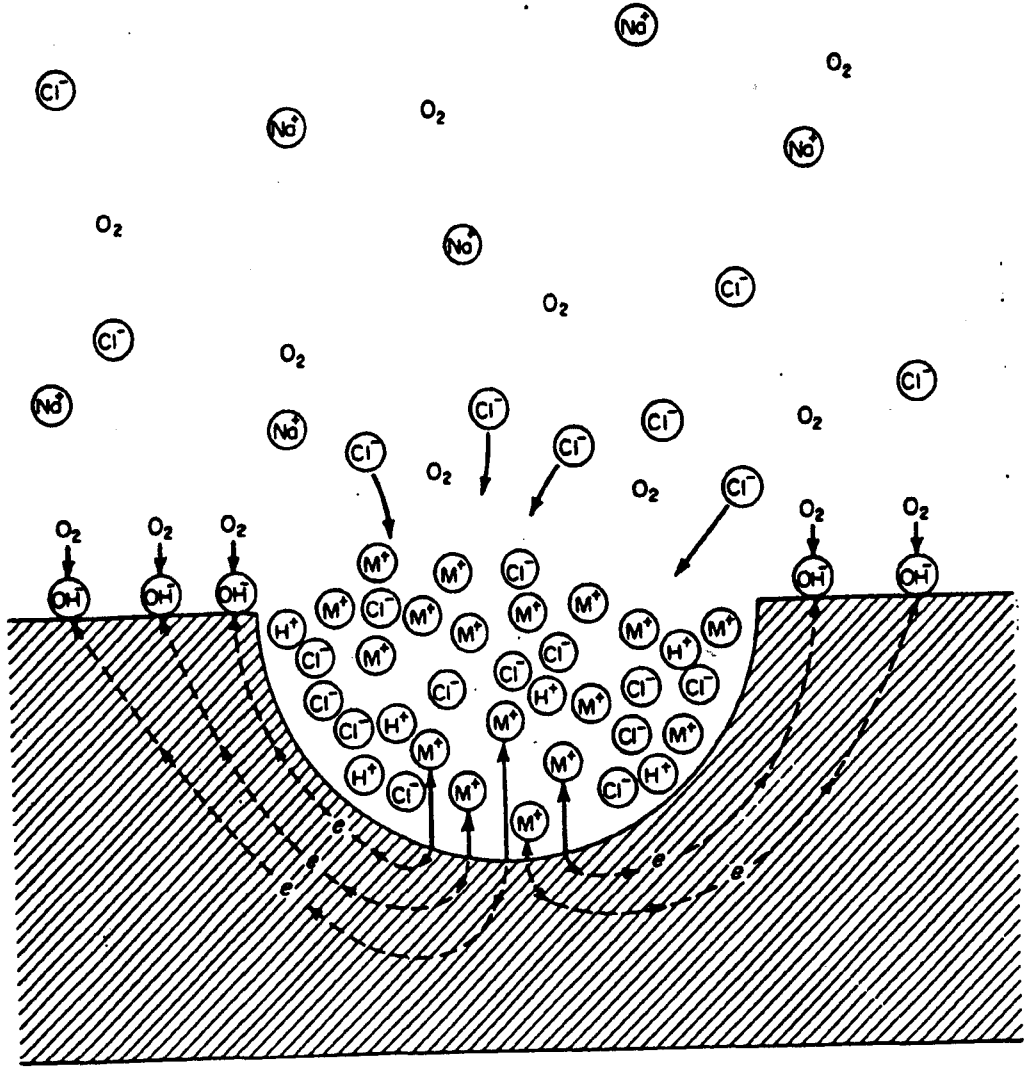
pit growth

rarely on downward-facing surfaces;

pit growth

Gravity is involved.

<u>Mechanism</u>: Has some features in common with CREVICE CORROSION.... consider metal M being pitted by aerated NaCl solution...

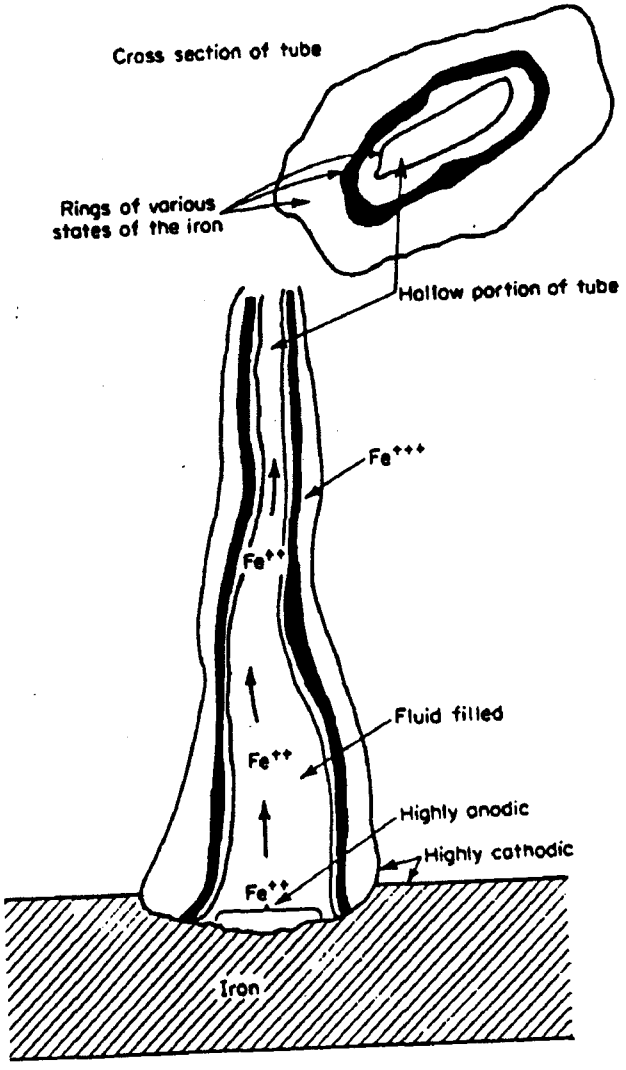


Autocatalytic processes occurring in a corrosion pit .

Remember:

- **inside pit - anodic, rapid dissolution;**
- **outside pit - cathodic, O_2 reduction;**
- **most M^+ will hydrolyse, form H^+;**
- **positive charges attract Cl^- ions;**
- **H^+ and Cl^- accelerate metal dissolution;**
- **high ionic concentrations in pit make O_2 solubility very low;**
- **high density of solution within pits means pits are more stable when growing downwards.**

At high pH (i.e., high OH^- concentration), precipitation of ion hydroxides and oxidation to Fe^{3+} oxides can lead to corrosion product "caps" or "tubes" around pits on steels.



Corrosion tube growth mechanism.

Metals Susceptible to Pitting

Most often, passivating metals, especially stainless steels, often in passivating environments (e.g., containing oxygen) but with agents such as Cl^- that attack the passive oxide film.

SENSITIZED SS particularly vulnerable: (its heat treatment has depleted the grain boundaries of Cr by precipitating chromium carbide).

COLD WORKING increases pitting attack, perhaps dislocation pattern is important.

DISCUSS

ETCHED or GROUND surfaces more likely to pit than polished surfaces.

Stainless Steel more susceptible than Carbon Steel (though CS will have more rapid GENERAL CORROSION).

Some alloys developed especially to resist pitting.

Effects of alloying on pitting resistance of stainless steel alloys

Element	Effect on pitting resistance
Chromium	Increases
Nickel	Increases
Molybdenum	Increases
Silicon	Decreases; increases when present with molybdenum
Titanium and columbium	Decreases resistance in $FeCl_3$ other mediums no effect
Sulfur and selenium	Decreases
Carbon	Decreases, especially in sensitized condition
Nitrogen	Increases

Source: N. D. Greene and M. G. Fontana, *Corrosion* 15:25t (1959).

Pitting Environments

Usually, solutions containing chloride or chlorine-containing ions (e.g., hypochlorites [bleaches]) have strong pitting tendencies.

Bromides are also aggressive, but fluorides and iodides are not.

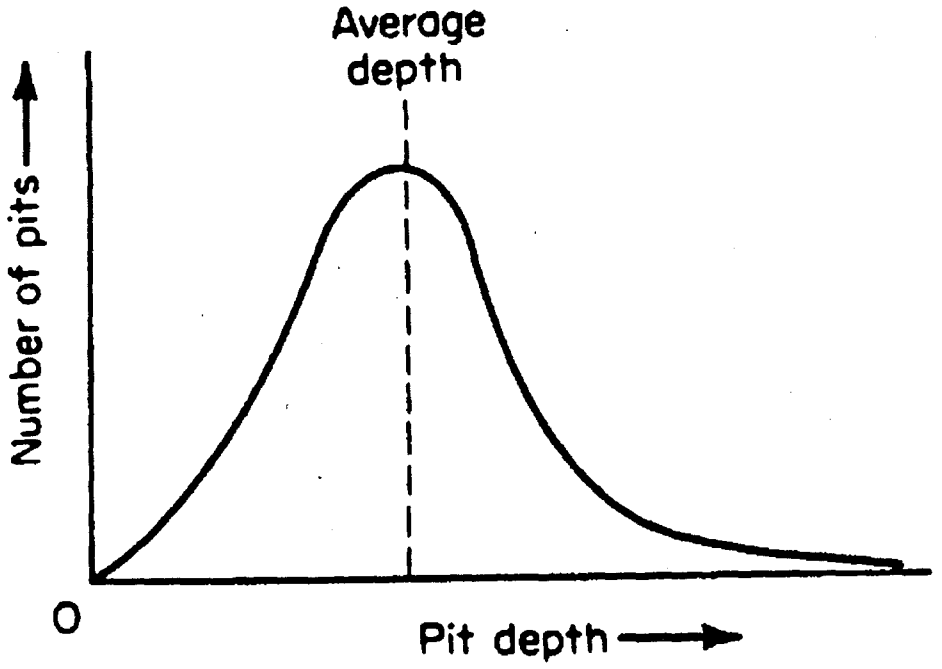
Cupric, ferric and mercuric ions promote pitting . . . easily reduced cathodically and do not require dissolved O_2; $CuCl_2$ and $FeCl_3$ are extremely aggressive (latter used as a test solution).

Thiosulphate ion ($S_2O_3^{2-}$) may also promote pitting.

Evaluating Pitting Attack

Weight loss of test specimens no good (. . . why ?).

Measurement of pit depth complicated because of statistical variations.

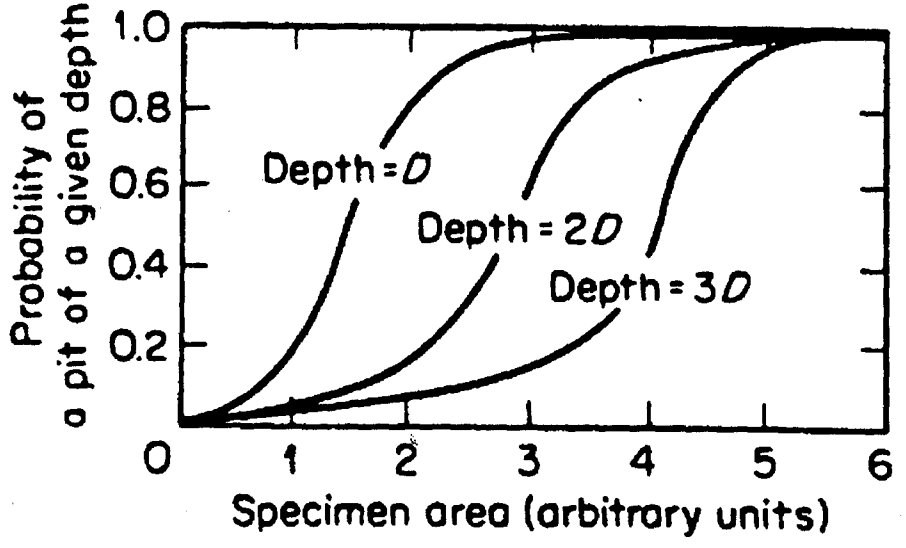


Relationship between pit depth and the number of pits appearing on a corroded surface.

Average pit depth of little use, since it is the deepest pit that causes failure.

MAXIMUM PIT DEPTH can be a useful way of expressing pitting corrosion, and for comparing pitting resistance of standard test samples.

HOWEVER, statistical nature of pitting means that sample size is important.



Pit depth as a function of exposed area.

Should never predict lifetime of plant component tests on small samples.

Prevention of Pitting

- **Reduce aggressiveness of environment (e.g., [Cl⁻], T, acidity, oxidizing agents).**
- **Use resistant materials:**

	Type 304 ss
Increasing	**Type 316 ss**
Resistance	**Hastelloy F, Nionel, Durimet 20**
	Hastelloy C, Chlorinet 3
	Titanium

- **Line with resistant materials.**
- **Modify design to eliminate stagnant areas, avoid sludge and deposit build-up, have proper drainage.**
- **Add inhibitor AFTER CAREFUL REVIEW: if attack not stopped completely might make situation worse.**