WHAT IS CORROSION?

Usually: reaction of a metal with its environment

e.g. rusting of iron:

4 Fe + $3O_2$ + $2H_2O \rightarrow 4$ Fe OOH (lepidocrocite)

BUT high temperature corrosion of iron:

3 Fe + $4H_2O \rightarrow Fe_3O_4$ (magnetite) + $4H_2$

Sometimes, non-metals are said to corrode

e.g. degradation of graphite moderator in a CO₂ reactor (nuclear)

 $C + CO_2 \rightarrow 2CO$ (may be inhibited by addition of CH_4)

Discussion:

- Other examples of metal corrosion?
- Do buildings corrode (brick, stone, concrete)?
- What about erosion? is it a corrosion phenomenon?
- Can corrosion be desirable?
- Other types of corrosion (e.g., plastic, wood, etc.)?

CORROSION IS A SPONTANEOUS PROCESS:

Energy is released as material proceeds towards "natural" state i.e. the thermodynamically stable state.

Thus, rusting of iron is a reversion towards the (hydrated - usually) ore; e.g., if lepidocrocite is dehydrated, we get:

Corrosion, especially of metals, is <u>usually</u> an oxidative process

- the metal loses electrons:

e.g.,
$$4 \text{ Cu} + \text{ O}_2 \rightarrow 2 \text{ Cu}_2\text{O}$$

$$Zn + 2H \text{ Cl} \rightarrow Zn \text{ Cl}_2 + \text{H}_2$$
metal Oxidation states? ion oxidation states?

CORROSION IS A SPONTANEOUS PROCESS (continued)

Regard such oxidations as two separate reactions occurring simultaneously e.g. for metal M:

$$M \rightarrow M^{Z+} + Z. e$$
 (oxidation)

Z. e. +
$$---$$
 O₂ \rightarrow --- O²⁻ (reduction)

$$Z$$
 $M + \longrightarrow O_2 \longrightarrow M O_{Z/2}$ (combined)

$$Zn \rightarrow Zn + 2e$$

2 H Cl + 2e \rightarrow H₂ + 2 Cl

what is the reduced species?

COST OF CORROSION

How do costs of corrosion arise?

Costs arise from:

- replacement of components (e.g., car mufflers ≤ \$ 100 muclear steam generators ≤ \$ 100 mm);
- loss of production (equipment or process downtime);
- extra process control to minimize corrosion (e.g., chemical additives and corrosion inhibitors);
- application and maintenance of coatings (e.g., Cr-plated bumpers; paints; sheathing of nuclear fuel);
- loss of process efficiency (e.g., fouling of Heat Exchangers by corrosion products, plugging of columns by corrosion products);
- radioactivity build-up (in reactor coolants from activation of corrosion products);
- cleaning (to restore appearance, to restore performance, to decontaminate, etc.);
- others?
 - inspection to verify that safety/regulatory limits have not been exceeded.

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COST OF CORROSION (continued)

Cost estimated at ≈ 300 billion (U.S.)/ Annum for metallic corrosion alone in

U.S.A. in 1993 (figure extrapolated from a 1975 study)

Equivalent for Canada ≈ \$ 40 billion (Can.)Annum

NOTE: Most of these costs are UNAVOIDABLE (i.e., avoiding them would cost known technology to reduce corrosion)

U.S.A. ≈ \$40 billion (U.S.) /Annum

Canada ≈ \$ 6 billion (Can.) /Annum

Many industries rely on corrosion:

- Muffler Shops,
- Paint Manufacturers,
- Nuclear Steam Generator Manufacturers;
- Steel companies;
- Others

Is corrosion a good thing?

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SOME COST CONSIDERATIONS

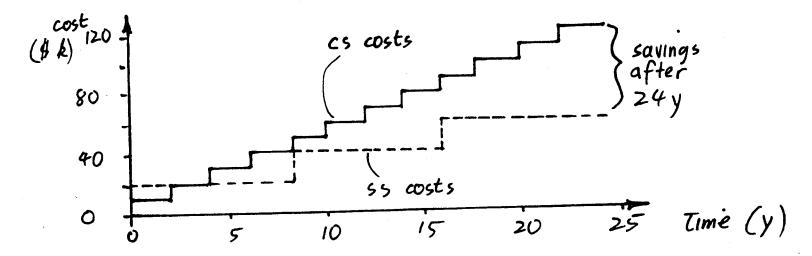
Decision to replace a material with a more corrosion-resistant and therefore more expensive material depends upon:

- difference in initial "investment" or cost of installation;
- what the extra "investment" would earn elsewhere (e.g., in the bank)

If the "return on investment", ROI, for the more expensive material is low, then it is cheaper to keep replacing more often with the same, cheap material.

EXAMPLE (from Fontana)

A carbon steel HX costs \$10k, has to be replaced every 2 years. Is it worthwhile to substitute stainless steel (SS) which costs \$20K but lasts 8 years?



ROI =
$$\frac{2.5k}{y} \times \frac{1}{10k} \times 100\% = \frac{25\%}{y}$$

In general

where:

a & b : present and proposed (i.e., alternative) installations respectively;

O = annual costs (maintenance, operation, losses, etc.);

| = "investment" (installation cost);

n = anticipated lifetime 9 years);

ROI = "return on investment" (% / year).

Most accurate estimates involve compound interest calculations:

"present value" (PV) and

"future value" (FV) or

"present worth" and "future worth" (equivalent concepts)

FV and PV are related by the compound interest calculation:

$$FV = PV (1+i)^n$$

where i = interest rate (fraction / period);

n = number of periods.

(N.B. compounding period usually = 1 year).

EXAMPLE (after FONTANA)

\$1.0k invested for 10 years at 6%

$$FV = $1,000 (1 + 0.06)^{10}$$
$$= $1,790.85.$$

In other words, the PRESENT VALVE of an investment of \$ 1,790.85 made in 10 years time at an interest rate of 6% is \$ 1,000 IN CONSTANT DOLLARS (no inflation)

For a series of anticipated (i.e., future) cash flows, C, the PRESENT VALVE formula

$$PV = \frac{FV}{(1+i)^n}$$

can be generalized to the NET PRESENT VALVE, NPV

NET PRESENT VALVE, NPV:

NPV =
$$-1 + \frac{C_1}{(1+i)^1} + \frac{C_2}{(1+i)^2} + \dots + \frac{C_n}{(1+i)^n}$$

where:

I = initial investment

 C_1 = cash flow in year 1

 $C_2 = "$

 $C_n =$ " n

NOTE: costs (expenses) are negative, gains (profits) are positive, C can be +ve <u>OR</u> -ve.

For corrosion costs:

- I could be initial installation cost of a material;
- C could be future operating, maintenance, replacement costs (-ve) combined with profits, gains etc. (+ve)

EXAMPLE (after Fontana)

Which is the cheapest Heat Exchanger material over an 8-year period, assuming an interest rate of 10%:

- (1) Carbon Steel (CS), costing \$8,000 and lasting 2 years?
- (2) Anodically-protected (AP) carbon steel costing \$8,000, requiring a \$7,000 potentiostat and lasting > 8 years with costs = \$ 1,100/year? or
- (3) Stainless Steel (SS) costing \$20,000 and lasting 8 years?

ANNUAL COSTS (\$)

<u>year</u>	<u>cs</u>	CS (AP)	<u>ss</u>
0	8,000	15,000	20,000
1	-	1,100	-
2	8,000	1,100	-
3	-	1,100	-
4	8,000	1,100	-
5	•	1,100	-
6	8,000	1,100	-
7	, =	1,100	-
8		1,100	

Carbon Steel:

NPV =
$$-8000 - 8000 - 8.000 - 8.000 - 8.000 - (1.1)^2 - (1.1)^6$$

Carbon Steel (Anodically-protected):

NPV =
$$-15000 - \underline{1,100} - \underline{1,100} - \underline{1,100} - \dots - \underline{1,100}$$

 $(1.1)^1 (1.1)^2 (1.1)^3 (1.1)^8$
= $-\$ 20,869$.

Stainless Steel:

$$NPV = -20,000.$$

i.e., at 10% interest, SS is least cost

N.B., CS (AP) is cheapest at i between 14.7% and 24.1%; above an interest rate of 24.1%, CS becomes cheapest.

Let's introduce some positive cash flow. What happens in the example if the reduced heat transfer of the Stainless Steel decreases revenue by 40%?

<u>year</u>	<u>CS</u>	CS (AP)	<u>ss</u>
0	- 8,000	-15,000	-20,000
1	•	-1,100	
	+ x	+ x	+0.6x
2	-8,000	-1,100	
_	+ x	+χ	+0.6x
3		-1,100	
	+x	+χ	+0.6x
4	-8,000	-1,100	
	+ x	+χ	+0.6x
5		-1,100	
	+χ	+ x	+0.6x
6	-8,000	-1,100	
	+x	+ x	+0.6x
7		-1,100	
	+x	+x	+0.6x
8		-1,100	
	+x	+x	

CS: NPV =
$$-8,000 + \frac{x}{(1.1)^1} - \frac{(8,000-x)}{(1.1)^2} + \frac{x}{(1.1)^3} - \frac{(8,000-x)}{(1.1)^4} + \dots \frac{x}{(1.1)^8}$$

= $-24,592 + x \left(\frac{1}{(1.1)} + \frac{1}{(1.1)^2} + \dots \frac{1}{(1.1)^8} \right)$
= $-24,592 + 5.34 \times$

CS (AP):

$$NPV = -20,869 + 5.34 x$$

<u>SS:</u>

NPV =
$$-20,000 + 0.6 * 5.34 x$$

= $-20,000 + 3.20 x$

For SS to be cheaper than CS x < \$2,275/year (VERY SMALL!)