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 CO_2 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:

$$2Fe\ OOH \rightarrow Fe_2O_3 \text{ (haematite)} + H_2O$$

Corrosion, especially of metals, is usually an oxidative process

- the metal loses electrons:

e.g., $4\ Cu + O_2 \rightarrow 2\ Cu_2O$

$Zn + 2H\ Cl \rightarrow Zn\ Cl_2 + H_2$

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:

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

$$Z.\,e. + \frac{Z}{4} O_2 \rightarrow \frac{Z}{2} O^{2-} \qquad \text{(reduction)}$$

$$M + \frac{Z}{4} O_2 \rightarrow M\,O_{Z/2} \qquad \text{(combined)}$$

Therefore:

$$Zn \rightarrow Zn + 2\,e$$

$$2\,H\,Cl + 2e \rightarrow H_2 + 2\,Cl^-$$

what is the reduced species?

COST OF CORROSION

How do costs of corrosion arise?

Costs arise from:

- **replacement of components (e.g., car mufflers $\leq$ \$ 100
nuclear steam generators $\leq$ \$ 100 M);**
- **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.**

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?

SOME COST CONSIDERATIONS

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

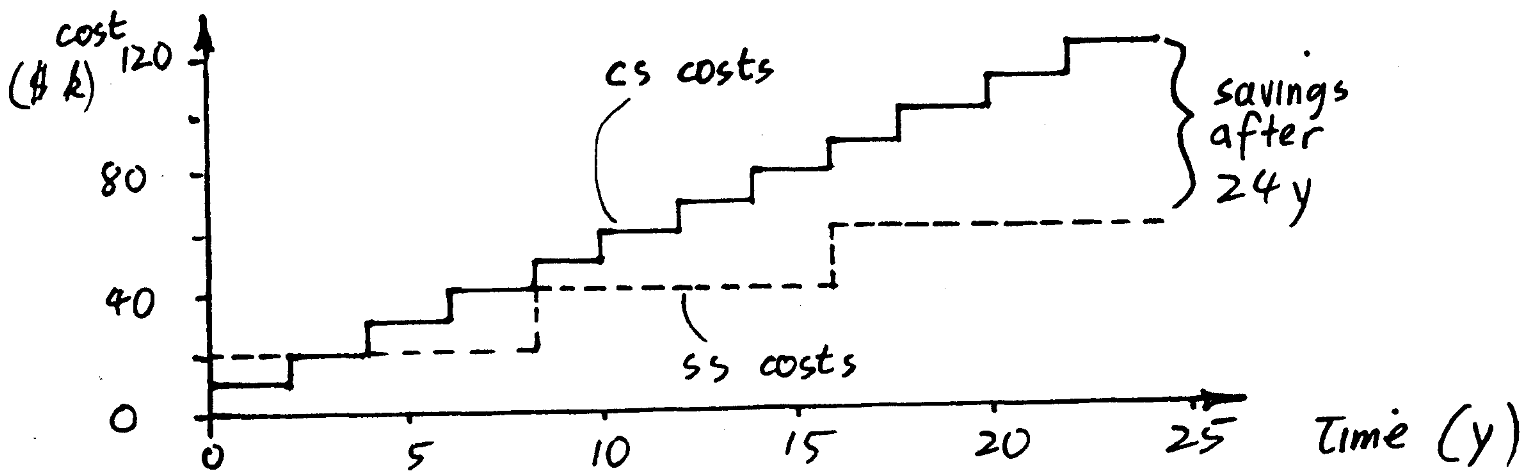
- **difference in initial "investment" or cost of installation;**
- **what the extra "investment" would earn elsewhere (e.g., in the bank)**

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?



saving after 24 y = \$12k - \$60k

average "return" = $\dfrac{\$120k - \$60k}{24}$ = \$2.5k/y

initial "investment" (= difference in cost)
= \$20k - \$10k - \$10k

ROI = $\dfrac{\$2.5k}{y} \times \dfrac{1}{\$\,10k} \times 100\% = \dfrac{25\%}{year}$

In general

$$ROI = \frac{\left(O_a + \frac{I_a}{n_a}\right) - \left(O_b + \frac{I_b}{n_b}\right) \times 100\%}{I_b \; - \; Ia}$$

where:

a & b : present and proposed (i.e., alternative) installations respectively;
O = annual costs (maintenance, operation, losses, etc.);
I = "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).

Therefore:

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

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:

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

where:

I	=	initial investment
C_1	=	cash flow in year 1
C_2	=	" " 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 ($)

year	CS	CS (AP)	SS
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:

$$\text{NPV} = -8000 - \frac{8000}{(1.1)^2} - \frac{8.000}{(1.1)^4} - \frac{8.000}{(1.1)^6}$$

Carbon Steel (Anodically-protected):

$$\text{NPV} = -15000 - \frac{1.100}{(1.1)^1} - \frac{1.100}{(1.1)^2} - \frac{1.100}{(1.1)^3} - \ldots\ldots - \frac{1.100}{(1.1)^8}$$

$$= -\$\ 20{,}869.$$

Stainless Steel:

$$\text{NPV} = -20{,}000.$$

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%?

TABLE OF CASH FLOWS (x = revenue)

year	CS	CS (AP)	SS
0	- 8,000	-15,000	-20,000
1		-1,100	
	+x	+x	+0.6x
2	-8,000	-1,100	
	+x	+x	+0.6x
3		-1,100	
	+x	+x	+0.6x
4	-8,000	-1,100	
	+x	+x	+0.6x
5		-1,100	
	+x	+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

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

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

$$= \underline{-24{,}592 + 5.34\,x}$$

CS (AP):

$$NPV = -20{,}869 + 5.34\,x$$

SS:

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

$$= -20{,}000 + 3.20\,x$$

For SS to be cheaper than CS (AP)

$$-20{,}000 + 3.20\,x > -20{,}869 + 5.34\,x$$

$$2.14\,x < 869$$

or $x <$ \$406/year (TRIVIAL!)

For SS to be cheaper than CS

$x <$ \$2,275/year (VERY SMALL!)