

Processes P6: Corrosion and Sustainability

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PRRE1003

Resources, Processes & Materials Engineering

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LECTURE 10

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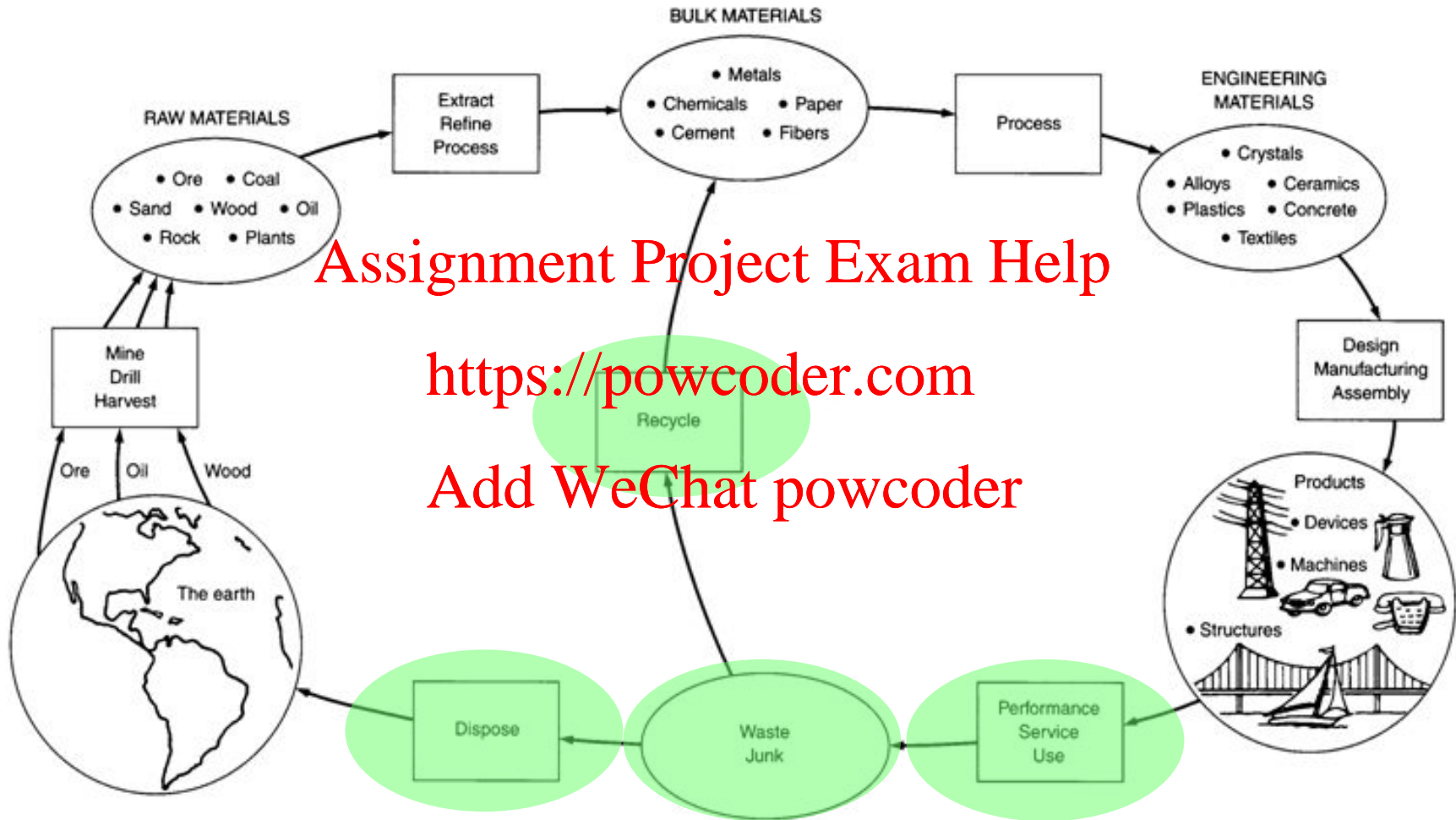
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Lecture focus



Reproduced from "Materials and Man's Needs", National Academy of Sciences, Washington D.C., 1974.

Lecture Outline

- Corrosion
 - oxidation, reduction, redox reactions
 - pH
 - standard reduction potential E_0
 - types of corrosion
 - corrosion protection

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- Sustainability
 - life cycle of materials
 - embodied energy
 - carbon footprint
 - circular economy



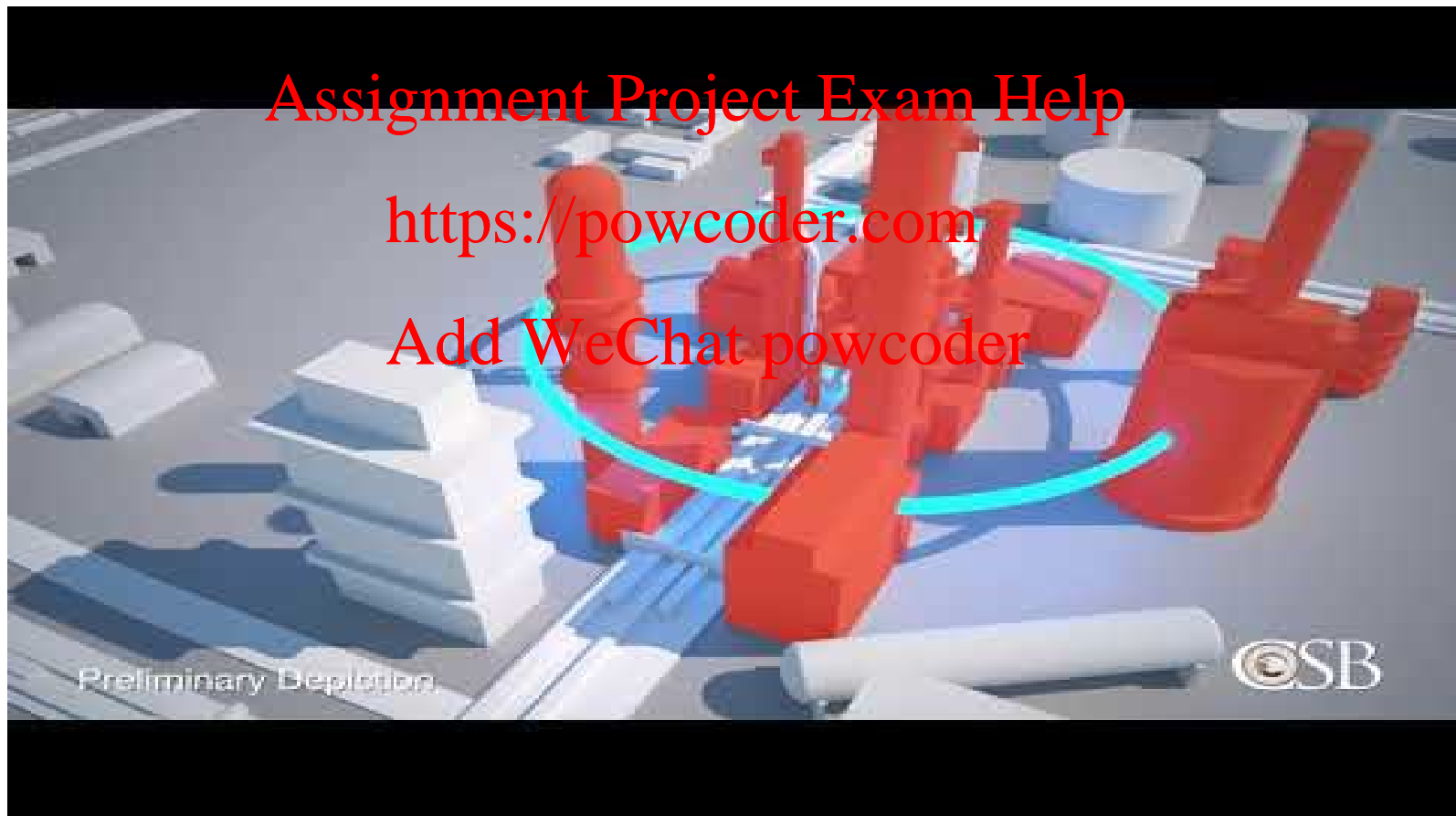
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The Cost of Corrosion

On June 21, 2019, a pipe elbow that had corroded to about half the thickness of a credit card ruptured in a Philadelphia refinery's alkylation unit, releasing process fluid that included over 2260 kg of hydrofluoric acid that formed a large ground-hugging vapour cloud. Two minutes later, the cloud ignited, causing a fire and multiple explosions that effectively closed the refinery, the largest on the US East Coast. It is estimated that most of the 300,000 kg of hydrocarbons released in that incident was burnt. The refinery was closed down, and it filed for bankruptcy in July.





The Cost of Corrosion

- The piping was susceptible to corrosion from the hydrofluoric acid that was in the process fluid. The elbow that ruptured corroded faster than the rest of the piping as a result.
- While pipe thickness in this section of the unit was periodically measured to monitor corrosion rates, the thickness of the elbow that failed had not been monitored for corrosion.
- The piece of piping that failed had a high nickel and copper content. Various industry publications have found that carbon steel with a higher percentage of nickel and copper corrodes at a faster rate than carbon steel with a lower percentage when used in a process with hydrofluoric acid.

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Corrosion and degradation

What is corrosion?

Corrosion is the process, or damage caused by the process, of destruction or deterioration of a material due to its reaction with its environment.

Corrosion usually deals with metals, which are the engineering materials most susceptible. The electrochemical oxidation of the metal, usually to form oxides, hydroxide or sulphate, is the most common type of corrosion.

Example: Rusting

The reddish-brown colour of Fe_2O_3 is formed when Fe is oxidised.

What is degradation?

Degradation is sometimes used interchangeably with the word corrosion, but can have a broader meaning. For example, material may degrade by its use – such as materials being stretched beyond its elastic limit and therefore experience mechanical degradation. Materials can also degrade due to UV light (e.g. fading, also known as photo-degradation).

When corrosion occurs in polymers or ceramics, it is normally referred to as degradation.



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Corrosion of Metals: Redox Reactions

Corrosion of metals refers to its chemical or electrochemical oxidation, in which the metal undergoes a valence change from zero to a positive value.

The corrosion process requires at least two reactions that must occur in a particular environment – *anodic* and *cathodic* reactions.

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Example: zinc corrosion in hydrochloric acid (HCl)

Oxidation at anode: $Zn \rightarrow Zn^{2+} + 2e^{-}$

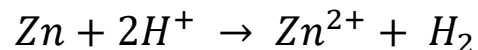
Reduction at cathode: $2H^{+} + 2e^{-} \rightarrow H_2$

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The anodic reaction, in which electrons are lost from a metal, is called *oxidation*. In the cathodic reaction, electrons are accepted by the ions to form H_2 , and this is called *reduction*.

The overall reaction is called a *redox reaction* (reduction + oxidation):



Acid and atmospheric corrosion

Example, the corrosion of copper metal in aqueous H_2SO_4 :

Copper is **oxidised** in water:



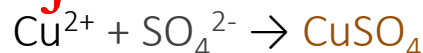
Sulphuric acid provides H^+ ions:



H^+ ions are **reduced** to H_2 molecules:



Corrosion product (**scale**) formation:



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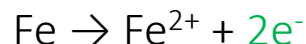
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Corrosion in alkaline media also takes place in a similar manner:

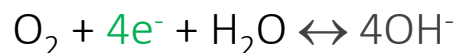
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Example, the corrosion of steel (iron based metals) in atmospheric environment:

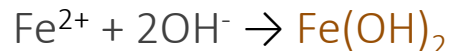
Iron is **oxidised** in water or moisture film:



Oxygen in atmosphere is **reduced**:



Corrosion product (**rust**) is formed:



Standard Reduction Potential E_0

The **standard reduction potential** is the likelihood that a particular molecule or atoms gains electrons, that is reduced. It is expressed in volts, at standard conditions (pressure of 1 atm), at 298 K and with 1M solutions; these values are determined experimentally.

When two metals are in solution, the one with the most negative E_0 value most readily loses electrons (oxidises).

	Reduction Half-Reaction	E^0 (V)	
Strongest oxidizing agent	$\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-(\text{aq})$	2.87	Weakest reducing agent
	$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.78	
	$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	1.51	
	$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$	1.36	
	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	1.33	
	$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.23	
	$\text{Br}_2(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Br}^-(\text{aq})$	1.09	
	$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	0.80	
	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	0.77	
	$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	0.70	
	$\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{aq})$	0.54	
	$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$	0.40	
	$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	0.34	
	$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq})$	0.15	
	$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0	
	$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.13	
	$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.26	
	$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cd}(\text{s})$	-0.40	
	$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.45	
	$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76	
	$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83	
	$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Al}(\text{s})$	-1.66	
	$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.37	
	$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71	
Weakest oxidizing agent	$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.04	Strongest reducing agent

Corrosion in liquids: pH

In aqueous solutions, water dissociates to give H^+ and OH^- ions:



The molar concentration of ions is denoted by square brackets, and in pure water, the concentration (mol/L) of H^+ and OH^- ions is constant:

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 $[H^+].[OH^-] = \text{constant} = 10^{-14}$

Therefore,

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 $[H^+] = [OH^-] = 10^{-7}$

Definition of pH:

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 $pH = -\log_{10}[H^+]$

Therefore, the pH of pure water is: $pH = -\log_{10}[10^{-7}] = 7$

When acids dissociate in aqueous solution, they increase the $[H^+]$ to values above 10^{-7} , and therefore, reduce the pH to below 7.

Corrosion occurs in pure water, if oxygen is available, and is enhanced by impurities, acids and alkalis.

Corrosion in liquids: pH

Example:

Household vinegar has a pH of 2.8. What is the molar concentration of $[H^+]$ ions?

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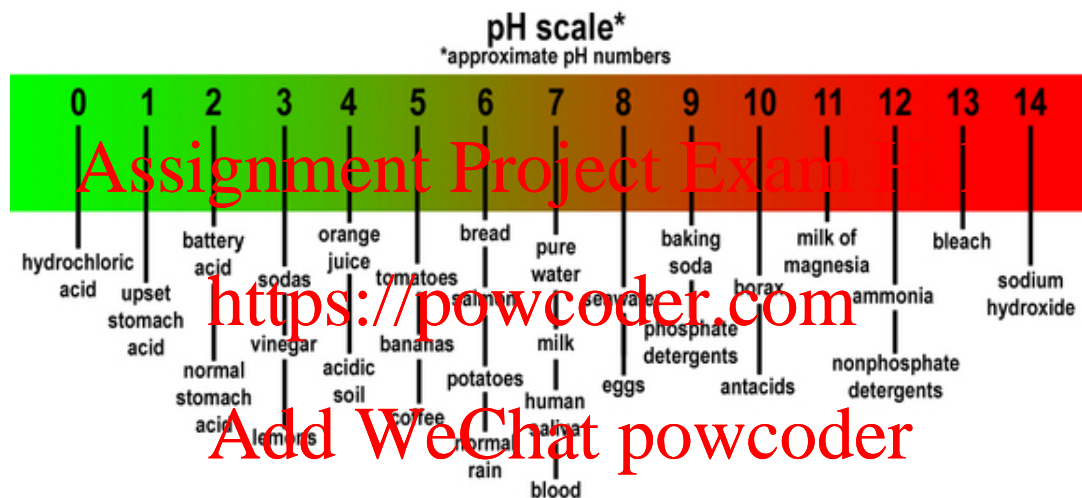
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Answer: 0.001585 or 1.585×10^{-3} mol/L

Corrosion in liquids: oxidation and reduction

Corrosion in acids and alkalis is an electrochemical reaction.



Sulphuric acid provides H^+ ions and this *decreases* the pH:



Sodium hydroxide provides OH^- ions and this *increases* the pH:



Types of corrosion

Classification of corrosion is not identical across textbooks or literature, but the major types are listed here:



General Corrosion (corrosive attack dominated by uniform thinning)

- Atmospheric – on steel tanks, containers etc.
- Galvanic – between dissimilar metals/alloys or microstructural phases
- Liquid Metal – on SS exposed to a NaCl environment
- **Biological** – on steel (Cu/Zn alloys in seawater)
- Stray-Current – on a pipeline near a railroad

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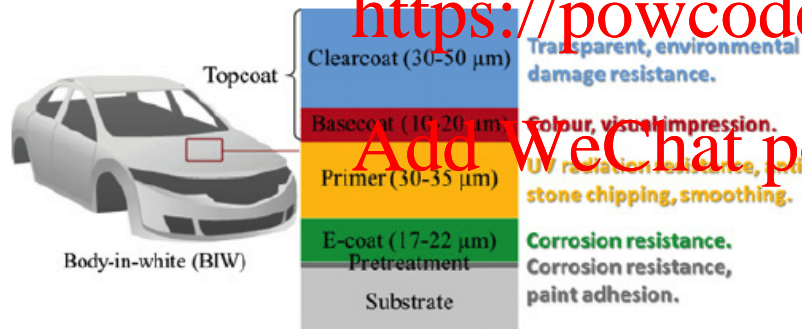


Localised Corrosion (high rates of penetration at specific sites)

- Crevice – associated with a stagnant electrolyte, occurring on metal/alloy surface holes, flange surfaces, etc.
- Filiform – a type of crevice corrosion, occurring underneath a protective film. Common on food and beverage cans
- **Pitting** – extremely localized, causing destructive pits
- Oral – on dental alloys exposed to saliva
- Biological – due to fouling organisms on steel in marine environments
- Selective Leaching – a metal removal process from the base alloy matrix (e.g. dezincification in brass)

Corrosion Protection

- 1) **Material Choice.** Choosing the correct material for the environment is the best option for preventing corrosion.
- 2) **Protective Coatings.** These prevent corrosion primarily by forming a physical barrier separating metal substrates from corrosive environment. Some coatings can also act as a sacrificial layer or serve as a reservoir for corrosion inhibitors. Coatings are the most common corrosion control strategies (88.3% of total cost of corrosion control). Coatings can eventually degrade from UV exposure, chemical attack, poor surface preparation, etc.



Xu, Zhenhai et al. (2015). MATEC Web of Conferences. 21. 05012. 10.1051/mateconf/20152105012.

<https://higherlogicdownload.s3.amazonaws.com/NACE/cedda8a4-c3c0-4583-b1b6-3b248e6b1f2/UploadedImages/Resources/pdf/ccsupp.pdf>

- 3) **Corrosion Inhibitors.** These are chemicals that reduce or inhibit the rate of corrosion. Some work by modifying the pH of the environment, or by suppressing the anodic or cathodic steps of the redox reaction. Polymers, chromates, calcium bicarbonate and thiourea are examples of corrosion inhibitors for different purposes.

Corrosion and Sustainability

In the *Resources* section of this unit, we learnt about the origins of all of the world's products. Much of the global debate about plastics, in particular, are about their origins in non-renewable fuels, and also their limited recyclability and/or high cost of disposal.

The following video provides a perspective on materials in the average household. When you watch it, consider how material choices impact safety, cost, lifestyle and sustainability.

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Learning Outcome Check

- ❑ Differentiate between corrosion and degradation.
- ❑ Calculate the pH of a solution, by using its $[H^+]$, or $[OH^-]$ concentration.
- ❑ Understand the concepts of oxidation and reduction, with regards to the loss or gain of electrons.
- ❑ Write a redox reaction, and also the relevant oxidation and reduction half-reactions.
- ❑ Use the standard electrode potential to predict the potential for corrosion.
- ❑ Recognise whether a given occurrence of corrosion is *general* or *localised*.
- ❑ Understand how corrosion prevention plays a part in the sustainable use of materials.

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Sustainability

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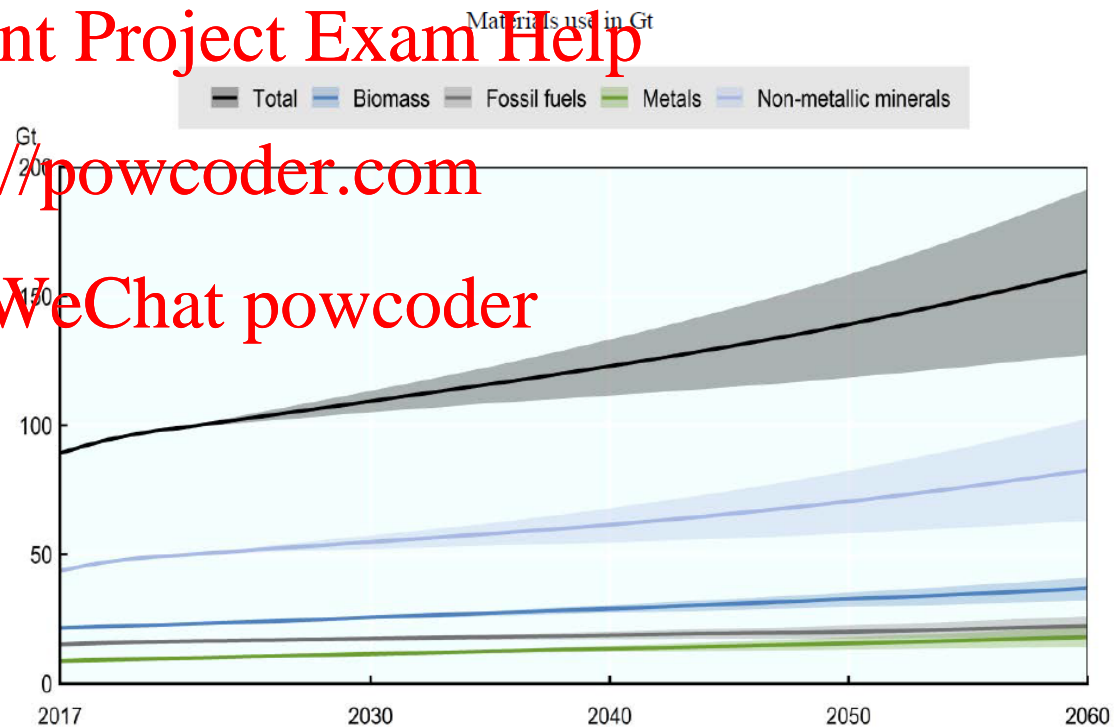
The Problem: World Consumption of Materials

The global consumption of materials is increasing and is expected to reach >160 billion tonnes per year by 2060, as shown in the Figure below. Approximately 10 billion tonnes of engineering materials are produced each year. Steel, wood (for construction purposes) and concrete are the engineering materials with the largest production rates by mass.

Whilst metals, polymers and ceramic constitute most of the engineering materials produced, the others listed below are also growing at an unsustainable rate, most matching the global production of alloys by mass, despite being a lot lighter:

- Structural woods – for construction
- Man-made fibres – polyesters, nylon, plastics, polyurethanes etc
- Natural fibres = hemp, linen, cotton, wool, silk etc
- Carbon-fibre – used to reinforce high-performance composites

Figure 1.5. Uncertainties on materials use is especially large for non-metallic minerals



Source: OECD ENV-Linkages model.

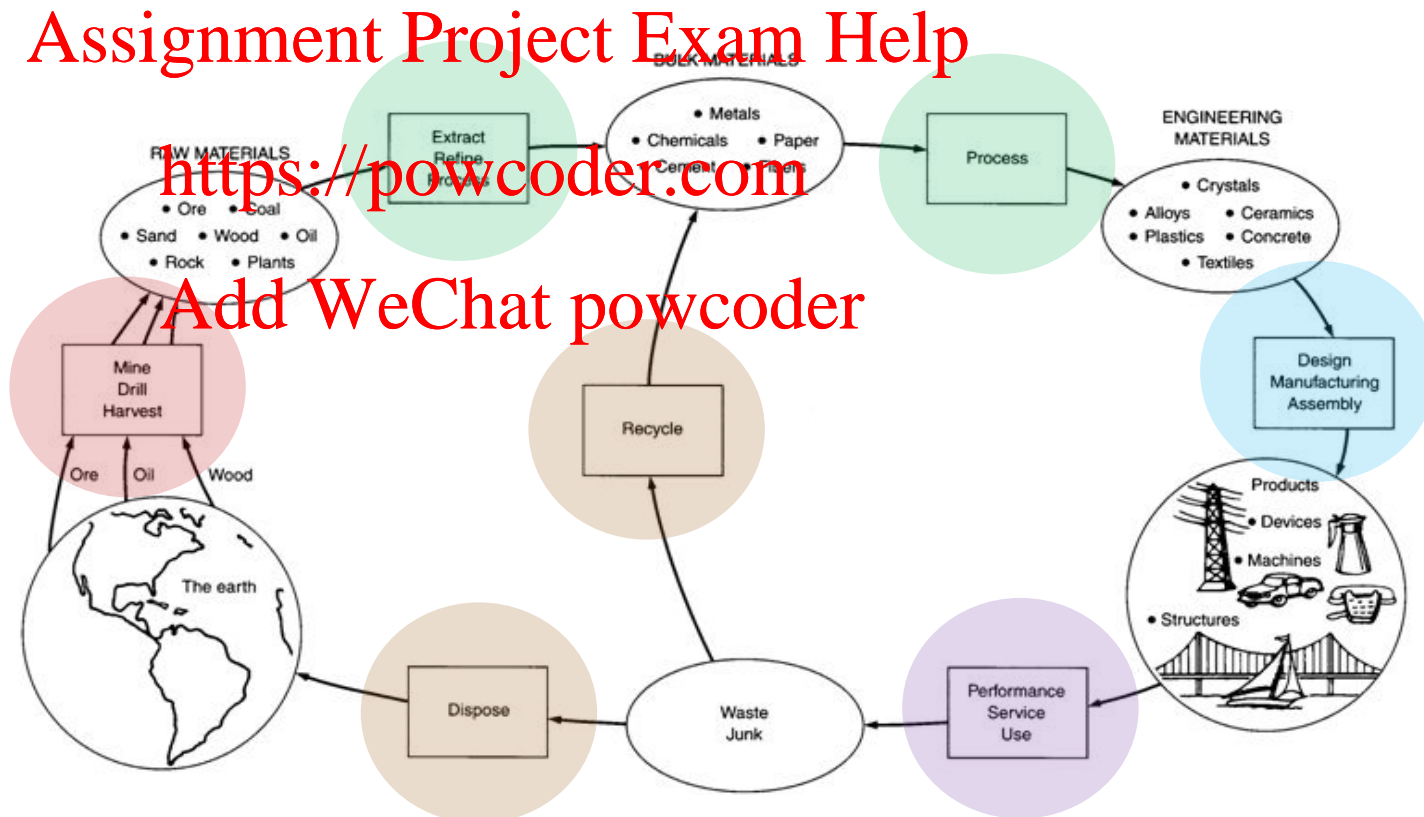
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Life cycle analysis

Whether we consider bulk material or engineering material production, the many processes that raw materials undergo for conversion into useful materials require both other materials and also energy. In a LCA, we lump these processes together to call them Material Production.

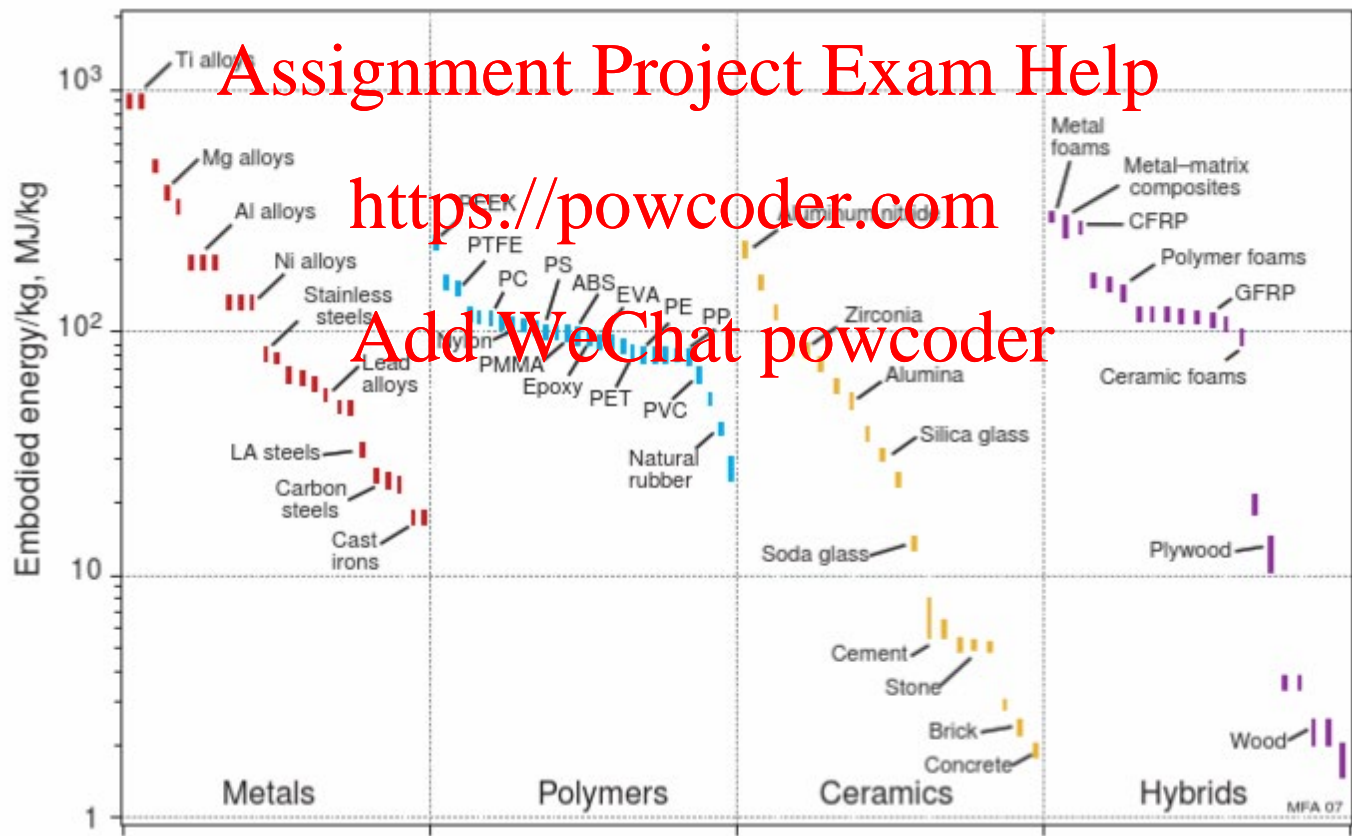
A traditional life cycle analysis (LCA) is divided into 5 steps:

1. Raw Material Acquisition
2. Material Production
3. Product Manufacture
4. Product Use
5. Product Disposal



Embodied energy

Embodied energy is a measure of the energy per unit mass required to produce 1 kg (or 1 m³ if by volume) of a material (bulk or engineering material), and is measured in MJ/kg. Production energy expenditure encompasses all processes from resource to raw material production to final material in its required form. The embodied energy is highly dependent upon the processes, labour and even location.



Carbon footprint

The carbon footprint of a material, $CO_{2,e}$ is the associated release of CO_2 , adjusted to include the carbon-equivalent of other associated emissions, in kg/kg. Carbon footprint, like embodied energy, is highly dependent upon the processes, labour and even location.

Example:

An aluminium alloy (0.75 mm thickness) is used for the casing of a power tool. It is proposed to replace it with a polypropylene (PP) moulding of the same area but 3 mm thickness. Does this increase/decrease the embodied energy, and carbon footprint, given the following data?

	Density (kg/m ³)	Embodied energy (MJ/kg)	Carbon footprint (kg/kg)
Aluminium alloy	2700	210	12.5
Polypropylene (PP)	900	80	3.15



From a Linear to a Circular Economy

The recycle fractions of current materials is shown in the chart below. As observed, most of the lead, about half of the steel and a third of aluminium is recycled. Recycling is well below 10% for most plastics, ceramics and other products, except notably for paper, cardboard and a few selected materials.

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Current unsustainability in material production and usage leads to.

- Increasing landfill
- Increasing pollution of land, water and atmosphere
- Decreasing supplies of resources

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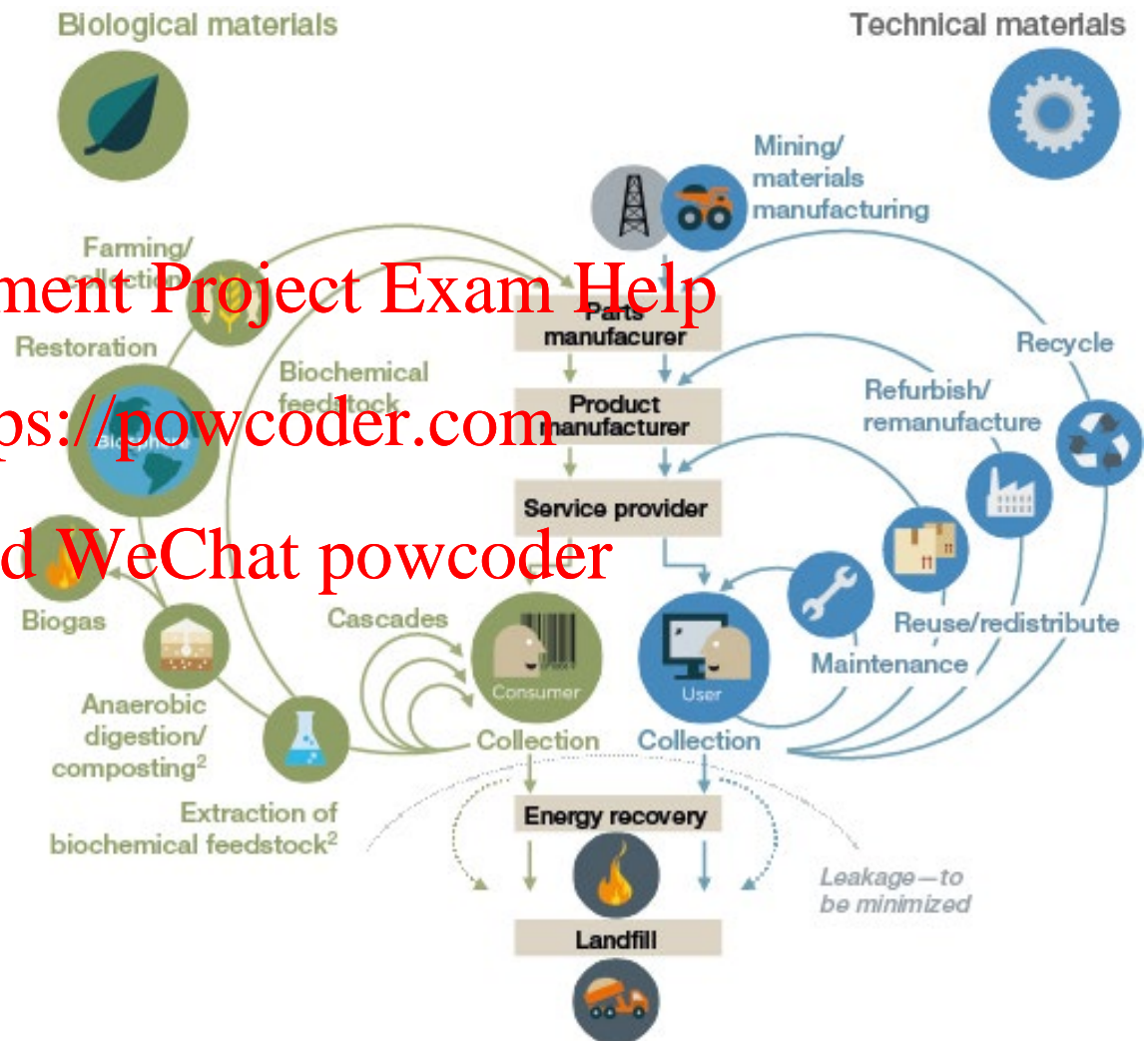
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This necessitates a different model of material production and consumption. In 2013, the Ellen McArthur Foundation and McKinsey Company commissioned a report that proposed a circular model, to replace the linear model of material production, usage and disposal (with a small fraction of recycle).

From a Linear to a Circular Economy

The model of the Circular Economy aims to design out waste, by designing products for a cycle of disassembly and reuse. The key components of a circular economy are as follows:

1. Design out waste.
2. Build resilience through diversity.
3. Rely on energy from renewable sources. Think in systems.
4. Think in 'systems'.
5. Waste is food.



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From a Linear to a Circular Economy

The key components of a circular economy are as follows:

1. **Design out waste.** Waste does not exist when the biological and technical components of a product are designed for disassembly and refurbishment. The biological nutrients are non-toxic and can be simply composted. Technical nutrients—polymers, alloys, and other man-made materials are designed to be used again.
2. **Build resilience through diversity.** Modularity, versatility, and adaptivity are prized features that need to be prioritised in an uncertain and fast-evolving world.
3. **Rely on energy from renewable sources.** Systems should ultimately aim to run on renewable sources. Working towards efficiency alone—a reduction of resource and fossil energy consumed per unit of manufacturing output—will not alter the finite nature of their stocks but can only delay the inevitable.
4. **Think in 'systems'.** The ability to understand how parts influence one another within a whole, and the relationship of the whole to the parts, is crucial. Elements are considered in their relationship with their infrastructure, environment, and social contexts.
5. **Waste is food.** On the biological nutrient side, the ability to reintroduce products and materials back into the biosphere through non-toxic, restorative loops is at the heart of the idea. On the technical nutrient side, improvements in quality are also possible; this is called upcycling. The drive to shift the material composition of consumables from technical towards biological nutrients and to have those cascade through different applications before extracting valuable feedstock and finally reintroducing their nutrients into the biosphere, rounds out the core principles of a restorative circular economy.

Learning Outcome Check

- ❑ What are the 5 key steps in a *life cycle analysis (LCA)* of materials?
- ❑ What is the definition of *embodied energy*, and what factors can give a different embodied energy for the same end product?
- ❑ Consider the Resources and Processes that are the source of key Engineering Materials (metals, polymers, ceramics, and hybrids), and compare those with the highest range of embodied energy (100-1000 MJ/kg) and the lowest range of embodied energy (1-10 MJ/kg) (see Figure on page 22).
- ❑ Define the term *carbon footprint*.
- ❑ Use the concepts of embodied energy and carbon footprint to make decisions on choice of product.

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From a Linear to a Circular Economy

As engineers of the future, you have an enormous opportunity to create a new future.

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<https://youtu.be/zCRKvDyyHmI> (3:48 mins)

Lecture Summary

✓ Corrosion

- oxidation, reduction, redox reactions
- pH
- standard reduction potential E_0
- types of corrosion
- corrosion protection

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✓ Sustainability

- life cycle of materials
- embodied energy
- carbon footprint
- circular economy