Industrial Inorganic Chemistry (chem427)
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Chapter one : Manufacture Of Portland Cement

introduction :

Portland cement is a fine powder generally gray in color. Although the method of making cement has been improved the basic process has remained same. Finely ground powders and all have the important property that when mixed with water a chemical reaction (hydration) takes place. Hydration produces a very hard and strong binding medium for the aggregate particles. The cement to be used in a particular concrete or mortar will be selected on the basis of the particular properties required.
History of cement:

- The name Portland cement given originally due to the resemblance of the color and quality of the hardened cement to Portland stone – Portland island in England.
- Cement production in Saudi Arabia was first started in Jeddah by al-Arabiya Cement Factory in 1955 AD.
- Today the annual cement production in Saudi Arabia is more than 370 million tons from more than 14 cement factories all over the country.
- Southern Province Cement factory, Yamamah Cement factory, Yanbu Cement factory, etc.
Manufacture of Portland cement:

- Raw materials:
  - Calcareous material – such as limestone or chalk, as a source of lime (CaO).
  - Clayey material – such as clay or shale (soft clayey stones), as a source of silica (SiO$_2$) and alumina (Al$_2$O$_3$).

- Methods of cement manufacturing:
  - Wet process: grinding and mixing of the raw materials in the existence of water.
  - Dry process: grinding and mixing of the raw materials in their dry state. (most common)

- The process to be chosen depend on the nature of the used raw materials.
**Definitions:**

- **Portland Cement**: Material made by heating a mixture of limestone and clay in a kiln at about 1450 C, then grinding to a fine powder with a small addition of gypsum. Other types of Portland cement include White Portland Cement and Sulfate Resisting Portland Cement (SRPC).

- **Clinker**: Portland cement is made by grinding clinker and a little added gypsum. Clinker is a nodular material before it is ground up. The nodules can be anything from 1mm to 25mm in diameter.

- **Concrete**: is a composite material which is made up of a filler and a binder. The constituents used for the binder are cement and water, while the filler can be fine or coarse aggregate.

- **Aggregate**: Cobbles, pebbles, gravel, sand and silt - the 'rock' component of all particle sizes in concrete.
Chemical composition of Portland cement:

- **Alite**: tricalcium silicate or $C_3S$: $Ca_3SiO_5$ in terms of its oxides is $3CaO.SiO_2$. The CaO term is shortened to C and the SiO$_2$ to S. The compound thus becomes $C_3S$.

- **Belite**: dicalcium silicate or $C_2S$: Similarly, $Ca_2SiO_4$ is $2CaO.SiO_2$, which is shortened to $C_2S$.

- **Tricalcium aluminate**: aluminate phase’ or $C_3A$: $Ca_3Al_2O_6$ is $3CaO.Al_2O_3$. The Al$_2$O$_3$ term is shortened to A and the compound becomes $C_3A$.

- **Tetracalcium aluminoferrite**: (‘ferrite’ phase) or tetracalcium aluminoferrite or $C_4AF_2(Ca_2AlFeO_5)$ is $4CaO.Al_2O_3.Fe_2O_3$. Fe$_2$O$_3$ is shortened to F and the compound becomes $C4AF$. 
In addition to the main compounds mentioned above, there exist minor compounds, such as MgO, TiO$_2$, Mn$_2$O$_3$, K$_2$O and Na$_2$O. Two of the minor compounds are of particular interest: K$_2$O and Na$_2$O, known as the alkalis (about 0.4-1.3\% by weight of cement). They have been found to react with the reactive silica found in some aggregates, the products of the reaction causing increase in volume leading to disintegration of the concrete. The increase in the alkalis percentage has been observed to affect the setting time and the rate of the gain of strength of cement.
Usual Composition Limits of Portland Cement:

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Content %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>60-67</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>17-25</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>3-8</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.5-6</td>
</tr>
<tr>
<td>MgO</td>
<td>0.5-4</td>
</tr>
<tr>
<td>Alkalis (as Na$_2$O)</td>
<td>0.3-1.2</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>2-3.5</td>
</tr>
</tbody>
</table>
Flow diagram:

Figure 2.1 Portland cement manufacturing process
Dry process kilns:
Dry process kilns:

- A rotary kiln is a long cylinder (50 m) rotating about its axis once every minute or two.
- The kiln is inclined at a slight angle, the end with the burner being lower.
- The rotation of the kiln causes the raw meal to gradually pass along from where it enters at the cool end, to the hot end where it eventually drops out and cools.
- The blended raw material enters the kiln via the pre-heater tower.
- Hot gases from the kiln, and probably the cooled clinker at the far end of the kiln, are used to heat the raw meal.
Production Steps of Portland Cement:

- Crushing, screwing, and stockpiling the raw materials
- Calculating the proportions of raw materials
- Preparing the raw mix by blending
- Feeding the raw mix into rotary kiln
- 100°C: Free water is evaporated.
- 150-300°C: Loosely bound water is evaporated.
- 500°C: More firmly bound water is evaporated.
- 600°C: $\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$
- 900°C: $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
- Reaction between lime and clay starts.
- 1300°C: Major compound formation starts.
- 1400-1600°C: Output temperature.
- (Around 1600°C clinker forms C3A, C2S, C3S, C4AF)
- Clinker cooled and stored.
- Clinker is ground with gypsum.
- Storing and marketing.
Composition percent:

- **Grinding**: The feed to the grinding process is consists of 80% limestone, 9% silica, 9% flyash, and 2% iron ore.

- These materials are ground to 75 micron in a ball mill. Grinding can be either wet or dry.

- **Pyro-processing**: The raw meal from the mill is heated with the hot exhaust gas from the kiln before being fed into the rotary kiln to form a semi-product known as clinker. The ash from fuel used is also absorbed into the clinker. The particle size range for clinker is from about 2 inches to about 10 mesh.
Reactions in the kiln:

- Decomposition of raw materials - temperatures up to about 1300 °C. This includes:
  - Water evaporation in the raw feed, if any.
  - Loss of carbon dioxide from the limestone (i.e.: calcining: decarbonation of calcium carbonate at 1 atmosphere takes place at 894 °C).
  - Decomposition of the siliceous and aluminosilicate fractions of the feed, immiscible. The initial silicate product is belite (C2S).
  - Some calcium aluminate and ferrite phases also start to form (C3A, C4AF)
Reactions in the kiln:

- Formation of a sulfate melt phase (sulfates combined with calcium and alkalis form a liquid phase. This is separate from the aluminate and aluminoferrite-based liquid formed in the burning zone - the two liquids are Alite formation and other reactions at 1300 °C - 1450 °C.
- The clinker is in the burning zone for 10-20 minutes.
- The proportion of clinker liquid increases and nodules form.
- Intermediate phases dissociate to form liquid and belite $C_2S$.
- Belite reacts with free lime to form alite $C_3S$.
- Some volatile phases evaporate.
Reactions in the kiln:

<table>
<thead>
<tr>
<th>T °C</th>
<th>Reaction</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>Evaporation of water</td>
<td>Solid phase reactions, endothermic</td>
</tr>
<tr>
<td>&gt;500</td>
<td>Evolution of combined water from the clay</td>
<td>Solid phase reactions, endothermic</td>
</tr>
<tr>
<td>900</td>
<td>Crystallization of amorphous dehydration products</td>
<td>Solid phase reactions, endothermic</td>
</tr>
<tr>
<td></td>
<td>Carbon dioxide evolution from CaCO₃</td>
<td></td>
</tr>
<tr>
<td>900-1200</td>
<td>Main reactions between lime and clay to form clinker</td>
<td>Fusion reactions, exothermic</td>
</tr>
<tr>
<td>1250-1280</td>
<td>Beginning of liquid formation</td>
<td>Fusion reactions, endothermic</td>
</tr>
<tr>
<td>1280-1550</td>
<td>Further liquid formation and final cement formation</td>
<td>Fusion reaction, endothermic</td>
</tr>
</tbody>
</table>
Reactions in the kiln:

- The main reactions which give the real strength of cement:
  
  \[
  2\text{CaO} + \text{CaO.SiO}_2 \overset{900-1200}{\longrightarrow} \text{CaO} + 2\text{CaO.SiO}_2 \overset{1200-1500}{\longrightarrow} 3\text{CaO.SiO}_2
  \]

- \(2\text{C} + \text{CS} = \text{C} + \text{C}_2\text{S} = \text{C}_3\text{S}\)
The main constituents of clinker

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Common name</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>2CaO·SiO₂</td>
<td>C₂S Dicalcium silicate</td>
<td>Together with 3CaO·SiO₂, responsible for final strength (1 year)</td>
</tr>
<tr>
<td>3CaO·SiO₂</td>
<td>C₃S Tricalcium silicate</td>
<td>Responsible for early strength i.e. 7-8 days</td>
</tr>
<tr>
<td>3CaO·Al₂O₃</td>
<td>C₃A Tricalcium aluminate</td>
<td>Causes fast hardening; needs retardation by gypsum by forming 3CaO·Al₂O₃·CaSO₄·3H₂O</td>
</tr>
<tr>
<td>3CaO·Al₂O₃·Fe₂O₃</td>
<td>C₄AF Tetracalcium alumino-ferrate</td>
<td>Improves chemical resistance</td>
</tr>
</tbody>
</table>
Cooling of the clinker:

- As the clinker cools, the main liquid phase crystallizes to form aluminate phase, ferrite and a little belite.

- **Fast cooling** of clinker is advantageous - it makes for more hydraulically-reactive silicates and lots of small, intergrown, aluminate and ferrite crystals.

- **Slow cooling** gives less hydraulically-reactive silicates and produces coarse crystals of aluminate and ferrite.

- Over-large aluminate crystals can lead to erratic cement setting characteristics.

- **Very slow cooling** allows alite to decompose to belite and frelime.
Oxide composition of a Portland cement:

**Elemental analysis:**
- Main phases or mineral (C₃S 65%)
- (C₂S 15%)
- (C₃A 7%)
- (C₃AF 8%)

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Range (wt%)</th>
<th>Cement #135 (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>60.2 – 66.3</td>
<td>63.81</td>
</tr>
<tr>
<td>SiO₂</td>
<td>18.6 – 23.4</td>
<td>21.45</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.4 – 6.3</td>
<td>4.45</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.3 – 6.1</td>
<td>3.07</td>
</tr>
<tr>
<td>MgO</td>
<td>0.6 – 4.8</td>
<td>2.42</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>--</td>
<td>0.11</td>
</tr>
<tr>
<td>TiO₂</td>
<td>--</td>
<td>0.22</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.05 – 1.20 (Na₂O equiv)</td>
<td>0.83</td>
</tr>
<tr>
<td>K₂O</td>
<td>--</td>
<td>0.20</td>
</tr>
<tr>
<td>SO₃</td>
<td>1.7 – 4.6</td>
<td>2.46</td>
</tr>
</tbody>
</table>

**The lime saturation factor (LSF):**

\[
\text{CaO}/(2.8 \text{ SiO}_2 + 1.18 \text{ Al}_2\text{O}_3 + 0.65\text{ Fe}_2\text{O}_3)
\]

At equilibrium = 1

Typical = 0.92–0.98

A mix with LSF > 1: means free CaO

Silica Ratio (SR) = SiO₂ / (Al₂O₃ + Fe₂O₃)

Silica modulus typical = 2.0–3.0

Alumina Ratio (AR) = Al₂O₃ / Fe₂O₃

Alumina modulus typical = 1.0–4.0

**Loss on Ignition** -- 0.81

**Insoluble residue** -- 0.16

**Free CaO** -- 0.64
Test methods:

**Lime Saturation Factor (LSF)**

The LSF controls the ratio of alite to belite in the clinker.

A clinker with a higher LSF will have a higher proportion of alite to belite than will a clinker with a low LSF.

Typical LSF values in modern clinkers are 0.92-0.98. Values above 1.0 indicate that free lime is likely to be present in the clinker. This is because, in principle, at LSF=1.0 all the free lime should have combined with belite to form alite.

**Silica Ratio (SR)**

The Silica Ratio (also known as the Silica Modulus) is defined as:

\[
SR = \frac{SiO_2}{(Al_2O_3 + Fe_2O_3)}
\]

A high silica ratio means that more calcium silicates are present in the clinker and less aluminate and ferrite. SR is typically between 2.0 and 3.0.
Test methods:

- **Alumina Ratio (AR)**
  The alumina ratio is defined as: \[ AR = \frac{\text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3} \]
  - An increase in clinker AR means there will be more aluminate and less ferrite in the clinker.
  - the AR is usually between 1 and 4.
Bogue calculation:

- is used to calculate the approximate proportions of the four main minerals in Portland cement clinker (C3S, C2S, C3A, C4AF).

- $C_3S = 4.0710CaO - 7.6024SiO_2 - 1.4297Fe_2O_3 - 6.7187Al_2O_3$
- $C_2S = 8.6024SiO_2 + 1.0785Fe_2O_3 + 5.0683Al_2O_3 - 3.0710CaO$
- $C_3A = 2.6504Al_2O_3 - 1.6920Fe_2O_3$
- $C_4AF = 3.0432Fe_2O_3$
Example of a Bogue calculation:

From the cement analysis below find the ratio of C3S, C2S, C3A, and C4AF phases.

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>21.5%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.2%</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.8%</td>
</tr>
<tr>
<td>CaO</td>
<td>66.6%</td>
</tr>
<tr>
<td>MgO</td>
<td>1.0%</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.6%</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.2%</td>
</tr>
<tr>
<td>SO₃</td>
<td>1%</td>
</tr>
<tr>
<td>LOI</td>
<td>1.5%</td>
</tr>
<tr>
<td>IR</td>
<td>0.5%</td>
</tr>
<tr>
<td>Total</td>
<td>98.9%</td>
</tr>
</tbody>
</table>

Free kime = 1.0% CaO

- Combined CaO = (66.6% - 1.0% free lime) = 65.6%

- From the analysis we have:
  - CaO = 65.6%
  - SiO₂ = 21.5%
  - Al₂O₃ = 5.2%
  - Fe₂O₃ = 2.8%
Example of a Bogue calculation:

- The Bogue calculation is therefore:
  - $C_3S = 4.0710\text{CaO} - 7.6024\text{SiO}_2 - 1.4297\text{Fe}_2\text{O}_3 - 6.7187\text{Al}_2\text{O}_3$
  - $C_2S = 8.6024\text{SiO}_2 + 1.1\text{Fe}_2\text{O}_3 + 5.0683\text{Al}_2\text{O}_3 - 3.0710\text{CaO}$
  - $C_3A = 2.6504\text{Al}_2\text{O}_3 - 1.6920\text{Fe}_2\text{O}_3$
  - $C_4AF = 3.0432\text{Fe}_2\text{O}_3$
- Therefore:
  - $C_3S = (4.0710 \times 65.6)-(7.6024 \times 21.5)-(1.4297 \times 2.8)-(6.718 \times 5.2) = 64.7\%$
  - $C_2S = (8.6024 \times 21.5)+(1.0785 \times 2.8)+(5.0683 \times 5.2)-(3.0710 \times 65.6) = 12.9\%$
  - $C_3A = (2.6504 \times 5.2)-(1.6920 \times 2.8) = 9.0\%$
  - $C_4AF = 3.0432 \times 2.8 = 8.5\%$
Uses of cement:

- Main use is in the fabrication of concrete and mortars. Modern uses include:
  - Building
  - Transport (roads, pathways, crossings, bridges, etc.)
  - Water (pipes, drains, canals, dams, etc.)
- Cement used for railway sleepers shall additionally satisfy the following chemical/mineralogical requirements and shall be designated.
Glossary:

- **Accelerators**: Admixtures that decrease the setting time of cement by increasing the rate of hydration.
- **Admixture**: A material other than water, aggregates, or cement that is used as an ingredient of concrete or mortar to control setting and early hardening, workability, or to provide additional cementing properties.
- **Aggregate**: Inert solid bodies such as crushed rock, sand, gravel.
- **Calcination**: Decomposition due to the loss of bound water and carbon dioxide.
- **Cement**: Finely powdered mixtures of inorganic compounds which when combined with water hardens with hydration.
- **Cement paste**: Cement plus water. When the mass has reacted with water and developed strength it is called hardened cement paste.
- **Clay**: Type of soil consisting of very fine particles.
- **Clinker**: The material that emerges from the cement kiln after burning. It is in the form of dark, porous nodules which are ground with a small amount of gypsum to give cement.
- **Concrete**: A hard compact building material formed when a mixture of cement, sand, gravel, and water undergoes hydration.
Glossary:

- **Gypsum**: Calcium sulfate dihydrate, CaSO$_4$.2H$_2$O added to cement to regulate setting.
- **Hydration**: The reaction of cement with water to form a chemical compound.
- **Kiln**: High temperature oven.
- **Limestone**: Mineral rock of calcium carbonate.
- **Pozzolan cement**: Volcanic rock powdered and used in making hydraulic cement.
- **Portland cement**: A cement consisting predominantly of calcium silicates which reacts with water to form a hard mass.
- **Retardants**: Admixtures that increase the setting time by slowing down hydration.
- **Setting time**: The time taken for Transformation of cement paste or concrete from a fluid-like consistency to a stiff mass.
- **Workability**: How easily fresh concrete can be placed and consolidated in forms.
Chapter two : Manufacture of ammonia \( \text{NH}_3 \)
Manufacture of ammonia NH₃ introduction:

- Free ammonia was prepared for the first time in 1774 by J. Priestly and C. Berthollet using ammonium carbonate.
- About 1900 Fritz Haber began investigating the ammonia equilibrium reaction and evaluating effect of temperature. (Making ammonia from the elements).
- In 1913 the first commercial Plant was started in Ludwigshafen (30 tons per day).
- **Saudi Arabian Fertilizer Company** the first petrochemical company in Saudi Arabia was established 1965.
- The first production of ammonia was in 1970 with 20 tones every year.
- **Today** the production reached up to 2.3 million tons every year.
Uses of ammonia:

- The manufacture of fertilizers is by far the most important use of ammonia. These include urea\((\text{CO(NH}_2\text{)}_2)\), ammonium salts \((\text{(NH}_4\text{)}_3\text{PO}_4 - \text{NH}_4\text{NO}_3 - 5\text{Ca(NO}_3\text{)}_\text{NH}_4\text{NO})\) and solutions of ammonia.
The manufacture of ammonia from nitrogen and hydrogen takes place in two main stages:

- the manufacture of hydrogen
- the synthesis of ammonia (the Haber Process)
the manufacture of hydrogen:

- Hydrogen is produced from a variety of feedstocks, mostly from natural gas, coal or naphtha. The ways in which hydrogen is obtained from these feedstocks are dealt with separately.

- Hydrogen from natural gas (methane) This involves two stages:
  - the manufacture of synthesis gas
  - the removal of the carbon monoxide and production of a mixture of hydrogen and nitrogen (the shift reaction)
the manufacture of synthesis gas:

- Whichever way the methane is obtained, it will contain some organic sulfur compounds and hydrogen sulfide, both of which must be removed. Otherwise, they will poison the catalyst needed in the manufacture of synthesis gas. In the desulfurisation unit, the organic sulfur compounds are often first converted into hydrogen sulfide, prior to reaction with zinc oxide. The feedstock is mixed with hydrogen and passed over a catalyst of mixed oxides of cobalt and molybdenum on an inert support (a specially treated alumina) at 700 K.

\[ R-\text{SH}(g) + H_2(g) \rightarrow R-H(g) + H_2S(g) \]
the manufacture of synthesis gas:

- Then the gases are passed over zinc oxide at ca 700 K and hydrogen sulfide is removed:
  \[
  \text{ZnO(s)} + \text{H}_2\text{S(g)} \rightarrow \text{ZnS(s)} + \text{H}_2\text{O(g)}
  \]

- Primary steam reforming converts methane and steam to synthesis gas, a mixture of carbon monoxide and hydrogen:
  \[
  \text{CH}_4\text{(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO(g)} + 3\text{H}_2\text{(g)} \quad \Delta H^\circ = +210 \text{ kJ mol}^{-1}
  \]

- High temperatures and low pressures favour the formation of the products (Le Chatelier's Principle)
the manufacture of synthesis gas:

- Secondary steam reforming reacts oxygen from the air with some of the hydrogen present and the resulting mixture is passed over a nickel catalyst. The steam and heat produced from the combustion reforms most of the residual methane. Among the key reactions are:

  \[
  2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) \quad \Delta H^\ominus = -482 \text{ kJ mol}^{-1}
  \]
  \[
  \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \quad \Delta H^\ominus = +210 \text{ kJ mol}^{-1}
  \]
The shift reaction:

- His process converts carbon monoxide to carbon dioxide, while generating more hydrogen.
- It takes place in two stages. In the first, the high temperature shift reaction, the gas is mixed with steam and passed over an iron/chromium(III) oxide catalyst at 700 K in a fixed bed reactor:

\[
\text{CO(g) + H}_2\text{O(g) \rightleftharpoons CO}_2\text{(g) + H}_2\text{(g)} \quad \Delta H^\circ = -42 \text{ kJ mol}^{-1}
\]

- In the second stage, the low temperature shift reaction, the mixture of gases is passed over a copper-zinc catalyst at ca 500 K. The carbon monoxide concentration is further reduced to 0.2%.
- The reaction is done in two stages for several reasons. The reaction is exothermic.
Hydrogen from naphtha / coal:

- If naphtha is used as the feedstock, an extra reforming stage is needed. The naphtha is heated to form a vapour, mixed with steam and passed through tubes, heated at 750 K and packed with a catalyst, nickel supported on a mixture of aluminium and magnesium oxides. The main product is methane together with oxides of carbon, and is then processed by steam reforming, as if it was natural gas, followed by the shift reaction.

- If coal is used, it is first finely ground and heated in an atmosphere of oxygen and steam. Some of the coal burns very rapidly in oxygen (in less than 0.1 s) causing the temperature in the furnace to rise and the rest of the coal reacts with the steam:

\[
C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)
\]
Hydrogen from coal:

- The gas emitted contains ca 55% carbon monoxide, 30% hydrogen, 10% carbon dioxide and small amounts of methane and other hydrocarbons. This mixture is treated by the shift reaction.

- The main problems of using coal includes the large amounts of sulfur dioxide and trioxide generated in burning coal and the significant amounts of other impurities such as arsenic and bromine, all of which are very harmful to the atmosphere and all of which are severe poisons to the catalysts in the process. There is also a massive problem with disposal of the ash.
The manufacture of ammonia (The Haber Process)

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H^\circ = -92 \text{ kJ mol}^{-1}$$

- The heart of the process is the reaction between hydrogen and nitrogen in a fixed bed reactor. The gases, in stoichiometric proportions, are heated and passed under pressure over a catalyst.
- The proportion of ammonia in the equilibrium mixture increases with increasing pressure and with falling temperature (Le Chatelier's Principle).
- A wide range of conditions are used, depending on the construction of the reactor. Temperatures used vary between 600 and 700 K, and pressures between 100 and 200 atmospheres.
- As the reaction is exothermic, cool reactants (nitrogen and hydrogen) are added to reduce the temperature of the reactors.
The manufacture of ammonia (The Haber Process)
Chapter three: Anhydrous acids
Manufacture of Nitric acid $\text{HNO}_3$

introduction:

- Jaber Bin Hayyan is the first chemist who prepared nitric acid from saltpeter he named it ma alfeda. WHY?
- Nitric acid occurs in nature in the form of nitrate salts. Initially, large scale production of nitric acid began with sodium nitrate as a feed stock.
- Three techniques were used industrially:
  - Production of NO by reacting $\text{N}_2$ and $\text{O}_2$ at greater than 2000 °C, abandoned because of poor energy efficiency.
  - Production of ammonia by hydrolysis of calcium cyanamide, not widely accepted.
  - Production of ammonia from $\text{N}_2$ and H2. (Haber-Bosch Process)
Uses of Nitric acid:

- By far the principal use of nitric acid (80%) is in the manufacture of fertilizers.
- Of this 96% is used to make ammonium nitrate and calcium ammonium nitrate.
- A small amount of ammonium nitrate is used to make explosives.
- Some nitric acid is used in the manufacture of adipic acid to make polyamides and TDI (toluene diisocyanate).
Manufacture of nitric acid:

- one of the process of nitric acid production:
  - The Ostwald Process
Ammonia is converted to nitric acid in stages:

One: in the presence of a catalyst such as platinum

\[ 4 \text{NH}_3 (g) + 5 \text{O}_2 (g) \rightarrow 4 \text{NO} (g) + 6 \text{H}_2\text{O} (g) \quad (\Delta H = -905.2 \text{ kJ/mol}) \]

This reaction is strongly exothermic making it a useful heat source once initiated.

Two: Oxidation of NO

\[ 2 \text{NO} (g) + \text{O}_2 (g) \rightarrow 2 \text{NO}_2 (g) \]

Three: Absorption by water:

\[ 3 \text{NO}_2 (g) + \text{H}_2\text{O} (l) \rightarrow 2 \text{HNO}_3 (aq) + \text{NO} (g) \]

Last stage is carried out in air:

\[ 4 \text{NO}_2 (g) + \text{O}_2 (g) + 2 \text{H}_2\text{O} (l) \rightarrow 4 \text{HNO}_3 (aq) \]
The Ostwald Process:
Manufacture of Sulfuric acid $\text{H}_2\text{SO}_3$

**introduction:**

- Sulfuric acid is a very important commodity chemical, and indeed, a nation's sulfuric acid production is a good indicator of its industrial strength. World production in 2018 was about 280 million tones.
- Jaber Bin Hayyan Hayyan is the first chemist who discovered Sulfuric acid

And he named it (zayt alzaaj)
Uses of Sulfuric acid

- By far the largest amount of sulfuric acid is used to make phosphoric acid, used, in turn, to make the phosphate fertilizers.
- Used in metal processing for example in the manufacture of copper and the manufacture of zinc.
- Used in cleaning the surface of steel sheet.
- It is also used to make caprolactam.
- Amongst its many other uses is in the manufacture of hydrofluoric acid and phenol with propanone.
Manufacture of sulfuric acid:

The process for producing sulfuric acid has four stages:

1. extraction of sulfur
2. conversion of sulfur to sulfur dioxide
3. conversion of sulfur dioxide to sulfur trioxide
4. conversion of sulfur trioxide to sulfuric acid
Extraction of sulfur:

- Easily the most important source of sulfur is its recovery from natural gas and oil. These contain sulfur compounds both organic and hydrogen sulfide both of which must be removed before they are used as fuels or chemical feedstock. Another important source of sulfur is as sulfur dioxide from metal refining. Many metal ores occur as sulfides and are roasted to form an oxide and sulfur dioxide for example in the manufacture of lead.

\[
2\text{PbS}_\text{(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{PbO}_\text{(s)} + 2\text{SO}_2\text{(g)}
\]

\[
2\text{ZnS}_\text{(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{ZnO}_\text{(s)} + 2\text{SO}_2\text{(g)}
\]
Extraction of sulfur:

The most important way to extract sulfur is the Frisch process.

Three concentric tubes are introduced into the sulfur deposit.

Superheated water (165 °C, 2.5MPa) is injected into the deposit via the outermost tube. Sulfur (m.p. 115 °C) melts and flows into the middle tube. Water pressure alone is unable to force the sulfur into the surface due to the molten sulfur's greater density, so hot air is introduced via the innermost tube to froth the sulfur, making it less dense, and pushing it to the surface. To extract ton of sulfur in this way requires 15 tons of water vapor. The sulfur obtained can be very pure (99.7 - 99.8%).
Extraction of sulfur:

- The **Claus process** is the most significant gas desulfurizing process recovering elemental sulfur from gaseous hydrogen sulfide. Small amounts of hydrogen sulfide occur in crude petroleum but natural gas can contain up to 90% for example, in the hydro-desulfurization of refinery naphtha's and other petroleum oils is converted to sulfur in Claus plants. The reaction proceeds in two steps:

  \[
  2 \text{H}_2\text{S} + 3 \text{O}_2 \rightarrow 2 \text{SO}_2 + 2 \text{H}_2\text{O}
  \]

  \[
  4 \text{H}_2\text{S} + 2 \text{SO}_2 \rightarrow 3 \text{S}_2 + 4 \text{H}_2\text{O}
  \]
conversion of sulfur to sulfur dioxide:

If sulfur is the feedstock, it must first be converted to sulfur dioxide. Molten sulfur is sprayed into a furnace and burnt in a blast of dry air at about 1300 K. The sulfur burns with a characteristic blue flame:

\[ S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)} \]

Elemental sulfur is burnt in air to form sulfur dioxide (Oxidation of S):

\[ S_{(l)} + O_{2(g)} \rightarrow SO_{2(g)} \quad \Delta H = -297 \text{kJmol}^{-1} \]

Reaction occurs at high temperature (about 1000°C) but normal atmospheric pressure Reaction is complete.

The very negative change in enthalpy for this reaction means it is very exothermic.

This means heat is generated so the heater needs to be cooled by water. Achieved by running through pipes. The steam produced is used in other parts of the plant.
The catalyst, vanadium(V) oxide on silica is generally in the form of small pellets, to which cesium sulfate has been added as a promoter. The function of the promoter is to lower the melting point of vanadium(V) oxide so that it is molten at 700 K.

Platinum used to be the catalyst for this reaction however as it is susceptible to reacting with arsenic impurities in the sulfur feedstock. Vanadium(V) oxide (V$_2$O$_5$) is now preferred.

To prevent the ‘poisoning’ of the catalyst by purifying the raw materials.

Catalyst used:
- Finely divided platinum – expensive, (more efficient)
- Or vanadium(V) oxide, V$_2$O$_5$ (cheaper)
To Increase Yield of SO$_3$ gas Increase Rate of Reaction:

- Decrease Temperature (exothermic reaction)
- Increase Pressure
- Excess Reactants are added
- Add Catalyst
- Le Chatelier’s principle says if temperature is lowered, more products would be produced
- However the reaction is basically complete in the absorption tower. Any extra production would not be enough to justify cost of cooling tower.
To Increase Yield of SO$_3$ gas Increase Rate of Reaction:

- By removing sulphur trioxide.
- Not by dissolving sulphur trioxide in water as the reaction is highly exothermic and vaporize the acid.
- The acid fume is hazardous to the operator and harmful to the machinery.
- Dissolving sulphur trioxide in concentrated sulphuric acid to form oleum (fuming sulphuric acid)

\[ \text{SO}_3(g) + \text{H}_2\text{SO}_4(l) \rightarrow \text{H}_2\text{S}_2\text{O}_7(l) \]

Oleum is then carefully diluted in right proportion to give concentrated sulphuric acid

\[ \text{H}_2\text{S}_2\text{O}_7(l) + \text{H}_2\text{O}(l) \rightarrow 2\text{H}_2\text{SO}_4(l) \]
conversion of sulfur trioxide to sulfuric acid:

- The sulfur trioxide gas is absorbed into very concentrated sulfuric acid (a 98 percent solution of H₂SO₄ in water) producing a thick fuming liquid called oleum. The oleum is mixed carefully with water and the sulfur trioxide in the oleum reacts with the water as follows:

  \[
  \text{H}_2\text{SO}_4 \text{ (l)} + \text{SO}_3 \text{ (g)} \rightarrow \text{H}_2\text{S}_2\text{O}_7 \text{ (l)}
  \]

  \[
  \text{H}_2\text{S}_2\text{O}_7 \text{ (l)} + \text{H}_2\text{O} \text{ (l)} \rightarrow 2 \text{H}_2\text{SO}_4 \text{ (l)}
  \]
The contact process is the current method of producing sulfuric acid in the high concentrations needed for industrial processes:

Figure 9.1 The manufacture of sulphuric acid, $\text{H}_2\text{SO}_4$, through the Contact Process
phosphoric acid (H$_3$PO$_4$) production introduction:

- The main source of phosphoric acid is the raw phosphate which is the remains of the bones of the ancient marine organisms, so we find in the phosphate mines shells, snails and sea shells in addition to sodium chlorine and salts that resulted from the evaporation of sea water. Most of the raw phosphate are in Shape of Fluoroapatite (Ca$_5$(PO$_4$)$_3$F). The world production 43 million tones.

- Maaden company have phosphate mine and beneficiation plant at Al Jalalid in the north of Saudi Arabia and a processing complex at Ras Az Zawr on the Kingdom’s East coast consisting of four plants producing sulphuric acid, ammonia, phosphoric acid and, DAP.
Uses of phosphoric acid:

- About 90% of the phosphoric acid produced is used to make fertilizers.
- Phosphates are also used in a variety of other ways, including in soft drinks and as a supplement in feed given to cattle, pigs and poultry.
- triple superphosphate (TSP)
- di ammonium hydrogen phosphate (DAP)
- mono ammonium dihydrogen phosphate (MAP)
Manufacture of phosphoric acid:

- Phosphoric acid is made by two processes:
  - The wet process
  - Thermal process
- The thermal method normally produces a more concentrated and purer product, but is energy intensive (because of the manufacture of phosphorus itself. Acid produced by the 'wet' route is less pure but is used in the manufacture of fertilizers.
The wet process:

- Phosphoric acid is produced from fluorapatite, known as phosphate rock, $\text{Ca}_5(\text{PO}_4)_3\text{F}$ by the addition of concentrated (93%) sulfuric acid in a series of well-stirred reactors. This results in phosphoric acid and calcium sulfate (gypsum) plus other insoluble impurities.

- Water is added and the gypsum is removed by filtration along with other insoluble materials (e.g. silica).

- Fluoride, as $\text{H}_2\text{SiF}_6$, is removed at a further stage by evaporation.

$$\text{Ca}_3(\text{PO}_4)_2(\text{s}) + 3\text{H}_2\text{SO}_4(\text{l}) \rightarrow 2\text{H}_3\text{PO}_4(\text{l}) + 3\text{CaSO}_4(\text{s})$$
The wet process:

- However, there are side reactions; for example with calcium fluoride and calcium carbonate present in the rock:

  \[ 3\text{CaF}_2(s) + \text{SiO}_2(s) + 3\text{H}_2\text{SO}_4(l) \rightarrow \text{H}_2\text{SiF}_6(l) + 3\text{CaSO}_4(s) + 2\text{H}_2\text{O}(l) \]
  
  \[ \text{CaCO}_3(s) + \text{H}_2\text{SO}_4(l) \rightarrow \text{CaSO}_4(s) + \text{H}_2\text{O}(l) + \text{CO}_2(g) \]

- Fluorosilicilic acid is an important by-product from this and from the manufacture of hydrogen fluoride. It can be neutralized with sodium hydroxide to form sodium hexafluorosilicate. The acid is also used to make aluminum fluoride, used in turn in the manufacture of aluminum.
The wet process:

- Calcium sulfate is filtered off and the acid is then concentrated to ca 56% P2O5 using vacuum distillation.
- The product from the wet process acid is impure but can be used, without further purification, for fertilizer manufacture.
Wet Process Flow Diagram

Phosphate Rock → Mill → Reactor

93% H₂SO₄

Mill → Reactor → Filter

CaSO₄, H₃PO₄

Filter → Evaporator

CaSO₄·2H₂O, Dilute H₃PO₄

Absorption Tower

H₂SiF₆

Gases

Dilute H₃PO₄

75% H₃PO₄
Thermal process :

- The raw materials for this process are phosphorus and air:

\[
P_4(l) + 5O_2(g) \rightarrow 2P_2O_5(g)
\]

- Initially, phosphorus is sprayed into the furnace and is burnt in air at about 1800-3000 K.
Thermal process:

- The products from the burner tower pass directly into a hydration tower where the gaseous phosphorus oxide is absorbed in recycled phosphoric acid:

\[ \text{P}_2\text{O}_5(\text{g}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_3\text{PO}_4(\text{l}) \]
Thermal process:

- This method allows heat to be recovered and reused. Burning and direct hydration as previously described, creates highly corrosive conditions.

The equipment is constructed from stainless steel or is carbon brick-lined.

To reduce corrosion the walls of the burner and hydrator towers are cooled, but the reactor products emerge at a temperature too low for useful heat recovery.

The product acid has a concentration of 85%.
Phosphates :

- The salts of phosphoric acid, the phosphates, are the compounds that are widely used in agriculture, industry and in the home.

- **(a)** Ammonium phosphates \((\text{NH}_4)_3\text{PO}_4\)

- Monoammonium dihydrogenphosphate and diammonium hydrogenphosphate are much used as fertilizers and are made by mixing the correct proportions of phosphoric acid with anhydrous ammonia in a rotating drum.

- The choice of which ammonium phosphate to use depends on the proportion of nitrogen and phosphorus needed for the crop.
Phosphates:

- **(b)** Calcium phosphates $\text{Ca(H}_2\text{PO}_4\text{)}_2$
- The calcium phosphates are used extensively as fertilizers. Calcium dihydrogenphosphate, $\text{Ca(H}_2\text{PO}_4\text{)}_2$, is produced by the reaction of phosphate rock with sulfuric acid:

  \[
  \text{Ca}_3(\text{PO}_4)_2 + \text{H}_2\text{SO}_4 \rightarrow \text{Ca(H}_2\text{PO}_4\text{)}_2 + 2\text{CaSO}_4
  \]

  This is known as superphosphate. It contains ca 20% $\text{P}_2\text{O}_5$.

- If phosphate rock is treated with phosphoric acid, rather than sulfuric acid, a more concentrated form of calcium dihydrogenphosphate is produced with an overall higher $\text{P}_2\text{O}_5$ level (50%):

  \[
  \text{Ca}_3(\text{PO}_4)_2 + 4\text{H}_3\text{PO}_4 \rightarrow 3\text{Ca(H}_2\text{PO}_4\text{)}_2
  \]
This is known as triple superphosphate. The higher level of phosphate is achieved because the product is no longer diluted with calcium sulfate.

(c) Sodium phosphates

- $\text{NaH}_2\text{PO}_4$ used in metal cleaning
- $\text{Na}_2\text{HPO}_4$ corrosion inhibitor in water treatment
- Tri sodium phosphate ($\text{Na}_3\text{PO}_4$) is used in heavy-duty cleansers.
- Disodium pyrophosphate ($\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$) is used as a leavening agent in bread/cakes.
Chapter four : Fertilizers
Introduction:

For healthy growth, plants require many different nutrients. Of these, nitrogen is needed for leaf growth and protein production, phosphorus promotes root and early seedling growth, while potassium regulates the transport of other nutrients and water within the plant. Sulfur is essential for protein synthesis and magnesium is required for the formation of chlorophyll. Other necessary elements include Ca, Na, Fe, Mn, B, Cu, Zn and Co. Deficiencies in a particular soil can be treated by the addition of appropriate fertilizers.
Before using any fertilizers, it is important to understand how to read a fertilizer label.

All fertilizers are labeled as %N - %P2O5 - %K2O.

For example, a fertilizer labeled as a 15-5-10 means that the product contains, by weight:

- 15 percent N
- 5 percent P₂O₅
- 10 percent K₂O
Nitrogen fertilizers: introduction:

- Inorganic N fertilizers are produced by fixing N from the atmosphere.

- Natural gas is used as the energy source and is a major component of the cost of N fertilizers.

- The following section lists the primary N materials used by the fertilizer industry.
Nitrogen fertilizers : Urea \( \text{CO(NH}_2\text{)}_2 \) :

- In 1828, the German chemist Friedrich Wöhler obtained urea artificially by treating silver cyanate with ammonium chloride.
  \[
  \text{AgNCO} + \text{NH}_4\text{Cl} \rightarrow (\text{NH}_2\text{)}_2\text{CO} + \text{AgCl}
  \]
- Soluble, readily available source of N.
- Produced by reacting ammonia (NH\(_3\)) with carbon dioxide under pressure at an elevated temperature.
- Contains the highest percentage of N of all dry fertilizers.
- Applying too much near germinating seeds can kill seedlings due to NH\(_3\) release.
- Rapid hydrolysis to ammonium carbonate can cause significant N losses as NH\(_3\) gas when urea is applied to the surface of soil:
  \[
  \text{CO(NH}_2\text{)}_2 + \text{H}_2\text{O} \rightarrow 2\text{NH}_3(g) + \text{CO}_2
  \]
- Incorporation or injection into the soil is important to avoid NH\(_3\) gas volatilization losses. Rainfall or irrigation (0.5 inches or more) will prevent volatilization.
Ammonium nitrate $\text{NH}_4\text{NO}_3$:

- The industrial production of ammonium nitrate entails the acid-base reaction of ammonia with nitric acid:
  \[ \text{HNO}_3 + \text{NH}_3 \rightarrow \text{NH}_4\text{NO}_3 \]
- Soluble, readily available source of N.
- Dry fertilizer product.
- 50% of the N is present as ammonium ($\text{NH}_4^+$).
- 50% of the N is present as nitrate ($\text{NO}_3^-$), which is the form susceptible to leaching and denitrification losses.
- $\text{NH}_3$ volatilization is not an issue unless applied to high pH soils (i.e., >7.5).
- Strong oxidizer that can react violently with other incompatible materials.
- Should be stored properly to prevent risk of explosion.
- Natural affinity to absorb moisture limits bulk storage during summer.
Ammonium sulfate \((\text{NH}_4)_2\text{SO}_4\):

- is an inorganic salt with a number of commercial uses. The most common use is as a soil fertilizer. It contains 21% nitrogen and 24% sulfur.
- Ammonium sulfate is made by treating ammonia, often as a by-product from coke ovens, with sulfuric acid:

\[
2\text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4
\]
Phosphoric Fertilizers:

- The basic ingredient for producing phosphorus (P) fertilizers is rock phosphate.
- Most rock phosphate comes from the mineral apatite, a calcium phosphate mineral that is mined out of the ground.
- Ma'aden produces the most widely used ammonium phosphate in modern agriculture, such as Diammonium phosphate (DAP) and monoammonium phosphate (MAP).

https://www.youtube.com/watch?v=s-Qw8KLvopM
Di ammonium phosphate \((\text{NH}_4)_2\text{HPO}_4\):

- is one of a series of water-soluble ammonium phosphate salts that can be produced when ammonia reacts with phosphoric acid.
  \[(\text{NH}_4)_2\text{HPO}_4(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{NH}_4\text{H}_2\text{PO}_4(\text{s})\]
- Soluble, readily available source of P and N.
- Dry fertilizer product.
- Initial soil reaction can produce free \(\text{NH}_3\), which can cause seedling injury if too much fertilizer is placed near the seed.
- Acid-forming fertilizer.
Monoammonium phosphate $\text{NH}_4\text{H}_2\text{PO}_4$:

- Monoammonium phosphate (MAP) is a widely used source of phosphorus (P) and nitrogen (N).
- Monoammonium phosphate is industrially prepared by the exothermic reaction of phosphoric acid and ammonia in the correct proportions:
  \[
  \text{NH}_3 + \text{H}_3\text{PO}_4 \rightarrow (\text{NH}_4 \text{H}_2\text{PO}_4
  \]
- Crystalline MAP then precipitates.
- It is water soluble and dissolves rapidly in soil if adequate moisture is present.
Chapter five Manufacture of chlorine gas $\text{Cl}_2$ and $\text{NaOH}$
Introduction:

- Around 1630, chlorine gas was first synthesised in a chemical reaction, but not recognised as a fundamentally important substance.
- Because of its great reactivity, all chlorine in the Earth's crust is in the form of ionic chloride compounds.
- Elemental chlorine is commercially produced from brine by electrolysis.
- Brine is a high-concentration solution of salt in water.
Uses of chlorine gas:

- Chlorine kills bacteria – it is a disinfectant. It is used to treat drinking water and swimming pool water. It is also used to make hundreds of consumer products from paper to paints, and from textiles to insecticides.

- About 20% of chlorine produced is used to make PVC. This is a very versatile plastic used in window frames, car interiors, electrical wiring insulation, water pipes, blood bags and vinyl flooring.

- Another major use for chlorine is in organic chemistry. It is used as an oxidising agent and in substitution reactions. 85% of pharmaceuticals use chlorine or its compounds at some stage in their manufacture.

- In the past chlorine was commonly used to make chloroform and carbon tetrachloride. However, both of these chemicals are now strictly controlled as they can cause liver damage.

- Chlorine gas is itself very poisonous, and was used as a chemical weapon during the First World War.
Uses of sodium hydroxide NaOH:

- Used to manufacture soaps.
- Used to help manufacture a variety of medicines and pharmaceutical products.
- Water treatment facilities use sodium hydroxide to control water acidity and to help remove heavy metals from water.
- Used to extract alumina from naturally occurring minerals.
Manufacture of chlorine gas and NaOH

- The most common method is the electrolysis of brine (chloralkali process):

- Membrane cell electrolysis. This method is more efficient than the diaphragm cell and produces very pure sodium hydroxide at about 32% concentration but requires very pure brine.
Saturated brine is passed into the first chamber of the cell where the chloride ions are oxidised at the anode, losing electrons to become chlorine gas:

\[ 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \]

At the cathode, positive hydrogen ions pulled from water molecules are reduced by the electrons provided by the electrolytic current, to hydrogen gas, releasing hydroxide ions into the solution:

\[ 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \]

The ion-permeable ion exchange membrane at the center of the cell allows the sodium ions (\(\text{Na}^+\)) to pass to the second chamber where they react with the hydroxide ions to produce caustic soda (\(\text{NaOH}\)).

The overall reaction for the electrolysis of brine is thus:

\[ 2\text{NaCl} + 2\text{H}_2\text{O} \rightarrow \text{Cl}_2 + \text{H}_2 + 2\text{NaOH} \]
Chapter six: Extraction of metals
Introduction:

- Metals can be found in nature:
- uncombined or free they are limited to metals of very low reactivity, for example silver, gold, copper, platinum, nickel.
- combined in the form of ores These include the majority of metals. Chief ores of economic importance are metal oxides, sulphides, chlorides and carbonates.
Extraction of Iron:

 قال تعالى: (وَأَنْزَلْنَا الْحَدِيدَ فِيهِ بَاسْتِ شَدِيدٍ وَمَنَافِعَ لِلنَّاسِ وَلَيْغَلَّمَ اللَّهُ مَنْ يَصْرِهِ وَرَسُلُهُ بِالْغَيْبِ إِنَّ اللَّهَ قَوِيٌّ عَزِيزٌ)
Extraction of Iron:

introduction:

- Several iron ores exist. The most popular method of iron extraction uses the **Blast Furnace**. This is a cylindrical tapering tower about 30-40m high constructed of steel lined with refractory bricks.

- The principle of the method is the reduction of iron(III) oxide with carbon.

- Saudi iron and steel co. (Headed) was established 1979.

- And the production reached 6 million tons per year.
Uses of iron:

- Most is used to manufacture steel, used in civil engineering (reinforced concrete, girders etc) and in manufacturing.
- Alloy steels are carbon steels with other additives such as nickel, chromium, vanadium, tungsten and manganese. These are stronger and tougher than carbon steels and have a huge variety of applications including bridges, electricity pylons, bicycle chains, cutting tools and rifle barrels.
- Stainless steel is very resistant to corrosion. It is used in architecture, bearings, cutlery, surgical instruments and jewellery.
- Cast iron contains 3–5% carbon. It is used for pipes, valves and pumps. It is not as tough as steel but it is cheaper. Magnets can be made of iron and its alloys and compounds.
- Iron catalysts are used in the Haber process for producing ammonia, and in the Fischer–Tropsch process for converting syngas (hydrogen and carbon monoxide) into liquid fuels.
Types of iron:

- **Pure iron** is too soft and reactive to be of much real use.
- **Pig iron**, basic raw iron is called pig iron produce from blasting furnace.

  is an alloy containing about 90–95 percent iron, 3–4 percent carbon, and traces of other elements such as silicon, manganese, and phosphorus, and is much harder than 100 percent pure iron.

- **Cast iron**: is the liquid iron that has been cast. roughly has 3–4% carbon. it's hard and brittle, it's virtually impossible to shape
Types of iron:

- **Grey iron** which contain very small amounts of carbon and other impurities but 1.2-3% slag, is softer than cast iron and much less tough.

- **Steel** another type of iron alloy which contain from 0.08 to 0.8% carbon.

- **Hard steel** which contain 0.8 to 1.5% carbon

- **Alloy steels**: or special steels which besides carbon contain one or more metals such as Ni, Cr, W, V, Mo, Mn.

- **Stainless steels** contain a high proportion of Cr and Ni, are very resistant to corrosion and other chemical reactions
The Types ores of iron:

<table>
<thead>
<tr>
<th>The ore</th>
<th>Chemical symbol</th>
<th>Scientific name</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite</td>
<td>Fe$_3$O$_4$</td>
<td>Magnetic iron oxide</td>
<td>Black</td>
</tr>
<tr>
<td>Haematite</td>
<td>Fe$_2$O$_3$</td>
<td>Iron III oxide</td>
<td>Blood red</td>
</tr>
<tr>
<td>Limonite</td>
<td>Fe$_2$O$_5$ . 3H$_2$O</td>
<td>Hydrate iron II oxide</td>
<td>Yellow</td>
</tr>
<tr>
<td>Siderite</td>
<td>FeCO$_3$</td>
<td>Iron II carbonate</td>
<td>Yellowish grey</td>
</tr>
</tbody>
</table>
The extraction of iron from the ores:

- The process of extraction include three stages:
  - Dressing of iron ore.
  - Reduction of iron ore.
  - Production on of iron.
  - Roasting process.
The extraction of iron from the ores:

- Crushing process: It's the process of converting the large size of the iron ore to small size to be easily reduced.

- Purification and concentration of the ore by using two methods:
  This process removes most of the impurities such as rocks by using one or more of several mechanical and physical processes.

- Sintering process: A process of converted the fine particles of the iron ore to large particles to be easily reduced.

- Roasting process: Heating the ores in air strongly to:
  - Increase the percentage of iron in the ore.
  - Oxidation of some impurities: such as (S, P)

\[
\begin{align*}
\text{FeCO}_3 + O_2 & \rightarrow \text{FeO} + \text{CO}_2 \rightarrow \text{Fe}_2\text{O}_3 \\
\text{Fe}_2\text{O}_3\cdot 3\text{H}_2\text{O} + O_2 & \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \\
\text{S} + O_2 & \rightarrow \text{SO}_2 \\
4\text{P} + O_2 & \rightarrow 2\text{P}_2\text{O}_5
\end{align*}
\]
Raw materials:

- The main raw materials of iron:
  - Iron ores (magnetite, hematite) – iron oxides with earth impurities;
  - Coke, which is both reducing agent and fuel, providing heat for melting the metal and slag.
  - Limestone – calcium silicate fluxes, forming a fluid slag iron ore and limestone or dolomite. Coking coal is used as fuel.

The fuel serves two purposes:

- To heat the furnace and to produce CO which acts as the reducing agent.
- To make special steels other materials such as nickel, chromium, cobalt are added.

- The ores include red hematite (Fe₂O₃), the less inferior brown hydrated hematite also known as limonite (2Fe₂O₃.3H₂O), the magnetic magnetite (Fe₃O₄) which is black in colour and pyrites (FeS₂).
- The hematite is easily reduced.
- Magnetite contains about 72% pure metal and it is reduced with some difficulty.
Iron factory:
Removal of impurities in iron ore:

- The presence of impurities in the iron ore not only reduce the iron content in the ore but also increase production costs.
- The main impurities in iron ore are silica and alumina.
- Silica and alumina in the presence of limestone makes the ore self-fusing.
- At high temperatures the flux reacts with alumina and silica to form a complex of calcium-magnesium aluminum silicate known as slag.
- Sulphur and phosphorus impurities: sulphides FeS, sulphates CaSO$_4$ and phosphates Ca$_3$(PO$_4$)$_2$ or Fe$_3$(PO$_4$)$_2$.

Steel should not contain more than 0.05% Sulphur and 0.05% phosphorus.

- Fuel
  - Coke is the fuel used to melt the ore and also to reduce the iron ore to metallic iron.
  - Good quality coke has about 80% carbon and 20% ash.
  - It is consumed at the rate of one ton per ton of pig iron.
Manufacture of iron:
The blast furnace

- CO₂ is formed when limestone is added to remove impurities.
- CO₂ is produced from burning fuel during the coking and sintering process.
- Iron and CO₂ are formed in the furnace.
- Additional CO₂ is formed when carbon is removed from the pig iron with pure oxygen to make steel.
- Limestone is also added during the steel refining.

Ingredients:
- Limestone
- Coke
- Coal
- Iron Ore
- Sintered Iron Ore
The Extraction Of Iron using the Blast Furnace:

- **Step 1**: Dried heated iron ore, limestone (calcium carbonate) and coke (carbon) are fed into the top of the furnace.

- **Step 2**: Hot air is blown into the furnace near the bottom. The hot air burns the coke producing carbon dioxide and generating great heat.

\[
C(s) + O_2(g) \rightarrow CO_2(g)
\]

- **Step 3**: The carbon dioxide is then reduced to carbon monoxide by the hot coke.

\[
CO_2(g) + C(s) \rightarrow 2CO(g)
\]

- **Step 4**: The carbon monoxide reduces the hot iron ore to molten iron which runs to the bottom of the furnace

\[
Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)
\]

OR

\[
Fe_3O_4(s) + 4CO(g) \rightarrow 3Fe(l) + 4CO_2(g)
\]
The Role of lime stone $\text{CaCO}_3$ :

- It decomposed by heat to calcium oxide and carbon dioxide
  \[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]

- Calcium oxide reacts with acidic oxides
  \[ \text{CaO} + \text{SO}_2 \rightarrow \text{CaSiO}_3 \]
  \[ \text{CaO} + 2\text{Al}_2\text{O}_3 \rightarrow \text{Ca(Al}_2\text{O}_3)_2 \]
  \[ 3\text{CaO} + \text{P}_2\text{O}_5 \rightarrow \text{Ca}_3(\text{PO}_4)_2 \]

- The slage floats on the top of molten iron and protects it from oxidation by the current of air.

- The slage is used in brick industry, cement and asphalt.
Step 1: \( \text{C(s)} + \text{O}_2(g) \rightarrow \text{CO}_2(g) \)

Step 2: \( \text{CO}_2(g) + \text{C(s)} \rightarrow 2\text{CO}(g) \)

Step 3: \( \text{3CO}(g) + \text{Fe}_2\text{O}_3(s) \rightarrow 3\text{CO}_2(g) + 2\text{Fe}(l) \)

Step 4: Molten Fe(l) flows to bottom

Step 5: \( \text{CaO} \) (from thermal decomposition of \( \text{CaCO}_3 \)) reacts with acidic impurities to form molten slag

Molten slag floats on the molten iron and is tapped off separately

Hot air blast at base

Waste Gases (\( \text{CO}_2, \text{CO} \))
Midrex process:

- The midrex using the midrex shaft furnace to converts iron oxide in pellets or lumps form into highly metallized direct reduces iron.
- Most naturally occurring iron exist as hematite.
- In this process the chemically bonded oxygen in the iron ore is removed using high temperature reducing gas composed of $\text{H}_2$ and CO to produce iron.
- To create reducing gas from natural gas:
  \[
  \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2
  \]
  \[
  \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2
  \]
- The reaction occurring in the shaft furnace is the well-known reduction reaction of iron:
  \[
  \text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2
  \]
  \[
  \text{Fe}_2\text{O}_3 + 3\text{H}_2 \rightarrow 2\text{Fe} + 3\text{H}_2\text{O}
  \]
Midrex process:

MIDREX® Direct Reduced Flowsheet

- Process Gas System
  - Process Gas Compressors
  - Top Gas Scrubber
- Reformer
- Shaft Furnace
- Heat Recovery
- Ejector Stack
- Natural Gas
- Flue Gas
- Main Air Blower
- Reducing Gas
- Combustion Air
- Fuel Gas
- Cooling Gas Scrubber

Iron Oxide

MIDREX® Direct Reduced Iron
Alloys:

- It is a substance formed from two metals and sometimes formed from metals and other element in a certain ratio.

- Methods of preparation of alloys:
  - Melt method: The metals are melt together and then leave the metal to cool gradually.
  - Electro position method: Two metals or more are deposited at the same time from solution on the surface other elements such as electro plating iron handles with brass (Cu + Zn).
### Types of alloys:

<table>
<thead>
<tr>
<th>Interstitial alloy</th>
<th>Substitutional alloy</th>
<th>Intermetallic alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>It is formed when a metal introduces to the structure of another pure metal.</td>
<td>It is formed when a some atom of the crystalline lattice of pure metal is replaced by the atoms of other metal added.</td>
<td>It is formed when two metals or more combine with each other chemical compounds with new properties.</td>
</tr>
</tbody>
</table>
| Such as separated carbon in iron carbon alloy. | such as stainless steel – copper – gold alloy – iron – nickel alloy which they are distinguished by:  
   a- The same crystalline structure.  
   b- The same chemical properties.  
   c- The same diameter. | Such as alloy of cementite Fe₃C which distinguished by:  
   a- It is hardness (solid).  
   b- It is valency which does not obey the low of valency.  
   c- It can not be formed by the metals of the same group in the periodic table. |
Types of alloys:

- To differentiate between two alloys one of them contain separated carbon (interstitial alloy) and other contains combined carbon and a bad odour is ppt. in the case of combined carbon.
Microstructure of Steel:

- Five main constituents:
  - Ferrite
  - Austenite
  - Cementite
  - Pearlite
  - Martensite
**Ferrite**: The structure of pure iron. Has a body-centred cubic (BCC) crystal structure. It is soft and ductile and imparts these properties to the steel. Very little carbon (less than 0.01% carbon will dissolve in ferrite at room temperature). Often known as iron.

**Austenite**: This is the structure of iron at high temperatures (over 912 deg C). Has a face-centre cubic (FCC) crystal structure. This material is important in that it is the structure from which other structures are formed when the material cools from elevated temperatures. Often known as iron. Not present at room temperatures.
- **Cementite**: A compound of iron and carbon, iron carbide (Fe$_3$C).
  It is hard and brittle and its presence in steels causes an increase in hardness and a reduction in ductility and toughness.

- **Pearlite**: A laminated structure formed of alternate layers of ferrite and cementite.
  - It combines the hardness and strength of cementite with the ductility of ferrite and is the key to the wide range of the properties of steels. The laminar structure also acts as a barrier to crack movement as in composites. This gives it toughness.

- **Martensite**: A very hard needle-like structure of iron and carbon.
  - Only formed by very rapid cooling from the austenitic structure.
## Properties of Carbon Steels:

<table>
<thead>
<tr>
<th>Carbon content wt %</th>
<th>Properties</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 - 0.1</td>
<td>Soft, ductile, no useful hardening by heat treatment except by normalizing, but can be work-hardened. Weldable.</td>
<td>Pressings where high formability required</td>
</tr>
<tr>
<td>0.1 - 0.25</td>
<td>Strong, ductile, no useful hardening by heat treatment except by normalizing, but can be work-hardened. Weldable. Ductile-brittle transition temperature is just below room temperature</td>
<td>General engineering uses for a mild steel</td>
</tr>
<tr>
<td>0.25 - 0.6</td>
<td>Very strong, heat treatable to produce a wide range of properties in quenched and tempered conditions. Difficult to weld. Can become brittle below room temperature.</td>
<td>Bars and forgings for a wide range of engineering components. Connecting rods, springs, hammers, axle shafts requiring strength and toughness.</td>
</tr>
</tbody>
</table>
Describe, in detail, the specific reactions taking place in any two distinct regions of the blast furnace.

Distinguish between the technical terms given in the following pairs, in 2-3 sentences each:

- Batch type furnace and continuous type furnace
- Carbon steel and alloy steel
- Low carbon ferro-alloy and high carbon ferro-alloy
- Iron and steel
Extraction of Aluminum:

introduction:

- Aluminum is very abundant in the earth’s crust, but is never found in its free state.
- Aluminum is found mainly in the form of aluminosilicates of which bauxite (Al$_2$O$_3$) is the chief source.

The crude/mined bauxite is either:
- heated to 3000°C to produce calcined bauxite
- Converted to pure alumina (Al$_2$O$_3$)
Uses of Aluminum:

- used in a huge variety of products including cans, foils, kitchen utensils, window frames, beer kegs and airplane parts.
- used as an alloy because aluminium itself is not particularly strong. Alloys with copper, manganese, magnesium and silicon are lightweight but strong.
- used in electrical transmission lines.
In 2009, Maaden established the world’s third-largest aluminum producer, to build the world’s most efficiently integrated aluminum project in Saudi Arabia. It includes a bauxite mine, a refinery, a smelter and one of the world’s most advanced rolling mills.

Feedstock comes from large bauxite deposits in Al Baitha, which includes the mine as well as the ore-crushing and handling facilities. The mine’s estimated production is 4 million tonnes per year of bauxite, and is transported via the new North-South railway line to Ras Al Khair.

Ras Al Khair hosts the refinery, the smelter and the rolling mill. Maaden refinery is the first alumina refinery in the Middle East; it can produce 1.8 million tonnes per year of alumina, all of which is processed in our smelter. The smelter’s annual production capacity is 740,000 tonnes per year of primary aluminum.

The rolling mill has a capacity of 380,000 tonnes per year.

https://www.youtube.com/watch?v=RpkQwQHL6D4
Extraction of Aluminum:

- The process for extracting aluminum from alumina is electrolysis.
- In the current process of extracting aluminum from bauxite, an electrolytic cell made of steel using graphite electrodes is used. The current used is 100,000A and the temperature is 1,223K.
- Pure alumina (aluminum oxide) which melts at 2050°C is dissolved in molten cryolite Na$_2$AlF$_6$ (sodium aluminum fluoride).
- The addition of the cryolite lowers the temperature to 950°C, because the presence of an impurity lowers the melting point of a substance.
- The presence of the cryolite also gives the melt better conducting properties and, in addition, it does not mix with the aluminum metal formed in the electrolysis.
Extraction of Aluminum:

- Aluminum is discharged at the graphite cathode, which lines the chamber. The product is 99% pure, the chief impurities being silicon and iron.

- Liquid aluminum is tapped off at the end of the cell.

\[
\text{Al}^3+(l) + 3e^- \rightarrow \text{Al}(l)
\]

- Oxygen is the other product that is produced at the anode.

\[
2\text{O}_2^-(l) + 4e^- \rightarrow \text{O}_2(g)
\]

- Overall equation:

\[
2\text{Al}_2\text{O}_3 (l) \rightarrow 4\text{Al}(l) + 3\text{O}_2(g)
\]
Electrolysis of Aluminum:

Bauxite ore is purified to Al₂O₃, which is mixed with cryolite, a mixture of NaF and AlF₃, which melts at 1000 °C.
Extraction of Copper: introduction:

- The method used to extract copper from its ores depends on the nature of the ore.
- The ores typically contain low percentages of copper and have to be concentrated before refining (e.g., via froth flotation).
- In 2015, Saudi Arabia produced about 34,750 tons of copper.
- Jabal Sayid copper mine in Madinah province. Contains a proven reserve of up to 99 million tons of copper ore.
Uses of Copper

- electrical wiring. It is a very good conductor of electricity and is easily drawn out into wires.
- domestic plumbing. It does not react with water, and is easily bent into shape.
- boilers and heat exchangers. It is a good conductor of heat and does not react with water.
- making brass. Brass is a copper-zinc alloy. Alloying produces a metal harder than either copper or zinc individually. Bronze is another copper alloy, but with tin.
- coinage. In many countries, as well as the more obvious copper-colored coins, "silver" coins are also copper alloys - this time with nickel; these are known as cupronickel alloys. UK pound coins and the gold-colored bits of euro coins are copper-zinc-nickel alloys.
Extraction of Copper:

- The finely crushed ore is concentrated by Froth-Floatation process. The finely crushed ore is suspended in water containing a little amount of pine oil. A blast of air is passed through the suspension. The particles get wetted by the oil and float as a froth which is skimmed. The gangue sinks to the bottom.
Extraction of Copper:

- The concentrated ore is then roasted in a furnace in the presence of a current of air. Sulphur is oxidized to $\text{SO}_2$ and impurities of arsenous and antimony are removed as volatile oxides.

- The following reaction takes place:

$$2\text{CuFeS}_2 + \text{O}_2 \rightarrow \text{Cu}_2\text{S} + 2\text{FeS} + \text{SO}_2$$
$$\text{S} + \text{O}_2 \rightarrow \text{SO}_2$$
$$4\text{As} + 3\text{O}_2 \rightarrow \text{As}_2\text{O}_3$$
$$4\text{Sb} + 3\text{O}_2 \rightarrow 2\text{Sb}_2\text{O}_3$$
Extraction of Copper:

- Cuprous sulphide and ferrous sulphide are further oxidized into their oxides.

\[
\begin{align*}
2\text{Cu}_2\text{S} + 3\text{O}_2 &\rightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2 \\
2\text{FeS} + 3\text{O}_2 &\rightarrow 2\text{FeO} + 2\text{SO}_2
\end{align*}
\]

- The roasted ore is mixed with coke and silica (sand) SiO\textsubscript{2} and is introduced into a blast furnace. The hot air is blasted and FeO is converted into ferrous silicate (FeSiO\textsubscript{3}).

\[
\begin{align*}
\text{FeO} + \text{SiO}_2 &\rightarrow \text{FeSiO}_3 \\
\text{Cu}_2\text{O} + \text{FeS} &\rightarrow \text{Cu}_2\text{S} + \text{FeO}
\end{align*}
\]
Extraction of Copper:

- Copper metal is extracted from molten matte through bessemerization. The matte is introduced into a Bessemer converter which is upheld by tuyères. The air is blown through the molten matte. Blast of air converts Cu$_2$S partly into Cu$_2$O which reacts with remaining Cu$_2$S to give molten copper.

$$2\text{Cu}_2\text{S} + 3\text{O}_2 \rightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2$$

$$2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \rightarrow 6\text{Cu} + \text{SO}_2$$
Extraction of Copper:

- Blister copper is refined by electrolysis
  
  \[ \text{Cu} \rightarrow \text{Cu}^{+2} + 2e^- \text{ (at the anode)} \]
  
  \[ \text{Cu}^{+2} + 2e^- \rightarrow \text{Cu} \text{ (at the cathode)} \]

  This electrically refined copper is 100% pure.
Chapter seven: manufacture of Ceramics
Introduction:

- Ceramics: are generally inorganic, non-metallic, dense, hard and brittle solid materials of one or more metals with a non-metallic element (usually silicon, boron, oxygen) that may be used as a single structural component or as one of the several layers that are used in the fabrication of a ceramic based prosthesis.
Ceramic Crystal Structure:

- Contains at least 2 and often 3 or more atoms
- Usually compounds between:
  - Metallic ions (e.g. Fe, Ni, Al): called cations and
  - Non-metallic ions (e.g. O, N, Cl): called anions
- Bonding will usually have some covalent character but is usually ionic.
Ceramic Crystal Structure:

- **Rock-salt structure**: $\text{AX}(\text{NaCl})$
- **Perovskite structure**: $\text{ABX}_3(\text{BaTiO}_3)$
- **Fluorite structure**: $\text{AX}_2(\text{CaF}_2)$
Classification of Ceramics based on application:

- **Traditional ceramics**
  - Whitewares
  - Structural Clay Products
  - Brick and Tile
  - Abrasives
  - Refractories
  - Cement

- **Advanced Ceramics**
  - **Electroceramics**
    - Electronic Substrate, Package Ceramics
    - Capacitor Dielectric, Piezoelectric Ceramics
    - Magnetic Ceramics
    - Optical Ceramics
    - Conductive Ceramics
  - **Advanced Structural ceramics**
    - Nuclear Ceramics
    - Bioceramics
    - Tribological (Wear-Resistant) Ceramics
    - Automotive Ceramics
Traditional Ceramics:

- Used in traditional applications such as construction, earthenware, and glassware.
- Made from three basic components:
  - **The clay**: provides work-ability of the material before firing hardens it and constitutes the major body material.
  - **The silica** (flint): has a high melting temperature and is the refractory component of traditional ceramics.
  - **Potash feldspar**: has a low melting temperature and turns into a glass with burning. It bonds the refractory components together.
Ceramics Raw Materials:

- Naturally occurring minerals
- Synthetic minerals
Naturally occurring minerals:

- The types of minerals found in nature are controlled mainly by the abundance of the elements and their geological characteristics.
- Since oxygen, silicon and aluminum together account for about 85% of the elements in the earth's crust it is not surprising that the dominant minerals are **aluminum silicates**.

**Composition:**
- **Silicate Raw Materials**: Mica – Clays – Feldspar – SILICA
- **Non-Silicate Raw Materials**: Chrome ore - High-alumina raw materials - Carbonate raw materials
Silicate Raw Materials:

- **silica** $\text{SiO}_2$:
  - Major source: Sand - Quartz, the principal silica mineral is a constituent of igneous rocks such as granite.
  - They are widely used because: Inexpensive - chemically stable - Hard - have the ability to form glasses.

- **Feldspar** (anhydrous aluminum silicates):
  - Major source: Soda feldspar (albite) $\text{Na(AlSi}_3\text{O}_8$ - Lime feldspar (anorthite) $\text{Ca(Al}_2\text{Si}_2\text{O}_8$.
  - Potash feldspar (microcline) $\text{K(AlSi}_3\text{O}_8$.

- **Clays**:
  - Major source: $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$ is the most common minerals used in ceramics.
  - Clay is the primary ingredient in traditional ceramics.

- **Mica**:
  - The mica group consists of 37 minerals two types: True micas ($\text{Na}^+$)
  - And brittle micas ($\text{Ca}^{2+}$).
Non-Silicate Raw Materials :

- High-alumina Raw Materials:
  They are used together with bauxite to raise the alumina content of kaolinitic clays from about 40 to 80% in order to form the refractory mullite phase \((3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2)\) on firing up to 1500°C.

- Carbonate Raw Materials Mainly composed of:
  magnesite \((\text{MgCO}_3)\) - dolomite \(\text{CaMg(CO}_3)_2\) - calcite \((\text{CaCO}_3)\)

- Chrome ore: It consists mainly of chromite mineral, which is a complex solid solution of \((\text{Mg, Fe}_2) (\text{Al}_3, \text{Fe}_3, \text{Cr}_3)_2\text{O}_4\) beside some magnesium silicate minerals as impurities.
Synthetic Materials:

- Synthesized from either natural materials or pure chemicals.
- Examples
  - Elements: carbon C
  - Halides: lithium fluoride (LiF)
  - Oxides: CaO - MgO - Al₂O₃ - SiO₂ - ZrO₂ - TiO₂ - ThO₂ and UO₂
  - Nitrides: Si₃N₄ - TiN - BN
  - Carbides: SiC and B₄C
  - Borides: TiB₂
  - Phosphates: Ca₅(OH)(PO₄)₃
  - Silicates: Al₆Si₂O₁₃ - LiAl₂Si₂O₉ - Mg₂Al₄Si₅O₁₈
  - Titanates: BaTiO₃ and Al₂TiO₅.
  - Spinels: Mg₄Al₂O₄ and MgFe₂O₄
Traditional Ceramics:

(a) shows the work part during the sequence

(b) shows the condition of the powders

Usual steps in traditional ceramics processing:
(1) preparation of raw materials
(2) shaping
(3) drying
(4) firing
Traditional Ceramics: White wares:

- Made from: clay - silica - feldspar.
- Examples:
  - Electrical porcelain.
  - Dinner china.
  - Sanitary ware.
- They are usually coated with a transparent or opaque glassy silicate layer, i.e. glaze.
- The water absorption of such ceramic products mostly exists below 1 %.
Traditional Ceramics:
Structural Clay Products:

- Made of natural clay, which contains all three basic components: clay, silica, feldspar.
- The water absorption of these products should be less than 5%.
- Portland cement and gypsum are used as binding agents.
- Examples:
  - Building brick
  - Sewer pipe
  - Drain tile
  - Roofing tile
  - Floor tile
Traditional Ceramics: Structural Clay Products:

- **Brick and Tile**:

  Formed from clay or shale or mixtures and burned (fired) in a kiln, or oven, to produce strength, hardness, and heat resistance.

  Structural clay products, manufactured as standard units, used in building construction.
Traditional Ceramics: Abrasives:

- Is a material, often a mineral, that is used to shape or finish a workpiece through rubbing which leads to part of the workpiece being worn away.
Traditional Ceramics: Refractories:

- It retains its strength at high temperature and possess high resistance to melting, thermal shock and reaction with the solid, liquid and gaseous phases in contact with their linings in industrial kilns under service conditions.

- They are generally processed from:

  Kaolinitic clays, magnesite and dolomite, bauxite, zircon and corundum as well as chromite and graphite.

- Examples:
  - Kiln linings
  - Gas fire radiants
  - Steel
  - Glass making crucibles
Advanced Ceramics:

- They are suited for industrial applications that provide a physical interface between different components.
- Due to their ability to withstand high temperatures, vibration and mechanical shock.
- Exhibit a high degree of industrial efficiency.
- Used in specialized, recently developed applications.
- Advanced ceramics often have simple chemical compositions, but they are difficult to manufacture.
Advanced Ceramics: Electro ceramics:

- It is a class of ceramic materials used primarily for their electrical properties.
- Further classified to:
  - Dielectric ceramics
  - Fast ion conductor ceramics
  - Piezoelectric ceramics
  - Magnetic Ceramics
  - Optical Ceramics
Dielectric ceramics:

- Are capable of storing large amounts of electrical charge in relatively small volumes.
- Is an electrical insulator that can be polarized by an applied electric field.
- Dielectric materials can be solids, liquids, or gases.
- Solid dielectrics are perhaps the most commonly used dielectrics in electrical engineering, and many solids are very good insulators.
Fast Ion Conductor Ceramics:

- solid electrolytes and superionic conductors
- are solids in which ions are highly mobile.
- These materials are important in the area of solid-state Ionics
- These materials are useful in:
  - solid oxide fuel cells.
  - Batteries
  - various sensors.
Piezoelectric Ceramics:

- Piezoelectric ceramic materials are categorized as functional ceramics.
- In sensors they make it possible to convert forces, pressures and accelerations into electrical signals.
- In sonic and ultrasonic transducers they convert electric voltages into vibrations or deformations.
Magnetic Ceramics:

- Magnetic ceramics are made of ferrites.
- They are crystalline minerals composed of iron oxide in combination with some other metal, $M(\text{Fe}_x\text{O}_y)$.
Optical Ceramics:

- are polycrystalline materials produced through controlled crystallization of base glass.
- Glass-ceramic materials
  - have the fabrication advantage of glass as well as special properties of ceramics.
  - Glass-ceramic materials share many properties with both glasses and ceramics
  - has a variety of properties such as:
    - High strength
    - Toughness
    - Translucency or opacity
    - Low or even negative thermal expansion
    - High temperature stability.
Advance Structural Ceramics:

- Further classified to:
  - **Nuclear Ceramics**: ceramic materials employed in the generation of nuclear power and in the disposal of radioactive nuclear wastes.
  - **Bio-ceramics**: Ceramics are now commonly used in the medical fields as dental and bone implants.
  - **Tribological Ceramics**: ceramic materials that are resistant to friction and wear.
  - **Automotive Ceramics**: advanced ceramic materials that are made into components for automobiles.
Chapter eight : manufacture of glass
Introduction:

- Glass is an amorphous, hard, brittle, transparent or translucent, super-cooled liquid, obtained by fusing a mixture of a number of metallic silicates, most commonly Na, K, Ca and Pb.
- It possesses no sharp melting point, crystalline structure and definite formula.

\[ xR_2O \cdot yMO \cdot 6SiO_2 \]

- R = monovalent alkali metals like Na, K
- M = Divalent metals like Ca, Pb, Zn, etc
- x & y = whole numbers

Approximate composition of ordinary glass (Soda lime glass) is \( Na_2O \cdot CaO \cdot 6SiO_2 \).
General Properties of glass:

- Amorphous Solid
- No definite melting point
- Very brittle
- Softens on heating
- Can absorb, reflect and transmit light
- Good electrical insulator
- Affected by alkalis
- Not affected by air, water, acid or chemical reagents. But soluble in HF which converts into SiF4
- Possesses high compressive strength and since it doesn’t have any crystalline structure no slippage between planes can occur. Light in weight because it has homogeneous internal structure similar to liquids.
### Raw materials of glass:

<table>
<thead>
<tr>
<th>SL. No</th>
<th>Name of the element</th>
<th>Source of the element</th>
<th>Name of the glass produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sodium (Na)</td>
<td>Na₂CO₃, Na₂SO₄</td>
<td>Soft glass</td>
</tr>
<tr>
<td>2</td>
<td>Potassium (K)</td>
<td>Potash, K₂CO₃, KNO₃</td>
<td>Hard glass</td>
</tr>
<tr>
<td>3</td>
<td>Calcium (Ca)</td>
<td>Lime, limestone</td>
<td>Glass with high RI</td>
</tr>
<tr>
<td>4</td>
<td>Barium (Ba)</td>
<td>BaCO₃</td>
<td>Glass with high RI</td>
</tr>
<tr>
<td>5</td>
<td>Lead, red lead</td>
<td>Litharge, red lead</td>
<td>Flint glass</td>
</tr>
<tr>
<td>6</td>
<td>Zinc</td>
<td>Zinc Oxide</td>
<td>Heat &amp; Shock proof glass</td>
</tr>
<tr>
<td>7</td>
<td>Borate</td>
<td>Borax, boric acid</td>
<td>Heat &amp; shock proof glass</td>
</tr>
<tr>
<td>8</td>
<td>Silica</td>
<td>Sand, quartz</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Colors Yellow</td>
<td>Ferric Salt</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Green</td>
<td>Ferrous and chromium</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Blue</td>
<td>Cobalt salt</td>
<td></td>
</tr>
</tbody>
</table>
Glass Manufacturing:

- Melting
  - Pot furnace
  - Tank furnace
- Forming and shaping
- Annealing
- Finishing
Melting:

- Raw materials in proper proportions (sand, soda ash and lime stone) are mixed and finely powdered.
- The homogenous mixture known as Batch is fused with some broken glass, called “Cullet” in any of the two types of furnaces.
- The homogeneous mixture is melted either in:
  - Pot furnace or
  - Tank furnace
- The batch melts and fuses at 1800°C.
Melting:

Pot furnace

Tank furnace.
The chemical reactions involved in both the furnaces are:

\[ \text{Na}_2\text{CO}_3 + \text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3 + \text{CO}_2 \]

\[ 2\text{Na}_2\text{SO}_4 + 2\text{SiO}_2 \rightarrow 2\text{Na}_2\text{SiO}_3 + \text{O}_2 + 2\text{SO}_2 \]

\[ \text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{CaSiO}_3 + \text{CO}_2 \]

▶ At 1400°C silica also in silicates of calcium and sodium

\[ \text{Na}_2\text{SiO}_3 + \text{CaSiO}_3 + 4\text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3\cdot\text{CaSiO}_3\cdot4\text{SiO}_2 \]
Forming and shaping:

- Molten glass is converted to desired shape by blowing or moulding or pressing between rollers - “Forming and Shaping”
- Articles are then cooled gradually at room temperature. - “Annealing”
- The longer the annealing period better the quality of glass
- After annealing, the articles are subjected to cleaning, polishing, cutting, sand blasting etc., - “Finishing”
Types of glasses:

- soda glass
- hard glass
- Lead glass
- Pyrex glass
- Alumina silicate glass
- Glass wool
Soft glass:

**Raw Materials**
- Silica
- CaCO₃
- Soda ash

**Properties**
- Low cost
- Resistant to water
- Attacked by acids
- Melts easily
- Moulded easily to any shape
- Poor thermal & chemical resistance

**Uses**
Window glasses, electric bulbs, bottles, jars, table wares etc.,

**Composition**
\[ \text{Na}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2 \]
Hard glass:

**Raw Materials**
- Silica
- CaCO₃
- K₂CO₃

**Properties**
- High Melting point
- Not attacked by acids, alkali and other solvents
- Costlier than soda-lime glass

**Uses**
Combustion tubes, chemical apparatus

**Composition**
K₂O . CaO . 6SiO₂
Lead glass:

**Raw Materials**
- Silica
- Lead Oxide
- Potassium Oxide

**Properties**
- Bright, lustrous and possesses high specific gravity
- Expensive to manufacture, than ordinary lime-soda glass
- Lower softening temperature than soda-lime glass
- Higher refractive index and excellent electrical properties

**Uses**
- High quality table wares, neon sign tubings, optical lenses
- High dense glasses are used for windows to protect from X-rays and gamma rays

**Composition**
\[ \text{K}_2\text{O} \cdot \text{PbO} \cdot 6\text{SiO}_2 \]
Pyrex-glass:

**Raw Materials**
- Silica
- Small amount of alumina
- Some oxides

**Properties**
- Substitution of alkali ($\text{Na}_2\text{O}$) and basic alkaline earth oxides ($\text{CaO}$) of the soda glasses by boron and aluminium oxides results in low thermal co-efficient
- High softening point and excellent resistivity (shock proof)
- High chemical resistance

**Uses**
Industrial pipeline for corrosive liquids, gauge glasses, superior laboratory apparatus etc.
Alumino Silicate glass:

**Raw Materials**
- 5% more of alumina
- Addition of alumina makes glass heat resistant

**Properties**
- Exceptionally high softening temperature
- Chemically durable
- Resistance to hydrolysis
- Affected by moisture due to high surface area

**Uses**
- High pressure mercury discharge tubes, chemical combustion tubes, specific domestic equipments
- Fibre glass
Glass wool:

- Fibrous wool-like material, composed of intermingled fine threads (or) filaments of glass
- Alkali free
- Glass filaments are obtained by forcing molten glass through small orifices which measures about 0.0005 to 0.0007 mm in diameter

Properties
- Very good fire-proof and heat proof
- Very low electrical conductivity and thermal conductivity
- Resistance to water and most chemicals
- Tensile strength is 8X of steel

Uses
- Heat insulation purpose
- Electrical and sound insulation
- Filtration of corrosive liquids like acids
- Manufacturing fibre-glass, by blending with plastic resins
Chapter nine: purification of water
Introduction:

- Water is a transparent, tasteless, odorless, and nearly colorless chemical substance, which is the main constituent of Earth's streams, lakes, and oceans, and the fluids of most living organisms.

- It is vital for all known forms of life, even though it provides no calories or organic nutrients. Its chemical formula is $\text{H}_2\text{O}$, meaning that each of its molecules contains one oxygen and two hydrogen atoms connected by covalent bonds.

- Water is the name of the liquid state of $\text{H}_2\text{O}$ at standard ambient temperature and pressure.

- It forms precipitation in the form of rain and aerosols in the form of fog. Clouds are formed from suspended droplets of water and ice, its solid state. When finely divided, crystalline ice may precipitate in the form of snow. The gaseous state of water is steam or water vapor.

- Water moves continually through the water cycle of evaporation, transpiration (evapotranspiration), condensation, precipitation, and runoff, usually reaching the sea.
Chemical and physical properties:

- Pure water has a low electrical conductivity, which increases with the dissolution of a small amount of ionic material such as common salt.

- Water is a good solvent and is often referred to as the universal solvent. Substances that dissolve in water, e.g., salts, sugars, acids, alkalis, and some gases – especially oxygen, carbon dioxide (carbonation) are known as hydrophilic (water-loving) substances, while those that do not mix well with water (e.g., fats and oils), are known as hydrophobic (water-fearing) substances.

- Pure water has a concentration of the hydroxide ion (OH\(^-\)) equal to that of the hydrogen ion (H\(^+\)), which gives a pH of 7 at 25 °C.

- Rain is generally mildly acidic, with a pH between 5.2 and 5.8 if not having any acid stronger than carbon dioxide. If high amounts of nitrogen and sulfur oxides are present in the air, they too will dissolve into the cloud and rain drops, producing acid rain.
Water's hardness is determined by the concentration of multivalent cations in the water. Multivalent cations are positively charged metal complexes with a charge greater than 1+. Usually, the cations have the charge of 2+. Common cations found in hard water include Ca$^{2+}$ and Mg$^{2+}$. These ions enter a water supply by leaching from minerals within an aquifer. Common calcium-containing minerals are calcite and gypsum. A common magnesium mineral is dolomite (which also contains calcium). Rainwater and distilled water are soft, because they contain few ions.

The following equilibrium reaction describes the dissolving and formation of calcium carbonate and calcium bicarbonate (on the right):

$$\text{CaCO}_3 (s) + \text{CO}_2 (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{Ca}^{2+} (aq) + 2\text{HCO}_3^- (aq)$$

The reaction can go in either direction. Rain containing dissolved carbon dioxide can react with calcium carbonate and carry calcium ions away with it.

The calcium carbonate may be re-deposited as calcite as the carbon dioxide is lost to atmosphere, sometimes forming stalactites and stalagmites.

Calcium and magnesium ions can sometimes be removed by water softeners.
Temporary hardness is a type of water hardness caused by the presence of dissolved bicarbonate minerals (calcium bicarbonate and magnesium bicarbonate). When dissolved, these minerals yield calcium and magnesium cations (Ca\(^{2+}\), Mg\(^{2+}\)) and carbonate and bicarbonate anions (CO\(_3^{2-}\), HCO\(_3^{-}\)). The presence of the metal cations makes the water hard.

However, unlike the permanent hardness caused by sulphate and chloride compounds, this "temporary" hardness can be reduced either by boiling the water, or by the addition of lime (calcium hydroxide) through the process of lime softening.

Boiling promotes the formation of carbonate from the bicarbonate and precipitates calcium carbonate out of solution, leaving water that is softer upon cooling.

\[
\text{Ca(HCO}_3\text{)}_2 \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \\
\text{Mg(HCO}_3\text{)}_2 \rightarrow \text{MgCO}_3 + \text{CO}_2 + \text{H}_2\text{O}
\]

Permanent hardness is a type of hardness that cannot be removed by boiling.

When this is the case, it is usually caused by the presence of calcium sulphate/calcium chloride and/or magnesium sulphate/magnesium chloride in the water, which do not precipitate out as the temperature increases. Ions causing permanent hardness of water can be removed using a water softener, or ion exchange column.

Washing soda (sodium carbonate - Na\(_2\)CO\(_3\)) is easily obtained and has long been used as a water softener for domestic laundry, in conjunction with the usual soap or detergent.
Ca\((HCO_3)_2\) + Na\(_2\)CO\(_3\) \rightarrow Ca CO\(_3\) + 2NaHCO\(_3\)

Mg\((HCO_3)_2\) + Na\(_2\)CO\(_3\) \rightarrow MgCO\(_3\) + 2NaHCO\(_3\)

CaCl\(_2\) + Na\(_2\)CO\(_3\) \rightarrow Ca CO\(_3\) + 2NaCl

MgCl\(_2\) + Na\(_2\)CO\(_3\) \rightarrow MgCO\(_3\) + 2NaCl

CaSO\(_4\) + Na\(_2\)CO\(_3\) \rightarrow CaCO\(_3\) + Na\(_2\)SO\(_4\)

MgSO\(_4\) + Na\(_2\)CO\(_3\) \rightarrow MgCO\(_3\) + Na\(_2\)SO\(_4\)
اللهم انفعنا بما علمتنا و قنا عذاب النار