US03CICV21

UNIT-1

SYLLABUS

- **Water**- Impurities and hardness of natural water, Water for steam making and industrial processes, Boiler water treatments, Calculations on water treatments.
- **Fuels**-Classification, Advantages and disadvantages, Analysis of fuels, heating media.
- **Air-** Specification for industrial uses of air. Industrial applications of CO_2, O_2, N_2 and H_2

WATER

WATER

- INTRODUCTION
- Water is nature’s most wonderful, abundant and useful compound.
- Without water human and plant cannot be survive. Water is one the most essential compound like air, food, shelter for human.
- It also occupies unique position in industries too. The most important use is in the steam generation.
- Water is also widely used in production of steel, rayon, paper, atomic energy, textiles, chemicals, ice and for air-conditioning, drinking, bathing, sanitary, washing, irrigation, fire-fighting etc.

SOURCES OF WATER

- Surface waters
- Rain water
- It is probably the purest form of natural water, since it is obtained as a result of evaporation from the surface water. However, during the journey downwards through the atmosphere, it dissolves a considerable amount of industrial gases (like CO2, SO2, NO2, etc.) and suspended solid particles, both of organic and inorganic origin.
- River water
- Rivers are fed by rain and spring waters. Water from the sources flow over the surface of land, dissolves the soluble minerals of the soil and finally falls in rivers. In general, the greater the contact that water has with the soil, or the more soluble the minerals of the soils with which it has come in contact, the greater is the amount of dissolved impurities in river water.

- River water thus contains dissolved minerals of the soil such as chlorides, sulfates, bicarbonates of sodium, calcium, magnesium and iron. River water also contains the organic matter, derived from the decomposition of plants, and small particles of sand and rock in suspension. Thus, river water contains considerable amounts of dissolved as well as suspended impurities.
- Lake water
- It has a more constant chemical composition. It, usually, contains much lesser amounts of dissolved minerals than even well water, but quantity of organic matter present in it is quite high.
- Sea water
- It is the most impure form of natural water. Rivers join sea and throw in the impurities carried by them.
- Moreover, continuous evaporation of water, from the surface of sea, makes sea water continuously richer in dissolved impurities. Sea water contains, on an average, about 3.5% of dissolved salts, out of which about 2.6% is sodium chloride.
- Other salts present are sulfate of sodium; bicarbonates of potassium, magnesium and calcium; bromides of potassium and magnesium and a number of other compounds. Surface water, generally, contains suspended matter, which often contains the disease-producing (or pathogenic) bacteria. Hence, such waters as such are not considered to be safe for human consumption.

- **Underground waters**
- A part of the rain water, which reaches the surface of the earth, percolates into the earth. As this water journeys downwards, it comes in contact with a number of mineral salts present in the soil and dissolves some of them.
- Water continues its downwards journey, till it meets a hard rock, when it retreads upwards and it may even come out in form of 'spring’.
- **Spring and well water or underground water** In general, is clearer in appearance due to the filtering action of the soil, but contains more of the dissolved salts.
- Thus, water from these sources contains more hardness. Usually, underground water is of high organic purity.

COMMON IMPURITIES PRESENT IN NATURAL WATER

- Dissolved minerals: These are carbonates, bicarbonates, sulfates and chlorides of calcium, magnesium, sodium and potassium.
- Dissolved gases: mainly air and Carbon dioxide
- Suspended matter: consists of mineral matter, giving turbid or muddy water, Organic matter may also be present.
- Microscopic matter: of plant and bacterial life giving colour, taste and odour.

EFFECT OF WATER ON ROCKS AND MINERALS

- When water flow over/percolates through the ground rocks or solid, it gets contaminated due to the following physical and chemical changes:
- Dissolution of mineral
- Mineral constituents of rocks like sodium chloride, gypsum ($CaSO_4.2H_2O$), etc., readily dissolve in water.
- Hydration
- Some minerals like anhydrite ($CaSO_4$), olivine (Mg_2SiO_4), etc., readily undergo hydration, leading to the formation of products of increased volume; and consequently, leading to the disintegration of such mineral-bearing rocks. Thus:

$$\underset{\text{Anhydride}}{CaSO_4 + 2H_2O} \xrightarrow{\text{Hydration}} \underset{\text{Gypsum (of 33\% more volume)}}{CaSO_{4.}2H_2O}$$

$$\underset{\text{Olivine}}{MgSO_4 + x\,H_2O} \longrightarrow \underset{\text{Serpentine}}{Mg_2SiO_{4.}x\,H_2O}$$

Action of dissolved oxygen

Oxidation and hydration reactions are brought by dissolved oxygen,

$$\underset{\text{Magnetite}}{2Fe_3O_4} \xrightarrow[\text{Oxidaton}]{+1/_2\,O_2} \underset{\text{Haematite}}{3Fe_2O_3} \xrightarrow[\text{Hydration}]{2\,H_2O} \underset{\text{Limonite}}{3Fe_2O_{3.}\,2H_2O}$$

$$2FeS_2 + 2H_2O + 7O_2 \xrightarrow[\text{Hydration}]{\text{Oxidaton and}} 2FeSO_4 + 2H_2SO_4$$

Action of dissolved carbon dioxide

(a) Converts insoluble carbonates of Ca, Mg and Fe into soluble bicarbonates

$$\underset{\text{(Insoluble)}}{CaCO_3 + CO_2 + H_2O} \longrightarrow \underset{\text{(Soluble)}}{Ca(HCO_3)_2}$$

$$\underset{\text{(Insoluble)}}{MgCO_3 + CO_2 + H_2O} \longrightarrow \underset{\text{(Soluble)}}{Mg(HCO_3)_2}$$

(b) Converts rock-forming silicates and alumino-silicates of Na, K, Co and Fe into soluble carbonates, bicarbonates and silica

$$K_2O.Al_2O_{3.}6SiO_2 + CO_2 + 2\ H_2O \longrightarrow Al_2O_{3.}2SiO_{2.}2H_2O + K_2CO_3 + 4\ SiO_2$$

Dissolved salts, fine clay and silica finally collect in water.

HARDNESS OF WATER

Hardness in water is that characteristic, which "prevents the lathering of soap". This is due to presence in water of certain salts of calcium, magnesium and other heavy metals dissolved in it. A sample of hard water, when treated with soap (sodium of potassium salt of higher fatty acid like oleic, palmitic or stearic) does not produce lather, but on the other hand forms a white scum or precipitate. This precipitate is formed, due to the formation of insoluble soaps of calcium and magnesium. Typical reactions of soap (sodium stearate) with calcium chloride and magnesium sulfate are depicted as follows

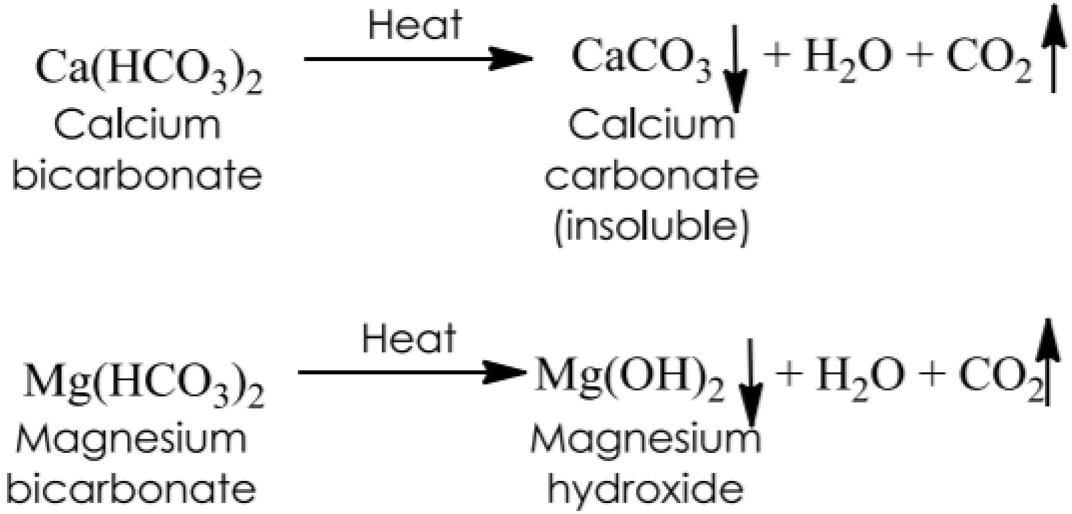
$$\underset{\substack{\text{Sodium stearate} \\ \text{(Sodium soap)}}}{2C_{17}H_{35}COONa} + \underset{\text{(Hardness)}}{CaCl_2} \longrightarrow \underset{\substack{\text{Calcium stearate} \\ \text{(Insoluble)}}}{(C_{17}H_{35}COO)_2Ca} \downarrow + NaCl$$

$$2C_{17}H_{35}COONa + MgSO_4 \longrightarrow \underset{\substack{\text{Mangesium stearate} \\ \text{(Insoluble)}}}{(C_{17}H_{35}COO)_2Mg} \downarrow + Na_2SO_4$$

Thus, water which does not produce lather with soap solution readily, but forms a white curd, is called **hard water**. On the other hand, water which lathers easily on shaking with soap solution, is called **soft water**. Such water, consequently, does not contain dissolved calcium and magnesium salts in it.

Temporary or carbonate hardness

It is caused by the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals and the carbonate of iron. Temporary hardness is mostly destroyed by mere boiling of water, when bicarbonates are decomposed, yielding insoluble carbonates or hydroxides, which are deposited as a crust at the bottom of vessel. Thus,



$$Ca(HCO_3)_2 \xrightarrow{\text{Heat}} CaCO_3\downarrow + H_2O + CO_2\uparrow$$

$$Mg(HCO_3)_2 \xrightarrow{\text{Heat}} Mg(OH)_2\downarrow + H_2O + CO_2\uparrow$$

Permanent or non-carbonate hardness

- It is due to the presence of chlorides and sulfates of calcium, magnesium, iron and other heavy metals. Unlike temporary hardness, permanent hardness is not destroyed on boiling.

DETERMINATION OF HARDNESS

- There are two methods
- 1.Clark's method or Soap method
- In this sample test, 70 ml. of water is taken in a 300ml bottle. A standard soap solution is added from a burette and the bottle is shaken. The volume of soap required to produce lather stable for 5 minutes is noted and hardness is calculated. After some experience fairly accurate results can be obtained. It is estimated that if about 2 kg. Of common soap is added to 100 liters of water of hardness 100 mg.-liter, it would get precipitated by the salts present in the water. Lather would be produced only if more than this amount of soap is used.

- 2.Complexometric method or EDTA (Versenate solution) method
- This method gives more accurate results than previous method. Fixed amount of water with indicator erichrome black T is taken into the flask. Buffer solution of pH=10 is added to the flask because in acidic solution indicator (EBT) will polymerize to red-brown product. So to prevent this, buffer solution is added.
- The solution becomes light red in colour. If EDTA (Ethylene diamine tetra acetic acid) is added to such a solution, the calcium and magnesium ions will form complex with EDTA.
- When the formation of complex with the free ions is completed, EDTA extracts the ions from dye and solution turns blue. This is the end point. Hardness is calculated in parts per million (ppm) from the reading obtained and ml. of water taken.
- Total hardness (X) In terms of CaCO3

$$= \frac{\text{Burette reading} \times 106}{\text{ml. of water taken}}$$

$$= X \text{ ppm}$$

UNITS OF HARDNESS

- Parts per million (ppm) It is the parts of calcium carbonate equivalent hardness per 106 parts of water, i.e. 1 ppm = 1 part of CaCO3 eq. hardness in 106 parts of water.
- Milligrams per liter (mg/L)
- It is the number of milligrams of CaCO3 equivalent hardness present per liter of water.
- Thus,
- 1 mg/L = 1 mg of CaCO3 eq. hardness per L of water But 1 L of water weighs

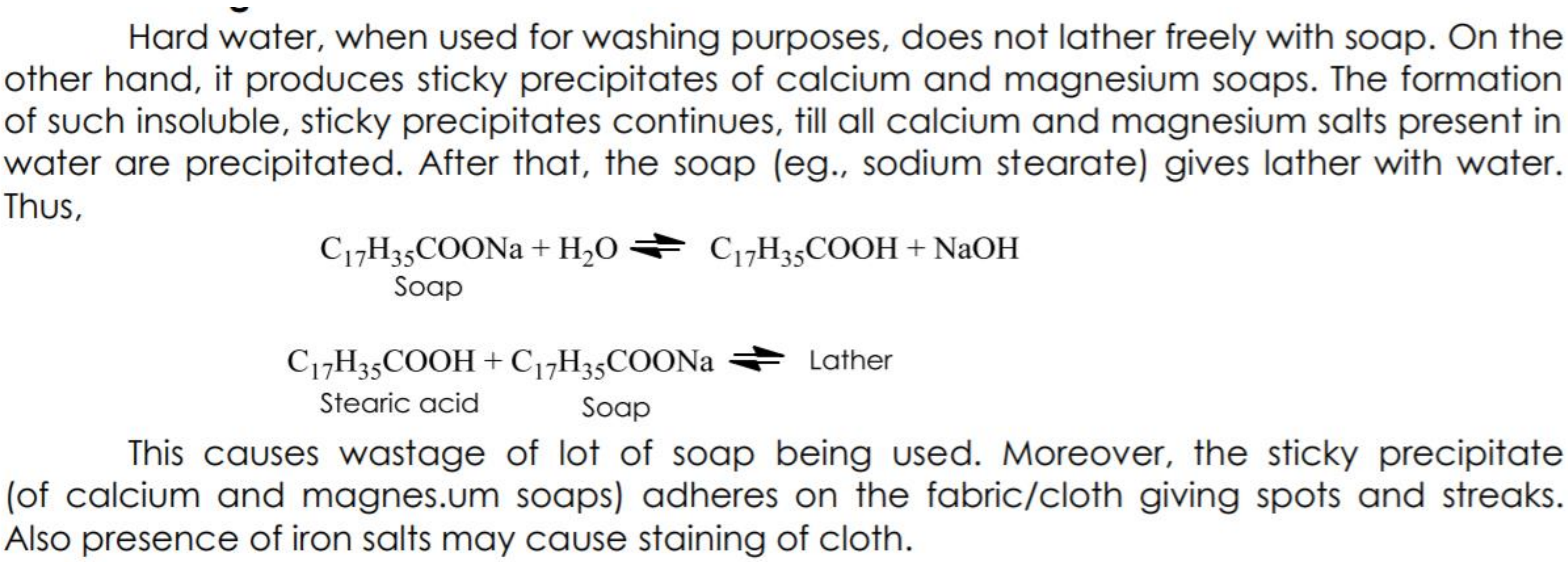
= 1 kg = 1,000 g = 1,000 X 1,000 mg = 106 mg.

1 mg/L = 1 mg of CaCO3 eq. per 106 mg of water

= 1 part of CaCO3 eq. per 106 parts of water = 1 ppm.

DISADVANTAGES OF HARD WATER

- Domestic use
- Washing



Hard water, when used for washing purposes, does not lather freely with soap. On the other hand, it produces sticky precipitates of calcium and magnesium soaps. The formation of such insoluble, sticky precipitates continues, till all calcium and magnesium salts present in water are precipitated. After that, the soap (eg., sodium stearate) gives lather with water. Thus,

$$\underset{\text{Soap}}{C_{17}H_{35}COONa} + H_2O \rightleftharpoons C_{17}H_{35}COOH + NaOH$$

$$\underset{\text{Stearic acid}}{C_{17}H_{35}COOH} + \underset{\text{Soap}}{C_{17}H_{35}COONa} \rightleftharpoons \text{Lather}$$

This causes wastage of lot of soap being used. Moreover, the sticky precipitate (of calcium and magnesium soaps) adheres on the fabric/cloth giving spots and streaks. Also presence of iron salts may cause staining of cloth.

- Bathing
- Hard water does not lather freely with soap solution, but produces sticky scum on the bath-tub and body. Thus, the cleansing quality of soap is depressed and a lot of it is wasted.
- Cooking
- Due to the presence of dissolved hardness-producing salts, the boiling point of water is elevated. Consequently, more fuel and time are required for cooking. Certain foods such as pulses, beans and peas do not cook soft in hard water. Also tea or coffee, prepared in hard water, has an unpleasant taste and muddy-looking extract. Moreover, the dissolved salts are deposited as carbonates on the inner walls of the water heating utensils.

- Drinking
- Hard water causes bad effect on our digestive system. Moreover, the possibility of forming calcium oxalate crystals in urinary tracks is increased.

Industrial use

- Textile industry
- Hard water causes much of the soap (used in washing yarn, fabric, etc.) to go as waste, because hard water cannot produce good quality of lather. Moreover, precipitates of calcium and magnesium soaps adhere to the fabrics. These fabrics, when dyed latter on, do not produce exact shades of colour. Iron and manganese salts-containing water may cause coloured spots on fabrics, thereby spoiling their beauty.

- Sugar industry
- Water containing sulfates, nitrates, alkali carbonates, etc., if used in sugar refining, causes difficulties in the crystallization of sugar. Moreover, the sugar so-produced may be deliquescent.
- Dyeing industry
- The dissolved calcium, magnesium and iron salts in hard water may react with costly dyes, forming undesirable precipitates, which yield impure shades and give spots on the fabrics being dyed.
- Paper industry
- Calcium and magnesium salts tend to react with chemicals and other materials employed to provide a smooth and glossy (i.e., shining) finish to paper. Moreover, iron salts may even affect the colour of the paper being produced.

- Laundry
- Hard water, if used in laundry, causes much of the soap used in washing to go as waste. Iron salts may even cause coloration of the clothes.
- Concrete making
- Water containing chlorides and sulfates is used for concrete making, affects the hydration of cement and the final strength of the hardened concrete.
- Pharmaceutical industry
- Hard water, if used for preparing pharmaceutical products (like drugs, injections, ointments, etc.,) may produce certain undesirable products in them.

Steam generation in boilers

- For steam generation, boilers are almost invariably employed. If the hard water is fed directly to the boilers, there arise many troubles such as

1. Carry over
2. Corrosion
3. Scale formation
4. Caustic embrittlement
5. Turbine deposits

MAJOR BOILER TROUBLES

- Carry over
- As steam emerges from the surface of the water, it is associated with tiny droplets of water. Such steam is called wet steam. The droplets may carry with them suspended matter besides the dissolved matter present in the boiler water. Such carryover of water by steam along with suspended and the dissolved solids are called carry over. It is mainly due to priming and foaming.

- Priming
- It is such rapid or violent boiling of water occurring in the boiler that water is carried into the steam outlet in the form of spray.
- Priming is because of

➢ Very high water level

➢ Presence of excessive foam filling the steam space

➢ High steam velocity

➢ Sudden steam demand leading to sudden boiling

➢ Faulty boiler design

- Priming is controlled by

- ➢ Keeping the water level as low as possible. Slight lowering of water level greatly reduces priming
- ➢ Avoid sudden steam demands, (by suddenly taking out a quantity of steam from boiler, the pressure in the boiler is reduced, the boiling point of water is reduced and super heated water is suddenly converted into steam minimizing foaming)

- Foaming
- It is the formation of small but stable bubbles above the surface of water. These are carried over along with steam, leading to excessive priming.
- Foam formation takes place when the concentration of solid in the surface layer is different from that in the mass of the liquid.
- This means that the solid must change the surface tension of water and promote foaming.
- Presence of fatty oil may form soap with the alkalinity. Soap greatly reduces surface tension of water.
- Foaming can be controlled by the use of anti-foaming chemicals. e.g. Castor oil, which spreads on the surface of the water. This oil is used for low-pressure boilers.
- Only satisfactory way for foaming is blow down, i.e. removal of concentrated boiler water and replacing if by fresh feed water.

- Carry over is undesirable because

- A considerable amount of heat is wasted by the removal of hot boiler water (i.e. in case of blow down).
- Water reduces superheat of steam in the super heaters.
- water takes along with it grit which strikes on the surface at high velocity and damages the walls
- Water contains large amount of dissolved solids which gradually get deposited and restrict the passage in the pipelines, causing corrosion and insulation,
- Water entering the steam engine cylinder causes serious trouble because of its incompressibility and inability to escape quickly through the steam parts.
- Foaming of water makes it difficult to know the exact level of water in the gauge glass.

- Corrosion
- It is one of the most serious problems caused by the use of unsuitable water. Boiler tubes, drums, economizers, super heaters and condensers are the most affected parts.
- The corrosion problem extends even to parts, which are not directly. In connect with boiler water because gases like O2 and CO2 are released during heating of water.
- These gases have corrosive effects corrosion is because of:

➢ Dissolved oxygen

➢ Mineral acids

➢ Dissolved CO2

➢ Galvanic cell formation

- Dissolved oxygen
- Dissolved oxygen in water is mainly responsible for corrosion in boilers. Dissolved O2 in presence of moisture and at high temperature readily attacks iron. At high pressure, O2 will dissolve more and high temperature reduces O2 content. Solubility of O2 in pure water is more than in the impure water.
- Dissolved oxygen can be removed by
- (a) Mechanical deaerator:
- (b)Pre-heating:
- (c)Chemical treatment:

- (a) Mechanical deaerator: Various types of deaerators have been designed. In a cylindrical chamber, water falls through perforated plates or is sprayed, so that larger surface is exposed. The deaerator is connected to a vacuum line, which sucks out the gases.
- (b)Pre-heating: Solubility of a gas decreases with rise in temperature. Air begins to be expelled at temperature of about 65°C and is completely removed at the boiling point. Water is sprayed in a cylindrical equipment and steam moving in opposite direction. Steam heats and carries away the gases, which have been liberated.
- (c)Chemical treatment: for complete removal of O_2 chemical treatment is required. This is done by adding a reducing agent, sodium sulphite being commonly used, which reacts as follows:
- $2Na_2SO_3 + O_2 \rightleftarrows 2Na_2SO_4$

- Ferrous sulfate is also used. It gives precipitate of Fe(OH)2 which is oxidized to Fe(OH)3. In high-pressure boiler, even traces of O2 are undesirable hydrazine is added in such amounts that after reacting as under, residual hydrazine is about 0.02 mg/litre.
- $N2H4 + O2 \rightleftharpoons 2H2O + N2$
- Thus no solid is added to the boiler. Hydrazine should be handled carefully; usually its solutions are used.

Mineral acids

Natural waters are alkaline. Waters in the mining areas are often acidic. In industrial areas the water may become acidic due to acidic industrial waste discharge into water.

Magnesium salts may hydrolyze to produce acidity as follows:

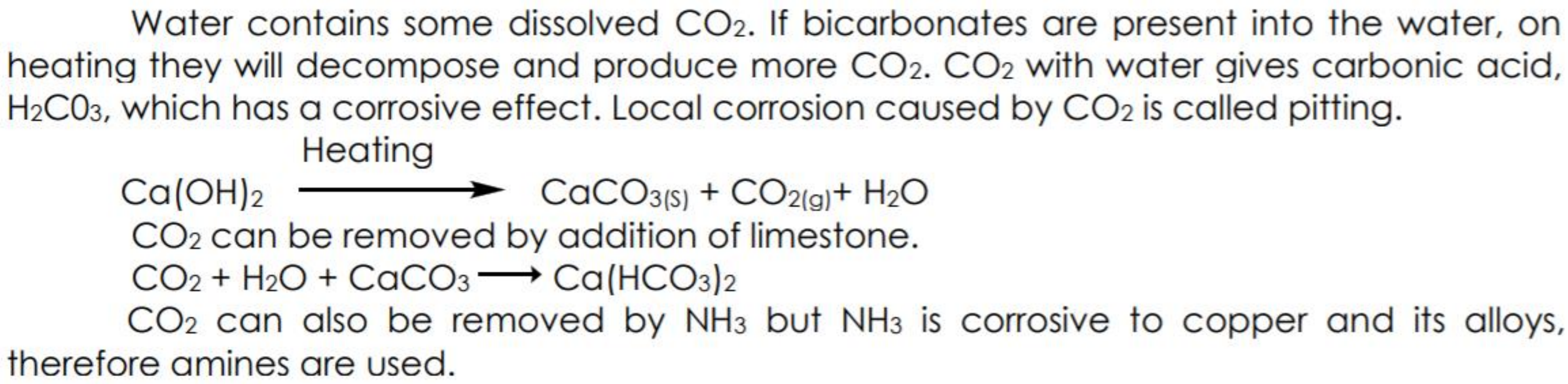
$MgCl_2 + 2H_2O \rightleftharpoons Mg(OH)_2 + 2HCl$(Mineral acid)

$Fe + 2HCl \rightleftharpoons FeCl_2 + H_2$

$FeCl_2 + 2H_2O \rightleftharpoons Fe(OH)_2 + 2HCl$

Thus small amount of $MgCl_2$ will cause corrosion of a large amount of iron by producing HC1. Boiler water should have a pH value of about 10.5 so that acid may not attack iron.

Carbon dioxide



Water contains some dissolved CO_2. If bicarbonates are present into the water, on heating they will decompose and produce more CO_2. CO_2 with water gives carbonic acid, H_2C0_3, which has a corrosive effect. Local corrosion caused by CO_2 is called pitting.

$$Ca(OH)_2 \xrightarrow{\text{Heating}} CaCO_{3(S)} + CO_{2(g)} + H_2O$$

CO_2 can be removed by addition of limestone.

$$CO_2 + H_2O + CaCO_3 \longrightarrow Ca(HCO_3)_2$$

CO_2 can also be removed by NH_3 but NH_3 is corrosive to copper and its alloys, therefore amines are used.

- **Galvanic cells**
- Galvanic cells which iron forms with some of the boiler fittings made of other materials or with impurities, which cause corrosion. Zn is more electropositive than iron hence it is anodic to iron and gets dissolved first and iron is saved.

Scale formation

- Water containing impurities is fed into the boiler and pure water is removed in the form of steam leaving behind the impurities. Some of the deposits stick to the metal surface and are known as scale.
- If they are in the form of soft and muddy deposits, which can be removed easily, are known as sludges. Scale formation takes place because of salt like $Ca(HCO3)2$ which gives off $CO2$ and insoluble $CaCO3$ is precipitated on boiler surface giving the scale.
- Some salts having lower solubility at high temperature cause crystallization, e.g. $CaSO4$ crystalizes out on the surface at high temperature. Silicate of Calcium and magnesium or other silicates deposit cause trouble because they are poor thermal conductor.

Disadvantages of scale formation

Waste of Fuel: The scales are bad conductors of heat, therefore they act as a insulator on the surface. This results in reduction in the heat transfer rate hence large quantity of fuel is required to maintain the rate of heat transfer.

Overheating of the boiler tubes: This is explained by following figure

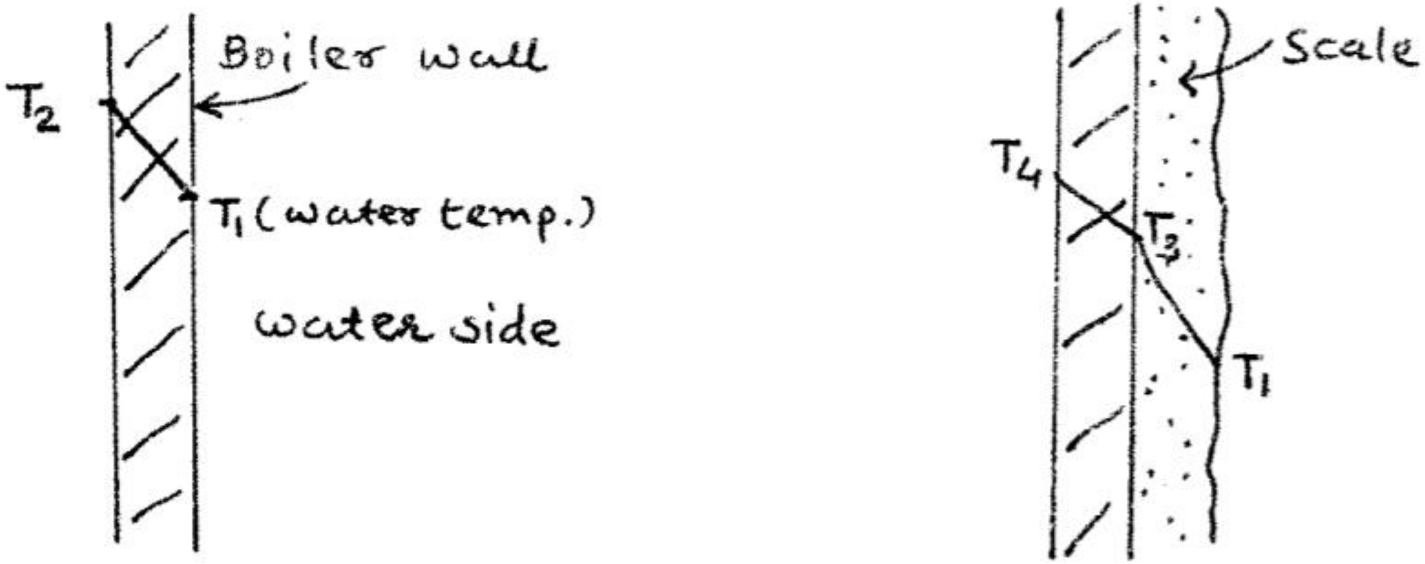


Figure: 1 Insulating effect of scales

The figure to the right represents surface with scale. Therefore, heating the water to $T_1{}^{0}$C the metal surface in the heat source side is heated to$T_4{}^{0}$C which is higher than $T_2{}^{0}$C.

- At high temperature metal becomes weak and cannot withstand high pressure. This becomes dangerous.
- Prevention of scale formation
- External treatment: It is given outside the boiler to remove the calcium and magnesium salts and silica from water which forms scale. For this, external equipment is needed which requires an investment.
- Internal treatment: Chemicals are added into the water entering the boiler, to convert the remaining salts into more insoluble salts that will be in form of nonstick sludge. This can be easily removed.
- Blow down: In spite of giving external and internal treatment, concentration of impurities goes on increasing and practical solution is to make a blow down, i.e. remove the portion of the concentrated water which contains a large amount of dissolved matter. Along with it some sludge is also removed.

Caustic embrittlement

- Caustic embrittlement Sometimes boiler failure is due to metal plate becoming brittle and cracks having been formed in the metal. This happens in areas which are under stress.
- Alkali metal carbonates and bicarbonates present in water give rise to caustic alkalinity at high temperature and pressure,
- $NaHCO3 \longrightarrow NaOH + CO2$
- Alkali metal Caustic Bicarbonate The concentration becomes greater near the rivets because of bad circulation of water and also the leaks through which steam escapes leaving behind water with a higher concentration of caustic alkalinity.

- Turbine deposits
- To avoid or to minimize the turbine deposit, chemical analysis throughout the steam and water line is carried out. Chemicals are added properly and mixed properly. Operate demineralization plant properly to avoid the dissolved mineral matters.

METHODS OF BOILER WATER TREATMENT

- The common treatments given to the boiler water to overcome from the troubles are described below
- **Preliminary treatments** They may include simple treatments like

- sedimentation
- coagulation and
- filtration.

Sedimentation and Coagulation

- Sedimentation means simple settling.
- It is the process by which the force of gravity acts on particles heavier than water and causes them to move downwards and settle.
- For this purpose water is kept in huge tanks, called sedimentation tanks in which water moves very slowly.
- Time required for sedimentation depends on the weight, size and shape of particles and the viscosity and factional resistance of water.
- Because viscosity varies with temperatures the settling rate varies in differ at season. Sedimentation requires 4-12 hours. Generally, only 70% of suspended matter settles down by plain sedimentation.
- Further removal of matter is done by addition of coagulants like, alum, ferrous sulfate, ferric chloride, sodium aluminate etc. Generally about 95% suspended matter is removed by coagulation.
- Coagulation reactions are salt hydrolyses and produce a flow of the hydroxide e.g. $Al(OH)3$ and $Fe(OH)3$. The flocculent precipitate so produce has a large surface area and the floe removes the finally divided matter by adsorption or electrical attraction of oppositely charged particles, which quickly settle down.

Filtration

- It is the process of passing a liquid containing suspended matter through a suitable porous material in such a manner as to effectively remove the suspended matter from liquid.
- Two types of filters are used viz., gravity filters and pressure filters

Pre-heating

- It is heating feed water before enters the boiler.
- Very often blow down and low pressure steam is available. Hot fuel gas also is used for pre-heating.
- Water may be heated in a heat exchanger.

Advantages

- Save fuel
- Removes temporary hardness

  $Ca(HCO_3)_2 \xrightarrow{\qquad} CaCO_3(s) + CO_2 + H_2O$

- Removes dissolved O_2 + CO_2. Initially at 65°C dissolved gases are removed from water and almost completely removed at boiling point. Thus removal of corrosive gases is advantageous.
- Use of hot water in chemical treatments such as lime-soda process, greatly helps in the process

Lime-soda process

- It is used for feed water treatment for low and medium pressure boilers.
- Lime and soda convert the soluble impurities, into insoluble salts, which get precipitated and after settling they are filtered off.
- Lime is generally 10% excess is added to water. Its advantages are Temporary hardness is removed by the following reactions:
- $Ca(HCO3)2 + Ca(OH)2 \xrightarrow{\qquad} 2CaCO3 + 2H2$
- $Mg\ (HCO3)2 + 2Ca(OH)2 \xrightarrow{\qquad} 2CaCO3 + Mg(OH)2 + 2H2O$
- CaCO3 & Mg(OH)2 are precipitated.
- The removal of temporary hardness by lime does not introduce any soluble salt in water and reduce the total dissolve solids.

- **Lime also removes all permanent magnesium - hardness**
- $MgSO_4 / MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2(s) + CaSO_4 / CaCl_2$
- An equivalent amount of permanent calcium hardness is introduced, which has to be removed by soda treatment. Here, there is no softening.
- **Lime also removes free acids, CO_2 and H_2S**
- Soda Treatment: It removes the remaining calcium permanent hardness.
- $CaSO_4/CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3(s) + Na_2SO_4/2NaCl$

Lime - soda process

Batch process

Continuous process

Batch process

- In this process chemicals are added in batches in water taken in tanks, agitated for necessary time and the precipitate allowed to settle and then filtered.
- Fresh water is again taken into the tank and the operation is repeated.

Continuous process

- Water together with lime and soda solutions enters a smaller tank continuously at a predetermined rate.
- The chemicals and water to be treated enter a bigger tank or chamber.
- The second chamber is tall structure having a larger cross section at the top than at the bottom.
- As chemical reactions settle down, because towards the upper portion of chamber the velocity in less due to larger cross section, clear water is removed continuously from the top and sludge from the bottom.
- A part of sludge is recycled which helps in reuse of excess chemicals left behind in the sludge and also helps in precipitation by providing nuclei.

Cold lime soda process

- When the chemicals are added to water at atmospheric temperature, the process is **known as cold lime soda process.**
- At this temperature precipitate is finely divided and do not settle easily, nor can it be easily filtered.
- Therefore it is necessary to add coagulants like alum, aluminum sulfonate, sodium aluminate etc.
- Coagulants get hydrolyzed and form flocculent and gelation's precipitated which entraps the finely divided particles and settle down readily or are easily filtered off.
- Ferrous sulfate and sodium aluminate are costlier than alum. Ferrous sulfate helps to remove oxygen and sodium aluminate helps the removal of silica and also oil.

Hot lime soda process

- When this treatment is given at a higher temperature the process is **known as hot lime soda process.**
- Water is heated by waste steam or hot gases and calculated amount of chemicals is added as in cold process.
- **Advantages**

➢ As reactions proceed, quickly at higher temperature, the reactions are completed in about 15 min., whereas in the cold process, several hours are needed. This greatly increases the capacity of the plant.

➢ Precipitate and sludge formed settle rapidly at higher temperature; hence coagulants are not needed.

- Filtration becomes easier because of the bigger size, of the particles and the reduced viscosity of solution at the higher temperature; hence the capacity of the filter is also increased.
- Residual hardness, i.e. hardness of softened water needs careful consideration. Solubility of calcium salts is very slightly higher at low temperature. More than this, the time taken for the completion of the reaction at a lower temperature is greater. In the hot process the reaction time is less with the result that the hot process gives softer water. In some places, water is highly alkaline, and contains considerable amounts of sodium bicarbonates. On adding lime, calcium carbonate precipitates forming sodium carbonate.

$$2NaHCO3 + Ca(OH)2 \longrightarrow CaCO3 + Na2CO3 + 2H2O$$

- In such a case, soda may not be heated for the removal of permanent hardness. As a matter of fact, cases are known where gypsum has to be added to remove soda so produced.
- $Na2CO3 + CaSO4 \longrightarrow Na2SO4 + CaCO3(s)$

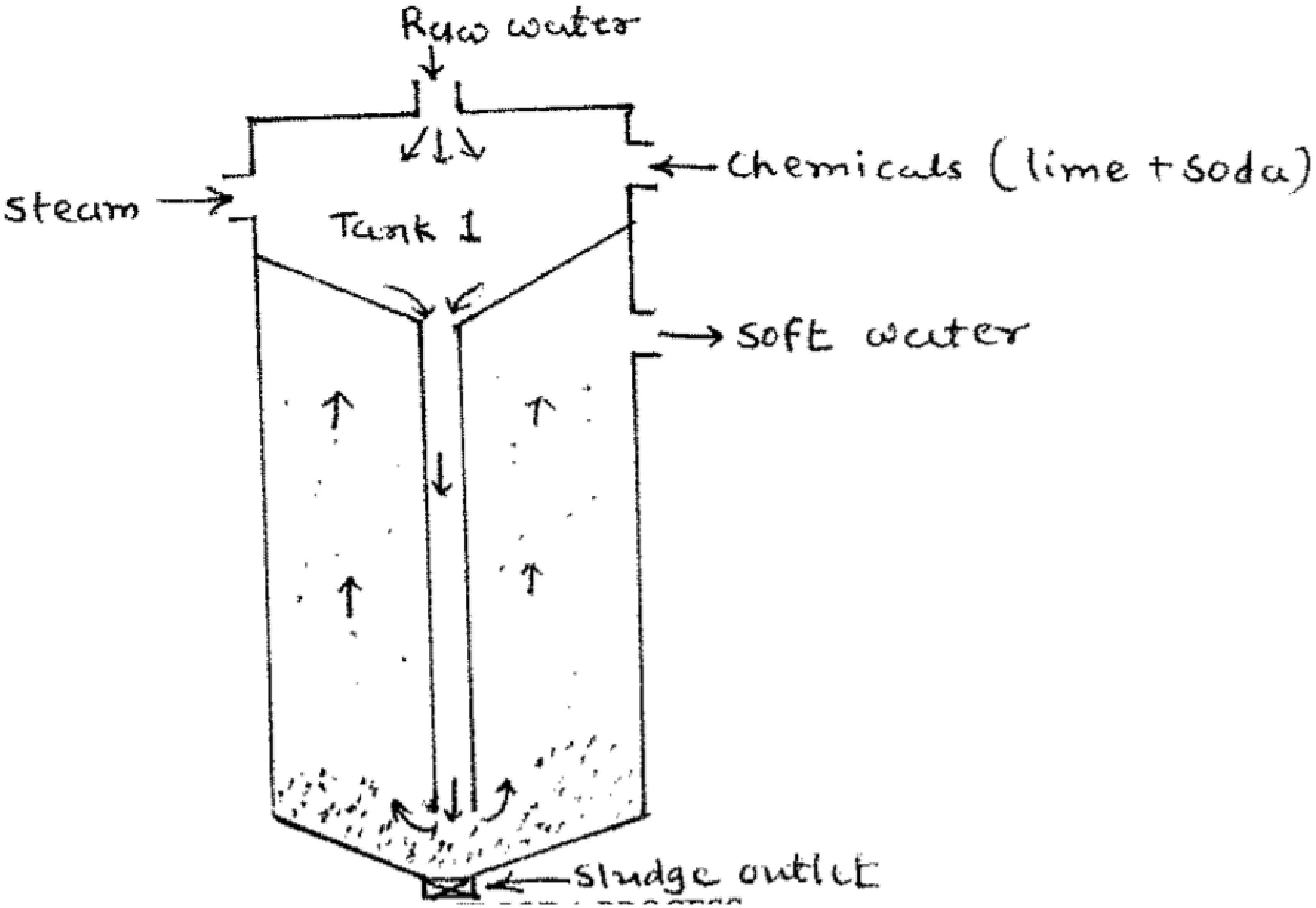


Figure: 2 Hot lime soda process

zeolite process

- Zeolites are natural or synthetic complex compounds, consisting of hydrated sodium aluminum silicates approximately corresponding to the chemical formula $Na_2O.Al_2O_3.2SiO_2.6H_2O$ Zeolites are insoluble.
- They introduce Na^+ in place of Ca^{+2} and Mg^{+2}. As these exchange bases, they are also known as base exchangers.
- If Na_2Z represents Zeolite, the reactions taking NaCl may be represented thus:
- $Ca(HCO_3)_2 + Na_2Z \longrightarrow 2NaHCO_3 + CaZ$
- $MgSO_4 + Na_2Z \longrightarrow Na_2SO_4 + MgZ$

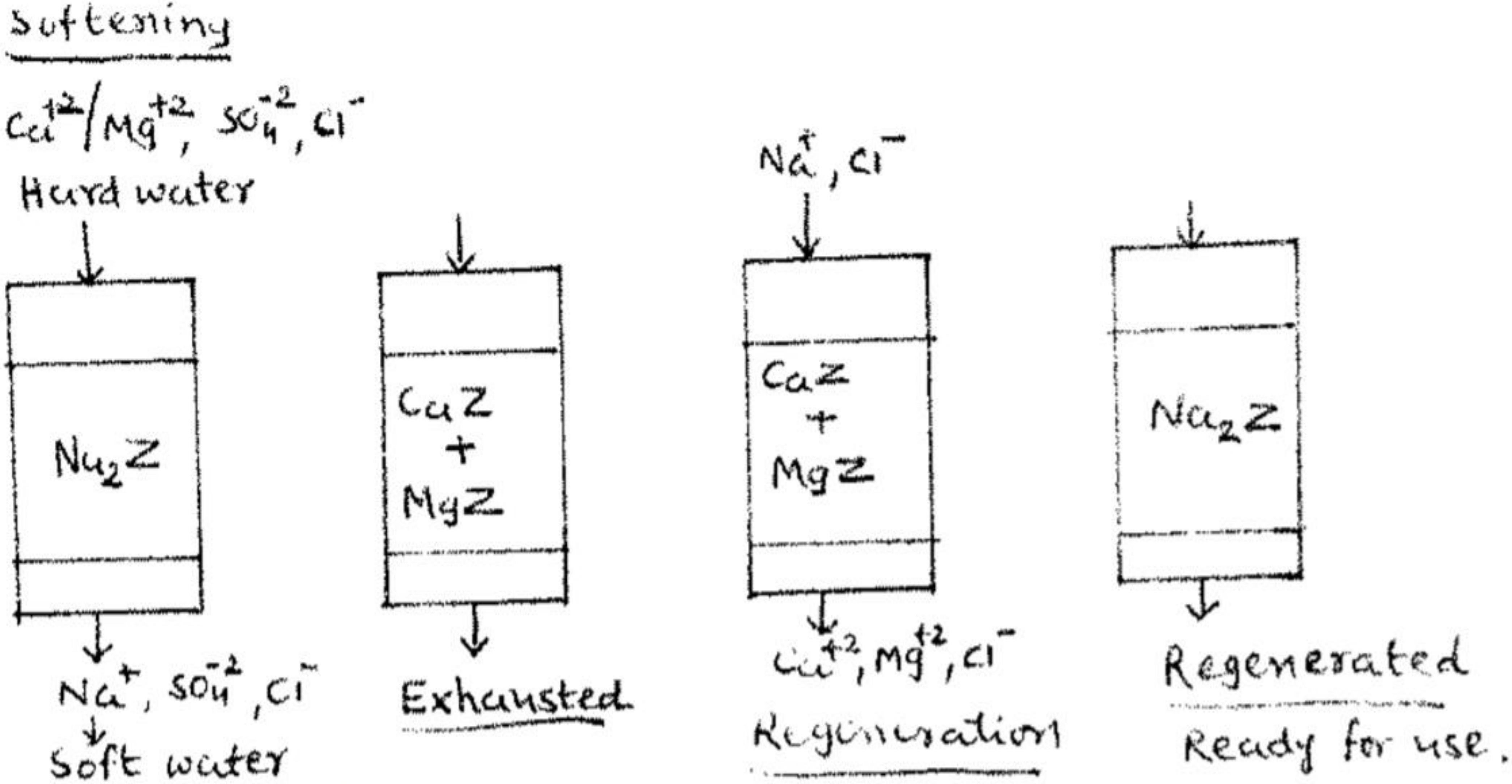


Figure: 3 Water softening by Zeolite process.

- Zeolites are kept in cylinders, which act as filter beds. Hard water is passed through them.
- The hardness causing substances are retained as insoluble compounds according to the reactions given above. After use for some time the zeolite is converted into Calcium or magnesium zeolite and then it stop to soften water.
- At this stage it has to be regenerated by treatment with a conc. sodium chloride solution. When the original sodium zeolite is recovered
- $CaZ + 2NaCl \xrightarrow{\hspace{2cm}} Na2Z + CaCl2$
- The Zeolite bed is again ready for use.
- Turbidity will clog the pores and restrict the flow, excess acidity alkalinity will attack the zeolite, therefore pH value should be around 7, iron or manganese salts will produce iron or manganese zeolites from which it cannot be easily regenerated.
- Therefore, these should be removed before passing water through zeolite bed. Hot water is not passed through zeolite bed because zeolite tends to dissolve in hot water.

- The temporary hardness will give water containing $NaHCO_3$ which dissociates inside the boiler giving high alkalinity
  $NaHCO_3 \longrightarrow NaOH + CO_2$

  Alkalinity causes caustic embrittlement.
- CO_2 with steam makes condensed water acidic, hence corrosive. Thus it is necessary to remove temporary hardness as far as possible before using zeolite.
- **Advantages**

➢It removes the hardness completely.

➢Equipment is a compact unit occupying a small space

➢It automatically adjusts itself to different hardness and can be worked under pressure, therefore plant can be installed in the water supply line and avoid double pumping

➢Impurities are not precipitated; there is no danger of sludge formation at a later stage.

Deionizer or Demineralizers

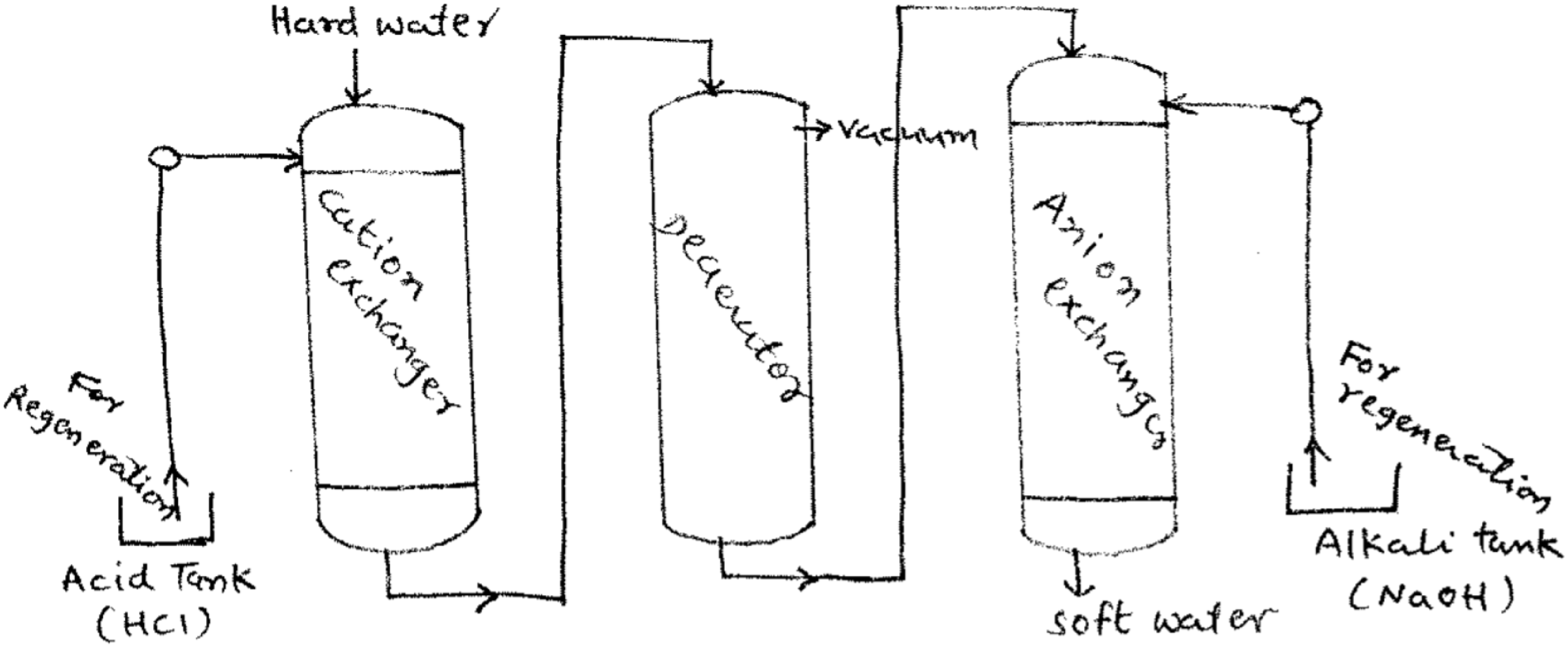


Figure: 4 Water softening by deionizer or demineralizer process

- Several organic substances - resins of complex chemical structures - which behave similar to the zeolites. By this process all the ions are removed. The cations are replaced by OH- . Water is treated in two cylinders containing the resins, one of which removes cations and other anions.
- When resins get used up, they are regenerated by acid and alkali treatment Suppose the first and second cylinders contain resins represented by the formulas H2R' and (OH)2R"the reactions may be represented thus :
- $CuSO_4 \xrightarrow{\qquad} Ca^{+2} + SO_4^{-2}$
- **Cylinder I**: $H_2R' + Ca^{+2} \xrightarrow{\qquad} 2H^+ + CaR'$
- Water coming out from cation exchanger is highly acidic. Water from nature contains large amount of carbonates and bicarbonates.
- These ions like other anion can be removed by passing through union exchanger. CO_3^{-2} & HCO_3^- in presence of H^+ form H_2CO_3 - (or $H_2O + CO_2$). The loud on anion Exchanger is reduces by having a deaerator which will remove CO_2.

- **Cylinder II:** $(OH)_2R'' + SO_4^{-2} \longrightarrow 2OH^- + SO_4R''$
- H^+ and OH^- unite to form H_2O, thus not solid is added to water. When the plant does not soften any more, the first cylinder is regenerated by passing a dil. Solution through it and second cylinder by passing dilute alkali.
- **Reactions for regeneration**
- **Cylinder I**: $CaR' + 2HCl \longrightarrow H_2R' + CaCl_2$
- **Cylinder II**: $SO_4R'' + 2NaOH \longrightarrow (OH)_2R'' + Na_2SO_4$
- Mixed bed deionizers are also now available. The main disadvantage of process is the equipment is costly and more expensive chemicals are needed for regeneration. If water contains turbidity or large amount of dissolved salts then the output is reduced.
- This process is very good for water for very high pressure boilers. For low pressure boiler, the equipment is rather costly and water may be treated more economically by other processes.

FEED WATER CONDITIONING

- It is treatment given to correct undesirable tendencies.
- **Phosphate treatment** In the lime- soda process, calcium is precipitated as $CaCO_3$, which is quite insoluble. However a small amount remains in solution. This can be removed by sodium phosphate (Na_3PO_4) which precipitates the less soluble $Ca_3(PO_4)_2$, thus hardness is further reduced.
- For the best results, the pH value of water should not be less than 9.5. For this purpose NaOH is added.
- $MgCl_2 + 2NaOH \longrightarrow Mg(OH)_2 + 2NaCl$
- $Ca(HCO_3)_2 + 2NaOH \longrightarrow CaCO_3 + Na_2CO_3 + 2H_2O$
- $3CaCO_3 + 2Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 3Na_2CO_3$
- Na_3PO_4 and NaOH precipitate magnesium as hydroxide and calcium as phosphate. These reagents are costlier than lime and soda. Na_3PO_4 treatment also helps to control pH value of water.
- Na_3PO_4 gives alkaline reaction and can be used to increase the pH value. This treatment is often given after lime-soda treatment.
- It has disadvantage of causing “after precipitation”, that is gradual precipitation in pipes, equipment, etc.

- **Sodium aluminate treatment** Sodium aluminate precipitates calcium and magnesium as insoluble aluminates $NaAlO_2$ hydrolyses also, giving $NaOH$ and $Al(OH)_3$.
- $NaOH$ so produced precipitates some of the magnesium as $Mg(OH)_2$. Flocculent precipitates of $Al(OH)_3$ and $Mg(OH)_2$ are produced which remove finely suspended and colloidal impurities., including silica and oil droplets, which are ordinarily difficult to remove.
- Sodium aluminate is cheaply available from bauxite refineries.
- **Treatment for microbiological growth** The growth of greenish matter may be commonly observed in stagnant waters. Similar growth may take place in heat exchangers, condensers and cooling systems.
- They restrict the flow of water and also retard the heat transfer. Sometimes they may come out suddenly in large masses and clog the pipe or the pump. Algae and slime are present in such water.

- Bacteria produce gas which can attack stainless steel and cause pitting.
- Chlorine is very effective to remove algae and slime. $CuSO_4$ is more effective for algae than for slime. It cannot be used is pH value is above 8.5 as copper hydroxide will be precipitated. Chromates are used for corrosion control and for control of algae and slime.
- Chloramine is also used. Bleaching powder mixed with NH_3 and when NH_3 and Cl_2 combine to Chloramine is formed which destroy the microbiological growth.
- **Fe and Mn Removal** These are present in small amounts in water in absence of dissolved O_2, Fe and Mn give red and black precipitates, respectively, when water comes in contact with air.
- They are highly undesirable in water for dye and tanning industries and for laundries. They also give metallic taste to water.
- They are remove in forms of insoluble $Fe(OH)_3$ & $Mn(OH)_2$ by oxidation, followed by coagulation and filtration. The oxidation may be by blowing of air in water.

- **Silica Removal**
- About 5-8 mg/lit silica is present in natural water. After lime-soda process because of alkalinity of water, during filtration through sand bed Silica dissolves in water.
- Calcium and Magnesium silicates act as cements and bind together other particles into a hard scale.
- Soluble silica is removed by the use of magnesium compounds like MgO. For high pressure boiler silica is removed by strongly basic anion exchangers.
- **Oil removal**
- Generally, natural waters are free from oil but small amounts are likely to come from the oils used for lubrication of the pumps.

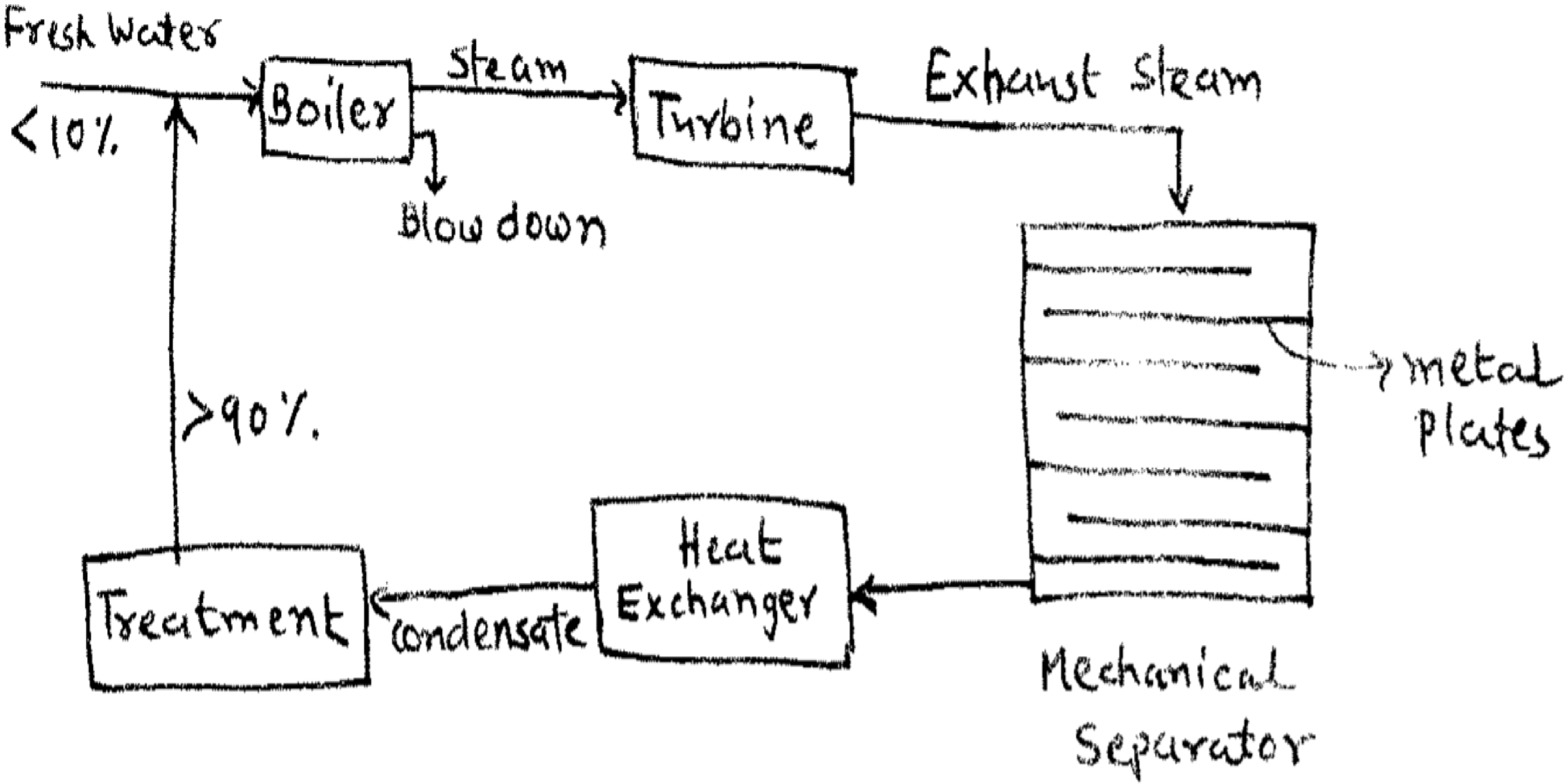


Figure: 5 Oil removals by mechanical separator

- For removal of oil the exhaust steam is passed through mechanical oil separators, which consists of a chamber with a number of metal plates.
- As the steam with droplets of oil passes over the plates, droplets of oil are retained on the metal surface. Thus most of the oil is removed. Sodium aluminate is added to the condensate, which removes remaining oil.
- If oil is vegetable or animal oil, it may get hydrolyzed producing fatty acids, which may have corrosive action. Fatty acids may combine with the alkalinity, producing soap, which forms sticky coating on the metal surface. These will attract other impurities and form thicker deposits.

- **O2 removal** Write down about preheating, deaerater and reducing agents in this topic, which you previously studied.
- **Boiler compounds** The inorganic constituents of boiler compounds precipitate the scale forming salts and also help to control the corrosion.
- The organic constituents are characterized by high molecular weights. These form large particles, which are adsorbed on the metal surface and then prevent the formation of hard scale.
- Boiler compounds are more expensive than the ingredients brought separately.

FUEL

INTRODUCTION

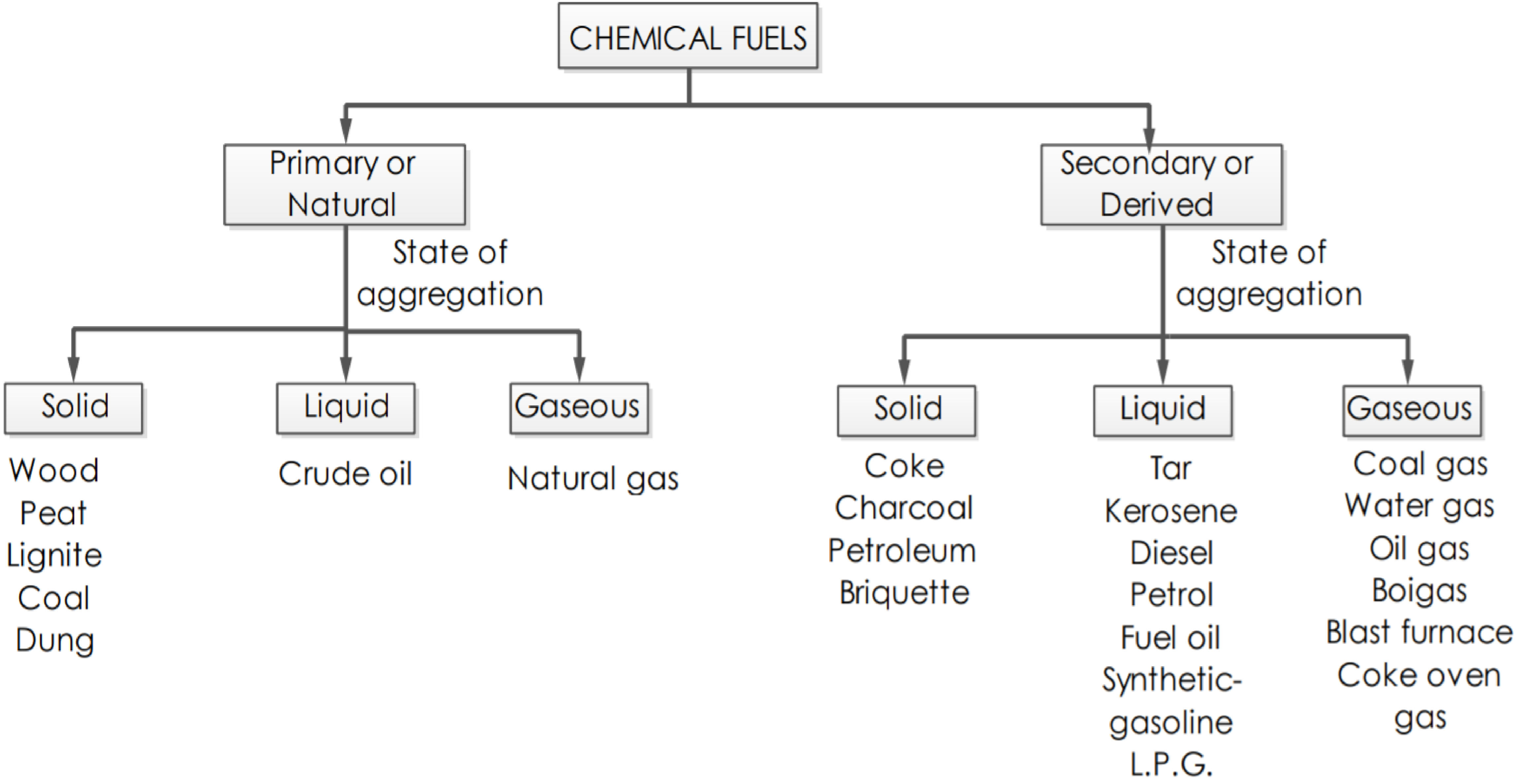
- Fuel is a combustible substance, containing carbon as main constituent, which on proper burning gives large amount of heat, which can be used economically for domestic and industrial purposes. Wood, charcoal, coal, kerosene, petrol, diesel, producer gas, oil gas, etc. are some of the fuels.
- During the process of combustion of a fuel (like coal), the atoms of carbon, hydrogen, etc. combine with oxygen with the simultaneous liberation of heat at a rapid rate.
- This energy is liberated due to the "rearrangement of valence elections" in these atoms, resulting in the formation of new compounds (like CO2, H2O, etc.).
- These new compounds have less energy (or heat content) in them and, therefore, the energy (or heat) released during the combustion process is the difference in the energy of the reactants (C, H, and O of fuel) and that of the products formed.

$$\underset{\text{More heat energy content}}{\text{Fuel}} + O_2 \longrightarrow \underset{\text{Lesser heat energy content}}{\text{Products}} + \text{Heat}$$

The primary or main sources of fuels are coals and petroleum oils, the amounts of which are dwindling day-by-day. These are stored fuels available in earth's crust and are, generally, called **'fossil fuels'.**

CLASSIFICATION OF FUELS

- **According to Occurrence (and preparation)**
- (a) Natural or primary fuels, which are found in nature as such, e.g., wood, peat, coal, petroleum, natural gas, etc.
- (b) Artificial or secondary fuels are those which are prepared form the primary fuels. For example, charcoal, coke, kerosene oil, diesel oil, petrol, coal gas, oil gas, producer gas, blast furnace gas, etc.
- **According to the state of aggregation**
- (a) Solid fuels; (b) liquid fuels, and (c) gaseous fuels.



CHEMICAL FUELS

- Primary or Natural
  - State of aggregation
    - Solid
      - Wood
      - Peat
      - Lignite
      - Coal
      - Dung
    - Liquid
      - Crude oil
    - Gaseous
      - Natural gas
- Secondary or Derived
  - State of aggregation
    - Solid
      - Coke
      - Charcoal
      - Petroleum
      - Briquette
    - Liquid
      - Tar
      - Kerosene
      - Diesel
      - Petrol
      - Fuel oil
      - Synthetic-gasoline
      - L.P.G.
    - Gaseous
      - Coal gas
      - Water gas
      - Oil gas
      - Boigas
      - Blast furnace
      - Coke oven gas

UNITS OF HEAT

Calorie

- Calorie is the amount of heat required to raise the temperature of one gram of water through one degree Centigrade (15-16°C).

Kilocalorie

- Kilocalorie (or Kilogram centigrade units) is equal to 1,000 calories. This is the unit of metric system and may be defined as 'the quantity of heat required to raise the temperature of one kilogram of water through one degree Centigrade. Thus
- 1 kcal = 1,000cal

British thermal unit (B.T.U.)

- BTU is defined as "the quantity of heat required to raise the temperature of one pound of water through one degree Fahrenheit (60-61°F). This is the English system unit.
- 1B.T.U. = 252cal = 0.252 kcal or
- 1 kcal = 3.968 B.T.U.

Centigrade heat unit (C. H. U.) CHU is "the quantity of heat required to raise the temperature of 1 pound of water through one degree Centigrade." Thus

1 kcal = 3.968 B.T.U. = 2.2 C.H.U.

CALORIFIC VALUE

- Calorific value of a fuel is "the total quantity of heat liberated, when a unit mass (or volume) of the fuel is burnt completely“

➢ **Higher or gross calorific value**

- Usually, all fuels contain some hydrogen and when the calorific value of hydrogen containing fuel is determined experimentally, the hydrogen is converted into steam. If the products of combustion are condensed to the room temperature (15°C or 60 °F), the latent heat of condensation of steam also gets included in the measured heat, which is then called "**higher or gross calorific value".**
- So, gross or higher calorific value (HCV) is "the total amount of heat produced, when unit mass / volume of the fuel have been burnt completely and the products of combustion have been cooled to room temperature" (i.e., 15 °C or 60 °F).

➢Lower or net calorific value

- In actual use of any fuel, the water vapour and moisture, etc., are not condensed and escape as such along-with hot combustion gases. Hence, a lesser amount of heat is available.
- So, net or lower calorific value (LCV) is "the net heat produced, when unit mass/ volume of the fuel is burnt completely and the products are permitted to escape".
- Alternatively, net or lower calorific value (LCV)

= HCV - Latent heat of water vapour formed

= HCV - Mass of hydrogen x 9 x Latent heat of steam

because 1 part by mass of hydrogen produces 9 parts by mass of water. The latent heat of steam is 587 kcal/kg or 1,060BTU/lb. of water vapour formed at room temperature (i.e., 15°C).

➢Units of calorific value

- The calorific value is, generally, expressed in calorie/gram (cal/g) or kilocalorie/kg {kcal/kg) or British thermal unit/lb. (B.T.U/lb.) in case of solid or liquid fuel.
- In case of gaseous fuels, the units used are kilocalorie/cubic metre (kcal/m3) or B.T.U./cubic feet (B.T.U./ft3).

CHARACTERISTICS OF A GOOD FUEL

- **High calorific value**
- A fuel should possess high calorific value, since the amount of heat liberated and temperature attained thereby depends upon the calorific value of fuel.
- **Moderate ignition temperature**
- Ignition temperature is the lowest temperature to which the fuel must be pre-heated so that it starts burning smoothly.
- Low ignition temperature is dangerous for storage and transport of fuel, since it can cause fire hazards. On the other hand, high ignition temperature causes difficulty in kindling (or igniting) the fuel, but the fuel is safe during storage, handling and transport.
- Hence, an ideal fuel should have "moderate" ignition temperature.
- **Low moisture content** The moisture content of the fuel reduces the heating value and involves in a loss of money, because it is paid for at the same rate as the fuel. Hence, fuel should have low moisture content.

➢**Low non-combustible matter content**

- After combustion, the non-combustible matter remains, generally, in the form of ash or clinker.
- The non-combustible matter also reduces the heating value, besides additional cost of storage, handling and disposal of the waste products produced.
- Each per cent of non-combustible matter in fuel means a heat loss of about 1.5%. Hence, a fuel should have low content of non-combustible matter.

➢**Moderate velocity of combustion**

- If the rate of combustion is low, then the required high temperature may not be possible, because a part of the heat liberated may get radiated, instead of raising the temperature.
- On the other hand, too high combustion rates are also not required.

➢**Products of combustion should not be harmful**

- Fuel, on burning, should not give out objectionable and harmful gases.
- In other words, the gaseous products of combustion should not pollute the atmosphere. CO, SO2, H2S, etc., are some of the harmful gases.

➢**Low cost**

- A good fuel should be readily available in bulk at a cheap rate.

➢**Easy to transport**

- Fuel must be easy to handle, store and transport at a low cost. Solid and liquid fuels can easily be transported from one place to another. On the other hand, transportation of gaseous fuels is costly and can even cause fire hazards.

➢**Combustion should be easily controllable**

- Combustion of the fuel should be easy to start or stop, when required.

➢**Should no undergo spontaneous combustion**

- Spontaneous ignition can cause fire hazards.

➢**Storage cost**

- In bulk should be low.

➢**High efficiency**

- It should burn in air with efficiency, without much smoke.

➢**Uniform size**

- In case of solid fuel, the size should be uniform so that combustion is regular

COMPARISON BETWEEN SOLID, LIQUID AND GASEOUS FUELS

Solid fuels

Advantages

- Easy to transport
- Convenient to store, without any risk of spontaneous explosion
- Low cost of production
- Possess moderate ignition temperatures

Disadvantages

- High ash content
- Low thermal efficiency i.e. Large proportion of heat is wasted during combustion
- Burn with clinker formation
- Combustion operations cannot be controlled easily
- High cost of handling
- Lower calorific value as compared to that of liquid fuels
- Require large excess of air for complete combustion
- Cannot be used as internal combustion engine fuels

Liquid fuels

Advantages

- Possess higher calorific value per unit mass than solid fuels
- Burn without forming dust, ash, clinkers, etc.
- Their firing is easier and also fire can be extinguished easily by stopping the liquid fuel supply
- Easy to transport through pipes
- They can be stored indefinitely, without any loss
- The flame produced by burning liquid fuels can easily be controlled by adjusting the liquid fuel supply
- Generally, handled by pipes and one man can easily regulate a large number of furnaces simultaneously
- Clean in use and economic in labor
- Loss of heat to chimney is very low, due to greater cleanliness
- Require less excess of air for complete combustion
- Require less furnace space for combustion
- No wear and tear of grate bars and cleaning of fires, etc., unlike solid fuels.
- Can be used as internal combustion fuels

- **Disadvantages**
- Higher cost as compared to solid fuels
- Costly special storage tanks are required
- Higher risk of fire hazards, particularly in case of a highly inflammable and volatile liquid fuel.
- They give bad odour
- Specially constructed burners and spraying apparatus are required for efficient burning of liquid fuels
- Choking of sprayers (during liquid fuel combustion) is a drawback of oil firing

Gaseous fuels

Advantages

- Conveyed easily through pipelines to the actual place of need, thereby eliminating manual labour in transportation
- Can be lighted at moment's notice
- Have high heat content and hence, help us in having higher temperatures
- Economy in heat because it can be pre-heated by the heat of hot waste gases
- Their combustion can readily be controlled for changes in demand like oxidizing or reducing atmosphere, length of flame, temperature, etc.
- Burn without any soot (or smoke) and are ash less, so there is no labour involved in ash handling, etc.
- Clean in use
- Do not require any special burner

- They can be produced by using even the poorest quantity of coal, etc.
- Burn without heat loss, due to convection currents
- Burn in slight excess of air supply
- Free from solid and liquid impurities. Hence, they do not affect the quality of metal produced, when used as a metallurgical fuel
- Complete combustion without pollution is possible, due to uniform mixing of air and fuel
- Have high calorific values
- Can also be used as internal combustion engine fuels

Disadvantages

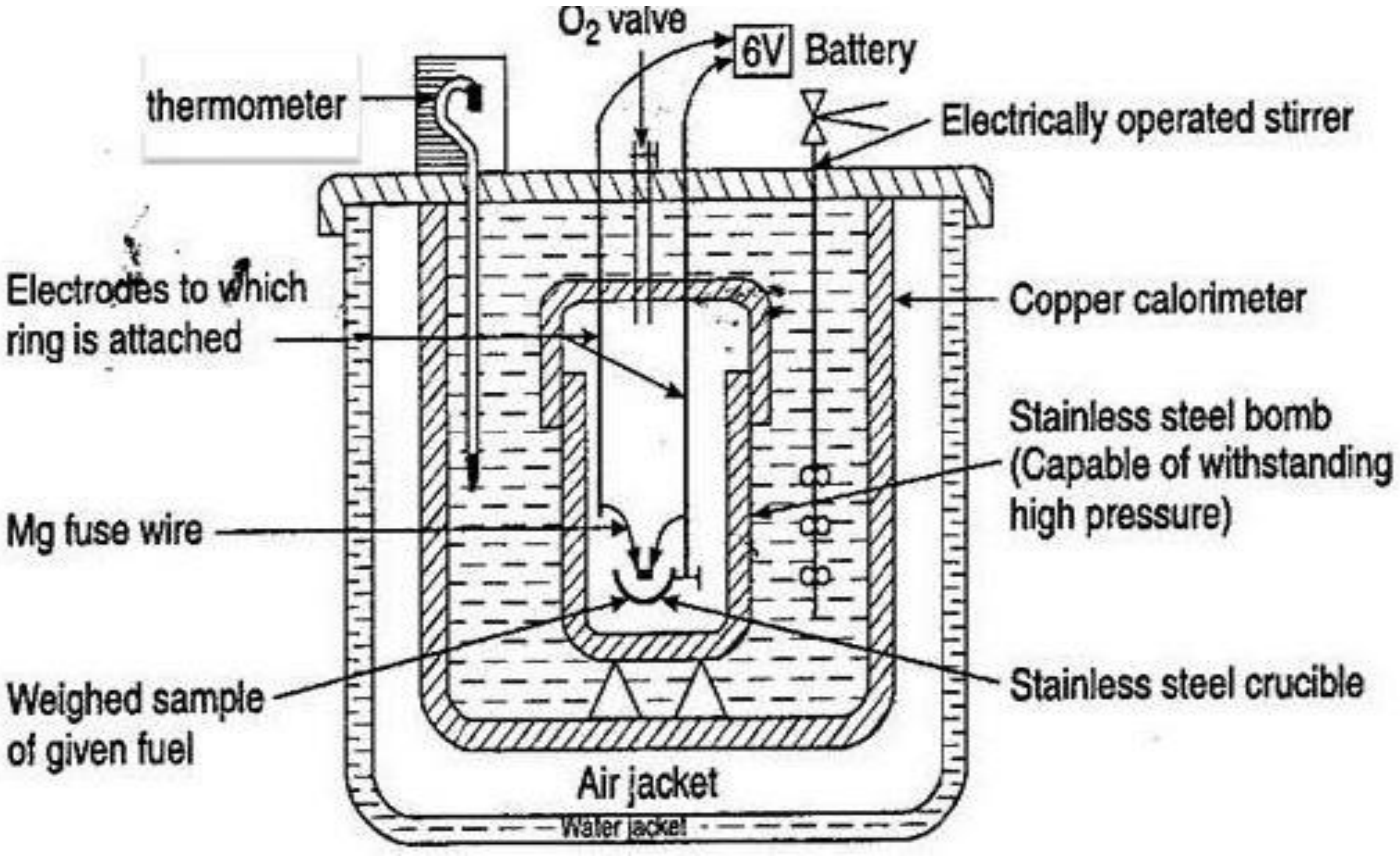
- Very large storage tanks are needed for them
- Highly inflammable, so chances of fire hazards are high in their use
- More costly as compared to solid and liquid fuels

Table: 1 Relative merit of solid, liquid and gaseous fuels.

Solid fuels	Liquid fuels	Gaseous fuels
Easily available and cheap.	More costly than solid fuels, but cheap only in the countries of origin.	Except natural gas, other gaseous fuels are costly.
Transport, storage and handling is convenient, without any risk of spontaneous explosion.	Can easily be transported through pipes, but care must be taken to store them in closed containers only.	Must be stored in leak proof voluminous storage tanks and can be distributed through pipelines.
There is least risk of fire hazards.	There is greater risk of fire hazards.	They are highly inflammable, so chances of fire hazards are high in their use.
Combustion is a slow process and its control and stopping is not easy.	Quick combustion takes place; and it can be controlled or stopped, when needed.	Combustion takes place rapidly and more efficiently and greater flexibility in usage is available by controlling air supply.
Labour is required in their storage, transport, etc.	Lesser handling cost is required.	Lesser handling cost is required.
Ash is always produced and its disposal is a problem. Smoke is invariably produced.	No ash problem and burning is clean, but high carbon and aromatic liquid fuels may produce smoke	Neither ash nor smoke is produced.
Cannot be used in Internal combustion engines.	Can be used in internal combustion engines.	Can also be used as internal combustion engine fuels.
Burn in large excess of air.	Burn in slight excess of air.	Also burn in slight excess of air.
W/W calorific value is least.	W/W calorific value is higher.	W/W calorific value is highest.
Their thermal efficiency is least.	Their thermal efficiency is higher than that of solid fuels.	Their thermal efficiency s highest.

BOMB CALORIMETER

This apparatus is used to find the calorific value of solid and liquid fuels.



Construction

- It consists of a strong cylindrical stainless steel bomb in which the combustion of fuel is made to take place.
- The bomb has a lid, which can be screwed to the body of bomb so as to make a perfect gas-tight seal.
- The lid is provided with two stainless steel electrodes and an oxygen inlet valve. To one of the electrodes, a small ring is attached.
- In this ring, a nickel or stainless steel crucible can be supported.
- The bomb is placed in copper calorimeters, which is surrounded by an air-jacket and water-jacket to prevent heat losses due to radiation.
- The calorimeter is provided with an electrically operated stirrer and Beckmann's thermometer, which can read accurately temperature difference up to 1/100th of a degree.

Working

- A known mass (about 0.5 to 1.0 g) of the given fuel is taken in clean crucible.
- The crucible is then supported over the ring. A fine magnesium wire, touching the fuel sample, is then stretched across the electrodes.
- The bomb lid is tightly screwed and bomb filled with oxygen to 25atm pressure.
- The bomb is then lowered into copper calorimeter, containing a known mass of water.
- The stirrer is worked and initial temperature of the water is noted- The electrodes are then connected to 6-volt battery and circuit completed.
- The sample burns and heat is liberated. Uniform stirring of water is continued and the maximum temperature attained is recorded.

Calculations

- Let x = mass in g of fuel sample taken in crucible;

  W = mass of water in the calorimeter;

  w = water equivalent in g of calorimeter, stirrer, thermometer, bomb, etc.;

  t1= initial temperature of water in calorimeter;

  t2 = final temperature of water in calorimeter;

  L = higher calorific value in fuel in cal/g.

$\therefore$ Heat liberated by burning of fuel =x L and

Heat absorbed by water and apparatus $= (W + w)(t_2 - t_1)$

But heat liberated by the fuel = Heat absorbed by water, apparatus, etc.

$$\therefore \quad xL = (W + w)(t_2 - t_1)$$

or HCV of fuel (L) $= \dfrac{(W + w)(t_2 - t_1)}{x}$ cal/g(or kcal/kg) ….(2)

Corrections

- To get more accurate results, the following corrections are applied;
- **Fuse wire connection**
- The heat liberated, as measured above, includes the heat given out by ignition of the fuse wire used.
- **Acid correction**
- Fuels containing S and N are oxidized, under high pressure and temperature of ignition, to H_2SO_4 and HNO_3 respectively.

$$S + 2H + 2O_2 \xrightarrow{} H_2SO_4 + \text{Heat}$$

$$2N + 2H + 3O_2 \xrightarrow{} 2HNO_3 + \text{Heat}$$

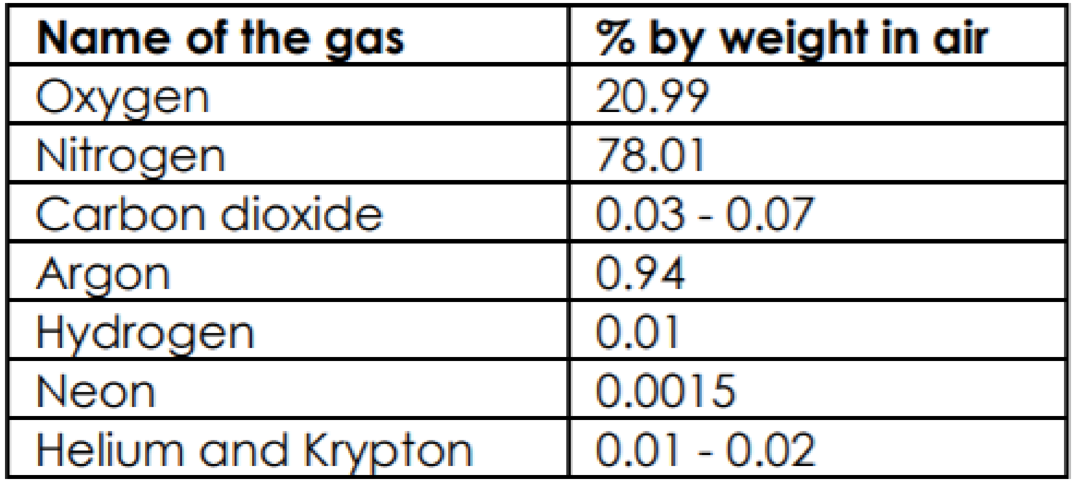
- Formations of these acids are exothermic reactions. So, the measured heat also includes the heat given out during the acid formation. The amount of these acids is analysed from washings of bomb by titration; while H_2SO_4 alone is determined by precipitation as $BaSO_4$. The correction for 1 mg of S is 2.25cal; while for 1 mL of N/10 HNO_3 formed is 1.43 cal.
- **Cooling correction**
- Time taken to cool the water in calorimeter from maximum temperature to room temperature is noted. From the rate of cooling (7minute) and the actual time taken for cooling (t minutes), the cooling correction of dtxt is added to the rise in temperature.

$$\therefore \quad L = \frac{(W + w)(t_2 - t_1 + coolingcorrection) - [Acid + fuse corrections]}{Massoffuel(x)} \quad \ldots.(4)$$

AIR

ANALYSIS OF AIR

- Air mainly consist of two gases oxygen and nitrogen, which are practically considered to constitute 1/5 and 4/5 of air by volume respectively.
- The list of various gases present in air by weight percent is as under



Name of the gas	% by weight in air
Oxygen	20.99
Nitrogen	78.01
Carbon dioxide	0.03 - 0.07
Argon	0.94
Hydrogen	0.01
Neon	0.0015
Helium and Krypton	0.01 - 0.02

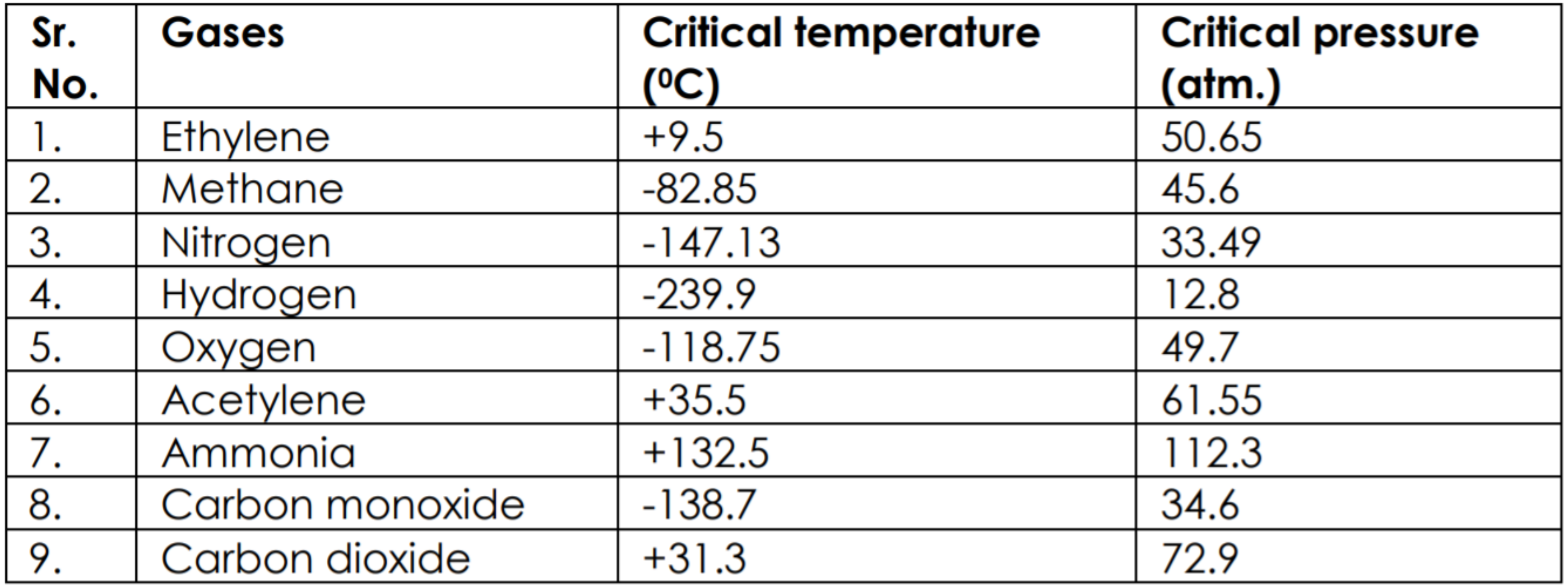
- Except CO2 the concentration of all the gases listed above are present in air are constant.
- However water vapour and traces of ozone and iodine are present in air in variable amounts.
- Also, composition of air also depends on altitude and distance to sea, in neighbourhood of industry, built up urban areas, nearby volcanic phenomena. Other gases such as CO, H2S and NO2 are also present in air.

KINETICS AND THEORY OF GASES

- According to kinetic theory a gas consists of swiftly moving molecules some molecules collide with one another.
- During away from one another, these phenomena leaving an average distance between the molecules. At lower pressure the average distance is large, and at high pressure the molecules are brought near to one another.
- In all the three state of matter, molecules have two tendencies i.e. Attraction tendency and Repulsive tendency. The repulsive tendency is most predominant in gases, and least prominent in solids.
- While in most of liquids the attractive tendency in molecules is more than the repulsive tendency, so that the molecules remain together, but the attracting tendency is still less than in comparison of solids there so liquid is in fluid state.
- In the gases as the temperature raises the repulsion tendency increases, and pressure remaining constant the average distance between molecules increases i.e. the volume increases. Hence with fall of temperature the distance diminishes and, the molecules come closer together.
- Thus it becomes apparent that the average distance of molecules will progressively diminish with fall of temperature, and rise of pressure. Change of average distance of gas is quantitatively expressed by $PV/T = \text{constant}$

- **Critical temperature**
- When by decreasing the distance the molecules of a gas are brought close together the gas assumes the liquid form provided the repulsive tendency has been diminished beyond a certain point known as critical temperature which is different for different gases.
- Critical temperature is the temperature below which any gas can be liquefied by increasing the pressure. Above the critical temperature any gas cannot be liquefied by compression.

- **Critical pressure**
- Above critical temperature the gas will never liquefy under any pressure.
- The minimum pressure under which gas liquefies at the critical temperature is called as critical pressure.
- Therefore air should be cooled at very high pressure and low temperature for cooling purpose. The liquid form is obtained when the kinetic energy and the potential energy of the substance is approximately equal.
- The critical temperature and critical pressure of some gases are as follows.



Sr. No.	**Gases**	**Critical temperature (^{0}C)**	**Critical pressure (atm.)**
1.	Ethylene	+9.5	50.65
2.	Methane	-82.85	45.6
3.	Nitrogen	-147.13	33.49
4.	Hydrogen	-239.9	12.8
5.	Oxygen	-118.75	49.7
6.	Acetylene	+35.5	61.55
7.	Ammonia	+132.5	112.3
8.	Carbon monoxide	-138.7	34.6
9.	Carbon dioxide	+31.3	72.9

APPLICATIONS OF INDUSTRIAL GASES

- **Oxygen**

➢It is used to produce oxyacetylene flame to cutting and welding the metals

➢Used in L. D. process for steel production

➢Used for artificial respiration in case of patients

➢Used for mountain climbers and high attitude aero planes flights

- **Nitrogen**
  - Used in manufacture of synthetic ammonia, nitric acid
  - Used in manufacture organic nitrates like propellants and explosives,
  - Synthetically produced nitrates are key ingredients of industrial fertilizers
  - Used in producing nitrogen oxide.
  - Applied to create inert atmosphere.
- **Carbon dioxide**
  - As solid CO2 in refrigeration process
  - Liquid CO2 is needed in carbonated.
  - Used in creating inert atmosphere.
  - As fire extinguisher
  - Gaseous CO2 used as a neutralizing agent
  - Gaseous CO2 is the basic raw material for production of Na2CO3, NaHCO3

- **Hydrogen**

- In fertilizer industries to produce NH3 which is converted into (NH4)2SO4, urea and HNO3
- In hydrogenation of oils to make fats or in hardening of fatty oils
- In hydrogenating coal, low temperature carbonization tar and water gas to produce gasoline
- In hydrogenating water gas to produce methanol
- In production of HCl, which is used in large quantity in industries
- For filling in metrological balloons which are essential for upper air observation to guide the air flights
- In making oxy-hydrogen flame used for melting of platinum, quartz and in auto welding of lead
- In producing an inert media and in making tungsten filaments for electric lamps, mixture of nitrogen and hydrogen is used