

ASSIGNMENT-1
ENGINEERING CHEMISTRY

submitted by: YASH VINAYVANSHI
B.TECH (2nd SEM)
SECTION - C; SR. 72
JAMIA MILLIA ISLAMIA

submitted to: PROF. MASOOD ALAM
DEPT. OF APPLIED SCIENCE
JMI FET

Q1(a) Discuss Caustic Embrittlement in the boilers.
How can it be controlled?

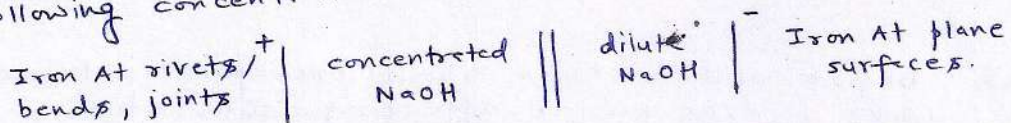
Caustic Embrittlement is a type of boiler corrosion caused by using highly alkaline water in the boiler. During softening of water by lime soda process, some excess soda (Na_2CO_3) may remain free in small proportion in softened water.

In high pressure boilers, Na_2CO_3 decomposes to give sodium hydroxide and carbon dioxide.

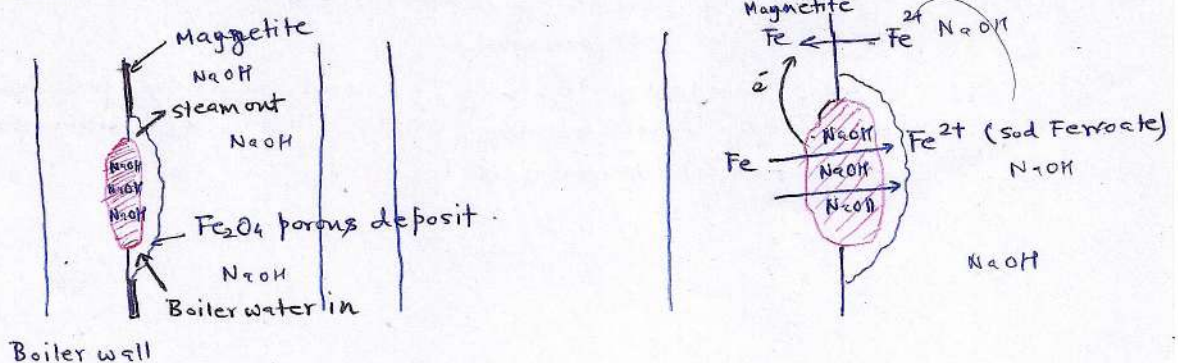


This makes boiler water caustic. NaOH containing water flows into minute hair cracks, always present in the inner side of boiler, by capillary action. Here water evaporates by boiler action and caustic soda concⁿ increases progressively. This caustic soda attacks the surrounding area thereby dissolving iron of boiler as sodium ferroate. This causes embrittlement of boiler parts, particularly stressed parts (bends, joints, rivets etc), potent of even failing the boiler.

Caustic cracking can be explained by considering following concentration cell.



The iron surrounded by dilute NaOH becomes the cathodic side; while iron in contact with rather conc. NaOH becomes anodic side, which is consequently dissolved or corroded.



Prevention of Caustic Embrittlement

- (i) By using sodium phosphate as softening agent
- (ii) By adding tanning and lignin to boiler water
(Blocks cracks \rightarrow preventing infiltration of Na_2CO_3)
- (iii) By adding sodium sulphate (Na_2SO_4)
(Blocks cracks \rightarrow preventing infiltration of Na_2CO_3)

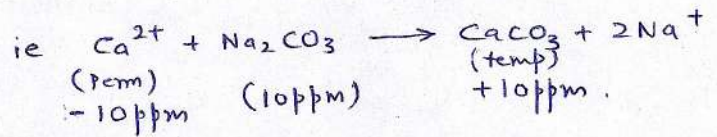
Q1 (b) Calculate CH & NCH of a water sample measuring 100L and having the following impurities.

- $\text{NaCl} : 10 \text{ ppm}$; $\text{MgCl}_2 : 10 \text{ ppm}$
- $\text{Na}_2\text{CO}_3 : 10 \text{ ppm}$; $\text{Ca}(\text{HCO}_3)_2 : 10 \text{ ppm}$
- $\text{KCl} : 20 \text{ ppm}$; $\text{CaCl}_2 : 20 \text{ ppm}$
- $\text{Mg}(\text{HCO}_3)_2 : 20 \text{ ppm}$;

| | salt | conc ⁿ | MF | eq. hardness of CaCO_3 |
|-----|-----------------------------|-----------------------------|---------|---------------------------------|
| CH | $\text{Mg}(\text{HCO}_3)_2$ | 20 ppm | 100/146 | 2000/146 ppm |
| | $\text{Ca}(\text{HCO}_3)_2$ | 10 ppm | 100/162 | 1000/162 ppm |
| | CaCO_3 | 10 ppm | 100/100 | 1000/100 ppm |
| NCH | MgCl_2 | 10 ppm | 100/95 | 1000/95 ppm |
| | CaCl_2 | 20 ppm 10 ppm | 100/111 | 1000/111 ppm |

(10 ppm Na_2CO_3 will

reduce Ca^{2+} perm hardness by 10 ppm & increase Ca^{2+} temp. hardness by 10 ppm



$\therefore \text{CH} = \frac{2000}{146} + \frac{1000}{162} + \frac{1000}{100} = 29.87 \text{ ppm}$

$\text{NCH} : \frac{1000}{95} + \frac{1000}{111} = 19.53 \text{ ppm}$

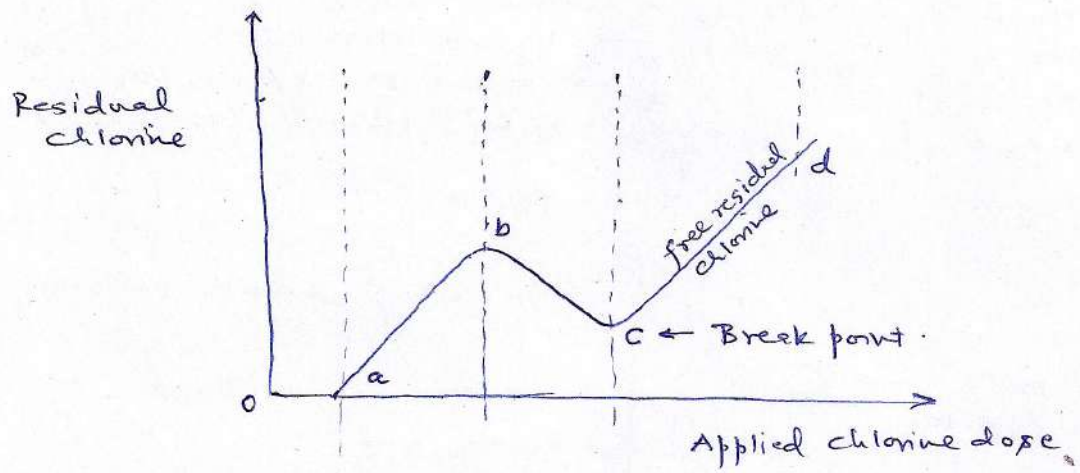
Q1 (c) Define and discuss about breakpoint chlorination. Also discuss factors affecting chlorination.

Breakpoint chlorination (or free residual chlorination) involves in addition of sufficient amt. of chlorine to oxidise

- (a) organic matter
- (b) reducing substances.
- (c) free ammonia

in raw water, leaving behind mainly free chlorine, which possesses disinfecting action against disease producing (pathogenic) bacteria.

When the dosage of applied chlorine to water rich in organic compound or ammonia is gradually increased, four stages occur which can be graphically represented as:



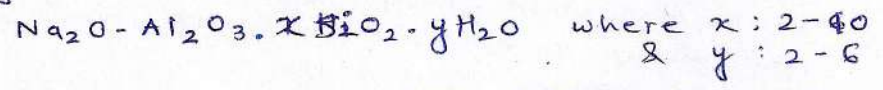
- 0-a : oxidation of reducing compounds by chlorine
- a-b : formation of chloro-organic compounds and chloramines.
- b-c : Destruction of chloro-organic " & chloramines.
- c-d : free residual chlorine increases.

→ Advantages of breakpoint chlorination :

- (i) It oxidises completely organic compounds, ammonia and other reducing compounds.
- (ii) It removes colour in water due to OCS.
- (iii) It destroys completely all disease producing bacteria.
- (iv) Removes odour and taste from water.
- (v) Prevents growth of any weeds in water.

Q2 (a) What are zeolites? Discuss their functioning while softening impure water, Discuss its advantages & disadvantages,

→ Zeolite is hydrated sodium aluminosilicate, capable of exchanging reversibly its sodium ions for hardness producing ions in water. Chemical structure of sodium zeolite may be represented as



Zeolites are also known as permutits and are of two types :

- (i) Natural Zeolites. (~~porous~~ non porous)
- (ii) Synthetic zeolites. (porous & gel structure)
(Higher exchange capacity / unit weight than natural zeolites)

→ Zeolite Process.

For softening of water by zeolite process, hard water is percolated at a specified rate through a bed of zeolite, kept in a cylinder. The hardness causing ions (Ca^{2+} , Mg^{2+} etc)

are retained by zeolites such as CaZ, MgZ; while the outgoing water contains sodium salts. Reactions taking place during the softening process are

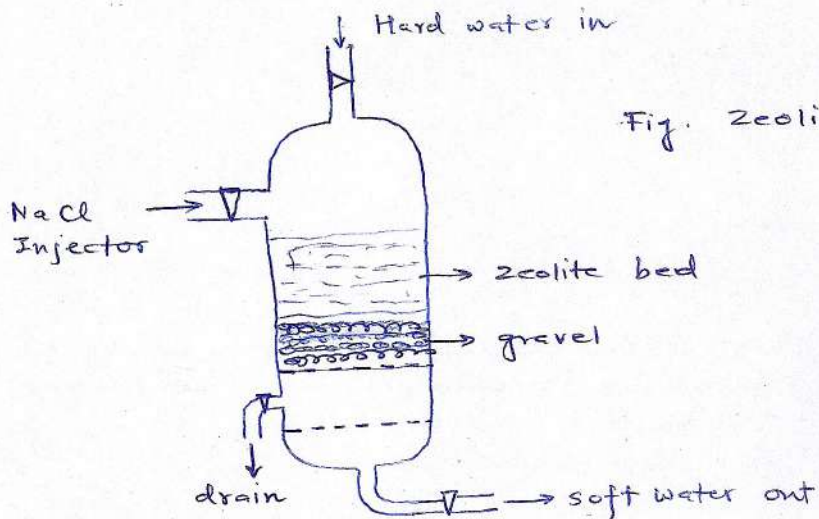
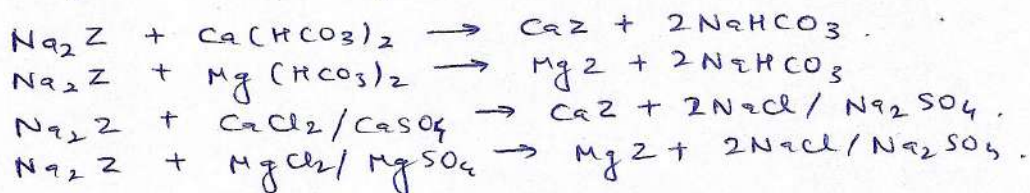
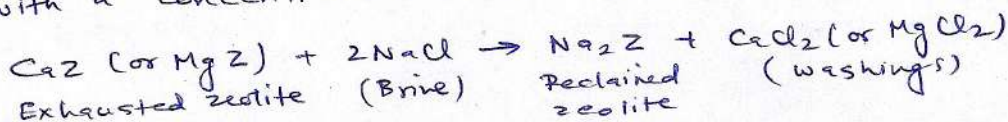


Fig. Zeolite softening column

After some time, sodium zeolite is completely converted into Calcium and magnesium zeolites & ceases to soften water i.e. gets exhausted. At this stage, supply of hardwater is stopped and the exhausted zeolite is reclaimed by treating the bed with a concentrated (10%) brine (NaCl) solⁿ.



The washings (containing $CaCl_2$ & $MgCl_2$) are led to drain and regenerated zeolite bed thus obtained is used again for softening purpose.

→ Advantages

- (i) It removes hardness almost completely (upto 10 ppm)
- (ii) Compact equipment.
- (iii) No impurities precipitated → no danger of sludge formation
- (iv) process automatically adjusts itself for variation in hardness of incoming hard water.
- (v) Less maintenance, less complex mechanism.

→ Disadvantages

- (i) Treated water contains more sodium salts than lime soda process
- (ii) only replaces Ca^{2+} & Mg^{2+} ions by Na^+ ions, but leaves all acidic ions (like HCO_3^- , CO_3^{2-}) as such. Hence softened water containing Na_2CO_3 ; $NaHCO_3$ can cause corrosion in boilers.
- (iii) High turbidity water cannot be treated efficiently as. Impurities can block zeolite bed.

Q2 (b) 100 mL of water sample consumed 10 mL and 40 mL of N/50 HCl in the presence of phenolphthalein and methyl orange indicators respectively. Calculate the alkalinity of water in terms of components.

Vol. of HCl consumed upto phen end pt = P mL
 " " " " MO end pt = M mL

since $P (10 \text{ mL}) < \frac{M}{2} (20 \text{ mL})$

- NaOH $\equiv 0$ ppm.
- Na₂CO₃ $\equiv 2P$ ppm
- NaHCO₃ $\equiv M - 2P$ ppm.

∴ component hardness,

OH⁻ = 0 ppm

CO₃²⁻ = $\frac{1 \text{ eq/L} \times 20 \text{ mL}}{50} \times 30 \text{ g/eq} \times \frac{1}{100 \text{ mL}} \times 10^6$
strength of Acid volume of Acid for CaCO₃ (in L) eq. wt of CaCO₃ per volume of water sample

= 120 ppm

HCO₃⁻ = $\frac{1 \text{ eq/L} \times 20 \text{ L}}{50} \times 61 \text{ g/eq} \times \frac{1}{100 \text{ mL}} \times 10^6$
 = 244 ppm

Q2 (c) 10⁵ litres of tube water sample on analyses gave following results.

- CaCl₂ : 10 ppm NaHCO₃ : 10 ppm
- AlCl₃ : 20 ppm NaAlO₂ : 20 ppm
- MgCl₂ : 10 ppm CO₂ : 20 ppm

Treated water contains.

OH⁻ : 10 ppm. +L

Calculate the dose of lime and soda in kg if their purity is 80%.

| Salt | Amount | Need |
|--------------------|--------|------|
| CaCl ₂ | 10 ppm | S |
| MgCl ₂ | 10 ppm | S+L |
| AlCl ₃ | 20 ppm | S+L |
| NaHCO ₃ | 10 ppm | L-S |
| NaAlO ₂ | 20 ppm | -L |
| CO ₂ | 20 ppm | +L |

∴ Lime req. = $\frac{74}{100} [10 + 20 + 10 - \frac{20}{2} + 20] \times 10^{-6} \times 10^5 \times \frac{100}{80} = 4.625 \text{ kg}$

Soda req = $\frac{106}{100} [10 + 10 + 20 - 10] \times 10^{-6} \times 10^5 \times \frac{100}{80} = 3.975 \text{ kg}$

Q3 (a) Define and differentiate b/w HCV and LCV for a fuel sample (6)

→ Higher Calorific / Gross calorific value HCV.

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 room temperature, the latent heat of condensation of steam also gets included in the measured heat, which is called higher calorific value.

Def: Hence HCV is the total amount of heat produced, when unit mass or unit volume of fuel has been burnt completely and the products of combustion are cooled to room temperature (ie 15°C or 60°F)

→ Lower / Net calorific value (LCV)

In actual use of any fuel, the water vapour & moisture etc, are not condensed and escape as such along with hot combustion gases. Hence a lesser amount of heat is available.

Def: ∴ LCV is the net heat produced, when unit mass or volume of the fuel is burnt completely and the products are permitted to escape

$$\begin{aligned} \text{LCV} &= \text{HCV} - \text{Latent Heat of water vapour formed} \\ &= \text{HCV} - \text{Mass of Hydrogen} \times 9 \times \text{Latent heat of steam} \end{aligned}$$

Because 1 part by mass hydrogen produces 9 parts by mass water. The latent heat of steam is 587 kcal/kg of water vapour formed at r.t (15°C).

Q3 (b) Calculate HCV and LCV for the following coal sample weighing 1 kg with following analyses.

C = 85%; N = 2%; S = 1%; O = 1%; H = 10%; Ash = 1%

By Dulong formula

$$\begin{aligned} \text{HCV} &= \frac{1}{100} [8080C + 34500(H - \frac{O}{8}) + 2240S] \\ &= \frac{1}{100} [8080 \times 85 + 34500(10 - \frac{1}{8}) + 2240 \times 1] \\ &= \frac{1}{100} [686800 + 342927.5] \\ &= \boxed{10297.28 \text{ kcal/kg}} \end{aligned}$$

$$\begin{aligned} \text{LCV} &= \text{HCV} - 9M_H \times 587 \text{ kcal/kg} \\ &= 10297.28 - 9 \times \frac{10}{100} \times 1 \times 587 \\ &= 10297.28 - 528.3 \text{ kcal/kg} \\ &= \boxed{9768.98 \text{ kcal/kg}} \end{aligned}$$

Q3 (c) Discuss the functioning of Bomb Calorimeter by drawing simple sketch of it. How is HCV & LCV determined using this calorimeter?

→ Bomb Calorimeter

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 nichel or stainless steel crucible can be supported. The bomb is placed in copper calorimeter, which is surrounded by 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 diffn upto 1/100th of a degree.

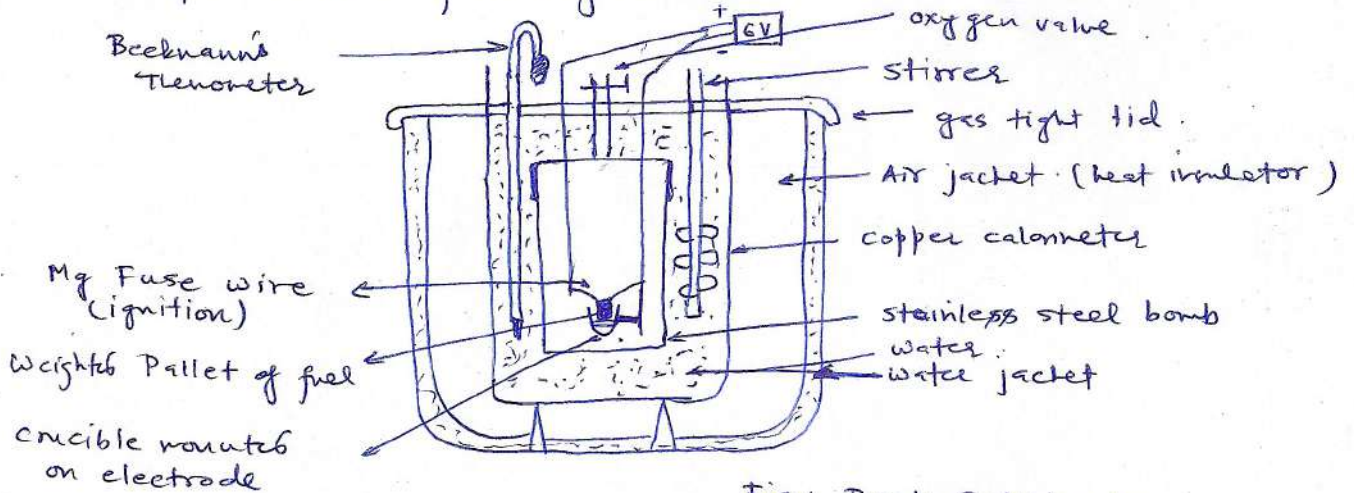


Fig: Bomb Calorimeter.

→ working

A known mass of given fuel is taken in a clean crucible. The crucible is then supported on the ring. A fine magnesium wire, touching the fuel sample stretched b/w electrodes - Bomb lid is tightly screwed and filled with oxygen at high pressure. The Bomb is then lowered into copper calorimeter containing known mass of water. The stirrer is worked and initial temp. is noted. short circuited terminals ignite fuel which burns & heat is liberated. Uniform stirring of water is continued and maximum attained temperature is recorded.

→ calculation

- let x : mass in gm of fuel sample taken in crucible
- W : mass of water in calorimeter
- w : water equivalent of in gm of calorimeter, stirrer, thermometer, bomb etc.
- t_1 : initial temperature of water in calorimeter
- t_2 : final " " " " " "
- L : HCV of fuel in cal/g.

Heat liberated by burning fuel : xL

Heat absorbed by water & apparatus : $(W+w)(t_2-t_1)$

Heat liberated by fuel = Heat Absorbed by water, apparatus

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

$$\therefore \text{HCV of fuel } L = \frac{(W+w)(t_2-t_1)}{x} \text{ cal/g}$$

if H is % of hydrogen in fuel, then:

$$\frac{9H}{100} \text{ gm} = \text{Mass of H}_2\text{O from 1 gm of fuel} = 0.09H \text{ g}$$

$$\therefore \text{Heat taken by water in forming steam} = 0.09H \times 587 \text{ cal}$$

latent heat of steam

$$\begin{aligned} \text{LCV} &= \text{HCV} - \text{Latent heat of water formed} \\ &= \text{HCV} - 0.09H \times 587 \text{ cal/g or kcal/kg} \end{aligned}$$

