Unit 2 - Boiler Problems and Softening Methods

Unit Overview -

→ A **boiler** is a closed vessel in which water is heated to produce steam under pressure. This steam runs turbines and engines and is used for heating and in many industrial processes.

→ Natural water carries dissolved salts of Ca and Mg, dissolved gases, oil and suspended matter. When such water is fed to a boiler it causes **sludge**, **scale**, **priming**, **foaming**, **corrosion** and **caustic embrittlement**.

→ These troubles waste fuel, shorten the life of the boiler and can even cause an explosion. The feed water must therefore be **softened** before use.

What You Will Learn -

1. Requirements of boiler feed water.
2. Sludge and scale: formation, disadvantages, removal and prevention.
3. Internal treatment (conditioning) of boiler water.
4. Priming and foaming.
5. Boiler corrosion and caustic embrittlement.
6. Softening methods: lime-soda, zeolite and ion-exchange processes.
7. Related numerical problems.

Key Terms -

Term	Meaning
Boiler feed water	Water that is fed into the boiler to make steam.
Sludge	Soft, loose, slimy deposit in the cooler parts of a boiler.
Scale	Hard, adherent coating on the inner wall of a boiler.
Priming	Carrying of water droplets along with the steam (wet steam).
Foaming	Formation of persistent bubbles or foam on the water surface.
Carry-over	Combined result of priming and foaming: water and salts go out with the steam.
Blow-down	Draining out a part of the concentrated boiler water and replacing it with fresh water.

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Term	Meaning
Caustic embrittlement	Cracking of boiler metal caused by concentrated NaOH.
Softening	Removal of hardness causing Ca^{2+} and Mg^{2+} from water.
Zeolite	Hydrated sodium alumino-silicate, used as a cation exchanger (Na_2Ze).
Regeneration	Restoring an exhausted exchanger to its original form.

Boiler Feed Water -

→ The water fed to the boiler is called boiler feed water. It should be as pure as possible, because every impurity ends up as a deposit or a corrosive agent inside the boiler.

Impurity	Trouble it causes in the boiler
Hardness salts	sludge and scale
Dissolved solids, oil	priming and foaming
Dissolved O_2 and CO_2	corrosion of the boiler metal
Salts like $MgCl_2$	acid formation and corrosion
Alkali (NaOH)	caustic embrittlement
Silica	very hard silicate scale

→ So the ideal boiler feed water has zero hardness, no dissolved gases, no oil or suspended matter and very low dissolved solids and alkali.

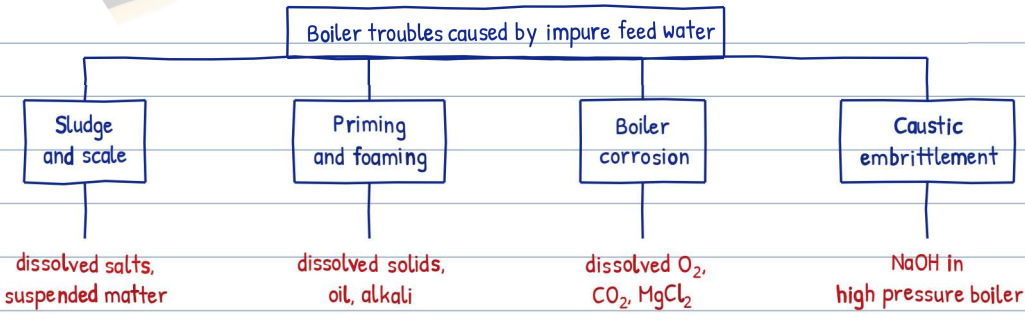


Fig 2.1 Boiler troubles and their causes

Sludge and Scale -

→ In a working boiler water keeps changing into steam, so the dissolved salts left

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behind become more and more concentrated. When a salt crosses its solubility limit it is thrown out of solution as a deposit.

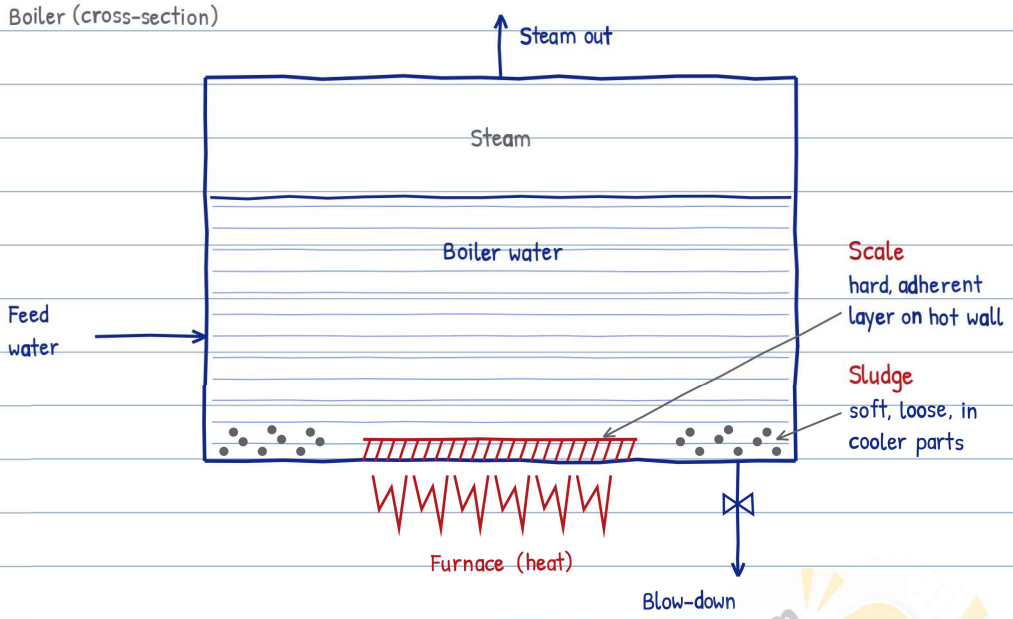


Fig 2.2 Sludge and scale in a boiler

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1. Sludge

→ Sludge is a soft, loose and slimy precipitate. It does not stick to the surface; it collects in the cooler parts of the boiler, where the water flows slowly (bottom, corners, bends).

→ Formed by salts such as $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$ and by suspended matter in the feed water.

Disadvantages –

→ (i) Sludge is a poor conductor of heat, so it wastes some fuel.

→ (ii) It settles where circulation is slow and can choke pipes and outlets.

→ (iii) If it forms along with scale, it gets trapped in the scale and becomes a part of it.

→ Removal and prevention – use of soft water, and frequent blow-down (draining the concentrated water from the bottom).

2. Scale

→ Scale is a hard, adherent coating on the inner surface of the boiler. It forms at the hotter parts, directly above the furnace, and cannot be removed with a simple brush.

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Reasons for the formation of scale –

(i) Decomposition of $Ca(HCO_3)_2$ at the boiler temperature:

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

⟶ $CaCO_3$ is a soft scale at low pressure. In high pressure boilers it changes to the more soluble $Ca(OH)_2$, so it is not a serious trouble there.

(ii) Deposition of $CaSO_4$: its solubility falls as the temperature rises: about 3200 ppm at 15 °C, but only 55 ppm at 320 °C. In hot superheated water it is almost insoluble and forms a very hard scale on the hottest tubes. It is difficult to remove.

(iii) Hydrolysis of magnesium salts at high temperature:

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 \downarrow + 2HCl$$

⟶ $Mg(OH)_2$ deposits as a soft scale. The HCl formed also attacks the boiler (see corrosion).

(iv) Presence of silica: even a little SiO_2 deposits as $CaSiO_3$ and $MgSiO_3$. These are extremely hard, adherent scales and are the most difficult ones to remove.

REMEMBER

Scale = hard + adherent + hot parts. Sludge = soft + loose + cooler parts.

$CaSO_4$ is the worst scale former because its solubility decreases at high temperature.

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Disadvantages of scale –

1. Wastage of fuel: scale conducts heat very poorly, so more fuel is needed to raise the same amount of steam. The wastage grows quickly with the thickness of the scale.

Thickness of scale (mm)	0.325	0.625	1.25	2.5	12
Fuel wasted	10 %	15 %	50 %	80 %	150 %

2. Overheating and loss of safety: the metal under the scale becomes very hot, loses its strength and gets distorted.
3. Danger of explosion: a thick scale cracks because of uneven expansion. Water then touches the red-hot metal suddenly, a large amount of steam forms at once and the pressure shoots up.
4. Lower efficiency: scale on pipes, valves and condensers reduces the flow of water and steam.

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5. **Cost:** the boiler has to be shut down and cleaned again and again.

Removal of scale -

Method	How it works
Mechanical	Loose scale is removed with a scraper, wire brush or hammer.
Thermal shock	Brittle scale: the boiler is heated and then suddenly cooled with cold water; the scale cracks and falls off.
Blow-down	Loose scale is flushed out by draining water at high pressure.
Chemical	$CaCO_3$ scale is dissolved by 5 to 10 % HCl. $CaSO_4$ scale is dissolved by EDTA solution (soluble Ca-EDTA complex). Silica scale needs HF.

Sludge vs Scale

Point	Sludge	Scale
Nature	soft, loose, slimy	hard, adherent, stuck to the wall
Formed by	$MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$	$CaCO_3$, $CaSO_4$, $Mg(OH)_2$, $CaSiO_3$
Where formed	cooler parts, slow flow	hotter parts, above the furnace
Heat conduction	poor	very poor
Removal	blow-down	scraping, thermal shock, chemicals
Danger	chokes pipes	overheating, explosion

Internal Treatment of Boiler Water -

→ In internal treatment (conditioning) a chemical is added directly to the boiler water. It either throws the scale forming salts out as a loose sludge that is removed by blow-down, or converts them into soluble compounds.

→ It is used after external softening to remove the last traces of hardness.

Method	Chemical	Action
Colloidal	kerosene, tannin, agar-agar	Coat the precipitate, which then stays loose and non-sticky and is removed by blow-down. Low pressure boilers.
Phosphate	Na_3PO_4 (or Na_2HPO_4, NaH_2PO_4)	Gives soft, non-adherent $Ca_3(PO_4)_2$ sludge. High pressure boilers.

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Method	Chemical	Action
Calgon	sodium hexametaphosphate $Na_2[Na_4(PO_3)_6]$	Forms a soluble complex with Ca^{2+}, so there is no scale and no sludge.
Carbonate	Na_2CO_3	Converts $CaSO_4$ into loose $CaCO_3$. Low pressure boilers only.

$$3CaCl_2 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2 \downarrow + 6NaCl \quad \text{(phosphate)}$$

$$2CaSO_4 + Na_2[Na_4(PO_3)_6] \rightarrow Na_2[Ca_2(PO_3)_6] + 2Na_2SO_4 \quad \text{(calgon)}$$

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4 \quad \text{(carbonate)}$$

REMEMBER

Na_2CO_3 is not used in high pressure boilers because it hydrolyses to NaOH and causes caustic embrittlement.

Priming and Foaming (Carry-over) -

→ When steam is produced very fast it carries some water along with it. This wet steam is of poor quality and carries dissolved salts into the pipes and turbines. The trouble is called carry-over and it has two forms: priming and foaming.

1. Priming

→ Priming is the carrying of water droplets along with the steam that leaves the boiler.

Causes -

→ (i) presence of a large amount of dissolved solids in the boiler water.

→ (ii) high steam velocity and a sudden increase in the rate of steam production.

→ (iii) sudden boiling of the water, e.g. when the steam stop valve is opened suddenly.

→ (iv) faulty boiler design (too little steam space) and too high a water level.

Prevention -

→ (i) fit mechanical steam purifiers (anti-priming pipes, baffles).

→ (ii) keep the steam production steady and the water at the proper level.

→ (iii) use soft water, filter it and remove the extra concentrated water by blow-down.

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2. Foaming

→ Foaming is the production of persistent foam or bubbles on the water surface in the boiler. The bubbles do not break easily and are carried out with the steam.

→ Cause - oil and grease in the water react with alkali in the boiler to form soap. Soap lowers the surface tension and makes the bubbles stable.

Prevention -

→ (i) add anti-foaming agents such as castor oil or synthetic polyamides; they spread on the surface and break the bubbles.

→ (ii) remove the oil from the water with coagulants such as sodium aluminate or aluminium hydroxide.

→ (iii) blow-down and avoiding excess alkali.

Point	Priming	Foaming
What happens	water droplets go out with the steam	persistent bubbles on the water surface
Main cause	dissolved solids, high steam velocity, sudden boiling	oil and alkali forming soap
Remedy	steam purifier, steady firing, soft water	castor oil, coagulants, blow-down

Disadvantages of carry-over -

1. Dissolved salts in the droplets deposit on superheater tubes, turbine blades and valves and reduce their efficiency.
2. Wet steam has less heat content, so fuel is wasted.
3. The actual height of the water level cannot be judged, so the level is difficult to control.
4. The salts in wet steam cause corrosion of pipes and machinery and can spoil the product (food, paper, textile).

Boiler Corrosion -

→ Boiler corrosion is the decay of the boiler metal (iron) by the chemical or electrochemical attack of the water in it. It has three main causes: dissolved O_2, dissolved CO_2 and acids formed from dissolved salts.

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1. Dissolved oxygen

→ Water holds about 8 ppm of O_2 at room temperature. On heating, the O_2 comes out and attacks iron at the high boiler temperature, forming rust.

$$2Fe + 2H_2O + O_2 \rightarrow 2Fe(OH)_2$$

$$4Fe(OH)_2 + O_2 \rightarrow 2[Fe_2O_3.2H_2O] \quad \text{(rust)}$$

Removal of dissolved O_2 -

→ (i) Chemical: add a calculated amount of sodium sulphite, hydrazine or sodium sulphide.

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$

$$Na_2S + 2O_2 \rightarrow Na_2SO_4$$

→ Hydrazine is the best: its products N_2 and H_2O are harmless and leave no salt in the boiler.

→ (ii) Mechanical de-aeration: the feed water is sprayed over perforated plates in a tower that is heated and connected to a vacuum pump. High temperature and low pressure reduce the solubility of O_2 and CO_2, and the pump removes them.

2. Dissolved carbon dioxide

→ CO_2 comes from the air and from the decomposition of bicarbonates on heating. It forms carbonic acid, which attacks iron slowly.

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

$$CO_2 + H_2O \rightarrow H_2CO_3$$

→ Removal - add a calculated amount of ammonia, or use mechanical de-aeration.

$$2NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O$$

3. Acids from dissolved salts

→ Salts such as $MgCl_2$ and $CaCl_2$ hydrolyse at the boiler temperature and give HCl, which attacks the iron.

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl$$

$$Fe + 2HCl \rightarrow FeCl_2 + H_2\uparrow$$

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

→ The HCl is formed again in the last step, so it works like a chain: a small amount of $MgCl_2$ corrodes a large amount of iron.

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→ Prevention - soften the water, remove salts by blow-down and keep the boiler water slightly alkaline.

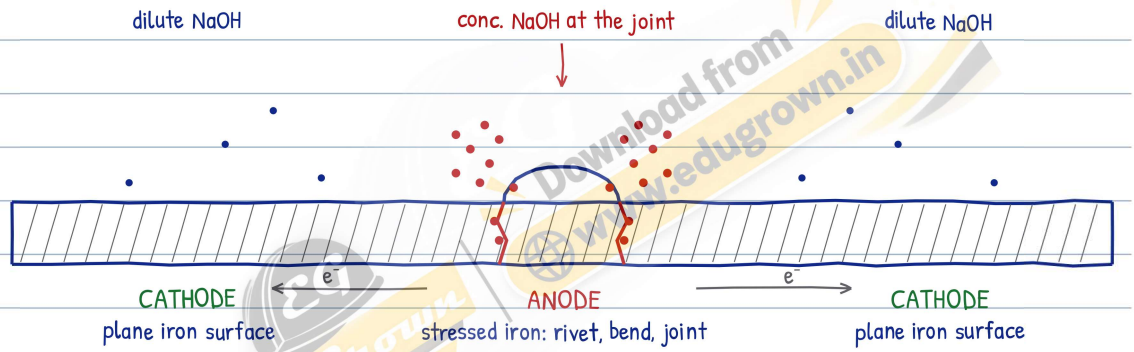
Caustic Embrittlement -

DEFINITION

Caustic embrittlement is a type of boiler corrosion caused by a high concentration of NaOH in the boiler water. It gives brittle, inter-crystalline cracks in the boiler metal, mostly at stressed parts such as rivets, bends and joints.

→ Cause - water softened by the lime-soda process still contains some Na_2CO_3. In high pressure boilers it hydrolyses to NaOH, which makes the water caustic.

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2 \uparrow$$



At the anode: $Fe + 2NaOH \rightarrow Na_2FeO_2 + H_2$

Iron dissolves at the stressed part, so the crack widens and the boiler fails.

Fig 2.3 Caustic embrittlement - concentration cell at a stressed joint

Mechanism -

1. The caustic water enters the tiny hair-cracks near rivets, bends and joints by capillary action.
2. The water in the cracks evaporates, so the NaOH there becomes more and more concentrated.
3. The concentrated NaOH dissolves the iron as sodium ferroate:

$$Fe + 2NaOH \rightarrow Na_2FeO_2 + H_2 \uparrow$$

4. A concentration cell is set up: the stressed iron in contact with concentrated NaOH is the anode, the plane iron surface in contact with dilute NaOH is the cathode. The anode dissolves, the cracks widen and the boiler fails.

Prevention -

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→ (i) use sodium phosphate (Na_3PO_4) instead of Na_2CO_3 for softening.

→ (ii) add tannin or lignin to the boiler water; they block the hair-cracks.

→ (iii) add Na_2SO_4; it enters the cracks first and blocks them. The ratio Na_2SO_4 : NaOH is kept at 1:1, 2:1 and 3:1 in boilers working up to 10, 20 and 30 atm and above.

→ (iv) soften the water by the zeolite or ion-exchange method, so that no Na_2CO_3 is left.

Boiler troubles at a glance

Trouble	Main cause	Effect	Remedy
Sludge	$MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$	chokes pipes, poor heat transfer	soft water, blow-down
Scale	$CaSO_4$, $CaCO_3$, silica	fuel wastage, overheating, explosion	softening, conditioning, scraping
Priming	dissolved solids, high steam rate	wet steam, salt deposits	steam purifier, steady firing
Foaming	oil and alkali (soap)	water carried with steam	castor oil, coagulants
Corrosion	O_2, CO_2, $MgCl_2$	rusting, thinning	de-aeration, hydrazine, softening
Caustic crack	NaOH from Na_2CO_3	inter-crystalline cracks	Na_3PO_4, tannin, Na_2SO_4

Softening of Water -

→ Softening is the process of removing the hardness causing salts (Ca^{2+} and Mg^{2+}) from water. It is done in two ways.

→ Internal treatment is done inside the boiler (already discussed). External treatment is done before the water enters the boiler. The three external methods of the syllabus are explained below.

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