# Chemical Process Utilities
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## Lecture - 13
## Water Chemistry

Welcome to the next chapter of water chemistry under the aegis of chemical process utilities. We have covered about we were discussing the source of water; we were discussing the various water chemistry in which we have discussed the various contaminants present in the water.

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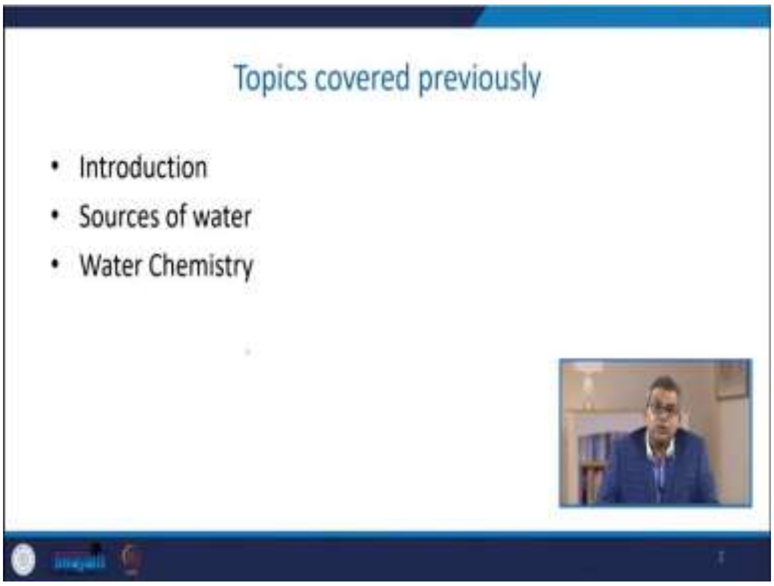

Topics covered previously

- Introduction
- Sources of water
- Water Chemistry

We had already discussed how these contaminants are important, especially the determination and removal, because they may seriously affect the process. May seriously affect the presence of these contaminants may seriously affect energy efficiency economic aspect, may cause wear and tear to the equipment, and moreover may catalyze the reaction so that any unwanted product may become part and parcel of our chemical processes.

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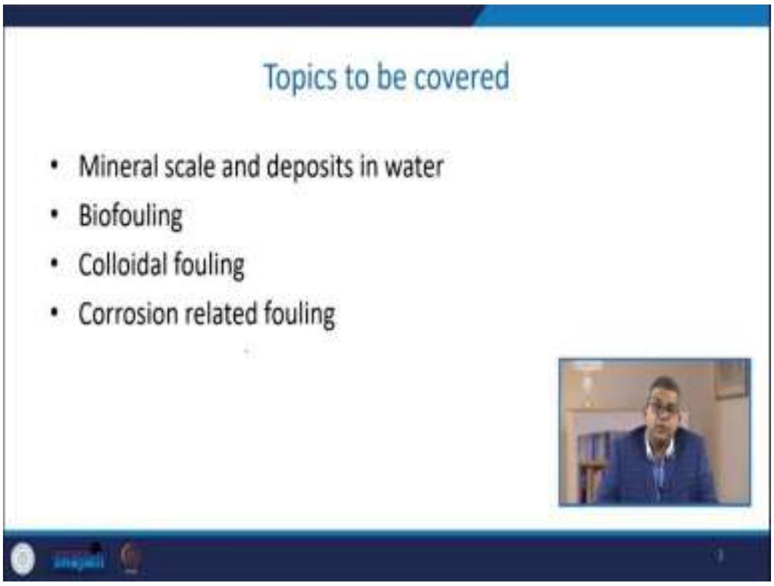

## Topics to be covered

- Mineral scale and deposits in water
- Biofouling
- Colloidal fouling
- Corrosion related fouling

This particular lecture will cover the concept of mineral scale and deposits in the water. We discuss the idea of biofouling and colloidal fouling and corrosion-related fouling.

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## Mineral Scale and Deposits

**Foulants commonly encountered in industrial water systems are of two types:**

- Mineral scales, which are hard, dense, crystalline precipitates of calcium carbonate, calcium sulfate, barium sulfate, calcium fluoride, calcium phosphate, etc.
- Deposits, such as colloidal and suspended matter, biological growth, corrosion products, etc.

Let us have the first thing in a picture: the mineral scale and deposits. Foulants commonly encountered in the industrial water system are of two types. Basically, there are two types. One is the mineral scales, which are hard, dense, crystalline precipitates of calcium carbonate, calcium sulfate, barium sulfate, calcium fluoride, calcium phosphates etc. So, we are discussing so many chemicals etc.

But are very much important the knowledge their concentration their sometimes the controlled removal all these things are essential. Second is; deposits like colloidal or suspended matters, biological growth, corrosion products etc.

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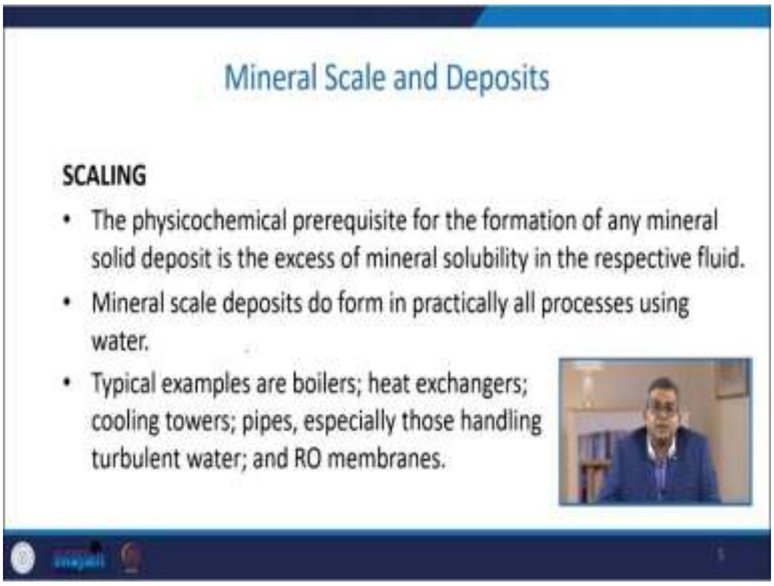

Mineral Scale and Deposits

SCALING

- The physicochemical prerequisite for the formation of any mineral solid deposit is the excess of mineral solubility in the respective fluid.
- Mineral scale deposits do form in practically all processes using water.
- Typical examples are boilers; heat exchangers; cooling towers; pipes, especially those handling turbulent water; and RO membranes.

So, first, we will discuss the scaling. This is the physicochemical prerequisite for forming any mineral solid deposits in excess of mineral solubility in the respective fluid. Mineral scale deposits do form in practically all processes using water. We can enlist several examples: boilers, heat exchangers, cooling towers, pipes, especially those handling turbulent water or reverse osmosis membranes, etc.

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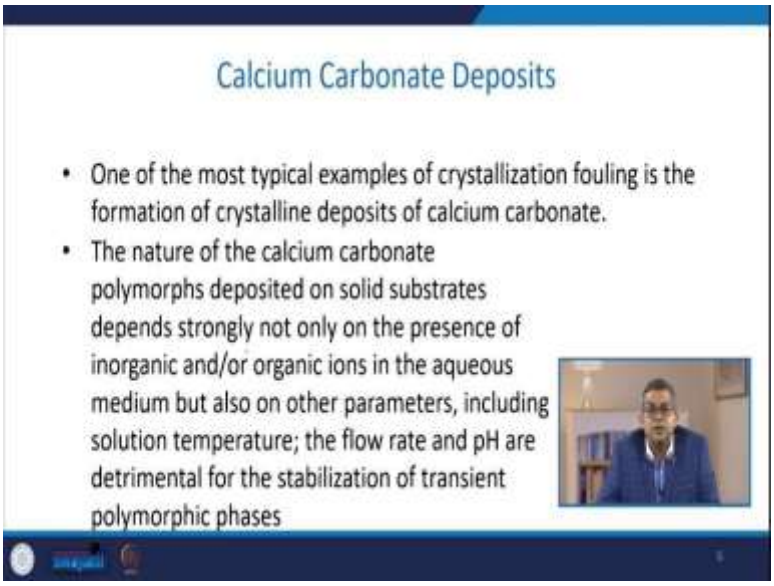

Calcium Carbonate Deposits

- One of the most typical examples of crystallization fouling is the formation of crystalline deposits of calcium carbonate.
- The nature of the calcium carbonate polymorphs deposited on solid substrates depends strongly not only on the presence of inorganic and/or organic ions in the aqueous medium but also on other parameters, including solution temperature; the flow rate and pH are detrimental for the stabilization of transient polymorphic phases

One thing is that scales do not offer any kind of a heat effect but hinder the smooth passage of the heat transfer, which is very important. Let us have a discussion about the calcium carbonate deposits. One of the most typical examples of crystallization fouling is the formation of crystalline deposits of calcium carbonate. The nature of calcium carbonate polymorphs deposits on the solid substrate depends strongly on the presence of the inorganic or the organic ion in the aqueous medium.

But also, other parameters like solution temperature, the flow rate, and the pH are detrimental to the stabilization of transient polymorphic phases.

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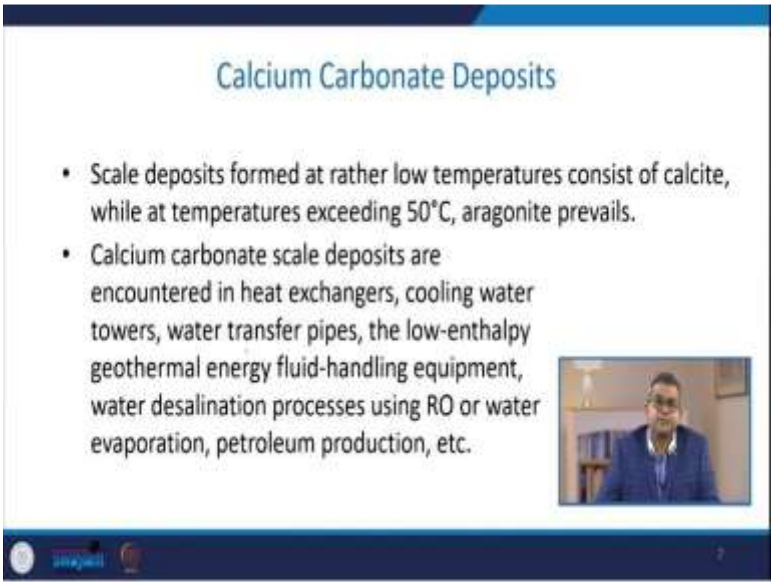

Calcium Carbonate Deposits

- Scale deposits formed at rather low temperatures consist of calcite, while at temperatures exceeding 50°C, aragonite prevails.
- Calcium carbonate scale deposits are encountered in heat exchangers, cooling water towers, water transfer pipes, the low-enthalpy geothermal energy fluid-handling equipment, water desalination processes using RO or water evaporation, petroleum production, etc.

Scale deposits usually formed at rather low temperatures consist of calcite. While the temperature exceeding at 50 degrees Celsius, aragonite prevails. Calcium carbonate scale deposits are encountered in heat exchangers, cooling water towers, water transfer pipes, the low enthalpy geothermal energy fluid handling equipment, water desalination processes using RO or water evaporation petroleum production etc.

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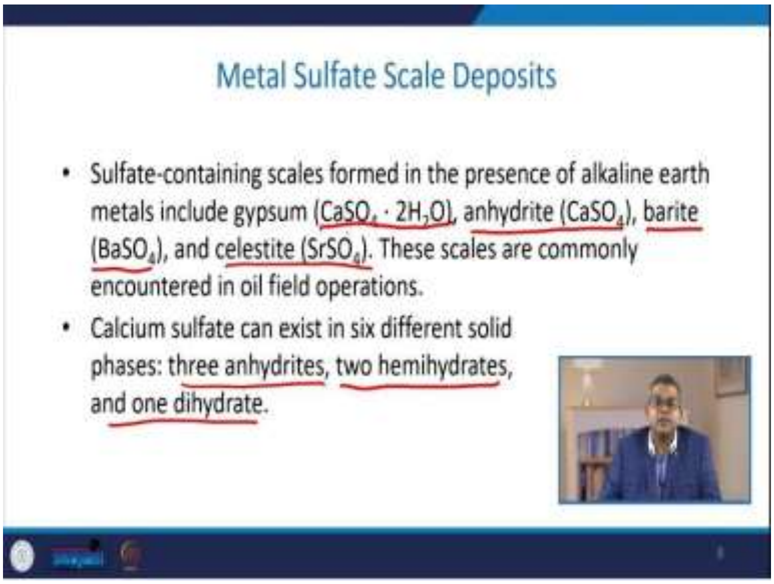

Metal Sulfate Scale Deposits

- Sulfate-containing scales formed in the presence of alkaline earth metals include gypsum ($CaSO_4 \cdot 2H_2O$), anhydrite ($CaSO_4$), barite ($BaSO_4$), and celestite ($SrSO_4$). These scales are commonly encountered in oil field operations.
- Calcium sulfate can exist in six different solid phases: three anhydrites, two hemihydrates, and one dihydrate.

Let us discuss the metal sulfate scale deposits. Sulfate-containing scales formed in the presence of alkaline earth metal includes the gypsum with the basic formula $CaSO_4.2H_2O$, anhydrite that is $CaSO_4$, barite or sometimes referred as barium sulfate $BaSO_4$, celestite that is $SrSO_4$ so these scales are commonly encountered in oil field operations. So, we need to find out we need to know the concentration, and then we need to treat it accordingly.

Calcium sulfate can exist in six different solid phases 3 anhydrides, two hemi hydrates, and one dihydrides.

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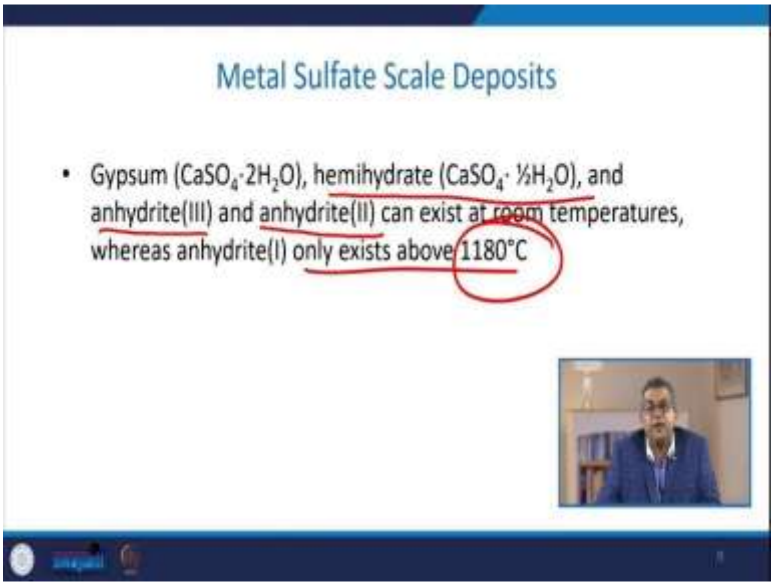

Metal Sulfate Scale Deposits

- Gypsum ($CaSO_4 \cdot 2H_2O$), hemihydrate ($CaSO_4 \cdot ½H_2O$), and anhydrite(III) and anhydrite(II) can exist at room temperatures, whereas anhydrite(I) only exists above 1180°C

Gypsum $CaSO_4.2H_2O$ or hemihydrates having the chemical formula of $CaSO_4.1/2H_2O$ and anhydrite (III) and anhydrite(II) can exist at room temperature where anhydride one only exists above the temperature of 1180 degrees Celsius.

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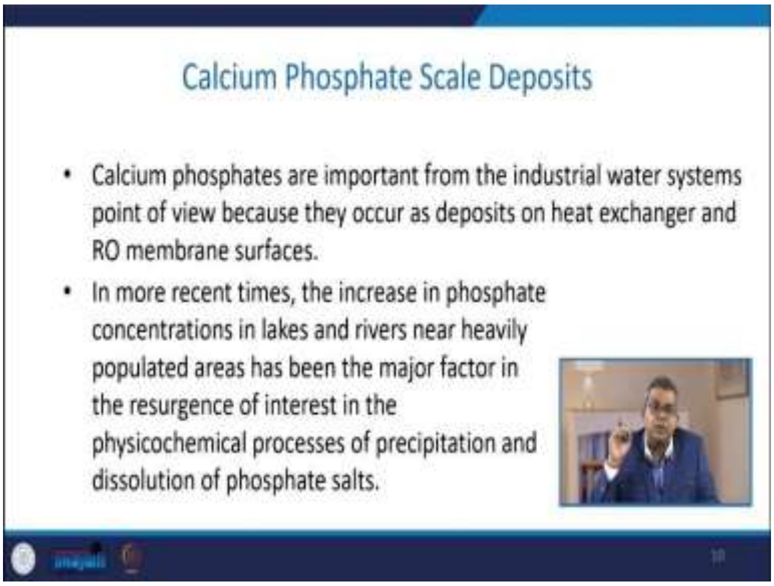

## Calcium Phosphate Scale Deposits

- Calcium phosphates are important from the industrial water systems point of view because they occur as deposits on heat exchanger and RO membrane surfaces.
- In more recent times, the increase in phosphate concentrations in lakes and rivers near heavily populated areas has been the major factor in the resurgence of interest in the physicochemical processes of precipitation and dissolution of phosphate salts.

Let us have a discussion about the calcium phosphate scale deposition. Calcium phosphates are important from the industrial water system point of view if you talk about because they occur as deposits on the heat exchanger and reverse osmosis membrane surface. So, it can clog the pores of these reverse osmosis membranes. In more recent times, the increase in phosphate concentration in lakes and rivers near a heavily populated areas.

This has been the major factor in the resurgence of interest in physiochemical processes of precipitation and dissolution of a phosphate salt.

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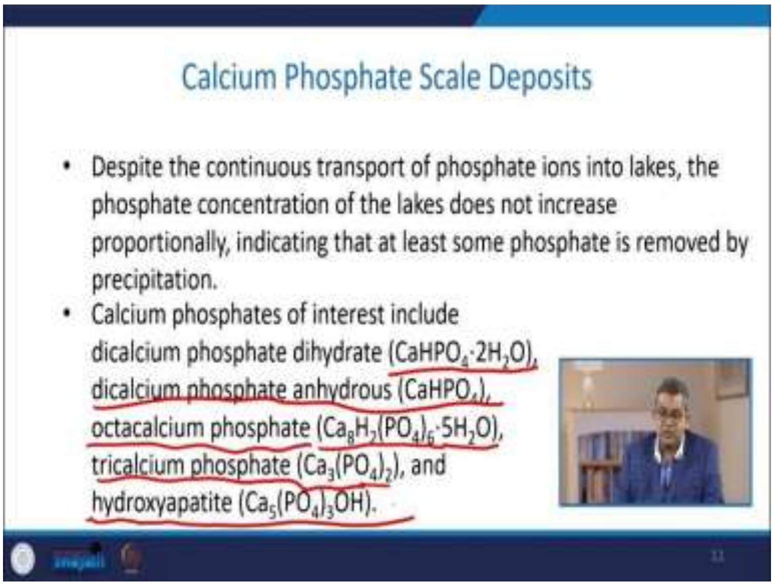

## Calcium Phosphate Scale Deposits

- Despite the continuous transport of phosphate ions into lakes, the phosphate concentration of the lakes does not increase proportionally, indicating that at least some phosphate is removed by precipitation.
- Calcium phosphates of interest include dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$), dicalcium phosphate anhydrous ($CaHPO_4$), octacalcium phosphate ($Ca_8H_2(PO_4)_6 \cdot 5H_2O$), tricalcium phosphate ($Ca_3(PO_4)_2$), and hydroxyapatite ($Ca_5(PO_4)_3OH$).

- Despite the continuous transport of phosphate iron into the lakes, the phosphate concentration of the lake does not increase proportionally. Calcium phosphates of interest include dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$), dicalcium phosphate anhydrous

($CaHPO_4$), octacalcium phosphate ($Ca_8H_2(PO_4)_6 \cdot 5H_2O$), tricalcium phosphate ($Ca_3(PO_4)_2$), and hydroxyapatite ($Ca_5(PO_4)_3OH$).

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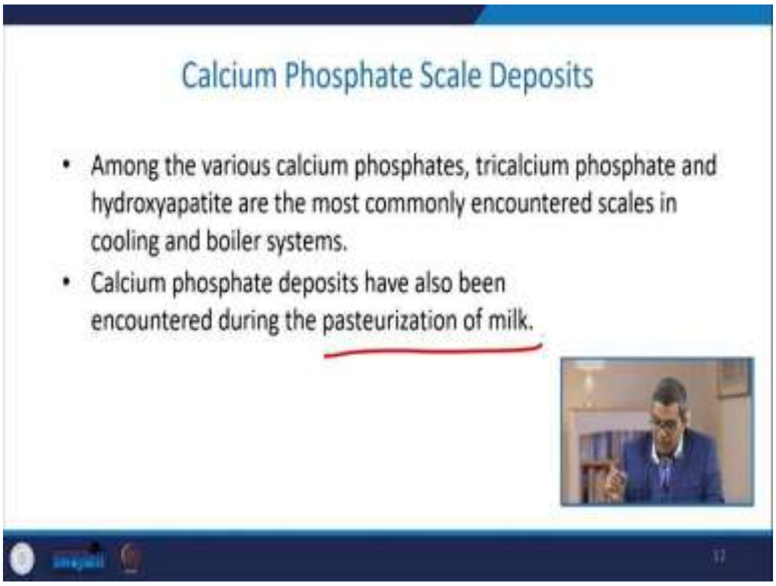

## Calcium Phosphate Scale Deposits

- Among the various calcium phosphates, tricalcium phosphate and hydroxyapatite are the most commonly encountered scales in cooling and boiler systems.
- Calcium phosphate deposits have also been encountered during the pasteurization of milk.

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## Silica/Metal Silicates

- The markedly different solubilities between amorphous and crystalline silica in neutral pH is the main factor responsible for supersaturation with respect to silicate and metal silicate salts
- The silicate-based scale deposits in cooling water systems consist mainly of silica, calcium, magnesium, and aluminosilicates.
- If magnesium is present in high-enough concentrations, magnesium silicate scaling will occur at a pH of 8.5.

Let us have a discussion about the silica metal silicates. The different significant solubilities between amorphous and crystalline silica in neutral pH are the main factor responsible for supersaturation with respect to silicate and metal silicate salts. The silicate-based scale deposits in the cooling water system consist mainly of silica, calcium, magnesium, and aluminosilicate.

If you see that magnesium is present in high enough concentration, magnesium silicate scaling will occur at a pH of 8.5.

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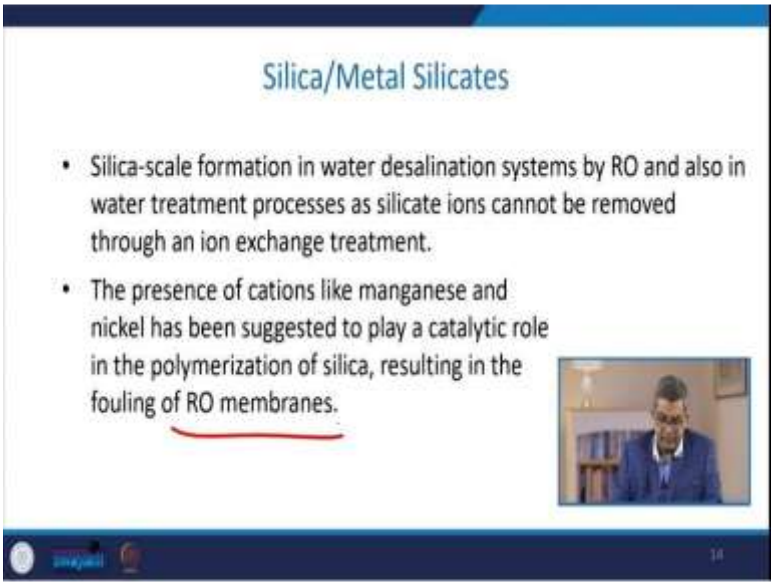

## Silica/Metal Silicates

- Silica-scale formation in water desalination systems by RO and also in water treatment processes as silicate ions cannot be removed through an ion exchange treatment.
- The presence of cations like manganese and nickel has been suggested to play a catalytic role in the polymerization of silica, resulting in the fouling of RO membranes.

Silica scale formation in water desalination system by reverse osmosis and also water treatment processes as a silicate ion cannot be removed through an ion-exchange treatment. The presence of cations like manganese and nickel has been suggested to play a catalytic role in the polymerization of silica, may result in the fouling of the reverse osmosis membrane.

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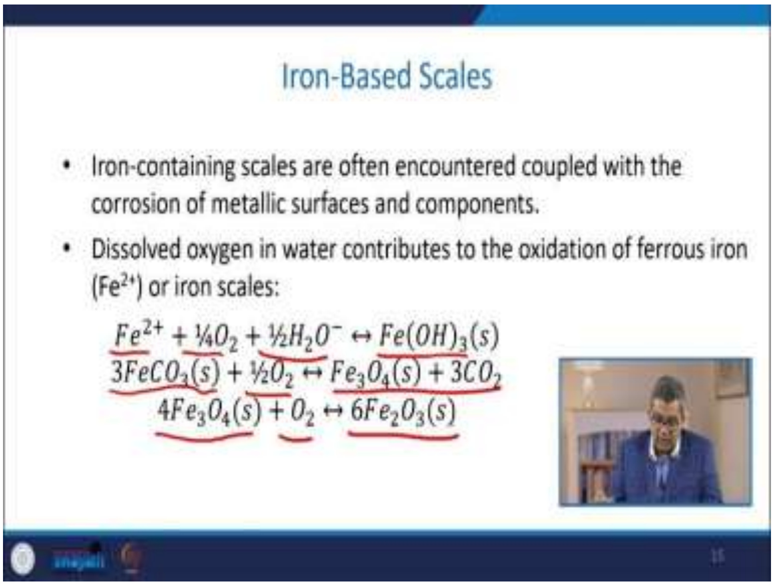

## Iron-Based Scales

- Iron-containing scales are often encountered coupled with the corrosion of metallic surfaces and components.
- Dissolved oxygen in water contributes to the oxidation of ferrous iron ($Fe^{2+}$) or iron scales:

$$Fe^{2+} + \frac{1}{4}O_2 + \frac{1}{2}H_2O^- \leftrightarrow Fe(OH)_3(s)$$
$$3FeCO_3(s) + \frac{1}{2}O_2 \leftrightarrow Fe_3O_4(s) + 3CO_2$$
$$4Fe_3O_4(s) + O_2 \leftrightarrow 6Fe_2O_3(s)$$

Let us have a discussion about the iron-based scales. Iron-containing scales are often encountered coupled with corrosion of metallic surfaces and components. Dissolved oxygen in water sometimes contributes to the oxidation of ferrous iron Fe 2 + or iron scales. These are the sum of the chemical reactions like

$$Fe^{2+} + ¼O_2 + ½H_2O^- \leftrightarrow Fe(OH)_3(s)$$

$$3FeCO_3(s) + ½O_2 \leftrightarrow Fe_3O_4(s) + 3CO_2$$

$$4Fe_3O_4(s) + O_2 \leftrightarrow 6Fe_2O_3(s)$$

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## Iron-Based Scales

- The rate of corrosion of the iron metal has little relationship to the amount of iron that actually goes into the water, primarily due to the deposition of oxidized iron or other compounds into a scale that serves as a large reservoir of corrosion by-products.
- Iron scales are very heterogeneous, consisting of a large variety of compounds.

When we; talk further about the iron-based scales, the rate of corrosion of the iron metal has little relationship to the amount of iron that actually goes into the water, primarily due to the deposition of oxidized iron or other compounds into a scale that serves a large reservoir of corrosion by-product. Iron scales are very heterogeneous, consisting of a large variety of compounds.

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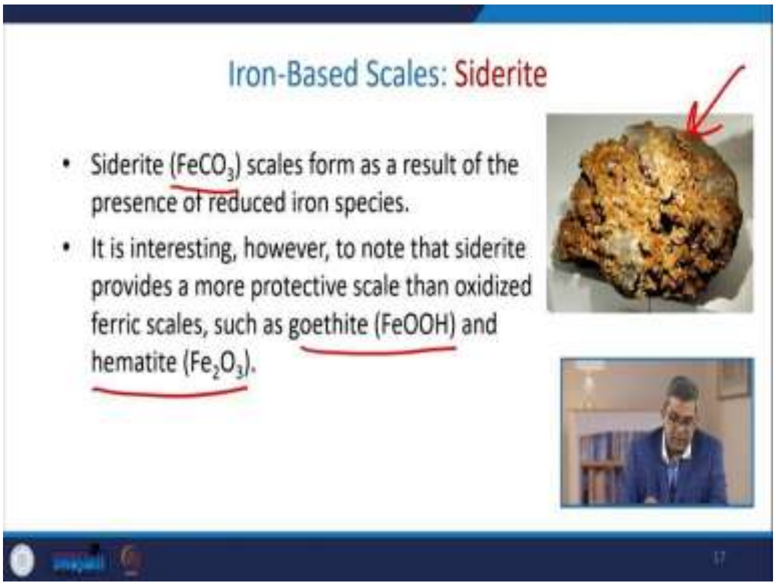

## Iron-Based Scales: Siderite

- Siderite ($FeCO_3$) scales form as a result of the presence of reduced iron species.
- It is interesting, however, to note that siderite provides a more protective scale than oxidized ferric scales, such as goethite (FeOOH) and hematite ($Fe_2O_3$).

One of the iron-based scales is siderite. Siderite is a $FeCO_3$ scale you can have a look at this picture. Their scales form as a result of the presence of reduced iron species. is interesting, however that to note that siderite provides a more protective scale than oxidized ferric scales, such as goethite that is FeOOH and hematite $Fe_2O_3$.

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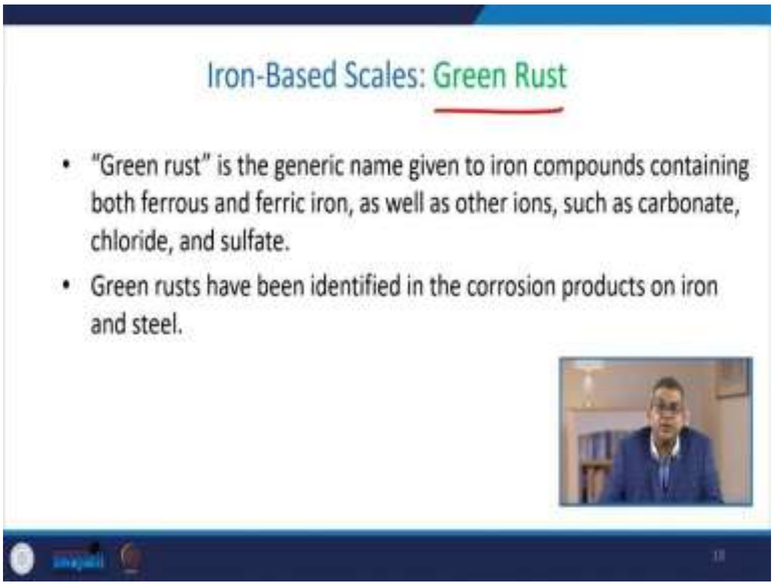

Iron-Based Scales: Green Rust

- "Green rust" is the generic name given to iron compounds containing both ferrous and ferric iron, as well as other ions, such as carbonate, chloride, and sulfate.
- Green rusts have been identified in the corrosion products on iron and steel.

Green rust, green rust is the generic name given to the iron compound containing ferrous and ferric iron and ions such as carbonate, chloride, and sulfate. This green rust has been identified in the corrosion product on iron and steel.

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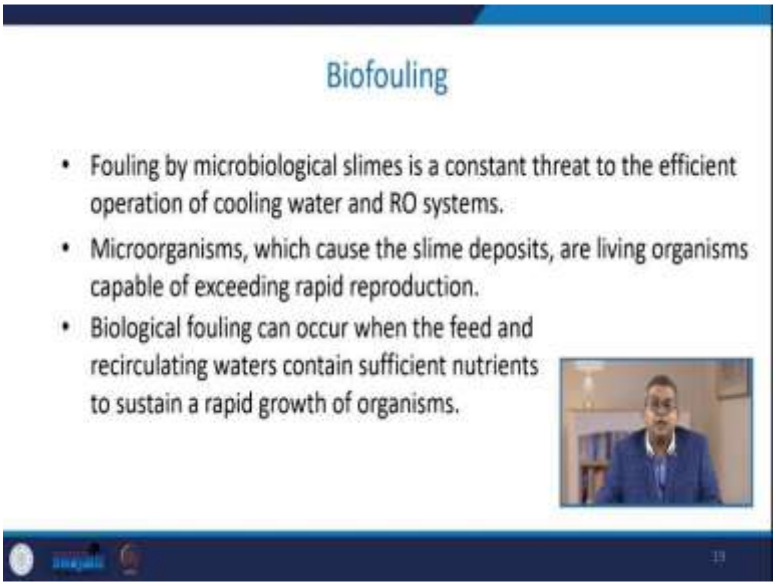

Biofouling

- Fouling by microbiological slimes is a constant threat to the efficient operation of cooling water and RO systems.
- Microorganisms, which cause the slime deposits, are living organisms capable of exceeding rapid reproduction.
- Biological fouling can occur when the feed and recirculating waters contain sufficient nutrients to sustain a rapid growth of organisms.

Let us have a discussion about biofouling. Fouling occurs by microbiological slimes is a constant threat to the efficient operation of cooling water and reverse osmosis system. Microorganisms, which cause the slime deposit, are living organism capable of exceeding rapid reproduction. So, biological fouling can occur when the feed and recirculating water contains sufficient nutrients to sustain a rapid organism's growth.

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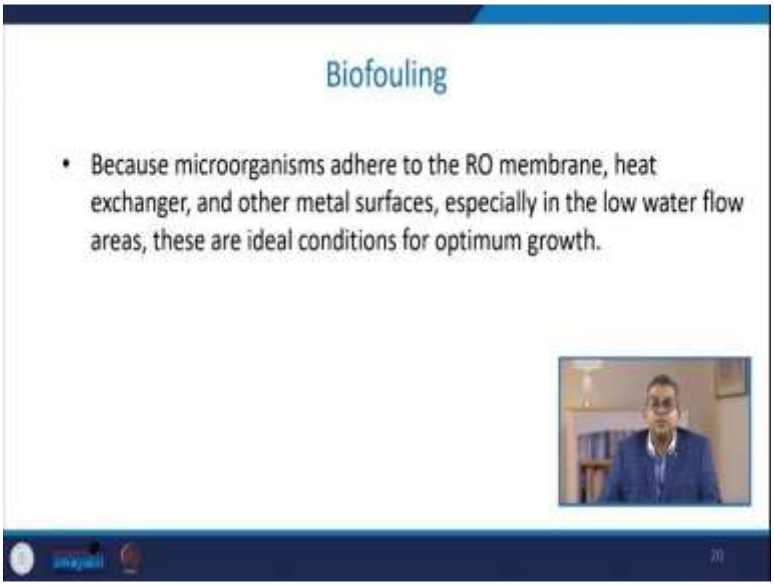

## Biofouling

- Because microorganisms adhere to the RO membrane, heat exchanger, and other metal surfaces, especially in the low water flow areas, these are ideal conditions for optimum growth.

Because microorganisms adhere to the reverse osmosis membrane heat exchanger and other metal surfaces, especially in the low water flow area, these are ideal conditions for optimal growth.

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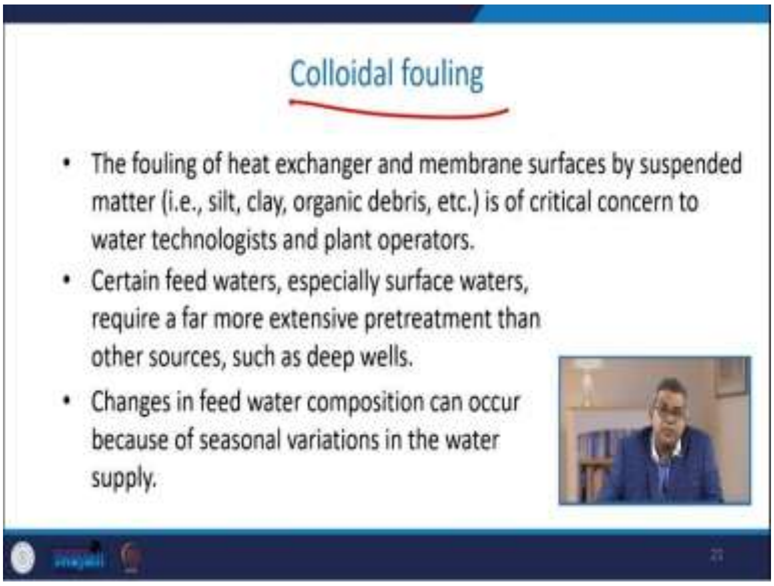

## Colloidal fouling

- The fouling of heat exchanger and membrane surfaces by suspended matter (i.e., silt, clay, organic debris, etc.) is of critical concern to water technologists and plant operators.
- Certain feed waters, especially surface waters, require a far more extensive pretreatment than other sources, such as deep wells.
- Changes in feed water composition can occur because of seasonal variations in the water supply.

Let us have a discussion about colloidal fouling. The fouling of heat exchanger and membrane surfaces by suspended matter that is maybe silt, clay, organic debris etc. This is a critical concern to water technologists, water conditioning persons, and plant operators. Certain feed waters, especially the surface water, require a far more extensive pretreatment than other sources, such as deep wells etc.

Changes in sometimes the feed water composition can occur because of the seasonal variation in the water supply.

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Colloidal fouling

- Feed waters containing suspended matter are typically treated with inorganic and organic clarification agents.
- The effectiveness of a surface treatment to reduce suspended matter is dependent upon the proper selection and concentration of clarifying agents, pH, mixing, and residence time.
- Commonly used water clarification agents include aluminum chloride, ferric chloride, and cationic polymers.

Feedwater containing suspended matter is typically treated with inorganic or inorganic clarification agents. The effectiveness of surface treatment to reduce suspended matter is usually dependent upon the proper selection and concentration of clarifying agent pH, whatever pH we are using at the mixing, the mixing time, and the residence time. We may list certain commonly used water clarification agents, including aluminium chloride, ferric chloride, some cationic polymers etc., are commonly used water clarifiers. There are certain fouling are related to corrosion. Corrosion is a very common phenomenon and usually occurs in all chemical process industries. So, let us have a brief description of the corrosion.

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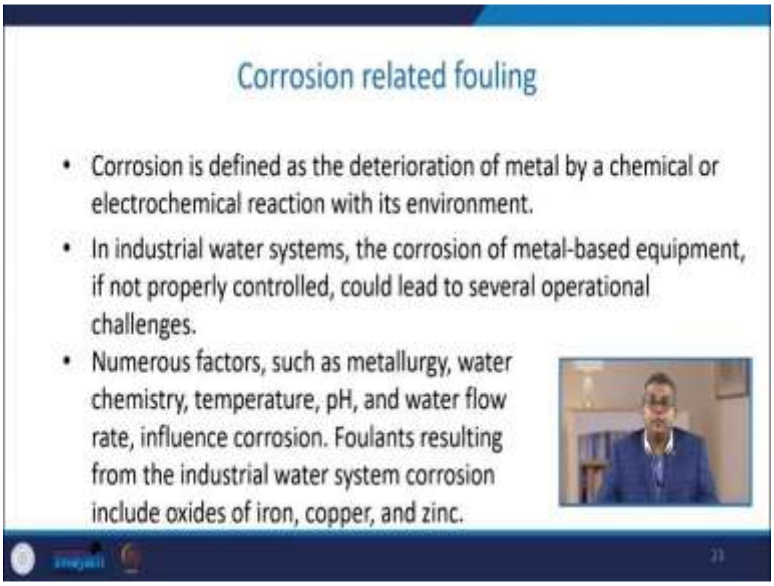

## Corrosion related fouling

- Corrosion is defined as the deterioration of metal by a chemical or electrochemical reaction with its environment.
- In industrial water systems, the corrosion of metal-based equipment, if not properly controlled, could lead to several operational challenges.
- Numerous factors, such as metallurgy, water chemistry, temperature, pH, and water flow rate, influence corrosion. Foulants resulting from the industrial water system corrosion include oxides of iron, copper, and zinc.

It is defined as the deterioration of metal by chemical or electrochemical reaction with its environment. So, you can see it is a broad spectrum or a broad definition. When we talk about the industrial water system, the corrosion of metal-based equipment is not properly controlled. If we are unable to control it, this may lead to several operational challenges and sometimes may create a serious hazard to the safe environment or safe working conditions apart from the environmental problem, energy issues, various wear, and tears etc. So, numerous factors such as metallurgy, water chemistry, temperature, knowledge about the pH, and water flow rate influence corrosion. Foulants resulting from the industrial water system corrosion include the oxide of iron, copper, and zinc.

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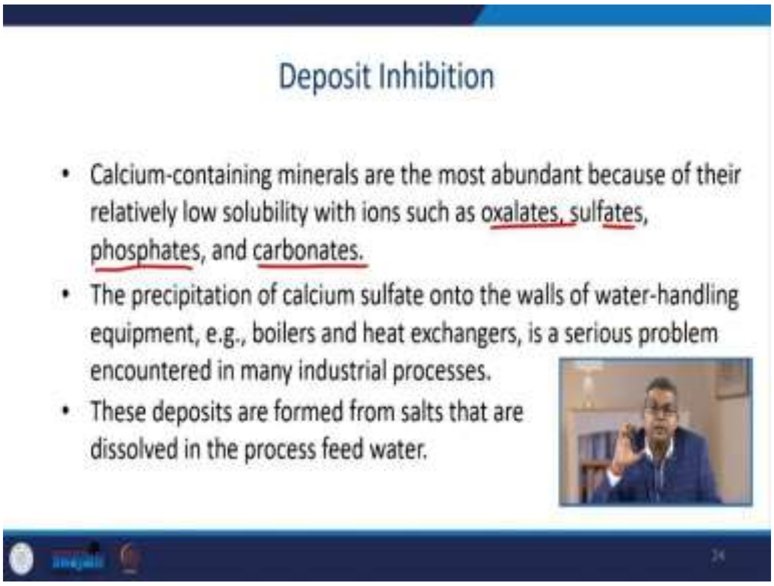

## Deposit Inhibition

- Calcium-containing minerals are the most abundant because of their relatively low solubility with ions such as oxalates, sulfates, phosphates, and carbonates.
- The precipitation of calcium sulfate onto the walls of water-handling equipment, e.g., boilers and heat exchangers, is a serious problem encountered in many industrial processes.
- These deposits are formed from salts that are dissolved in the process feed water.

Let us have a discus discussion about deposit inhibition. Inhibition is again very important because earlier, we had discussed the various fouling aspects. Now, we understand that fouling is, again, extremely you can say, detrimental for any kind of chemical operation. So, we need to think about the inhibition of all kinds of these deposits. How we can go ahead? What are the surface preparation?

What are the different types of chemistry involved in this kind of inhibition disinhibition aspect? So, let us have a brief discussion, and in due course of time and the subsequent time we will discuss this inhibition aspect. Calcium-containing minerals are the most abundant because of their relatively low solubility with ions such as oxalate, sulfates, phosphates, carbonates etc.

The precipitation of calcium sulfate onto the walls of water handling equipment, maybe the tube may be the pipes etc. These are used in the boiler and heat exchanger. This is a serious problem encountered in various industrial operations. These deposits are formed from salts that are dissolved in the processed feed water. I am giving you one example: if you repeatedly heat the water, then what the salts may get deposited over the inner lining of the other vessel or a pot in which you are depositing.

It is a very common phenomenon, and even you can try it in your home also. Moreover, this sometimes creates a very problem because, over time, the concentration of these salts keeps increasing, increasing, and increasing. Sometimes, the process water this becomes super saturated with respect to these salts during the process.

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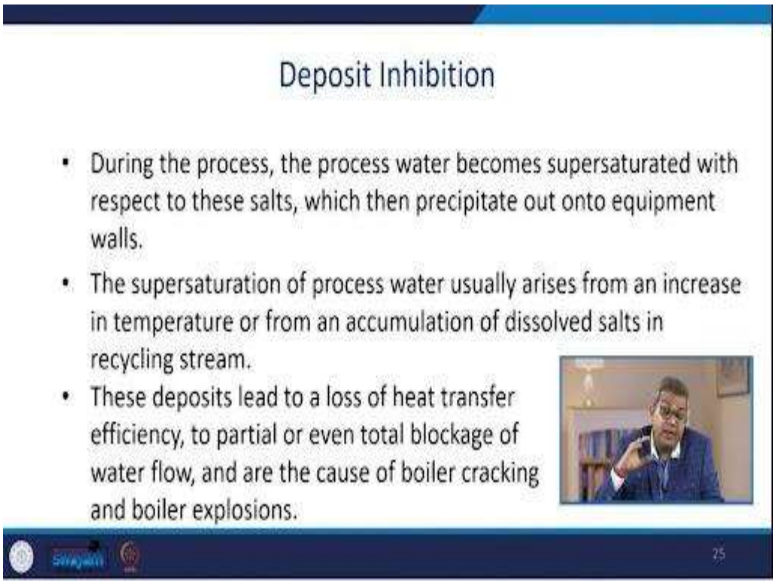

Deposit Inhibition

- During the process, the process water becomes supersaturated with respect to these salts, which then precipitate out onto equipment walls.
- The supersaturation of process water usually arises from an increase in temperature or from an accumulation of dissolved salts in recycling stream.
- These deposits lead to a loss of heat transfer efficiency, to partial or even total blockage of water flow, and are the cause of boiler cracking and boiler explosions.

And then it intends to precipitate out into equipment walls which I discussed with an example in the previous slide. The supersaturation of processed water usually arises from an increase in temperature or from an accumulation of dissolved salt in the recycling stream. These deposits sometimes lead to the loss of heat transfer efficiency to partial or even total blockage of water flow, and that causes the boiler cracking boiler explosion.

Obviously, when these are occurring, you definitely see that is a serious hazard because the boiler is not only producing steam but is a pressure vessel. It may create a serious problem for industrial affairs. Now, scaling may be defined as a solid layer deposition on the surface arising primarily from dissolved inorganic salt in a flowing solution.

That exhibits the supersaturation under the process condition. For example, this is the pipeline and scale may get deposited at the inner line.

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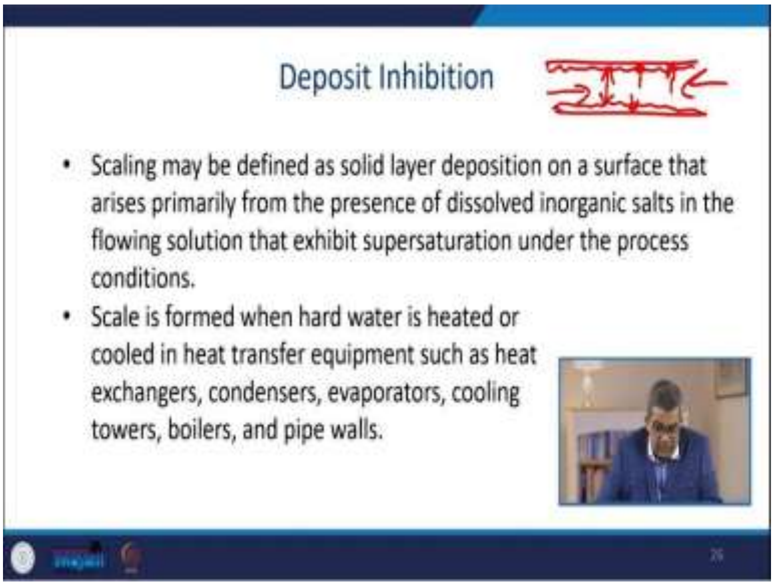

Deposit Inhibition

- Scaling may be defined as solid layer deposition on a surface that arises primarily from the presence of dissolved inorganic salts in the flowing solution that exhibit supersaturation under the process conditions.
- Scale is formed when hard water is heated or cooled in heat transfer equipment such as heat exchangers, condensers, evaporators, cooling towers, boilers, and pipe walls.

So, the effective inner diameter may reduce this, thereby creating a flow disturbance this, thereby creating the problem in the heat transfer. And similarly, if these tubes are being used in the boiler, then again creates a problem and which we had already discussed in the previous slide. Scales are formed when hard water is heated or cooled in heat transfer equipment such as heat exchangers, condensers, evaporators, cooling towers, boiler tubes, pipe walls etc.

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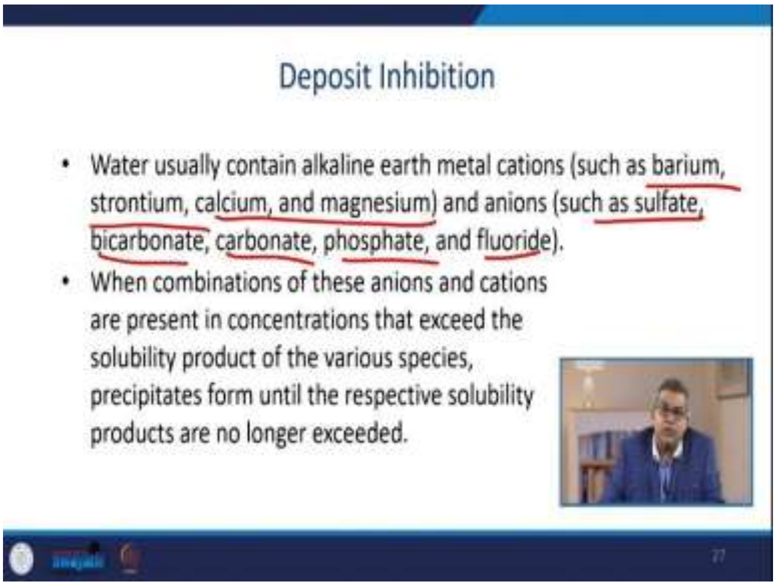

## Deposit Inhibition

- Water usually contain alkaline earth metal cations (such as barium, strontium, calcium, and magnesium) and anions (such as sulfate, bicarbonate, carbonate, phosphate, and fluoride).
- When combinations of these anions and cations are present in concentrations that exceed the solubility product of the various species, precipitates form until the respective solubility products are no longer exceeded.

So, water usually contains alkaline earth metal cations such as barium, strontium, calcium, and magnesium, and sometimes anions such as sulfates, bicarbonates, carbonates, phosphate, and fluorides. Now, when a combination of these anions and cations are present in a concentration that exceeds the solubility product of the various species, precipitates from form until the respective solubility products are no longer exceeded.

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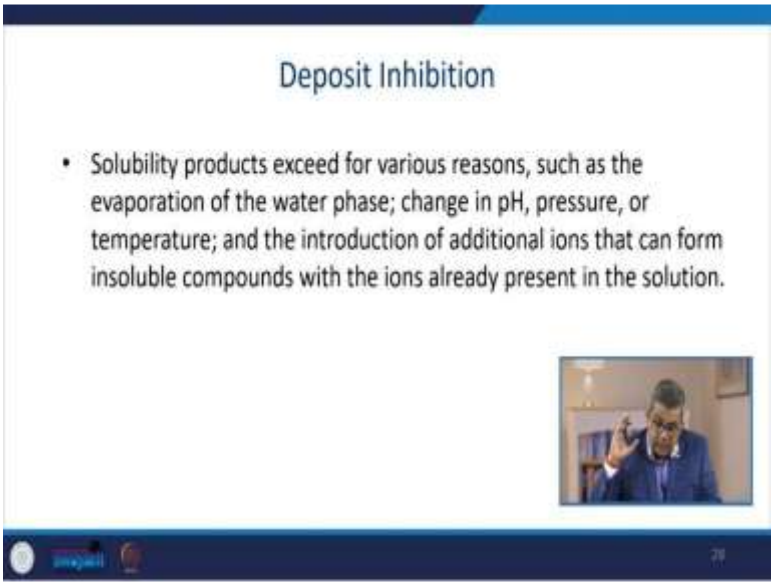

## Deposit Inhibition

- Solubility products exceed for various reasons, such as the evaporation of the water phase; change in pH, pressure, or temperature; and the introduction of additional ions that can form insoluble compounds with the ions already present in the solution.

Now, solubility products exceed for various reasons such as evaporation of water phase, change in pH, pressure, and temperature. Again, you see that the pressure and temperature have a wide range, and sometimes the introduction of additional ions that makes that can form insoluble compounds with the ion already present in the solution. So, every time do not think that these are the negative aspect. This gives you useful information to prevent the deposit inhibition.

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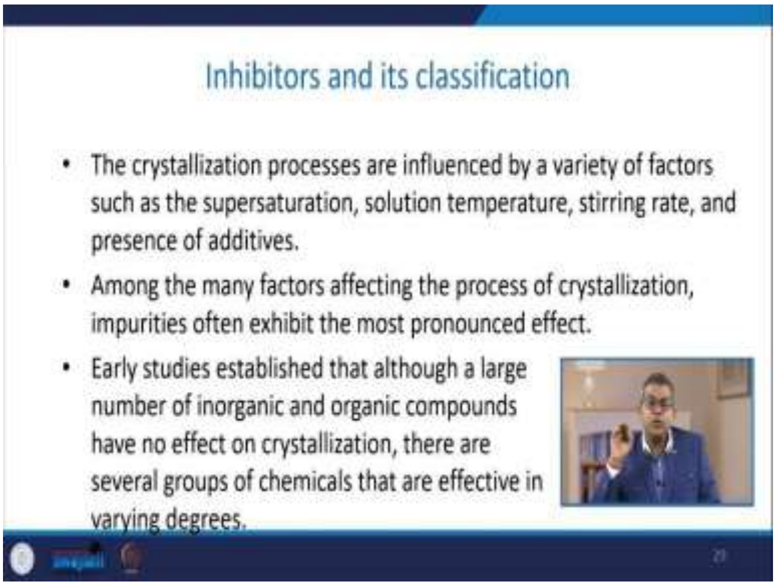

## Inhibitors and its classification

- The crystallization processes are influenced by a variety of factors such as the supersaturation, solution temperature, stirring rate, and presence of additives.
- Among the many factors affecting the process of crystallization, impurities often exhibit the most pronounced effect.
- Early studies established that although a large number of inorganic and organic compounds have no effect on crystallization, there are several groups of chemicals that are effective in varying degrees.

Now, since we were talking about deposit inhibition. Inhibitors; if we look into the deposit inhibition, we have to look into the concept of inhibitors and how we can classify these inhibitors because there are different scales. So, we need to have a similar type of classification scheme for inhibitors. So, the crystallization processes usually are influenced by a variety of factors such as supersaturation, solution temperature, sometimes stirring rate, sometimes the presence of additives etc.

Among the many factors affecting the process of crystallization, the impurities often exhibit the most pronounced effect. Early studies usually established that although many inorganic and organic compounds have no effect on crystallizations, there are several groups of chemicals that are effective in varying degrees.

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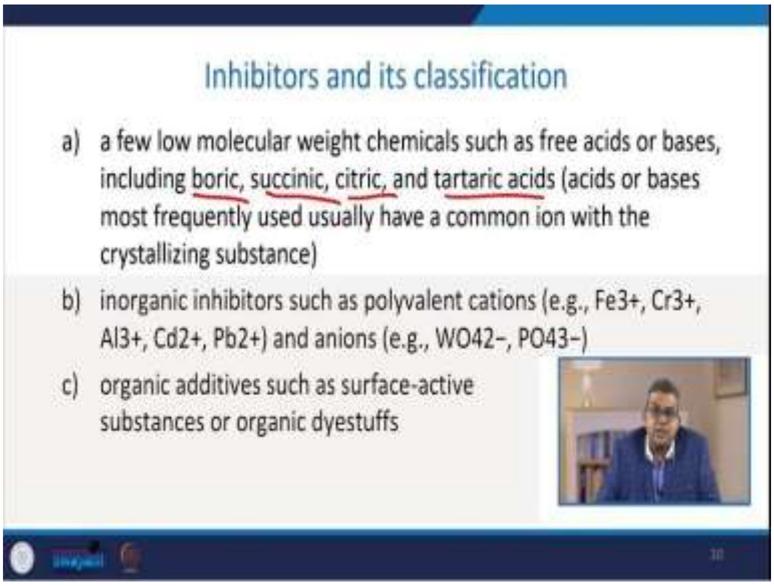

## Inhibitors and its classification

a) a few low molecular weight chemicals such as free acids or bases, including boric, succinic, citric, and tartaric acids (acids or bases most frequently used usually have a common ion with the crystallizing substance)

b) inorganic inhibitors such as polyvalent cations (e.g., Fe3+, Cr3+, Al3+, Cd2+, Pb2+) and anions (e.g., WO42−, PO43−)

c) organic additives such as surface-active substances or organic dyestuffs

When we talk about the classification, very few molecular weight chemicals such as free acids or bases, including boric, succinic, citric, tartaric acids, acid or bases most frequently used, usually have a common ion with the crystallizing substance. Inorganic inhibitors such as polyvalent cations like ($Fe^{3+}$, $Cr^{3+}$, $Al^{3+}$, $Cd^{2+}$, $Pb^{2+}$) and anions (e.g., $WO_4^{2-}$, $PO_4^{3-}$). Organic additives such as surface-active substances or organic dye stuffs.

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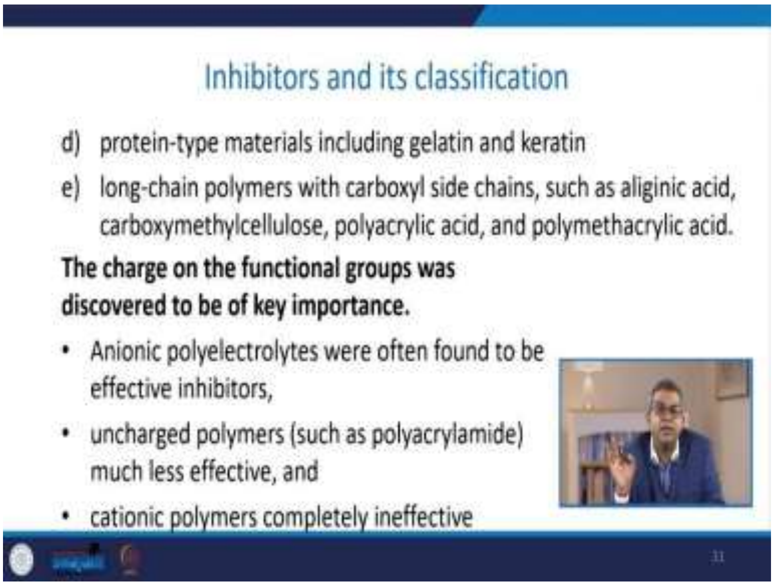

Inhibitors and its classification

d) protein-type materials including gelatin and keratin

e) long-chain polymers with carboxyl side chains, such as aliginic acid, carboxymethylcellulose, polyacrylic acid, and polymethacrylic acid.

**The charge on the functional groups was discovered to be of key importance.**

- Anionic polyelectrolytes were often found to be effective inhibitors,
- uncharged polymers (such as polyacrylamide) much less effective, and
- cationic polymers completely ineffective

Another is the protein-type materials, including gelatin and keratins. Long-chain polymers with the carboxyl side chains, such as allergenic acids, carboxymethylcellulose, polyacrylic acid, poly methacrylic acids. The charge on the functional groups was usually discovered to be the key importance that is crucial and very important. Now, anionic polyelectrolytes are often found to be effective inhibitors.

Uncharged polymers such as polyacrylamide are much less effective, and cationic polymers are completely ineffective. Now, let us discuss the mechanism of inhibition, how it works and what is important, etc. This is again a very crucial aspect to inhibit the skill deposition.

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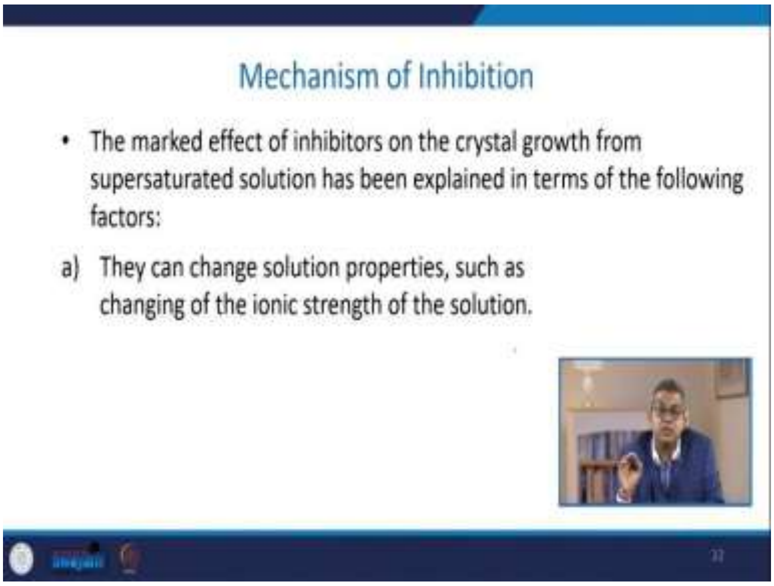

Mechanism of Inhibition

- The marked effect of inhibitors on the crystal growth from supersaturated solution has been explained in terms of the following factors:

a) They can change solution properties, such as changing of the ionic strength of the solution.

The marked effect of inhibitors on the crystal growth from supersaturated solution has been explained in terms of different factors. One is that it can change solution properties, such as changing of ionic strength of the solution.

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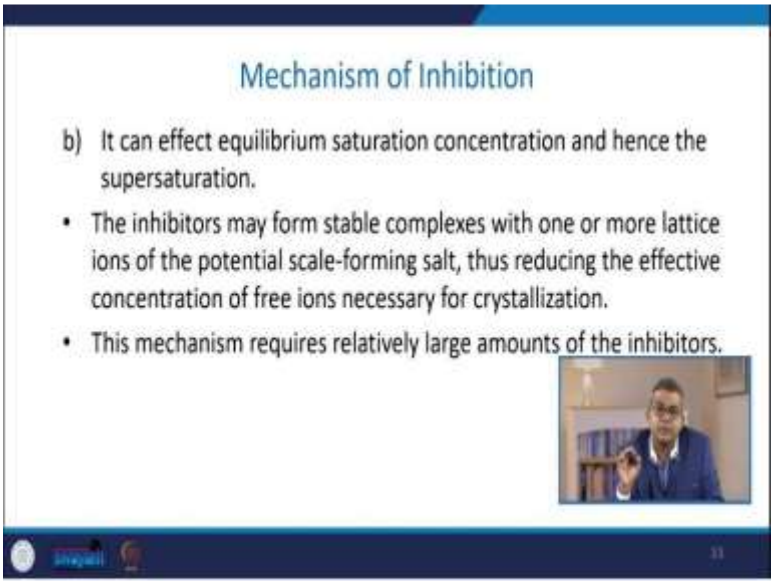

Mechanism of Inhibition

b) It can effect equilibrium saturation concentration and hence the supersaturation.

- The inhibitors may form stable complexes with one or more lattice ions of the potential scale-forming salt, thus reducing the effective concentration of free ions necessary for crystallization.
- This mechanism requires relatively large amounts of the inhibitors.

It can affect the equilibrium saturation concentration and, therefore, supersaturation. So, the inhibitors may form stable complexes with one or more lattice science of the potential scale forming a salt. Therefore, reducing the effective concentration of free ions is necessary for crystallization. This mechanism requires a relatively large amount of inhibitors.

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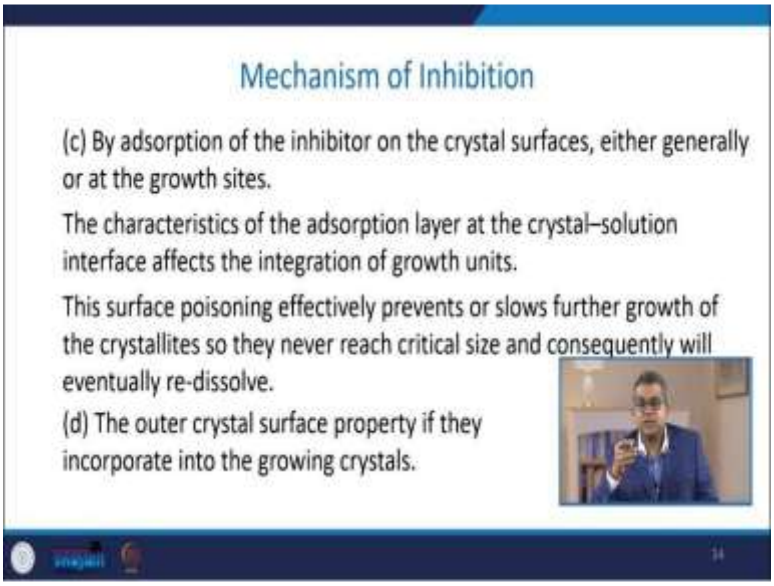

## Mechanism of Inhibition

(c) By adsorption of the inhibitor on the crystal surfaces, either generally or at the growth sites.

The characteristics of the adsorption layer at the crystal–solution interface affects the integration of growth units.

This surface poisoning effectively prevents or slows further growth of the crystallites so they never reach critical size and consequently will eventually re-dissolve.

(d) The outer crystal surface property if they incorporate into the growing crystals.

Another is by adsorption of the inhibitor on the crystal surface, are either generally on or at the growth sites. The characteristics of the adsorption layer at the crystal solution interface affect the integration of the growth unit. This surface poisoning is usually termed as surface poisoning. This effectively prevents or slows further growth of the crystallites. So, never reach the critical size and consequently will eventually redissolve.

So, it creates a barrier between the surface and the targeted sides. The outer crystal surface property if it is incorporated into the growing crystal.

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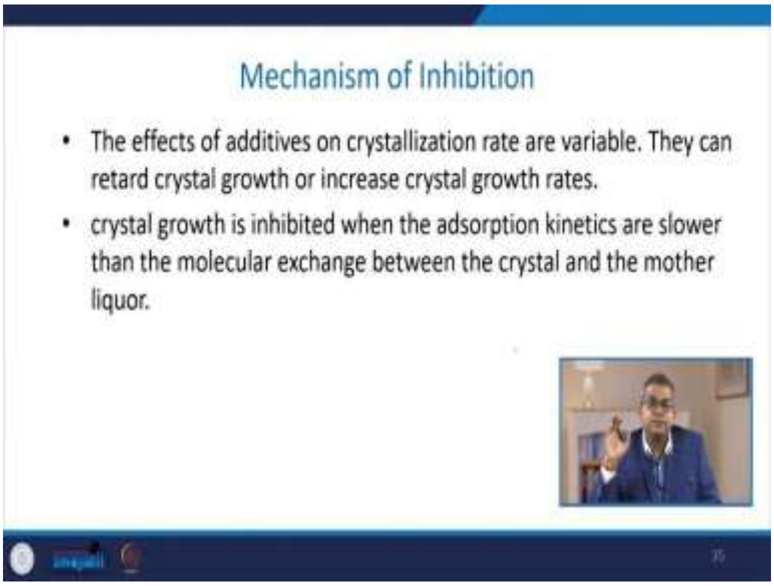

## Mechanism of Inhibition

- The effects of additives on crystallization rate are variable. They can retard crystal growth or increase crystal growth rates.
- crystal growth is inhibited when the adsorption kinetics are slower than the molecular exchange between the crystal and the mother liquor.

The effects of additives on crystallization rate are variable. It can retard the crystal growth or sometimes increase the crystal growth rates. Crystal growth is usually inhibited when the adsorption kinetics are slower than the molecular exchange between the crystal and the mother liquor.

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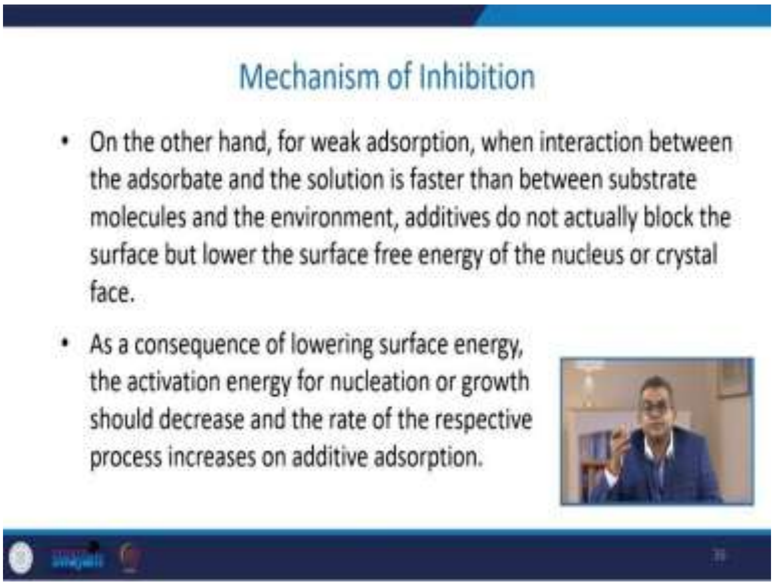

### Mechanism of Inhibition

- On the other hand, for weak adsorption, when interaction between the adsorbate and the solution is faster than between substrate molecules and the environment, additives do not actually block the surface but lower the surface free energy of the nucleus or crystal face.
- As a consequence of lowering surface energy, the activation energy for nucleation or growth should decrease and the rate of the respective process increases on additive adsorption.

On the other hand, for weak adsorption, when the interaction between the adsorbate and the solution is faster than between the substrate molecules and the environment, additives do not actually block the surface but lower the surface free energy of the nucleus or crystal phase. So, the surface knowledge about the surface free energy is important because this is again the key factor of skill inhibition in this particular category.

So, as a consequence of lowering surface energy, the activation energy for nucleation or growth should decrease, and the rate of the respective process increases on additive adsorption. So, earlier reported that the additive promotes growth at a low concentration and at high concentration in the same system. In most cases, the presence of additives reduces the overall crystal growth rate.

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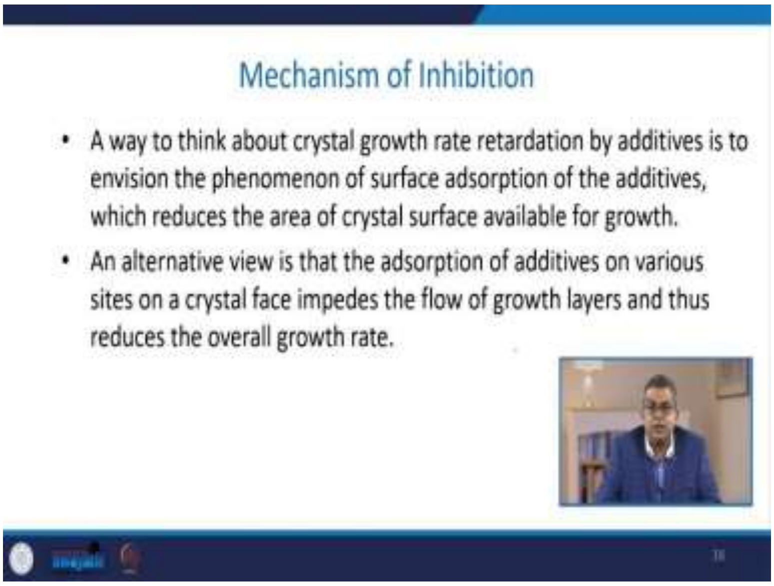

## Mechanism of Inhibition

- A way to think about crystal growth rate retardation by additives is to envision the phenomenon of surface adsorption of the additives, which reduces the area of crystal surface available for growth.
- An alternative view is that the adsorption of additives on various sites on a crystal face impedes the flow of growth layers and thus reduces the overall growth rate.

A way to think about the crystal growth rate retardation usually by the additives is to envision the phenomenon of surface adsorption of the additives, which reduces the area of crystal surface available for growth. An alternative view is that the adsorption of additives on various sites on the crystal face impedes the flow of the growth layer and therefore reduces the overall growth rate.

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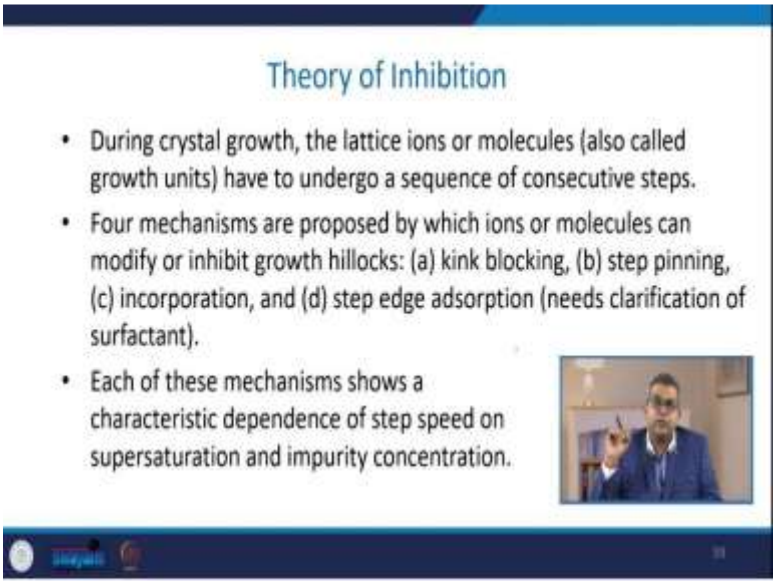

## Theory of Inhibition

- During crystal growth, the lattice ions or molecules (also called growth units) have to undergo a sequence of consecutive steps.
- Four mechanisms are proposed by which ions or molecules can modify or inhibit growth hillocks: (a) kink blocking, (b) step pinning, (c) incorporation, and (d) step edge adsorption (needs clarification of surfactant).
- Each of these mechanisms shows a characteristic dependence of step speed on supersaturation and impurity concentration.

Now, let us discuss the theory of inhibition. Now, during crystal growth, the lattice ion or molecules, also called the growth units, have to undergo consecutive steps. So, people have suggested the four mechanisms by which ions or molecules can modify or inhibit growth hillocks; one is kink blocking, the other is step pinning, and the third is incorporation.

And the fourth one is the step edge adsorption. This needs the clarification of surfactants. These mechanisms show a characteristic dependence of step speed on supersaturation and impurity concentration.

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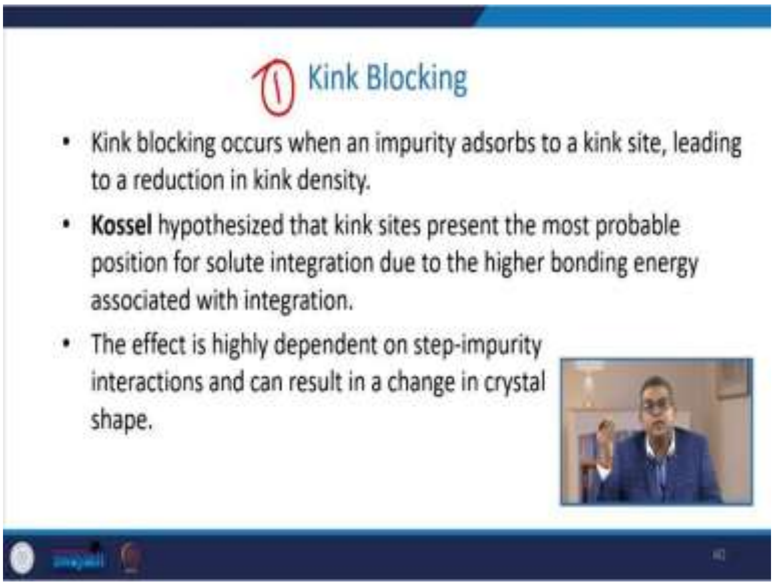

### ① Kink Blocking

- Kink blocking occurs when an impurity adsorbs to a kink site, leading to a reduction in kink density.
- **Kossel** hypothesized that kink sites present the most probable position for solute integration due to the higher bonding energy associated with integration.
- The effect is highly dependent on step-impurity interactions and can result in a change in crystal shape.

So, let us take the first one which is kink blocking. Now, kink blocking occurs when an impurity adsorbs to the king side, reducing kink density. Kossel's hypothesis is that the kink sites present the most probable position for solute integration due to higher bonding energy associated with integration. The effect of highly dependent on step impurity interaction and can result in a change in crystal shape.

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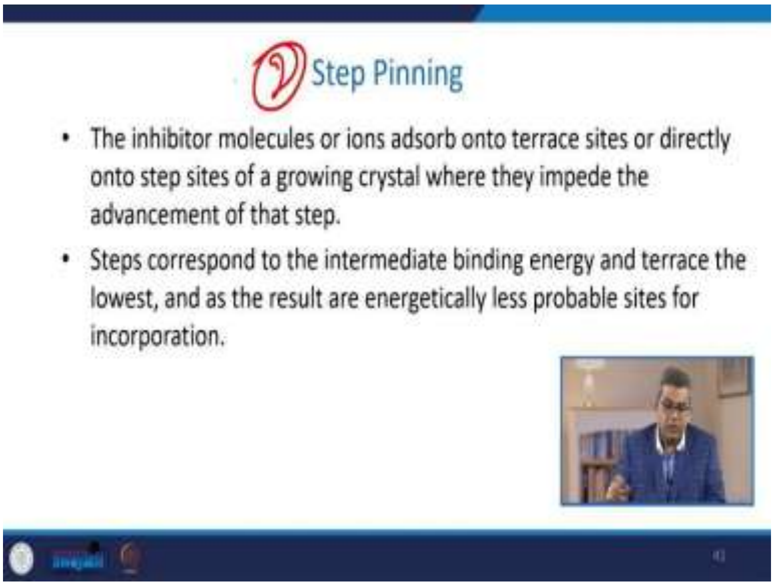

### ② Step Pinning

- The inhibitor molecules or ions adsorb onto terrace sites or directly onto step sites of a growing crystal where they impede the advancement of that step.
- Steps correspond to the intermediate binding energy and terrace the lowest, and as the result are energetically less probable sites for incorporation.

Next is the step pinning. The inhibitor molecules or ions adsorb onto the terrace sites or directly onto the step size of the growing crystal, where they impede the advancement of that step.

Now, step corresponds to the intermediate binding energy and terrace the lowest and as a result are an energetically less probable site available for incorporation. However, the next step is able to move around and squeeze through the neighboring inhibitors.

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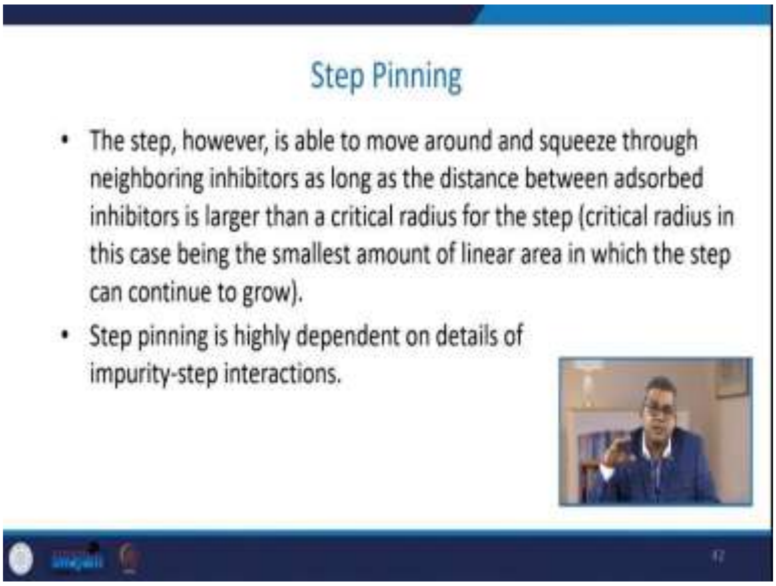

## Step Pinning

- The step, however, is able to move around and squeeze through neighboring inhibitors as long as the distance between adsorbed inhibitors is larger than a critical radius for the step (critical radius in this case being the smallest amount of linear area in which the step can continue to grow).
- Step pinning is highly dependent on details of impurity-step interactions.

As long as the distance between adsorbed inhibitors is larger than a critical radius for the step, the critical radius in this case being the smallest amount of linear area in which the step can continue to grow. The step pinning is highly dependent on details of impurity step interactions. Therefore, ion or molecules that may block one step may have no effect on the other steps. In this way, step pinning can lead to a drastic change in the hillocks and overall crystal shape.

Since the growth process consists of a surface diffusion of solute diffusion along the step to a kink and incorporation into the lattice at the kinks side.

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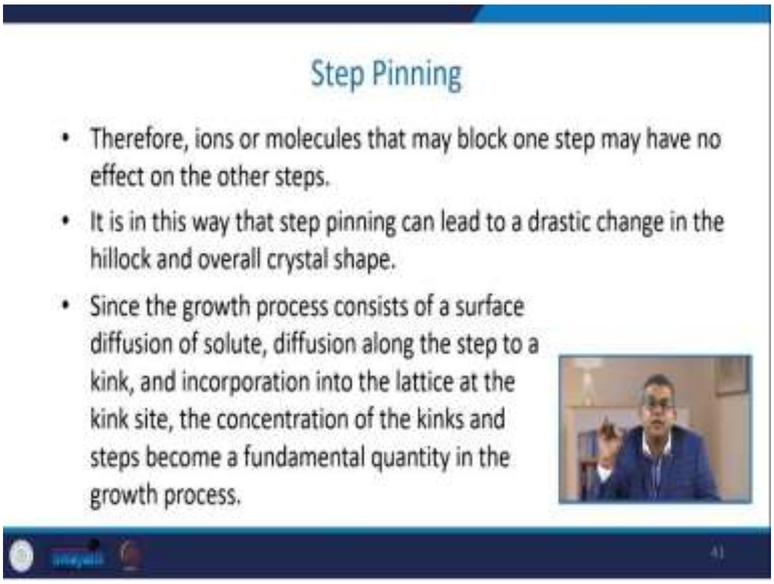

## Step Pinning

- Therefore, ions or molecules that may block one step may have no effect on the other steps.
- It is in this way that step pinning can lead to a drastic change in the hillock and overall crystal shape.
- Since the growth process consists of a surface diffusion of solute, diffusion along the step to a kink, and incorporation into the lattice at the kink site, the concentration of the kinks and steps become a fundamental quantity in the growth process.

The concentration of the kinks and steps becomes a fundamental quantity in the growth process. So, in this lecture, we have discussed the various aspects of inhibitors and their knowledge. So, we have already discussed why it is so important to prevent scale formation, which ultimately reduces the various efficiencies of our operation, and we discuss the various theories and mechanisms involved in the innovation aspects.

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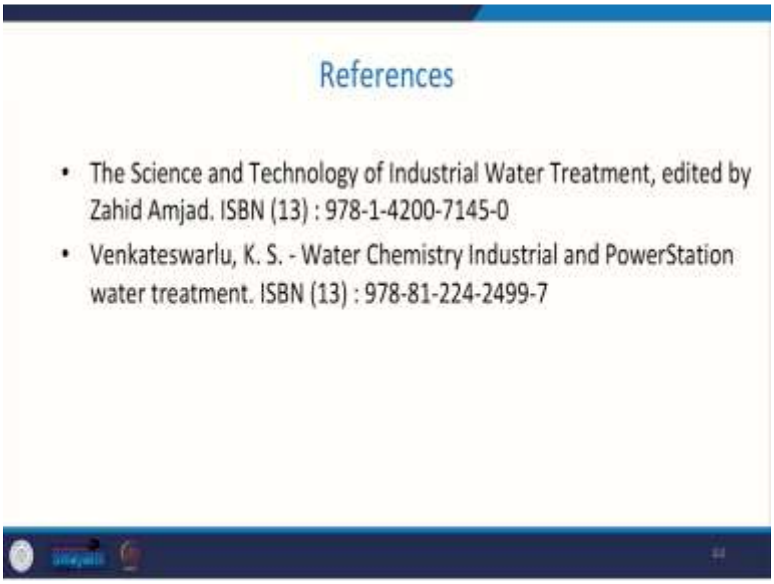

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- Venkateswarlu, K. S. - Water Chemistry Industrial and PowerStation water treatment. ISBN (13) : 978-81-224-2499-7

For your convenience we have enlisted various references you can go ahead if you wish to have a further knowledge. Thank you very much.