Chemical Process Utilities

Prof. Shishir Sinha
Department of Chemical Engineering
Indian Institute of Technology Roorkee

Module No # 12

Lecture No # 57

Thermodynamic Principles and Corrosion in Refractories

Welcome to the thermodynamic principle and corrosion aspect of refractories under the ages of chemical process utility. Now before we go into the detail of the thermodynamic aspect of refractories let us have a brief outlook about the topics which we covered in the previous lecture. So, previously we discussed about the introductory aspect of refractories this we discussed about the important requirement for uses and pertaining to the classification of refractories then we discussed about the properties of refectories.

When we were discussing about the properties we segregated the properties in 3 different spectrums, physical properties. Under the physical properties we discussed about the density, porosity, abrasion strength etc. Whereas in the thermal properties, we discussed about the thermal shock, thermal conductivity, thermal diffusivity. Then we discussed about the chemical properties with respect to the erosion and corrosion.

And apart from this, we discussed about the various ceramic properties and we started that particular lecture about; the production of refractories concept.

(Refer Slide Time: 01:44)

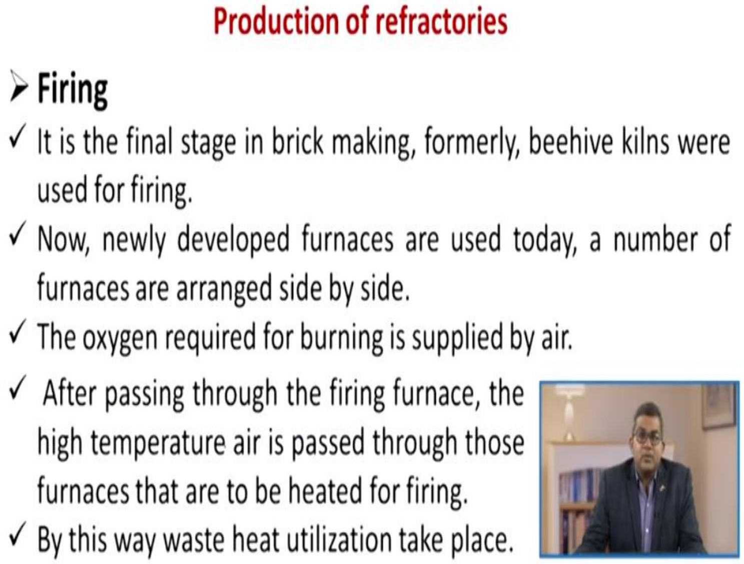
Topics to be covered?

- Production of Refractories
  - Firing
- Thermodynamic principles
  - Free energy, enthalpy, entropy, chemical equilibrium, chemical stability etc.
- Corrosion in refractories
  - Stage-I corrosion
  - Stage-II corrosion
  - Stage-III corrosion

Now in this particular lecture we are going to discuss about the concept of production of refractories under this we will discuss about the firing aspect. Then we will discuss about the thermodynamic principle because this is you can see the theoretical backbone of the refractories. Under this aspect we will discuss about the free energy enthalpy, entropy, chemical equilibrium, chemical stability all these things we will discuss.

Then we will discuss about the different stages of corrosion like; stage 1 corrosion, stage 2 corrosion and stage 3, corrosion.

(Refer Slide Time: 02:17)



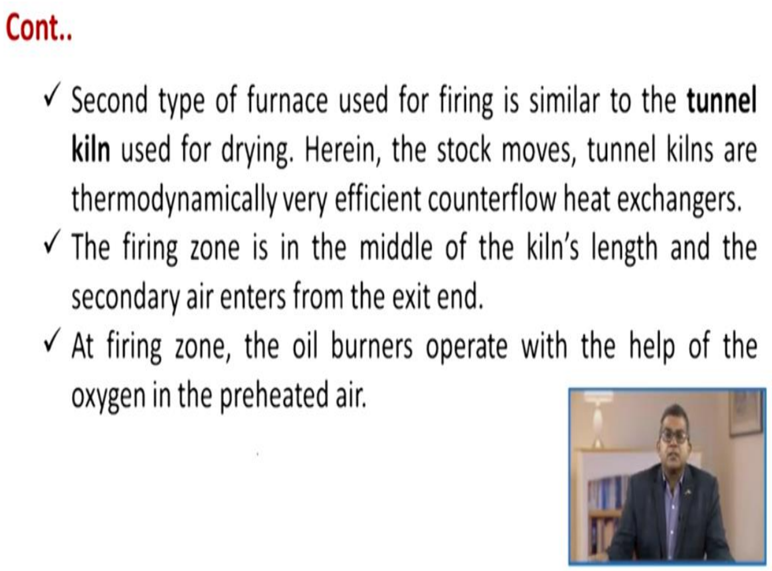
Production of refractories

- Firing
  - ✓ It is the final stage in brick making, formerly, beehive kilns were used for firing.
  - ✓ Now, newly developed furnaces are used today, a number of furnaces are arranged side by side.
  - ✓ The oxygen required for burning is supplied by air.
  - ✓ After passing through the firing furnace, the high temperature air is passed through those furnaces that are to be heated for firing.
  - ✓ By this way waste heat utilization take place.

So let us start with the firing. Now it is the final stage in brick making and formerly beehive kilns used for firing. Now newly developed furnace those who are used today number of furnaces. They are arranged side-by-side since during the firing oxygen is a key component. And usually the oxygen is whatever oxygen is required of a burning is usually supplied through air.

Now after passing through the firing furnace the high temperature air is passed through those furnaces that are to be heated for firing. Now by this way the waste heat utilization takes place.

(Refer Slide Time: 03:04)



Cont..

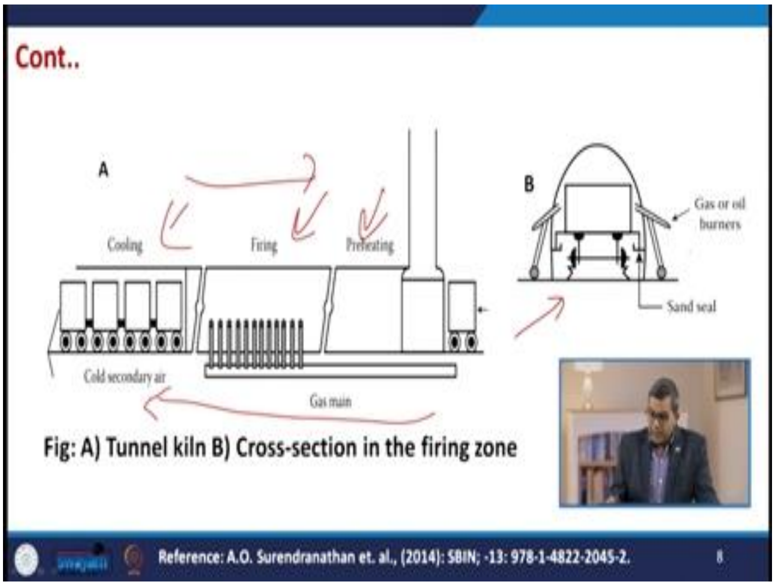
- ✓ Second type of furnace used for firing is similar to the **tunnel kiln** used for drying. Herein, the stock moves, tunnel kilns are thermodynamically very efficient counterflow heat exchangers.
- ✓ The firing zone is in the middle of the kiln's length and the secondary air enters from the exit end.
- ✓ At firing zone, the oil burners operate with the help of the oxygen in the preheated air.

Now second type of furnace is used for firing is the similar to the tunnel kiln which we discussed in the previous lecture and that is used for the drying. Now in this the stock moves tunnel kiln are thermodynamically very efficient counter flow heat exchanger. The firing zone is in the middle of the Kiln's length and the secondary air enters from the exit end. Now at the firing zone, the oil burner they usually operate with the help of oxygen in the preheated air.

Now from the firing zone the combustion product they carry heat and pass through the preheating zone. Now as the green big bricks pass through this particular zone. They absorb heat from combustion products and they are preheated. The firing temperature is usually maintained at least as high as the working temperature for sufficiently long enough to ensure that all possible reactions are completed and that dimensional stability is attained.

Now, in recent year the NC2 firing has been introduced. That is the bricks are not separately fired. The green bricks are made and equipment such as furnace is built. Now during the operation of furnace the bricks get fired.

(Refer Slide Time: 04:34)



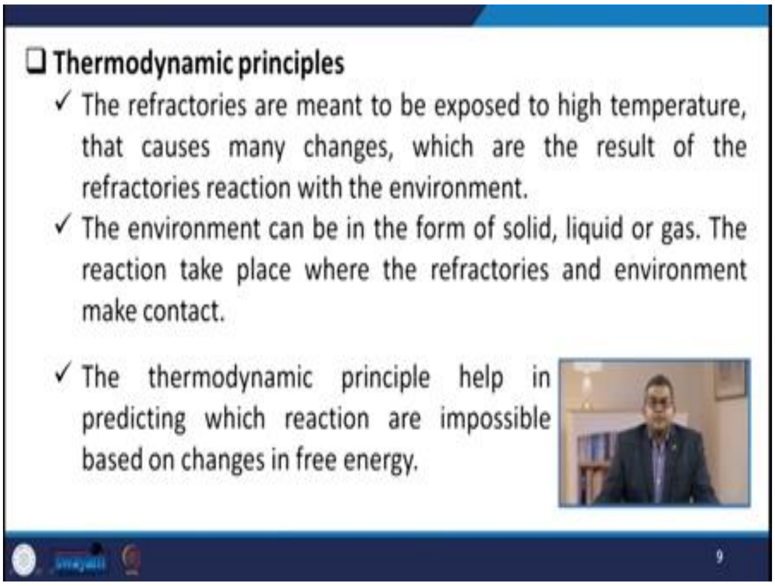
Cont..

Fig: A) Tunnel kiln B) Cross-section in the firing zone

Reference: A.O. Surendranathan et. al., (2014): SBIN; -13: 978-1-4822-2045-2.

Now, here you see that this is the tunnel kiln here. Now, as we discussed in the previously there is a preheating zone and a firing zone and a cooling zone. And the movement usually goes in this particular direction. Now in this, particular figure shows the cross section of firing zone here you see that this is the gas or oil burner and with the help of a sand seal.

(Refer Slide Time: 05:02)

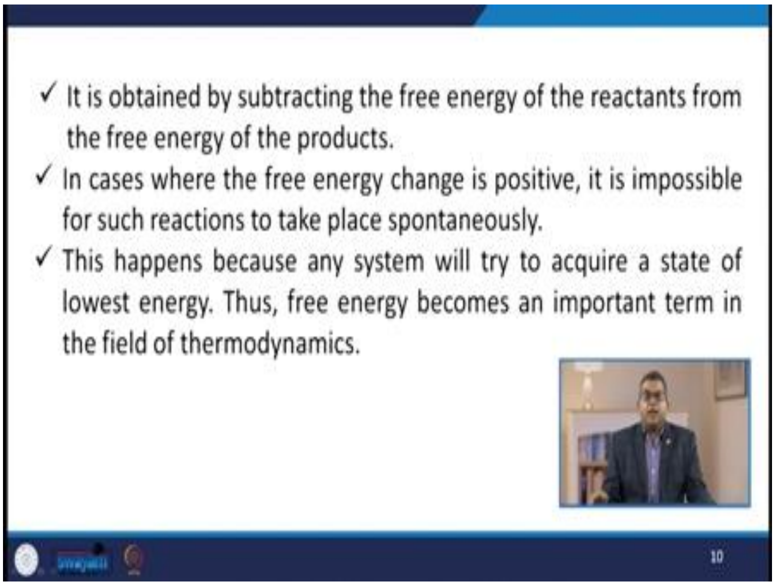


❑ Thermodynamic principles

- ✓ The refractories are meant to be exposed to high temperature, that causes many changes, which are the result of the refractories reaction with the environment.
- ✓ The environment can be in the form of solid, liquid or gas. The reaction take place where the refractories and environment make contact.
- ✓ The thermodynamic principle help in predicting which reaction are impossible based on changes in free energy.

Now let us discuss about the thermodynamic principles. The refractories are mean to be exposed to high temperature and that causes many changes which are the result of the refractories reaction with the environment. The environment can be in the form of solid, liquid or gas the reaction take place where the refractories and environment make contact. The thermodynamic principle helps in predicting which reactions are impossible based on changes in free energy.

(Refer Slide Time: 05:36)

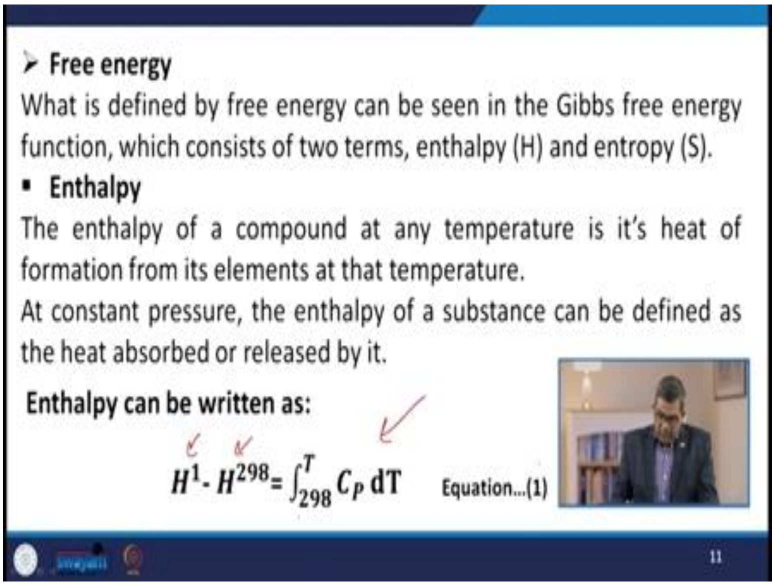


- ✓ It is obtained by subtracting the free energy of the reactants from the free energy of the products.
- ✓ In cases where the free energy change is positive, it is impossible for such reactions to take place spontaneously.
- ✓ This happens because any system will try to acquire a state of lowest energy. Thus, free energy becomes an important term in the field of thermodynamics.

Now it is obtained by subtracting the free energy of the reaction from the free energy of the product. Now in case where the free energy change is positive it is impossible for such reaction to take place spontaneously. Now this happens because any system will try to acquire a state of lowest energy. Therefore the free energy becomes an important term in the field of thermodynamics. Now let us talk about the free energy that what is defined by free energy?

This can be seen in the Gibbs free energy function which consists of 2 terms enthalpy and entropy. Let us have a brief outlook about the enthalpy.

(Refer Slide Time: 06:24)



➢ **Free energy**

What is defined by free energy can be seen in the Gibbs free energy function, which consists of two terms, enthalpy (H) and entropy (S).

- **Enthalpy**

The enthalpy of a compound at any temperature is it's heat of formation from its elements at that temperature.

At constant pressure, the enthalpy of a substance can be defined as the heat absorbed or released by it.

Enthalpy can be written as:

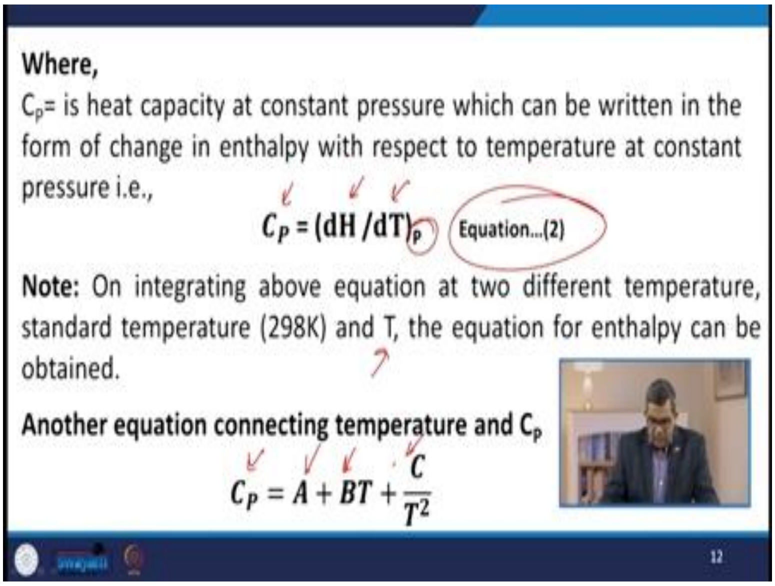
$$H^{1} - H^{298} = \int_{298}^{T} C_P \, dT \quad \text{Equation...(1)}$$

The enthalpy of a compound at any temperature is its heat of formation from its element at that particular temperature. Now at constant pressure the enthalpy of a substance can be defined as the heat absorbed or released by it. Now enthalpy you can write the enthalpy as H^1 is H - H^{298} that is 298 Kelvin temperature is equal to integration 298 to T Cp dT and that is equation number 1.

(Refer Slide Time: 06:59)

Equation for enthalpy

$$H^1 - H^{298} = \int_{298}^{T} C_P \, dT$$



Where,

C_p= is heat capacity at constant pressure which can be written in the form of change in enthalpy with respect to temperature at constant pressure i.e.,

$$C_P = (dH/dT)_p \quad \text{Equation...(2)}$$

Note: On integrating above equation at two different temperature, standard temperature (298K) and T, the equation for enthalpy can be obtained.

Another equation connecting temperature and C_p

$$C_P = A + BT + \frac{C}{T^2}$$

Now C p is the heat capacity at constant pressure which can be written in the form of change in enthalpy with respect to temperature at constant pressure. Now Cp you can represent as a C p = dH over dT at constant pressure that is equation number 2. Now if we integrate this equation at 2 different temperatures say from T1 to T2 or standard temperature 298 Kelvin and T the equation for enthalpy can be obtained. Now another equation connecting the temperature and C p now Cp = A + BT + C over T Square.

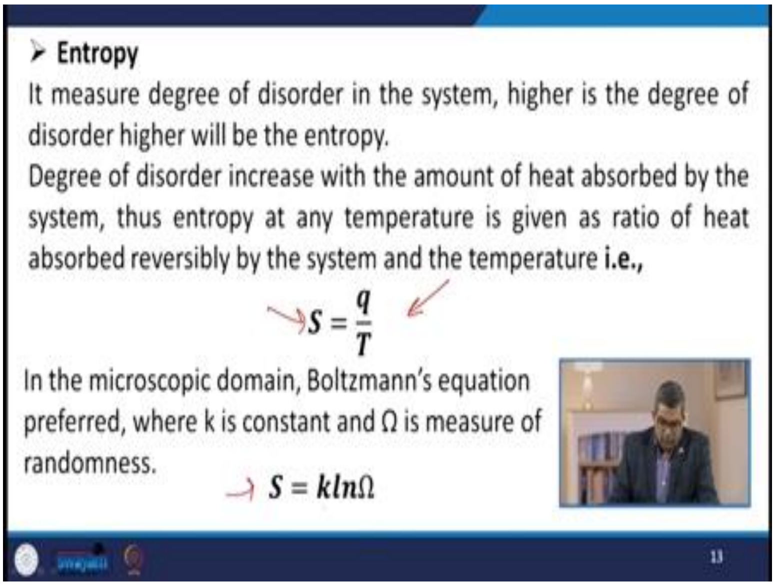
(Refer Slide Time: 07:52)

Heat capacity at constant pressure, can be written as

$$C_P = \left(\frac{dH}{dT}\right)_p$$

Another equation connecting temperature and C_P

$$C_P = A + BT + \frac{C}{T^2}$$



➢ **Entropy**

It measure degree of disorder in the system, higher is the degree of disorder higher will be the entropy.

Degree of disorder increase with the amount of heat absorbed by the system, thus entropy at any temperature is given as ratio of heat absorbed reversibly by the system and the temperature **i.e.,**

$$S = \frac{q}{T}$$

In the microscopic domain, Boltzmann's equation preferred, where k is constant and Ω is measure of randomness.

$$S = kln\Omega$$

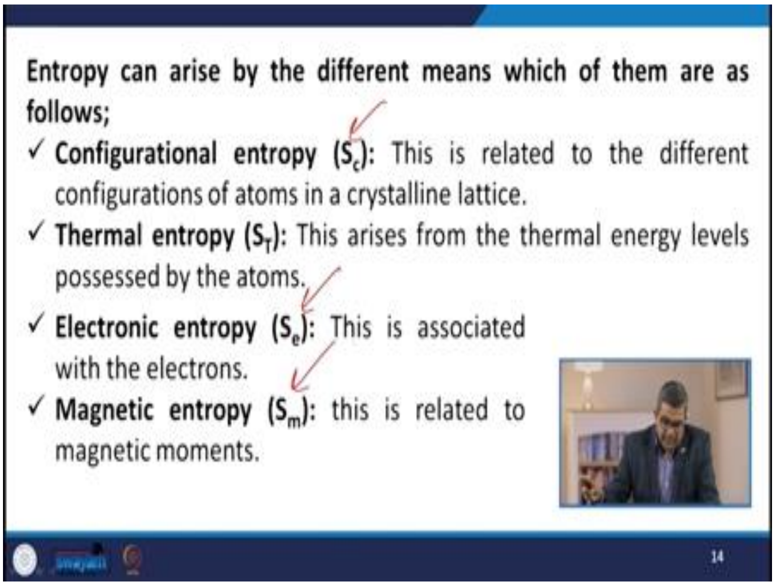
Now A B C, are constants. Entropy it measures the degree of disorder in the system. Higher the degree of disorder higher with the entropy degree of disorder increases with the amount of heat absorbed by the system. Thus entropy at any temperature is given as the ratio of heat absorbed reversibly by the system and the temperature. So in a broad spectrum entropy can be written as or entropy can be represented as S = q over T.

In the microscopic zone the Boltzmann's equation preferred where K is constant and omega is the measure of randomness so it can be represented as S = Kln omega.

(Refer Slide Time: 08:46)

Entropy at any temperature can be written as;

$$S = kln\Omega$$

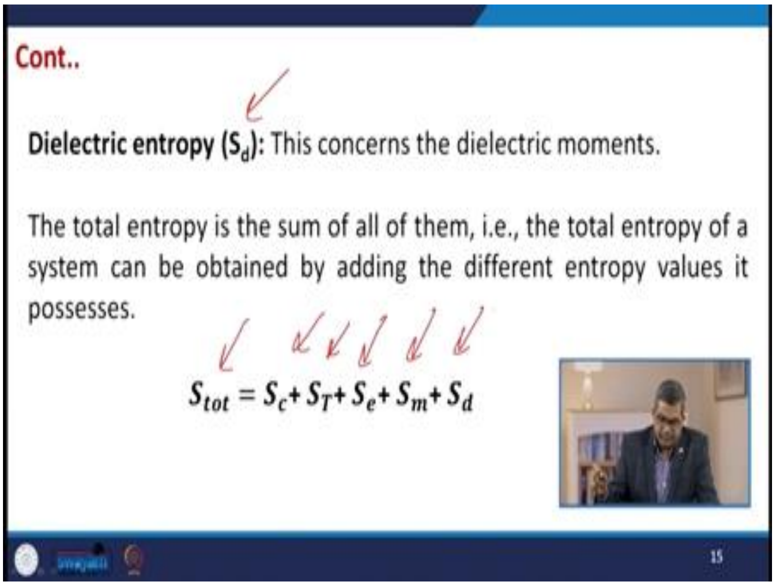


Entropy can arise by the different means which of them are as follows;

- ✓ **Configurational entropy (S_c):** This is related to the different configurations of atoms in a crystalline lattice.
- ✓ **Thermal entropy (S_T):** This arises from the thermal energy levels possessed by the atoms.
- ✓ **Electronic entropy (S_e):** This is associated with the electrons.
- ✓ **Magnetic entropy (S_m):** this is related to magnetic moments.

Now entropy can rise by the different means which of them are follows like configurational entropy and represented as SC. Now this is related to the different configuration of atom in a crystalline lattice. The thermal entropy ST this arises from the thermal energy level possessed by the atom. Then electronic in Tempe entropy and that is represented by a Se this is associated with electrons then the magnetic entropy Sm. This is related to the magnetic moment.

(Refer Slide Time: 09:27)



Cont..

Dielectric entropy (S_d): This concerns the dielectric moments.

The total entropy is the sum of all of them, i.e., the total entropy of a system can be obtained by adding the different entropy values it possesses.

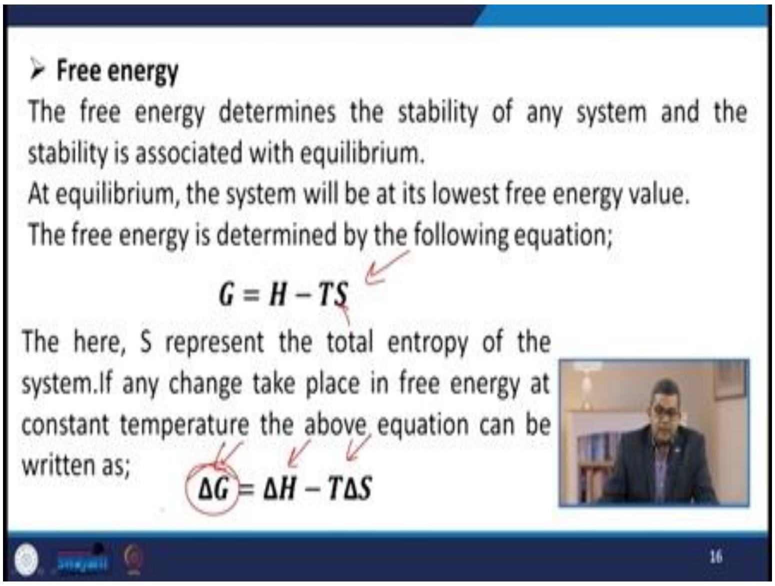
$$S_{tot} = S_c + S_T + S_e + S_m + S_d$$

Then the dielectric entropy Sd this concerns the dielectric moment. The total entropy is the sum of all of them that is a total, entropy of a system can be obtained by addition of different entropies or entropy value it possesses like S total is SC St Se Sm + Sd.

(Refer Slide Time: 09:55)

Total entropy can be written as;

$$S_{total} = S_c + S_T + S_e + S_m + S_d$$



- **Free energy**

The free energy determines the stability of any system and the stability is associated with equilibrium.

At equilibrium, the system will be at its lowest free energy value.

The free energy is determined by the following equation;

$$G = H - TS$$

The here, S represent the total entropy of the system.If any change take place in free energy at constant temperature the above equation can be written as;

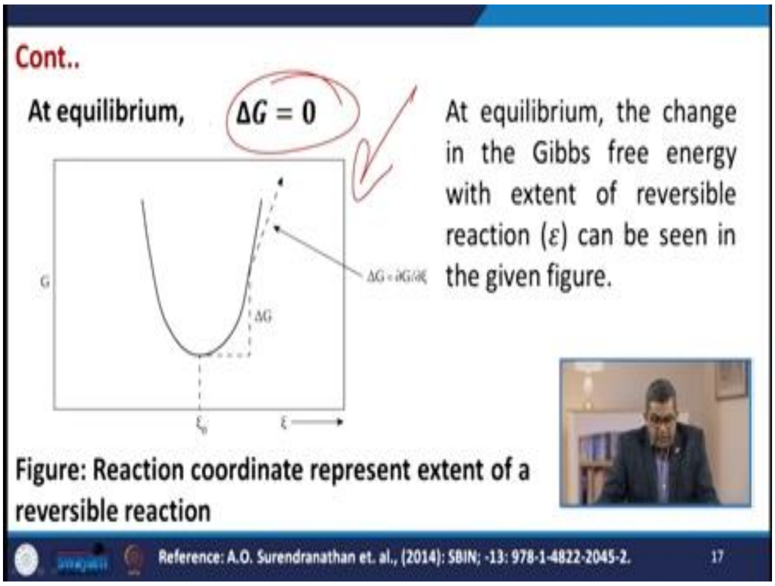
$$\Delta G = \Delta H - T\Delta S$$

Let us talk about free energy. Now the free energy determines the stability of any system and the stability is associated with equilibrium. Now at equilibrium the system will be at its lowest free energy value. The free energy is determined by the equation G =H - TS. Now here the S represents the total entropy of the system now if any changes or any change take place in the free energy at constant temperature this particular equation can be written as delta G = delta H - T delta S.

(Refer Slide Time: 10:38)

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S$$



Cont..

At equilibrium, $\Delta G = 0$

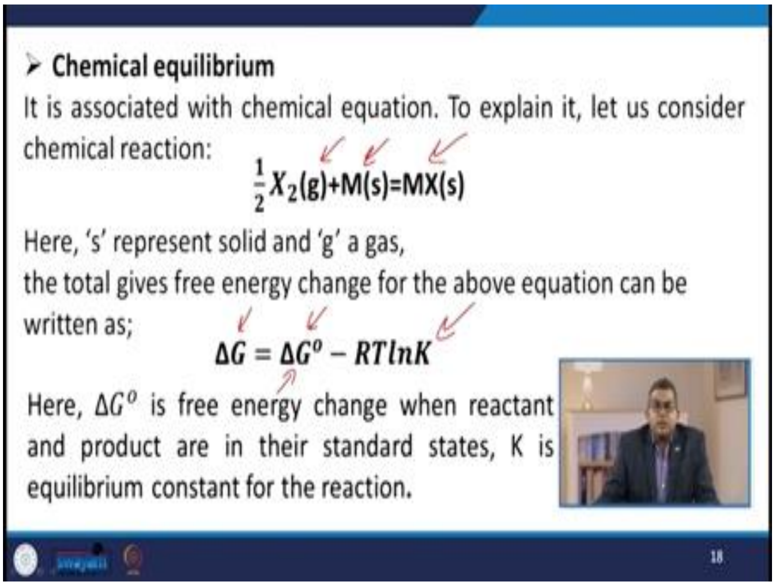
At equilibrium, the change in the Gibbs free energy with extent of reversible reaction (ε) can be seen in the given figure.

Figure: Reaction coordinate represent extent of a reversible reaction

Reference: A.O. Surendranathan et. al., (2014): SBIN; -13: 978-1-4822-2045-2.

So now here at equilibrium the change in the Gibbs free energy and this delta G refers to be the change in Gibbs free energy. So at equilibrium the change in; the Gibbs free energy with the extent of reversible reaction Psi. This can be seen in this particular figure. Now at equilibrium it is quite evident that delta G = 0.

(Refer Slide Time: 11:03)



➢ **Chemical equilibrium**

It is associated with chemical equation. To explain it, let us consider chemical reaction:

$$\frac{1}{2}X_2(g)+M(s)=MX(s)$$

Here, 's' represent solid and 'g' a gas,

the total gives free energy change for the above equation can be written as;

$$\boldsymbol{\Delta G = \Delta G^o - RTlnK}$$

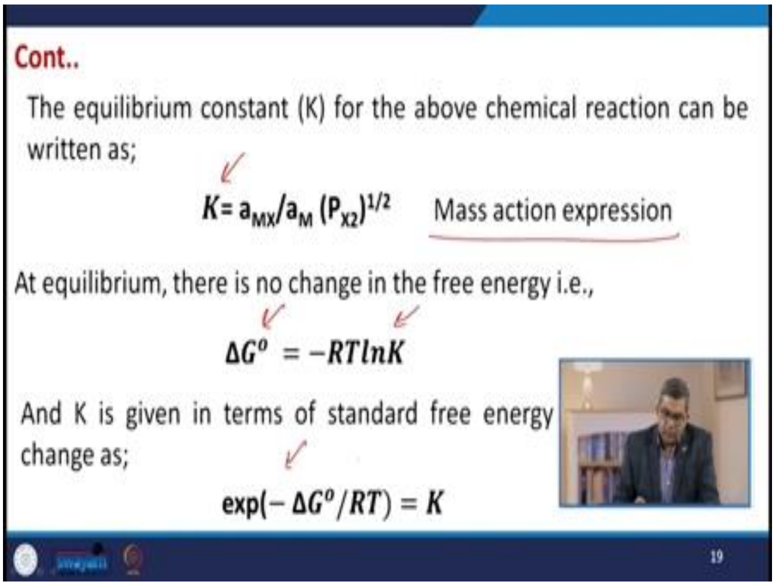
Here, ΔG^o is free energy change when reactant and product are in their standard states, K is equilibrium constant for the reaction.

Let us talk about the chemical equilibrium it is associated with the chemical equation. Now to explain let us consider a chemical reaction. Let us say that half X 2 g that is in the gaseous form +M is in the solid form and it gives you MX in the solid form. Now this total gives free energy change for the above equation. This can be written as delta G that is the change in the Gibbs free energy is equal to delta G naught –RT ln K. Here this delta G naught is the free energy change when reactant and product are in their standard state and K is the equilibrium constant for the reaction.

(Refer Slide Time: 11:56)

Total gives free energy change for above equation can be written as;

$$\boldsymbol{\Delta G = \Delta G^o - RTlnK}$$



Cont..

The equilibrium constant (K) for the above chemical reaction can be written as;

$$K= a_{MX}/a_M\,(P_{X2})^{1/2}$$ Mass action expression

At equilibrium, there is no change in the free energy i.e.,

$$\Delta G^o = -RT\ln K$$

And K is given in terms of standard free energy change as;

$$\exp(-\,\Delta G^o/RT) = K$$

Now the equilibrium constant K from this particular reaction can be written as K = a MX over a M into P x2 to the power half that is the mass action expression. Now at equilibrium as we understand that there is no change in the free energy. And that is delta G naught = -RT ln K and K is given terms is the standard free energy change and it can be expressed as K is equal to exponential of minus delta G naught over RT.

(Refer Slide Time: 12:42)

Equilibrium constant for above chemical reaction can be written as;

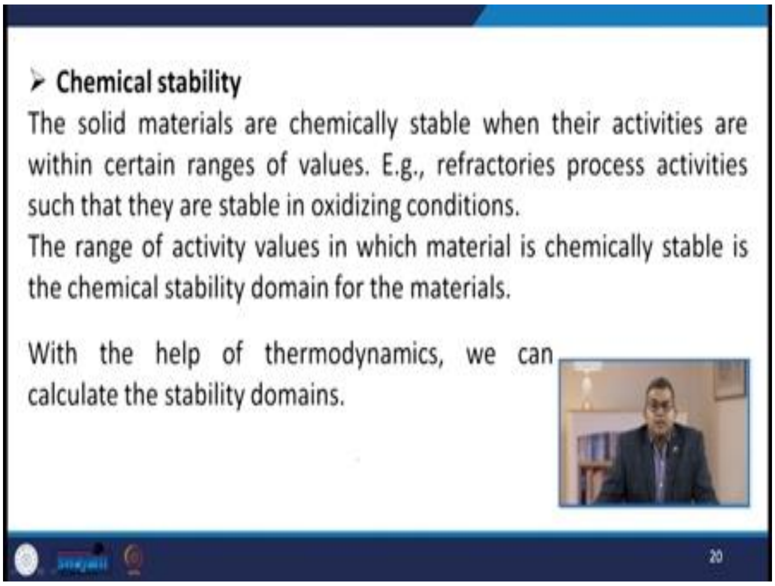
$$K = \frac{a_{MX}}{a_M}\,(P_{X2})^{\frac{1}{2}}$$

Free energy change

$$\Delta G = -RTlnK$$

K in the terms of standard free energy change as

$$\exp(\Delta G^o/RT) = K$$



➢ Chemical stability

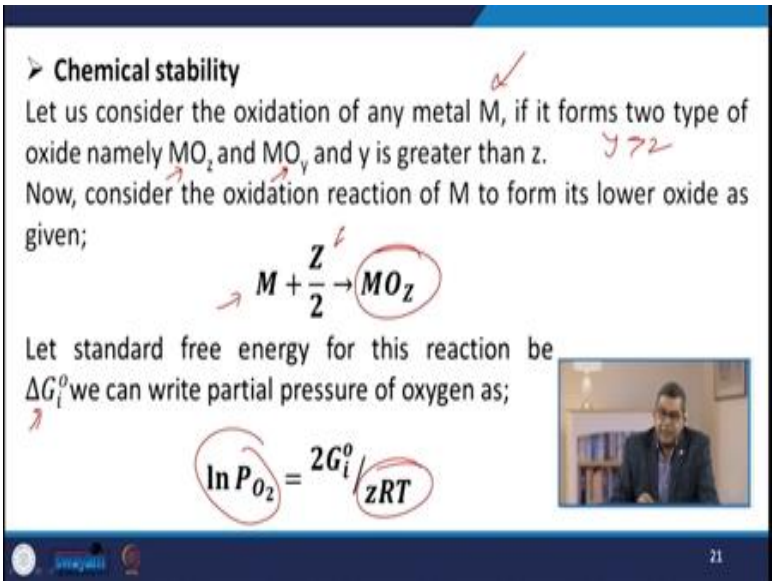
The solid materials are chemically stable when their activities are within certain ranges of values. E.g., refractories process activities such that they are stable in oxidizing conditions.

The range of activity values in which material is chemically stable is the chemical stability domain for the materials.

With the help of thermodynamics, we can calculate the stability domains.

Let us talk about the chemical stability the solid material are, chemically stable when their activities are within certain range of values. That is the refractory is process activities such that they are stable in oxidizing condition. The range of activity values, in which material is chemically stable, is the chemical stability domain for the material. With the help of thermodynamics, we can calculate the stability domains.

(Refer Slide Time: 13:15)



➢ Chemical stability

Let us consider the oxidation of any metal M, if it forms two type of oxide namely MO_z and MO_y and y is greater than z. $y > z$

Now, consider the oxidation reaction of M to form its lower oxide as given;

$$M + \frac{Z}{2} \rightarrow MO_Z$$

Let standard free energy for this reaction be ΔG_i^o we can write partial pressure of oxygen as;

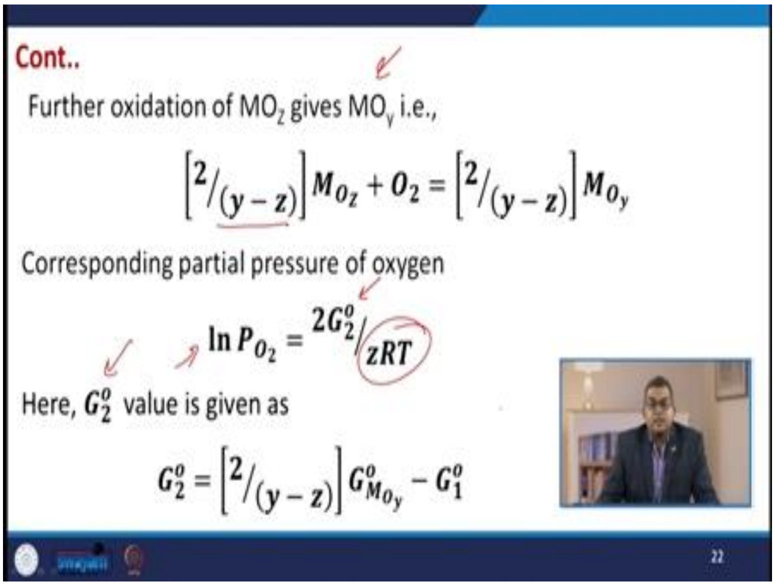
$$\ln P_{O_2} = 2G_i^o / zRT$$

Now let us consider the oxidation of any metal M. Now if it forms 2 types of oxides like MO z and MO y and y is greater than z. Now consider the oxidation reaction of M to form its lower oxide and that is M + Z by 2 = MO z. Now let the standard free energy for this particular reaction be delta Gi naught. So we can write the partial pressure of oxygen as ln Po naught = 2 Gi naught over z RT.

(Refer Slide Time: 14:02)

Let standard free energy for this reaction be ΔG_i^o we can write partial pressure of oxygen as;

$$\ln P_{O_2} = {}^{2G_i^o}/_{zRT}$$



Cont..

Further oxidation of MO_Z gives MO_y i.e.,

$$\left[{}^{2}/_{(y-z)}\right] M_{O_Z} + O_2 = \left[{}^{2}/_{(y-z)}\right] M_{O_y}$$

Corresponding partial pressure of oxygen

$$\ln P_{O_2} = {}^{2G_2^o}/_{zRT}$$

Here, G_2^o value is given as

$$G_2^o = \left[{}^{2}/_{(y-z)}\right] G^o_{M_{O_y}} - G_1^o$$

Now further oxidation of MO z gives MO y and that is 2 over y - Z into MO z + O2 = 2 over y - z Mo y. Now corresponding partial pressure of oxygen can be represented as ln Po2 = 2G naught 2g 2 naught over z RT. Now here G2 naught value is given as G 2 naught = 2 over y - z G naught GMO y naught – G 1 naught. This G naught represents the standard condition.

(Refer Slide Time: 14:46)

Further oxidation of MO_Z gives MO_y i.e.,

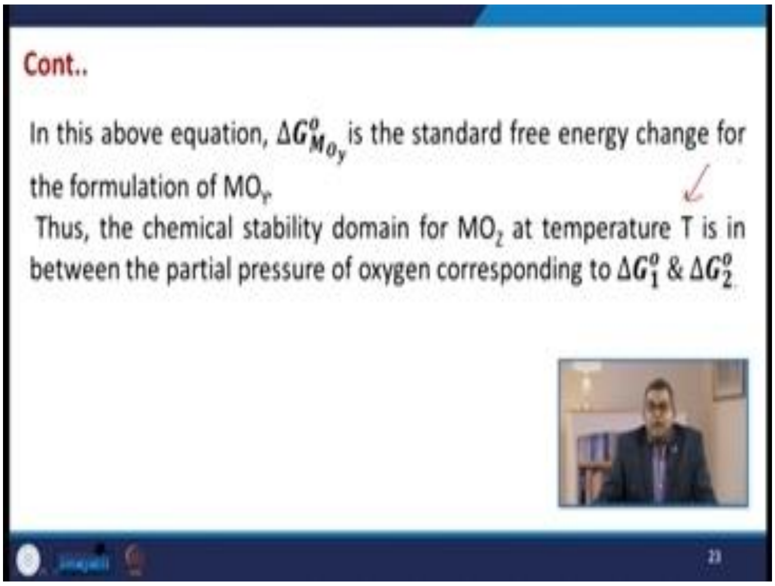
$$\left[{}^{2}/_{(y-z)}\right] M_{O_Z} + O_2 = \left[{}^{2}/_{(y-z)}\right] M_{O_y}$$

Corresponding partial pressure of oxygen

$$\ln P_{O_2} = {}^{2G_2^o}/_{zRT}$$

Here, G_2^o value is given as

$$G_2^o = \left[{}^{2}/_{(y-z)}\right] G^o_{M_{O_y}} - G_1^o$$



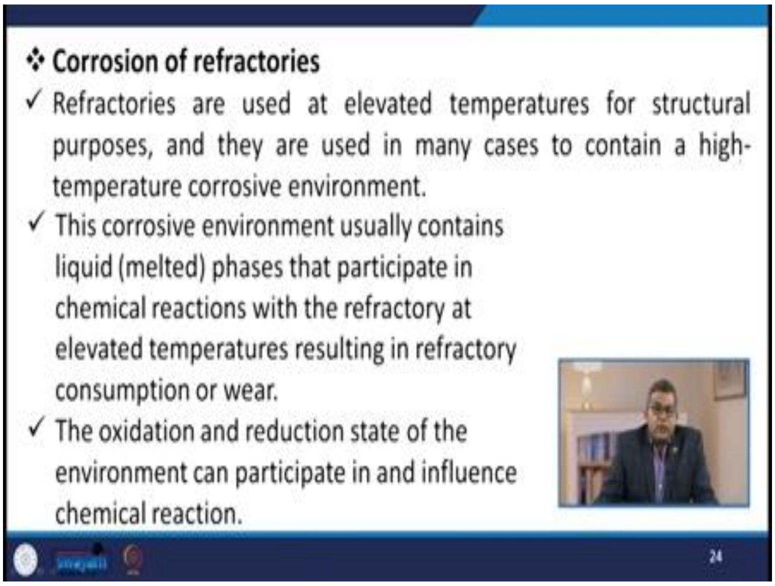
Cont..

In this above equation, $\Delta G^o_{MO_y}$ is the standard free energy change for the formulation of MO_y.

Thus, the chemical stability domain for MO_2 at temperature T is in between the partial pressure of oxygen corresponding to ΔG^o_1 & ΔG^o_2

Now in this equation delta GM oy naught is the standard free energy change for the formulation of MO y. Thus the chemical stability domain for a MO 2 at temperature T is in between the partial pressure of oxygen corresponding to delta G 1 naught and delta G 2 naught.

(Refer Slide Time: 15:15)



❖ Corrosion of refractories

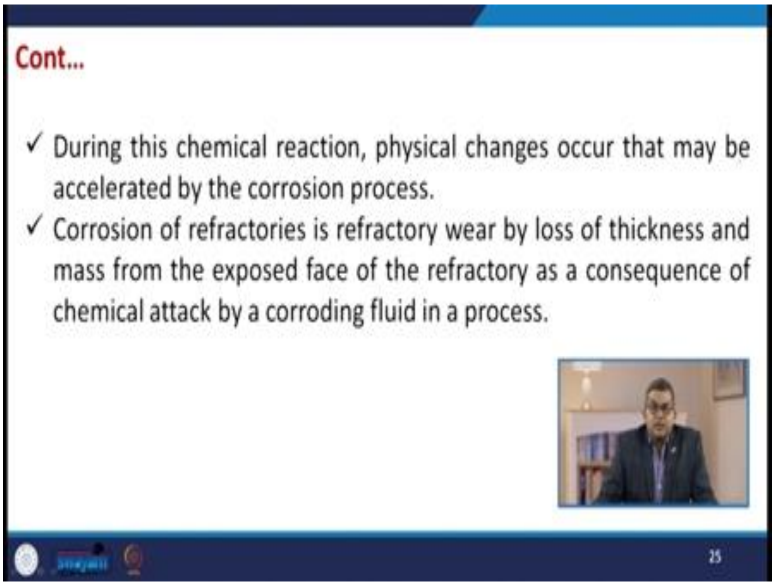
✓ Refractories are used at elevated temperatures for structural purposes, and they are used in many cases to contain a high-temperature corrosive environment.

✓ This corrosive environment usually contains liquid (melted) phases that participate in chemical reactions with the refractory at elevated temperatures resulting in refractory consumption or wear.

✓ The oxidation and reduction state of the environment can participate in and influence chemical reaction.

Now let us talk about the corrosion of refractories. Now refractories are used at elevated temperatures for structural purpose and they are used in many cases to contain a high temperature corrosive environment. Now this corrosive environment usually contains liquid that is in the melted phase and that participate in a chemical reaction with the refractory at elevated temperatures resulting in refractory consumption or wear. The oxidation and reduction state of environment can participate in and influence chemical reaction.

(Refer Slide Time: 15:54)



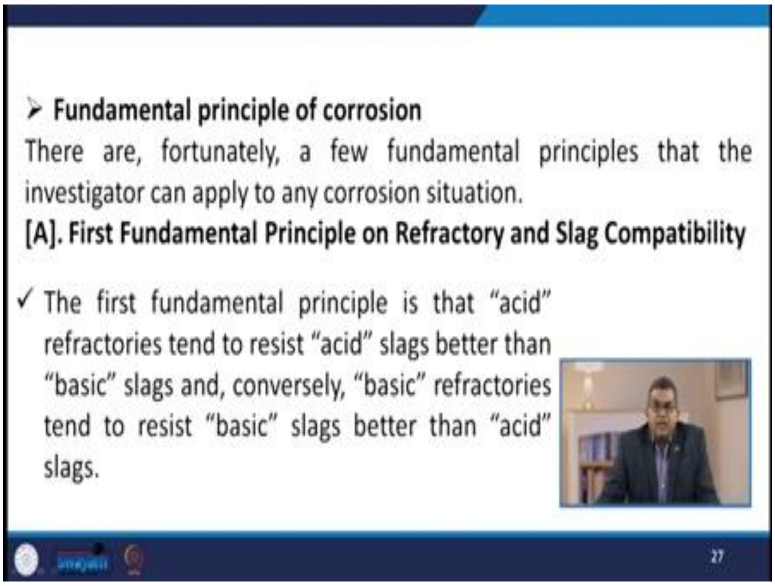
Cont...

- ✓ During this chemical reaction, physical changes occur that may be accelerated by the corrosion process.
- ✓ Corrosion of refractories is refractory wear by loss of thickness and mass from the exposed face of the refractory as a consequence of chemical attack by a corroding fluid in a process.

During this particular chemical reaction the physical changes occur that may be accelerated by the corrosion process. Corrosion of refractories is the refractory wear by loss of thickness and mass from the exposed face of the refractory as a consequence of chemical attack by corroding fluid in a process. And this particular the refractory and corroding fluid react together and approaching the chemical equilibrium in the zone of contact between the refractory and the fluid.

The phase equilibrium diagram this can be used to analyze the corrosion situation and to predict the chemical strategies to minimize the corrosion and wear rates. Now while we are discussing the corrosion then the let us talk about briefly the fundamental principle of corrosion. Now there are fortunately a few fundamental principles that the investigator can apply to any corrosion situation.

(Refer Slide Time: 17:04)



➢ **Fundamental principle of corrosion**

There are, fortunately, a few fundamental principles that the investigator can apply to any corrosion situation.

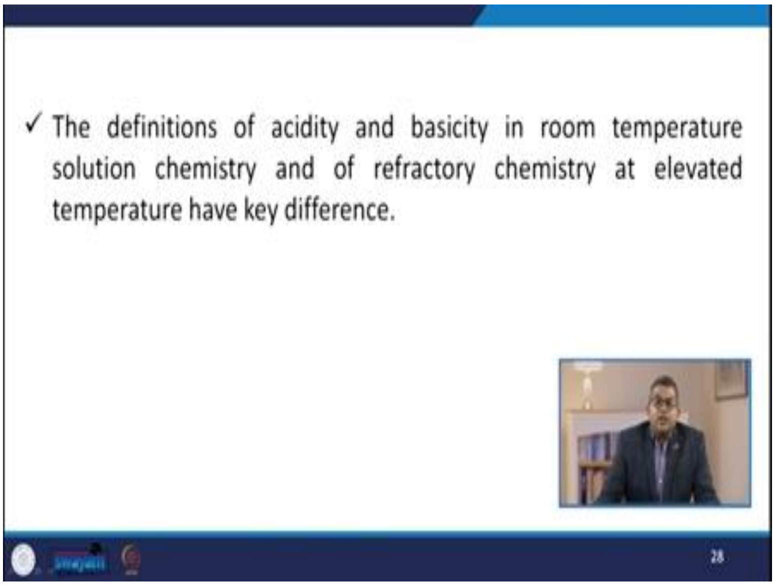
[A]. First Fundamental Principle on Refractory and Slag Compatibility

✓ The first fundamental principle is that "acid" refractories tend to resist "acid" slags better than "basic" slags and, conversely, "basic" refractories tend to resist "basic" slags better than "acid" slags.

27

Now first fundamental principle on refractory and slag compatibility. The first fundamental principle is that acid refractories tend to resist acid slag better than the basic slag and conversely the basic refractories is tend to resist the basic slag better than acid slags.

(Refer Slide Time: 17:19)

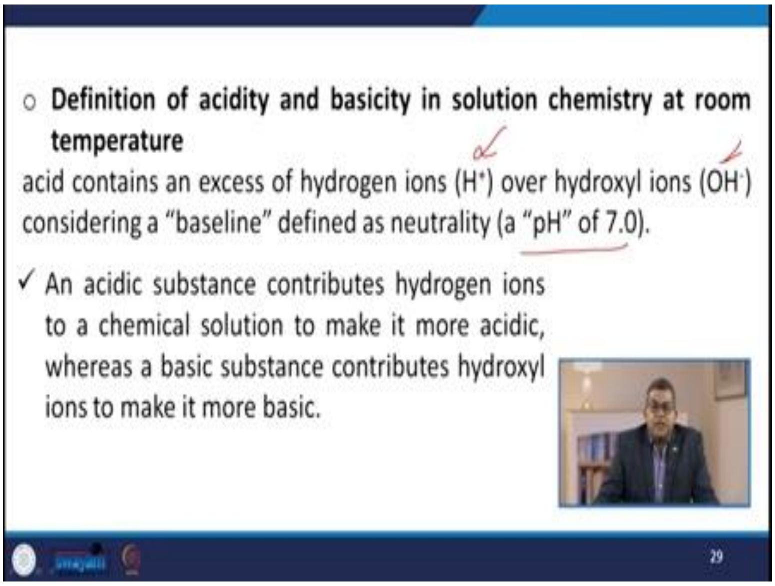


✓ The definitions of acidity and basicity in room temperature solution chemistry and of refractory chemistry at elevated temperature have key difference.

28

The definition of acidity and basicity in room temperature solution; of any kind of refractory chemistry at elevated temperature have the key difference.

(Refer Slide Time: 17:31)



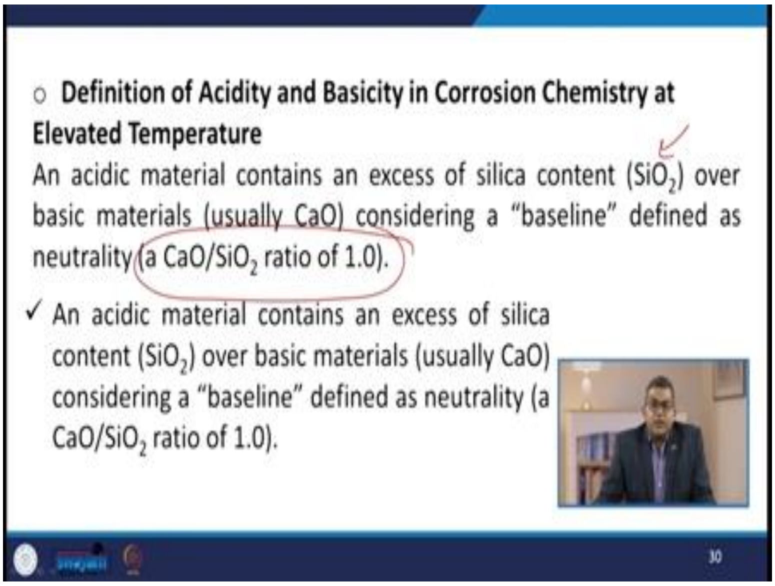
- Definition of acidity and basicity in solution chemistry at room temperature

acid contains an excess of hydrogen ions (H^+) over hydroxyl ions (OH^-) considering a "baseline" defined as neutrality (a "pH" of 7.0).

✓ An acidic substance contributes hydrogen ions to a chemical solution to make it more acidic, whereas a basic substance contributes hydroxyl ions to make it more basic.

Now the definition of acidity and basicity in solution chemistry at room temperature, now acid contains an excess of hydrogen ions H+ over hydroxyl ions OH minus considering that baseline defined as neutrality at Ph of 7. Now an acidic substance contributes hydrogen ions to chemical solution to make it more acidic whereas a basic substance contributes hydroxyl ion to make it more basic.

(Refer Slide Time: 18:06)



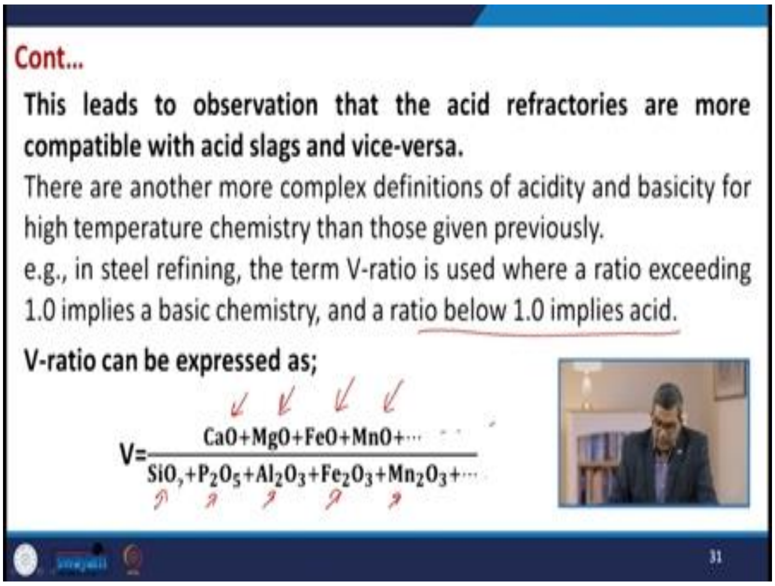
- Definition of Acidity and Basicity in Corrosion Chemistry at Elevated Temperature

An acidic material contains an excess of silica content (SiO_2) over basic materials (usually CaO) considering a "baseline" defined as neutrality (a CaO/SiO_2 ratio of 1.0).

✓ An acidic material contains an excess of silica content (SiO_2) over basic materials (usually CaO) considering a "baseline" defined as neutrality (a CaO/SiO_2 ratio of 1.0).

Now an acidic material contains an excess of silica contain SiO 2 over basic material; usually in this case calcium oxide considering a baseline defined as the neutrality at CaO over SiO 2 ratio of 1. Now an acidic material contains an excess of silica content SiO 2 over basic material usually in this case is CaO considering a baseline defined as neutrality at the CaO over SiO 2 ratio of 1.

(Refer Slide Time: 18:44)



Cont...

This leads to observation that the acid refractories are more compatible with acid slags and vice-versa.

There are another more complex definitions of acidity and basicity for high temperature chemistry than those given previously.

e.g., in steel refining, the term V-ratio is used where a ratio exceeding 1.0 implies a basic chemistry, and a ratio below 1.0 implies acid.

V-ratio can be expressed as;

$$V=\frac{CaO+MgO+FeO+MnO+\cdots}{SiO_2+P_2O_5+Al_2O_3+Fe_2O_3+Mn_2O_3+\cdots}$$

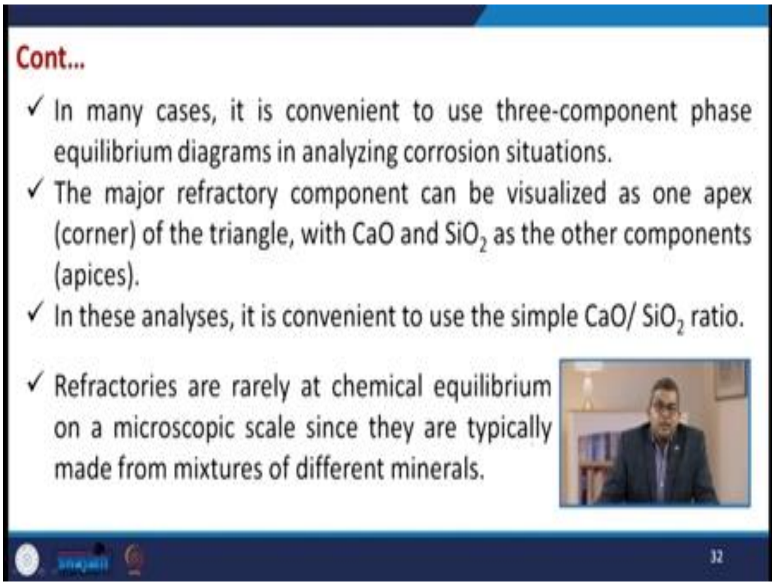
This led to the observation that the acid refractories are more compatible with acid slag or vice versa. Now, there are another more complex definition of acidity and basicity for high-temperature chemistry than those given previously like in steel refining. The term V ratio is used where a ratio exceeding1.0 implies a basic chemistry and the ratio of below 1.0 implies acid.

Now this V ratio question arises that how we can define the V ratio or how we can express the real V ratio. So, the V ratio is expressed as V = CaO + MgO + FeO + MnO + and so on over SiO 2 + P_2O_5 + Al_2O_3 + Fe_2O_3 + Mn_2O_3 + and so on.

(Refer Slide Time: 19:41)

V-ratio can be expressed as;

$$V=\frac{CaO+MgO+FeO+MnO+\cdots}{SiO_2+P_2O_5+Al_2O_3+Fe_2O_3+Mn_2O_3+\cdots}$$



Cont…

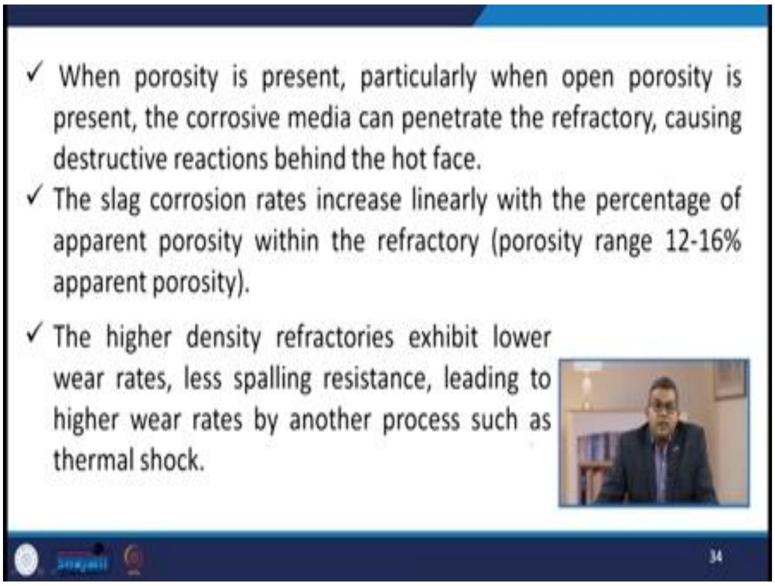
- ✓ In many cases, it is convenient to use three-component phase equilibrium diagrams in analyzing corrosion situations.
- ✓ The major refractory component can be visualized as one apex (corner) of the triangle, with CaO and SiO_2 as the other components (apices).
- ✓ In these analyses, it is convenient to use the simple CaO/ SiO_2 ratio.
- ✓ Refractories are rarely at chemical equilibrium on a microscopic scale since they are typically made from mixtures of different minerals.

In many cases it is convenient to use the 3 component phase equilibrium diagram in analysis of corrosion situation. The major refractory component can be visualized as one apex of the triangle with CaO and SiO_2 as the other component. Now in this analysis it is convenient to use the simple CaO over SiO_2 ratio. The refractories are rarely in chemical equilibrium on microscopic scale since they are typically made from a mixture of different minerals.

Now second fundamental principle on the porosity and corrosion rates most refractories contain void spaces or porosity. This may be open pores that can be penetrated by a fluid media that is apparent porosity or it may be closed porosity that is not easily penetrated by fluid media if a refractory contained no porosity or brick joints or expansion joints or construction joints. The corrosion reaction is limited only to the phase exposed, to the corrosive media that is called the hot face.

Now when porosity is present particularly when open porosity is there that corrosive material or corrosive media can penetrate the refractory causing the destructive reaction behind the hot face. The slag corrosion rates increase linearly with the percentage of apparent porosity within the refractory and that is a porosity range from 12 to 16% apparent porosity.

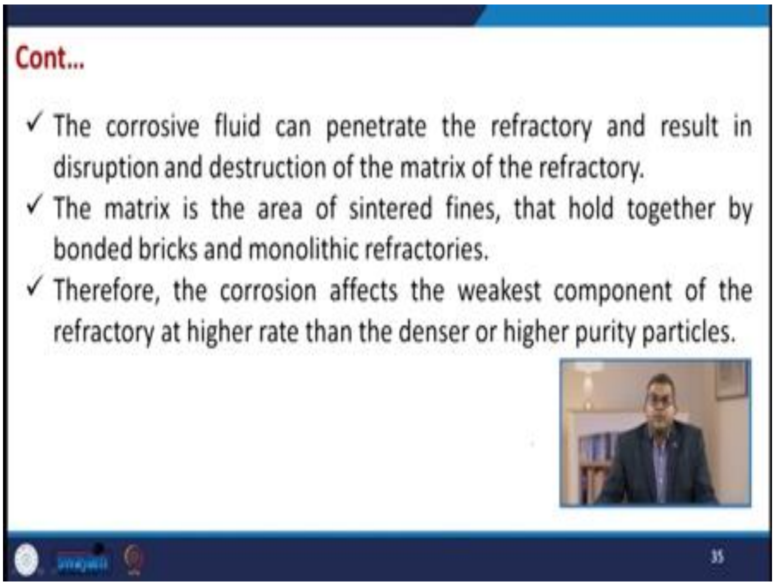
(Refer Slide Time: 21:25)



- ✓ When porosity is present, particularly when open porosity is present, the corrosive media can penetrate the refractory, causing destructive reactions behind the hot face.
- ✓ The slag corrosion rates increase linearly with the percentage of apparent porosity within the refractory (porosity range 12-16% apparent porosity).
- ✓ The higher density refractories exhibit lower wear rates, less spalling resistance, leading to higher wear rates by another process such as thermal shock.

The higher density refractories exhibits lower wear rates and less spalling resistance leading to higher wear rates by another process such as thermal shock

(Refer Slide Time: 21:32)

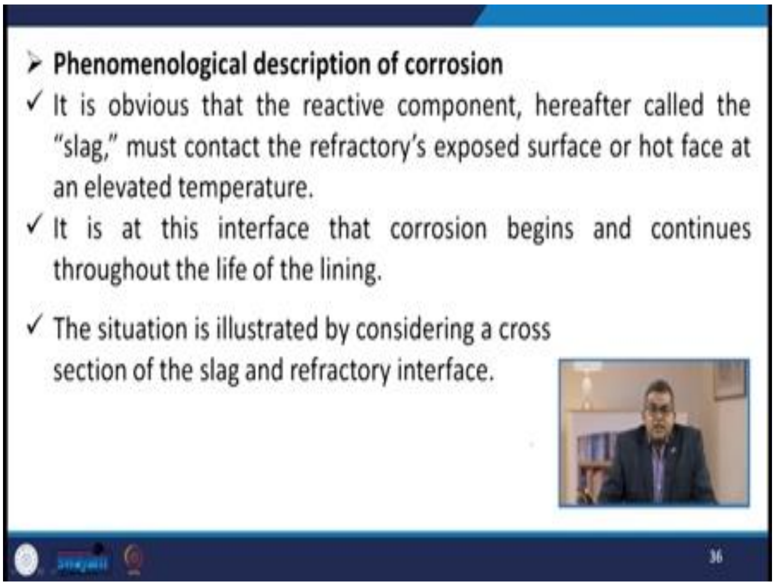


Cont...

- ✓ The corrosive fluid can penetrate the refractory and result in disruption and destruction of the matrix of the refractory.
- ✓ The matrix is the area of sintered fines, that hold together by bonded bricks and monolithic refractories.
- ✓ Therefore, the corrosion affects the weakest component of the refractory at higher rate than the denser or higher purity particles.

Now the corrosive fluid can penetrate the refractory and result in the disruption and destruction of matrix of the refractor. Now the matrix is the area of sintered fines that hold together by a bonded bricks and monolithic refractories. Therefore the corrosion affects the weakest component of the reflected higher rate than the denser or higher purity particles.

(Refer Slide Time: 22:01)

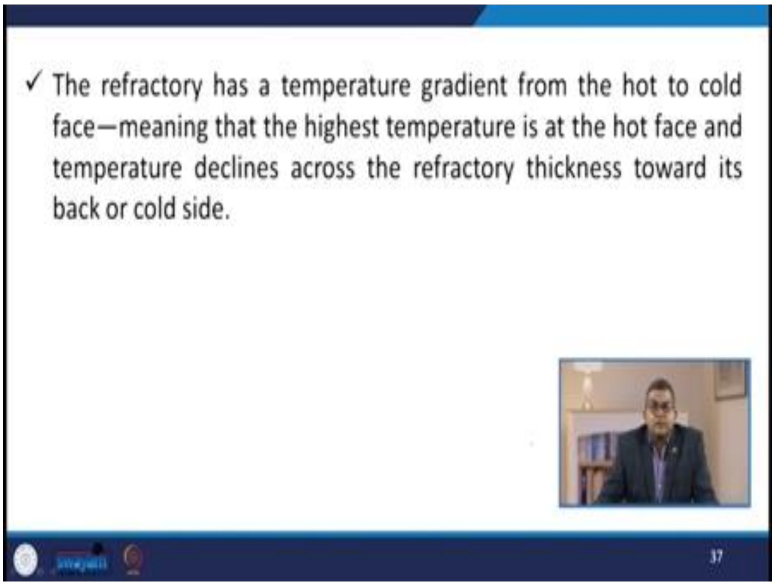


➢ **Phenomenological description of corrosion**

- ✓ It is obvious that the reactive component, hereafter called the "slag," must contact the refractory's exposed surface or hot face at an elevated temperature.
- ✓ It is at this interface that corrosion begins and continues throughout the life of the lining.
- ✓ The situation is illustrated by considering a cross section of the slag and refractory interface.

Detailed description of corrosion now it is obvious that the reactive component thereafter called the slag that must contain the refectory exposed to surface or hot face at an elevated temperature. Now it is at this interface that corrosion begins and continues throughout the life of the lining.

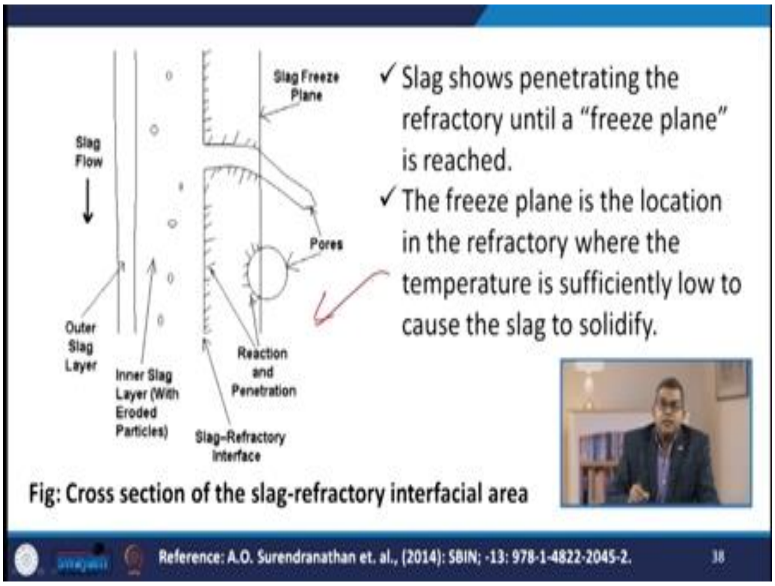
(Refer Slide Time: 22:30)



- ✓ The refractory has a temperature gradient from the hot to cold face—meaning that the highest temperature is at the hot face and temperature declines across the refractory thickness toward its back or cold side.

Now the situation we can understand by considering a cross-section of slag and refractory interface. Now the refractory has a temperature gradient from the hot to cold face. Meaning that the highest temperature is at the hot face and the temperature declines across the refractory thickness towards it back or cold side.

(Refer Slide Time: 22:55)



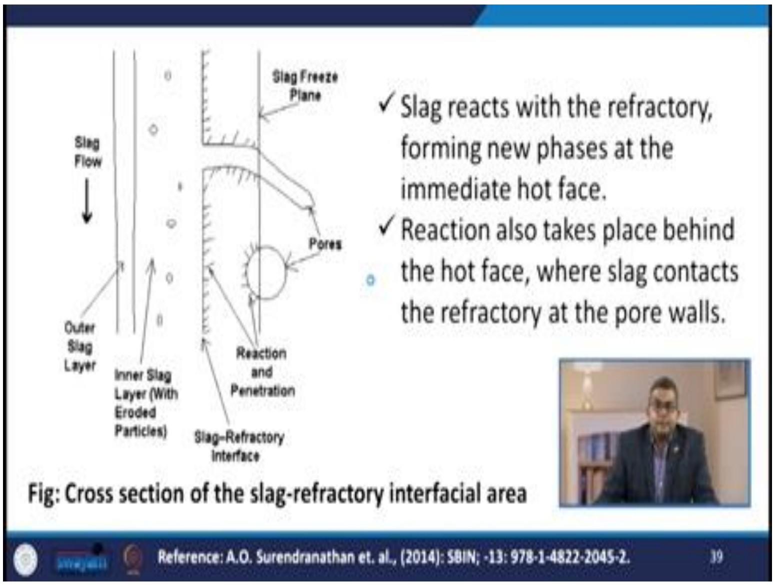
- ✓ Slag shows penetrating the refractory until a "freeze plane" is reached.
- ✓ The freeze plane is the location in the refractory where the temperature is sufficiently low to cause the slag to solidify.

Fig: Cross section of the slag-refractory interfacial area

Reference: A.O. Surendranathan et. al., (2014): SBIN; -13: 978-1-4822-2045-2.

Now here you see the cross section of slag refractory, interfacial area. Now the slag shows penetrating refectory until the freeze plane is achieved. Now the freeze plane is the location in the refractory where the temperature is sufficiently low to cause the slag to solidify.

(Refer Slide Time: 23:11)



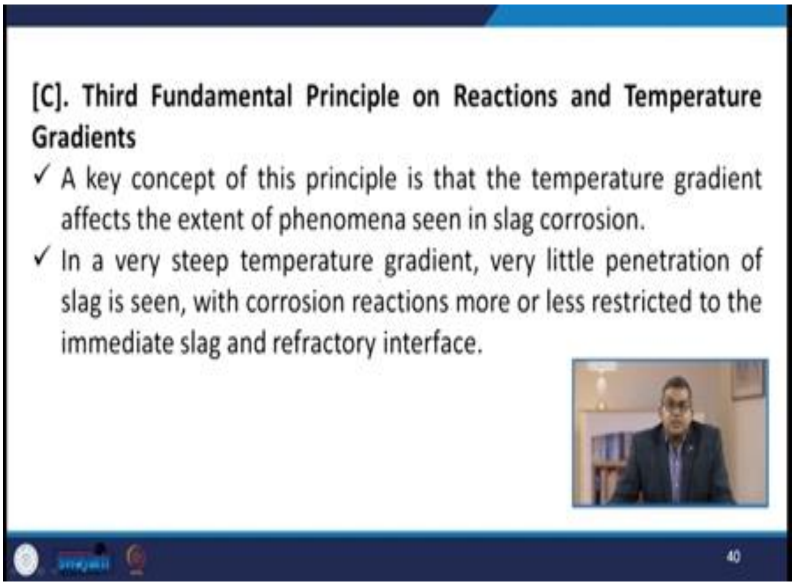
- ✓ Slag reacts with the refractory, forming new phases at the immediate hot face.
- ✓ Reaction also takes place behind the hot face, where slag contacts the refractory at the pore walls.

Fig: Cross section of the slag-refractory interfacial area

Reference: A.O. Surendranathan et. al., (2014): SBIN; -13: 978-1-4822-2045-2.

Now slag reacts with the refractory forming new faces at the immediate hot face. Now reactions may also take place behind the hot face where the slag contacts are the refractory at the pore walls.

(Refer Slide Time: 23:26)

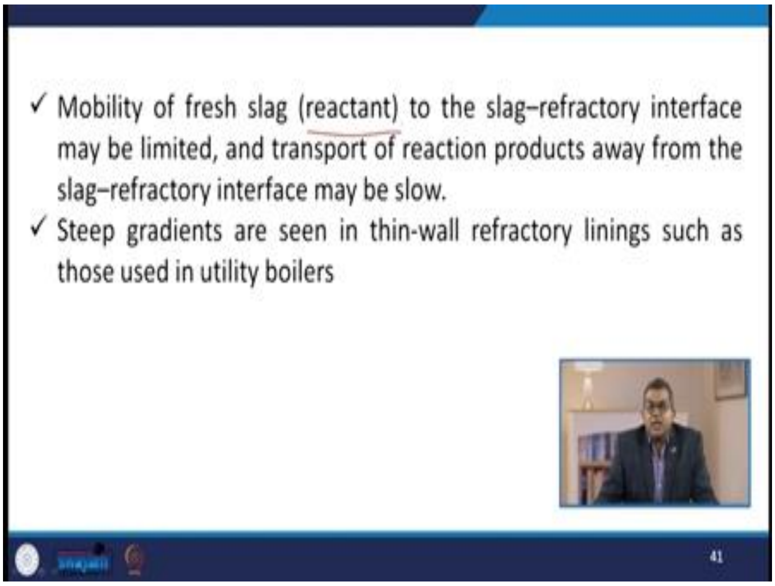


[C]. Third Fundamental Principle on Reactions and Temperature Gradients

- ✓ A key concept of this principle is that the temperature gradient affects the extent of phenomena seen in slag corrosion.
- ✓ In a very steep temperature gradient, very little penetration of slag is seen, with corrosion reactions more or less restricted to the immediate slag and refractory interface.

Now the third fundamental principle of reaction and temperature gradients a key concept of this particular principle is that the temperature gradient affects the extent of phenomena seen in the slag corrosion. Now in a very steep temperature gradient a very little penetration of slag is seen with corrosion reaction more or less restricted to the immediate slag and refractory interface.

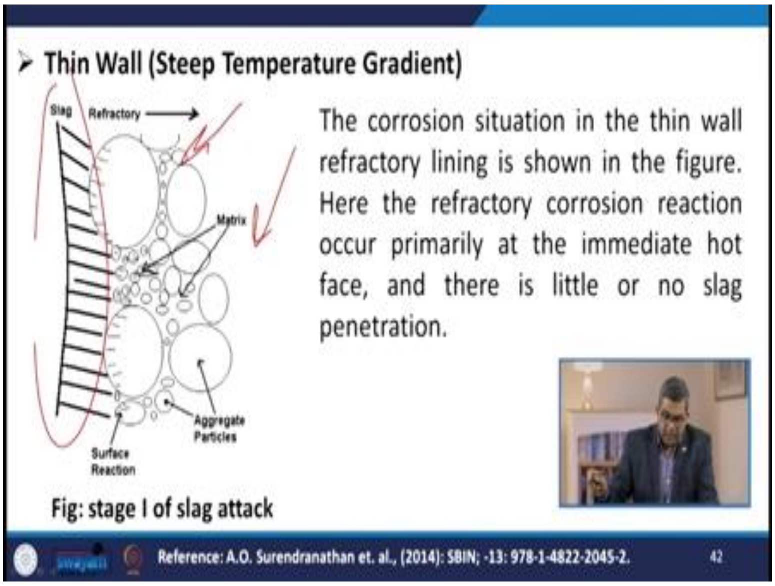
(Refer Slide Time: 23:59)



- ✓ Mobility of fresh slag (reactant) to the slag–refractory interface may be limited, and transport of reaction products away from the slag–refractory interface may be slow.
- ✓ Steep gradients are seen in thin-wall refractory linings such as those used in utility boilers

The mobility of fresh slag sometimes referred as a reactant to the slag refractory interface, may be limited and transport of a reaction products away from the slag refectory interface that may be slow. The steep gradients can be seen in the thin-walled refractory lining such as those used in the utility boilers.

(Refer Slide Time: 24:17)



- Thin Wall (Steep Temperature Gradient)

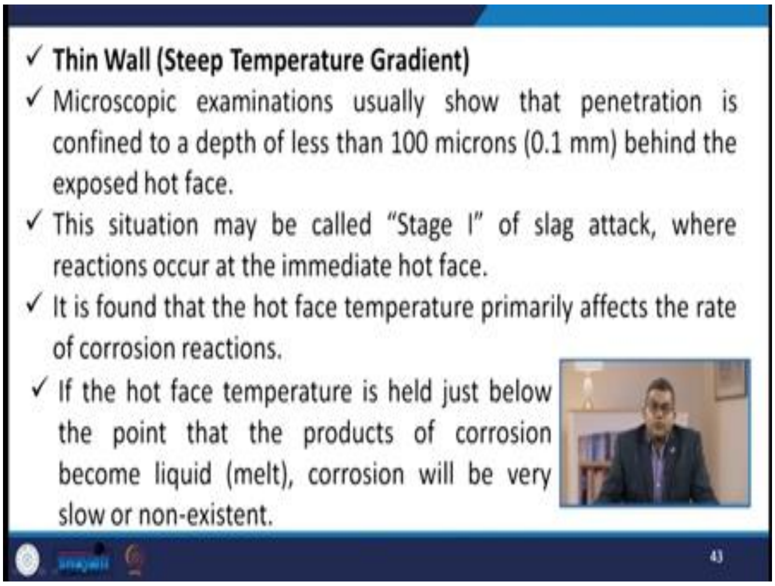
The corrosion situation in the thin wall refractory lining is shown in the figure. Here the refractory corrosion reaction occur primarily at the immediate hot face, and there is little or no slag penetration.

Fig: stage I of slag attack

Reference: A.O. Surendranathan et. al., (2014): SBIN; -13: 978-1-4822-2045-2.

Now here you see that thin wall or steep temperature gradient. The corrosion situation in the thin wall refractory lining this is particularly shown in this particular figure. Now here the refractory corrosion reaction; each occur primarily at the intermediate hot face and then there is a little or no slag penetration. Here you see that this is the slag zone and you see that particular phenomena in this particular figure.

(Refer Slide Time: 24:44)

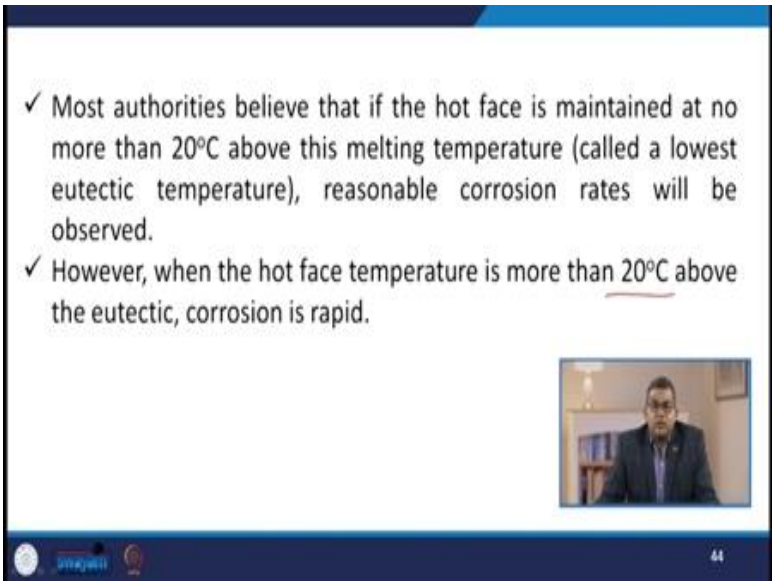


- ✓ Thin Wall (Steep Temperature Gradient)
- ✓ Microscopic examinations usually show that penetration is confined to a depth of less than 100 microns (0.1 mm) behind the exposed hot face.
- ✓ This situation may be called "Stage I" of slag attack, where reactions occur at the immediate hot face.
- ✓ It is found that the hot face temperature primarily affects the rate of corrosion reactions.
- ✓ If the hot face temperature is held just below the point that the products of corrosion become liquid (melt), corrosion will be very slow or non-existent.

Now microscopic examination usually shows that the penetration is confined to a depth of less than 100 microns or 0.1mm behind the exposed hot surface. Now this situation may be called as a stage 1 or it slag attack where the reaction, occur at the intermediate hot face. Now it is found that the hot face temperature primarily affect the rate of corrosion reaction. Now if; hot face temperature is held just below the point that the product of corrosion becomes liquid corrosion will be very slow or non-existent.

So most of the authority they believe that if the hot face is maintained at not more than say 20 degrees Celsius above this melting temperature that is called the lowest eutectic temperature, reasonable corrosion rates will be observed.

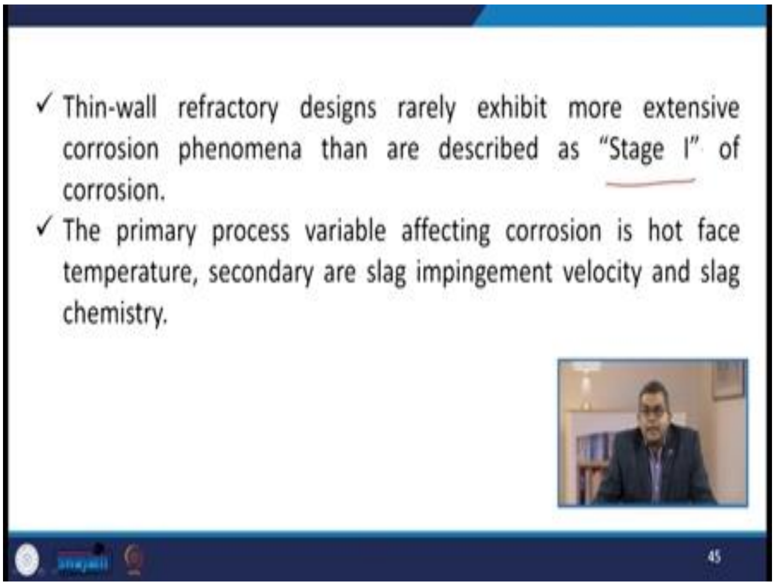
(Refer Slide Time: 25:44)



- ✓ Most authorities believe that if the hot face is maintained at no more than 20°C above this melting temperature (called a lowest eutectic temperature), reasonable corrosion rates will be observed.
- ✓ However, when the hot face temperature is more than 20°C above the eutectic, corrosion is rapid.

However when the hot face temperature is more than say to 20 degree Celsius above the eutectic temperature, then corrosion is rapid.

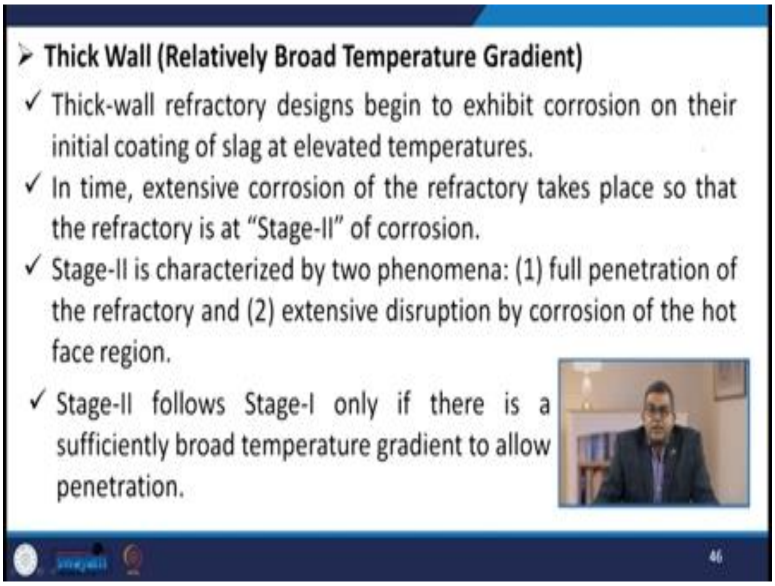
(Refer Slide Time: 25:50)



- ✓ Thin-wall refractory designs rarely exhibit more extensive corrosion phenomena than are described as "Stage I" of corrosion.
- ✓ The primary process variable affecting corrosion is hot face temperature, secondary are slag impingement velocity and slag chemistry.

Now thin wall refractory design rarely this exhibits more extensive corrosion phenomena then they described as a stage one of the corrosion. The primary process variable affecting corrosion is hot face temperature. Secondly are; the slag impingement to velocity and slag chemistry.

(Refer Slide Time: 26:10)



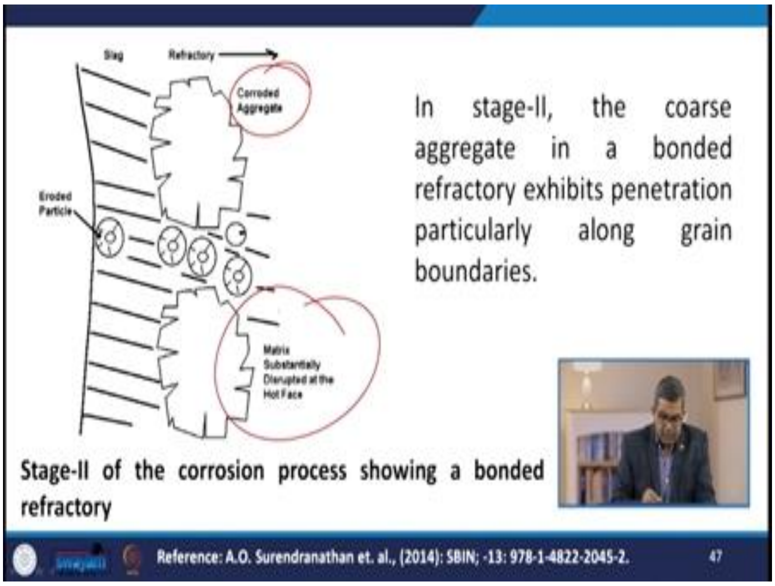
➢ **Thick Wall (Relatively Broad Temperature Gradient)**

- ✓ Thick-wall refractory designs begin to exhibit corrosion on their initial coating of slag at elevated temperatures.
- ✓ In time, extensive corrosion of the refractory takes place so that the refractory is at "Stage-II" of corrosion.
- ✓ Stage-II is characterized by two phenomena: (1) full penetration of the refractory and (2) extensive disruption by corrosion of the hot face region.
- ✓ Stage-II follows Stage-I only if there is a sufficiently broad temperature gradient to allow penetration.

Now let us talk about the thick wall. That is relatively broad temperature gradient. Now, thick-wall refractory, design begins to exhibit corrosion on their initial coating of slag at elevated temperature. In time extensive corrosion of the refractory takes place so that the refractory at stage 2 of corrosion. Now stage 2 is the characterized by 2 phenomena. One is the full penetration of the refractory and second is the extensive disruption by corrosion of the hot face region.

Now stage 2 follows is stage one only if there is a sufficiently broad temperature gradient to allow penetration.

(Refer Slide Time: 26:52)



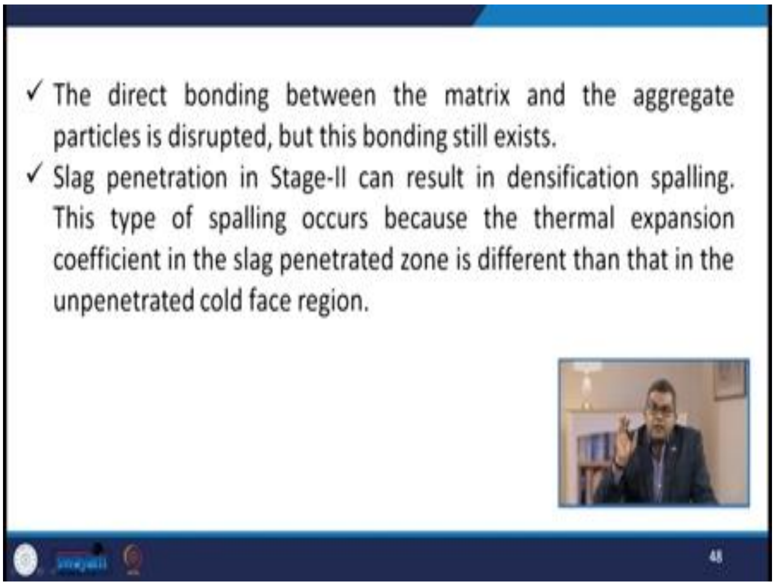
In stage-II, the coarse aggregate in a bonded refractory exhibits penetration particularly along grain boundaries.

Stage-II of the corrosion process showing a bonded refractory

Reference: A.O. Surendranathan et. al., (2014): SBIN; -13: 978-1-4822-2045-2.

Now here you see that the stage 2 of the corrosion process, this showing a bonded refectory. Now in stage 2 the coarse aggregate in the bonded refractory exhibits the penetration particularly along the grain boundary. Here you see that the corroded aggregate and this matrix are substantially disrupted at the hot to face.

(Refer Slide Time: 27:14)

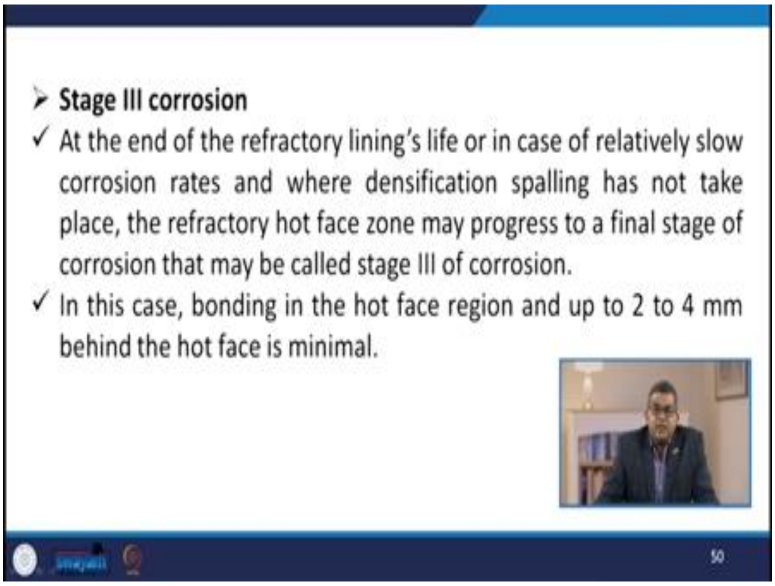


- ✓ The direct bonding between the matrix and the aggregate particles is disrupted, but this bonding still exists.
- ✓ Slag penetration in Stage-II can result in densification spalling. This type of spalling occurs because the thermal expansion coefficient in the slag penetrated zone is different than that in the unpenetrated cold face region.

Now the direct bonding between the matrix and aggregate particle is disrupted, but this bonding is still exists. Now the slag of penetration in stage 2 can result in densification spalling this type of spalling occurs because the thermal expansion coefficient in the slag penetrated zone is different than that in the unpenetrated cold face region. So on continued thermal excursion may be cooling or heating spalling can occur at the line of demarcation between the penetrated and unpenetrated areas.

The residual lining after spalling, then begins the corrosion process, new progressing from stage 1 to stage 2 again. Let us have a brief outlook about the stage 3 corrosion at the end of the refractory linings life or in case of relatively slow corrosion rate. Whereas the densification is spalling has not take place.

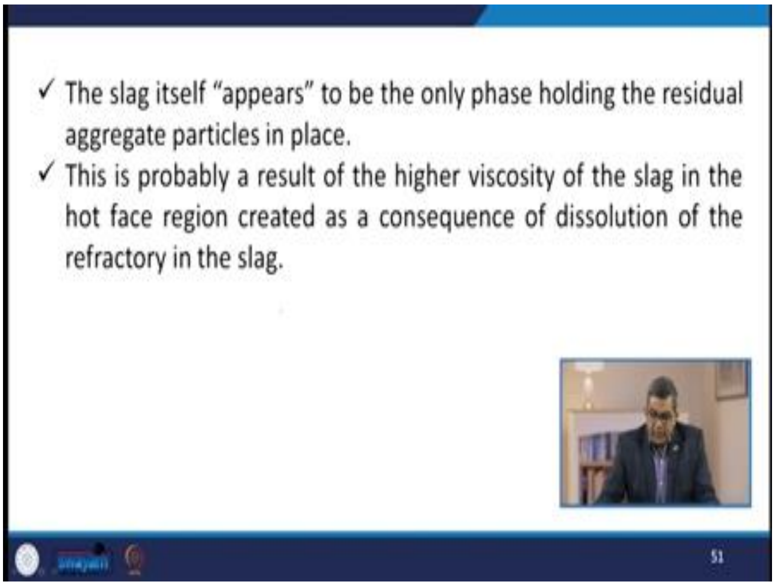
(Refer Slide Time: 28:21)



- **Stage III corrosion**
- ✓ At the end of the refractory lining's life or in case of relatively slow corrosion rates and where densification spalling has not take place, the refractory hot face zone may progress to a final stage of corrosion that may be called stage III of corrosion.
- ✓ In this case, bonding in the hot face region and up to 2 to 4 mm behind the hot face is minimal.

The refractory hot face zone may progress to a final stage of corrosion that may be called the, stage 3 corrosion. In this particular case the bonding in the hot face region and up to say 2 to 4 mm behind the hot face is minimal.

(Refer Slide Time: 28:40)



- ✓ The slag itself "appears" to be the only phase holding the residual aggregate particles in place.
- ✓ This is probably a result of the higher viscosity of the slag in the hot face region created as a consequence of dissolution of the refractory in the slag.

The slag itself appears to be the only face holding the residual aggregate particles in place. Now, this is probably a result of higher viscosity in the slag in hot face region and created as a consequence of dissolution of the refractory in the slag.

(Refer Slide Time: 29:00)

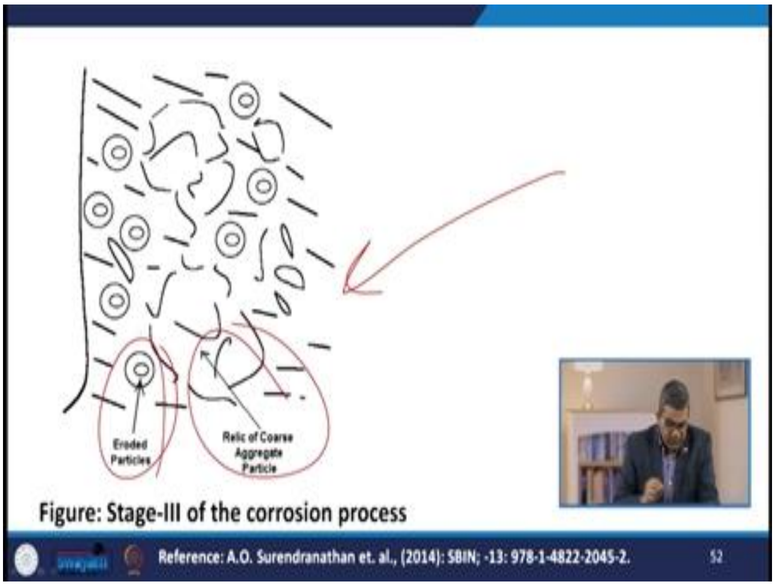
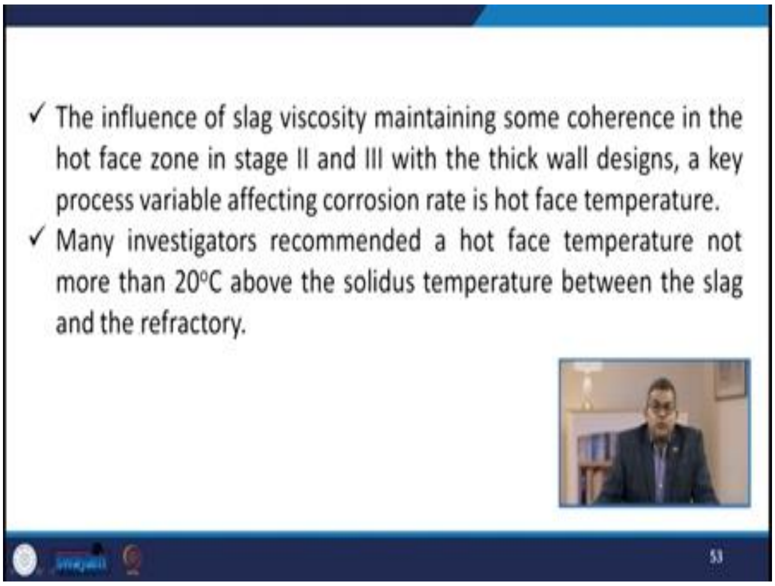


Figure: Stage-III of the corrosion process

Reference: A.O. Surendranathan et. al., (2014): SBIN; -13: 978-1-4822-2045-2.

Now here you see that the stage 3 of the corrosion process. Here you see that the relic coarse aggregate particles and this one are the eroded particles.

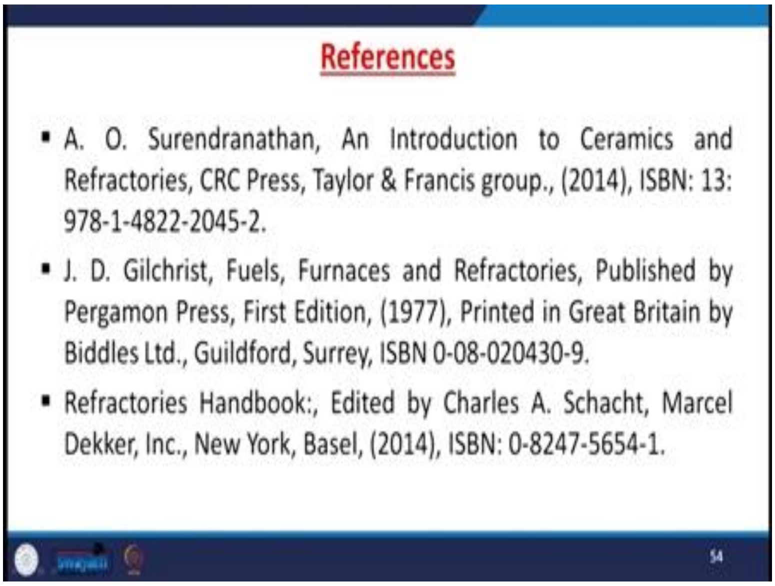
(Refer Slide T1ime: 29:10)



- ✓ The influence of slag viscosity maintaining some coherence in the hot face zone in stage II and III with the thick wall designs, a key process variable affecting corrosion rate is hot face temperature.
- ✓ Many investigators recommended a hot face temperature not more than 20°C above the solidus temperature between the slag and the refractory.

Now the influence of slag viscosity maintaining some coherence in the hot face zone in stage 2 and 3 with the thick wall design a key process variable affecting corrosion rate is hot face temperature. Many investigators recommended a hot face temperature not more than 20 degrees Celsius above the solidus temperature between the slag and refractory zone. So in this particular chapter or in this particular lecture we have discussed about the various thermodynamic concept, pertaining to the refractory operation apart from this we discussed about corrosion aspect in the refractory.

(Refer Slide Time: 29:54)



References

- A. O. Surendranathan, An Introduction to Ceramics and Refractories, CRC Press, Taylor & Francis group., (2014), ISBN: 13: 978-1-4822-2045-2.
- J. D. Gilchrist, Fuels, Furnaces and Refractories, Published by Pergamon Press, First Edition, (1977), Printed in Great Britain by Biddles Ltd., Guildford, Surrey, ISBN 0-08-020430-9.
- Refractories Handbook:, Edited by Charles A. Schacht, Marcel Dekker, Inc., New York, Basel, (2014), ISBN: 0-8247-5654-1.

And for your convenience we have listed several references and further reading, you may utilize those references. Thank you very much.