Iron Making and Steel Making
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Module - 05
Lecture – 22
Blast Furnace Products and Their Utilization

In this lecture, I will talk about the Blast Furnace Products and Their Utilization. This will include hot metal composition and its control, blast furnace slag, and gas and their usage.

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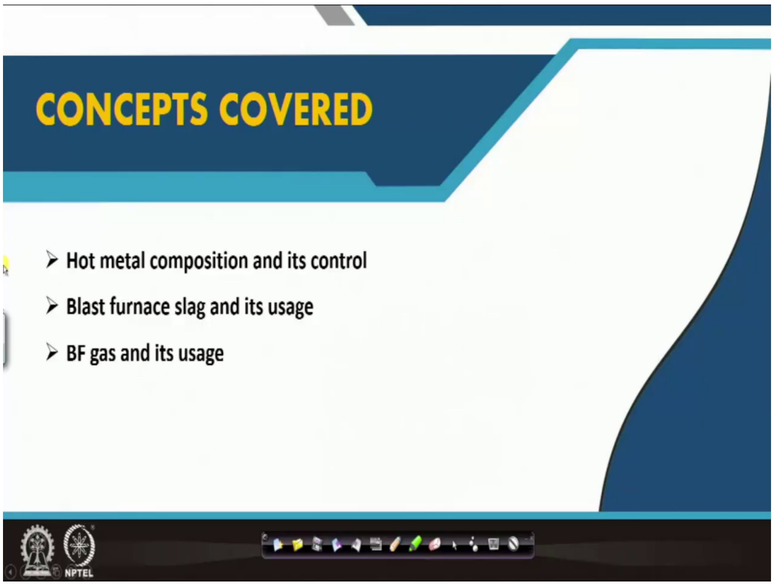

CONCEPTS COVERED

- Hot metal composition and its control
- Blast furnace slag and its usage
- BF gas and its usage

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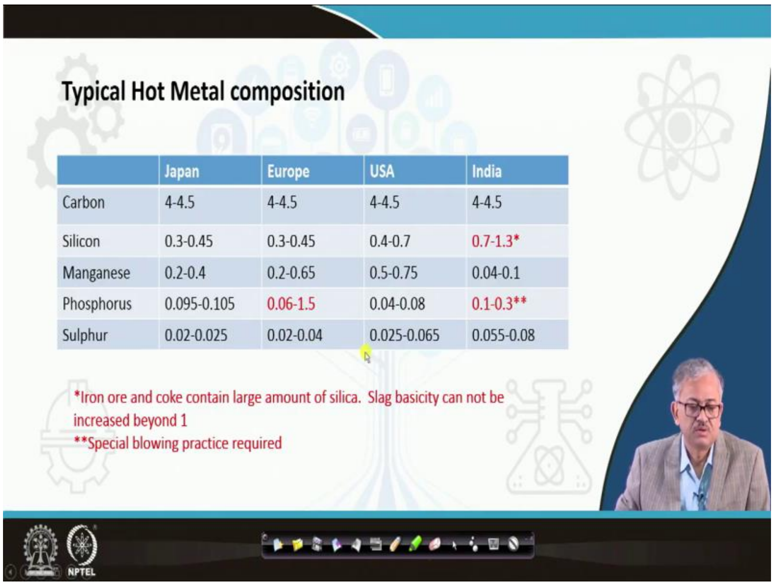


Typical Hot Metal composition

	Japan	Europe	USA	India
Carbon	4-4.5	4-4.5	4-4.5	4-4.5
Silicon	0.3-0.45	0.3-0.45	0.4-0.7	0.7-1.3*
Manganese	0.2-0.4	0.2-0.65	0.5-0.75	0.04-0.1
Phosphorus	0.095-0.105	0.06-1.5	0.04-0.08	0.1-0.3**
Sulphur	0.02-0.025	0.02-0.04	0.025-0.065	0.055-0.08

*Iron ore and coke contain large amount of silica. Slag basicity can not be increased beyond 1

**Special blowing practice required

The slide above, compares the Indian hot metal composition with that of other hot metal from other countries.

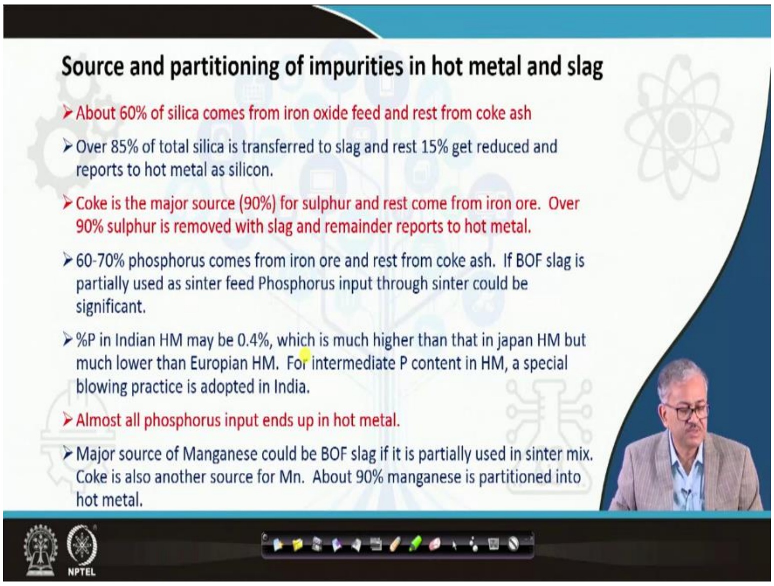
You may note that carbon percentage is usually same in all hot metal irrespective of countries, and it varies from 4 to 4 5 percent. Because, the liquid iron is saturated with the carbon under blast furnace condition.

If you consider silicon, you may note variation; in our hot metal it ranges from 0.7 to 1.3 weight percent, while in Japan it ranges from 0.3 to 0.45, in Europe it ranges from 0.3 to 4 5 and in USA it is from 0.4 to 0.7. So, compared to other countries we have lot of silicon in hot metal. It is mainly due to silica rich iron ore in India. Besides, our coal is also notorious for high ash, that results in comparatively high ash coke, which also contributes significantly to silicon addition to hot metal. It may be further noted that coke as burns at raceway, silicon directly enters into hot metal. Another factor is that due to high alumina content in blast furnace slag, we have very narrow window for fluid slag in blast furnace operating condition; and consequently we have very little option to increase the slag basicity that may help in partitioning silica more to the slag phase. Under Indian condition slag basicity may be varied between 1 to 1.2 only.

You may note that manganese is quite low in Indian hot metal ranging 0.04 to 0.1 wt%, compared to overseas hot metal ranging from 0.2 to 0.75. It might be due to the fact that we do not regularly recycle BOF slag, which could be major source of manganese, in a larger quantity for sinter making.

Regarding phosphorus, you may note that European steel have wide range of variation of phosphorus, ranging from 0.06 to 1.5. Some Europian countries processes high phosphorus iron ore that may result in very high phosphorus to the tune of 1.5. That is why they have special refining technique for treating high phosphorus hot metal. Either, they make a double slag practice or they use the lime powder along with the oxygen, called the LDAC process; Rotating LD vessel called KALDO is also used for treating such hot metal. Special slag evolution in LD could also be helpful. Note that USA has the lowest phosphorus in the range 0.04 to 0.08% and also Japan has quite low phosphorous up to 0.09 to 0.1, which may be attributed to very good qulity iron ore containing very low phosphorus. In India phosphorus content is intermediate in the range 0.1 to 0.3.So, we have also some special technique, we basically control it by the blowing practice.

Regarding sulphur, Indian hot metal is found to contain the high sulphur in the range 0.06 to 0.08%, which may be attributed to high coke ash and difficulty in maintaining high slag basicity in blast furnace in presence of significant alumina (detail slag evolution will be discussed later). (Refer Slide Time: 05:38)



Source and partitioning of impurities in hot metal and slag

- About 60% of silica comes from iron oxide feed and rest from coke ash
- Over 85% of total silica is transferred to slag and rest 15% get reduced and reports to hot metal as silicon.
- Coke is the major source (90%) for sulphur and rest come from iron ore. Over 90% sulphur is removed with slag and remainder reports to hot metal.
- 60-70% phosphorus comes from iron ore and rest from coke ash. If BOF slag is partially used as sinter feed Phosphorus input through sinter could be significant.
- %P in Indian HM may be 0.4%, which is much higher than that in japan HM but much lower than Europian HM. For intermediate P content in HM, a special blowing practice is adopted in India.
- Almost all phosphorus input ends up in hot metal.
- Major source of Manganese could be BOF slag if it is partially used in sinter mix. Coke is also another source for Mn. About 90% manganese is partitioned into hot metal.

Now, let us discuss the source and partitioning of the impurities in hot metal. Source of silicon in hot metal is silica in ore and coke. Generally, around 60 percent of silica, comes from the iron ore feed rest 40% from the coke ash; and over 85 percent of the total silica is transferred to the slag with low alumina and high basicity slag and 15 percent get reduced and reports to the hot metal. Under Indian condition with basicity of the order of 1 to 1.2 the silicon partition in slag is rather restricted and silicon reports to hot metal significantly. In India, coke contributes to more than 70% of the total silica input, which burns at raceway and adds to hot metal directly and silicon partitioning to slag in hearth is not very effective.

Then coke is also the major source of sulphur; 90 percent of the sulphur in the hot metals come from the coke sulphur. And over 90 percent of the sulphur is removed to the slag under highly reducing condition and basic slag in blast furnace, specially with low alumina slag. In spite of the fact that sulphur contained in the India coke ash also quite less, we have very high sulphur in the hot metal compared to that Japan because we have some limitation in the slag basicity, as mentioned earlier.

60 to 70 percent phosphorous comes from the iron ore and rest from the coke ash. If BOF slag is partially used as a sinter making, then such slag also acts as a source of phosphorus and phosphorous in hot metal becomes high. It may be noted that BOF slag has a very less utility and sometimes recycled for the sinter making. Because, BOF slag also contained around 20 percent iron oxides; but it also contain undesirable P_2O_5. It also contains CaO, which might be helpful for fluxing sinter, if recycled for sinter making. So, BOF slag is partially recycled into sinter making. Approximately 100% P_2O_5 in iron ore and coke ash reports to hot metal under reducing blast furnace condition.

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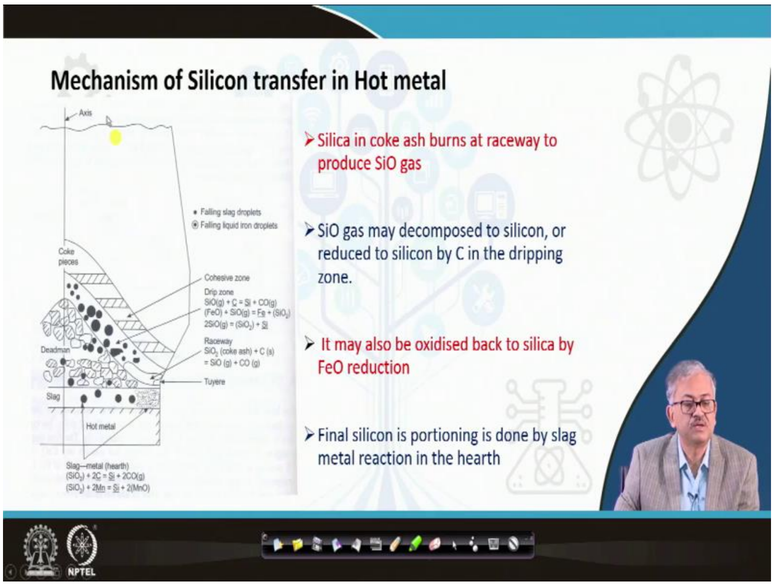

Mechanism of Silicon transfer in Hot metal

- Silica in coke ash burns at raceway to produce SiO gas
- SiO gas may decomposed to silicon, or reduced to silicon by C in the dripping zone.
- It may also be oxidised back to silica by FeO reduction
- Final silicon is portioning is done by slag metal reaction in the hearth

Now, let us consider the mechanism of silicon transfer in the hot metal. How the silicon is transferred into the hot metal? First silica in the coke ash burns at raceway to produce the SiO gas;. and when this SiO gas move up through the dripping zone, SiO gas react with the dissolved carbon and forming silicon and CO gas and SiO gas can also directly be decomposed to Si (see equations 22.1 to 22.3)..

$$SiO_2(coke\ ash) + C(s) = SiO(g) + CO(g)$$

(22.1)

$$SiO(g) + \underline{C} = \underline{Si} + CO(g)$$

(22.2)

$$SiO(g) = (SiO_2) + \underline{Si}$$

(22.3)

FeO is less stable compared to the SiO_2. So, FeO in slag can also reduce the SiO gas to silicon (equation 22.4).

$$SiO(g) + (FeO) = \underline{Si} + (SiO_2)$$

(22.4)

Final silicon partitioning is done at the slag metal interface in the hearth following the equation 22.5.

$$\underline{Si} + 2(FeO) + 2(CaO) = (SiO_2.2CaO) + 2[Fe] \tag{22.5}$$

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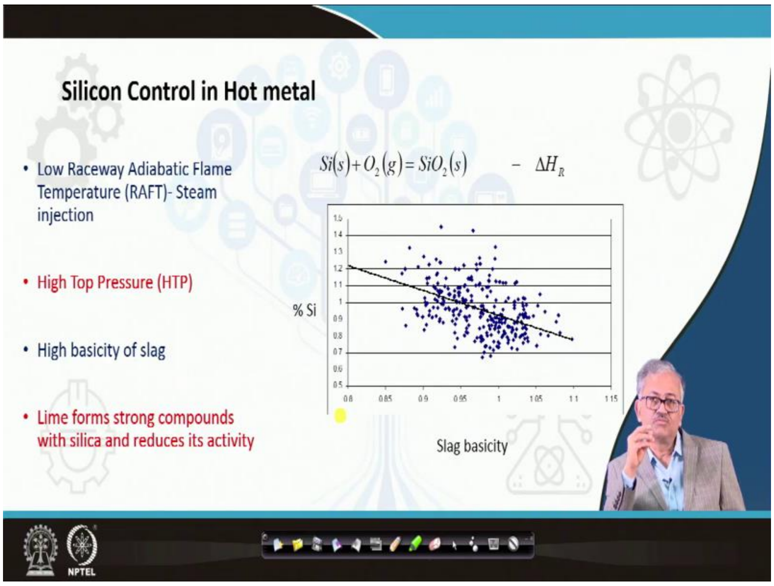

Silicon Control in Hot metal

- Low Raceway Adiabatic Flame Temperature (RAFT)- Steam injection
- High Top Pressure (HTP)
- High basicity of slag
- Lime forms strong compounds with silica and reduces its activity

$$Si(s)+O_2(g)=SiO_2(s) \quad -\Delta H_R$$

Parameters on which silicon content in hot metal depends: Silicon in hot metal depends on hot metal temperature, high top pressure, slag basicity. Silicon oxidation is an exothermic reaction and this reaction will be retarded at high temperature; in other words if hot metal temperature increases, it will retard the silicon oxidation and as a result partitioning of silicon in slag will be reduced, leading to high silicon in hot metal. High top pressure will assist silicon oxidation by increasing the partial pressure of oxygen and consequently increase silicon partitioning in slag and reduce the silicon in hot metal. Slag basicity will also promote silicon partitioning by decreasing silicon activity in slag. The Figure 22.1 shows the variation of silicon content in hot metal as a function of slag basicity based on Indian plant data. A clear decrease in hot metal silicon content is observed with increase in basicity.

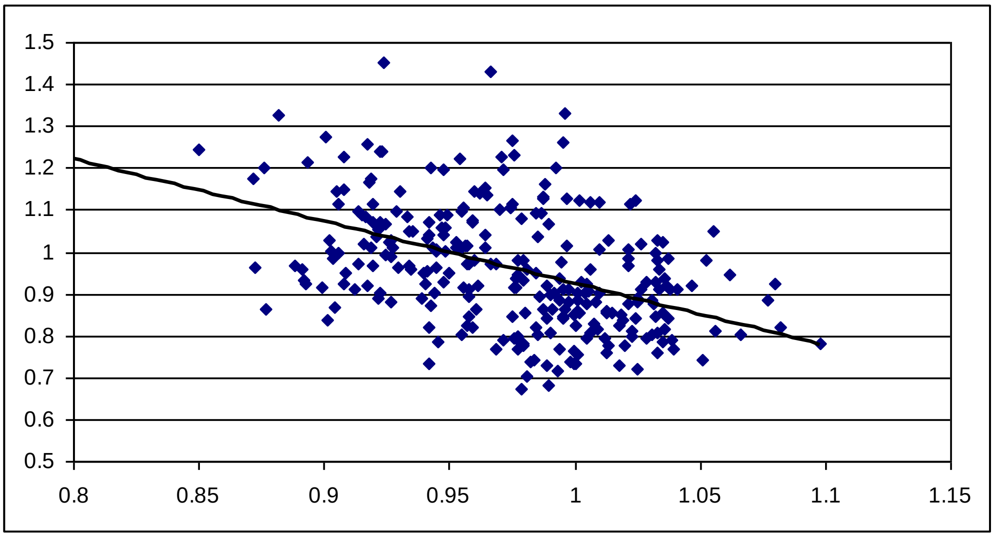

Figure 22.1 Variation of silicon content in hot metal with basicity.

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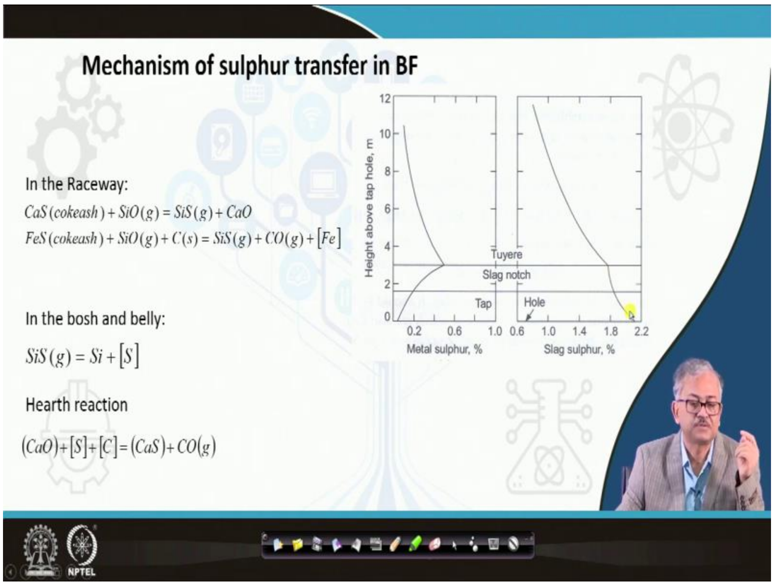

Mechanism of sulphur transfer in BF

In the Raceway:

$$CaS\,(cokeash) + SiO(g) = SiS(g) + CaO$$

$$FeS\,(cokeash) + SiO(g) + C(s) = SiS(g) + CO(g) + [Fe]$$

In the bosh and belly:

$$SiS(g) = Si + [S]$$

Hearth reaction

$$(CaO) + [S] + [C] = (CaS) + CO(g)$$

Mechanism of Sulphur transfer in blast furnace:

Sulphur in coke ash (in the form of CaS,or FeS) react with the SiO gas at the raceway forming SiS gas which subsequently decompose to silicon and sulphur in the bosh region and reports to hot metal (equations 22.6 & 8)

$$(CaS) + SiO(g) = SiS(g) + (CaO)$$

(22.6)

$$FeS(coke\ ash) + SiO(g) + \underline{C} = SiS(g) + CO(g) + [Fe]$$

(22.7)

$$SiS(g) = \underline{Si} + \underline{S}$$

(22.8)

Final partitioning of sulphur takes place at the slag metal interface in the hearth by the following reaction (equation 22.9.

$$(CaO) + \underline{S} + \underline{C} = (CaS) + CO(g)$$

(22.9)

The evolution of sulphur in iron and slag across the height above tuyer level may be given by the figure 22.2.

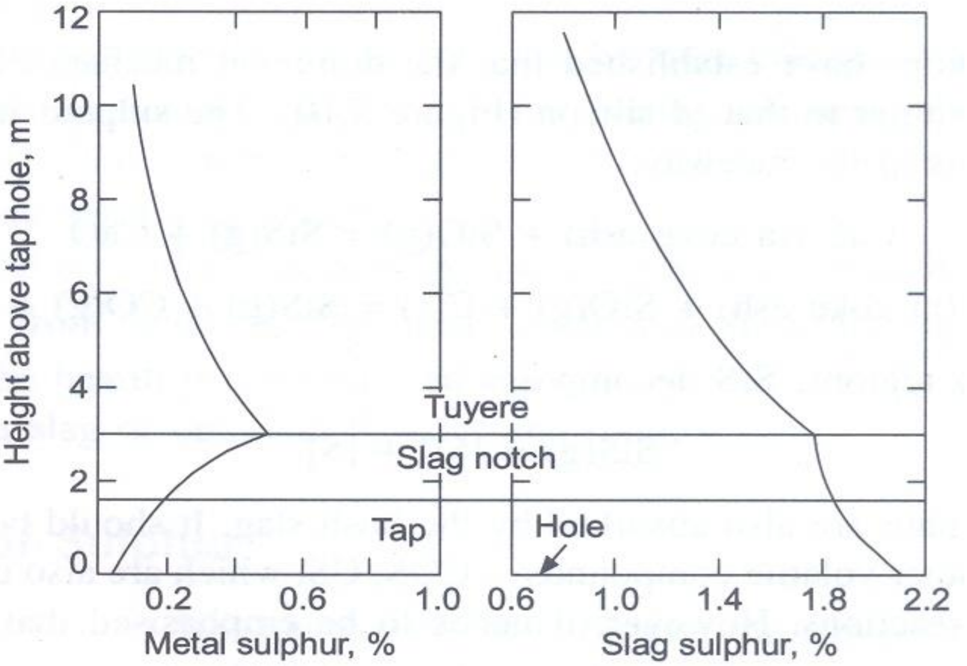

Figure 22.2: Evolution of sulphur in iron and slag across the height above the tuyer level (Courtesy: Ghosh, Chatterjee)

Sulphur in the iron increases axially in blast furnace from top of the furnace towards the tuyer line and then decreases in the hot metal. Sulphur in iron and slag becomes maximum at tuyer level through the reactions mentioned in equations (12.6 to12.8); then it decreases in hot metal and increases in slag by sulphur partitioning at slag metal interface(equation 12.9) , which is favoured under reducing condition and basic slag, prevalent in blast furnace.

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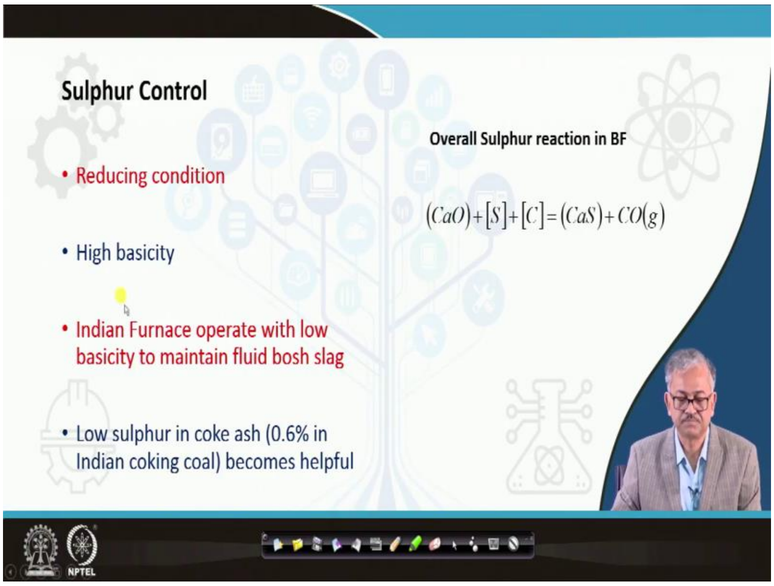

Sulphur Control

- Reducing condition
- High basicity
- Indian Furnace operate with low basicity to maintain fluid bosh slag
- Low sulphur in coke ash (0.6% in Indian coking coal) becomes helpful

Overall Sulphur reaction in BF

$$(CaO)+[S]+[C]=(CaS)+CO(g)$$

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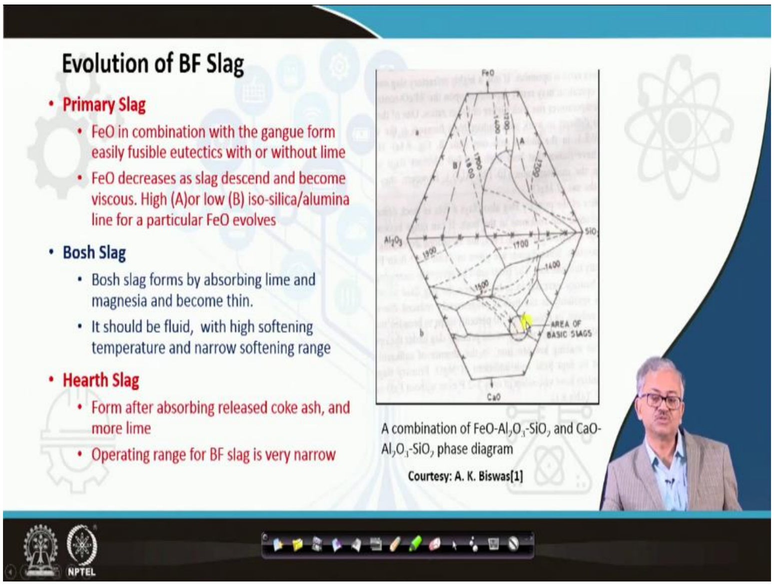


Evolution of BF Slag

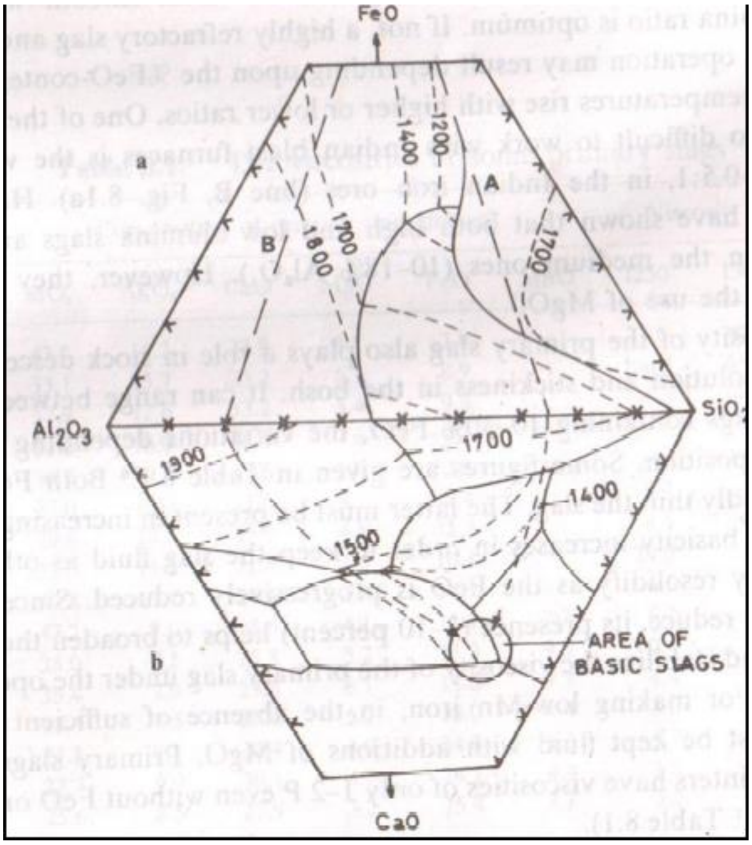
- **Primary Slag**
  - FeO in combination with the gangue form easily fusible eutectics with or without lime
  - FeO decreases as slag descend and become viscous. High (A)or low (B) iso-silica/alumina line for a particular FeO evolves
- **Bosh Slag**
  - Bosh slag forms by absorbing lime and magnesia and become thin.
  - It should be fluid, with high softening temperature and narrow softening range
- **Hearth Slag**
  - Form after absorbing released coke ash, and more lime
  - Operating range for BF slag is very narrow

A combination of FeO-Al_2O_3-SiO_2 and CaO-Al_2O_3-SiO_2 phase diagram

Courtesy: A. K. Biswas[1]

Let us now see how the blast furnace slag evolves with time, or the distance from top of the furnace towards the hearth. When the higher oxides of iron are reduced to wustite in the upper part of the furnace, wustite can combine with MnO, SiO_2 and Al_2O_3 forming the primary slag, which is quite viscous. Depending on the ratio of SiO_2/Al_2O_3 in the slag, the slag could be fluid or viscous. As seen from the figure below (Fig. 22.3), where the primary slag is shown in a SiO_2, Al_2O_3, FeO ternary system, we find that the slag can evolve along two lines; one with high SiO_2/Al_2O_3 (3 to 4), and the other with low SiO_2 to Al_2O_3 ratio (~0.5). The first one is represented by line A and the second one is represented by line B and it is found that A has comparative lower liquidus from 1200^oC to 1700^oC ; while the B-lines passes through liquidus >1800^oC. It is also found that as the slag moves down its viscosity increases as the percentage of FeO in the slag decreases by its direct reduction of FeO to Fe.

As the slag enters the Bosh, the CaO starts dissolving in the slag and FeO reduces to zero and thus the slag system converts to Al_2O_3, SiO_2 and CaO system. Slag starts becoming fluid and CaO percentage in the slag goes on increasing until the slag joins the hearth, where coal ash also joins the slag and make the slag most fluid with liquidus at 1250 to 1350^oC. This is called the hearth slag. Here the basicity of the slag remains 1 to 1.2. It may be observed that the slag composition window in blast furnace is very limited.



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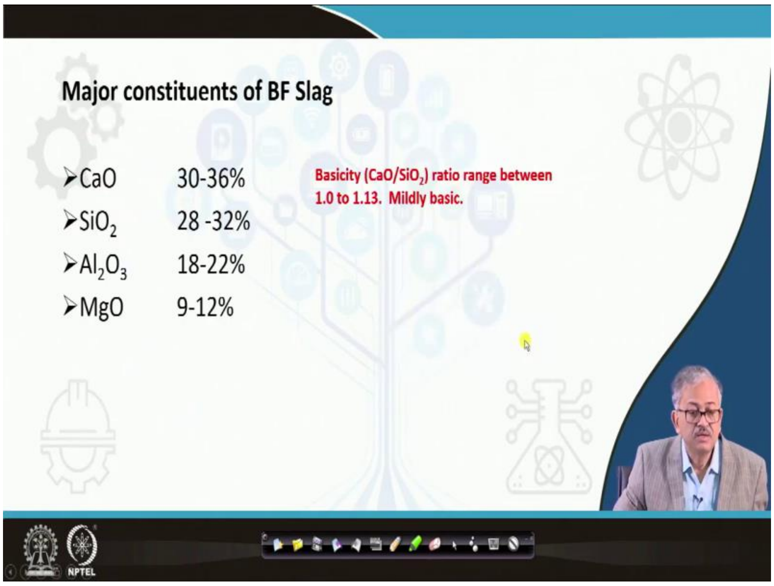

Major constituents of BF Slag

- CaO 30-36%
- SiO$_2$ 28 -32%
- Al$_2$O$_3$ 18-22%
- MgO 9-12%

Basicity (CaO/SiO$_2$) ratio range between 1.0 to 1.13. Mildly basic.

The hearth slag composition becomes: CaO is around 30 to 36 percent SiO$_2$ 20 to 32 percent. And here the basicity lies between 1 to 1.13 and Al$_2$O$_3$ is around 18 to 22 percent and MgO 9 to 12 percent.

MgO is added additionally sometimes to make the slag fluid; but there is some limitations.

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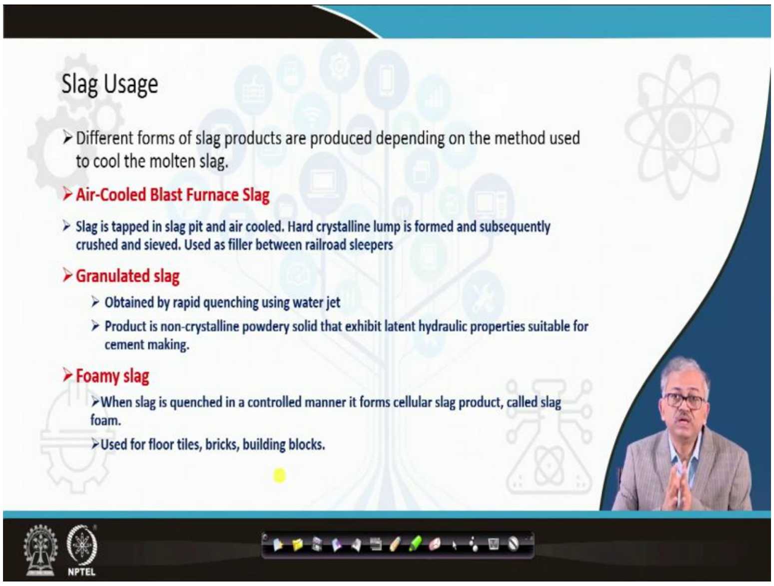

Slag Usage

- Different forms of slag products are produced depending on the method used to cool the molten slag.
- **Air-Cooled Blast Furnace Slag**
- Slag is tapped in slag pit and air cooled. Hard crystalline lump is formed and subsequently crushed and sieved. Used as filler between railroad sleepers
- **Granulated slag**
  - Obtained by rapid quenching using water jet
  - Product is non-crystalline powdery solid that exhibit latent hydraulic properties suitable for cement making.
- **Foamy slag**
  - When slag is quenched in a controlled manner it forms cellular slag product, called slag foam.
  - Used for floor tiles, bricks, building blocks.

Slag usage: Different forms of slags products are produced from the blast furnace slag. Blast furnace slag is very usable. When blast furnace slag is slowly cooled in a slag pit under the normal air, a crystalline solid lump of slag forms; after crushing it is used between the rail sleepers or in the railroads sleeper.

The most popular use of BF slag is in cement industry. For this purpose BF slag is granulated by quenching it under forced water jet, which does not allow crystallization of slag and slag remains completely amorphous and powdery mass. Such granulated slag has a very cementitious property; it exhibit latent hydraulic properties suitable for the cement making. So, majority of the blast furnace slag goes to the cement plant.

A foamy slag forms when the cooling rate not too high, or not too low; in this case quenching is done through water air mixture, allowing flexibility in cooling rate. Slag foam with a cellular slag structure can be used for making floor tiles, bricks, building blocks etc.

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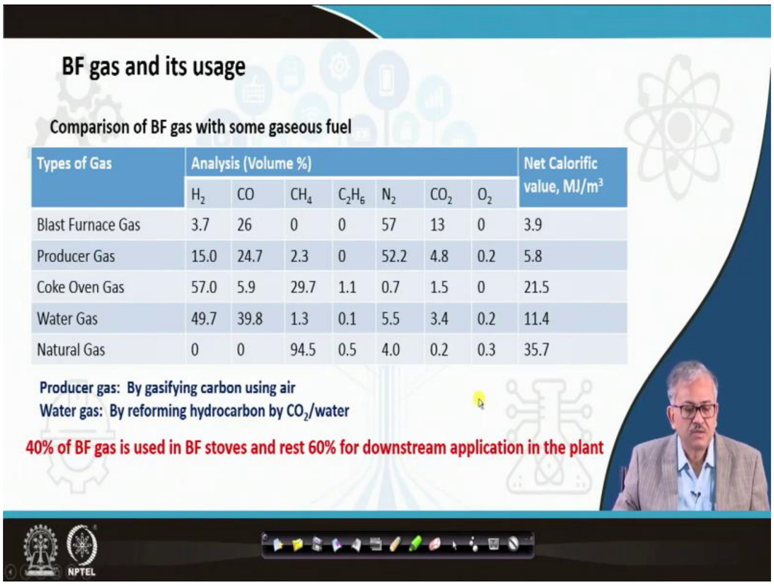

BF gas and its usage

Comparison of BF gas with some gaseous fuel

Types of Gas	Analysis (Volume %)							Net Calorific value, MJ/m^3
	H_2	CO	CH_4	C_2H_6	N_2	CO_2	O_2	
Blast Furnace Gas	3.7	26	0	0	57	13	0	3.9
Producer Gas	15.0	24.7	2.3	0	52.2	4.8	0.2	5.8
Coke Oven Gas	57.0	5.9	29.7	1.1	0.7	1.5	0	21.5
Water Gas	49.7	39.8	1.3	0.1	5.5	3.4	0.2	11.4
Natural Gas	0	0	94.5	0.5	4.0	0.2	0.3	35.7

Producer gas: By gasifying carbon using air

Water gas: By reforming hydrocarbon by CO_2/water

40% of BF gas is used in BF stoves and rest 60% for downstream application in the plant

Let us discuss blast furnace gas and its usage. The slide above compares the blast furnace gas with other synthetic gases. Blast furnace gas is 26% CO, 4% H_2, 13% CO_2 and rest 57% N_2 with a calorific value of 3.9 MJ/m^3 (900 kcal/m^3) Producer gas is synthetically prepared by gassifying carbon in air and steam mixture and it has 15% H_2, 25% CO, and 2 to 3% methane with a calorific value of 5.8MJ/m^3(1400 kcal/m^3). Coke oven gas, a by product of coking process, has 57% H_2 and 6% CO and 30% methane with a calorific value of 21.5MJ/m3 (5000 kcal/Nm^3). Water gas is obtained by gassifying carbon by steam and it has a composition of 50% H_2 and 40% CO with a calorific value of 11.4 MJ/m^3 (2700 kcal/m^3). High percentage of hydrogen in water gas is obtained by promoting the water gas shift reaction where CO reduce water to hydrogen and it itself oxidized to CO_2. Finally, natural gas has 95% methane and calorific value 35.7MJ/m^3 (8500 kcal/m^3).

So, it may be noted that BF gas and coke oven gas are the product gases; producer and water gas are two synthetic gases and the other is natural gas. Obviously, BF gas with least calorific value but usable. In fact BF gas after cleaning, is used for preheating air blast. Not only that, but also around 60% cleaned BF gas is used for downstream application in the plant (in coke oven and sinter plant).

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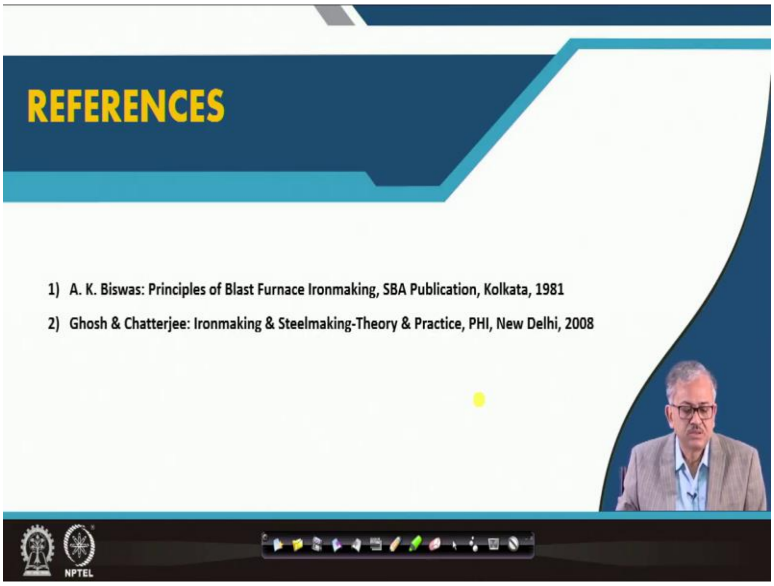

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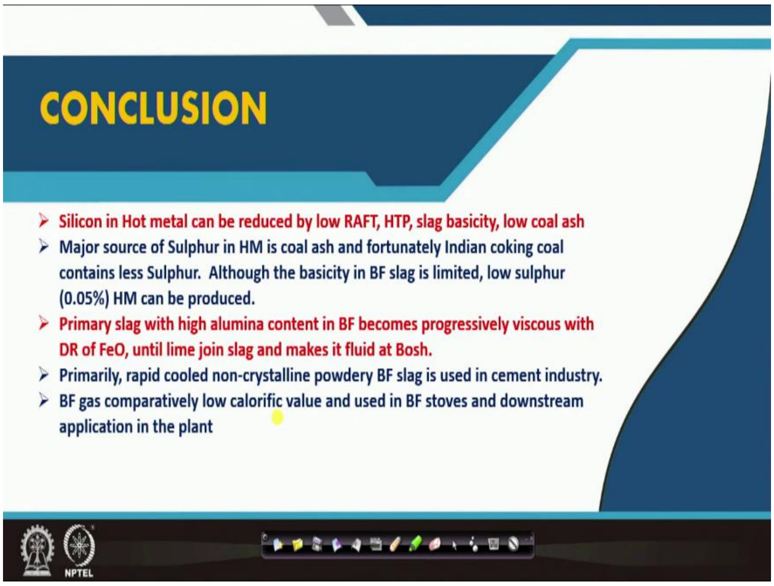

CONCLUSION

- Silicon in Hot metal can be reduced by low RAFT, HTP, slag basicity, low coal ash
- Major source of Sulphur in HM is coal ash and fortunately Indian coking coal contains less Sulphur. Although the basicity in BF slag is limited, low sulphur (0.05%) HM can be produced.
- Primary slag with high alumina content in BF becomes progressively viscous with DR of FeO, until lime join slag and makes it fluid at Bosh.
- Primarily, rapid cooled non-crystalline powdery BF slag is used in cement industry.
- BF gas comparatively low calorific value and used in BF stoves and downstream application in the plant

Conclusion: Indian hot metal contains high silicon, primarily due to coke ash that burns at raceway and directly incorporate silicon in the hot metal. Silicon in hot metal can be reduced by low RAFT, high top pressure, and high slag basicity.

90 percent of the sulphur in hot metal is contributed by coke ash. Significant amount of sulphur is partitioned in BF slag. The operating window for fluid slag in BF with high alumina under Indian condition is rather limited and therefore basicity of slag can not

exceeds 1.2. Such limitation reduces the sulphur capacity of slag. Comparatively low sulphur (0.6%) in in coke ash is helpful.

Granulated, amorphous, powdery BF slag produced under high speed quenching is the major product of slag that is used in cement industry. Cleaned BF gas is used for air blast preheating and downstream application.