Iron Making and Steel Making.

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Module – 07
Lecture - 31
LD Steelmaking: Basics, Process steps emulsion formation and stabilization

In this lecture, I will discuss the LD Steelmaking. Topics covered in this lecture will include the basics of LD steelmaking, process steps, emulsion formation and stabilization.

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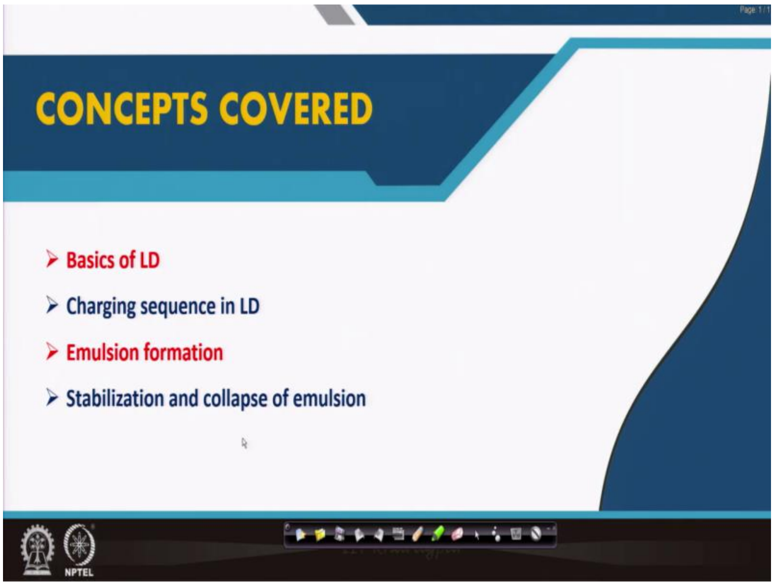

CONCEPTS COVERED

- Basics of LD
- Charging sequence in LD
- Emulsion formation
- Stabilization and collapse of emulsion

Figure 31.1 shows the schematics of LD furnace. Pure oxygen is charged from the top using top lance. The shape of the vessel is similar to that of Bessemer vessel; the major difference being the oxygen lancing from the top at supersonic velocity that creates emulsion for very fast refining without any nozzle flooding problem, unlike in Bessemer where air in injected through bottom tuyere.

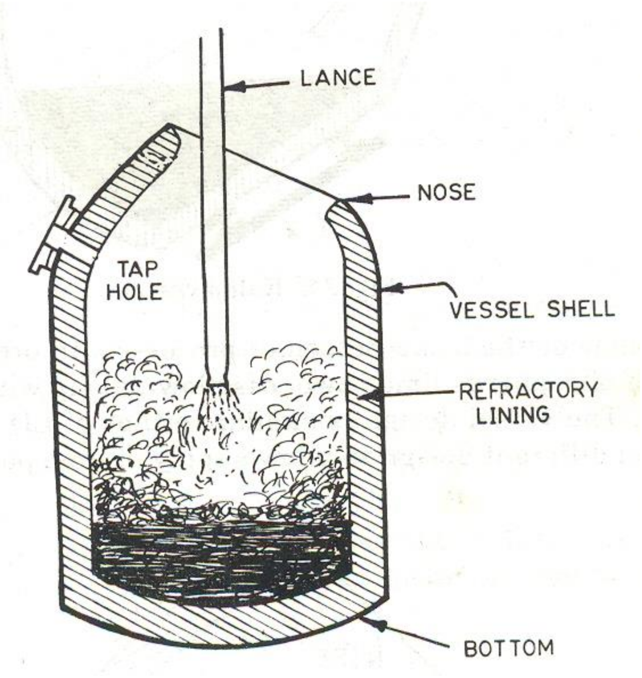

Figure 31.1 Schematics of LD furnace[3].

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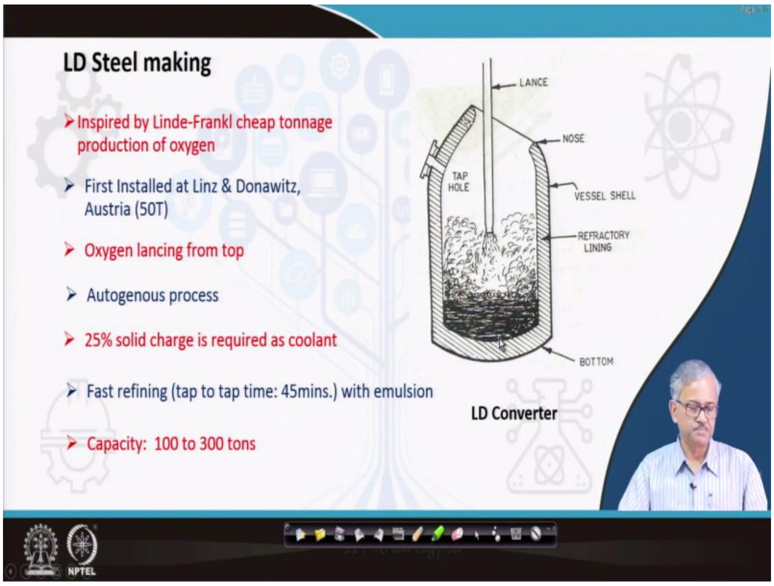

LD Steel making

- Inspired by Linde-Frankl cheap tonnage production of oxygen
- First Installed at Linz & Donawitz, Austria (50T)
- Oxygen lancing from top
- Autogenous process
- 25% solid charge is required as coolant
- Fast refining (tap to tap time: 45mins.) with emulsion
- Capacity: 100 to 300 tons

LD possess is inspired by the Linde Frankl cheap tonnage production of oxygen, because similar idea was also conceived by Bessemer; but cheap oxygen was not available at that time and he was satisfied with using air. But air had major problem because it introduced lot of nitrogen into the liquid steel.

So, Linde Frankl process was responsible for LD to take birth, and this Linde Frankl process is basically based on fractional distillation air, but with some process innovation; that is why this process is very cheap.

LD furnace derived its name from two cities in Austria, Linz and Donawitz, where it was first installed with 5 ton capacity. Oxygen is lanced from the top at supersonic velocity that creates gas-slag-metal emulsion with tremendous increase in surface area for superfast refining. It is autogenous process because it does not require supply of any external heat; impurity oxidation generates heat that is more than sufficient to self-sustain this process. Surplus heat is generated such that coolant is required to maintain the bath temperature at 1600^oC. Temperature in excess affect the life of the refractory. Around 25% scrap is added to contain the temperature to the desired limit. Bessemer was also autogenous but it could not accept scrap due to heat limitation. Obviously, while using pure oxygen, oxygen partial pressure as well as kinetics is faster leading to higher heat generation.

Due to superfast kinetics total refining time in LD is just 20 minutes and tap to tap time is 45 minutes; this is in contrast to Open Hearth Furnace where best possible tap to tap time was 6 hours.

LD furnace capacity ranges from 100 to 300 tons. Most of the plants have LD furnaces of 150 ton capacity; furnaces with 300 ton capacity are very rear.

Refractory lining is highly basic. Liquid metal is tapped through the tap hole, placed on the side wall near the bottom, by tilting the furnace. It may be noted that vessel corners are rounded to facilitate the mass transfer into the liquid steel bath. Let us now discuss the charging sequence in LD process.

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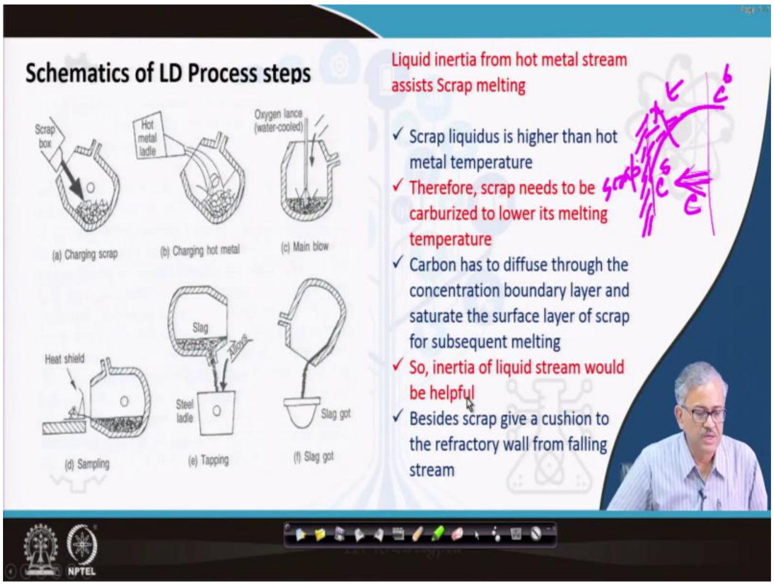
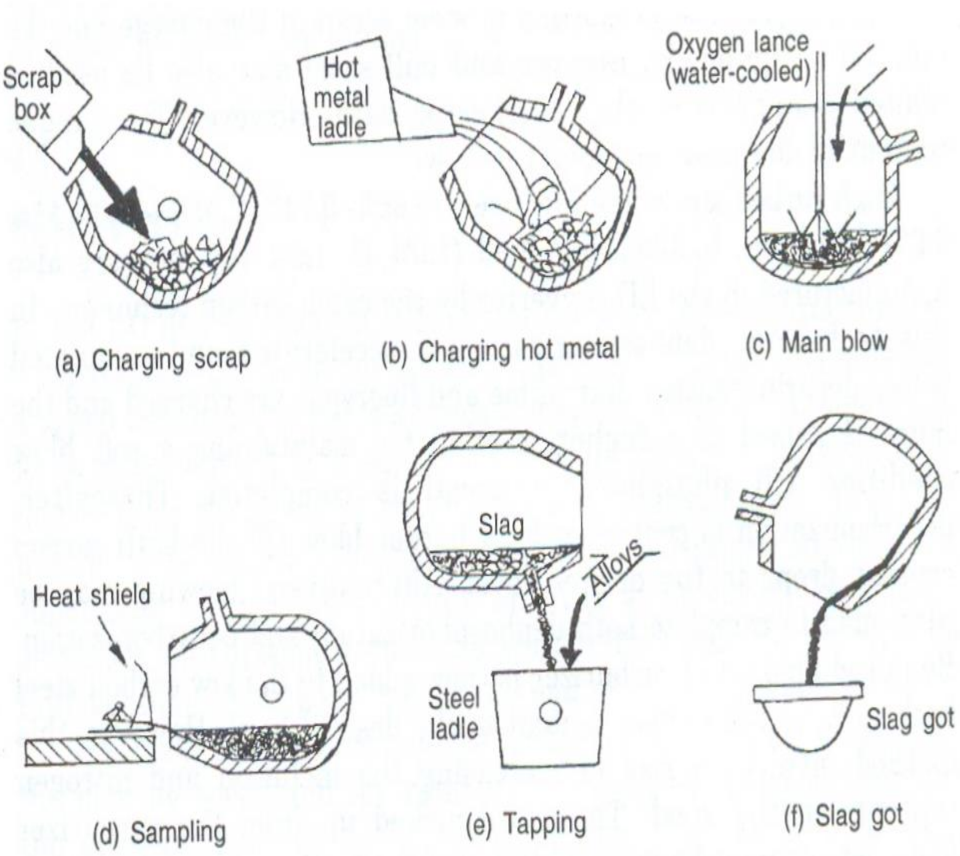


Schematics of LD Process steps

Liquid inertia from hot metal stream assists Scrap melting

- ✓ Scrap liquidus is higher than hot metal temperature
- ✓ Therefore, scrap needs to be carburized to lower its melting temperature
- ✓ Carbon has to diffuse through the concentration boundary layer and saturate the surface layer of scrap for subsequent melting
- ✓ So, inertia of liquid stream would be helpful
- ✓ Besides scrap give a cushion to the refractory wall from falling stream

Figure 31.2 shows the schematics of the process sequence.



(a) Charging scrap (b) Charging hot metal (c) Main blow

(d) Sampling (e) Tapping (f) Slag got

Figure 31.2: Schematics of the process sequence[3]

First, the scrap is charged directly on the vessel from the scrap box. It has two advantages: i) one thing is that if you charge the scrap first and then you put the hot metal over it, then hot metal does not directly hit the refectory wall and avoids chemical erosion of the wall. Thus, scrap provides a cushioning effect over the refractory.

Secondly, charging the hot metal over the scrap helps in the scrap melting. Scrap melting is heat and mass transfer controlled and when liquid falls over scrap, its inertia may be utilized for scrap melting. It may be noted that besides steel scrap, other coolants like DRI/briquettes of iron bearing solid waste could also be utilized.

After charging, oxygen lancing and main blow starts, and refining through emulsion formation continues. Superfast refining takes place within very short time, maybe 20 minutes only.

Then sampling is done by turning the vessel to check whether the desired steel composition has been achieved or not. Finding the time for end blow is a difficult task and several offline and online models are available to predict the end of blow period when the desired steel composition and temperature has been attained. Prolonging blowing unnecessarily enhances cost of operation and decreases yield and productivity.

The final step is tapping the metal. Metal is tapped by tilting the furnace directly to the ladle. Draining of slag to the metal at the end of tapping is a concern because carryover slag interferes with subsequent deoxidation of bath by reversion of impurities from slag to metal when bath oxygen is lowered to very small value. To arrest the slag, some kind of float with density between that of slag and metal is used, which block the taphole when metal has been drained and slag starts draining. But clear cut transition from metal to slag does not happen due to drain sink formation. Therefore, some sensors have also been used which indicates the traces of slag in metal flow through the nozzle when the tapping could be stopped. Inspite of all efforts some carryover of slag could not be avoided with due consideration to the metal yield; but definitely its amount could be restricted.

Deoxidation and alloying is also sometimes done in the ladle by adding blocks of aluminum and ferroalloy at the vessel bottom to utilize the inertia of the falling stream.

Now let us briefly discuss how liquid inertia from hot metal stream assist in the scrap melting during charging in LD vessel. As I have said that scrap melting is heat and mass transfer controlled. For low carbon scrap, which is usually the case, the scrap melting is mass transfer controlled and for high carbon steel scrap, scrap melting could be heat transferred controlled.

For low carbon steel scrap, the scrap liquidus is very high; it is higher than that of hot metal. Then how you can melt the scrap? So, to melt the scrap, it needs to be carburized first to lower its liquidus, atleast in the near surface region; such that scrap liquidus goes below the hot metal temperature enabling hot metal to melt it. Now the transfer of carbon from hot metal to scrap surface is controlled by mass transfer of carbon through the concentration boundary layer at the scrap-hot metal interface. Such boundary mass transfer is facilitated by turbulence in the boundary layer, which could be derived from the falling stream over the scrap. When the scrap liquidus is lower than hot metal temperature, then heat transfer across the boundary layer might also control the scrap melting. In this case also liquid inertia derived from falling stream will be helpful in enhancing heat transfer across the boundary layer.

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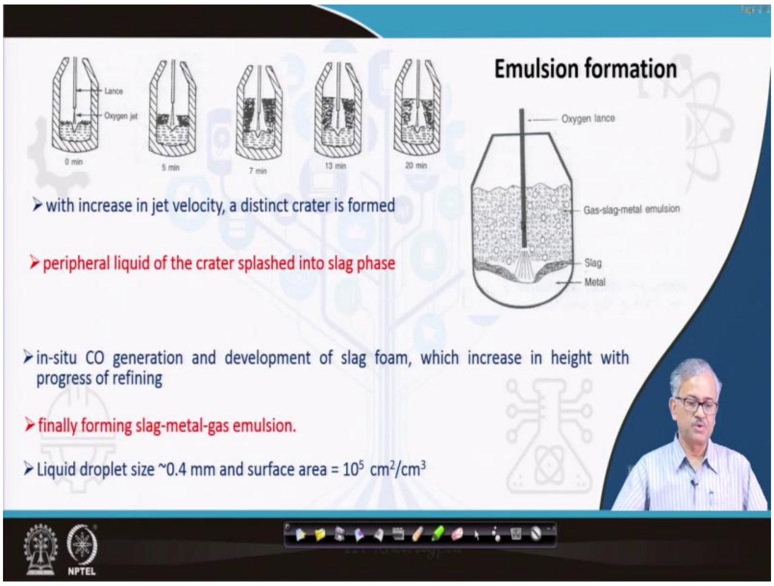

Emulsion formation

- with increase in jet velocity, a distinct crater is formed
- peripheral liquid of the crater splashed into slag phase
- in-situ CO generation and development of slag foam, which increase in height with progress of refining
- finally forming slag-metal-gas emulsion.
- Liquid droplet size ~0.4 mm and surface area = 10^5 cm^2/cm^3

Now, let us discuss the emulsion formation. What are the steps of emulsion formation? With increase in the jet velocity distinct crater is formed. So, peripheral liquid of the crater ie teared off and splashed into the slag phase above. Slag metal reaction will take place at the ejected metal droplet slag interface and mostly it is the decarburization that will initiate first because carbon is the major impurity in steel and forms a stable gaseous product at steelmaking temperature. So in-situ CO generation will take place that will form slag foam. With progress of refining such foam will increase in height. Continuously ejected metal droplets into the foam will form slag-gas-metal emulsion. When a full fledged emulsion forms other impurities also starts removing. Phosphorus removal starts when the basic slag forms. Carbon content of the bath is judiciously controlled by proper blowing practice such that carbon stays in the bath and supports emulsion and impurity removal till the end of the process.

Liquid droplet size may be of the order of 0.4 millimeter and the specific surface area becomes of the order of 10^5 cm^2/cm^3, which is much larger than nominal slag metal interfacial area; and that is basically responsible for a very high kinetics of the process.

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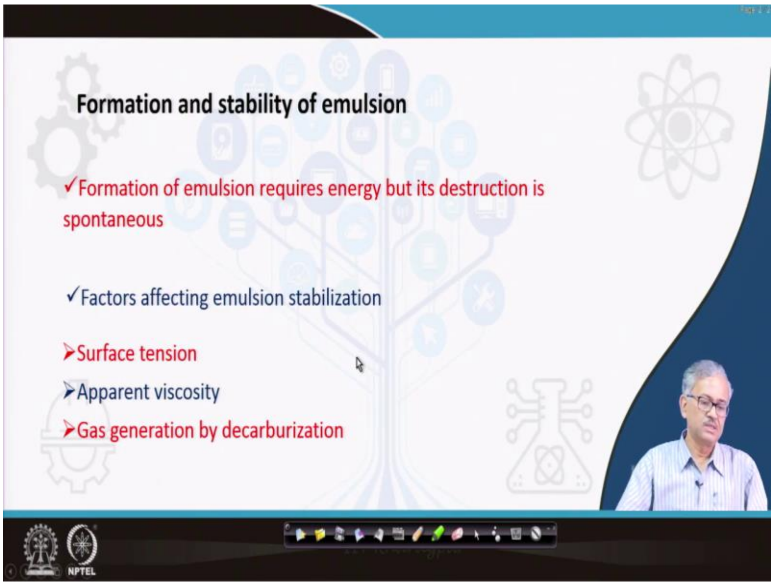


Formation and stability of emulsion

✓Formation of emulsion requires energy but its destruction is spontaneous

✓Factors affecting emulsion stabilization

- Surface tension
- Apparent viscosity
- Gas generation by decarburization

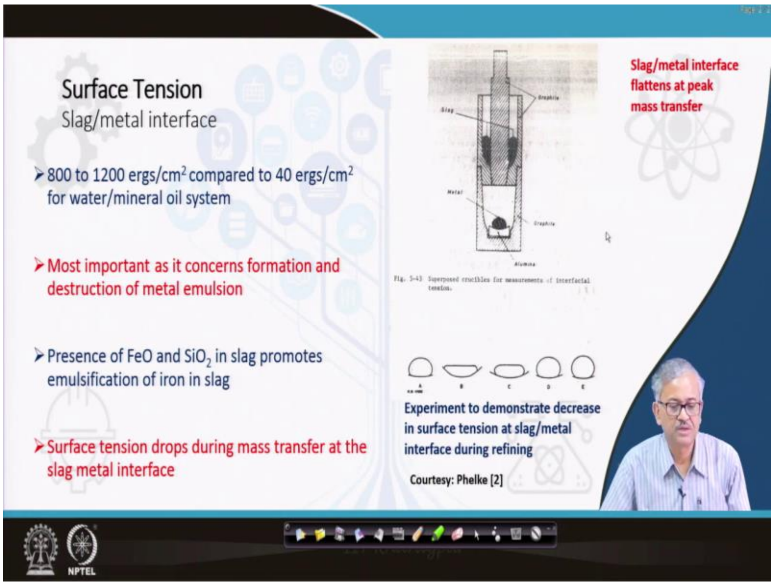
Now, see the formation and stability of the emulsion. Now, formation of emulsion requires energy. Why it requires energy? Because when you are making the droplet, you are just tearing the liquid metal and creating a new surface. As a result, you have to provide energy, the surface energy. So, that is why formation of emulsion requires energy and oxygen jet is continuously pumping the energy for generating this liquid droplets, and throwing them into the slag phase. So, formation of emulsion requires energy and you are getting it from the oxygen lancing. But its destruction is spontaneous. Why collapse of emulsion is spontaneous? Because in the emulsion you have droplets and small bubbles with lots of surface area and associated surface energy. So, emulsion is a very high energy product;

and always it will try to collapse and go to the nominal slag metal interface by minimizing its energy.

So how to stabilize this emulsion? What are the factors that can stabilize the emulsion?There are 3 factors: one is the surface tension at different interfaces like slag-metal interface, slag-gas interface, metal-gas interface. And if these surface tension forces are higher, then the surface energy also will be higher and emulsion will be much less stable. So, your aim should be to reduce the surface tension at all interfaces.

And apparent viscosity of slag is also another factor. If slag viscosity is higher, then the gas bubbles and the liquid droplets will have more residence time due to enhanced drag force.

Thirdly, the most important thing is the gas generation by the decarburization; because when the bath gets decarburized CO bubbles forms and that CO bubbles basically stabilizes the foam by buoyancy. Since bubble essentially escape to atmosphere, a continuous supply because CO bubble will ensure the emulsion stabilization. (Refer Slide Time: 23:48)



Surface Tension
Slag/metal interface

- 800 to 1200 ergs/cm^2 compared to 40 ergs/cm^2 for water/mineral oil system
- Most important as it concerns formation and destruction of metal emulsion
- Presence of FeO and SiO_2 in slag promotes emulsification of iron in slag
- Surface tension drops during mass transfer at the slag metal interface

Slag/metal interface flattens at peak mass transfer

Fig. 5-43 Superposed crucibles for measurements of interfacial tension.

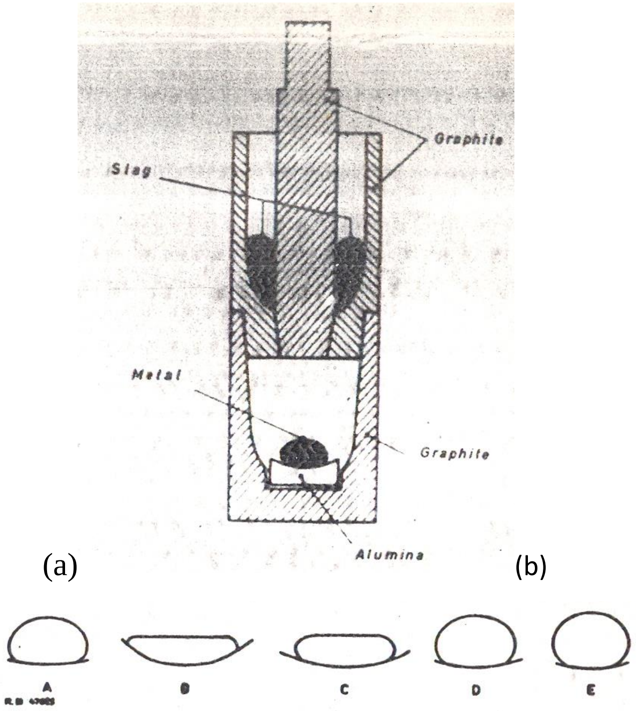
Experiment to demonstrate decrease in surface tension at slag/metal interface during refining

Courtesy: Phelke [2]

Let us now examine what are the surface tension of different interfaces. For example, if we consider the slag-metal interface, the value of surface tension is 800 to 1200 ergs per centimeter square.And if we compare this value with water- mineral oil system, a low temperature analogue of metal-slag system, it is only 40 ergs per centimeter square. slag-metal interface is most important, as it concerns the formation formation and destruction of metal emulsion; because if surface tension is less, then it is easier to generate the droplets, and again if the surface tension is less then also the total energy in emulsion will be less and stability of the emulsion will also be higher.

Presence of the FeO and SiO_2 in the slag has been found to emulsify the iron better in the slag. Both FeO and SiO2 are surface active compounds and modify the slag-metal interface for better emulsification of iron in slag.

And most importantly, it has been found by experiment that the surface tension decreases significantly during the impurity transfer across the slag-metal interface. Figure 31.3 (a) shows the experimental setup. A metal droplet is taken in an alumina crucible and then slag is allowed to fall on it. Thereafter the contact angle of the metal slag interface is monitored. Figure 31.3(b) shows the evolution of contact angle at slag-metal interface with time. It is found that initially the metal droplet is round with high contact angle between metal-gs interface. When slag poured over it and time passes, the contact angle at slag-metal interface decreases and the interface flattens and it becomes almost horizontal at peak mass transfer and then onwards again the contact angle starts increasing. Finally when the mass transfer is over the metal droplet regains its spherical shape.



(a) (b)

Figure 31.3 (a) the experimental setup, (b) the evolution of contact angle between slag metal interface during impurity transfer[2]

So, during the refining process, the surface tension at slag-metal interface decreases significantly, that helps in reducing the emulsion surface energy and helps in stabilizing it. Besides, presence of FeO and SiO2 also enhances the emulsification of iron in slag.

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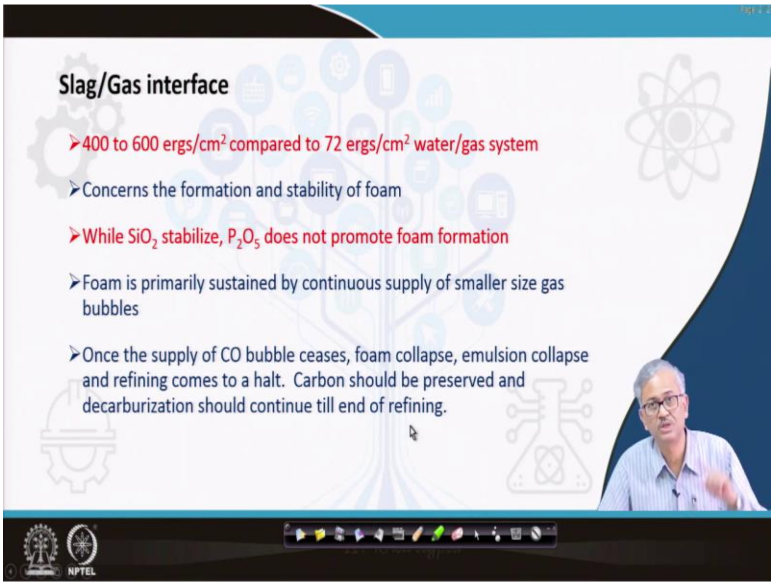

Slag/Gas interface

- ➢400 to 600 ergs/cm^2 compared to 72 ergs/cm^2 water/gas system
- ➢Concerns the formation and stability of foam
- ➢While SiO_2 stabilize, P_2O_5 does not promote foam formation
- ➢Foam is primarily sustained by continuous supply of smaller size gas bubbles
- ➢Once the supply of CO bubble ceases, foam collapse, emulsion collapse and refining comes to a halt. Carbon should be preserved and decarburization should continue till end of refining.

Now let us consider the gas-slag interface. For slag-gas interface also interfacial tension not very low and of the order of 400 to 600 ergs per centimeter square. If you compare this value to 72 ergs per centimeter square for the water-gas system; this is also quite high.And it concerns the formation and stability of the foam. And it has also again be found that SiO 2 promote foam formation, while P_2O_5 does not.

And finally, the foam is primarily sustained by the continuous supply or small sized bubbles; because at steady state a large amount of bubbles are required to sustain foam by buoyancy.. So, as long as CO bubbles are there foam is stabilized as well as emulsion is stabilized. When foam collapse, emulsion will also collapse.

So, in case of the LD refining carbon has to be preserved to the end of the process, such that decarburization continue to the end and it sustain the foam as well as emulsion.. Once the supply of CO bubbles ceases, foam collapse, emulsion collapse and refining comes to a halt.

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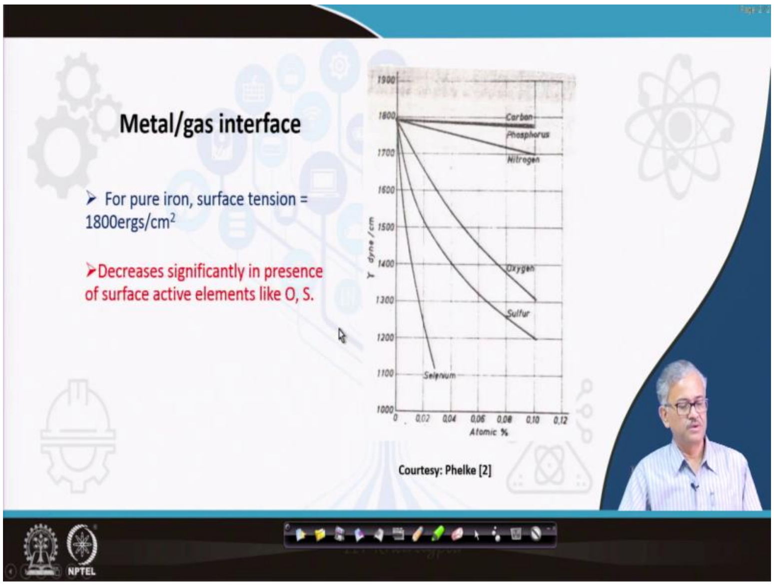

Metal/gas interface

- For pure iron, surface tension = 1800ergs/cm^2
- Decreases significantly in presence of surface active elements like O, S.

Courtesy: Phelke [2]

Finally, examine the metal-gas interface; for pure iron, the surface tension is 1800 ergs per meter square. The surface tension at metal-gas interface can be reduced significantly by using the surface active element.

Figure 31.4 shows the variation of surface tension at the liquid iron-gas interface in presence of oxygen and sulphur dissolved in liquid iron.

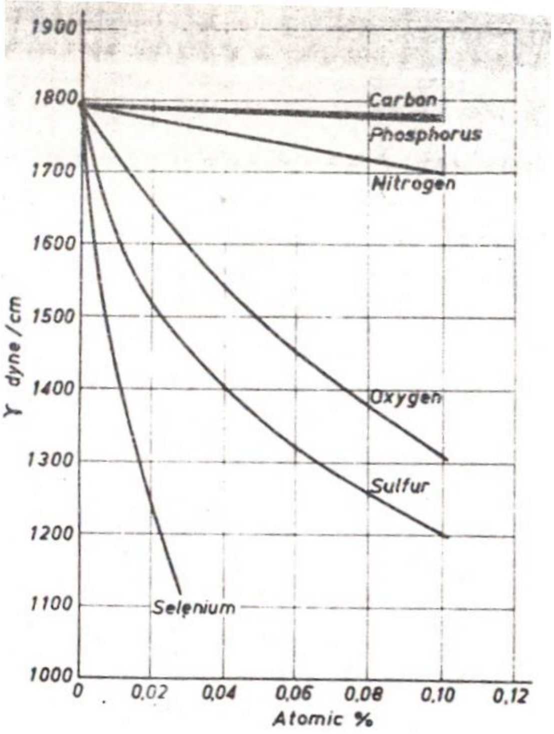

Figure 31.4: variationof surface tension of liquid iron-gas interface in presence of surface active elements like oxygen and Sulphur [2]

Oxygen and Sulphur are surface active elements and in their presence surface tension at liquid iron-gas interface is fund to decrease from 1800 to 1200 dynes/cm. So, with oxygen, this value drops from 1800 to 1300 at oxygen atomic percent of 0.1 dissolved in liquid iron. Similrly, in presence of sulphur, with same concentration of sulphur in liquid iron(0.1 atomic percentage) the value drops to 1200 dynes/cm.

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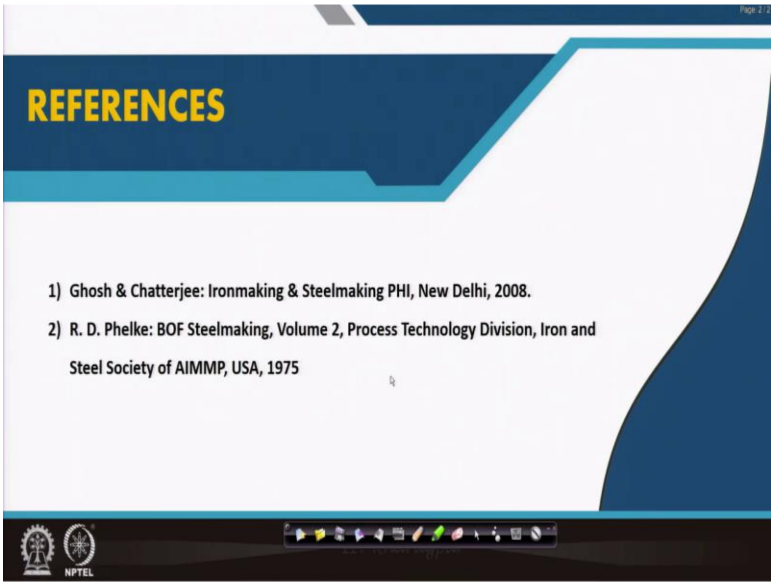

REFERENCES

1) Ghosh & Chatterjee: Ironmaking & Steelmaking PHI, New Delhi, 2008.
2) R. D. Phelke: BOF Steelmaking, Volume 2, Process Technology Division, Iron and Steel Society of AIMMP, USA, 1975

Reference 3. R.H. Tupkary: Modern Steelmaking, Khanna publishers.

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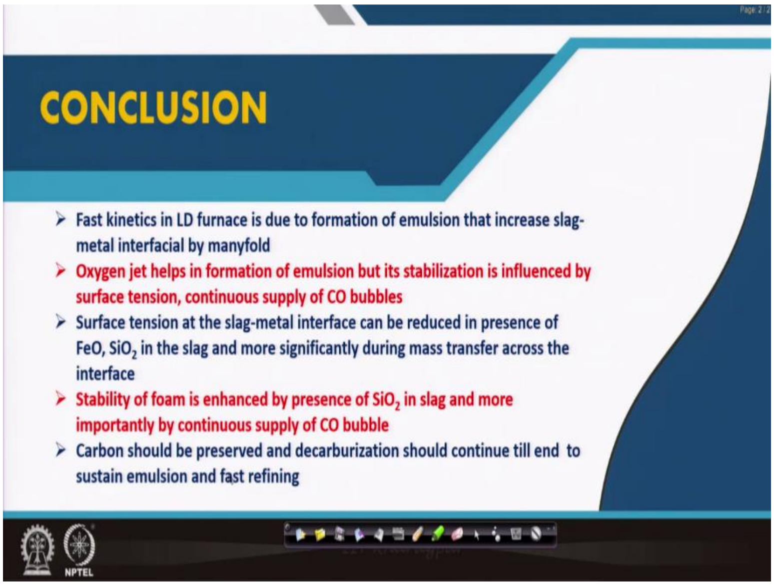

CONCLUSION

- Fast kinetics in LD furnace is due to formation of emulsion that increase slag-metal interfacial by manyfold
- Oxygen jet helps in formation of emulsion but its stabilization is influenced by surface tension, continuous supply of CO bubbles
- Surface tension at the slag-metal interface can be reduced in presence of FeO, SiO_2 in the slag and more significantly during mass transfer across the interface
- Stability of foam is enhanced by presence of SiO_2 in slag and more importantly by continuous supply of CO bubble
- Carbon should be preserved and decarburization should continue till end to sustain emulsion and fast refining

Conclusion: The super first kinetics in the LD furnace is due to formation of emulsion that increases the slag metal interfacial by many-fold. And the oxygen jet help in formation of the emulsion and its stabilization is influenced by the surface tension at various heterogeneous interfaces and continuous supply of CO gas bubble through decarburization.

The surface tension in the slag-metal interface decreases significantly during refining. FeO and SiO_2 in slag also helps in emulsifying the metal in slag.

In case of the foam (gas-slag interface) it is the continuous supply of the CO bubble that is important. SiO_2 in the slag also stabilizes foam.

Surface tension in the metal-gas interface decreases significantly in presence of surface active element like oxygen and Sulphur.

Finally, continuous supply of CO bubble can stabilize the emulsion and therefore, we should have a proper blowing practice, such that decarburization can be controlled most efficiently and economically and carbon remains to the end of the process.