Iron Making and Steel Making

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Module – 06

Lecture 27

Properties of Slag

In this lecture I will talk about the properties of slags.

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CONCEPTS COVERED

- Structure of slag and basicity
- Oxidation property of slag
- Viscosity of slag

Because steelmaking represents slag metal reaction, we need to understand the stag structure and the slag properties. So, first we will discuss about the structure of the slag and subsequently the concept of basicity, oxidation potential of the slag and viscosity of the slag will be discussed.

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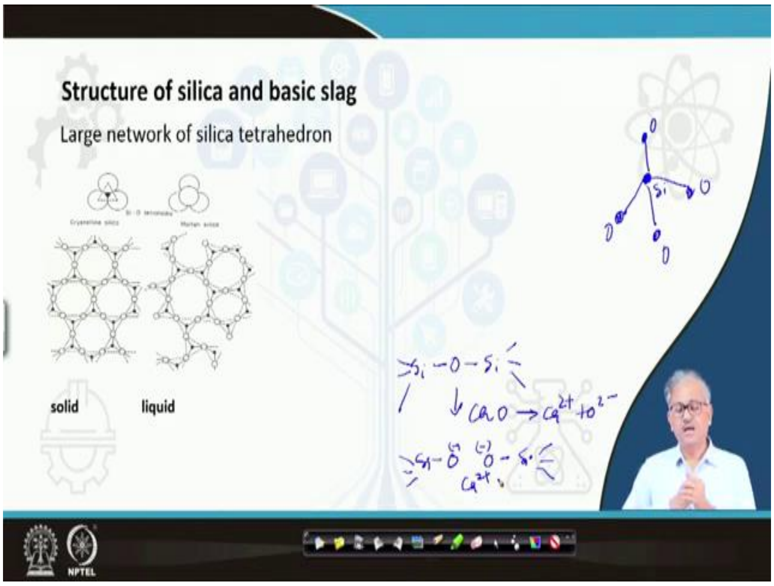


Structure of silica and basic slag

Large network of silica tetrahedron

$$>Si-O-Si<$$

$$\downarrow CaO \rightarrow Ca^{2+} + O^{2-}$$

$$>Si-\overset{(-)}{O}\ \ \overset{(-)}{O}-Si<$$

$$Ca^{2+}$$

Since silica is one of the major acidic constituents of the steelmaking slag, let us discuss its structure and how it evolve in presence of another major basic constituents of slag like lime (CaO).

Now, silica forms a large polymeric network of silica tetrahedron. In each silica tetrahedron silica is seating at the core and four oxygen atoms at four corners of the tetrahedron connected through covalent bonds (see Figure 27.1). In liquid silica also such polymeric network is maintained and only some bonds might be broken. As a result, usually the silica melt is very viscous with higher liquidus.

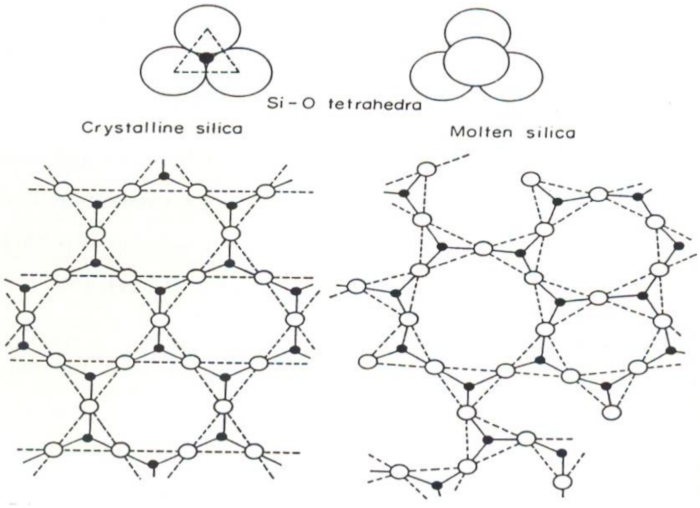


Figure 27.1 Schematics of silica network [1,3]

Let us see, how such silica networks evolves in presence of lime. Lime depolymerize the silica network by breaking the bonds. With increase in lime the polymeric network breaks and become simpler. How do they do that? In slag CaO ionize completely to calcium cation and oxygen anion following equation (27.1) and supplies the oxygen anions to the silica structure to break a bond. When bond breaks one electron on oxygen become free making it $O^{(-)}$. The cation neutralize the two negative charge on two free oxygen atoms, as shown in Figure (17.2).

$$CaO = Ca^{2+} + O^{2-} \tag{17.1}$$

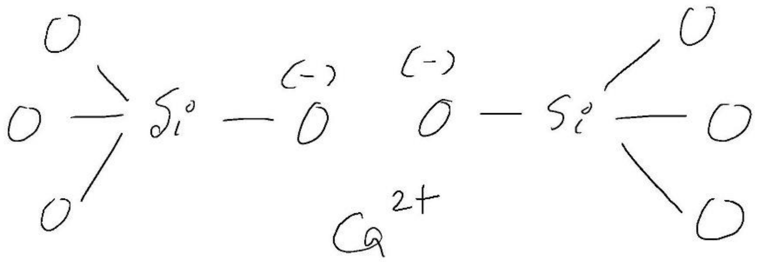
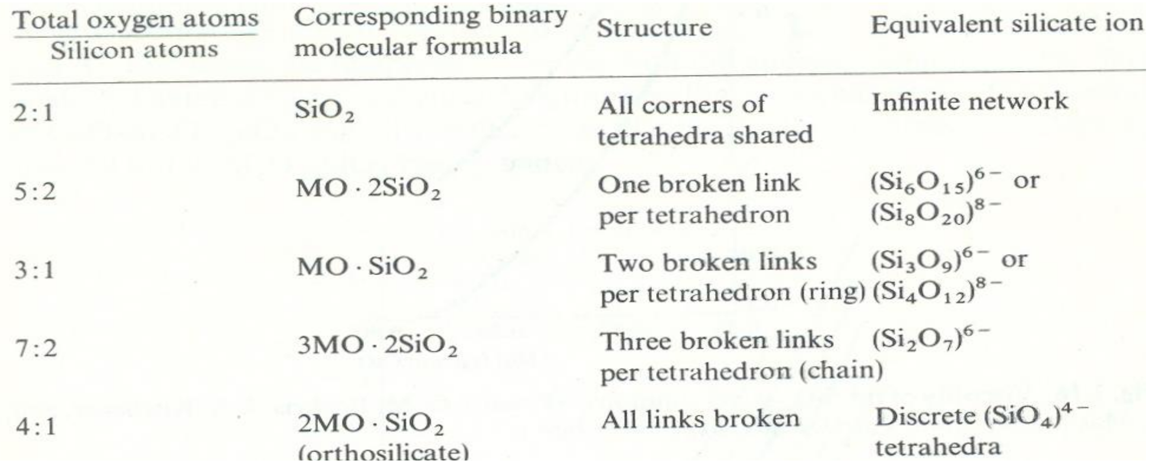


Figure 27.2: Schematically showing the single bond breaking in silica network in presence of lime

Number of bond breaking depends on the CaO/SiO_2 ration or O/Si ratio. When, CaO/SiO_2 ratio is 1:2, or O/Si ratio is 5:2, then only one bond breaks. As these ratio increases, the number of bond breaking increases. When the CaO/SiO2 ratio is 1:1 and O/Si is 3:1, two bonds break and the anionic complexes also simplify as shown in Table (17.1).

Table 17.1 Evolution of silica structure with addition of basic oxide (MO). In case of lime as basic oxide, M represents Ca[4].



Total oxygen atoms / Silicon atoms	Corresponding binary molecular formula	Structure	Equivalent silicate ion
2:1	SiO_2	All corners of tetrahedra shared	Infinite network
5:2	$MO \cdot 2SiO_2$	One broken link per tetrahedron	$(Si_6O_{15})^{6-}$ or $(Si_8O_{20})^{8-}$
3:1	$MO \cdot SiO_2$	Two broken links per tetrahedron (ring)	$(Si_3O_9)^{6-}$ or $(Si_4O_{12})^{8-}$
7:2	$3MO \cdot 2SiO_2$	Three broken links per tetrahedron (chain)	$(Si_2O_7)^{6-}$
4:1	$2MO \cdot SiO_2$ (orthosilicate)	All links broken	Discrete $(SiO_4)^{4-}$ tetrahedra

The anionic complexes preferentially form ring structures (Figure 27.3) and becomes simpler with increase in CaO/SiO2 ratio.

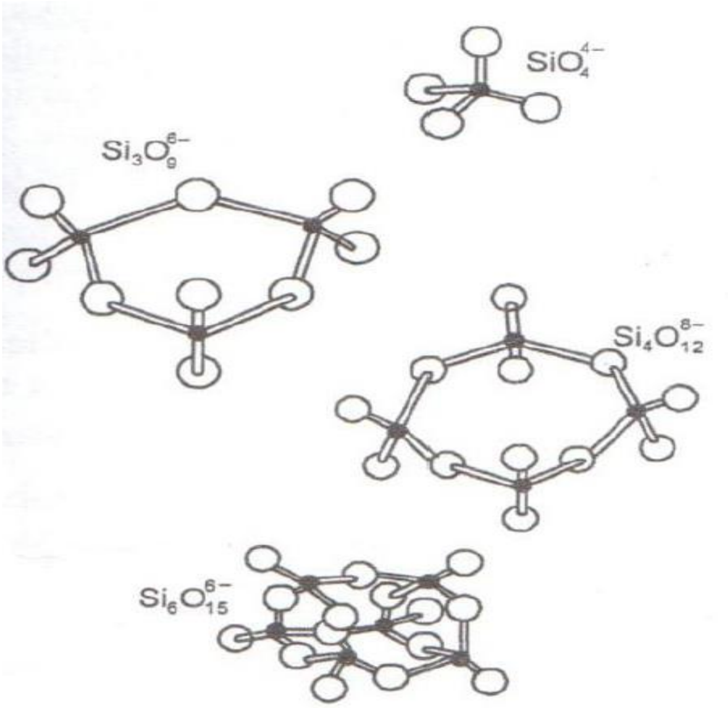


Figure 27.3: Anionic complexes in ring structures[3]

When the CaO/SiO_2 ratio becomes 3:2, or O/Si becomes 7:2, three bonds are broken (liner structure) and finally when the CaO/SiO_2 ratio becomes 2:1, or O/Si becomes 4:1, all four bonds are broken and the simplest anion of silica appears in the form SiO_4^{4-} (Figure 27.4)

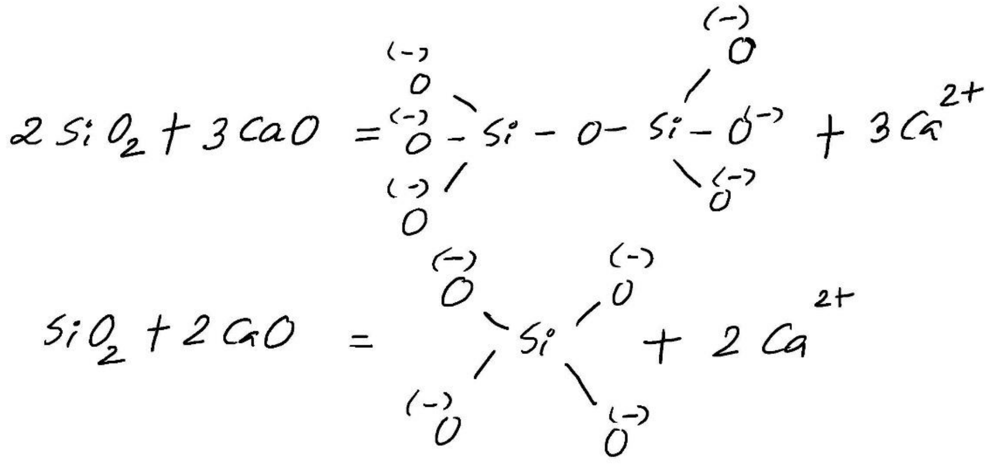


Figure 27.4 Equations showing the bond breaking at O/Si ratio of 7:2 and 4:1.

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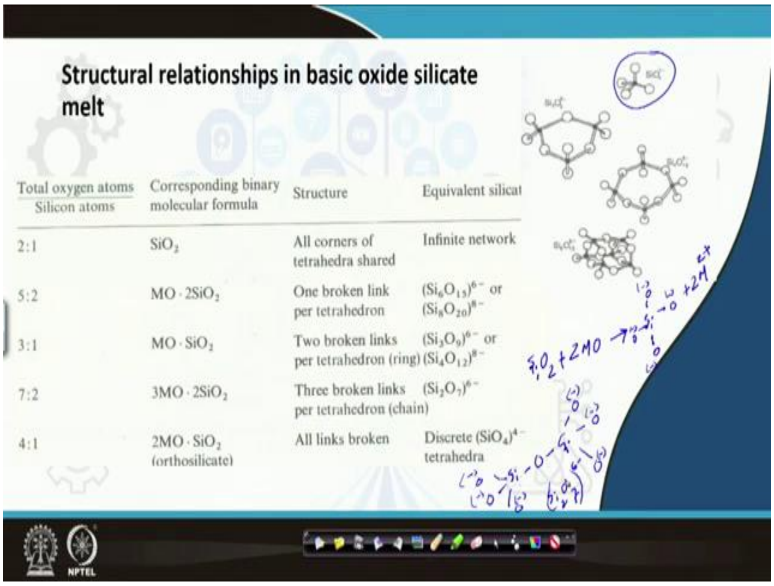

Structural relationships in basic oxide silicate melt

Total oxygen atoms / Silicon atoms	Corresponding binary molecular formula	Structure	Equivalent silicat
2:1	SiO_2	All corners of tetrahedra shared	Infinite network
5:2	$MO \cdot 2SiO_2$	One broken link per tetrahedron	$(Si_6O_{15})^{6-}$ or $(Si_8O_{20})^{8-}$
3:1	$MO \cdot SiO_2$	Two broken links per tetrahedron (ring)	$(Si_3O_9)^{6-}$ or $(Si_4O_{12})^{8-}$
7:2	$3MO \cdot 2SiO_2$	Three broken links per tetrahedron (chain)	$(Si_2O_7)^{6-}$
4:1	$2MO \cdot SiO_2$ (orthosilicate)	All links broken	Discrete $(SiO_4)^{4-}$ tetrahedra

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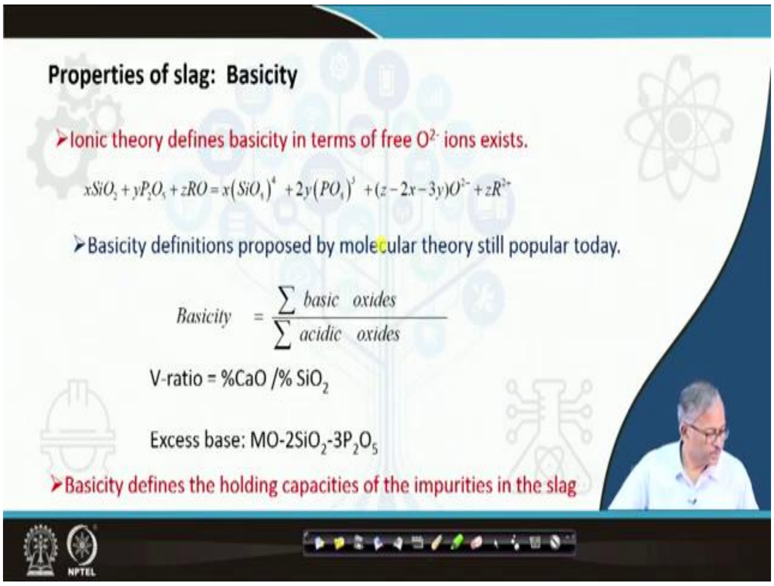


Properties of slag: Basicity

- Ionic theory defines basicity in terms of free O^{2-} ions exists.

$$xSiO_2 + yP_2O_5 + zRO = x(SiO_4)^{4} + 2y(PO_4)^{3} + (z-2x-3y)O^{2-} + zR^{2+}$$

- Basicity definitions proposed by molecular theory still popular today.

$$Basicity = \frac{\sum basic \quad oxides}{\sum acidic \quad oxides}$$

V-ratio = %CaO /% SiO_2

Excess base: MO-2SiO_2-3P_2O_5

- Basicity defines the holding capacities of the impurities in the slag

Now, let us discuss about the properties of slag.. Basicity of slag is a measure of its holding capacity for impurities in the slag. According to ionic theory, basicity is defined in terms of the free oxygen ion activity, which is defined by the equation (27.2).

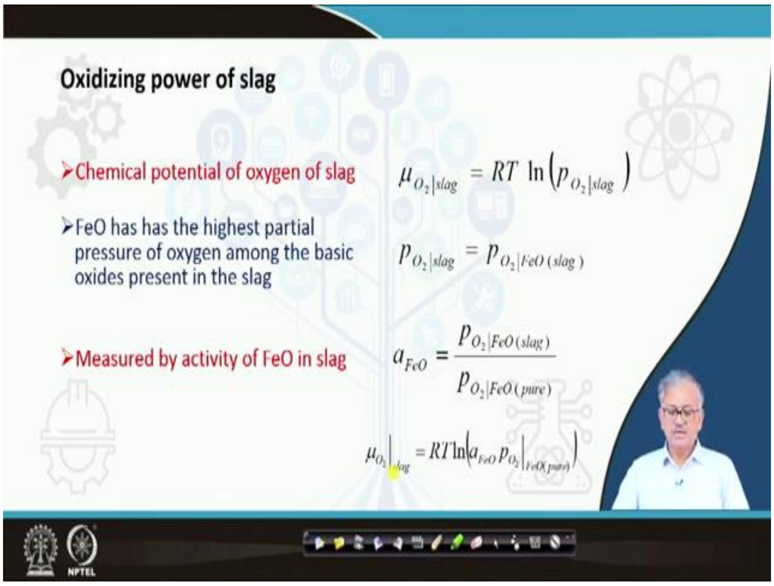
$$xSiO_2 + yP_2O_5 + zRO = x\left(SiO_4\right)^{4-} + 2y\left(PO_4\right)^{3-} + (z-2x-3y)O^{2-} + zR^{2+} \tag{27.2}$$

The equation represents free oxygen ion available after complete reaction in a slag containing x moles of SiO_2, y moles P_2O_5 and z moles of CaO. x moles of SiO_2 requires 2x moles of CaO for its complete depolymerization, forming the simplest anionic complex SiO_4^{4-}. Similarly, y moles of P_2O_5 will require 3y moles of CaO. After complete neutralization, the free oxygen anions available will be given by (z-2x-3y), which is defined as the basicity.

According to molecular theory of slag, where neutral compounds are supposed to exists in slag, the basicity may be defined in various ways. The simplest definition is represented as the ratio of summation of all basic oxides to the summation of acidic oxides. It is called the common basicity; but it is not a very proper definition of basicity because all the basic oxide are not are not equally efficient to retain the impurity oxides in the slag or the oxygen ion activity will not be similar for all the basic oxides. Such common basicity also fails to correlate the holding capacity of slag for impurities.

The second definition of basicity by molecular theory is called the V-ratio, defined as the ratio of CaO/SiO_2. This is found to be very effective definition because CaO is the most effective and major constituents of basic oxides in slag and SiO_2 is also the most influencing and major acid oxides in the slag. This definition is very popular in the industry.

The other basicity index by molecular theory is called the excess base and it is defined as total moles of lime minus twice the moles of SiO_2 minus thrice the moles of P_2O_5in slag. This definition is quite similar to the definition of oxygen ion activity in slag. Such definition has been found to correlate the phosphate capacity of slag quite reasonably; while common basicity fails to do so. (Refer Slide Time: 18:43)



Oxidizing power of slag

- Chemical potential of oxygen of slag $\mu_{O_2|slag} = RT\ \ln\left(p_{O_2|slag}\right)$
- FeO has has the highest partial pressure of oxygen among the basic oxides present in the slag $p_{O_2|slag} = p_{O_2|FeO(slag)}$
- Measured by activity of FeO in slag $a_{FeO} = \frac{p_{O_2|FeO(slag)}}{p_{O_2|FeO(pure)}}$

$$\mu_{O_2}\Big|_{slag} = RT\ln\left(a_{FeO}\,p_{O_2}\Big|_{FeO(pure)}\right)$$

Next important property of slag is the oxidizing power of the slag. Oxidizing power of the slag can be expressed in terms of chemical potential of oxygen of the slag, defined by equation (27.3)

$$\mu_{O_2}\big]_{slag} = RTln\left(p_{O_2}\big]_{slag}\right) \tag{27.3}$$

where $p_{O_2}\big]_{slag}$ represents the partial pressure of oxygen that exists in equilibrium with the slag. The major constituents of steel making slag are SiO_2, CaO, FeO and P_2O_5, MnO, MgO are also present. Interestingly, if you have a look at the Ellingham diagram, you can find that iron oxide is placed much above compared to the other oxides like CaO, SiO_2, MnO, MgO; and although P_2O_5 is very close to FeO in pure state, but under basic steel making condition P_2O_5 line dips much much below than that of FeO. So, FeO is the least stable with highest partial pressure of oxygen among other oxides present in the slag. So, the partial pressure oxygen that will be in equilibrium with the iron oxide that will eventually be in equilibrium with the rest of the oxides present in the slag. So, partial pressure of oxygen in equilibrium with the slag may be estimated by calculating the partial pressure of oxygen that will be in equilibrium with FeO in slag (equation 27.4)

$$p_{O_2|slag} = p_{O_2|FeO(slag)} \tag{27.4}$$

The RHS of equation (27.4) may further be expressed in terms of activity of FeO in the slag, from definition of activity as follows (Equation 27.5).

$$a_{FeO} = \frac{p_{O_2|FeO(slag)}}{p_{O_2|FeO(pure)}} \tag{27.5}$$

The denominator in the equation (27.5) represents the partial pressure of oxygen that will remain in equilibrium with the FeO pure, which is known. So, the numerator of the equation (27.5), can be known by knowing the activity of FeO in slag and finally the chemical potential of oxygen of slag may be estimated by the equation (27.6).

$$\mu_{O_2}\Big|_{slag} = RT\ln\left(a_{FeO}\, p_{O_2}\Big|_{FeO(pure)}\right) \tag{27.6}$$

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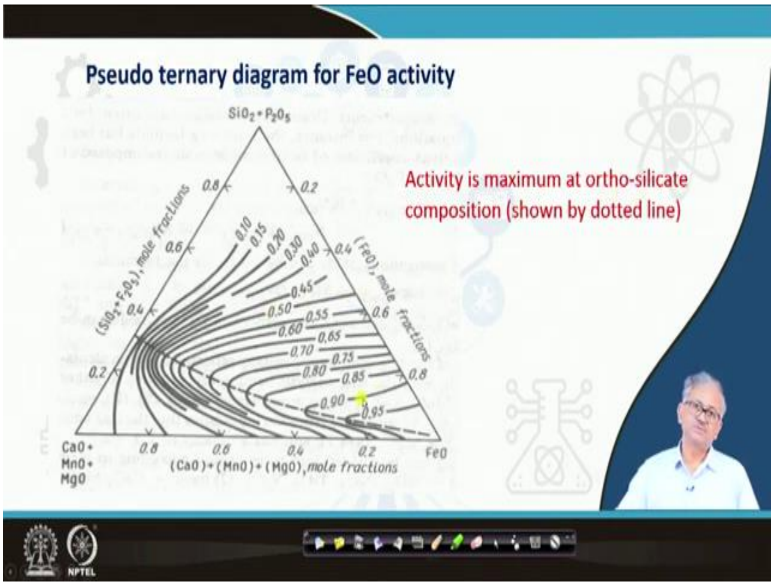

Pseudo ternary diagram for FeO activity

Activity is maximum at ortho-silicate composition (shown by dotted line)

Activity of FeO at different slag compositions is reported in literature in terms of iso-activity line of FeO in pseudo ternary diagram (Figure 27.5).

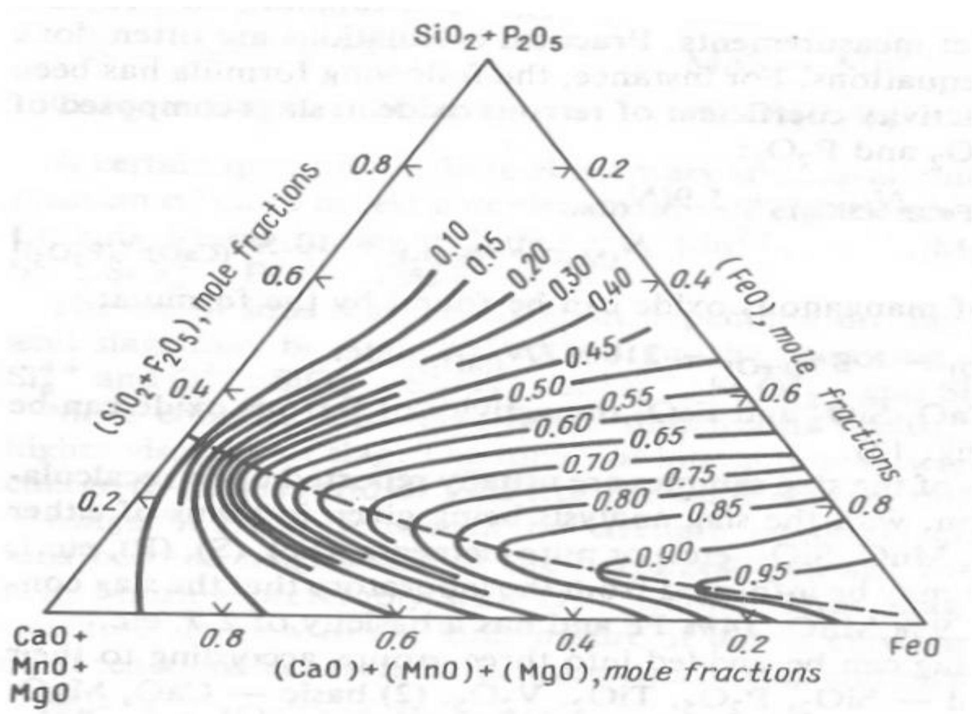

Figure 27.5: Pseudo-ternary diagram showing the iso-activity lines for FeO[2]

The dotted line in the figure refers to the composition of the di-calcium silicate ($2CaO.SiO_2$), where CaO is completely engaged in the silica structure forming the simplest silica anion (SiO_4^{4-}), where FeO is relatively free and showing maximum activity of FeO.

This diagram may be used to calculate the activity of FeO in steel slag of certain composition, which will finally yield the oxidation potential of the slag.

So, activity of FeO in slag primarily defines the potential of slag towards oxygen supply for impurity oxidation; in other words the oxygen potential of slag. While activity of CaO, or free oxygen ion in the slag defines the potential of the slag to retain the impurities in it.

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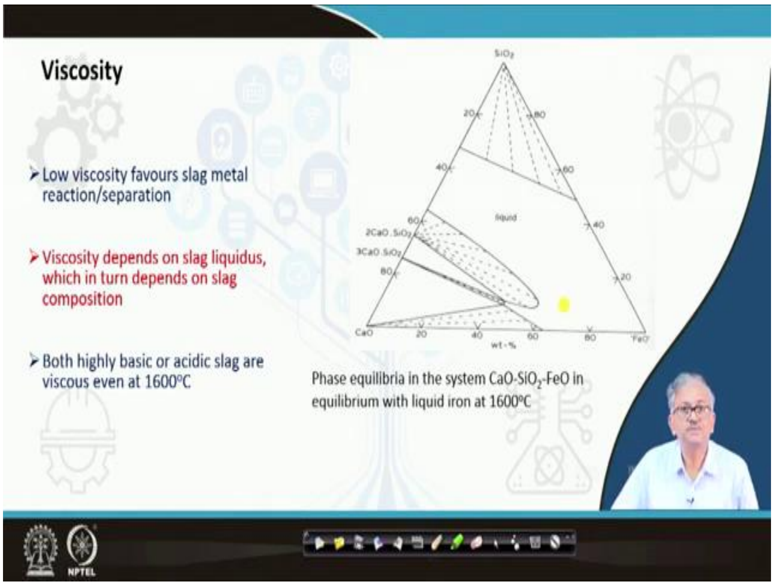

Viscosity

- Low viscosity favours slag metal reaction/separation
- Viscosity depends on slag liquidus, which in turn depends on slag composition
- Both highly basic or acidic slag are viscous even at 1600°C

Phase equilibria in the system CaO-SiO_2-FeO in equilibrium with liquid iron at 1600°C

Now, come to the viscosity. Viscosity is another very important property of the slag because slag has to be fluid to assist the mass transport of species through slag and more importantly to facilitate slag/metal separation.

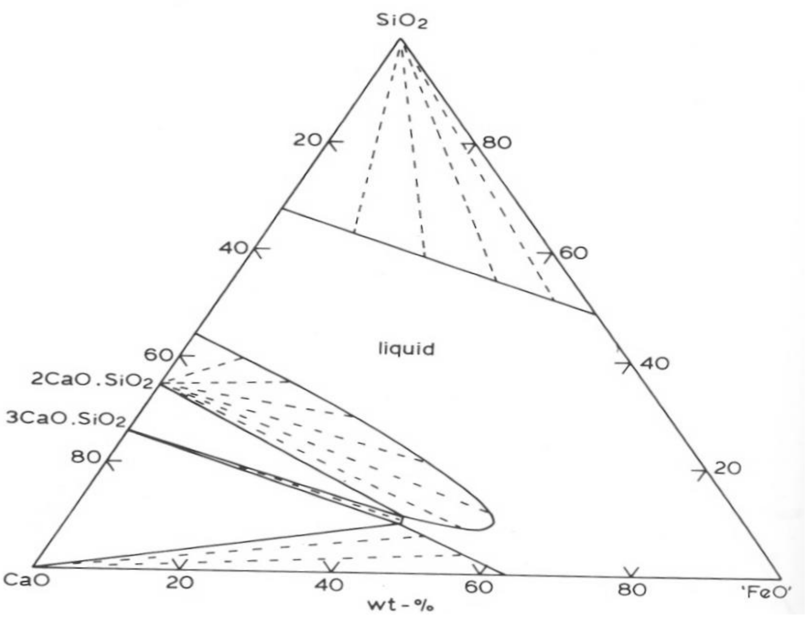

Figure 27.6: Slag liquidus in ternary diagram constituted by three major constituents of steelmaking slag[1,2]

Slag liquidus has to be low to make the slag fluid, which in turn depends on the composition of the slag. The liquidus of slag at various composition of slag is presented in the ternary diagram (Figure 27.6).

It is seen that there is a wide area for liquid zone. Slag is viscous, or semi-solid at higher activity of silica or CaO in the slag; otherwise rest of the regions are liquid. Such wide liquid region allows us to operate the slag in a wide range of basicity (V-ratio in the range 2 to 4). This is in contrast to the narrow window of operation for blast furnace slag, which restricted the basicity of the slag in the range 1 to 1.2 only.

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REFERENCES

1) E. T. Turkdagon: Fundamental of Steelmaking, Institute of Materials, London, 1996, 188
2) Ghosh & Chatterjee: Ironmaking & Steelmaking PHI, New Delhi, 2008.
3) H. S. ray: Introduction to melts, molten salts, slag & glasses, Allied publishes Pvt. Ltd., Kolkata, 2006

The references are given above. One more reference is missed there. (4) Geiger & Poirier: Transport phenomena in Metallurgy

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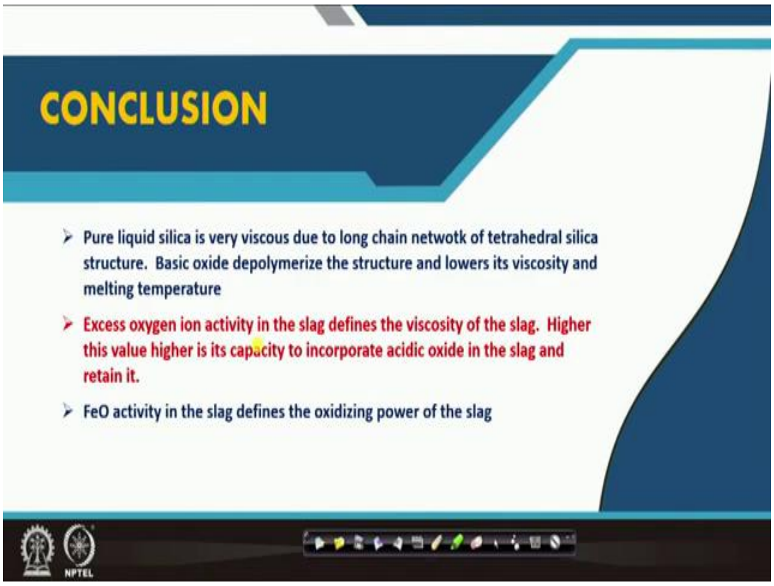
CONCLUSION

- Pure liquid silica is very viscous due to long chain netwotk of tetrahedral silica structure. Basic oxide depolymerize the structure and lowers its viscosity and melting temperature
- Excess oxygen ion activity in the slag defines the viscosity of the slag. Higher this value higher is its capacity to incorporate acidic oxide in the slag and retain it.
- FeO activity in the slag defines the oxidizing power of the slag

Conclusion: Pure liquid silica is very viscous due to long chain network of individual tetrahedral silica and basic oxide depolymerize the silica structure and make it less viscous and fluid. The simplest silica anion after complete breakup of the silica structure is SiO_4^{4-}

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Three major properties of the slag are basicity, oxidation potential and viscosity. Basicity defines the holding capacity of slag for the impurities and it is represented by oxygen ion activity in slag (according to ionic theory). Another definition of basicity that is more popular in industry (based on molecular theory) is called the V-ratio (CaO/SiO2), defined the ratio of the two major and influential constitutents like CaO and SiO_2. The simple minded definition of slag basicity by the ratio of summation of all basic oxides to acidic oxides does not correlates to the holding capacity of the slag for impurities. Because all basic oxides are not equally efficient to hold the impurities in slag. CaO is most efficient followed by MgO and FeO is the least.

Since FeO is the least stable oxide among all the oxides present in steelmaking slag, with maximum partial pressure of oxygen, activity of FeO in slag rather defines the oxygen potential of the slag.

A fluid slag is efficient for mass transfer of species through slag and most importantly it allows easy separation of liquid slag and metal. Fluidity of slag depends on viscosity, which in turn depends on the slag composition. It is found that there exists a wide operating window for fluid slag, where basicity of the slag can safely be maintained in the range between 2- 4 , which is required for steelmaking.