Iron Making
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Lecture - 25
Iron Making Lecture 25

Now we will focus on manganese reaction after silicon reaction.

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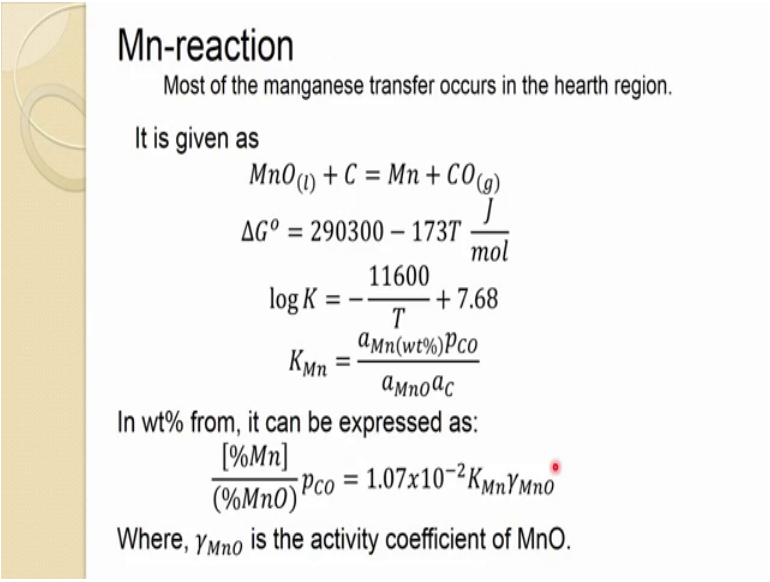

Mn-reaction

Most of the manganese transfer occurs in the hearth region.

It is given as

$$MnO_{(l)} + C = Mn + CO_{(g)}$$

$$\Delta G^o = 290300 - 173T \frac{J}{mol}$$

$$\log K = -\frac{11600}{T} + 7.68$$

$$K_{Mn} = \frac{a_{Mn(wt\%)} p_{CO}}{a_{MnO} a_C}$$

In wt% from, it can be expressed as:

$$\frac{[\%Mn]}{(\%MnO)} p_{CO} = 1.07x10^{-2} K_{Mn} \gamma_{MnO}$$

Where, γ_{MnO} is the activity coefficient of MnO.

So, most of the manganese transfer occurs in the hearth region; however, the higher oxide get reduced to amino in the ore by the time it comes to the bosh region, but transfer of manganese mostly it occurs in the hearth region a little bit it can occur in the dropping zone, when it comes in contact with liquid iron, but not really that much.

So, in the hearth region this is given as manganese oxide plus carbon which is there in dissolved form in the iron, keep to manganese and CO. The free energy of this reaction is given in this and equilibrium constant of the reaction is given in this form and this k the rate constant for this equation can be expressed in this term and in weight percentage form usually activity of carbon if it is saturated with the iron is saturated with the carbon, then activity of carbon can be taken h 1.

So, and this one converting into the weight percentage it can be written in this form. So, where gamma m no the activity coefficient of manganese, and sometimes this is also known as the fugacity. Value of this can be calculated at various temperatures which are available in various references. So, I am not going too much into the detail of this is a part of a physical chemistry or I hope you might have studied a little bit about reaction kinetic parts in steelmaking or the separate course.

So, I will not be talking much about this, and I assumed you know how these quantities are defined and how to calculate them.

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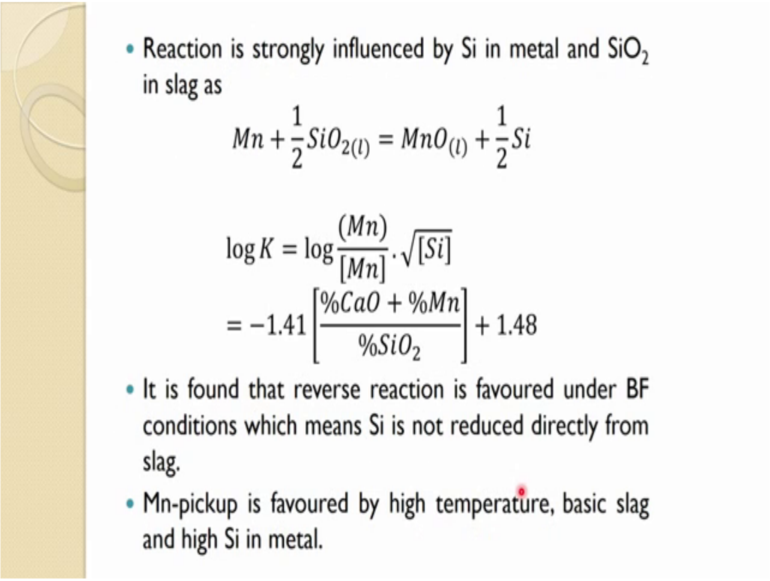

- Reaction is strongly influenced by Si in metal and SiO_2 in slag as

$$Mn + \frac{1}{2}SiO_{2(l)} = MnO_{(l)} + \frac{1}{2}Si$$

$$\log K = \log\frac{(Mn)}{[Mn]}\cdot\sqrt{[Si]}$$
$$= -1.41\left[\frac{\%CaO + \%Mn}{\%SiO_2}\right] + 1.48$$

- It is found that reverse reaction is favoured under BF conditions which means Si is not reduced directly from slag.
- Mn-pickup is favoured by high temperature, basic slag and high Si in metal.

This reaction also manganese reaction is strongly influenced by silicon in the metal and SiO 2 in the slag which is again expressed as M n plus half SiP 2. So, MnO plus half Si those silicon does not reduce that much by this reaction that we will see later so on.

So, the reaction constant for this is given by this equation and in terms of this is really nothing like you are the basicity of the. So, sometimes this one is defined at a percentage of CaO plus percentage of manganese by percentage of SiO 2. So, this is its nothing like a basicity of the slag. So, there is a relation experimentally, it is found that this constant can be represent is using this relation also.

So, one once you substitute these values or the basicity you can get the value of k. So, it is found that the reverse reaction is favored under blast furnace conditions, which means silicon is not reduced directly from the slag. So, that is a sort of a reverse reaction is favored in blast furnace condition, in steelmaking it could be different manganese pickup is favored by high temperature.

Basic slag and high silicon content in the metal. So, these are the three condition which favored the magnet pickup and your hot metal.

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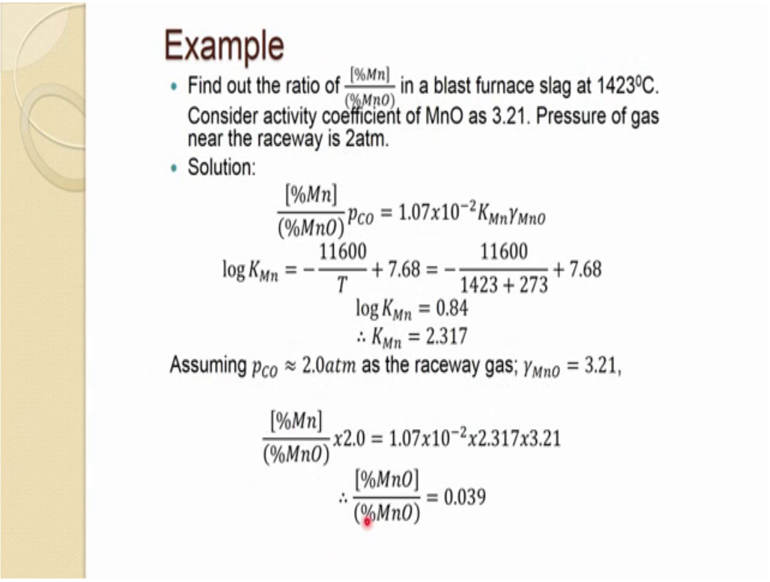

Example

- Find out the ratio of $\frac{[\%Mn]}{(\%MnO)}$ in a blast furnace slag at 1423⁰C. Consider activity coefficient of MnO as 3.21. Pressure of gas near the raceway is 2atm.
- Solution:

$$\frac{[\%Mn]}{(\%MnO)}p_{CO} = 1.07x10^{-2}K_{Mn}\gamma_{MnO}$$

$$\log K_{Mn} = -\frac{11600}{T} + 7.68 = -\frac{11600}{1423+273} + 7.68$$

$$\log K_{Mn} = 0.84$$

$$\therefore K_{Mn} = 2.317$$

Assuming $p_{CO} \approx 2.0atm$ as the raceway gas; $\gamma_{MnO} = 3.21$,

$$\frac{[\%Mn]}{(\%MnO)}x2.0 = 1.07x10^{-2}x2.317x3.21$$

$$\therefore \frac{[\%MnO]}{(\%MnO)} = 0.039$$

So, based on that we have one example here find out the ratio of manganese percentage in iron and a MnO percentage in slag in a blast furnace slag at 1423 3 degrees Celsius consider the activity coefficient of MnO as 3.21, pressure of gas near the raceway is about 2 atmosphere.

So, as we know the manganese transfers etcetera in this way in the hearth region; which forms the CO bubbles and the CO bubble if we neglect the hydrostatic pressure of the slag. So, pressure in that one can be assumed whatever pressure is pre is prevailing in near the respiration. So, pco can be assumed in like a two atmosphere, and using this equation we can easily calculate the percentage. So, this is which is reproduced here and what we need the convenient constant and this coulomb constant is given by this equation is mentioned, before and t is the temperature which is always of course, in degree Kelvin.

So, converting that into degree Kelvin and substituting the values essentially what we get it can I mean equilibrium constant value is 2.32 and now we got this. So, we can substitute these over here. Activity coefficient of MnO is given and as we mentioned the pco can be taken as two atmospheres, which is the pressure near the raceway.

So, substituting all these value that keeps the ratio is about 0.03 9.04. So, once you have this percentage. So, that is can gives you the manganese percentage sorry this is actually mn. So, manganese percentage in hot metal only suppose if this is a 5 percent say about 0.2 percent manganese in the hot metal. So, this is sort of an example by which one can calculate the weight percent of manganese in the hot metal giving the various conditions.

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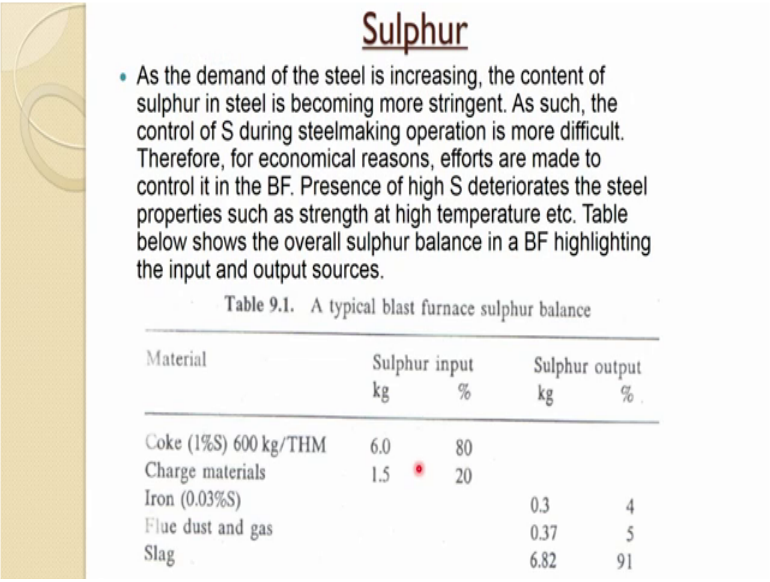

Sulphur

- As the demand of the steel is increasing, the content of sulphur in steel is becoming more stringent. As such, the control of S during steelmaking operation is more difficult. Therefore, for economical reasons, efforts are made to control it in the BF. Presence of high S deteriorates the steel properties such as strength at high temperature etc. Table below shows the overall sulphur balance in a BF highlighting the input and output sources.

Table 9.1. A typical blast furnace sulphur balance

Material	Sulphur input		Sulphur output	
	kg	%	kg	%
Coke (1%S) 600 kg/THM	6.0	80		
Charge materials	1.5	20		
Iron (0.03%S)			0.3	4
Flue dust and gas			0.37	5
Slag			6.82	91

Now, we move to another element, which is important in blast furnace and not in the blast furnace more also in steelmaking. So, that is sulphur as the demand of the steel is increasing the content of sulphur in steel is becoming more and stringent. So, separation is not desirable that much in steel in most of the steel. So, that between more stringent and a stringent as the demand of the steel is increasing.

As such the content of sulphur during the steel making operation is more difficult therefore, for economical reasons efforts are made to control in the blast furnace. So, presence of high sulphur deteriorate the steel property such as strength at high temperature etcetera, table below shows the overall sulphur balance in a blast furnace highlighting the input and output sources.

So, you get quite a lot sulphur from the coke if you assume 1 percent sulphur you get almost 6 kg and from the charge material, you get about 1.5 kg mostly it comes from iron and sometime from the flux also it comes. And sulphur out usually in the iron is about 0.3 and flue dust goes is.

So, 2.37 but most of the sulphur goes with the slag; so 6.82. So, 91 percent with the slag and about 4 percent with a iron and 5 percent goes into flue cases.

So, this is a typical sulphur balance in the blast furnace. So, as you can see most of the sulphur is absorbed by the slag or some amount of sulphur goes into iron and as we had mentioned sulphur is not desirable, in steelmaking that much and it is difficult also to remove sulphur though one can do the desulphurization action to remove the sulphur to very low level in steelmaking, but that is not that much economical.

However, in the blast furnaces I mentioned before it is not easy to control silicon sulphur and phosphorus though, still we try to reduce sulphur content in iron by other means sometimes you put it de sulphurising agent it during tapping interrupt and like that by which you can reduce it.

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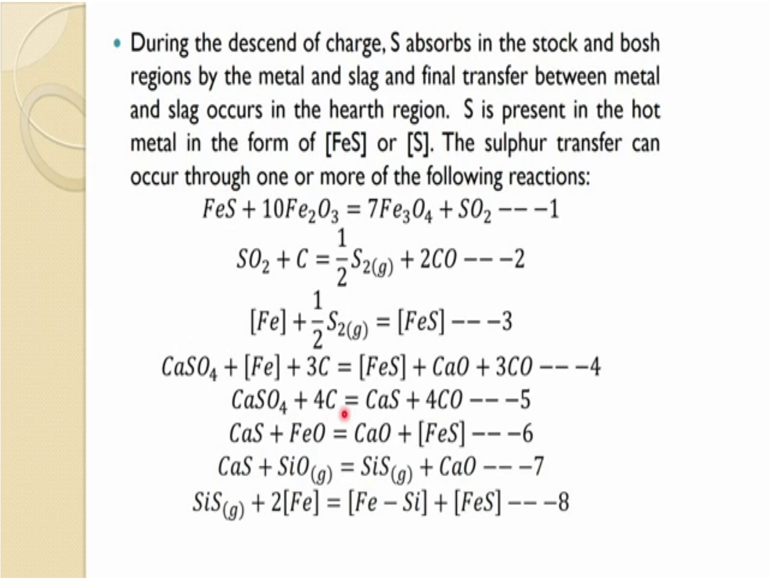

- During the descend of charge, S absorbs in the stock and bosh regions by the metal and slag and final transfer between metal and slag occurs in the hearth region. S is present in the hot metal in the form of [FeS] or [S]. The sulphur transfer can occur through one or more of the following reactions:

$$FeS + 10Fe_2O_3 = 7Fe_3O_4 + SO_2 --- 1$$

$$SO_2 + C = \frac{1}{2}S_{2(g)} + 2CO --- 2$$

$$[Fe] + \frac{1}{2}S_{2(g)} = [FeS] --- 3$$

$$CaSO_4 + [Fe] + 3C = [FeS] + CaO + 3CO --- 4$$

$$CaSO_4 + 4C = CaS + 4CO --- 5$$

$$CaS + FeO = CaO + [FeS] --- 6$$

$$CaS + SiO_{(g)} = SiS_{(g)} + CaO --- 7$$

$$SiS_{(g)} + 2[Fe] = [Fe - Si] + [FeS] --- 8$$

So, during the descent of charge sulphur absorbs in the stock and bosh region by the metal and slag.

So, its absorbs by both and final transfer between metal and slag occurs in the hearth region. So, sulphur is present in the hot metal in the form of iron sulphide or sulphur dissolve the sulphur transfer can occur through one of more of the following reaction. So, this is these are the few reaction by which the sulphur transfer can occur. So, if some sulphur associated with iron that in the upper zone of the blast furnace it can go in the form of gas or it can converge at elemental sulphur gas, which I can combine with iron and quite a bit sulphurs also comes from fluxes.

So, calcium sulfate that is again goes with iron and it is a rigidity reduces with carbon, then calcium sulfide and this calcium sulfide and FeO when they react. So, sulphur goes to iron and with SiO is confirmed a Si s and again some of that goes through the liquid metal. So, you can see liquid metal is picking up these are mostly the relation reaction which occurs in the bosh region, and sulphur pickup can occur by liquid metal in a good quantity.

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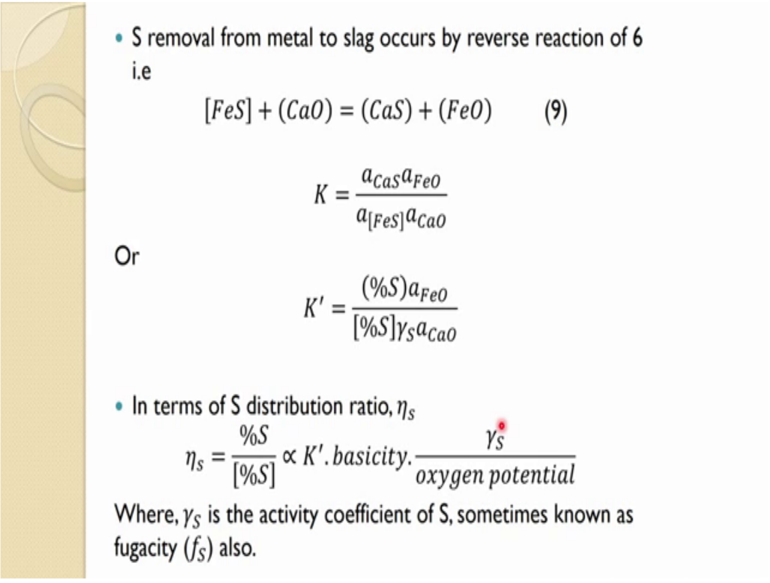

- S removal from metal to slag occurs by reverse reaction of 6 i.e

$$[FeS] + (CaO) = (CaS) + (FeO) \qquad (9)$$

$$K = \frac{a_{CaS} a_{FeO}}{a_{[FeS]} a_{CaO}}$$

Or

$$K' = \frac{(\%S) a_{FeO}}{[\%S] \gamma_S a_{CaO}}$$

- In terms of S distribution ratio, η_s

$$\eta_s = \frac{\%S}{[\%S]} \propto K'.basicity.\frac{\gamma_S}{oxygen\ potential}$$

Where, γ_S is the activity coefficient of S, sometimes known as fugacity (f_S) also.

However, in the hearth region most of the removal of the sulphur occur. So, sulphur removal from metal to slag occurs by a reverse reaction as we had seen this, so mostly the reverse of this reaction its sort of a removing the sulphur. So, if you have a more line or more basic slag in one way the sulphur removal it is good from the metal. So, for this reaction you can write the equilibrium constant in terms of activities.

So, activity of calcium sulfide FeO and iron sulfide CaO and in terms of rate percentage these tubes you can put in this form and where this is the activity coefficient, the sulphur and if you look at this is really nothing its a distribution ratio of sulphur between the slag and metal and its proportional to a equilibrium point modified equilibrium constant into basicity as we said into the best basicity, and the activity of the sulphur and oxygen potential that from the oxygen potential from there.

So, this is the activity coefficient sulphur and sometime known as the fugacity also and the fugacity, it is mentioned in that one that way. So, efficiency our supreme person depends on this parameter.

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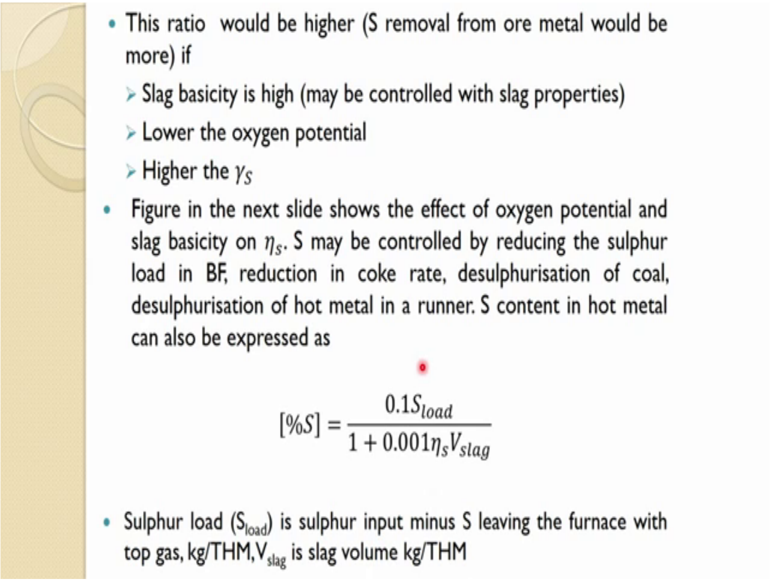

- This ratio would be higher (S removal from ore metal would be more) if
  - Slag basicity is high (may be controlled with slag properties)
  - Lower the oxygen potential
  - Higher the γ_S
- Figure in the next slide shows the effect of oxygen potential and slag basicity on η_S. S may be controlled by reducing the sulphur load in BF, reduction in coke rate, desulphurisation of coal, desulphurisation of hot metal in a runner. S content in hot metal can also be expressed as

$$[\%S] = \frac{0.1S_{load}}{1 + 0.001\eta_S V_{slag}}$$

- Sulphur load (S_{load}) is sulphur input minus S leaving the furnace with top gas, kg/THM, V_{slag} is slag volume kg/THM

So, this ratio would be higher or sulphur removal from all metal would be more if select basicity is high. So, as we said. So, this would be proportional to the basicity.

Basicity is high then removal between good and or oxygen potential is low or activity is small. So, that is lowered the oxygen potential sulphur removal from or metal would be more and higher activity coefficient of the sulphur. So, figure in the next slide shows the effect of oxygen potential and slag basicity on distribution ratio of sulphur.

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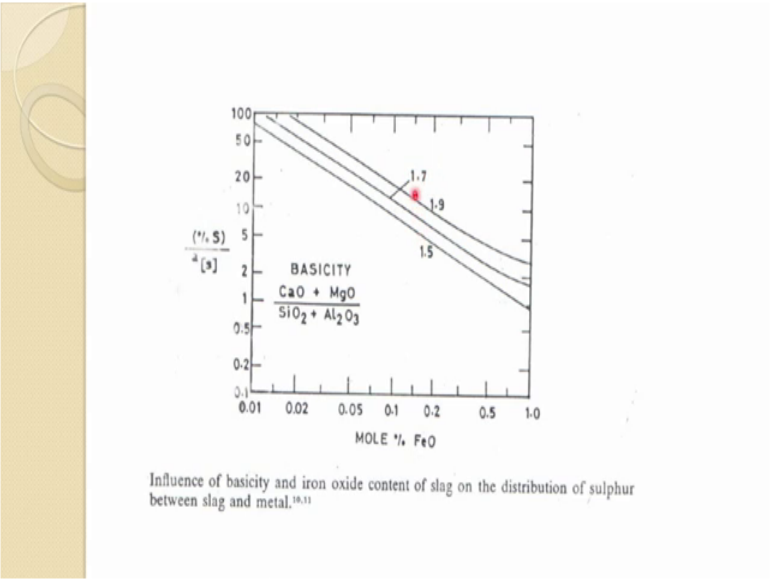

Influence of basicity and iron oxide content of slag on the distribution of sulphur between slag and metal.[10,11]

So if you look at. So, distribution ratio of sulphur, as the basicity increases this ratio increases or if the oxygen potential is increases then this basicity essentially decreases.

I know the ns the distribution ratio decreases and that is what actually we have seen from this equation, essentially it is showing the same thing in terms of values in terms of basicity and oxygen potential the same thing. So, sulphur may be controlled by reducing the sulphur load in the blast furnace, reduction in coke rate because in the coke most of the sulphur is coming from coke, desulphurization of coal desulphurization of hot metal in a runner.

Sulfur content in hot metal can also be expressed as 0.1 sulphur load divided by 1 plus 0.001 eta s as you know that sulphur distribution ratio and we select which is the volume slag volume in kg per ton of hot metal. So, sulphur load is the is the sulphur input minus sulphur leaving from the furnace with the top gas and kg per ton of hot metal. So, these are easy to measure in the industry as you have seen in this one we know what is the input and what is the output this can be easily measured in the flue gases.

So, that is called the surfer load and we know slag volume of course, we can know easily, when the blast furnace is working and distribution ratio. So, this percentage sulphur or sulphur contained the hot metal can be calculated. This is useful in the industry because these parameter can easily be available.

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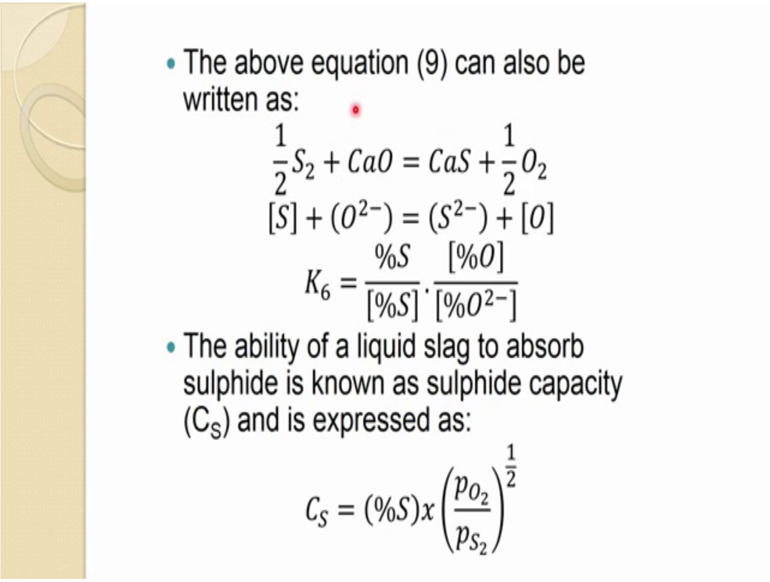

- The above equation (9) can also be written as:

$$\frac{1}{2}S_2 + CaO = CaS + \frac{1}{2}O_2$$

$$[S] + (O^{2-}) = (S^{2-}) + [O]$$

$$K_6 = \frac{\%S}{[\%S]} \cdot \frac{[\%O]}{[\%O^{2-}]}$$

- The ability of a liquid slag to absorb sulphide is known as sulphide capacity (C_S) and is expressed as:

$$C_S = (\%S)x\left(\frac{p_{O_2}}{p_{S_2}}\right)^{\frac{1}{2}}$$

So however, as we said the equation 9 we said about the this equation this equation can be written in various form one of the form is this, and if you put it in an ionic form the same equation is represented in this form.

And now, again the constant equilibrium constant for this, reaction can be written in this form which is an in terms of oxygen percentage in the weight percentage. Now why we are writing this one sometime it is useful because it is good to define one parameter. So, the ability of a liquid slag to absorb sulphide is known as sulphide capacity of that slag and is expressed as in this form.

So, this is a definition of the sulphide capacity which is which was proposed by Richardson in 1953. And it is a very good parameter for to know how much the capacity of slag or slag has the capacity to observe the sulphide. So, that that is how it is known as sulphide capacity and this essentially can be put in this form when we have put writing this equation in ionic form that fit well with this.

So, really if you look at this. So, this is nothing gas. So, that get square root p o 2 and ph 2 so, that to the power half and the percentage of sulphur silicon which is coming in this one. So, with the help of this equation you can represent all also in the form of this equilibrium constant the sulphur sulphide capacity. So, it is a measure of a slag capacity how efficient it can and remove the sulphur it is quite useful in the industry.

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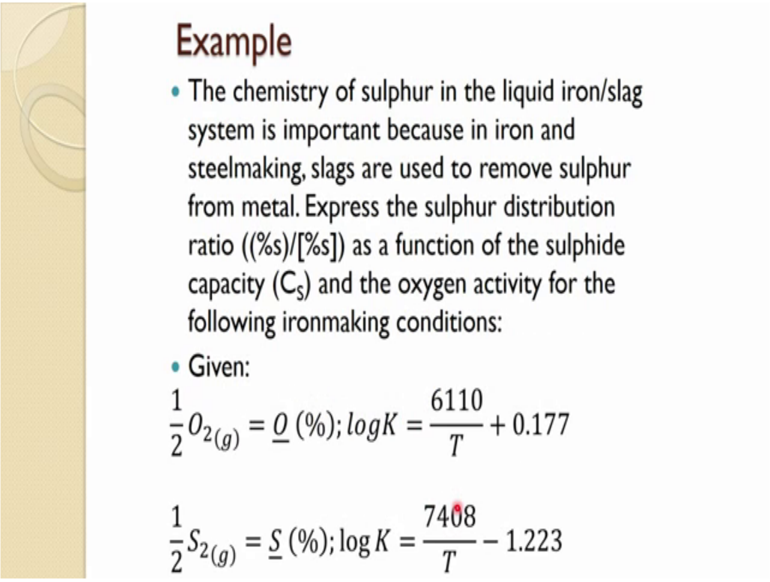

Example

- The chemistry of sulphur in the liquid iron/slag system is important because in iron and steelmaking, slags are used to remove sulphur from metal. Express the sulphur distribution ratio ((%s)/[%s]) as a function of the sulphide capacity (C_S) and the oxygen activity for the following ironmaking conditions:
- Given:

$$\frac{1}{2}O_{2(g)} = \underline{O}\,(\%); logK = \frac{6110}{T} + 0.177$$

$$\frac{1}{2}S_{2(g)} = \underline{S}\,(\%); \log K = \frac{7408}{T} - 1.223$$

So, we will have an example based on this. So, the chemistry of sulphur in the liquid iron slag system is important because in iron and steelmaking select they are used to remove sulphur for metal. So, sometimes you put you make the slag like that, in iron especially in the steelmaking that it can absorb more sulphur so, it can remove. So, slags are used to remove sulphur from metals.

So, express the sulphur distribution ratio which we have seen before, as a function of the sulphide capacity and the oxygen activity. So, express sulphur distribution ratio funks as a function of sulphide capacity and the oxygen activity for the following iron making condition. So, these are given.

So, oxygen get to dissolve its going to the iron as a FeO. So, the equilibrium constant for the reaction is given for this, similarly for the sulphur the equilibrium constant is given for these. So, these two who are the parameter which are given so, based on these information we have to calculate the sulphur distribution ratio is a function of sulphide capacity and oxygen potential. As we have seen this I think if we use these equation these two we can express the distribution ratio in terms of sulphide capacity and let us see how we will do it.

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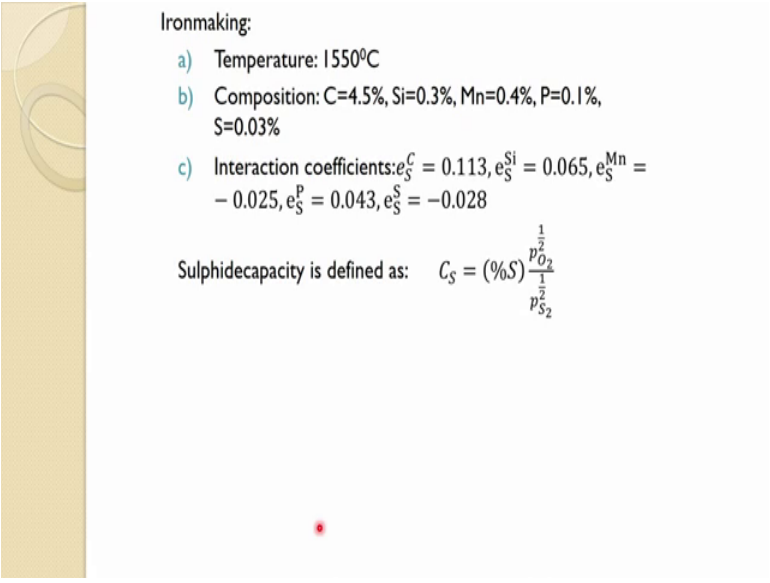

Ironmaking:

a) Temperature: 1550⁰C
b) Composition: C=4.5%, Si=0.3%, Mn=0.4%, P=0.1%, S=0.03%
c) Interaction coefficients: $e_S^C = 0.113, e_S^{Si} = 0.065, e_S^{Mn} = -0.025, e_S^P = 0.043, e_S^S = -0.028$

Sulphidecapacity is defined as: $C_S = (\%S)\dfrac{p_{O_2}^{\frac{1}{2}}}{p_{S_2}^{\frac{1}{2}}}$

So, for and these are other parameter which are giving temperature is about 1550 degree celsius composition of carbon 4.5, silicon 0.3, manganese 0.4, phosphorus 0.1 and sulphur is 0.03 data composition of the matter which is given and the interaction coefficient for the different element as follows sulphur carbon, sulphur silicon, sulphur manganese, sulphur phosphorous and for sulphur.

So, these are the interaction coefficient which can be used to find out the activity coefficient of fugacity. So, sulfide capacity is defined in this form.

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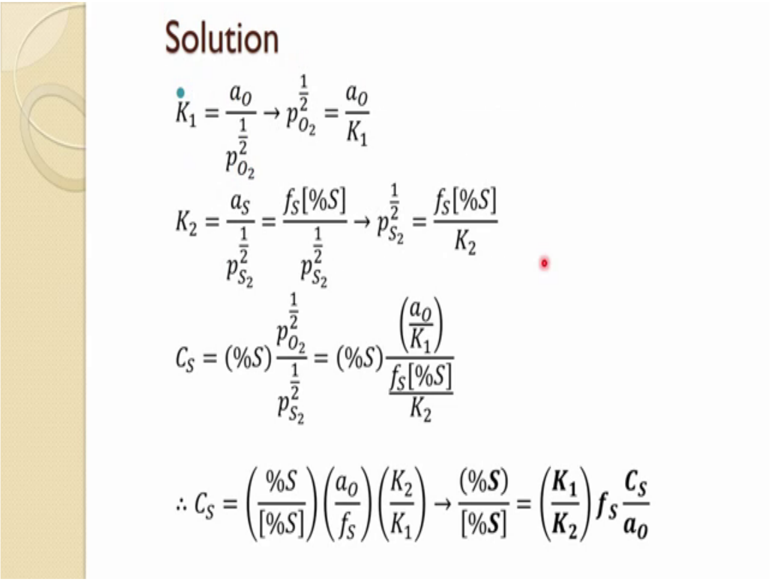

Solution

$$K_1 = \frac{a_O}{p_{O_2}^{\frac{1}{2}}} \rightarrow p_{O_2}^{\frac{1}{2}} = \frac{a_O}{K_1}$$

$$K_2 = \frac{a_S}{p_{S_2}^{\frac{1}{2}}} = \frac{f_S[\%S]}{p_{S_2}^{\frac{1}{2}}} \rightarrow p_{S_2}^{\frac{1}{2}} = \frac{f_S[\%S]}{K_2}$$

$$C_S = (\%S)\frac{p_{O_2}^{\frac{1}{2}}}{p_{S_2}^{\frac{1}{2}}} = (\%S)\frac{\left(\frac{a_O}{K_1}\right)}{\frac{f_S[\%S]}{K_2}}$$

$$\therefore C_S = \left(\frac{\%S}{[\%S]}\right)\left(\frac{a_O}{f_S}\right)\left(\frac{K_2}{K_1}\right) \rightarrow \frac{(\%\boldsymbol{S})}{[\%\boldsymbol{S}]} = \left(\frac{\boldsymbol{K_1}}{\boldsymbol{K_2}}\right)\boldsymbol{f_S}\frac{\boldsymbol{C_S}}{\boldsymbol{a_O}}$$

Now with the help of these 2-3 reaction we know from the first reaction that if you look at this. So, from this reaction a half O 2 it is your k. So, a o half. So, square root of p o 2. So, the this gives po 2 equal to a naught divided by K 1.

Similarly, we can do for sulphur. So, activities of sulphur square root of sulphur or half p s 2. So, that is equilibrium constant; so these activities in terms of weight percentage change if I put it. So, to multiply with the fugacity or activity coefficient and which now we can write the p s 2 in this form the same way as we did for this now for sulphide capacity we know it is expressed in this form.

So, po 2 we have already got it ph 2 we gotten this. So, sulphide these we can now put this value over here in the pg arrange it. So, this percentage of ratio percentage of this or slag metal a naught fs and K 2 K 1. So, this comes into this form. So, really our question is find out the distribution ratio, they express the sulphur distribution ratio as a function of sulphide capacity and oxygen potential.

So, we rearranged this one. So, that we get the sulphide capacity oxygen potential here and K 1 K 2 fs these actually are non K 1 we can calculate it is already given, K 1 temperature is given. So, we can calculate K 1 from this K 2 from this we can calculate it again to temperature is given 15 1550 degree Celsius.

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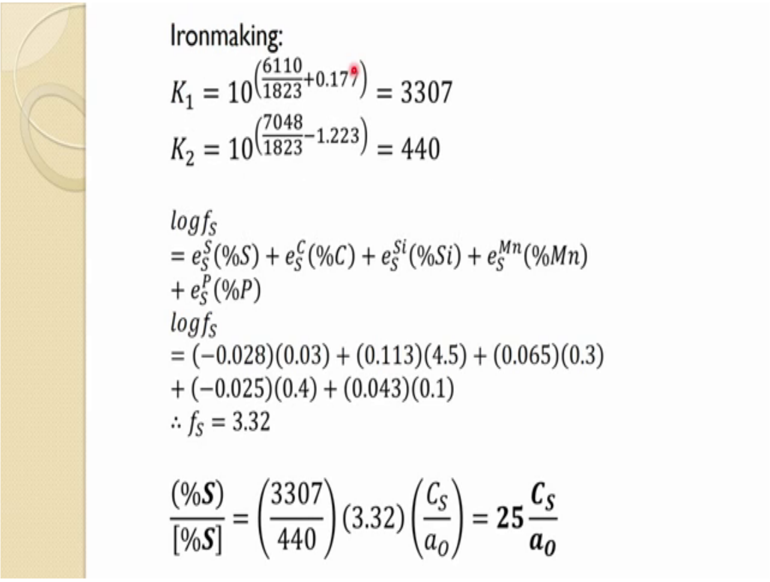

Ironmaking:

$$K_1 = 10^{\left(\frac{6110}{1823}+0.177\right)} = 3307$$

$$K_2 = 10^{\left(\frac{7048}{1823}-1.223\right)} = 440$$

$$\log f_S$$
$$= e_S^S(\%S) + e_S^C(\%C) + e_S^{Si}(\%Si) + e_S^{Mn}(\%Mn)$$
$$+ e_S^P(\%P)$$
$$\log f_S$$
$$= (-0.028)(0.03) + (0.113)(4.5) + (0.065)(0.3)$$
$$+ (-0.025)(0.4) + (0.043)(0.1)$$
$$\therefore f_S = 3.32$$

$$\frac{(\%\boldsymbol{S})}{[\%\boldsymbol{S}]} = \left(\frac{3307}{440}\right)(3.32)\left(\frac{C_S}{a_O}\right) = \mathbf{25}\frac{\boldsymbol{C_S}}{\boldsymbol{a_O}}$$

So, if we put those values. So, K 1 because in terms of log. So, essentially K 1 comes to 33307 and K 2 is 440. Now in order to get the fugacity this is the relation for the fugacity this again as I said you should be aware of it, if you have gone through those reaction physical chemical reaction of iron steel making then this would be known to you.

So, log fs the fugacity is given by this because these are the composition, which are mentioned in the question. So, we have to take those composition and these are the interaction coefficient and these interaction coefficient are given to us and even the composition of the hot metal is given.

So, if we put those values for example, the interaction coefficient sulphur to sulphur is minus 0.028 and sulphur composition of hot metal is 0.03. So, we put that values first one come to these, similarly other values we can put it and once we put that and this is a log fs. So, fs we calculate it comes to 3.32.

So, once you put now the now we got the fugacity, we got the equilibrium constant value we substitute into this we can get the distribution ratio in terms of sulphide capacity and the oxygen potential. So, which is 25 C s divided by a naught.

So, I hope you understood this question.