Using a thermodynamic database and

Researchers at Steel Authority of India Ltd (SAIL) have been using thermodynamic databases and FactSage 6.4 software to optimise the parameters of slag basicity and slag oxygen potential in order to optimise the desulphurisation of liquid steel in the ladle. By **Snehangshu Roy, Rajeev Kumar Singh, A. Paul, A. Gupta, N. Banerjee, N. Pradhan and S. Ghosh**

USING the simulation software FactSage the role of various parameters on the effectiveness of desulphurisation of steel during secondary ladle treatment were assessed for three different deoxidation practices. For Al killed steels, CaO is already close to the saturation line and further increases in lime cannot assist desulphurisation. For mixed Al + Si deoxidation, improved desulphurisation is achieved by adding lime to make the CaO/SiO_2 ratio around 3.0 to 3.5 and the FeO and MnO content of slag is <1.0% for both. For Si-Mn killed steels again, addition of lime to make the CaO/SiO_2 ratio around 1.9 aids desulphurisation and is especially important for hydrogen sensitive steels. In this case, deoxidation of the slag also improves desulphurisation and increases the slag volume by addition of a synthetic slag of the same basicity.

The Steel Authority of India Ltd (SAIL) is the largest state-owned steel making company in India. In recent years, SAIL has undergone major up-grades and modernisation with the aim of capacity enhancement and production of special quality steel.

For the production of special quality steels, secondary metallurgy plays a very important role. One of the main purposes of the slag in secondary steelmaking slag is to remove any remaining sulphur in the steel while held in the ladle. This requires a proper understanding of the impact of different process parameters on the ability to desulphurise to design an optimum slag chemistry to improve the degree of sulphur removal. Thermodynamic database software can be applied as a tool to understand the impact of process

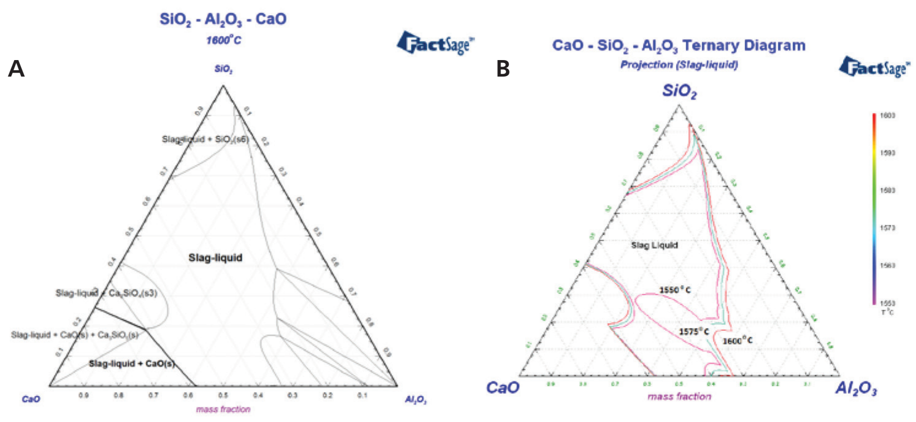

Fig 1.(A)Ternary diagram of CaO-SiO_2-Al_2O_3 slag system

Fig 1.(B) Projection of liquid slag phase in range of 1550 to 1600°C

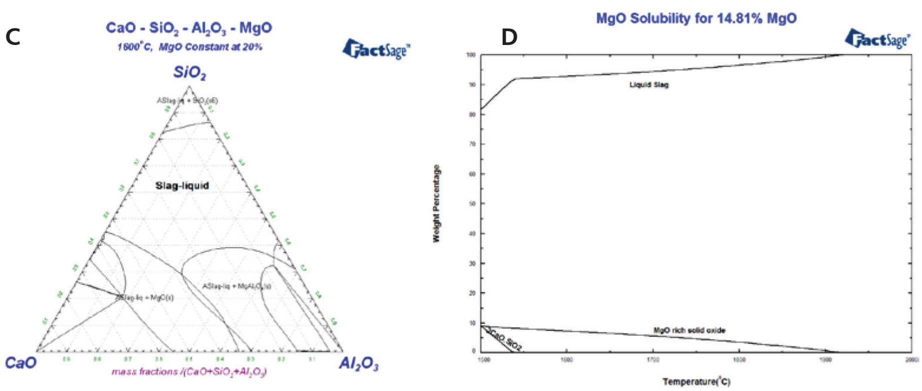

Fig 1.(C) Effect of MgO on liquid slag window of CaO- SiO2-Al2O3 slag system

Fig 1.(D) Solubility of MgO vs Temperature for 14.81% MgO

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l FactSage to optimise slag parameters

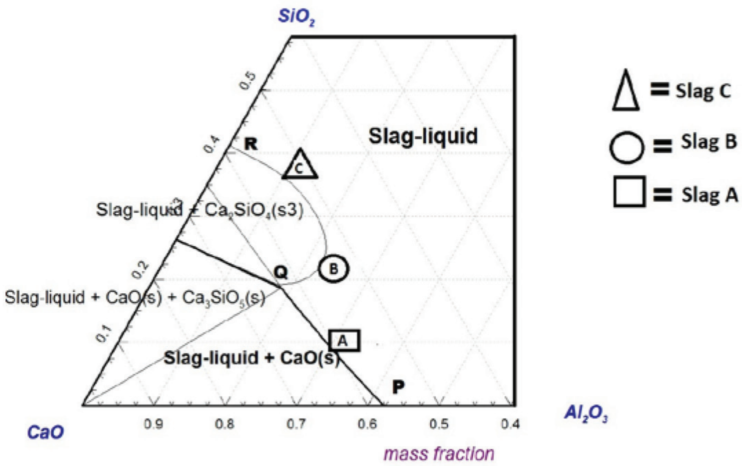

Fig 2. Operating window of different SAIL steel plants in CaO- SiO_2-Al_2O_3 system

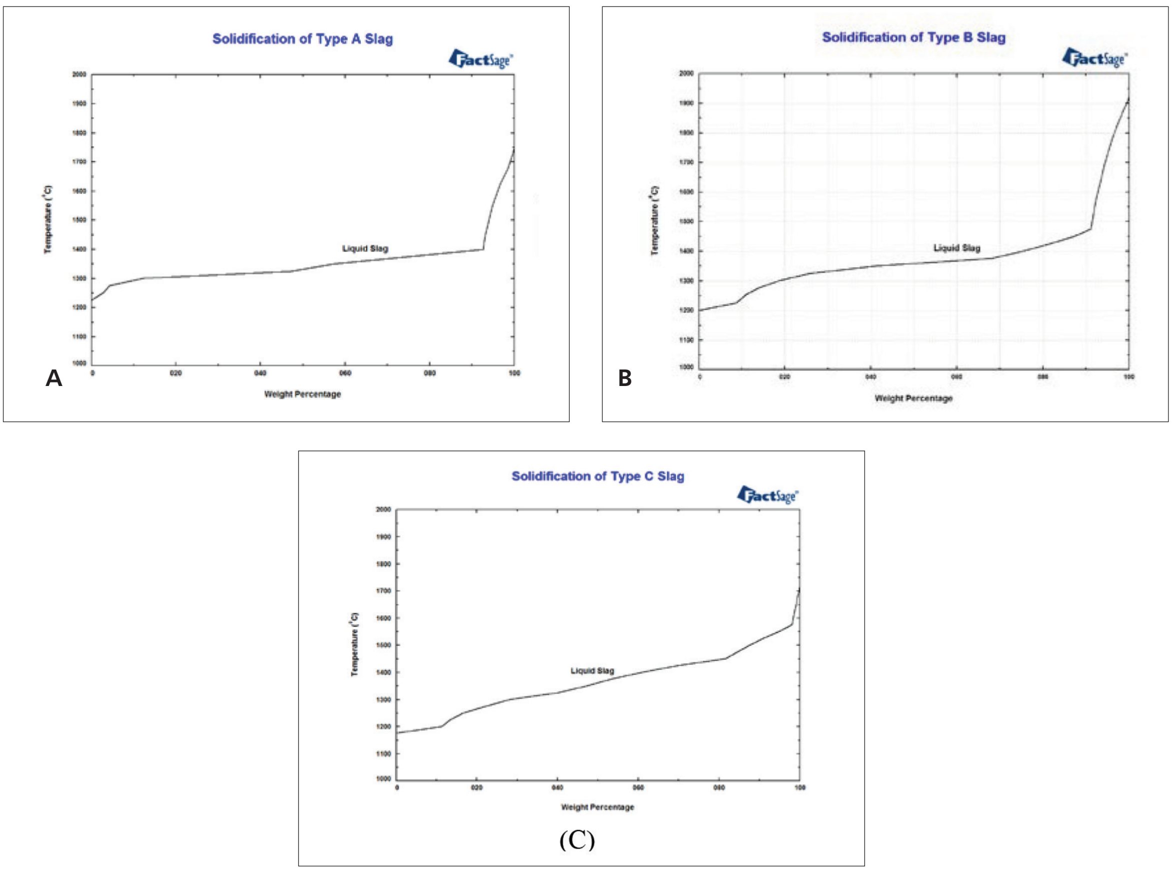

Fig 3. (A),(B),(C) Equilibrium solidification of A, B and C slag types calculated using FactSage

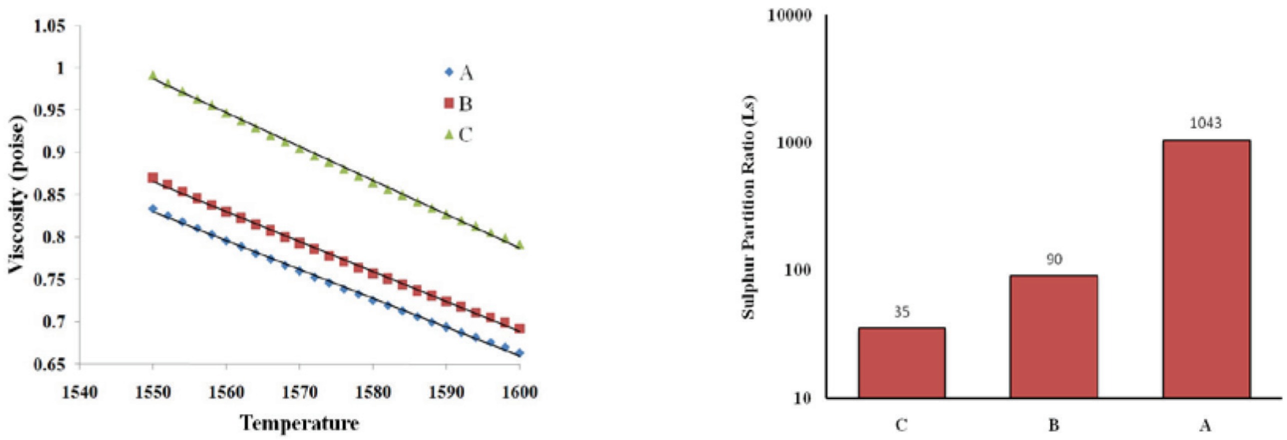

Fig 4. Comparison of (A) viscosity (in poise) and (B) Sulphur partition ratio of different slag Types

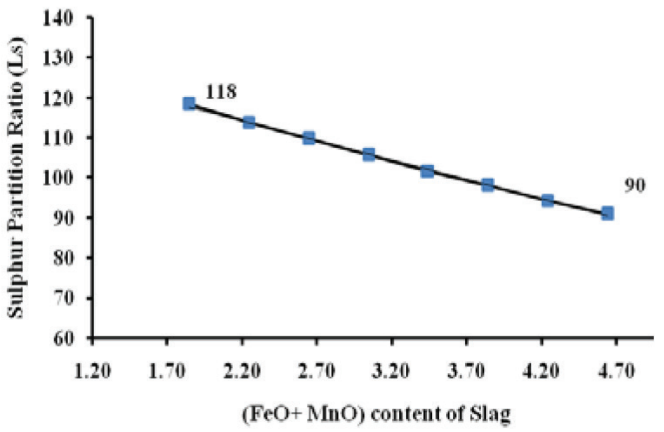

Fig 5. Change in Ls with (A) (FeO+MnO) wt% in slag and (B) with Al wt% in steel

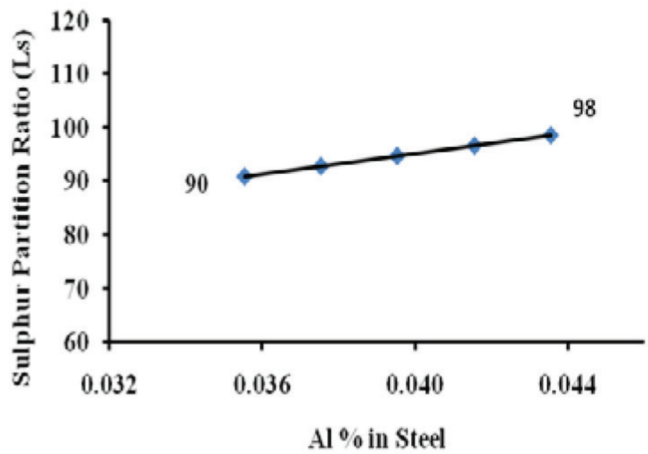

Fig 6. Effect of slag basicity (CaO/SiO_2 mass ratio) on Ls of Slag B

parameters on desulphurisation. Compared to pyrometallurgical experiments of slag metal reactions, thermodynamic modelling has the advantages of shorter time required for optimisation, no experimental equipment required and ability to operate over a wide variation of parameters. FactSage thermodynamic software, which is fusion of FACT and ChemSage, hold a large database of slags, oxides and steel phases[1] which can be applied for thermodynamic characterisation of ladle top slags and the simulation of slag metal equilibrium to evaluate the equilibrium sulphur partition ratio.

Phases present in the slag play important roles in refining so calculation of phase diagrams is also important to determine the operating window for better desulphurisation.

Thermodynamics of desulphurisation

Holappa[2] has reviewed the theoretical basis for sulphur removal during ladle treatment by the slag–metal reaction. For sulphur removal from steel, it is better to utilise the general ionic form of the desulphurisation reaction, ie,

$$[S] + (O^{2-}) = (S^{2-}) + [O] \qquad (1)$$

[S] is the sulphur in the steel, (O^{2-}) is the oxygen ion in the slag, (S^{2-}) is the sulphur ion in the slag and [O] is the oxygen in the metal.

One important parameter is the equilibrium sulphur partition ratio between slag and metal (Ls)[3, 4]:

$$Ls = (WS)/[WS] \qquad (2)$$

Where [WS] & (WS) are the weight of sulphur in the steel and slag respectively)

To achieve the most effective desulphurisation, one should carefully consider the thermodynamic parameters that are responsible for desulphurisation. In the CaO-SiO_2-Al_2O_3 slag system, the optimum slag chemistry should be in the liquidus region for faster mass transfer, lower viscosity and higher liquid slag volume. The activity of CaO in the slag should be close to unity to facilitate the exchange of dissolved sulphur in the steel with the oxygen ion[5].

Thermodynamic models and database

Well-known thermochemical softwares with large thermodynamic databases for steelmaking are[6] CEQCSI, FactSage, MPE, MTDATA and Thermo-Calc. FactSage, holds the databases that are used for thermodynamic simulation of

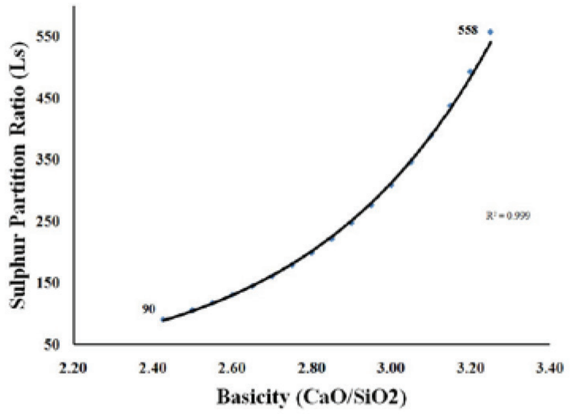

Fig 7. Activity of CaO vs slag basicity (CaO/SiO2 mass ratio) for slag type B

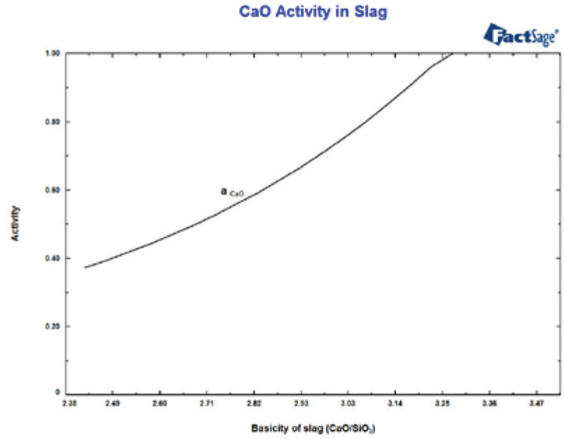

Fig 8. MgO solubility vs temperature at 10% MgO (wt %) for Slag B

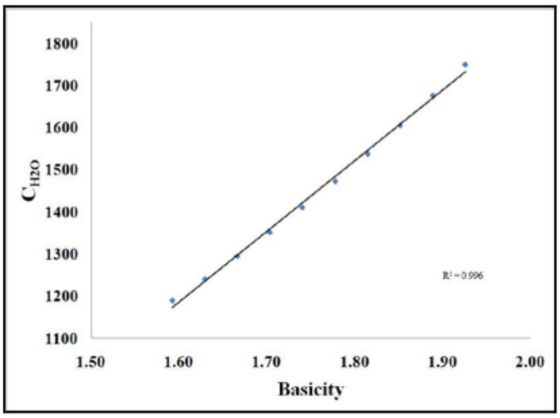

Fig 9. Effect of slag basicity (CaO/SiO_2 mass ratio) on water capacity of slag for Slag C

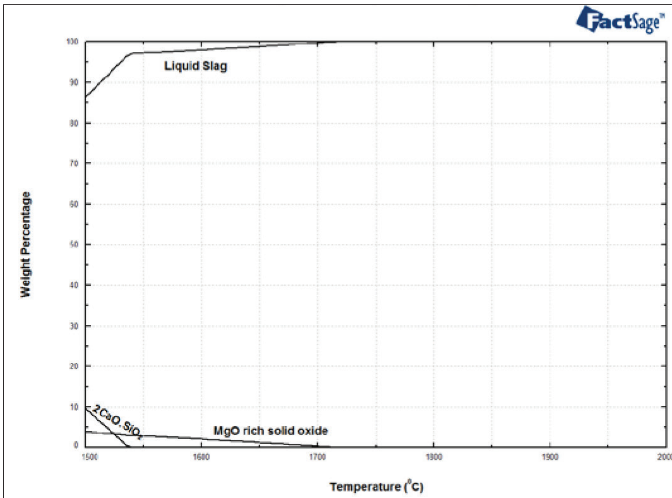

Fig 10. Effect of basicity (CaO/SiO_2 mass ratio) on Ls of Slag C

the steelmaking process. These include FToxide, FSstel and Fact. Earlier attempts by researchers such as Wcisło et al used FactSage to study the role of secondary slag in the ladle metallurgical process. The researcher showed that deoxidation of the slag has a positive influence on the desulphurisation process. Gaye et al[8] analysed the reaction mechanisms of desulphurisation involving metals, slag and fluxes. They studied the sulphur partition ratio in slag for Al-killed and Si-killed steels and concluded that for Al-killed steel, a very large equilibrium sulphur partition ratio can be obtained for CaO-Al_2O_3-SiO_2 slags with high lime saturation.

Experimental

Ladle top slags and related process data was collected from different SAIL plants and categorised on the basis of their deoxidation and fluxing practice. Category A is for fully aluminium killed steel, B for aluminium and silicon mixed killed and C for silicon manganese mixed killed. The average values of the ladle top slag analysis and corresponding metal analysis are given in **Tables 1 & 2**. The percentages desulphurisation achieved for A, B & C types were around 70%, 30% and 15% respectively.

The CaO-SiO_2-Al_2O_3 phase diagram at 1600°C and the projection of the liquid slag zone in the temperature range 1550°C to 1600°C in the ternary phase diagram was calculated and is shown in **Figs 1A** and **1B**. The calculated CaO-SiO_2-Al_2O_3 ternary phase diagram has consistency with diagrams presented by other researchers[5]. The effect of MgO on the liquid fraction of slag was also calculated in the pseudo-ternary phase diagram (**Fig 1C**). It was found that the liquid window becomes smaller at lower temperature and higher MgO content of the slag and the solid phase is mainly MgO rich periclase. (**Fig 1D**).

Fig 2 shows the operating window of slags for aluminium killed steel (A), silicon-aluminium mixed killed steel (B) and silicon-manganese killed steel (C). Thermodynamic analysis of the slag-metal reaction was carried out for different slag types to find out the equilibrium sulphur partition ratio (Ls) and the effect of different parameters on this. Equilibrium solidification of ladle top slag of slag types A, B and C is shown in **Figs3A**, **3B** and **3C**. The metal-to-slag weight ratio was kept at 100:2 to find the equilibrium sulphur partition ratio (Ls) at 1600°C for all calculations. For optimisation

		Ladle Top Slag Analysis (Weight %)					
Slag Type		SiO_2	CaO	MgO	FeO	MnO	Al_2O_3
A (Al-killed)	Typical Range	5-6	52-54	7-9	<0.5	<0.5	30-32
	Average	5.09	54.08	8.86	0.50	0.34	31.10
B (Si-Al killed)	Typical Range	18-20	43-46	14-16	3-4	1-2	17-19
	Average	18.79	44.38	14.30	3.18	1.46	17.95
C (Si-Mn Killed)	Typical Range	27-29	44-47	10-12	~2.5	~2.5	8-10
	Average	28.50	46.39	11.29	2.23	2.35	9.24

Table 1.Typical ladle top slag analysis from different deoxidation practices

	Metal Analysis (Weight %)					
Type	C	Mn	P	S	Si	Al
A (Al-killed)	0.09	0.41	0.027	0.008	0.075	0.045
B (Si-Al killed)	0.10	0.60	0.039	0.022	0.11	0.040
C (Si-Mn killed)	0.68	1.13	0.022	0.024	0.18	0.007

Table 2 Metal analysis for various deoxidation practices

				Average Viscosity (poise)		
Slag Type	Average Solidus (°C)	Average Liquidus (°C)	Average Ls	1550 °C	1575 °C	1600°C
A	1227	1738	1043	0.84	0.75	0.67
B	1205	1914	90	0.87	0.77	0.69
C	1197	1711	35	0.99	0.87	0.79

Table 3 Evaluation of parameters of slags calculated using FactSage

of secondary slag, the slag parameters considered are the (FeO+MnO) content, the CaO/SiO_2 ratio and the, MgO content and its effect on slag solidification and the Al level in the steel. The effect of slag volume (Metal/Slag mass ratio) was also checked.

Result and discussion

The simulation of the present practice using FactSage indicates Ls for A, B & C slags to be approximately 1000, 90 and 35 respectively. From the equilibrium solidification of slag (**Figs 3A, 3B & 3C**) it can be seen that the solidus points of each slag were close to each other varying from 1197°C to 1227°C and the liquidus point varied from 1711°C to 1914°C. The calculated values for solidus, liquidus, Ls and viscosity of current slag systems are shown in **Table 3**.

The calculated result shows that slags of types A and B are less viscous than C which is Silicon-Manganese killed. Comparison of the viscosity and equilibrium sulphur partition ratio of the three slag types are shown in **Figs 4A & 4B**. The operating windows for the different type of slags are shown on the CaO-SiO_2-Al_2O_3 ternary diagram (**Fig 2B**) and reveal that the slag chemistry in aluminium killed practice (type A) is very much close to the CaO saturation line but for the other two slag types B & C there is an opportunity to increase the lime content to reach saturation. Further increases in CaO in slag A will result in forming solid CaO, which will not take part in the desulphurisation reaction. The sulphur partition ratio obtained for that slag is above 1000, which also indicates lime saturation of the slag[8].

The change in Ls of slag B with (FeO+MnO) content, Al content in the steel and the CaO/SiO_2 ratio is shown in **Figs 5A**, **Fig 5B** and **Fig 6** respectively. The CaO/SiO_2 ratio has the greatest impact on increase

For the Ls of the ladle top slag, the simulation result shows that Ls change from 90 to 558 by varying the CaO/SiO_2 ratio from 2.43 to 3.25. Ls also increased with a decrease in the (FeO+MnO) content in the slag (**Fig 5A**) and an increase in Al in the steel (**Fig 5B**), but that increase is marginal compared to the increase due to a higher CaO/SiO_2 ratio. The combined effect of increasing the CaO/SiO_2 ratio and decreasing (FeO+MnO) on Ls is quite substantial, with the Ls at around 800. In **Fig 2**, the Al-Si killed slag was projected in Slag B. The calculated value of activity of lime (CaO) for the current chemistry is around 0.38. For the condition of complete liquid slag, the nearest lime saturation point is at the point Q in **Fig 2** and for improved desulphurisation the slag needs to follow the path B to Q. From the theoretical calculation it is shown that activity of CaO reaches a value of 1 around a basicity of 3.25 (**Fig 7**). That is the optimisation point of type B slag. From the calculations, it was also found that the saturation point of MgO in slag is near 8-10% and this is optimum for a fluid slag[9]. For Type C slag, generally basicity is kept around 1.5 for hydrogen sensitive grades. One major reason to keep the basicity low is to prevent hydrogen pick-up in the steel after degassing. During vacuum degassing hydrogen is removed from the steel but it does not effectively remove the OH- concentration in the slag. After vacuum treatment, hydrogen can be picked up in the steel from this slag[10]. Researchers correlate the hydrogen pick-up from slag after degassing with the water capacity (CH_2O) of the slag [10,11], which is defined as

$$C_{H20} = \frac{H_2Oppm}{\sqrt{P_{H20}}} \qquad (3)$$

Here, H_2O ppm is the H_20 content in the slag and pH_2O is the partial pressure of steam in the system. It is reported by the researchers that hydrogen pick-up is severe when CH_2O is greater than 1650°C[10].

The CH_2O value of slag C is calculated according to equitation(9) and plotted in **Fig 9**. The CH_2O increases to above 1650°C when slag basicity is more than 1.9 and calculation showed that to achieve a liquid slag in this condition the Al_2O_3 content of the slag should be around 15%. So the optimum basicity for type C slag is 1.9. For a CaO/SiO_2 ratio of 1.9 the Ls obtained is 100 as shown in **Fig 10**

The FeO and MnO level can be reduced by a slag deoxidation technique such as addition of Fe-Si fines to the slag[12]. However achieving a lower equilibrium sulphur in steel, with the same slag composition, can be achieved by increasing the slag volume, which can be reached by the addition of synthetic slag. In **Table 4**, at a metal to slag mass ratio of 100:3, the equilibrium sulphur content of the metal was 0.0050% whereas at a 100:2 ratio the value was 0.0062%.

Conclusions

For fully aluminium killed steels the current parameters of operation are close to the optimal condition resulting in a high equilibrium partition ratio > 1000 for this type of slag.

For mixed aluminium and silicon deoxidation practice, better desulphurisation can be achieved, when the CaO/SiO_2 ratio is around 3.0 to 3.5 and the FeO and MnO content of the ladle top slag is minimised to below 1.0% for both FeO and MnO. In industrial practice, this condition can be achieved by early addition of aluminium in the ladle during tapping the BOS. Implementation of these measures will increase removal of sulphur to 60% from the 30% previously.

For the case of Silicon-Manganese killed steels the CaO/SiO_2 ratio should be around 1.9, especially for hydrogen sensitive steels. Deoxidation of the slag should be adopted to decrease slag oxygen potential to improve desulphurisation by the slag. In addition to this, lower levels of sulphur in the steel can be achieved by increasing the slag volume by addition of a synthetic slag of the same basicity. ■

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