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Control of sulphur and minimisation of centre line segregation for Rail Steel

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Abstract : Rail is the most important constituent of the track structure and plays a very vital role in the reliability of railway system as a whole. Quality of rail steel with reference to its chemical composition has been a matter of prime importance for the manufacturers as well as Railways. Sulphur is a detrimental element in rails since it causes hot shortness during rolling, centerline segregation during casting, poor weldability for the rails etc. To improve quality of rails, a substantially low range of sulphur < 0.015% (Railway's specified norms <0.03%) has been targeted in Bhilai Steel Plant by adequate sulphur control measures in steelmaking process. A two stage de-sulphurisation treatment is now employed in which the blast furnace hot metal is first treated by co-injection of Mg and CaC_2 reagents, and subsequent treatment with a synthetic slag former (CaO-Al_2O_3) added to the ladle during tapping from the Basic Oxygen furnace. Improvement in the internal quality of the cast bloom has been established by introduction of Electro Magnetic Stirring. The centerline segregation is minimized vis-a-vis the properties of the cast product and rails improved by the successful implementation of step by step control measures.

Keywords : Sulphur, Centreline segregation, Synthetic slag and Electro magnetic stirring.

INTRODUCTION

Rail is the most important constituent of the track structure. It plays a very vital role in the reliability of railway system as a whole. Steel Authority of India Limited (SAIL) is sole supplier of rails to Indian Railways. It is the most prestigious product of SAIL and therefore, Steel Melting Shop (SMS) - II, Bhilai Steel Plant (BSP), Bhilai has been earmarked for the production of rails. The best metallurgical facilities for steel making, rolling and post manufacturing inspection are available to produce about 1.0 Mt rails annually. Improvement in the quality of rails is the prime importance with the view of steel making to meet the stringent chemical specification. Significant work has been carried out in secondary steel making after introduction of RH degasser to achieve low gaseous content especially hydrogen content below 1.5 ppm. Addition of synthetic slag in the steel ladle for sulphur arresting is an established process for its secondary refining. Recently, hot metal de-sulphurising facility and electromagnetic stirring for blooms has been commissioned for additional control of sulphur and to enhance cast properties respectively.

Sulphur is a detrimental element in rails since it causes hot shortness during rolling, centerline segregation during casting, poor weldability for the rails etc. The ill effect of hot shortness due to formation of FeS can be eliminated by improving the [Mn]/[S] ratio > 8:1 to form high melting point MnS inclusion. D. M. FEGREDO et.al.[1] has studied the effect of sulphide inclusion for rails and concluded as "increasing sulphur content, i.e. increasing MnS inclusion content, causes subsurface cracks due to MnS deformation in the sheared surface layer influences wear rate". Hodgson and Preston et.al.[2] has investigated for rails and particularly

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for steel [S] and concluded as "Sulphur is generally positive in helping reduce hydrogen troubles but negative in toughness and wear. A balance was found in a typical range of 0.010% to 0.015% [S]".

On Indian Railways, rails are accepted as per strict guidelines IRS-T-12-96 for chemical composition, physical tests and dimensional checks. A rigorous testing of iron and steel products is necessary for ensuring conformity and quality in the manufactured product. Various tests are conducted during and after the operation which includes online ultrasonic test, surface quality tests, chemical analysis, tensile test, sulphur print, falling weight test, hydrogen content etc. Any test failure even for single rail results the rejection of the corresponding lot of rails. In the present work, study and optimization of steelmaking process in the view of new facilities have been incorporated for sulphur control and minimization of centerline segregation. A substantially low range of sulphur < 0.015% (Railway's specified norms <0.03%) in liquid rail has been targeted and achieved at BSP through Hot Metal De-Sulphurisation (HMDS) - Basic Oxygen furnace (BOF) - Argon Rinsing Unit (ARU) - Ladle Furnace (LF) - RH Degasser - Bloom Continuous Casting (CC) route.

Steel making and Sulphur control

The favorable metallurgical conditions for sulphur removal are a) reducing condition, b) high basicity, and c) high temperature. In BOF, condition of high basicity and temperature can be achieved but due to oxidizing condition, the sulphur removal has limitation. Hot metal contains silicon and carbon as impurities which provide the best reducing condition for sulphur removal before it's charging to BOF. Removal of hot metal impurities like carbon, silicon, phosphorus etc by its oxidation takes place in a 120t BOF. The steel after BOF treatment contains low carbon (~0.05%) and therefore petro coke in the quantity of 700 - 800 kg is added in the steel ladle during tapping for achieving the specified carbon (0.6%) in the steel bath. The addition of coke increases sulphur in the steel by 0.04 - 0.08 %. Rails are Si - killed steel and therefore, the de-sulphurisation in ladle metallurgy has metallurgical limitations. To enhance sulphur removal before its casting, high sulphur capacity secondary slag by the addition of suitable synthetic slag is essential.

Desulpurisation of Hot Metal

SMS II has installed a HMDS station having two stands. It is based on co-injection technology involving use of calcium carbide and magnesium based reagent to reduce hot metal [S] ~ 0.01% from hot metal [S] ~0.45 - 0.7%. The HMDS process uses co-injection technology with single lance injection at different ratio and rates where, nitrogen was used as carrier gas. Presently, the ratio of CaC_2 and elemental Mg is kept at 5:1. Mg reagent has good desulphurising ability. It keeps the treatment time low with minor decrease in the hot metal temperature. The specifications of the reagents and desulphurising process parameters are mentioned in Table 1 & Table 2 respectively.

Table 1: Specification of reagents

CaC_2 Reagent		Elemental Mg		
Technical carbide	70 %	Typical	Mg	97%
CaC_2 (Chemical)	52 ± 2 %	Analysis	Coating	3 %
Gas generating Hydrocarbon	5 %	Typical sizing		1.0 X 0.15 mm^2
				2% max. > 1200 mm
CaO	Rest			10 % max. < 150 mm
Bulk Density	1000 kg/m^3	Mg Chemistry		99.8 % min.
Grain Size	85% min, 63 micron	Bulk Density		0.88 - 0.98 g/cm^3

Table 2 : Desulphurising process parameters

Operating Parameters	Specification
Heat weight	120 t
N_2 flow rate	30 - 50 Nm^3/hr
CaC_2 : Mg reagent ratio	5:1
Avg. CaC_2 consumption	160 kg/heat
Avg. Mg Consumption	32 kg/heat
Avg input [S]	0.035 %
Aim [S] after HMDS	0.01 %
Avg %S drop	70 %
Avg injection time	5 min.

Hot Metal Slag Skimming

After HMDS treatment, the complete removal of slag from the hot metal ladle is pre-requisite to prevent its entry to BOF. The process of skimming becomes difficult and less effective due to increase in refractoriness and viscosity, and entrapment of iron. The poor skimming resulted in higher sulphur reversal in BOF and thereby nullifying the effect of external HMDS process. It is also associated with considerable metal loss. A need was considered to improve hot metal slag characteristic for its easy and effective skimming.

The addition of slag conditioner improves the slag fluidity and reduces the iron entrapment and thereby increases slag - metal stratification for its efficient removal. The best way of using the modifying agent is to mix it with the desulphuring reagents viz. CaC_2 in a predetermined ratio (2 - 5% of CaC_2 reagent wt) before taking the reagent in the silo. In this way, the slag modifier will be injected simultaneously with the desulphurising reagents and will help to improve the slag properties.

Desulphurisation by Synthetic Slag

Synthetic slag is low melting point CaO - Al_2O_3 compound which helps in formation of CaO - Al_2O_3 - SiO_2 type refining slag[3, 4]. It helps in desulphurisation of steel by increasing the sulphur partition ratio with increasing CaO and alumina contents. The efficiency of desulphurisation in ladle depends upon the activity of the oxygen and circulation rate of steel bath. Desulphurisation of Si- killed steel (rail steel) has less favorable thermodynamic condition than Al - killed steel. There are instances of desulphurisation of Si- killed steels with sulphur partition ratio of up to 50 achieved through SiC deoxidation[5]. Better efficiency of the desulphurisation using synthetic slag may be achieved by ensuring adequate deoxidation level.

Electro Magnetic Stirrer

Mould Electro Magnetic Stirrer (Figure 1) has been installed along with electro-mechanical mould oscillator in a existing bloom caster of steel melting shop. Some of the important electrical characteristics of EMS coil are a) Maximum frequency: 6 Hz (frequency range: 2-6 Hz), b) Maximum Intensity: 500 Amps (per phase), and c) Maximum Voltage: 415 V (380-420 V). The EMS has been installed within the mould assembly with introduction of tubular moulds replacing the plate mould assembly for its effective utilisation.

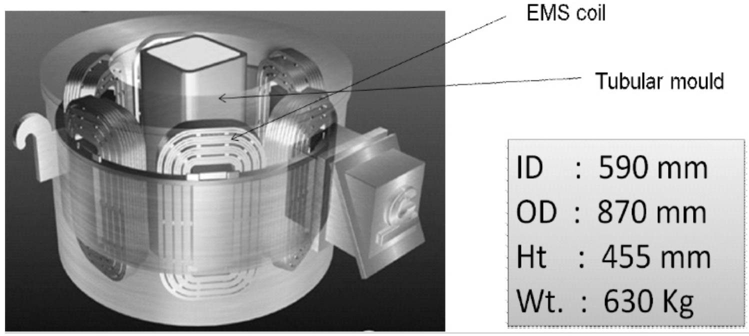

Fig. 1 : Mould Electro Magnetic stirrer

Plant trials

With the view to ascertain the sulphur control in each and every step of steelmaking processes, sulphur mapping was conducted. BOF operation has its own limitation and ~ 30% [S] is achievable. Therefore, the major sulphur control and process optimization has been targeted primarily at two stages i.e. HMDS & secondary steelmaking. The blast furnace hot metal is first treated by co-injection of Mg and CaC_2 reagents. The modified CaC_2 reagent with a suitable slag conditioner was also tried for some time to study its effect for modifying hot metal slag characteristic and efficient slag removal prior to BOF process. Subsequently, the previous practice of synthetic slag (CaO-Al_2O_3-SiO_2) addition in steel ladle during BOF tapping for its further refining has been modified as per steel [S]. Continuing with its efforts towards quality improvement, electromagnetic stirring along with a modern electro-mechanical mould oscillation system has been introduced in Bloom Caster. Since the work involves retrofitting of a new system into the earlier system, the process optimization of EMS parameters with the issues related to quality improvement like centre line segregation in cast bloom has been carried out. Various samples of processed rails after rolling were collected and sulphur prints were analyzed for the effect of EMS to minimize centre line segregation.

RESULTS & DISCUSSION

Sulphur Mapping and Hot Metal Desulphurisation

More than hundred numbers of heats were monitored using HM-DeS-BOF- ARU- LF-CC route with and without synthetic slag addition. Mapping of these two routes (with and without synthetic slag) are shown in Fig. 2 and Fig. 3 respectively. The sulphur reversal in BOF is common due to poor slag skimming after HMDS. A high and varying sulphur pick-up to the

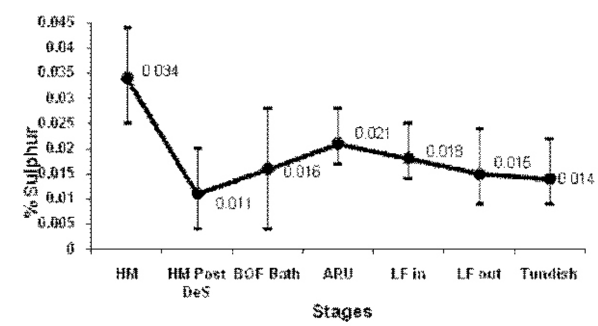

Fig. 2 : Sulphur mapping for rail heats with synthetic slag addition

extent of 0.012% was observed. The average pickup of sulphur was 0.005 %. A large number of heats (40 % heats) were observed with sulphur pick -up of $\geq$ 0.005 %. The sulphur mapping spells about the necessity to adopt a good slag skimming procedure.

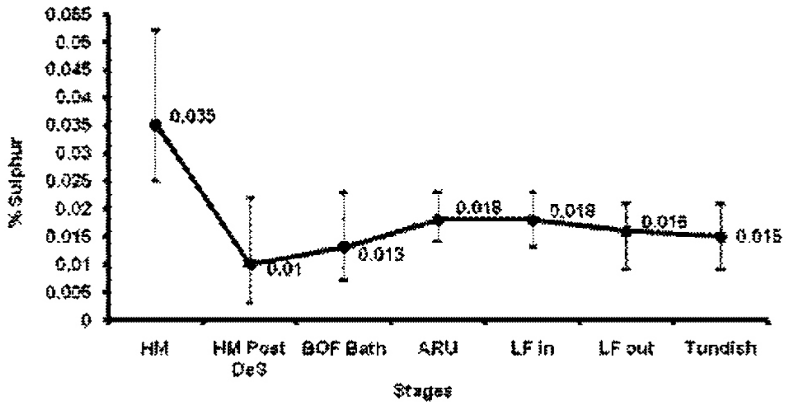

Fig.3 : Sulphur mapping for rail heats with no synthetic slag addition

Average steel [S] ~ 0.005% increase can also be observed from BOF to ARU due to addition of petro coke in the ladle during tapping. Depending on the steel [S] at BOF, synthetic slag addition has been made. The sulphur mapping shows that the secondary refining by synthetic slag addition is necessary to keep steel [S] < 0.015%.

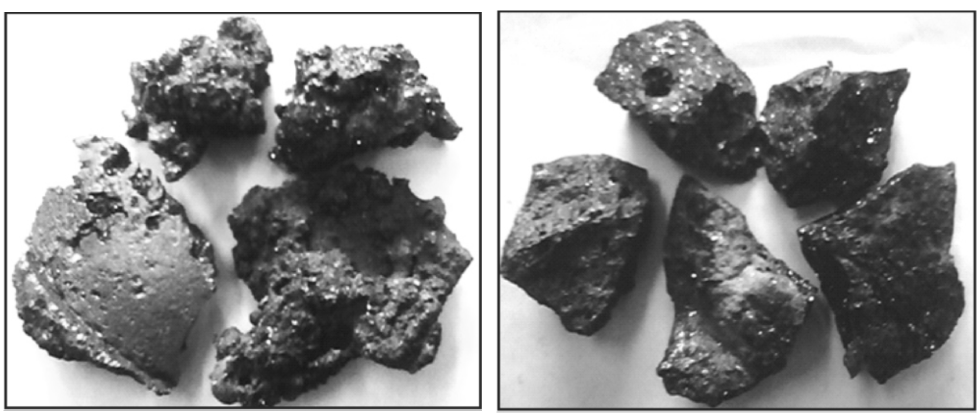

Fig. 4 (a & b) : Photographs of post de-sulphurised slag samples a) Base period - metallic & heavier, and b) Trial period - brittle & light

The morphology of hot metal ladle top slag after HMDS is important for its efficient removal. It is basically composed of blast furnace slag, high sulphur reaction products and a good quantity of metal entrapped within the slag. The entrapment of metal occurs due to vigorous mixing of the top slag and metal during tapping. It may also happens due to solidification of metal on the surface of formation of high melting products like MgS, MgO, CaS etc inside the hot metal bath and subsequently, float up to join the top slag. A study trial was conducted with the modified CaC_2 reagent for more than 80 heats. The slag samples after HMDS were collected. A comparative study was carried out for base period (previous practice without slag modifier) and trial period (modified practice with modified CaC_2 reagent with slag modifier) and tabulated in Table 3. Typical photographs of slag samples are shown in Fig. 4 (a & b).

Fig. 4a shows the slag of base period which are metallic and heavier due to higher content of metal. The slag samples of trial periods are shown in Fig. 4b which are brittle and light. This shows that addition of slag modifier has helped reduced the metallic content in slag. The outcome has a good impact on slag fluidity and slag - metal stratification, which resulted in easy slag removal and improvement in slag skimming efficiency & time. No negative impact on desulphurization efficiency was observed. However remarkable reduction in sulphur reversal in BOF operation was observed.

Optimization of Steel Desulphurization in Steel Ladle

Studies were conducted on the amount of synthetic slag addition in steel ladle based on the sulphur level attained in BOF. Nomogram 1 was proposed to get the objective to maintain final sulphur below 0.02%. Addition of 300 - 500 kg synthetic slag in the heats having BOF bath sulphur >0.018% was done while no synthetic slag addition was proposed for bath sulphur below 0.018% in BOF. The addition practice of synthetic slag was redefined in subsequent trial with a new modified Nomogram 2. Both the nomograms are tabulated in Table 4.

Table 3 : Comparative analysis of de-S parameters

Parameters	Base Period	Trial Period
HM Sulphur, %	0.044	0.040
Reagent Consumption		
CaC_2 Reagent, Kg/t	1.66	1.52
Mg Reagent, Kg/t	0.333	0.305
HM [S] after treatment, %	0.009	0.0085
BOF Bath [S], %	0.018	0.0143
BOF [S] Reversal, %	0.009	0.006
Texture of ladle slag after treatment	Metallic & Heavier	Glassy & light
Slag Metal separation	Poor	Good
Slag Skimming Time	3 - 8 min	2 - 5 min

Table 4 : Synthetic slag addition regime

Nomogram 1		Nomogram 2	
Bath Sulphur (%)	Addition of Synthetic slag (kg/heat)	Bath Sulphur (%)	Addition of Synthetic slag (kg/heat)
Upto 0.018	Nil	Upto 0.015	Nil
0.019 - 0.021	300	0.016 - 0.020	300
0.022 - 0.024	400	0.021 - 0.025	500
0.025 & above	500	0.026 & above	600

Trial was conducted in 46 nos of rail heats as per nomogram 1. Only in three cases, the final sulphur was found to be more than 0.02%. The average final sulphur was found to be 0.017 %. In the second stage, trial was conducted as per nomogram 2 in 20 nos of heats to achieve sulphur $\leq$ 0.015%.

Casting of Rail Steel

Under the application of EMS technology, the stirring motion improves the heat transfer from the product axis to the skin as compared to simple convection and thus accelerates the dissipation of super heat and hence helps in enlarging the equiaxed structure. In addition to this the rotational force created by EMS drives the inclusions and gases to the centre of the liquid core of the strand and coalescence takes place, which facilitate floating. This is the basis of EMS in continuous casting, which has been found to enhance equiaxed zone and reduce axial segregation.

Fig. 5 : Macro of processed Rail from unstirred bloom

Fig. 6 : Sulphur print of processed Rails from stirred bloom

The central pipe and porosity which was present in unstirred cast bloom results in segregation line mark in the web portion of processed Rail as shown in Fig. 5. The line segregation mark of unstirred processed Rail is significantly reduced in case of stirred processed Rail Samples as shown in Fig. 6.

CONCLUSIONS

Rail is the most prestigious product of SAIL and SMSII, BSP is earmarked for the production of rail steel. Improvement in the quality of rails is the prime importance with the view of steel making to meet the stringent chemical specification as per the guideline (IRS-T-12-96) of Indian Railways. In continuation to improve the quality of rails, hot metal de-sulphurising facility and electromagnetic stirring for blooms has been commissioned. Therefore, overall process of steelmaking process for betterment of quality of steel has been looked and modified accordingly. A substantially low range of sulphur < 0.015% in rail has been targeted through HMDS - BOF - ARU - LF - RH - CC route. A two stage de-sulphurisation treatment is now employed in which the blast furnace hot metal is first treated by co-injection of Mg and CaC_2 reagents, and subsequent treatment with a synthetic slag former (CaO-Al_2O_3) added to the ladle during tapping from the BOF. The sulphur pick up in BOF is a concern due to poor slag skimming. Studies carried out by modified carbide reagent containing slag modifier. Improved hot metal top slag after HMDS was observed w.r.t. increased slag fluidity and slag - metal stratification, which resulted in easy slag removal and improvement in slag skimming efficiency and reduction in skimming time. No negative impact on desulphurization efficiency was observed.

Addition of petro coke in the steel ladle during BOF tapping increases the steel [S], therefore, an effective secondary steelmaking slag is essential by the addition of synthetic slag for the further refining of rail steel. Introduction of EMS in the bloom caster has improved the cast product to control internal properties w.r.t. equiaxed structure, reduce axial segregation etc. The sulphur prints of the processed rails were obtained. Centreline segregation was dispersed and no porosity & centerline pipe was observed. Line segregation in web portion of final rail samples has been significantly reduced.

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