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Hot Metal De-Sulphurisation by KR Process

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Abstract**: The objective of this project is to present an analysis of the use of residual mixtures in the pig iron desulphurization process. This study involves the Effect of Aluminium dross, fluorspar, and lime. These mixtures were made and added to a liquid hot metal with known chemical composition at a temperature of 1300 to 1420^{0}C. The mass of each element was calculated from its chemical analysis and compared with an industrial mixture. All of the mixtures used in the experiments were stirred by a mechanical stirrer. Samples were collected, and analysis was performed to check sulphur variation in the bath with time. The results were analyzed and the verified that it was possible to use as a desulfurizers. This project seeks to optimize parameters, reduce the cost of desulphurization and the consumption of operation about KR pre-treatment of hot metal. Based on the theoretical analysis of physical chemistry in metallurgy, simulation experiments of the KR desulphurization of hot metal were in a laboratory and the composition of the desulphurization was optimized, by means of chemical analysis. The optimized parameters of the process are put forward.

Key wards: sulphur, lime, aluminium dross, fluorspar, raking, stirring, ladle, impeller

I. INTRODUCTION

Sulphur is a detrimental impurity which causes brittleness and granular cracks in steels and adversely affects mechanical properties such as ductility and impact toughness. Sulphur (S) may dissolve in liquid iron (Fe) at any concentration. However solubility of sulphur in solid iron is limited: 0.002% in α-iron at room temperature and 0.013% in γ-iron at 1832°F (1000°C). Factors determine negative influence of sulphide inclusions on the mechanical properties. Cracks may be initiated at brittle sharp edge inclusions. Sulphide inclusions especially arranged in a chain form also make easier the cracks propagation along the grain boundaries. The negative effect of sulphur on the steel properties becomes more significant in large ingots and castings, some zones of which are enriched by sulphur (macro segregation of sulphur).

The properties negatively affected by sulphur:

A. Ductility,
B. Impact toughness,
C. Corrosion resistance, & Weld ability.

Therefore, hot metal from blast furnace must be treated prior to the oxygen steelmaking in order to obtain steels with low sulfur content in the desulfurization process, powdered reagents are injected into the hot metal through an immersed lance using nitrogen as carrier gas .The reagents chemically react with the sulfur forming lower density slag that ascends to the top of hot metal. Lime, calcium carbide and magnesium are the powdered reagents commonly employed for the hot metal desulfurization systems based on the injection, namely co-injection or mono-injection.

Stirring desulphurization process in hot metal ladle (hereinafter called KR process) in order to reduce operation cost, to achieve high productivity of hot metal desulphurization, and also to meet the increasing demands for low S steel grades.

II. LITERATURE SURVEY

The hot metal desulphurization process is an external pre-treatment of iron. It takes advantage of the high content of carbon, which implies a low activity of oxygen. A low activity of oxygen makes the desulphurization process more effective according the hot metal ladle is fully filled and the weight is measured, it is transported to the desulphurization station. Before starting the desulphurization process, a temperature and a composition sample of the hot metal are taken. The composition analysis gives the initial content of sulfur, which is one important parameter to decide the amount of desulfurizing reagent to be added. The desulfurizing reagent is a powder mixture of calcium carbide (CaC2) and carbon.

The injection system can be described as follows: The powder is stored in a silo, which is connected with a dispenser to ensure a better control of the reagent flow. Calcium carbide is dangerous in contact with any moisture. Therefore, the storage of calcium

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carbide is completely closed and is kept dry. The gas carrier used is nitrogen gas and the lance is a straight bottom discharger with 1 hole. The lance is lowered through the hood opening in the center of the hot metal ladle for injecting the desulphurization agent. The direction of the gas flow is along the long center of ladle. The turbulence is introduced when injecting powder and gas is the only way used to stir the melt during the desulphurization process.

The amount of reagent is recommended by the Level-2 system based on four parameters:

A. Temperature of hot metal,
B. Initial content of sulfur,
C. Final content of sulfur and
D. The amount of hot metal

During injection of the desulphurization agent, the reaction is intensive inside the ladle, which leads to splashing of hot metal outside of the ladle and a strong shaking of the lance. The flow rate of Lime/Calcium carbide is about 40-50 kg/min and Magnesium is about 8-10 kg/min for the Desulphurization process. The final composition sample is taken from the hot metal. The sulfur content after desulphurization is aimed < 0.010.

E. CaC_2powder

The desulphurization reaction of CaC_2 with sulfur is shown as follows:

$$CaC_2(s) + S \leftrightarrow CaS(s) + 2C$$

The affinity between calcium and sulfur is strong, which can lead to a direct reaction between the elements, reaction can be more easily achieved if the powder is directly injected to melt .The desulphurization process uses CaC_2 blended with coke powder. This reaction is endothermic and thus it reduces the temperature of the pig iron.

F. Mg powder

The desulphurization reaction can be written as follows:

$$Mg\ (g) + S \leftrightarrow MgS(s)$$

With Mg powder, very low sulfur contents can be achieved. The problem with Mg powder is that the vapor pressure of Mg is high, so that Mg bubbles forms when Mg powder is injected to the hot metal. Mg powder is usually blended with other desulfurizers to avoid too violent reaction in the hot metal.

G. Cao powder

Lime plays a major role in steel making in desulphurization. It is low cost and easily available therefore it's an economic desulfurizer's reagent. The desulphurization reaction of Cao with sulfur is shown as follows:

$$2Cao + 2S = 2CaS + O2$$

After completion of treatment ladle is sent for slag skimming. Before slag removal, both temperature and composition samples are taken. The most common method to remove the sulfur-rich slag is to tilt the transport ladle and rake the slag by a slag skimmer. During slag raking there will be iron losses in slag which is separated by magnetic separator and charged as scrap in converter. After de-slagging process, the hot metal is ready for charging into a BOF to produce crude steel.

III. PROBLEM DEFINITION AND OBJECTIVES

A. Problem definition

Problems observed in injection process are listed below:

1) Cac2 and Mg using as a reagent in injection process and these reagent material highly inflammable and more harmful to human body

$$CaC2 + H2O\text{- - >} Ca\ (OH)\ 2 + C2H2\ (\text{Acetylene})$$
$$Mg + O2\text{ --- >} MgO +$$

2) Injection process system is complicated as compare to KR process.
3) Injection based on pneumatic system and KR based on mechanical stirring system.
4) For material injection by injection lance in injection process but in KR material charge while impeller rotation
5) Compare to KR process cast is more per drop per ton of hot metal i.e 0.00

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6) Foster to removing sulphur into hot metal as compare to injection process
7) Sulphur revert is less, good rakability as compare injection because more concentration in cac2 treatment that slag becomes more viscou
8) More automation required to injection process as compare KR. In injection reagent are injected by pneumatically by using carrier gas as N2. Sometimes malfunction operation can happening due to its complex ability of operation
9) njection process have both material stored in dispenser and that can pressurized for making fluidity and dispenser have load cell that load cell will condition the percentage of valve opening, but sometimes error of load cell injection line andForeign material may enter while transporting/ grinding.
10) Dust collector should be good condition otherwise lot of material enters in to atmosphere and create unhealthy atmosphere.

B. Objectives
1) To increase the productivity.
2) To reduce the production cost.
3) To reduce the time duration for treatment.
4) To produce electric and infrastructure steel grades with low cost.
5) To eliminate the use of carrier gas in treatment.
6) To eliminate the utilization of harmful and inflammable reagents in treatment.

IV. MECHANICAL STIRRING PROCESS(K R PROCESS)

KR is hot metal pre-treatment system for desulphurization process in which reaction takes place by addition of reagents and mixing through mechanical stirring refractory impeller. It utilizes the efficiency of CaO as lime is cheap and easily available from lime plant. As compared to Injection system it is very simple process, further the treatment time is very short.
Since the final Sulphur achievement at KR is consistently very less as compared to injection process, nitrogen consumption is very less this process is very cheap as far as reagent consumption is concerned. Apart from that it equipped with less automation unlike injection equipment's, valves, lance handling and sophisticated logics. As far as safety is concern lime is also non-hazardous and safe to keep, since calcium carbide requires more stringent monitoring system for moisture control.

A. Kr Plant Major Equipment's
1) Impeller drive system
2) Reagent storage silos
3) Hot metal ladle car
4) De-dusting system
5) Slag racking machine
6) Impeller exchange unit

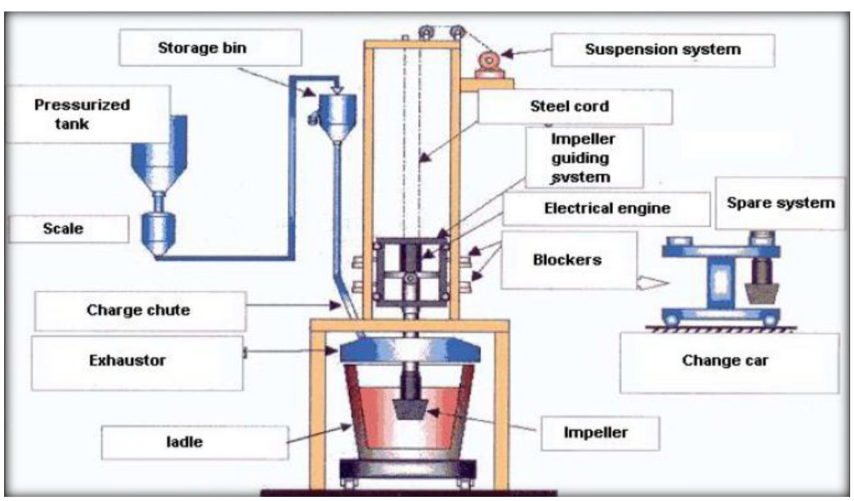

Fig 4.1 KR PROCESS OVERVIEW

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B. Process Description

1) *Pouring section*: Pouring station is the first section of KR process, where the received Torpedo ladles are tilted towards the empty hot-metal ladles placed down at the ground Level. Torpedo ladles can be received in tracks. Each track has 2 ladle cars, and the hot metal ladle capacity is 190 ton, hot metal is poured in the hot metal ladle by the tilting of Torpedo ladle, after completion of pouring of hot metal, taken the sample and temperature it's known by "BDS sample and BDS temp".
2) *Pre raking section:* Pre raking section is the Raking of blast furnace slag from the hot metal it was comes from the torpedo ladle, it is for better desulphurization efficiency. The skimmer basically rakes the surface of the hot metal, moving the slag accumulated on top into a separate slag dumping area. Tilters are provided to tilt the ladle into position so that the material moved by the skimmer falls into the slag dumping area in a safe way. A hydraulic system is used to generate the hydraulic pressure required to tilt the ladle for skimming and to operate the skimmer.
3) *Treatment section:* Place the Hot metal ladle for treatment, before starting the treatment assume all the desired materials in the charging bin (weigh hopper), after that start the treatment by the automation system, impeller will be lowered in the hot metal bath to certain immersion depth with the speed of 30 rpm, the time taken for the reaching of impeller to hot metal stirring position (HMS position) is about 2 minute 30 sec, after that the rotation speed will be increased in ramps and at a defined speed that is 70 rpm, after 30 seconds the all De-S (Cao+ Al dross / Cao + Fluorspar) material will be charged into the hot metal ladle It will takes 2 minute 30 sec, afterwards the impeller speed will be increased up to the maximum set point speed i.e. 90 rpm and follow that speed until the end of the stirring phase, the stirring is carried up to the time of 12 minutes, adjust the impeller rotation speed for aiming the desired Sulphur, The exact adjustment of rotation speed and impeller immersion depth, together with the special impeller design ensures the optimum bath mixture which is the key for optimum Sulphur removal. A strong downward metal stream initiated by rotating impeller with a high speed, desulphurization reagent particles are engulfed and dispersed deeply and uniformly into hot metal bath. During their stay in hot metal bath, hot metal [S] is reacted with CaO component and removed from hot metal as Cas. Below fig. 4.2 shows the treatment cycle.

$$Cao + [S] = Cas + [O]$$

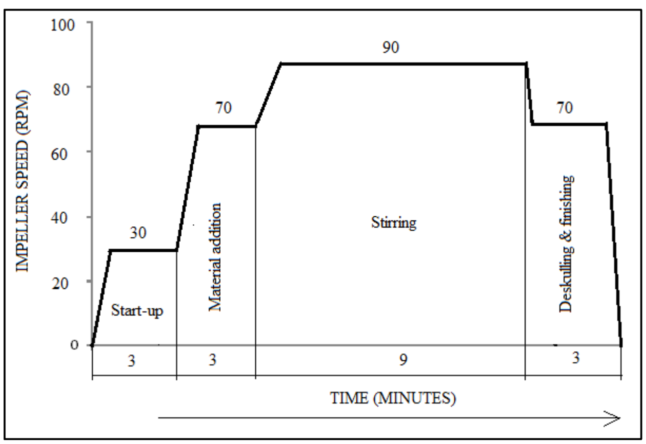

Fig. 4.2 KR treatment cycle

4) *Post raking section:* After completion of KR Desulphurization operation, Hot Metal Ladle will be sent to Post Raking Section for removing the slag from the Hot Metal with the help of Slag Raking Machine. After the treatment it is very important to remove slag to avoid reversal of Sulphur from slag into metal, therefore slag raking/skimming is done. Slag if not properly removed can cause early slag formation during blowing, resulting in slopping, slow de-carburization, extend of blow, oxidized converter slag and high S % in end chemistry and low end temperature. Raking operation will be performed by tilting of the Hot Metal Ladle to a suitable angle (controlled by HMLC Hydraulic System) & by using different movement of Raking Arm (controlled by the Raking Machine Hydraulic System). After completion of post raking taken the sample and temperature it's known by "ADS sample and ADS temp", after that confirm the ADS sample analysis then send the hot metal ladle to charging bay.

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C. Critical parameters in KR process

1) *Effective surface area ratio:* An index of effective surface area ratio is introduced to investigate the impeller shape design. The calculation formula is as follows;

Effective surface area ratio = (2w+t) x n x h / (D x H)

w	=	Propeller length of impeller
t	=	Propeller thickness of impeller
h	=	Propeller height of impeller
n	=	Number of propellers
D	=	Diameter of hot metal ladle
H	=	Bath depth

As shown in Fig.4.3, 2w+t means impeller diameter, n and h are fixed value to be 4 and 850mm – 900 mm, respectively. D and H are given values (also fixed value) in the target plant. Thus, the effective surface area ratio is proportional to impeller diameter.

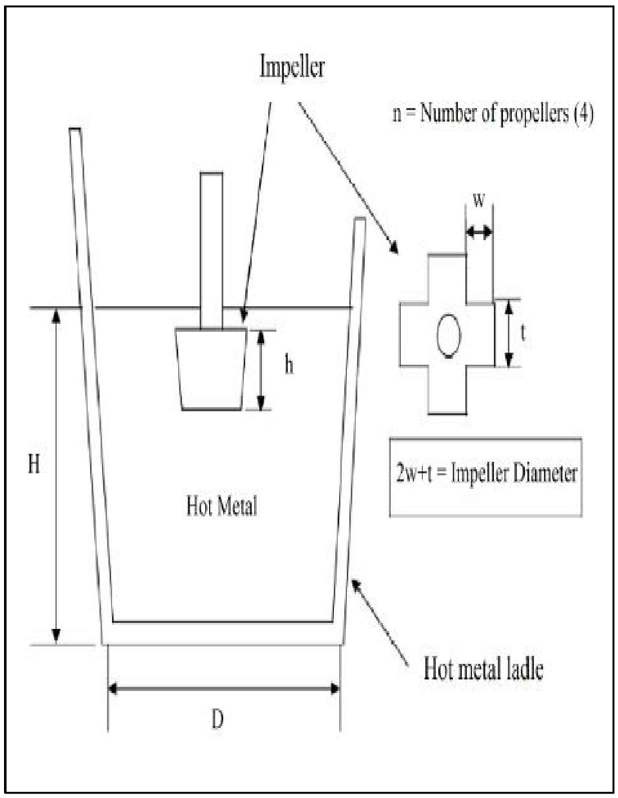

Fig.4.3 Symbol of effective surface area ratio

2) *Impeller Design:* The impeller is the critical parts and its dimension must be carefully designed depending on the target plant conditions. The followings are the dimensions to be designed and their symbols are indicated in Figure.4.4

a) *Propeller height: This* value usually ranges between 700mm and 900mm, but should be finalized aiming around 0.35 of the effective surface area ratio

b) *Propeller thickness and propeller width:* Once propeller thickness is decided, propeller width is automatically decided. Propeller thickness is designed based on the structural strength of propeller itself and castable refractory wearing rate. Usually propeller thickness is around 500 mm for 200 heats

c) *Angle*: This angle (α)is critical to refractory wearing of lower part of propeller which is mainly damaged in KR operation. Minimum cast able thickness is the distance between low edge of core metal and the outer surface of cast able. To be 200 heat life, this thickness is around 150 mm and the angle (α) can be calculated, for example, 4^0in No.2 steelmaking Shop of JSW steel limited

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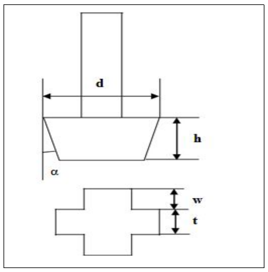

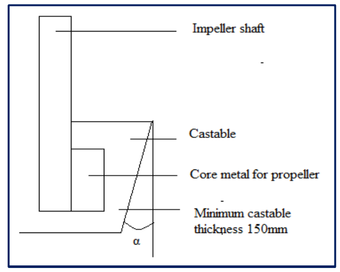

Fig 4.4 Impeller design

V. RESULTS

Formula for determine the specific consumption (kg/1drop) of material used to reduce the sulphur in hot metal in both processes i,e INJECTION method and KR process

$$\frac{\text{TOTAL CONSUMPTION OF MATERIAL}}{\text{WEIGHT OF HOT METAL * TOTAL SULPHUR DROP *(0.001)}}$$

A. Cao and AL dross heats

S. No	BDS temp	ADS temp	BDS (S)	ADS (S)	CaO	Aldross	RPM
1	1310	1280	0.023	0.0002	2190	188	105
2	1368	1330	0.035	0.001	2106	161	95
3	1360	1320	0.035	0.002	2106	231	100
4	1327	1285	0.038	0.002	1525	169	95
5	1362	1310	0.044	0.0004	2300	217	110
6	1364	1310	0.044	0.001	2288	208	90
7	1342	1310	0.044	0.002	2241	203	90
8	1343	1320	0.044	0.005	2362	200	95
9	1362	1320	0.045	0.0003	2394	320	100
10	1357	1330	0.046	0.002	2552	206	105

Table: 1

B. Cao and Fluorspar Heats:

S. No	BDS temp	ADS temp	BDS (S)	ADS (S)	Cao	Fluorspar	RPM
1	1355	1273	0.034	0.001	1708	154	105
2	1360	1277	0.034	0.001	1743	181	95
3	1366	1310	0.034	0.001	1710	133	100
4	1350	1305	0.036	0.0002	1927	176	95
5	1296	1266	0.038	0.0005	2161	450	110
6	1300	1270	0.038	0.0008	1926	294	90
7	1384	1354	0.038	0.0002	1648	145	90
8	1387	1357	0.038	0.001	1987	200	95
9	1336	1288	0.04	0.0002	1929	263	100
10	1360	1293	0.04	0.0005	1757	138	105

Table: 2

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C. Cac2 & Mg treatment in Injection system

Calcium carbide and magnesium are the reagents used for co-injection in injection system.

SL NO.	LADLE NO.	BDS (TEMP)	BDS (S)	ADS (S)	CAC2	MG
1	18	1327	0.045	0.001	0.524	73
2	9	1329	0.055	0.001	0.511	82
3	6	1343	0.044	0.002	0.696	83
4	18	1343	0.044	0.002	0.661	100
5	18	1300	0.032	0.002	0.75	89
6	17	1329	0.055	0.002	0.668	100
7	3	1350	0.121	0.002	0.963	130
8	3	1350	0.041	0.002	0.45	70
9	3	1348	0.083	0.002	0.81	122
10	10	1312	0.054	0.003	0.797	107

Table: 3

D. Comparison of material consumption for treatment to hot metal in KR & INJECTION system

Average consumption for 10 heats	Cao + CaF_2	Cao + Al dross
Cao (kg)	1953	2192
CaF_2/ A ldross (kg)	223	230
BDS (Sulphur)	0.045	0.046
ADS (Sulphur)	0.0006	0.002
Cao (kg/t)	10.28	11.53
CaF_2/ Al dross (kg/t)	1.17	1.21
Cao (kg/1 drop of Sulphur /t)	0.023	0.026
CaF_2/ Al dross (kg/1 drop of Sulphur /t)	0.0026	0.0027

Average consumption for 10 heats	CAC2 + MG
Cac2 (kg)	683
MG (kg)	95
BDS (Sulphur)	0.057
ADS (Sulphur)	0.002
Cac2 (kg/t)	3.69
MG (kg/t)	0.52
Cao (kg/1 drop of Sulphur /t)	0.067
MG (kg/1 drop of Sulphur /t)	0.0092

Table: 4(a) Table: 4(b)

Above table shows that (table 4,(a) material consumption for KR process and table 4(b) shows that material consumption For

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Injection process.

E. *Comparison of cost for treatment for hot metal weight of 190t.*

The table no 5.a shows that cost required for KR process. And table 5.b shows that cost required for Injection system.

Cost of Cao = 6 rupees
Cost of CaF_2 = 15 rupees
Cost of Al dross = 21 rupees

Average cost for 10 heats	Cao + CaF_2	Cao + Al dross
Cao (kg)	1953	2192
CaF_2/ Al dross (kg)	223	230
Cost of Cao (Rs)	1953*6 = 11718	2192*6 = 13152
Cost of CaF_2/ Al dross (Rs)	223*15 = 3345	230*21 = 4830
Total Cost (Rs)	15063	17982

Table: 5 (a)

Cost of Cac2 = 37 rupees
Cost of MG = 192 rupees

Average cost for 1s0 heats	CAC2 + MG
CAC2 (kg)	683
MG (kg)	95
Cost of CAC2 (Rs)	683*37=25271
Cost of MG (Rs)	95*192 = 18240
Total Cost (Rs)	43511

Table: 5 (b)

F. *Graph & discussion:*

1) *Cost difference in both treatments:* Table no.5 shows that cost difference between both Injection method and KR treatment process. Below graph 5.1 shows KR process is economic as compare to injection process.

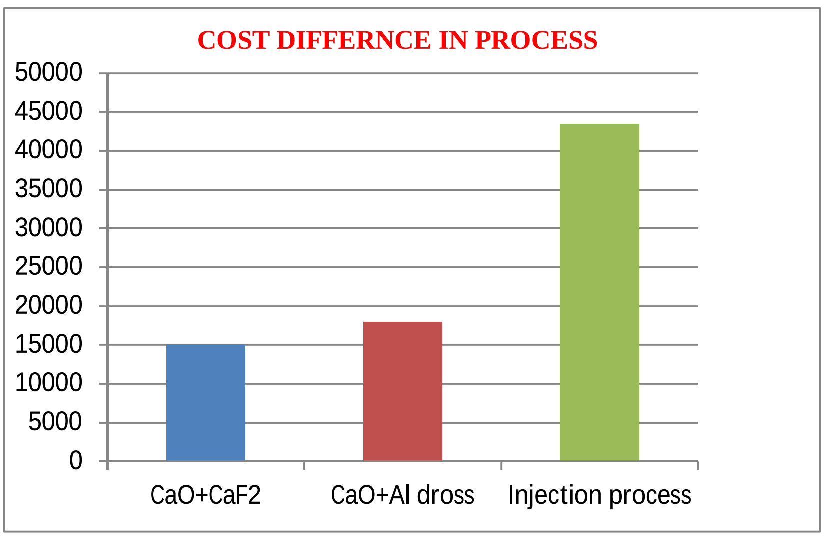

Fig 5.1

2) *Impeller rotation speed:* Below graph 5.2 shows the relation between impeller rotation speed and desulphurization ratio, which is described in the original patent (now expired). Desulphurization ratio is dramatically increasing at 95 rpm to 110 rpm of impeller rotation speed. The curve becomes flat; however, over 120 rpm of impeller rotation speed. So the target impeller rotation speed should be from 95 rpm to 110 rpm.

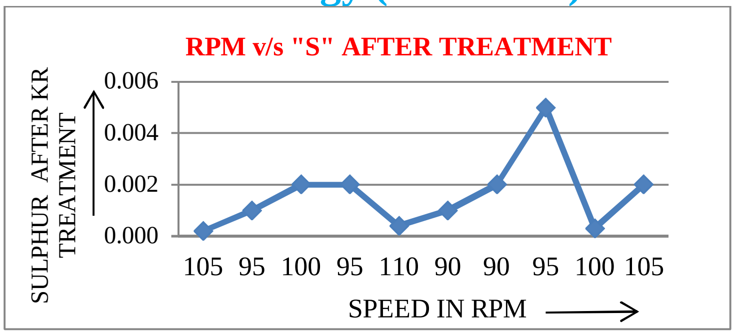

Fig 5.2

VI. CONCLUSIONS

In this study, an attempt was made to compare the two desulphurization reagent mixtures (CaO+CaF2 and Cao+ Al dross) used in KR desulphurization process based on the metallurgical performance and the costs. The numbers mentioned in this study should not be considered solid, as most of them are averages and estimates based on experience and literature (of which most are unrealistically positive about the performance of their own installation or method). Local circumstances and fluctuations are not considered in this study; however, based on this study some conclusions can be drawn

A. These results were achieved because the addition of CaF_2did not permits the formation of solid layer of Cas, which occurred when it was added Cao. This fact favoured the desulphurization reaction, leading to a better result.

B. The CaF_2reduces the mixture fusion point $CaO+CaF_2$, which produces a greater amount of liquid phase and, consequently, the mass transport is facilitated, favouring the desulphurization. Besides reducing the point of the mixture fusion, CaF_2also reduces the viscosity of the formed slag and also there is no formation of a possible calcium-silicate that would delay the desulphurization process.

C. The largest Desulphurization degree is obtained with the treatment of $CaO+CaF_2$mixture in reaction to the Cao+ al dross.

D. Considering the performance and the operational costs, the treatment with $CaO+CaF_2$mixture is better for achieving good results compared to the treatment with Cao+ al dross mixture.

E. Raking operation is more comfortable and less time consuming in treatment with $CaO+CaF_2$mixture than the treatment with Cao+ al dross mixture.

F. Less skull building around the impeller, ladle jam and raking plate, in the treatment with the$CaO+CaF_2$mixture compared to the treatment with Cao+ al dross mixture.

G. Finally, this study suggests that $CaO+CaF_2$mixture, gathers interesting characteristics from both the thermodynamics as well as kinetic aspect to its use in the process of desulphurization.

VII. ACKNOWLEDGMENT

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