

AN EFFICIENT PROCESS FOR DESULPHURIZATION OF FERROUS MELTS

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The paper describes a desulphurization process developed at the N.M.L. which offers high degree of desulphurization efficiency on both hot metal and steel. Results from the laboratory experiments presented in the paper show that it is possible to reduce sulphur from the normal hot metal levels of 0.05% to 0.09% down to less than 0.01%, by employing agents amounting to 1.2% to 1.5% of the metal weight.

Unlike the other presently popular desulphurizing agents, such as CaC_2 or Mg base materials, the present process is less susceptible to upward trend in raw material cost and also does not suffer from pollution hazards inherent in soda ash or CaC_2 treatment. The process is based on desulphurization by Mg vapour, formed in-situ from its compounds under the conditions of the molten bath.

INTRODUCTION

Low sulphur in steel is essential for improved notch toughness, tensile ductility, cold pressing properties and to avoid cracking failure as well as directional anisotropy in mechanical properties on hot working. Demand has been steadily on the rise in recent years for extra low sulphur ($\leq 0.01\%$) in quality steels for super-duty applications.

It is easier to desulphurize hot metal than steel, since activity coefficient of sulphur in the presence of higher carbon and silicon is five to ten times greater in hot metal than in steel (1). Desulphurization is also dependent on oxygen level, which is necessarily higher in steels. As a consequence of these factors and the inherent lower metal oxygen content, the equilibrium sulphur level in hot metal is orders of magnitude lower than in steel. Even though it is advantageous to desulphurize hot metal in the blast furnace, where even now bulk of the sulphur removal (90%-95%) takes place, the growing trend in recent years has been to supplement it with external desulphurization in order to increase the throughput rate and thermal efficiency of blast furnace. An external desulphurization station

between the blast furnace and steel melting shop has come to be a permanent feature in most of the integrated steel plants. For many alloy and special steels, additional desulphurization after steelmaking is also becoming a necessity.

Of the four alkali, alkaline and rare earth metals (Na, Mg, Ca, Ce) with high affinity for sulphur, which together with their compounds form bulk of the desulphurizing agents, the Ca and Mg base reagents have been more successful in industrial applications from the point of view of efficiency, cost and consistency of results. Ce, although by far the most efficient desulphurizer, is too expensive. Soda ash, the common Na base agent, though the least expensive, has limited desulphurizing capacity. It is good for higher sulphur ranges only, and suffers from inconsistency in performance and causes pollution problem due to generation of noxious fumes and gas during treatment.

Of the calcium base reagents, lime (CaO), although inexpensive and holds considerable promise for the future, has not gained much in popularity, since large application rate of the reagent causes unmanageable slag volume and handling problem. Calcium carbide

TABLE 1
Performance and Efficiency of Desulphurizing Agents

Reagent(R)	%S/kg/R:THM	Kg.R/ 0.01 %S/ THM	Sulphur Range (%)	Rate of R Addition Kg/THM
Mg granules	0.06	0.18	0.05-0.01	0.7
Mag-coke	i) 0.037 ii) 0.035	0.28	0.05-0.005	1.2
65 Mg/35 Al 50 Mg/50 Al	0.055-0.044 0.035	0.18-0.23	0.048-0.022	0.7
Soda ash	.007	1.5	0.10-0.035	10
CaC ₂				
(i) Injection	0.0073	1.3	0.05-0.02	4.0
(ii) Agitation	0.0099	1.0	0.05-0.02	3
(iii) NSC with reaction acid	0.0121	0.83	0.04-0.01	2.5
(iv) ATH with CAD i)	0.0055	1.83	0.04-0.01	5.5
Mix ii)	0.0077	1.29	0.055-0.02	4.5
Lime				
(i) Injection	0.0026	3.8	0.05-0.02	11.5
(ii) Agitation	0.0031	3.2	0.05-0.02	9.5
(iii) Injection with H.C.gas	0.0040	2.5	0.05-0.02	7.5
(iv) Lime/Soda (9:1) Injection	.0040	2.5	0.05-0.02	7.5
(v) Lime/Soda (9:1) Agitation	0.0051	2.0	0.05-0.02	60

(CaC₂), the most popular desulphurizing agent to date is efficient but the capital cost for infrastructures for dispensing the reagent either by pneumatic lance injection or by mechanical stirring method is very high. Besides, safety problems are encountered in handling the after-treatment slag due to generation of acetylene gas in the presence of moisture. As for magnesium, it is being used in the following forms - (i) granules (2) injected via stream of carrier gas; (ii) proprietary "Mag-Coke" (3,4) plunged through graphite bell; (iii) Mg-Al alloys (3) and (iv) Mg powder mixed in lime as in lime-mag process (5). The last two utilize injection technology and have been in commercial use with considerable success. Table-1 (6) lists the relative performance efficiencies of the common desulphurizing agents in hot metal, showing the superiority of Mg as a desulphurizing agent over others.

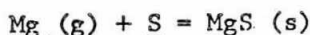
Both Ca and Mg metals are products of energy intensive processes and

both are subjected to steep cost growth rates in line with the rise in energy costs in recent years. It was, therefore, the objective of the present research programme to develop a process which combines the high desulphurization efficiency of Ca or Mg with a compromise on infrastructural capital cost. The present process developed as a result combines both the above advantages and more importantly it is not handicapped by the escalating price hike of Mg metal which is the desulphurizing agent used here.

The selection of Mg as the desulphurizing agent is based on the consideration of many advantages associated with it, such as (i) low equilibrium sulphur levels approaching the theoretically attainable values; (ii) virtual instantaneous reactivity with sulphur - the high kinetics of the reaction is due to the existence of Mg in vapour phase in hot metal, which renders thorough agitation and mixing of Mg vapour with liquid metal and rapid partitioning of sulphur through

gas-liquid interface; (iii) higher reaction efficiency with decreasing bath temperature, contrary to other agents, due to the reduction in Mg and S solubility product with decreasing temperature; (iv) easy slag disposal, as the slag is crusty-solid and also low in volume, (v) insensitivity to blast furnace carry-over slag; (vi) secondary desulphurization due to the presence of residual magnesium in solid solution, the level of solubility being higher and so better in Mg than in Ca; (vii) absence of toxic fume or pollution problem. Calcium as metal satisfies many of the above properties and, in particular, it is capable of bringing down sulphur in steel to much lower level than possible by Mg (1.0×10^{-7} wt.% equilibrium residual sulphur with Ca vs. 2.4×10^{-3} wt.% with Mg) (8), a property which has been successfully utilized in TN-process for desulphurization of steel. However, in addition to Ca metal being expensive, high capital cost for injection station is associated with the process.

The effective desulphurization capacity of Mg in hot metal can be ascertained by calculating the equilibrium residual sulphur from thermochemical analysis of the reaction:



The reference state for Mg and MgS is pure substance and for sulphur pure liquid iron in infinitely dilute

solution. The equilibrium constant of the above reaction given by

$$K = a_{\text{Mgs}} / P_{\text{Mg}} \cdot a_{\text{S}}$$

is calculated from free energy - temperature relations to be 18,500 for hot metal at 1370°C and 412 for steel at 1600°C (8). Assuming that MgS does not form solid solution with other constituents in the slag, its activity could be set to one. Assuming one atmosphere for Mg vapour, the equilibrium S activity is then given by

$$a_{\text{S}} = \frac{1}{K} = \frac{1}{18,500} \quad \text{for hot metal at } 1370^{\circ}\text{C}$$

$$\text{and } a_{\text{S}} = \frac{1}{K} = \frac{1}{412} \quad \text{for steel at } 1600^{\circ}\text{C}$$

Since $a_{\text{S}} = f_{\text{S}} \cdot [\% \text{S}]$, taking activity coefficient of sulphur, f_{S} , to be 5 for typical hot metal composition (1) and one for steel, the equilibrium S contents with one atmosphere of Mg vapour for hot metal and steel come out to be 1.1×10^{-6} and 2.4×10^{-3} , respectively. Similar calculations done by Pehlke (8) for equilibrium sulphur levels in hot metal and steel with Ca, CaC_2 , lime and Ce, for an f_{S} value of 5 for hot metal is shown in Table 2 (8), showing the relative desulphurization capacity of several other potent agents in respect to that of Mg.

TABLE 2

Reactant	Desulphurising Reaction	WT % Equilibrium Residual Sulphur	
		Hot Metal	Steel
Mg	$\text{Mg(g)} + \underline{\text{S}} = \text{MgS (s)}$	1.1×10^{-5}	2.4×10^{-3}
Ca	$\text{Ca(l)} + \underline{\text{S}} = \text{CaS (s)}$	2.8×10^{-10}	-
	$\text{Ca(g)} + \underline{\text{S}} = \text{CaS (s)}$	-	1.0×10^{-7}
Ce	$2\text{Ce} + 20\underline{\text{S}} = \text{Ce}_2\text{O}_{20}\text{S}$	-	$\frac{1.3 \times 10^{-20}}{\% \text{Ce } \% \text{O}}$
CaC_2	$\text{CaC}_2(\text{s}) + \underline{\text{S}} = \text{CaS(s)} + 2\text{C(s)}$	5.0×10^{-7}	-
CaO	$\text{CaO(s)} + \underline{\text{S}} + \text{C(gr)} = \text{CaS} + \text{CO(g)}$	1.0×10^{-3} (at 1300°C)	-
	$\text{CaO(s)} + 2\underline{\text{S}} + \text{Si(s)} = 2\text{CaS(s)} + \text{SiO}_2(\text{s})$	2.5×10^{-5} (at 1300°C)	-

EXPERIMENTAL

As mentioned earlier, the process is based on desulphurization via Mg metal which is obtained from inexpensive raw material sources, wherefrom Mg is liberated in-situ under high temperature conditions of ferrous bath. The raw material used is in the form of calcined dolomite (dolime) or a mixture of CaO and MgO or MgO alone in combination with suitable reductants comprising Si, Al or Ca or their alloys along with flux constituents. Close proximity and large interface area of contact between the different reactants, essential for the progress of the reaction, are achieved by using the constituents in very finely powdered form and compacting the mixture under pressure into the form of briquettes. Owing to their low density (approximately 2 g/ml) the briquettes are required to be plunged into the molten bath, as otherwise they float and burn off on the surface of the bath.

From thermodynamical considerations high temperature is essential for thermal decomposition of MgO. The kinetics of the reaction is, on the other hand, favoured under reduced pressure, since the reaction product, Mg, is in gaseous state (b.p. of Mg: 1107°C). Plunging briquettes into the bath increases pressure in the reaction zone due to the ferrostatic head, which slows down the reaction kinetics. On the other hand, the liberated Mg vapour traversing through larger metal volume achieves greater surface area of contact with the molten metal, resulting in better utilization of Mg and higher desulphurization efficiency. Thus the depth of plunging of the briquette and temperature of the molten bath together can offer an element of flexibility to the reaction kinetics and the degree of utilization of Mg, similar to what is being experienced in Mag-Coke operation also.

Experiments were carried out in the laboratory in magnesite lined open-bath induction furnaces of capacities 10 kg and 30 kg. The melting stock in general was m.s. rods to which weighed additions of graphite, Fe-Si & Fe-Mn were made and the molten metal deoxidised with Al to ensure low metal oxygen content. This was followed by controlled addition of FeS to increase the bath sulphur to hot metal level, i.e. 0.05% to 0.09%. To add the reagents two types of plungers were used. The graphite plunger

used in the first phase of experiments was made from spent graphite electrodes. The refractory plunger used subsequently was made from kayanite cups, pressed and fired to high temperatures, which was attached at its base to a steel rod covered with fired refractory sleeves, similar to the arrangement for stopper rod-stopper head assembly. Both types of plungers had holes drilled into the sides of the bells (cups) at several locations to allow for escape of Mg vapour during plunging. The temperature of the bath varied from 1600°-1650°C. The power input to the furnace was regulated to maintain the above temperature range, as the bath temperature increased with the progress of reaction, accelerating the rate of reaction further and resulting in throwing off of molten metal by the rapidly escaping Mg vapour. A mixture of CaO+CaF₂ or CaO+Al₂O₃ powder was sprinkled on the bare bath before and during plunging to maintain a slag cover on the bath for entrapment of the reaction product, MgS, which otherwise tends to get oxidized reverting the sulphur back into the metal.

The reagents were used in fine powder form (-100 mesh) and compacted to briquettes under a pressure of 4-20 T/sq. in. Reagents amounting to approximately 1.0 to 1.6 per cent of the metal weight, made up in several briquettes of known weight, were used in the experiment. Depending upon the experimental parameters and the condition of the bath, the reaction rate varied from moderate to extreme briskness, even to the extent of throwing off molten metal around. In all cases, bright flame characteristic of Mg burning in air was noticeable, the intensity of the flame increasing with the increasing briskness of reaction. Owing to the shallow plunging of briquettes into the molten metal in order to avoid excessive metal throw off, and the limited volume of metal involved, the liberated Mg vapour in most occasions escaped in profusion and burnt above the bath, as testified by the appearance of bright flashes of light during the entire course of plunging.

Button samples for chemical analysis were collected before plunging and subsequently at the completion of each plunging operation, marked by complete consumption of briquettes into the metal and disappearance of burning Mg flame outside. Premature withdrawal of

plunger from the metal bath was indicated by the flame of burning Mg coming out from the remainder briquettes lodged inside the cup. At times due to vigorousness of reaction or ineffective plunging, broken pieces of briquettes floated up on the bath issuing Mg flame. However, results from such experiments were deleted while compiling this report.

RESULTS

The results of chemical analysis for sulphur and other constituents in the treated metal as a function of desulphurizing agents addition are shown in a series of graphs, Figs.1 to 6 and the detailed results and other related information are tabulated in Table 3A and 3B. For an assumed theoretical 100% conversion of MgO into Mg, the corresponding liberated Mg, the actual desulphurizing agent here, is shown along the same X-axis together with the briquette, both expressed in weight percents.

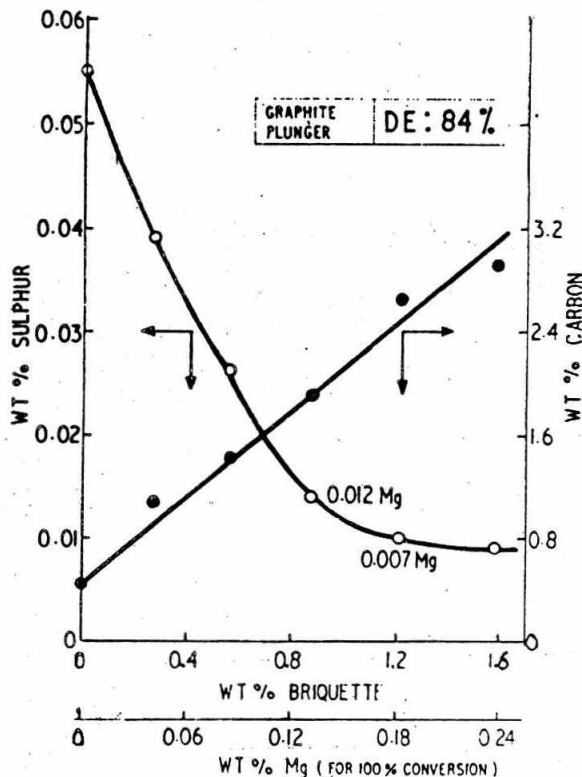


Fig. 1 Sulphur and carbon content in metal vs. weight per cent briquette and Mg for heat no. 85J2. Appropriate scales indicated by arrows. Residual Mg for two samples indicated on sulphur curve.

Fig.1 shows the plots of wt.% Sulphur and Carbon against wt.% briquette additions for heat no. 85J2, wherein the reductant amounted to 20 wt.% of the briquetting mixture, the other constituents in the briquette being dolomite: 79% and CaF_2 : 1%. A drop of sulphur from 0.055% to less than 0.01%, estimated by evolution method of wet chemical analysis, is observed for an addition of 1.2 wt.% briquette or, in terms of Mg, for 0.18% theoretically available Mg. As is the normal case, at lower ranges of S the rate of requirement of the briquette is observed to go up considerably for each quantum drop in S. The residual Mg level in the metal at low sulphur ends is shown for two cases on the sulphur curve. The figure also shows a plot of bath carbon which steadily increases from a starting 0.4% to 2.85% at the end, due to a pick-up from dissolution of the graphite plunger which bore mark of considerable erosion during the experiment. A high order of desulphurization efficiency (D.E.) of 84% was achieved in this case.

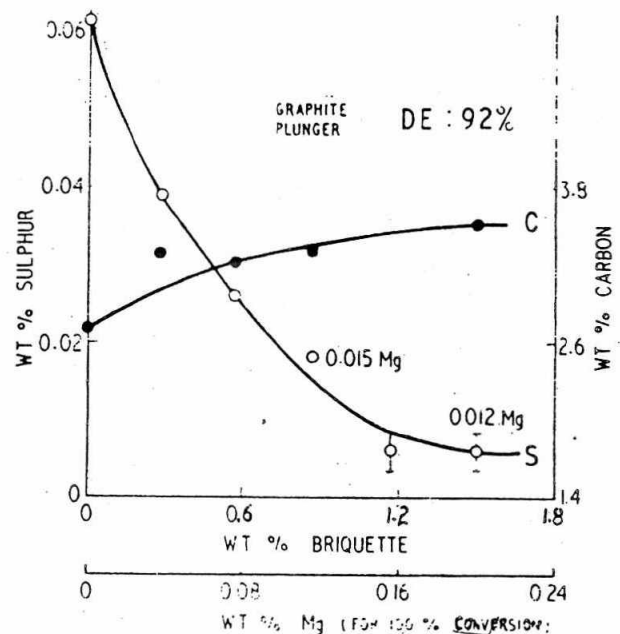


Fig. 2 Sulphur and carbon content in metal vs. weight per cent briquette and Mg for heat no. 88J5. Residual Mg for two samples indicated on sulphur curve.

Fig.2 shows the results for heat no. 88J5. The starting material here was pig iron but further pick-up of carbon occurred during the experiment bringing the level to 3.51% from the original 2.7% C. A high order of

desulphurization from 0.061% down to 0.006% S was obtained in the presence of a theoretical 0.16% Mg, from a 1.2 wt.% briquette addition giving a D.E. of 92%. Residual Mg levels of 0.012%-0.015% was obtained in the final metal. In this experiment, a combination of reductants comprising FeSi and Al were used.

Fig.3 shows the results for heat no. 90J7, using a combination of reductants dominated by CaSi. The reaction was late in initiation and considerably subdued throughout. Nonetheless, a DE of 85% was obtained with a drop of S from 0.052% to 0.008%. Also, considerable pick-up of carbon in the bath from 1.15% to 1.95% occurred, even though residual Al, added in large excess to ensure low bath oxygen, dropped from 0.34% down to 0.24% between two subsequent briquette plungings. When CaSi was replaced by FeSi in the mixture, the reaction was suppressed as indicated by the inert nature of the resultant briquettes.

All the results hereafter described are for experiments conducted with refractory plunger (Table-3B), while the above results were based on the use

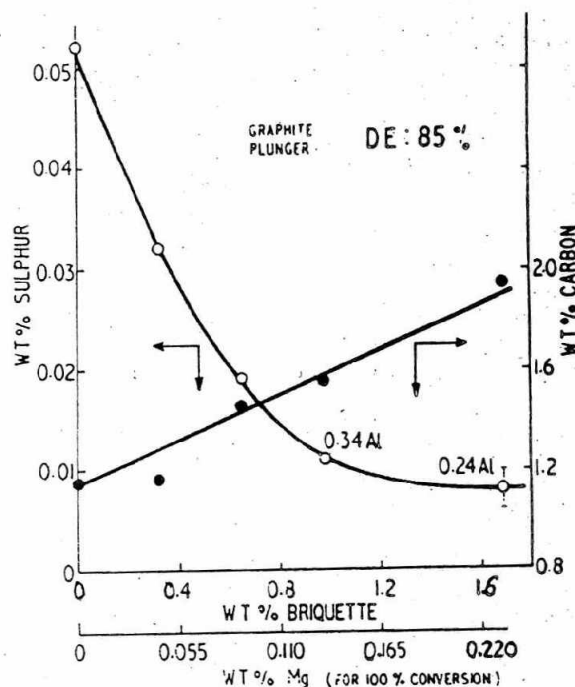


Fig.3 Sulphur and carbon content in metal vs. weight per cent briquette and Mg for heat no. 90J7. Bath Al for two samples indicated on sulphur curve.

TABLE 3A

Heat No.	Element	Original	BATH ANALYSIS					DESULPHURISATION EFFICIENCY		Mg Utilisation Factor (%)
			After sequential addition of briquettes					DE ^I Si-Sf/Si x 100* (%)	DE ^{II} %S/0.17Mg**	
			1st	2nd	3rd	4th	5th			
85J2	S	0.055	0.039	0.026	0.014	0.009	0.009	84	0.026	23
	C	0.41	1.09	1.40	1.90	2.65	2.85			
	Mg	-	-	-	0.012	0.007	-			
88J5	S	0.061	0.039	0.026	0.018	0.006	0.006	92	0.028	33
	C	2.7	3.29	3.20	3.33	-	3.51			
	Mg	-	-	-	0.015	0.005	0.012			
90J7	S	0.052	0.032	0.019	0.011	-	0.008	85	0.020	23
	C	1.15	1.15	1.45	1.55	-	1.95			
	Al	-	-	-	0.34	0.24	-			
95J10	S	0.090	0.074	0.061	0.045	0.035	-	(1.1)	0.036	25
	Al	0.46	-	-	-	0.28	-	61		

Heat Size: 8 kg; Reagent weight: 100 gm; Plunger: Graphite except Refractory for 95J10; Briquetting Pressure: 6T/sq.in. MgO in dolime: 30%.

* DE^I: for application of 1.5 wt.% desulphurising agent (for 95J10 the application rate: 1.1 wt.%)

** DE^{II}: for sulphur range given by initial S to final S in each.

TABLE 3B

Heat No.	Element	Original	BATH ANALYSIS				DESULPHURIZATION EFFICIENCY		Mg Utilisation Factor (%)
			After sequential addition of briquettes				DE ^I $S_i - S_f / S_i \times 100^*$ (%)	DE ^{II} 7S/0.1Mg%**	
			1st	2nd	3rd	4th			
106J18	S	0.070	0.031	0.028	0.025		64	0.014	12
	C	0.54	-	-	0.46				
	Si	0.22	-	-	0.23				
	Mn	0.73	-	-	0.83				
107J19	S	0.048	0.038	0.017	0.011		73	0.012	13
	C	0.42	-	-	0.45				
	Si	0.26	-	-	0.38				
	Mn	0.83	-	-	0.92				
108J20	S	0.054	0.035	0.019	0.012		74	0.013	15
	C	0.45	-	-	0.46				
	Si	-	-	-	0.47				
	Mn	0.82	-	-	0.97				
120J25	S	0.042	0.020	0.013	0.009		76	0.011	13
	C	0.32	-	0.30	-				

Heat size: 10 kg; Reagent weight: 150 gm; Plunger: Refractory;
Briquetting Pressure: 20T/sq.in.; MgO in dolime: 40%

* DE^I : for application of 1.5 wt.% desulphurising agent

** DE^{II}: for sulphur range given by initial S to final S in each.

of graphite plunger (Table-3A). Experiments with refractory plungers were conducted to study the efficacy of the process for desulphurization of steel, since bath composition remains unaltered in this case.

Fig.4 shows results for heat no. 95J10, using the same combination of reductants as in heat no. 88J5 (Fig.2) with the exception that a refractory plunger instead of a graphite plunger was used here. Also, the starting material here is steel having C in the range of 0.4% which remained unaltered throughout the experiment. A marked drop of Al from 0.46% to 0.28% can be noticed here, indicating continuous reduction of oxides of Mn and Si as also some ingress of oxygen into the bath. Sulphur dropped from 0.090% to 0.035% giving a D.E. of 61%.

Fig.5 shows results for heat no. 106J18, using the same reductant as in 85J2. Owing to the use of refractory plunger, the bath composition remained more or less unaltered throughout the experiment as shown by the C, Si, Mn analyses in the figure. In fact, carbon registers a decrease from 0.54% to 0.46% while Mn as usual shows a slight pick-up. A DE of 64% is obtained for a

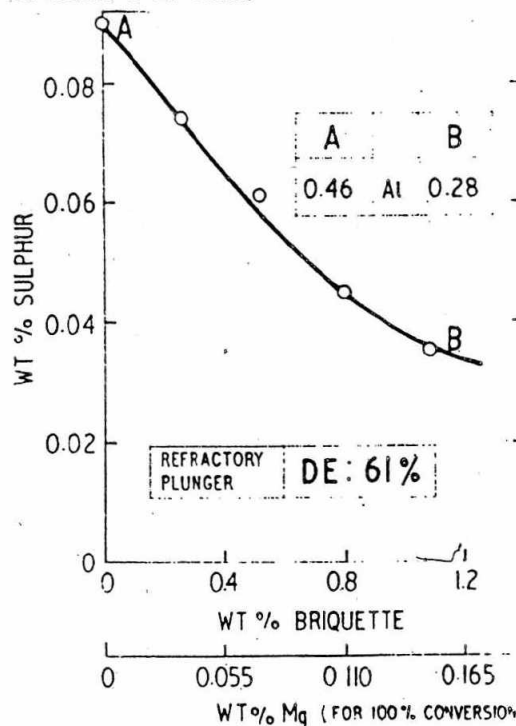


Fig.4 Bath sulphur vs. weight per cent briquette and Mg for heat no. 95J10. Initial and final levels of bath Al indicated in attached box.

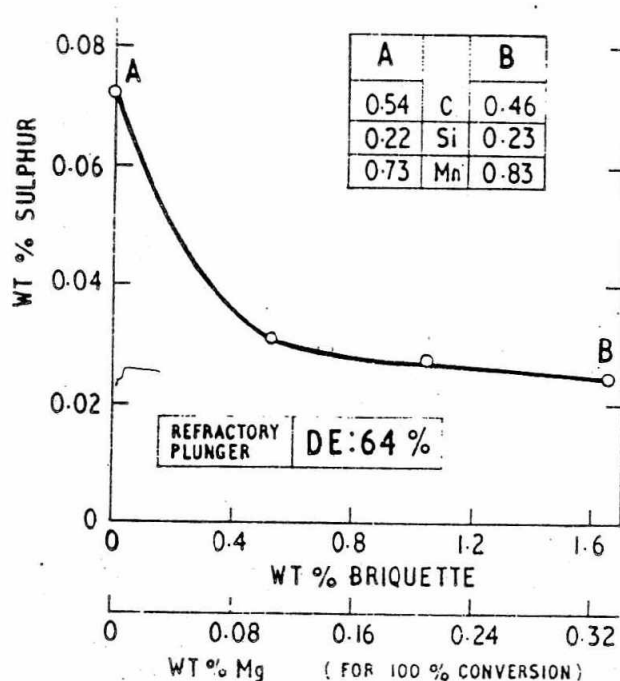


Fig. 5 Sulphur and carbon content in metal vs. weight per cent briquette and Mg for heat no. 106J18. Bath analysis for C, Si, Mn at starting and end of experiment shown in attached box.

drop of S from 0.070% to 0.025%, as compared to 84% for 85J2 where the bath carbon was much higher.

A combined plot for three heats, viz. 107J19 (Curve Y), 108J20 (Curve X) and 120J25 (Curve Z), all employing refractory plunger is shown in Fig. 6. The corresponding reductants being used are Al plus CaSi; Al plus FeSi and Al plus CaSi plus FeSi, respectively. Comparable order of D.E. is obtained in all three cases, although 120J25 heat appears to be somewhat more efficient (D.E.-79%), since here both the initial (0.042%) and the final (0.009%) S levels are lower than in the other two heats. Next in order of efficiency comes heat no. 107J19 with D.E. of 77% for a reduction of S from 0.048% to 0.011%, closely followed by heat no. 108J20 with a D.E. of 78% and a reduction of sulphur from 0.054% to 0.012%. Bath carbon analysis in all three cases remained unaffected during the experiment while only minor alterations in the levels of Si & Mn were noticed.

Thus, results in Table 3B and that of heat no. 95J10 in Table 3A, pertain to desulphurization reaction as applied

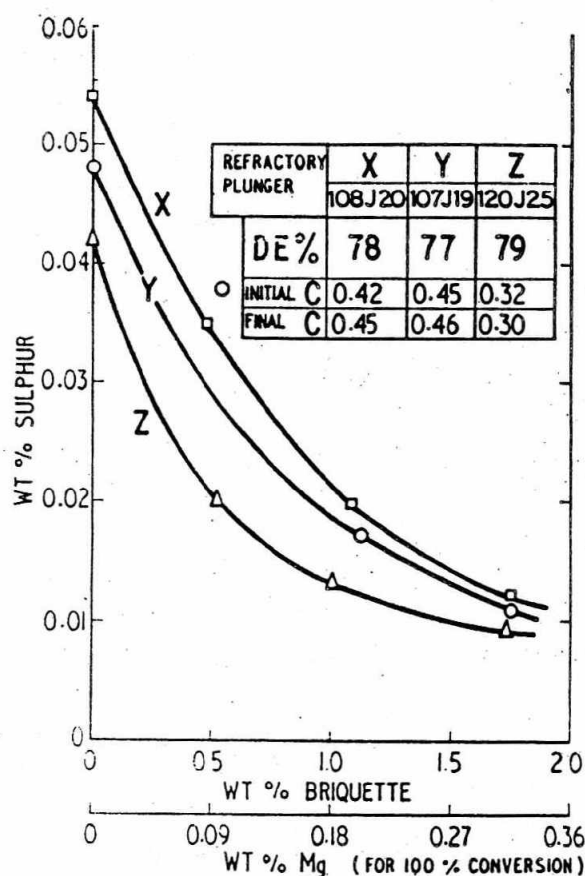


Fig. 6 Bath sulphur vs. weight per cent briquette and Mg additions for heat nos. 107J19, 108J20 and 120J25. Initial and final C for each heat indicated in attached box along with degree of desulphurization attained.

to steel bath, while the rest of the results in Table 3A approximate the case for hot metal, with the provision that Si content, and in one case (90J7) also the C content of the bath, both of which aid in desulphurization, were considerably below normal levels encountered in hot metal.

DISCUSSION

Detailed results showing bath analysis for different elements, desulphurization efficiency and Mg utilization factor are shown in Table 3A and 3B. Desulphurization efficiency (D.E.) is expressed here in two ways. D.E. I defined in the normal manner $DEI = \frac{(S_{initial} - S_{final})}{S_{initial}} \times 100$ is tabulated for all the heats for an uniform application rate of 1.5 wt.% of the reagent. In

one experiment, viz. 95J10, where the application rate was less than 1.5 wt.%, the results are based on 1.1 wt.% of the reagents. DE^I is shown also in Figs. 1 to 6 where it is calculated on the basis of maximum desulphurization obtained (i.e. minimum s_f) corresponding to the maximum available application of the reagents. This shows somewhat higher DE^I values for the steel samples compared to those in Table 3B. This is because desulphurization rates being comparatively slower in steel than in carbon rich baths, a plateau in the curves is still not reached at 1.5wt.% reagent level. Therefore, small differences in application rates beyond 1.5 wt.% still made differences in DE^I values.

A high order of DE^I varying from 84% to 92% is seen to be attained in carbon rich baths as in 85J2, 88J5 and 90J7 heats. For steel compositions which refer to the remaining heats, experimented with refractory plunger, DE^I is comparatively lower, varying from 61% to 76%. The results show the decided advantage of higher bath carbon for efficient desulphurization. This is understandable, since both C and Si (as also Al and P) increase the activity coefficient of sulphur, f_s , in molten iron (9) (f_s in hot metal being five to ten times higher than in steel) and the equilibrium residual sulphur in hot metal is lower by orders of magnitude than in steel, see Table 2. In the present case, even for the carbon rich heats, the bath composition fell short of hot metal composition, since whilst carbon was picked up in the bath from graphite plunger, Si remained unaltered at the original level which is considerably lower than that in hot metal. It is conceivable that with hot metal composition, the present technique should be capable of offering an even higher degree of desulphurization efficiency (DE^I) that obtained in the laboratory heats.

Desulphurization efficiency as expressed above does not convey explicitly an idea regarding the relative efficiency of the reagents employed for comparison with one another. For this reason, it is customary now to correlate the percentage drop in sulphur with weight of the reagent and the bath size. It is expressed in two ways, in terms of percent S removed per kg of reagent per ton of hot metal (THM), (%S/kg/THM), or as kg of reagent per 0.01 percent drop

in sulphur per ton of hot metal, (kg/0.01%S/THM). In the present case, the desulphurization efficiency, DE^{II} is calculated adopting the former convention, with the modification that since these heats were done on kg scale only, rather than converting the figures to tonnage scale, DE^{II} is redefined as,

$$DE^{II} = \%S/0.1\% \text{ Mg.}$$

This appears reasonable, since kg/THM amounts to 0.1% of the reagent and Mg is the active desulphurizing agent in this case. DE^{II} as defined above varies with the range of sulphur being considered, increasing with higher levels of initial and final sulphur and vice versa.

In Tables 3A and 3B, DE^{II} values are presented for the range of sulphur given by the corresponding initial and final sulphur values in the table, which are different for different heats. The DE^{II} values can be compared with the industrial trial results on hot metal for several Mg base agents, given in Table 1.

For the sake of comparison of relative efficiency, it would be preferable to calculate DE^{II} for definite sulphur ranges which is shown in Table 4, for the ranges 0.05%-0.02%S, 0.05%-0.015%S and 0.05%-0.01%S. Results from industrial trials on Mag-coke (3,4,10), Mg-Al alloys (3,10), Mg granule (2,10) and Lime-Mag (5,10) for the above sulphur ranges are also presented for comparison. As for Mag-coke and Mg-Al alloys, the results from Table 1 which are given in terms of kg of reagent weight were recalculated for kg of contained Mg in each case, assuming 45% Mg in Mag-coke and 65% and 50% Mg, respectively, in the two Mg-Al alloys. The results show that the DE^{II} values for the laboratory heats are two (for Mag-coke, Mg-Al alloy) to three (Mg granule, Lime-Mag) times lower than those for the industrial heats using the more established techniques.

This is, however, not surprising for two reasons. Whilst all the industrial processes utilise Mg metal directly contained in the reagents being used, the present technique in effect involves a two-stage process. In the first stage, Mg metal is generated from its compound by thermal decomposition involving a solid-solid interface reaction and in the second stage the liberated Mg is utilized for desulphurization reaction. Each process operates with a certain

TABLE 4

Desulphurization Efficiency (DE^{II}) at Different Sulphur Ranges for Mg base Agents

	Sulphur Range (%)		
	0.05-0.02	0.05-0.015	0.05-0.01
85J2	0.032	0.031	0.024
88J5	0.038	0.035	0.031
90J7	0.036	0.033	0.027
Mag-coke	0.078 ⁽³⁾	0.068 ⁽¹⁰⁾	
65Mg-35Al	0.077 ⁽³⁾	0.068 ⁽¹⁰⁾	
50Mg-50Al	0.07 ⁽³⁾		
Mg granule		0.09 ⁽¹⁰⁾	0.06 ⁽²⁾
Lime-Mag		0.11 ⁽¹⁰⁾	

efficiency factor, which is being compounded for the two-stage reaction in the present case. Secondly, the present experiments were carried out in less than ideal condition for proper utilization of Mg vapours being released. The factors responsible for low utilization of Mg (Table 3A and 3B) are: (1) limited volume of metal being treated; (2) shallow bath depth with inappreciable ferro-static head and (3) induction stirring effect preventing continuous slag cover over the bath with the resultant continuous ingress of oxygen.

The Mg utilization factor was calculated assuming an ideal 100% recovery of Mg from its compounds. This was compared against the sum of stoichiometric requirement of Mg for removal of sulphur and the residual Mg content in the metal, the latter being calculated theoretically from the available Mg-S solubility product values. The residual Mg being reciprocally related to the sulphur content is significant only at low sulphur ranges. To account for the low degree of Mg utilization, calculation was also made for consumption of Mg in reacting with oxygen dissolved in the bath. For this, in the absence of available data with oxygen analysis, a $[S]/[O]$ of 10 was assumed to arrive at an estimate of bath oxygen level (7). The resultant consumption of Mg was, however, found to be inappreciable. Thus, the low utilization factor in this

case arises primarily from the physical loss of Mg vapour due to its rapid rise to the surface through a shallow metal bath.

It is reported (11) that highest degree of Mg utilisation is attained when Mg vapour is released and is allowed to rise through the metal as individual bubbles, as in Lime-Mag process (10). Such a situation is obtained only with a small rate of Mg consumption or with a sufficiently high ferrostatic head pressure. Departure from these conditions lead to the transition of gas-liquid stream structure from individual bubbles to foam and finally to channel structure, in which state Mg vapour forms gas voids of great length reaching up to the metal surface, accompanied by bright flashes of light, ejection of molten metal and a sharp drop in the degree of Mg utilisation. Similar phenomena were noticed in the present case suggesting the low degree of utilisation of Mg to be due to the existence of a low ferrostatic head and the resultant escape of Mg in channels from the metal surface. In industrial heats, where the ferrostatic head height can be much higher such wasteful escape of Mg vapour can be minimized and a higher degree of utilisation of Mg should be possible to achieve. The utilisation factor of Mg in hot metal, added in the form of Mg ingots using a bell type of evaporator, was found to increase by 11.7% when the depth of immersion was increased by 0.5 mm (12). Similar improvements in Mg utilisation factor were found while treating hot metal with Mag-Coke, giving higher values for treatment in transfer ladles than in torpedocars having shallower bath(3). In effect, the ferrostatic head plays the dual role of regulating the rate of release of Mg through its effect on the kinetics of thermal decomposition of MgO, and the rate of escape of the liberated Mg vapour through the metal. Deep plunging helps in better utilisation of Mg, but will hinder the rate of decomposition of MgO, while shallow plunging will lead to the reverse situation. An optimum control of plunging depth, which will necessarily vary with bath temperature, can give a compromise between high degree of Mg utilisation and a minimum treatment time. Besides, a more effective slag cover can be also maintained in a ladle for the entrapment of the reaction product, MgS, thereby preventing its oxidation and consequent reversion of sulphur back into the metal.

which was not possible in the induction furnace heats.

From the limited data collected for residual Mg in the desulphurised metal in heats 85J2 and 88J5, the solubility product, $[Mg] \cdot [S]$ is found to vary from 27×10^{-5} to 7×10^{-5} . This can be compared with a value of $(10-12) \times 10^{-5}$ obtained for hot metal at comparable sulphur levels (4). A low solubility product value of 7×10^{-5} obtained in both the heats above for the lowest sulphur range can arise from the following causes:

- i) presence of soluble Mg at lower than equilibrium level, owing to the rapid rise of Mg vapour through shallow metal depth and faster rate of fading of Mg through the bare bath due to melting in an induction furnace.
- ii) effective removal of reaction products like MgS and MgO by induction stirring, which otherwise if present in the metal give an erroneously high value for Mg and S and hence their solubility product, (reduction of Mg-S solubility product has been reported to be achieved by Argon stirring of hot metal, through removal of suspended MgS particles (13)).
- iii) a higher than usual bath temperature for these experiments ($\sim 1650^\circ\text{C}$), since the solubility product has been found to decrease with increasing metal temperature (7).

As regards variations in the bath composition, Mn content was found to increase by approximately 15% presumably through reduction of its oxides in the slag by the escaping Mg vapour and Al in the bath. Same argument holds true for Si as well, although in this case the throw-back from the slag is comparatively less, due to the comparative higher stability of the oxide.

CONCLUSION

1. It is possible to thermally decompose MgO to liberate Mg in ferrous bath conditions by suitable control of process parameters.

2. A high degree of desulphurization in hot metal and to a lesser extent in steel, can be achieved by adding the reagents in the form of briquettes using a plunger device. Reagents comprise MgO in suitable combination with reductants and fluxes based on Ca, Al and Si metals and their compounds.
3. In order to achieve high utilisation factor of Mg and high desulphurization efficiency, deep plunging of the briquettes into the metal bath is essential.
4. Since while using a refractory plunger, the bath composition is not significantly altered, the process is suitable for desulphurization of both hot metal and steel.
5. The active reagent Mg being derived from inexpensive and relatively abundant raw material sources, the process has significant cost advantage and is unaffected by the rising cost of Mg.

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