A KINETIC STUDY OF HOT METAL DESULPHURIZATION BY CALCIUM CARBIDE POWDER INJECTION

(C) L. K. Chiang, B.Sc

by

A Thesis

Submitted to the School of Graduate Studies in Partial Fulfillment of the Requirements

for the Degree

Doctor of Philosophy

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A KINETIC STUDY OF HOT METAL DESULPHURIZATION

BY CALCIUM CARBIDE POWDER INJECTION

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TITLE: A Kinetic Study of Hot Metal Desulphurization by Calcium Carbide Powder Injection.

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ABSTRACT

Currently, sulphur is the most problematic impurity which affects the physical and mechanical properties of steel. Therefore all the integrated steel producers desulphurize iron before steelmaking. Calcium carbide is one of the reagents used to desulphurize not metal from the blast furnace, yet the kinetic reaction phenomena are not clear. The present work was initiated to study the kinetics of hot metal desulphurization by calcium carbide powder injection at the 3 Tonne scale.

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The most important variables which affect the rate and efficiency of calcium carbide desulphurization are the type of top slag, the injection conditions and the oxygen activity in the hot metal.

The present results quantitatively demonstrate these effects. The experimental results indicate that control of the initial slag condition can effectively improve the rate and efficiency of calcium carbide desulphurization. It was found that lower solid loading is kinetically favorable for both slag/metal and plume desulphurization. Oxygen activity measurements show that oxygen plays a crucial role in desulphurization, particularly to achieve' extra-low sulphur levels.

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A steady-state, one-dimensional, three-phase model

was developed to model the plume desulphurization kinetics. The model permits a quantitative analysis of the present experimental results. The computed results from the model are found to be consistent with the experimental data.

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The author Wishes to express his sincere gratitude to Professor G. A. Irons for his guidance during the course of this project, and his countless efforts which led to the successful completion of this project. Thanks are also due to Professor W -K. Lu, whose direction and encouragement throughout this work were invaluable. The help from the other member of the supervisory committee, Professor J. Vlachopoulos, is greatly appreciated.

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• . •	LIST OF SYMBOLS
A	slag/metal reaction interfacial area, m2,
A _p	surface area of calcium carbide particle, m2.
Apt	area of plume, m ² .
B	proportionality constant, m-1/2
с _s	sulphide capacity, wt%.
C ^D S	sulphur concentration in bulk phase, mole/m3.
C ^{SL}	sulphur concentration in slag phase, mole/m ³
C ^{p1}	sulphur concentration in the plume. mole/m3
C ⁱ * ^m	equilibrium sulphur concentration in metal phase at interface of slag/metal, mole/m3.
C _s i,st	equilibrium sulphur concentration in slag phase at interface of slag/metal, mole/m ³ .
C _s	equilibrium sulphur concentration at interface of CaC ₂ particle, mole/m ³
c ^{eq} s,CaC ₂	equilibrium sulphur concentration with CaC ₂ , mole/m ³ .
C ^{pow,b}	sulphur concentration in powder (trapped on the bubble), mole/m ³ .
C ^{pow} ,p	sulphur concentration in powder (in the melt), mole/m ³ .
C _{dg}	gas drag coefficient.
Cdp	particle drag coefficient.
C _{pt}	liquid heat capacity at constant pressure, J/kg.
D _s	diffusivity of sulphur in molten iron, m ² /s.
Deff,s(v)	equivalent effctive duffusivity of gaseous sulphur through the reaction product lawar

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•	•	and the second secon	
:		-34	•
• .	D	m4 <u>×</u> 8.	· .
	^U eff,ca(v)	effective diffusivity of calcium vapor through the reaction product layer, m2/s.	
	DL	ladle diameter, m.	
- · · ·	Dp	plume, diameter, m.	•
	D	diameter of agitator, m.	
	dp	particle diamater, m.	
	dE	equivalent bubble diameter. m	
al source a sure and a		diameter_of_crucible_cell_m_	
	E	measured cell E.M.F. my	
	F	Faraday constant, 23061 cal/v equivalent	
	F ^b gp	buoyancy_force on the gas-powder (in gas) mixture, N/m.	
	Fp	buoyancy force on the powder in the liquid, N/m.	
•	Fgp-t	drag force on the gas-powder (in gas) mixture, N/m.	•
•	F <mark>p−£</mark>	drag force on the powder in the liquid. N/m	
	F	fraction of powder inside cas bubbles	
	f'	fraction of powder in the melt.	
	G ₁	heat transfer function for radiation. W/m3/K4	•
·	G ₂ , G3, G ₄	heat transfer functions for convection, W/m ³ /K.	
	9	gravitational acceleration, m/s2.	
	н	depth of the melt, m.	
•	h	y bubble height, m.	:
	h	heat transfer coefficient, W/m2/k	
	J _{ca(v)}	calcium vapor flux, mole/m ² /s.	

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	K J²(^)	equivalent sulphur vapor flux, mole/m2/s.	
	K J2(V)	equivalent sulphur vapor flux, mole/m2/s.	· · · · · · · · · · · · · · · · · · ·
	J₅(v) K	equivalent sulphur vapor flux, mole/m2/s.	1
	J₂(v) K	equivalent sulphur vapor flux, mole/m2/s.	
	К Л ^{2 (^)}	equivalent sulphur vapor flux, mole/m2/s.	• :
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		GIMENSIONIESS COnstant.	n n n Maria de la composición de la composición de la composición de la composición de la composición de la comp
	Kea	equilibrium constant of reaction	
	K		•
	im _o	rirst order reaction rate,1/s.	
	Kov,b	product of the overall mass transfer coefficient and reaction interface (for CaC ₂ particles which are trapped on the bubble surface), m ³ /s.	-
•	K _{ov,p}	product of the overall mass transfer coefficient and reaction interface (for CaC2 particles which are dispersed in the melt), m ³ /s.	
	k _s	sulphur mass transfer coefficient in slag phase, m/s.	· •
· · ·	к _ғ	first order forward reaction rate.	
	к _b	first order backward reaction rate.	
	κ _b	mass transfer coefficient to bubble. m/s.	: : :
	κ _p	turbulent mass transfer coefficient. m/s.	:
	ĸ	kinetic energy of turbulence. m/s2.	· .
1	ĸ	thermal conductivity, W/m/k.	•
l	L. States and States	solid to gas ratio, kg/Nm ³ .	
	Ms	molecular weight of sulphur, ko.	
I	[%M]	metallic element concentration in metal phase, wt%.	•
ſ	^m s.	solid mass flow rate, kg/s.	•
r	ng	gas mass flow rate, kg/s.	••••
t	^N sh	Sherwood number.	• •
1	Nac	Schmidt number.	
١	^N Gr	Grashof number.	
	NRe .	Reynolds number.	
· .		xiii	

NPT	Prandtl number.
NPe	Peclet number.
N	rotation speed, r.p.s.
.m/s	
N _S	rate of sulphur transfer from metal phase to slag/metal interface, mole/s. /
N ^{KX}	rate of chemical reaction at the slag/metal interface, mole/s.
Nst	rate of sulphur transfer from the slag/metal interface to the slag phase.
N _s	desulphurization term in plume.
NE	Entrainment number.
n .	rate of ion transfer, mole/s.
Πp	particle number.
n•a₁	number of particles in the melt.
[%0]	oxygen concentration in metal phase, wt%.
P	gas pressure, atm.
Pca, CaC 2	equilibrium calcium partial pressure with CaC ₂ , atm.
PCa,1	equilibrium calcium partial pressure with sulphur at particle interface, atm.
69 s(g),i)	equivalent equilibrium sulphur partial pressure with calcium at particle interface, atm.
P ^{eq} Ps(g),CaC ₂	equivalent equilibrium sulphur partial pressure with CaC ₂ , atm.
Q	gas flow rate, Nm³/t/min.
R	gas constant, 8.3144 Joule/degree/mole.
r _i .	radius of unreacted core of calcium carbide,m.

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	•	
•	гь	bubble radius, m.
	ro	outer radius of calcium carbide, m.
	гр	particle radius, m.
• •	۵r	thickness of reaction product layer, m.
•	S	rate of surface renewal.
	(%5)	sulphur concentration in slag phase, wt%.
۰.	[%5]	sulphur concentration in metal phase, st%.
	Ť 🔶	temperature, k.
	t	time, s.
•	te	exposure time, s.
	U	velocity, m/s.
21	v _m	liquid entrainment rate, m ³ /s.
	V _P	volume of single CaC2 particle, m3.
· .	Wst	slag weight, kg.
	Wmet	metal weight, kg.
	X	mole fraction.
•	z	vertical distance from bottom of plume, m.
	α	thermal diffusivity, m ² /s.
	α	volume fraction of gas within plume.
•	Г	the excess concentratioin of solute in the surface film, mole/m2.
	8	Stefan-Boltzman constant, W/m2/k4.
	3	energy dissipation per unit mass, m2/s3
`` `	3	emissivity.
	n	equilibrium partition ratio of sulphur between slag and metal phase.
	θţ	the fractional surface coverage of surfactant.

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XV

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critical particle volume fraction. phase volume concentration. effective viscosity, kg/m/s. molecular viscosity, kg/m/s. turbulent viscosity, kg/m/s. kinematic viscosity, m2/s. density, kg/m³. mixing time, s. surface factor.

θ_{pc}

^µeff

ש_e'

۳t

ν

SUBSCRIPTS

atm	atmospheric.	•	•	•	
b	bubble.			_	
bt	bulk liquid.	•		1	A
eq	equilibrium.			*** [*]	\bigcirc
9	9as .			,	
9P	particle in gas.				
2	liquid.			•	
L	ladle.				~
m	mixture, mean, metal.			•	
met	metal.		.	•	
þ	particle.				-
P£	plume, particle in liquid.	•			•
ŕ	relative.				
5	sulphur.		· · ·		
5 £	slao.				

xvi

3

terminal.

).

SUPERSCRIPTS

bubble. equilibrium. interface. metal. slag.

ь

ea

m

s L

pow

0

powder. at inlet.

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Effect of immobilized factor on average CaC₂ desulphurization efficiency (gas flow rate: 160 L/min, CaC₂ injection rate: 6 kg/min).

Fraction of control for each mass transfer step as a function of distance from the bottom of the plume (sulphur concentration: 0.08 wt%, gas flow rate:160 L/min, CaC₂ injection rate 2 kg/min).

Cumulative CaC₂ plume desulphurization efficiency as a function of distance from the bottom of the plume (sulphur concentration: 0.08 wt%, gas flow rate: 160 L/min, CaC₂ injection rate: 2 kg/min).

Fraction of control for each mass transfer step as a functioin of distance from the bottom of the plume (sulphur concentration: 0.08 wt%, gas flow rate: 160 L/min, CaC₂ injection rate 6 kg/min).

CaC₂

5.188 .

Figure

5-16B

5.17A

5.17B

5.18A

desulphurization efficiency as a function of distance from the bottom of the plume (sulphur concentration: 0.08 wt%, gas flow rate: 160L/min, CaC2 injection rate 6 kg/min).

Cumulative

5.19A

Fraction of control for each mass transfer step as a function of distance from the bottom of the plume (sulphur concentration: 0.08 wt%, gas flow rate: 160 L/min, CaC₂ injection rate 10 kg/min).

5.19B

Cumulative CaC2 plume desulphurization efficiency as a function of distance from the bottom of the plume (sulphur concentration: 0.08 wt%, gas flow rate: 160 L/min, CaC2 injection rate: 10 kg/min).

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CHAPTER 1

Introduction

Ladle metallurgy operations have proven to be very effective in improving steel quality and reducing production costs. However these processes have been developed in the plant, and consequently the kinetics of the processes are poorly understood and the processes are far from optimized. Therefore the present study of hot metal desulphurization by powder injection technology was undertaken to increase our understanding of desulphurization kinetics.

Few well-controlled injection experiments on ladie metallurgy reactions such as desulphurization have been carried out. The current experiments were performed in the three Tonne scale furnace equipped with extensive instrumentation. Therefore the experimental conditions could be accurately measured and controlled. The particular system chosen to work with was calcium carbide desulphurization of carbon-rich iron (hot metal).

Forty eight injection tests were carried out under four different top slag initial conditions, namely;

(a) no slag,

(b) a dry slag, a mechanical mixture of 60% CaO and

40% SiO2 by weight,

- (c) a liquid slag, a commercially available continuous casting powder (nominally 33% CaO, 26% SiO₂, 7% Al₂O₃, 6% MnO₇ 7% Na₂O, 7% C, 6% F with a melting point of 1135 °C),
- (d) a dry slag modified by plunging aluminium into the melt before carbide injection.

The calcium carbide contained 81% CaC_2 , 11% CaO and 7% ash and the average particle size was 24 µm. A wide range of injection conditions were studied (1.3 to 7.6 kg reagent/Tonne metal, 2.5 to 11 kg reagent/min, 0.05 to 0.24 Nm³/min Argon carrier gas, solid to gas loading 16 to 154 kg/Nm³).

The experiments have focused on the following three important parameters:

- (a) the effect of top slag,
- (b) the effect of injection conditions, and
- (c) the effect of oxygen potential.

The present results quantitatively demonstrate these effects on the desulphurization kinetics. A steadystate, one-dimensional, three-phase kinetic model was developed to model the reactions in the plume. Reasonable

- 2

agreement is obtained from the comparisions of the model predictions with the experimental data. The model demonstrates that the best desulphurization results are attained when conditions are adjusted so that the plume and top slag reaction zones work together.

CHAPTER 2

2.1 Introduction

The importance of powder injection technology in steelmaking processes has grown rapidly during the last two decades. The use of powder injection technology to treat hot metal or steel is a key step for mass production of higher quality steel with low cost. The main purposes of this technology for steelmaking processes can be outlined in the following advantages from both the technical and economic points of view.

(A) Technical advantages:

A favourable kinetic condition for refining reaction can be obtained, i.e, a large contact area between reactants is possible because the reagents are in powder form. Furthermore, the carrier gas provides the stirring and mixing to enhance the heterogenous mass transfer process and homogenize the melt simultaneously. Since the refining reaction can be carried out in the transfer ladle or simple vessels, these places can provide locations which allow the refining processes to be divided into several separate stages so as to eliminate thermodynamic conflicts between
various refining reactions (eg, desiliconization and desulphurization). Advancements in powder injection technology have greatly changed the philosophy of steelmaking. The conventional single vessel process (B.O.F) has been divided into a multi-vessel process to achieve high efficiency of the refining operation[1]. Therefore, this newly developed steelmaking process is the combination of the pretreatment of hot metal (for the removal of silicon, phosphorous and sulphur), B.O.F. operation (for decarburization and temperature control), and secondary steelmaking (for the extra-low residual elements and inclusion shape control). The success of O.R.P. process developed at Kimitsu Works, Nippon Steel Corp. has been recognized as a great step for powder injection technology[1]. Super clean steel with low residual elements such as sulphur, oxygen and phosphorous can be made commercially through the use of this technology.

(B) Economic advantages

Powder injection technology is a suitable way for mass production of high grade steel. This is because these injection processes are carried out in transfer ladles which allow the fluctuations in operation of major reactors,i.e.,blast furnace, B.O.F. and continuous casting machine to be smoothed out so that the steel is more consistent and of higher quality. It is possible to make each of the three major reactors to operate under the most profitable and stable conditions[1]+[11]. Furthermore, the powder injection systems can be built with comparatively little capital investment. The payback period on the investment is usually only a few months from the savings of fuel, fluxes and alloy additions in ironmaking and steelmaking. However, due to the local economics and the availability of existing facilities, only the desulphurization of hot metal is currently being used in the steelmaking industry of North America.

2.2 Industrial application of powder injection technology

2.2.1 Secondary steelmaking

About 1920, R. Perrin developed a tapping process for the desulphurization of steel in the ladle. A synthetic lime alumina slag was put into a transfer ladle together with molten steel to achieve rapid and efficient desulphurization. This process has been considered as the predecessor of today's ladle treatment technology. In the 1950's, vacuum degassing was orignally developed for the purpose of solving the hydrogen problem. Later on, application of this technology was extended to improve the inclusion cleanliness and chemical composition control. In order to meet the increasing demand for higher quality steel in the 1960's, a more sophisticated ladle treatment process

was developed. It provided versatile refining capability such as degassing, deoxidation and desulphurization and was equipped with the heating facility to prevent temperature loss due to the prolonged treatment. These are known as the ladle furnace processes, examples of which include ASEA- ~ SKF[12], AOD[13] process.

In the early 1970's, powder injection techniques were under development. Due to significantly lower installation costs, the T.N. process (developed by Thyssen-Niederrhein)[14], CAB process (calcium-argon-blowing)[15] and Scandinavian Lances injection system[16], became very important tools for the successful mass production of high quality steel. These processes are based on the injection of a CaSi reagent. The positive effect of Ca on steel properties and the castability is well documented. In order to obtain good desulphurization results, a lining with stable refractory of low oxygen potential and deoxidation of steel with aluminium addition prior to the injection treatment are essential for sulphur removal and inclusion modification[14],[17]. However, the efficiencies of CaSi utilization are low and generally in the range of 15-25 π [14]-[16].

2.2.2 Desiliconization of hot metal

Although the powder injection treatment of steel subsequent to the primary steel making operation has proved to be the most effective method for improving steel quality, it is not an economic way to reduce the impurities such as sulphur due to the low reagent efficiencies and large temperature drop. Furthermore, the thermodynamic conflicts between desulphurization and dephosphorization would hinder the optimization of the refining process and cause serious phosphorous reversal from the primary steel making slag. In fact, some residual elements in the melt can be more easily removed prior to the B.Q.F. operations.

Recently, external hot metal treatment technology has played a very important role in the overall steelmaking process.) There are many pretreatment processes available for commercial plant operation. These refining processes are carried out in a transfer ladle, torpedo ladle or even in a blast furnace runner. The characteristics of the processes are dependent on the type of reagent, slag system and impurity elements to be treated. Generally they can be classified into three categories as follows:

(A) desiliconization;

 (B) simultaneous desulphurization and dephosphorization;

(C) desulphurization alone.

Currently there is a great deal of research activity being

conducted in Japan on desiliconization, and the simultaneous dephosphorization and desulphurization of hot metal. In North America, phosphous has not been regarded as much of a problem since the phosphous content in iron ore is low enough to be managed during steelmaking. Therefore, all efforts are directed towards the reduction of sulphur content in hot metal.

In Japan, there are several reasons for desiliconization, even though the silicon content of hot metal produced from the blast furnace is at a low level (less than 0.5 wt%). The benefits of hot metal desiliconization gained in steelmaking are[18],[19]:

(A) increased oxygen efficiency;

(8) reduced flux consumption;

(C) increased yield due to less FeO and entrained iron losses in the slag;

(D) smooth B.O.F. operation, thus improving end point control with less refractory wear.

A further reason has been that a minimal silicon content in hot metal (0.10-0.15% Si) is necessary for the effectiveness of simultaneous desulphurization and dephosphorization[20]. The dephosphorization reaction by sodium carbonate can be described by the reaction [21].

 $4/5 P + Na_2CO_3 = (Na_2O) + 2/5 (P_2O_5) + C$

10

(2.1)

The reason for the strong dependence of the degree of desulphurization on the initial silicon content may be attributed to the reaction of sodium carbonate with silicon when the silicon content of hot metal is higher.

For the silicon removal by hot metal pretreatment, reagents such as iron oxide or oxygen are added onto the hot metal in the blast furnace runner or in the transfer ladle by the injection method. Generally lime is added as a basic slag to decrease the activity of silica so as to improve the desiliconization efficiency.

2.2.3 Simultaneous desulphurization and dephosphorization

The advantages of simultaneous desulphurization and dephosphorization can be outlined as follows[22]:

- (A) fast reaction rate in terms of treatment time
 due to simultaneous desulphurization and
 dephosphorization;
- (B) lower slag volume in the subsequent B.O.F. process;
- (C) the ability to handle any phosphorus level from hot metal.

The use of sodium carbonate or calcium oxide based reagents for simultaneous desulphurization and dephosphorization has been known for some time. Pravious work [23]-[26] has shown that simultaneous desulphurization and dephosphorization reactions in a silicon free or low silicon hot metal are possible with the above-mentioned reagents. The thermodynamic and kinetic aspects of simultaneous desulphurization and dephosphorization can be briefly summarized as follows:

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(A) Dephosphorization and desulphyrization are known to be in contradiction to each other in term of thermodynamics. Higher oxygen partial pressures and lower temperatures favor dephosphorization, while the reverse conditions are favorable for desulphurization. A freageant such as sodium carbonate will decompose to form sodium oxide or sodium vapor which has a high affinity for both phosphorus and sulphur. The slag containing the reaction product of Na₂O will make dephosphorization and desulphurization insensitive to oxygen. At 1400 °C, as shown by Suito[156] in Figure 2.1, both the equilibrium sulphur and phosphorus activities with Na20 are expected to be less than 0.001 % for P_{O2} ranging from 10^{-1} to 10^{-4}



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Activities of P and S in hot metal in equilibrium with Na2O and CaO[156]. atm. Thus dephosphorization and desulphurization can take place simultaneously.

- (B) For the calcium oxide based reagent, the simultaneous reaction can be enhanced through the proper control of oxygen potential in the melt and slag compositions. Generally, slag fluxes such as CaF_2 , NaF and $CaCl_2$ are added onto the surface of hot metal to form a slag with high sulphide and phosphate capacity. The oxygen potential can be controlled through the co-injection of FeQ, Fe_2O_3 or O_2 with CaO based reagent to increase the oxygen potential in the melt so as to promote dephosphorization.
- (C) Low silicon content (0.10-0.15%) of hot metal is necessary for effective dephosphorization.

(D) Intensive stirring is required for effective desulphurization and dephosphorization.

There has been a growing interest in the industrial applications of simultaneous dephosphorization and desulphurization of hot metal in Japan. The ORP process[1] consists of three separate oxidizing processes between the blast furnace and the continuous casting machine on the basis of thermodynamics. These three oxidizing processes are desiliconization, simultaneous dephosphorization and

desulphurization, and decarburization. The fluxes used in these three stages of oxidation are mill scale for desiliconization, mill scale (FeO), CaO, CaF₂, and CaCt₂ for desulphurization and dephosphorization, and O₂ for decarburization. Similar refining processes for the extralow residual element were also developed by Kawasaki Steel[157]. The flux comprising CaO (CaCO₃)-CaF₂ (Fe₂O₃) or Na₂CO₃ (+Fe₂O₃) mixed with oxygen (+N₂) is injected into the transport vessel for the desulphurization and dephosphorization of hot metal. It was reported that this newly developed refining process is suitable for mass production of high quality steel at a low cost.

2,2.4 Desulphurization

Since 1970, there has been an increasing demand for steels with extra low sulphur specifications. The detrimental effects of sulphur on the steel properties can be summarized as follows:

> (A) surface defects: There is a trend of increasing surface cracks with high sulphur content in steel. Experience has shown that surface defects can be significantly reduced with sulphur content below, 0.02%[27].

the physical and mechanical properties of steel[28].

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Therefore in almost every integrated steelplant, the hot metal is externally treated from the blast furnace. The reasons for this are as follows:

- (A) At lower slag basicity, higher sulphur operation of the blast furnace increases productivity of the blast furnace and reduces the fuel rate[10],[11].
- (B) low slag basicity is favorable for alkali removal from the blast furnace[29].
- (C) The activity coefficient of sulphur in the hot metal is higher than that of sulphur in steel which means desulphurization can be more easily accomplished in hot metal.

There is great diversity in the installations and world wide development of external hot metal desulphurization. The current desulphurization processes available in commercial operation differ vastly between North America, Europe and Japan. A critical comparison made by Koros[30] in terms of process characteristics, reagent options and performance among these processes is shown in Tables 2.1 to 2.3. He concluded that the reasons for these differences are mainly

Table 2.1

Hot Motal Desulfarization Rangest (1 = Favorable, Best Attribute = M

its. Acceptable in Most Situations cosptable Attribute for Most Situa 11

Precess Attribute	Soda Abh	Carbide	(Passivatad)	Magneelum With Lime	Line	-Lime-Spar
Predictability (Low S)	3	2	1	t .	2	-1
Low S (<0.005) Attainment	3.	2	ī			:
Temperature Sensitivity ((1350-C)	ī	3	· ·	1 .		4 .
Temperature Loss in Treatment			:		3	4
Slag Interference	· •	*	4		3	្រ
From B F. Stee Soilt		-	· · ·			
To BOE by R. Culturing	. 2	3	4 1 1 1 1	1	1	- L -
Tone Wold France (Tone	3	_ 3	1.	1	2	1
THOM THEN TO THE TO THE	. 1	3	1 .	12	3	1
Process Speed	1.	2	1	ī	3	
Freeboard Requirement (Sub or Ladle)	. 3	2	3		ĩ	:
Precticality of High S to Low S Treatment	3	2		÷ .	:	
Vessel Demars (Slag Accretions als Attack)		_ · · · ·			3	2
Vessel Share Sensitivity (Length/Dismount	ĩ			*	I.	2. •
Environmental Control Differenties	3	· •	1	I.	1	1
Report Cost Realing	J	2	2	1	1	2
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Japas	1	2	3		; ; .	. :
U.S	1	3	-			:
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	•					
	Precess Attribute Predictability (Low S) Low S ((0.002) Attainment. Temperature Sensitivity ((1350 °C) Temperature Loss in Treatment Slag Interference Pron B.F. Slag Solil To BOF by Re-Subtrisation: Iron Yield Loss to Slag Process Speed Precisionity of High S to Low S Treatment Vessel Damage Slag Accretions at Attacki Vessel Shape Sensitivity (Langth/Dismotor) Environmental Control Difficulties Reseant Cost Rankings Canada Europe Japan U.S.	Precess Attribute Sodia Abh Predictability (Low S) 3 Low S (0.008) Attainment: 3 Temperature Sensitivity ((1350°C) 1 Temperature Loss in Treatment 2 Stag Interference 2 From B.F. Stag Spill 2 To BOF by Re-Sufficiencia 3 Iron Yield Loss to Stag 1 Process Goed 1 Presed Requirement (Sub or Ladie) 3 Presed Shape Sensitivity (Langth/Dismeter) 3 Eavironmental Control Difficulties 3 Leased 1 Japes 1 U.S. 1	Precess Attribute Sodi Abh Carbide Predictability (Low S) 3 2 Low S (0.008) Attainment: 3 2 Temperature Sensitivity ((1350°C) 1 3 Temperature Loss in Treatment 2 3 Stag Interference 2 3 From B.F. Stag Spiil 2 3 To BOF by Re-Sufficientistic 3 2 Process Speed 1 3 Process Speed 1 2 Presend Requirement (Sub or Ladle) 2 3 Process Speed 3 2 Vessel Damps (Sug Accretions 40 Attackt 3 2 Vessel Damps Cost Antickings 3 2 Canada 1 2 Japes 1 2 U.S. 1 3	Precess AttributeSodia AbhCarbideMagnesisms (Passivated)Predictability (Low S)321Low S (0.008) Attrainment:321Temperature Sensitivity (0.150°C)131Temperature Loss in Treatment232Stag interference231Process Speed131Process Speed321Process Speed321Process Speed323Prestoard Requirement (Sub or Ladle)323Presteinalty of High S to Low S Treatment323Vessel Dampe Sing Acturcity (Langth/Diameter)312Respent Cost Rankings123Canada1233U.S.1323	Precess AttributeSodi AbhCarbideMagnesium (Panivated)Magnesium With LinePredictability (Low S)3211Low S (0.008) Attrainment:3211Temperature Sensitivity (0.150°C)1311Temperature Loss in Treatment2321Stag Interference2311Process Good2311Process Good1211Process Good1211Precess Good1211Precess Speed3211Precess Speed3211Precess Speed3221Respected Control Difficulties3221Respecting1233Uses Deps1233Langes1233Uses Control Difficulties322Langes1233U.S.1322	Precess Attribute Sodi Abb Carbide Magnesium (Pamivated) Magnesium With Line Line Predictability (Low S) 3 2 1 1 2 Low S (0.008) Attainment 3 2 1 1 3 Temperature Sessitivity ((1350°C) 1 3 1 1 3 Temperature Loss in Treatment 2 3 2 1 1 3 Stag Interference 7 3 1 1 2 3 2 1 3 Process Speed 1 3 1 2 3 1 1 2 Process Speed 1 2 1 1 3 1 1 Prestoard Requirement (Sub or Latile) 1 2 1 1 3 1 1 2 3 1 1 3 1 2 3 1 1 3 1 3 1 3 3 1 3 3 1

Table 2.2

	Carbide (ATH)	Magnesium		Lime-Based			
•		Lime-Meg ^(*)	Passivated	Lime-Alooet	Line-Al ^{un}	Lime-Spar*	
Predictability (Lot	0.005	0.006	0.007	0.005			
Practicality for < 0.005S	Diff.	Eary	Fare	None	(D)// 1000	C	
Trestment Pactors		,		((OUB	(1)((1)	Caty .	
Respont Flow, karmin./t	0.36	0.50	0.11	0.98	. 0.47	0.00	
Transport Gas. N1/min/t	6.0	48	18.7	1 0 1	0.40	0.50	
Sulfur Removal Rate*		0.04	19.7	9.01	1.0.00	5.0	
Temperature Loss (Milmin)	1.0	0.00	0.10	0.04	0.09	0.10	
Recent Efference former		0.5	0.4	1.0		1.2	
nongene Linconey Index.", "	43.	59.	160	8,0	11.	12.	
Sing Characterization	D,T	T	F	D.T		F	
O.05-0.015S	· ·	•				•	
Injection Time, Min.	12	20	12	20			
Temperature Loss. *C.	12	10 \		30	1101	1101	
Slag Generation key	10			30	(15)	(20)	
Slag Generation, kgrt *Sulfur Removal Rate $\left(\ln \frac{S_1}{S_2}\right) \bullet \left($	بة (<u>+</u>)	6.2	5 1.5	30 8.5	(15) 4.2		

Indicates Estimated From Available Information 3

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**Reagent Efficie Index, % đ١ 100 S.

D = Dry T = Thick F = Fluid

Table 2.3

Selected Parameters for Process Comparison - Transfer Louis Treatments

	Cashida	Magnoalum-Lime			Magnanium-Passivated			Lime Sparth
	Carology	Pre-Mixed J&L		Lime-PMg UEL	Pellemag	USIRMAG	U.S.S.R.*	(K.tt)
		.30% Mg	20% Mg**	(Variable Mg Rate)	_ 1121			
Predictability (1c) Practicality for (0.005S Freeboard Needed, cm Treatment Factors	Diff. 30	0.003 Easy Nil	0.005 Easy Nil	0.005 Medium 15	0.005 Eanv 50	Easy	1251	0.003 Easy
Respect Flow, kg/min./t Transport Gas Nimin./t Sultur Removal Rate* Temperature Loss (*C/Min.) Respent Efficiency Index*,5 Siag Characterization* Typical Treatment Performance	0.47 3.5 0.10 1.3 23 D.T	0.25 2.2 0.20 2.7 80 D	0.65 NE 0.42 <1 80 D	1.13 Nii 0.25 2.5 61 D,T	0.05 2.1 0.10 1.1 fi1 F	0.08 0.21 66 F	0.11 14 0.25 0.0 1 60 F	KR KR 0.42 26 E
60.035-0.010S) Injection Time, Min Temperature Loss, "C Sing Generation, Egit	13 17 7.0	6.5 15 2.0	3 • C10 1.9	4.5 11 5.0	12 14 1.0	. 6 . (15) 0.5	5 15 0.5	- 3

*Refer to Table II. **Dual dispenser operation: Lime/L-20% Mg/Lime

dependent on availability of facilities and reagent economics. In summary, the desulphurization processes which have been used for hot metal desulphurization are as follows:

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Magnesium based methods

- (A) Mag-coke process[31].
- (B) Lime-Mag process[32].
- (C) Mag-Al process[33].
- (D) Salt-coated granules process[34].

Lime based methods

- (A) Lime-spar process[35].
- (B) Lime-Al process[36],[37].
- (C) Lime alone process[38].
- (D) Limestone-spar process[158]

Calcium carbide based methods

- (A) KR method[39].
- (B) Porous-plug method (PDS method)[39].

(C) A.T.H. Injection method[40].

Sodium carbonate based method

- (A) Soda-ash-paving method[39]. in which the bottom of the ladle is "paved" with soda ash before tapping steel on it.
- (B) Injection method.

2.3 Fundamentals of hot metal desulphurization

2.3.1 Thermodynamic aspects

According to the reagent types and desulphurization mechanism, the desulphurizers commonly used for hot metal and steel desulphurization can be classified into three groups, namely

- (A) The use of Mg, Ca, Sr, or La in metallic form to react with sulphur to form stable metal sulfide.
- (B) The use of oxide, carbide or carbonate compound to react with sulphur to form stable metal sulphide.
- (C) The use of fluid, highly basic slags to remove sulphur through slag/metal reaction.

For the group types of reagent (A) and (B), the desulphurization reaction in general is governed by the

oxide/sulphide equilibrium.

$Me_{X}O_{Y} + Y \underline{S} = Me_{X}S_{Y} + Y \underline{O}$ (2.2)

For unit activity of oxide and sulphide, the critical ratio of sulphur to oxygen for desulphurization to proceed is given by the equilibrium constant K. This equilibrium activity ratio of sulphur to oxygen in the melt can be calculated from the free energy of oxide and sulphide formation at the temperature of interest. Figure 2.2 shows the thermodynamic calculation of sulphur/oxygen activity ratio in liquid iron for the sulphide-oxide equilibria in the temperature range 1300 to 1450 oC[41]. At a fixed oxygen potential, a low value of the ratio represents higher desulphurization potential. It can be seen from this diagram that the desulphurization ability of the metallic element or oxides increases downwards in the order MgO, CaO, SrO, BaO, and Na₂O

Kay and Kumar[42] prepared the phase stability diagram for the system of metal-sulphur-oxygen (Figure 2.3). It is possible to use this diagram to predict the lower limit of desulphurization under a fixed oxygen potential condition. With magnesium, calcium and rare earth (or their oxides), it can be seen from this diagram that the La203 La202S, CaO/CaS and MgO/MgS equilibria lines intersect the



Figure 2.2:

The sulphur/oxygen activity ratio in liquid iron for the indicated sulphideoxide equilibria at hot metal temperature[41].





C/CO (Pco=latm) line at h_s values of 4.46X10-4, 5.62X10⁻³ and 7.94X10-1%, respectively. These values represent, on a thermodynamic basis, the lower limits of desulphurization with La or La203+ Ca or CaO and Mg or MgO at 1773-K. The results indicate that, at a fixed oxygen potential (C/CO , Pco=latm), Mg and MgO are not effective desulphurizers. However, Mg has a relatively high solubility in carbonsaturated molten fron. When hot metal is saturated with Mg (0.26 wt% at 1773K[43]), the oxygen potential can be reduced to a h_o value of 3.16X10⁻⁸%. This oxygen potential corresponds to a hs value of 3.16X10-4. The use of aluminium for deoxidation of hot metal can effectively enhance desulphurization. Figure 2.3 shows the La₂03/La₂02S, and Ca0/CaS equilibria lines intersect the h_{A2} =0.2 line at a h_s^2 value of 1.90X10⁻⁴ and 1.69X10⁻³% respectively. The significance of this difference is that the desulphurization power of La203/La202S and Ca0/CaS can be enhanced by decreasing the oxygen potential of the hot metal by aluminium addition. Figure 2.3 also indicates the saturation of CaC₂ gives very low oxygen potential with a hs value of 3.55X10-7% which corresponds to a h_s value of 2.51X10⁻⁵%. However, due to the low solubility of Ca in a carbon-saturated melt, Kay and Kumar pointed out that the dissolved calcium can not provide any protection against reoxidation and consequent sulphur reversion. Therefore, the use of Ca in the form of carbide can improve the

effectiveness of the utilization of Ca by providing a continuous source of Ca.

The thermodynamics of the slag/metal sulphur reaction has been the subject of the most extensive studies of all the slag/metal reactions in iron and steelmaking. Sulphur is only slightly soluble in atomic form and is present as sulphide ions or sulphate ion depending on the oxygen pressure. When Po2 is less than 10-6 atm, sulphide can be formed according to equation[44].

 $1/2 S_2 + (0^{-2}) = 1/2 O_2 + (S^{-2})$

Under current iron and steelmaking conditions, reaction (2.3) governs slag/metal sulphur reactions. When Po_2 exceeds 10^{-4} atm, sulphate can be formed which can be represented by the following equation:

(2.3)

(2.4)

 $1/2 S_2 + 3/2 O_2 + (0^{-2}) = (S_0^{-2})$

The activity of the oxygen ion and the activity coefficient of the sulphur ion can not be evaluated in an ionic melt. For the sake of convenience, the concept of

sulphide capacity was introduced by Fincham and Richardson[44] to describe the sulphur affinity of a slag,

25

$C_{s} = (wt \% S) (Po_2 / Ps_2) 0.5$ (2.5)

where Po2 and Ps2 are the equilibrium partial pressures of oxygen and sulphur, respectively, and (w2%s) is the sulphur solubility in the slag. A slag with a high value of sulphide capacity means more sulphur can be held in the slag.

Selected data[45] on the sulphide capacity of binary oxide melts, ferrites, aluminate, silicates and phosphates are shown in Figure 2.4. As can be seen from this diagram, the sulphide capacity increases with increasing concentration of basic oxide.

Figure 2.5 shows the correlation of sulphide capacity with an empirical basicity ratio in a wide range of slag systems such as $CaO-SiO_2$, $CaO-Al_2O_3-SiO_2$, $CaO-MgO-SiO_2$ and $CaO-MgO-Al_2O_3-SiO_2[48]$. This correlation provides a more useful form for the estimation of sulphide capacity.

In a study of the influence of the metal composition on the kinetics of desulphurization, both Goldman et al[49] and Turkdogan et al[50] found



Figure 2.4: Sulphide capacities of binary oxide melts[45].

N ...



independently that C, S, Mn, and Al enhance the rate of desulphurization. They explained that this experimental observation is due to the effect of solute elements Si, Mn and Al in removing the oxygen dissolved in the metal phase. They proposed the overall sulphur reaction based on the molecular theory as

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However, this sulphur reaction mechanism is inconsistent with the ionic theory of slag-metal sulphur reaction mechanism and is therefore incapable of explaining the effect of applied voltage on desulphurization kinetics.

[S]+(O)=[O]+(S)

Rosenqvist[51] was first to suggest the electrochemical mechanism to explain the phenomena of sulphur reaction. According to this mechanism, slag-metal reactions are redox exchange reactions which are accompanied by an exchange of electrons between the reacting species as they are transferred to and from a non-polar metallic phase and ionic molten slag. Therefore the transfer of sulphur from metal to slag is a cathodic reaction:

[S]+2e-=(S-2)

(2.7)

(2.6)

In order to fulfil the electrical neutrality, the accompanying anodic reactions take place simultaneously, for example:

$$[Fe] = Fe^{+2} + 2e^{-} \qquad (2.8)$$

$$[Si] = Si^{+4} + 4e^{-} \qquad (2.9)$$

$$[Mn^{-}] = Mn^{+2} + 2e^{-} \qquad (2.10)$$

$$(0^{-2}) + C = \{CO\} + 2e^{-} \qquad (2.11)$$

The overall desulphurization rate can be balanced by the above various anodic half-cell transfer reactions

$$2n_{s} = 2n_{Fe} + 4n_{S1} + 2n_{Mn} + 2n_{co}$$

(2.12)

where n is the rate of transfer or evolution in mole/s. The overall rate of desulphurization will be dominated by the step which is sufficiently slow compared to those of the other steps.

For the prediction of the equilibrium condition of desulphurization, the equilibrium sulphur partition ratio is generally used. The partition of sulphur between slag and metal can best be represented by the reaction(2.6). Through the combination of Eqn(2.3) and Eqn(2.5), the appropriate gas-metal reaction can be expressed as follows:

 $1/2 0_2 + [S] = 1/2 S_2 + [O]$ (2.13)

30

$K_{eq} = ([a_0]/[a_s])(Ps_2/Po_2)^{0.5}$ (2.14)

Where

 $\log K_{eg} = -935 / T + 1.375$ (2.15)

Using the thermodynamic data for the equilibrium constant of Egn(2.14), the sulphur partition can be expressed as function of sulphide capacity, activity coefficient of sulphur in hot metal, and oxygen activity in the hot metal.

Log((%S)/[%S])= Log f + Log K + Log C

- Log a_o

(2.16)

The presence of carbon and silicon in hot metal increases the activity coefficient of sulphur by a factor varying between 5 and 10. Consequently, at a given condition the sulphur partition in iron making will be increased by a factor of 5 to 10 higher than that in steelmaking. Furthermore, in ironmaking the oxygen potential in blast furnace approaches C/CO equilibrium at about 2 atm CO pressure and a carbon activity of 0.8[52]. The corresponding oxygen potential has the value equivalent to about 10⁻¹⁶ atm at 1500 oC. For the slag under steelmaking conditions, the estimated oxygen potential is about 10-9 atm at 1600 $^{\circ}$ C. Therefore, the value of (%S)/[%S] would be lowered roughly by a factor of 10-2, indicating that desulphurization in the steelmaking process is very ineffective.

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Figure 2.6[53] shows the variation of the computed equilibrium sulphur partition with temperature and concentration of aluminium in hot metal and CaO in calcium aluminate melts. It can be seen that the sulphur partition ratio increases with increasing CaO content in slag melt. The sulphur partition ratio is also enhanced by an increase of the concentration of dissolved aluminium in liquid steel, Although an increase of temperature will improve the sulphur capacity of slag, the equilibrium partition ratio decreases with increasing temperature, since an increase in temperature will increase the oxygen activity in liquid steel according to aluminium and oxygen equilibrium.

2.3.2 Kinetic aspects

Powder injection refining processes are carried out in a transfer ladle in which the solid reagents are injected together with a carrier gas. The solid reagents remain in the powder form (eg CaC₂ or CaO) or are vaporized to the gas phase (eg Mg or Ca). The overall processes of injection refining are in general considered to consist of





Variation of the computed equilibrium distribution ratio (%)/[%] with temperature and concentration of aluminium in solution in iron and calcium oxide in calcium aluminate melts[53].

several consecutive steps. Because the reagent may be in solid or vapor form, a variety of situations may exist, each requiring a somewhat different analysis of the mass transfer phenomena involved.

2.3.2.1 Mass transfer in dispersed system

During the flotation of a rising particle a boundary layer will develop. Adjacent to the particle's surface, the fluid velocity is slow and mass transport normal to the surface is therefore governed by molecular diffusion. In most metallurgical operations, the system is so turbulent that mixing occurs not only by diffusion but by the movement of turbulent eddles, bulk movement and convection. Therefore, the mass transfer rate may be more conveniently expressed as

 $N = k_m A (C_b - C_f)$ (2.17)

where k_m is a mass transfer coefficient. Eqn(2.17) is used under the assumption that a steady state equilibrium existed across the film. However, this is not always true because it takes some time to establish equilibrium conditions across the film with the formation of the solid-fluid hetergenous interface. Higble [54] proposed a "penetration theory" to describe the contact between two fluids during this nonequilibrium period. Through the solution of Fick's second

law, Higble obtained the mass transfer coefficient for the absorption of gas in time "te" by a stagnant liquid.

$k_{\rm m} = 2 \ (D/\pi t_{\rm e})^{0.5}$ (2.18)

where te is the exposure time of the liquid to the gas. Based on the modification of the Higble penetration theory, Dankwerts et al[55] proposed surface renewal theory to relate the mass transfer coefficient to the fractional rate of surface renewal:

$k_{\rm m} = (DS)^{0.45}$

where S is the rate of surface renewal which depends on hydrodynamic conditions and geometry of the system.

Mass transfer for flow past single spheres has been the subject of much study[56],[57]. The phenomenon of mass transfer between a sphere surrounded by fluid can be described by the dimensionless group which is used to correlate the mass transfer.

^NSh = F(NRe,NSc,NGr)

(2.20)

(2.19)

For the condition of no natural convection $(N_{Gr=0})$ the correlation for the mass transfer from a sphere can be expressed as

35

 $N_{Sh}= 2.0 + C N_{Re}^{0.5} N_{Sc}^{0.33}$ (2.21)

where C is constant which falls in the range 0.3-1.0. For Reynolds numbers from 20 to 2000, it is suggested by Rowe[57] that the value of C is 0.63 for gases and 0.76 for liquids. This type of empirical correlation was based on the assumption that mass transfer was controlled by the potential flow over the front or upper surface of the particle and there was no transfer through the wake. A more appropriate correlation which takes account of the mass transfer due to the wake has been proposed by the previous authors[58],[59] and is of the form.

 $N_{Sh} = C_1 N_{Re}^{0.5} N_{Sc}^{0.33} + C_2 N_{Re}^{0.5} N_{Sc}^{0.5}$ (2.22)

Where the second term represent the mass transfer to the wake.

For the agitated system, the mean relative velocities between particles and fluid flow is greatly

system. affected by the turbulence of the Although Eqn(2.21) and (2.22) are applicable to estimate the mass transfer coefficient for particles in turbulent flow, an appropriate velocity to use for the calculation of the Reynolds number has to be estimated with caution. However for particles with very small diameter in a highly turbulent system, the corresponding Reynolds number will be small enough (Re<1) to ignore this turbulent effect on mass transfer. Therefore, Kolmogoroff's theory of local isotropy is used to account for the influence of the local turbulent flow field on mass transfer of a particle. The detail of the Kolmogoroff's theory were described by Hinze[60]. For particles with very small diameter, the average statistical /turbulent properties around these particles are determined by the local energy dissipation per unit mass. For a baffled stank the average energy dissipation per unit mass is given by[61].

= K N3D2 *

ε≕ Ugg. g

(2.23)

where K is a dimensionless constant, N rotation speed in r.p.s., D diameter of agitator. For gas stirred bubble columns, the average energy dissipation per unit mass is given by [62].

(2.24)

where Ug is the bubble velocity, and g is gravitational acceleration. It has been found that mass transfer between small particles and turbulent liquid is a function of energy input per unit mass. Sano et al[62] in their study of mass transfer to solid particle proposed the following correlation for dimensionless mass transfer coefficients by using Kolmogoroff's theory of local isotropy in agitated systems.

 $N_{Sh}^{=} [2 + 0.4(sd_{p}^{3})1/4N1/3]$ (2.25)

where d_p is the diameter of particle v is the kinematic viscosity and ϕ is the surface factor.

Apart from the hydrodynamic factors, the rate of mass transfer of the dissolved solute to the particle could be enhanced by Marangoni turbulence at the liquid-particle interface[63].

Studies on the disintegration and coalesence of bubbles during flotation were reviewed by Sano et al[66]. They proposed the following empirical equation for the estimation of bubble size in the plume.

(2.26)

 $d_{VS} = 0.091(\delta/\rho_{1})0.5V0.44$

The sizes of bubbles in molten iron estimated from this equation are in the range 20-100 mm.

The extensive literature review on mass transfer from bubbles to liquid are available in ref.[67],[68]. The bubble shape is affected by many factors, and Grace et al [69] provide guidance on methods of prediction. Small bubbles with diameters less than 2.5 mm behave as rigid spheres. In liquids of low and intermediate viscosities, bubbles larger than 10 mm in diameter are spherical cap in shape with open wake. By assuming potential flow over the front or upper surface of the bubble, the mass transfer coefficient for the front is given as[72]

 $k_{b} = 0.951 g_{0.25D}^{0.5d} = 0.25 (2.27)$

However, this is applicable to the idealized case of a spherical cap bubble rising vertically. Glinkov found that large bubbles are elliptical in shape and tend to slide sideways. Consequently the velocity at the bottom section of bubble is higher than the vertical velocity. Therefore the mass transfer at the bottom plate becomes important.However, transfer from the bottom section of the bubble is not as well understood. Weber[74] used the penetration theory to relate the observed mass transfer rate from the rear of bubbles. $k_{fr} = 0.29 g0.2500.50 - 0.25$ (2.28)

39

in aqueous systems, the presence of surfactants tends to reduce mass transfer rates for bubbles by interfering with circulation pattern or by immobilizing the bubble interface. Small amount of surface-active agents, such as oxygen dissolved in silver, may substantially decrease the mass transfer rate of bubbles[75]. The fractional surface coverage of surfactant,0, is well described by Langmuir's adsorption isotherm[65].

 $K_{1} = \frac{\theta_{1}}{(1-\theta_{1}) \theta_{1}}$ (2.29)

The presence of surfactant at the liquid surface will cause a variation in the concentration of the solute on the gasliquid surface, resulting in the uneven distribution of surface tension. The relation between the excess concentration of solutes and the surface tension is given by the Gibbs' adsorption equation.

(2.30)

where **r** is the excess concentration of the solute in the

surface film; mole/m2, a is the thermodynamic activity of the solutes in the bulk phase, r is the surface tension. Owing to the existence of the uneven surface force at the liquid/gas interface, the surface pressure will be created to cause the retardation of the interfacial movement. Consequently, it reduces the mass transfer rate. In aqueous systems, the mass transfer rates immobilized by surfactant have been found to be lowered by a factor of 2 to 10 in comparison with the mass transfer coefficient obtained from the penetration theory[162].

2.3.2.2 The kinetics of slag metal desulphurization

The kinetics of sulphur transport between slag and molten iron has been the subject of much study[76]-[97]. Due to the large volume of literature available in this area, several of the important observed experimental facts on the rates of desulphurization between slag and metal are summarized below:

- (1) The , rate of reaction is enhanced with the increasing slag basicity.
- (2) The existence of reducible oxide in the slag reduces the rate of desulphurization.
- (3) Improvement of bath stirring enhances the desulphurization rate .
Sulphur is present as sulphide ions in iron making slags due to the low oxygen potential, thus the slag/metal desulphurization can be described by an ion exchange reaction.

$$5^{-2} + 0 = 5 + 0^{-2}$$
 (2.31)

The kinetics of sulphur transport between slag and hot metal have been reported to follow first order reaction kinetics with respect to sulphur[98],[99]. The overall transport process may involve the following three elementary steps as shown in Figure 2.7 namely:

(A) Transfer of sulphur from the metal phase to slag/metal interface.

$$Nm/s = k A (Cb - Ci,m)$$
(2.32)

(B) Chemical reaction at the metal/slag interface

$$NRx = k_f A C_{i,m} - k_h A C_{i,sl} \qquad (2.33)$$

(C) Transfer of sulphur from the slag/metal interface to the slag phase



Figure 2.7:

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Time-average concentration-distance curves across the phase boundary for a reaction involving a metal and slag under conditions of mixed control.

Γ-

$$N_{st} = k_A (C_{i,st} - C_{st})$$
 (2.34)

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Rearranging Eqn (2.32), (2.33), and (2.34) gives

$$Nm/s / k_{m}^{A} = Cb_{s} - Ci_{s}m \qquad (2.35)$$

$$\frac{NRx}{s} / k_f A = Ci, m - k_f / k_f Ci, sl \qquad (2.36)$$

$$N_{s}^{m} / k_{A} = C_{1}^{i} s_{a}^{i} - C_{s}^{i}$$
(2.37)

At steady state, we can combine Eqn(2.35) and (2.36), and divide Eqn (2.37) by the equilibrium partition ratio η to obtain

$$1/k_{m}^{A} + 1/k_{f}^{A}$$
)Nm/s = Cb - k_/ k_Ci,sl
s s b/ fs
(2.38)

(2.39)

Ę¢.

and

$$(1/\eta k_A) Nm/s = 1/\eta C_1 st - 1/\eta C_st$$

Using partition ratio $\eta = k_f/k_b$ and combining Eqn (2.38) and (2.39) gives

$$\frac{Nm/s}{s} = A / (1/k_{f} + 1/k_{f} + 1/\eta k_{s}) (C_{s}^{b} - C_{s}^{st}/\eta)$$

(2.40)

where the term ($Cb_s - Cst/\eta$) represents the driving force in terms of concentration, Cst/η is the concentration in the metal that is in equilibrium with concentrion Cst_s , the bulk concentration of slag.

The reaction rate is controlled by the steps which are slowest. For the case of high temperature metallurgical systems, the chemical reactions are so fast that equilibrium can be assumed to be attained[163]. Therefore, the overall reaction rate constant can be simplied to

 $K_{m/s} = A/(1/k_{m} + 1/\eta k_{s})$ (2.41)

Whether the reaction rate is controlled by the transport kinetics in the metal side or slag side depends on the value of $1/k_m$ and $1/\eta k_s$. If the value of $1/k_m$ is much larger than $1/\eta k_s$, the overall reaction rate is dominated by mass transfer in the metal. The overall reaction rate expression contains the equilibrium partition ratio. Therefore the reaction rate will be affected by oxygen potential and slag composition. Low oxygen potential and high basicity of slag composition are favorable for high reaction rate. For deoxidized hot metal with high slag basicity, it is reasonable to assume that the reaction rate is dominated by the transport kinetics in the hot metal.

The effect of hydrodynamic conditions such as stirring on the slag-metal reaction rate has been studied by many previous investigators. The positive effects of intensive stirring on the rate of reaction in general can be appreciated in the following steps[100]-[113].

- (A) Improvement of the convection rate on both the hot metal and slag phases to increase the transfer of solute element to and from the reaction site;
- (B) Improvement of reaction interface due to the intensive stirring at the slag metal interface;
- (C) Improvement of mass transfer coefficient due to the increase of interfacial turbulence.

Mass transfer experiments regarding the transfer of solute between two immiscible phase have been reported in detail elsewhere[100]-[105]. Robertson et al[144] measured

mass transfer coefficients in algam-aqueous solution and lead-molten salt systems which do not involve interfacial turbulence during reaction. They successfully correlated the mass transfer coefficient with gas flow rate and vessel diameter by the relationship.

$$= B (D Q/ d2) 0.5$$

(2.42)

where B is a proportionality constant,m-1/2, D the diffusion coefficient, Q the total gas flow rate and d the vessel diameter. The values of the proportionality constants are found to vary for metal and slag control and metal depth. For high depth metal control, B is approximately 109.5 m-1. Under the condition of the low depth metal control, B is estimated to be 89.4 m⁻¹. For the case of slag control, B is estimated to be 70.7 m^{-1/2} The proportionality constant B has also been estimated based on plant studies and a value of 480 m^{-1/2} was obtained for slag-metal desulphurization of steel in transfer ladle stirred by deep argon injections[106].

The effect of gas flow rate on the rate of mass transfer has been investigated[108]-[112]. For a constant volume of liquid, the mass transfer rate can be defined as a product of the reaction interfacial area and mass transfer coefficient. However, it is found that the mass transfer

coefficient is only slightly dependent on the gas flow rate. Therefore the strong dependence of gas rate on the rate of mass transfer can be attributed to the increase of reaction interface due to the turbulence near the interface. The previous results which included both high temperature slag/metal and room temperature water model experiments indicated that the rate of reaction increased with an increase in the intensity of stirring. Table 2.4 shows these results which were summarized and tabulated by Asai et al[136].

2.4 Deoxidation of hot metal

A critical review of the previous work on the deoxidation of steel is beyond the scope of this section. Reference should be made to Turkdogan et al[114],[155] which provide a comprehensive coverage of past work on steelmaking deoxidation.

Aluminium has been known as the strongest deoxidizer commonly used in steel deoxidation. Recently it has also been used to deoxidize the hot metal to enhance the rate of desulphurization [37],[115]-[117]. The use of aluminium addition to improve the hot metal desulphurization has been successfully demonstrated at J&L steel's Aliquippa Works[37]. The reason for the use of aluminium addition to deoxidize hot metal before lime injection is that aluminium

• • • • •	Correl	ation of mas	s transfer i iquid-liquid	n 'system	
System	Stirring	Reaction	Correlation	Remarks	Ref.
Slag-Steel	Ar gas	Desulphur- ization	K « c ^{0 + 25} ;c<60w/ton K « c ^{2 - 1} ;c>60w/ton	2.5ton converter q<1502/min. ton 150 <q<240< td=""><td>[135]</td></q<240<>	[135]
water-Hg …	N ₂ gas	Reduction of quinone	K = E	q<58 ∳=0.22	[137]
Slag-Steel T	Ar gas mechani- cal stirring	Dephosphor- ization	K = c ^{0 - 6 0}	30 <q<160< td=""><td>[138]</td></q<160<>	[138]
Slag-Steel	Ar gas	<u>Cu</u> +(Cu)	K = c ^{0 - 27}	q<100 ,	[139]
Slag-Steel	<u> </u>	Desulphur- ization	K = c ^{1 • 9}		[1.40]
011-water		•	K = c ^{0.33}		[141]
Amalgams- aqueous sol.		[In]+3(Fe ³⁺) (In ³⁺) +3(Fe ²⁺)	K _{II} = e ^{0 + 3 3} K _S = e ^{0 - 5 2}	q<10 φ=0.5	[142]
n-hexane- aqueous sol.	N ₂ gas	I2+20H I0 +I +H20 3I0-I03 +2I-	K = c ^{6:72}	199 <q<994 ¢=0.5</q<994 	[143]
Amalgams- aqueous so Lead- noltensal	n. It		K = e ^{0 • 5}	q<130 ¢=0.5	[144]
Slag-Steel	O ₂ gas	Dephosphor- ization	K = e*- 5*	50 <q<80< td=""><td>[145]</td></q<80<>	[145]
iiquid paraffin -water			K = c ^{3 + 0}	30 <q<80 80<q<200 #=0.17</q<200 </q<80 	[134]
etraline- aqueous sol.	air		Kαε ⁰⁺³⁶	q<150 150 <q<650< td=""><td>[136]</td></q<650<>	[136]

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Table 2.4

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q∝c is assumed K:capacity coefficient of mass transfer c:mixing power density ¢:fraction of slag

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can enhance the desulphurizing ability of lime due to the formation of liquid calcium aluminate slag with higher sulphide capacity. Furthermore, as stated in section 2.3, low oxygen potential is thermodynamically favorable for effective desulphurization to occur.

In general, the solubility of the deoxidation products in liquid iron alloys is represented by

 $M_{X}O_{Y} = X\underline{M} + Y\underline{O}$ (2.43)

for which the equilibrium constant is

2

eq^ª ^AX ^AY / ^AM 0 × ∨

(2.44)

 $K_{eq} = [\%]X [\%]Yfxfy (2.45)$

Theoretically the equilibrium constant represents the deoxidation power of the deoxidizer. Table 2.5 shows selected deoxidation equilibrium constants for liquid iron saturated with the respective oxide. It can be seen that TABLE 2.5

Deoxidation equilibrium constants for liquid iron saturated with the respective or

•

Equilibrium constant K*	Composition range	K at 1 600°C	log K
[art]2[a0]4	<1 ppm Al	1-1 × 10-15	$-\frac{71600}{7}+23\cdot28$
[avi]2[ao]3	>1 ppm Al	- 4·3 × 10-14	$-\frac{62}{2}\frac{780}{78}+20.17$
[<i>a</i> _B] 2 [<i>a</i> ₀] ³		1.3 × 10-8	· · ·
[ac][a ₀]	>0-02%C	2.0 × 10 ⁻³	$-\frac{1}{200}$ - 2.07
(1 atm CO)	• •		T
[acr]2[a ₀]4	<3%Cr	4.0×10^{-6}	$-\frac{50\ 700}{7}+21\cdot70$
[a _{Cr}]a[a ₀]3	>3%Cr	1·1 × 10-4	$-\frac{40}{7}\frac{740}{7}+17.78$
[akn][ao]	>1%Mn	5•1 × 10-2	$-\frac{14450}{450}+6.43$
[a _{EI}][a ₀]2	>20 ppm Si	2·2 × 10-5	$-\frac{30.410}{$
[a ₁₁][a ₀] ²	<0-3%Ti	2.8 × 10 ⁻⁶	.
[a ₁₁][a ₀]	>5%TI	1.9 × 10-3	
[av][a_0] ⁴	<0•1%V	8-3 × 10-8	
$[a_V]^2[a_0]^3$	>0.3%V	3.5 × 10-6	•
^{Activities are chosen such the}	at $a_{\mu} \equiv %M$ and $a_{0} \equiv %O$ as	%M → 0	

aluminium has the strongest deoxidation power.

The determination of oxygen in steel or hot metal has been intensively studied for several decades. Oxygen can exist in iron both in the form of oxide and dissolved oxygen. Typical total oxygen contents of hot metal are reported in the range of 10-100 ppm[37],[117]. Obviously these total oxygen values are far in excess of those expected for equilibrium with either carbon or silicon. Therefore most oxygen is in the form of oxide. it is not practical to use the total oxygen content to determine the oxidation level of the hot metal so as to control the refining condition. Recently, the developments of the oxygen galvanic cell can provide a rapid and accurate measurement of the dissolved oxygen activity in steel or hot metal.

The oxygen galvanic cell consist of two electrodes with oxygen chemical potential which are separated by the solid oxide electrolyte. For an oxygen cell using Cr-Cr₂O₃ as a reference electrode, and partially magnesium-stabilized zirconia as the electrolyte, the galvanic cell can be represented by

Cr-Cr203 Zr02(MgO) 0 (in Fe alloy)

51

The cell reaction is

12

$$2/3 \text{ Cr}_{(s)} + 0 = 1/3 \text{ Cr}_{2}^{0}_{3} (s)$$
 (2.46)

 $\Delta Go = -90180 + 20.45 T (J)$ (2.47)

If the cell conducts purely ionically, then the free energy change for the cell reaction and the measured EMF's are related by the Nernst equation.

Therefore

$$\Delta E = E - E_0 = RT/nF \ln a_0 \qquad (2.49)$$

where Eo is the EMF for the reference electrode pure Cr and Cr_2O_3 , n=2 and F is the Faraday constant (23061 cal/v equivalent).Substitution of the known value of Eo from the available thermodynamic data[118], the activity of oxygen is given by

Log a = (4.62 - 13580 - 10.08E) / T

(2.50)

(2.48)

In fact, the oxygen cell usually exhibts some electronic conduction under the steelmaking condition. Wagner[119] and Schmalzried[120] proposed the following equation to take into account the effect of electronic conduction.

 $\frac{1}{2} = \frac{1}{2} \left[\frac{(Po'1/4 + Pe1/4)}{Exp(EF/RT)} - \frac{Pe1/4}{2} \right]$

(2.51)

(2.52)

Where Keq is the equilibrium constant for the reaction.

Po' is the equilibrium oxygen partial pressure of the reference electrode. Pe is a constant which represents the oxygen partial pressure where the ionic transport (ti)and electronic transport numbers te are equal (i.e., ti=te=0.5).

At ironmaking temperatures, for example 1350 oc, the electronic conduction requires only a 3% correction. On the contrary, at steelmaking conditions, 1650 $^{\circ}$ C, it requires a 30-40% correction.

2.5 Fluid dynamic aspects of powder injection

 $1/2 \ O_2 \ (g) = O_1 \ w/o$

Recently, the role of powder injection has become

of particular importance in pyrometallurgical operations. There is a great deal of literature available which deals with the hydrodynamic phenomena of this technology. A physical reaction model of powder injection has been proposed by Lehner[121]. During powder injection refining, the reagent powder is injected along with the carrier gas into the melt. The ladie can be divided into several zones (Figure 2.8).

- (1) jet zone 😳
- (2) central plume zone (formed by the rising gas bubbles and reagents).
- (3) breakthrough zone
- (4) slag zone
- (5) dispersion zone
- (6) lining zone
- (7) bulk zone

This reaction model is useful because it simplifies the complicated reaction model and illustrates the fundamental concepts regarding the possible reaction zones during injection refining. Through fundamental studies of turbulence intensity associated with reaction kinetics, it is found that the central plume zone has the





ß

highest reaction rate and is considered to be the best place for the reaction to take place[121],[164].

56

particles are injected into the melt, each When particle either penetrates into the melt or is entrapped inside the bubble, depending on the surface properties and hydrodynamic situation of the system. There are many investigations which have been carried out to achieve a better understanding of the behavior of the gas injection into the melt[122]-[128]. However, little is known about the behavior of injected particles. The most important physical parameter to determine whether the injection particle will penetrate the gas/liquid interface is σ , the contact angle of the solid with liquid. For the maximum penetration, the contact angle should be zero or as low as possible. Engh et al[129] used a momentum balance on a single particle injected normal to the bubble/liquid interface to determine the minimum size of particle required for the penetration. Farias and Robertson[130] proposed a dimensionless group called the Entrainment number to predict the onset of jetting of gas-powder mixtures. The Entrainment number is given by

 $N_{E} = \frac{3}{8} \left(\frac{m}{s} \frac{m}{g} \right) \left(\frac{h}{r} \right) \left(\frac{r}{r} \right) \left(\frac{\rho}{\rho} \frac{\rho}{t} \right)$

(2.53)

It was found that the use of small particle sizes at high loading lead to a high value of N_E which causes the gaspowder mixture to form a jet.

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Irons and Tu [131], in their studies of powder injection in molten lead, 'also found that the size of particle and loading influences the formation of a bubbling or jetting regime. They proposed a critical loading criterion to predict jetting/bubbling of the gas-powder mixtures injection. With high loading of small particle size, the gas and particles are travelling at the same velocity. Due to the dense two phase transport, the momentum boundary layer of the particles is large enough to overlap adjacent ones, so that most of the gas travels with the particles in a coupled state. Therefore on exit from the lance nozzle, the gas will flow with the particle to form a jet. The critical loading is a function of the boundary layer thickness which can be analyzed in terms of particle Reynolds Number. Thus the critical loading proposed by them is given as follows:

 $\theta_{\text{PC}} = \pi / [6(6/(2 \text{ Rep })^{0.5} + 1)3]$

13

For the prediction of penetration depth of a gas-

(2.54)

balance of the particles with-buoyancy force acting on the displaced liquid which was originally proposed by Engh et al[129]. Recently, Farias and Irons[133] investigated the injection of powder into liquid by physical modelling and multi-phase fluid dynamic modelling. The measured penetration depth of submerged jets in water and lead and top jets in water were described by equating the momentum balance of the jet and its buoyancy.

The influence of stirring on the rate of refining has been investigated by many previous workers[134]-[145]. Various stirring methods such as electromagnetic, mechanical and argon injection have been developed in the steel industry.

Based on the intensive study of mixing phenomena in a 50 ton argon stirred melt, 200 ton R.H. vacuum degasser and 65 kg water model experiments, Nakanishi et al [134] correlated the mixing time as a function of the rate of energy dissipation. The proposed empirical equation is

 $\tau = (600 \pm 100) \epsilon^{-0.4}$ (2.55)

where τ is the mixing time to be defined as 95% homogenization in the stirred melt, ε the rate of energy dissipation. W/t.

For gas stirred melts, the rate of energy dissipation based on the assumption that the kinetic and thermal expansion energies of gas are small enough to be neglected, can be expressed as follows:

= 6.183 \times 10-3 VT/W Ln (1 + ρ gH/105P)

(2.56)

59

where V is the gas flow rate in m3/min, T is the melt' temperature, K. W is the mass of the melt in ton. ρ is the density of the melt ,g is the gravity acceleration , H is the depth of the gas inlet in m, P is the gas pressure at inlet in bar.

There have been few studies carried out to examine the influence of powder injection on mixing phenomena[165]-[167]. Sinha and McNallan injected sand into water and found that the mixing times were shorter than those from gas alone at the same flow rate[166]. However, Narita et al[167]. found that the mixing times of liquid in the powder injection process is not affected by the kinetic energy of injected particles. More recently, Irons[168], in his study of water modelling of a torpedo car, found that the kinetic and potential energy of the injected particles generally have little effect on mixing times, in comparison with the

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potential energy of the gas. However the particles can improve the mixing time when the particles carry the gas deeper than the gas would have gone without the particles.

Recently, an increasing effort[146]-[152] has been devoted to numerical solution of the turbulent hydrodynamic transport equations in an attempt to predict the recirculating flow field occuring in various metallurgical operations. In general, the relevant turbulent hydrodynamic equations governing the motion of flow can be expressed in vectorial form as

equations of continuity

equation of motion

∇ U = 0

^µeff

DU/Dt =-1/ρ V P + 1/1 V τ + F

(2.58)

(2.57)

60

For modelling turbulence, the effective viscosity, µeff can be calculated by the two equation turbulence model of Launder and Spalding[153]. For this case, the effective viscosity takes the form of where 1 is the Prandtl mixing length and K is the kinetic energy of turbulence.

61

(2.60)

Fairly good agreement between the measurements and computed results of these equations were reported by several authors[146]-[152]. The success of these models is due partly to the assumption of simplying the two-phase nature of the fluid as a single phase by using a mixture model. Therefore it is possible to have well defined boundary conditions for the governing equations of fluid flow. However, it is not true for the gas agitated reactor because the discreteness of each phase is ignored by these model. Farias and Irons[154] developed a one-dimensional steady-state model to describe the fluid dynamic processes in a rising plume for gas-liquid-solid mixing. This model consists of equations of continuity, momentum and energy for each phase (gas-solid-liquid). This model can be extended to include mass transfer calculation in the plume as described in Chapter 5.

and

 $\mu_{\perp} = \rho t K 1/2$

CHAPTER 3

APPARATUS AND PROCEDURE

The present work was carried out on a 3 tonne induction furnace, located at the pilot plant of STELCO Inc. in Burlington, Ontario.

3.1 Apparatus

3.1.1 Powder dispenser

A pilot-scale powder dispenser was specially modified for the present study. Extensive preliminary calibration trials indicated that the powder feed rate was dependent on the pressure, orifice diameter of the outlet valve, and the characteristics of the powder. A schematic diagram of the pilot scale dispenser is shown in Figure 3.1.

During an injection, the powder injection rate was controlled by the difference between the bottom pressure of the dispenser and the pipeline pressure directly below the outlet valve of the dispenser. The main carrier gas flow rate was accurately and reproducibly controlled by a needle valve. Only 5 to 10 % of the gas flow was found to be going through the dispenser during injection. By properly adjusting the needle valve, the fluctuations of the gas flow rate were minimized so as to maintain constant gas flow



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Figure 3.1:

Schematic diagram of powder dispenser and conveying line. The powder dispenser was equipped with a load cell and mass flow meter for continuous measurement of dispenser weight and total gas flow rate, respectively. Capacitance transducers and pressure transducers were also installed at 2 points in the pipeline for monitoring the instantaneous volume fraction of solid and static pressure[64]. Figure 3.2 shows a photograph of the powder dispenser.

The gas and powder flow rate, pipeline pressure, and solid volume fraction were recorded 60 times per second with a customized DEC LSI 11/2 computer.

3.1.2 Furnace configuration

rate

Details of the lance and furnace arrangements are shown in Figure 3.3. The lance was located at the center of the furnace. The lance was submerged into the hot metal 650mm(±25 mm). The total hot metal weight used for the present study was between 2.2 and 2.6 tonne.

Typical chemical analysis of furnace lining are shown in Table 3.1. The lance consisted of a metallic tube with a refractory lining of castable material (stopper rod siéeves). Lance life varied from one to several treatments. Table 3.2 shows the typical chemical analysis of castable refractory. Figure 3.4 (shows a photograph of the lance



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Figure 3.2:

Photograph showing induction furnace and powder dispenser.

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SCHEMATIC REPRESENTATION OF HOT METAL TREATMENT.

Figure 3.3: Cross-section showing lance, furnace and metal levels, to scale.

Table 3.1

Typical Chemical Analysis of

Furnace Lining			
AL ₂₀₃	90 %		
MgO	7.0 7		
Other	3.0 %		
•			

Table 3.2

Typical Chemical Analysis of

Castable Refractory			
A£203	90.5 %		
MgO 1	4.0 %		
TIO2	1.7 %		
St02	1.4 %		
Fe ₂₀₃	0.2 %		
CaO	0.2 %		
Other	2.0 %		

Figure 3.4:

Photograph showing lance for powder injection.

68

together with the cover.

3.2 Oxygen probe 🔪

The Celox oxygen probes (Celox2/CII), used in the present study to measure the oxygen activity in the hot metal, were commercial, single-use electrochemidal oxygen cells. The cell consists of a ZrO_2 electrolyte partially stabilized with MgO and a Cr/Cr_2O_3 reference electrode.

The disposable oxygen probe was plugged into a holder and then plunged directly into the liquid hot metal. About 10 to 15 seconds were required to give a stable E.M.F. reading for both the melt temperature and oxygen activity.

The measured cell E.M.F.(mv) is converted into oxygen activity by the recommended calibration equation[160]:

 $Log(a_0) = 1.36 + 0.0059[E + 0.54(T-1550) + 0.00021E(T-1550) (3.1)]$

where a_0 is the oxygen activity (ppm). T is the temperature oC, and E is the measured cell E.M.F.(mv). This calibration equation was developed for steelmaking conditions so it should be used cautiously in the iron making condition. A comparison between the theoretical relationships such as Eqn(2.51) and the calibration equation is in Appendix I. The

results are shown in Figure 3.5 which indicated that a comparative-good agreement are obtained between Eqn(2.51) and the recommended calibration equation. The recommended calibration equation is approximately 20% higher over the range of oxygen activity in the present study. It was decided to use this calibration equation to relate the measured E.M.F and oxygen activity throughout the present study.

3.3 Materials

The composition of the principal materials used in this study are listed in Tables 3.3 to 3.6. Four different initial top slag conditions were used:

- * (1) No slag
 - (2) A dry slag which was a mechanical mixture ofCaO and SiO₂ in a weight ratio of 1.2 : 1.
 - (3) A liquid siag which was a commercially available continuous casting powder with the composition shown in Table 3.4 and a liquid temperature of 1150 °C.
 - (4) The dry slag used above, modified in most cases by the plunging of 4 kg alumimium before calcium carbide injection. This slag appeared liquid. Two injections were performed using a



y	prea		•
	Hot	Metal Composition"	
		•	
•	Ċ	3.5 - 4.0 %	
	Si	0.2 - 1.5 %	
	Mn	/ 0.5 %	
	P	0.04 - 0.045	7.

Table 3.3

72

* The details of hot metal composition are listed

in Appendix II.

Table 3.4

Typical Chemical Analysis of 1/STG Continuous Casting Powder*

CaO	31.5 - 33.5 %
510 ₂	25.0 -27.0 %
A1203	6.5 - 7.5 %
MnO	5.0 - 6.0 %
Na ₂ 0	6.5 - 7.5.%
Total C	615 - 715 %
F	5.5 - 6.5 %

Melting temperature 1135 °C

-	Typical	Chemic	al Anal	ysis of
	DSR"	Grade	Desulph	urizer
				······································
	CaC2	2 '	. 81.	0 %
	Ca0	* 1	10.	6 %
	CaS	-	, 0.9	7.
	С	. •	0.5	7.
	MgO	-	0.3	7
	Ash		6.3	7.
c	diaméter	is 24	um.	•



Mean particle

Table 3.6

Typical Compo	sition of Flu
CaO	45%
CaF2	20%
A1	30%
C	5%

Table 3.5

flux to modify the slag. The composition of flux is listed in Table 3.6.

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These four sing conditions were chosen so as to determine the significance of this variable. Generally 10 kg of top sing was used, and more than 10 kg of calcium carbide was injected so that at the end of injection the sing was solid or semisolid:

The calcium carbide was a commercially available desulphurizing reagent (DSR) as shown in Table 3.5. Note that no diamide lime (CaCO₃) was used for most of the runs.

3.4 Procedure

The detailed experimental procedure is shown in Figure 3.6. Prior to the injection test, the initial sulphur content of the iron was adjusted to the desired level by plunging a box containing sulphur into the bath. The temperature was controlled at 1350 \pm 5°C. Before the injection test, the oxygen activity and hot metail temperature were measured simultaneously by oxygen probe. A pair of slag and metal samples were taken before the start of injection. The injection lasted between 1 and 6 minutes. This was dependent on the rate of solid injection . One or two minutes of argon gas bubbling was conducted after the calcium carbide injection for the the purpose of slag/metail reaction studies. During the injection and Argon gas





 Flowchart for experimental procedure during a heat.

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bubbling treatment, hot metal samples were taken every 15 to 20 seconds. After the injection and bubbling treatment, the oxygen activity and bath temperature were measured. A pair of slag and metal samples was also taken as a measure of final slag and metal chemistry. The top slag was then thoroughly skimmed off the furnace. The furnace was covered by a loose-fitting lid during the treatment to prevent large splashes.

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3.5 Operating condition

The ranges of injection conditions are shown in Table 3.7 and a loading diagram for all the runs is shown in Figure 3.7.

3.6 Chemical analysis

The slag samples were crushed and screened to separate the metal droplets from the slag. The slag powder were then analysed for the chemical contents of S, SiO_2 , CaO, MgO, Al₂O₃, and metallic Fe.

The metal droplets from the slag were weighed and then immersed for 30 minutes in 20% hydroflouric acid for thorough surface cleaning before chemically analysing for silicon and carbon contents.

The pin samples of metal which were taken from the hot metal during the injection tests, were cut into small
Experimental Con	ditions
Carrier gas	Argon
Hot metal temperature	1350 <u>+</u> 5 oC
Powder consumption (Kg/t)	1.3 - 7.6
Powder injection rate (Kg/min)	2.5 - 11.0
Gas flow rate (Nm3/min)	0.05 - 0.24
Solid/gas ratio (Loading)	16 - 154

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Table	3.7	
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pieces weighing approximately 0.5 gram. For each analysis, at least 4 pieces were taken at random from the sound portions of samples, and sent for chemical analysis of sulphur. Some selected metal samples were also analysed for the content of Si and Al. Duplicate analyses gave results reproducible within 8 % of the amount of S in the sample for the 95 % confidence limit.

Table 3.8 shows the technique and analyser accuracy which were used for the slag and metal sample analysis.

STELC	O Chemical Analysis Techniqu	18 5
Substance	<u>Technique</u>	Accuracy (%)
Slag		
FeO	Oxidation of ferrous ion	to a
<u>`````````````````````````````````````</u>	to ferric by KMnO4	_0.2
SiOZ		
^{A £} 203 Ca0	Sodium tetra borate fusion ARL 72000 X - ray	<u>+</u> 0.1
Mgo		· · ·
S	Combustion CS-144 (Leco)	<u>+</u> 0.002
Hot Metal/Iron		
s	Combustion CS-144 (Leco)	<u>+</u> 0.002
c))		+0.1
Si	ARL-72000 X-ray	<u>+</u> 0.02
Acid Soluble Aluminum	Acid dissolution-Atomic Emission Spectrospan III	±0.002

Table 3.8

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

Forty-eight injection tests were carried out in the present study. The injection tests were divided into four groups according to the initial slag conditions; namely no slag, dry slag, liquid slag, and modified dry slag.

The injections with no top slag were performed in the summer of 1982. The control of the system was not as good as in the subsequent tests, but they are reported for the sake of comparsion. Several other aspects were briefly examined in the 1982 injections. Both DSR and CAD commercial grade calcium carbide containing diamide lime (CaCO3) were used. An attempt was also made to use the co-injection technique; in the later stage of the injection, salt-coated magnesium was simultaneously injected from a separate dispenser. The co-injection period was 20 to 30 seconds. The injection rate of salt-coated magnesium was between 0.85 and 3.0 kg/min. The operating conditions and results are shown in Table 4.1 and Appendix III.

In 1983-84, thirty-seven successful injection tests, with initial slag conditions of dry slag, liquid

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SUDS:11	ARGON	RATE (Nm ³ /min)	52°0	0.25	0.25 ³	0.25 ³	0.25 ¹	. 0.25 ^{3 -}	0.25 ¹	0.25	0.25 ³	6.25	0.25 ³		1	0.164		0.155	0.155	0.163	012'0	0.118	0.127	N01.0
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VDLF.4.1 - SI	3 (DSR)	QUANTITY (kg)	20.02	34.6	4.50	16.0	14.7	12.71	16.9	11.2	10.01	13.61	611		1	3.65	1	16.5	3.52	£71	FH	15.0	611	¥ E 1
4	3	ltATE (tg/min)	8.41 ³	667	5.10	7.76	4.83	7.14	6.04	5.05	7.17	6.70 ¹	5.6		Ŧ	2.66	T	10.0	11.5	26.7	80.0	6,¢0	9.49	¥ C
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slag, and modified dry slag, were performed with very accurate control of the injection conditions. The desulphurizer used in the injection tests was DSR grade commercial carbide with a particle size of 24 µm. Details of slag conditions, operating conditions, and changes in sulphyr contents are shown in Table 4.1.

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The discussion of these results is divided into three sections:

- (1) the effect of top slag,
- (2) the effect of injection conditions, and
- (3) the effect of oxygen.

4.2 Effect of top slag

4.2.1 Results

The typical curves of sulphur change with time, during the treatment, are shown in Figures 4.1A and 4.1B. The four injections shown in Figures 4.1A and 4.1B were selected because the starting sulphur, gas flow rate, and solid flow rate were very similar; the only difference was the top slag. A significant difference was found between no slag and dry slag cases on one hand, and liquid slag and modified dry slag cases on the other hand. The amount of initial slag used in most of injection tests was about 10







Sulphur versus time for injection H9R3 with liquid top slag and injection H14R2 with aluminium-modified dry slag. Note the absence of an incubation time.

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kg. For no slag and dry slag cases, the hot metal sulphur level did not decrease significantly for an initial 30 to 50 seconds of injection time, resulting in inefficient calcium carbide utilization and slow desulphurization. This phenomenon was termed an incubation period. The sulphur curves for both liquid slag and modified dry slag cases exhibited no incubation period as seen in Figure 4.18. A survey of all the sulphur versus time curves given in Appendix III shows that this observation is true for all the injection runs. Figure 4.2 shows the apparent sulphur partition ratio as a function of the amount of calcium carbide injected. The apparent sulphur partition ratio is calculated based on the assumption that all the sulphur removed from the hot metal is transferred to the top slag. Thus the apparent sulphur partition ratio is the ratio of the sulphur concentration in the slag, which is calculated from the change of sulphur in the hot metal, over the sulphur concentration in the hot metal. As can be seen from Figure 4.2, the apparent sulphur partition ratio is small and increases slowly during the incubation period. However, after passing through the incubation period, the apparent sulphur partition ratio is seen to increase rapidly. Based on examination of the sulphur versus time curves, it was found that the injection of 3.5 kg (1.4 kg/t.H.M.) of calcium carbide was required to end the incubation period. Therefore high calcium carbide injection rates result in a



 Apparent sulphur partition ratio versus amount of calcium carbide injected (dry slag condition).

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short incubation period.

Figure 4.3 shows the plot of apparent sulphur . partition ratio against amount of calcium carbide injected for liquid slag condition. It shows that a relatively high sulphur partition ratio is observed in the initial stage of injection in comparison with that of dry slag condition. An estimate of sulphur partition ratio at the beginning of injection can be obtained by the intercept of the regression. line with the Y axis where the CaC_2 weight is zero. Thus the apparent sulphur partition ratio for liquid slag was estimated to be 4.5 at the start of injection. Using the same method, a value of 0.1 was obtained for the dry slag condition. It can be seen that liquid slag possesses better desulphurization properties than dry slag does initially. Therefore the liquid slag has the ability to immediately dissolve the initial quantity of CaS due to the relatively high slag volume and better slag properties. Consequently, the incubation phenomenon was not observed. Similarly, no incubation phenomenon was observed in the case of modified dry slag.

For the purpose of obtaining the rate of slag/metal desulphurization, the post bubbling stirs were carried out and lasted for 1 to 3 minutes after most injection runs. If the slag/metal desulphurization is a first order reaction, the rate can be expressed as:



 $d[\% S] / dt = K_m ([\% S] - (\% S) / \eta)$

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(4pd)

where [%S] is the sulphur concentration in metal in Wt%; (%S) is the sulphur concentration in the slag in Wt%; η is the equilibrium partition ratio of sulphur between slag and metal; K_m is the overall reaction rate in 1/s.

The refining capacity of CaC_2 -saturated top siag after injection was found to be very powerful for desulphurization. A high equilibrium sulphur partition ratio is expected to cause (%S)/ η to be small in comparison with [%]. Therefore, Eqn(4.1) can be written as

 $-d[\% S]/dt = K_m[\% S]$ (4.2)

Rearranging and integrating gives

 $\ln ([\% S_t)/[\% S_i]) = -K_m t$ (4.3)

where [%St] is the sulphur content at any time t and [%Si] is the initial sulphur content.

The plots of the logarithm of the sulphur ratio versus time are shown in Figures 4.4 to 4.6 for the initial



Figure 4.4: Logarithm of sulphur ratio versus time (dry slag condition).







slag conditions of dry slag, liquid slag and modified dry slag. respectively. It is found that the assumption of first order kinetics of slag/metal desulphurization is verified by the linear slope of desulphurization curves. The values of desulphurization rate constant calculated from the semilogarithmic plots for all injection tests are given in Tables 4.2A to 4.2C.

The effects of gas flow rate and slag weight on the rate of the slag/metal reactions have been examined in the present study. The plots of the reaction rate as a function of gas flow rate are shown in Figures 4.7 and 4.8 for the initial slag condition of dry slag and liquid slag. The corresponding slag weight for each post-bubbling test is also indicated in the above figures. Multiple regression of desulphurization rates on the slag weights and the gas flow rates were performed. The resulting equations, with correlation coefficients of 0.78 and 0.75 for the initial slag conditions of dry slag and liquid slag, respectively, are expressed as follows:

For the initial dry slag condition

 $\kappa_{\rm m} = 2.31 \times 10 - 6 \times Q^{0.68} \times W^{3.25}$ (4.4)

For the initial liquid slag condition

 $K_{\rm m} = 9.46 \times 10^{-7} \times 20.47 \times 3.19$ (4.5)

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•	Run	Gas flow rate (Nm ³ /t.min)	Slagweight (Kg)	Desulphurization rate (1/s)
	H5R2	0.0654	14.65	2.80 X 10 ⁻³
	H6R1	0.0596	26.53	18.7 X 10-3
	H6R3	0.0669	27.90	19.4 X 10 ⁻³
	H7R1	0.0899	24.35	19.0 X 10 ⁻³
	H7R2	0.0470	24,98	12.6 X 10 ⁻³
	H9R1	0.0607	22.68	6.21 X 10 ⁻³
	HIOR	1 0.0305	22.77	5.24 X 10 ⁻³
	HIORZ	0.0193	22.77	5.10 X 10 ⁻³
	HIORE	0.0227	22.93	3.19 X 10 ⁻³
	HIOR4	0.0206	22.77	5.85 X 10 ⁻³
	HIZR3	0.0645	21.83	, 3.08 X 10 ⁻³
	H15R1	0.0603	16.62	3.07×10^{-3}

(Initial Slag condition : Dry Slag)

Table 4.2A

Rate of Slag / Metal Desulphurization

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Rate of Slag / Metal Desulphurization (Initial Slag Condition: Liquid Slag)

74.847762.2459499743 (300 746).74	Run	Gas flow rate (Nm ³ /t.min)	Slag weight (Kg)	Desulphurization rate (1/s)	
Z	H7R3	- 0.0506	24.87	5.10 X 10-3	
	H7R4	0.0691	23.41	5.90 X 10 ⁻³	
	H8RI	0.0468	18.23	1.55 X 10-3	х. Х
	H8R3	0.0665	24.81	8.59 × 10 ⁻³	
•	H8R4	0.0934	21.91	∧ 7.70 X 10 ⁻³	
· ,	H9R2	0.0487	22.68	4.80 X 10 ⁻³	
•	H9R3	0.0657	22.68	5.55 × 10 ⁻³	
	H9R4	0.0897	22.96	7.83 X 10 ⁻³	
	HIIRI	0.0292	21.83	4.26 X 10 ⁻³	
	H11R2	0.0189	23.23	4.91 X 10 ⁻³	
•	H11R4	0.0210	18.12	2.75 X 10 ⁻³	
	H11R5	0.0209	29.98	1.02 × 10 ⁻³	
	H12R1	0.0449	z1.55	3.40 X 10-3	
	H12R2	0.0483	21.54	7.21 X 10 ⁻³	

Table 4.2C

Rate of Slag / Metal Desulphurization (Initial Slag Condition: Modified Dry Slag)

Run	Gas flow rate (Nm3/t.min)	Slag weight (Kg)	Desulphurization rate (1/s)
H14R2	0.0625	22.50	21.10 × 10 ⁻³
H14R4	0.0638	22.95	9.74 X 10-3
H15R3	0.0673	22.95	25.50 X 10 ⁻³
H15R4	0.0329	22.96	9.05 X 10 ⁻³
HIGR3	0.0646	32: Ì)	28.10 X 10 ⁻³

Table 4.3

Typical Chemical Analysis of

Slag [*] Comp	osition
′s –	2.84 %
STO2	9.0 %
ĊaO	67.7 7
^{A £} 203	I.08 %
MnO	0.49 %
Met. Fe	18.9 %

*Initial slag condition: dry slag (after calcium carbide injection).





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where K_m is the rate of desulphurization in 1/s; Q is the gas flow rate in N^{m3}/t/min; W is the CaC₂ weight in kg.

The coefficient of the exponent on gas flow rate for the dry slag initial condition is found to be 0.68 and that of liquid slag initial condition is 0.47. The influence of slag weight on the rate of reaction are also shown in the above-mentioned correlation equations. The correlated value of the exponent on the weight of top slag for both the dry slag and the liquid slag are 3.25 and 3.19, respectively.

The typical results of slag chemistry after injection are shown in Tables 4.3 to 4.5. for the three slag types. There was a considerable number of metal droplets embedded in the slag. The size distribution and weight percent of metal droplets are shown in Table 4.6 for the dry slag. Approximately 50-70% of the slag weight was found to be iron, mostly in the form of spherical droplets, and 20-30% of the metal droplets were in the form of very finely dispersed iron (less than 300 μ m) mixed with slag powder. The estimated contact surface for the dispersed metal in the slag is in the range 3 to 5 m2/(kg. of slag). Figure 4.9 shows photographs of metal droplets.

The metal droplets were cleaned to completely remove the adhering slag, and analysed for C and Si. The results are shown in Table 4.7. The carbon and silicon

contents were higher than the corresponding bulk concentrations of hot metal.

In order to calculate the efficiency of reagent utilization, the stoichiometric equations for desulphurization with CaC₂ and lime in the DSR mixture are used:

CaO(s) + S = CaS(s) + Q (4.6)

and

 $CaC_{2(s)} + S = CaS_{(s)} + 2C_{(s)}$ (4.7)

Thus if the drop in sulphur content from the initial value [%S(i)] to the final value after post bubbling [%Sb] corresponded to that expected from the total amount of CaC2 and CaO injected and reacted according to Eqn(4.6) and Eqn(4.7), the desulphurization efficiency would be 100%. Since the DSR reagent used was nominally 81% CaC₂ and 10.6% CaO, the ratio of desulphurization from each component would be expected to be similar for all injections.

Figures 4.10 to 4.13 shows these efficiencies of desulphurization plotted as a function of initial sulphur content. One can see that the efficiency increased with

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Typical Chemical Analysis of			
Stag*	Composition		
S	3.98 %		
\$10 ₂	13.4 %		
CaO	63.5 %		
A±203	6.0 %		
MnO	1.2 %		
Met. Fe	11.9 %		

Table 4.4

*Initials.lagcondition:liquid slag (after calcium carbide injection).

I	Ъ	l	e	4	•	5	

ypical Chemic	al Analysis	of	
Slag [*] Composition			
		*	
S	4.05%	•	
SiO2	7.6%		
CaO	41.5%	•	
A\$203	25.4%		
MnO	1.05%	•	
Met. Fe	20.47		

 Initial slag condition: modified dry slag(after calciumcarbide injection).

104

c

Table 4.6

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Typical Screen Analysis of

	netal Droplets	
Nesh	Size (mm.)	2
4	4.75	10 - 30
8	2.36	15 - 25
10	1.70	7 - 15
16	1.0	10 - 15
28	0.6	10 - 20
48	0.3	10 - 20

Table 4.7

Typical Chemical Analysis of Netal Droplets Injection run Si 🐒 C 🞜 H8R3 bulk conc. 0.10 4.07 droplet conc. 0.18 4.26 H8R4 bulk conc. 0.12 4.20 droplet conc. 0.18 4.22 H9R3 bulk conc. 0.14 4.15 droplet conc. 0.18 4.19

HIORS bulk conc. 0.13 4.12 droplet conc. 4.39 0.146 H14R4 bulk conc. 3.94 0.46 droplet conc. 4.53 H15R4 bulk conc. 1.53 4,03 droplet conc. 4.55



Figure 4.9: Photograph showing metal droplets from top slag.

sulphur content. It can be seen by comparing Figures 4.11 to 4.13, the efficiencies are improved slightly by moving from dry slags to liquid slag, and improved even more by the use of dry slag modified with aluminum. The efficiency also depends on loading (L) and this will be discussed in Section 4.3.

The degree of sulphur removal was simply the fraction of sulphur removed:

$$\frac{([\% S_i] - [\% S_e])}{[\% S_i]} \times 100\%$$
(4.8)

These quantities are plotted as a function of Kg of DSR added per tonne of hot metal for the four different slag initial conditions in Figures 4.14 to 4.17. One can see that the fraction of sulphur removed increased with the amount of addition, and improved progressively through the four different top slag conditions. In fact, for the aluminiummodified dry slag, the degree of sulphur removal was well over 95% corresponding to final sulphur levels of 0.001 to 0.003%.

In order to develop a useful index for the rate of desulphurization, it was decided to use,



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flow rate.

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1.

Ln ([% Se] / [% St])

Strictly speaking, this expression can be applied only to kinetic processes which are first order with respect to sulphur content. Clearly, the present results show the slag/metal reaction are first order reaction kinetics after injection. The plume CaC₂ desulphurization was also found to be close to first order reaction kinetics as shown in Figure 4.24. Thus the overall reaction kinetics should appear to be first order with respect to sulphur by the summation of both plume and slag/metal reactions except during sulphur reversion from the top slag. It may be reasonable to use this index to represent the extent of the reaction rate for CaC₂ desulphurization.

This index is plotted as a function of the powder injection rate for the three different top slag conditions in Figures 4.19 to 4.21. Once again one sees that there is a small, but progressive improvement in rate in moving from a dry slag to a liquid slag and finally to the aluminummodified dry slag. From Figures 4.13,4.17, and 4.21, it is found that the use of double modified dry slag significantly improves the efficiency, rate, and fraction of sulphur removal.

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4.2.2 Discussion

4.2.2.1 Effect of no slag and dry slag

As can be seen from Figure 4.1A, the incubation period appeared at the initial stage of injection. The phenomenon of incubation period can be explained as sulphurreversal from top slag with poor desulphurization. properties, or the inability of the top slag to physically or chemically hold the reaction product of calcium sulphide particles. The formation of a sulphide-saturated Fe-O-S-CaO liquid slag could provide a possible explanation of this sulphur reversion phenomenon. It has been reported[99],[169] that both FeO and CaS are effective fluxes for lowering the liquidus temperature of the CaO-based slags. For the injections in which the hot metal was initially uncovered by a top slag, the hot metal was liable to be oxidized by atmospheric oxygen. It is speculated that the oxidation of the hot metal will form a liquid layer of highly active FeO on the surface of hot metal. This highly oxidizing slag melt is thought to flux the reaction product, calcium sulphide, to form a sulphide-saturated liquid slag. Therefore, the sulphur in the slag will tend to revert to the hot metal. Later on (30 to 50 seconds later) the unreacted calcium carbide in the top slag will be sufficient in quantity to deoxidize the slag and desulphurize the hot metal. Consequently, the reversion will stop and the incubation

period will be over. In the dry slag condition, the mixture of calcium oxide (CaO) and silica, (SiO2) is chemically unable to dissolve calcium sulphide due to the solid state of calcium oxide in this dry slag mixture but physically able to hold calcium sulphide from the slag/metal interface to reduce the extent of sulphur reversal. This results in a slight shortening of the incubation period. After passing through the incubation period, the accumulation of the unreacted calcium carbide at the top slag may not only dilute the FeO content in the slag, but also turn the slag into a "dry and reducing condition". Therefore, the slag/metal desulphurization can be described as the solid desulphurizer/metal reaction which forms a stable reaction product of CaS. In fact, this reducing condition has been confirmed according to the present experimental results that the carbon and silicon contents in the metal droplets are higher than that in the metal bulk. Furthermore, Figure shows that the apparent sulphur partition ratio 4.2 increased rapidly to a higher value after passing through the incubation period, indicating that the top slag possesses very strong desulphurization capability. Based on the experimental observations, the presence of a large amount of the unreacted calcium carbide mixed with the metal droplets at the top slag implies that there was excess calcium carbide available for the desulphurization. The rate of slag/metal desulphurization can be described as:

^Ns =- kmA[%S]

(4.10)

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It can be seen from this equation that high reaction rates are expected with large interfacial area and high sulphur mass transfer coefficient. The large slag/metal interfacial area (in the range 3 to 5 m2/(kg of slag)) can explain the high desulphurization rate during injection and postbubbling period with the dry slag.

Similar incubation phenomena are also observed in both hot metal desulphurization and steel desulphurization in full scale plant operation. Figure 4.22 shows the typical hot metal desulphurization curve of calcium carbide injection at Stelco's Lake Erie Works. An incubation period of slow desulphurization occurred during the injection. Approximately 40 to 50 percent of the torpedo cars desulphurized were reported to exhibit this phenomenon[170]. Bruder and Haastert et a![172] used the T.N. process to desulphurize steel with various desulphurizers such as calcium silicide, calcium carbide or magnesium. They also found that no sulphur removal was observed with no top slag on the steel melt. They explained this phenomenon as a result of the oxidation of the sulphur-bearing reaction product by atmospheric oxygen at the surface of the steel melt. This caused constant resulphurization during injection treatment. Consequently,





a synthetic top slag is usually used for steel desulphurization or sulphide shape control.

4.2.2.2 The effect of liquid slag and modified dry slag

As can be seen from Figure 4.18, no incubation period was observed at the initial stage of injection for both the initial liquid slag and modified dry slag conditions. The sulphide capacity of the initial liquid slag can be calculated by the empirical expression proposed by Haughton et al[171].

 $Log(C_{s}) = -5.704+3.15 XFeO$

+ 2.65 X_{CaO} + 0.12 X_{MgO} + 0.77 X_{T1O2} + 0.75(X_{Na2O} + X K2O) (4.11) 126

where X is the mole fraction of the constituent oxides. The above empirical expression is based on the measurement of the solubility of sulphur in blast-type aluminosilicate melts. Because the composition ranges are similar to those in the liquid slag used in the present work, it was decided to use this equation to calculate the sulphide capacity of the initial liquid slag. For an average oxygen activity of 2.7 ppm, the correspoding sulphur equilibrium partition ratio is calculated to be 5. This theoretical equilibrium sulphur partition ratio is in good agreement with the apparent sulphur partition ratio shown in Figure 4.3. Since the melt was covered by 10 kg of liquid sing, in terms of thermodynamics, the sing can hold 1.6 moles of CaS from plume reaction with 0.05 wt% sulphur in hot metal. The reaction product of CaS from plume desulphurization is produced at the rate of 0.26 mole/s based on the injection conditions of 6 Kg/min CaC2 with 10% efficiency. Therefore, at the initial stage of injection, the reaction product CaS is absorbed by this liquid sing to prevent sulphur reversal.

For the condition of modified dry slag, even higher sulphur partition ratio can be obtained due to the lower oxygen activity in the melt and the formation of molten calcium aluminosilicate with high sulphide capacity. The equilibrium sulphur partition ratio is calculated to be 2000. (The oxygen activity effects are more fully discussed in Section 4.4). Again the sulphur reversal was prevented initially by both the higher slag volume and equilibrium sulphur partition ratio. Similarly the effect of slag flux agent on the hot metal desulphurization can be explained by the formation of liquid slag with sufficiently high slag volume to dissolve calcium sulphide.

4.2.2.3 The effect of slag volume and gas flow rate on slag/metal desulphurization

The refining rates of CaC2-saturated top slags during or after injection were found to be dependent on their volume/weight and the injection gas flow rate. The rate of desulphurization was correlated with the gas flow rate and the slag weight. The regression equations are given in Eqns.(4.4) and (4.5) for initial dry slag and liquid slag conditions, respectively. The statistical analysis shows that the desulphurization rate obtained from these two different type of slags have a similar standard error at 0.05 significant level. The t test statistics indicate that the mean value of the dry slag desulphurization rate has a significantly higher value than that of liquid slag. This is due to the different types of reaction mechanisms involved in those two slag/metal reactions. For the initial dry slag condition, the slag compositions were developed during injection. The accumulation of unreacted calcium carbide turns the slag into "dry and reducing" condition, in which the CaC2-saturated dry slag behaves as a solid desulphurizer. Therefore, good desulphurization is expected. In contrast, for liquid slag initial conditions, due to the presence of large amounts of liquid slag, the slag will develop into the "semi-dry" condition. The liquid portion of the slag could provide a path for the sulphur to reverse as

the slag becomes saturated with sulphide. Therefore, a relatively lower desulphurization rate was observed. Although an incubation period was observed for dry slag, the strong desulphurization rate after the incubation period compensated for this slow desulphurization and made the overall desulphurization similar to the liquid slag condition.

As stated in the previous section, the rate constant of desulphurization is defined as (K_mA/V) If we fix the value of hot metal volume as a constant, the rate constant is directly proportional to mass transfer coefficient k_m and slag/metal reaction interface. It is very difficult to separate the mass transfer coefficient km from the reaction interface A. However, the mass transfer coefficient can be predicted by using Eqn(2.42). This equation shows that the mass transfer coefficient is proportional to $Q_{0.5}$ which means that higher gas flow rates will enhance the desulphurization rate. According to the previous work of Asai et al[136], the slag/metal reaction rates are enhanced by the increase of the gas flow rate. Figure 4.23 shows the comparison of the present results with the previous work in terms of the exponent, n, in the relation of $K_m ext{ aQn}$, against gas flow rate per unit mass of liquid, Q. The exponent of the gas flow rate varied from 0.2 to 2.1. It can be seen that the present results are



consistent with most of the previous works. Asai et al also pointed out that the slag/metal reaction nate does not strongly depend on the mass transfer coefficient but mainly rely on the increase of the reaction interface. In their study of the mass transfer rate of benzoic acid between tetraline (slag phase) and water (metal phase), they found that the mass transfer rate is proportional to the gas flow rate. They found that there is a critical gas flow rate above which the abrupt change of the exponent on Q is observed. They attributes this to an entrapment of water droplets into the tetraline due to the turbulent condition. In their system, the critical gas flow rate is approximately 110 (N1/t/min). However, in the present work, a considerable number of metal droplet's were found in the slag even when the gas flow rate were very low (20 NL/t/min). Therefore, it is apparent that the critical gas flow rate varies from system to system, and probably depends on the injection conditions, type of slag, and furnace size and geometry.

The strong dependency of the slag/metal desulphurization rate on slag volume/weight (the exponents in Eqn(4.4) and Eqn(4.5) are 3.25 and 3.19 for the dry and liquid slag conditions, respectively) can also be attributed to the metal droplet formation. If there were a constant number, distribution and residence time of the metal droplets in the slag, the exponent would be one. Therefore these quantitles apparently change as the slag volume increases. This is an interesting area for further study.

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In summary, the effect of slag on the rate of desulphurization can be outlined as follows:

(1) The type of slag is important.

The liquid slag is good only under the conditions of high basicity and low oxygen activity in hot metal. The liquid slag with relatively low sulphur capacity will cause serious resulphurization when it reaches the refining limit. However, the liquid slag can initially prevent the sulphur reversal if the sufficiently high liquid slag volume are presented. The CaC_2 -saturated dry slag behaves as solid desulphurizers, therefore relatively high desulphurization rates are observed.

(2) The gas flow rate is important.

The higher gas flow rate is favorable for the improvement in desulphurization rates.

(3) The slag weight/volume is important. The higher slag volume is favorable for the rate of desulphurization due to the large amount of slag/metal interface.

.3 Effect of injection condition

4.3.1 Results

As was mentioned in the previous section, the loading has a significant impact on the efficiency of desulphurization, fraction of sulphur removed and desulphurization rate. The loading parameter used in the this study, L, is the solid feed rate (kg/min) divided by the carrier gas flow rate at normal conditions (Nm³/min). Thus L is the solid to gas ratio in kg/Nm³.

One can see that in Figures 4.10 to 4.13 for efficiency, Figures 4.14 to 4.17 for fraction of sulphur removed and Figures 4.18 to 4.21 for desulphurization rate that lower loading improves the results regardless of the top slag condition. Therefore for comparable solid addition amounts and rates, more carrier gas has a beneficial effect.

The sulphur removal rate due to plume desulphurization was obtained by subtracting the sulphur change due to the slag/metal reaction from the total sulphur change. The typical semi-logarithmic plots of sulphur change versus time are shown in Figure 4.24. The linear slope of the desulphurization curve in this figure indicates that the plume calcium carbide desulphurization is close to first order kinetics with respect to sulphur. The desulphurization rate constant calculated from the semilogarithmic plots for





all injection tests are listed in Table 4.8. As should be the case, the rate of plume desulphurization shows no trend with slag conditions.

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/ The dimensions of the plume were determined experimentally from the visual observation of the 'breakthrough zone'. Photographs of break through zone were taken by a camera. Figure 4.25 shows a photograph of the hot metal surface during injection. The uncovered area shown in the photograph is the so called 'break through zone'. The diameter of 'break through zone' was measured from the pictures taken under various injection gas flow rates. A plot of plume diameter versus gas flow rate is shown in Figure 4.26. It is found that the plume diameter is proportional to the injection flow rate in the present experiments.

4.3.2 Discussion

The positive effect of the low loading injection on the rate and efficiency of CaC2 desulphurization can be explained by the following:

- The creation of large slag/metal reaction interface by the high gas flow rate.
- (2) The improvement of plume reaction kinetics is mainly due to the intensive mixing and the

lable 4.8

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Run Ga	asflowrate (Nm ³ /min)	CaC ₂ injection D rate (Kg/min)	lesulphurization rate (1/s)
H10R2	0.050	5.15	2.92 X 10-4
HIOR3	0.057	9.24	1.30 X 10 ⁻³
H10R4	0.050	3.67	1.12 X 10 ⁻³
HI3R2	0.050	3.76	7.25 X 10 ⁻⁴
HI 1R2	0.049	5.80	1.52 X 10-3
H11R4	0.051	1.56	9.28 X 10 ⁻⁴
H11R5	0.049	2.55	5.23 X 10-3
HIORI ·	0.082	4.80	1.61 X 10 ⁻³
HIIRI	0.078	5.54	1.09 X 10-3
H15R4	0.080	9.72	2.20×10^{-3}
H7R2	0.118	5.00	2.99 X 10-3
H9R2	0.126	7.10	2.40 X 10^{-3}
H12R1	0.120	4.31	
H8R1	0.125	2.35	9.35 X 10^{-4}
H12R2	0.120	4.44	1.62 X 10-3
HGR2	0.155	5.71	2.67×10^{-3}
HERI	0.155	10.02	1.98 X 10-3
HGR3	0.168	7.32	2.23×10^{-3}
H9R1	0.162	10.00	1.89 X 10-3

•		-		
H15R1	.0.161	3.50		1.15 × 10 ⁻³
H7R4	0.168	3.80		3.96 X 10-3
H8R3	0.167	9.12		2.50 X 10 ⁻³
- H9 6 3	0.165	6.25		5.88 X 10-3
H14R4	0.155	9.30	-	3.47 X 10 ⁻³
H12R3	0.162	5.70	•	3.20 X 10-3
H14R2	0.162	6.94		3.07 X 10 ⁻³
H16R3	0.162	6.50	•	1.88 X +0-3
H15R3	0.169	7.42		1.61 X 10 ⁻³
H13R1	0.220	3.56		2.41 X 10-3
H7R1	0.240	6.38	•	2.89 X 10 ⁻³
H8R4	0.227	8.10		5.38 X 10-3
H9R4	0.218	5.50		4.38 X 10 ⁻³
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Figure 4.25: Photograph showing plume during CaC₂ injection.

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larger reaction interface provided by gas bubbles for CaC2 to reside and react with sulphur.

The details regarding plume desulphurization kinetics will be discussed in Chapter 5.

1.4 Effect of oxygen

4.4.1 Results

As Table 4.1 indicates, oxygen probe readings were taken before and after most of the injection tests. For the injection tests with no aluminium addition, the EMF values show a slight downward trend which is probably due to the temperature drop after the injection (Figure 4.27).

For the injection tests (H14 and H15, Figures 4.28 and 4.29) in which aluminum additions was used, one can see that the aluminium plunging lowers the EMF to between -150 and -200 mv. Immediately after the CaC₂ injection, it rose to between -100 and -150 mv. The next aluminum addition, in preparation for the next injection, depresses the EMF value again. Clearly, the aluminium lowers the dissolved oxygen content in the hot metal.

The calibration equation suggested by the probe manufacturer to determine the dissolved oxygen is:



.27: EMF readings from the oxygen probe before and after reagent injection for the cases in which no aluminium was used.



Figure 4.28:

EMF readings from the oxygen probe during heat HI4. Note that the 'aluminium depresses the oxygen, while the holding periods and injection of carbide raises it.



Figure 4.29:

EMF readings from the oxygen probe during heat H15. Note that the aluminium depresses the oxygen, while the holding periods and injection of carbide raises it. $\frac{\text{Log}(a_0)}{+0.0021(T - 1550)} = 1.36 + 0.0059(E+0.54(T - 1550))$ (4. 12)

Thus -50 and -200 mv correspond to 2.7 ppm and 0.35 ppm oxygen activity respectively in the hot metal at 1350 oc. The former value is quite close to silica saturation with silicon in the hot metal, which is expected to control oxygen in the carbon-rich (unsaturated) hot metal at such low temperatures. The equilibrium oxygen activity can be calculated according to the reaction.

$\underline{Si} + 2 \underline{Q} = SiO_2(s)$ (4.13)

where the free energy change of reaction (4.13) ΔoG is

 $\Delta G_0 = -594128.0 + 230.1T (J) \qquad (4.14)$

The activity coefficient of oxygen and silicon in iron alloys may be estimated by

 $Log f_{\underline{O}} = \Sigma eo[\% j]$

(4.15)

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 $Log f = \sum_{si=1}^{j} e_{si} [\%j]$ (4.16)

where [%j] are the concentration of the alloying elements and e_0^j , e_{si}^j are the interaction coefficients for the effect of element j on oxygen and silicon, respectively. It is important to note that Eqn(4.15) and (4.16) are approximations, reasonable only for low concentrations of alloying elements. The equilibrium constant K_{eq} for reaction (4.13) is given by

∆Go = -R T Ln K_{eq}

i.e

 $q = a_{sio2}/(a_{sia_0}) = e(-\Delta Go /RT)$

(4.18)

(4.17)

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where the activity of silica is relative to the pure solid state. For the Si and O dissolved in hot metal, the activity is referenced to infinite dilution with 1 weight percent as standard state. Introducing Eqns (4.15) and (4.16) into equation (4.18), and assuming that the activity of SiO2 is unity.

 $Log(a_{0}) = -15600/T + 6.02 - 0.5 Log(f_{5i})$ -0.5 Log(Wt% Si) (4.19) Figures 4.30 and 4.31 show the comparison of oxygen activities calculated from Eqn (4.19) and the measured oxygen activities from the oxygen probe. The equilibrium oxygen activities based on the C-O equilibrium, on the assumption that P_{co} is one atmosphere, in hot metal at 1350 oC are also shown in the lower curves of Figures 4.30 and 4.31. Very good agreement is obtained between the oxygen activity calculated from Si-O equilibrium and the measured oxygen activity by oxygen probe. This indicated that the oxygen activity is close to the Si-O equilibrium, rather than to that of C-O equilibrium.

4.4.2 Discussion

Aluminium is the strongest deoxidizer commonly used in steelmaking. Recently there have been many trials carried out to deoxidize the hot metal for the purpose of improving the desulphurization rate and reagent efficiency. The standard free energy change for deoxidation of hot metal with aluminum addition is represented by the reaction:

$2 \underline{A1} + 3\underline{0} = A1_{203(s)}$

(4.20)

$\Delta G \circ = -1219050 + 394 T (J)$

(4.21)



Figure 4.30:

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Measured molten iron oxygen levels compared to values predicted by sillicon-oxygen and carbon-oxygen equilibria (before injection).



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where the oxide activity is relative to the pure solid state as sfandard state; the activities of Al and O dissolved in bot metal are relative to I Wt% as standard state.

In the present study, the oxygen activity after such large additions of aluminium should be below 10-3 ppm. However, in such an open system oxygen is available from many sources, i.e inclusions in hot metal, air in the atmosphere, reducible oxides in the slag, and furnace lining. Therefore instantaneous oxygen reading is just the balance point between the rate at which oxygen is entering the metal and the rate at which it is being consumed by the dissolved aluminium. This is consistent with the fact that 'the oxygen readings drifted upward during or after the injection.

The role of oxygen must be carefully considered for both the plume and top slag reactions.

4.4.2.1 Plume reactions

Oxygen can also compete for calcium carbide according to:

$CaC_{2(s)} + Q = CaO(s) + 2C(s)$ (4.22)

and in fact this reaction is more favored than the desired

desulphurization reaction at normal hot metal temperatures. The calcium carbide desulphurization in general can be described as follow:

$CaC_{2(s)} + S = CaS(s) + 2C(s)$ (4.23)

The free energy changes of these two reactions are plotted as a function of oxygen activity for Eqn (4.22) and sulphur activity for Eqn (4.23). One can see (Figure 4.32) that at equal oxygen and sulphur activity, the deoxidation is more favored. Therefore for desulphurization to occur, there must be a much higher sulphur activity. The lowest achievable hot metal sulphur content can be predicted from the competition between oxygen and sulphur for calcium carbide, and is governed by calcium oxide/calcium sulphide equilibrium.

CaS + <u>0</u> = CaO + <u>S</u>

(4.24)

The theoretical minimum sulphur to oxygen activity ratio (one weight percent Henrian scale) for desulphurization to proceed is plotted as a function of temperature in Figure 4.33. The pilot plant experiments were conducted at 1350 oC, at which this ratio is 90. This ratio becomes



Figure 4.32:

Free energy of reaction of calcium carbide with oxygen and sulphur as a function of Henrian activities of oxygen and sulphur.



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smaller at higher temperature as Figure 4.33 indicates.

Using the measured oxygen activities of 2.7 and 0.35 ppm, one would predict on a thermodynamic basis that the lowest sulphur levels attainable would be 0.009 and 0.001 wt%, respectively (assuming that the sulphur activity coefficient is 2.7). This agrees well with the plant results from Stelco's Lake Erie Works[170]. However for some injection tests without deoxidization, sulphur levels below these values were obtained. This could be attributed to the desulphurization through the slag-metal reaction.As might be expected in the late period of carbide injection, the oxygen potential is reduced to a very low level in the slag. The estimated value of oxygen activity is approximately 1 ppm (calculated based on the silicon activity in the metal droplets) which is a factor of two lower than that of the metal bulk. Therefore further desulphurization is possible : by the slag/metal reaction.

For the injection runs of HIR1, HIR2, and H2R3, the salt coated magnesium was simultaneously injected from a separate dispenser for the purpose of stirring and deoxidation. The results show that very low sulphur levels were easily obtained (< 0.010 wt%). For the injection runs with aluminium additions (modified dry slag with aluminium additions), the results of all the final sulphur were at very low levels. This again indicate the importance of

deoxidation for the low sulphur desulphurization.

4.4.2.2 Top slag reactions

The dry top slag possessed negligible desulphurization capacity. However as the injection progressed there was an increasing amount of calcium carbide in the top slag. This unreacted calcium carbide can continue to react with sulphur at the slag/metal interface and with sulphur in iron droplets entrained into the slag.

The liquid slags or dry slags modified by aluminium which become liquid can be analysed by conventional slag/metal thermodynamics as discussed in Chapter 2.

The oxygen potential Po₂ is, in theory, governed by the predominant redox equilibrium. For initial slag conditions of dry and liquid slag, the oxygen potential at the slag/metal interface can be calculated by the reaction:

 $Si + 20 = (Si0_2)^{-1}$

For the modified dry slag with aluminium additions, the oxygen potential is governed by the reaction:

2 A1 + 3 Q = (A1203)

» (4.26)

(4.25)

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The silicon and carbon contents in the metal droplets obtained from the slags were found to be higher than those in the hot metal. This indicates that a strongly reducing condition was formed during the carbide injection. From a thermodynamic point of view, the starting temperature for the silica reduction is 1200°C, based on the assumption that activities of both the silica and carbon in the slag are unity and that the silicon content is 1.2 wt%. Therefore for the present experimental temperature of 1350 °C, it is reasonable to expect an increase in the silicon content in the metal droplets. The calculated slag/metal interfacial oxygen activity, based on the assumption that the activity of SiO2 in the slag was approximated by its molar fraction, was found to be a factor of two to three lower than that in the bulk metal. This suggests that a relatively higher equilibrium partition ratio can be achieved in the droplet stage of carbide injection. Figure 4.34 shows the dependence of the sulphur. partition ratio for the liquid slag in the present study at 1350 °C calculated according to Eqn(2.16). One can see that the equilibrium sulphur partition ratio, at normal hot metal oxygen activity of 2.7 ppm, is 5. This is very low compared to that of modified dry slag. However, the partition ratio increases to moving from 2.7 ppm oxygen activity to 0.35 ppm. Therefore the deoxidation of hot metal can improve the desulphurization capability of slag.



The lime and aluminum are two essential ingredients for effective deoxidation and desulphurization of liquid hot metal because of the formation of calcium aluminate or calcium aluminosilicate as the reaction product. The extent of deoxidation and desulphurization is determined by temperature, slag composition, and concentration of residual aluminum in liquid hot metal.

The oxygen potential at the slag/metal interface can be calculated by Eqn (4.26). Since the reliable values for Al₂O₃ activity in CaO-Al₂O₃-SiO₂ slags at hot metal temperature of 1350-1400 °C are not yet available, the activity of Al₂O₃ could be assumed to be the same value of its molar fraction. For instance, if the liquid metal contains 0.2% Al in equilibrium with alumina in the slag, the calculated equilibrium oxygen activity would be 10^{-2} ppm which corresponds to an equilibrium sulphur partition ratio of 2000. To compare this with the liquid slag (without aluminium addition), the sulphur partition ratio is calculated to be 400 time higher than that of the liquid slag (without aluminium addition).

In summary, the reduction of oxygen activity is benefical for both the plume reaction and the slag/metal reaction, so that both are desulphurizing effectively together. The use of aluminium addition or magnesium coinjection deoxidize hot metal may be an effective way to

ultimately solve the extra-low sulphur problem in this study.

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CHAPTER 5

Kinetic Model for Calcium Carbide

5.1 Introduction

In order to analyze the present experimental data quantitatively, a kinetic model has been developed to describe the calcium carbide desulphurization. This model extends the model of Farias and Irons[154] for momentum and heat transfer in the plume to include mass transfer and chemical reaction. The present model calculates the volume fractions, velocities, temperatures and compositions of the gas, liquid, and solid phases in the rising plume during calcium carbide injection.

Desulphurization of the hot metal occurs in the ascending plume and at the top slag/metal interface. A number of previous investigations[173]-[175] have been carried out to clarify the importance of both the top slag/metal desulphurization (permanent contact reaction) and the plume desulphurization (transitory reaction) during the powder injection. Figure 5.1 shows the schematic representation of the plume and top slag/metal reactions. The overall rate equation can be generally expressed as follows:



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Figure 5.2 schematically shows the physical and chemical phenomena of calcium carbide desulphurization in the rising plume. A jet of calcium carbide and argon issues from the lance tip and penetrates until its momentum is dissipated. At the bottom of the jet, a plume forms comprising gas, particles, and liquid which rise to the bath surface. The contact of calcium carbide particles with liquid hot metal is a complicated hydrodynamic phenomenon. Calcium carbide particles could be in the melt, on the bubble surface, or in the bubbles. The calcium carbide particles which come into contact with liquid metal are heated rapidly to reach the plume temperature. At this temperature, calcium carbide is partially thermally dissociated to form calcium vapor. The calcium vapor diffuses through the reaction product layer to react with sulphur at the surface of particles. Meanwhile the carrier gas controls the rate of liquid recirculation in the ladle to pump fresh sulphur-rich liquid metal into plume where reaction occurs. Once the particles reach the bath surface they are incorporatd in the top slag and continue desulphurization through slag-metal reactions.

Ratept + Rates/m

(5.1)

The proposed calcium carbide desulphurization kinetic model consists of two parts, viz,



Figure 5.2:

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Schematic representation of the physical and chemical phenomena of calcium carbide desulphurization in a rising plume.

(a) Desulphurization of a single calcium carbide particle.

A model has been developed to describe a single calcium carbide particle desulphurization phenomena. This model is based on the reaction mechanism proposed by Talballa et al.[176].

(b) Nodel for overall sulphur balance in the plume.

A differential equation based on the sulphur balance over a control volume unit in the plume is developed to simulate the overall rate phenomena of calcium carbide desulphurization during injection. This model extends the abovementioned model of Farias and Irons to - calculate fluid flow, heat, and mass transfer rate.

5.2 The plume model for fluid flow and heat transfer

A non-isothermal, steady-state, one dimensional three phase plume model has been developed by Farias and Irons. The predictions of liquid velocity were found to be in reasonable agreement with the previous experimental data[152],[177],[178]. Therefore, it is decided to adopt this plume model to plume desulphurization kinetics.

5.2.1 Equations for plume momentum conservation

In their plume model, separate momentum equations have been written for the three phases, in which the velocity of solid, gas and liquid can be calculated.

5.2.1.1 Model assumptions

- (a) Plume geometry is known from experiment.
- (b) Liquid entrainment into the plume is governed by drag forces only.

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- (c) A "top hat" profile has been assumed for the velocity and momentum flow rate of the phases in the plume.
- (d) Viscous forces have been ignored.
- (e) Gas and powder concentrations are low so as to ignore bubble-bubble and particle-particle interactions.
- (f) The ladle is sufficiently large that the pressure gradient outside the plume is given by the head of liquid.

5.2.1.2 Mathematical formulation

The bubbles are assumed to be composed of a mixture of gas and a fraction of the particles so that the

mixture density can be written as

^рm= Өдрд + f Өррр

where f is the fraction of the particles residing with the gas. Therefore, the conservation of mass in the bubbles can be expressed as

$$\frac{d(\rho_{mUgApt})}{d Z} = 0$$

where A_{pt} is the plume cross-sectional area. Similarly for the powder in the liquid.

$$\frac{d(1-f)\theta_{p}\rho_{p}U_{p}A_{pt}}{dz} = 0$$
 (5.4)

It should be noted that liquid mass is not conserved because liquid is entrained into the plume by the drag from the bubbles and particles.

The momentum of bubble and particle phases is increased by the buoyancy forces, while the drag forces from the liquid phase will resist this acceleration:

 $\frac{\frac{1}{2}mU_{g}^{2}Pt}{dZ} = Fb - Fd$

o

(5.5)

(5, 2)

(5.3).



While the liquid experiences the reactive component of the drag forces:

$$\frac{d\theta_{lpl}U_{l}^{2}A_{pl}}{d Z} = Fd + Fd \qquad (5.7)$$

The buoyancy forces for the gas and powder in the bubbles and the powder in the liquid, respectively are:

$$Fb = [\rho_{\pounds}(\theta_{g} + f\theta_{p}) - \rho_{m}]gAp_{\pounds} \qquad (5.8)$$

 $F_{p}^{b} = (1 - f)(\rho_{t} - \rho_{p})\theta_{p}g_{Apt}$

(5.9)

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The interphase drag functions were developed as the product of the drag force on one particle or bubble and the number of particles or bubbles per unit volume of plume. For the bubbles rising in the liquid, the interphase drag functions are given as



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For the particles rising in the liquid

$$F_{p-1}^{d} = \frac{0.75_{\rho_{1}}C_{dp}(U_{p} - U_{1})^{2}(1 - f)\theta_{p}A_{p1}}{d_{p}}$$
(5.11)

The gas density is a function of temperature and pressure.

$$\frac{P_{\text{atm}} + \rho_{\text{f}} g (H - Z)}{R T_{g}}$$

5.2.2 Equations for energy conservation

5.2.2.1 Model assumptions

(a) The assumptions of the isothermal model are still valid.

(5\12)

- (b) There is no exchange of mechanical and thermal energy, thus only thermal energy balances need be considered.
- (c) The specific heat capacity of all phases do not

vary significantly with pressure or temperature.

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- (d) The heat of watting the solids is negligible.
- (e) The particles are sufficiently small so that internal temperature gradients can be ignored.
- (f) Conduction of heat radially and axially is negligible in comparison to that of convective transport.
- (g) The important heat transfer mechanisms are:
 - (i) Radiation from liquid to particles uniformly dispersed inside the bubble (G_1) .
 - (ii) Convection from liquid to particles in the liquid (G2).
 - (iii) Convection from liquid to the bubbles(G_3).
 - (iv) Convection from gas to particles inside
 - the bubbles (G₄). The particles are assumed to be dispersed inside the bubble.
- (h) The cooling effect of the lance is ignored.
- (i) The entrained liquid is at the bulk bath temperature.

5.2.2.2 Mathematical formulation

The heat flow rate balance per unit volume of

plume is written for each phase:

 $\theta_{\text{tPtUtCpt}} dT_{\text{t}} / dZ = -G_1 (T_{\text{t}}^4 - T_{\text{pg}}^4)$

 $-G_2(T_t - T_{pt})$

- G₃ (T₂ - T₃)

+ PECpE(The - TE) detue / dZ

(5.13)

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Particles in the liquid

 $(1 - f)\theta_{p}\rho_{p}U_{g}C_{pp} dT_{pt}/dZ = G_{2}(T_{t} - T_{pt})$

Particles in the gas

(5.14)

 $f_{\theta_{p}\rho_p}U_gC_{pp}$ d T_{pg} / dZ = G₁ ($T_{t}^4 - T_{gp}^4$)

+ G4 (Tg - T_{gp})

(5.15)

Gas phase

$$\theta_{g\rho}gU_{g}C_{\rho g} d T_{g} / dZ = G_3 (T_{f} - T_{g})$$

- G4 (T_{g} - T_{gp})

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(5.16)

(5.18)

For the radiation mechanism the particles were assumed to behave as gray bodies with a radiaton shape of one, thus

$$G_{I} = \frac{6 f \theta_{p \sigma}}{dp}$$

$$G_{I} = \frac{6 f \theta_{p \sigma}}{f \theta_{p}} d_{b} / ((\theta_{g} + f \theta_{p}) d_{p} \varepsilon_{t}) + 1 / \varepsilon_{p} - 1$$

$$(5.17)$$

For convection to the particles in the liquid

$$G_2 = \frac{G_p}{d_p} \left(1 - f \right) \theta_p$$

where the heat transfer coefficient h_p was obtained from the Ranz-Marshall correlation for spheres.

$$Nu = 2 + 0.6 \frac{\text{Re}1/2}{\text{P}} \frac{\text{Pr}1/3}{2}$$
(5.19)

*



^{6 h}gpf^θp G₄ ⊒ _____

(5.23)

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Where

h_{gp =} Nu K_g dp

(5.24)





The drag coefficient on the particles follows Stokes law,

thus

^ρpgd² ^Ur= _____p 18μg

(5.27)

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5.3 Nodel for single calcium carbide desulphurization

5.3.1 Model Assumptions

In order to develop a model for a single calcium carbide particle desulphurization, the following assumptions are made:

- (a) The resistance due to chemical reaction rate is negligible. (Desulphurization and calcium carbide decomposition reach equilibrium.)
- (b) The effective diffusivity and total concentration of calcium vapor are constant at the temperature of interest.
- (c) Quasi-steady state prevails within the product layer of calcium carbide particle.

(d) The calcium carbide particles are assumed to be spherical in shape. Their initial chemical composition of calcium carbide, is constant throughout their volume and the excess C and CaO do not participate in the reaction.

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- (e) While the desulphurization is taking place, the reaction product layer of the calcium sulphide is assumed to be evenly formed around the carbide particle. The outer diameter of calcium carbide particle (is increasing due to the formation of calcium sulphide.
- (f) Due to the low solubility of calcium in the carbon-rich hot metal and the fast reaction rate of calcium vapor with sulphur, the reaction site is assumed to be at the carbide/hot metal interface.

(g) The densities of pure, dense CaC₂, CaS and C are used for calculation, although diffusion likely occurs through micropores.

5.3.2 Mathematical formulation

When calcium carbide is injected into the carbonrich hot metal, it partially decompose to form calcium vapor and grapite. The calcium vapor diffuses through the reaction product layer of calcium sulphide and residual graphite, and reacts with sulphur transported from the hot metal. It forms calcium sulphide at the surface of calcium carbide particle adjacent to liquid hot metal.

The overall plume calcium carbide desulphurization is postulated to involve the following individual steps as sketched in Figures 5.2 and 5.3.

- (a) Mass transfer of sulphur through the boundary layer to the calcium carbide particle surface.
- (b) Thermal decomposition of calcium carbide.
- (c) Diffusion of calcium vapor through the micropores of the reaction product layer to the outer surface of calcium carbide.
- (d) Chemical reaction of calcium with sulphur takes place at the interface of the calcium carbide particle and liquid hot metal.

For high temperature metallurgical reactions, the chemical reaction rate is generally very fast. Therefore the rate of steps (b) and (d) are fast enough to be ignored. At steady state, the above-mentioned mass transfer and diffusion steps must occur at the same rate. Thus, in terms of sulphur and calcium vapor, the following two rate equations are equal:



Figure 5.3:

Schematic representation of the concentration profile of calcium vapor and sulphur along a sectioned spherical CaC₂ particle.



boundary layer.

(b) Diffusion of calcium vapor through the reaction product layer.

(a) Mass transfer of sulphur through solid/liquid



At steady state, the equilibrium concentrations of calcium vapor and sulphur at the calcium carbide particle surface can be calculated according to the equations:

$$N_{s} = N_{C_{z}}$$

and

(5.31) (5

(5.30)

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Keq = PCa hs

(5.32)

where the standard states are pure calcium sulphide (CaS), pure calcium vapor at 1 atm, and one weight percent for sulphur in the carbon-rich liquid hot metal.

x .

For mathematical simplicity, we consider that the sulphur at the liquid surface diffuses inwards through the reaction product layer and reacts with calcium vapor at the interface of the unreacted core, rather than to use the more likely mechanism of calcium vapor diffusion through the reaction product layer. The flux of calcium was converted mathematically to a numerically equal flux of sulphur vapor so that consecutive steps of sulphur transport could be used for convenience.

For the equivalent sulphur diffusion, the transfer of sulphur from the liquid hot metal to the interface of the unreacted core of calcium carbide takes the form of the concentration profile shown in Figure 5.3. The hypothetical concentration of sulphur vapor at the calcium carbide/hot metal surface is assumed to be in equilibrium with the surface concentration of sulphur in the hot metal. Thus the equilibrium constant or partition ratio $\eta = C_{s(g)}^{i}/C_{s}^{i}$ can be calculated by the reaction (5.33).

 $\underline{S} = S_{(g)}$

(5.33)

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 $\Delta G^{O} = +293697.1 - 84.24 T (J) (5.34)$

Rearranging Eqn(5.28) and (5.29) gives



• • • •

The term ($C^{b} - Ceq_{s(g),CaC2} / \eta$) represents the driving force in term of sulphur concentration. $Ceq_{s(g),CaC2}$ is the sulphur concentration in the liquid hot metal which is hypothetically in equilibrium with the pure calcium carbide. The left handside of Egn(5.38) represents the sum of the transport resistances: The first terms corresponds to mass transfer through boundary layer and the second term corresponds to diffusion through the reaction product layer. These transport resistance term are conveniently expressed as follows:

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 $R2 = \frac{4\pi n_p r_1 r_0 n_p}{4\pi n_p r_1 r_0 n_p}$

Thus, the overall rate constant of the reaction is expressed as follows:

R1 + R2

(5.41)

(5.40)

The equivalent effective diffusivity of sulphur

vapor through the micropores of the reaction product layer

can be obtained by equating the vapor diffusion flux of calcium to that of sulphur vapor.

$$JCa(g) = \frac{D_{eff,Ca(g)}}{\Delta r} \left(\frac{Peq}{Ca,CaC2} - \frac{Peq}{Ca,i} \right)$$

$$R T$$
(5.42)

Fixing $JCa(g) = J_{S}(g)$, the equivalent effective sulphur -diffusivity can be obtained as follows:

(5.44)

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5.4 Equation for plume sulphur conservation

5.4.1 Model assumptions

The model for the overall sulphur balance in the plume developed for the present study is mainly based on the following assumptions: (a) The plume is cylindrical in shape; the size of plume is measured experimentally.
(b) The diffusion flux due to the gradient of sulphur in plume is negligible.

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- (c) The calcium carbide desulphurization is confined to the plume for the transitory reaction.
- (d) It is assumed that the calcium carbide particles are evenly spread and well mixed at the surface of the bubbles.
- (e) The size of bubble is taken to be 25 mm in equivalent diameter and constant during rise.
- (f) The calcium carbide particles after travelling through the plume are absorbed by the top slag.

5.4.2 Mathematical formulation

After injection from the lance tip, the gas and calcium carbide particles penetrate together as a jet until its momentum is dissipated. At the bottom of the jet, a plume forms comprising gas, particles, and liquid, which rises to the bath surface. During the rise of the particles, the calcium carbide continuously reacts with sulphur. Once the particles reach the bath surface they are incorporated in the top slag. The rate of desulphurization in plume can be described by formulating the conservation equation of sulphur over the control volume unit. At steady state, the sulphur balance over the control volume unit in plume, as shown in Figure 5.4, is as follows:



The terms of the above sulphur balance can be written in a differential form.

$$\frac{d\theta_{t}C_{s}^{ptA_{ptU_{t}}} + C^{b}V_{m} - N^{Rx,s=1}}{dz s}$$

(5.46)

The first term on the left-hand side is the convective flux of sulphur into the plume for a control volume of thickness ΔZ with plume cross sectional area A_{pl} . The second term on the left-hand side is the amount of sulphur entrained into the plume from the bulk of hot metal. Both the convective and entrained flux of sulphur are principally controlled by the the carrier gas flow rate. The rate of hot metal entrainment can be obtained by the hot metal mass balance.







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At steady state, the rate of change of hot metal mass is equal to the sum of the rate of the hot metal convection and entrainment.

$$\frac{d \theta_{LPL} A_{PL} U_{L}}{d Z} + \rho_{L} V_{m} = 0 \qquad (5.48)$$

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Thus the liquid entrainment rate V_{m} is

$$V_{\rm m} = \frac{-1 \, d\theta_{\rm gp} A_{\rm pg} U_{\rm g}}{\rho_{\rm g} \, d \, Z}$$
(5.49)

The third term on the left-hand side of Eqn(5.46) is the desulphurization term which has a negative value as the reaction represents conversion of sulphur to calcium sulphide. The desulphurization term contains the overall mass transfer cofficient, $K_{OV,b}$ which accounts for the two mass transfer steps:

(1) The mass transfer of sulphur through the boundary layer to the surface of particle.

(2) The diffusion of calcium vapor through the
reaction product layer to the reaction interface.

The desulphurization term can be expressed

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$$NRx,b = (1 - f)A_{pt}Ub\theta p \frac{s}{dz}$$

(5.50)

Where

$$\frac{d Cpow,b}{S} = -\frac{K_{ov,b}}{R_{ov,b}} (Cp! - Ceq) \\ d Z = R_{p}V_{pUb} (Cp! - Ceq) \\ eq, CaC2 (n_{p})$$

(5.51) Putting Eqn(5.49) and (5.50) into Eqn(5.46) gives

$$\frac{\theta_{\ell}C_{S}^{p\ell}A_{p\ell}U_{\ell}}{dZ} = \frac{C_{S}^{b}d\theta_{\ell}\rho_{\ell}A_{p\ell}U_{\ell}}{\rho_{\ell}} \frac{dZ}{dZ} - \frac{(1-f)\theta_{p}K_{ov,b}A_{p\ell}}{n_{p}V_{p}}(C_{S}^{p\ell} - C_{S}^{eq}), CaC2^{/\eta}}{(5-52)}$$

where f is the powder fraction in the gas phase, θ_p the solid fraction of powder particles in the plume, V_p the volume of particle. This differential equation is the general statement of sulphur conservation in the system of one-dimensional, three-phase desulphurization kinetics.

Since the calcium carbide particles are assumed to be retained on the surface of bubbles, the dissolved sulphur is considered to diffuse onto the surface of bubbles to react with calcium carbide. Thus, by assuming potential flow developed over the front or upper surface of the bubble, the theoretical value of the mass transfer coefficient can be obtained by the Baird & Davidson[72] formula.

$k_{b=0.82} D_{s}^{1/2} U_{b-s}^{1/2} r_{b}^{-1/2}$ (5.53)

where D_s is the diffusivity of sulphur in the melt. U_{b-1} the relative velocity between gas phase and solid phase.rb the radius of the bubble.

5.5 Methods of solution

Eqns(5.2) to (5.53) constitute the complete mathematical formulations of fluid flow, heat transfer, and mass transfer of sulphur for calcium carbide desulphurization in the plume. These equations were solved With proper initial and boundary conditions in conjunction with the rate equation of slag/metal desulphurization Eqn(4.1) so as to obtain the overall rate of desulphurization during injection.

5.5.1 Solution procedure for plume reaction

5.5.1.1 The boundary conditions for fluid flow equations

The velocity of powder particles at the lance tip is given below.

 $U_{p} = 0.5 U_{g}$

(5.54)

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Thus, the corresponding volume fraction of powder particles can be calculated as follows:

 $\theta^{O=} (m_{p/\rho_{p}}) (0.5 m_{g}/\rho(g) STP + m_{p}/\rho_{p})^{-1}$ (5.55)

and

 $\begin{array}{ccc} \theta \circ = 1 & - & \theta \circ \\ g & p \end{array}$

The initial conditions for the liquid, solid, and gas fraction at the bottom of the jet (Z=0) are calculated by the following equations:

 $\theta_{g=0} = \theta_{g} - \theta_{t} \theta_{g}$

(5.57)

(5.56)

Previous work [154] of Irons and Farias indicated that the liquid volume fraction is not very high at the bottom of the jet. We therefore chose θ_{\pm} to be 0.1. The gas and powder velocity at the bottom of jet can be calculated by the equations shown as follows:

 $\theta_{p=} \theta_{p}^{O} - \theta_{t} \theta_{t}$

and

(5.60)

(5.59)

(5.58)

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The liquid velocity at the bottom of jet is determined by using the average recirculating velocity from Sano and Mori[177], Viz;

$$U_{t} = U_{re} = \frac{1.17(Q g H A_{pt}^{2})0.339}{\pi/4(D_{c}^{2} - D_{c}^{2})}$$
(5.61)

Where Q is the gas flow rate at the bulk liquid temperature

and mean pressure.

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5.5.1.2 The boundary conditions for heat transfer equations

The temperature of calcium carbide and gas at the bottom of the jet (Z = 0) are assumed to be 250C (room temperature). For liquid temperature, it is assumed to have the same value as that of bulk metal temperature.

5.5.1.3 The boundary conditions for plumesul phur

conservation equation

At the jet bottom, the sulphur concentration in the plume is assumed to have the same value as that of bulk concentration. The initial sulphur content in the powders is assumed to be zero. Thus

Cpow= 0 at Z=0

(5.62)

Using the Gear's method[179] for stiff first order ordinary differential equation, the fluid flow and heat transfer equation have been solved simultaneously with plume sulphur conservation equation. The details of computer program is listed in Appendix V. The solution procedures and the important parameters involved in the calculation is presented in the following sections. 5.5.2 Solution procedure for slag/metal reaction

As has been stated in Section 2.3.2.2, the slag/metal desulphurization generally can be described by Eqn (4.1). The rate of slag/metal desulphurization is increased during injection due to the constant increase of slag volume.

For a short period of reaction time, the value of reaction rate can be considered constant. Thus the solution of Eqn (4.1) is given as

 $\frac{Cb}{s,t} = \frac{Cst}{s} + (\frac{Cb}{s,i} - \frac{Cst}{s} + \eta) \text{ Exp } (-Km t)$

(5.63)

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Where Cb is the sulphur content in hot metal at time t, and Cb is the initial sulphur content of hot metal. Since desulphurization rate is varied during injection. the empirical correlations of Eqn (4.4) and (4.5) are used for the calculation of the rate constant of desulphurization. However, for the dry slag initial condition, the incubation period at the early stage of injection can simulated by the interplay of desulphurization and be resulphurization. The criterion for the resulphurization to take place is given as follows:

 $\frac{1}{100 \text{ Ms}} ((\%S) -\eta [\%S]) = (CSl - \eta Cb)$

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(5.64)

Where M_s is the molecular weight of sulphur, ρ is the density of hot metal, η is the apparent equilibrium sulphur partition ratio which was obtained directly from experimental data. (i.e., the apparent sulphur partition ratio was correlated as a function of calcium carbide injection weight.) The sulphide-saturated slag will continuously reverse sulphur to the hot metal until the value for the criterion of resulphurization (Eqn(5.64)) is negative. According to the present experimental observations, this incubation period is equivalent to the time for the first 1.4 Kg/t.H.M. of calcium carbide injection.

Since the sulphur removed from the plume is absorbed by the top slag, the sulphur contents in the slag varied during injection. Using a mass balance of sulphur in the system, based on the assumption that all of the sulphur removed from the plume is transferred to the slag phase, the sulphur content in the slag phase at any time t can be calculated according to the equation:

$$\begin{array}{c} Csl \\ s,t \end{array} = (Csl \\ s,i \end{array}) + (Cb \\ s,i \\ s,i \end{array} - Cb \\ s,t \end{array}) \frac{w_{met}}{w_{met}}$$

 $W_{st} = W_{st,i} + W t$ (5.66)

where Cb and Cst are the initial sulphur contents in metal and slag, respectively. W_{met} and W st are the masses of hot metal and slag, respectively. The term Cb = Cb is the total amount of sulphur removed from the hot metal in a time interval. W is the calcium carbide injection rate.

5.6 Computed results

As has been stated previously, a steady-state, one-dimensional, three-phase model for the plume desulphurization kinetics has been solved simultaneously with fluid flow equations and heat transfer equations. The computed results and the experimental data of the plume desulphurization rate are shown in Figures 5.5 to 5.9 for five different gas flow rates. The computed results and the experimental first order reaction rates are found in reasonable agreement under such a wide range of injection conditions. Furthermore they show no trend with the type of top slag, providing strong support for the validity of the model.





First-order rate constants for desulphurization in the plume from experimental data and the present model for various solid injection rates (50 L/min).



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The typical simulation results for the CaC₂ desulphurization are shown in Figures 5.10 and 5.11 for the initial slag conditions of dry slag and liquid slag, respectively. The filled circles in these diagram are the experimental desulphurization data obtained during injection. It clearly shows that good agreement is obtained between the results of model predictions and experiments.

Figure 5.12 presents the computed volume fraction for solid, liquid and gas phase in a rising plume. One can see that at the bottom of the plume there is a large amount of gas phase. However, the liquid is entrained quickly into the rising plume. The computed average volume fraction are approximately 10% and 0.2% in the plume for the gas phase and solid phase, respectively. Figure 5.13 shows the computed velocity profile for gas, solid and liquid phase in the rising plume. In Figure 5.14, the temperature profiles for the gas (TG), liquid (TL), and solid (TPL) phases are presented. The particles dispersed in the melt are found to be heated very quickly to the liquid metal temperature. On the contrary, the gas phase is heated slowly to the liquid temperature.

5.6.1 Effect of initial conditions

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The equations of fluid flow are made very stiff by the choice of initial conditions. Low density gas is placed



Comparison of desulphurization curve between the experimental data and the computed results from the present model (162 L/min, 10.7 kg/min, dry slag).

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at near zero velocity in a high density liquid. The resulting forces accelerate the gas to its terminal velocity in a very short distance. It was found that the initial conditions of phase fraction and velocity could be changed quite dramatically without any appreciable difference in the end results. However, when the initial gas velocity was set too high (comparable to Ut), the predicted velocities turned out larger. Farias and Irons[180] pointed out that the highly unstable conditions chosen for the initial conditions should quickly rearrange themselves to bubbles rising through the melt with a terminal velocity with respect to the liquid. Velocity solutions were also very insensitive to the choice of liquid velocity at Z=0.

5.6.2 Effect of bubble size

The bubble size in the plume is dependent on liquid properties and gas flow rates. An estimate of the bubble size can be made from the experimental result of Sano and Mori[66]. For the iron system, the bubble diameter is likely to be between 20 and 100 mm. Therefore in the present model, the bubble diameter has been chosen to be 25 mm and the calculations were performed on the assumption that all of the CaC2 particles are evenly spread and well mixed at the interface of the bubbles. Due to the complicated hydrodynamic situations in the plume, the bubble size may vary during injection. It was therefore necessary

to examine the sensitivity of the rate and efficiency of CaC₂ desulphurization to the variation of the bubble $\sqrt[3]{2}$ diameter. The computed plume desulphurization rates and efficiencies for various bubble diameters, under the injection conditions of 6 kg/min of CaC₂ and 160 1/min of carrier gas rate, are shown in Figures 5.15A and 5.15B. It may be noted that the computed values of the plume desulphurization rate is significantly influenced by the variation of bubble diameter. An increase of bubble diameter by a factor of two results in a 33% decrease in calcium carbide efficiency. However, small bubble size leads to a higher plume desulphurization rate and CaC2 efficiency. This is because more bubble surface is available for the reaction to take place which can effectively improve the contact of . calcium carbide with hot metal. In metallurgical systems, it is well known that surface-active agents reduce mass transfer rates for spherical cap bubbles. This is generally due, to the immobilization of the bubble surface, rather than to a reduction of free sites on the bubbles. In a similar manner, the residence of CaC2 on the bubbles surface could cause the reduction in surface tension. This may be related to the extent of the stagnant region, resulting in a reduction of mass transfer rates. As can be seen from Figures 5.16A and 5.16B, a modified factor to reduce mass transfer rate was introduced to take account of the immobilization effect on the overall desulphurization rate



e 5.15A Effectiof bubble diameter on average CaC₂ desulphurization rate (gas flow rate: 160 L/min, CaC₂ injection rate: 6 kg/min).





Figure 5.16A: Effect of immobilized factor on average CaC₂ desulphurization rate (gas flow rate: 160 L/min, CaC₂ injection rate: 6 kg/min).

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and efficiency. Thus, if the bubble surfaces are immobilized by CaC2 particles, one would expect the desulphurization rate and efficiency to decrease. The immobilized factors of 1 and 0.1 represent estimates for the limiting case of free circulating and totally stagnant region, respectively. As can be seen the desulphurization rate and efficiency decrease slightly with decreasing immobilized factor. An immobilized factor of 0.5 leads to a 10% reduction in the desulphurization rate and efficiency. This is ascribed to the fact that the reaction is dominated by the product layer control. Therefore, the rate and efficiency of the reaction is rather insensitive to the mass transfer rate of sulphur in the melt. However, a further reduction of the mass transfer rate of sulphur would change the control mode into the step of sulphur mass transfer. Thus, a modified factor of 0.1 results in a 55% reduction in the desulphurization rate and efficiency.

5.6.3 Effect of solid, gas flow rates, and sulphur content

It is well known that the chemical reactions in most high temperature metallurgical refining systems are very fast and irreversible. Under these conditions, the rate of CaC₂ desulphurization is controlled by the transport of sulphur or calcium to the reaction interface. Whether the control lies solely in the steps of mixing (i.e. pumping control), mass transfer of sulphur in the hot metal (i.e.

contact control), or diffusion of calcium vapor through the reaction product layer (i.e. product layer control), or whether there is mixed control by these steps, depends mainly on the injection conditions and sulphur content of hot metal. Figures 5.17A, 5.18A and 5.19A show the variation of the control for each transport step in the rising plume, computed for 0.08 wt% sulphur in hot metal various injection conditions. The corresponding and cumulative efficiencies of CaC2 desulphurization are also shown in Figures 5.178, 5.188 and 5.198. As can be seen from these diagrams, the low loading injections are kinetically favorable for CaC2 desulphurization. At a fixed carrier gas flow rate, lower loading injection results in less CaC2 being injected along with carrier gas. Therefore, the thickness of the CaC₂ layer on the bubble surface is thinner than that of higher loading injection. At the bottom of the plume, control mainly lies with the pumping control and contact control, but the product layer control gradually dominates as the CaC₂ particles rise towards the surface of the melt. This can be explained by the large amount of gas which exists in the bottom of the plume. Accordingly, there is less hot metal which can bring sufficient sulphur into the bottom of the plume for the reaction. Consequently, both the pumping and contact control dominate initially. Later as the CaC₂ particles rise towards the surface of the melt, the reaction product layer thickens, and control gradually



Figure 5.17A: Fraction of control for each mass transfer step as a function of distance from the bottom of the plume (sulphur concentration: 0.08 wt%, gas flow rate: 160 L/min, CaC₂ injection rate 2 kg/min).





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Figure 5.18A: Fraction of control for each mass transfer step as a functioin of distance from the bottom of the plume (sulphur concentration: 0.08 wt%, gas flow rate: 160 L/min, CaC₂ injection rate: 6 kg/min).







Figure 5.19A: Fraction of control for each mass transfer step as a function of distance from the bottom of the plume (sulphur concentration: 0.08 wt%, gas flow rate: 160 L/min, CaC₂ injection rate 10 kg/min).

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shifts to mixed contact control and product layer control. Finally, as the reaction product layer. continues growing to further retard the calcium vapor diffusion rate, the product layer control prevails. Figure 5.20 illustrates the sulphur profile in the plume during CaC₂ injection. The computed sulphur content in the rising plume is seen to be decreased sharply at the bottom of the plume until reaching the minimum sulphur content, and then starts increasing to the surface of the plume. This phenomenon is attributed to the fresh hot metal being entrained into the rising plume to increase the sulphur content of the hot metal. Furthermore, due to the slow reaction rate of CaC₂ at the upper portion of the plume, the CaC₂ can not effectively and completely remove the entrained sulphur.

As the sulphur content of the hot metal decreases from 0.08 wt% to 0.02 wt%, the computed results shows that a Significant change in the reaction controlling mechanism occurs. Figure 5.21A indicates that the contact control becomes important and has more influence on the reaction at a low sulphur content compared with at 0.008% S. At a lower sulphur content, less sulphur is transported to the reaction interface due to the lower chemical potential of sulphur. Consequently, the efficiency of CaC₂ utilization is low. Figure 5.21B shows the corresponding CaC₂ efficiency. The control sequence of CaC₂ desulphurization is varied



Figure 5.20: Plot of sulphur concentration profile in a rising plume under various injection conditions.



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during the overall injection process. Figure 5.22A shows computed results of the change of the fraction of control for each transport step during injection. At the start of injection with higher sulphur content in the hot metal, the control lies mainly with the product layer control. As the desulphurization proceeds, the sulphur in the melt continuously decreases and therefore the control gradually shifts to the contact control. Figure 5.22B shows the corresponding CaC2 plume efficiency change during injection.

5.6.4 Effect of plume geometry

The recirculation rate of hot metal in the plume was obtained according to the equation:

Vm=02ULApt

(5.67)

/ cylindrical plume was assumed for the present model calculations. Therefore, the area of plume can be taken to be the breakthrough zone which is observed on the bath surface. There is controversy about the plume geometry. Fruehan and Martonik[181] proposed that the plume is cylindrical in shape above the injection point. More recently, Irons and Farias[180] used a water model to simulate the downward injection and found that the rising



Figure 5.22A: Fraction of control for each mass transfer step as a function of sulphur concentration in hot metal (gas flow rate: 160 L/min, CaCz injection rate: 6 kg/min).

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plume is roughly cylindrical. However, Hsiao et al[178] and Szekely et al[182] have suggested that the rising plume is conical in shape. Therefore, it was necessary to examine the effect of plume geometry on the rate of desulphurization. Calculations based on a conical plume shape were carried out. The computed results show an insignificant effect of the plume geometry on the rate of desulphurization because mixing does not dominate the reaction.

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5.6.5 Effect of temperature

Both good particle-liquid contact and sufficient thermal energy are essential for fast and efficient CaC2 desulphurization. Therefore, the CaC2 particles must be in contact with the hot metal and heated rapidly to reach the hot metal temperature. As stated in Section 5.5, the CaC_2 . particles in the melt have been assumed to be trapped on bubbles and free to circulate on the bubble surface. the Thus all CaC2 particles are assumed to come into contact with the hot metal, (i.e. in this case f=0). Consequently, the CaC2 particles are assumed to be heated rapidly to reach the hot metal temperature. However, the present model does not take into account the heating of the particles on the bubble surface, therefore, cautions must be paid on the sensitivity of the temperature variation of calcium carbide

particles on the rate of CaC_2 desulphurization. Figures 5.23A and 5.23B show that the rate and efficiency of CaC2 desulphurization are affected by the temperature. Lower temperature leads to a lower rate and efficiency of CaC2 desulphurization. This is mainly due to the fact that the thermal decomposition of CaC2 is an endothermic reaction. A decrease of 50oC of particle temperature causes a 15% reduction in the CaC2 efficiency and desulphurization rate.

5.7.6 Effect of calcium vapor diffusivity

The effective diffusivity of calcium vapor deduced from the data of Taballa et al.[176]. is in the range of 1.0X10-5 to 1.0X10-7 m2/s. A value of 1.0X10-6 m2/s was used for the present model calculation, and fairly good agreement between the experimental results and the computed results of plume desulphurization were obtained. Furthermore, for a better understanding of the effect of the effective diffusivity on the rate of desulphurization, calculations have been carried out to examine the sensitivity of the desulphurization rate due to a change in the effective diffusivity. Figures 5.24A and 5.24B show the effects of variations in the effective diffusivity of calcium vapor on the rate and efficiency of desulphurization. Increasing the effective diffusivity by a factor of five results in a 30% improvement in the calcium carbide efficiency, showing that the desulphurization rates are very sensitive to the







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Figure 5.24A: Effect of Ca vapor effective diffusivity on CaC2 desulphurization rate (gas flow rate: 160 L/min, CaC2 injection rate: 6 kg/min).



effective diffusivity of calcium vapor. This is mainly due to the fact that the product layer control dominates desulphurization for most conditions studied. Therefore, calcium carbide desulphurization could be improved if the rate of calcium vapor diffusion could be increased, either by thinning the product layer or by enhancing the diffusivity of calcium vapor.

5.6.7 Effect of calcium carbide particles position

The position of the particles (i.e. in the bubbles, on the bubble surfaces, or in the melt) strongly influences the calcium carbide efficiency and the desulphurization rate. For a better understanding of the effect of calcium carbide contact with hot metal on plume desulphurization. four other particle-liquid contact pattern were chosen for the investigation besides the present model assumption of CaC2 trapped on the bubble surface (Table 5.1). Case 1, the present model assumption, corresponds to all calcium carbide being trapped on the interface by surface tension because calcium carbide does not wet hot metal. The calcium carbide is assumed to be free to circulate on the interface, and thus all calcium carbides react. This is similar to a model proposed by Engh[129] for liquid fluxes. Case 2 is based on the findings of Irons and Farias[183] that the bath cooling rate for powder injection was only 30 percent of that which would be expected if all

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Table 5.1 Cases Used to Investigate Particle-Liquid Contact

Case Description Contact Control Factor .100% of particles on diffusion of sulphur to bubble interface bubble interface .particles circulate .diffusion of sulfur to .same as case 1, except 30% of particles are bubble interface and to dispersed in liquid particles in liquid .same as case 2, except З. .same as case 2, except particles on interface that only a monolayer are stagnant of particles on bubble reacts .100% particles in liquid .diffusion to particles 100% of particles as .diffusion to bubbles stagnant layer on bubble with monolayer reaction Interface

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the particles were in melt. For the calcium carbide in the melt, an extra desulphurization term is added to the overall plume sulphur balance equation (Eqn(5.52)). The desulphurization term for the calcium carbide in the melt is given as follows:

$$NPOW_{P} = f' A_{pt} U_{p} \theta_{p} \frac{d CPOW_{P}}{d z}$$
(5.68)

where

$$\frac{d C_{pow,p}}{d z} = -\frac{K_{ov,p}}{n_{p,m} V_{p} U_{p}} (C_{s}^{pt} - C_{eq}^{eq} / \eta)$$

(5.69)

where fr is the fraction of CaC_2 in the melt. Turbulent mass transfer coefficients[62] were used to calculate the mass transfer flux to the CaC_2 particles.

$$N_{sh} = \frac{k_{p} d_{p}}{D_{s}} [2 + 0.4 (\epsilon d_{p} / v_{3})] / 4 N_{sc}]$$

(5.70)

Owing to the small particle size, the mass transfer coefficient k_p calculated from the above equation is close to the one calculated under the condition of a single sphere

at rest in a large volume of stagnant fluid. (i.e. $N_{Sh}=2$, the limiting value of Sherwood Number for radial diffusion.)

Case 3 was the same as case 2 except that the particles on the pubble surface are stagnant which was chosen to show the effects of very slow particle recirculation. Thus, only a monolayer of calcium carbide particles on bubble surface reacts. For case 4, it is assumed that 100% particles are in liquid which represents an estimates for the fastest reaction rate. Case 5 is based on the assumption that all the particles form a stagnant. layer on the bubble surface which represents an estimate for slowest reaction rate. The various contact control cases are compared with the experimental first order rate constants for the plume reactions for two carrier gas flow rates (50 1/min and 160 1/min, Figures 5.25 and 5.26). All the data fall between the limiting cases of all the particles in the liquid (case 4) and stagnant particles on the bubble interface (case 5). It is difficult to choose the contact pattern among the cases 1,2 and 3 due to the scatter in the data. Nevertheless, a significant fraction of the particles are obviously on the bubble interface and, therefore, techniques to improve particle-liquid contact should improve desulphurization rate and calcium carbide efficiency. For example, Irons and Farias[133] have found that the use of inclined or "hockey-stick" lances and the use of gas release



Figure 5.25: First-order rate constants for desulphurization in the plume from experimental data and the present model for various solid injection rates and powder dispersion conditions (50 L/min).



for various solid injection rates and nowder dispergion conditions (160

agent (i.e. CaCO3 in the case of CaC2 injection) improve particle-liquid contact as measured by bath cooling rates[183].

5.6.8 Desuriphurizing contribution of slag/metal reaction and plume reaction

The results of the present model analysis indicate that the desulphurizing contributions made by both slag/metal reaction (permanent-contact reaction) and plume reaction (transitory reaction) varied during injection. Whether the desulphurization is dominated by the slag/metal reaction or by the plume reaction, mainly depends on the type of slag, injection conditions, and the amounts of CaC_2 injected.

Figures 5.27 and 5.28 show the computed results of the cumulative slag/metal desulphurizing contribution as a function of CaC_2 injection rates after 12 kg of CaC_2 injection for the initial slag conditions of dry slag and liquid slag, respectively. As can be seen from Figures 5.27, for the case of initial dry slag condition, the slag/metal desulphurizing contributions are only weakly affected by the CaC_2 injection rate. This is because the plume desulphurization rate is mainly dominated by the bubble surface area which can be calculated from gas flow rate. At a fixed gas flow rate, the plume desulphurization rate is



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Figure 5.27: Effect of gas flow rate and CaC₂ injection rate on contribution factor of slag/metal desulphurization (dry slag).



Figure 5.28: Effect of gas flow rate and CaC₂ injection rate on contribution factor of slag/metal desulphurization (liquid slag).

not sensitive to the CaC₂ injection rate (see Figures 5.5 to 5.9). Thus, a decrease of CaC₂ injection rate only slightly reduces the plume reaction rate and consequently results in a slow improvement of the slag/metal desulphurizing contribution. For the same amount of CaC₂ injected into the hot metal, Figure 5.27 also indicates that lower gas flow rates favor slag/metal desulphurization. Although it is known from the present work that both the plume and slag/metal desulphurization rates are affected by the gas flow rate, the plume desulphurization is found to be more sensitive to the gas flow rate than that of the slag/metal reaction. Therefore, the decrease of gas flow rate will strongly reduce the plume desulphurization rate and consequently result in an increase in the slag/metal desulphurizing contribution.

Figures 5.29 and 5.30 show the effect of the amount of CaC_2 injection on the cumulative slag/metal desurphurizing contribution. It can be seen that the slag/metal desurphurizing contribution is dependent on the total amount of CaC_2 injected. As explained in Chapter 4, the rate of slag/metal desurphurization is increased proportionally to the slag weight. More CaC_2 injection implies that more slag weight is formed. Therefore, the slag/metal desurphurizing contribution can be improved due to the increase of the total amount of CaC_2 injected. Since





Figure 5.30: Effect of amount of CaC, injected on contribution factor of slag/metal desulphurization (dry slag, gas flow rate: 160 L/min).

the contact pattern of calcium carbide in the plume has a strong influence on the plume desulphurization rate, it is necessary to check the sensitivity of the contact pattern on the slag/metal desulphurizing contribution. As can be seen all the experimental data fall between the limiting cases of all the particles in the melt (case 4) and stagnant particles on the bubble surface (case 5).

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Similar phenomena are also found in the case of initial liquid slag. Figure 5.28 shows the computed results of the cumulative slag/metal desulphurizing contribution as a function of CaC₂ injection rate under two different gas flow rates of 50 \pounds /min and 160 \pounds /min. It can be seen that the liquid slag is more sensitive to gas flow rate, therefore, the decrease in the gas flow rate results in the rapid increase of slag/metal desulphurization. Figures 5.31 and 5.32 show the computed results of the cumulative slag/metal desulphurizing contribution as a function of the amount CaC₂ injected for the gas flow rate of 50 \pounds /min and 160 \pounds /min, respectively. Good agreement is obtained between the computed results fall between the two limiting cases of contact pattern.

According to the present model calculations, it indicates that the slag/metal desulphurizing contribution of dry slag and liquid slag are roughly equal which is



Figure 5.31: Effect of amount of CaC₂ injected on contribution factor of slag/metal desulphurization (liquid slag, gas flow rate: 50 L/min).



consistent with the experimental results. Although an incubation period was found initially in dry slag condition, the high desulphurization rate was obtained after passing through the incubation period which compensates for the initial slow desulphurization rate.

5.7 Discussion

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5.7.1 Desulphurization mechanism

Calcium carbide is produced in submerged arc furnaces. The reaction stoichiometry is given by the overall equation.

(5.71)

$Ca0 + 3C = CaC_2 + CO$

The binary phase diagram CaC_2-CaO (Figure 5.33) shows a eutectic point at 1850^{OC} at 53% $CaC_2[184]$. Commercially available calcium carbide is produced with a higher CaC_2 content. The typical composition is approximately 80% CaC_2 with the remainder being mainly CaO. Since calcium carbide does not melt at the temperature of hot metal desulphurization and is not fluxed at reducing conditions with an oxygen activity of $2 - 3\times10^{-4}\%$ in carbon-rich hot metal, the desulphurization reaction is a solid-liquid reaction between calcium carbide particles and liquid hot metal. The process of desulphurization with solid CaC_2 possibly takes place by the diffusion of sulphur or calcium



Figure 5.33: Binary phase diagram of CaC_{2-CaO} system [184].

atoms through the reaction product layer of calcium sulphide and graphite. However, the diffusivity of sulphur in a calcium sulphide matrix is approximately $4.9 \times 10^{-15} \text{m}^2/\text{s}$ in the temperature range of 1375° to 1600° [185]. This value is about the order of magnitude that one would expect if solid-state diffusion dominates. Similarly, the diffusivity of Ca atom in a CaO single crystal is approximately 5×10^{-16} m²/s at 1350° [186]. Such heterogeneous reactions involving solid-state diffusion are extremely slow.

Few studies on the mechanism of calcium carbide desulphurization have been reported. The mechanism proposed by Meischsner [187] and Oeter's [188] is based on the findings that CaC₂ and CaS have similar crystal structures and form solid solutions over the entire composition range [189]. They postulated that sulphur in hot metal is absorbed due to the substitution of carbon in the lattice of calcium carbide. The reaction based on this mechanism can be expressed as

 $2 \operatorname{CaC}_2 + \underline{S} = \operatorname{Ca}(\operatorname{C}_2, \underline{S}) + 2\underline{C}$ (5.72)

where $Ca(C_2,S)$ represents the solid solution of CaC2 and CaS. The sulphur substituted by carbon of calcium carbide has to dissolve at the surface of calcium carbide first and then diffuse inside the calcium carbide particle. As has

been explained previously, such heterogeneous reactions involving solid state diffusion are kinetically rather unfavorable and the reaction rate is extremely slow. Consequently, the desulphurization rate of calcium carbide is expected to be very slow. This is in conflict with the fact that calcium carbide is an effective desulphurization agent.

Oeter[188] postulated that sulphur is transported to the surface of the particle and reacted with calcium carbide to form a sulphide ionic melt. Thus the concentration gradient of S^{-2} ions between the surface and unreacted core of calcium carbide is built up for the sulphide ions diffusion. The reaction at the interface of calcium carbide particle and hot metal which was suggested by Oeters[188] is given as follows:

 $[S] + C_2^{-2} = S^{-2} + 2 [C]$ (5.73)

The fact is that calcium carbide has to remain in solid state under the conditions of hot metal desulphurization. The reason for this has been explained previously. Even if it were possible to form slag meit at the surface of calcium carbide particle, low sulphide and carbide diffusivities would also make the reaction rate very slow. In general, the element diffusivity in the slag meit is in the range of 10-9

to 10-12 m²/s[190], which is three to five orders of magnititude lower than the effective diffusivity of calcium vapor deduced from Talballa's experimental results. Furthermore, the reaction(5.73) occurs in the presence of carbon saturated hot metal. The carbon in calcium carbide would not tend to dissolve into the hot metal in this situation. This has been confirmed by the experimental findings of Talballa (see Appendix IV). In their study of the mechanism of calcium carbide desulphurization, the carbon content of hot metal did not change as the calcium carbide desulphurization proceeds. Consequently, the reaction (5.73) proposed by Oeters is unlikely to be true. It is more likely, therefore, that desulphurization with calcium carbide is topochemical reaction. The desulphurization occurs via the diffusion of the decomposed calcium vapor through the micropores of the reaction product layer.

Once the calcium carbide contacts the hot metal, calcium vapor is produced due to the high temperature. The equilibrium calcium partial pressure can be calculated according to the following equation.

$$CaC_2 = Ca_{(g)} + 2C_{(s)}$$
 (5.74)

At 1350° , the equilibrium partial pressure of calcium vapor is 1.44 x 10^{-4} atm which corresponds to a concentration of

1.08 × 10⁻³ mole/m³ calcium vapor. Thermodynamic calculations[191] have shown that monatomic sulphur gas is the predominant gas species escaping from carbon-saturated hot metal; CS, S₂ and COS are of lesser importance. The equilibrium partial pressure of monatomic sulphur gas can be calculated from Eqn(5.33) and (5.34). For a hot metal with a sulphur activity coefficient of 3.0 and a sulphur content of 0.05 wt%, the equilibrium partial pressure of monatomic sulphur vapor is 1.34 × 10⁻⁶ atm at 1350° C. This value is two order of magnitude lower than the equilibrium partial pressure of calcium vapor. Therefore it is reasonable to ignore the effect of sulphur vapor diffusion in the present model.

It has been reported that the retention time of the solid desulphurizer in the melt is very short and generally is close to the time of the desulphurizer travelling through the melt[192],[193]. In order to check this point, the chemical analysis of sulphur for the metal sample taken shortly after the injection test were compared with another sample taken after a holding period of several minutes. The results (H12R4 and H16R4) show that the sulphur^o contents for both metal samples have the same value, indicating that the retention time of the calcium carbide is very short and the calcium carbide floats up quickly after the injection. This can be attributed to the poor

wettability and the low density of calcium carbide which reduces the retention time of calcium carbide in the melt. Ogawa et al. [194] in their study of dispersion of particles in a powder injection process, also concluded that the behavior of dispersion is influenced by the wettability of the powder. In the case of poor wettability, all the particles float up quickly.

5.7.2 Two-Dimensional effects

In the present one-dimensional model, the other two dimensions are handled by assuming that the plume dimension are determined experimentally and that the plume' is axisymmetric. The model parameters are averaged evenly over the plume cross-section. It is well known from experiment that void fraction, liquid and gas velocities vary across the plume, and are usually fitted to a Gaussian distributition. Since the calcium carbide particles are likely trapped on the surface of the bubble and dispersed in the melt, the retention time of calcium carbides is affected by the Gaussian distribution of bubble and solid velocities. In the present work, both the bubble and solid velocities are averaged evenly across the cross-section of the plume. It is believed that the velocities of bubble and solid calculated from the present model represents the average value from the Gaussian distribution; the efficiency of calcium carbide based on the present model should have the

same value as that of using Gaussian distribution for the bubble and solid velocity.

5.7.3 Axial mixing

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The extent of axial mixing can be measured by the turbulent Peclet number, for example, an extremely large Peclet number represents negligible axial mixing. The turbulent Peclet number is defined by

(5.75)

(5.76)

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It can be seen that the turbulent Peclet number is the ratio of the strength of convection and turbulent diffusion. Since this is not a molecular process, the turbulent sulphur diffusivity would be expected to vary with the fluid temperature, intensity of turbulence and kinematic viscosity of the fluid. In the turbulent system involving molecular diffusion, the turbulent Schmidt number can be approximated to be of the order of unity[161]. Thus, the turbulent diffusivity can be obtained according to the turbulent Schmidt number given as follows: The effective viscosity,^µt, has been modelled by Sahai and Guthrie[167] to describe turbulent mixing in an gas-stirred vessels. In this case the average effective viscosity formula is given as follows:

$$g Q(1 - \alpha)$$

 $\mu_{e=5.5 \times 10-3p_{L}} L[-0]$

(5.77)

where ρ_{ℓ} is the density of the liquid, α is the volume fraction of gas within the plume, L is the depth of the liquid in the vessel, D is diameter of the vessel, Q is the gas flow rate.

Since the turbulent diffusivity can be calculated based on those formulae, an estimate of the turbulent Peclet number in the present situation is approximately in the range of 400 to 600, indicating that the diffusion type of process is not important. This is consistent with the present model assumption of ignoring the influence of diffusion mass transfer within the plume.

5.7.4 Comparison with other mathematical models

Few mathematical models describing desulphurization kinetics for submerged injection of powders have been reported. El-Kaddah and J. Szekely[164] proposed a model, in which a set describing (Navier-Stokes

equations) together with $\kappa - \epsilon$ turbulence model are solved simultaneously to obtain the fluid flow velocity and turbulence fields. A convective-diffusive equation for sulphur conservation was used in their model to examine the influence of turbulence and fluid flow properties on the mass-transfer process. The predictions based on their mode 1 were found to be in good agreement with experimental measurements obtained from 6 and 40 t ladles. Obguchi and Robertson [173] developed a model to simulate the desulphurization kinetics by submeraged powder injection. Kinetic rate equations for transitory reaction and permanent-contact reaction were used to take account of the P desulphurization due to plume reaction and slag/metal reaction, respectively. This model was used to simulate small-scale powder injection experiments (injection of CaObased powder into 3.5 kg hot metal), in which the contributions of the permanent-contact and transitory reaction were found to be roughly equal.

The present model differs from the above-mentioned models in that the volume fractions, velocities, temperatures and compositions of the gas, liquid, and solid phases in the rising plume can be calculated during powder injection. However, the EI-Kaddah and Szekely model ignored the discreteness of each phase, in which the three phase region was treated as a single homogenous phase. Obguchi and

Robertson's model did not take into account the hydrodynamic effect on the reaction kinetics; they simply assumed a residence time for the particles.

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In the present model, the detailed reaction mechanism of CaC2 particle desulphurization and the plume desulphurization model were developed. The computed results are found to be consistent with the experimental data. In El-Kaddah and Szekely's model, the behaviour of the solid reagent desulphurization was over simplified. It was assumed that the reaction occured at the surface of the injected particles where the reaction products will form a liquid film which adheres to the solid surface. They assumed that the diffusion of the reactants through this liquid film was the rate-limiting step. However, in their model, no mention was made of the diffusivity of sulphide ions through this liquid film. In fact, the rate equation (Eqn 24 in their paper) used to describe the diffusion through this liquid product layer actually represents sulphur mass transfer through the liquid boundary layer. In their model, no mention was made regarding the particle position in the rising plume.

In Obguchi and Robertson's model, the controlling mechanism regarding the CaO-CaF₂-AL₂O₃ based reagent in the transitory reaction is not reported. They assumed the flux was in liquid state and evenly spread around the bubble. For
the purpose of evaluating the transitory reaction, the parameter E, which is a measure of the efficiency of the transitory reaction, was introduced to fit the experimental data. A value of 0.14 for the efficiency of the transitory reaction was used to force good agreement between their model and experimental data.

The present model clearly shows the important factors affecting the desulphurizing contributions made by the transitory and permanent-contact reaction. In general, the desulphurizing contribution of these two reactions are dependent on the type of initial slag conditions, injection conditions and the amount of reagent injected. In El-Kaddah and Szekely's model, they did not report any details of the relative desulphurization contribution of plume reaction and slag/metal reaction. In Obguchi and Robertson's model, they found that contributions made by the plume reaction and slag/metal reaction were roughly equal. However, due to the simplicity of their model, it is difficult to use their method to evaluate the influence of injection conditions on the desulphurization contribution of slag/metal and plume reaction.

5.7.5 Implication for the industrial practice

Increasing the carrier gas flow rate from 50 to 230 1/min enhanced the plume reactions as indicated by Figures

5.5 to 5.9. This result is due to better hot metal mixing and more bubble surface area at increased flow rates. ' Normally, commercial operators minimize the carrier gas flow rate. This situation only appears to be contradictory; the gas release from the limestone in the commercial mixtures is generally an order of magnitude greater than the carrier gas flow rate, which generates considerable mixing and bubble surface area. Nevertheless, in torpedo car desulphurization, an additional resistance to sulphur transport exists because of poor mixing in the ends of the car[73]. This aspect was not included in the present model because the small scale induction furnace is close to being well-mixed.

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CHAPTER 6

This investigation was initiated to study the kinetics of calcium carbide desulphurization of hot metal by powder injection. Forty-eight successful injections of commercial-grade calcium carbide(DSR) into 2.5 Tonne heats of hot metal were carried out. Four slag initial conditions were studied: no slag, a dry top slag; a liquid slag and the dry slag modified by pre-plunging of aluminum. The experimental conditions of the solid to gas loadings ranged between 15 and 160 kg/Nm³. After an analysis of the experimental results, the following conclusions were drawn:

(1) The most important parameters which affect the rate and efficiency of calcium carbide desulphurization are the type of top slag, injection conditions(i.e. solid to gas loading) and oxygen activity in the hot metal.

(2) The type of initial slag condition has a significant influence on the rate and efficiency of calcium carbide desulphurization. With the use of no slag or dry slag as an initial slag condition, a 30 to 50 second incubation period was observed. This can be explained as sulphur reversion to the hot metal due to poor properties of the top slag. Control of the initial slag condition through

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addition_of liquid slag (without deoxidation) or modified dry slag (deoxidation) can effectively improve the top slag properties, and eliminate the incubation period.

- (3) The post-bubbling results of slag/metal desulphurization demonstrated that the slag/metal desulphurization is first order with respect to sulphur content in the hot metal.
- (4) The plume desulphurization rates were obtained by subtracting the slag/metal desulphurization from the overall desulphurization. The plume desulphurization reaction appeared to be close to a first order reaction with respect to the sulphur content in the hot metal.
- (5) Lower loading injections are kinetically favorable for both slag/metal desulphurization and plume desulphurization. Therefore, it is benefical to the calcium carbide utilization, the fraction of sulphur removed and the reaction rate.
- (6) Oxygen activity measurements indicated that aluminum additions were associated with low oxygen activity and excellent desulphurization.
- (7) A plume desulphurization kinetic model was developed to simulate the plume desulphurization kinetics. The computed results are consistent with the experimental

(8) Mathematical model for the plume desulphurization indicates that diffusion through the reaction product layer on the calcium carbide particles offers the most significant resistance to the overall desulphurization. The experimental plume reaction rate is slower than that, predicted if all the calcium carbide particles were in the liquid, suggesting that significant numbers of the particles are in the carrier gas bubble interfaces. Furthermore, mixing in the plume, as influence by carrier gas flow rate, exhibits some control over the processes.

results.

- (9) As a result of the present study, the contribution made by slag/metal reaction(permanent-contact reaction) toward the overall desulphurization is dependent on the injection conditions, initial slag condition, and amount of calcium carbide injected. In general, lower calcium carbide injection rates, lower carrier gas flow rates and higher total amounts of calcium carbide injection favour the slag/metal reaction.
- (10)The experimental work and mathematical modelling quantitatively demonstrate that both the slag/metal and plume reactors must be working together for effective desulphurization.

CLAIN TO ORIGINALITY

Several aspects of this Thesis constitute, in the Author's opinion, new and distinct contributions to knowledge. The major contributions are:

- (1) Although the importance of slag/metal desulphurization has been appreciated previously, this work systematically demonstrates and explains the important parameters which affect slag/metal desulphurization such as the type of initial slag conditions, gas flow rate, and slag volume. Furthermore, this is the first time that the effects of dry slag have been studied.
- (2) This is the first time that the calcium carbide powder injection experiments were carried out at the 3 Tonne pilot scale over a wide range of injection conditions. This quantitatively demonstrates the effect of solid loading on both slag/metal and plume desulphurization.
- (3) In the present work, it is shown that calcium carbide plume desulphurization is close to a first order reaction, which has not been reported in the literature previously.
- (4) A quasi-steady state model for calcium carbide desulphurization of a single particle was developed. It

successfully explains the kinetic phenomena of calcium carbide desulphurization.

- (5) This is the first time that a steady-state, onedimensional, three-phase model was developed to model the plume desulphurization kinetics. This provides a thorough investigation of plume desulphurization.
- (6) The present work clearly demonstrates and explains the important parameters affecting the desulphurization contribution made by both slag/metal and plume reactions which had not been previously understood.

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APPENDIX 1

Appendix I

The Calculations of Oxygen Activity

Solid oxide electrolyte cells have been used as a measuring tool to control oxygen activities in steel melts. In general, the E.M.F. of an oxygen concentration cell is dependent on the difference of oxygen potential at the two electrodes and the transport properties of the solid oxide electrolyte. However at low oxygen activity and high temperature, one has to be aware of the various sources of error in electromotive force measurements. The possible experimental errors are:

(a) Electronic conduction.

(b) Dissolution of the unstable ceramic oxide of

the cell which is in contact with liquid metal.

(c) Thermoelectric voltage in the cell.

For the Celox oxygen probe used in this study, the correlation suggested by the oxygen manufacturer to determine the dissolved oxygen activities is as follows:

 $Log a_0 = 1.36 + 0.0059(E + 0.54(T - 1550 R) + 0.00021(T - 1550 C))$ (1)

This recommended calibration equation has been determined empirically in the steelmaking shop on the basis of the theoretical consideration of Eqn(2).

A comparison of this probe calibration with those of using theoretical equations was carried out. The require is the use of the empirically determined parameter P'_e . Then, the true oxygen activity in the melt can be obtained according to equation:

$$\Delta G^{O} \frac{1/4}{R T} = \frac{11}{1} \frac{1}{4} \frac{1}{1} \frac{1}{4} \frac{1}{4} \frac{1}{1} \frac{1}{4} \frac{1}{$$

where F is Faraday's constant, 23050cal/mole-volt, and R is gas constant, 1.987 cal/degree-mole. E' is the modified, E.M.F. after the correction of the thermoelectric voltage created by Mo and Fe conducting electrodes, thus[1]

E' = -(E + E'')/1000 Volt (3)

where E'' is the thermoelectric voltage generated due to Mo and Fe conducting electrodes[2].

10000C < T < 15360C

E''= (-685.9 + 0.861 X T)0.5 mv

1536°C < T < 1700 °C

E''= (7.44 + 0.001124 X T) mv

 ΔGo is the standard free energy change for the dissolution of oxygen in the melt[3].

$$0.50_2 = 0$$

 $\Delta GO = -137124.3 + 7.8T (J)$ (7)

Pii is the equilibrium oxygen partial pressure with Cr-Cr203 reference electrode which can be calculated according to the reaction[3]:

> $Cr_{2O3} = 2Cr + 3/2 O_2$ (8) $\Delta G^{O=} 1077733.8 - 232.5 T (J)$ (9)

Pe is the characteristic oxygen partial pressure due to electronic conductivity which is defined as the oxygen partial pressure at equal ionic and electronic conductivity.

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(5)

(6)

The characteristic oxygen partial pressure depends on the temperature and the composition of solid oxide electrolyte. For the type of partially stabilized ZrO_2 (7 mole%) in the temperature range of 1300 to 1600 °C, the value of Pe can be expressed, as[4]

74370 Log P_{e =} - <u>T</u> + 24.42 (Pe, bar) (10)

With the use of Eqn(2), the calculated oxygen activity are listed in Table 1 to compare with these from the calibration equation (Eqn(1)). A comparatively good agreement is obtained between the oxygen activity using Eqn(2) and the calibration equation. An 20% difference is estimated for the calculation under the conditions of -50mv and 1350 oc.

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	tivity Relations	hip at 1350 oC			
leasured EMF (m	v) Oxygen	Oxygen Activity (ppm)			
•	Equation[2]	Calibration	Eqn.		
-25	2.97	3.76			
-50	2.05	2.68			
-75	1.42	1.91			
-100	0.98	1.36			
-125	0.67	0.97			
-150	٥.46	0.69			
-175	. 0.31	0.49			
-200	0.21	0.35			
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		•	Appendix		· •	
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•	HSRI	3.57	0.50	0.042	0.20	•
•	H5R2	3.62	0.50	0.042	0.23	· · · ·
	H6R2	3.81	0.49	0.040	0.21	
	H6R3	3.85	0.48	0.040	0.20	•
	H6R4	3.86	0.48	0.039	0.20	· .
	H7R1	3.94	0.50	0.041	0.18	
	H7R2	3.83	0.48	0.039	0.18	
•	H7R3	3.87	0.46	0.038	0.17	,
	H7R4	3.94	0.49	0.040	0.17	• •
•••	H8RI	4.14	0.48	0.042	0.08	
	H8R2	4.13	0.50	0.041	0.13	·
	H8R3	4.07	0.53	0.043	0.10	
	H8R4	4.20	0.54	0.044	0.12	·.
,	H9R 1	4.05	0,53	0.044	0.12	
	H9R2	4.04	0.54	0.042	0.14	
	H9R3	4.15	0.54	0.041	Q.14	
•	H9R4	4.15	0.53	0.041	0.13	
	HIORI	4.13	0.53	0.044	0.13	., 44
	H10R2	4.12	0.52	0.043	0.13	
	H10R3	4.12	0.51	0.041	0.13	
	H10R4	4.12	0.52	0.044	0.10	
	H11R1	4.10	0.53	0.046	0.13	
	H11R2	4.11	0.55	0.043	0.11	
	HIIR3	4.13	0.55	0.043	0-11	

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			• • •			•	•	
	H11R4	- 4.12	0.56	0.042	0.09	2	84	
	H11R5	4,12	0.56	0.043	0.10	•	•	
	H12R1	3.98	0.58	0.043	0.35		ພິ	
	H12R2	3.94	0.62	0.043	0.31	· · ·		
	H12R3	4.04	0.64	0.044	0.32			
	H12R4	4.01	0.63	0.046	0.37	• • •	•	
	H13R1	3.95	0.61	0.046	0.34	•	•	•
	H13R2	3.91	0.58	0.040	0.38	•		
•	H13R3	3.95	0.59	0.043	0.42			•
	HI3R4	3.95	0.60	0.043	0.42			
	H14R1	3.92	0.59	0.043	0.44	•		
	H14R2	3.85	0.60	0.043	.0.48	.	•	
	H14R3	3.89	0.58	.0.042	0.42		•	
	H14R4	3.94	0.59	0.045	0.46		•	
	H15R	4.03	0.97	0.046	1.53		-	1
	. H15R	4.03	0.84	0.035	1.63			
	HIGR	4.02	0.80	0.041	1.47			
	H16R	4.01	0.82	0.044	1.52			
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APPENDIX III

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APPENDIX IV

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Appendix IV

Estimation of the Effective Diffusivity of Calcium Vapor through the Porous Reaction Product Layer

The mechanism of calcium carbide desulphurization was clearly described in Chapter 5. It was found that the formation of the calcium sulphide and graphite layer will reduce the rate of desulphurization. The reason for this is that the diffusion of calcium vapor is hindered by the reaction product layer. This phenomenon can be described by the following rate equation in spherical co-ordinates.

 $(N_{Ca})_{r,t} = 4 \Pi r^{2D}_{eff,Ca} (\frac{1}{2})$ (1)

where (NCa)r,t is the rate of calcium vapor diffusion.

Deff,Ca is the effective diffusivity of calcium vapor through the reacted layer.

r is the distance from the center of the particles.

t is the time of reaction.

When desulphurization is occuring, the interface of the

unreacted core moves towards the center of the calcium carbide particle. Therefore the effective cross sectional area for diffusion of calcium vapor is changing constantly. Since the rate of diffusion is much greater than the movement of the reaction interface, it is reasonable to assume that quasi-steady state is attained within the particle. Therefore by integrating Eqn (1) with respect to the distance only, one obtains

$$N_{Ca} = -\frac{4\pi r_{ori}}{(r_{o} - r_{i})} \quad D_{eff,Ca} (C_{Ca} - C_{Ca}^{eq})$$
(2)

Where rist the radius of the unreacted core of calcium carbide.

ro is the outer radius of the calcium carbide particle.

Deff,Ca is the effective diffusivity of calcium vapor through the reacted layer.

Figures 1A and 1B show the desulphurization results of Talballa et al[1]. The effective diffusivity can be calculated based on such data. In their experiments, a hole of 56 mm in diameter and a depth of 20 mm was made in the center of the calcium carbide block and a small amount of

iron-carbon sulphur alloy weighing 5 grams was placed in thehole. Experiments were carried out at two, different temperatures, i.e, 1370 °C and 1450°C. The reaction time was precisely controlled. After finishing the experiments, the argon stream was used to quench the crucible and samples. The samples were then analysed by microprobe and X-ray diffraction techniques in the interface region between the calcium carbide and carbon alloy metal. The results of their microprobe analysis are shown in Figure 2A. Figure 2B shows the the schematic representation of the unreacted calcium carbide together with a product layer consisting of calcium carbide and residual graphite. According to their results, it is evident that calcium carbide decomposes to form graphite and calcium vapor. The calcium vapor diffuses through the reaction product layer and reacts with sulphur at the interface to form calcium sulphide. As the reaction proceeds, the graphite layer recedes towards the center of the particle. In the meantime, the calcium sulphide layer is growing outwards from the original interface.

It is apparent that the desulphurization curves can be divided into 3 regions for the purpose of analysis. For all the curves, the desulphurization were found to be fast initially (region A), then slowing down to a plateau (region B), and finally the desulphurization power of carbide were resumed again (region C). Their microprobe

data indicate that the reaction of region A is due to a large amount of dissociated calcium available at the interface of the carbide and melt. Thus fast desulphurization is observed. The reaction of region B can be explained as the region in which the reaction product layer retards the diffusion of calcium vapor. The resumption of calcium carbide desulphurization of region C may be caused by the development of fissures and cracks at the interface to provide a fresh calcium carbide surface. Therefore more calcium is available to react with sulphur. According to this experimental observations, it is reasonable to consider that the reaction of region B could be the limiting step due to the reaction product layer control which dominates the desulphurization kinetics. Therefore the effective diffusivity of calcium vapor through the reacted layer can be calculated by this isolated desulphur ration mechanism. The effective diffusivity is defined as the ratio of the diffusate flux over the diffusate concentration gradient. Thus the effective diffusivity of calcium vapor can be expressed as follows:

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 $D_{eff,Ca} = \frac{J_{Ca}(v)}{\Delta C / \Delta r}$ (3)

where $J_{Ca,(v)}$ is the flux of calcium vapor, $\Delta C/\Delta r$ is the

concentration gradient of calcium vapor across the reaction product layer.

For the purpose of obtaining the calcium vapor diffusion flux, the desulphurization data is used to calculate the sulphur flux removed by the reaction. Then the equilvalent calcium vapor flux can be indirectly obtained through the stoichiometical relationship of the reaction:

 $CaS = Ca(v) + \underline{S}$ (4)

It is noted that the consumption of one mole of calcium vapor requires one mole of sulphur. For instance, the initial and final reaction time of region B can be estimated from Figure 18. The amount of sulphur flux removed by the reaction is found to be about 2.96×10^{-5} mole/ m²/s at 1370 °C. The thickness of the reacted layer can be calculated by the stoichiometic relationship:

 $CaC_2 = Ca(v) + 2 C$ (5)

Since the amount of sulphur removed by the reaction is known, the density of calcium carbide, the reaction product layer of calcium sulphide, and residual graphite are also known, the thickness of the reaction product layer of calcium sulphide and graphite can be calculated accordingly. For the present case, the thickness of the graphite and the reaction product of calcium sulphide are calculated to be $1.7X10^{-5}$ and $2.1X10^{-5}$ m, respectively.

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The equilibrium calcium vapor concentration can be calculated by the following equation:

$$C_{Ca}(v) = \frac{P_{Ca}}{R T}$$

where P_{Ca} is the equilibrium partial pressure of calcium vapor with pure calcium carbide, R is the gas constant, 8.314 J/ mole/K, T is the temperature, K.

The equilibrium partial pressure of calcium vapor with pure calcium carbide can be obtained by the reaction:

$CaC_2 = Ca(v) + 2 C(s)$ (7)

At 1370 °C, the equilibrium partial pressure of calcium vapor is calculated to be 1.74×10^{-4} atm. Therefore, the corresponding calcium vapor concentration is 1.3×10^{-3} mole/m3. The concentration gradient is calculated to be

33.9 mole/m4. Finally the effective diffusivity can be calculated from Eqn(3). The calculated effective diffusivity is about 9.35X10⁻⁷ m2/s at 1370 °C. The other calculations at various initial sulphur contents are shown in Table 1.

In summary, the value of the effective diffusivity of calcium vapor through the reaction product layer of calcium sulphide and residual graphite is estimated approximately to bein the range 1.0×10^{-5} to 1.0×10^{-7} m² /s.

Table 1

The Effective Diffusivity of

Calcium	Vapor at	1370	οC

5%	D (m²/s)	
0.5 %	4.14X10 ⁻⁶	
0.4 %	9:35X10-7	
0.2 7	3.77X10-7	

Reference

M. Talballa et al, 'Mechanism of Desulphurization--of

Liquid Iron Carbon Alloy with Solid CaC2 and CaO', AFS

Transactions, 76-122, pp.775 - 786.



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Figure 2A

Microprobe results of Ca, S, Fe, and C concentration profile across Fe/CaC₂ interface after 5 minutes reaction time at 1370 oC. 316

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Figure 2B

Schematic representation of the reaction product layer in the reaction region between CaC_2 and Fe.



Figure 3

in ...

Carbon content of liquid iron versus time in desulphurization of iron. Note that carbon contents did not change during desulphurization.

APPENDIX

PROGRAM ONEPLDS As dicussed in ChapterS, a ONEPLDS FORTRAN-language computer program was developed to model hot metal desulphurization kinetics by calcium carbide powder injection. This program uses Gear's method to solve a set of ordinary differential equations for momentum, heat , and mass transfer in a rising plume. The model calculates the volume fractions, velocities, temperatures, and compositions of the gas, liquid and solid phases as they rise in the plume. Ealcium carbide powder injection. This program uses Gear's method C solve a set of ordinary differential equations for momentum, heat C d mass transfer in a rising plume. The model calculates the volumeC ctions, velocities, temperatures, and compositions of the gas, C uid and solid phases as they rise in the plume. IMPLICIT REAL(A-Z) COMMON RHOP, PD, MFRP, P, FP, RMUL, RMUG, SRCE. TLB COMMON RHOP, PD, MFRP, F, FP, RMUL, RMUG, SRCE. TLB COMMON CPLA, CPLB, CPLC, CPCA, CPCB, CPCA, CPCB, CPCC COMMON SIO, EPSL, EPSP, RKL, RKG, AML, AMP, AMO, HPL, HBL, HPC, REPO COMMON SIO, EPSL, EPSP, RKL, RKG, AML, AMP, AMO, HPL, HBL, HPC, REPO COMMON SIO, EPSL, EPSP, RKL, RKG, AML, AMP, AMO, HPL, HBL, HPC, REPO COMMON SIO, EPSL, EPSP, RKL, RKG, AML, AMP, AMO, HPL, NBL, MPC, MCM COMMON VSU, J, API, THL1, DTHL, METWIT, LSSG, DEFFS, ROI, RO2, DX, CBS1 COMMON VASC, LP, DJ, FROI, GAMI INTEGER N, METH, MITER, INDEX, IMA(9), IER, K, L REAL Y(8), WK(180), H, X, TOL, XEND, MFRG, MFRL, MFRP, XKVIS REAL, Z(200), TG(200), TL(200), FFI(200), FFG(200), CBS2(200) REAL EFFF(200), RATEE(200), CFF1(200), PAT2(200), CFF3(200), CBS2(200) REAL EFFF(200), DAP2(200), DTHL2(200), PAT2(200), CDNC(200), THL(200) NHB G=9, 81 ECTION CONDITIONS is the volumeC the gas-INJECTION CONDITIONS C PRINT*, 'IMPUT REAGENT INJECTION RATE(KG/MIN)' READ(3, *)MR MFRP=MR/60.0 PRINT*, 'IMPUT GAS FLOW RATE(L/MIN)' READ(3, *)GR MFRG#1, 44*1.01E5/298.0/296.5/60.0/1000.0*GR C LANCE IMMERSED DEPTH DEPLM=0.63 C LADLE DIAMETER C CCC HOT METAL CONDITIONS C HOT METAL CONDITIONS C PRINT+, 'IMPUT HOT METAL TEMPERATURE C' READ(5,*)TEMP PRINT+, 'IMPUT HOT METAL WEIGHT KQ' READ(5,*)METWI PRINT+, 'IMPUT INITIAL SULPHUR CONTENT IN WTX' READ(5,*)WTS PRINT+, 'IMPUT SILICON CONTENT IN WTX' READ(5,*)WTS PRINT+, 'IMPUT CARBON CONTENT IN WTX' READ(5,*)WTC PRINT+, 'IMPUT MN CONTENT IN WTX' READ(5,*)WTC C HOT METAL DEPTH DEPLG=METWI/(0.385*7000.0) C DISTANCE BETWEEN LANCE TIP AND BOTTOM OF LADLE C MODER 0-0.45 c CH=DEPLG-0. 65 EFFECTIVE DIFFUSIVITY OF Ca VAPOR PRINT*, 'IMPUT'EFFECTIVE DIFFUSIVITY OF Ca VAPOR' READ(5,*)DEFCA CCC CALCULATION OF SULPHUR DIFFUSIVITY DSUL=7. 4E-3+EXP (-21000. 0/(1. 987*(TEMP+273. 0)))+1. 0E-4 CALCULATION OF PLUME DIAMETER DIAPL=0. 01*(0. 102+0R+31. 6) REAGENT PARTICLE SIZE DPR=24. 0E-6 PD=24. 0E-6

CCC ATOMIC WEIGHT OF IRON AWL=56. CCC DENSITY OF IRON . RHOL=7000. CCC VISCOSITY OF LIQUID IRON AT 1600C, POSE RHUL=. 006 000 THERMO CONDUCTIVITY OF LIQUID IRON AT 1600C RKL=33. CCC EMISSIVITY OF LIQUID IRON EP6L=. 9 CCC SIGMA FOR RADIATION OF HEAT 8IG=. 5669E-07 HEAT CAPACITY COEFF. OF LIQUID IRON CPLA=10. CPLB=0. CPLC=0. CCC ATOMIC WEIGHT OF POWDER AWP=64. CCC DENSITY OF POWDER RHOP=2220. CCC EMISSIVITY OF POWDER EPSP=. 5 CCC HEAT CAPACITY COEFF. OF POWDER CPPA=14. 4 CPPB=. 284E-02 CPPC=-. 207E+06 ATOMIC WEIGHT OF ARGON GAS ANG=40. C ENGINEERING GAS CONSTANT č · R=296. 5 ATMOSPHERIC PRESSURE Ĉ PATM=101300. CCC DRAQ COEFF. FOR BUBBLE IN THE LIGUID RCD=2. 66 C CALCULATION OF INITIAL BUBBLE DIAMETER IN THE PLUME BD1=0.025 BD=BD1/2.0 CALCULATION OF REAGENT PARTICLE NUMBER PATNO1=MFRP/(2220.0*(4.0/3.0)*3.14*(12.0E-6)**3.0) CALCULATION OF INITIAL SULPHUR CONC. METVOL=NETWT/7000.0 TCPOWS1=METWT*(WTS/100.0)/0.032 CBS1=TCPOWS1/METVOL ĉ CALCULATION OF PARTICLE VOLUME

```
VPON=4. 0/3. 0+3. 14+(12. 0E-6)++3. 0
   CCC
      CALCULATION OF PARTICLE SURFACE AREA
           APON=4. 0+3. 14+(12. 0E-6)++2
   CCC
     DENSITY OF Cas
      .
        DENCAS=2500. 0
   c
   č
     DENSITY OF CaC2
           DENCAC=2220. 0
   CCC
    INITIAL CONDITION OF SOLID REACTED LAYER
           THRT=1.0E-9
                             .
  CCC
     INITIAL CONDITION OF ROL, RO2
           R01=12.0E-6
R02=12.0E-6
                                    .
  C C C
    VISCOSITY OF CAS AT ROOM TEMPERATURE
         RMUC=. 3213E-04
  CCC
    THERMO CONDUCTIVITY OF GAS
          RKQ=. 051
  ç
    HEAT CAPACITY COEFF. OF GAS
          CPCA=6. 66
CPGB=: 102E-02
CPGC=0.
 CCC
    INITIAL CONDITION POWDER FRACTION
       F=. 0001
 000
    DENSITY OF CAS AT S. T. P.
         ROGSTP=PATM/R/298.
 c
    FRACTION OF CAB
 ē
      FP=1.-F
 C
    THETA FOR THE POWDER INITIALLY
 ç
    THP=(MFRP/RHOP)/(.5+MFRG/ROGSTP+MFRP/RHOP)
CCC
   THETA FOR THE GAS
         TH#1, -THP
RHOP=2220.0
UG=0.001+0R/0.0000785
RHOM=RHOP=THP+R00STP#TH
UMO=(RHOP=THP+R00STP#TH#UG)/(RHOP#THP+R00STP#TH)
FR01=UMD#22.0/(0.01*9.8)/(RHOL/RHOM-1.0)
GAM1=RHOL/RHOM
   CALCULATION OF JET PENETRATION DEPTH
       CALL JET10
LP=0.01+LP
DJ=0.01+LP
DJ=0.04-CH/LP
LP=0.01+CH/CH/LP
LP=CH
ENDIF
HE=0.65+LP
LP=CH
ENDIF
HE=0.65+LP
CAP=MFRC/(0.25+3.14+DP(0+DP(0))
FLXP=MFRC/(0.25+3.14+DP(0+DP(0)))
000
  THETA FOR THE LIQUID
        THL=. 1
с
```

CALCULATION OF THETA FOR THE PONDER THP=THP-THL+THP 11 . CALCULATION OF THETA FOR THE GAS TH=TH-THL+TH CROSS SECTION AREA OF PLUME AT Z=0.0 AP=. 25+3. 1416+LP1+LP1 INITIALIZE Z=0.0 ĉ X=0. 0 TEMPERATURE OF LIQUID BATH TLB=1350. TEMPERATURE OF GAS AT Z=0.0 TCO=300. C TEMPERATURE OF LIQUID AT Z=0.0 TL0=1350.

321

1

CCC TEMPERATURE OF POWDER AND LIQUID AT Z=0,0 TPL0=300.

TEMPERATURE OF POWDER AND GAS AT Z=0.0 TPG0=300.

SET 20=0.0

CCC

CCC

CCC

CCC

20=X RATE1=0.0 RRATE1=0.0

VARIABLES INITIALIZED

Y(4)=TL0 Y(5)=TPL0 Y(6)=TPC0 Y(7)=TC0

HTS+METWT/0.032/100.0/METV CBS: 2011

AVERAGE LOGARITHMIC HYDRAULIC STATIC PRESSURE PM=(RHOL+Q+HE)/ALOO((PATM+RHOL+Q+HE)/PATM) MEAN GAS FLOW RATE AT LIQUID METAL TEMPERATURE GGM=MFR0+R+TLB/PM INITIAL CIRCULATING FLOW RATE OF LIQUID

QLC=1. 17+(QGM+G+HE+(, 785+DP0+DP0)++2.)++. 339 INITIAL LIQUID VELOCITY FROM SAND AND MORI USM=1. 17*(QQM+G+HE/, 785/DPO/DPO) ++. 346-

INITIAL LIQUID VELOCITY FROM SAMAI AND GUTHRIE USQ=4, 176+00Mat, 333+HE++, 25/(DLAD/2,)++, 333

DENSITY OF GAS INITIAL CONDITION

RHDG=(PATM+RHOL+G+(HE-X))/R/TOD INITIAL CONDITION

Y(1)=NFRG/AP/TH/RHOQ Y(3)=MFRP/AP/THP/RHOP Y(2)=GLC/.783/(DLAD+DLAD-DPO+DPO) C MASS FLOW RATE OF LIQUID

MFRL=AP+RHOL+THL+Y(2)

FLUX OF LIQUID

FLXL(1)=MFRL/AP

REQUIREMENTS FOR DOEAR

TOL=0.000	01
H=0.00001	
NETH=2	-
MITER=2	•
INDEX=1	

CCC

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C PRINTING OF THE CONSTANTS USED

	MATE(3/ 77/	the state and share shares and sh
	WRITE(3,102)	HE, DLAD, RHOL, RHOP, ROOSTP
1	WRITE(3,101)	· · · · · · · · · · · · · · · · · · ·
	PRINT 101	· · · · ·
	UBTTE/2 (03)	
•	1011E 3/102/	
	PRINT 102, RC	Dribbi FFRQ, FLXQ
	WRITE(3, 1000)
	PRINT 1000	
	UDITE/2 LOAL	A C OD MCOO CLYD (
÷.	MUTIE(3) 1001	
	PRINT 1001, F	PD, MFRP, FLXP
1	WRITE(3,1002	
	WRITE(3, 1003	
	UPTTE (3.100	
	MULIC(3) 1003	/ AHCIAHPIANU
	WRITE(3, 1005	}
	WRITE(3, 1001) RKL, RKQ, EPSL, EPSP
	WRITE(3, 100A	
	UDITE (3. 1003	COLA COLO COLO
÷.	10116(3) 1003	
	WRITE(3, 1007	
	WRITE(3, 1003) CPPA, CPPB, CPPC
	WRITE(3, 1008)	
	WRITE(3, 1003	CROA. CROR. CROC
	UPTTE/2. 1021	F VI WIT VI WUT VI WV.
	WRC11E(3)104)	- X; Y (1); Y (2); Y (3); TH; THP; MFR(; DJ

AVERAGE, ZERO

SUM1=0.
C10/2-0
SUNJ#0.
SUM4=0.
SUM5=0
CINK - A
SKCE=0.
SUM7=0.
THI 1 STHE
ADIAD
UC 1 THE
T1=0,0
L=89

C THE DO LOOP FOR THE CALCULATION OF PLUME DIAMETER AS FUNCTION OF Z

CS S

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DO 10 K=1,L XEND=FLOAT(K)/(FLOAT(L)/HE) DX=XEND=X

C CALCULATION OF PLUME DIAMETER

C AP=3. 14/4+DIAPL+DIAPL C CALCULATION OF MASS TRANSF

CALCULATION OF MASS TRANSFER COEFFICIENT KSUL1=0. 82*(DSUL+(Y(1)-Y(2))/BD)**0./5

C CALCULATION OF BUBBLE SURFACE AREA

P1=(1.01E5+7000.0+9.8+(HE-XEND))/1.01E5 GR1=GR/1000.0+(Y(7))/(P1+60.0+298.0) NDBLB=GR1/(4.0/3.0+3.14+BD++3.0) TAREA-NDBLB+4.0+3.14+BD++2.0 APOW+4.0+3.14+(12.0E-6)++2.0

CALCULATION OF CALCIUM CARBIDE PARTICLES RESIDING ON BUBBLES PATNO2=TAREA/(3,14+12,0E-6++2,0)

```
IF (PATNO2, LT. PATNO1 ) THEN PATNO=PATNO2
            RSTS1=1.0/(PATNO+KSUL1+APOH)
           ELSE

PATNO=PATNO1

RST91=1.0/(PATNO+KSUL1+APOW)

ENDIF

F=(PATNO1-PATNO)/PATNO1

IF(F.LT:0.0001)THEN

F=0.0001

ENDIF

FP=1-F
CCC
   CALCULATION OF EQUILIBRIUM PARTITION RATIO OF SULPHUR BETWEEN GAS/METAL PHAS
          CULATION OF EQUILIBRIUM PARTITION RATIO OF SULPHUR BETWEEN

QCASG=-B67331.5+253 1*(TEMP+273.0)

LGKCAS=CASG/(-2.303*8.314*(TEMP+273.))

KCAS=10.0+H.GKCAS

KCAS1=KCAS**(-1.0)

OSGG=293486.48-84.18*(TEMP+273.0))

LGKSE=GSSG/(-2.303*8.314*(TEMP+273.0))

KSS=10.0+*(LGKSS)

LGFS=0.11*HTC-0.026*HTMN+0.028*HTP+0.0066*HTSI-0.028*HTS

FS=10.0+*(LGKSS)

LGFS=0.11*HTC-0.026*HTMN+0.028*HTP+0.0066*HTSI-0.028*HTS

LSSG=FS*KSS/(0.1799*(TEMP+273))

ACTS=HTS*FS

MS1=PATNO+KSUL1*APOW

MS3=12.36*PATNO+R02*RO1*DEFCA/THRT

GCAC=218070.1-60.88*(TEMP+273.0)

LGPCA=GCAC/(-2.303*8.314*(TEMP+273.0))

CCA=PCA*1.01E5/8.314/(TEMP+273)

CSI=1.01E5/LSE/8.314/(TEMP+273)

CI1*MS1*Y(8)

CI1*MS1*Y(8)

CI3=MS3*CCA
              2=MS1+CS1
             I3=M83+CCA
          E1=C11-C13
IF(E1.LT.0.000)THEN
RSTS1=1.0/(PATNO+KSUL1+APOW)
RSTS3=0.0
          ELSE
PSI=(CI1-CI3)/CI2
  CALCULATION OF EQUIVALENT EFFECTIVE SULPHUR VAPOR DIFFUSIVITY
          DEFFS=DEFCA+(PCA/PSI)
  CALCULATION OF FRACTION OF CONTROL FOR CONTACT CONTROL
          RSTS1=1.0/(PATNO+KSUL1+APOW)
  CALCULATION OF FRACTION OF CONTROL FOR PRODUCT LAYER CONTROL
          RSTS3=1.0/((PATND+LSSG+R02+R01+DEFFS)/THRT)
ENDIF
  CALCULATION OF OVERALL CONTROL
          RSTS4=R8TS1+RSTS2+RSTS3
 USE DEGEAR
      CALL DGEAR(N, FCN1, FCN2, X, H, Y, XEND, TOL, METH, MITER, INDEX, IWK, WK, IER)
 EVALUATION OF VARIABLES USING RETURNED Y VALUES
 CALCULATION OF GAS PHASE DENSITY IN RISING PLUME
         RHOG=(PATM+RHOL+G+(HE-X))/R/Y(7)
 CALCULATION OF GAS PHASE VOLUME FRACTION
```

and the state

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No. of Concession, Name

TH=MFRG/AP/Y(1)/RHOG CALCULATION OF SOLID PHASE VOLUME FRACTION

THP=MFRP/AP/RHOP/(FP+Y(3)+F+Y(1))

CALCULATION OF MIXTURE DENSITY OF GAS AND SOLID PHASE
```
RHOM=RHOO+TH+RHOP+F+THP
000
    CALCULATION OF LIQUID PHASE VOLUME FRACTION
            THL=1. -TH-THP
THLL(K)=THL
CCC
   CALCULATION OF LIQUID CIRCULATION RATE
            MFRL=AP+RHOL+THL+Y(2)
CCC
    CALCULATION OF THE THICKNESS OF THE REACTION PRODUCT LAYER
           CULATION OF THE THICKNESS OF THE REACTION PROL
CPOWS4=TCPOWS3/PATNO1
TCPOWS5=TCPOWS3
CPLMS=TCPOWS3/METVOL
WTS1=(CPLMS#METVOL+0.032)/METWT*100.0
WTS2=WT91+HTS2
RIN=0.064*CPOWS4/(2220.0*4.0*3.14*RO1+*2.0)
THRIN=RIN
ROUT=0.072*CPOWS4/(2500.0*4.0*3.14*RO2**2.0)
THROUT=ROUT
THROUT=ROUT
THROT=RIN
RO2=ROUT
THRT=THRIN+THR
    CALCULATION OF CALCIUM CARBIDE EFFICIENCY
             EFF=(12,0E-6**3.0-RD1**3.0)/12.0E-6**3.0*100.0
PRINT*, 'EFFICIENCY OF PARTICLE',EFF
   EVALUATION OF SOURCES TERM
CALCULATION OF FLUX OF LIGUID GOING THROUGH PLUME
0000
             J=K+1
FLXL(J)=MFRL/AP
CCC
    INCREMENT OF LIQUID FLUX AS FUNCTION OF DISTANCE
             SRCE=(FLXL(J)-FLXL(K))/DX
CCC
    RENOLD NUMBER
             REP=RHOL*PD*(Y(3)-Y(2))/RMUL
CCC
    ACCUMULATION
            SUM1=MFRL*DX+SUM1
SUM2=Y(2)*DX+SUM2
SUM3=TH*DX+SUM3
SUM3=TH*DX+SUM3
SUM5=Y(1)*DX+SUM4
SUM5=Y(3)*DX+SUM6
SUM7=SUM7+RATE*DX
SUM8=SUM8+KSUL1*DX
AP1=AP
DTHL=(THLL(K)-THLL(K-1))/DX
H=SUM4/XEND
T2=XEND/H
    ŝ
 CCC
    CALCULATION OF CALCIUM CARBIDE DESULPHURJZATION RATE
C RATE=LOG(WTS/(WTS-WTS2))/T2
C STORING DATA FOR SUBSEGUENT PRINTING
EFFF(K)=EFF
RATEE(K)=RATE
KOVSS(K)=KOVS
Z(K)=X
TL(K)=Y(4)
TG(K)=Y(4)
TG(K)=Y(5)
              TPL(K)=Y(5
              TPG
             TPG(K)=Y(6)
CPS(K)=Y(8)
PHPL(K)=HPL
PHBL(K)=HPL
PHPG(K)=HPG
PRNUSO(K)=RNUSG
PREPG(K)=REPG
CF1=RSTS1/(RSTS1+RSTS2+RSTS3)
CF3=RSTS2/(RSTS1+RSTS2+RSTS3)
CF3=RSTS3/(RSTS1+RSTS2+RSTS3)
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CFF2(K)=CF2 CFF3(K)=CF2 CFF3(K)=CF3 DAP2(K)=DAP DTHL2(K)=DTHL PAT2(K)=PAT CON=Y(G)=METVOL+0.032/METWT+100.0 CONC(K)=CON PRINTING OF FLUID DYNAMIC DATA ē WRITE(3, 104) X, Y(1), Y(2), Y(3), TH, THP, MFRL, DP, RHOO, RHOM CONTINUE ·10 FINAL SUM OF THE AVERAGES PRINT+, 'EFFICIENCY OF CAC2', EFF, 'RATE=', RATEE(K) SUM1=SUM1/HE SUM2=SUM2/HE SUM3=SUM3/HE SUM3=SUM4/HE SUM3=SUM4/HE SUM3=SUM4/HE 000 SUMA=SUMA/HE SUMA=SUMA/HE SUMA=SUMA/HE SUMB=SUMB/HE PRINT*, 'EFFICIENCY', EFF PRINT*, 'RATE OF DESULPHURIZATION', RATE RESIDENCE TIMES FOR GAS AND PARTICLES RTC=HE/SUM4 RTP=HE/SUM6 CCC PRINTING OF AVERAGE VALUES TRINT 107, SUM1, SUM2 WRITE (3, 107) SUM1, SUM2 PRINT 110, SUM3, SUM4 WRITE (3, 110) SUM3, SUM4 PRINT 111, SUM5, SUM6 WRITE (3, 111) SUM5, SUM6 PRINT 112, RT0, RTP WRITE (3, 112) RT0, RTP PRINT 113, USM, USG WRITE (3, 113) USM, USG CCC PRINTING HEAT TRANSFER DATA WRITE(3,1110) WRITE(3,104) ZO, TLO, TGD, TPLO, TPGO DO 40 K=1,L WRITE(3,104) Z(K), TL(K), TG(K), TPL(K), TPG(K), PHPL(K), PHBL(K) , PHPG(K), PRNUSG(K), PREPG(K) 40 CCC ERROR MESSAGES FROM DGEAR CONTINUE FRINT 108 WRITE(3,108) PRINT 105, IER, XEND, H. X, INDEX WRITE(3,105) IER, XEND, H. X, INDEX STOP 20 C C C C FORMAT STATEMENTS 99 FORMAT(///,3X, 'H, M', 8X, 'DLAD, M', 5X, 'RHL, KG/M3', 2X, 'RHOP, KG/M3', +2X, 'RHOGSTP') 101 FORMAT(/,3X, 'CDRAG', 6X, 'BD, M', 7X, 'MFRG, KG/S', 2X, 'FLXG, KG/S/M2/') 102 FORMAT(X, 3(E11, 4)) 1000 FORMAT(/,3X, 'FINGAS', 5X, 'DP, M', 7X, 'MFRP, KG/S', 2X, 'FLXP, KG/S/M2') 1001 FORMAT(X, 4(E11, 4)) 1002 FORMAT(/,3X, 'DJET, M', 5X, 'DPLUME, M', 3X, 'ALFA, DEG') 1003 FORMAT(1X, 3(E11, 4)) 325

1004 1005 1006 1007 1008 FORMAT(/, 3X, FORMAT(/, 3X, FORMAT(/, 3X, FORMAT(/, 3X, FORMAT(/, 3X, ALWL', 7X, ATWP',7X, ATWO') KL, W/M/DO',2X, KG, W/M/DO',2X, 'EPSL',7X, 'EPSP') 'CPLA',7X, 'CPLB',7X, 'CPLC') 'CPPA',7X, 'CPB',7X, 'CPPC') 'CPGA',7X, 'CPOB',7X, 'CPGC') 'SPLA',7X, 'CPOB',7X, 'CPGC') ČPOČI) 5%, 10 DTHL1,6%,1% P.D.B1, Ξx. Ī17 CRMAT(//, X, 'CONC') PLU A SX) 118 326

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