MASS TRANSFER STUDIES BETWEEN GAS-BUBBLES AGITATED METAL AND SLAG SYSTEMS

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By

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "MASS TRANSFER STUDIES BETWEEN GAS-BUBBLES AGITATED METAL AND SLAG SYSTEMS" in fulfilment of the requirement for the award of the Degree of Doctor of Philosophy, submitted in the Department of Metallurgical Engineering of the University is an authentic record of my own work carried out during a period from Sept.80 to Oct. 1985 under the supervision of Dr. M.L. Kapoor, Dr. R.D. Agrawal and Dr. S.S. Gupta.

The matter embodied in this thesis has not been submitted by me for the award of any other degree.

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ABSTRACT

Drops and bubbles are of great importance to the extractive metallurgists in his attempts to speed up processes by the use of sprays, foams, and jets. The metallurgist is doing this by using discontinuous phases so as to increase the surface area across which reactions take place, and to make convective processes in the vicinity of these surfaces as vigorous as possible.

It is well known that the presence of sulphur in steels unfavourably affects its mechanical and physical properties. Further, it has been observed that the sulphur present in pig iron directly goes to the steels in more or less same amount. So, for quality steel production it is necessary to reduce the sulphur content in the pig iron which is used as raw material in the various steel-making processes. Extensive work has been done in past in removal of sulphur during extraction and refining but at the cost of productivity and economy. However, external desulphurisation has off-late proved to be quite useful process for removal of sulphur in between iron making and steelmaking stages. Still, substantial work may be done to optimize the external desulphurisation process with regard to the technology and desulphurising agents used to improve the economy of the process. In external or ladle desulphurisation use of soda base slags have been

established to be very useful for bringing down the sulphur level in the melts. However, no systematic kinetic study has been reported in literature on external desulphurisation using soda-base slags with gas bubble stirring.

The present work has, therefore, been taken-up to study systematically the kinetics of desulphurisation of nitrogen gas bubble- stirred pig iron melt by soda-base slag. The effect of variables, such as, amount of slag-140, 210 & 280 gms per 1000 gms of pig iron; gas flow rate-4.6, 9.4,23.7,38,0.48.0 & 61.3 l/hr; Na_2O/SiO_2 molar ratio-0.6,0.8,1.0,1.2,1.4 & 1.6 ; addition of Al_2O_3- 0, 1.5, 8.06% at Na_2O/SiO_2 molar ratio of 1.0 ; addition of CaF_2-0, 2.886, 5.538% at Na_2O/SiO_2 molar ratios 0.6 & 1.0 ; addition of FeO- 0, 0.807, 2.59% at Na_2O/SiO_2 molar ratio 0.6 & 0, 1.768, 3.94% at Na_2O/SiO_2 molar ratio 1.0 ; and temperature -1280,1350 & 1400°C on transfer of sulphur from pig iron to soda-base slag have been studied.

The entire text of the dissertation has been divided into four chapters.

Chapter I has been devoted to the brief introduction of the problem and critical review of literature comprising of preparation of reagents, contacting techniques, desulphurising reagents, method of sulphur analysis, thermodynamic studies and kinetic studies with emphasis on the kinetics of desulphurisation and finally the formulation of the problem.

Chapter II deals with the experimental set-up, materials used, preparation of slags, and actual experimental runs.

In Chapter III the experimental results and discussion have been reported. Results of present work are compared, wherever possible, with the relevant data in literature.

Finally, Chapter IV lists the major conclusions drawn from the present investigation.

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CONTENTS

		Page No.
	CERTIFICATE	(i)
	ABSTRACT	(ii)
	ACKNOWLEDGEMENTS	(v)
	CONTENTS	(viii)
	LIST OF FIGURES	(xi)
	LIST OF TABLES	(xiv)
	NOMENCLATURE	(xv)
CHAPTER-I	GENERAL	1-60
	1.1 Introduction	1
	1.2 Literature Survey	3
	1.2.1 Preparation of reagents	3
	1.2.2 Contacting techniques	4
	1.2.3 Reagents	7
	1.2.3.1 Soda-base reagents	7
	1.2.3.2 Calcium-base reagents	8
	1.2.3.3 Magnesium-base reagents	10
	1.2.3.4 Miscellaneous reagents	11
	1.2.4 Method of sulphur analysis	12
	1.2.5 Thermodynamic studies	14
	1.2.6 Kinetic studies	21
	1.2.6.1 General	21
	1.2.6.2 Theoretical analysis	21

1.2.6.2.1 Derivation of mass transfer expression 21

1.2.6.2.2 Models proposed to explain mass transfer across a phase boundary 26

1.2.6.3 Role of stirring in liquid phase mass transfer 31

1.2.6.4 Gas bubble-agitated liquid reactive systems 32

1.2.6.4.1 Characteristics of bubbles formed at an orifice in a gas-stirred liquid bath 32

1.2.6.4.2 Analysis of gas-bubble characteristics 38

1.2.6.4.3 Experimental investigation related to mass transport in agitated reactive systems 41

1.2.7 Typical experimental investigations on desulphurisation-effects of reagents and techniques adopted 44

1.3 Formulation of the Problem 52

CHAPTER-II EXPERIMENTAL 61-73

2.1 Experimental Set-Up 61

2.1.1 Gas purification train 61

2.1.2 Gas mixing unit 63

2.1.3 Slag preparation unit 65

2.1.4 Gas-bubble agitated slag-metal contacting unit 65

2.2 Materials Used 68

2.3 Preparation of Slags 69

2.3.1 Preparation of FeO 69

2.3.2 Purification of quartz 71

2.3.3 Blending and melting of slags 71

2.3.4 Homogenisation of slags 72

2.4 Experimental Runs 72

2.5 Chemical Analysis 73

CHAPTER-III RESULTS AND DISCUSSION 74-150

3.1 Effect of Change in Slag Weight 129

3.2 Effect of Gas Flow Rate 132

3.3 Effect of Slag Basicity 138

3.4 Effect of Alumina 140

3.5 Effect of Calcium Fluoride 142

3.6 Effect of FeO 143

3.7 Effect of Temperature 144

3.8 Comparison with Others 146

CHAPTER-IV SUMMARY AND CONCLUSIONS 151-154

4.1 Summary 151

4.2 Conclusions 151

SUGGESTIONS FOR FUTURE RESEARCH PROGRAMMES 155

REFERENCES 156-174

LIST OF FIGURES

Fig.No.	Title	Page No.
2.1	Schematic block diagram of experimental set-up.	62
2.2	Schematic diagram of nitrogen purification train.	64
2.3	Gas mixing unit	66
2.4	Sulphur transfer study unit.	67
3.1	Effect of slag weight on rate of sulphur removal from pig iron.	107
3.2	Effect of slag weight on rate of sulphur transfer from pig iron to slag.	108
3.3	Effect of slag weight on rate of desulphurisation of pig iron.	109
3.4	Effect of gas flow rate on rate of sulphur removal from pig iron.	110
3.5	Effect of gas flow rate on rate of sulphur transfer from pig iron to slag.	111
3.6	Effect of gas flow rate on rate of desulphurisation of pig iron.	112
3.7	Effect of Na_2O/SiO_2 molar ratio on rate of sulphur removal from pig iron.	113
3.8	Effect of Na_2O/SiO_2 molar ratio on rate of sulphur transfer from pig iron to slag	114
3.9	Effect of Na_2O/SiO_2 molar ratio on rate of desulphurisation of pig iron.	115
3.10	Effect of Al_2O_3 addition to slag on rate of sulphur removal from pig iron.	116

3.11 Effect of Al_2O_3 addition to slag on rate of sulphur transfer from pig iron to slag. 117

3.12 Effect of Al_2O_3 addition to slag on rate of desulphurisation of pig iron. 118

3.13 Effect of CaF_2 addition to slag on rate of sulphur removal from pig iron. 119

3.14 Effect of CaF_2 addition to slag on rate of sulphur transfer from pig iron to slag. 120

3.15 Effect of CaF_2 addition to slag on rate of desulphurisation of pig iron. 121

3.16 Effect of addition of FeO to slag on rate of sulphur removal from pig iron. 122

3.17 Effect of addition of FeO to slag on rate of sulphur transfer from pig iron to slag. 123

3.18 Effect of addition of FeO to slag on rate of desulphurisation of pig iron. 124

3.19 Effect of temperature on rate of sulphur removal from pig iron. 125

3.20 Effect of temperature on rate of sulphur transfer from pig iron to slag. 126

3.21 Effect of temperature on rate of desulphurisation of pig iron. 127

3.22 Spherical cap bubble showing wake, and by arrows directions of flow relative to the bubble. 135

3.23 Effect of gas flow rate on mass transfer. 137

3.24 Effect of Na_2O/SiO_2 molar ratio, Al_2O_3, CaF_2, and FeO content of slag on mass transfer. 139

3.25 Mass transfer in various systems as a function of gas throughput 147

3.26 Mass transfer as a function of surface renewal time in various systems. 149

LIST OF TABLES

Table No.	Title	Page No.
1.1	Results of typical desulphurisation studies.	53-59
2.1	Characteristics of soda-slags used in the present investigation.	70
3.1-3.32	Run No. 1-32 .	75-106
3.33	Summary of results.	128
3.34	Mass transfer coefficient in metal and slag phases.	131
3.35	Bubble frequency and diameter at different gas flow rate.	134
3.36	Surface renewal time for different gas flow rate .	150
4.1	Mass transfer coefficient for different operating variables.	152-153

NOMENCLATURE

A	interfacial area
A_B	bubble front cross section
B	slag basicity
B^*	special function defined by eqs.(1.11 and 1.12)
C_S	sulphur capacity of slag
$[C_b]_t$	molar concentration in bulk metal phase at time, t
$(C_b)_t$	molar concentration in bulk slag phase at time, t
$[C_b]_\infty$	molar concentration in bulk metal phase at infinite time
$(C_b)_\infty$	molar concentration in bulk slag phase at infinite time
$[C_i]_t$	interfacial molar concentration in metal phase at time, t
$(C_i)_t$	interfacial molar concentration in slag phase at time, t
D	diffusivity
F	frequency of bubble formation
G	gas flow rate (gas throughput)
H	depth of orifice in liquid
J	rate of sulphur transfer
K	equilibrium constant
L	distribution coefficient
$N_{M^{x-}}$	ionic fraction of M^{x-} ions
N_{MO}	mole fraction of MO
N_{Mo}	Morton's number

$N_{Re,O}$	orifice Reynold's number
$N_{Re,b}$	bubble Reynold's number
N_{We}	Weber's number
P	pressure
S	rate of production of fresh surface per unit area
T	temperature
V_M	volume of metal
V_S	volume of slag
V_b	bubble volume
a_i	activity of component i
d_b	bubble diameter
d_{be}	volume of a sphere of volume equal to bubble (equivalent spherical bubble diameter)
d_{bvs}	volume surface mean diameter of the bubble (defined by eq.1.43)
d_o	orifice diameter
f_X	activity coefficient of X
g	acceleration due to gravity
g_c	conversion constant for eq.(1.46)
h_M	height of metal phase
h_S	height of slag phase
k	mass transfer coefficient
k_M	mass transfer coefficient in metal phase
k_S	mass transfer coefficient in slag phase

$n_{O^{2-}}$	number of gram ions of oxygen in 100 gms of slag in addition to the oxygen requirements for formation of SiO_4^{4-}, PO_4^{3-} and $Al_2O_3^{3-}$ ions
$\dot{n}$	total flux
p_g	partial pressure of g
t_R	residence time of bubble in the liquid
t_e	exposure time
u	rising velocity of bubble
u_t	terminal velocity of bubble
wt% S	weight % sulphur
$[wt\%S_b]_o$	initial weight % sulphur in bulk metal phase
$[wt\%S_b]_t$	weight % sulphur in bulk metal phase at time, t
$(wt\%S_b)_t$	weight % sulphur in bulk slag phase at time, t
$[wt\%S_b]_\infty$	weight % sulphur in bulk metal phase at infinite time (equilibrium weight % sulphur in bulk metal phase)
$(wt\%S_b)_\infty$	weight % sulphur in bulk slag phase at infinite time (equilibrium weight % sulphur in bulk slag phase)
β	special function defined by eq.(1.13)
δ	thickness of the boundary film
Δt	surface renewal time
μ_S	viscosity of slag
μ_l	viscosity of liquid
η_A	rate of transfer per unit area

ρ_M	density of metal phase
ρ_S	density of slag phase
ρ_g	density of gas phase
σ	surface tension

Because of these adverse effects of sulphur, the metallurgists have, in general, concentrated their efforts for a long time to minimise the contents of this harmful element in metals and alloys and in particular in steels. Sulphur enters the reduced metal in pyrometallurgical processes from raw materials mainly the fuel viz. coal, coke or liquid fuels. In different smelting and refining operations, it gets partitioned between the metal and the slag phases. Therefore, for control of sulphur during these operations, different operating variables such as slag volume, viscosity and basicity, oxygen content of bath, temperature etc. must be precisely controlled. It has also been observed that efficiency of desulphurisation is much higher while treating hot metal or the pig iron, for external desulphurisation or in the iron blast furnace practice as compared to steel-making processes, primarily because activity coefficient of sulphur and therefore its reactivity and transfer into slag-phase is several orders of magnitude greater under reducing conditions of blast furnace or external desulphurisation as compared to oxidising conditions of steel-making. In blast furnace operation also, the extent of desulphurisation is limited. Hence external desulphurisation using a variety of techniques and reagent-combinations, has been considered a preferred technique.

Several efforts have, therefore, been made in the past to study behaviour of this element in metallurgical systems encountered generally in extraction and refining of metals. Both thermodynamic and kinetic studies on

1.2.2 Contacting Techniques

Different techniques used for contacting either in batch or continuous operation includes :

(a) Addition to metal stream- reagents have been added to metal stream either in the forehearth or onto the metal during tapping operation and either directly[9] or using a nozzle arrangement[10]. Powdered reagent such as ground lime, aluminium powder etc., are generally used for introduction just below the surface of metal whereas in the lumpy form these are added to the runner[8]. Primary limitations of this technique include inconsistency of results and the poor degree of desulphurisation[11]. Both concurrent and counter-current flow of reagent and metal can be used.

(b) Addition to the ladles- reagents forming both solid[12,13] and liquid slags[14-16] have been added in the ladles. Soda ash[15] is normally placed at the bottom of the ladle before tapping. A variation of this technique used for addition of cerium alloy[8] and recently with magnesium-based reagents also consists of introduction inside a steel holder into the metal by means of a weighted rod arrangement. Solid desulphurising agents such as lime, calcium carbide and cynamide require excessively long contact time[17]while using this technique.

(f) Reaction within seperate vessels - many different types of vessels, particularly designed for intimate mixing of desulphuring agent and molten metal but requiring additional capital outlay to attain the increased desulphurising efficiency have been used, e.g., a shaking ladle[27,28], capable of variable speed eccentric rotation, has been used for desulphurisation with burnt lime or calcium carbide. A rocking ladle[29,30] using calcium carbide has been used for desulphurisation of cast iron and also foundry iron and hot metal for steel-making with excellent desulphurisation efficiency at low reagent rates. The bottom blown ladle technique uses injection of air or gas through the bottom of a ladle using tuyere arrangement or porous plugs technique [31-33]. Air or nitrogen has been used to introduce calcium carbide or soda ash. The improved agitation of bath & contact between reactants results in high desulphurisation efficiency at faster rate. The centrifugal ladle technique has the advantage of faster and more efficient desulphurisation specially with lighter materials due to intimate mixing[34]. Rotary reactors for desulphurising iron, bring powdered lime and metal into close contact resulting in very rapid and almost complete desulphurisation[35-38]. Syphon ladle[39] is claimed to result in reduced reagent consumption, e.g., in case of soda ash and soda-lime mixtures by about 50%. A suction cup arrangement[40]involving two cups has been used for rapid desulphurisation of pig iron using soda ash. Electromagnetic mixing[41]has also been used but is costly to prevent commercial application. It is thus observed that a variety of techniques and also reagents have been used for desulphurisation. Choice in any specific case depends upon, (i) degree of desulphurisation required, (ii) final sulphur level, and, (iii) prevailing works condition.

1.2.3 Reagents

Various desulphurisation reagents used either singularly or in combination are based either on alkali or alkaline - earth metals with high affinity for sulphur. The calcium and magnesium based reagents have proved more efficient, cost effective and yield more consistent results. The metal cerium and its compounds, although, most efficient desulphuriser, is too expensive for industrial application.

1.2.3.1 Soda-base reagents

Soda-ash, the common sodium based reagent is comparatively cheap but (a) has limited desulphurising capacity (b) is more effective for higher sulphur ranges only, (c) suffers from inconsistency in performance, (d) causes serious environmental pollution problems resulting from noxious fumes and gases produced during treatment (d) the slag produced being highly corrosive, substantially shortens the life of hot metal ladles due to severe refractory attack[42,43], (f) results in occasional problems due to blocking of lance in injection process, and (g) use of pure Na_2O accelerates slagging of silicon of hot metal so that the basicity and therefore the sulphur partition is not improved[44]. Soda ash has also been used mixed with other materials such as lime-soda mixtures, soda ash-fluorspar mixtures, and, even an alloy of sodium and cerium. Advantages of use of soda over other reagents, however, include (a) Na_2O reduces viscosity of synthetic slags and improves their refining capacity[45,46], (b) Na_2CO_3 is a powerful flux for both dephosphorisation and desulphurisation[47-56], and, a Na_2CO_3 - Na_2SO_4 mixed-flux is considered very effective for simultaneous dephosphorisation and desulphurisation[57-61], (c) oxidation of manganese and carbon in hot metal is minimum with soda treatment[62], and, (d) after recovery of soda ash, the waste slag does not have the property of disintigration and is as stable as ballast made from blast furnace slag and is therefore useful as a building material[62].

1.2.3.2 Calcium-base reagents

Lime[42,50,63] is inexpensive but results in high slag volume and therefore handling problems. It can be used in granulated form or as powder but needs intense mixing with hot metal. Desulphurising capacity of lime falls as initial sulphur falls in metal and hence comparatively larger quantities are necessary for equivalent desulphurisation capacity. It also tends to coagulate on storage which in turn reduces the effective surface area for reaction. Advantages of use of lime include, (a) production of a solid slag, which is less corrosive towards refractories, (b) ready availability in the blast furnace plant, and, (c) comparable cost with other desulphurisers.

Calcium carbide[6,42,43,63-66] is very useful desulphuriser with high efficiencies possible, produces a dry granular slag comparatively easy to seperate from the metal, results in much less associated silicon losses compared to soda ash and therefore, much less fume emmision problem. However, capital cost of infra structure for dispensing the reagent either by pneumatic lance injection or by mechanical stirring methods is very high, stringent conditions in its storage and handling are to be observed to minimise risk of acetelene explosion specially in slags formed on desulphurisation in presence of moisture.

Calcium cynamide, although used by several workers[11,13], is not as effective desulphuriser as calcium carbide or lime-soda mixtures and its availability is also limited. However, the slag formed is dry, no hazardous fumes are evolved and the nitrogen released on decomposition of the cynamide, which dissolves in molten iron, can be easily removed during subsequent steel-making processes.

1.2.3.3 Magnesium-base reagents

Magnesium has been used in various forms viz. (i) granules injected via stream of carrier gas [1,2,67-70] - (ii) propritery 'mag-coke' plunged through graphite bell [71] (iii) magnesium aluminium alloy [72] and, (iv) magnesium powder mixed with lime as in 'lime-mag' process [73,74]. The last two forms, using injection technology, have also been commercially utilised with considerable success [68,75,76]. Although magnesium [1,2,77] is much superior desulphuriser but is highly energy intensive (cf. metallic calcium) and results in high cost of treatment due to high cost of metal. Also, its low boiling point and therefore increased evaporation losses necessitate its use in blended form. The main advantages of magnesium includes, (a) low equilibrium sulphur levels approaching the theoretically attainable values, (b) virtual instantaneous reactivity towards sulphur- due to its presence in vapour phase in the hot metal resulting in intense agitation and turbulent mixing of magnesium vapour with liquid metal and partitioning of sulphur through gas -liquid interface, (c) higher reaction efficiency with decreasing bath temperature - a characteristic contrary to other reagents resulting from reduction in magnesium and sulphur solubility - product with decreasing temperature, (d) a crusty- solid slag of low volume with consequent ease of slag disposal, (e) insensitivity to blast furnace carry over slag, (f) secondary desulphurisation due to the presence of residual magnesium in solid solution, resulting from sufficient solubility in Fe-C melts- the level of solubility for Mg is higher than for calcium and therefore the consequent desulphurisation effect also , (g) absence of toxic fumes and therefore no environmental pollution problems. Metallic calcium is also comparable in many respects, reduces sulphur in steel to much lower levels than magnesium viz. 1.0×10^{-7} wt% equilibrium residual sulphur with calcium compared to 2.4×10^{-3} wt% with magnesium. Magnesium compounds such as dolomite or magnesite require suitable reductants viz. silicon, aluminium, calcium or their alloys alongwith flux constituents for use as desulphurisers, require very finely powdered form compacted as briquettes which needs plunging into molten bath due to their lower density to prevent them from floating and burning-off at the surface of the molten metallic bath. Depth of plunging of the briquettes and temperature of molten bath controls reaction kinetics and the degree of utilization of magnesium-also experienced in the 'mag-coke' treatment.

1.2.3.4 Miscellaneous reagents

Use of lime-soda mixtures[11,22], fluorspar-soda mixtures or cerium alloys[8] has already been mentioned. Many other mixtures and variations have also been used, e.g., sodium chloride and lime mixtures[78], also resulting in emission of noxious and copious fumes, calcium carbide-sodium chloride mixtures[79], slags containing sodium carbonate-sodium hydroxide and calcium carbide [78], mixtures of calcined lime and dolomite [80], blast furnace slag either alone [16] or mixed with soda ash and lime [81], mixtures of soda ash and lime with metallic magnesium-calcium-sodium etc. [72,82,83] introduced into the metal by inert gas injection. Use of hydrocarbon gases e.g. methane in conjunction with desulphurising agents such as lime or lime-calcium carbide mixtures [84], N_2-10% H_2 gaseous mixture [85] have also been reported.

From the above discussion on reagents preferential position of soda-base desulphurisers primarily due to economic reasons and higher desulphurisation efficiency is obvious.

1.2.4 Methods of Sulphur Analysis

Use of different methods for analysis of sulphur have been reported in literature. However in general combustion method has been adopted. Moriya & Fujii [49] have used combustion method for analysis of carbon in metal samples and fluorescent X-rays method for other elements like S, P and Si. Bhuchar et al [86] have also used combustion method for analysis of sulphur in steel samples employing combustion in an oxygen flask with a new type of combustion boat. Inoue & Suito [59,87] adopted coulometric titration method for analysis of C and S in metal samples. They also employed methylene blue method for analysis of samples with sulphur content below 0.01% and no difference was found within the limit of analytical errors. Total sulphur in slag was determined by gravimetric determination of sulphur precipitated as barium sulphate. Takenouchi et al[88] used infrared absorption method for carbon and sulphur. LECO analyser used by Prasad[89] has also been used in the present investigation because of limited choice of available-reliable method of sulphur estimation in metal and slag samples. This method is based on infrared radiation, absorption and detection principle. Infrared source consists of a nichrome wire which is resistance heated to approximately 850°C. Infrared source radiates visible energy as well as all wavelengths in the infrared spectrum.LECO analyser consists of three subsystems - measurement unit, induction furnace, and control console. A pan balance is also built into the measurement unit. Following description refers to the carbon portion of the measuring system ; performance of the sulphur portion is identical to this with only the necessary change to accomodate a different gas SO_2. Total carbon, as carbon-di-oxide, is detected on a continuous and a simultaneous basis. Carbon-di-oxide (CO_2) absorbs infrared energy at a precise wavelength within the infrared spectrum. Energy is absorbed as the gas passes through the cell body in which the infrared energy is being transmitted. Thus at the detector, less energy is received. All other infrared energy is eliminated from reaching the detector by a precise wavelength filter. Thus, the absorption of infrared energy can be attributed to only carbon-di-oxide and the concentration of CO_2 is detected as change in energy at the detector. Accuracy of sulphur determination for above mentioned equipment is ± 0.0002 or ± 5% of the sulphur present, for sulphur concentrations less than 0.1%, and, ± 0.001 or ± 2% of sulphur present, for concentrations greater than 0.1% sulphur. Its weighing accuracy is ± 0.001 gms.

1.2.5 Thermodynamic Studies

The thermodynamic reaction of liquid iron by molten slag may be expressed as,

$$[S] + (MO) = (MS) + [O] \qquad \ldots(1.1)$$

the equilibrium constant, K_1 and distribution coefficient, L_1 as defined by Holbrook[90] and Holbrook & Joseph[91] for the above reaction may be expressed as,

$$K_1 = \frac{a_{MS} \cdot a_O}{a_{MO} \cdot a_S} = \frac{(\% MS) . f_{MS} \cdot a_O}{a_{MO} . [\% S] . f_S} \qquad \ldots(1.2)$$

and,

$$L_1 = \frac{(\% MS)}{[\% S]} = \frac{K_1 . a_{MO} . f_S}{a_O . f_{MS}} \qquad \ldots(1.3)$$

where, the symbols [ ] and ( ) indicate constituents dissolved in metal and slag phases respectively; a is the activity; f, the activity coefficient; K_1, the equilibrium constant; and, L_1, the distribution coefficient. Since fused slag is an ionic melt and liquid iron, a conductor of electrons, the slag-metal reactions are considered to proceed electrochemically. Therefore, electrochemical approaches were also used by several investigators[92-96] for study of these. According to ionic theory of slag, the reaction of desulphurisation may be expressed in terms of the ionic species as follows,

$$[S] + (O)^{2-} = (S)^{2-} + [O] \qquad \ldots (1.4)$$

the above expression involves no assumptions concerning the cations associated with oxygen and sulphur in slag. The equilibrium constant, K_4, for the above reaction may be expressed as,

$$K_4 = \frac{a_{S^{2-}} \cdot a_O}{a_S \cdot a_{O^{2-}}} \qquad \ldots (1.5)$$

Eq. (1.5), on rearrangement of terms yields,

$$\frac{a_{S^{2-}}}{a_S} = K_4 \frac{a_{O^{2-}}}{a_O} \qquad \ldots (1.6)$$

if one consider the Henrian behaviour for all components (standard state : 1 gram-ions of oxygen in 100 gms of **slag**), one may write the above equation as follows,

$$\frac{(wt\%S)}{[\%\ S]} = K_4 \frac{n_{O^{2-}}}{[\%\ O]} \qquad \ldots (1.7)$$

where, $n_{O^{2-}}$ is the number of gram-ions of oxygen in 100 gms of slag in addition to the oxygen requirements for formation of SiO_4^{4-} , PO_4^{3-} and $Al_2O_3^{3-}$ ions[97].

On the basis of data after Fetters et al[98] and Grant et al[99] on equilibrium sulphur distribution between slag and metal at 1600°C, Carter[100] by plotting (wt%S)/[%S] versus $n_{O^{2-}}$ /[%O] observed the linear behaviour of eq.(1.7). Frohberg[101] calculated the activity coefficients of oxide ion ($f_{Fe^{2+}} \cdot f_{O^{2-}}$) and sulphide ion ($f_{Fe^{2+}} \cdot f_{S^{2-}}$)

function of basicity of slag, though several different ways[99,109-114] were proposed to define 'basicity' of slag, Schenck et al[104] obtained the following equation for $CaO-MgO-Al_2O_3-SiO_2$ quaternary slag system,

$$\log (\%S)/a_S = 1.06\ B^{*2} - 0.65 \qquad \ldots (1.10)$$

where, for $N_{CaO}/N_{SiO_2} < 1.39$,

$$1.06\ B^{*2} = \beta \left\{ \frac{0.6\ N_{Al_2O_3}}{N_{SiO_2}} - \frac{0.31}{1.06} \beta \left(\frac{N_{CaO}}{N_{SiO_2}} \right)^2 \cdot \frac{N_{Al_2O_3}}{N_{SiO_2}} + \frac{N_{CaO}}{N_{SiO_2}} \right\}^2 \qquad \ldots (1.11)$$

and, for $N_{CaO}/N_{SiO_2} > 1.39$,

$$1.06\ B^{*2} = \frac{\beta\ N^2_{CaO}}{\left\{ 0.8\ N^2_{Al_2O_3} - \left(\frac{1.55\ N_{Al_2O_3}}{\beta} \right) \left(\frac{N_{SiO_2}}{N_{CaO}} \right)^2 + N_{SiO_2} \right\}^2} \qquad \ldots (1.12)$$

where, β in above expression is defined as,

$$\beta = 19\ N^2_{MgO} + 1.06 \qquad \ldots (1.13)$$

Giedroyc et al[105] defined basicity, B , of a slag by following simple relationship,

$$B = \frac{(\%CaO) + (\%MgO)}{(\%SiO_2) + (\%Al_2O_3)} \qquad \ldots (1.14)$$

and arrived at the following expression for distribution coefficient of sulphur,

$$\log (\% S)/a_S = 1.60 B - 0.38 \qquad \ldots (1.15)$$

Effect of sulphur and other elements on the activity coefficient of sulphur were investigated by a number of workers[58,60-62,115-127]. In general, deoxidisers, such as carbon, silicon, aluminium etc. increase the activity coefficient of sulphur in iron. Further, the content of oxygen in iron containing these elements will be low. Therefore, remarkable desulphurisation may be expected in such an iron. However, Suito et al [60] observed a remarkable reduction in desulphurisation and dephosphorisation in the presence of silicon as a result of consumption of flux Na_2CO_3-Na_2SO_4 for the oxidation of silicon present in iron.

Kalyanram et al[114] equilibrated the slag systems CaO-Al_2O_3-SiO_2, CaO-MgO-SiO_2 and CaO-MgO-Al_2O_3-SiO_2 with CO-CO_2-SO_2 gas mixtures at 1500°C and used their results to assess the activity of lime in these slags. They expressed their data in the form of a parameter A_{CaO} ($a_{CaO}\ \gamma^o_{CaS}/\ \gamma_{CaS} = (\% S)\ A^o/(\%S^o)\ A$; where superscript 'o' refers to a standard slag with unit lime activity and $A(= p_{S_2}^{1/2}\ /\ p_{O_2}^{1/2}$), proportional to sulphur capacity, C_S, [103,128,129]). Values of A_{CaO} were found to be a simple function of the ratio $(N_{CaO} + N_{MgO}/2\ )/(N_{SiO_2} + N_{Al_2O_3}/3\ )$. Shim & Ban-ya [21] found that SiO_2 markedly decreased the distribution ratio of sulphur between liquid iron and Fe_tO-MgO, Fe_tO-SiO_2-MgO, and

$Fe_tO-SiO_2-CaO-MgO$ system slags saturated with MgO in the temperature range of 1550-1650°C.

Toop & Samis[130], Masson[131], Whiteway, Smith & Masson[132,133], Kapoor & Frohberg [134-138], Yokokawa & Niwa[139,140], Hajra & Narayanan[141], Gaskell[142] and Richardson[143] made extensive contributions towards the understanding and prediction of the thermodynamic properties of simple binary and ternary silicate systems. Loslish[144] examined the $FeO-CaO-P_2O_5$ slag and reported that the FeO-rich slags have more desulphurising power than P_2O_5-rich slags. Toporishchev et al [145] observed that small initial values of FeO accelerate the initial desulphurisation process but retard the establishment of equilibrium. Equilibrium was established more rapidly by introducing strong deoxidising agents over a period of time . Additions of Al_2O_3 and CaF_2 contributed to considerable increase of the lime desulphurisation capacity because of liquefaction of the slag formed[88,121,146].

Several fundamental studies on external desulphurisation of hot metal using soda ash have been reported in literature[9,44,107,108]. The sulphur partition, particularly, between carbon-saturated iron and Na_2O-SiO_2 slags was studied by Korber & Oelsen [107], Oelsen[108], Domalski et al[44], and Neudorf & Elliott [147]. The sulphur partition between carbon-saturated iron melts and Na_2O-SiO_2 slags was also studied at 1250 and 1350°C in the Na_2O/SiO_2 ratios of 0.33, 0.5 and 1.5 by Inoue & Suito[87] under SO_2-CO_2-H_2 gaseous mixture atmosphere to show that sulphide capacities of Na_2O-SiO_2 slags lay between those of the CaO-CaF_2 and CaO-SiO_2 slags. Sahab Prasad[89] too studied the sulphur capacities of binary Na_2O-SiO_2 and ternary CaO-Na_2O-SiO_2 slags of different compositions at 1373,1473 and 1573 K and concluded that in case of binary Na_2O-SiO_2 slags, (i) logarithm of sulphur capacity varied linearly with N_{Na_2O} / N_{SiO_2} ratio at all temperatures of investigation, (ii) logarithmic sulphur capacity and temperature were related by reciprocal linear relationship, (iii) values of sulphur capacity of Na_2O-SiO_2 slags lie in between those of CaO-SiO_2 and CaO-CaF_2 slags. In case of ternary CaO-Na_2O-SiO_2 slags, the author concluded that, (i) with lime additions to soda slags upto 25% CaO, there is a sharp initial increase in sulphur capacity which then becomes less pronounced, (ii) at constant lime concentrations sulphur capacity increased with N_{Na_2O}/ N_{SiO_2} ratio, (iii) at constant silica levels, sulphur capacity decreased with decreased lime concentrations, (iv) iso-sulphur capacity contours showed higher logarithmic sulphur capacity values away from silica end, and, an empirical equivalence between lime and soda could be established and finally, (v) temperature causes a significant positive effect on sulphur capacities.

1.2.6 Kinetic Studies

1.2.6.1 General

In a heterogeneous reacting system the overall reaction rate may be controlled either by the rate of transport processes or of chemical reaction at the interface or both. However, at elevated temperatures, the interfacial chemical reaction is generally known to much faster than the transport processes. Therefore, chemical equilibrium is assumed to prevail at the interface and only transport processes are considered to control the overall rate of reaction.

1.2.6.2 Theoretical analysis

1.2.6.2.1 Derivation of mass transfer expression

Since slag-metal reaction is heterogeneous in nature, the overall reaction involves following steps :

i) Transport of reactants from bulk to the slag-metal interface.

ii) Interfacial chemical reaction between slag and metal, and,

iii) Transport of products from interface to the bulk.

The overall rate of transfer of dissolved elements from metal to slag will, therefore, be determined by the slowest of the above steps. The rate determining step may also change according to the experimental conditions of the reactive system under study and is not always the same for any particular reaction. Experimental determination of the rate-determining step is very difficult, because the rate of individual steps can not be measured independently.

As already pointed out at elevated temperatures because of the fast chemical reaction rates, the mass transport step controls the overall rate of reaction and chemical equilibrium is considered to exist at the interface. Thus for desulphurisation reaction, the rate of sulphur transfer J, (gm/sec) from metal to slag across the interface under steady state conditions, can be expressed by the relationship,

$$\begin{aligned} J &= - k_M A \{ [C_b]_t - [C_i]_t \} \\ &= - k_S A \{ (C_i)_t - (C_b)_t \} \qquad \ldots (1.16) \end{aligned}$$

where, k_M & k_S are respectively the mass transfer coefficients for sulphur in metal and slag phases, (cm/sec); A, the interfacial area, (cm^2); $[C_b]_t$ & $(C_b)_t$, the concentrations of sulphur in bulk metal and slag phases respectively at time t, (gm/cm^3); and, $[C_i]_t$ & $(C_i)_t$, the interfacial concentrations of sulphur on metal and slag side respectively at time t, (gm/cm^3). Further since chemical equilibrium prevails at the interface, assuming Henrian behaviour of sulphur in metal and slag phases, one can write the following expression for the distribution coefficient, L,

$$L = \frac{(C_i)_t}{[C_i]_t} \qquad \ldots (1.17)$$

It is to be noted that L, will be a function of temperature and compositions of slag- and metal- phases.

The above expression can also be rewritten as,

$$L = \frac{\rho_S (\text{wt\% } S_i)_t}{\rho_M [\text{ wt\% } S_i]_t} \qquad \ldots (1.18)$$

where, ρ_M & ρ_S are respectively the densities (gm/cm^3) of metal and slag phases; and $(\text{wt\% } S_i)_t$ & $[\text{wt\% } S_i]_t$ respectively, the interfacial sulphur weight percents on slag and metal sides. Also under steady state conditions,

$$J = \frac{d}{dt} \{ V_M \, [C_b]_t \}$$

$$= V_M \rho_M \frac{d \, [\text{wt\% } S_b]_t}{dt} \qquad \ldots (1.19)$$

where V_M & V_S are respectively the volumes of metal and slag phases.

Therefore, using eq.(1.17) and eq.(1.19), eq.(1.16) may be rewritten as,

$$V_M \rho_M \frac{d [\text{ wt\% } S_b]_t}{dt} = - k_M A \{ [C_b]_t - [C_i]_t \}$$

$$= - L k_S A \{ [C_i]_t - (C_b)_t / L \} \qquad \ldots (1.20)$$

which on rearrangement of terms gives,

$$\frac{V_M \rho_M}{A} \frac{d [\text{ wt\% } S_b]_t}{dt} = \frac{[C_b]_t - (C_b)_t / L}{\frac{1}{k_M} + \frac{1}{L k_S}} \qquad \ldots (1.21)$$

Further, from mass balance criteria,

$$V_M[C_b]_t + V_S(C_b)_t = V_M[C_b]_\infty + V_S(C_b)_\infty \qquad \ldots (1.22)$$

where, $[C_b]_\infty$ & $(C_b)_\infty$ are respectively the concentrations of sulphur in bulk metal and slag phases at infinite time.

Further since interfacial concentration will be equal to the bulk concentration at infinite time, so one can write eq.(1.21) in the following alternative form,

$$\frac{d[\text{wt\% } S_b]_t}{dt} = -\frac{\frac{1}{h_M} + \frac{1}{Lh_S}}{\frac{1}{k_M} + \frac{1}{Lk_S}} \{[\text{wt\% } S_b]_t - [\text{wt\% } S_b]_\infty\} \qquad \ldots (1.23)$$

where, h_M & h_S are respectively the heights of metal and slag columns in the reaction vessel.

Integration of above equation leads to the following expression,

$$\ln \frac{[\text{wt\% } S_b]_t - [\text{wt\% } S_b]_\infty}{[\text{wt\% } S_b]_o - [\text{wt\% } S_b]_\infty} = -\frac{\frac{1}{h_M} + \frac{1}{Lh_S}}{\frac{1}{k_M} + \frac{1}{Lk_S}}\, t \qquad \ldots (1.24)$$

where, $[\text{wt\% } S_b]_o$, is the wt% sulphur in bulk metal at time $t = 0$.

Eq. (1.24) can also be written as,

$$\ln \frac{[\text{wt\% } S_b]_t - [\text{wt\% } S_b]_\infty}{[\text{wt\% } S_b]_o - [\text{wt\% } S_b]_\infty} = -k\left(\frac{1}{h_M} + \frac{1}{Lh_S}\right) t \qquad \ldots (1.25)$$

where, k, the overall mass transfer coefficient is defined by the expression,

$$\frac{1}{k} = \frac{1}{k_M} + \frac{1}{Lk_S} \qquad \ldots(1.26)$$

Two specific cases arise from the above general relationship :

Case I : Assuming L to be large and therefore $Lk_S >> k_M$ and also $Lh_S >> h_M$, one gets,

$$\frac{1}{k_M} + \frac{1}{Lk_S} \simeq \frac{1}{k_M} \qquad \ldots(1.27)$$

and therefore, eq.(1.24) takes the following form,

$$\ln \frac{[\text{wt\% } S_b]_t - [\text{wt\% } S_b]_\infty}{[\text{wt\% } S_b]_o - [\text{wt\% } S_b]_\infty} = - \frac{k_M}{h_M} t \qquad \ldots(1.28)$$

In other words, for this case, the rate of overall chemical reaction will be controlled by the mass transfer in metal phase.

Case II : Assuming L to be very small and therefore $Lk_S << k_M$ and $Lh_S << h_M$, one gets,

$$\frac{1}{k_M} + \frac{1}{Lk_S} \simeq \frac{1}{Lk_S} \qquad \ldots(1.29)$$

and therefore eq.(1.24) reduces to,

$$\ln \frac{[\text{wt\% } S_b]_t - [\text{wt\% } S_b]_\infty}{[\text{wt\% } S_b]_o - [\text{wt\% } S_b]_\infty} = - \frac{k_S}{h_S} t \qquad \ldots(1.30)$$

meaning thereby that in this case the reaction will be controlled by the mass transfer of sulphur in slag phase.

In all other cases, the overall reaction rate will be controlled jointly by the mass transfer of sulphur in both slag- and metal-phases as indicated by eq. (1.24).

1.2.6.2.2 Models proposed to explain mass transfer across a phase boundary

Following theories have been proposed to explain the mass transfer across an interface in an agitated/stirred system.

a) The two-film theory :

In this theory [148] , it is assumed that turbulence dies out at the interface and a laminar layer exists in each of the two fluids. Outside the laminar layer, turbulent eddies supplement the action caused by the random movement of the molecules, and the resistance to transfer becomes progressively smaller. For equimolecular counter-diffusion, the concentration gradient close to the interface is therefore linear and gradually becomes less at greater distance. The basis of the theory is the assumption that the zones in which the resistance to transfer lies can be replaced by two hypothetical layers, one on each side of the interface, in which the transfer is entirely by molecular diffusion. The concentration gradient is therefore linear in each of these layers and zero outside. Equilibrium is assumed to exist at the interface.

The mass transfer is treated as a steady state process and therefore the theory can be applied only if the time taken for the concentration gradients to become established is very small compared with the time of transfer, or if the capacity of the film is negligible. The rate of transfer per unit area η_A, in terms of the two-film theory for equimolecular counterdiffusion may be expressed for the first phase (phase-1) by following relationship,

$$\eta_A = \frac{D_1}{\delta_1} (C_{o1} - C_{i1}) = k_1 (C_{o1} - C_{i1}) \quad ..(1.31)$$

where D_1, is the diffusivity; δ_1 the thickness of the film; C_{o1}, the molar concentration outside the film; C_{i1}, the molar concentration at the interface; and, k_1, the mass transfer coefficient, for this phase.

For the second phase (phase-2), using similar notations,

$$\eta_A = \frac{D_2}{\delta_2} (C_{i2} - C_{o2}) = k_2 (C_{i2} - C_{o2}) \quad ... (1.32)$$

Because material does not accumulate at the interface, the two rates of transfer expressed by eqs. (1.31 & 1.32) must be identical. Therefore,

$$\frac{k_1}{k_2} = \frac{C_{i2} - C_{o2}}{C_{o1} - C_{i1}} \quad ... (1.33)$$

The flow conditions are too complex for the film thickness to be evaluated. However, these are progressively decreased as the turbulence of the fluid is increased.

b) The penetration theory :

This theory [149] assumes that the eddies in the fluid bring an element of fluid to the interface where it is suddenly exposed to the second phase for a definite interval of time, for reaction to proceed, after which the surface element is mixed agains with the bulk fluid. It is further assumed that equilibrium is immediately attained by the surface layers and that a process of unsteady state molecular diffusion then occurs and also that the element is remixed after a fixed interval of time. In the calculation, depth of the liquid element is assumed to be infinite and this is justifiable if the time of exposure is sufficiently short for penetration to be confined to the surface layers. Throughout, the existence of velocity gradients within the fluids is ignored and the fluid at all depths is assumed to be moving at the same rate as the interface.

With the boundary conditions,

$t = 0 \quad 0 < y < \infty \quad C_A = C_o$

$t > 0 \quad y = 0 \quad C_A = C_i$

and,

$t > 0 \quad y = \infty \quad C_A = C_o$

where, C_o is the concentration in the body of the phase; and, C_i, the equilibrium value at the interface. The rate of transference per unit area, η_A, across the phase may thus be given as,

$$\eta_A = (C_i - C_o) \sqrt{\frac{D}{\pi t}} \qquad \ldots (1.34)$$

This equation gives the instantaneous transfer rate when the surface element under consideration has an age t. If the element is exposed for a time t_e, the average rate of transfer is given by,

$$\eta_A = 2\,(C_i - C_o)\sqrt{\frac{D}{\pi t_e}} \qquad \ldots(1.35)$$

Thus, the shorter the time of exposure, the greater is the rate of mass transfer. No precise value can be assigned to t_e in any practical equipment, but its value will clearly becomes less as the degree of agitation of the fluid is increased.

c) The random surface renewal theory :

In this theory [150] it is considered that each element of surface would not be exposed for the same time, but a random distribution of ages would exist. It is assumed that the probability of any element of surface becoming destroyed and mixed with the bulk of the fluid was independent of the age of the element.

By supposing the rate of production of fresh surface per unit total area of surface to be S, and that S is independent of the age of the element, the overall rate of transfer per unit area, when the surface is renewed in a random manner can be expressed as,

$$\eta_A = (C_i - C_o)\sqrt{D\,S} \qquad \ldots\ (1.36)$$

conditions are similar to those in the Two- Film Theory.

The boundary conditions are same as in the Penetration Theory, but the third boundary condition is applied at $y = \delta$, the film thickness, and not at $y = \infty$. With these boundary conditions the rate of mass transfer was given by,

$$\frac{\delta^2}{Dt} \geq \pi, \quad \eta_A = (C_i - C_o)\sqrt{\frac{D}{\pi t}}\ \{1 + 2e^{-\delta^2/Dt}\} \quad ..(1.37)$$

$$\frac{\delta^2}{Dt} \leq \pi, \quad \eta_A = (C_i - C_o)\ \frac{D}{\delta}\ \{1 + 2e^{-\pi^2 Dt/\delta^2}\} \quad ...(1.38)$$

The mass transfer rates given by eqs. (1.37 & 1.38) are point values at surface elements of age t. The mean transfer rates can be obtained, by assuming that all surface elements are exposed for the same time t_e, or by assuming a random age distribution. For very short time of exposure eq. (1.37) reduces to eq. (1.34) for the Penetration Theory, and for long exposures eq. (1.38) reduces to eq.(1.31) for the Two- film Theory. The difficulty in applying eqs. (1.37 & 1.38) are that they involve two quantities, the film thickness and the time of exposure, neither of which is readily known.

1.2.6.3 Role of stirring in liquid phase mass transfer

Improvement in the overall rate of reaction in a heterogeneous system as a result of stirring due to enhanced mass transport is well - known. Different methods used for stirring include mechanical stirring, pneumatic stirring, electromagnetic stirring, gas bubbles stirring etc. [7,23-25,152-160].

1.2.6.4 Gas bubble-agitated liquid reactive systems

A reactive liquid system can be gas-bubble agitated due to, (i) evolution of dissolved gas resulting from decreased solubility, e.g., hydrogen and nitrogen evolution from molten steel on cooling, (ii) production of gas due to chemical reaction within the liquid phase, e.g., CO evolution in molten steel resulting from deoxidation with carbon, and, (iii) flow of an inert gas through the liquid bath.

1.2.6.4.1 Characteristics of bubbles formed at an orifice in a gas-stirred liquid bath

At very low gas flow rates through an orifice, the bubble diameter and the frequency of bubble formation may be determined [161] by the balance between the buoyancy and the surface tension forces. Thus for $N_{Re,O} < 500$,

$$\frac{\pi}{6} d_b^3 g (\rho_l - \rho_g) = \pi d_o \sigma \qquad \ldots (1.39)$$

where, d_b and d_o, are respectively the bubble and orifice diameters; ρ_l and ρ_g, respectively the liquid and gas densities; $N_{Re,O}$, the orifice Reynold's number; and, σ, the surface tension. As evident from the above expression, the bubble diameter is independent of flow rate of the gas. Under these conditions, frequency of bubble formation is proportional to the volumetric flow rate and the orifice diameter.

At intermediate gas flow rates ($500 < N_{Re,O} < 2100$), the bubble size depends upon the gas flow rate and nozzle diameter. The frequency of bubbles emerging from the orifice increases with an increase in the gas flow rate until a limiting value is reached. For the air-water system, Davidson & Emick [162] presented the following empirical relationships,

$$d_b = 0.54\ (G\ .\ d_o^{0.5})^{0.289} \qquad \ldots (1.40)$$

and,

$$F_{max} = 6.7\ G^{0.13}\ d_o^{0.43} \qquad \ldots (1.41)$$

where, G is the gas flow rate; and, F_{max}, the maximum frequency of bubble formation which may range from 25 bubbles/sec for a 1.6 cm diameter orifice to 75 bubbles/sec for a 0.035 cm diameter orifice.

Variation of mean bubble diameter with gas flow rate and orifice diameter, expressed in terms of the orifice Reynold's number was also studied by Leibson et al [163] for the air-water system. In laminar region ($N_{Re,O} < 2100$), they presented the following correlation,

$$d_b = 0.29\ d_o^{0.5}\ N_{Re,O}^{0.333} \qquad \ldots (1.42)$$

At high gas flow rates, small bubbles of varying sizes are formed at about 10 cm above the orifice by disintegration of large irregular bubbles formed at the orifice. Leibson et al [163] proposed the following equation for bubble diameter in the turbulent range,

$$d_{bvs} = 0.71\, N_{Re,O}^{-0.05} \qquad \ldots (1.43)$$

where, d_{bvs} is the volume surface mean diameter of the bubble and $N_{Re,O} > 10000$ in above equation.

The velocity at which bubble rises through a liquid is determined principally by the buoyancy force that drives the bubble upwards, and the viscous and form drag that tend to retard this motion. When these forces are equal, the bubble rises at a constant velocity. The principal parameters which characterise the motion of bubble include

i) bubble Reynold's number, $N_{Re,b} = \dfrac{d_{be} . u . \rho_1}{\mu_1}$ ...(1.44)

ii) Weber number, $N_{We} = \dfrac{d_{be} . u^2 \rho_1}{g_c . \sigma}$ ...(1.45)

and, iii) Morton number, $N_{Mo} = \dfrac{g\, \mu_1^4}{\rho_1 (g_c \sigma)^3}$ ...(1.46)

where, d_{be} is the diamter of a sphere of volume equal to the bubble under study; u, the rising velocity of the bubble; μ_1, viscosity of the liquid; and, g_c, the conversion constant. With the help of these parameters, behaviour of bubbles in accordance with [164] can be classified into four categories.

(a) Very small bubbles: small bubbles, for which $N_{Re,b}<2$, rise at a terminal velocity determined by Stokes' law, expressed as,

$$u_t = \frac{d_b^2}{18\mu} g (\rho_l - \rho_g) \qquad \ldots(1.47)$$

these very small bubbles behave like rigid spheres, because the surface tension inhibits circulation of the gas.

(b) Intermediate size spherical bubbles : these bubbles with $2 < N_{Re,b} < 400$, are still spherical and rise in a rectilinear path, but their rising velocity may be as much as 50% greater than that predicted for very small bubbles.

(c) Spheroidal and ellipsoidal bubbles : the bubbles in this region, with $400 < N_{Re,b} < 5000$, may be spheroidal or ellipsoidal and rise in the fluid in a spiral path.

(d) Spherical cap bubbles : bubbles of diameter above 1 cm with $N_{Re,b} > 5000$ and $N_{We} > 18$, are of spherical-cap shape and rise at a terminal velocity which is independent of the properties of the liquid. The rising velocity of such bubbles may be expressed by the following expression derived by Davies & Taylor [165] ,

$$u_t = 1.02 \left(\frac{g.d_b}{2} \right)^{0.5} \qquad \ldots(1.48)$$

Growth of bubbles takes place due to diffusion of gas from the liquid to the gas-phase and during their rise in the liquid, because its pressure decreases with decreasing liquid head. Since the velocity of rising bubble is related to its size, for calculating its residence time, the change in bubble size with distance above the orifice must be taken into account. In the spherical-cap bubbles, the terminal rising velocity can be related to the bubble volume by the following expression,

$$u_t \simeq 0.8\, g^{1/2}\, V_b^{1/6} \qquad \ldots(1.49)$$

where, the bubble volume $V_b = \pi\, d_b^3\, /6$

For $g = 980$ cm/sec^2 one gets,

$$u_t \simeq 25\, V_b^{0.167} \qquad \ldots(1.50)$$

By denoting the vertical distance of the bubble from the orifice, by x and assuming that the terminal velocity corresponding to a certain bubble size is attained very rapidly, one may write,

$$u_t = \frac{dx}{dt} = 25\, V_b^{0.167} \qquad \ldots(1.51)$$

In order to integrate above equation it is necessary to relate the bubble volume to the vertical co-ordinate x. For an isothermal system, the pressure- volume relationship in the bubble can be expressed by the ideal gas,

$$P_x\, V_x = P_o\, V_o \qquad \ldots(1.52)$$

where, V_x & V_o are the bubble volumes respectively at a distance x from the orifice and at the orifice; and P_x & P_o, the corresponding pressures. The pressure at orifice can be calculated by adding the atmospheric pressure above the bath and the liquid head. Thus,

$$P_o = P_{atm} + \rho_l \, g \, H \qquad \ldots(1.53)$$

where, H is the depth of orifice in the liquid (in cm). The pressure, P_x, on the bubble at a distance x from the orifice may be expressed as,

$$P_x = P_o - \rho_l g \, x \qquad \ldots(1.54)$$

By combining eqs. (1.50-1.52) with eq. (1.54), one gets,

$$\frac{dx}{dt} = 25 \left(\frac{P_o \, V_o}{P_o - \rho_l g \, x} \right)^{0.167} \qquad \ldots(1.55)$$

and on subsequent integration of eq. (1.55) between the limits,

$x = 0$, at $t = 0$

and $x = H$, at $t = t_R$

where, t_R is the residence time of the bubble in the liquid, one arrives at the following expression,

$$t_R = \frac{P_o^{1.167} - (P_o - \rho_l g \, H)^{1.167}}{29.2 \, \rho_l \, g \, (P_o \, V_o)^{0.167}} \qquad \ldots(1.56)$$

In derivation of eq.(1.56), it was assumed that the expanding bubble attains its new terminal velocity instantaneously, i.e., with a negligible time lag. This assumption is valid for practically all gas-liquid systems.

1.2.6.4.2 Analysis of gas-bubble characteristics

Hughes et al [166], Hayes et al [167] and Sullivan et al [168] studied the characteristics of the gas bubbles under laminar flow conditions at the orifice and observed that volume of the bubble formed was initially independent of the gas flow rate. However, as the gas flow rate and hence the orifice Reynolds number was increased, the frequency of bubble formation increased in this region. With further increase in the gas flow rate, the frequency of bubble formation reached a maximum and the volume of the bubble formed at the orifice increased significantly. Haberman & Morton [169], Hartunian & Sears [170], Garner & Hammerton [171], Peebles & Garber [172], Davies & Taylor [165] also carried out extensive studies on the characteristics of gas bubbles in aqueous type liquids. Lanauze & Harris [173], Kumar et al [174], Siemes & Haufmann [175], Siemes [176], Davidson & Schuler [177,178] tried to model their experimental findings with various degrees of success. Papamantellos et al [179] put forward a mathematical model which is adaptable to practical conditions to describe the purging of liquid steel with an inert gas. Sano & Mori [180] investigated the nitrogen mercury & nitrogen - silver systems at 25°C & 1000°C respectively and observed a transition from varying to constant bubble formation frequency in both systems. Bulk of their work was carried out under constant flow conditions. Under laminar flow conditions, Andreini et al [181] studied the characteristics of gas bubbles injected into molten tin, lead, and, copper. They found that the bubble size generated for a particular orifice diameter was dependent upon the magnitudes of the orifice, and the Frude and Weber numbers. Several other workers [182-188] reported theoretical and experimental studies on mass transfer into rising bubbles in metallurgical systems. Guthrie & Bradshaw [185] reported experimental data on the transfer of oxygen to molten silver during bubble rise. These studies followed earlier work [183,184] using CO_2 in aqueous solutions and were designed to test the applicability of general mass transfer theory to these types of systems. Baird & Davidson [189] developed a theoretical model for the mass transfer into spherical cap bubbles based on unsteady state diffusion. The model considers only transfer to or from the front surface. Following expression was arrived at for mass transfer coefficient, k,

$$k = 0.975\, d_{be}^{-1/4}\; D^{1/2}\; g^{1/4} \qquad \ldots (1.57)$$

where, d_{be}, is the diameter of a spherical bubble with a volume equal to that of the spherical cap bubble (equivalent spherical bubble) ; D, the diffusivity in the metal; and g, the acceleration due to gravity. This equation was tested for solutes in water & alcohol [184, 189] and for oxygen in liquid silver [183,185] and it was found that the equation was valid within about 20%. Richardson [190,191] carried out the work on drops and bubbles in liquid metals and represented the rate of transfer of gaseous solute between the liquid and the bubble in terms of an average mass transfer coefficient, k_M, in the metal by the following equation,

$$\dot{n} = k_M . A \{ [C_b] - [C_i] \} \qquad \ldots(1.58)$$

where, $\dot{n}$, is the total flux; A, the bubble area; and, $[C_b]$ & $[C_i]$, respectively the bulk and interfacial concentrations in the metal.

In liquid steel, bubbles smaller than 2 mm are spherical shaped, but with increasing volume they tend to become elliptical. With diameters greater than 8 mm, the bubble ascending in stagnant liquid layer are cap shaped [183,185,192,193], their ascending velocity is determined only by their size. Kraus [194] derived relationship for the ascending velocity for bubbles less than 8 mm diameter and Davies & Taylor [165] for ascending velocity for bubbles greater than 8 mm diameter. Guthrie & Bradshaw [183], Richardson [195] and Johnson et al [196] derived relationship for the mass transfer across the flat phase boundary area of the bubble cap.

Sano and Mori [197] presented a mathematical model to describe circulating flow in a molten metal bath with inert gas injection. The model is based principally on the energy balance for the liquid phase. In the model, effects of gas hold-up in the bubble plume zone and energy dissipation due to bubble slip are taken into account. It has been shown by them that the 'liquid velocity' and the 'liquid circulating flow rate' are both directly proportional, and, 'mixing time', inversely proportional to one-third power of the gas flow rate or stirring power of gas. Asai et al [198] also developed theoretically a correlation between mixing time and mixing power density for gas agitation from the view point of transport phenomenon and confirmed the theoretical results by the water model experiments. They concluded from their studies that same formulation can be employed both in 'gas agitation 'and 'mechanical agitation' as far as the relationship between fluid velocity and mixing power density is concerned.

1.2.6.4.3 Experimental investigation related to mass transport in agitated reactive systems

Little work has however been reported on the mass transfer between gas bubble agitated slag metal systems. Patel et al [199] studied the transfer of chromium between molten iron and FeO bearing slag at 1600°C in the presence of gas bubbles and observed that the bubbles noticeably increased the mass transfer. Linder [200] studied turbulent mass transfer between slag and bath and presented an analysis of the mass transfer of irregularities or waves on the liquid-solid surface and used the results to study the hydrodynamics and transfer in a gas-sitrred ladle. Richardson et al [201] measured the mass transfer coefficients in two reacting bubble-stirred systems: one involving the transfer of Cd from Hg to an aqueous phase, the other of Zn from Pb to a molten salt and observed that the rates are independent of whether the gas was supplied in a single stream or in multiple streams, and that, in shallow systems, the depth of the metal affects the mass transfer coefficients.

Narita et al [20] studied the desulphurisation kinetics in a calcium injection process. Behaviour of injection was evaluated using water modelling experiments and then a mathematical model of desulphurisation rate was formulated. By using the mathematical model, desulphurisation in industrial operations was explained by assuming that the rate- determining step is diffusion of sulphur. Further, it was determined that the desulphurisation rate is greatly affected by the immersion depth of the lance, the diameter of the nozzle and the argon flow rate. A mathematical model was also developed by Kaddah & Szekely [202] for desulphurisation kinetics in argon stirred ladles. This model has three key components viz. the velocity field is represented through the solution of the turbulent Navier-Stokes equations, in conjunction with a two equation model, the actual desulphurisation kinetics are represented in terms of sulphur transfer and reaction in a turbulent recirculating melt. The predictions based on the model were found to be in reasonably good agreement with experimental measurements obtained using both 6 or 40 ton ladles. It was found that the rate of desulphurisation depends both on the rate at which sulphur is being transferred in melt to the reaction zone and on equilibrium conditions prevailing in this reaction zone. It was therefore concluded that the fluid-flow phenomena and turbulence are key parameters in desulphurisation kinetics. Nakanishi et al [203] studied desulphurisation of hot metal in an open ladle stirred by an impeller, modified by gas injection. They confirmed by water model experiments that the gas injected, efficiently breaks up the cone -shaped agglomerate of desulphurising agents at the bottom of rotational vortex formed around the impeller shaft and makes it disperse homogeneously into the bath so that the chemical efficiency of desulphurisation rises to a greater extent than that without gas injection. Reduction of sulphur-content from 0.050 to 0.012% was reported by treating it with calcium carbide at the rate of 3 kg (75% in purity) per ton of hot metal for 11 min under the condition of 77 rpm in revolution rate and 3 Nm^3/min of nitrogen injection rate. The content of rate of desulphurisation was interpreted in terms of the rate of sulphur transfer in hot metal.

Though the desulphurising reaction proceeds as a combination of several reaction - steps, effects of various factors on the sulphur transfer rate were also examined. Effect of slag composition was studied by Ward & Salmon [204] , Marukawa et al [62] , Yamamoto et al [55, 56] , Inoue & Suito [59] , Smirnov et al [205] , and Takenouchi et al [88] . It was observed that the rate increases with an increase in slag basicity. Effect of basicity on the mass transfer coefficients was studied by Ching Chang & Goldman [206] and Saito & Kawai [207] . They found that mass transfer coefficient of sulphur in metal, k_M, increased with increasing slag basicity, but that in the slag, k_S, decreased. The temperature dependence of sulphur transfer from metal to slag was studied by Marukawa et al [62] , Moriya et al [49] , Inoue & Suito [59] , and Suito et al [60] , who found that the desulphurisation reaction was suppressed considerably with increasing temperatures. However, Inoue & Suito [87] did not observe any temperature dependance of sulphur partition between carbon-saturated iron melt and sodium-silicate slag.

1.2.7 Typical experimental investigations on desulphurisation-effects of reagents and techniques adopted

Lime and other calcium base-reagents were used by a number of workers for desulphurisation of iron and steel. Gatellier & Olette [208] , while studying removal of dissolved S and O in a liquid iron-base alloy by an electrochemical process using solid and liquid electrolytes, found that the best results were obtained with electrolytes containing Ca^{2+} ions, even at low concentrations. Orsini et al[209] studied the desulphurisation of low-C steel with rare earths in a medium-frequency vacuum induction furnace in magnesia-lined crucible and obtained the desulphurisation efficiency varying from 55-90%. Nakanishi et al[203] , Kaddah & Szekely [202] , Cameron & Dastur [6],Asano[210], Narita et al [20] , Haida et al [63], and, Fray [64]also desulphurised hot metal by lime and/or calcium carbide. Asano [210] in an excellent paper on 'Recent developments on desulphurisation of pig iron in a Torpedo Car' described introduction of an injection process for desulphurisation at one plant, the improvements in the desulphurisation reaction efficiency and also the developments in desulphurising reagents. He also reported improvements in CaC_2 desulphurising reagent and development of another desulphurising agent consisting of CaO compound. Haida et al [63] also developed a lime-base powder mixture with fine grain size and improved fluidity and observed that resulphurisation occuring during teeming of hot metal from blast furnace into torpedo cars, to which calcium carbide injection was made, was prevented by lime injection. Haida et al[63] , Ohya et al[66] , and Koros et al [75] observed that the lime-based reagent was cheaper than calcium carbide. Cameron & Dastur [6]observed that injection of fine calcium carbide for desulphurising hot metal was feasible in torpedo cars as the desulphurisation efficiency was fairly consistent and sulphur contents below 0.01% were easily obtained provided the calcium carbide injected was ground fine, preferably to -200 mesh size. Frey [64] described desulphurisation of off-grade blast furnace casts using carbide injection with nitrogen for preparing feed for BOF steelmaking and observed that 3 lb of carbide injected at nitrogen flow rate of 1.6 ft^3/lb of carbide removed 0.01% sulphur from 1 ton of hot metal.

Koros et al [75] and Orton et al [211] described the lime-mag injection process for desulphurisation of hot metal and steel. Orton et al [211] also observed that tonnage production of 0.005% S (max.) steel can be achieved by injection in a basic-lined steel ladle.

Dyudkin & Krupman [124] recommended injection of $CaO-CaF_2$ mixtures for desulphurisation of hot metal outside blast furnace. Folmo et al [212] desulphurised the steel injecting CaSi, $CaO-CaF_2$, and, $CaO-CaF_2-CaSi$ mixtures in the ladle and obtained sulphur levels of 0.008% by either of the treatments. Carlsson [7] studied powder injection in ladle at MEFOS in co-operation with Scandinavian Steel Works and concluded that good desulphurisation can be achieved by powder injection and argon stirring. He also reported that the thermodynamics of the system has to be kept under close control for obtaining reproducible results.

Inoue et al [213] studied simultaneous desulphurisation of pig iron with $CaO-CaCl_2$ flux and concluded that,

(i) it was possible to couple the cathodic reactions such as desulphurisation and reduction of Fe^{2+} and Mn^{2+} ions with anodic dephosphorisation, (ii) high viscosity of CaO-based slag could be reduced by addition of Al_2O_3 and SiO_2, and (iii) phosphate-and sulphide- capacities of $CaO-CaCl_2$ flux were much higher than those of conventional slags. Parma et al [121], using levitation melting method, studied effects of liquefactive additions of Al_2O_3 and CaF_2 on desulphurisation efficiency of lime and concluded that both these additives considerably increase the desulphurising capacity of lime, essentially due to the liquefaction of slag and improvement kinetic conditions favouring desulphurisation.

Gladyshev et al [214] reported 75-80% sulphur removal from hot metal by a slag mixture consisting of lime, fluorspar, aluminium and sodium nitrate.

A number of investigations[1,2,21,24,43,65,67-70, 73,76,215-223] have been reported on desulphurisation of hot metal and steel by magnesium and magnesium- base alloys. Haastert[3] , Moore[4] , and, Lehner [5] have described experiments wherein magnesium mixed with lime fluorspar or alumina was injected in steel for desulphurisation. In the hot metal desulphurisation too, magnesium was used in blended form[77] so as to reduce the turbulence in ladle caused by evaporation of the metal ($T_{bp,Mg}$ = 1380K). However, Voronova[1,2] injected pure magnesium for desulphurisation of hot metal with air and found that granular magnesium is the best form for desulphurisation. He also observed that by using granular magnesium with natural gas stream instead of compressed air stream, specific magnesium consumption per unit weight of sulphur removed decreased by 25%. Efimenko et al [224] observed that in addition to desulphurising and deoxidising hot metal, magnesium injection treatment also reduced the content of nitrogen and hydrogen gas dissolved in metal. Dvoryaninov et al [76] used a secondary magnesium alloy containing upto 86% Mg, which had the advantage of being cheaper than pure magnesium, and found that the quality of the desulphurised iron was not affected adversely.

Silva et al [218], Ishiro Honjo [67], and, Hausen & Schutz [225] found the mag-coke process using an inert gas, to be the best method of obtaining low-sulphur steels at low cost. Yamaguchi et al [43] and Sandberg [65] compared the mag-coke process with the carbide treatment and found that the former process was better than the latter from both economic and metallurgical view points. Reduction of sulphur levels from 0.030-0.045% to 0.008% and even less using approximately 1.2 kg/ton mag-coke were reported by Yamaguchi et al [43].

Torloiu [226] studied desulphurisation of foundry cast iron by mixtures of pulverised $CaCO_3$ and Na_2CO_3 in different proportions in the temperature range 1350-1450°C and observed that best results were obtained by addition of 1.2% by weight of the mixture of particle size range 1-5 mm, the slag formed was also viscous and easy to remove. Kozielewicz & Ciupka [227] studied the effect of additions of 2.7,3.9, and, 4.45 wt. percent soda and 1.66% soda - 6% Na_2CO_3 to coke briquettes on desulphurisation of pig iron in coupola. Desulphurisation to the extent of 18.5-22.8% was recorded and similarities between effects of sodium carbonate and fluoride were observed. Further, relatively low rates of desulphurisation were attributed to formation of sodium-silicate which had the retarding effect on desulphurisation. Takenouchi et al [88] studied the influence of slag composition on the rates of desulphurisation and dephosphorisation for producing steels with ultra-low sulphur and phosphorus and concluded that $CaO-CaF_2$ based slags containing Na_2O, B_2O_3, $Na_2B_4O_7$, or , k_2O have high rates of desulphurisation and dephosphorisation .Korbut & Veselovsky [228] observed upto 60% sulphur removal from initial contents of ~0.06% from steel samples by lime-soda treatment at 1600-1640°C. Kohler et al [229] while studying desulphurisation on plant scale, obtained sulphur levels upto 0.005% in hot metal by treating it in batches of 5-45 tons with $CaO-Na_2CO_3$ mixtures and in some cases with the addition of CaC_2 also with a consumption of $CaO-Na_2CO_3$ (in ratio 9:1) upto 10 kg/ton and CaC_2 upto 8 kg/ton of steel. Domalski et al [44] reviewed the different processes of desulphurisation and described results of experimental studies in an integrated steel plant to conclude that use of pure Na_2O accelerates slagging of

Si, so that the basicity and therefore the sulphur-partition is not improved. Addition of CaO to Na_2O improves basicity and lowers the liquidus temperature also. They also compared the cost of various desulphurising procedures and concluded that the Ostberg process with 50% CaO and 50% Na_2O was the cheapest. Smirnov et al [205] also arrived at similar conclusions.

Yamamoto et al [55] reported that Na_2CO_3 is a powerful flux for simultaneous dephosphorisation and desulphurisation in oxidising atmosphere. Phosphorus content of treated metal is affected by Si and P content of hot metal, and, can be easily lowered to below 0.010%. Yamamoto et al [56] observed that by using 40 gm Na_2CO_3 per kg of hot metal with P=0.10% and S=0.040% initially , the final P and S contents of treated metal could be lowered down to 0.003 and 0.001% respectively. Schenck et al [47] obtained the sulphur level of 0.019% from an initial value of 0.098% in pig iron in a counterflow system by using about 5.8 kg soda/tonne of iron and for a supply of 310 kg pig iron/min. Sulphur levels of 0.010-0.012% and 0.007-0.008% in treated metal were reported by Lovenfosse[48] using process of double-transfer and double-deslagging with additions of Na_2CO_3. The melt temperature also decreased by 15°C at each transfer stage. Voronova et al [230] desulphurised liquid iron in a barrel ladle by charging soda at the bottom of the ladle, then pouring in molten iron and injecting air through tuyere in the ladle wall and claimed 75-90% desulphurisation with initial sulphur contents of 0.078-0.160%, with a consumption of 1.5% Na_2CO_3 of metal weight. Schulz [11], analysing operational results from a number of steel plants concluded that higher degrees of desulphurisation right on specification can be obtained using immersed lances or stirrers, irrespective of the temperature, composition, and, initial sulphur content of pig iron. Bahout et al [231] studied external desulphurisation of hot metal of composition C=4.2-4.3%, Si= 0.5-1.4%, Mn= 0.6-1.3%, P= 0.13-0.16%, S= 0.013-0.031% by pneumatic injection of soda ash in 200 ton ladles and concluded that deep injection (at 2 m depth) of soda ash considerably improves the desulphurisation efficiency as compared to classical techniques and also that, (i), the specific consumption of soda ash decreased from more than 12 kg/ton in classical techniques to 4 kg/ton of hot metal while using deep injection to bring down the sulphur levels from 0.030% to 0.015%, (ii) very low sulphuf levels 0.005% could be reached in deep injection technique by using approximately 7 kg soda ash per ton of hot metal. The improvements in the desulphurisation efficiency of soda ash were attributed to the fine dispersion of desulphurising reagent in the metal, the reduction in soda ash loss, and the boiling effect of the reaction. They also observed that the treatment time could be reduced to 30 min or less by using a soda ash flow rate greater than 40 kg/min.

TABLE- 1.1 RESULTS OF TYPICAL DESULPHURISATION STUDIES

Reagent system	Rate of reagent addition, technique used and other relevant experimental parameters	Typical results	Reference
1	2	3	4
Lime (CaO)	7.5 kg/ton pig iron;lance injection	(i) 40% desulphurisation achieved and S-level from 0.04% reduced to 0.025% (ii) Degree of desulphurisation falls as the initial S concentration falls.	Pliskanovskii et al [232]
Calcium carbide (CaC_2)	10-15 kg/ton pig iron; lance injection with nitrogen flowing at 21-28 m^3/hr	60% S removal achieved	Watkins & McFarland [19]

Contd.......

1	2	3	4
CaC_2	3 kg/ton pig iron; lance injection	S level from 0.030-0.034% reduced to 0.015%	Wittenberger et al [233]
CaC_2	3-11 kg/ton pig iron; lance injection	i) If the minimum possible level of S in iron is considered to be 0.008% then 100% desulphurisation is possible ii) 0.008% S level may be obtained.	Schulz [11]
CaC_2^*	Injection of fine CaC_2 in hot metal in torpedo cars.	S contents less than 0.01% achieved and fairly consistent desulphurisation efficiency.	Cameron & Dastur . [6]
Calcium cynamide($CaCN_2$)	10-30 kg/ton iron; addition to ladles.	S levels from initial 0.10-0.60% reduced to below 0.035%.	Hatch et al [13]
Calcium silicide (Ca-Si)	1.5-3.0 kg/ton treated steel; injection	i) Average S removal was 37% with some peaks upto 72%. ii) S content after treatment attained upto 0.005%.	Centomo et al[234]

Contd.....

1	2	3	4
Lime-Mag*	Injection in a basic lined steel ladle	S-levels upto 0.005% in treated steel could be obtained.	Orton et al [211]
Calcined Lime* and dolomite	1.5% of metal weight	30% desulphurisation achieved.	Shparber [235]
CaSi, $CaO-CaF_2$*, $CaO-CaF_2-CaSi$	Injection in ladle	Final sulphur levels upto 0.008% attained.	Folmo et al [212]
$CaO-Na_2CO_3$(9:1) and CaC_2	$CaO-Na_2CO_3$ 10 kg/ton and CaC_2 8 kg/ton steel; addition in batches of 5-45 ton steel.	Sulphur levels reduced upto 0.005%	Kohler et al [229]
Lime base flux* containing CaF_2, Na_2CO_3, Fe_2O_3, $Na_2B_4O_7$	N.A.	Simultaneous dephosphorisation and desulphurisation is possible with S-removal greater than 80% and P-removal 40-50% in 20-25 min time.	Cho et al [146]
$CaO-CaF_2-Al$ $-Na_2NO_3$	Addition to pig iron in runner (0.5 ton/min), with a device for bottom blowing of metal through a porous refractory block.	75-80% desulphurisation achieved.	Gladyshev et al [214]

Contd.....

1	2	3	4
Lime-soda*	Addition at 1600-1640°C.	60% desulphurisation attained from initial level of 0.06%.	Korbut & Veselovsky [228]
Calcined dolomite, $CaO-MgO$, MgO	1.2-1.6% of the metal weight-alongwith suitable reductants like Si,Al or Ca or their alloys; plunged into molten bath of 8 and 10 kg with the help of graphite or kayanite (refractory) plunger in magnesite lined open-bath induction furnaces of capacities 10 kg and 30 kg	S-level from 0.05-0.09% brought down to less than 0.01%	Chakrabarti et al [236,237]
Mag-coke	1.2 kg/ton; plunging into 145 ton/heat capacity hot metal ladle.	S-level from 0.030-0.045% reduced to 0.008%.	Yamaguchi et al [43]
Mag-oxide* -Al powder	N.A.	Mean degree of desulphurisation achieved ~66%.	Rubkin et al [72]

Contd....

1	2	3	4
Na_2CO_3	40 g/min; injection with argon gas, 7.5 l/min through bottom in 15 kg pig iron melt at 1430°C.	Sulphur level from 0.15% reduced to less than 0.005% in 10 min.	Kawakami [238]
Na_2CO_3	40 g/kg HM; continuous refining in specially designed furnace to take advantages of counter-current refining.	P and S brought down from initial 0.10 and 0.04% to 0.003 and 0.001% respectively.	Yamamoto et al [56]
Na_2CO_3	1.5% of cast iron; charging soda on the bottom of the ladle then pouring in the cast iron and injecting air through a tuyere in the ladle wall.	75-90% desulphurisation achieved from initial S level of 0.078-0.160%.	Voronova et al [230]
$Na_2CO_3^*$	Desulphurisation in two ladles.	Sulphur level from 0.03% in transfer car reduced to 0.023% in first ladle and 0.012% in the second ladle.	Lovenfosse [48]

Contd....

1	2	3	4
Soda slag	5.8 kg/tonne pig iron; desulphurisation produced in counterflow channel.	Sulphur content reduced from 0.098% to 0.019% for a supply of 310 kg pig iron/min.	Schenck et al [47]
Soda-ash	4 kg/ton hot metal; deep injection (2m) of soda ash in 200 ton ladles.	i) Sulphur level brought down from 0.03 % to 0.015%. ii) Use of soda ash approximately at a rate of 7 kg/ton HM could reduce the sulphur levels upto 0.005%.	Bahout et al [231]
Soda ash*	Treatment of pig iron in shaking ladle.	In 10 min, the sulphur-level reduced from 0.08% to 0.01-0.008%.	Anon [28]
Soda ash*	N.A.	Degree of desulphurisation attainable is 90%.	Schulz [11]
Lumpy lime-soda ash-fluorspar for primary desulphurisation and alloy of cerium for secondary desulphurisation.	Soda-potash 0.8% of metal weight; addition to hot metal stream/ladles.	Sulphur levels in the pig iron reduced to 0.002-0.005%.	Voronova [8]

Contd.....

1	2	3	4
Soda-potash* mixture and calcined soda	2.0-2.2% of the weight of cast iron with 1.5-3.0% iron ore for oxidation and slagging of phosphorus.	i) Average levels of removal achieved for S=63-66% and for P=35-50%. ii) For same degree of desulphurisation and dephosphorisation, expenditure of soda-potash mixture is higher than calcined soda.	Baby et al [239]
Na_2CO_3-Na_2SO_4	10% by weight of pig iron; desulphurisation in induction furnace.	70-92% desulphurisation achieved from initial S content of 0.02%.	Egger & Hiebler [61]
Na_2CO_3-NaOH-CaF_2	1.5% of metal weight.	Sulphur levels to below 0.02% were obtained.	Meunier [80]

*Details not available. (information collected from Metals Abstract)

Al_2O_3, and CaF_2 contents, temperature of reaction, and, nitrogen gas flow rate will be used as experimental parameters for arriving at the optimum conditions for desulphurisation. Weighed amounts of slag and metal brought in intimate contact in liquid state due to bubbled nitrogen gas, will be treated at different temperatures. Samples of slag and metal will be withdrawn at regular intervals and analysed for their sulphur contents to monitor the progress of desulphurisation reaction. For theoretical analysis of experimental data, an expression will be derived for mass transfer coefficient of solute in gas bubble agitated metal-slag reaction systems. From the experimental data so obtained, distribution coefficient of sulphur between the slag-and metal-phases will be graphically estimated and using its values mass-transfer coefficient of sulphur will be computed for different sets of operating conditions using expressions arrived at in this work. Where-ever possible the data so obtained will be compared with the values reported by other workers.

CHAPTER-2

EXPERIMENTAL

Inert gas bubble agitation method has been adopted for contacting soda-based slags and hot metal for the present investigation. Brief account of design and fabrication of experimental set-up, actual experimental runs for desulphurisation, and, analysis of sulphur in metal and slag samples is presented below.

2.1 EXPERIMENTAL SET-UP

Fig.(2.1) shows the schematic block-diagram of experimental set-up used in the present investigation. The essential components of this set-up, designed and fabricated locally, include : a gas purification train, slag preparation unit, a gas mixing unit-for obtaining gaseous mixtures (air+N_2) of desired composition for study with Fe-oxide bearing slags, and, a bubble-agitated slag-metal contacting unit for desulphurisation with thermostatic temperature controller. Significant details of the different units are very briefly presented below.

2.1.1 Gas Purification Train

High purity nitrogen procured from M/S Modi Gas and Chemicals Ltd., Modi Nagar, was further purified by removal

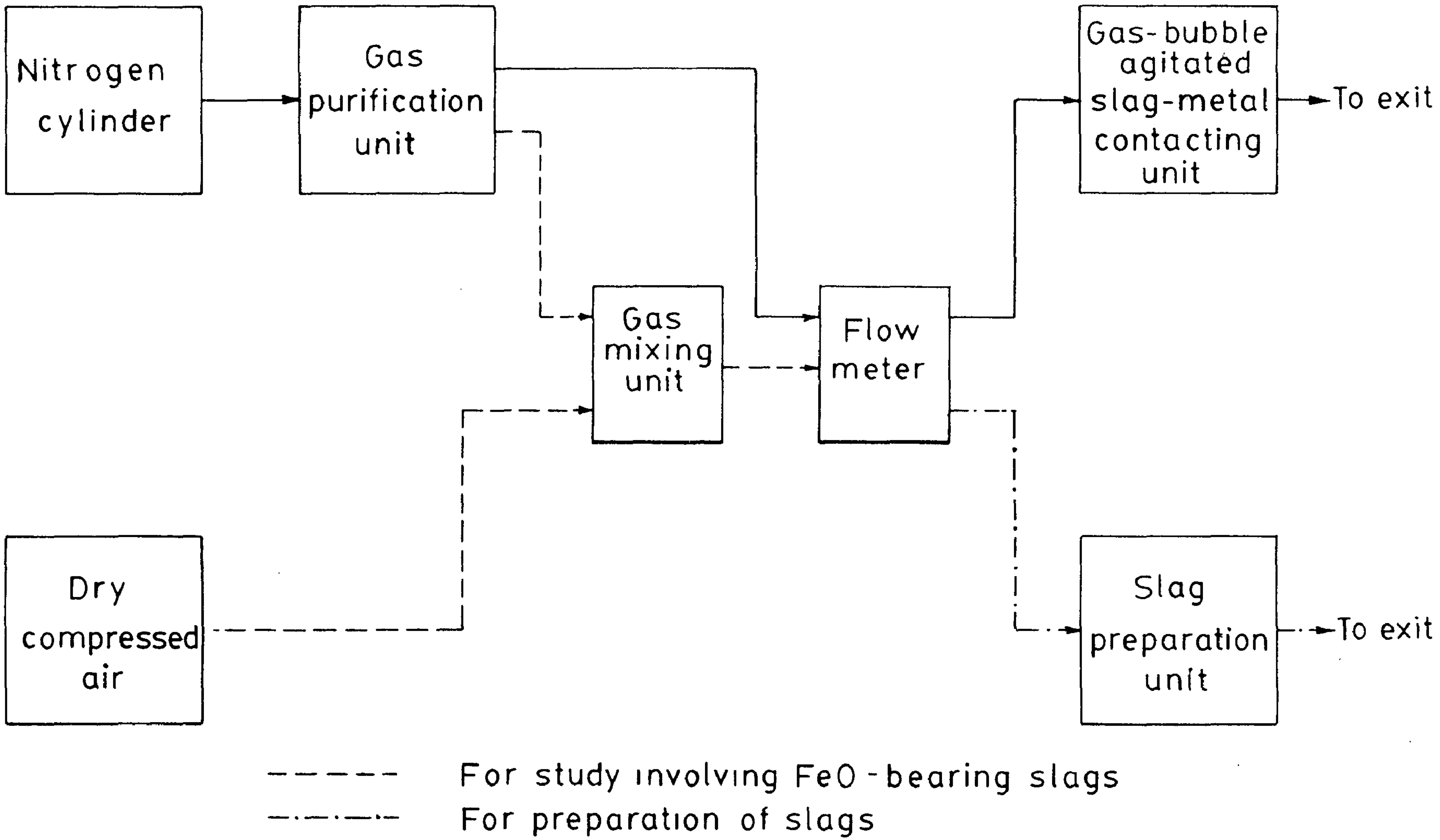

FIG. 2.1 SCHEMATIC BLOCK DIAGRAM OF EXPERIMENTAL SET-UP.

of associated moisture vapour and oxygen using a simple purification train shown schematically in Fig.(2.2). Nitrogen gas from the cylinder was first bubbled through alkaline pyrogallol solution and conc. sulphuric acid and then contacted with phosphorus pentaoxide powder, contained in a series of bubblers. Ten pyrex-glass bubblers were connected in series with the first, fourth, seventh, and, tenth bubblers kept empty to avoid mixing of different reagents used. The second and third bubblers contained alkaline pyrogallol solution, fifth and sixth, conc. sulphuric acid, and, the eighth and ninth, powdered phosphorus pentaoxide. The bubbled gas was then passed over copper turnings, iron turnings, and, graphite pieces of 1-2 mm size, kept in three different tubular furnaces maintained respectively at 480,480 and 800°C temperature. Finally, the purified gas was passed through a copper coil immersed in a water tank, for cooling before entering either the slag preparation unit or the bubble-agitated slag-metal contacting unit for desulphurisation-either directly or through a gas mixing unit. Flow rate of gas was measured with a 'flow meter' located before the gas-bubble agitated slag-metal contacting unit as shown in Fig.(2.1).

2.1.2 Gas Mixing Unit

For preparing the N_2-air gaseous mixture of desired composition, used in the experimental runs for study of

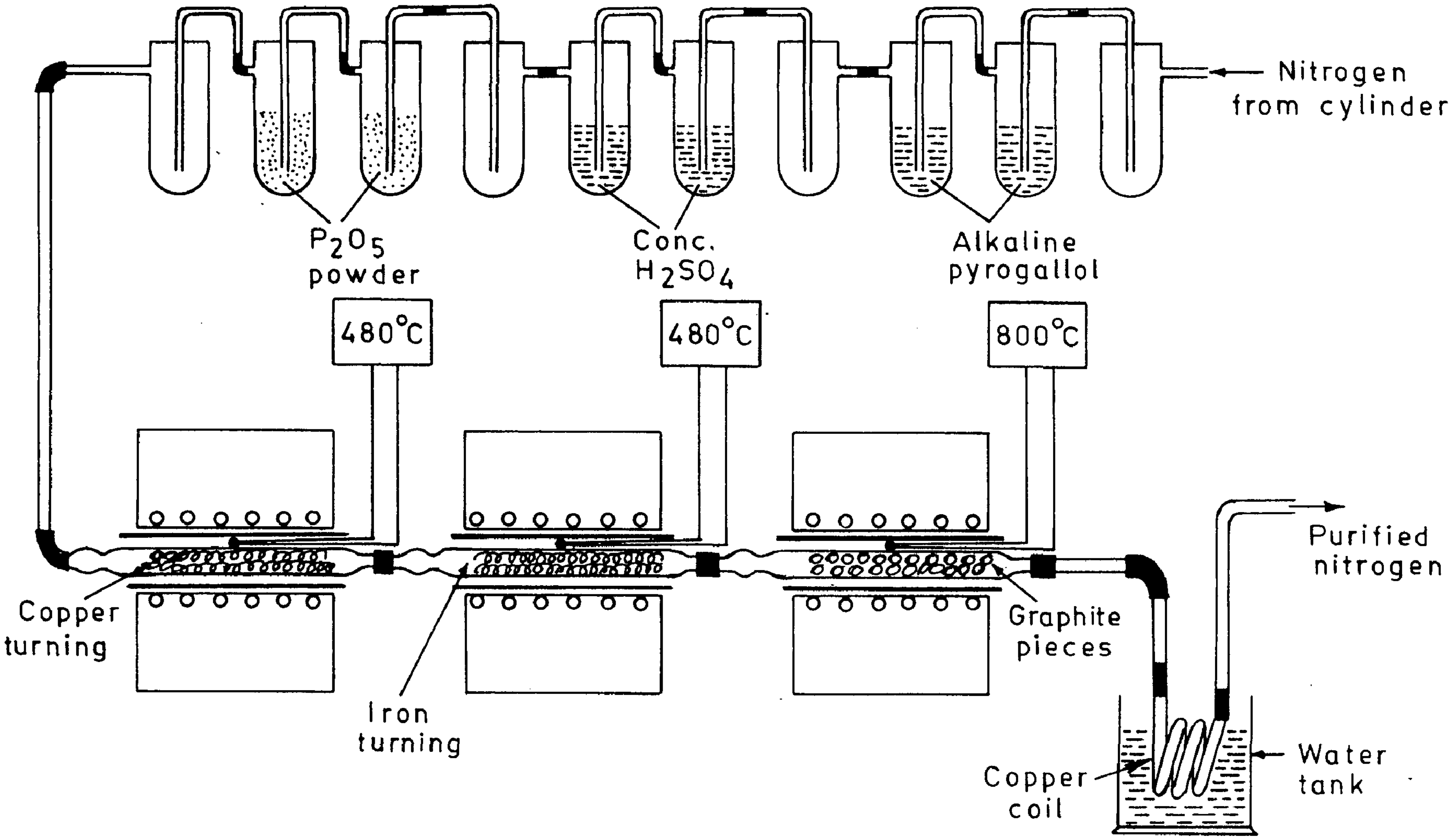

FIG. 2.2 SCHEMATIC DIAGRAM OF NITROGEN PURIFICATION TRAIN.

effect of FeO on kinetics of desulphurisation, a constant pressure head flowmeter type gas mixer was used. By adjusting the flow rates of N_2 and dry compressed air, a gaseous mixture of desired composition could be obtained in this unit.

An Orsat- apparatus was introduced in the line, between the gas mixing unit and reaction unit, to facilitate rapid and frequent analysis of gaseous mixture. Alkaline pyrogallol was used for O_2-absorption for calculation of partial pressure of oxygen in the gaseous mixture. Fig.(2.3) shows the gas mixing unit.

2.1.3. Slag Preparation Unit

Two tubular resistance furnaces one placed vertically and other horizontally, with super kanthal wire winding, were used for melting and homogenisation of all slags used in the present investigation. Temperature of these furnaces were controlled by means of automatic temperature controller (APLAB make), employing Pt/Pt-13% Rh thermocouples. All the slags were melted in graphite crucibles in inert atmosphere of purified nitrogen.

2.1.4 Gas-Bubble Agitated Slag-Metal Contacting Unit

Details of the gas-bubble agitated slag-metal contacting unit used for desulphurisation is shown in Fig.(2.4). Essential components of this unit include,

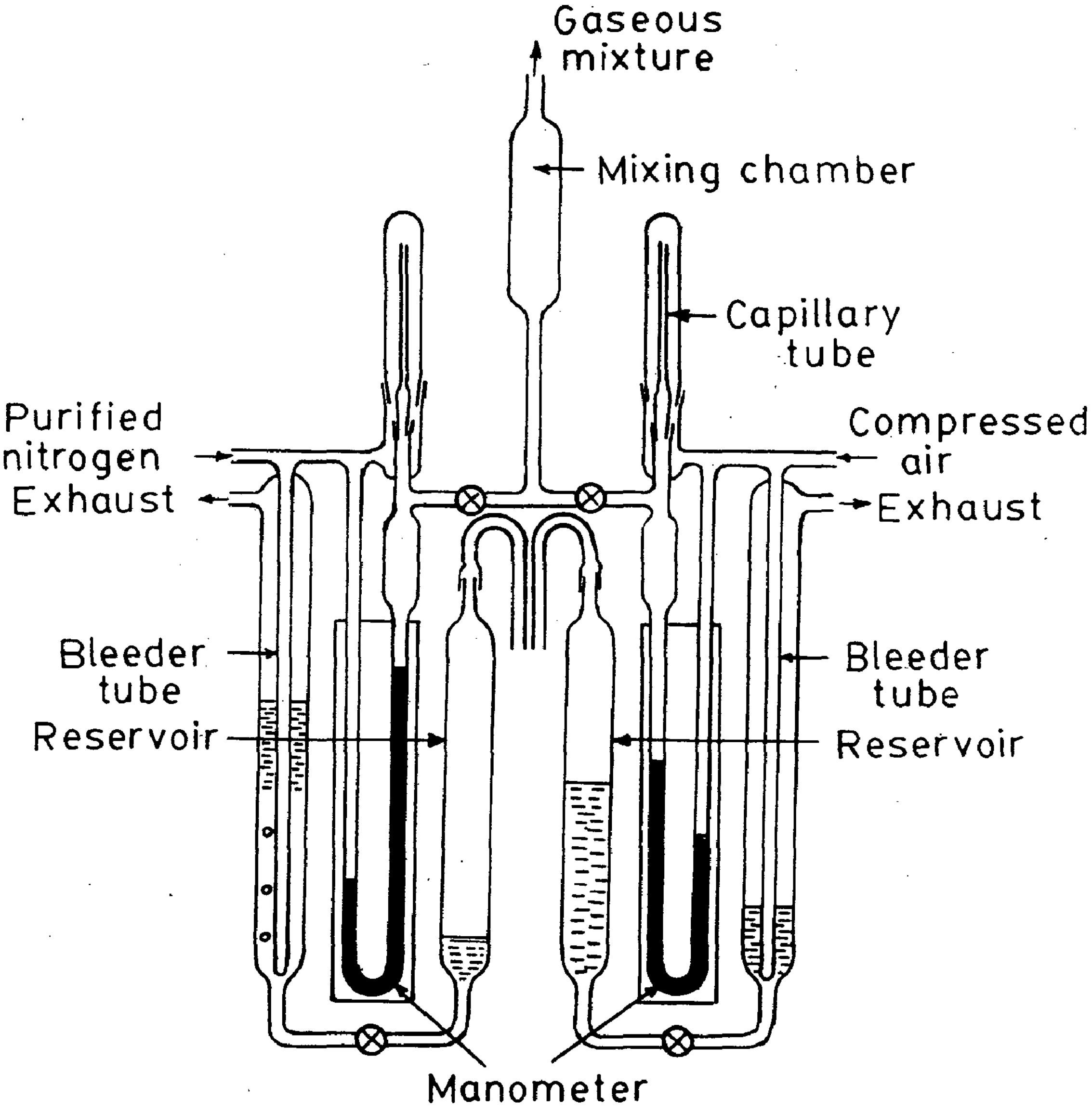

FIG. 2.3 GAS MIXING UNIT.

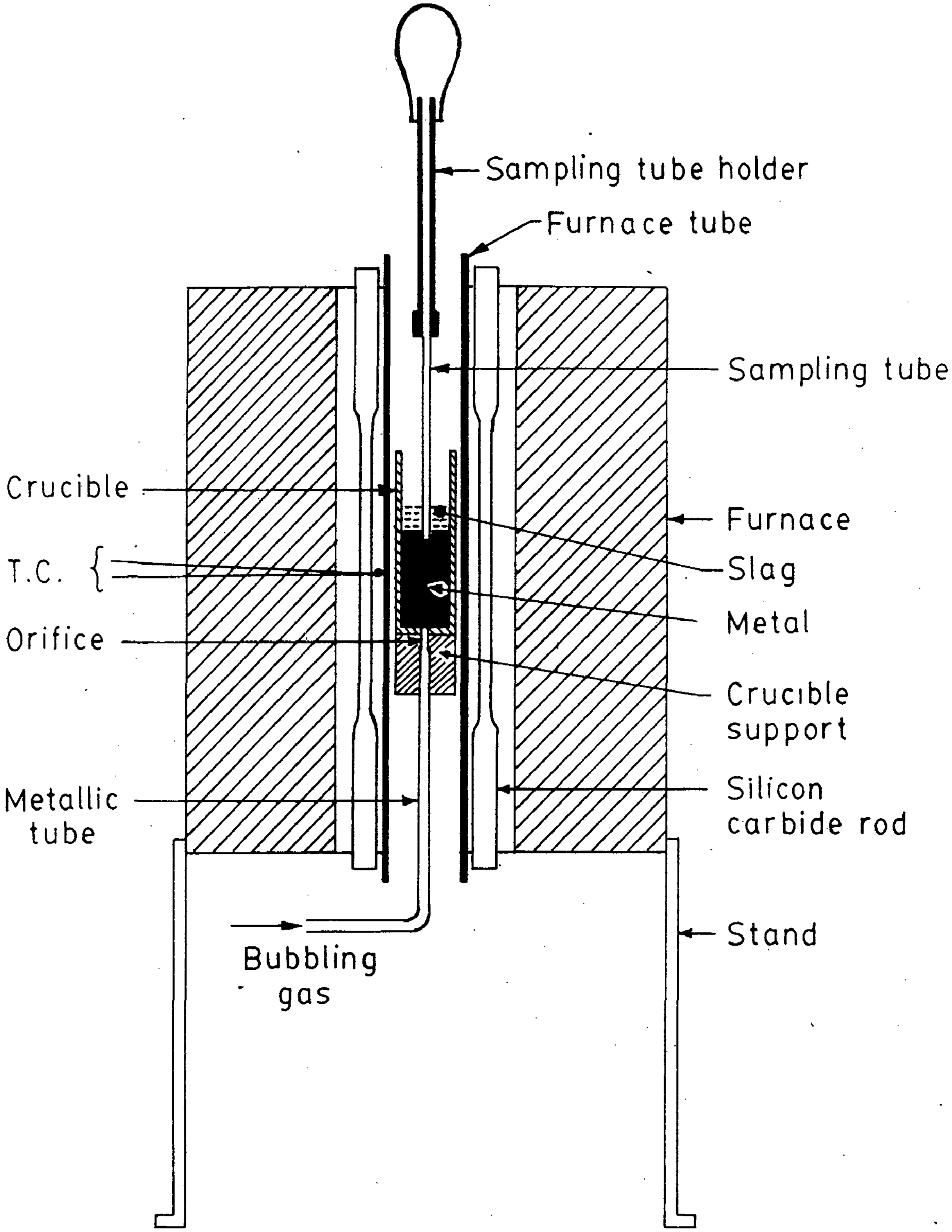

FIG. 2.4 SULPHUR TRANSFER STUDY UNIT.

a) Furnace assembly : A vertical glober furnace with both ends open and employing silicon-carbide rods as heating element , was used for melting the charge. Recrystallised high alumina tube of 75 mm OD and 65 mm ID was vertically placed between the four silicon carbide rods. Temperature of the furnace was controlled within ± 2°C by an APLAB make automatic temperature controller, employing Pt/Pt-13% Rh thermocouple.

b) Alumina reaction crucible : Recrystallised high alumina crucibles of 60 mm OD, 55 mm ID and 140 or 210 mm hight , depending upon weight of charge used, were used for desulphurisation. This was placed centrally in the alumina tube in furnace assembly for experimental runs.

c) Sampling device : Recrystallised high alumina tube of 5 mm ID were used to withdraw metal and slag samples from the crucible during contacting of slag and metal at different intervals of time to study the progress of desulphurisation of metal.

2.2 MATERIALS USED

Nearly pure quartz lumps were picked up from a quarry near Delhi. Analar grade chemicals- anhydrous sodium carbonate, conc. hydrochloric acid, conc. sulphuric acid, ammonium ferrous sulphate, and alumina powder, all procured from Glaxo Laboratories (India) Ltd., Bombay, calcium fluoride from Robert Johnson (India) Ltd., electrolytic grade iron powder from Sarabhai Merck Ltd., Baroda, and, copper turnings, iron turnings, pyrogallol, graphite pieces etc. were used for the present work. Pig iron was procured from Bharat Heavy Electricals Ltd., Hardwar.

2.3 PREPARATION OF SLAGS

Soda-silica slags of Na_2O/SiO_2 molar ratios ranging from 0.6 to 1.6 with adequate additions of FeO, Al_2O_3,CaF_2 etc. were used for the study. Compositions, solidus and liquidus temperatures, and, the melting and homogenisation temperatures of different slags used are presented in Table (2.1). Following techniques were adopted for preparation of FeO, purification of quartz, and, melting and homogenisation of slags.

2.3.1 Preparation of FeO

To obtain FeO, used for study of its effects on desulphurisation, first α-Fe_2O_3 was produced by thermal decomposition of analar grade ammonium ferrous sulphate. This was carried out in two stages- initially ammonium ferrous sulphate was heated at 900°C for 48 hours and the product so obtained was reheated at 1150°C for 24 hours. Electrolytic grade iron powder, in slight excess over the stoichiometric amount required to form FeO, was added to

TABLE-2.1 CHARACTERISTICS OF SODA-SLAGS USED IN THE PRESENT INVESTIGATION

Molar Na_2O/ SiO_2 ratio	Chemical analysis			Solidus temperature* (^oC)	Liquidus temperature* (^oC)	Slag melting temperature (^oC)	Homogenisation temperature (^oC)
	wt% Na_2O	wt% SiO_2	equivalent[x] Na_2CO_3				
0.6	38.2716	61.7284	65.4321	1022	1195	1300	900
0.8	45.2555	54.7445	77.3723	1022	1060	1160	900
1.0	50.8197	49.1803	86.8853	837	1080	1180	700
1.2	55.3571	44.6429	94.6428	837	1008	1110	700
1.4	59.1281	40.8719	101.0900	837	920	1020	700
1.6	62.3116	37.6884	106.5327	837	850	950	700

[x] equivalent Na_2CO_3 = wt% Na_2O. $\frac{MW_{Na_2CO_3}}{MW_{Na_2O}}$

[*] data obtained from Na_2O-SiO_2 phase diagram.

α-Fe_2O_3. This mixture was compacted in a die at a pressure of 440 MNm^{-2} (~44 atm). These compacts were placed in an iron boat, heated to 1150°C and maintained at this temperature for 8 hours in an inert atmosphere of purified nitrogen to prevent reoxidation. The product so obtained was first furnace-cooled upto 700°C and then rapidly- cooled to room temperature by drawing the iron-boat containing these compacts towards the cooler region of the furnace tube and also increasing the flow rate of nitrogen to facilitate faster cooling.X-ray diffraction analysis was used to test for and ensure complete conversion of oxides to FeO state in the final product.

2.3.2 Purification of Quartz

Quartz lumps, picked up from quarry, were crushed and ground to -48 mesh size . This powdered material was treated with conc. hydrochloric acid several times to remove completely the acid soluble impurities, washed repeatedly with distilled water to remove associated clay and finally dried at 110°C. Chemical analysis of the treated product showed + 99% SiO_2.

2.3.3 Blending and Melting of Slags

Accurately weighed quantities of purified silica and anhydrous sodium carbonate (together with Al_2O_3, CaF_2 and/or FeO for slags to be used for study of effects of these additives) were mixed thoroughly in a hand mortar and the resulting mixtures transferred to graphite crucibles for melting in a vertical tubular furnace at temperatures approximately 100°C above their respective liquidus temperatures (Table2.1) under purified nitrogen atmosphere for nearly six hours to ensure completion of slag-formation reaction. The molten slags were withdrawn from the furnace and air-cooled. The solidified slags were again crushed and ground in hand-mortar and remelted in nitrogen atmosphere to prevent damage to graphite crucible for six hours. The doubly melted slags were finally crushed and ground for homogenisation.

2.3.4 Homogenisation of Slags

The doubly-melted slag powders, were placed in high alumina boats and heated in horizontal tubular furnace in presence of air at temperatures nearly 100°C below their normal solidus points (Table 2.1) for about 24 hours for homogenisation and for elimination of carbon picked-up during melting from graphite crucibles, if any.

2.4 EXPERIMENTAL RUNS

For experimental runs initially, optimum weight of slag (140 gms) to be used for subsequent runs was determined by contacting 1000 gms of pig iron with varying weights of slag for 1 hour. For subsequent experimental runs for study of kinetics of desulphurisation, 1000 gms of pig iron and

140 gms of slag were placed in the recrystallised high alumina reaction crucible, which was then heated to melt the charge under purified nitrogen atmosphere. However, in case of FeO containing slags, 5-7% air was also mixed with nitrogen to minimise or eliminate possibility of the reduction of FeO in contact with pig iron. Nitrogen gas was passed at slow controlled rate during initial heating and melting period but once the desired temperature for desulphurisation was attained, its flow rate was adjusted to result in the desired degree of agitation in bubble-stirred slag-metal reacting system. Samples of metal and slag were withdrawn, using recrystallised high alumina sampling tubes, at regular intervals of 3 minutes and analysed for their sulphur contents.

2.5 CHEMICAL ANALYSIS

Rapid instrumental analysis technique was used for estimation of sulphur in both metal and slag samples collected during the experimental runs in the laboratories of Bharat Heavy Electricals Ltd., Hardwar and Modi Steels, Modi Nagar using LECO analyser. This was done due to limited choice of reliable and rapid analytical method for sulphur.

CHAPTER-3

RESULTS AND DISCUSSION

Effect on desulphurisation has been studied as a function of relative amounts of metal and slag; gas flow rate; basicity of slag; Al_2O_3, CaF_2, and FeO additions to slag; and temperature. Results of different experimental runs are given in Tables (3.1-3.32) and plotted in Figs.(3.1-3.21) as summarised in Table (3.33).

The different tables (Table 3.1-3.32) of the experimental runs represent the variation of sulphur concentration in both metal as well as slag phases, as a function of time. It is evident from these tables that the concentration of sulphur in metal phase initially decreased rapidly (and that in slag phase initially increased rapidly) and finally attained a constant value as desulphurisation progressed. The last value given in these tables did not change even after a long time of experimentation and thus refer to the ultimate or equilibrium value of sulphur in the respective phases i.e., $[\,\mathrm{wt\%}\ S_b\,]_\infty$ and $(\mathrm{wt\%}\ S_b)_\infty$, respectively the weight percent S in bulk metal and slag phases at infinite time. These equilibrium values were used to calculate the distribution coefficient, L, of sulphur between metal and slag using the relation,

$$L = \frac{\rho_S(\mathrm{Wt\%}\ S_b\ )_\infty}{\rho_M[\,\mathrm{Wt\%}\ S_b\,]_\infty} \qquad \ldots\ (3.1)$$

Table - 3.1 Run No.1

Crucible diameter = 5.50 cms

Nozzle diameter = 0.15 cms

Metal weight = 1000 gms

Slag weight = 140 gms

Na_2O/SiO_2 ratio = 1.0

Temperature = 1400°C

Flow rate = 6.0 l/h

S.No.	Time, t (min)	$[wt\% S_b]_t$	$(wt\% S_b)_t$	$\ln \frac{[wt\% S_b]_t - [wt\% S_b]_\infty}{[wt\% S_b]_o - [wt\% S_b]_\infty}$
1	3	0.1145	0.1821	-0.2081
2	6	0.0958	0.3157	-0.3941
3	9	0.0795	0.4321	-0.5903
4	12	0.0662	0.5271	-0.7849
5	15	0.0554	0.6043	-0.9767
6	18	0.0467	0.6664	-1.1633
7	21	0.0388	0.7229	-1.3695
8	24	0.0324	0.7686	-1.5747
9	27	0.0270	0.8071	-1.7881
10	30	0.0227	0.8379	-1.9981
11	45	0.0121	0.9136	-2.8563
12	60	0.0043	0.9693	-

Distribution coefficient, L =70

Mass transfer coefficient k = 5.6932×10^{-3} cm/sec

Table - 3.2 Run No.2

Crucible diameter = 5.50 cms
Nozzle diameter = 0.15 cms
Metal weight = 1000 gms
Slag weight = 210 gms
Na_2O/SiO_2 ratio = 1.0
Temperature = 1400°C
Flow rate = 6.3 l/h

S.No.	Time, t (min)	$[\text{wt\% } S_b]_t$	$(\text{wt\% } S_b)_t$	$\ln \dfrac{[\text{wt\% } S_b]_t - [\text{wt\% } S_b]_\infty}{[\text{wt\% } S_b]_o - [\text{wt\% } S_b]_\infty}$
1	3	0.1088	0.1486	-0.2602
2	6	0.0933	0.2224	-0.4199
3	9	0.0756	0.3067	-0.6402
4	12	0.0650	0.3571	-0.8000
5	15	0.0529	0.4148	-1.0203
6	18	0.0440	0.4571	-1.2203
7	21	0.0371	0.4900	-1.4086
8	24	0.0319	0.5148	-1.5784
9	27	0.0263	0.5414	-1.8006
10	30	0.0222	0.5610	-2.0018
11	45	0.0110	0.6143	-2.9400
12	60	0.0038	0.6486	-

L = 53

k = 6.1243×10^{-3} cm/sec

Table - 3.3 Run No.3

Crucible diameter = 5.50 cms

Nozzle diameter = 0.15 cms

Metal weight = 1000 gms

Slag weight = 280 gms

Na_2O/SiO_2 ratio = 1.0

Temperature = 1400°C

Flow rate = 5.9 l/h

S.No.	Time, t (min)	$[\text{wt\%}\, S_b]_t$	$(\text{wt\%}\, S_b)_t$	$\ln \dfrac{[\text{wt\%}\, S_b]_t - [\text{wt\%}\, S_b]_\infty}{[\text{wt\%}\, S_b]_o - [\text{wt\%}\, S_b]_\infty}$
1	3	0.1086	0.1121	-0.2601
2	6	0.0912	0.1743	-0.4400
3	9	0.0724	0.2414	-0.6794
4	12	0.0609	0.2825	-0.8603
5	15	0.0504	0.3200	-1.0600
6	18	0.0426	0.3479	-1.2394
7	21	0.0347	0.3761	-1.4612
8	24	0.0285	0.3982	-1.6781
9	27	0.0242	0.4136	-1.8620
10	30	0.0205	0.4268	-2.0528
11	45	0.0093	0.4668	-3.0644
12	60	0.0029	0.4896	-

L = 53

k = 6.4399×10^{-3} cm/sec

Table - 3.5 Run No.5

Crucible diameter = 5.50 cms

Nozzle diameter = 0.15 cms

Metal weight = 1000 gms

Slag weight = 210 gms

Na_2O/SiO_2 ratio = 1.0

Temperature = 1400°C

Flow rate = 6.0 l/h

FeO = 0.807 %

S.No.	Time, t (min)	$[\text{wt\% } S_b]_t$	$(\text{wt\% } S_b)_t$	$\ln \dfrac{[\text{wt\% } S_b]_t - [\text{wt\% } S_b]_\infty}{[\text{wt\% } S_b]_o - [\text{wt\% } S_b]_\infty}$
1	3	0.1250	0.0714	-0.3395
2	6	0.1183	0.1033	-0.5387
3	9	0.1128	0.1295	-0.7383
4	12	0.1075	0.1548	-0.9776
5	15	0.1036	0.1733	-1.1995
6	18	0.1007	0.1871	-1.4037
7	21	0.0987	0.1967	-1.5736
8	24	0.0963	0.2081	-1.8249
9	27	0.0948	0.2152	-2.0216
10	30	0.0942	0.2181	-2.1126
11	45	0.0898	0.2390	-3.3113
12	60	0.0879	0.2481	-

$L = 1.0$

$k = 2.8060 \times 10^{-3}$ cm/sec

Table - 3.6 Run No.6

Crucible diameter = 5.50 cms
Nozzle diameter = 0.15 cms
Metal weight = 1000 gms
Slag weight = 280 gms
Na_2O/SiO_2 ratio = 1.0
Temperature = 1400°C
Flow rate = 5.9 l/h
FeO = 0.807 %

S.No.	Time, t (min)	$[\text{wt\%}\,S_b]_t$	$(\text{wt\%}\,S_b)_t$	$\ln \dfrac{[\text{wt\%}\,S_b]_t - [\text{wt\%}\,S_b]_\infty}{[\text{wt\%}\,S_b]_o - [\text{wt\%}\,S_b]_\infty}$
1	3	0.1234	0.0593	-0.3392
2	6	0.1159	0.0961	-0.5407
3	9	0.1098	0.1079	-0.7411
4	12	0.1040	0.1286	-0.9779
5	15	0.0997	0.1439	-1.1988
6	18	0.0965	0.1554	-1.4020
7	21	0.0931	0.1675	-1.6757
8	24	0.0909	0.1754	-1.9035
9	27	0.0894	0.1807	-2.0952
10	30	0.0879	0.1861	-2.3325
11	45	0.0843	0.1989	-3.3621
12	60	0.0823	0.2061	-

L = 0.78

k = 2.9713×10^{-3} cm/sec

Table - 3.7 Run No.7

Crucible diameter = 5.50 cms
Nozzle diameter = 0.15 cms
Metal weight = 1000 gms
Slag weight = 140 gms
Na_2O/SiO_2 ratio = 1.0
Temperature = 1400°C
Flow rate = 6.3 l/h
FeO = 2.59 %

S.No.	Time, t (min)	$[\text{wt\%} S_b]_t$	$(\text{wt\%} S_b)_t$	$\ln \frac{[\text{wt\%} S_b]_t - [\text{wt\%} S_b]_\infty}{[\text{wt\%} S_b]_o - [\text{wt\%} S_b]_\infty}$
1	3	0.1299	0.0721	-0.4191
2	6	0.1270	0.0929	-0.5810
3	9	0.1232	0.1200	-0.8428
4	12	0.1207	0.1379	-1.0620
5	15	0.1184	0.1543	-1.3175
6	18	0.1171	0.1636	-1.4973
7	21	0.1156	0.1743	-1.7551
8	24	0.1147	0.1807	-1.9493
9	27	0.1136	0.1886	-2.2530
10	30	0.1131	0.1921	-2.4289
11	45	0.1113	0.2050	-3.6075
12	60	0.1105	0.2107	-

$L = 0.59$

$k = 1.560 \times 10^{-3}$ cm/sec

Table - 3.8 Run No. 8

Crucible diameter = 5.50 cms
Nozzle diameter = 0.15 cms
Metal weight = 1000 gms
Slag weight = 210 gms
Na_2O/SiO_2 ratio = 1.0
Temperature = 1400°C
Flow rate = 6.1 l /h
FeO = 2.59 %

S.No.	Time, t (min)	$[\text{wt\%}\,S_b]_t$	$(\text{wt\%}\,S_b)_t$	$\ln \dfrac{[\text{wt\%}\,S_b]_t - [\text{wt\%}\,S_b]_\infty}{[\text{wt\%}\,S_b]_o - [\text{wt\%}\,S_b]_\infty}$
1	3	0.1277	0.0586	-0.3801
2	6	0.1216	0.0876	-0.6406
3	9	0.1179	0.1052	-0.8396
4	12	0.1146	0.1210	-1.0583
5	15	0.1113	0.1367	-1.3386
6	18	0.1091	0.1471	-1.5816
7	21	0.1074	0.1552	-1.8204
8	24	0.1060	0.1619	-2.0718
9	27	0.1048	0.1676	-2.3527
10	30	0.1043	0.1700	-2.4978
11	45	0.1021	0.1805	-3.6610
12	60	0.1011	0.1852	-

L = 0.57
k = 2.1656×10^{-3} cm/sec

Table - 3.9 Run No.9

Crucible diamter = 5.50 cms
Nozzle diameter = 0.15 cms
Metal weight = 1000 gms
Slag weight == 280 gms
Na_2O/SiO_2 ratio = 1.0
Temperature = 1400°C
Flow rate = 5.9 l/h
FeO = 2.59 %

S.No.	Time, t (min)	$[\text{wt\%} S_b]_t$	$(\text{wt\%} S_b)_t$	$\ln \frac{[\text{wt\%} S_b]_t - [\text{wt\%} S_b]_\infty}{[\text{wt\%} S_b]_o - [\text{wt\%} S_b]_\infty}$
1	3	0.1262	0.0493	-0.3805
2	6	0.1194	0.0736	-0.6396
3	9	0.1141	0.0925	-0.9015
4	12	0.1098	0.1079	-1.1798
5	15	0.1072	0.1171	-1.3955
6	18	0.1048	0.1257	-1.6468
7	21	0.1029	0.1325	-1.9033
8	24	0.1011	0.1389	-2.2275
9	27	0.1003	0.1418	-2.4141
10	30	0.0993	0.1454	-2.7103
11	45	0.0972	0.1529	-3.9982
12	60	0.0964	0.1557	-

L = 0.50

k = 2.6078×10^{-3} cm/sec

Table - 3.10 Run No.10

Crucible diameter = 5.50 cms
Nozzle diameter = 0.15 cms
Metal weight = 1000 gms
Slag weight = 140 gms
Na_2O/SiO_2 ratio = 1.0
Temperature = 1400°C
Flow rate = 4.6 l/h

S.No.	Time, t (min)	$[wt\%\ S_b]_t$	$(wt\%S_b)_t$	$\ln \dfrac{[wt\%\ S_b]_t - [wt\%\ S_b]_\infty}{[wt\%\ S_b]_o - [wt\%\ S_b]_\infty}$
1	3	0.1114	0.2043	-0.2480
2	6	0.1006	0.2814	-0.3604
3	9	0.0893	0.3621	-0.4933
4	12	0.0769	0.4507	-0.6629
5	15	0.0662	0.5271	-0.8366
6	18	0.0571	0.5921	-1.0126
7	21	0.0518	0.6300	-1.1314
8	24	0.0424	0.6971	-1.3848
9	27	0.0393	0.7193	-1.4847
10	30	0.0392	0.7200	-1.4881
11	45	0.0242	0.8271	-2.2018
12	60	0.0098	0.9300	-

L = 16
k = 4.0412×10^{-3} cm/sec

Table - 3.11 Run No.11

Crucible diameter = 5.50 cms
Nozzle diameter = 0.15 cms
Metal weight = 1000 gms
Slag weight = 140 gms
Na_2O/SiO_2 ratio = 1.0
Temperature = 1400°C
Flow rate = 9.4 l/h

S.No.	Time, t (min)	$[\text{wt\%}\ S_b]_t$	$(\text{wt\%}\ S_b)_t$	$\ln \dfrac{[\text{wt\%}\ S_b]_t - [\text{wt\%}\ S_b]_\infty}{[\text{wt\%}\ S_b]_o - [\text{wt\%}\ S_b]_\infty}$
1	3	0.1004	0.2829	-0.3417
2	6	0.0795	0.4321	-0.5838
3	9	0.0657	0.5307	-0.7834
4	12	0.0511	0.6350	-1.0494
5	15	0.0398	0.7157	-1.3185
6	18	0.0310	0.7786	-1.5935
7	21	0.0238	0.8300	-1.8932
8	24	0.0190	0.8643	-2.1585
9	27	0.0151	0.8921	-2.4420
10	30	0.0128	0.9086	-2.6568
11	45	0.0063	0.9550	-3.7871
12	60	0.0032	0.9771	-

L = 76
k = 7.8808×10^{-3} cm/sec

Table - 3.12 Run No.12

Crucible diameter = 5.50 cms

Nozzle diameter = 0.15 cms

Metal weight = 1000 gms

Slag weight = 140 gms.

Na_2O/SiO_2 ratio = 1.0

Temperature = 1400°C

Flow rate = 23.7 l/h

S.No.	Time, t (min)	$[\text{wt\%}\,S_b]_t$	$(\text{wt\%}\,S_b)_t$	$\ln \dfrac{[\text{wt\%}\,S_b]_t - [\text{wt\%}\,S_b]_\infty}{[\text{wt\%}\,S_b]_o - [\text{wt\%}\,S_b]_\infty}$
1	3	0.0911	0.3493	-0.4415
2	6	0.0668	0.5229	-0.7642
3	9	0.0500	0.6429	-1.0698
4	12	0.0356	0.7457	-1.4357
5	15	0.0254	0.8186	-1.8109
6	18	0.0182	0.8700	-2.1987
7	21	0.0134	0.9043	-2.5782
8	24	0.0110	0.9214	-2.8405
9	27	0.0100	0.9286	-2.9741
10	30	0.0076	0.9457	-3.3939
11	45	0.0039	0.9721	-5.0293
12	60	0.0030	0.9786	-

L =127

$k = 1.0349 \times 10^{-2}$ cm/sec

Table - 3.13 Run No.13

Crucible diameter = 5.50 cms
Nozzle diameter = 0.15 cms
Metal weight = 1000 gms
Slag weight = 140 gms
Na_2O/SiO_2 ratio = 1.0
Temperature = 1400°C
Flow rate = 38.9 l/h

S.No.	Time,t (min)	$[\text{wt\% } S_b]_t$	$(\text{wt\% } S_b)_t$	$\ln \frac{[\text{wt\% } S_b]_t - [\text{wt\% } S_b]_\infty}{[\text{wt\% } S_b]_o - [\text{wt\% } S_b]_\infty}$
1	3	0.0867	0.3807	-0.4900
2	6	0.0544	0.6114	-0.9731
3	9	0.0364	0.7400	-1.3980
4	12	0.0234	0.8329	-1.8798
5	15	0.0151	0.8921	-2.3827
6	18	0.0100	0.9286	-2.8962
7	21	0.0068	0.9514	-3.4427
8	24	0.0059	0.9579	-3.6716
9	27	0.0046	0.9671	-4.1359
10	30	0.0038	0.9729	-4.5879
11	45	0.0026	0.9814	-6.5338
12	60	0.0024	0.9829	-

L = 127

k = 1.4193×10^{-2} cm/sec

Table - 3.14 Run No.14

Crucible diameter = 5.50 cms
Nozzle diameter = 0.15 cms
Metal weight = 1000 gms
Slag weight = 140 gms
Na_2O/SiO_2 ratio = 1.0
Temperature = 1400°C
Flow rate = 48.0 l/h

S.No.	Time, t (min)	$[wt\% S_b]_t$	$(wt\% S_b)_t$	$\ln \frac{[wt\% S_b]_t - [wt\% S_b]_\infty}{[wt\% S_b]_o - [wt\% S_b]_\infty}$
1	3	0.0790	0.4357	-0.5858
2	6	0.0493	0.6479	-1.0763
3	9	0.0332	0.7629	-1.4968
4	12	0.0207	0.8521	-2.0175
5	15	0.0131	0.9064	-2.5541
6	18	0.0084	0.9400	-3.1326
7	21	0.0055	0.9607	-3.7929
8	24	0.0042	0.9700	-4.3366
9	27	0.0035	0.9750	-4.8290
10	30	0.0030	0.9786	-5.4352
11	45	0.0024	0.9829	-
12	60	0.0024	0.9829	-

L = 127

k = 1.6082×10^{-2} cm/sec

Table - 3.15 Run No. 15

Crucible diameter = 5.50 cms
Nozzle diameter = 0.15 cms
Metal weight = 1000 gms
Slag weight = 140 gms
Na_2O/SiO_2 ratio = 1.0
Temperature = 1400°C
Flow rate = 61.3 l/h

S.No.	Time, t (min)	$[wt\% \; S_b]_t$	$(wt\% S_b)_t$	$\ln \dfrac{[wt\% \; S_b]_t - [wt\% \; S_b]_\infty}{[wt\% \; S_b]_o - [wt\% \; S_b]_\infty}$
1	3	0.0673	0.5193	-0.7499
2	6	0.0387	0.7236	-1.3285
3	9	0.0232	0.8343	-1.8813
4	12	0.0130	0.9071	-2.5463
5	15	0.0074	0.9471	-3.2771
6	18	0.0044	0.9686	-4.1374
7	21	0.0036	0.9743	-4.5893
8	24	0.0030	0.9786	-5.1489
9	27	0.0027	0.9807	-5.6190
10	30	0.0025	0.9821	-6.1298
11	45	0.0022	0.9843	-
12	60	0.0022	0.9843	-

L = 127

k = 1.9202×10^{-3} cm/sec

Table - 3.16 Run No.16

Crucible diameter = 5.50 cms
Nozzle diameter = 0.15 cms
Metal weight = 1000 gms
Slag weight = 140 gms
Na_2O/SiO_2 ratio = 0.6
Temperature = 1400°C
Flow rate = 5.9 l/h

S.No.	Time, t (min)	$[\text{wt\% } S_b]_t$	$(\text{wt\% } S_b)_t$	$\ln \dfrac{[\text{wt\% } S_b]_t - [\text{wt\% } S_b]_\infty}{[\text{wt\% } S_b]_o - [\text{wt\% } S_b]_\infty}$
1	3	0.1164	0.1636	-0.1962
2	6	0.0979	0.3007	-0.3823
3	9	0.0855	0.3893	-0.5299
4	12	0.0727	0.4807	-0.7091
5	15	0.0610	0.5643	-0.9069
6	18	0.0521	0.6279	-1.0888
7	21	0.0434	0.6900	-1.3058
8	24	0.0386	0.7243	-1.4494
9	27	0.0316	0.7743	-1.7044
10	30	0.0273	0.8050	-1.9009
11	45	0.0166	0.8814	-2.6783
12	60	0.0075	0.9464	-

L = 39

k = 5.2874×10^{-3} cm/sec

Table - 3.17 Run No.17

Crucible diameter	=	5.50	cms
Nozzle diameter	=	0.15	cms
Metal weight	=	1000	gms
Slag weight	=	140	gms
Na_2O/SiO_2 ratio	=	0.8	
Temperature	=	1400°C	
Flow rate	=	6.1 l/h	

S.No.	Time,t (min)	$[wt\% \ S_b]_t$	$(wt\%S_b)_t$	$\ln \frac{[wt\% \ S_b]_t - [wt\% \ S_b]_\infty}{[wt\% \ S_b]_o - [wt\% \ S_b]_\infty}$
1	3	0.1148	0.1800	-0.2075
2	6	0.0962	0.3129	-0.3940
3	9	0.0875	0.3750	-0.4948
4	12	0.0679	0.5150	-0.7680
5	15	0.0573	0.5907	-0.9542
6	18	0.0477	0.6593	-1.1591
7	21	0.0408	0.7086	-1.3377
8	24	0.0343	0.7550	-1.5412
9	27	0.0288	0.7943	-1.7531
10	30	0.0247	0.8236	-1.9467
11	45	0.0146	0.8957	-2.6933
12	60	0.0055	0.9607	-

L = 54

k = 5.5560×10^{-3} cm/sec

Table - 3.18 Run No.18

Crucible diameter = 5.50 cms
Nozzle diameter = 0.15 cms
Metal weight = 1000 gms
Slag weight = 140 gms
Na_2O/SiO_2 ratio = 1.2
Temperature = 1400°C
Flow rate = 6.3 l/h

S.No.	Time, t (min)	$[\text{wt\%} S_b]_t$	$(\text{wt\%} S_b)_t$	$\ln \dfrac{[\text{wt\%} S_b]_t - [\text{wt\%} S_b]_\infty}{[\text{wt\%} S_b]_o - [\text{wt\%} S_b]_\infty}$
1	3	0.1122	0.1986	-0.2279
2	6	0.0926	0.3386	-0.4270
3	9	0.0767	0.4521	-0.6238
4	12	0.0647	0.5379	-0.8031
5	15	0.0535	0.6179	-1.0056
6	18	0.0447	0.6807	-1.1996
7	21	0.0369	0.7364	-1.4100
8	24	0.0305	0.7821	-1.6235
9	27	0.0255	0.8179	-1.8291
10	30	0.0213	0.8479	-2.0420
11	45	0.0108	0.9229	-2.9415
12	60	0.0036	0.9743	-

L = 85

k = 6.0769×10^{-3} cm/sec

Table - 3.19 Run No.19

Crucible diameter = 5.50 cms
Nozzle diameter = 0.15 cms
Metal weight = 1000 gms
Slag weight = 140 gms
Na_2O/SiO_2 ratio = 1.4
Temperature = 1400°C
Flow rate = 5.9 l/h

S.No.	Time, t (min)	$[\text{wt\% } S_b]_t$	$(\text{wt\% } S_b)_t$	$\ln \dfrac{[\text{wt\% } S_b]_t - [\text{wt\% } S_b]_\infty}{[\text{wt\% } S_b]_o - [\text{wt\% } S_b]_\infty}$
1	3	0.1121	0.1993	-0.2281
2	6	0.0925	0.3393	-0.4265
3	9	0.0766	0.4529	-0.6226
4	12	0.0629	0.5507	-0.8292
5	15	0.0522	0.6271	-1.0267
6	18	0.0435	0.6895	-1.2222
7	21	0.0356	0.7457	-1.4404
8	24	0.0309	0.7793	-1.5971
9	27	0.0237	0.8307	-1.8981
10	30	0.0202	0.8557	-2.0853
11	45	0.0104	0.9257	-2.9444
12	60	0.0032	0.9771	-

L = 85

k = 6.0769×10^{-3} cm/sec

Table - 3.20 Run No.20

Crucible diameter = 5.50 cms
Nozzle diameter = 0.15 cms
Metal weight = 1000 gms
Slag weight = 140 gms
Na_2O/SiO_2 ratio = 1.6
Temperature = 1400°C
Flow rate = 6.3 l/h

S.No.	Time, t (min)	$[wt\% S_b]_t$	$(wt\% S_b)_t$	$\ln \dfrac{[wt\% S_b]_t - [wt\% S_b]_\infty}{[wt\% S_b]_o - [wt\% S_b]_\infty}$
1	3	0.1108	0.2086	-0.2383
2	6	0.0894	0.3614	-0.4580
3	9	0.0764	0.4543	-0.6197
4	12	0.0622	0.5557	-0.8324
5	15	0.0504	0.6400	-1.0518
6	18	0.0415	0.7036	-1.2564
7	21	0.0376	0.7314	-1.3612
8	24	0.0284	0.7971	-1.6631
9	27	0.0223	0.8407	-1.9293
10	30	0.0189	0.8650	-2.1157
11	45	0.0088	0.9371	-3.0533
12	60	0.0023	0.9836	-

L = 133

k = 6.1333×10^{-3} cm/sec

Table - 3.21 Run No.21

Crucible diameter	=	5.50	cms
Nozzle diameter	=	0.15	cms
Metal weight	=	1000	gms
Slag weight	=	140	gms
Na_2O/SiO_2 ratio	=	1.0	
Temperature	=	1400°C	
Flow rate	=	6.3	l/h
Al_2O_3	=	1.5 %	

S.No.	Time, t (min)	$[\text{wt\% } S_b]_t$	$(\text{wt\% } S_b)_t$	$\ln \dfrac{[\text{wt\% } S_b]_t - [\text{wt\% } S_b]_\infty}{[\text{wt\% } S_b]_o - [\text{wt\% } S_b]_\infty}$
1	3	0.1157	0.1736	-0.2001
2	6	0.0958	0.3157	-0.4003
3	9	0.0825	0.4107	-0.5605
4	12	0.0699	0.5007	-0.7405
5	15	0.0573	0.5907	-0.9601
6	18	0.0497	0.6450	-1.1205
7	21	0.0425	0.6964	-1.3005
8	24	0.0347	0.7521	-1.5409
9	27	0.0291	0.7921	-1.7580
10	30	0.0249	0.8221	-1.9587
11	45	0.0141	0.8993	-2.8060
12	60	0.0060	0.9571	-

L = 50

k = 5.5385×10^{-3} cm/sec

Table - 3.22 Run No.22

Crucible diameter = 5.50 cms
Nozzle diameter = 0.15 cms
Metal weight = 1000 gms
Slag weight = 140 gms
Na_2O/SiO_2 ratio = 1.0
Temperature = 1400°C
Flow rate = 6.1 l/h
Al_2O_3 = 8.06 %

S.No.	Time, t (min)	$[wt\% S_b]_t$	$(wt\% S_b)_t$	ln $\frac{[wt\% S_b]_t - [wt\% S_b}{[wt\% S_b]_o - [wt\% S_b}$
1	3	0.1165	0.1679	-0.1947
2	6	0.0977	0.3021	-0.3835
3	9	0.0857	0.3879	-0.5257
4	12	0.0728	0.4800	-0.7053
5	15	0.0612	0.5629	-0.8999
6	18	0.0522	0.6271	-1.0822
7	21	0.0437	0.6879	-1.2913
8	24	0.0386	0.7243	-1.4420
9	27	0.0317	0.7736	-1.6902
10	30	0.0275	0.8036	-1.8782
11	45	0.0169	0.8793	-2.6167
12	60	0.0072	0.9486	-

L = 41
k = 5.3012×10^{-3} cm/sec

Table - 3.23 Run No. 23

Crucible diameter = 5.50 cms
Nozzle diameter = 0.15 cms
Metal weight = 1000 gms
Slag weight = 140 gms
Na_2O/SiO_2 ratio = 0.6
Temperature = 1400°C
Flow rate = 6.1 l /h
CaF_2 = 2.886 %

S.No.	Time, t (min)	$[\text{wt\%}\, S_b]_t$	$(\text{wt\%}\, S_b)_t$	$\ln \dfrac{[\text{wt\%}\, S_b]_t - [\text{wt\%}\, S_b]_o}{[\text{wt\%}\, S_b]_o - [\text{wt\%}\, S_b]_o}$
1	3	0.1055	0.2464	-0.2998
2	6	0.0926	0.3386	-0.4398
3	9	0.0770	0.4500	-0.6405
4	12	0.0667	0.5236	-0.7992
5	15	0.0568	0.5943	-0.9798
6	18	0.0477	0.6593	-1.1807
7	21	0.0417	0.7021	-1.3394
8	24	0.0377	0.7307	-1.4611
9	27	0.0311	0.7779	-1.7014
10	30	0.0263	0.8121	-1.9214
11	45	0.0154	0.8900	-2.7401
12	60	0.0068	0.9514	-

L = 39
k = 5.4477×10^{-3} cm/sec

Table - 3.25 Run No.25

Crucible diameter = 5.50 cms

Nozzle diameter = 0.15 cms

Metal weight = 1000 gms

Slag weight = 140 gms

Na_2O/SiO_2 ratio = 1.0

Temperature = 1400°C

Flow rate = 6.3 l/h

CaF_2 = 2.886 %

S.No.	Time, t (min)	$[\text{wt\% } S_b]_t$	$(\text{wt\% } S_b)_t$	$\ln \dfrac{[\text{wt\% } S_b]_t - [\text{wt\% } S_b]_\infty}{[\text{wt\% } S_b]_o - [\text{wt\% } S_b]_\infty}$
1	3	0.1027	0.2664	-0.3197
2	6	0.0847	0.3950	-0.5204
3	9	0.0714	0.4900	-0.6998
4	12	0.0591	0.5779	-0.9008
5	15	0.0509	0.6364	-1.0605
6	18	0.0416	0.7029	-1.2799
7	21	0.0354	0.7471	-1.4585
8	24	0.0296	0.7886	-1.6606
9	27	0.0256	0.8171	-1.8284
10	30	0.0214	0.8471	-2.0413
11	45	0.0105	0.9250	-2.9979
12	60	0.0037	0.9736	-

L = 82

k = 6.0428×10^{-3} cm/sec

Table - 3.26 Run No.26

Crucible diameter = 5.50 cms

Nozzle diameter = 0.15 cms

Metal weight = 1000 gms

Slag weight = 140 gms

Na_2O/SiO_2 ratio = 1.0

Temperature = 1400°C

Flow rate = 6.3 l/h

CaF_2 = 5.538 %

S.No.	Time, t (min)	$[wt\% S_b]_t$	$(wt\% S_b)_t$	$\ln \frac{[wt\% S_b]_t - [wt\% S_b]_\infty}{[wt\% S_b]_o - [wt\% S_b]_\infty}$
1	3	0.1024	0.2686	-0.3203
2	6	0.0844	0.3971	-0.5196
3	9	0.0709	0.4936	-0.7005
4	12	0.0586	0.5814	-0.8997
5	15	0.0476	0.6600	-1.1192
6	18	0.0391	0.7207	-1.3296
7	21	0.0334	0.7614	-1.5004
8	24	0.0274	0.8043	-1.7187
9	27	0.0229	0.8364	-1.9207
10	30	0.0196	0.8600	-2.1001
11	45	0.0090	0.9357	-3.0969
12	60	0.0028	0.9800	-

L = 109

k = 6.3049×10^{-3} cm/sec

Table - 3.27 Run No.27

Crucible diameter = 5.50 cms
Nozzle diameter = 0.15 cms
Metal weight = 1000 gms
Slag weight = 140 gms
Na_2O/SiO_2 ratio = 0.6
Temperature = 1400°C
Flow rate = 5.9 l/h
FeO = 0.807 %

S.No.	Time, t (min)	$[wt\%\ S_b]_t$	$(wt\%\ S_b)_t$	$\ln \dfrac{[wt\%\ S_b]_t - [wt\%\ S_b]_o}{[wt\%\ S_b]_o - [wt\%\ S_b]_o}$
1	3	0.1284	0.0829	-0.3214
2	6	0.1219	0.1293	-0.5602
3	9	0.1171	0.1636	-0.7823
4	12	0.1133	0.1907	-1.0016
5	15	0.1105	0.2107	-1.2008
6	18	0.1084	0.2257	-1.3816
7	21	0.1060	0.2429	-1.6383
8	24	0.1045	0.2536	-1.8403
9	27	0.1037	0.2593	-1.9675
10	30	0.1019	0.2721	-2.3314
11	45	0.0993	0.2907	-3.3370
12	60	0.0978	0.3014	-

L = 0.96
k = 2.1352×10^{-3} cm/sec

Table - 3.28 Run No.28

Crucible diameter = 5.50 cms
Nozzle diameter = 0.15 cms
Metal weight = 1000 gms
Slag weight = 140 gms
Na_2O/SiO_2 ratio = 0.6
Temperature = 1400°C
Flow rate = 6.1 l/h
FeO = 2.59 %

S.No.	Time, t (min)	$[\text{wt\% } S_b]_t$	$(\text{wt\% } S_b)_t$	$\ln \dfrac{[\text{wt\% } S_b]_t - [\text{wt\% } S_b]_\alpha}{[\text{wt\% } S_b]_o - [\text{wt\% } S_b]_\alpha}$
1	3	0.1340	0.0429	-0.4000
2	6	0.1318	0.0586	-0.5988
3	9	0.1292	0.0771	-0.8999
4	12	0.1277	0.0879	-1.1265
5	15	0.1265	0.0964	-1.3539
6	18	0.1255	0.1036	-1.5931
7	21	0.1246	0.1100	-1.8718
8	24	0.1240	0.1143	-2.1130
9	27	0.1236	0.1171	-2.3136
10	30	0.1232	0.1200	-2.5650
11	45	0.1222	0.1271	-3.8177
12	60	0.1218	0.1300	-

L = 0.33
k = 1.0269×10^{-3} cm/sec

Table - 3.29 Run No.29

Crucible diameter = 5.50 cms
Nozzle diameter = 0.15 cms
Metal weight = 1000 gms
Slag weight = 140 gms
Na_2O/SiO_2 ratio = 1.0
Temperature = 1400°C
Flow rate = 6.3 l/h
FeO = 1.768 %

S.No.	Time, t (min)	$[\,wt\%\,S_b\,]_t$	$(\,wt\%\,S_b\,)_t$	$\ln \dfrac{[wt\%\,S_b]_t - [wt\%\,S_b]_\infty}{[wt\%\,S_b]_o - [wt\%\,S_b]_\infty}$
1	3	0.1292	0.0771	-0.3603
2	6	0.1247	0.1093	-0.5596
3	9	0.1198	0.1443	-0.8343
4	12	0.1174	0.1614	-1.0025
5	15	0.1145	0.1821	-1.2528
6	18	0.1123	0.1979	-1.4957
7	21	0.1106	0.2100	-1.7346
8	24	0.1094	0.2186	-1.9459
9	27	0.1084	0.2257	-2.1642
10	30	0.1074	0.2329	-2.4437
11	45	0.1054	0.2471	-3.4798
12	60	0.1043	0.2550	-

L = 0.76
k = 1.8918×10^{-3} cm/sec

Table - 3.30 Run No.30

Crucible diameter = 5.50 cms

Nozzle diameter = 0.15 cms

Metal weight = 1000 gms

Slag weight = 140 gms

Na_2O/SiO_2 ratio = 1.0

Temperature = 1400°C

Flow rate = 6.0 l/h

FeO = 3.94 %

S.No.	Time, t (min)	$[\text{wt\%}\,S_b]_t$	$(\text{wt\%}\,S_b)_t$	$\ln \dfrac{[\text{wt\%}\,S_b]_t - [\text{wt\%}\,S_b]_\infty}{[\text{wt\%}\,S_b]_o - [\text{wt\%}\,S_b]_\infty}$
1	3	0.1353	0.0336	-0.3985
2	6	0.1331	0.0493	-0.6588
3	9	0.1315	0.0607	-0.9024
4	12	0.1300	0.0714	-1.2016
5	15	0.1292	0.0771	-1.4075
6	18	0.1283	0.0836	-1.7047
7	21	0.1278	0.0871	-1.9183
8	24	0.1273	0.0907	-2.1903
9	27	0.1269	0.0936	-2.4779
10	30	0.1267	0.0950	-2.6603
11	45	0.1260	0.1000	-3.8642
12	60	0.1257	0.1021	-

L = 0.25

k = 8.3650×10^{-4} cm/sec

Table 3.31 Run No. 31

Crucible diameter = 5.50 cms
Nozzle diameter = 0.15 cms
Metal weight = 1000 gms
Slag weight = 140 gms
Na_2O/SiO_2 ratio = 1.0
Temperature = 1280°C
Flow rate = 6.1 l/h

S.No.	Time, t (min)	$[\text{wt\% } S_b]_t$	$(\text{wt\% } S_b)_t$	$\ln \frac{[\text{wt\% } S_b]_t - [\text{wt\% } S_b]_\infty}{[\text{wt\% } S_b]_o - [\text{wt\% } S_b]_\infty}$
1	3	0.1209	0.1364	-0.1673
2	6	0.1098	0.2157	-0.2791
3	9	0.0974	0.3043	-0.4209
4	12	0.0872	0.3771	-0.5548
5	15	0.0779	0.4436	-0.6948
6	18	0.0698	0.5014	-0.8350
7	21	0.0625	0.5536	-0.9808
8	24	0.0576	0.5886	-1.0922
9	27	0.0502	0.6414	-1.2881
10	30	0.0436	0.6886	-1.5025
11	45	0.0328	0.7657	-1.9989
12	60	0.0160	0.8857	-

L = 12
k = 3.6065×10^{-3} cm/sec

Table - 3.32 Run No.32

Crucible diameter = 5.50 cms
Nozzle diameter = 0.15 cms
Metal weight = 1000 gms
Slag weight = 140 gms
Na_2O/SiO_2 ratio = 1.0
Temperature = 1350°C
Flow rate = 5.9 l/h

S.No.	Time, t (min)	$[\text{wt\% } S_b]_t$	$(\text{wt\% } S_b)_t$	$\ln \dfrac{[\text{wt\% } S_b]_t - [\text{wt\% } S_b]_\infty}{[\text{wt\% } S_b]_o - [\text{wt\% } S_b]_\infty}$
1	3	0.1192	0.1486	-0.1733
2	6	0.0970	0.3071	-0.3990
3	9	0.0853	0.3907	-0.5422
4	12	0.0723	0.4836	-0.7298
5	15	0.0628	0.5514	-0.8932
6	18	0.0526	0.6243	-1.1048
7	21	0.0460	0.6714	-1.2701
8	24	0.0397	0.7164	-1.4585
9	27	0.0344	0.7543	-1.6500
10	30	0.0275	0.8036	-1.9715
11	45	0.0190	0.8643	-2.6008
12	60	0.0093	0.9336	-

L = 25
k = 5.1013×10^{-3} cm/sec

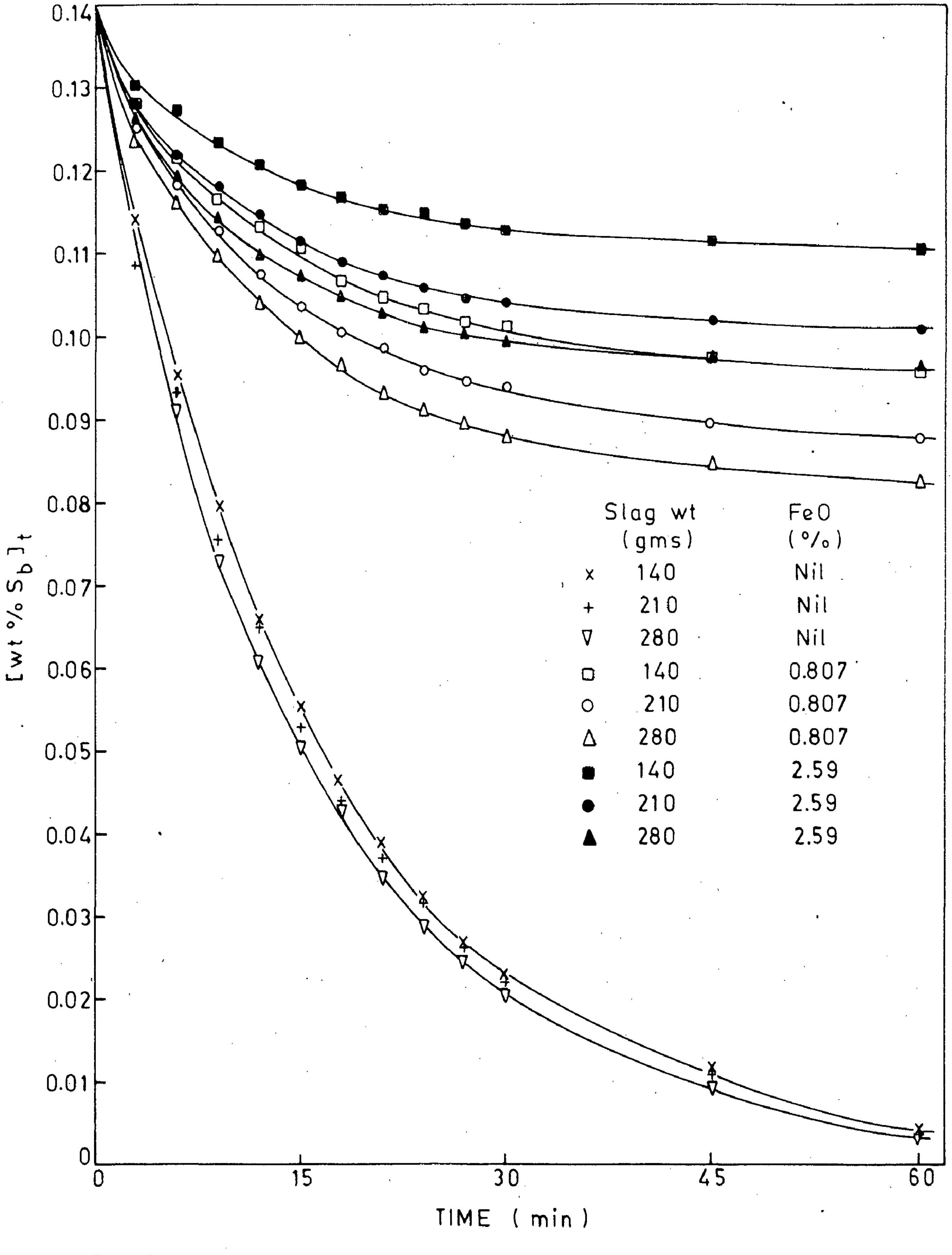

FIG. 3.1 EFFECT OF SLAG WEIGHT ON RATE OF SULPHUR REMOVAL FROM PIG IRON.

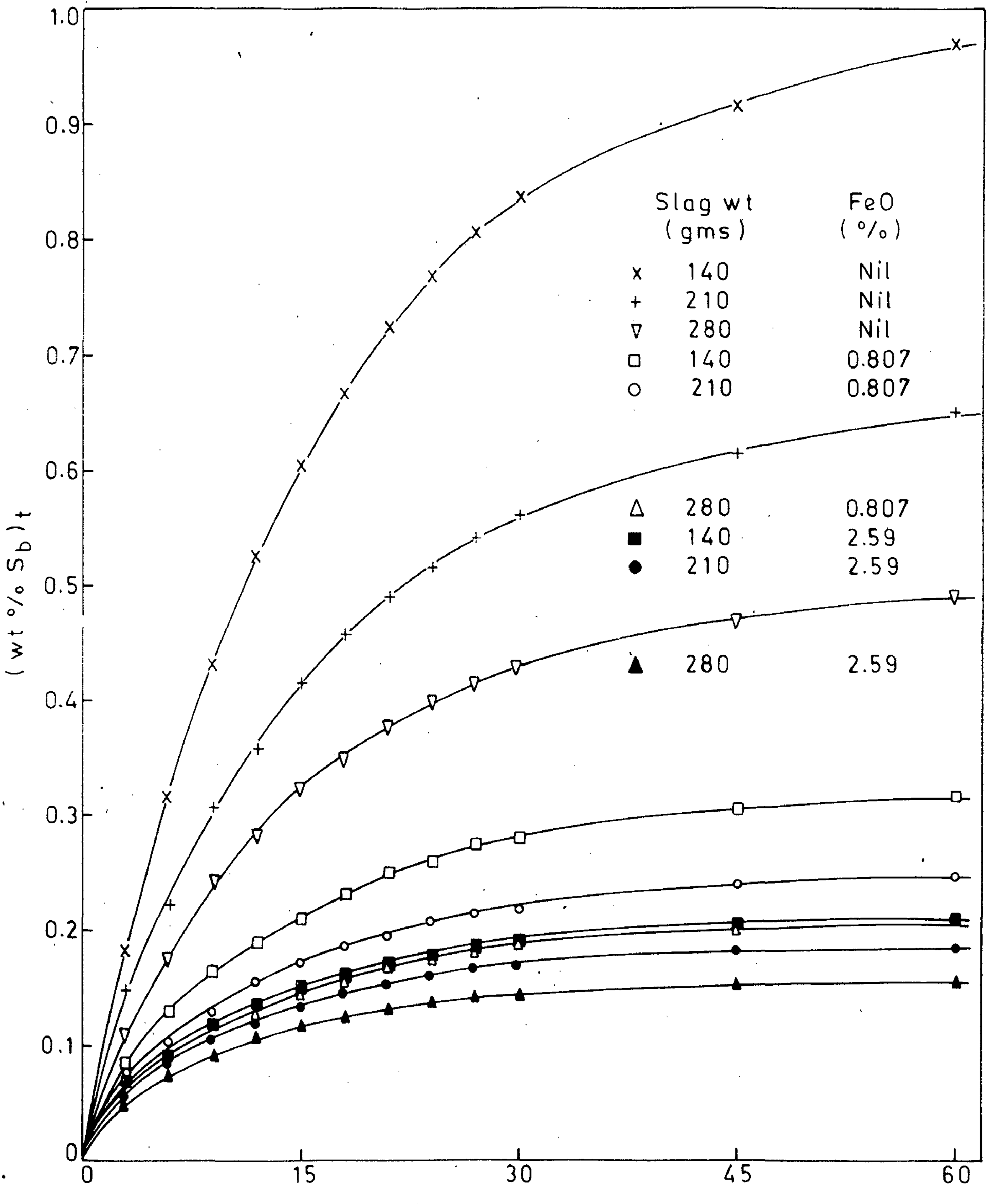

FIG. 3.2 EFFECT OF SLAG WEIGHT ON RATE OF SULPHUR TRANSFER FROM PIG IRON TO SLAG.

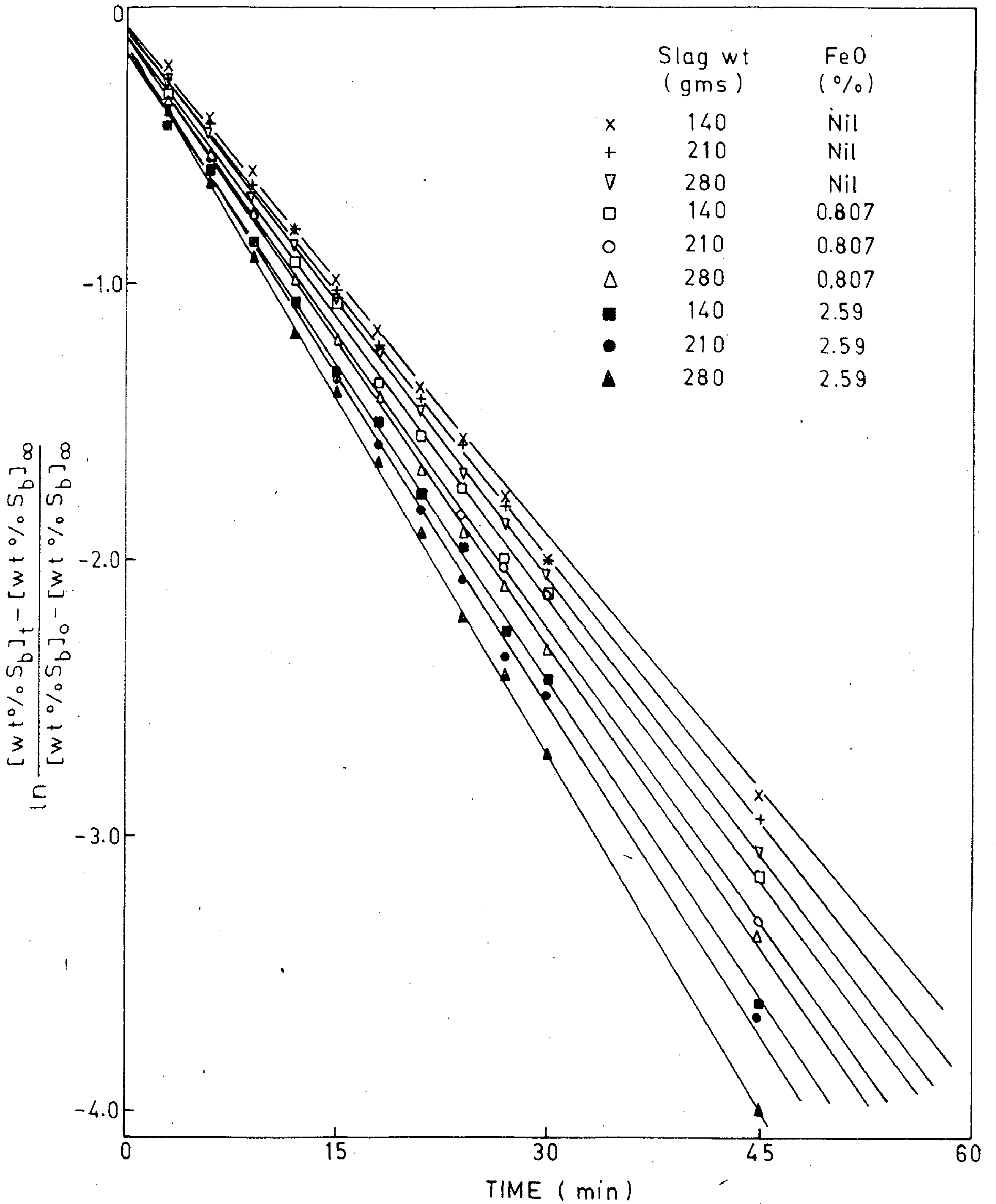

FIG.3.3 EFFECT OF SLAG WEIGHT ON RATE OF DESULPHURISATION OF PIG IRON.

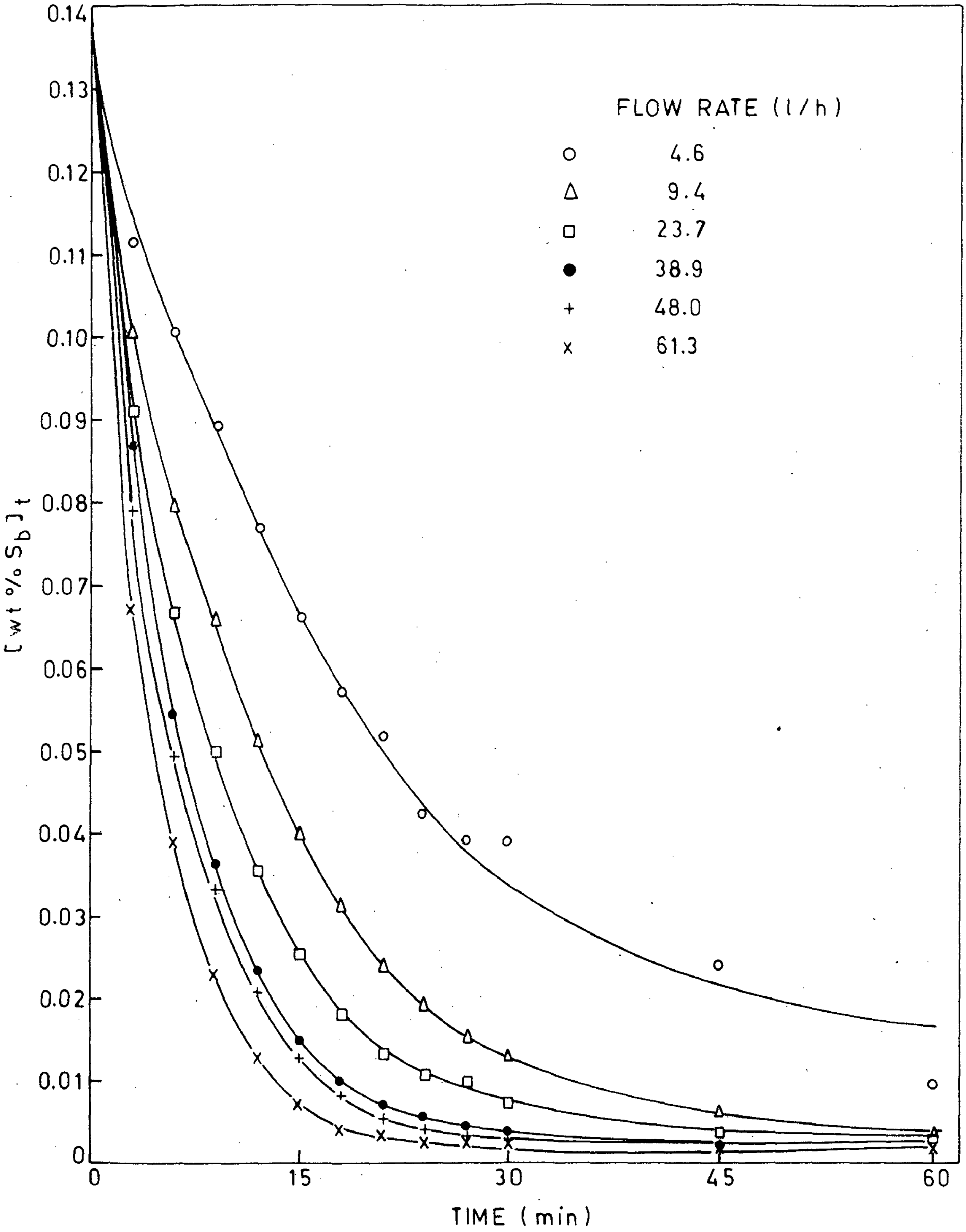

FIG.3.4 EFFECT OF GAS FLOW RATE ON RATE OF SULPHUR REMOVAL FROM PIG IRON.

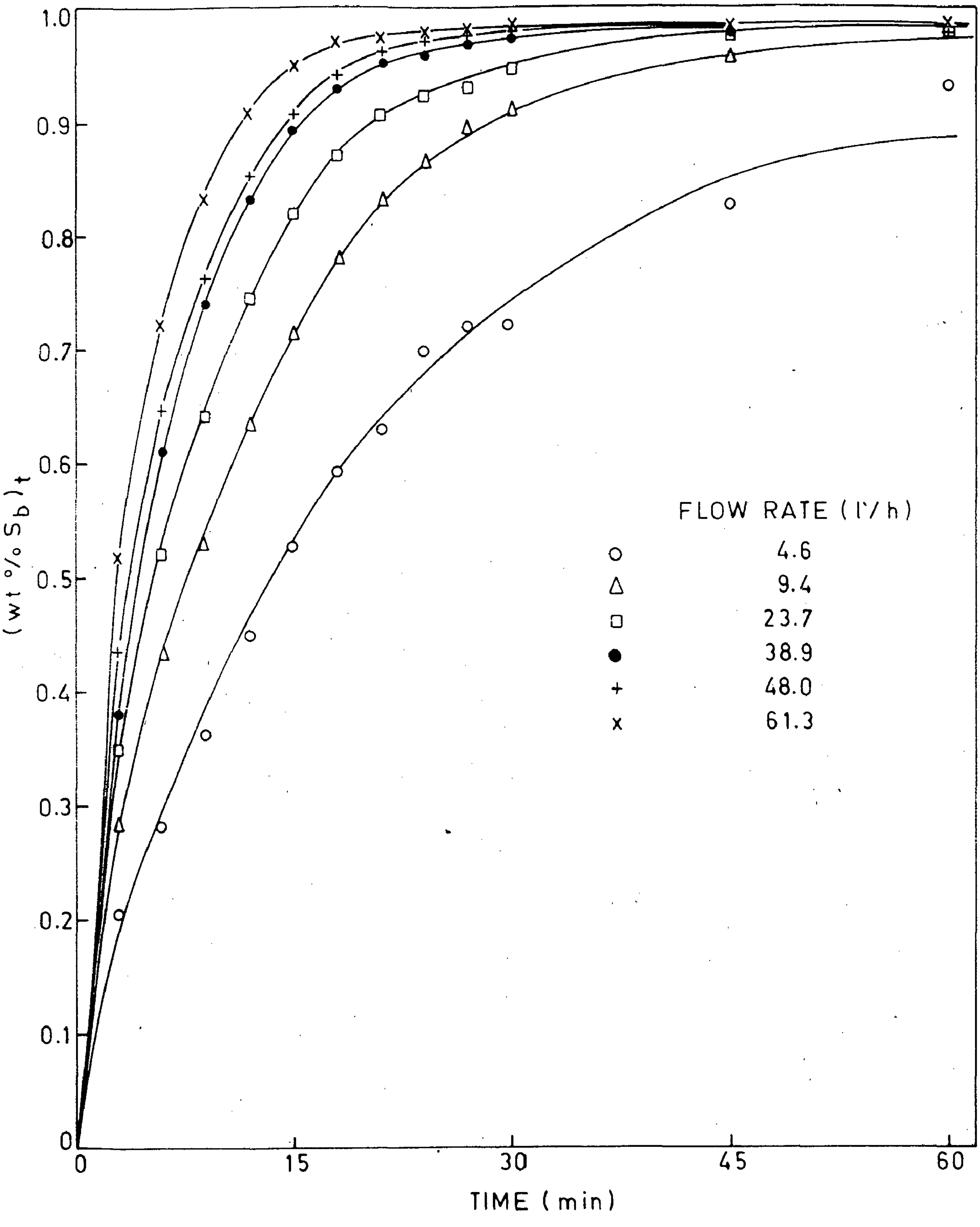

FIG. 3.5 EFFECT OF GAS FLOW RATE ON RATE OF SULPHUR TRANSFER FROM PIG IRON TO SLAG.

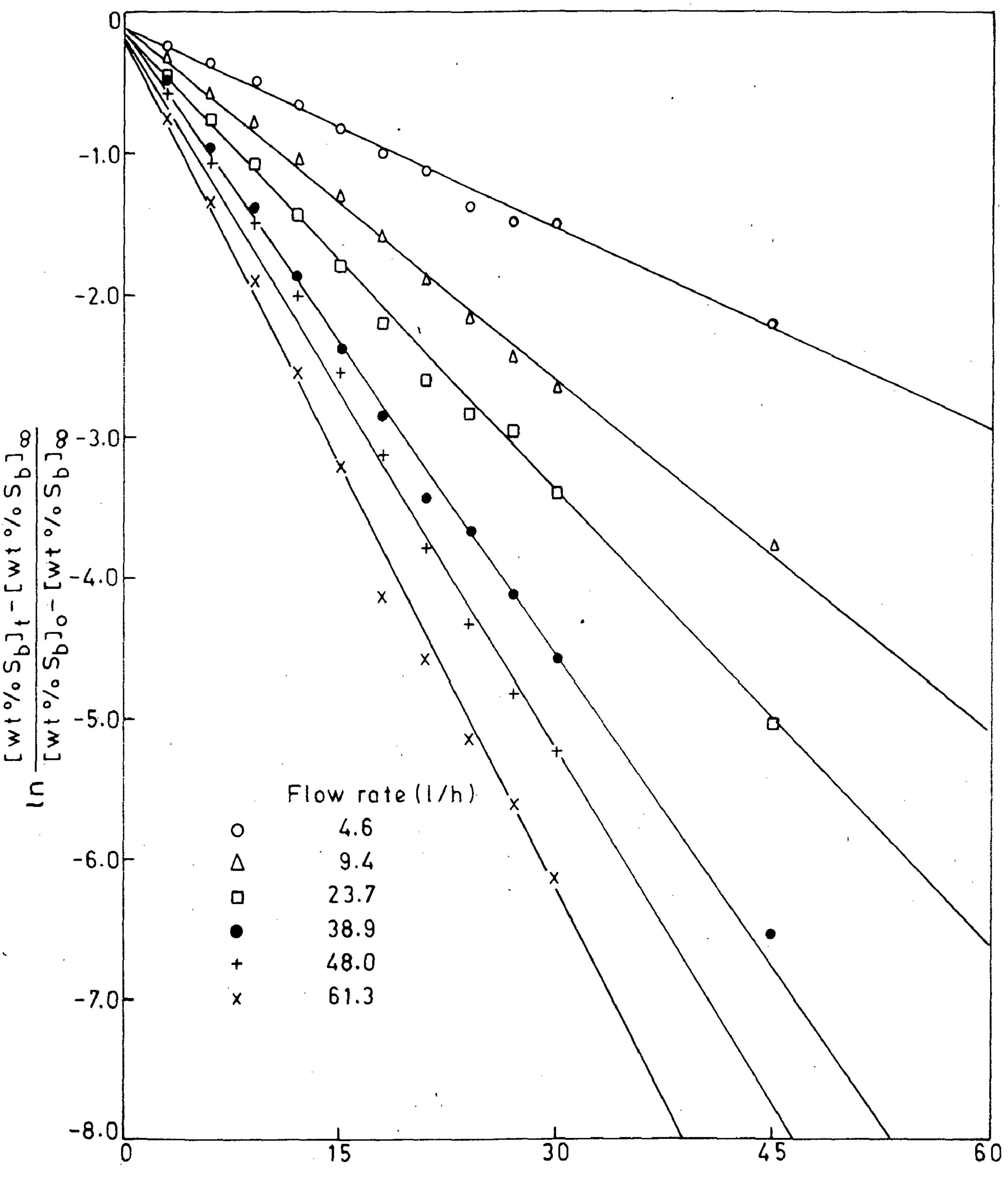

FIG.3.6 EFFECT OF GAS FLOW RATE ON RATE OF DESULPHURISATION OF PIG IRON.

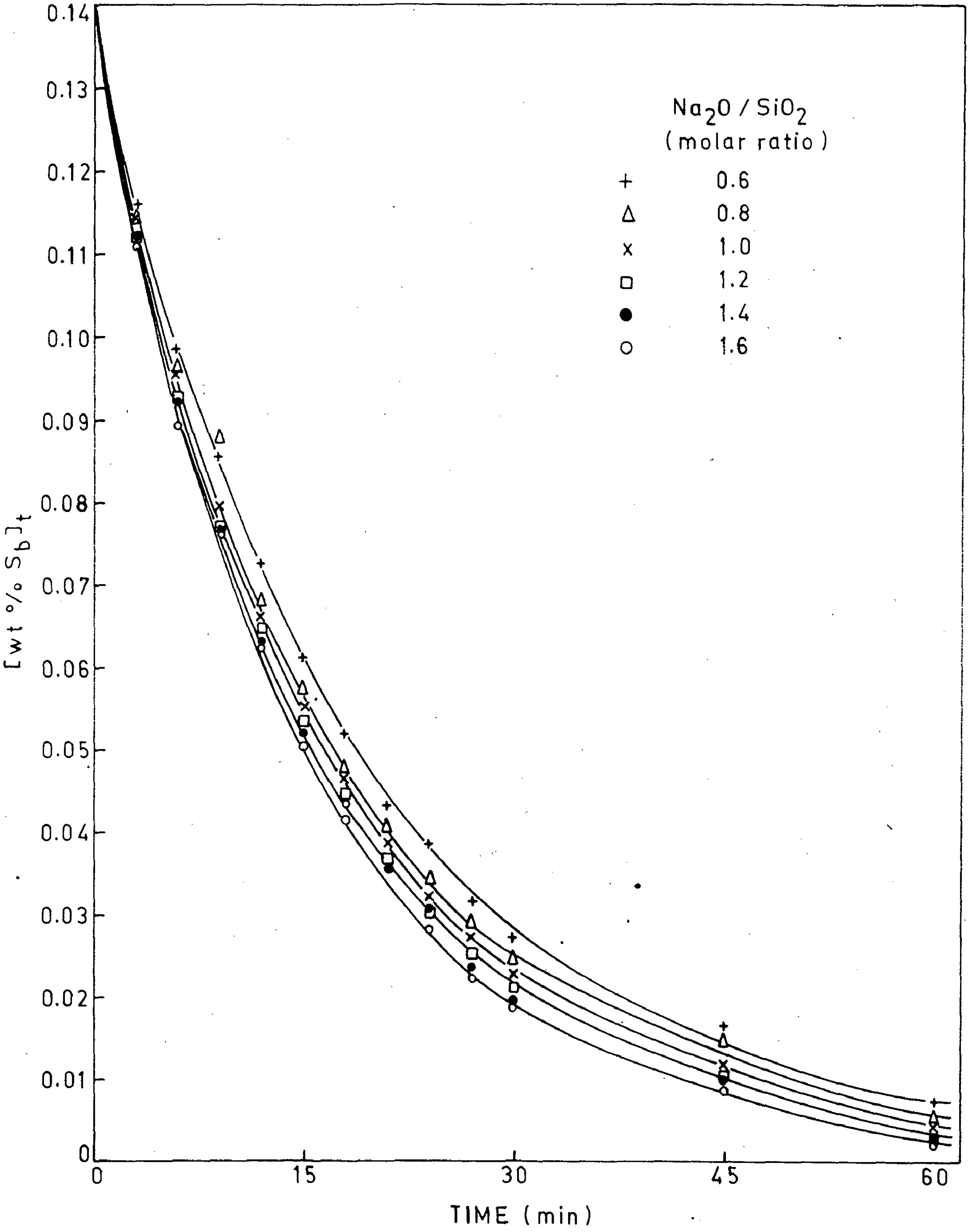

FIG. 3.7 EFFECT OF Na_2O/SiO_2 MOLAR RATIO ON RATE OF SULPHUR REMOVAL FROM PIG IRON.

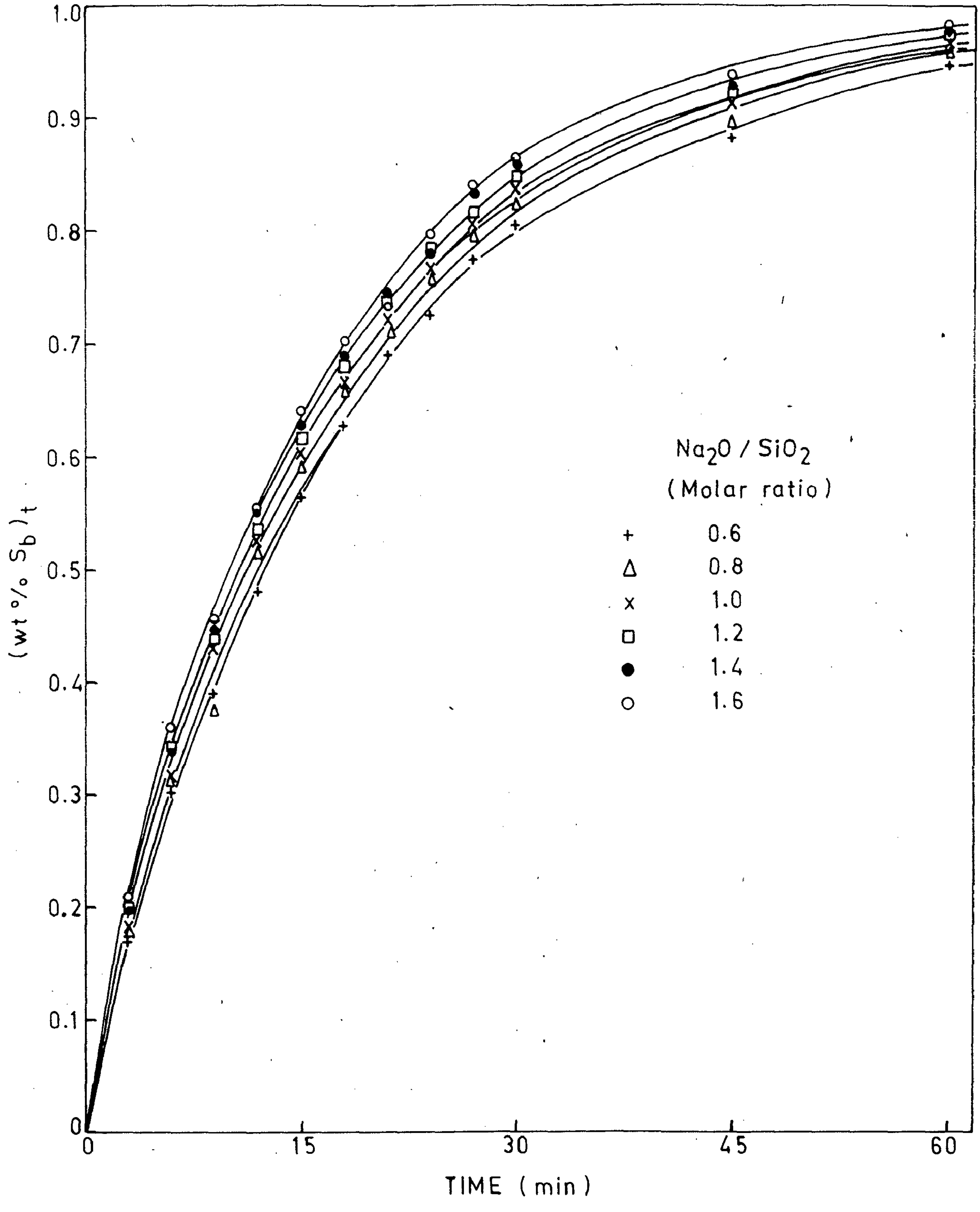

FIG. 3.8 EFFECT OF Na_2O / SiO_2 MOLAR RATIO ON RATE OF SULPHUR TRANSFER FROM PIG IRON TO SLAG.

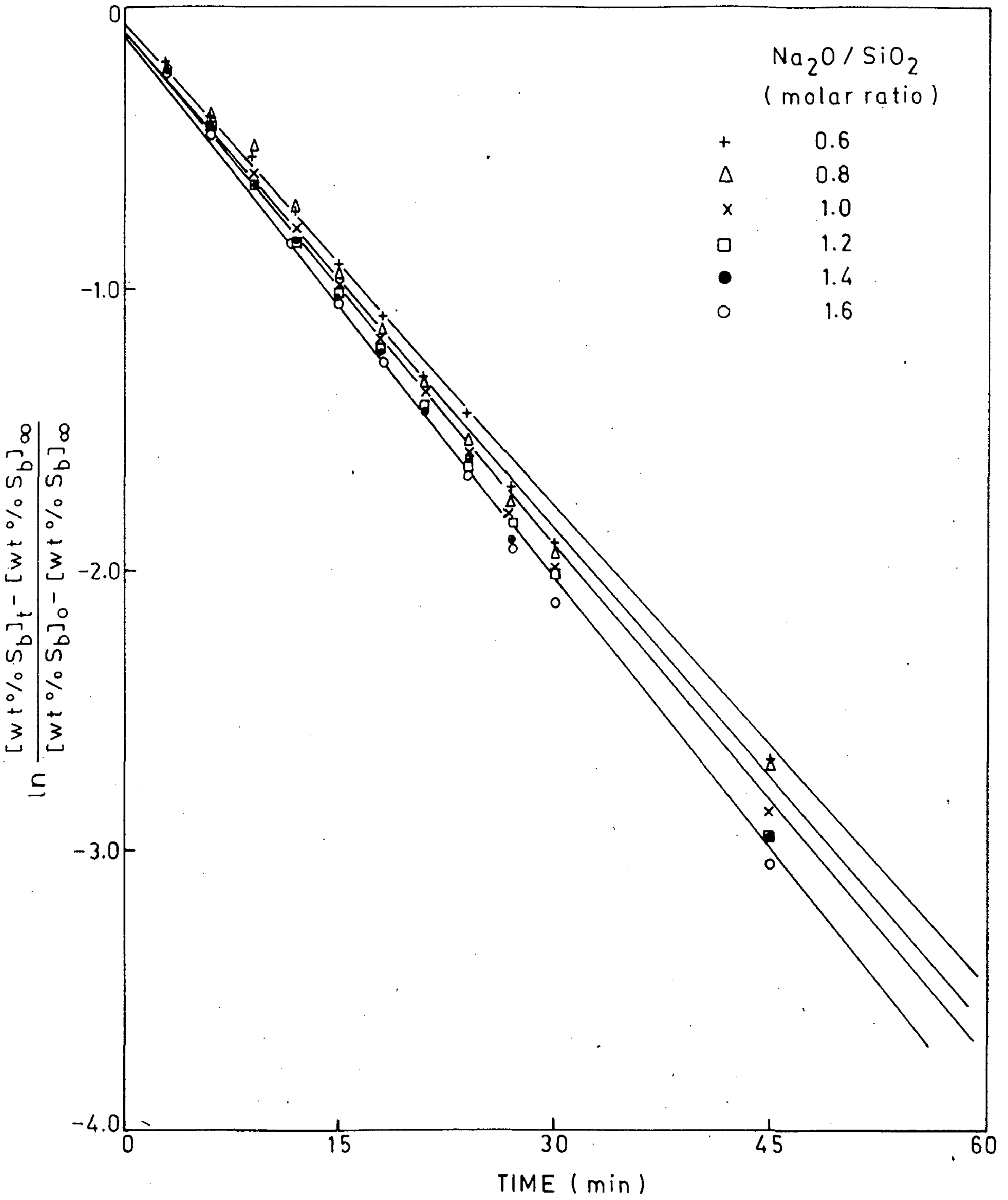

FIG.3.9 EFFECT OF Na_2O/SiO_2 MOLAR RATIO ON RATE OF DESULPHURISATION OF PIG IRON.

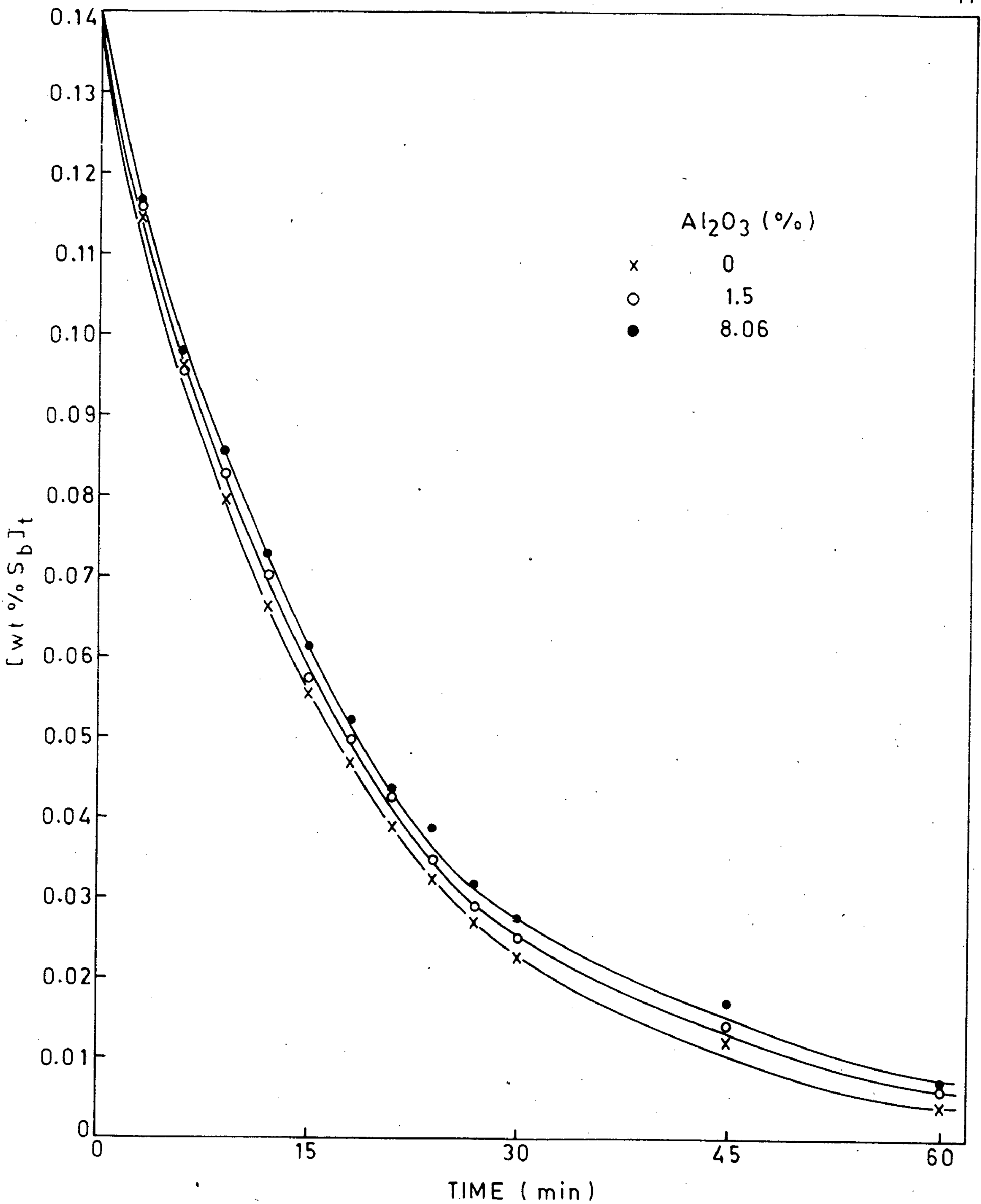

FIG. 3.10 EFFECT OF Al_2O_3 ADDITION TO SLAG ON RATE OF SULPHUR REMOVAL FROM PIG IRON.

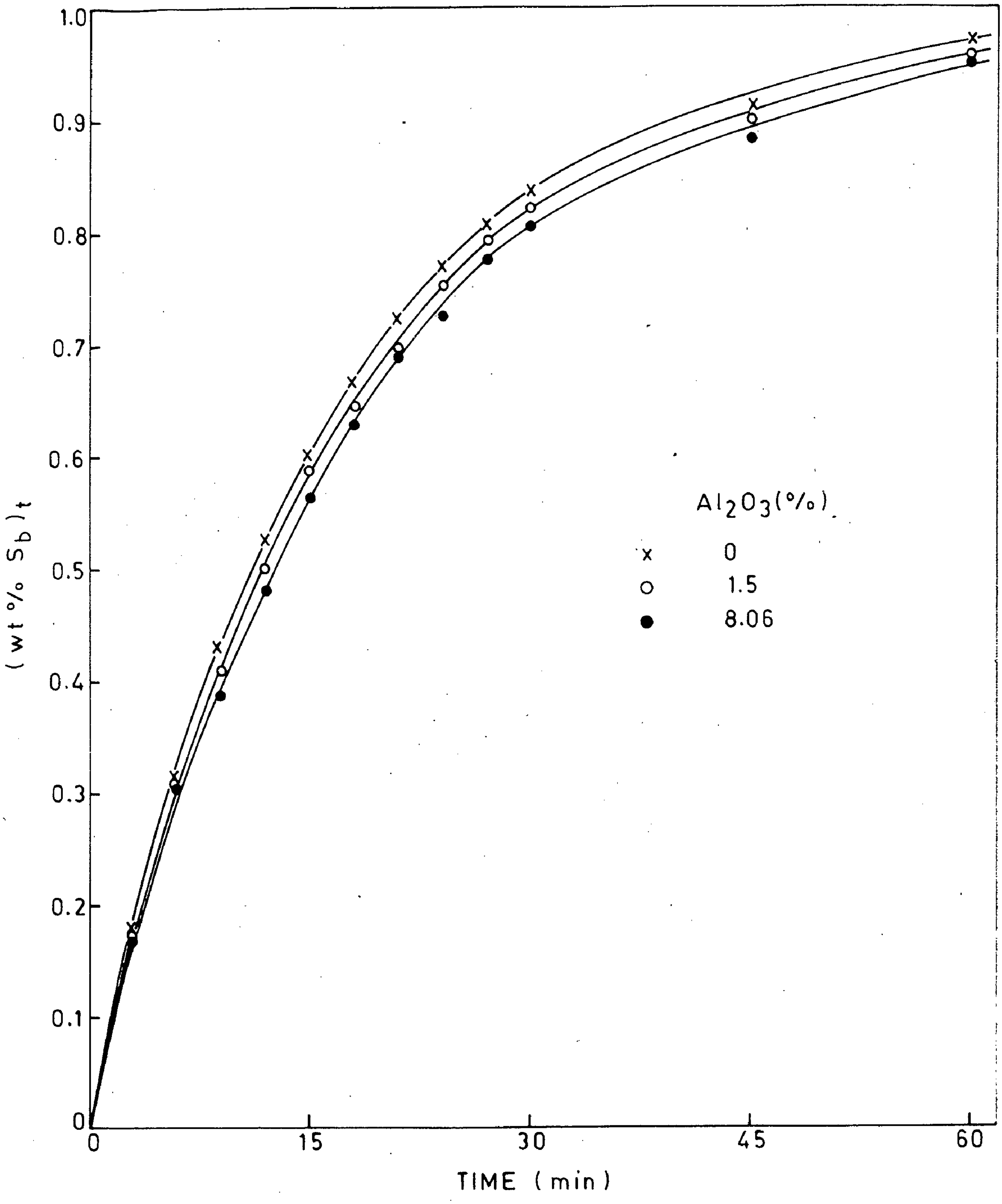

FIG. 3.11 EFFECT OF Al_2O_3 ADDITION TO SLAG ON RATE OF SULPHUR TRANSFER FROM PIG IRON TO SLAG.

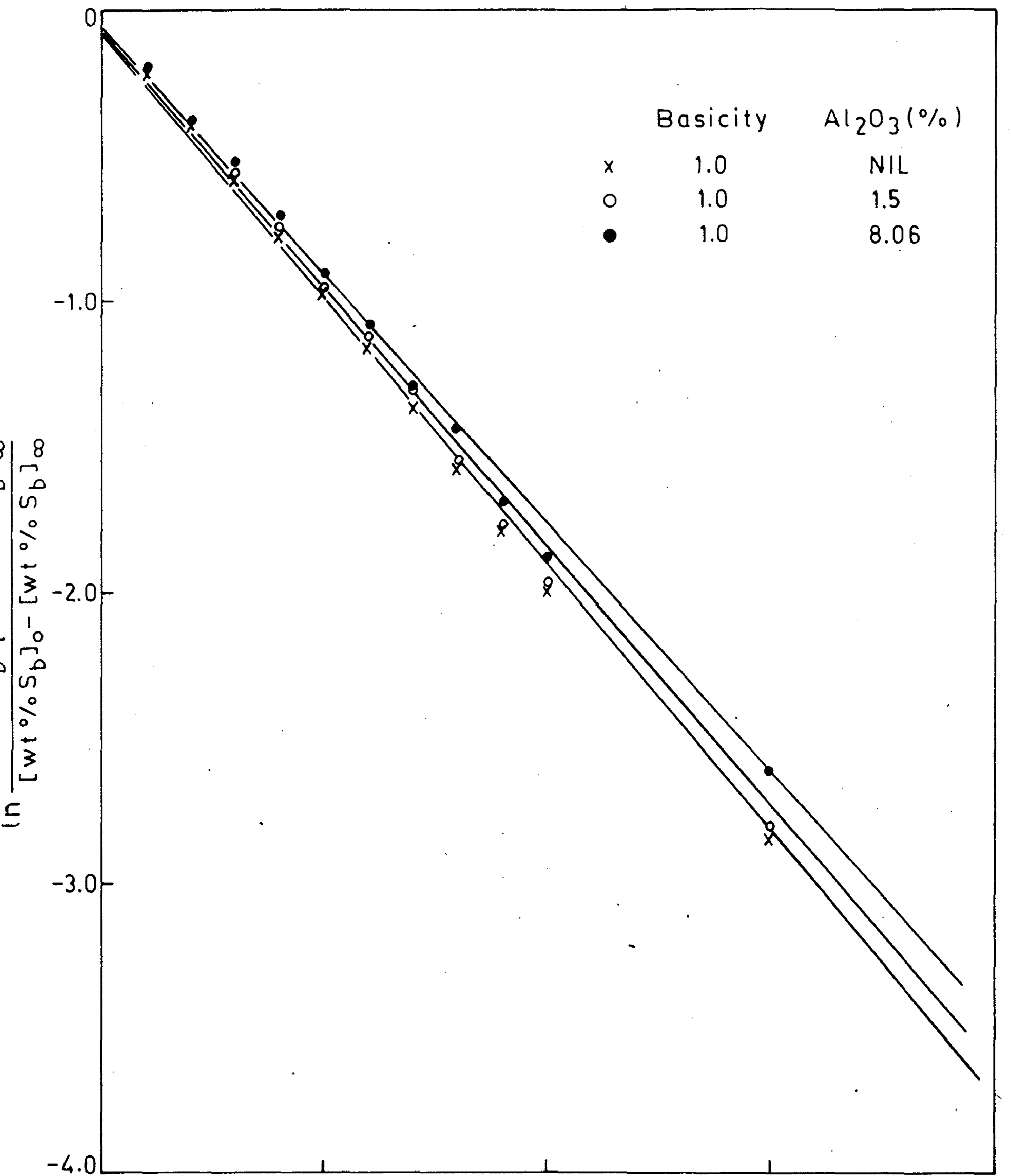

FIG. 3.12 EFFECT OF Al_2O_3 ADDITION TO SLAG ON RATE OF DESULPHURISATION OF PIG IRON.

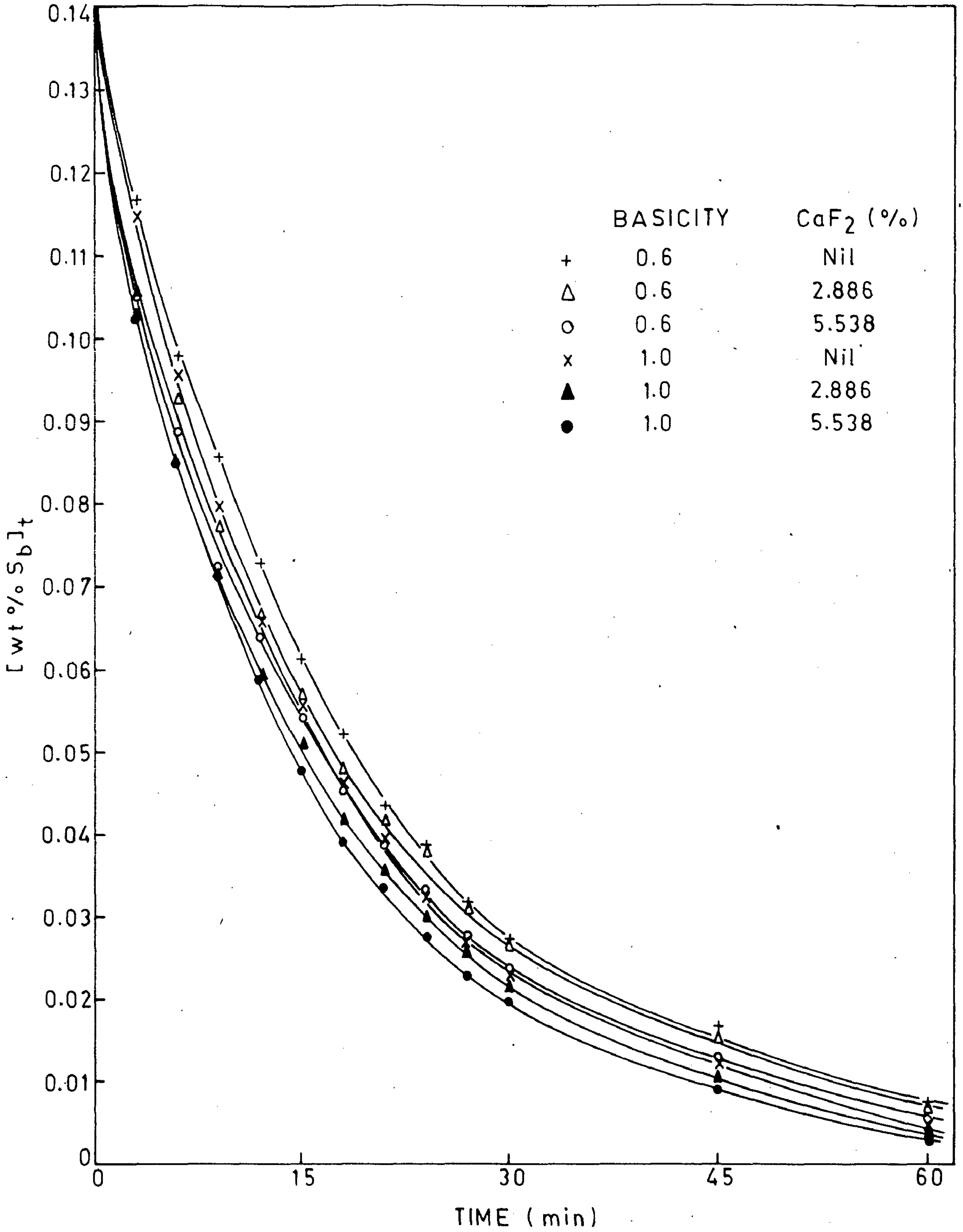

FIG. 3.13 EFFECT OF CaF_2 ADDITION TO SLAG ON RATE OF SULPHUR REMOVAL FROM PIG IRON.

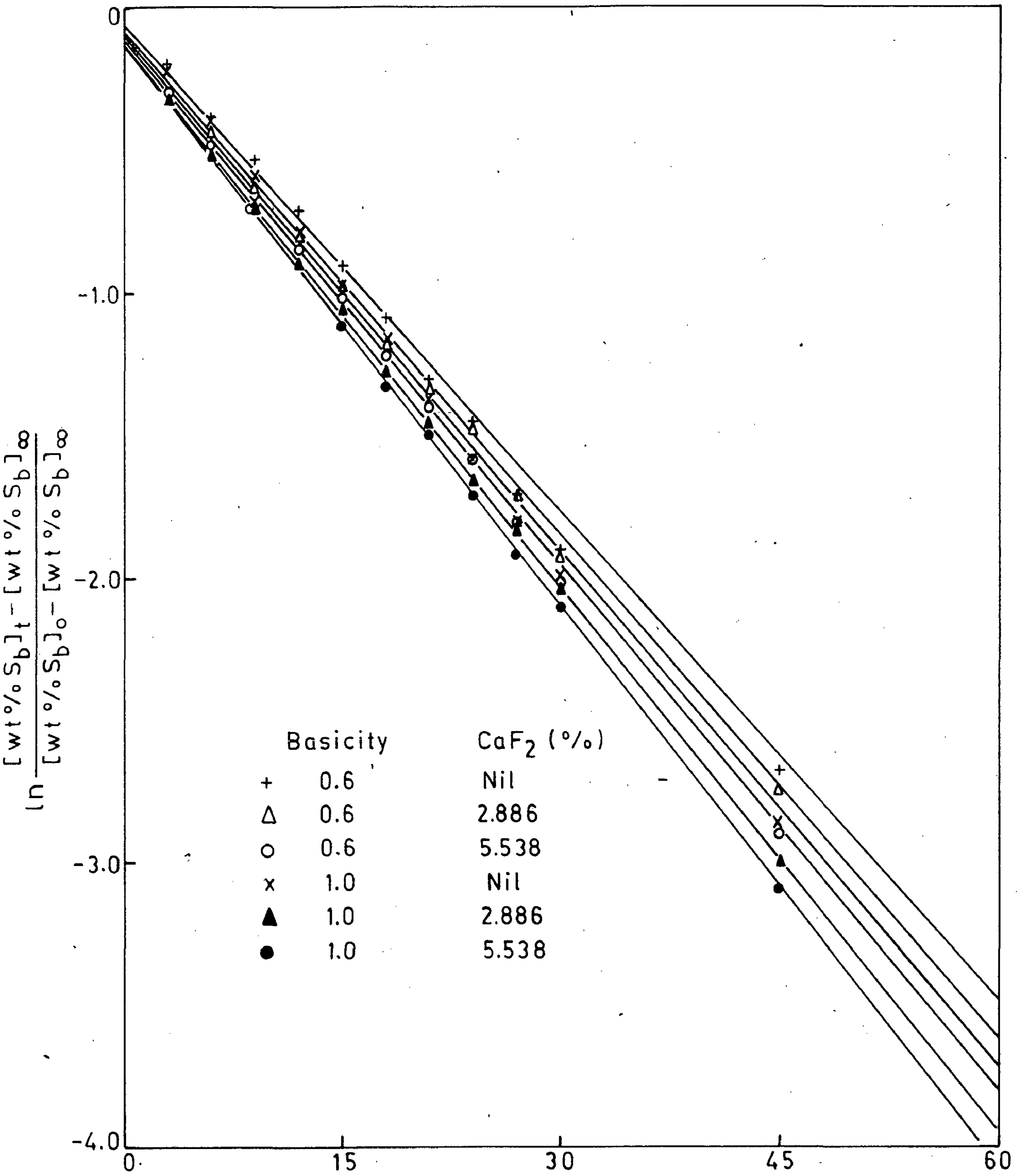

FIG. 3.15 EFFECT OF CaF_2 ADDITION TO SLAG ON RATE OF DESULPHURISATION OF PIG IRON.

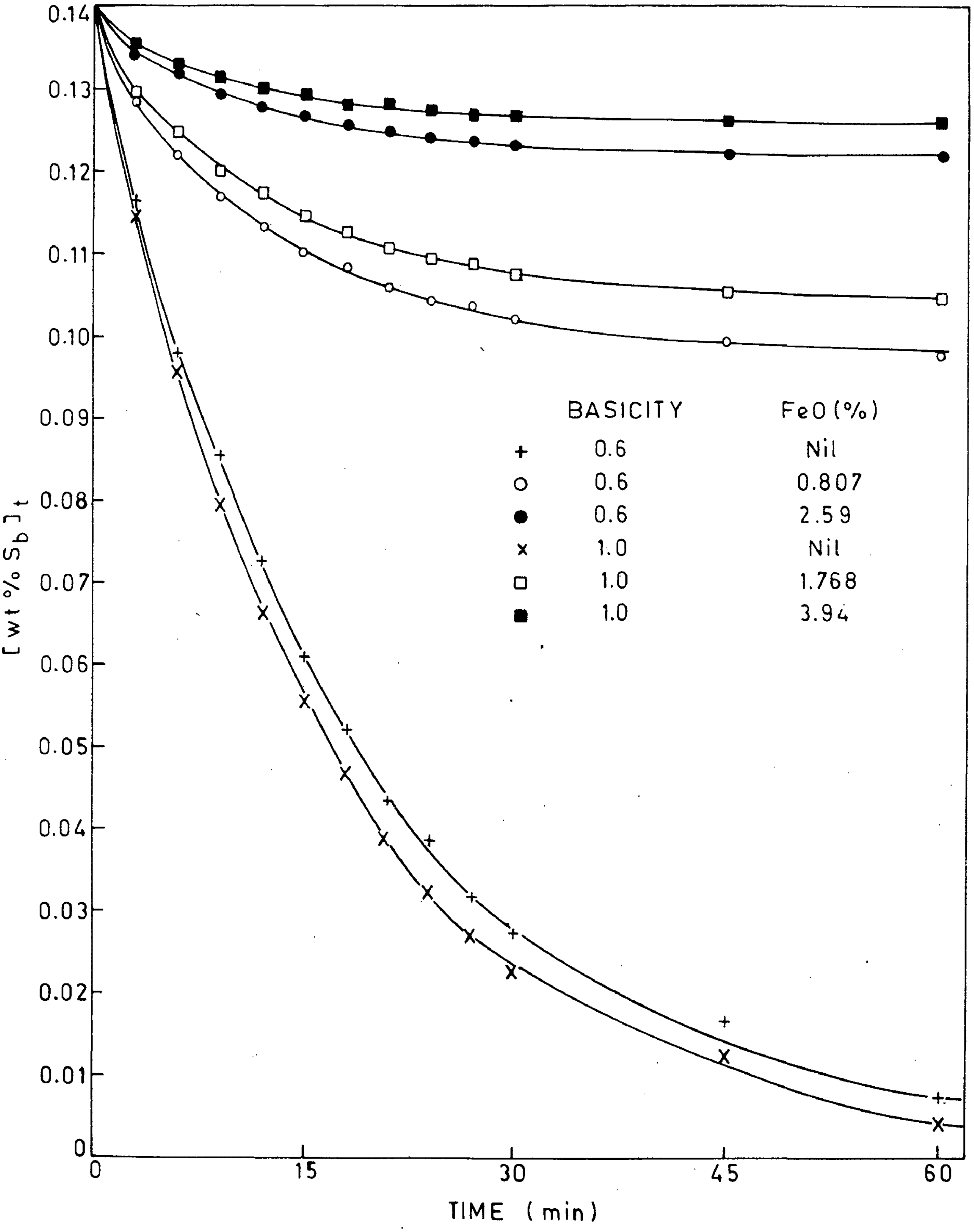

FIG. 3.16 EFFECT OF ADDITION OF FeO TO SLAG ON RATE OF SULPHUR REMOVAL FROM PIG IRON.

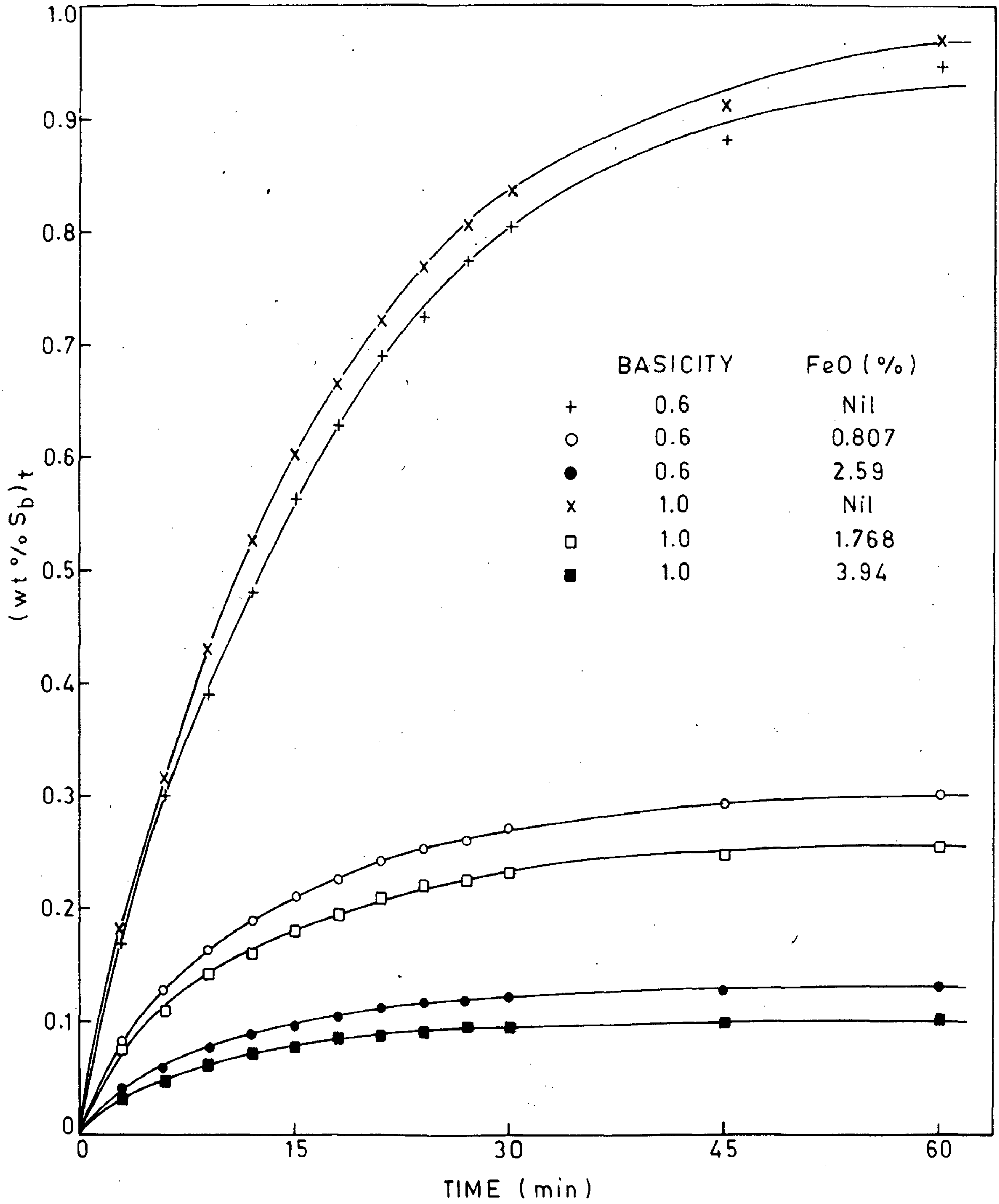

FIG. 3.17 EFFECT OF ADDITION OF FeO TO SLAG ON RATE OF SULPHUR TRANSFER FROM PIG IRON TO SLAG.

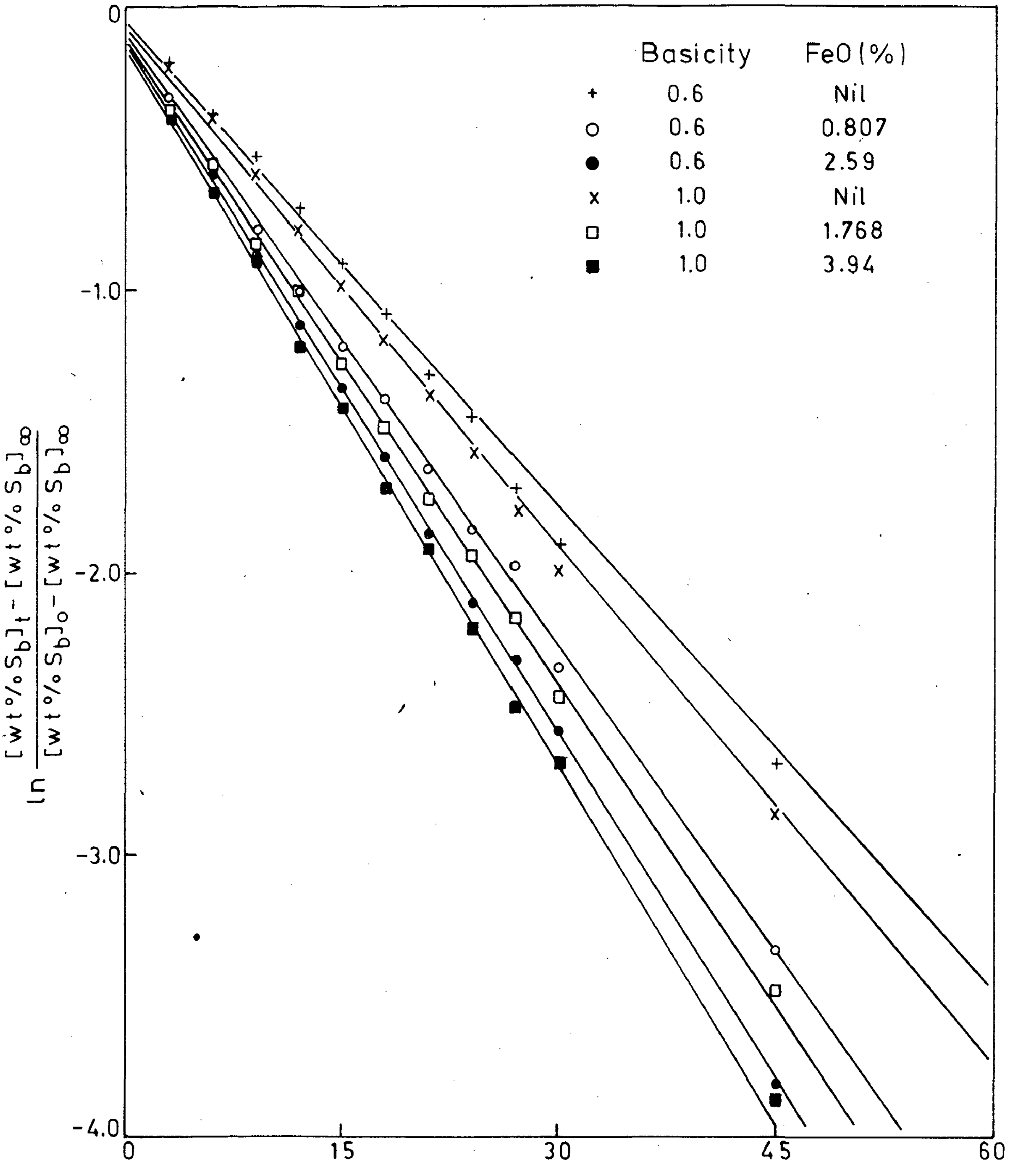

FIG. 3.18 EFFECT OF ADDITION OF FeO TO SLAG ON RATE OF DESULPHURISATION OF PIG IRON.

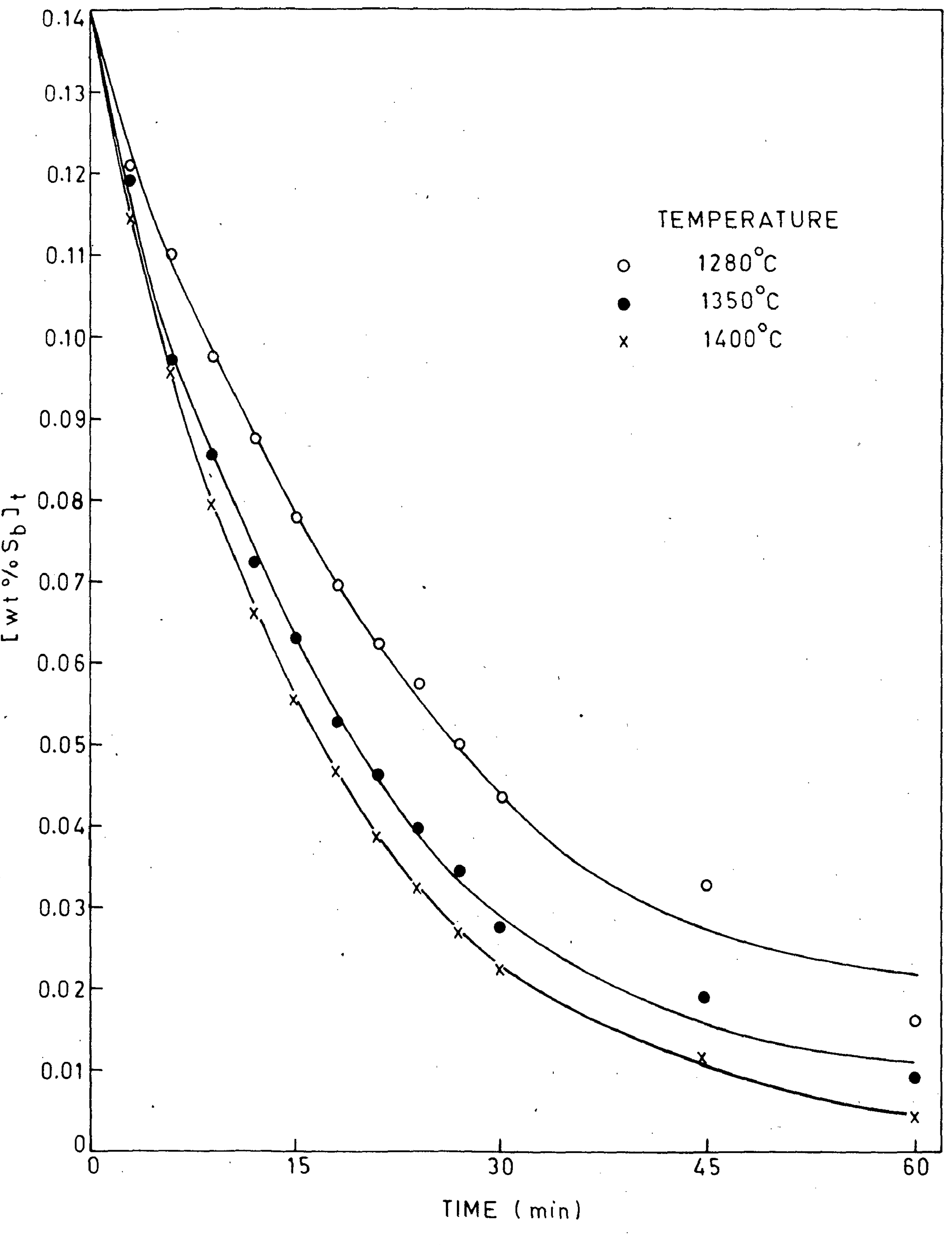

FIG. 3.19 EFFECT OF TEMPERATURE ON RATE OF SULPHUR REMOVAL FROM PIG IRON.

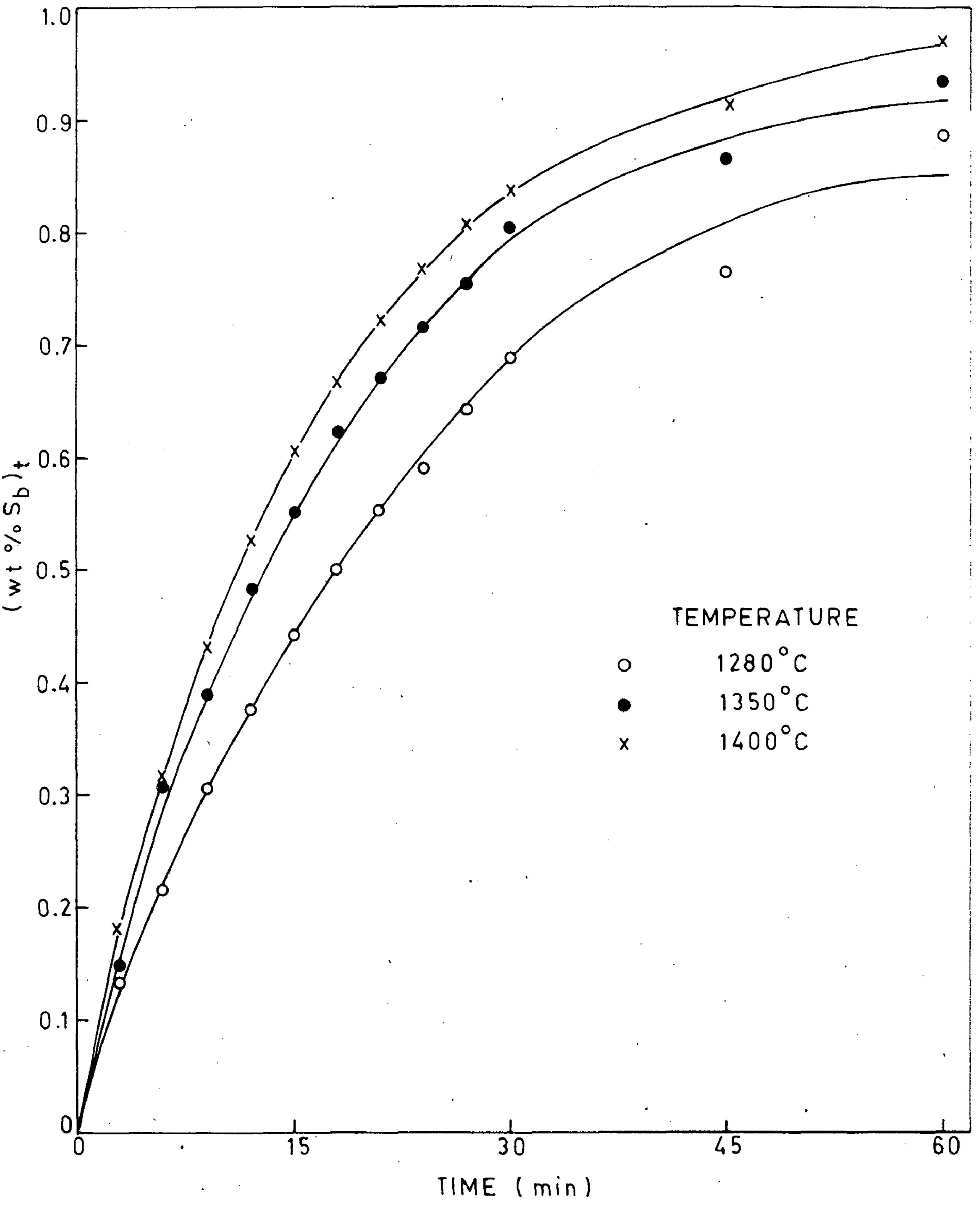

FIG.3.20 EFFECT OF TEMPERATURE ON RATE OF SULPHUR TRANFER FROM PIG IRON TO SLAG.

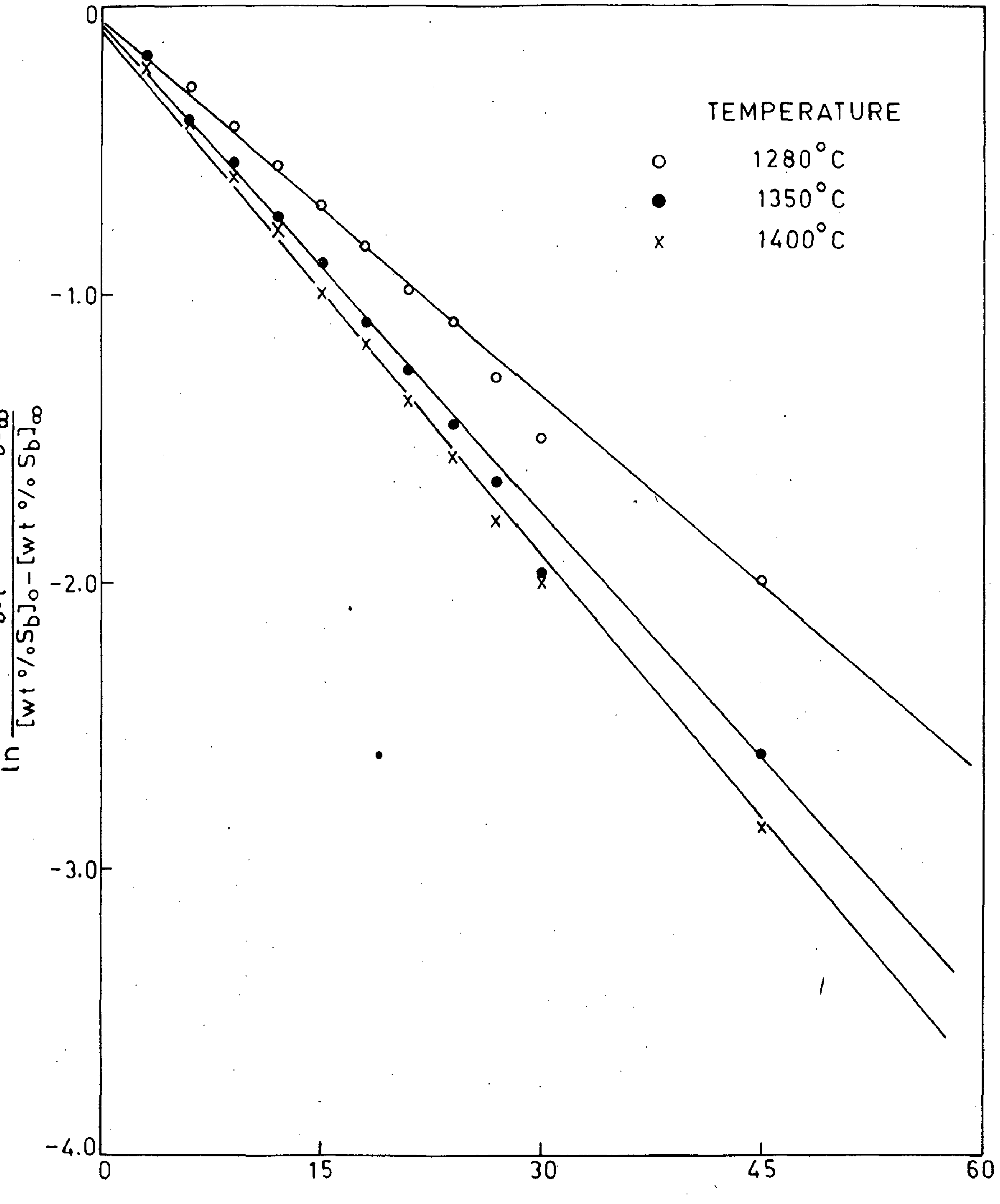

FIG. 3.21 EFFECT OF TEMPERATURE ON RATE OF DESULPHURISATION OF PIG IRON.

Table - 3.33 Summary of Results

S.No.	Parameter studied	Given in Tables	Plotted in Figure
1.	Relative amount of metal and slag	3.1 - 3.9	3.1 -3.3
2.	Gas flow rate	3.10-3.15	3.4 -3.6
3.	Basicity of slag	3.1 and 3.16-3.20	3.7-3.9
4.	Al_2O_3 addition to slag.	3.1, 3.21 and 3.22	3.10-3.12
5.	CaF_2 addition to slag	3.1,3.16 and 3.23-3.26	3.13-3.15
6.	FeO addition to slag	3.1,3.16 and 3.27-3.30	3.16-3.18
7.	Temperature	3.1,3.31 and 3.32	3.19-3.21

The value of L, so calculated for different experimental runs are given in the respective tables.

Figs.(3.3,3.6,3.9,3.12,3.15,3.18,3.21) are the plots of the calculated values of L.H.S. of the equation,

$$\ln \frac{[wt\%\ S_b]_t - [wt\%\ S_b]_\infty}{[wt\%\ S_b]_o - [wt\%\ S_b]_\infty} = -k\left(\frac{1}{h_M} + \frac{1}{Lh_S}\right)t \quad \ldots (1.25)$$

against time for the different experimental runs. From the slopes of these plots, values of overall mass transfer coefficient, k (cm/sec), are calculated and presented in the respective tables.

As described in chapter I, a slag metal reaction can be controlled basically by (a) transport processes and/or (b) chemical reactions. As at elevated temperatures of the present investigation, the chemical reaction at the interface is known to be much faster than the mass transfer rates, it can be assumed that for all practical purposes chemical equilibrium prevails at the interface. Therefore, under steady state conditions, the rate of sulphur transfer from metal to slag phase can be defined by eq. (1.25).

3.1 EFFECT OF CHANGE IN SLAG WEIGHT

Effect of change in weight of slag on the rate of sulphur transfer from metal to slag was studied mainly with an object to have an insight into the predominant rate controlling step, i.e., whether the rate controlling step lies in the metal phase or the slag phase. The results are given in Tables (3.1-3.9) and plotted in Figs.(3.1-3.3). The calculated values of the mass transfer coefficient, k, given in the above tables are found to vary between 5.6932×10^{-3} to 6.4399×10^{-3} cm/sec for slags without FeO.

Mass transfer coefficient in the metal phase, k_M, was calculated from the slopes (Fig.3.3) using the expression (eq. 1.28) which is reproduced below, on the assumption that resistance to mass transfer lies predominantly in the metal phase,

$$\ln \frac{[\text{wt\% } S_b]_t - [\text{wt\% } S_b]_\infty}{[\text{wt\% } S_b]_o - [\text{wt\% } S_b]_\infty} = -\frac{k_M}{h_M} t \quad \ldots(1.28)$$

Similarly, mass transfer coefficient in the slag phase, k_S, was calculated taking into account the change in bath depth using the expression (eq.1.30), reproduced below,

$$\ln \frac{[\text{wt\% } S_b]_t - [\text{wt\% } S_b]_\infty}{[\text{wt\% } S_b]_o - [\text{wt\% } S_b]_\infty} = -\frac{k_S}{h_S} t \quad \ldots(1.30)$$

on the assumption that resistance to mass transfer lies predominantly in the slag phase. The values of k_M and k_S so obtained are given in Table (3.34). It is clear from this table that the mass transfer coefficient k_M in the metal phase remains almost constant, whereas, the mass transfer coefficient in slag phase k_S increases with

Table - 3.34 Mass Transfer Coefficients in Metal and Slag

Gas flow rate(l/h)	Metal weight (gms)	Slag weight (gms)	k_M(cm/sec)	k_S (cm/sec)
6.0	1000	140	5.874×10^{-3}	2.643×10^{-3}
6.3	1000	210	6.295×10^{-3}	4.249×10^{-3}
5.9	1000	280	6.575×10^{-3}	5.917×10^{-3}

increase in slag weight. This leads to the conclusion that the amount of slag has little effect on the rate of mass transfer of sulphur from pig iron to soda-silica slag and therefore, the rate controlling step lies predominantly in the metal phase. This result accords with the data in literature on slag-metal relations [199] .

The small effect of the amount of slag on the overall mass transfer coefficient, k, can be explained by the second term in the relation for overall mass transfer coefficient, k,

$$\frac{1}{k} = \frac{1}{k_M} + \frac{1}{Lk_S} \qquad \ldots (1.26)$$

Due to the increase in slag amount, k_S and the amount of sulphur transferred from metal to slag phase has been slightly increased and the distribution coefficient slightly decreased as is clear from the data reported in Tables(3.1-3.3 and 3.34) and also from the Figs.(3.1-3.3) and thus the amount of slag has a very little effect on the overall mass transfer coefficient. Behaviour of FeO bearing slags will be discussed in sec. (3.6).

3.2 EFFECT OF GAS FLOW RATE

The size of gas bubbles was calculated for different gas flow rates, using the relation [240],

$$d_b = \left(\frac{6\,G}{\pi F}\right)^{1/3} \qquad \ldots (3.2)$$

where, d_b, is bubble diameter (cm); G, gas flow rate (cm^3/sec);F , frequency of bubbles formation (sec^{-1})

calculated from the relation $F = 6.7\ G^{0.13}\ d_o^{0.43}$ [162] where d_o is orifice diameter (cm).

The values so calculated are given in Table (3.35). Bubbles of these sizes (exceeding 1 cm dia) are reported to adopt the spherical cap or mushroom shape [191] . The geometry of fully developed spherical cap bubbles is found to be independent of their sizes, and their shapes and velocities are virtually independent of the liquid through which they rise whether they are mercury, steel, water or slag[183,184,190]. Such bubbles rise with velocities proportional to the square root of their diameter [165]and they carry behind them wakes as shown in Fig. (3.22). In a bath of metal, they cause vertical mixing by carrying up liquid in this wake, and exchanging it relatively slowly with the surrounding liquid as vortices are shed. The bubbles also provide lateral mixing by cleaving the liquid through which they pass. In swarms such bubbles tend both to break up due to turbulance, and to join together because large bubbles sweep up smaller bubbles which they overtake and drawn into their wakes as illustrated in Fig. (3.22). Because of this vertical and lateral mixing caused by the bubbles, transport distances are cut down and therefore, mass transfer coefficient in metal phase is increased. As this mixing effect increases with increase in gas flow rate therefore, with increase in gas flow rate mass transfer coefficient increases.

Large bubbles help mass transfer across the interface between the metal and slag. The bubble first pushes a

Table-3.35 Bubble Frequency and Diameter at Different Gas Flow Rates.

d_o = 0.15 cms.

Gas flow rate		Frequency of bubbles formation $F = 6.7\ G^{0.13}\ d_o^{0.43}$ (sec^{-1})	Bubble diameter $d_b = (\frac{6\ G}{\pi\ F})^{1/3}$ (cm)
l/h	cm^3/sec (G)		
4.6	1.278	3	0.934
9.4	2.611	3	1.185
23.7	6.583	4	1.465
38.9	10.806	4	1.728
48.0	13.333	4	1.853
61.3	17.078	4	2.013

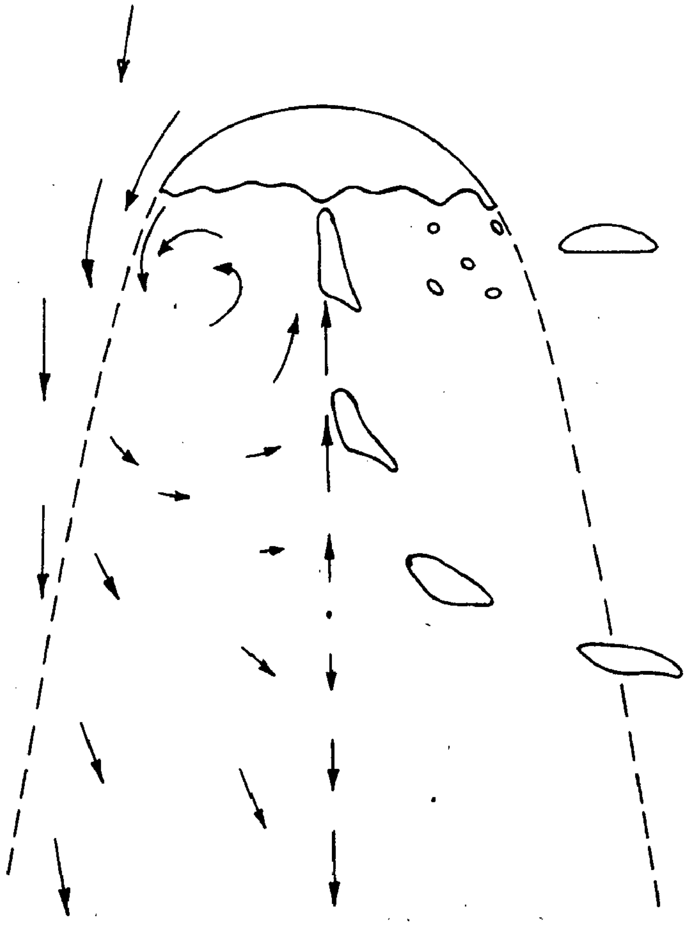

FIG. 3.22 SPHERICAL CAP BUBBLE SHOWING WAKE, AND BY ARROWS DIRECTIONS OF FLOW RELATIVE TO THE BUBBLE.

large dome of metal into the upper liquid, it then carries through into the upper slag phase a skin of liquid metal which drains away at the base. As the reaction taking place at the interface involves transfer of sulphur - a surface active substance, interfacial turbulence can also occur. This phenomena is associated with Marangoni effect [241], which arises when eddies in the metal phase which bring reactant to the interface, also bring about strong local changes in surface tension. The presence of sulphur in liquid metal lowers the surface tension strongly [242]. Thus, whilst the reaction is progressing, the surface tension varies from one part to another over the surface, the areas of high surface tension tend to contact whilst that of low surface tension tend to expand. Thus eddies in metal may bring about sufficiently large changes in surface tension for interfacial turbulence to be set up. This interfacial turbulence may greatly enhance the mass transfer coefficient which, therefore, increases with the gas flow rate. As the effect of gas flow rate is predominant in the metal phase than in the slag phase, it further confirms that rate controlling step lies predominantly in the metal phase. This effect of gas flow rate on mass transfer coefficient is depicted quantitatively in Fig. (3.23) which shows that the log k v/s log G plot is a straight line and follows the quantitative relation,

$$k = 3.4435 \times 10^{-3} G^{0.6} \qquad \ldots (3.3)$$

The values of k in Fig.(3.23) are calculated with the help

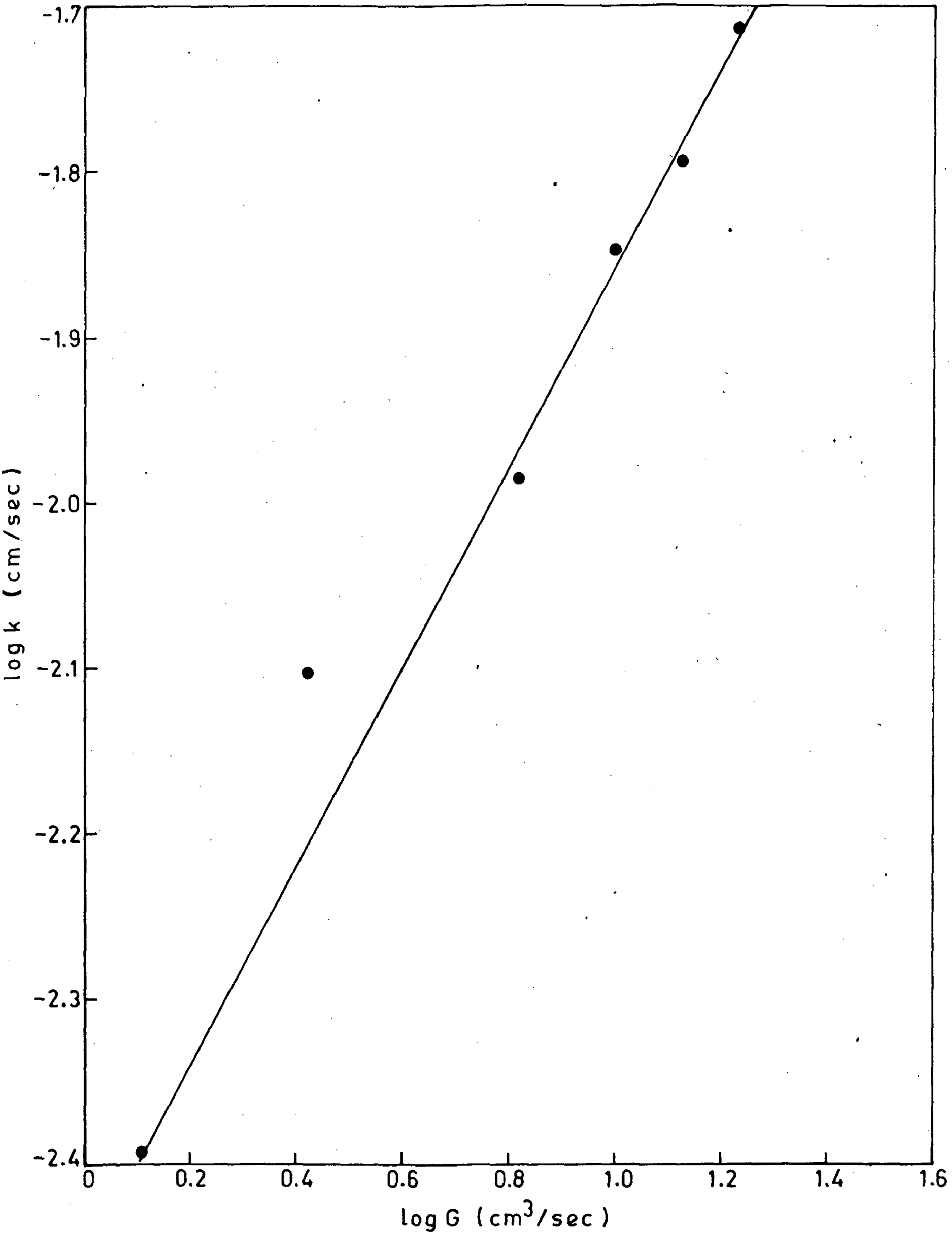

FIG. 3.23 EFFECT OF GAS FLOW RATE ON MASS TRANSFER.

of experimental data given in Tables (3.10-3.15) and plotted in Figs.(3.4-3.6).

3.3 EFFECT OF SLAG BASICITY

The results of experimental runs (Tables 3.1, 3.16-3.20) for different slag composition are plotted for a fixed gas flow rate of approximately 6 ± 0.3 l/h in Figs.(3.7-3.9). The values of mass transfer coefficient, k, obtained from the slopes of the plots of Fig.(3.9) are plotted against slag basicity in Fig. (3.24). The values of k seem to vary very slightly with basicity. This result also leads to the conclusion that the rate controlling step lies predominantly in the metal phase. This conclusion is further confirmed from the fact that the values of the distribution coefficient 'L' in the expression for overall mass transfer coefficient, reproduced below,

$$\frac{1}{k} = \frac{1}{k_M} + \frac{1}{L\ k_S} \qquad \ldots (1.26)$$

are very high (Table 3.1 and 3.16-3.20) and thus the effect of slag phase resistance to overall mass transfer becomes very small.

A little increase in the rate of desulphurisation with the basicity can be explained in terms of the second factor on the right hand side of the above relation, i.e., in terms of the properties of slag phase. Sahab Prasad[89], Denier[243], Nagashima & Katsura[244], Kapoor et al.[245], and Bahout et al[231] have reported that

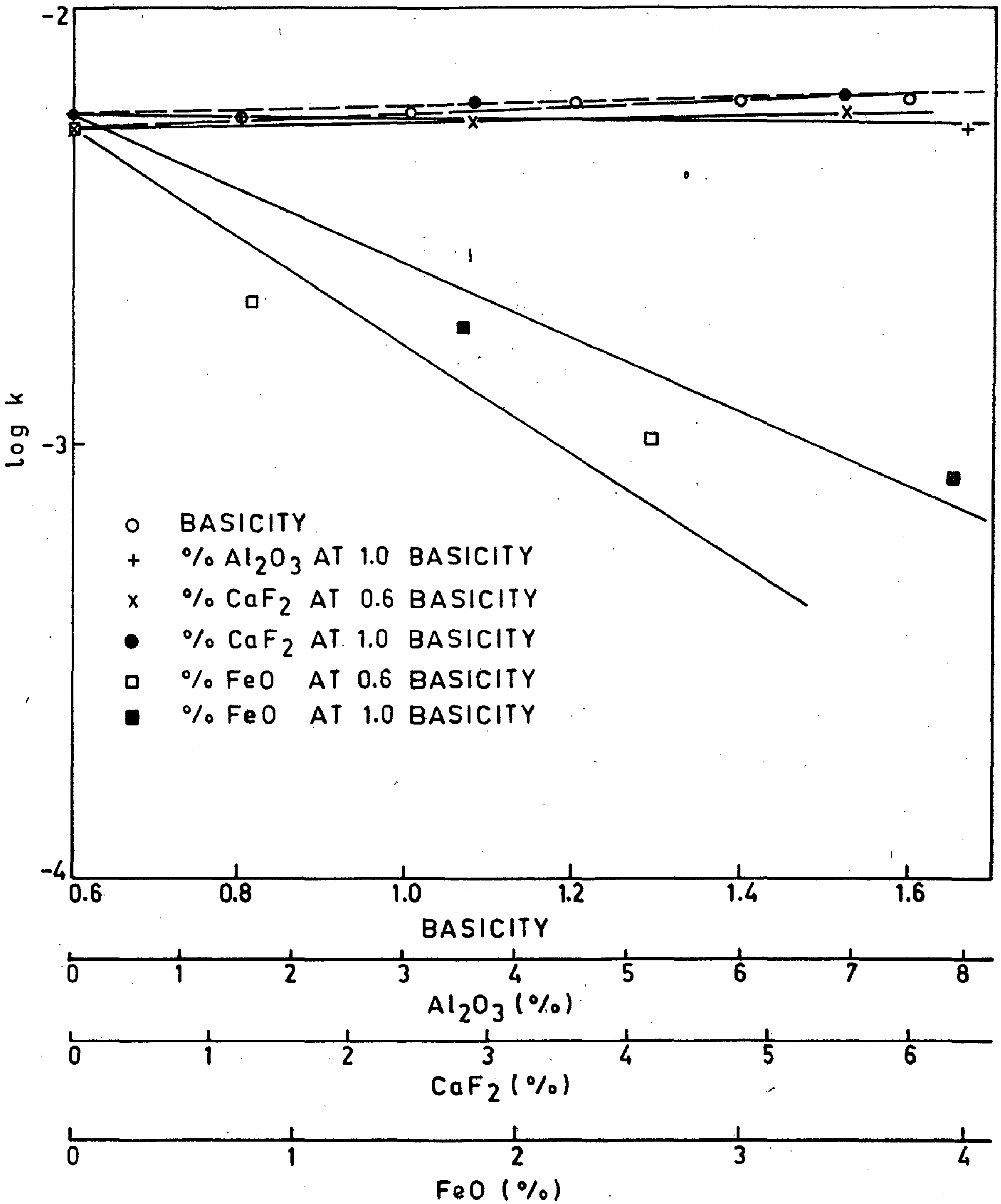

FIG. 3.24 EFFECT OF Na_2O/SiO_2 MOLAR RATIO, Al_2O_3, CaF_2, AND FeO CONTENT OF SLAG ON MASS TRANSFER.

logarithm of sulphur capacity of the Na_2O-SiO_2 slags increases approximately linearly with increase in basicity of the slag due to the increase in the activity of Na_2O in the binary sodium-silicate system. Also, Kawahara et al [246] , Kapoor et al [247], and Bockris et al [248] have reported that with increasing Na_2O/SiO_2 ratio the viscosity of silicate melts decreases, because the viscosity is a structure property. In case of polymeric solutions, as the case for silicate melts, it depends primarily on the size of the polymer in the melt. Formation of these polymers takes place by polymerisation of basic SiO_4^{4-} units and is the result of the overall chemical reation $O^0+O^{2-}=2O^-$. With an increase in content of silica above orthosilicate composition, the amount of O^0 will increase in the melt and hence the size of the polymer shall increase, which in turn will affect an increase in the viscosity of slag. Thus with an increase in silica content viscosity of the melt increases.

Thus due to the combined effect of decrease in viscosity and increase in sulphur capacity of the slag with increase in slag basicity, there is a little increase in the rate of desulphurisation, as is also clear from the increase in the value of distribution coefficient with increase in the basicity.

3.4 EFFECT OF ALUMINA

The results of experimental runs conducted at a constant gas flow rate of about 6 ± 0.3 l/h are presented alongwith other details in Tables (3.1, 3.21 and 3.22) for different percentage of alumina in slag. These results are plotted in Figs. (3.10-3.12). Value of k (5.6932×10^{-3}-5.3012×10^{-3} cm/sec) calculated from Fig. (3.12) is plotted against percentage alumina in Fig. (3.24). These Figs. (3.12,3.24) show that alumina has a lowering effect of very low intensity on the rate of desulphurisation. This effect can be explained on the basis of the thermodynamic investigations on sulphur capacity and viscosity measurements on Na_2O-SiO_2 slags.Kapoor et al [245] have reported that addition of alumina to a fixed Na_2O/SiO_2 ratio lowers slightly the sulphur capacity of slags in the temperature range 1100-1300°C and basicity 0.6-1.6. Kapoor et al [247] have also measured the viscosity of the ternary Na_2O-SiO_2-Al_2O_3 slags in temperature range 1100-1300°C, Na_2O/SiO_2 ratio between 0.6 to 1.6 and alumina content of 2.48 to 8.06%. They reported that presence of alumina increases the viscosity of slags. As a result of this the distribution coefficient is likely to decrease with increase in alumina content in the slag. The experimentally evaluated values of distribution coefficient 'L' for the different percentages of alumina additions of the present investigation are given in Tables (3.1, 3.21 and 3.22), from which it is clear that as alumina content increases the distribution coefficient decreases. Thus, due to the combined effects of sulphur capacity, viscosity, and distribution coefficient, the alumina has a minor effect of decreasing the mass transfer coefficient of sulphur.

3.5 EFFECT OF CALCIUM FLUORIDE

The results of present investigation made on the effect of calcium fluoride at different slag basicities (0.6 and 1.0) are given in Tables (3.1, 3.16 and 3.23-3.26) and are plotted in Figs. (3.13-3.15). Value of k (5.2874×10^{-3}-6.3049×10^{-3} cm/sec) calculated from Figs. (3.15) are plotted against percentage CaF_2 in slag in Fig. (3.24). The Figs. (3.15,3.24) show that there is only slight increase in the rate of desulphurisation with increase in the CaF_2 content. This can be attributed to the minor effect of the second factor in eq.(1.26) which has some impact on the overall mass transfer coefficient k. The report of investigation on sulphur capacity of Na_2O-SiO_2 slag [245] in the temperature range 1100-1300°C and basicity 0.6-1.6 shows that the presence of CaF_2 in slag increases its sulphur capacity due to its direct and indirect participation in overall sulphur transfer reaction. Kapoor et al [247] have also measured the effect of addition of CaF_2 (1.17-4.056%) to Na_2O-SiO_2 slag on its viscosity in the temperature range 1100-1300°C and basicity 0.6-1.6 and reported that for a given basicity of slag as the CaF_2 content in the slag increases the viscosity of slag decreases and that for a given amount of CaF_2 addition to slag, its viscosity decreases as basicity increases. The CaF_2, when present in slag, is known to be an efficient Si-O bond breaker and also lowers down the melting point of the slag. Thus due to increase in sulphur capacity and decrease in viscosity of the slag in presence of CaF_2, the distribution coefficient, L, is expected to increase. The calculated values of L for the experimental runs on the effect of CaF_2 addition to slag as reported in Tables (3.1,3.16 and 3.23-3.26) confirm this fact. Thus, due to the combined effects of sulphur capacity and viscosity of slag and therefore increase in distribution coefficient L, with increase in CaF_2 content of slag, the overall mass transfer rate is slightly increased.

3.6 EFFECT OF FeO

The effect of FeO on mass transfer was studied by bubbling through the system nitrogen gas mixed with 5-7% air to reduce the reduction of FeO in contact with pig iron. However, the change in composition of slag due to corrosion of alumina crucible could not be overcome.

Results of experimental runs conducted at basicities 0.6 and 1.0 and FeO content 0-3.94% at a gas flow rate of about 6 ± 0.3 l/h are presented in Tables (3.1-3.9, 3.16 and 3.27-3.30) alongwith other details. These results are plotted in Figs.(3.1-3.3 and 3.16-3.18). Fig. (3.24) depicts the effect of amount of FeO on k (5.6932×10^{-3} - 8.3650×10^{-4} cm/sec). From these Figs. (3.18,3.24) it is clear that the presence of FeO in slag decreases the rate of desulphurisation. This effect of FeO on desulphurisation can be explained by considering the equation,

$$\frac{1}{k} = \frac{1}{k_M} + \frac{1}{L\,k_S} \qquad \ldots \quad (1.26)$$

As it is clear from the above equation the value of overall mass transfer coefficient, k, depends also upon the distribution coefficient, L. In the present investigation the value of L decreases as we add FeO to Na_2O-SiO_2 slags (Tables 3.1-3.9,3.16 and 3.27-3.30) and therefore, the value of overall mass transfer rate also decreases. Similar effect of FeO has been found by Takenouchi et al [88]in case of desulphurisation of stainless steel with CaO-CaF_2-Al_2O_3-SiO_2 slags.

Kapoor et al [245,247] studied the effect of addition of FeO to Na_2O-SiO_2 slags, on the viscosity and sulphur capacity of these slags in the temperature range 1100-1300°C and basicity 0.6-1.6 and found that the addition of FeO decreases the viscosity of slag slightly and increases its sulphur capacity. However, as has been pointed out earlier the rate determining step lies predominantly in metal phase, the effect of change of properties of slag on the overall mass transfer coefficient shall be very less as compared to the effect of distribution coefficient on it.

3.7 EFFECT OF TEMPERATURE

The effect of temperature on the kinetics of desulphurisation of pig iron by Na_2O-SiO_2 slag was studied at 1280,1350 and 1400°C in the present investigation. The results are given in Tables (3.1,3.31 and 3.32) and plotted in Figs. (3.19-3.21). The Fig. (3.21) shows that there is slight increase in the rate of desulphurisation with increase in temperature from 1280 to 1400°C (k value from 3.6065×10^{-3} cm/sec at 1280°C increases to 5.6932×10^{-3} cm/sec at 1400°C). This increase in desulphurisation rate with temperature can be attributed to activation energy, distribution coefficient and viscosity of slag.

In the report of investigation on sulphur capacity of slags Kapoor et al [245]]have found a linear relationship between log C_S vs 1/T plots in the temperature range 1200-1400°C, which shows that the sulphur capacity of Na_2O-SiO_2 slag increases with increasing temperature. Sahab Prasad [89] , and Denier [243] have also reported the same effect of temperature on sulphur capacity of Na_2O-SiO_2 slag. This effect of temperature can be explained by the relationship,

$$C_S = K.a_{O^{2-}} \qquad \ldots (3.4)$$

where, K is the equilibrium constant for the reaction,

$$(O^{2-}) + \frac{1}{2} S_2 = (S^{2-}) + \frac{1}{2}O_2 \qquad \ldots (3.5)$$

In eq. (3.4) the value of K is expected to be a weak function of temperature as the reactant and product side in eq.(3.5) involve equal moles of similar phase. Further, activity of basic oxide in binary silicate systems is known to decrease with temperature, hence, the product $K.a_{O^{2-}}$, and, therefore sulphur capacity of the slag will increase with an increase in temperature. **Mitsuo** et al [127] have studied the effect of temperature on desulphurisation of

$Fe\text{-}C_{sat}\text{-}S$ melt by injecting lime and have reported a increase in desulphurisation rate with increasing temperature.

In a report on viscosity of $Na_2O\text{-}SiO_2$ slags Kapoor et al [247] have reported that the viscosity of these slags decreases with increasing temperature in temperature range 1100-1300°C and at a basicity of 1.0 They have found a linear relationship between $\log \mu_S$ vs $1/T$ curves (μ_S is viscosity). Thus, due to decrease in viscosity and increase in sulphur capacity of slag with increase in temperature, the distribution coefficient L, and, hence the mass transfer coefficient shall increase.

The value of overall mass transfer coefficient k has been found to increase by 41% for an increase in temperature from 1280 to 1350°C and 58% for an increase in temperature from 1280 to 1400°C. The activation energy for the mass transfer controlled reaction has been reported to be ~ 20 Kcal/mole [249].

3.8 COMPARISON WITH OTHERS

In Fig.(3.25) overall mass transfer coefficient is plotted against the gas throughput and compares the present experimental results with those of other investigators [199, 250-252]. The straight lines are seem to be more or less parallel. It is also noted from this figure that the effect of gas bubbles on material transfer is almost the same as reported by Patel et al [199] in their studies on 'The

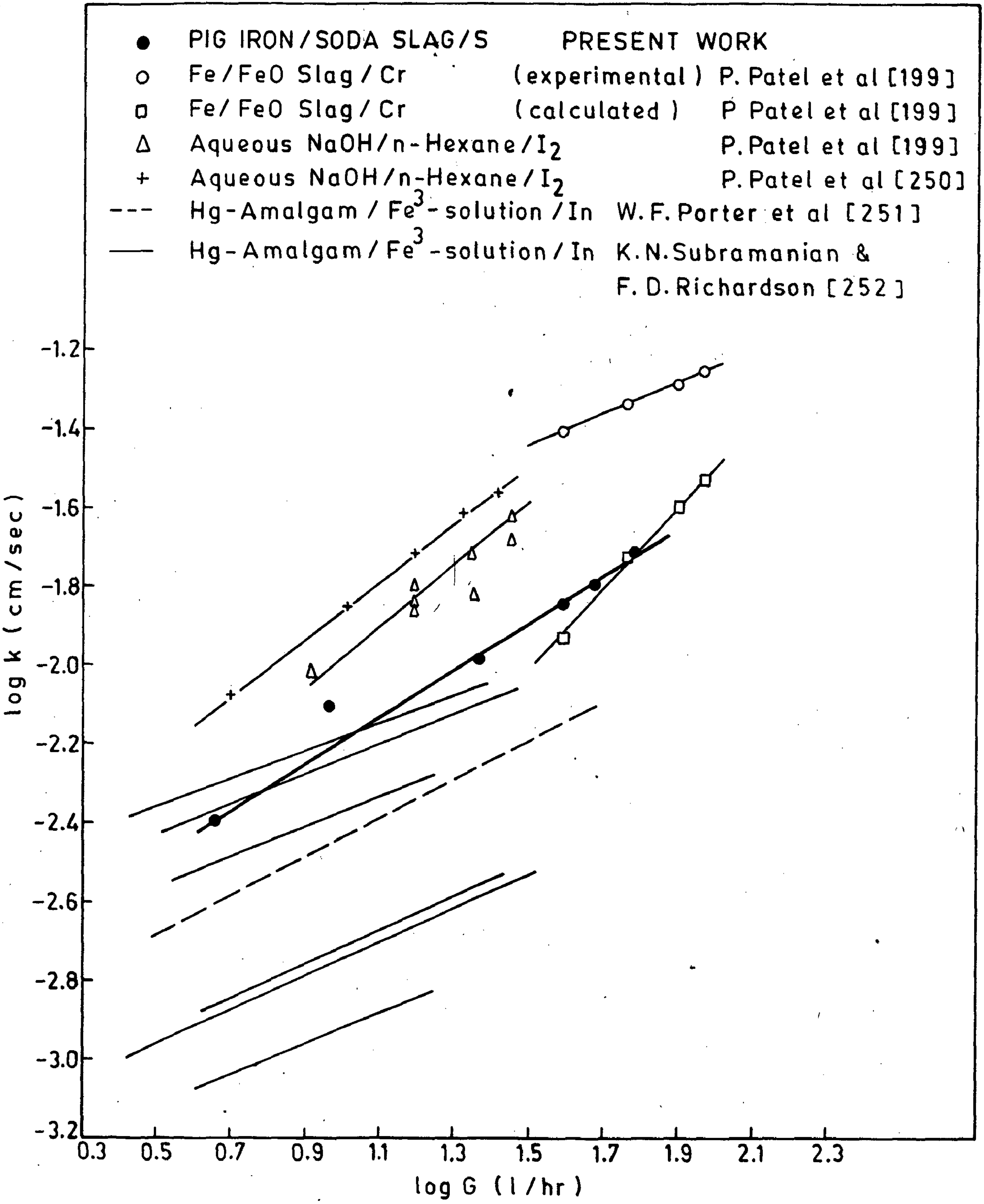

FIG.3.25 MASS TRANSFER IN VARIOUS SYSTEMS AS A FUNCTION OF GAS THROUGHPUT.

effect of rising gas bubbles on the mass transfer between liquid iron and FeO bearing slags'. Their results also indicate a rate-determining factor mainly in the metal phase.

In Fig. (3.26) overall mass transfer coefficient k is plotted against surface renewal time Δt (Table 3.36) defined by the relationship,

$$\Delta t = \frac{A}{F . A_B} \qquad \dots (3.6)$$

based on penetration theory. Where, A is the reaction surface (cm^2); F, the bubble frequency (sec^{-1}); and A_B, the bubbles front cross section (cm^2).

The results of other **investigators** [199,250-252] are also plotted in this figure for a comparison. It is clear from this figure that the plot of present work is more or less parallel with the plots of other workers. It may be concluded from Fig. (3.26) that as surface renewal time decreases, i.e., as the gas flow rate increases, mass transfer coefficient increases and thus the effect of gas bubbles on the mass transfer of sulphur from metal to slag can be defined with the help of penetration theory.

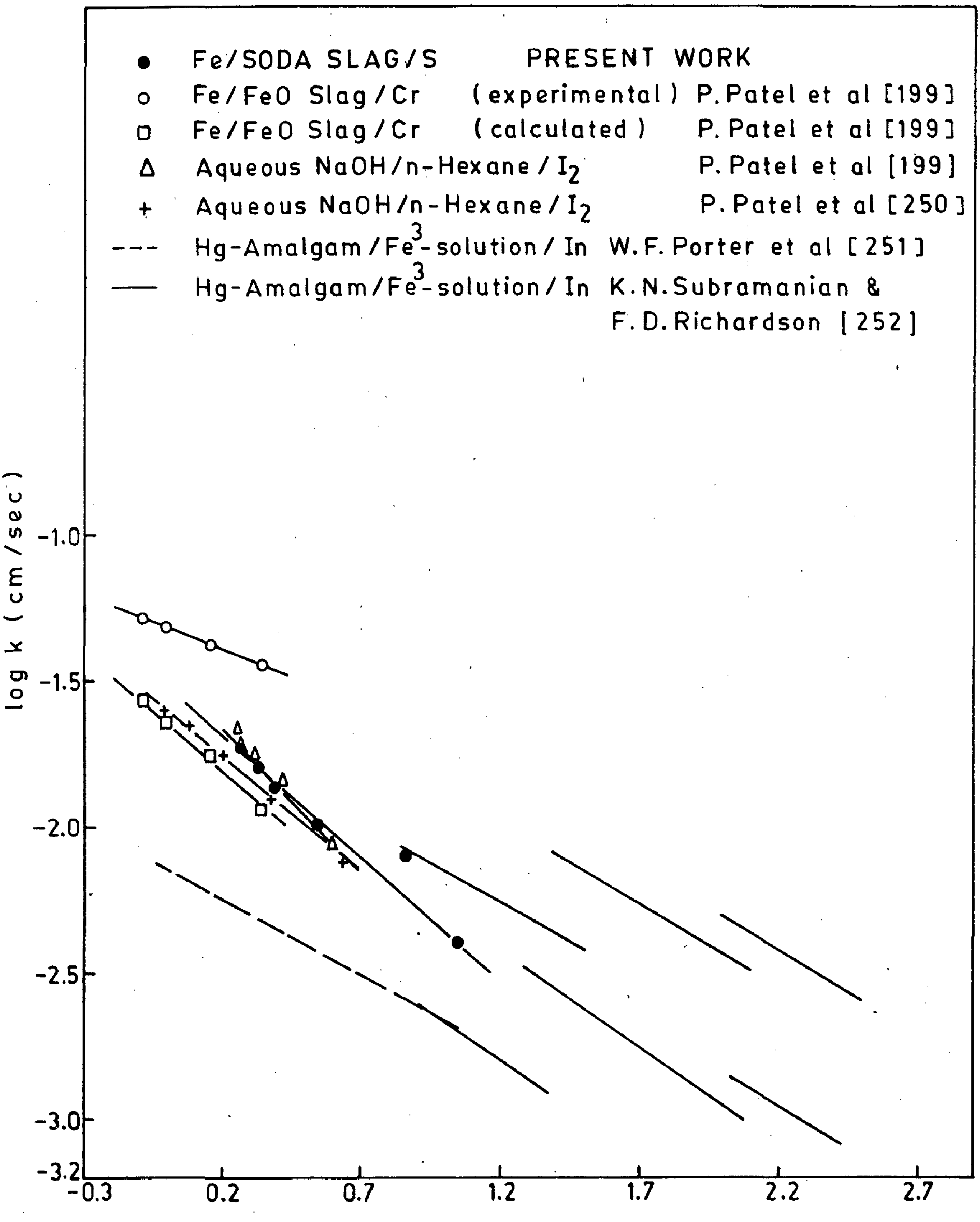

FIG.3.26 MASS TRANSFER AS A FUNCTION OF SURFACE RENEWAL TIME IN VARIOUS SYSTEMS.

Table-3.36 Surface Renewal Time for Different Gas Flow Rate

Gas flow rate		Reaction surface area A, (cm^2)	Frequency of bubbles F, (sec^{-1})	Bubble cross section A_B, (cm^2)	Surface renewal time Δt, (sec)
1/h	cm^3/sec				
4.6	1.278	23.7583	3	0.6844	11.57
9.4	2.611	23.7583	3	1.1021	7.19
23.7	6.583	23.7583	4	1.6852	3.52
38.9	10.806	23.7583	4	2.3452	2.53
48.0	13.333	23.7583	4	2.6976	2.20
61.3	17.078	23.7583	4	3.1819	1.87

CHAPTER-IV

SUMMARY AND CONCLUSIONS

In this chapter the experimental results on mass transfer studies in gas bubbles agitated metal and soda base slag systems have been summarised and concluded.

4.1 SUMMARY

Mass transfer coefficient determined for different operating variables are presented in Table (4.1).

4.2 CONCLUSIONS

On the basis of analysis of the present data for different operating variables the conclusions drawn are enumerated as follows:

(i) The rate controlling step for transfer of sulphur from metal to slag lies predominantly in metal phase.

(ii) Amount of slag has a very little effect on overall mass transfer coefficient.

(iii) By increasing gas flow rate (intensity of mixing), mass transfer coefficient increases and following quantitative relationship between mass transfer coefficient and gas flow rate has been established,

$$k = 3.4435 \times 10^{-3} G^{0.6} \qquad \ldots (3.3)$$

Table-4.1 Mass Transfer Coefficient for Different Operating Variables

Operating variables						
Na_2O/SiO_2 molar ratio	Gas Flow rate (l/hr)	Weight of metal (gms)	Weight of slag (gms)	Tempera-ture(^oC)	Slag additives (%)	Mass Transfer coefficient (cm/sec.)
1	2	3	4	5	6	7
1.0	6.0	1,000	140	1,400	-	$5.6932x10^{-3}$
1.0	6.3	1,000	210	1,400	-	$6.1243x10^{-3}$
1.0	5.9	1,000	280	1,400	-	$6.4399x10^{-3}$
1.0	6.1	1,000	140	1,400	FeO=0.807	$2.1066x10^{-3}$
1.0	6.0	1,000	210	1,400	FeO=0.807	$2.8060x10^{-3}$
1.0	5.9	1,000	280	1,400	FeO=0.807	$2.9713x10^{-3}$
1.0	6.3	1,000	140	1,400	FeO=2.59	$1.5604x10^{-3}$
1.0	6.1	1,000	210	1,400	FeO=2.59	$2.1656x10^{-3}$
1.0	5.9	1,000	280	1,400	FeO=2.59	$2.6078x10^{-3}$
1.0	4.6	1,000	140	1,400	-	$4.0412x10^{-3}$
1.0	9.4	1,000	140	1,400	-	$7.8808x10^{-3}$
1.0	23.7	1,000	140	1,400	-	$1.0349x10^{-2}$
1.0	38.9	1,000	140	1,400	-	$1.4193x10^{-2}$
1.0	48.0	1,000	140	1,400	-	$1.6082x10^{-2}$

Contd......

Table- 4.1 Contd....

1	2	3	4	5	6	7
1.0	61.3	1,000	140	1,400	-	1.9202×10^{-2}
0.6	5.9	1,000	140	1,400	-	5.2874×10^{-3}
0.8	6.1	1,000	140	1,400	-	5.5560×10^{-3}
1.2	6.3	1,000	140	1,400	-	6.0769×10^{-3}
1.4	5.9	1,000	140	1,400	-	6.0769×10^{-3}
1.6	6.3	1,000	140	1,400	-	6.1333×10^{-3}
1.0	6.3	1,000	140	1,400	$Al_2O_3 = 1.5$	5.5385×10^{-3}
1.0	6.1	1,000	140	1,400	$Al_2O_3 = 8.06$	5.3012×10^{-3}
0.6	5.1	1,000	140	1,400	$CaF_2 = 2.886$	5.4477×10^{-3}
0.6	6.1	1,000	140	1,400	$CaF_2 = 5.538$	5.7431×10^{-3}
1.0	6.3	1,000	140	1,400	$CaF_2 = 2.886$	6.0428×10^{-3}
1.0	6.3	1,000	140	1,400	$CaF_2 = 5.538$	6.3049×10^{-3}
0.6	5.9	1,000	140	1,400	$FeO = 0.807$	2.1352×10^{-3}
0.6	6.1	1,000	140	1,400	$FeO = 2.59$	1.0269×10^{-3}
1.0	6.3	1,000	140	1,400	$FeO = 1.768$	1.8918×10^{-3}
1.0	6.0	1,000	140	1,400	$FeO = 3.94$	8.3650×10^{-4}
1.0	6.1	1,000	140	1,280	-	3.6065×10^{-3}
1.0	5.9	1,000	140	1,350	-	5.1013×10^{-3}

(iv) Increase in slag basicity slightly improves the overall mass transfer coefficient.

(v) Presence of alumina in slag, slightly reduces the overall mass transfer coefficient.

(vi) Presence of CaF_2 in slag improves mass transfer coefficient slightly.

(vii) FeO, if present in slag reduces its desulphurising efficiency and the mass transfer coefficient.

(viii) Increase in temperature has a favourable effect on desulphurisation of pig iron with soda base slag.

(ix) Role of gas bubbles on transfer of sulphur from metal to slag can be explained with the help of penetration theory.

SUGGESTIONS FOR FUTURE RESEARCH PROGRAMMES

1. Experimental studies on the kinetics of simultaneous desulphurisation and dephosphorisation may be carried out.
2. Experimental studies on the kinetics of desulphurisation using soda base slag and a reactive gas may also be carried out.
3. Other alkali based system e.g. lithium oxide, potassium oxide in combination of silica and alumina could be the subject of interest in external desulphurisation, as they are likely to perform better in refining owing to their lower enthalpy values for silicate formation, and lower activation energy requirements for iónic conduction in comparison to other basic oxides.
4. Kinetics of desulphurisation may also be studied in an induction furnace with gas bubble agitation.

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