

Errata

(T. OKAZAKI , Ph.D thesis . University of London 1985)

1/3

	page	line	original	correction
1	3	17	Cu	Sn
			CuCl	SnCl ₂
2	4	22	copper	tin
			CuCl	SnCl ₂
3	4	23	Cu	Sn
4	4	20	8	28
5	6	16	them. the	them, the
6	8	18	k_{sp}	$k_s \rho_s$
7	34	Fig.3-1(a)	metal phase	-s
8	35	7	glas	gas
9	35	11	both	bath
10	51	eq.(3-50)	metal affected	affected by metal
			by composition	composition
11	52	17	1.0 : steel	1.1 : steel
12	53	Table 3-1	ref(7)	ref(17)
13	65	Fig.3-11	(vertical axis : Fig.3-11(a)= sulphur activity*10 ³ , Fig.3-11 (b)=oxygen activity*5*1000)	
14	87	24	x_{FeS}	x_{FeO}
15	93	17	phase zero	phase is zero
16	94	18,19	(neglect statement in the bracket)	
17	100	15	(3-6)	(3-50)
18	119	18	(neglect the following statement : The quantitative results are shown in Table 4-1.)	
19	124	Fig.4-15	entraine	entrain
20	125	8	4.14	4-14
21	131	18	-	(4-3) ; name of the equation
22	131	19	(4-3)	(4-4)
23	170	7	ϵ	ϵ'
24	171	18	.3	1.3
25	173,174	Fig.5-22	(one of two parameters' name is missing in the figures. η_{Cu} (%) : fraction of Cu removed. two parameters are wt%S and η_{Cu})	
25	181	8	Fig.5-28	Fig.5-27
26	187	6	(5-9)	(5-7)
27	199	1	K_{CL}^{eff}	K_{CO}^{eff}
28	228	eq.(A1-3)	(neglect g in the equation)	
29	260	Table A5-1	=	=dissolved in the molten iron
			-	-liquid
30	263	eq.(A6-7)	$\gamma_{Cu_2S}/(1-x_{FeS}^A)$	$\sqrt{\gamma_{Cu_2S}/(1-x_{FeS}^A)}$
31	263	eq.(A6-11)	$x_{Fe_{0.5}S_{0.5}}$ γ_{FeS}/x_{FeS}	$\gamma_{Fe_{0.5}S_{0.5}}$ $\sqrt{\gamma_{FeS}/x_{FeS}}$
32	263	eq.(A6-12)	γ_{Cu_2S}	$\sqrt{\gamma_{Cu_2S}/x_{Cu_2S}}$
33	267	eq.(A6-16)	$\gamma_{Na_2S}/(1-x_{FeS}^A)$	$\sqrt{\gamma_{Na_2S}/(1-x_{FeS}^A)}$
		eq.(A6-17)	γ_{Na_2S}/x_{Na_2S}	$\sqrt{\gamma_{Na_2S}/x_{Na_2S}}$
		eq.(A6-18)	$\gamma_{Cu_2S}/(1-x_{Na_2S})$	$\sqrt{\gamma_{Cu_2S}/(1-x_{Na_2S})}$
34	272	1	O.N.Carlson p.397	V.G.Leak et al p.409

page	line	original	correction
1.	xii	(missing left part of the page)	(exchange a whole page)
2.	4	23	4.9% of iron
3	12	17	lasser
4	15	2, 3, 9	(2-1)
5	16	9, 10, 11, 19	(2-2)
6	17	3	(2-1) and (2-2)
7	16	3	(2-4) and (2-5)
8	17	5	stirers
9	20	3	entrainment
10	20	9	3 kg wall above the
11	25	23	wall above the 3 kg
12	22	5, 6, 12	Davis
13	35	7	requires
14	35	20	required
15	42	Fig. 3-4 (a)	(2-3)
16	42	Fig. 3-5 (e)	slag
17	43	8	e.g. if
18	48	eg. (3-41)	e.g.
19	81	Fig. 3-20	$i = 40$
20	83	4, 5	$i + 40$
21	83	16	MS
22	127	3	MS _σ
23	131	17	($i = 49$)
24	154	Fig. 5-14	($i = 49$)
25	171	9	$M(8) \cdot N_{Na}$
26	180	Fig. 5-26	$M(8) \cdot N_{Na} + M(49) \cdot N_{SnS}$
27	166	after line 16	$\gamma_{FeS} = 0.1, \gamma = 1$
28	169	eq (5-4)	(delete this sentence)
29	170	16	Fig. 3-20
30	183	9	Fig. 3-19
31	214	6	(A1-5)
			(A1-9)
			$g (*g = g)$
			$\bar{g} \quad g = g$
			... 80 90
			... 80 90 110 160
			120
			(time)
			γ_{CuSO_4}
			γ_{FeS}
			80wt% Na ₂ SO ₄ - 20wt% FeS
			Na ₂ SO ₄ - FeS
			insert (1) Effect of
			argon bubbling.
			delete e in the equation
			Kituchi
			Kikuchi
			fairly
			3-2

ν	kinematic viscosity, [m^2/s]
ρ	density, [kg/m^3]
σ	stoichiometric constant
$\sigma(i_0, i)$	array for stoichiometric constant of the species- i (compound i_0)
φ	φ co-ordinate in the cylindrical system
$\varphi(t_r)$	distribution of t_r in the surface renewal theory
$\Delta \varphi$	electrical potential difference between two phases
ω	ratio of the total weight of the slag to metal phase

The removal of copper and tin from molten pig iron and steel
using sulphide slags

A thesis submitted to the
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CONTENT

	<u>PAGE</u>
<u>ABSTRACT</u>	iii
<u>ABBREVIATIONS AND SYMBOLS</u>	iv
(1) <u>INTRODUCTION</u>	1 - 5
(2) <u>PREVIOUS WORK</u>	
2-1 Mathematical modelling	6 - 11
2-2 Physical modelling	12 - 20
2-3 Chemistry and kinetics of decopperisation and detinning from carbon saturated iron and steel (de-Cu/de-Sn)	21 - 28
(3) <u>MATHEMATICAL MODELLING</u>	
3-1 Introduction	29 - 30
3-2 Description of mathematical models	31
3-2-1 Full model	31 - 49
3-2-2 Steady state model	50 - 61
3-3 Some applications	62
3-3-1 Dephosphorisation and desulphurisation from pig iron (de-P/de-S)	62 - 75
3-3-2 Decopperisation and detinning from carbon saturated iron and steel, (de-Cu/de-Sn)	76 - 101
3-3-3 Cr-slag cleaning	102 - 111
(4) <u>PHYSICAL MODELLING</u>	
4-1 Experimental techniques	112 - 115
4-2 Results	116 - 124
4-3 Interpretation and discussion of results	125 - 133
(5) <u>CHEMISTRY AND KINETICS OF DECOPPERISATION AND DETINNING</u> <u>(de-Cu/de-Sn)</u>	
5-1 Experimental techniques	134 - 145
5-2 Results	146 - 165
5-3 Interpretation of results	166 - 193
(6) <u>DISCUSSION</u>	
6-1 Overall aspects of the full model	194 - 200
6-2 Kinetics of decopperisation (de-Cu)	201 - 206
6-3 Kinetics of detinning (de-Sn)	207 - 212
6-4 Desulphurisation after decopperisation (de-Cu)	213
6-5 Behaviour of other elements during decopperisation and detinning (de-Cu/de-Sn)	213 - 218
6-6 Difference between carbon saturated iron and steel on decopperisation and detinning (de-Cu/de-Sn) using sulphide slags.	219 - 221
6-7 Evaluation of activity coefficients of sulphides in the slag phase	222
6-8 Performance of mechanical stirrer	222 - 224

PAGE(7) CONCLUSIONS

225 - 227

APPENDICES

1 Surface profile of forced vortex and free vortex

228 - 230

2 Terminal velocity

231 - 234

3 Derivations for the full model

235 - 246

4 Documentation of the full model

247 - 257

5 Thermodynamic and kinetic data

258 - 261

6 Activity and activity coefficient in the slag phase

262 - 268

REFERENCE

269 - 274

ACKNOWLEDGEMENT

275

Abstract

An industrially feasible method for copper and tin removal from molten pig iron/steel has not been established. Many studies have been carried out mainly on de-Cu/de-Sn from molten pig iron using sodium sulphide or sodium sulphate slag under the condition of lower temperature, say 1523K.

It is important to establish a method for decopperisation and detinning (de-Cu/de-Sn) not only at lower temperature for pig iron but also at higher temperature for steel. In this work, de-Cu/de-Sn from these two types of molten metal were studied.

The reactions involved in these systems are related to three phases, i.e. metal phase= Fe, C, S, O, Cu, Sn etc. slag phase= $\text{NaS}_{0.5}$, $\text{CuS}_{0.5}$, SnS, CaS, FeS etc. gas phase= $(\text{Na})_{\text{gas}}$, $(\text{SnS})_{\text{gas}}$ etc.

Mathematical model, which is based on thermodynamic and kinetic data was developed in this work. This model can include any elements and compounds whose thermodynamic and kinetic data are available. This model was used for evaluating the de-Cu/de-Sn characteristics of various kinds of slags. $\text{NaS}_{0.5}$ -FeS, CaF_2 -FeS, CaS-FeS and CaF_2 -CaS-FeS mixtures were chosen for experimental work.

These slags were added on the surface of molten pig iron at 1523K or 1873K and of steel at 1873K.

The physical mixing of slag and metal was investigated using a water model and a molten lead model with a mechanical stirrer.

The following conclusions were obtained:

- (1) Mathematical model can describe the experimental results in the sense of both thermodynamics and kinetics.
- (2) Optimum operating conditions for a mechanical stirrer have been established. e.g. optimum position of a stirrer and critical revolution rate for entrainment of slag.
- (3) $\text{NaS}_{0.5}$ -FeS mixture is good reagent for de-Cu from molten pig iron. For de-Sn, transport of a product, $(\text{SnS})_{\text{gas}}$, is important. Argon bubbling helps this transport.
- (4) It is more difficult to remove Cu from steel than from pig iron. Carbon in the metal phase plays an important role. CaS- CaF_2 -FeS mixture may work. Further work is worth doing with this slag. Higher temperature for steel is favourable condition for de-Sn, because of higher $(\text{SnS})_{\text{gas}}$ vapour pressure.

ABBREVIATIONS AND SYMBOLS

In order to save space and to clarify the text the following abbreviations have been used:

1. "de-P/de-S" denotes "dephosphorisation and desulphurisation".
2. "de-Cu/de-Sn" denotes "decopperisation and detinning".
3. "de-Si" denotes "desiliconisation".

a	activity
$a(i,j,k)$	array for activity of the species- i in the phase- j at the site- k .
$a_l(m)$	constant
C	molar concentration, $[\text{mol}/\text{m}^3]$
$C(j)$	array for molar concentration of the phase- j , $[\text{mol}/\text{m}^3]$
C_{Na}	total moles of sodium vaporised, $[\text{mol.}]$
d	diameter of a mechanical stirrer, $[\text{m}]$
d_p	diameter of a particle, $[\text{m}]$
D	i) diameter of a vessel, $[\text{m}]$ ii) diffusion coefficient, $[\text{m}^2/\text{s}]$
D_e	eddy diffusivity, $[\text{m}^2/\text{s}]$
$e_i^{(j)}$	first order j - i interaction coefficient in molten iron.
$E(i,j,k)$	array for equilibrium constant for the species- i at the phase- j /phase- k interface.
f	activity coefficient (Henrian standard)
Fr	Froude number defined by $Fr = N^2 \cdot d/g$
$f(i; a_0, a_s, NT_m)$	interfacial activity of species- i at the slag/gas interface.

g	gravitational acceleration, $[m/s^2]$
ΔG^0	standard Gibbs free energy change, $[cal/mol.]$ conversion factor to $[J/mol]$ is 4.1840. <u>$\Delta G^0 \times 4.1840 \quad [J/mol.]$</u>
G_{CO}	phenomenological rate parameter for CO evolution,, $[mol./m^2.s]$
H	i) depth of liquid in the vessel, $[m]$ ii) depth of gas inlet, $[m]$
ΔH	enthalpy change, $[cal/mol]$ <u>$\Delta H \times 4.1840 \quad [J/mol]$</u>
h_1, h_2, h_3	vertical dimensions for a mechanical stirrer - liquid system
$h(i; a_o, a_s)$	interfacial activity of the species- i at the metal/ slag interface
i	index of species
j	index of phases
J	flux, $[mol/s]$
k	i) index of sites which face to the phase- k ii) mass transfer coefficient, $[m/s]$
$k(i,j)$	array for mass transfer coefficient of the species- i in the phase- j , $[m/s]$
K	equilibrium constant for reaction.
l	clearance between the wall of a vessel and a stirrer, $[m]$

L	i) distribution coefficient using weight percentages ii) characteristic length for mass transfer [m]
L'	distribution coefficient using mole fractions
$L_{i,j}$	phenomenological constant in equation (2-1)
M	i) total moles, [mol] ii) molecular weight, [kg/mol]
M(i)	array for molecular weight of species-i, [kg/mol]
Mass (j)	array for total weight in the phase-j, [kg]
Δ Mass (j)	array for change of total weight in the phase-j during a particular time interval [kg]
M_{pow}	powder supplying rate in terms of weight per unit time, [kg/s]
n	number of droplets entering the nozzle per unit time, [1/s]
N	i) revolution rate of a mechanical stirrer, [r.p.m.], which is equal to $N \times 0.10472$ [rad/s] ii) flux density, [mol/m ² .s]
N(i,j,k)	array for flux density of the species-i from the phase-j to phase-k, [mol/m ² .s]
NT_m	total metal flux density, [mol/m ² .s]

p	i) partial pressure, [atm], which is equal to $p \times 1.0133 \times 10^5$ [Pa] ii) fraction of area renewed per unit time in the surface renewal theory, [1/s]
p_T	total pressure of the gas phase, [atm], which is equal to $p_T \times 1.0133 \times 10^5$ [Pa]
P_e	Peclet number defined by $Pe = L \cdot V_0 / D_e$
$q_1 - q_6$	constants
$\dot{q}$	argon gas flow rate at a particular temperature, [m^3/s]
$\dot{q}_N$	argon gas flow rate at room temperature in terms of [Nl/min] which is equal to $\dot{q}_N \times 1.667 \times 10^{-5}$ [Nm^3/s]
$\dot{Q}$	rate of powder supplying, [mol/s]
r	radial coordinate in the cylindrical system
R	gas law constant. $R = 1.987$ [cal/g-mol.K] $= 8.205 \times 10^{-5}$ [$m^3 \cdot atm/g-mol \cdot K$] $= 8.314 \times 10^3$ [$kg \cdot m^2/s^2 \cdot kg-mol \cdot K$]
R_1, R_2	radial positions in the cylindrical system
Re	Reynolds number defined by $Re = N \cdot d^2 / \nu$
S	interfacial area, [m^2]
ΔS	entropy change, [cal/mol K] <u>$\Delta S \times 4.1840$ [J/mol K]</u>
$S(j,k)$	interfacial area between phase-j and phase-k, [m^2]

t	time, [s]
Δt	time interval, [s]
t_r	residence time of fluid element at the surface in the penetration theory, [s]
t_{ref}	reference time defined by $t_{ref} = V_m/k_m \cdot S$, [s]
T	temperature, [K]
T_{gas}	gas temperature, [K]
U_B	rising velocity of a gas bubble in the molten metal, [m/s]
v	velocity, [m/s]
$v_{peripheral}$	peripheral velocity of a stirrer, [m/s]
V	volume, [m ³]
$V(j)$	array of a volume of the phase-j, [m ³]
V_0	characteristic velocity
V_G	gas flow rate, [Nm ³ /min] <u>$V_G \times 0.01667$ [Nm³/s]</u>
W	weight, [kg]
x	i) mole fraction ii) x co-ordinate in the rectangular system iii) = (weight of NaS _{0.5} slag)/(weight of metal)
x_{pow}	composition of powder supplied (mole fraction)
y	ratio of the total moles in the metal phase at a particular time to the initial

z

- i) z co-ordinate in the cylindrical system
- ii) constant

Greek

α	fraction of sodium vaporised
β	ratio of the total moles of the slag to metal phase
γ	activity coefficient of compounds in the slag phase (Roultian standard)
$\gamma(i,j)$	activity coefficient of species-i in the phase-j
Γ	circulation
δ	i) off-centre length of a stirrer in a cylindrical vessel, [m] ii) film thickness in the film theory [m]
$\delta_{i,j}$	function defined by: $\delta_{i,j} = \begin{cases} 1 & , \text{ when } i = j \\ 0 & , \text{ when } i \neq j \end{cases}$
ε	constant
ε_1	constant
ζ	multiplying factor for mass transfer coefficient in Cr-slag cleaning
η	fraction removed
θ	fraction of FeS decomposed
λ_f	latent heat of fusion, [cal/mol] <u>$\lambda_f \times 4.1840$ [J/mol]</u>
μ	viscosity, [kg/m s]

ν	kinematic viscosity, [m^2/s]
ρ	density, [kg/m^3]
σ	stoichiometric constant
$\sigma(i_0, i)$	array for stoichiometric constant of the species- i (compound i_0)
φ	φ co-ordinate in the cylindrical system
$\varphi(t_r)$	distribution of t_r in the surface renewal theory
$\Delta \varphi$	electrical potential difference between two phases
ω	ratio of the total weight of the slag to metal phase

Subscript

o	characteristic value
$1,2$	two specified systems in dimensional analysis
Ar	argon gas
cr	critical
M	element
MO or MO_{σ}	oxide
MS or MS_{σ}	sulphide
B	argon bubble

Superscript

b	bulk
eff	effective, e.g. K^{eff} denotes effective equilibrium constant defined by mole fractions
i	interface
0	initial
*	dimensionless

[]	dissolved in molten iron
{ }	liquid
() or () _{gas}	gas (unless otherwise stated)
< >	solid
wt%	weight percentage
Δ	$=\Delta_1 + \Delta_2$, [m]
Δ_1, Δ_2	vertical positions of liquid surface (see Fig. 4-5)
$\bar{X}$	mean value of X
∇	derivative

CHAPTER 1

INTRODUCTION

Steel scrap from motor cars contains typically 0.5 wt% Cu and 0.1 wt% Sn. These elements cause harmful effects on steel products. It is reported [44], [74]-[76] that Cu content and Sn content should be less certain levels of concentration in order to suppress hot-shortness during forming, which is one of the main harmful effects. As conventional steel making processes have no ability to remove Cu and Sn, it would obviously be useful to develop a process for this purpose.

Harmful effects of Cu and Sn on steel are described [59]-[61] below:

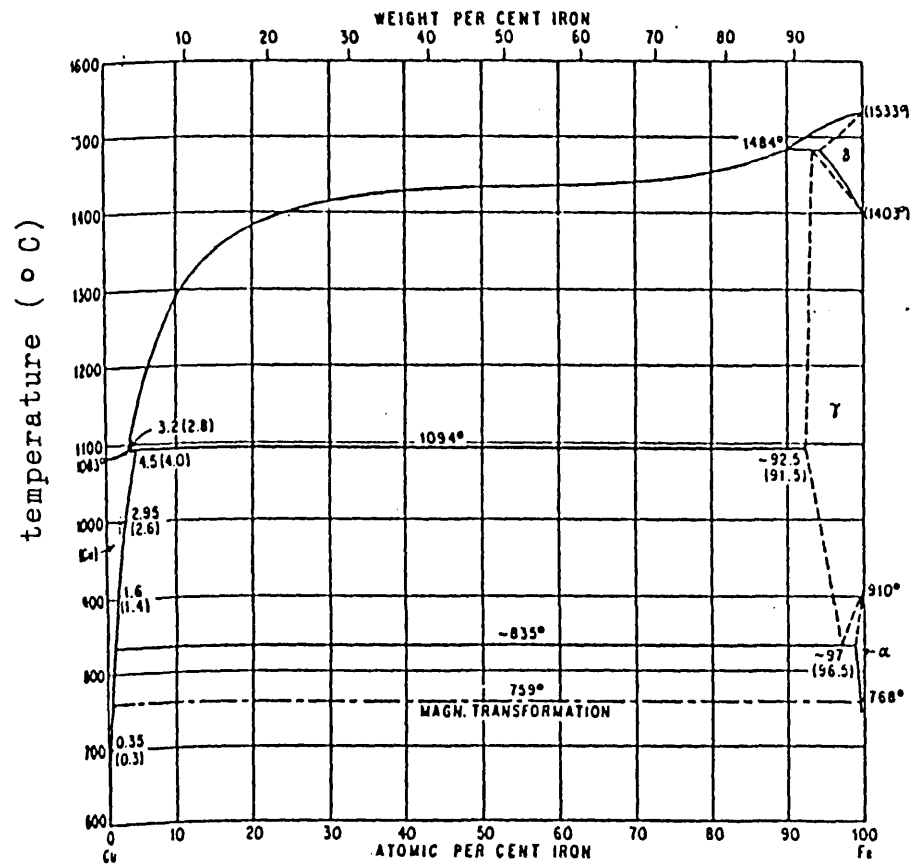
(1) Hot shortness : Cu in steel causes surface cracks in the later stages of hot forming, for example in the hot rolling of continuously cast slabs and sections. During the heating of steel slabs for hot rolling, Fe in the surface region is selectively oxidised. Cu is not oxidised and the Cu content in the surface region increases. The Cu-enriched alloy has a lower melting point, as shown in Fig. 1-1. In the surface region, some molten metal is formed which is enriched in Cu. This penetrates through grain boundaries and makes steel brittle. The tensile stress imposed by hot rolling causes surface cracks.

Sn aggravates any hot-shortness caused by Cu, because Sn decreases the solubility of Cu in austenite [48].

(2) Decreases of deep-drawability of steel sheet by Cu.

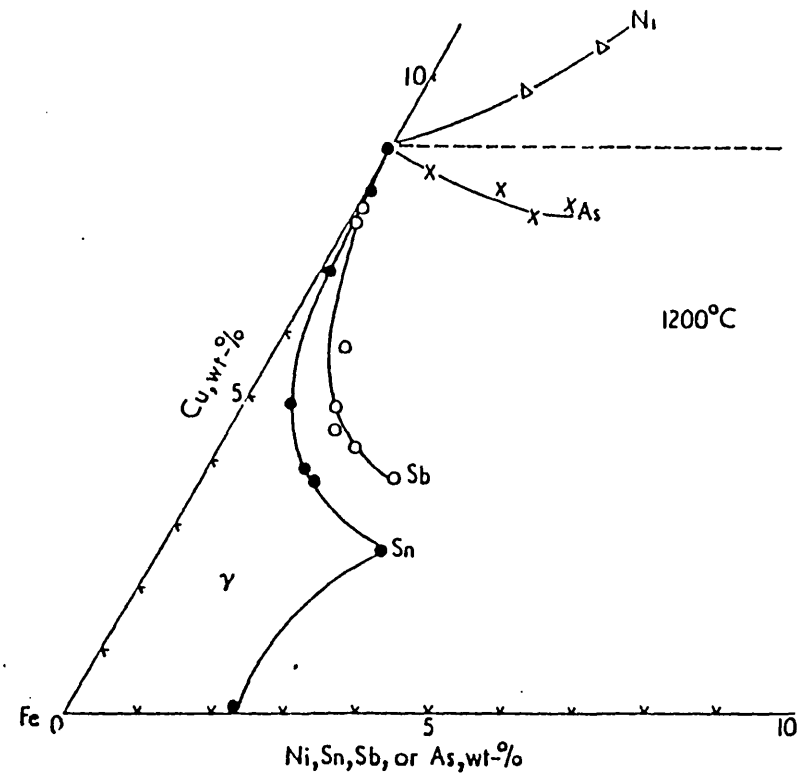
Various ideas have been put forward for copper and tin removal.

(i) Selective melting method : Cu and Sn are selectively sweated off the scrap by keeping the temperature higher than the melting point of



(a) Cu-Fe (30).

Fig.1-1 Cu-Fe(-Sn).



(b) Effect of small addition of Sn on the solubility of Cu in austenite at 1200° C.

the particular elements. (m.p. of Fe = 1536°C , m.p. of Cu = 1083°C , m.p. of Sn = 232°C); e.g. for copper removal a molten salt bath can be used at the temperature 1150°C - 1250°C .

(ii) Vacuum distillation method: using vacuum equipment, Cu and Sn are volatilised (vapour pressures of Cu and Sn, both at 1 wt% in molten iron, are 0.79mm Hg and 0.90mm Hg respectively at 1600°C). Vacuum distillation of tin coupled with the formation of volatile SnS has been reported by Sehgal [38] and this could form the basis of a successful process for tin removal. The rate of tin removal from 0.77 to 0.07 wt% under vacuum was enhanced by a factor of 5 times at a sulphur level of 0.16 wt%.

(iii) Sulphide formation method : using the fact that Cu and Sn have larger affinities for S than Fe has, it is possible to remove Cu and Sn from molten iron/steel by forming $\text{CuS}_{0.5}$ and SnS.

*S in
reducing
at. level
in?*

(iv) Other compounds : materials with high chlorine contents such as poly vinylchloride and hexachloroethane were used by Brown et al [40] in order to remove Sn from carbon saturated iron as SnCl_2 .

(v) $\text{CaSn}_{0.5}$ formation using metallic Ca and/or CaF_2 [55], [56], [58].

The characteristics of these methods are compared below. It is reported [42] that the final Cu content was approximately 0.3 wt% by the selective melting method. This method requires a large amount of thermal energy, about 240 kcal/kg steel, although the proportion of Cu removed is not high. If this method is installed in a conventional steelmaking process, e.g. combined with an LD converter, scrap can be heated up by the thermal energy of waste gas of the process and treated scrap which has a large amount of thermal energy can be directly charged into the refining process without any significant thermal loss. This improves the thermal efficiency in the whole system.

Vacuum treatment requires high temperatures from 1600 to 1800⁰C, so the thermal loss is significant. Because of the high temperature and vacuum, Mn escapes as vapour. It has been pointed out by Harris et al [35] that it is possible to increase the kinetics of Cu and Sn removal from molten iron by combining vacuum and argon gas bubbling, which increases the metal/gas interfacial area by forming both metal droplets and gas bubbles. In the case of slag-metal reaction most of the previous work has been concentrated on the study of copper removal from carbon saturated iron at the temperature range 1250⁰C - 1350⁰C. A great deal of slag (15-40% of the metal weight) is required for significant copper removal ($\eta_{Cu} \sim 70\%$), NaS_{0.5} slag has been thought the most suitable slag for copper removal from carbon saturated iron. It is more difficult to remove copper from steel than from carbon saturated iron due to the difference of C content and temperature. The higher the C content, the higher is the activity coefficient of Cu. NaS_{0.5} for copper removal from steel by the addition of a compound which increases the boiling point of the mixed compounds, e.g. AlS_{1.5}. NaS_{0.5} has many disadvantages, e.g. difficulty in handling because of hygroscopicity, high price, high reagent consumption, refractory attack. It is therefore necessary to investigate alternative fluxes for an industrial process. There are some reports ²⁸[6], [21] about copper removal using a method other than forming the sulphide. It is reported by Brown et al [40] that 85% of tin was removed as SnCl₂ (initial Sn 1.1 - 1.5 wt%). Simultaneously 4-9% of iron was removed - this loss of iron would be a serious limitation for a full scale process.

In the present work, copper and tin removal from carbon saturated iron and from steel has been studied, using sulphide slag.

Actual slags used in the experimental work are:-

- i) $\text{NaS}_{0.5}$ - FeS mixture.
- ii) CaF_2 - FeS mixture.
- iii) CaS - FeS - FeO mixture.
- iv) CaS - $\text{NaS}_{0.5}$ - FeS mixture.

The main aims were:-

- 1) to find an efficient condition for copper and tin removal from carbon saturated iron by varying the slag composition keeping [S] at a reasonably low value.
- 2) to find a suitable slag for copper and tin removal from steel.
- 3) to establish mathematical models which are able to simulate not only the behaviour of copper and tin in the various conditions but also to simulate various other kinds of pyrometallurgical problems which are relevant to metal-slag-gas reactions.

The full mathematical model which is a comprehensive version of the mathematical model predicts the behaviour of the system relating to both the rate phenomena and the local chemical equilibria at the interfaces.

The mathematical models may require some experimental verification. These models provide much information which is difficult to measure, and allows accurate predictions to be made on the basis of relatively few experiments.

The principal restrictions of the full model are :

- 1) As the rate of chemical reaction is not included, the chemical reaction rate should be faster than other rate phenomena.
- 2) Vigorous mixing, which creates droplets of slag and/or metal, is not included. This can be included by some modification of the coded programme or simply by an increase in the mass transfer coefficients.

CHAPTER 2

PREVIOUS WORK

2-1 Mathematical modelling

There are many mathematical models reported which are relevant to pyrometallurgical reactions. The majority are special models which are only applicable to a particular set of experimental conditions and were developed purely to understand their results. There are fewer general models which are applicable to a wider range of reaction conditions and which are based on very general governing equations. The present survey is restricted to the latter category of models.

The mathematical models for pyrometallurgical reactions mainly consider only the metal and slag phases. In iron and steelmaking processes these phases are important but the gas phase frequently also plays an important part in determining the course of the reactions.

Lu[63] and Froberg et al [62] applied electro-chemistry to the metal/slag reaction. According to them, the flux of the species- i across the interface, N_i , is related to the chemical and electrical potential difference between the two phases. After linearisation, using phenomenological parameters, L_{ij} , they obtained:-

$$N_i = - \sum_j L_{ij} (\Delta\mu_j/\delta + z_j F\Delta\phi/\delta) \quad (2-1)$$

Here $\Delta\mu_j$ and $\Delta\phi$ are chemical potential and electrical potential difference between the two phases respectively.

δ is a characteristic length for these potentials. F is Faraday's constant. z_j is the valency of the species - j .

In the case where the total current is zero,

$$\sum_i z_i N_i = 0. \quad (2-2)$$

This leads to the equation for determining $\Delta \varphi$

$$\Delta \varphi = - \sum_i \sum_j (z_i L_{ij} \Delta \mu_j) / \sum_i \sum_j (z_i L_{ij} z_j) F \quad (2-3)$$

In the right hand side of equation (2-1), the first term is the flux density caused directly by the chemical potential difference and the second term is the flux density caused by the electrical potential which is created by the collective effect of chemical potential differences of all species. Froberg et al [62] applied this model to de-S of an Fe-C-S melt. They derived $\Delta \mu_S$ from the experimental data of the distribution coefficient of sulphur defined by $(\text{wt\% S})_{\text{slag}} / [\text{wt\% S}]$. They then calculated the electrical potential induced and the flux density of oxygen and finally they calculated the rate of evolution of CO. They claimed that the calculated CO evolution and Fe transfer gave good agreement with the experimental data. Some of the assumptions in their model are debatable. e.g. the concentration of oxide in the slag phase was assumed to be constant and build up of oxygen in the metal phase was assumed to be negligible. They used many phenomenological parameters, and the results predicted by their model agreed fairly well with the experimental results. In the case of more complicated systems, e.g. when a greater number of elements are involved, their phenomenological parameters could hardly be determined. They assumed that the rate controlling step was the interfacial chemical reaction. It is thought more probable that the rate controlling step is mass transfer in the boundary layers.

Niwa et al [68] applied a reaction model based on an electrochemical mechanism to some problems; e.g. metal-slag transfer of manganese and sulphur. They included a diffusion process in the slag phase in their model. It is possible to discuss both chemical reaction rate and mass transfer rate in the slag phase. In the case where one anion $S^{=}$ and one

cation, e.g. Mn^{++} , are introduced, the problems are readily solved. Numerical methods using a computer are required in the case of multi-anion and/or cation problems due to the nonlinear nature of the governing equations.

Kawai et al [32] pointed out that many previous thermodynamic data were compiled on the basis of molar properties although a metal-slag reaction is thought to proceed electrochemically.

They established a model based on mass transfer as the rate controlling step. They applied it to simultaneous de-P/de-S from molten iron [67], MnO reduction into molten iron [64] and so on. In their model, the equation for the total flux density balance is equivalent to the equation for the charge neutrality (zero total electric current) condition in an electrochemical model. (see equation (2-2)). This model does not include CO evolution. If CO evolution plays an important role in the actual phenomena this model fails to describe the actual process correctly. In the case of MnO reduction [64], they used the interfacial concentration of FeO as a key variable and they determined the values of parameters, k_s , K_{Mn} defined by $(wt\% MnO)_{slag}^i / [wt\% Mn]^i (wt\% Fe_tO)_{slag}^i$ and L_O , defined by $(wt\% Fe_tO)_{slag}^i / [wt\% O]^i$ (which was assumed to be affected by MgO content due to dissolution of crucible in the slag phase). which gave minimum difference between calculated and experimental results, i.e.

$$\text{minimise } \sum_{\text{time}} ([wt\% Mn]^{calc} - [wt\% Mn]^{exp})^2 \text{ and}$$

$$\text{minimise } \sum_{\text{time}} ([wt\% O]^{calc} - [wt\% O]^{exp})^2, \text{ where superscripts}$$

calc and exp denote calculated and experimental result respectively.

They put all of the unknowns of thermodynamic data, eg. activity coefficients of compounds in the slag phase into K_{Mn} and L_O . Increasing the number of elements and compounds involved would cause difficulties in determining the values of parameters.

Fukuzawa et al [70] developed a reaction model based on mass-transfer as the rate controlling step and applied it to some problems of oxygen steelmaking processes. One of the essential parameters in their model is the oxygen delivery ratio which is defined by the ratio of oxygen consumed by FeO formation to the total oxygen blown.

The actual behaviour of oxygen could only be properly simulated by a metal-slag-gas reaction model, which can deal with oxygen transport in the slag phase, without introducing an empirical parameter such as the oxygen delivery ratio.

Robertson et al [16] developed a comprehensive reaction model which has the following characteristics:-

- 1) The rates were assumed to be controlled by multi-component transport in the metal and slag phases.
- 2) The model can be applied to both ferrous and non-ferrous systems, owing to its general nature.
- 3) The oxygen transport which played an important role in many problems was modelled by the introduction of metal/gas and slag/gas interface, which are relevant to CO formation and transport. They included the reduction mechanism of oxides by CO at the slag/gas interface and the oxidation mechanism of C by CO₂ at the metal/gas interface, as shown in Fig. 2-1.

Although this model requires some sophisticated computational techniques to solve simultaneous nonlinear equations, the solution leads to the better understanding of the actual phenomena observed in the experimental work for instance from calculated data which are experimentally unmeasurable.

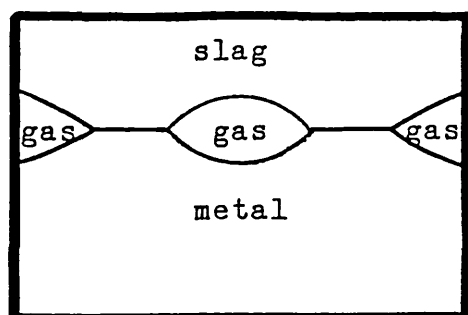
In the case of de-Cu/de-Su using $\text{NaS}_{0.5}$ slag which are relevant to the present study, Na vaporization, SnS vapour formation, $\text{NaS}_{0.5}$ decomposition and their transport to the bulk gas phase are important. In order to describe these phenomena, in the present work a mathematical model on the same basis as Robertson et al [16] was developed, as depicted in Fig. 2-2 and is explained in 3-2-1.

When thermodynamic and kinetic data are not available from previous literature they are kept as unknown parameters in the model. As long as the model is based on the correct governing equations, it is possible to evaluate these parameters by comparing the experimental and the computed results whilst changing the values of these parameters.

In the present work, some unknown parameters relevant to thermodynamics, e.g. $\gamma_{\text{CuS}_{0.5}}$, were determined from the steady state mathematical model and some unknown parameters relevant to kinetics were determined from the full mathematical model.

These kinetic parameters relate to the fluid dynamic properties of the system. Some attempts have been made [66], [69] to combine a fluid dynamic model and a chemical reaction model so as to simulate de-S with a dispersed slag in the metal phase. Their models agreed with the experimental data fairly well. Such models are useful for problems in which fluid dynamics play an important role.

As is pointed out by Robertson et al [16], there are some factors which are difficult to incorporate in the mathematical model, for example, the change of the product of mass-transfer coefficient and actual interfacial area during reaction due to the changes of interfacial tension and/or the changes of viscosity of the slag phase. These interfacial phenomena were reviewed by Berg [72]. The interfacial phenomena during de-S were discussed by Saelim et al [65].



(a) Phases.

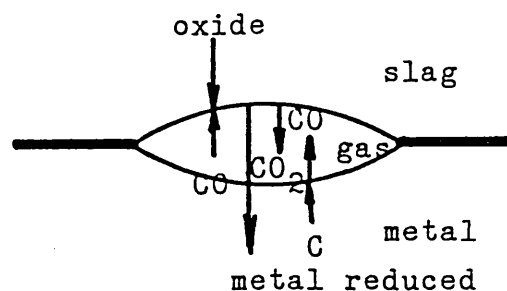
(b) CO, CO₂ reactions.

Fig.2-1 Schematic view of the metal-slag-gas reaction model developed by Robertson et al (16).

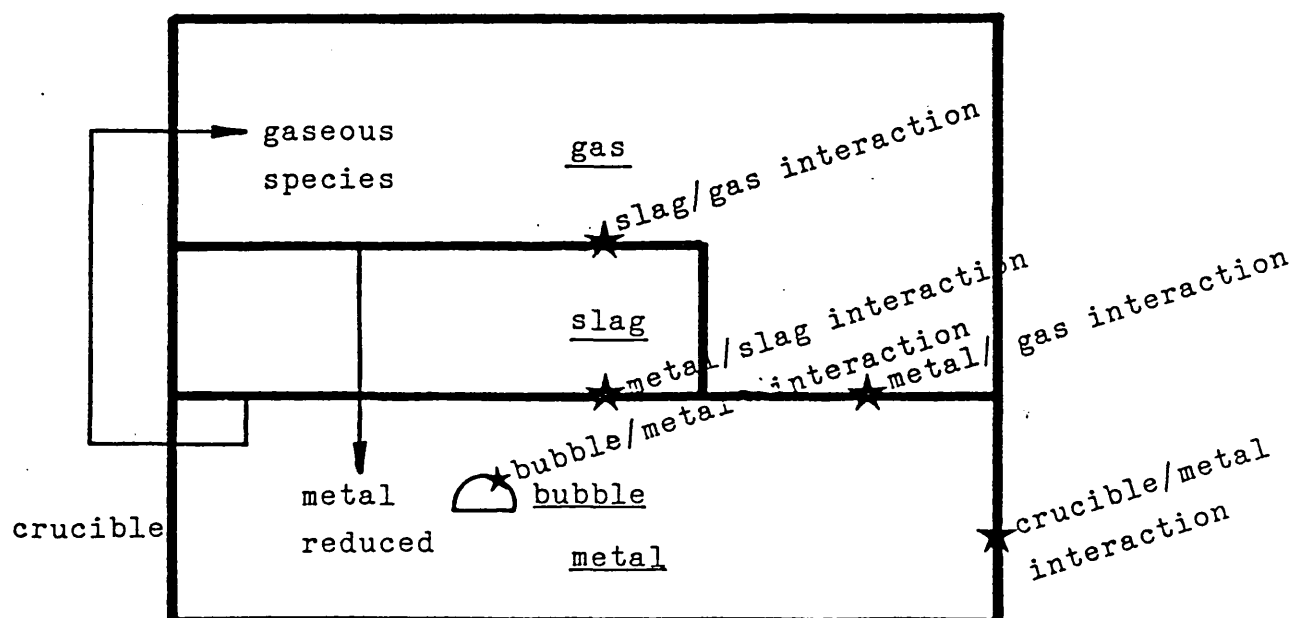


Fig.2-2 Schematic view of the metal-slag-gas reaction model (full model) in the present work.

2-2 Physical modelling.

In pyrometallurgy, the rate of a reaction is often controlled either by the mass transfer in the boundary layer close to a phase interface or by mixing in the bulk phases. Sometimes both mechanisms together have an influence on the rate. Chemical reactions at high temperatures are generally very fast so that they do not have a large effect on the overall rate of reactions involving phase to phase transport.

There are several means of enhancing mass transfer rates as follows:-

- 1) Mechanical stirring (by shearing stress), e.g. furnace rotation, impeller in the transfer ladle in steel industry [50].
- 2) Stirring by induction, e.g. electro-magnetic stirring.
- 3) Stirring by gas injection (see Fig. 2-3).

It has been pointed out by Joosten et al [1] that there have been many reports about the suspension of particles which are denser than the bulk liquid but a lesser number of reports about the entrainment of lighter particles in a heavier liquid. They determined the critical revolution rate of a stirrer and its power consumption for the entrainment of particles into a water bath by using various combinations of stirrers and baffles. In their definition, the critical revolution rate (called the minimum revolution rate in their paper) was the rotating rate of the stirrer which was just enough completely to remove any stagnant zone of floating particles on the surface of the liquid. This definition, as well as the observations, tended to be subjective. It was claimed that the reproducibility of the results was within 5% in their experiments as long as the experiment was carried out completely by the same person. The conclusions of

their experiments were :

- 1) The optimal flow pattern for suspension of the floating particles was obtained by rotating the liquid rapidly and disturbing the rotation with a fairly wide baffle placed above the stirrer and perpendicular to the wall of the vessel, (see Fig. 2-4).
- 2) Without a baffle, it seemed to be best to set the stirrer in an off-centre position. Thorough investigation of this was not carried out.
- 3) It was best to use a four-bladed and inclined-blade paddle in order to obtain a low critical revolution rate and low power consumption.
- 4) It was possible to decrease the critical revolution rate by increasing the d/D value. (Fig. 2-4).
- 5) The effect of h_3 (the distance between the bottom of the vessel and the bottom of the stirrer), on the critical revolution rate was small. The deeper the stirrer is set, the lower the critical revolution rate to some extent. The population of entrained particles was less below the stirrer than above it.
- 6) The effect of the density difference, $\Delta\rho$, between the floating particles and the liquid on the critical revolution rate N_{cr} is expressed by $N_{cr} \propto (\Delta\rho)^{0.21}$ according to the experimental results. It was thought that the effect of the size of particles on N_{cr} was negligible.

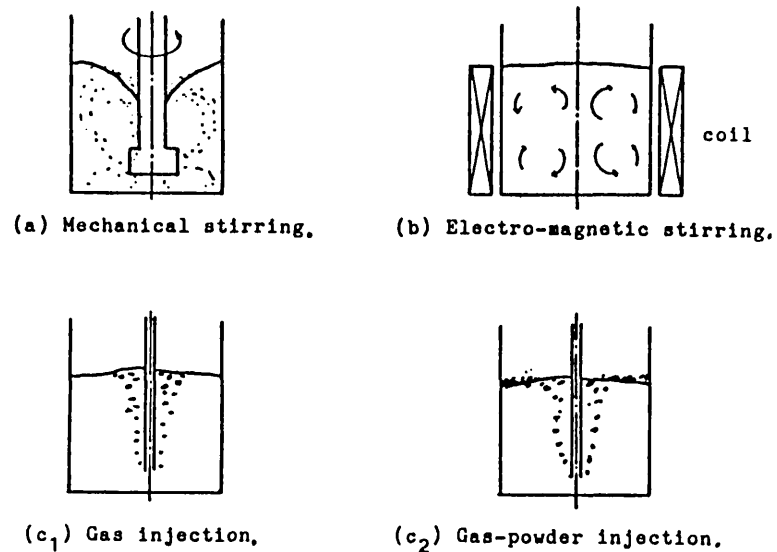


Fig.2-3 Methods for mixing.

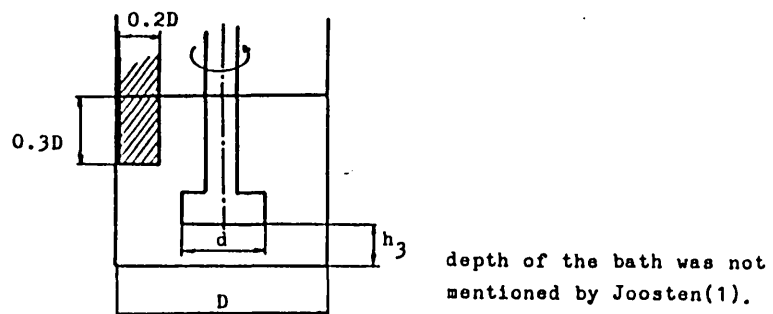


Fig.2-4 Optimal profile of baffle estimated by Joosten(1).

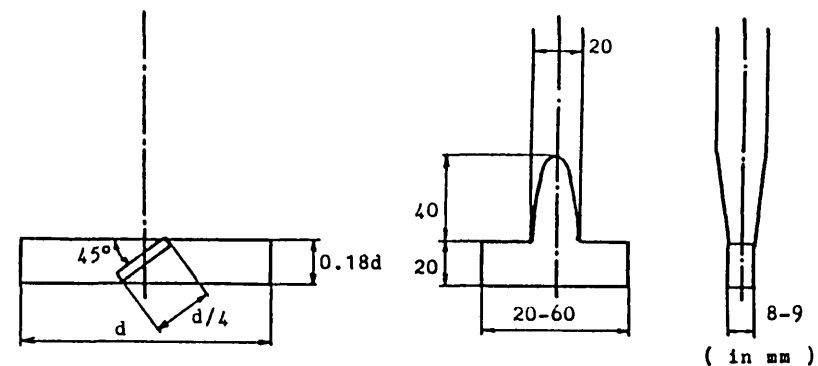


Fig.2-5 Stirrer profile used by Joosten(1).

Fig.2-6 Stirrer profile used in the present work.

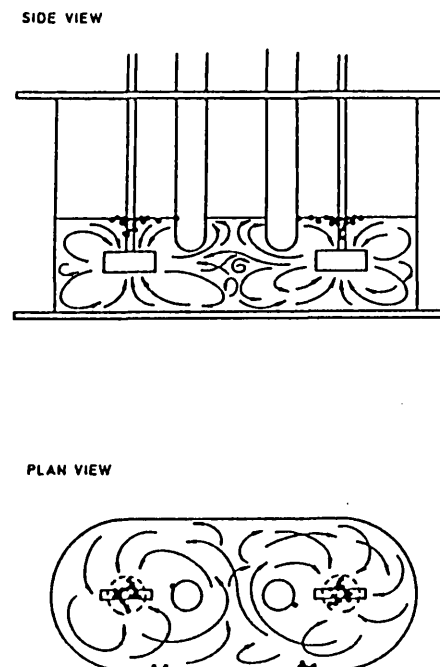


Fig.2-7 Water model for the submerged electric furnace and mechanical stirrer used by Lim(2).

- 7) The critical Froude number, the dimensionless critical revolution rate, was obtained from equation (2-4).

$$Fr_{Cr} = c \times \left(\frac{d}{D} \right)^{-3.65} \times \left(\frac{\Delta\rho}{\rho_L} \right)^{0.42} \quad (2-4) \quad \text{see 16.}$$

Fr : Froude number defined by $Fr = N^2 d/g$

c : experimental constant depending on the configuration of the stirrer and the baffle in case of the four bladed and inclined paddle, $C = 3.6 \times 10^2$

Applicable regions of the equation (2-4) :

$$0.27m \leq D \leq 1.8m$$

$$0.29 \leq d/D \leq 0.60$$

$$0.1 \leq \Delta\rho/\rho_L \leq 0.76$$

$$0.11 \leq h_3/D \leq 0.33$$

with $2mm \leq d_p$ (particle size) $\leq 13mm$

water { viscosity $\mu = 10^{-3}$ N.s/m²
only { density $\rho_L = 1000$ kg/m³

They used the stirrer profile depicted in Fig. 2-5 changing the d/D value between 0.29 and 0.6, the number of blades being 2,3,4 or 6, the number of baffles being 1 or 4. They achieved critical revolution rates at minimum power by choosing the inclined paddle which had larger d/D value and using the baffle which suppressed the swirling of the liquid.

Lim [2] used a low temperature model in order to obtain the basic data for both designing a new refining process and improving existing processes. He investigated the conditions for good entrainment of the particles by changing the revolution rate of the stirrer, the size of the stirrer, the viscosity of the liquid, the density and size of the particles and the system geometry. He measured the rate of entrainment of particles, using simple flat-bladed paddles.

He used a special geometry depicted in Fig. 2-7, which was similar to that in a submerged arc furnace for tin slag reduction by coal particles. There were two stirrers and two electrodes which acted as baffles. The main function of the stirrers was to entrain the floating reagent particles into the liquid and to disperse them. This enhanced the reaction rate. Lim's definition of the critical revolution rate was the rate which could just entrain 60 particles per minute. The critical Froude number was expressed by equation (2-5) which was derived from the experiments.

$$Fr_{cr} = 0.123 \times \left(\frac{d_p}{d}\right)^{0.43} \times \left(\frac{\ell}{d}\right)^{-0.33} \times \left(\frac{d}{D}\right)^{-1.95} \times \left(\frac{\Delta\rho}{\rho_L}\right)^{0.73} \quad (2-5)$$

Applicable regions of equation (2-) were not mentioned in Lim's paper. Regions investigated by him were:

$d = 127\text{mm}$ or 191mm (stirrer's size)

$h_3 = 50.8\text{mm}$ or 102mm (clearance between the bottom of vessel and stirrer)

$\nu = 0.9 \times 10^{-4} \sim 5.2 \times 10^{-4} \text{ m}^2/\text{s}$ (viscosity)

$\Delta\rho/\rho_L = 0.20, 0.46$ or 0.60

number of particles = 50, 120, 200 or 300 spheres

$d_p = 10$ or 20mm (particle size)

In equation (2-5), ℓ , which denotes the clearance between the wall of container and a stirrer, is expressed explicitly by

$\ell = (D - d)/2$. It is not reasonable to use three variables D, d and ℓ , which are not independent to each other, in the equation.

Although Lim showed a large effect of viscosity on the critical Froude number for entrainment in his paper, the critical Froude number decreasing with decreasing fluid viscosity, a viscosity term did not appear in the final correlation. The use of his work might lead to neglecting the effect of viscosity of the molten phase, e.g. slag phase.

The smaller and the heavier the particle, the lower was Fr_{cr} . The larger stirrer had lower Fr_{cr} values. The difference between equations (2-4) and (2-5) was mainly due to the difference of system geometry. Lim concluded that the deeper stirrer required a higher Reynolds number ($Re = d^2N/\nu$) to give entrainment. On the other hand, Joosten et al [1] concluded that, if anything, the deeper stirrer required the lower minimum revolution rate. In the present work, the effect of the depth of the stirrer on the critical revolution rate was carefully investigated.

The mechanical mixing of small foamed polystyrene particles floating on water in a cylindrical vessel was investigated by Ando et al [3]. They identified a region in the r.p.m./position plot which gave good performance for entrainment of the particles. The results are shown in Fig. 2-8(a). The effect of the revolution rate of the stirrer, the depth of the stirrer and the baffle on the entrainment and circulation of the particles were investigated. It was concluded by them that if the number of blades was increased from four to six, the critical revolution rate could be reduced by 30%. They also showed that a 5% pitch for the blade reduced the critical revolution rate by 10% in the case of the four-bladed stirrer. As is shown in Fig. 2-8(a), the baffle reduced the critical revolution rate to a great extent (~20%). Fig. 2-8(a) shows that the position of the stirrer should be deeper than some minimum value in order to entrain particles. This restriction for the depth can be relaxed by the use of the baffle.

Nakanishi et al [4] investigated the characteristics of mixing of water and particles for the combination of the gate type stirrer sketched in Fig. 2-8(b), and gas injection from the stirrer and applied the results of the water model to plant scale equipment which is used for de-S of 60 tonnes of molten iron. The stirrer caused a vortex in the centre of the liquid surface. The reagent for de-S gathered into

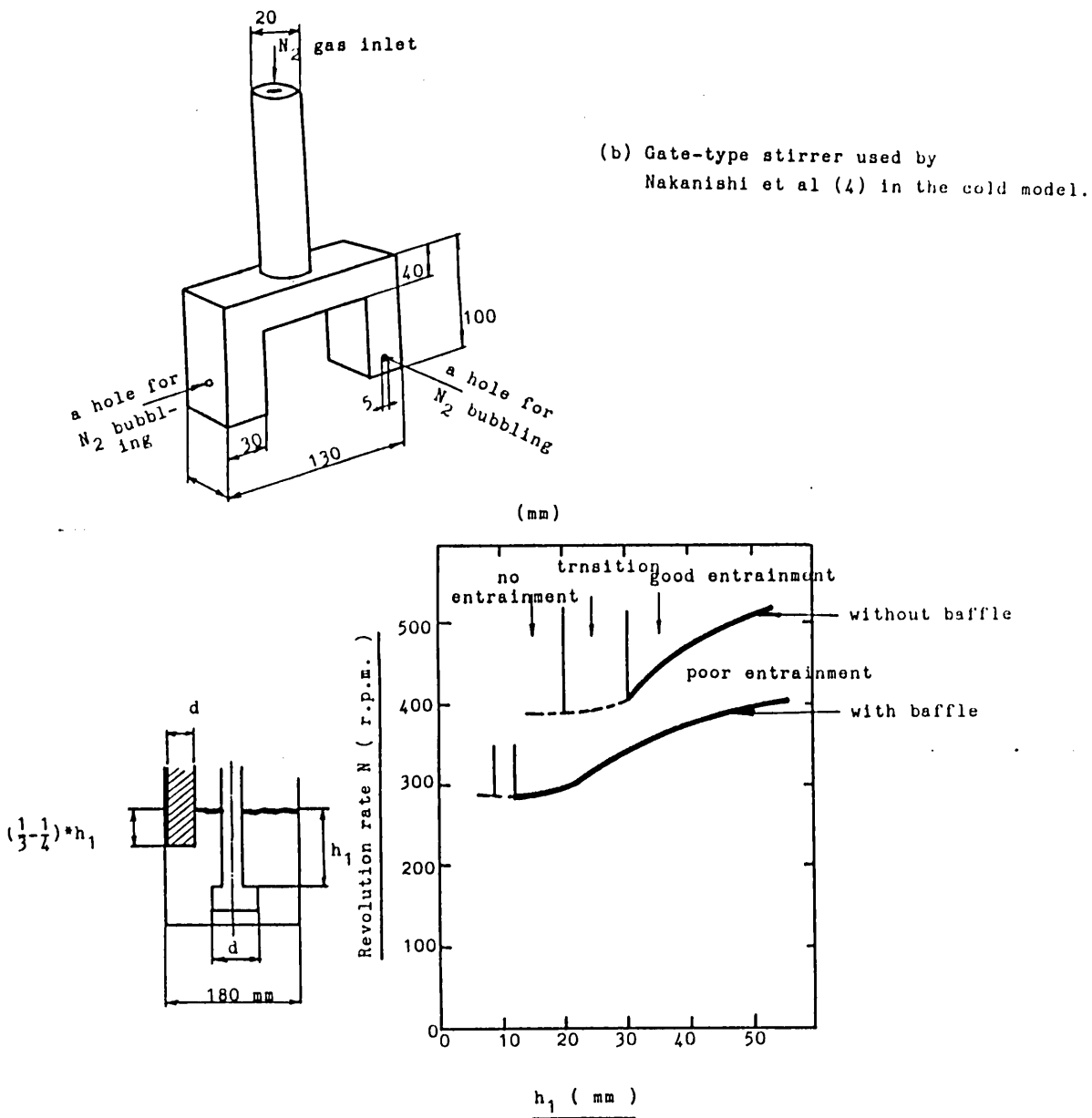


Fig.2-8 (a) Range of revolution rate and position of stirrer for various extent of the entrainment of floating particles. Ando et al (3).

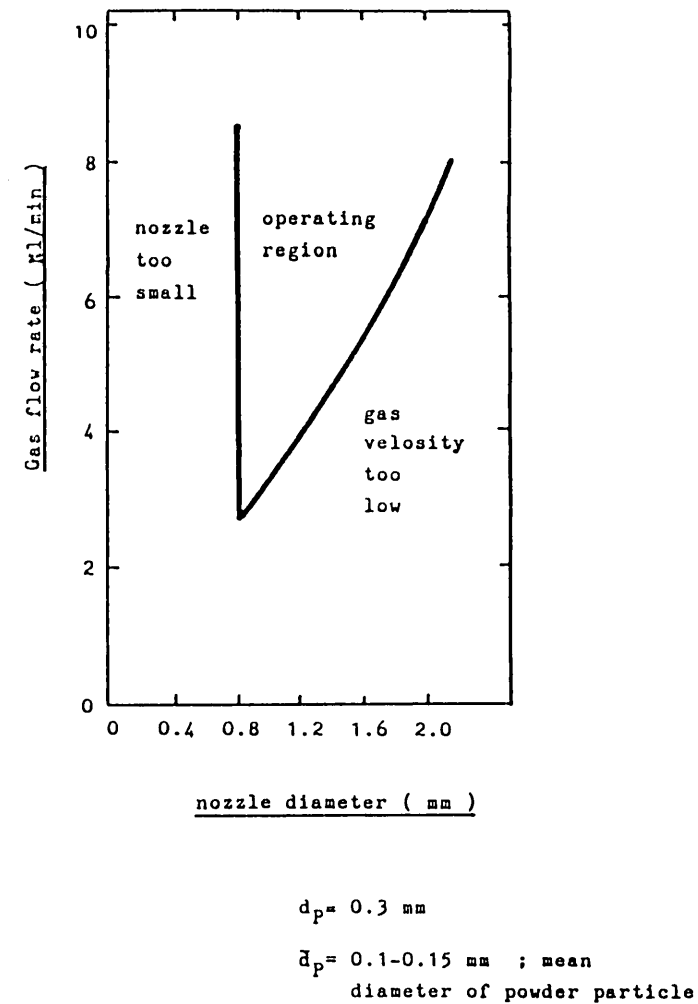


Fig.2-9 Stable condition for powder injection (10)

this vortex and then the reagent was entrained into the molten iron. Nitrogen gas injected from the stirrer helped dispersion of the reagent throughout the bulk phase. Their conclusions from the water model were :

- 1) The mixing time (defined by tracer-method) can be reduced only by the stirrer characteristics. The effect of gas injection on the mixing time was very small.
- 2) The reaction time, including mass transfer between the slag phase and the metal phase, was influenced by gas injection. Gas injection helped this mass transfer.

In the present work, water and lead were used to simulate the iron. In the present work it was aimed to obtain good suspension/suction performance using a flat-bladed stirrer which had smaller d/D value and no baffle. This increased the critical revolution rate required for entrainment to higher values than in the case of Joosten et al. (see Fig. 2-6). In the present work, the critical revolution rate, N_{cr} , was defined as the rate which could just entrain a floating particle. A mechanical stirrer was selected because it was found by Ohguchi [10] that it was difficult to inject gas powder mixtures on the small laboratory scale. The reasons for this are:-

- 1) The lance size has a minimum value below which blocking of solid flow will occur even in a tube transporting powder from one dry container to another.
- 2) The gas velocity must be sufficiently high to prevent nozzle blockage by liquid metal. You et al [8] have shown that, even during gas only injection, liquid penetration did occur and that its severity was reduced by increasing gas flow rate. In solid powder-gas injection the liquid penetration could cause nozzle blockage unless the gas velocity was above a critical value.

The gas injection rate dictated by factors 1) and 2) above was about 4 l/min in a 1 mm diameter nozzle and led to severe splashing in the 3κ wall above the melt. It was shown by Ohguchi [10] that the stable condition for injection was a very narrow region in the gas flow rate and nozzle diameter domain, as is shown in Fig. 2-9. This region for stable injection became narrower with advancing time because blockage became increasingly likely with time.

Blockage of horizontal nozzles during injection of gas into liquid cast iron was investigated by Davis et al [53]. They concluded that when the bubble rose from the nozzle tip, liquid metal moved to fill the space and if this metal has a sufficient component of momentum toward the nozzle, blocking would take place. Engh et al [54] found the relation between gas velocities at nozzle and the number of droplets that entered the nozzle per unit time, n . They also concluded that n was minimum for a horizontal nozzle.

You et al [8] studied the clogging of the nozzle in the case of gas injection with or without powder. He changed the orientation of nozzle. They concluded that horizontal position was most desirable and powder injection had a lower penetration depth of the liquid into the nozzle than the results for gas-only injections.

The transport of powder from tank to the vicinity of nozzle tip does not cause any problems. The fundamentals of this transport are given in the reference [51].

Because of the difficulties described above Ohguchi decided to supply the powder onto the surface of liquid and to entrain it into the liquid by a gas-only injection lance. However, accretions were still a problem and the slag/metal contacting was not very effective.

It was therefore decided to investigate the use of a mechanical stirrer in the present work.

2-3 Chemistry and kinetics of decopperising and detinning from carbon saturated iron and steel (de-Cu/de-Sn)

Studies of copper removal from carbon saturated iron have been influenced by the U.S. patent (1950) of Jordan [20]. He claimed the following items in this patent:

- 1) As S has greater affinity for Cu than for Fe, it is possible to get rid of Cu in the molten iron by forming copper sulphide.
- 2) $\text{NaS}_{0.5}$, $\text{KS}_{0.5}$ and $\text{AlS}_{1.5}$ were used as reagents for copper removal.
- 3) S in the initial metal phase helps copper removal.
- 4) Mn and Al have greater affinity for S than has Cu.
- 5) It is possible to suppress volatilisation loss of $\text{NaS}_{0.5}$ by adding $\text{AlS}_{1.5}$.
- 6) $\text{KS}_{0.5}$ has similar characteristics as $\text{NaS}_{0.5}$.
- 7) It is possible to remove Cu and S simultaneously by $\text{NaS}_{0.5}$.

The typical experimental results which he showed, are:
 initial metal composition (3.34 wt% C, 2.10 wt% Si, 0.10 wt% Mn, 0.30 wt% Cu, 0.155 wt% S)
 final metal composition (0.009 wt% Mn, 0.04 wt% Cu, 0.019 wt% S).
 by the action of the same weight of $\text{NaS}_{0.5}$ slag as metal at the temperature 1370°C.

S activity should be high enough to form copper sulphide significantly in order to remove Cu. Ideally both S and Cu should be low enough to give satisfactory mechanical properties in the final product. In order to satisfy these inconsistent demands, it is necessary to choose a refining slag composition which has a low activity coefficient of $\text{CuS}_{0.5}$ in the slag phase.

It is not absolutely necessary to remove Cu and S simultaneously, since sulphur can always be removed by a subsequent de-S step. However, it would obviously be uneconomic to have to remove too high a sulphur content after treatment for copper removal.

Although it is uneconomic to apply Jordan's method to the industrial scale operation, his suggestions are worthwhile for the reasons given below:

- i) He pointed out the importance of simultaneous copper and sulphur removal.
- ii) He pointed out the ability of $\text{NaS}_{0.5}$ for copper removal.
- iii) He pointed out the suppressing effect of $\text{AlS}_{1.5}$ on $\text{NaS}_{0.5}$ volatilisation loss at the elevated temperature.

Sodium sulphate (Na_2SO_4) was used for copper removal from carbon saturated iron by Harry et al [33]. They obtained the relation between x , which denoted the ratio of the slag weight to the metal weight, and η_{Cu} which denoted the fraction of copper removed, as equation (2-6) by η_{Cu} experiment

$$\eta_{\text{Cu}} = 1 - \exp(-3.23x) \quad (2-6)$$

$$x = (\text{weight of NaSO}_{0.5})/(\text{weight of metal})$$

$$\eta_{\text{Cu}} = \frac{(\text{initial Cu concentration}) - (\text{final Cu concentration})}{(\text{initial Cu concentration})}$$

$$0.45 \text{ wt\%} \leq (\text{initial Cu concentration}) \leq 1.5 \text{ wt\%}$$

$$\text{Temperature} \leq 1540^\circ\text{C}$$

They claimed that very low Cu contents were achieved, say less than 0.002 wt%. According to equation (2-6), $\eta_{\text{Cu}} = 0.90$ corresponds to $x = 0.71$, for instance. In other words, 710 g of slag is required for 90% of copper removal from 1000 g of metal. They tried to apply their experimental results to the industrial process. They could not establish economic feasibility, although they tried some efforts to improve the efficiency of reaction by means below:

- i) Various kinds of sulphate mixture were used in order to optimise slag composition.
e.g. Na_2SO_4 , K_2SO_4 , CaSO_4 , MgSO_4
- ii) Slag was recycled.
- iii) Both lump and powdered slag were used in order to compare the efficiency of copper removal.

They concluded that :

- 1) Pure Na_2SO_4 slag had a better performance for copper removal than sulphate mixtures.
- 2) Recycled slag worked well, improving the efficiency of copper removal.
- 3) Lump slag had better performance than powdered slag, because powdered slag was partly blown off from the vessel.

They proposed that lance injection may have given a better performance than dumping.

Topkaya [18] studied copper removal from carbon saturated iron systematically using sodium sulphide as the reagent. He estimated the effect of the following parameters on copper removal;

i) temperature, ii) revolution rate of a mechanical stirrer, iii) interfacial area for reaction, iv) length of a contact line of graphite, gas and slag, v) gas flow rate of argon, vi) material of crucible, e.g. graphite, recrystallised alumina, vii) weight ratio of slag to metal, viii) reaction time, e.g. long duration ~ 48 hr, ix) vacuum, x) closed system.

The following conclusions were quoted:

- 1) $\text{NaS}_{0.5}$ was adequate slag for copper, manganese and sulphur removal from carbon saturated iron.
- 2) The mechanism of resulphurisation was clarified.
- 3) Distribution coefficients defined by weight % ratios were 24 and 175 for Cu and Mn respectively.
- 4) These values were somewhat higher than the values which were derived from the pilot plant. In smaller scale experiment, it was possible to control the experimental conditions more accurately, e.g. higher purity of slag.
- 5) For copper removal from steel, it was necessary to choose stable slag composition in the elevated temperature.
- 6) In the closed system, loss of Fe and resulphurisation were small. Closed system had a good performance for copper and sulphur removal.
- 7) The reaction rate was controlled by the chemical reaction at the gas/slag and metal/slag interface and by diffusion of Na vapour in the gas phase. (This is not borne out by later work). It is one of the most important characteristics of his experimental results that the reaction rate was very slow, e.g. significant copper removal was observed after one hour in the system which contained 20g metal and 3g slag at 1250°C . Normally observations lasted for 8 hours.

The effect of C on copper removal was studied by Safiah et al [21]. They pointed out that there had been many reports on copper removal from carbon saturated iron or high carbon iron by $\text{NaS}_{0.5}$ slag but less from low carbon iron. They did experiments on copper removal, using slag which weighed 10% of metal weight at 1550°C and changing C content, e.g. saturated, 2 wt% and 0.01 wt%. Initial Cu content was 1.5 wt%. Their conclusions were:

- 1) Cu was removed more easily in the high carbon iron than in low carbon iron. This was explained by dependency of activity coefficient f_{Cu} of Cu on C content. As f_{Cu} (high carbon) was larger than f_{Cu} (low carbon), final content of Cu in high-carbon iron could be less than that in low carbon iron.

Their experimental results were :

	initial Cu	after 20 minutes
carbon saturated	1.5 wt%	0.8 wt%
2 wt% C	1.5 wt%	1.2 wt%
0.01 wt% C	1.5 wt%	1.35 wt%

- 2) Although it had been said that it was possible to remove both Cu and S by sulphide slag, they found that this occurred only in cases where the initial S content was sufficiently high. In their experimental condition, i.e. low initial S content, S was transferred from the slag phase to the metal phase. The amount of S pick-up in the metal phase was dependent on C content. The lower C content, the greater amount of S pick-up.
- 3) Na vapour was produced. This vapour reacted with oxygen in air to produce white fume which was $\text{NaO}_{0.5}$. This fume was harmful to the refractory. From this point of view, it was worth studying other slags, e.g. CaS , CaSO_4 .

The study of tin removal from molten iron or steel by compounds has only started recently. There was a feasibility study [39] and tin removal from carbon saturated iron by $\text{NaS}_{0.5}$ slag which weighed 15% of metal weight at 1250°C . Cu was selectively removed without any significant tin removal, say 0 - 10% tin removal without reproducibility.

The evaporation method [25] - [28], [35], [38] as tin metal or SnS and the method of Ca (and/or CaF_2) addition [55], [56], [58] have been the only successful methods for tin removal so far.

Sehgal [38] evaluated the effects of tin on the rate of loss of sulphur and of sulphur upon that of tin in the case of steel at 1580°C under vacuum condition. He concluded that the rate of removal of tin from steel containing sulphur and under low-pressure conditions consists of two components : one represents the normal rate loss and the other the effects of sulphur thereupon. The latter component follows second-order kinetics and is proportional to the product of the concentrations of tin and sulphur in the melt. It is also concluded that the removal of tin from steel under vacuum (2-3 μm pressure; Hg pressure) is limited but, by the addition of sulphur, it can be removed to low levels.

The effect of a third element (C, Cr, Si) on the volatilisation of Cu and Sn was studied by Morales et al [25], using the levitation technique. They criticised copper and tin removal methods which used sulphide slag and/or S in the metal phase. They pointed out that i) it had a slow reaction rate, ii) the amount of slag required was too much to apply it to the industrial process. They claimed that volatilisation of Cu and Sn metal by vacuum was the best method for copper and tin removal.

Many of the statements made in the paper by Morales are not in fact valid. Later work [41] has shown that $\text{NaS}_{0.5}$ reacts rapidly in well stirred systems and that very large slag masses are not required.

Sehgal [38] showed conclusively that vacuum evaporation of tin as SnS is a much faster process than the vacuum volatilisation of Sn metal. Of course making use of the volatility of SnS involves the addition of sulphur to the melt.

The reaction rate for the evaporation method was studied by Harris et al [28]. It had been thought that it was difficult to apply this method to the industrial scale, because the ratio of surface area to the volume decreased with increasing scale of the system. They clarified the reasons why the reaction rate in a large system was slow. The reasons, other than the simple surface volume ratio, were i) formation of an evaporation-

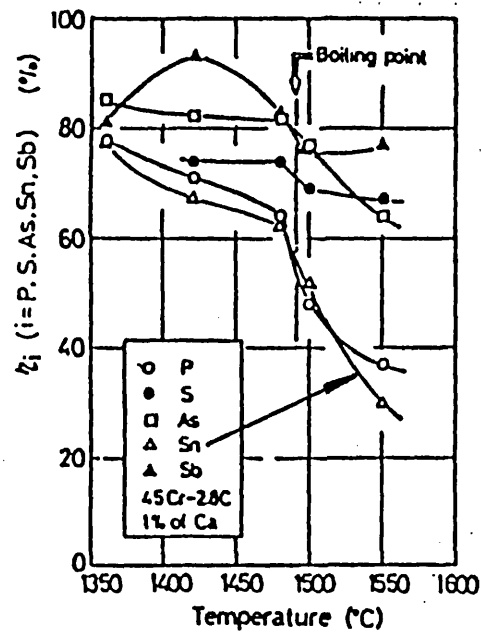
inhibiting film of oxide due to air leakage which is more probable in a larger system than a smaller one, ii) refluxing of Cu and Sn into the metal bath due to a greater distance to a condensation site for Cu and Sn vapour.

Later Harris et al obtained a U.S. patent [35] on increasing the kinetics in industrial scale operation. They proposed a combination of vacuum and gas bubbling. The gas bubbles, which rose into the vacuum vessel, cause violent dispersion of metal droplets. This increased the interfacial area for reaction and bulk gas flow diminished refluxing of copper and tin. They chose the pressure in the vacuum vessel 60-80% of the total vapour pressure of metals, which was the optimum pressure for maintaining the maximum transport of elements from the metal phase to the gas phase. Mn was also removed so that this process should be carried out before alloying.

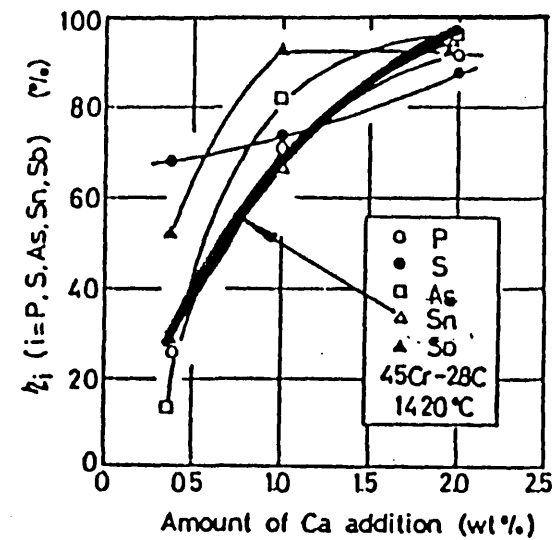
De-Sn using metallic Ca for $\text{CaSn}_{0.5}$ formation was studied by Janke [56], Kitamura et al [55] and Nakamura et al [58].

Kitamura et al [55] studied removal of impurities (P, S, As, Sn and Sb) from stainless steel. Their main interest was de-P from steel containing large amounts of Cr, say 10-48%. Under the oxidising conditions which is used in conventional oxidising refining processes, Cr is preferentially oxidised. They used metallic Ca for lower temperature melt (1350-1550°C) and CaC_2 - CaF_2 mixture for higher temperature melt ($\sim 1600^\circ\text{C}$) where they concentrated on studying de-P. As is shown in Fig. 2-10, metallic Ca for de-Sn is less effective in the higher temperature due to vaporising loss of Ca.

This method is very ineffective at higher temperature than 1500°C under the 1 atm atmospheric condition. Nakamura et al [58] estimated the ability of Ca- CaF_2 melt for removal of impurities (V-b in the periodic table, = N, P, As, Sb, Bi; VI - b = O, S, Se, Te; IV-b = Sn, Pb) from 18% Cr-8% Ni steel without substantial changes in the concentrations of metals (Cu, Zn, Al, Ni, Cr, Mn), C and Si. They pointed out that the vapour pressure of Ca in Ca- CaF_2 solution in which Ca metal is completely miscible with CaF_2 by decreasing Ca concentration at temperatures higher than the melting point of CaF_2 (1360°C) can be depressed by decreasing Ca concentration using ESR equipment. This is one way in which metallic Ca could be used under higher temperature conditions.



(a) Effect of bath temperature on the removal of Sn.



(b) Effect of Ca-amount added in melt on the removal of Sn.

Fig.2-10 De-Sn using metallic Ca(55).

Janke [56] obtained fairly good de-Sn using Ca and CaF_2 , $\eta_{\text{Sn}} \approx 90\%$ at 1550°C under the pressurised atmospheric conditions, 10 bar (argon), which helped high Ca content in the metal phase.

It is vital to keep a high activity of Ca to promote $\text{CaSn}_{0.5}$ formation. Ca solubility in steel is limited, especially at higher temperatures than boiling point (1497°C) under the 1 atm atmospheric condition e.g. Ca solubility is 0.032% at 1600°C [58]. Janke [56] showed the increase of Ca solubility in steel by introducing pressurised atmosphere and proved that Ca is a fairly good reagent for not only de-Sn but also de-P etc.

This pressurised atmospheric condition is hard to introduce in industrial larger scale operation.

There are many reports [19], [22], [23], [24], [31], [34], [36] on thermodynamic data related to the Fe-Cu-S-(Sn) system.

CHAPTER-3 MATHEMATICAL MODELLING

3-1 Introduction

In the present work, two mathematical models have been developed. One is the model which describes the unsteady state phenomena of reaction with metal/slag/gas phases. This is called the full model. The other is a simplified form of the full model which describes the steady state of the system. This is called the steady state model. The characteristics of these models are compared in Table 3-10.

The full model is related to the earlier model of Ohguchi et al [9]. The present model has been extended to include the following functions:-

- i) The effect of argon gas bubbling.
- ii) Various kinds of gas phase conditions.
i.e. inert, oxidising and reducing conditions.
- iii) A simplified mechanism of interaction between molten metal and the graphite crucible.

The rate phenomena are the most important aspects of the full model.

The rate of reaction is influenced by some of the following mechanisms:- i) bulk phase mixing ii) transport in the boundary layers iii) interfacial chemical reaction.

Bulk phase mixing occurs due to eddy diffusivity and bulk flow,

$$\frac{\partial C}{\partial t} + \underbrace{(\mathbf{v} \cdot \nabla)C}_{\text{convection}} = \underbrace{\nabla (D_e \nabla C)}_{\text{eddy diffusion}} + (\text{source or sink term})$$

where D_e is eddy diffusivity, which is not a molecular property but depends on the fluid dynamic characteristics of the system.

The relative importance between these terms is determined by the Peclet number, Pe , which is defined by:

$$\begin{aligned} Pe &= (\text{convection term})/(\text{eddy diffusion term}) \\ &= L \cdot V_0 / D_e \end{aligned}$$

Where L and V_0 are characteristic length and velocity respectively. When the Peclet number is large, eddy diffusion is negligible in comparison with the bulk flow.

Transport in or near the boundary layers is described by film theory, boundary layer theory, surface renewal theory or penetration theory.

The film theory is a statement of Fick's first law itself. Flux density, N , is proportional to gradient of concentration.

$$N = -D \cdot \frac{\partial C}{\partial x}$$

Concentration difference, $(C^b - C^i)/\delta$ is assumed to occur across thickness of a film δ . Then:

$$N = -D \cdot (C^b - C^i)/\delta$$

The mass transfer coefficient, k , can be expressed by:

$$k = D/\delta \quad [\text{m/s}]$$

D is the diffusivity, which is a molecular property. δ is a function of the velocity and properties of the fluid.

In the boundary layer theory, two-dimensional behaviour, e.g. velocity profile, can be dealt with.

In the penetration theory, it is assumed that an element of fluid appears at the surface and that the transferred species "penetrates" into the element during some particular time. The penetration occurs by unsteady state diffusion, governed by Fick's second law. The average flux density, N , during this period, t_r , is:

$$N = 2 \cdot \sqrt{D/\pi t_r} \cdot (C^i - C^b)$$

The mass transfer coefficient is therefore proportional to the square root of D .

$$K = 2 \cdot \sqrt{D/\pi t_r}$$

The surface renewal theory is based on the same idea as the penetration theory. In the surface renewal theory, however, t_r is not constant but has a distribution. The distribution of t_r is described by a function φ . In the case where p is the fraction of area renewed in a unit time period.

$$\varphi(t) = p e^{-pt}$$

Then average flux density N is:

$$N = \int_0^{\infty} N \cdot \varphi(t) \cdot dt$$

$$= \sqrt{D \cdot \rho} (C^i - C^b)$$

Mass transfer coefficient is:

$$k = \sqrt{D \cdot \rho}$$

In all these theories, the mass transfer coefficient is expressed in terms of a molecular property and fluid dynamic characteristics.

3-2 Description of mathematical models.

These models are based on the general governing equations, such as chemical equilibria, flux density continuity and mass balance. They can be applied to wide range of problems as far as the relevant thermo-dynamic data are available for any particular problem.

It does not matter that the mathematical model includes some phenomenological parameters. These parameters should ideally be determined by independent experiments.

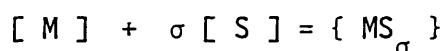
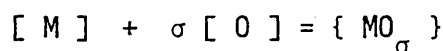
In the models in this work and in that of Ohguchi [10], the important parameters are mass transfer coefficients, i.e. k_m , G_{CO} etc. Once they are determined, it is possible to apply them in the model to predict performance under roughly similar physical conditions.

3-2-1 Full model

The characteristics of this model are briefly mentioned below:

- 1) Three phases are involved, i.e. metal, slag, gas.
- 2) The governing equations are those for the chemical equilibria both at the metal/slag interface and at the slag/gas interface; balance of flux density for each element at the interfaces and balance of mass in the three bulk phases.

- 3) Any number of elements can be involved so long as thermodynamic data for the elements are available. The reactions considered are shown below: Vaporization of all species



{ } is slag not gas

[] is element dissolved in molten iron

is considered. CO formation at the metal/slag interface, SO₂ formation CO oxidation, and CO₂ formation at the slag/gas interface and Na vaporization at the metal/slag interface are included.

- 4) It is possible to use the thermal balances in order to calculate temperature changes. In the present work, the temperature is kept at a constant value.
- 5) It is possible to include the effect of composition of the metal phase on activity coefficients of metallic elements through interaction parameters $e_i^{(j)}$.
- 6) The time step, Δt , for unsteady state calculation can be set to the maximum value which guarantees stability of calculation in each step of calculation. i.e. the criterion for the stable calculation is $\Delta x/x \ll 1$. Here x is the current mole fraction of a particular element and Δx is its change during the time step Δt . $\Delta x/x$ can be written in the equation (3-1) with a flux density N [mol/m²s], an interfacial area S [m²], the volume of the bulk phase V [m³] and molar concentration in the bulk phase C [mol/m³].

$$\begin{aligned}
 & V.C. \Delta x / \Delta t = -S.N \\
 & \left(\begin{array}{c} \text{total change of} \\ \text{moles in the bulk} \\ \text{phase per unit} \\ \text{time} \end{array} \right) = \left(\begin{array}{c} \text{flux coming into} \\ \text{the bulk phase} \\ \text{through} \\ \text{interface} \end{array} \right) \\
 & \therefore \frac{\Delta x}{x} = - \frac{S.N}{V.x.C} \Delta t \quad (3-1)
 \end{aligned}$$

Substituting this $\Delta x/x$ into the stability condition $\Delta x/x \ll 1$, one can obtain the restriction for Δt .

$$\Delta t \ll \frac{V \cdot x \cdot C}{S \cdot N}$$

- 7) Non-linear simultaneous equations are solved by the algorithm of Powell's non-linear equation method.
- 8) At the slag/gas interface, this model includes the following phenomena.

Reducing gas phase.

Oxides in the slag phase are reduced by the reducing gas, e.g. CO gas, to produce pure metal which is assumed to be transported to the bulk metal phase without further reaction. CO gas is oxidised to CO₂ gas and CO₂ gas leaves the slag/gas interface. Oxygen transport from the slag phase effectively occurs as shown in Fig. 3-1 (a)

Oxidising gas phase

FeO is oxidised by the oxidising gas, e.g. O₂ gas, to produce FeO_{1.5}. Oxygen transport from the gas phase to the slag phase occurs as shown in Fig. 3-1(b).

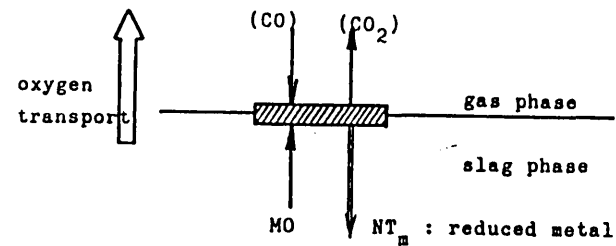
Volatilisation of oxides and sulphide

In the case of de-P and de-S of molten iron, the vapour pressures of any species are negligible. In the case of copper and tin removal, NaS_{0.5} and SnS vaporise substantially at the elevated temperature.

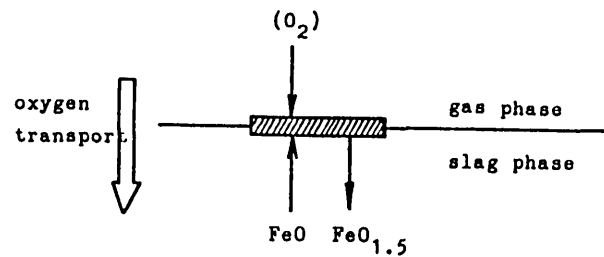
(1) Assumptions

The following assumptions are made for this model:

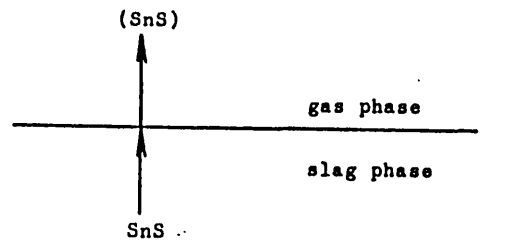
- i) The rate controlling step is mass transfer in the boundary layers on both sides of the interfaces.
- ii) The bulk phases are well mixed and have no concentration gradients within them.
- iii) Chemical equilibria are established at the interfaces.



(a) Reducing gas phase.

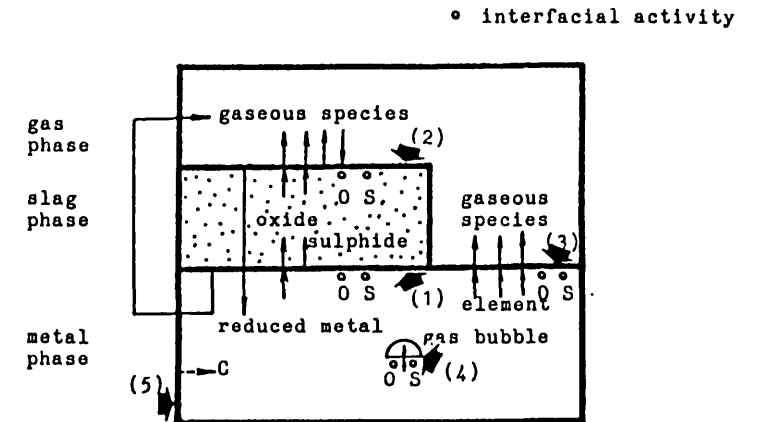


(b) Oxidising gas phase.



(c) Inert gas phase.

Fig.3-1 The phenomena occurred at the slag/gas interface.



- (1) At the metal/slag interface.
oxide and sulphide formation
 $M + \sigma O = MO_{\sigma}$
 $M + \sigma S = MS_{\sigma}$
gaseous species formation
 $C + O = (CO)$
 $Sn + S = (SnS)$
 $Na = (Na)$
- (2) At the slag/gas interface.
oxide and sulphide formation
 $M + \sigma O = MO_{\sigma}$
 $M + \sigma S = MS_{\sigma}$
 $S + 2 O = (SO_2)$
 $(CO) + O = (CO_2)$
vaporization
 $MO_{\sigma} = (MO_{\sigma})$
 $MS_{\sigma} = (MS_{\sigma})$
 $M = (M)$
 $O = (O_2)$
 $S = (S_2)$
- (3) At the metal/gas interface.
gaseous species formation
 $C + O = (CO)$
 $Sn + S = (SnS)$
vaporization
 $M = (M)$
 $O = (O_2)$
 $S = (S_2)$
- (4) At the metal/gas bubble interface.
 $Sn + S = (SnS)$
 $Sn = (Sn)$
 $C + O = (CO)$
- (5) At the metal/crucible interface (graphite crucible).
 $C = C : dissolved$

Fig.3-2 Metal/slag/gas reaction model (full model)
in the present work.

- iv) A mechanism of CO transportation is based on the model proposed by Ohguchi et al [9]. They used a phenomenological parameter G_{CO} [$\text{mol}/\text{m}^2\text{S}$]. Flux density of CO gas, N_{CO} , is expressed by the formula (3-2)

$$N_{CO} = G_{CO} (p_{CO} / p_T - 1) \quad (3-2)$$

Where p_T denotes the total pressure in the gas phase.

- v) Na vapour is allowed to vaporise both at the metal/slag interface and at the slag/gas interface. (Na) vaporised at the slag/gas interface obeys the same mechanism of transport as that of other species (Na) vaporised at the metal/slag interface is carried away by the argon gas flow which is used for bath stirring. Argon at a volumetric flow rate, $\dot{q}$, contains Na vapour at a partial pressure, p_{Na} [atm], at the metal/slag interface. Flux density of Na vapour, $N_{(Na)}$ is expressed in the formula (3-3).

$$N_{(Na)} = p_{Na} \cdot \dot{q} / R.T.S \quad [\text{mol}/\text{m}^2\text{S}] \quad \text{where } R \text{ is gas constant,} \\ (3-3) \quad T \text{ is temperature of injected} \\ \text{gas in the metal bath.}$$

- vi) All reactions are coupled through oxygen and sulphur potentials at the interfaces. These two potentials can be changed.
e.g. chlorine is chosen in the case of chloride formation.
- vii) No accumulation of mass at the interfaces.
- viii) The composition of the gas bulk phase is constant, except for rising gas bubbles.

(2) Governing equations and initial conditions

The following describes the system in which oxides and sulphides are the constituents of the slag phase. The main variables are activities of all species. It is necessary to define the relation between activities and mole fractions in order to formulate mass conservation equations for each phase and flux density continuity at each interface. Arrays are a very useful form for variables, because it is possible to formulate a general form of equation for each species. As is explained in detail in Appendix -3, activity, $a(i, j, k)$, denotes the activity of the species- i .

e.g. $i = 1$ (O), $i = 2$ (S), $i = 3$ & 4 (C), $i = 5$ & 6 (Fe),
 $i = 7$ (Cu), $i = 8$ (Na), $i = 9$ (Sn), $i = 10$ (Ca),
 $i = 11$ (Mn), $i = 12$ (Si), $i = 13$ (P), $i = 14$ (Mg),
 $i = 15$ (Al), $i = 16$ (Cr) etc. $i + 20$ for oxide and
 $i + 40$ for sulphide at the site facing to the phase-k

e.g. $j = 1$ (metal phase), $j = 2$ (slag phase), $j = 3$ (gas phase)
 in the phase - j

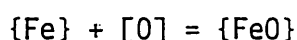
e.g. $k = 1$ (site facing to the metal phase), $k = 2$ (site facing to
 the slag phase), $k = 3$ (site facing to the gas phase)

i.e. $a(5, 1, 2)$ denotes the activity of iron ($i=5$) at the site
 facing to the slag phase ($k = 2$) in the metal phase ($j = 1$).

On the other hand, $a(5, 1, 1)$ is iron activity in the metal bulk
 phase.

Equilibrium constants for chemical reactions are also defined in
 similar form, $E(i, j, k)$.

i.e. For the reaction



at the metal/slag interface, the equilibrium constant for
 this is defined by $E(5 + 20, 1, 2)$. $E(5 + 20, 1, 2) =$
 $a(5 + 20, 2, 1)/a(5, 1, 2) \cdot a(1, 1, 2)$. This is same
 as the common expression:

$$K_{\text{Fe}} = a_{\{\text{FeO}\}} / a_{\{\text{Fe}\}} a_{[\text{O}]}$$

Using the general form of variables briefly explained above, one
 can obtain the generalised formulations of the governing equations.
 The following elements, however, are considered as special elements:

O, S : These two elements are directly coupled with
 all other elements.

C : C forms gaseous oxides, CO and CO₂.

[C] + [O] react on the metal/slag interface to form CO

Fe : Fe is allowed to form two oxides, FeO and FeO_{1.5}.

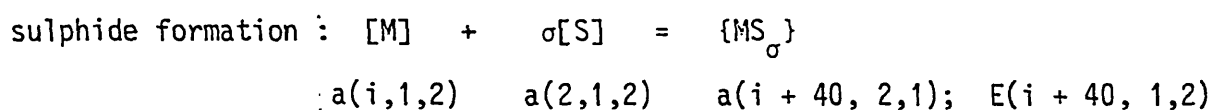
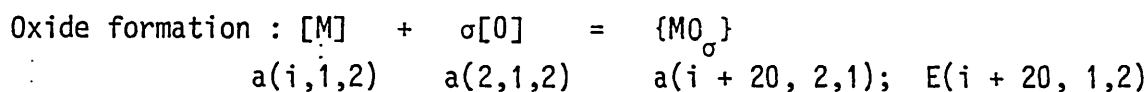
Na, Sn : Na vapour and SnS vapour at the metal/slag interface are carried away by argon gas flow. (see Fig. 3-2).

Sn : SnS vapour at the metal/slag interface is carried away by argon gas flow.

Oxides and sulphides have the form, MX_σ, where X denotes O or S. This form is advantageous mainly because i) activity coefficients for these compounds in any binary system are composition-independent if Tenkin's ideal solution is assumed. ii) reactant [M] and product {MX_σ} have a linear relation with all nonlinearity contained in the equation for O or S.

Equations for chemical equilibria at the interfaces are:

1) The metal/slag interface (see Fig. 3-3 (a)).



These two types of reactions are expressed in one generalised equation (3-4).

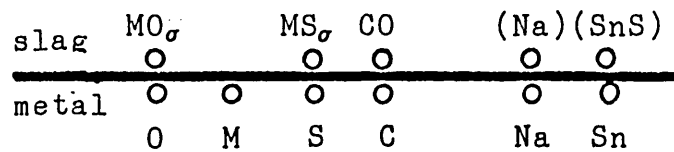
$$E(i+20i_o, 1,2) = a(i+20i_o, 2,1)/a(i,1,2) \quad a(i_o,1,2)^{\sigma(i_o i)} \\ \text{where } i \geq 3 \quad (3-4)$$

$$i_o = \begin{cases} 1 & \text{for oxide} \\ 2 & \text{for sulphide} \end{cases}$$

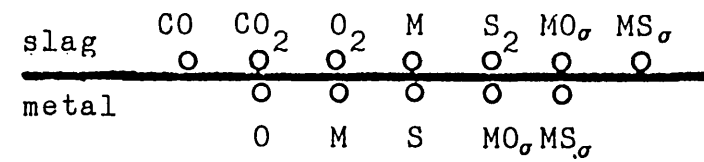
The CO reaction is included in the equation (3-4). (a(23,2,1) is a gaseous species CO and has a unit of partial pressure [atm].

Na vapour pressure at this interface, a(8,2,1), is calculated from the equilibrium [Na] = (Na).

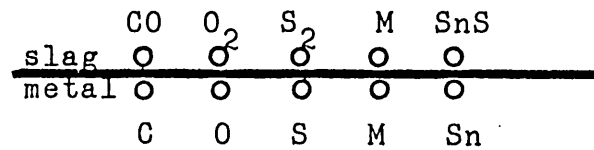
$$a(8,2,1) = E(8,3,2) \quad a(8,1,2) \quad (3-5)$$



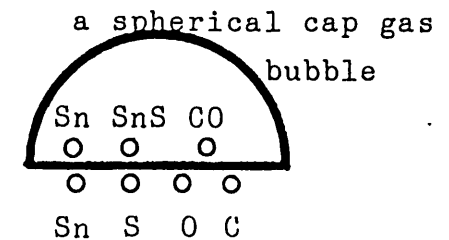
(a) Metal/slag interface.



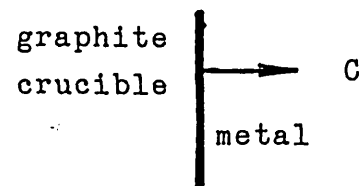
(b) Slag/gas interface.



(c) Metal/gas interface.



(d) Metal/gas bubble interface.



(e) Metal/crucible interface (in the case of the graphite crucible).

Fig.3-3 Chemical equilibria at the interfaces.

2) The slag/gas interface (see Fig. 3-1(b)).

It is possible to define activities of all species at this interface, metal, oxide and sulphide, although the metal itself is assumed not to dissolve in the slag bulk phase.

Oxide formation : $[M] + \sigma[O] = \{MO_{\sigma}\}$

$$a(i,2,3) \quad a(1,2,3) \quad a(i+20,2,3); \quad E(i+20,2,3)$$

sulphide formation : $[M] + \sigma[S] = \{MS_{\sigma}\}$

$$a(i,2,3) \quad a(2,2,3) \quad a(i+40,2,3); \quad E(i+40,2,3)$$

These two types of reactions are expressed in the generalised equation (3-6).

$$E(i+20i_o,2,3) = a(i+20i_o,2,3)/a(i,2,3) \cdot a(i_o,2,3)^{\sigma(i_o,i)}$$

$$\text{where } i \geq 5 \quad (3-6)$$

$$i_o = \begin{cases} 1 & \text{for oxide} \\ 2 & \text{for sulphide} \end{cases}$$

vaporization : $[M] = (M)$

$$a(i,2,3) \quad a(i,3,2); \quad E(i,3,2)$$

$$\{MO_{\sigma}\} = (MO_{\sigma})$$

$$a(i+20,2,3) \quad a(i+20,3,2); \quad E(i+20,3,2)$$

$$\{MS_{\sigma}\} = (MS_{\sigma})$$

$$a(i+40,2,3) \quad a(i+40,3,2); \quad E(i+40,3,2)$$

These three types of vaporization all have equilibrium constants of the form given by equation (3-7).

$$E(i+20i_o,3,2) = a(i+20i_o,3,2)/a(i+20i_o,2,3)$$

$$\text{Where } i \geq 5 \quad (3-7)$$

$$i_o = \begin{cases} 0 & \text{for metal} \\ 1 & \text{for oxide} \\ 2 & \text{for sulphide} \end{cases}$$

Elements of $i \leq 4$ are dealt with specially.

For $i = 1$ (oxygen), $[O] = \frac{1}{2} (O_2)$
 $a(1,2,3) \quad a(1,3,2); \quad E(1,3,2)$

For $i = 2$ (sulphur), $[S] = \frac{1}{2} (S_2)$
 $a(2,2,3) \quad a(2,3,2); \quad E(2,3,2)$

These two species are diatomic gases and obey Sieverts' law.

$$E(i,3,2) = a(i,3,2)^{\frac{1}{2}} / a(i,2,3) \quad (3-8)$$

Where $i = \begin{cases} 1 & \text{for oxygen} \\ 2 & \text{for sulphur} \end{cases}$

For $i=3=4$ (carbon), $[O] + (CO) = (CO_2)$
 $a(1,2,3) \quad a(23,3,2) \quad a(24,3,2); \quad E(24,2,3)$
 $[C] + [O] = (CO); \quad E(23,2,3)$

$$E(24,2,3) = a(24,3,2) / a(23,3,2) \cdot a(1,2,3)$$

$$E(23,2,3) = a(23,3,2) / a(3,2,3) \cdot a(1,2,3) \quad (3-9)$$

For $i=22$ (SO_2), $[S] + 2[O] = (SO_2)$
 $E(22,2,3) = a(22,3,2) / a(2,2,3) \cdot a(1,2,3)^2 \quad (3-10)$

3) The metal/gas interface.

If there is a metal/gas contacting interface, it is necessary to consider the formation of gaseous species at this interface, i.e. CO , SnS etc.

For O ($i=1$) and S ($i=2$),
 $E(i,3,1) = a(i,3,1)^2 / a(i,1,3) \quad (3-11)$

$$[O] = \frac{1}{2} (O_2) ; \quad E(1,3,1)$$

$$[S] = \frac{1}{2} (S_2) ; \quad E(2,3,1)$$

For C ($i=3$),
 $E(23,1,3) = a(23,3,1) / a(3,1,3) \cdot a(1,1,3) \quad (3-12)$

$$[C] + [O] = (CO) ; \quad E(23,1,3)$$

For M ($i \geq 5$),
 $E(i,3,1) = a(i,3,1) / a(i,1,3) \quad (3-13)$

$$[M] = (M) ; \quad E(i,3,1)$$

For (SnS) ($i=49$) formation,
 $E(49,1,3) = a(49,3,1) / a(9,1,3) \cdot a(2,1,3) \quad (3-14)$

$$[Sn] + [S] = (SnS) ; \quad E(49,1,3)$$

4) The metal/gas bubble interface.

Sn vaporization, SnS formation (gaseous species) and CO formation are considered. Other reactions are neglected at the metal/gas bubble interface.

For Sn ($i=9$) vaporization,

$$E(9,3,1) = a(9,3,1)/a(9,1,3) \quad (3-15)$$

$$[Sn] = (Sn) \quad ; \quad E(9,3,1)$$

For SnS ($i=49$) formation (gaseous species)

$$E(49,1,3) = a(49,3,1)/a(9,1,3).a(2,1,3) \quad (3-16)$$

$$[Sn] + [S] = (SnS) \quad ; \quad E(49,1,3)$$

For CO ($i = 23$) formation,

$$E(23,1,3) = a(23,3,1)/a(3,1,3).a(1,1,3) \quad (3-17)$$

$$[C] + [O] = (CO) \quad ; \quad E(23,1,3)$$

As no mass is allowed to accumulate at the interfaces, the flux density of each species for both sides of the interface are balanced. The flux density is proportional to the driving force which is the mole fraction difference between interface and bulk

1) The metal/slag interface.

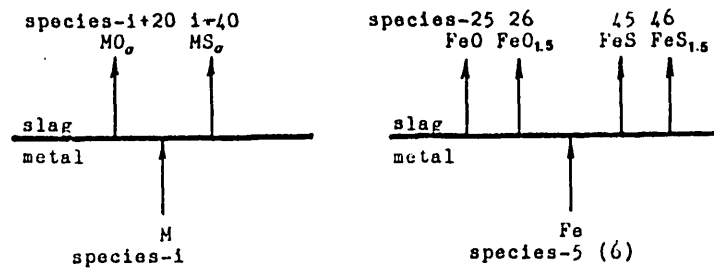
For the metallic species- i ($i \geq 7, i=8$), as is shown in Fig. 3-4(a), the flux density of species- i in the metal phase $N(i,1,2)$, balances the sum of the flux density of oxide MO_{σ} and sulphide MS_{σ} ,

$$N(i+20i_o, 2,1). N(i,1,2) = \sum_{i_o=1}^2 N(i + 20i_o, 2,1) \quad i \geq 7 (i \neq 8,9) \quad (3-18)$$

Where $N(i,1,2) = k(i,1).C(1). \{a(i,1,1) - a(i,1,2)\}/\gamma(i,1)$ and
 $N(i + 20i_o, 2,1) = k(i + 20i_o, 2) C(2) \{a(i + 20i_o, 2,1) - a(i + 20i_o, 2,2)\}/\gamma(i + 20i_o, 2)$
 $i_o = \begin{cases} 1 & \text{for oxide} \\ 2 & \text{for sulphide} \end{cases}$

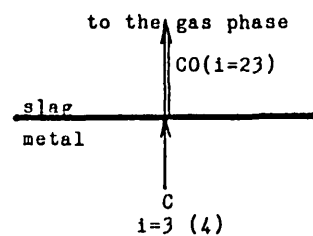
For Fe ($i = 5,6$), as is shown in Fig. 3-4(b), it is necessary to consider four species in the slag phase, FeO ($i=5+20$), FeO_{1.5} ($i=6+20$), FeS ($i=5+40$) and FeS_{1.5} ($i=6+40$)

$$N(5,1,2) = \sum_{i_o=1}^2 \sum_{i=5}^6 N(i+20i_o, 2,1) \quad (3-19)$$

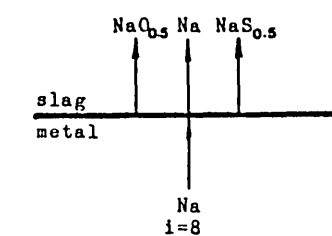


(a) Flux density of M.

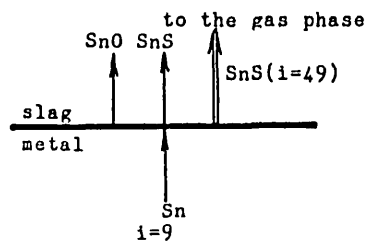
(b) Flux density of Fe.



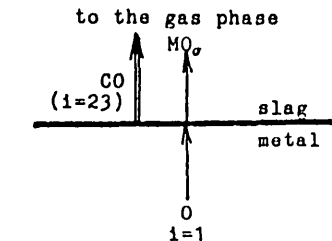
(c) Flux density of C.



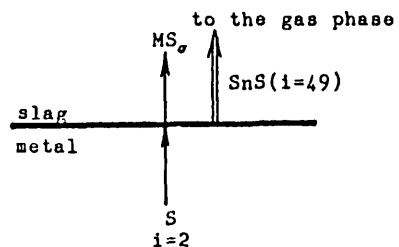
(d) Flux density of Na.



(e) Flux density of Sn.

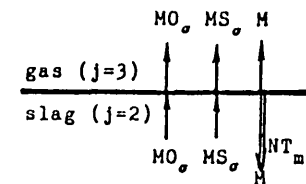


(f) Flux density of O.

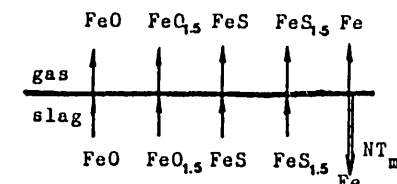


(g) Flux density of S.

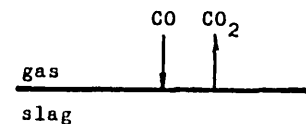
Fig.3-4 Continuity of the flux density at the metal/slag interface.



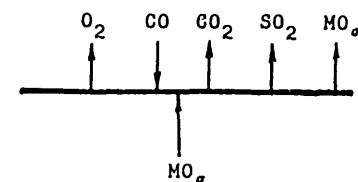
(a) Flux density of M.



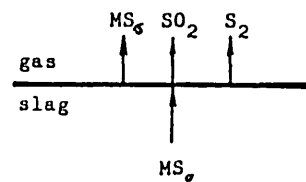
(b) Flux density of Fe.



(c) Flux density of C.



(d) Flux density of O.



(e) Flux density of S.

Fig.3-5 Continuity of the flux density at the slag/gas interface.

For C ($i=3,4$), as shown in Fig. 3-4(c), a phenomenological parameter G_{CO} is used for CO transport. In the case where the pressure of CO is less than a threshold value, which is chosen as equal to p_T , CO transport does not occur.

$$N(3,1,2) = N_{CO} \quad (3-20)$$

$$\text{where } N_{CO} = \begin{cases} G_{CO} \{a(23,2,1)/p_T - 1\}, & \text{if } a(23,2,1) > p_T \\ 0, & \text{if } a(23,2,1) \leq p_T \end{cases}$$

For Na ($i=8$) and SnS ($i=49$) as is shown in Fig. 3-4 (d), (e), Na vapour and SnS vapour carried away by argon gas flow must be included.

$$N(8,1,2) = \sum_{i_o=1}^2 N(8+20i_o, 2,1) + N_{Na} \quad (3-21)$$

$$N_{Na} = a(8,2,1) \cdot \dot{q} / R \cdot T_{gas} \cdot S$$

$$N(9,1,2) = \sum_{i_o=1}^2 N(8+20i_o, 2,1) + N_{SnS} \quad (3-22)$$

$$\text{where } N_{SnS} = E(49,1,2) \cdot E(49,3,2) \cdot a(9,1,2) \cdot a(2,1,2) \cdot \dot{q} / R \cdot T_{gas} \cdot S$$

For O ($i=1$), as is shown in Fig. 3-4 (f), oxygen is carried by oxides.

$$N(1,1,2) = \sum_{i=5}^{i_{max}} \{\sigma(1,i) \cdot N(i+20,2,1)\} + N_{CO} \quad (3-23)$$

For S ($i=2$), as is shown in Fig. 3-4 (g), sulphur is carried by sulphides.

$$N(2,1,2) = \sum_{i=1}^{i_{max}} \{\sigma(2,i) \cdot N(i+40,2,1)\} + N_{SnS} \quad (3-24)$$

2) The slag/gas interface (see Fig. 3-5).

For the element $M(i \geq 7)$, the flux densities of oxide and sulphide in the slag phase, the flux densities of oxide vapour and sulphide vapour and the flux densities of metal vapour and metal liquid drops are balanced.

$$\sum_{i_o=1}^2 N(i+20i_o, 2,3) = \sum_{i_o=0}^2 N(i+20i_o, 3,2) + NT_m \cdot a(i,2,3) / \gamma(i,2,3)$$

$$\text{where} \quad (i \geq 7) \quad (3-25)$$

$$N(i+20i_o, 2, 3) = C(2) \cdot k(i+20i_o, 2) \{a(i+20i_o, 2, 2) - a(i+20i_o, 2, 3)\} / \gamma(i+20i_o, 2)$$

$$i_o = \begin{cases} 1 & \text{for oxide} \\ 2 & \text{for sulphide} \end{cases}$$

$$N(i+20i_o, 3, 2) = C(3) p_T^{-1} \cdot k(i+20i_o, 3)$$

$$\times \{a(i+20i_o, 3, 2) - a(i+20i_o, 3, 3)\}$$

$$i_o = \begin{cases} 0 & \text{for metal} \\ 1 & \text{for oxide} \\ 2 & \text{for sulphide} \end{cases}$$

For Fe ($i=5,6$), all four compounds should be included.

$$\sum_{i_o=1}^2 \sum_{i=5}^6 N(i+20i_o, 2, 3) = \sum_{i_o=0}^2 \sum_{i=5}^6 N(i+20i_o, 3, 2)$$

$$+ NT_m \cdot a(5, 2, 3) / \gamma(5, 2) \quad (3-26)$$

For C ($i=3,4$), there is no transport in the slag phase and the flux densities of CO and CO₂ are balanced.

$$N(23, 3, 2) + N(24, 3, 2) = 0 \quad (3-27)$$

For O ($i=1$), in the slag phase oxygen can be transported only by oxides, MO_o, and in the gas phase oxygen can be transported by oxides and oxygen gas.

$$\sum_{i=5}^{i_{\max}} \{\sigma(1, i) N(i+20, 2, 3)\} = \sum_{i=5}^{i_{\max}} \{\sigma(1, i) N(i+20, 3, 2)\} + 2N(1, 3, 2) + 2 \cdot N(22, 3, 2) + N(23, 3, 2) + 2 \cdot N(24, 3, 2) \quad (3-28)$$

For S ($i=2$), in the slag phase sulphur can be transported only by sulphides, MS_{σ} , and in the gas phase sulphur can be transported by sulphides, SO_2 and S_2 gas.

$$\begin{aligned}
 & \sum_{i=5}^{i_{\max}} \{\sigma(2,i) \cdot N(i+40,2,3)\} \\
 & = \sum_{i=5}^{i_{\max}} \{\sigma(2,i) \cdot N(i+40,3,2)\} \\
 & + 2N(2,3,2) + N(22,3,2) \\
 & + NT_m \cdot a(2,2,3) / \gamma(2,2)
 \end{aligned} \tag{3-29}$$

3) The metal/gas interface (see Fig. 3-6).

For the element M, the flux densities of vapour and dissolved element are balanced.

$$N(i,1,3) = N(i,3,1) \quad i \geq 5, (i=9) \tag{3-30}$$

M vapour

For C ($i=3$),

$$N(3,1,3) = N(23,3,1) \tag{3-31}$$

CO gas

For Sn ($i=9$)

$$N(9,1,3) = N(9,3,1) + N(49,3,1) \tag{3-32}$$

metallic sulphide

For O ($i=1$),

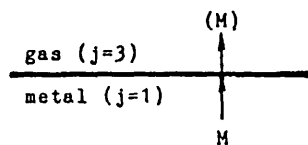
$$N(1,1,3) = 2N(1,3,1) + N(23,3,1) \tag{3-33}$$

O_2 gas CO gas

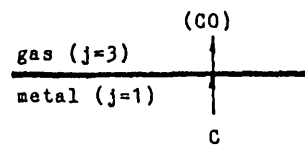
For S ($i=2$),

$$N(2,1,3) = 2N(2,3,1) + N(49,3,1) \tag{3-34}$$

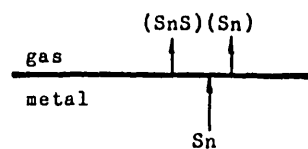
S_2 gas SnS gas



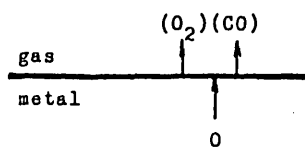
(a) Flux density of M.



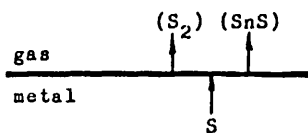
(b) Flux density of C.



(c) Flux density of Sn.

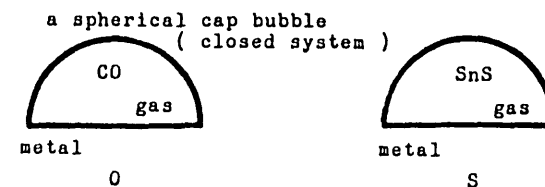


(d) Flux density of O.



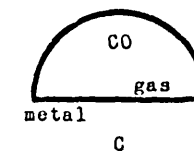
(e) Flux density of S.

Fig.3-6 Continuity of the flux density at the metal/gas interface.

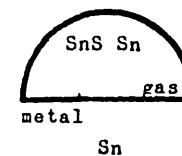


(a) Flux density of O.

(b) Flux density of S.



(c) Flux density of C.



(d) Flux density of Sn.

Fig.3-7. Continuity of the flux density at the metal/gas bubble interface.

4) The metal/gas bubble interface (see Fig. 3-7).

Rising time of a gas bubble is usually much less than the characteristic time of the reaction, t_{ref} .

Changes of gas bubbles during their rising period should be solved at each time step which is used for computing the evolution of the whole system. The main characteristics of this problem are the fact that the gas phase, i.e. bubble, is a closed system. It is necessary to solve the volume change, pressure change and composition change of gas bubbles. For simplicity, the reactions considered are CO formation, SnS formation (gaseous species) and Sn vaporization.

Flux density conservation equation for 0 ($i=1$) is

$$N(1,1,3) = N(23,3,1) \quad (3-35)$$

CO gas

For S ($i=2$),

$$N(2,1,3) = N(49,3,1) \quad (3-36)$$

SnS gas

For C ($i=3$)

$$N(3,1,3) = N(23,3,1) \quad (3-37)$$

CO gas

For Sn ($i=9$),

$$N(9,1,3) = N(9,3,1) + N(49,3,1) \quad (3-38)$$

Sn vapour SnS gas

It is required to derive mass conservation of each phase in order to describe evolution of all variables.

1) The metal phase.

The change of mass of each species in the metal phase during a time interval, Δt , is proportional to (flux density) (interfacial area) $\times$ (interval). This flux density should include reduced metal droplets created at the slag/gas interface in the case of reducing gas phase.

$$\Delta\{V(1).C(1).a(i,1,1)\}/\gamma(i,1).\Delta t$$

$$= -S(1,2).N(i,1,2) - S(1,3).N(i,1,3) + S(2,3).NT_m.a(i,2,3)/\gamma(i,2)$$

(3-39)

The total mass of the metal phase changes by $\Delta\text{Mass} (1)$ during time interval, Δt due to the change of mass of each species.

$$\begin{aligned} \Delta\text{Mass} (1) = & -S(1,2) \cdot \Delta t \cdot \sum_{i=1}^{i_{\max}} \{M(i) \cdot N(i, 1, 2)\} \\ & -S(1,3) \cdot \Delta t \cdot \sum_{i=1}^{i_{\max}} \{M(i) \cdot N(i, 1, 3)\} \\ & + S(2,3) \cdot \Delta t \cdot NT_m \sum_{i=2}^{i_{\max}} [M(i) \cdot a(i, 2, 3) / \gamma(i, 2)] \end{aligned} \quad (3-40)$$

It is allowed to supply carbon to the metal phase to compensate for carbon loss due to CO formation, if specified. The total amount of carbon supplied is counted. In this case, $\Delta\text{Mass} (1)$ is modified to :

$$\begin{aligned} \Delta\text{Mass} (1) = & \Delta\text{Mass} (1) \\ & + S(1,2) \cdot \Delta t \cdot M(3) \cdot N(3, 1, 2) \end{aligned}$$

The C content is kept constant with time. e.g. C content is kept at the saturated value at a particular temperature.

2) The gas phase

In the open system, the composition of the gas bulk phase is assumed to be constant.

The total mass of the gas phase changes by $\Delta\text{Mass} (3)$ during a time interval Δt due to all fluxes to and from the gas phase.

$$\begin{aligned} \Delta\text{Mass}(3) = & S(2,3) \cdot \Delta t \sum_{i_0=0}^2 \sum_{i=5}^{i_{\max}} \{M(i + 20i_0) N(i + 20i_0, 3, 2)\} \\ & + 2M(1) \cdot N(1, 3, 2) + 2M(2) \cdot N(2, 3, 2) \\ & + M(22) \cdot N(22, 3, 2) + M(23) \cdot N(23, 3, 2) \\ & + M(24) \cdot N(24, 3, 2) \\ & + S(1,2) \cdot \Delta t \cdot \sum_{i=1}^{i_{\max}} [M(23) \cdot N_{\text{CO}} + M(8) \cdot N_{\text{Na}}] \\ & + S(1,3) \cdot \Delta t \cdot \sum_{i=1}^{i_{\max}} \{M(i) \cdot N(i, 1, 3)\} \end{aligned} \quad (3-41)$$

Where $M(i)$ is a molecular weight [kg/mol] of the species - i

3) The slag phase.

The change of mass of each species in the slag phase during a time interval, Δt , is caused by the flux to and from the interfaces and powder supplied.

$$\begin{aligned} & \Delta \{ V(2) \cdot C(2) \cdot a(i + 20i_o, 2, 2) \} / \gamma(i + 20i_o, 2) / \Delta t \\ & = S(2, 1) \cdot N(i + 20i_o, 2, 1) - S(2, 3) \cdot N(i + 20i_o, 2, 3) \\ & + \dot{Q} \cdot x_{POW}(i + 20i_o) \end{aligned} \quad (3-42)$$

Here $\dot{Q} \cdot x_{POW}(i + 20i_o)$ denotes the rate of powder supplying of a particular species - $i + 20i_o$, [mol/s].

The total mass of the slag phase changes by $\Delta \text{Mass}(2)$ during a time interval, Δt . $\Delta \text{Mass}(2)$ should be balanced with the changes of mass of other phases and the amount of powder supplied during a time interval.

$$\begin{aligned} \Delta \text{Mass}(2) &= \{ \Delta \text{Mass}(1) + \Delta \text{Mass}(2) \} \\ &+ \dot{M}_{POW} \cdot \Delta t \end{aligned} \quad (3-43)$$

Here $\dot{M}_{POW}$ denotes a rate of mass supplied to the slag phase. All equations are coupled to form a set of simultaneous equations.

Activities of all species are the main variables. It is possible to reduce the number of variables in the simultaneous equations after some derivations explained in Appendix-3. These key variables are $a(1,1,2)$ and $a(2,1,2)$ at the metal/slag interface and $a(1,2,3)$, $a(2,2,3)$ and NT_m at the slag/gas interface.

Procedure and programme for computing are explained in Appendix-4.

3-2-2 Steady state model

The steady state model is a simplified version of the full model. The following modifications of the latter lead to the steady state model.

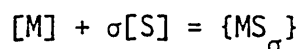
- i) All time derivatives of equations in the full model are put to zero.
- ii) The steady state model is not general model. It is applied only for de-Cu/de-Sn from carbon saturated iron/steel using a sulphide and/or oxide slag.
- iii) It includes three phases. i.e. metal, slag and gas.
The gas phase is simply involved in the reaction through Na vaporization, SnS vaporization and CO formation. CO formation is only considered in cases where oxidic slag is used.
Na and SnS vapour are transported by argon gas flow.

Strictly speaking, there is no steady state in the system, especially in the case where argon gas flow is introduced. In this steady state model, the total amount of argon gas blown is used to calculate the final state of the system in one step.

The following paragraphs deal with theoretical background of de-Cu/de-Sn and a description of the steady state model.

The conditions, which influence copper and tin removal from molten iron or steel are briefly stated as follows:-

A metallic component M in the metal phase is assumed to equilibrate with S and sulphide MS_{σ} in the slag phase.



where σ denotes stoichiometric constant (3-45)

The chemical equilibrium is described by an equilibrium constant K_M and activities a in equation (3-46)

$$K_M = a_{\{MS_{\sigma}\}} / a_{[M]} a_{[S]}^{\sigma} \quad (3-46)$$

K_M is dependent both on temperature and on the standard states which are chosen for activities.

In this work, the standard states selected are as follows:

- (1) Sulphides and oxides - pure stable substance in the liquid state, i.e. in the slag phase, pure MS_{σ} ($x_{\{MS_{\sigma}\}} = 1.0$) has activity $a_{\{MS\}} = 1$ (Raoultian standard).
- (2) Elements in the metal phase - infinite dilution, i.e. the activity coefficient f becomes unity when the solute is infinitely diluted (Henrian standard).
- (3) The solvent Fe. For Fe (Raoultian standard).

Using these definitions for the activities, the relation between an activity a and a mole fraction x is expressed in equations (3-47) and (3-48) with activity coefficients γ and f for Raoultian and Henrian standard states respectively.

$$a_{\{MS\}} = \gamma_{\{MS_{\sigma}\}} x_{\{MS_{\sigma}\}} \quad (3-47)$$

$$a_{[M]} = f_{[M]} \cdot x_{[M]} \quad (3-48)$$

Substituting these expressions for $a_{\{MS\}}$ and $a_{[M]}$ into equation (3-46), the distribution coefficient for the σ element M between the slag phase and the metal phase, defined in mole fractions, gives equation (3-49).

$$x_{MS_{\sigma}} / x_M = K_M f_M f_S^{\sigma} x_S^{\sigma} / \gamma_{MS_{\sigma}} = L_M^I ; \text{distribution coefficient} \quad (3-49)$$

Where brackets for subscripts are neglected. This rule is used in the following.

Thus, in the case where $M = Cu$

$$\frac{x_{Cu_{0.5}}}{x_{Cu}} = \boxed{K_{Cu}} \cdot \frac{\boxed{f_{Cu} \cdot f_S^{\frac{1}{2}} x_S^{\frac{1}{2}}}}{\boxed{\gamma_{CuS_{0.5}}}} = L'_{Cu} \quad (3-50)$$

affected by ^{metal} composition

affected by temperature

affected by slag composition

The greater value of L'_{Cu} the metal/slag system has, the larger is its capacity for copper removal.

The following considerations indicate how this factor can be influenced.

- i) The metal phase. L'_{Cu} increases with increasing f_{Cu} , $f_S^{\frac{1}{2}}$ and/or $x_S^{\frac{1}{2}}$. These activity coefficients depend on the composition in the metal phase. This dependency is quantitatively expressed by the interaction parameters $e_i^{(j)}$. For Cu, Sn and S, interaction parameters in molten iron are given [17] in Table 3-1.

Activity coefficients are calculated for the various molten metals. These are pig iron, iron after dephosphorising and desulphurising treatment, and steel. Assuming typical compositions, calculated results are given in Table 3-2.

The values of f_{Cu} $f_S^{\frac{1}{2}}$ are given below:

$$f_{Cu} \times f_S^{\frac{1}{2}} = \begin{cases} 3.7 : \text{pig iron} \\ 3.2 : \text{pre-treated de-P/de-S pig iron} \\ 1.1 : \text{steel} \end{cases}$$

In the case of steel, $f_{Cu} \times f_S^{\frac{1}{2}}$ is lowest and this means that it is the most difficult condition for copper removal among these three molten metals.

In equation (3-50) L'_{Cu} is also proportional to x_S . It is advantageous for copper removal to increase the S content of the metal phase. The S content should, however, be kept low in order to suppress harmful effect of S on the steel product. L'_{Cu} should therefore be increased without increasing S content.

- ii) The slag phase. L'_{Cu} increases with decreasing $\gamma_{CuS_{0.5}}$. It is thus essential to select the slag composition which keeps $\gamma_{CuS_{0.5}}$ low. Data on γ_{Cu_2S} in the FeS-Na₂S-Cu₂S system were reported by Topkaya [18]. In the present work, the FeS-NaS_{0.5} - CuS_{0.5} notation is used. Topkaya's data have been translated into this notation in Appendix -5.

Table 3-1 Interaction parameter $e_i^{(j)}$ in molten iron (ref.(17) unless otherwise stated).

$$\log f_i = e_i^{(j)} (\text{wt}\% j)_{\text{metal}}$$

at 1873 K

i \ j	O	S	C	Si	Cu	Sn
O	-0.20	-0.133	0.10*	-0.131	-0.013	-0.011
S	-0.27	-0.028	0.11	0.063	-0.008	0.103
C	0.08*	0.046	0.14	0.08	0.016	0
Si	-0.23	0.063	0.18	0.14	0.014	0.017
Cu	-0.065	-0.021	0.066	0.027	0.023	-
Sn	-0.11	-0.028	0.046**	0.057	-	0.0016

* ref.(43)

** ref.(24)

Table 3-2 Activity coefficient f_{Cu} , f_{Sn} and f_{S} in various molten metal compositions.

		pig iron	pre-treated pig iron	steel
wt%	C	4.3	4.0	0.1
	Mn	0.30	0.25	0.25
	Si	0.40	0	0
	P	0.10	0.020	0.010
	S	0.025	0.010	0.010
	O	-	-	0.10
	Cu	1.0	1.0	1.0
	Sn	1.0	1.0	1.0
activity	f_{Cu}	2.1	1.9	1.1
coeff.	f_{Sn}	1.7	1.5	1.1
	f_{S}	3.3	2.7	1.0

Table 3-3 Simulated cases for de-P/de-S (by the full model)

gas phase total pressure	no gas phase	reducing	oxidising
$p_T=10$ atm		DATA-1	
$p_T=1$ atm	DATA2-1 DATA2-2	DATA3-1 DATA3-2	DATA-4
$p_T=0.05$ atm		DATA-5	

- iii) Temperature. L_{Cu}^I increases with increasing equilibrium constant K_M^0 which is calculated by using Gibbs free energy change, ΔG^0 , for the formation of the sulphide.

$$[M] + [S] = \{MS_{\sigma}\} \quad \Delta G^0 = -RT \ln K_M$$

where R denotes the gas constant (3-51)

i.e. in case $M = Cu$

$$\Delta G^0 = -9655 - 1.61T \text{ [cal/mol]} \quad (3-52)$$

for $[Cu] + \frac{1}{2}[S] = \{CuS_{0.5}\}$.

[] denotes element dissolved in the molten iron.

{ } denotes element in the pure liquid state.

$$K_{Cu} = \exp (4862/T + 0.8107) \quad (3-53)$$

$$= \begin{cases} 54.7 & \text{at } 1250^{\circ}\text{C} \\ 30.2 & \text{at } 1600^{\circ}\text{C} \end{cases}$$

ΔG^0 for reactions between Cu and various possible refining slags based on $NaS_{0.5}$, $CaCl_2$, CaF_2 , KF , MnS , MgS , CaS , FeS and so on, are calculated in Appendix -5.

Temperature has an effect on activity coefficients

e.g. $RT \ln \gamma = \text{constant}$ for a regular solution.

The effect of the slag volume on copper and tin removal is roughly estimated by combining the equation for a chemical equilibrium (3-49) and the equation for a mass balance (3-55), yielding equation (3-56) for η_{Cu} which denotes the fraction of copper removed. The equation for a mass balance is:-

(initial total moles of Cu) = (final total moles of Cu)

$$M_m^0 \cdot x_{Cu}^0 = M_m \cdot x_{Cu} + M_s \cdot x_{CuS_{0.5}} \quad (3-54)$$

superscript o denotes the initial condition

subscript m denotes the metal phase

subscript s denotes the slag phase

M denotes the total moles in the particular phase

Assuming $M_m^0 \simeq M_m$, equation (3-54) can be rewritten as :

$$x_{Cu}^0 = x_{Cu} + \beta \cdot x_{CuS_{0.5}} \quad (3-55)$$

where $\beta = M_s/M_m$.

The fraction of copper removed, η_{Cu} , is derived, using equation (3-50) and (3-55)

$$\eta_{Cu} = (x_{Cu}^0 - x_{Cu})/x_{Cu}^0$$

or

$$\eta_{Cu} = 1 - 1/(1 + \beta L'_{Cu}) \quad (3-56)$$

η_{Cu} increases with increasing β and/or L'_{Cu} . If a low slag consumption is required (β is small), L'_{Cu} should be increased in order to keep η_{Cu} at the desired value. The relation between η_{Cu} , L'_{Cu} and β is shown in Fig. 3-8. The relation between η_{Cu} and x_s by changing the metal phase is shown in Fig. 3-9.

It is readily possible to estimate the effect of various changes of parameters on copper and tin removal by using the steady state model. Details, such as time-evolution, interfacial activity, transport phenomena and so on, are investigated for the important parameters by using the full model. In the steady state model, the following assumptions are made:-

- 1) Chemical equilibria are established between the metal phase and the slag phase through the reaction:



$M = Fe, Cu, Sn, Na, Mg, K, Ca, \text{ etc.}$

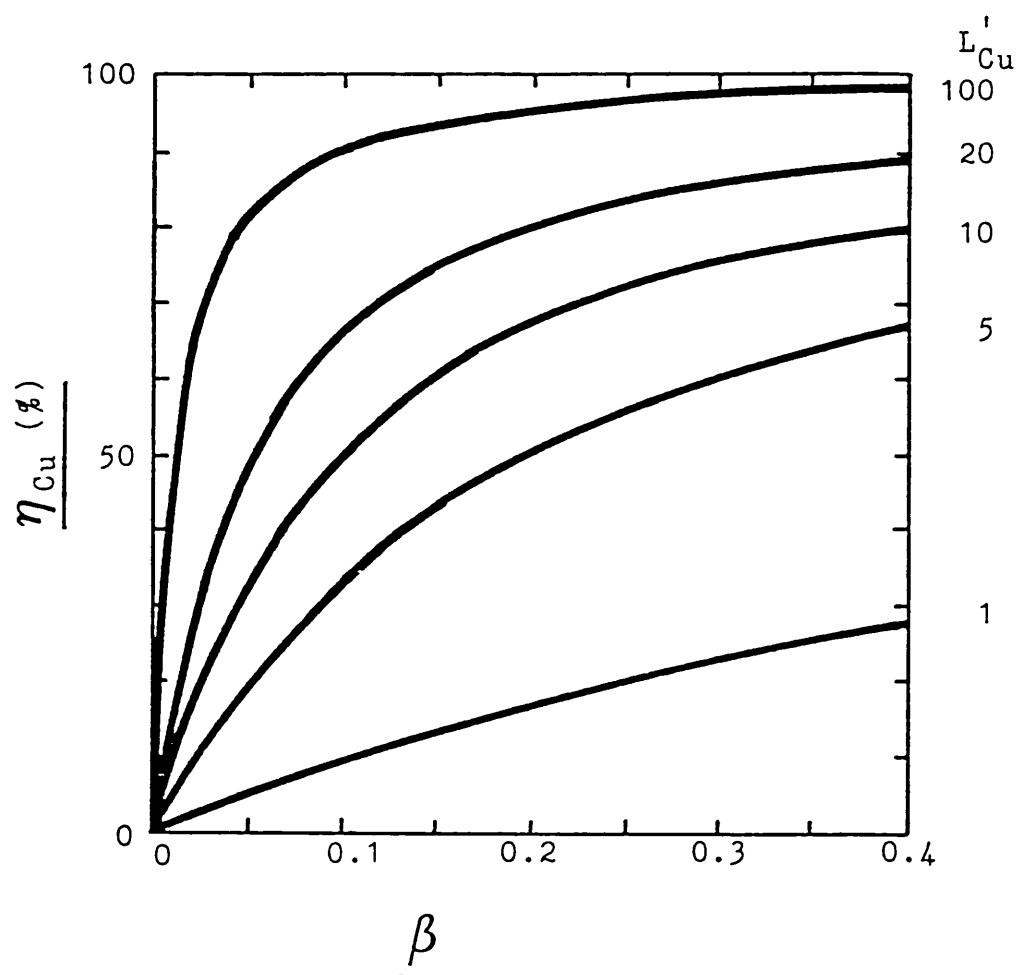
$X = S, F, Cl, \text{ etc.}$

- 2) Na and SnS are allowed to vaporise at the metal/slag interface.

$$[Na] = (Na) \quad (3-58)$$

$$\{SnS\} = (SnS) \quad (3-59)$$

This assumption is introduced in order to interpret the experimental results which were obtained by Topkaya [18] and Liu [41] in the case of copper removal by a pure $NaS_{0.5}$ slag.

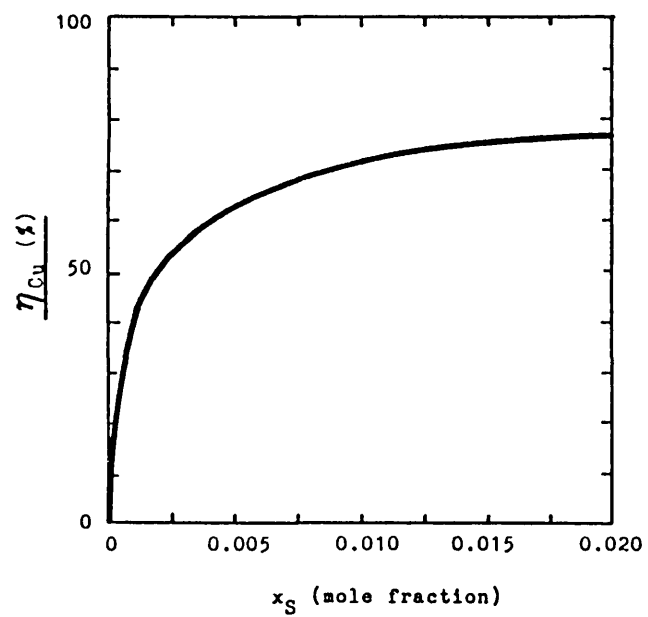


η_{Cu} : fraction of Cu removed

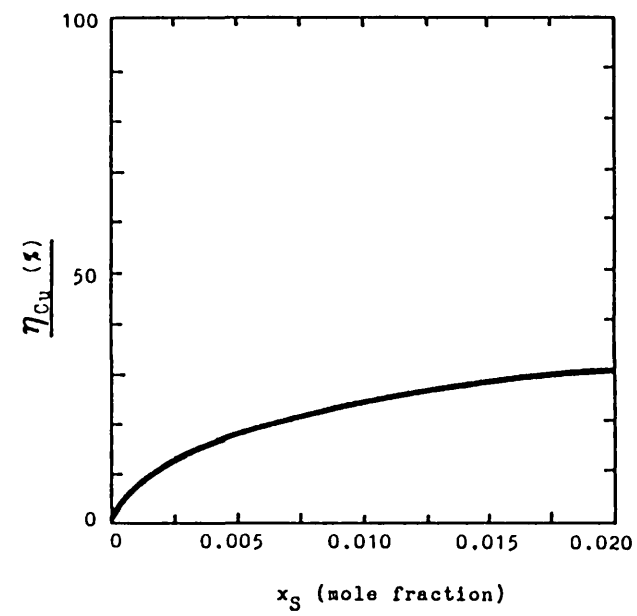
β : ratio of the total moles of the
slag phase to metal phase

L'_{Cu} : distribution coefficient of Cu
using mole fractions

Fig.3-8 Relation between η_{Cu} , L'_{Cu} and β .

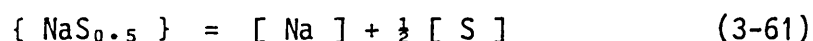
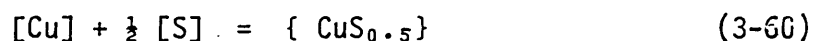


(a) De-Cu from carbon saturated iron at 1250° C
 ($\beta^0 \gamma_{CuS_{0.5}} = 0.1$, $f_{Cu} = 2.4$, $f_S = 3.4$).

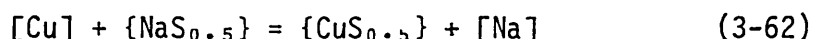


(b) De-Cu from steel at 1600° C
 ($\beta^0 \gamma_{CuS_{0.5}} = 0.1$, $f_{Cu} = 1$, $f_S = 1$).

Fig.3-9 Relation between η_{Cu} and x_S .



combined to form

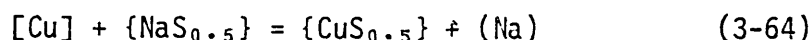


Reaction (3-62) is not favourable for the forward reaction at the temperature considered. By including

(3-63)



the overall reaction is described by equation (3-64)



Two assumptions are made to describe a mechanism of mass transfer for Na vapour produced at the metal/slag interface:

- i) Assumption 1 Sodium vapour is carried away by the argon gas flow which is supplied for bath stirring. If the argon gas flow rate is $\dot{q}$ [m^3/s], the flux of Na vapour carried away is

$$\text{Flux of } (\text{Na}) = p_{\text{Na}} \cdot \dot{q} / R.T_{\text{gas}} \quad (3-65)$$

- ii) Assumption 2 The fraction, α , of the total moles of Na in the initial slag as $\text{NaS}_{0.5}$ is lost with the release of S into the metal phase. α can be determined by the experimental results. In the steady state model, this simplest assumption α can be related to a particular value of argon gas flow rate $\dot{q}$.

The governing equations for the steady state model are for chemical equilibria and mass balances for each element. These simultaneous equations are solved under some initial conditions for the steady state solution.

Chemical equilibria

$$K_M = a_{MX_\sigma} / a_M \cdot a_X^\sigma \quad (3-66)$$

$$\text{for } [M] + \sigma [X] = [MX_\sigma]$$

In terms of mole fractions this equation is transformed to (3-67)

$$\begin{aligned} x_{MX_\sigma} / x_M x_X^\sigma &= f_M \cdot f_X^\sigma \cdot K_M / \gamma_{MX_\sigma} \\ &= K_M^{\text{eff}} \end{aligned} \quad (3-67)$$

This is the definition for the effective equilibrium constant K_M^{eff} in mole fractions.

Mass balance

Total mass or moles of each element must be conserved.

For element M :

$$M_m^0 \cdot x_M^0 + M_s^0 \cdot x_{MX_\sigma}^0 = M_m \cdot x_M + M_s \cdot x_{MX_\sigma} + \Delta_M \quad (3-68)$$

here Δ_M is the total moles lost as vapour. By assumption -2 above, this term is expressed in (3-69).

$$\Delta_M = \alpha_M M_s^0 \cdot x_{MX_\sigma}^0 \quad (3-69)$$

Where α_M is the fraction of the total moles of M lost as vapour.

$$\alpha_M = \begin{cases} 0 & M \neq \text{Na} \\ \alpha & M = \text{Na} \end{cases} \quad (3-70)$$

The equation (3-68) is rewritten, being divided by M_m^0 .

$$x_M^0 + (1 - \alpha_M) \cdot z^0 \cdot x_{MX_\sigma}^0 = y \cdot x_M + z \cdot x_{MX_\sigma} \quad (3-71)$$

$$\text{where } y \equiv M_m / M_m^0$$

$$z \equiv M_s / M_m^0$$

$$z^0 \equiv M_s^0 / M_m^0$$

Carbon is assumed to be inert

$$M_m^0 \cdot x_C^0 = M_m \cdot x_C$$

$$\therefore x_C = x_C^0 / y \quad (3-72)$$

For X, e.g. X=S, as X is coupled with other elements, it is necessary to sum them all.

$$\begin{aligned} M_m^0 \cdot x_X^0 + M_S^0 \cdot \sum_M (\sigma \cdot x_{MX_\sigma}^0) \\ = M_m \cdot x_X + M_S \cdot \sum_M (\sigma \cdot x_{MX_\sigma}) \end{aligned} \quad (3-73)$$

The equation (3-73) is rewritten, being divided by M_m^0

$$x_X^0 + z^0 \sum (\sigma x_{MX_\sigma}^0) = y \cdot x_X + z \sum (\sigma x_{MX_\sigma}) \quad (3-74)$$

Sum of mole fractions in the each phase are unity.

in the metal phase

$$\sum_M x_M = 1 \quad (3-75)$$

in the slag phase

$$\sum_M x_{MX_\sigma} = 1 \quad (3-76)$$

The number of variables is $(2n + 4)$. Where n denotes the number of metallic elements in the metal phase

$$\text{i.e. } \underbrace{x_X, x_C}_2, \underbrace{x_M}_n, \underbrace{x_{MX_\sigma}}_n, \underbrace{y, z}_2$$

The number of equations is also $(2n + 4)$ i.e.

$$\begin{aligned} \text{i.e. equations } & \underbrace{(3-67), (3-71)}_n, \underbrace{(3-72)}_n, \underbrace{(3-74)}_2, \\ & \underbrace{(3-75), (3-76)}_2. \end{aligned}$$

So that the problem can be solved.

After some manipulation, these $(2n + 4)$ equations can be reduced to three key equations for three variables, such as x_X , y and z . They are written below.

$$\left\{ \begin{array}{l} (1-x_X) \cdot y + z = \sum_M (u_M^0) + x_C^0 \end{array} \right. \quad (3-77)$$

$$\left\{ \begin{array}{l} x_X \cdot y - y \sum \left(\frac{\sigma u_M^0}{y+z \cdot K_M^{\text{eff}} x_X^\sigma} \right) = x_X^0 - \sum (\sigma x_{MX_\sigma}^0) \\ \quad \quad \quad + (1-\alpha_M) \cdot z^0 \cdot \sigma_{Na} \cdot x_{NaX_\sigma}^0 \end{array} \right. \quad (3-78)$$

$$\left\{ \begin{array}{l} x_X + x_C^0/y + \sum \left(\frac{u_M^0}{y+z \cdot K_M^{\text{eff}} \cdot x_X^\sigma} \right) = 1 \end{array} \right. \quad (3-79)$$

$$\text{Where } u_M^0 = x_M^0 + z^0 \cdot x_{MX_\sigma}^0.$$

These equations are solved by the computer programme which is described in Appendix -4.

3-3 Some applications

3-3-1 Dephosphorisation and desulphurisation(de-P/de-S)from pig iron

Some applications of the full model have been carried out in the present work. Simulated cases for de-P/de-S from pig-iron are summarised in Table 3-3.

A result predicted by the model in this work is compared with a result predicted by Ohguchi's model [10] which was itself confirmed by experimental results. The comparison of these two predictions is drawn in Fig. 3-10. The model in this work includes more general terms in the governing equations, i.e. volatilisation of all species, the effect of argon gas bubbling and so on.

There is no significant difference in the two predictions. This is considered to afford a good check for programming errors. Features of the results are, as are shown in Fig. 3-10, a time lag for start of de-P. In this case, the initial silicon content of the metal phase is $x=2.0 \times 10^{-3}$ mole fraction (0.10wt%) and the time lag is approximately 80 sec. This is due to low oxygen potential at the metal/slag interface in the initial stage when oxygen is consumed by silicon. On the other hand de-S and de-Si occur from the start. The time lag could be longer with higher initial contents of silicon, as was explained by Ohguchi [10]. After the end of powder addition, Mn-recovery and rephosphorisation of the metal take place.

In the full model, reagent can be supplied by an initial "dumping" and/or continuous feeding. It is almost impossible to start with no initial slag and continuous feeding. During the first time interval, which is used for unsteady state computation, a very small amount of reagent, which is generally far from chemical equilibrium with the initial metal phase, is fed. The composition of this slag phase changes too rapidly for the model to simulate properly because large driving forces for mass transfer between the metal phase and the slag phase cause large fluxes in the initial stage. It was found that 10g of the initial slag for 3000g of the metal phase and a time step of 0.001 in the dimensionless time are a good

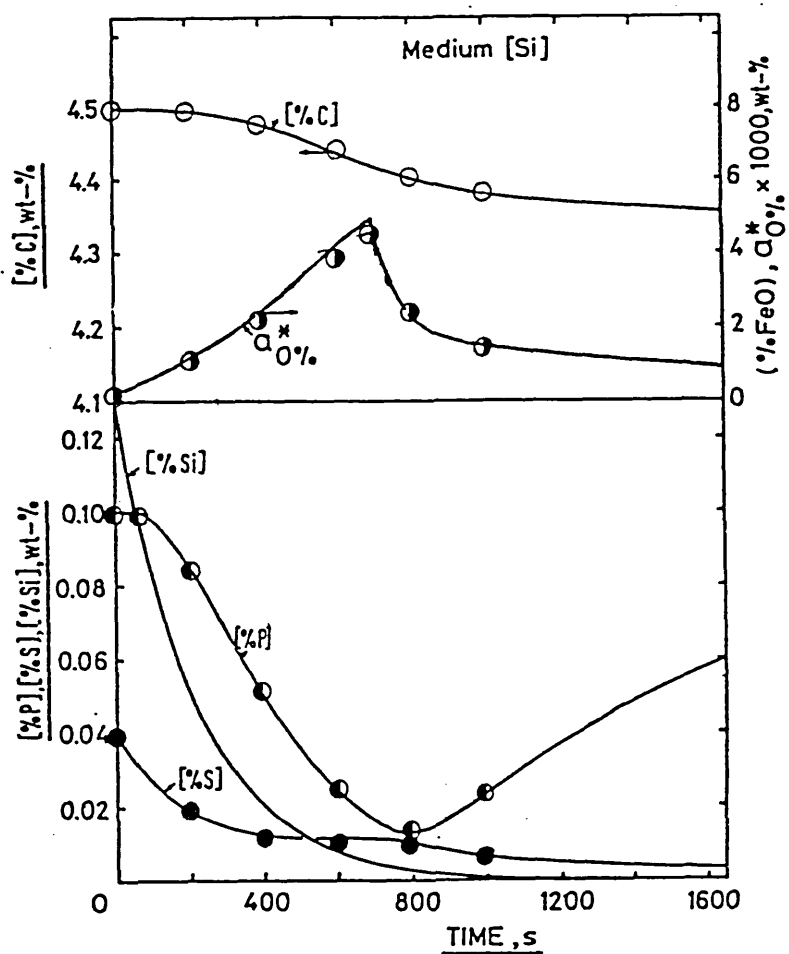


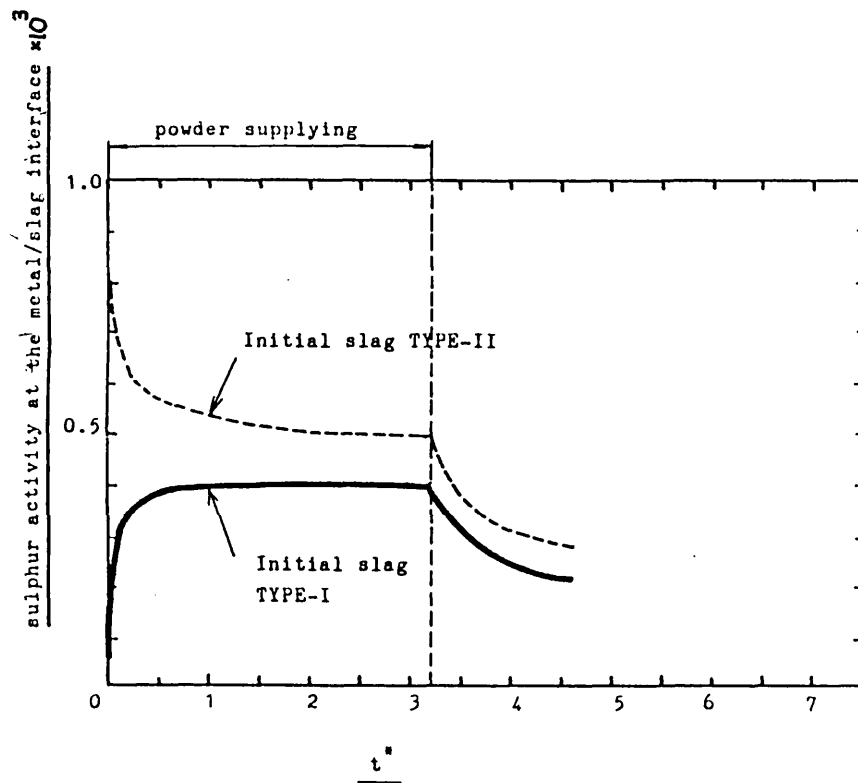
Fig.3-10 Comparison of calculated results by the metal-slag-gas reaction model (full model) in the present work with those of Ohguchi(10).

compromise for stable computation. The effect of the composition of the initial slag on the interfacial activities of oxygen and sulphur which are most sensitive to the initial slag composition are shown in Fig. 3-11.

Two types of slag are considered. Type I slag has a composition which is almost at equilibrium with the initial metal phase. Type II slag has the composition which contains excessive amount of sulphides to the steady state conditions. Higher interfacial activity of sulphur is predicted for Type II slag. There is no significant difference in the interfacial activity of oxygen.

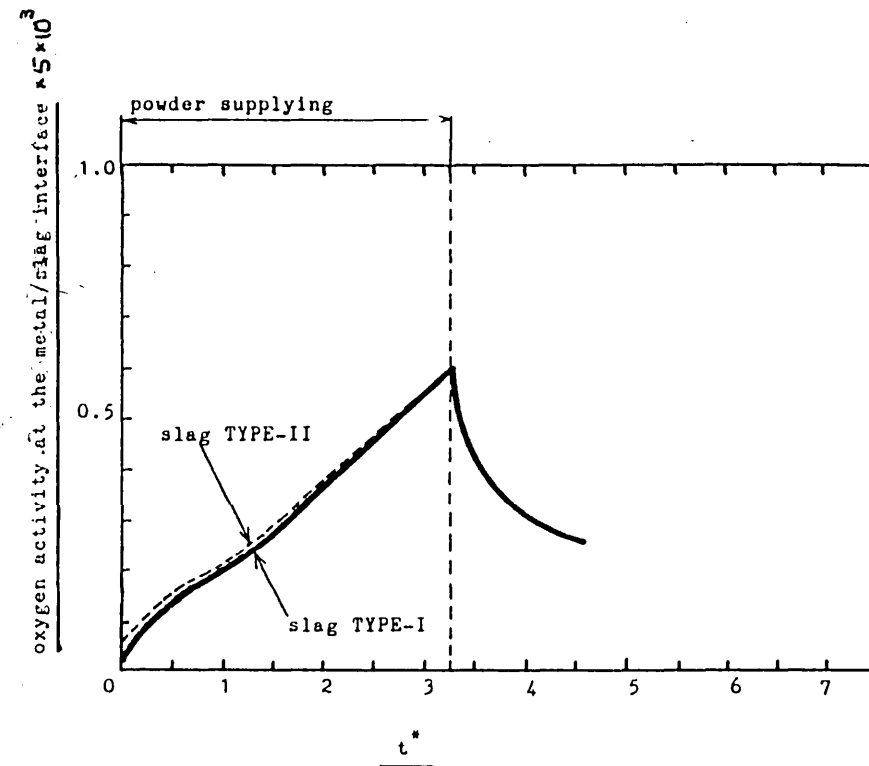
In the case of de-P/de-S of molten iron, the metal/slag interface is the major site for reaction. There are, however, some effects of the gas phase on the whole system. Three conditions for the gas phase are compared, i.e. no gas phase (except for CO evolution), reducing gas phase ($P_{CO}=1$ atm) and oxidising gas phase ($P_{O_2} = 0.1$ atm). The gas phase has influence on carbon losses, de-S/de-P, oxidation of FeO to $FeO_{1.5}$ and so on. The results are described in Table 3-5. There is little difference between the behaviour for these gaseous conditions. The reducing gas phase is slightly more favourable for de-S and the oxidising gas phase is slightly more favourable for de-P. In the case of the oxidising gas phase, oxygen transport occurs from the gas phase to the metal phase through the slag phase by $FeO_{1.5}$. As a result, CO evolution is enhanced in the case of an oxidising gas phase.

The effect of the total pressure of the gas phase, p_T , on de-P/de-S was investigated. The interfacial activity of oxygen is influenced by the total pressure through CO reaction and CO transport. This activity of oxygen influences all other species through reactions of the type $[M] + \alpha[O] = \{MO_\alpha\}$. The results are shown in Fig. 3-12. In the case of high pressure ($p_T = 10$ atm), CO transport from the metal is retarded and the interfacial activity of oxygen is high. This leads to favourable conditions for de-P. In the case of low pressure ($p_T = 0.05$ atm), CO transport is enhanced and interfacial activity of oxygen is low. This leads to favourable conditions for de-S and to unfavourable conditions for de-P.



(a) Interfacial sulphur activity at the metal/slag interface.

	slag TYPE-I	slag TYPE-II
FeO	6.8×10^{-4}	6.8×10^{-4}
SiO ₂	0.1	0.1
MnO	8.9×10^{-4}	8.9×10^{-4}
AlO _{1.5}	0.01	0.01
FeS	8.0×10^{-4}	0.011
MnS	4.7×10^{-3}	0.061
CaS	2.4×10^{-2}	5.0×10^{-2}
MgS	0.	1.8×10^{-5}



(b) Interfacial oxygen activity at the metal/slag interface.

Fig.3-11 Effect of the initial slag composition on interfacial activities of sulphur and oxygen (initial slag= 10g, metal=3000g, powder added=180g after 700s, at 1350° C, carbon saturated iron).

Table 3-4 Data for simulation (de-P/de-S,
by the full model).

1 Common data.

1) metal weight=3.0kg, slag weight=0.010kg(initial)

2) density of metal=7000kg/m³
density of slag =3000kg/m³

3) mass transfer coefficient

metal $k_m = 4 \times 10^{-4}$ m/s

slag $k_s = 2 \times 10^{-4}$ m/s

gas $k_g = 2 \times 10^{-2}$ m/s

CO transport $G_{CO} = 3 \times 10^{-3}$ mol/m²s

4) reaction area $S = 5 \times 10^{-3}$ m²

5) powder supplying

rate = 2.57×10^{-4} kg/s

duration = 700 s

total weight of powder supplied = 0.180 kg

composition = 0.30CaO-0.30FeO-0.40CaF₂ mole
fraction

6) initial metal composition (mole fraction)

O = 1.21×10^{-6}

S = 7.0×10^{-4}

C = 0.20

P = 1.81×10^{-3}

Si = 2.0×10^{-3}

Mn = 3.0×10^{-3}

7) initial slag composition (mole fraction)

FeO = 6.8×10^{-4}

SiO₂ = 0.10

MnO = 8.9×10^{-4}

CaO = 0.10

MgO = 0.01

AlO_{1.5} = 0.01

FeS = 1.9×10^{-2}

MnS = 6.1×10^{-2}

CaS = 5.0×10^{-2}

Table 3-4 (continued)

8) activity coefficient

$f_O = 2.64$, $f_S = 3.35$, $f_C = 4.41$, $\gamma_{Fe} = 0.85$,

$f_{Si} = 7.99$, $\gamma_{FeO} = 3.0$, $\gamma_{SiO_2} = 0.082$,

$\gamma_{CaS} = 1.0$,

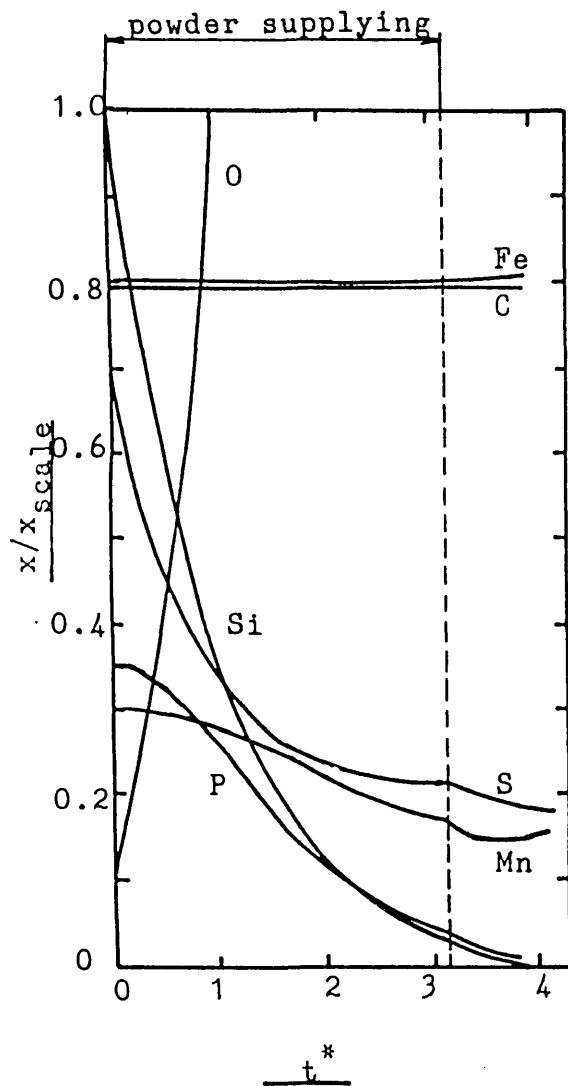
$\gamma_{PO_{2.5}} = 2.9 \times 10^{-10}$

9) temperature = 1623 K (1350° C)

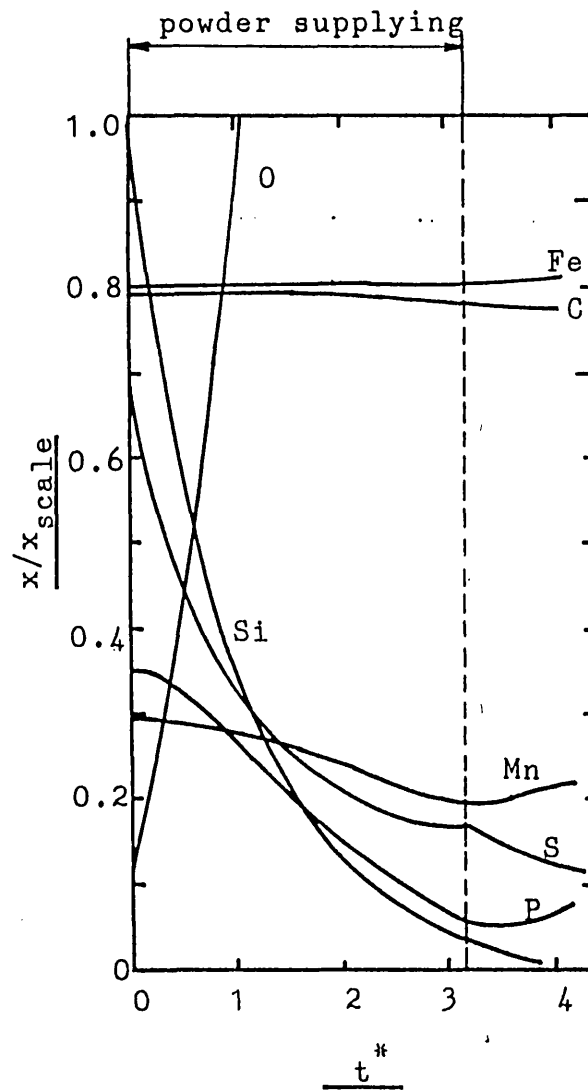
2 Data for each datafile.

	pressure (atm)			powder supply- ing rate (kg/s)	remarks
	P _T	P _{CO}	P _{O₂}		
DATA-1	10	10	0	2.57×10^{-4}	no gas lower sulphide content in the initial slag reducing gas phase
DATA2-1	(1)	(1)	(0)	2.57×10^{-4}	
DATA2-2	(1)	(1)	(0)	2.57×10^{-4}	
DATA3-1	1	1	0	2.57×10^{-4}	
DATA3-2	1	1	0	9.00×10^{-4}	
DATA-4	1	0	0.1	2.57×10^{-4}	
DATA-5	0.05	0.05	-	2.57×10^{-4}	

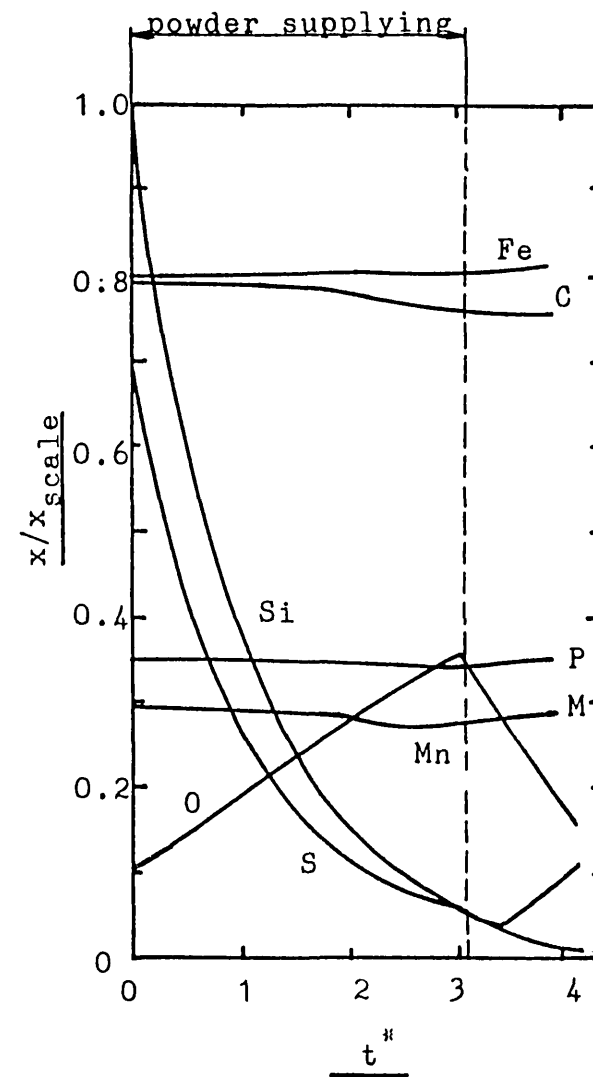
(continued)



(a) $p_T = 10.0$ atm

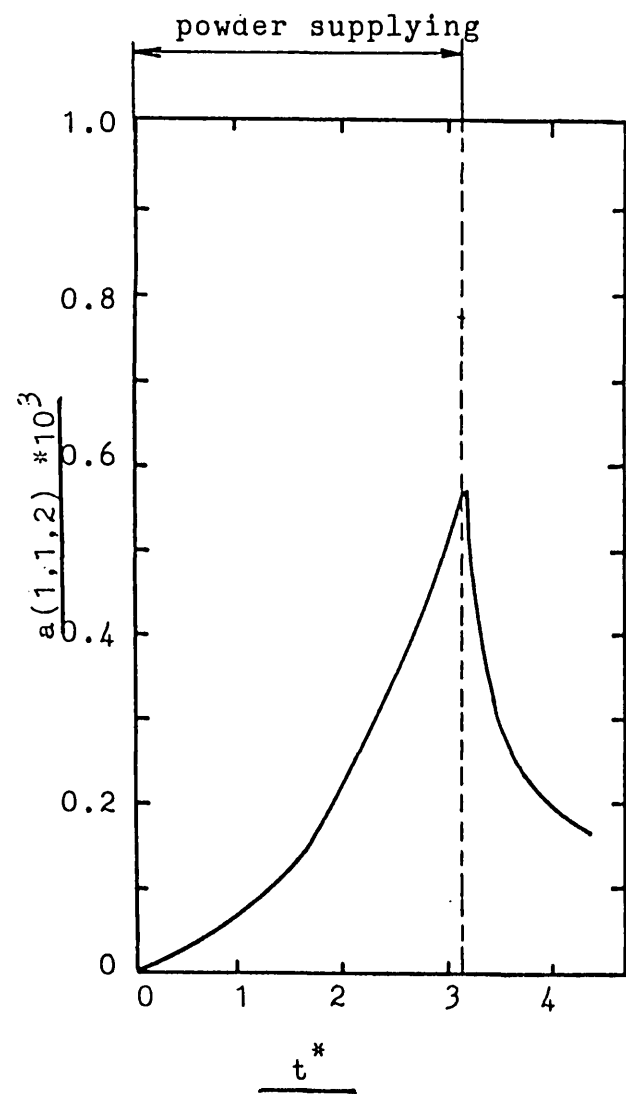


(b) $p_T = 1.0$ atm

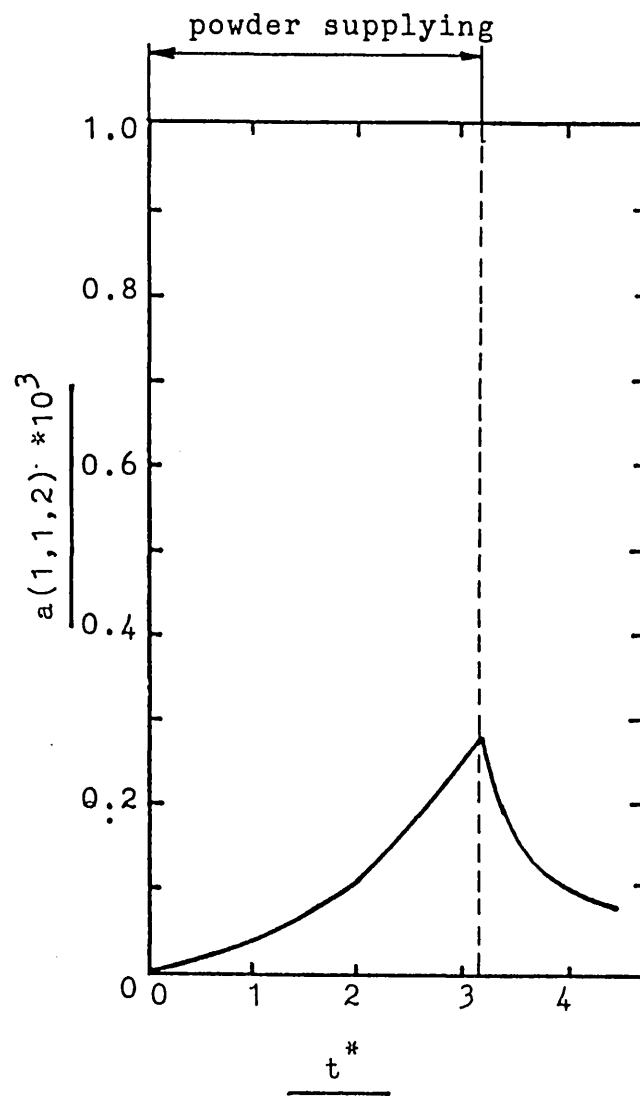


(c) $p_T = 0.05$ atm

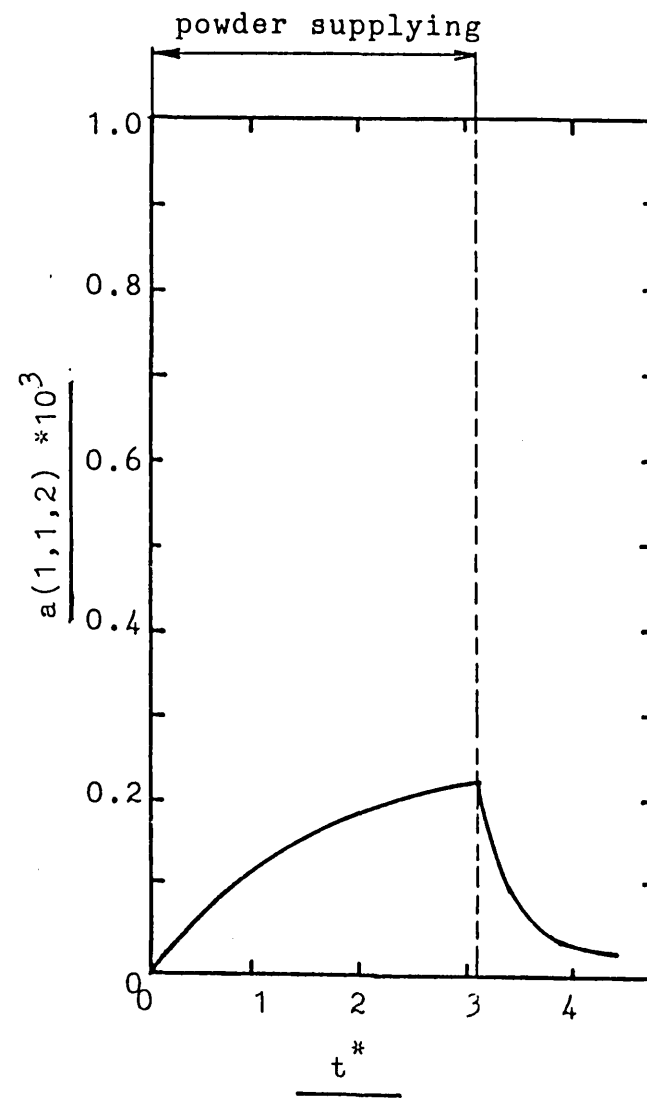
Fig.3-12 Effect of the total gas pressure on de-P/de-S ($t^* = t/t_{ref}$; $t_{ref} = V_m/k_m S$; $x_{scale} = 1 \cdot 10^{-5}$ for O, $= 1 \cdot 10^{-3}$ for S, $= 0.25$ for C, $= 1.0$ for Fe, $= 5 \cdot 10^{-3}$ for P, $= 2 \cdot 10^{-3}$ for Si, $= 1 \cdot 10^{-2}$ for Mn).



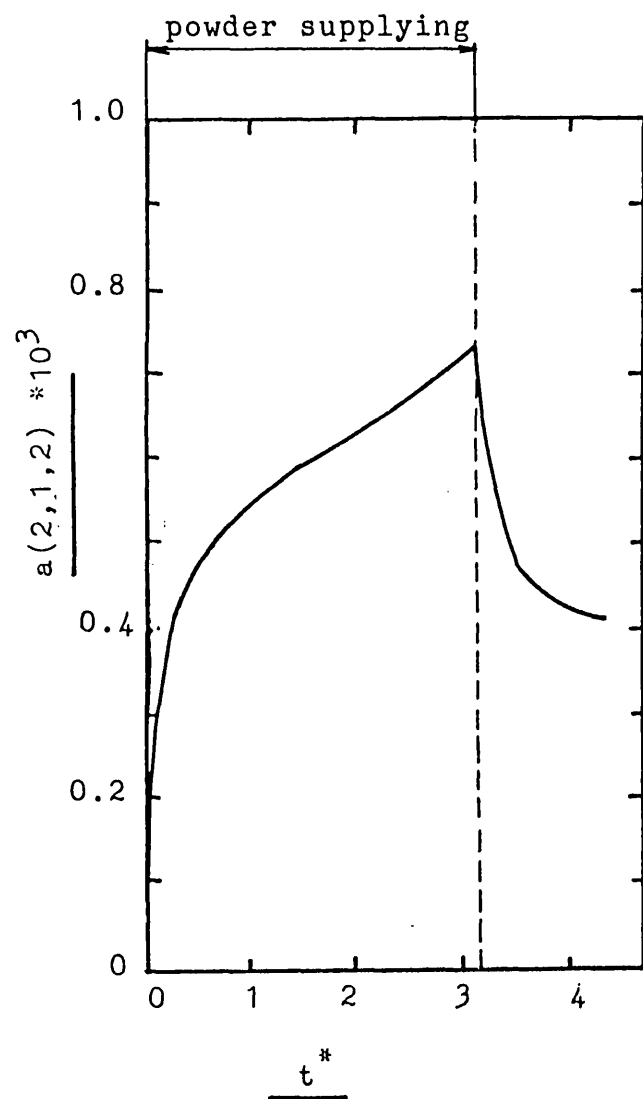
(d) $p_T = 10.0$ atm



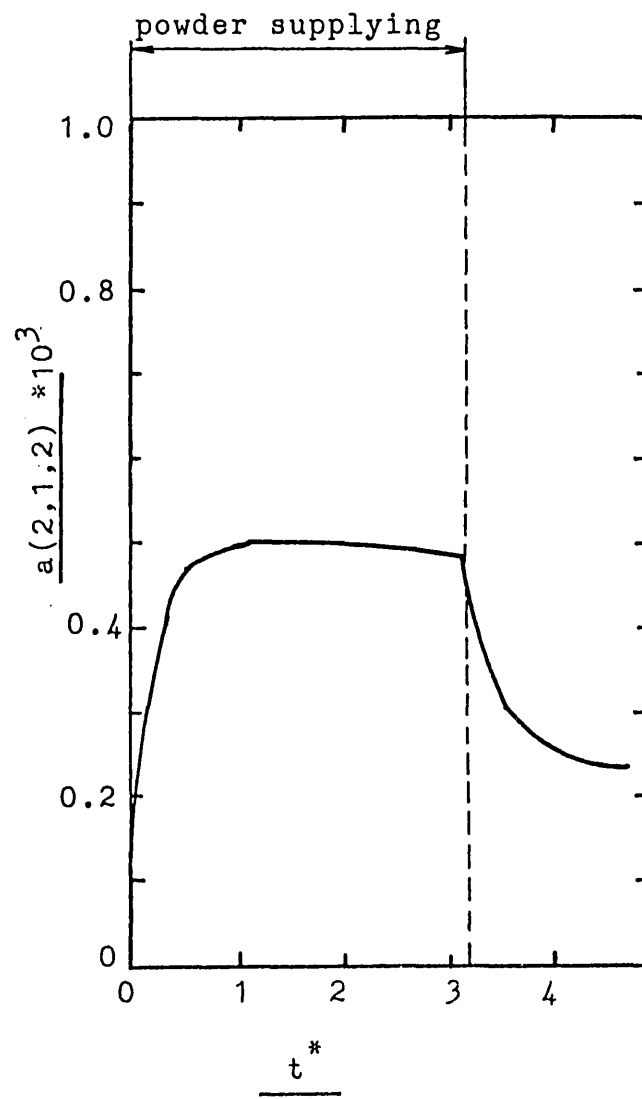
(e) $p_T = 1.0$ atm



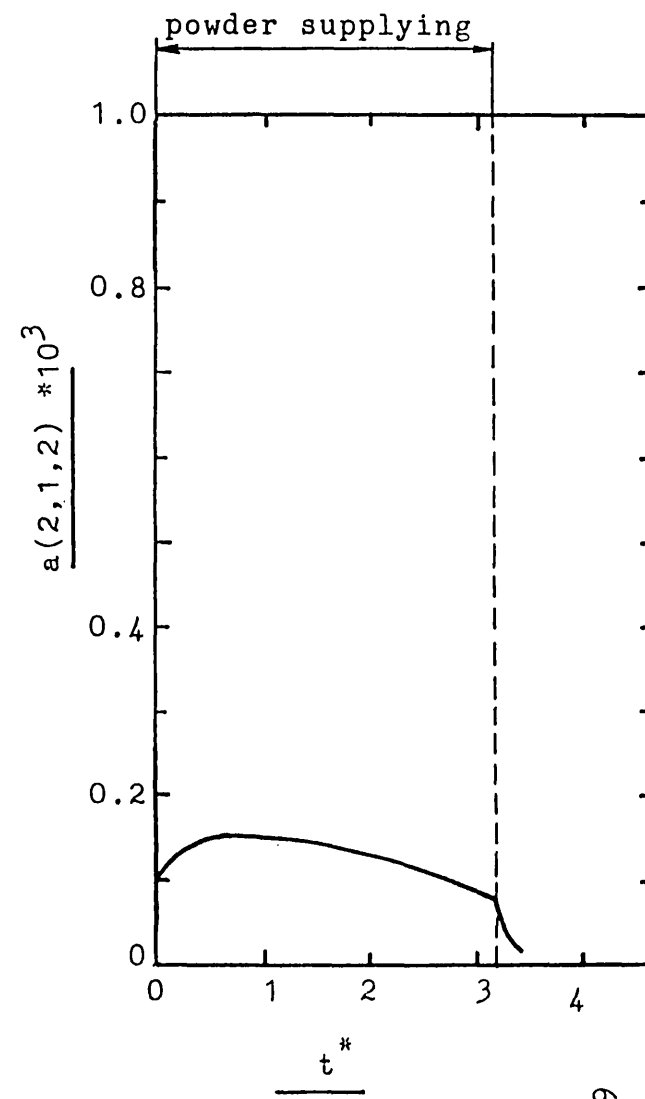
(f) $p_T = 0.05$ atm



(g) $p_T = 10.0$ atm



(h) $p_T = 1.0$ atm



(i) $p_T = 0.05$ atm

The interfacial activity of oxygen continuously increases until the end of powder feeding. The powder consists of 0.3 CaO-0.3FeO-0.4 CaF₂ (in mole fractions).

The results are summarised in Table 3-6.

The effect of the powder feeding rate on de-P/de-S was studied briefly. Two conditions for powder feeding rate were chosen. (see Table 3-7). Figs. 3-13 and 3-14 are for powder feeding rates of 0.257g/s and 0.900 g/s respectively. The effect of this rate on de-P/de-S was comprehensively studied by Ohguchi [10]. In the case of the higher feeding rate, a time lag of de-P does not occur.

Table 3-5 Effect of the gas phase on de-P/de-S from
carbon saturated iron at 1350° C.

(mole fraction)

Carbon losses

	t=0	t=990 s
no gas (DATA2-1)	0.20	0.1955
reducing (DATA3-1)	0.20	0.1955
oxidising (DATA-4)	0.20	0.1939

de-

	t=0	t=990 s
no gas (DATA2-1)	0.000700 (0.040wt%)	0.000092 (0.005wt%)
reducing (DATA3-1)	0.000700	0.000091
oxidising (DATA-4)	0.000700	0.000103

de-P

	t=0	t=990 s
no gas (DATA2-1)	0.00180 (0.100wt%)	0.00044 (0.024wt%)
reducing (DATA3-1)	0.00180	0.00045
oxidising (DATA-4)	0.00180	0.00025 (0.014wt%)

FeO & FeO_{1.5}

	t=0	t=990 s
reducing (DATA3-1)	FeO 6.8*10 ⁻⁴	1.35*10 ⁻²
	FeO _{1.5} 3.1*10 ⁻⁶	2.55*10 ⁻⁴
oxidising (DATA-4)	FeO 6.8*10 ⁻⁴	1.29*10 ⁻²
	FeO _{1.5} 3.1*10 ⁻⁶	3.74*10 ⁻³

Table 3-6 Effect of the total pressure p_T on de-P/de-S.

(mole fraction)

Carbon losses

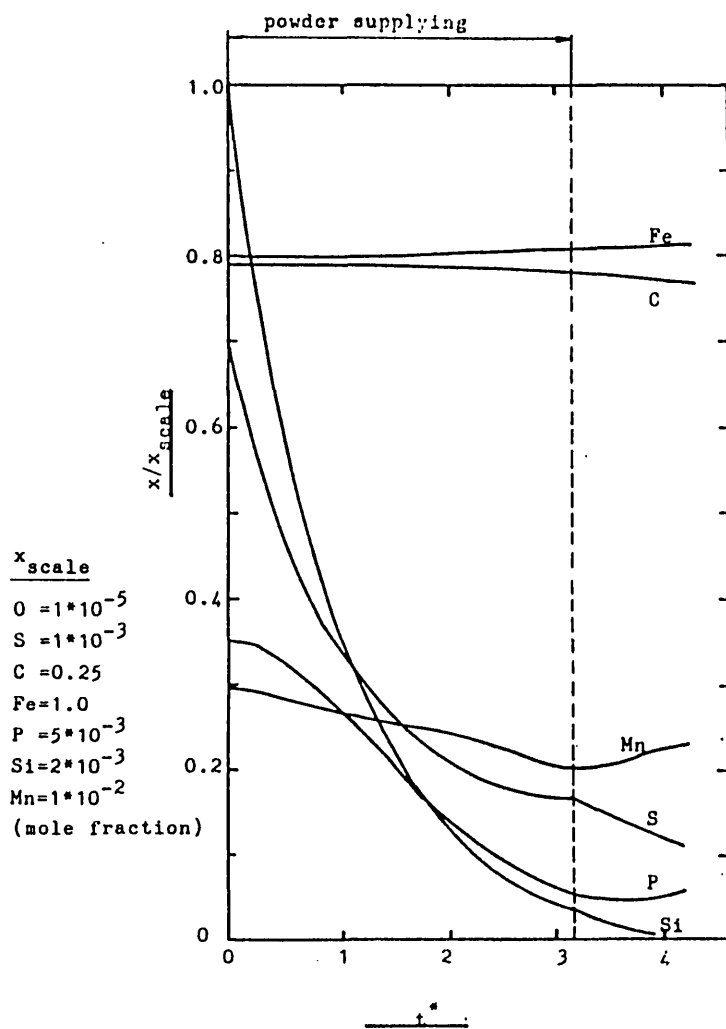
	t=0 s	t=1050 s
p _T =10 atm (DATA-1)	0.20	0.1992
p _T =1 atm (DATA3-1)	0.20	0.1953
p _T =0.05 atm (DATA-5)	0.20	0.1910

de-P/de-S

	t=0 s	t=1050 s
p _T =10 atm	S 0.00070	0.00014
	P 0.00180	0.000085
p _T =1 atm	S 0.00070	0.000085
	P 0.00180	0.00051
p _T =0.05 atm	S 0.00070	0.000013
	P 0.00180	0.00180

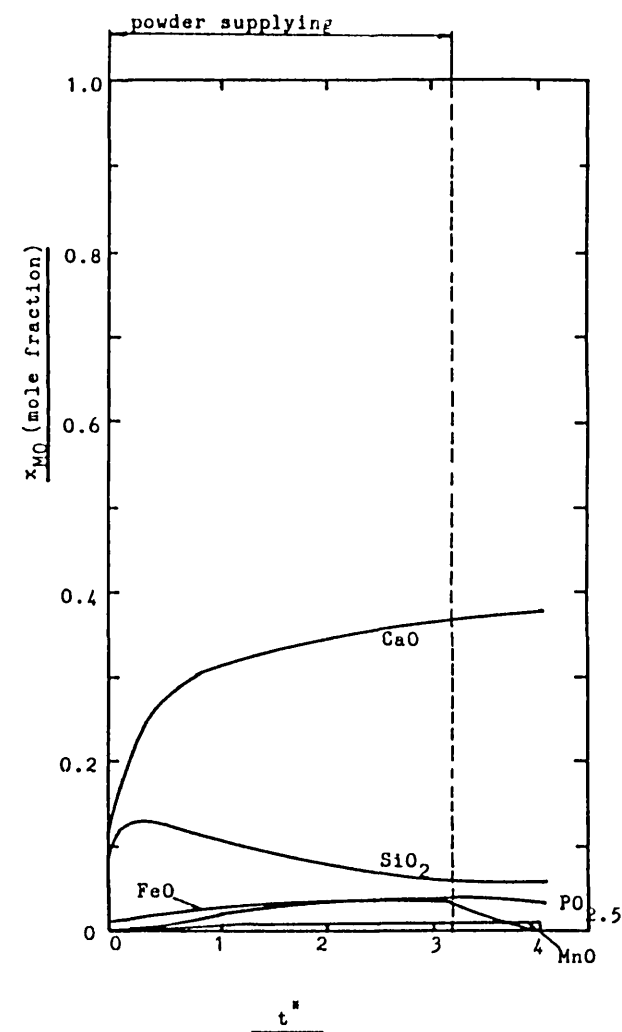
Table 3-7 Two conditions for powder supplying (rate).

data	duration	powder supplying rate (kg/s)	total amount
DATA3-1	700 s	2.57*10 ⁻⁴	0.180 kg
DATA3-2	200 s	9.00*10 ⁻⁴	0.180 kg

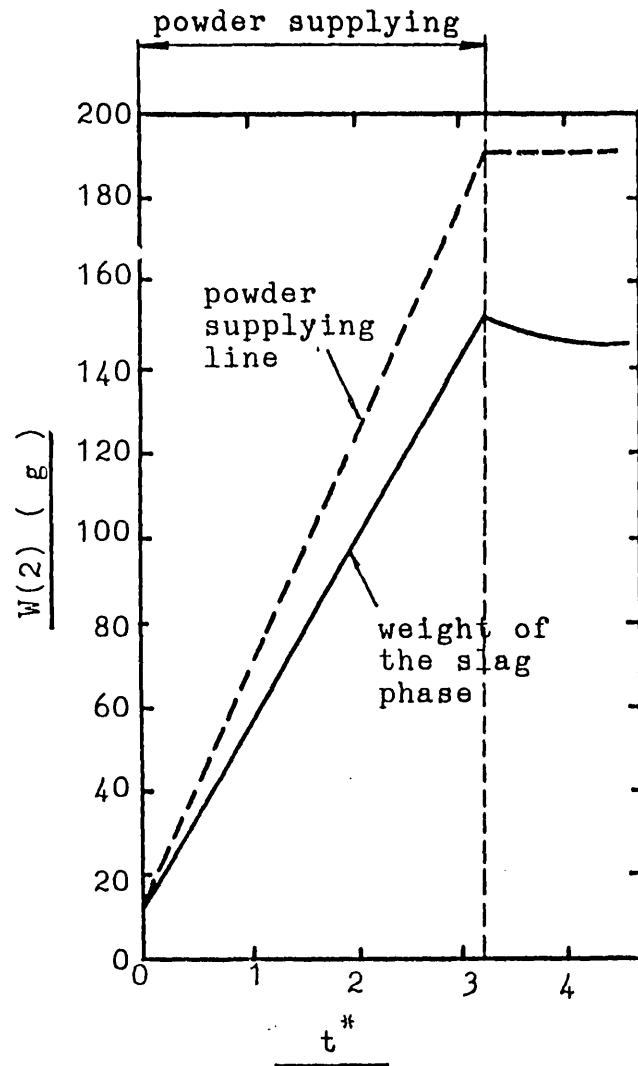


(a) Metal composition.

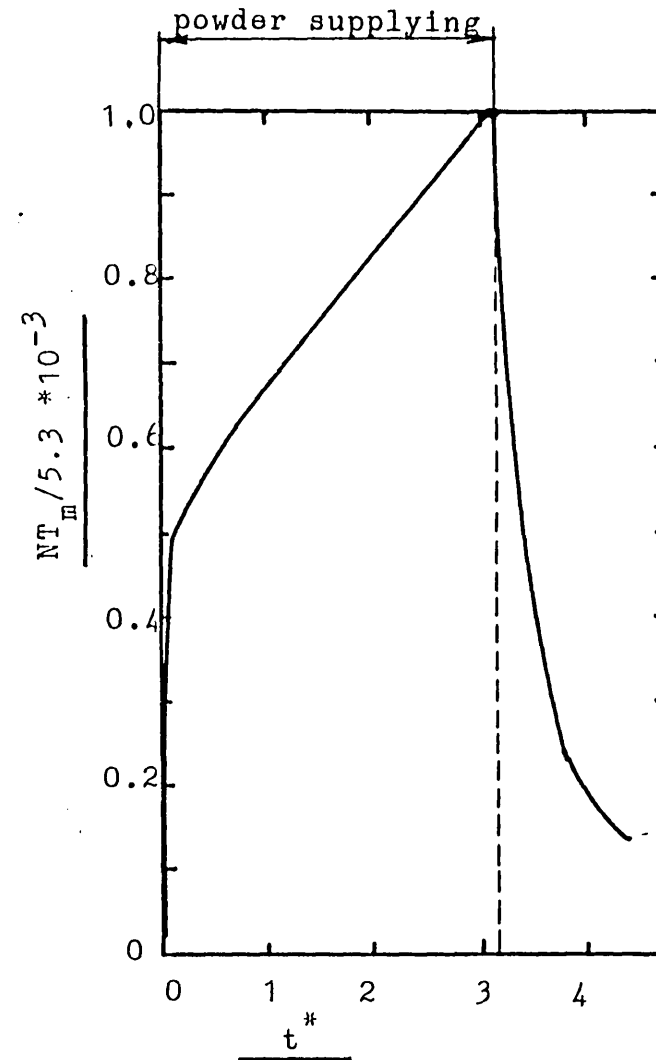
Fig.3-13 Evolution of composition in the case of standard gas pressure ($p_T = 1.0$ atm; DATA-3-1, $t^* = t/t_{ref}$, $t_{ref} = V_m/k_m S$ where V_m = volume of the metal phase, k_m = mass transfer coefficient in the metal phase, S = interfacial area).



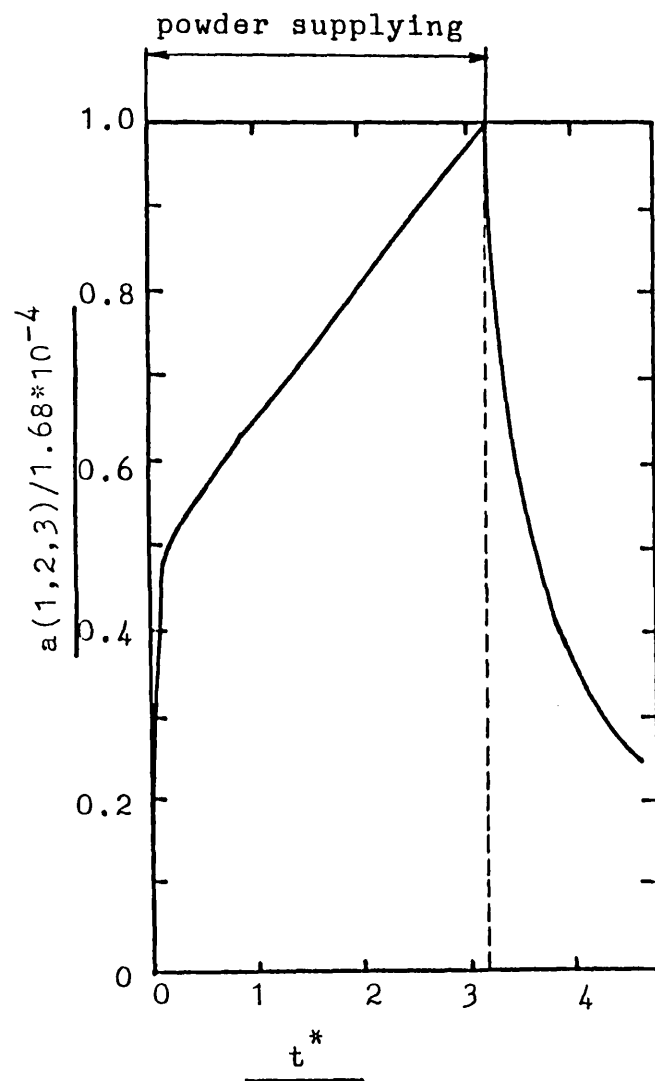
(b) Evolution of oxide in the slag phase.



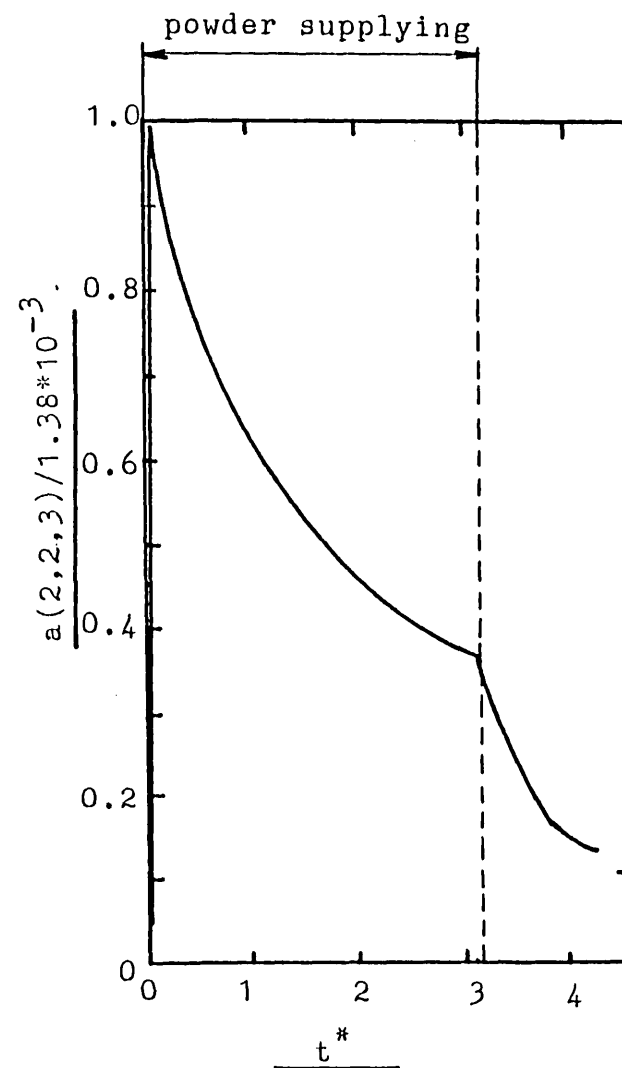
(c) Change of slag weight with time.



(d) Change of the flux density of metal reduced at the slag/gas interface.



(e) Interfacial activity of oxygen at the slag/gas interface.



(f) Interfacial activity of sulphur at the slag/gas interface.

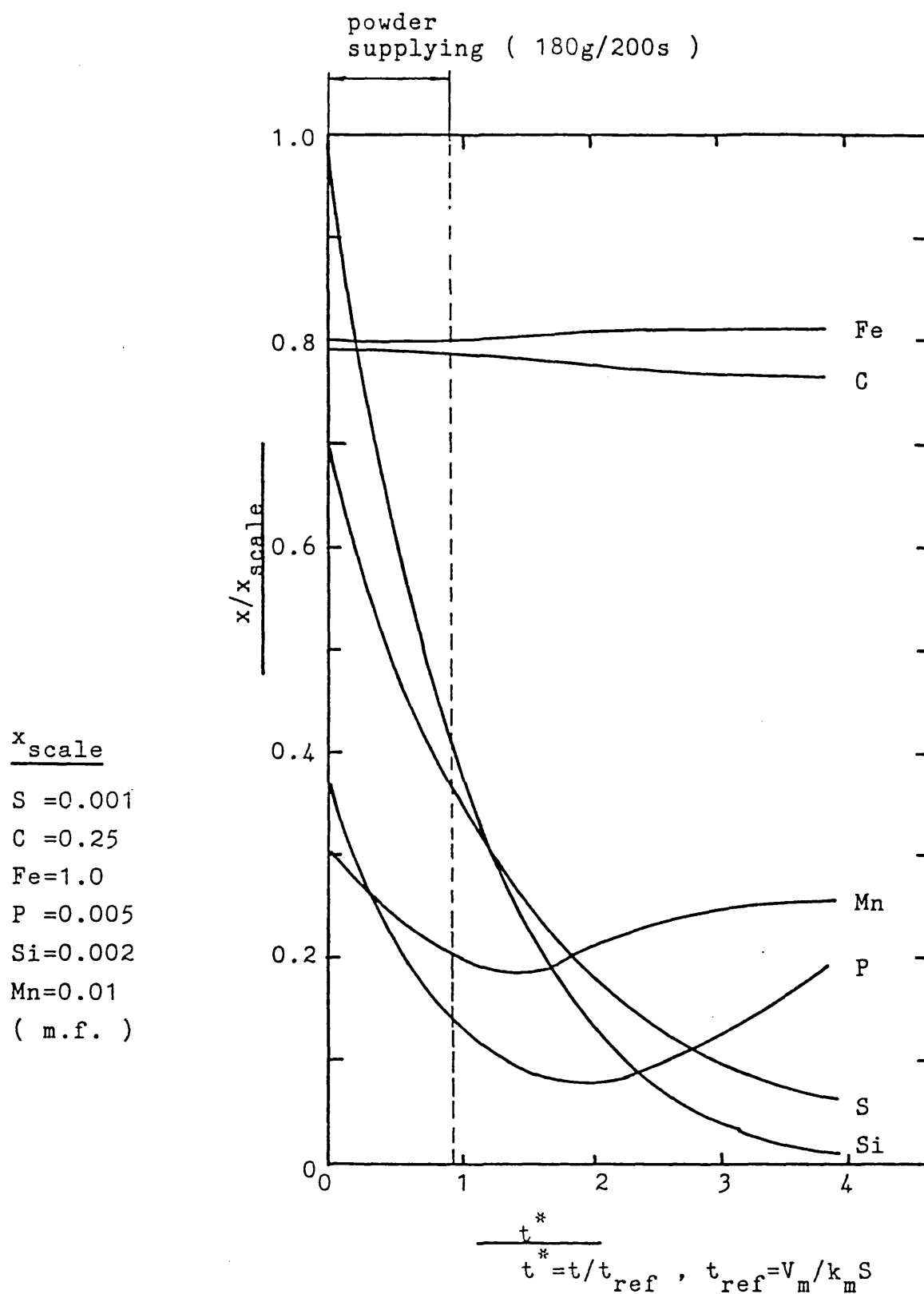


Fig. 3-14 Evolution of metal composition in the case of higher powder supplying rate (DATA-3-2).

3-3-2 Decopperising and detinning (de-Cu/de-Sn) from carbon saturated iron and steel.

Simulation of de-Cu/de-Sn from pig iron/steel was made using both the full model and the steady state model. The following thermodynamic data were used:

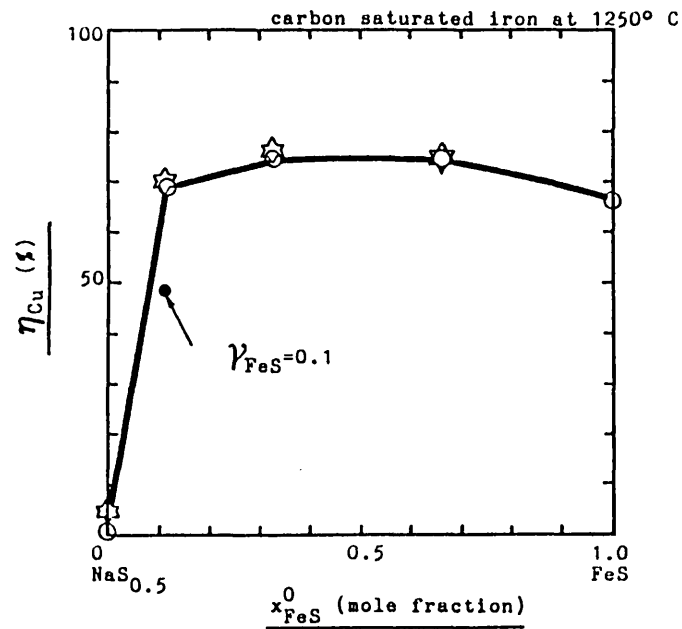
Calculated results for the relation between mole fraction and activity of sulphide and the change of Gibbs free energy are explained in Appendix -5 and -6 respectively. In the simulated results in this section, activity coefficients of sulphides are set unity unless otherwise stated. These activity coefficients are to be estimated after experimental work. Results predicted by the steady state model are summarised below:

- 1) Comparison of the results between the full model and the steady state model.

A fraction of copper removed, n_{Cu} , from carbon saturated iron by $NaS_{0.5}$ -FeS mixed slag is calculated by these two models individually. The results and computing conditions in detail are shown in Fig. 3-15. The results of the full model are the values at $t = 18$ minutes which represents approximately the steady state conditions in this model. The two sets of predictions agree well, although the full model predicts slightly higher copper removal than the steady state model, especially in the smaller x_{FeS}^0 region. γ_{FeS} influences copper removal through S released by FeS. In the case $\gamma_{FeS} = 0.1$, the results predicted by two models also agree well. n_{Cu} is approximately 70% except in the lower x_{FeS}^0 region, say $x_{FeS}^0 \leq 0.10$. This value agrees well with the experiments results of Liu [41], except in the lower x_{FeS}^0 region.

- 2) Effect of Na vaporisation at the metal/slag interface on copper and tin removal.

In Figs. 3-16 and 3-17 the relation between the fraction of Na vaporised, α , and n_{Cu} and n_{Sn} is shown. Na vaporization affects the results significantly in the lower x_{FeS}^0 region, say $x_{FeS}^0 \leq 0.3$ according to Fig. 3-20(a). In the case of pure $NaS_{0.5}$ slag, the effect of α on n_{Cu} and n_{Sn} is larger than in the case of 80 wt% $NaS_{0.5}$ - 20 wt% FeS mixed slag.



○ calculated result by the steady state model

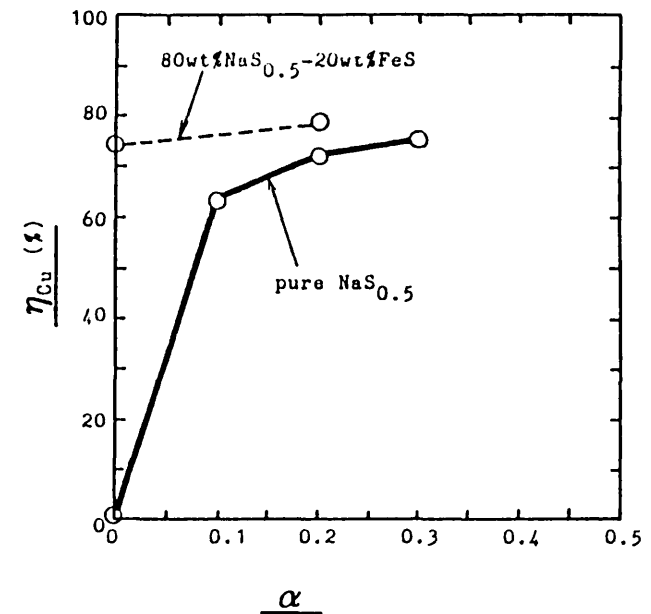
☆ calculated result by the full model

● by the steady state model

Computing conditions.

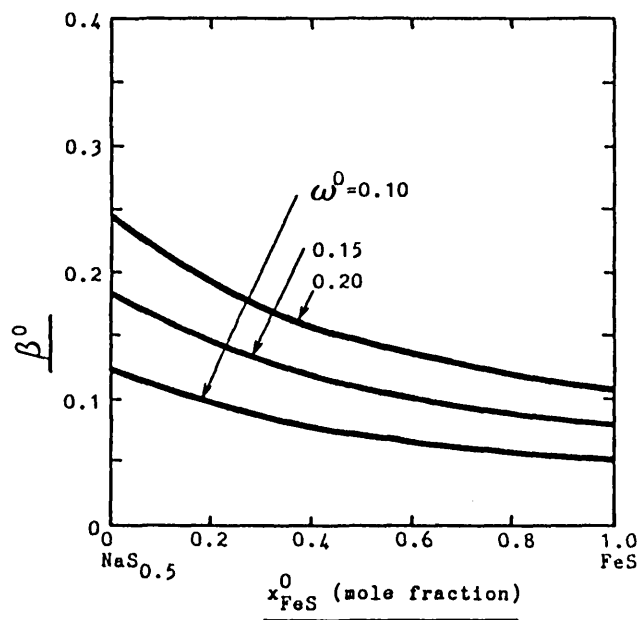
- 1) activity coefficients of sulphide are unity
- 2) slag=450g ($\text{NaS}_{0.5}$ -FeS mixture)
metal=3000g (carbon saturated iron with
 $x_{\text{Cu}}^0=0.01$, $x_{\text{Sn}}^0=0.002$ and $x_{\text{S}}^0=0$)
- 3) no Na vaporization allowed

Fig.3-15 Comparison of the calculated results by the full and steady state model.



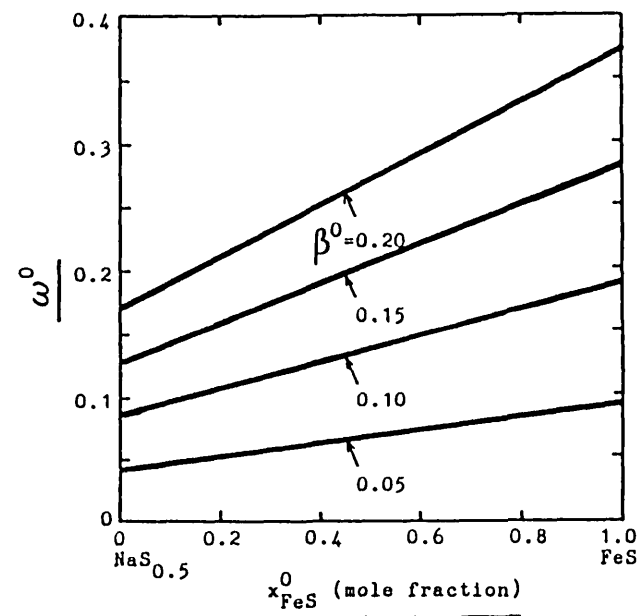
α : fraction of Na vaporised
at the metal/slag interface

Fig.3-16,17 Effect of Na vaporization at the metal/slag interface on de-Cu ($\beta^0=0.190$, carbon saturated iron at 1250°C , $x_{\text{Cu}}^0=0.01$, $x_{\text{S}}^0=0$).

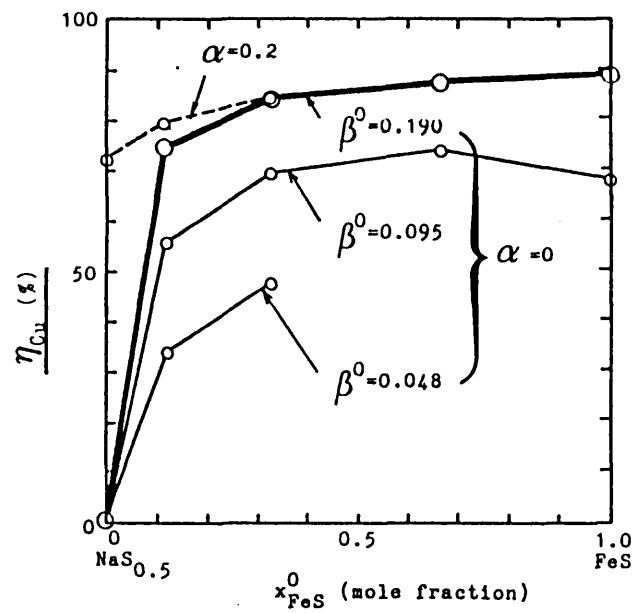


(a) Constant ω^0 -contour.

Fig.3-18 Relation between ω^0 and β^0 (ω denotes ratio of weight of the slag to metal phase, β denotes ratio of moles of the slag to metal phase and superscript 0 denotes an initial value).

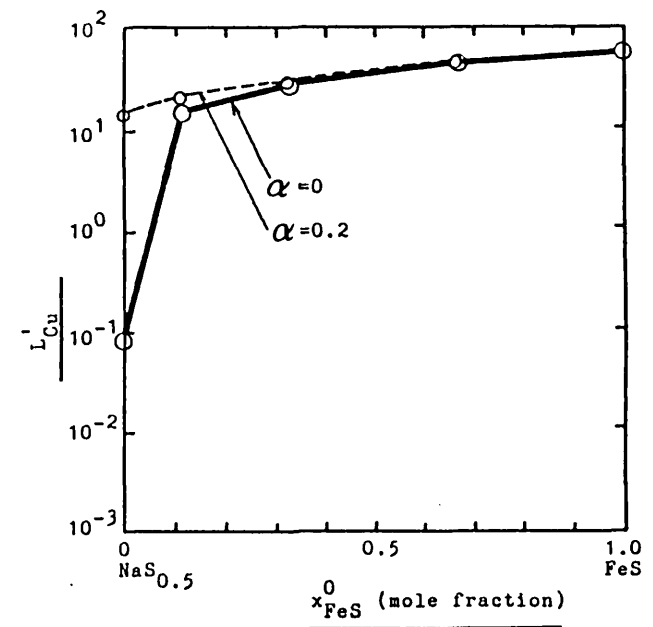


(b) Constant β^0 -contour.



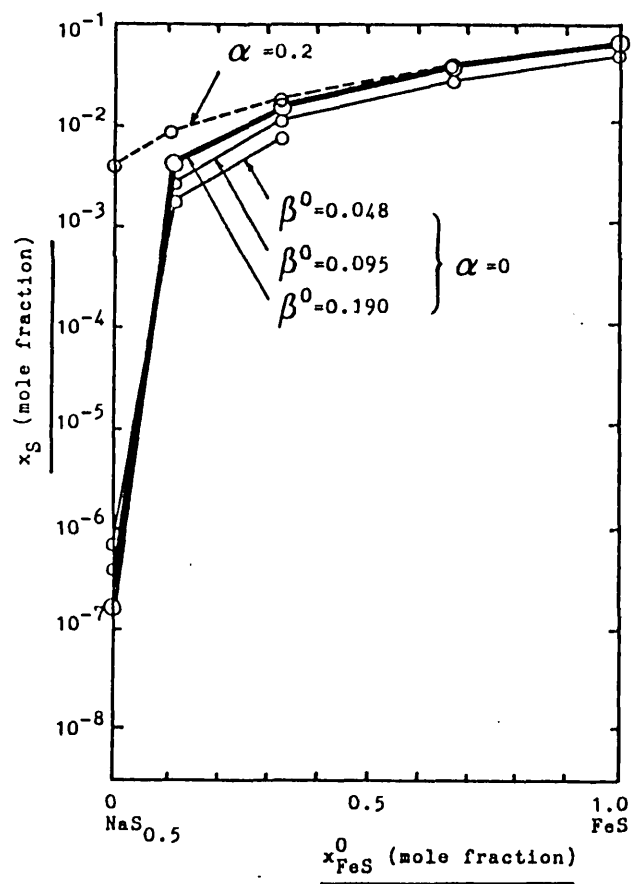
α : fraction of Na vaporised

(a) η_{Cu} .

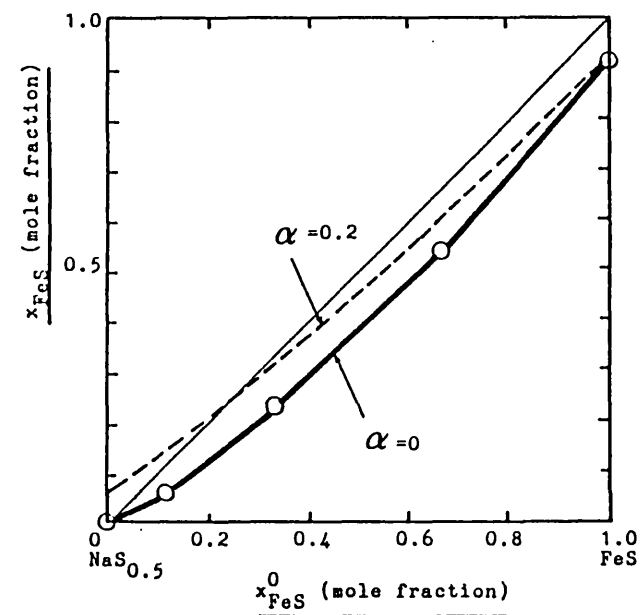


(b) Distribution coefficient of Cu, L_{Cu}^I
defined by mole fractions ($\beta^0=0.19$).

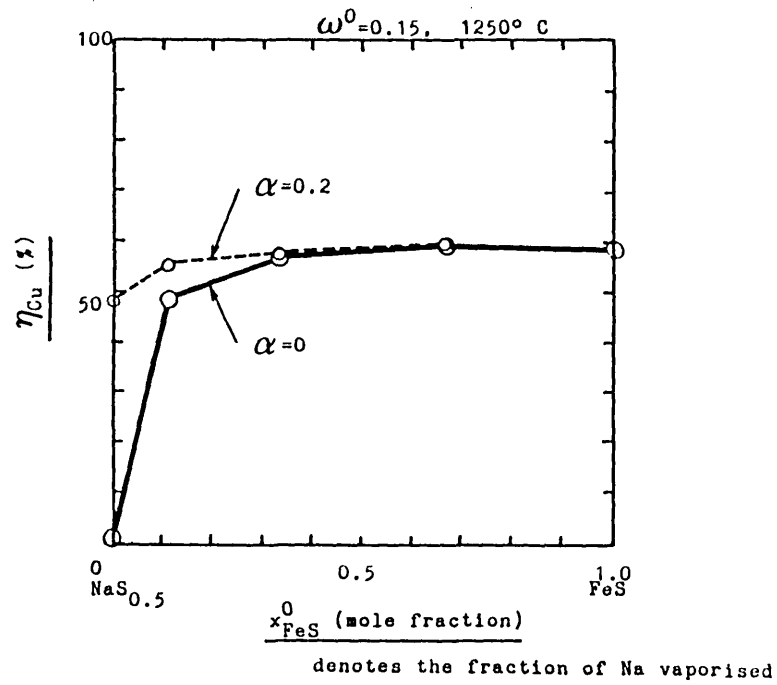
Fig.3-19 Effect of slag composition ($NaS_{0.5}$ -
FeS mixed slag) on de-Cu (constant
 β^0 -contour) from carbon saturated iron
at $1250^\circ C$ (predicted by the steady state
model).



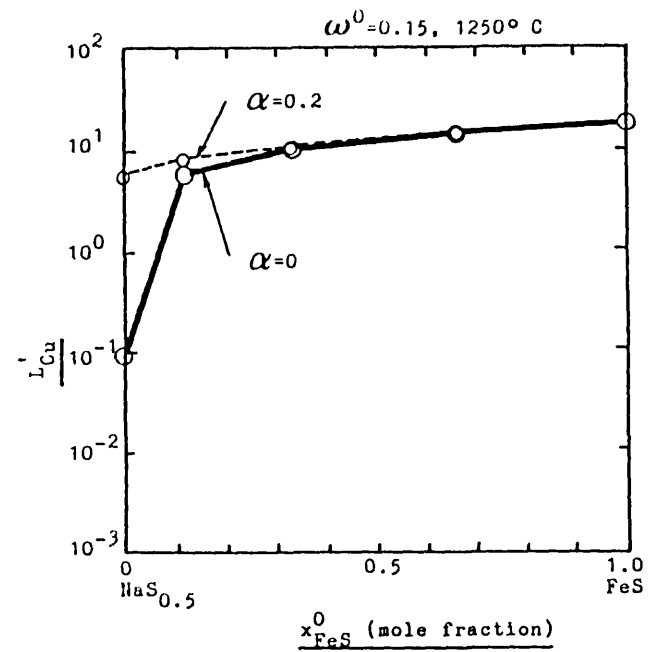
(c) Sulphur concentration in the metal phase.



(d) x_{FeS} vs x_{FeS}^0 ($\beta^0 = 0.190$).

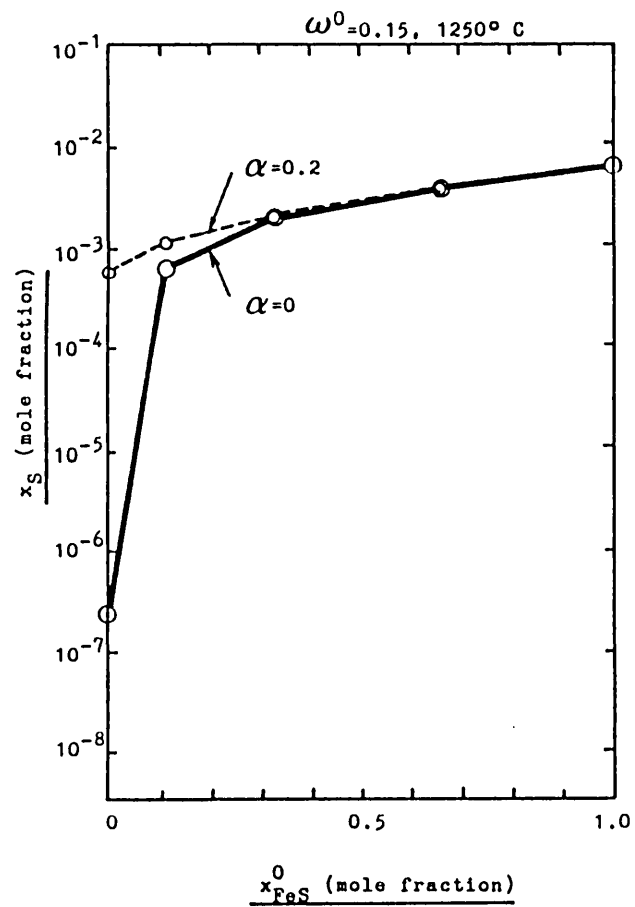


(a) x_{FeS}^0 vs η_{Cu} .

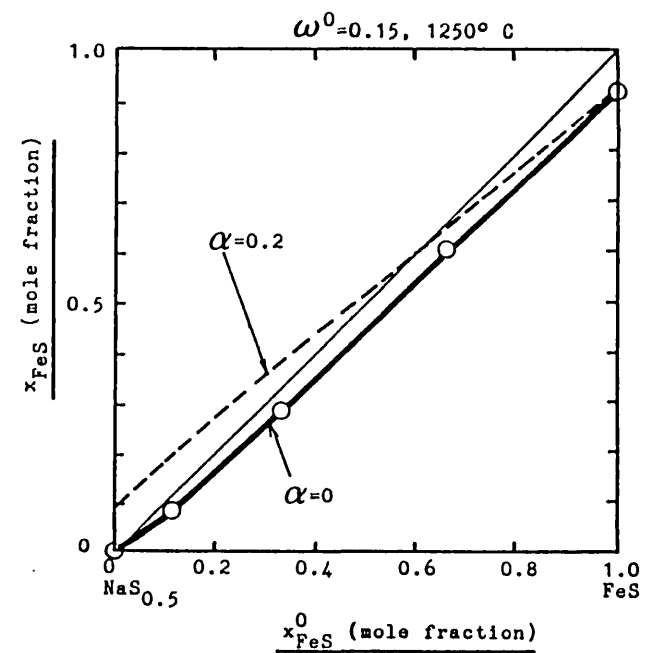


(b) Distribution coefficient of copper, L'_{Cu}
 ($L'_{\text{Cu}} = x_{\text{CuS}_{0.5}} / x_{\text{Cu}}$).

Fig.3-20 Effect of slag composition ($\text{NaS}_{0.5}$ -FeS mixed slag) on de-Cu from carbon saturated iron (predicted by the steady state model, $\gamma_{\text{FeS}} = 0.1, \gamma = 1$ for all other sulphides, metal=3000g, slag=450g).



(c) Sulphur concentration in the metal phase.



(d) FeS concentration in the slag phase.

3) Effect of activity coefficient of tin f_{Sn} on tin removal.

f_{Sn} is dependent mainly on the composition of the metal phase.

In the case of carbon saturated iron, f_{Sn} could be 1.7 according to the report of Schenck et al [32].

η_{Sn} decreased with decreasing f_{Sn} .

4) Effect of slag composition (binary mixture of $\text{NaS}_{0.5}$ and FeS) on copper and tin removal with constant ω^0 or constant β^0 .

Where ω denotes weight ratio of the slag phase to the metal phase.

Superscript ^{0} denotes the initial condition and β denotes molar ratio of the slag phase to the metal phase.

The relation between ω^0 and β^0 is explained in Table 3-8 and in Fig. 3-18. The results of the effect of x_{FeS}^0 on η_{Cu} , η_{Sn} , x_{S} , L'_{Cu} , L'_{Sn} and x_{FeS} are shown in Fig. 3-19 at constant β^0 values and in Fig. 3-20 at constant ω^0 values.

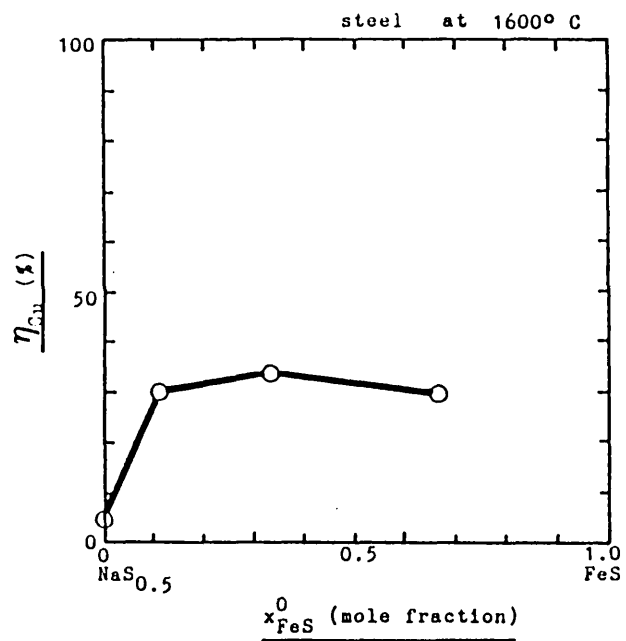
- In Fig. 3-19(a), η_{Cu} has a maximum value when $x_{\text{FeS}}^0 \approx 0.6 - 0.7$ with $\beta^0 = 0.095$.
- General trend is that η_{Cu} , η_{Sn} , x_{S} , L'_{Cu} , L'_{Sn} , and x_{FeS} increase with increasing x_{FeS}^0 .
- Na vaporization at the metal/slag interface has a significant effect on η_{Cu} , x_{S} , and L'_{Cu} in the lower x_{FeS}^0 region, say $x_{\text{FeS}}^0 \leq 0.3$.
- If β^0 is kept constant, ω^0 increases with increasing x_{FeS}^0 in the $\text{NaS}_{0.5} - \text{FeS}$ system.
- x_{FeS} is less than x_{FeS}^0 in all ranges of x_{FeS}^0 when $\alpha = 0$.
- when $\alpha > 0$, x_{FeS} is greater than x_{FeS}^0 in the low x_{FeS}^0 region.

5) Effect of β^0 on copper removal.

η_{Cu} increases with increasing β^0 , as shown in Fig. 3-19.

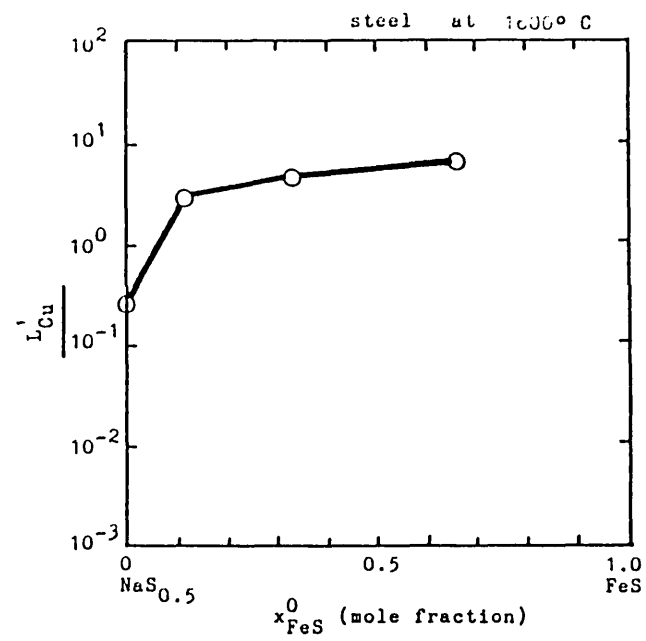
6) Comparison between carbon saturated iron and steel.

Results for steel are shown in Fig. 3-21 and a comparison between carbon saturated iron and steel is drawn in Fig. 3-22. Essential differences of conditions for these two types of melts are carbon content and temperature.

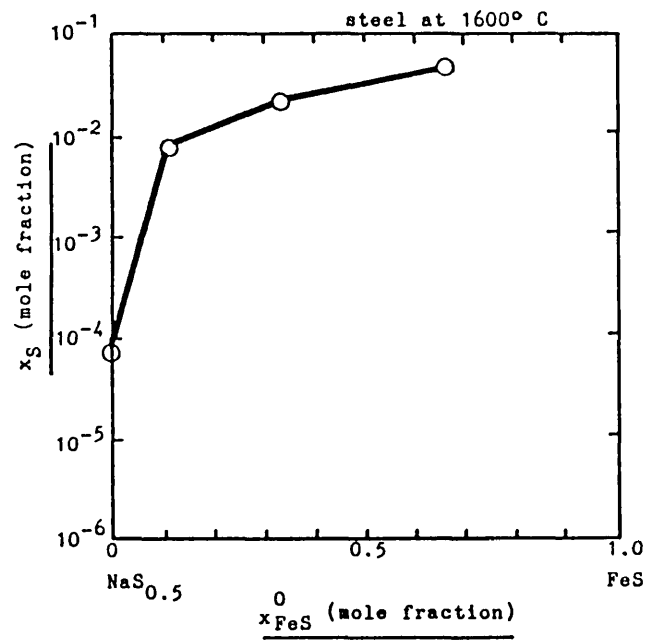


(a) x_{FeS}^0 vs η_{Cu} .

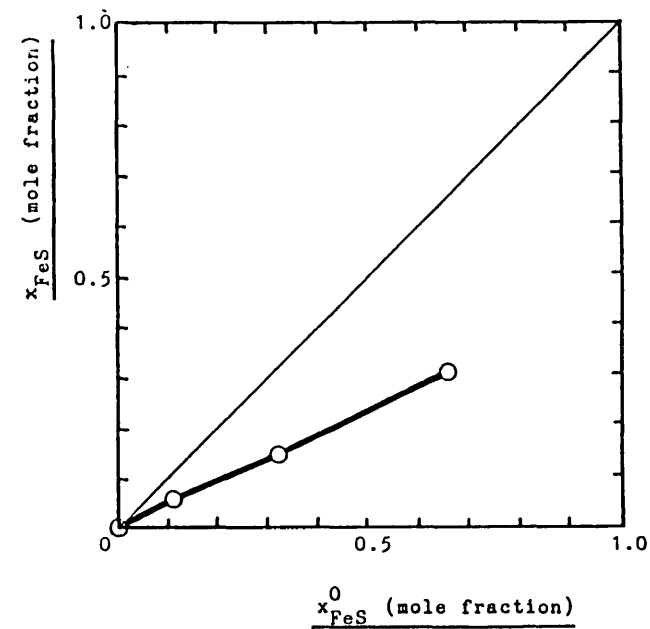
Fig.3-21 Effect of slag composition (NaS_{0.5}-FeS mixture) on de-Cu (metal=3000g with $x_{Cu}^0=0.01$ and $x_S^0=0$, slag=450g, calculated by the steady state model).



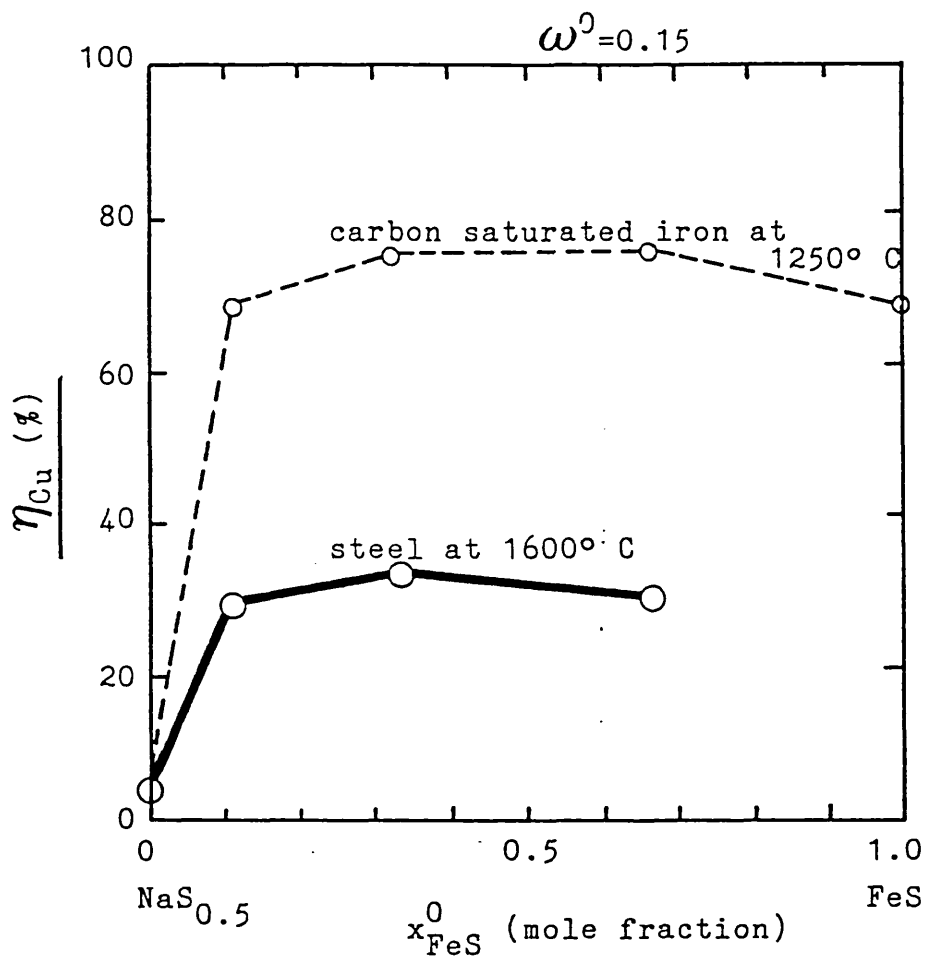
(b) Distribution coefficient of copper,
 $L'_{Cu} (=x_{CuS_{0.5}}/x_{Cu})$.



(c) Sulphur concentration in the metal phase.



(d) Initial vs final FeS concentration in the slag phase.



- 1) initial metal=3000g with $x_{Cu}^0=0.01$,
and $x_S^0=0$
- 2) initial slag=450g (NaS_{0.5}-FeS mixed
slag)
- 3) no Na vaporization allowed
- 4) calculated by the steady state model

Fig.3-22 Comparison between carbon saturated iron and steel (de-Cu using NaS_{0.5}-FeS mixed slag).

- In the case of steel, $\eta_{\text{Cu}} \sim 30\%$ and in the case of carbon saturated iron, $\eta_{\text{Cu}} \sim 70\%$ except in the lower x_{FeS}^0 region.
- The distribution coefficient of Cu :

$$L_{\text{Cu}}' \simeq 1-10 \text{ for steel}$$

$$L_{\text{Cu}}' \simeq 10-80 \text{ for carbon saturated iron}$$
- S pick-up in the metal phase is larger in steel than in carbon saturated iron.

Results predicted by the full model are summarised below:

- 1) Effect of slag composition binary mixture of $\text{NaS}_{0.5}$ and FeS on copper and tin removal from carbon saturated iron.

The results are shown in Figs. 3-23, 24 and 25(a) - (d) with x_{FeS}^0 increasing from 0 to 0.67.

- Significant change of composition finishes at approximately $t^* \simeq 3$ in the dimensionless time (approximately 11 minutes).
- C is an inert element in these computing conditions.
Change of x_{C} , means change of the total moles in the metal phase.
- η_{Sn} increases with increasing x_{FeS}^0 but η_{Cu} has a maximum value around $x_{\text{FeS}}^0 = 0.33$. This also shown in Fig. 3-15.
- As the initial S content is very low, e.g. $x_{\text{S}}^0 = 1 \times 10^{-6}$, x_{S} increases very quickly with time. The rate of this sulphurisation increases with increasing x_{FeS}^0 .
- $x_{\text{CuS}_{0.5}}$ increases with increasing x_{FeS}^0 . Slag weight at $t^* = 5.9$ decreases with increasing x_{FeO}^0 .
- FeO in the initial slag phase, $x_{\text{FeS}}^0 = 0.001$, is reduced by $\text{NaS}_{0.5}$, producing $\text{NaO}_{0.5}$

- 2) Effect of Na vaporization at the metal/slag interface on copper and tin removal.

The results are shown in Figs. 3-23, 24, 25(b) (b_1) and in Fig. 3-26.

- The change of weight in each phase is shown in Table 3-9.
- In the case (b_1), $x_{\text{NaS}_{0.5}}$ decreases almost linearly with time. x_{Fe} increases in the earlier stage and later (after $t^* = 1.5$) x_{Fe} decreases.

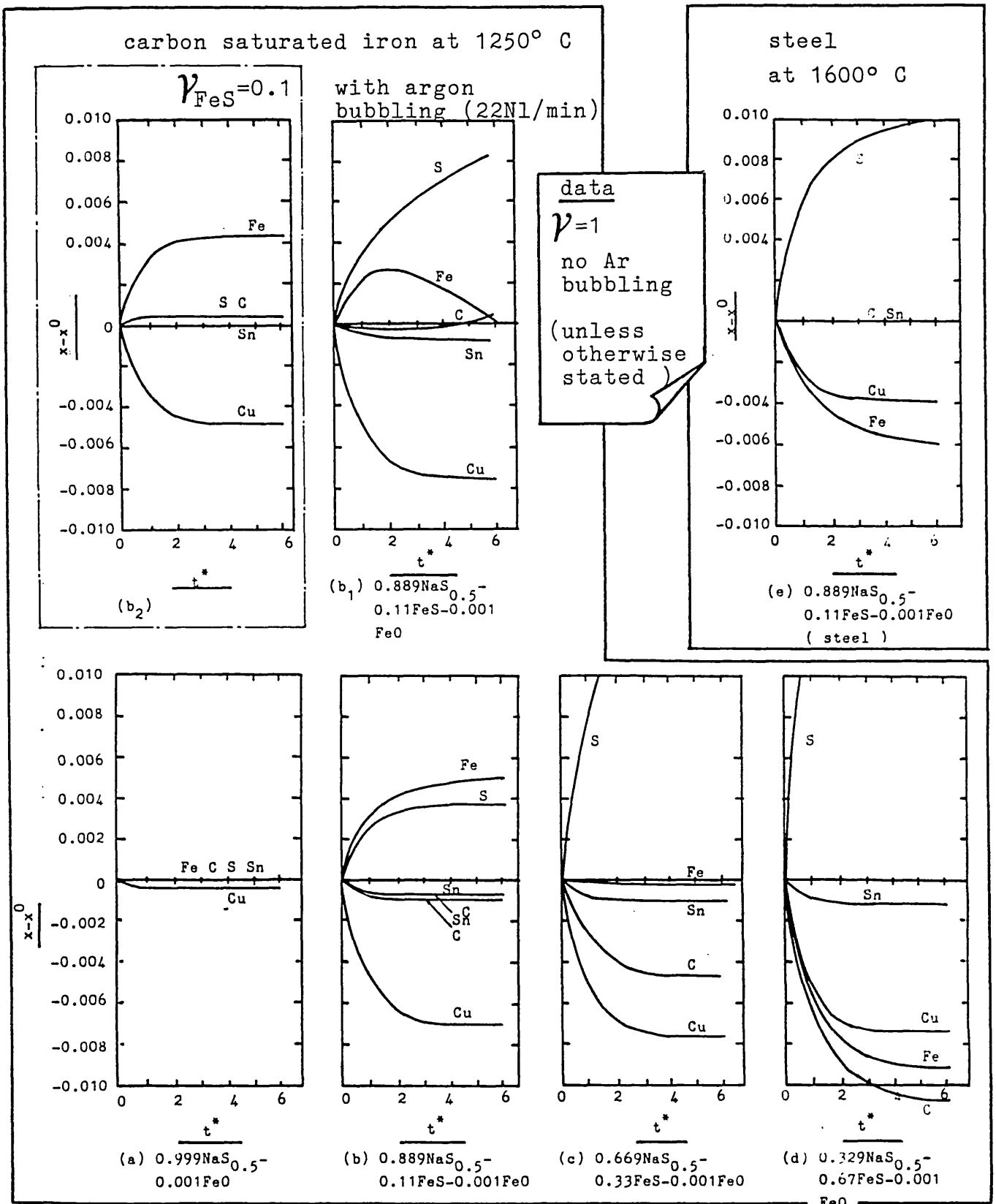


Fig.3-23 Change of composition of the metal phase with time

(t^* denotes dimensionless time defined by t/t_{ref} where $t_{\text{ref}}=V/k_m S$, vertical coordinate is the difference between the current and initial mole fraction ($=x-x^0$), calculated by the full model, metal=3000g, slag=450g, $S=5 \times 10^{-3} \text{ m}^2$, $x_{\text{Cu}}^0=0.01$, $x_{\text{Sn}}^0=0.002$).

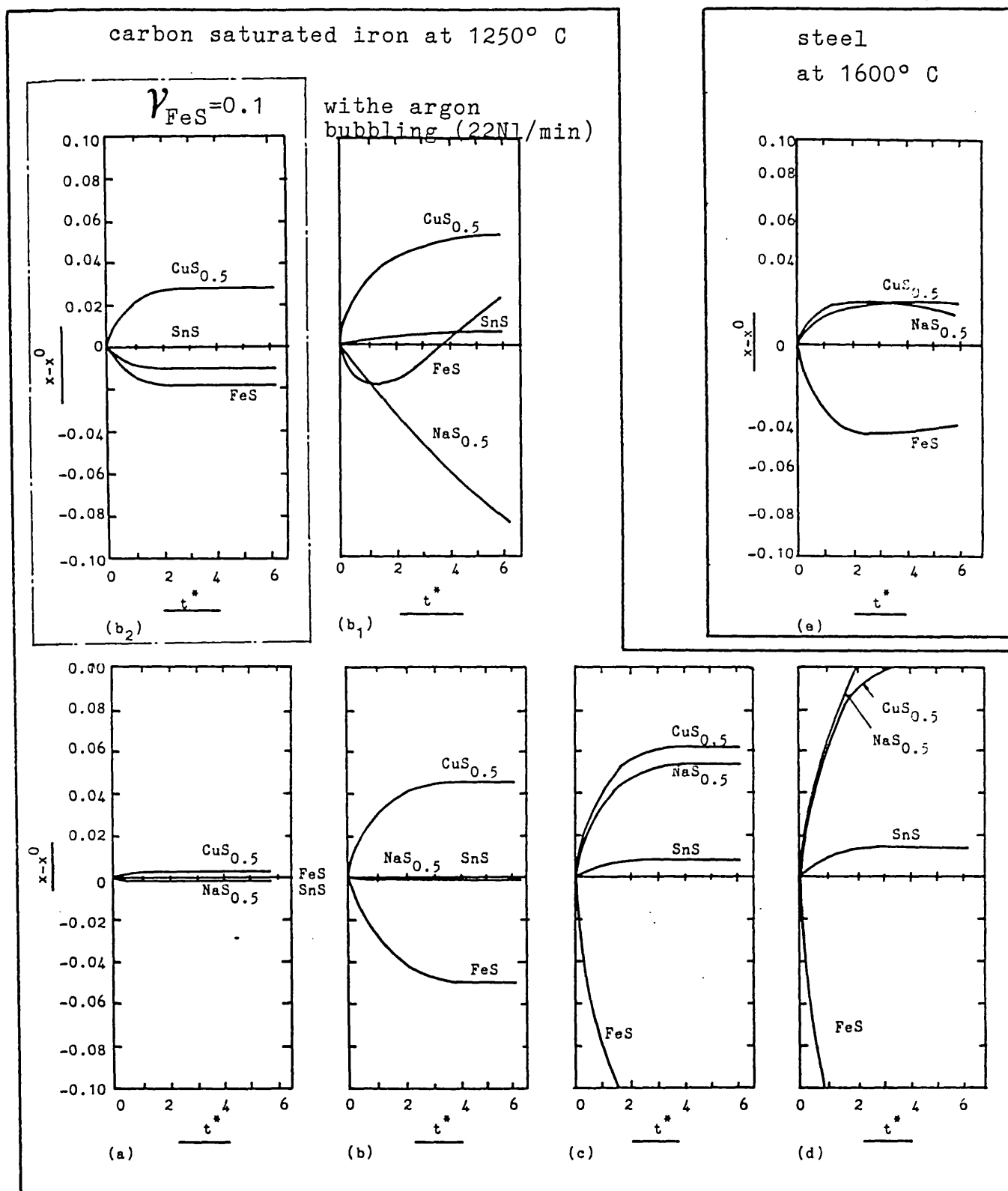


Fig.3-24 Change of composition of the slag phase with time (sulphide, simulation conditions are same as those of Fig.3-23).

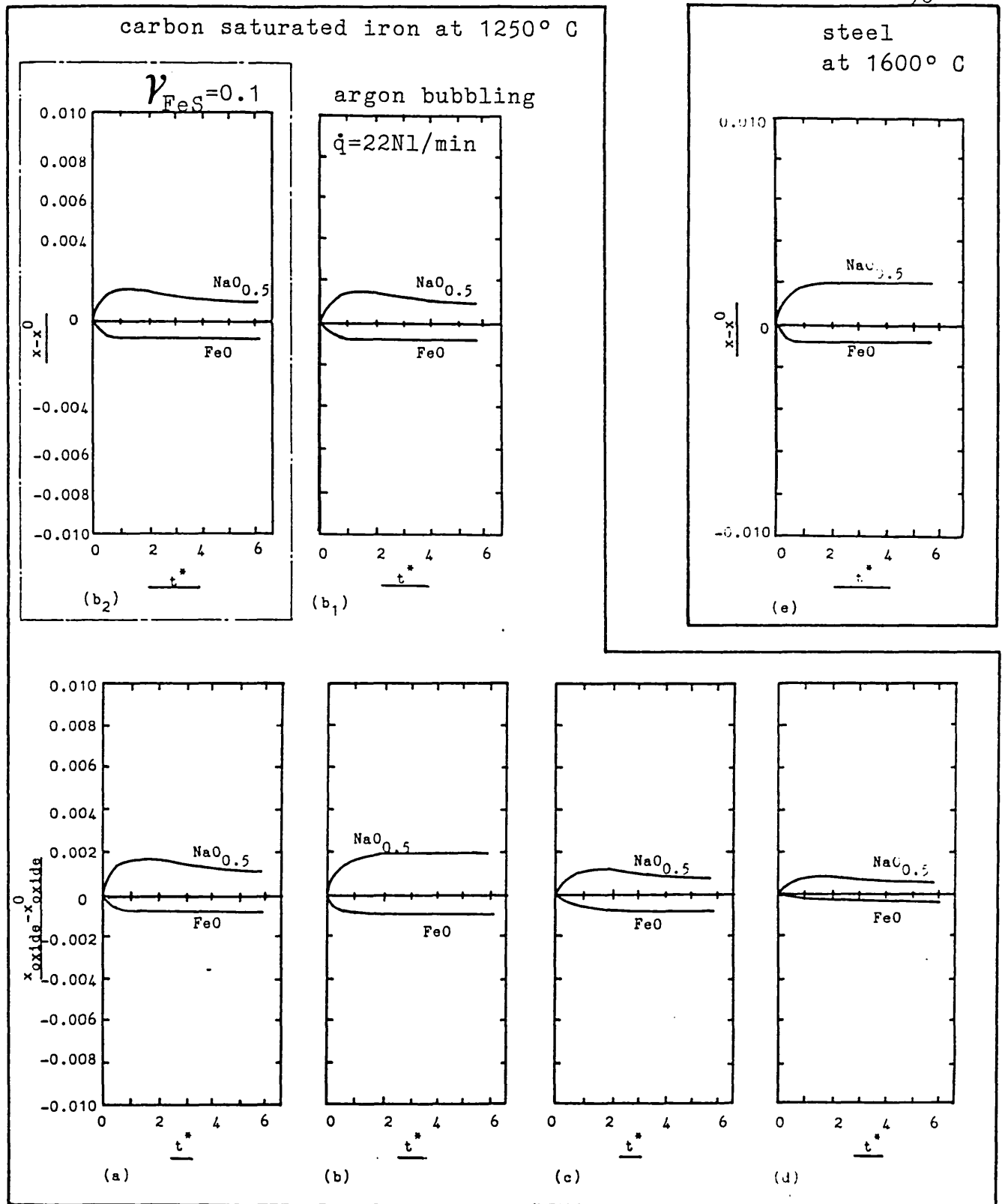
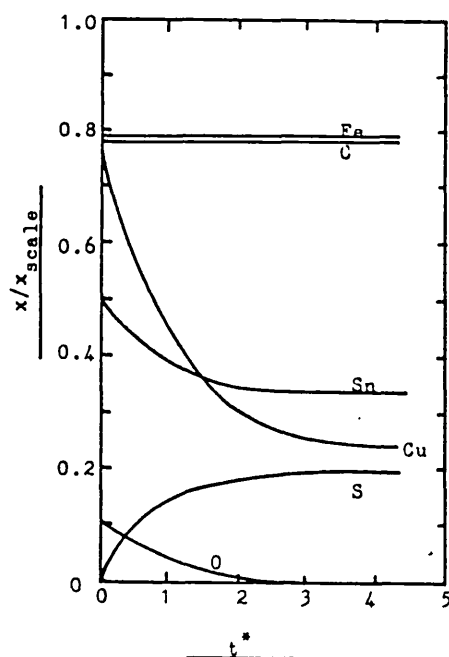


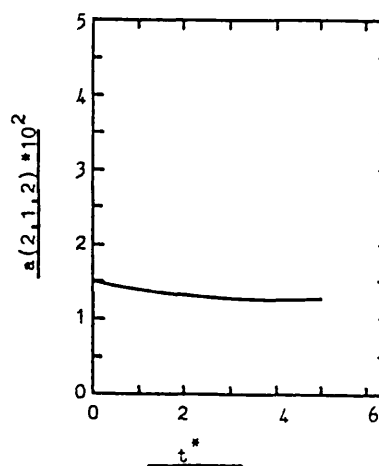
Fig.3-25 Change of composition of the slag phase with time (oxide, simulation conditions are same as those of Fig.3-23).

- The interfacial activity of sulphur (a_S^i at the metal/slag interface) has a larger value in case (b_1) than in case (b). In case (b), a_S^i decreases with time. On the other hand, a_S^i increases with time in case (b_1).
 - x_O decreases with time.
- 3) Comparisons between carbon saturated iron and steel.
The results are shown in Figs. 3-23, 24 and 25 (b) (e).
- S pick-up in the metal phase is larger in the case of steel than in the case of carbon saturated iron.
- 4) Effect of activity coefficient of iron sulphide γ_{FeS} on copper and tin removal from carbon saturated iron.
The results are shown in Figs. 3-23, 24 and 25(b) (b_2)
- S pick-up in the metal phase is larger in case $\gamma_{FeS} = 1(b)$ than $\gamma_{FeS} = 0.1 (b_2)$.
- 5) Change of weight of each phase.
The results are shown in Figs. 3-27.
- 3.4g of initial 450g $NaS_{0.5}$ has been transferred from the slag phase to the gas phase until $t = 3400$ sec. (at $1350^\circ C$). At $t = 870$ sec., the flux density of $NaS_{0.5}$ at the gas/slag interface is $6.5 \times 10^{-3} \text{ mol/m}^2 \text{ s}$ (interfacial area is $5 \times 10^{-3} \text{ m}^2$).
 - In the case where a mechanism of Na vaporization at the metal/slag interface is included, the change of weight of each phase enhanced.
 - With increasing x_{FeS}^0 , gain of the metal weight increases. In the case of steel, the loss of slag weight is larger than in the case of carbon saturated iron.
- 6) Effect of initial sulphur content x_S^0 on copper and tin removal.
The results are shown in Fig. 3-27.
- η_{Cu} and η_{Sn} increase with increasing x_S^0 .
 - FeS addition to the initial slag helps copper and tin removal. It is equivalent to an increased x_S^0 .
 - Neutral slag is slightly less effective than $NaS_{0.5}$ slag.

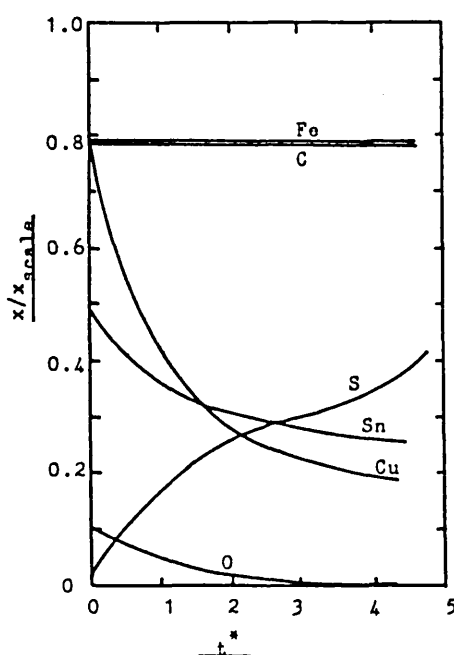


(a) Evolution of composition in the metal phase (without argon bubbling).

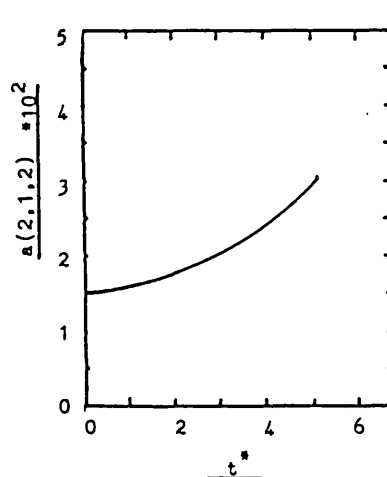
$x_{scale} :$ O = $1 \cdot 10^{-5}$
 S = 0.02
 C = 0.25
 Fe = 1.0
 Cu = 0.012
 Sn = 0.004



(b) Interfacial sulphur activity at the metal/slag interface.



(c) Evolution of composition in the metal phase (with argon bubbling=22 Nl/min).



(d) Interfacial sulphur activity at the metal/slag interface.

Fig.3-26 Effect of argon bubbling on de-Cu
 (80wt%NaS_{0.5}-20wt%FeS slag=450g,
 carbon saturated iron=3000g,
 calculated by the full model).

Discussion of above results

1) Comparison between the full model and the steady state model.

The characteristics of these two models are compared in Table 3-10. In cases where oxygen activity and evaporation of elements are not important, these two models provide equivalent solutions. In Fig. 3-15, η_{Cu} predicted by the full model is slightly larger than that by the steady state model. This is because the initial slag compositions are slightly different. The small amount of FeO ($x_{FeO}^0 = 0.001$) used in the full model causes a slight difference in η_{Cu} . $NaS_{0.5}$ is oxidised to $NaO_{0.5}$ and S is released. This S causes copper removal. There are two ways for $NaS_{0.5}$ to supply S. One is Na vaporization and another is oxidation of $NaS_{0.5}$. S₂?

2) Effect of Na vaporization at the metal/slag interface on copper and tin removal.

This effect is significant in the lower x_{FeS}^0 region. S, forming $CuS_{0.5}$ and SnS , is provided by $NaS_{0.5}$, FeS and initial sulphur content in the metal phase. Initial sulphur content in the metal phase ^{is} zero. Particularly in the case of pure $NaS_{0.5}$ slag, the distribution coefficient of copper L'_{Cu} is :

$$L'_{Cu} \approx 0.1 \quad \text{assuming no Na vaporisation}$$

$$L'_{Cu} \approx 16 \quad \text{assuming 20\% of Na vaporised at the metal/slag interface } (\alpha = 0.2).$$

The reported value [18] of the distribution coefficient, L_{Cu} , defined by the ratio of weight % in the slag and metal is approximately 7.4 under these conditions. This value can be transformed to the same definition as the present work (ratio of mole fractions) $L_{Cu} = 7.4$ is equivalent to $L'_{Cu} = 6.1$. It is not possible to explain the reported values for L_{Cu} without assuming Na vaporization. When the Na vaporization mechanism is included, the activity of sulphur at the metal/slag interface increases with time. This interfacial sulphur activity is higher than the bulk activity. It causes the sulphur flux from the interface to the metal phase, leading to the high sulphur content.

In the initial stage, sulphur is supplied by both FeS and $\text{NaS}_{0.5}$ and is consumed by $\text{CuS}_{0.5}$ and SnS formation. Afterwards, at about $t^* \geq 1.5$, Cu does not continue to react with sulphur to any extent and excess sulphur, released by $\text{NaS}_{0.5}$ decomposition, reacts with Fe, forming FeS. In this stage, Fe transport from the metal phase to the slag phase occurs. This causes Fe loss from the metal phase. There is also further sulphur pick-up in the metal phase. These deleterious phenomena can be avoided by terminating argon bubbling after a given period, say $t^* \approx 3$ and/or by deslagging.

3) Loss of $\text{NaS}_{0.5}$ weight by escape into the gas phase.

$\text{NaS}_{0.5}$ decomposes into the Na and S. The sodium and sulphur are vaporised from the slag/gas interface and sodium can react with oxygen in the gas phase.

In the case of $\text{NaS}_{0.5}$ slag, decomposition of $\text{NaS}_{0.5}$ is significant under the elevated temperature conditions. The experimental data measured by Topkaya [18] and the predicted result by the model in this work are compared in Fig. 3-27. According to Topkaya's data, the rate of loss of $\text{NaS}_{0.5}$ is approximately proportional to the interfacial area.

Mass transfer coefficient in the gas phase can be roughly estimated for Topkaya's data with mean vapour pressure $\bar{p}_{\text{Na}}$ and $\bar{p}_{\text{S}_2}$ which are predicted by the model in the present work.

$\bar{K}_g$ (Topkaya's experiment) $\approx 2.9 \times 10^{-2}$ [m/s]. This is fairly good agreement with the value used in the model in the present work.

$$(k_g = 2 \times 10^{-2} \text{ m/s})$$

4) Effect of slag composition on copper and tin removal.

Because of FeS decomposition into Fe and S, the sulphur content in the metal phase increases. With increasing x_{FeS}^0 at constant β^0 (or ω^0) this is favourable to copper and tin removal, but the slag weight decreases. Therefore, there is a maximum value of η_{Cu} , as is shown in Figs. 3-15 and 3-19. With constant ω^0 , $x_{\text{FeS}}^0 \approx 0.33$ gives a maximum value for η_{Cu} .

Addition of FeS in the slag helps copper removal. Small addition of FeS suppresses Fe transport from the metal phase to the slag phase. Sufficient addition causes Fe transport from the slag phase to the metal phase. Accuracy of prediction depends on the reliability of thermodynamic data, especially on activity coefficients of compounds in the slag.

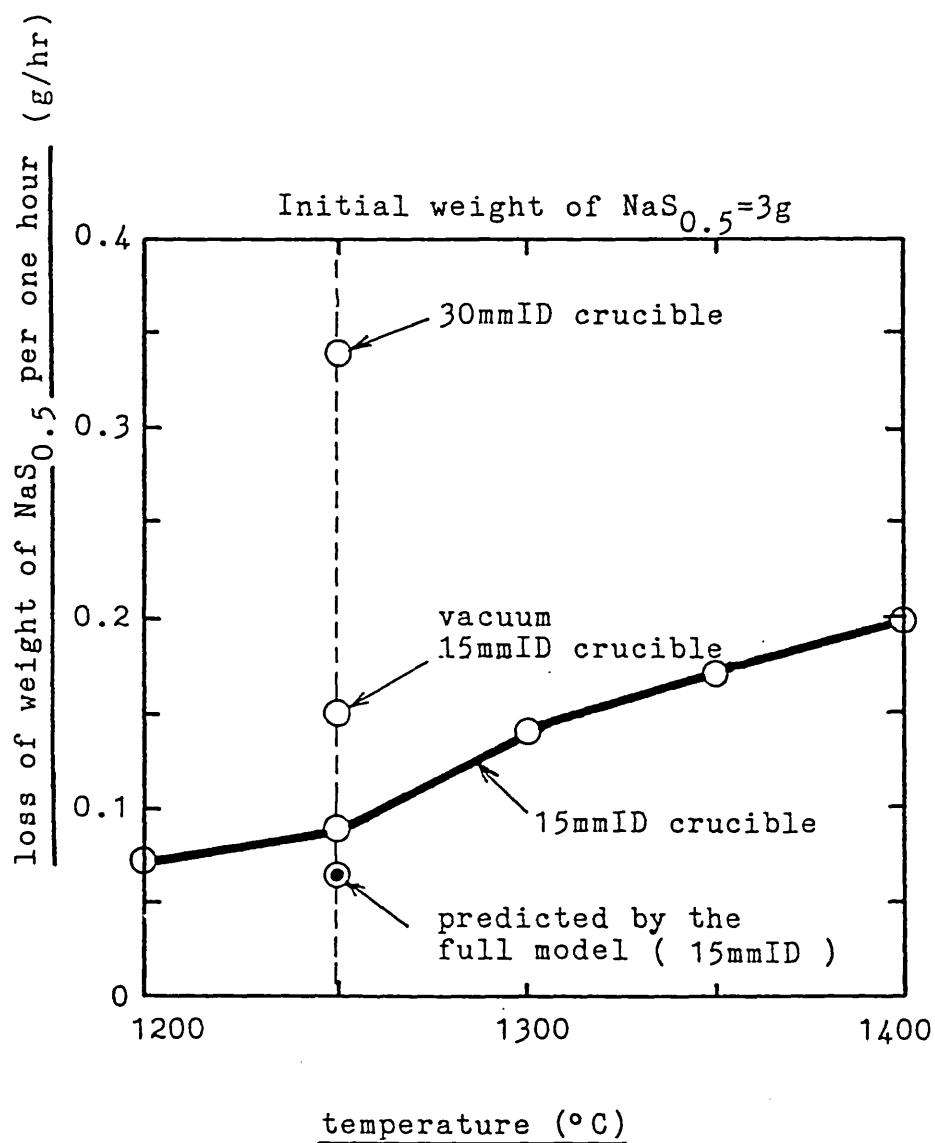
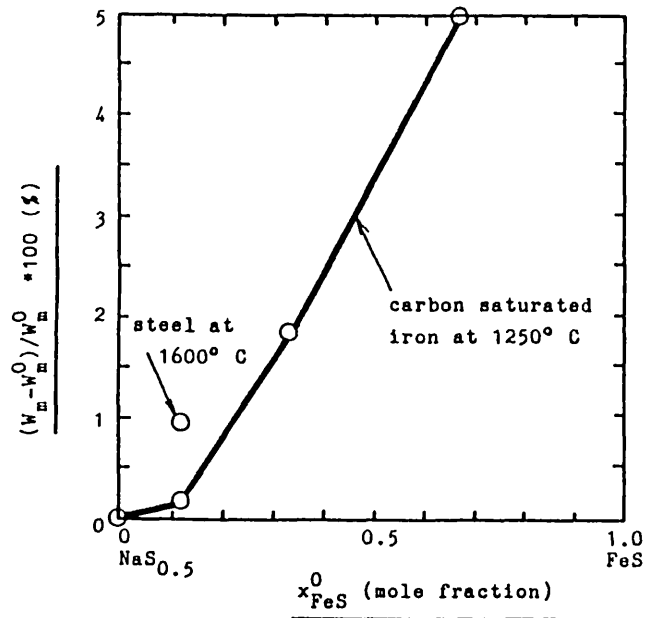
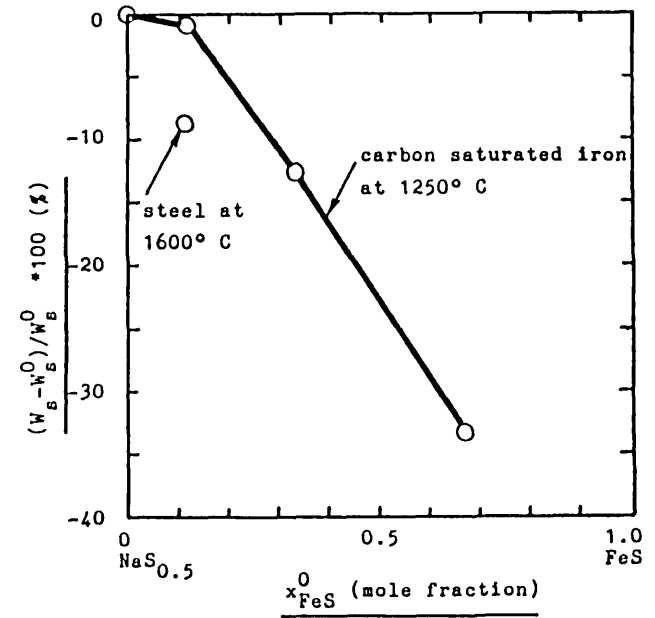


Fig.3-27(a) Thermal stability of $\text{NaS}_{0.5}$
 (decomposition rate of $\text{NaS}_{0.5}$
 measured by Topkaya (18) and
 predicted by the full model in
 the present work).

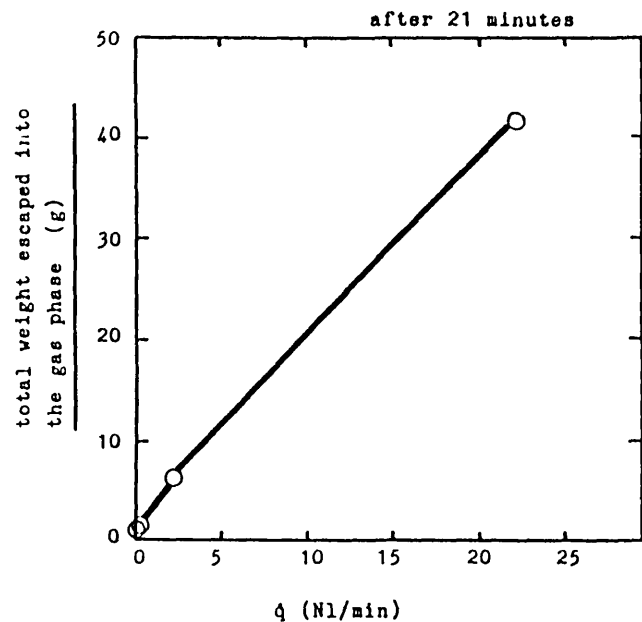


(b₁) Change of weight of the metal phase.

Fig.3-27. Change of weight of each phase (after 21 minutes, initial metal weight $W_m^0=3000g$, initial slag weight $W_s^0=450g$, $x_{Cu}^0=0.01$, activity coefficients of sulphides are unity).

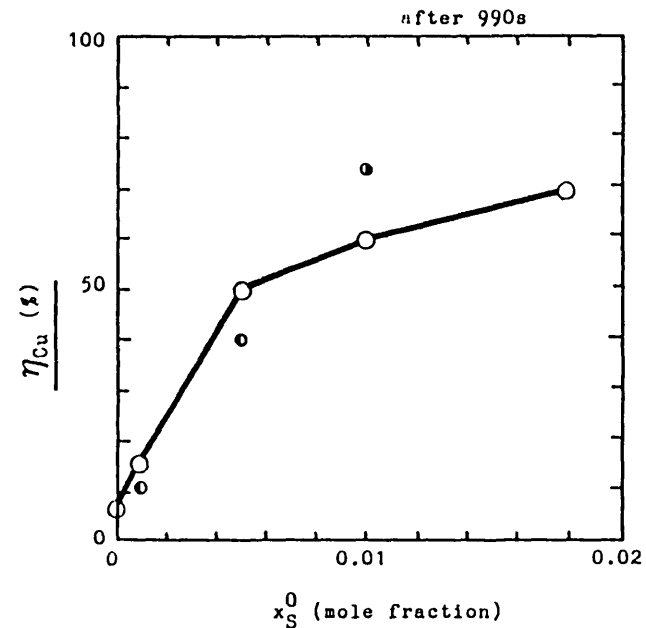


(b₂) Change of weight of the metal phase.



- q = argon gas flow rate
- 1) initial metal=3000g
 - 2) initial slag=450g (0.889NaS_{0.5}-0.11FeS-0.001FeO ; in mole fraction)
 - 3) carbon saturated iron at 1250° C
 - 4) calculated by the full model

Fig.3-27 (c) Relation between the total weight escaped into the gas phase and argon gas flow rate (for argon bubbling).



- pure NaS_{0.5} slag
- 0.80NaS_{0.5}-0.20FeS mixed slag
- inert slag, e.g. CaF₂

Fig.3-27 (d) Effect of the initial sulphur content in the metal phase on de-Cu (carbon saturated iron at 1350° C, no Na vaporization allowed, initial slag=450g, initial metal=3000 g, calculated by the full model).

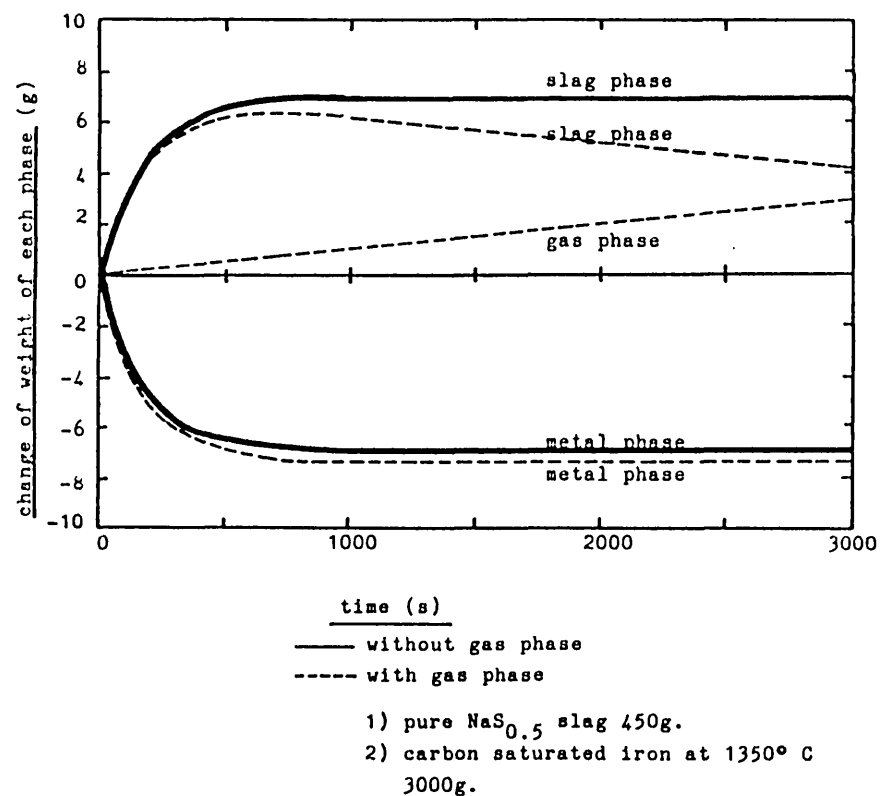


Fig.3-27(e) Effect of the gas phase on de-Cu/de-Sn (predicted by the full model).

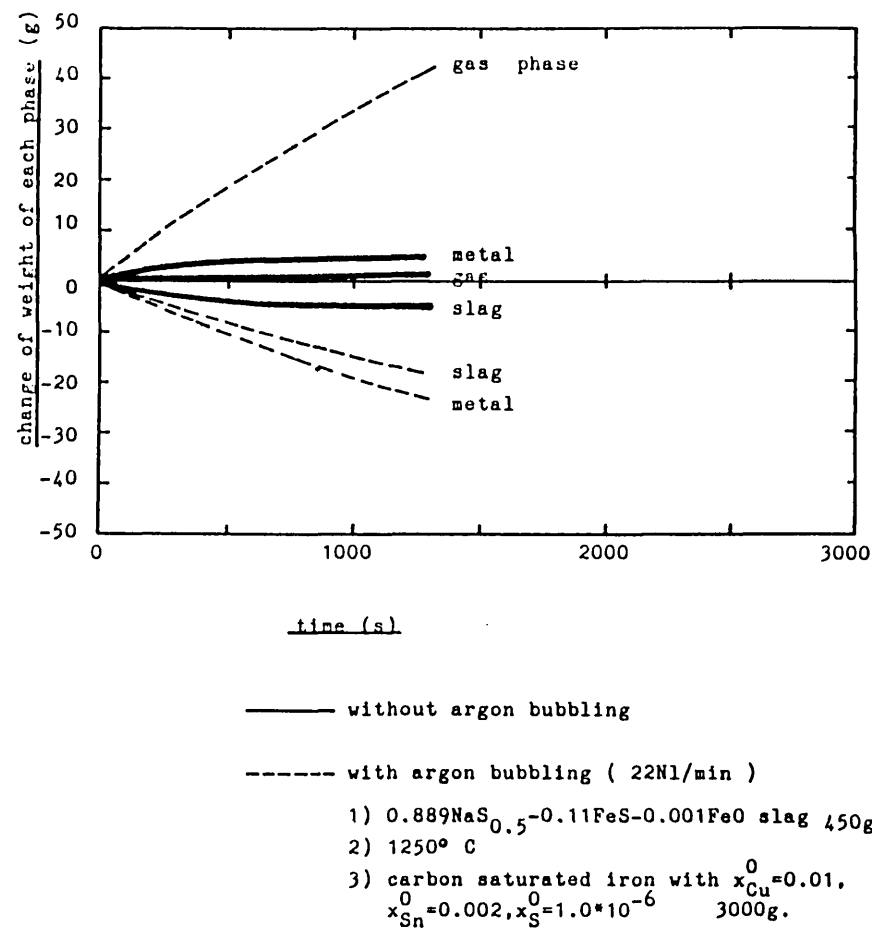


Fig.3-27 (f) Change of weight of each phase during de-Cu/de-Sn from carbon saturated iron (effect of argon bubbling).

Table 3-9 Weight of each phase (effect of Na vaporization).

	without Na vaporization	with Na vaporization
gas phase	increase 0.8g	increase 41.6g
slag phase (initially 450g)	$W_s = 445.2g$ (-4.8g)	$W_s = 431.8g$ (-18.2g)
metal phase (initially 3000g)	$W_m = 3004.0g$ (+4.0g)	$W_m = 2976.6g$ (-23.4g)
remarks	no argon bubbling	argon bubbling 22Nl/min

Table 3-10 Comparison of two models (the steady state and full model).

	Steady state model	Full model
phases involved	metal/slag/gas gas phase is involved through Na vaporization.	metal/slag/gas
key variable	sulphur activity	interfacial sulphur and oxygen activity at each interfaces (metal/slag, slag/gas, metal/gas, metal/bubble)
time evolution	no (steady state)	unsteady state, the rate of reaction is controlled by mass transfer in the films both side of interfaces
governing equations	chemical equilibria and mass balance	chemical equilibria at interfaces, flux density continuity and mass balance

- 5) Effect of initial sulphur content x_S^0 on copper and tin removal.

If there is a sufficient amount of sulphur in the metal, the slag phase composition is not important as long as there is sufficient capacity for absorption of $\text{CuS}_{0.5}$ and SnS .

- 6) Comparison between steel and carbon saturated iron.

Under the conditions described in Table 3-8,

$$(\eta_{\text{Cu}})_{\text{steel}} \sim 30\%$$

$$(\eta_{\text{Cu}})_{\text{carbon saturated iron}} \sim 70\%$$

This difference is mainly due to the different activity coefficients of Cu. Distribution coefficient for copper is defined by the equation (3-44) which is produced below:

$$\frac{x_{\text{CuS}_{0.5}}}{x_{\text{Cu}}} = K_{\text{Cu}} \frac{f_{\text{Cu}} \cdot f_{\text{S}}^{\frac{1}{2}} \cdot x_{\text{S}}^{\frac{1}{2}}}{\gamma_{\text{CuS}_{0.5}}}$$

According to $\{\text{Fe}\} + [\text{S}] = \{\text{FeS}\}$ equilibrium

$$x_{\text{S}} = \frac{1}{K_{\text{Fe}}} \cdot \frac{\gamma_{\text{FeS}}}{\gamma_{\text{Fe}} \cdot f_{\text{S}}} \cdot x_{\text{FeS}} / x_{\text{Fe}} \quad (3-80)$$

Substituting x_{S} in the equation (3-50) by the equation (3-80)

$$\begin{aligned} \frac{x_{\text{CuS}_{0.5}}}{x_{\text{Cu}}} &= \frac{K_{\text{Cu}}}{K_{\text{Fe}}^{\frac{1}{2}}} \cdot \frac{f_{\text{Cu}} \cdot \gamma_{\text{FeS}}^{\frac{1}{2}}}{\gamma_{\text{CuS}_{0.5}} \gamma_{\text{Fe}}^{\frac{1}{2}}} \cdot \frac{(x_{\text{FeS}})^{\frac{1}{2}}}{x_{\text{Fe}}} \\ &\approx \frac{K_{\text{Cu}}}{K_{\text{Fe}}^{\frac{1}{2}}} \cdot \frac{\gamma_{\text{FeS}}^{\frac{1}{2}}}{\gamma_{\text{CuS}_{0.5}} \gamma_{\text{Fe}}^{\frac{1}{2}}} \cdot \left(\frac{x_{\text{FeS}}^0}{x_{\text{Fe}}^0} \right)^{\frac{1}{2}} \cdot f_{\text{Cu}} \quad (3-81) \end{aligned}$$

putting the data for each case into the equation (3-81),

Table 3-8 Simulation conditions for de-Cu/de-Sn (by the steady state model).

	carbon saturated iron	steel
1) Initial composition (mole fraction)		
Fe	0.80	0.983
Cu	0.01	0.01
Sn	0.002	0.002
Na	1×10^{-8}	1×10^{-8}
C	0.188	0.005
S	0	0
FeS	x_{FeS}^0	x_{FeS}^0
NaS _{0.5}	$1-x_{FeS}^0$	$1-x_{FeS}^0$
CuS _{0.5}	0	0
SnS	0	0
2) Gibbs free energy change (cal/mol)		
Fe + S = FeS	$G^0 = 810 - 4.31T$	
$Cu + \frac{1}{2} S = CuS_{0.5}$	$G^0 = -9660 - 1.61T$	
Sn + S = SnS	$G^0 = 680 - 3.44T$	
$Na + \frac{1}{2} S = NaS_{0.5}$	$G^0 = -64200 + 10.76T$	
Na = Na	$G^0 = -6780 - 18.11T$	
3) Activity coefficient		
Fe	0.85	1.0
Cu	2.40	1.0
Sn	1.7	1.0
Na	1.0	1.0
C	4.41	1.0
S	3.36	1.0

	carbon saturated iron	steel
γ_{FeS}	1.0	1.0
$\gamma_{CuS_{0.5}}$	1.0	1.0
γ_{SnS}	1.0	1.0
$\gamma_{NaS_{0.5}}$	1.0	1.0
4) Temperature	1250° C	1600° C
5) Initial metal weight (kg)	W_m^0	
moles (mol)	M_m^0	
6) Initial slag weight (kg)	W_s^0	$\omega^0 = W_s^0 / W_m^0$
moles (mol)	M_s^0	$\beta^0 = M_s^0 / M_m^0$

Note : Relation between ω^0 and β^0 is derived below.

1) Molecular weight M (kg/mol). e.g. $M_{Fe} = 0.056$,
 $M_{NaS_{0.5}} = 0.039$, $M_{FeS} = 0.088$

2) Initial slag composition.

NaS_{0.5} : $1-x_{FeS}^0$ NaS_{0.5}-FeS mixed slag.
FeS : x_{FeS}^0

3) Relation between W_m^0 and M_m^0 .

$$M_m^0 (M_H x_H^0) = W_m^0$$

4) Relation between W_s^0 and M_s^0 .

$$M_s^0 (M_{NaS_{0.5}} (1-x_{FeS}^0) + M_{FeS} x_{FeS}^0) = W_s^0$$

5) Relation between ω^0 and β^0 :

$$\beta^0 \cdot \omega^0 = (M_H x_H^0) / (M_{NaS_{0.5}} (1-x_{FeS}^0) + M_{FeS} x_{FeS}^0)$$

6) The results are shown in Fig.3-6.

$$x_{\text{CuS}_{0.5}} / x_{\text{Cu}} = 20 \text{ for carbon saturated iron at } 1250^{\circ}\text{C},$$

$$x_{\text{FeS}}^0 = 0.11$$

$$x_{\text{CuS}_{0.5}} / x_{\text{Cu}} = 3.8 \text{ for steel at } 1600^{\circ}\text{C}, x_{\text{FeS}}^0 = 0.11$$

In order to increase the distribution coefficient, it is the most sensible to decrease $\gamma_{\text{CuS}_{0.5}}$ by choosing adequate slag composition.

3-3-3 Cr-slag cleaning

The Cr-slag reduction by carbon was simulated by the full model. All the necessary thermo-dynamic data on Cr alloys are not available. For simplicity, all activity coefficients are assumed to be unity. In the experimental work carried out by Taneka [57], Cr-slag is continuously added with carbon into a graphite crucible and is melted by a plasma. In the full model, the mechanism for reduction of Cr-slag is:

- i) Cr-slag reduction by carbon in the metal phase at the metal/slag interface.
Carbon is assumed to be supplied by erosion of the graphite crucible.
- ii) Cr-slag reduction by CO gas at the slag/gas interface.

Rate phenomena can be determined from three parameters.

- i) Mass transfer rate constant for CO evolution, G_{CO} [$\text{mol}/\text{m}^2 \text{ s}$].
- ii) Mass transfer coefficient in the metal k_m [m/s], which can be used to infer mass transfer coefficients in other phases.
- iii) Cr-slag feed rate, $\dot{M}_{\text{POW}}$ [kg/s]

Temperatures can affect the rate phenomena through driving force terms which are relevant to interfacial chemical equilibria.

- 1) The effect of G_{CO} was studied by varying it from 3×10^{-3} to 3×10^{-1} . $G_{CO} = 3 \times 10^{-3}$ [mol/m² s] was chosen because it was used in the case of de-P/de-S from carbon saturated iron by Ohguchi [10].

The effect of G_{CO} on reduction of Cr-slag was summarised in Fig. 3-28. CO flux is expressed by $(CO \text{ flux}) = S \cdot G_{CO} \cdot (P_{CO}/p_T - 1)$ [mol./s].

Reduction rate of Cr-slag can be enhanced by increasing the product $S \cdot G_{CO}$.

- 2) The effect of k_m . The same values of the mass transfer coefficients for all phases as used by Ohguchi were chosen [10]. These values were multiplied by a factor ζ and tested by checking the behaviour of the model for various values of ζ

i.e. base data

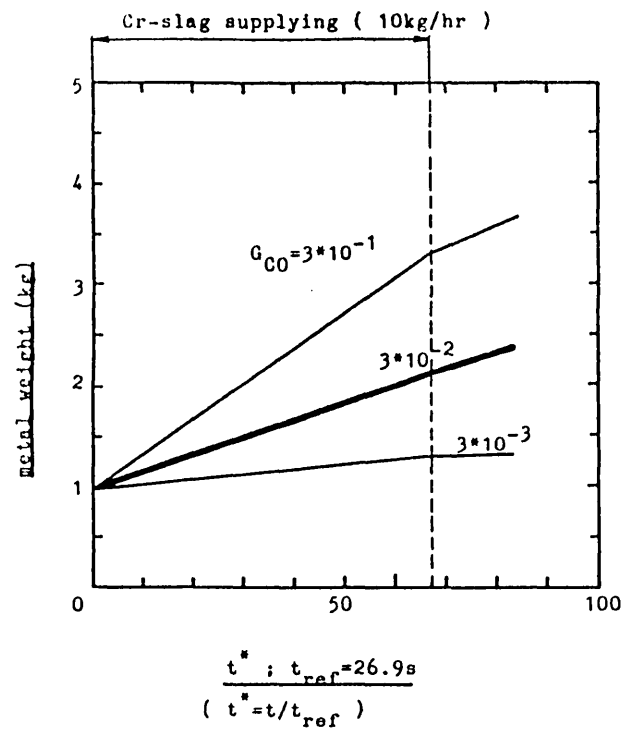
$$\begin{cases} k_m = 4 \times 10^{-4} & [\text{m/s}] \\ k_m = 2 \times 10^{-4} & [\text{m/s}] \\ k_g = 2 \times 10^{-2} & [\text{m/s}] \end{cases} \rightarrow \begin{cases} k_m = 4 \times 10^{-4} \zeta & [\text{m/s}] \\ k_s = 2 \times 10^{-4} \zeta & [\text{m/s}] \\ k_g = 2 \times 10^{-2} \zeta & [\text{m/s}] \end{cases}$$

The effect of ζ is summarised in Fig. 3-29.

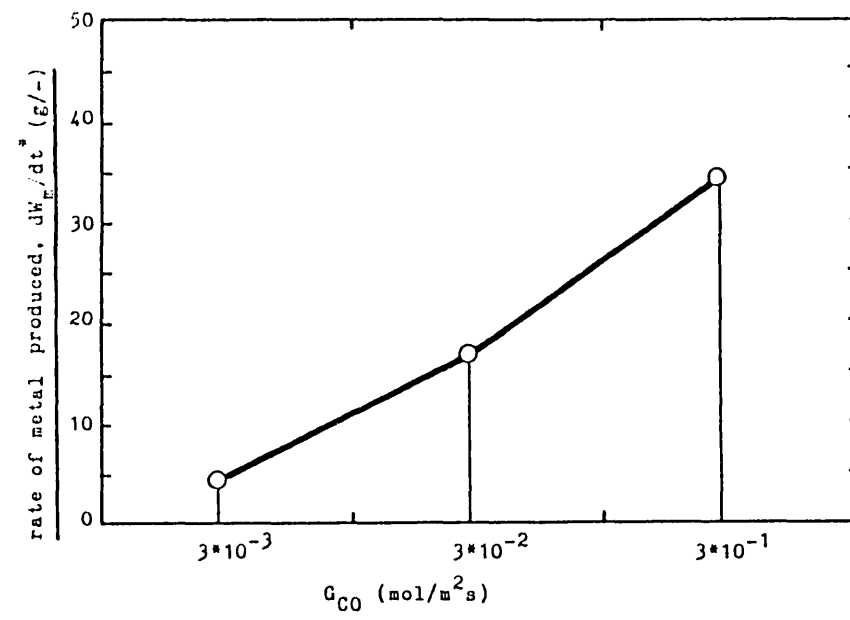
The rate of the metal weight increase is controlled by CO transport under the conditions investigated.

- 3) Cr-slag feed rate, $\dot{M}_{POW}$ [kg/s].

Simulating conditions are summarised in Table 3-11. In all cases, Cr-slag was supplied for 30 minutes at a rate varying from 5 kg/hr to 20 kg/hr. The results are shown in Fig. 3-30. Excess feed simply causes piling up of slag mass.

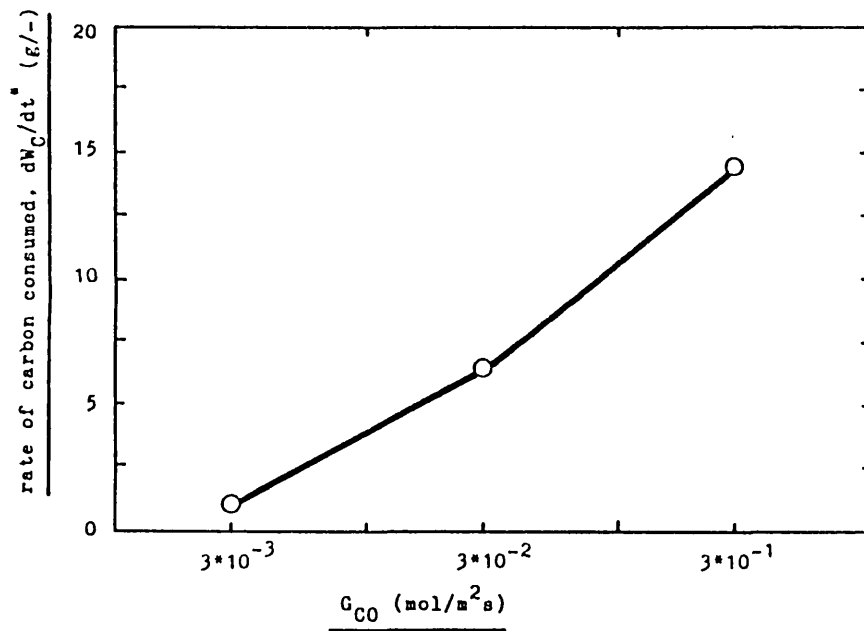


(a) Change of weight of the metal phase with time.

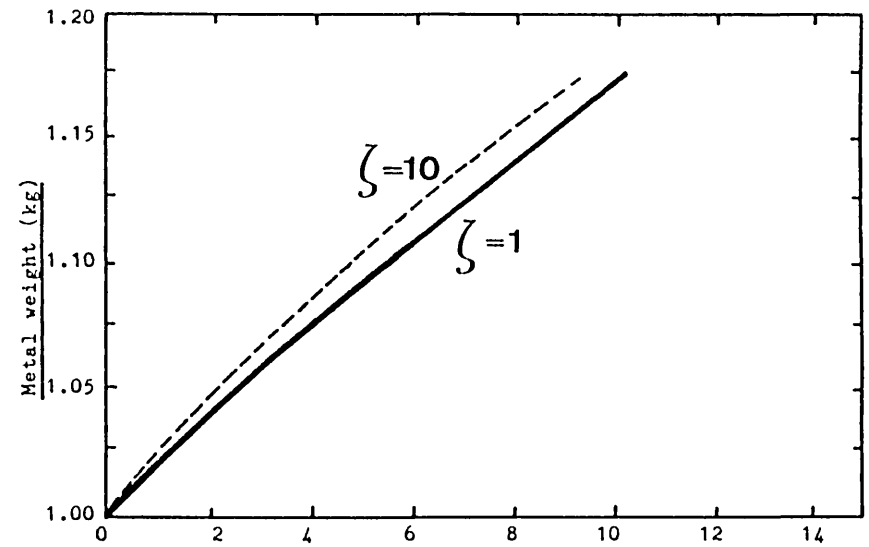


(b) The rate of metal produced (reduced by carbon).

Fig.3-28 Effect of mass transfer rate constant of CO, G_{CO} (mol/m²s), on Cr-slag cleaning (initial metal weight=1kg, at 1850° C).



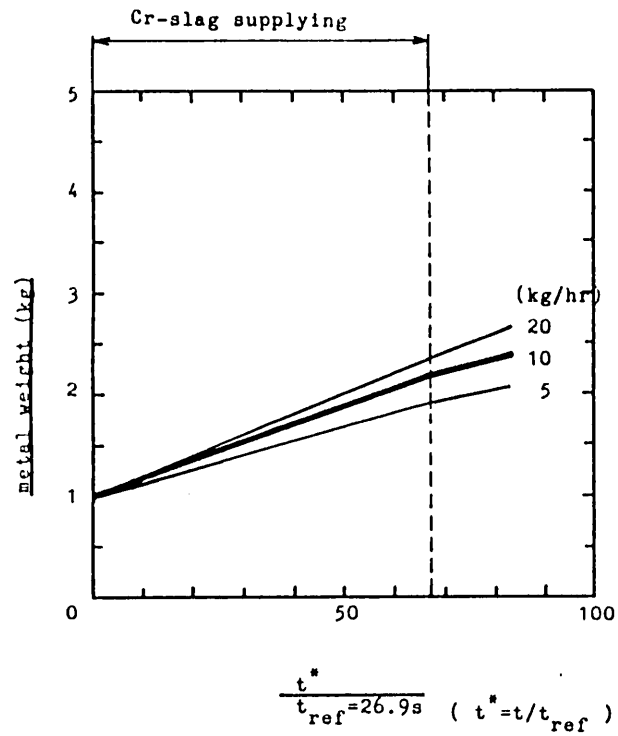
(c) The rate of carbon consumption.



$$\frac{t^*}{t_{ref} = 26.9s}$$

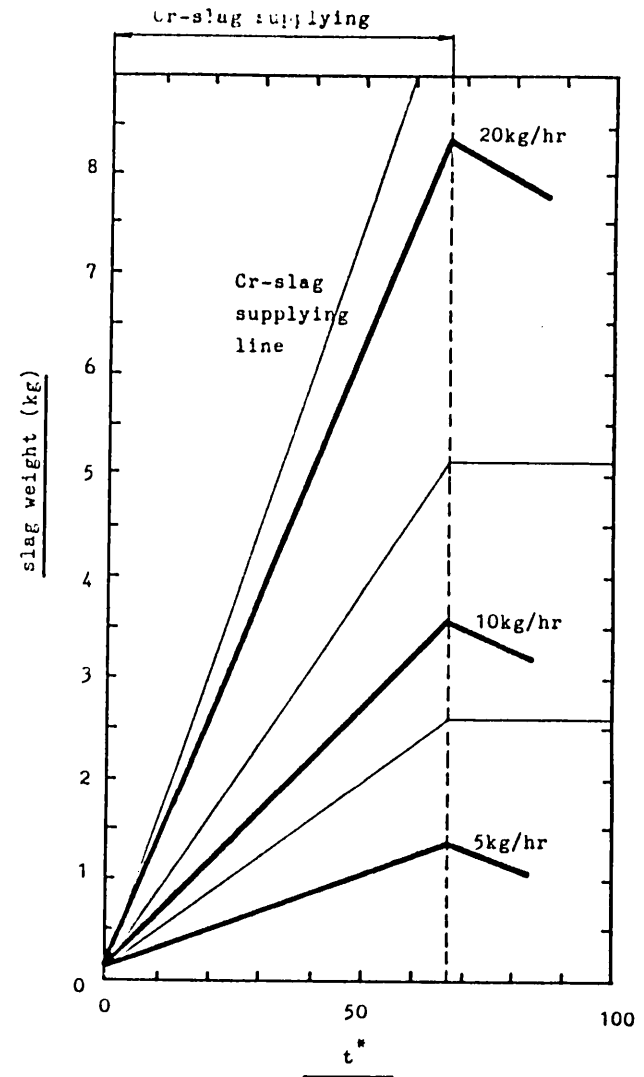
	k _m	k _s	k _g	G _{CO}	
————	4*10 ⁻⁴	2*10 ⁻⁴	2*10 ⁻²	3*10 ⁻²	{
-----	4*10 ⁻³	2*10 ⁻³	2*10 ⁻¹	3*10 ⁻²	
	(m/s)			(mol/m ² s)	

Fig.3-29 Effect of mass transfer coefficient on Cr-slag cleaning (initial metal=1kg, Cr-slag supplying rate=10kg/hr, at 1850° C).

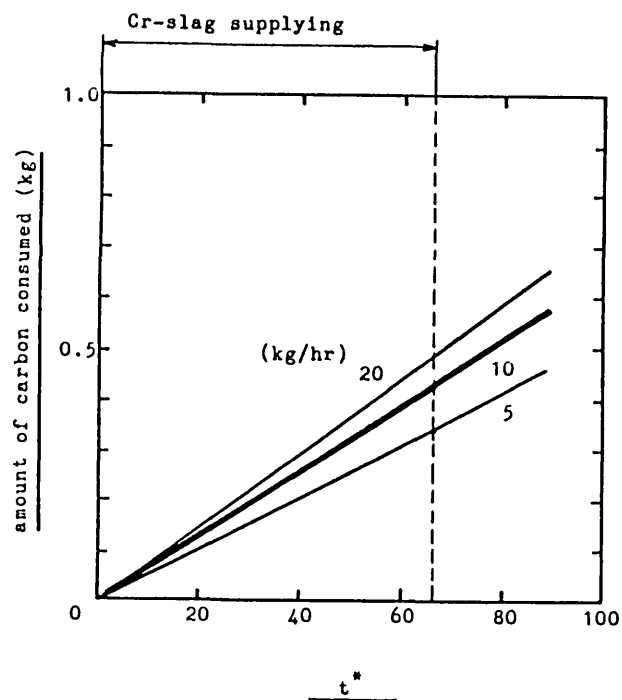


(a) Change of weight of the metal phase with time.

Fig.3-30 Effect of Cr-slag supplying rate (initial metal=1kg, at 1850° C).



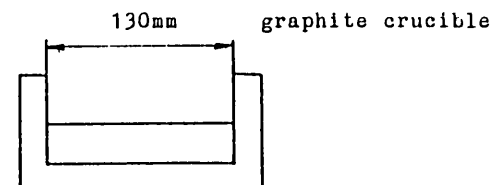
(b) Change of slag weight with time.



(c) Amount of carbon consumed.

Table 3-11 Simulation conditions for Cr-slag cleaning.

1) Configuration.



2) Initial conditions.

metal (1kg) ----

	wt%	mole fraction
Cr	67.9	0.5112
Fe	21.0	0.1469
C	10.0	0.3264
Si	1.0	0.0140
Mg	0.020	3.25×10^{-4}
Al	0.020	2.90×10^{-4}
Mn	0.10	7.05×10^{-4}

3) Cr-slag supplying rate = 5-20 kg/s.

4) Cr-slag composition ---

	wt%	mole fraction
CrO _{1.5}	57.0	0.472
FeO	14.3	0.125
SiO ₂	3.4	0.036
AlO _{1.5}	9.1	0.112
MgO	16.2	0.255

5) Cases of simulation.

Temperature (1650, 1750 and 1850° C)

Mass transfer coefficient

$$\begin{aligned}
 k_m &= 4 \times 10^{-3} - 4 \times 10^{-4} \text{ m/s} \\
 k_s &= 2 \times 10^{-3} - 2 \times 10^{-4} \text{ m/s} \\
 k_g &= 2 \times 10^{-1} - 2 \times 10^{-2} \text{ m/s} \\
 G_{CO} &= 3 \times 10^{-1} - 3 \times 10^{-3} \text{ mol/m}^2\text{s}
 \end{aligned}$$

4) The effect of temperature.

$$\{\text{CrO}_{1.5}\} = [\text{Cr}] + 1.5 [\text{O}] \quad \Delta G^0 = 95270 - 22.8T \text{ [cal/mol]} \quad (3-92)$$

$$[\text{C}] + [\text{O}] = (\text{CO}) \quad \Delta G^0 = 4740 - 225T \text{ [cal/mol]} \quad (3-93)$$

Combining the two equations, one can obtain a equation for over-all reaction,

$$\{\text{CrO}_{1.5}\} + 1.5 [\text{C}] = [\text{Cr}] + 1.5 (\text{CO}) \quad \Delta G^0 = 88160 - 56.6T \text{ [cal/mol]} \quad (3-94)$$

The higher the temperature, the more favourable the conditions are for Cr-slag reduction. The results are shown in Fig. 3-31.

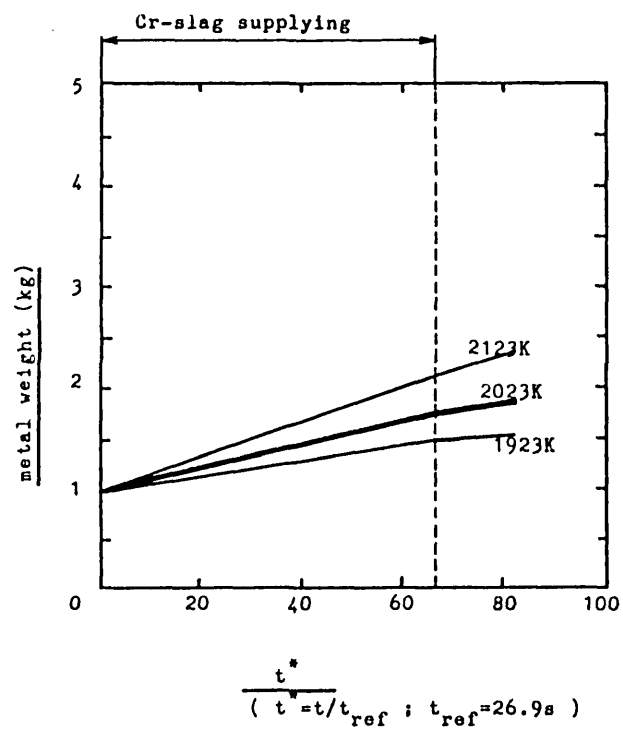
As is shown in Fig. 3-31(b), metal compositions depend on the temperature. The higher temperature, the higher concentration of Cr in the metal phase. Fe content increases with decreasing temperature under the constant carbon concentration in the metal phase.

5) Sites for reduction of Cr-slag.

There are two flux densities of Cr metal created by reduction of $\text{CrO}_{1.5}$. There are those at the slag/metal and at the slag/gas interfaces. They are compared in Fig. 3-32. Flux density of Cr metal at the metal/slag interface is dominant in the wide range of conditions which supposedly include the experimental conditions used by Tanaka [57].

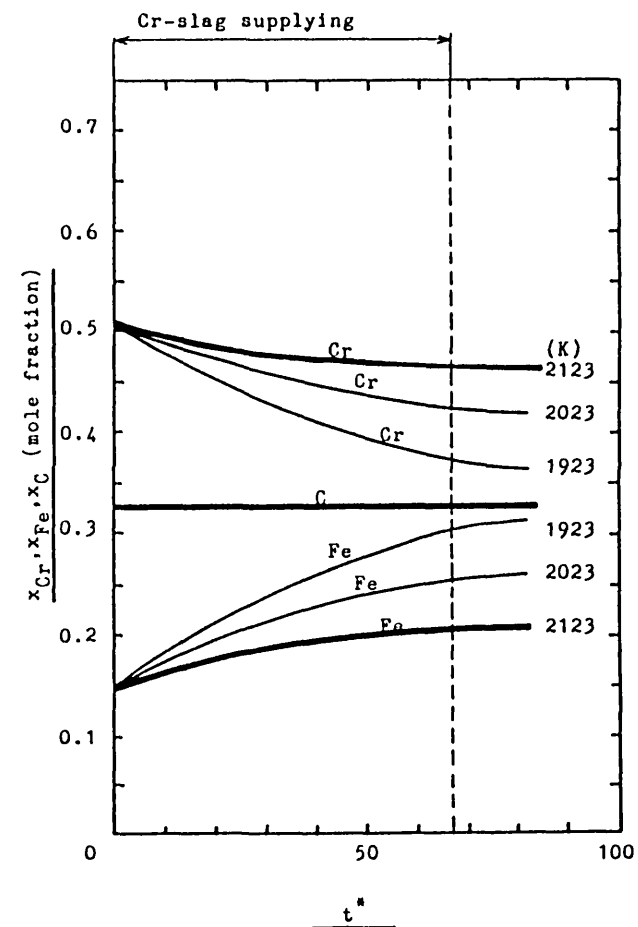
Flux densities of species at the metal/slag and slag/gas interface are shown in Fig. 3-32 (b) and (c) respectively. FeO flux density at the metal/slag interface does not change so much as that of $\text{CrO}_{1.5}$ with changing temperature.

At the slag/gas interface, metallic Mg vaporises under the higher temperature condition.

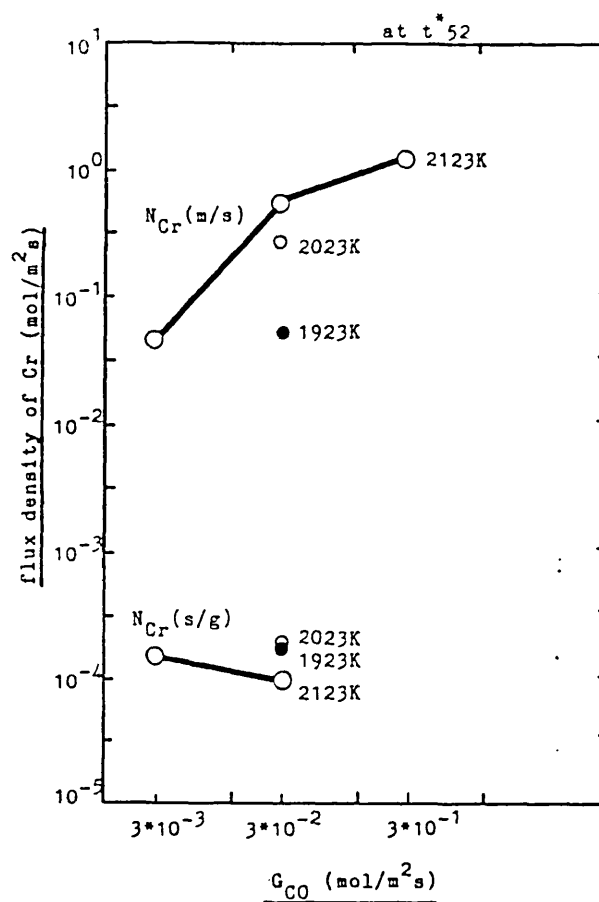


(a) Change of weight of the metal phase with time.

Fig.3-31 Effect of temperature on Cr-slag cleaning
(initial metal=1kg, Cr-slag supplying rate
=10kg/hr, $G_{CO}=3 \times 10^{-2}$ mol/m²s).



(b) Effect of temperature on the metal composition. (x_C is constant).

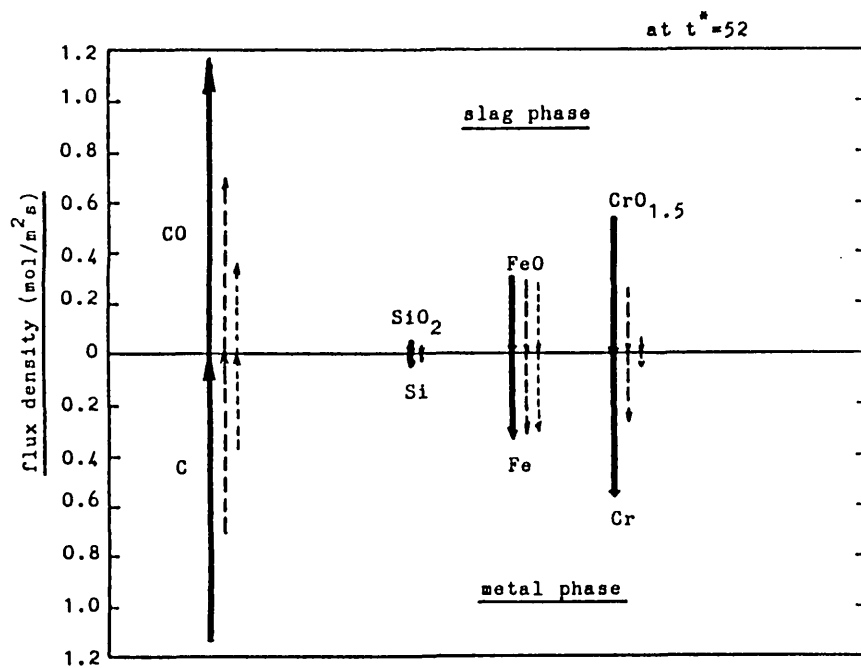


(a) Effect of G_{CO} on the flux densities of Cr metal reduced at interfaces.

Fig.3-32 Comparison of Cr metal formation (reduction) at the metal/slag and slag/gas interface.

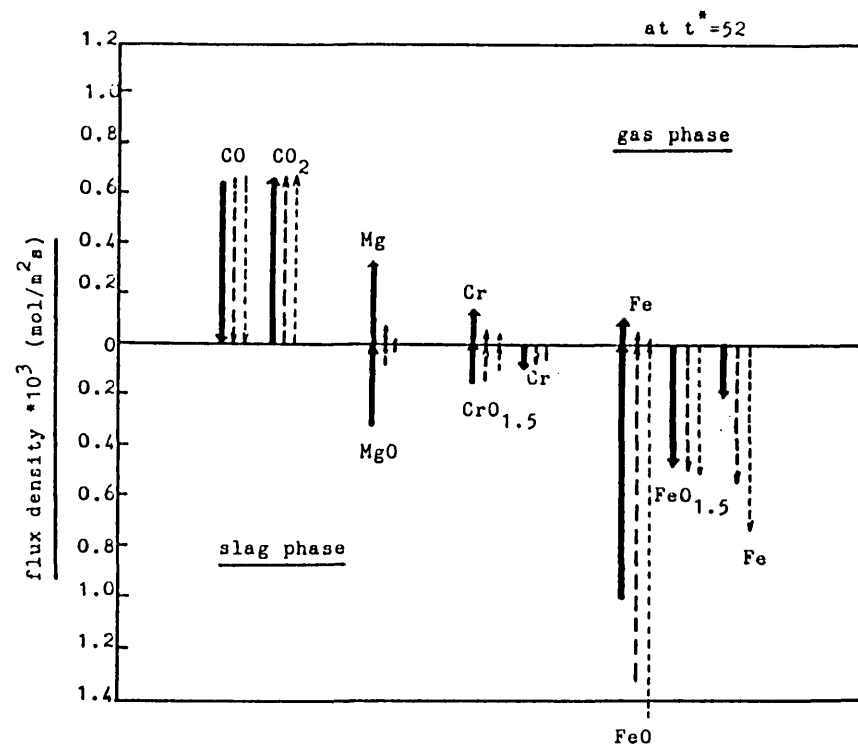
$N_{Cr}(m/s)$: flux density of Cr reduced at the metal/slag interface (mol/m²s).

$N_{Cr}(s/g)$: flux density of Cr reduced at the slag/gas interface (mol/m²s).



— 2123K
 - - - 2023K
 . . . 1923K

(b) Effect of temperature on the flux densities at the metal/slag interface.



— 2123K
 - - - 2023K
 . . . 1923K

(c) Effect of temperature on the flux densities at the slag/gas interface.

CHAPTER-4

PHYSICAL MODELLING4-1 Experimental techniques

In this work, the physical mixing of the particle that is supplied on the surface of the liquid is investigated in the mechanical stirrer-water-floating particle system. Some observations have been made in the mechanical stirrer-molten lead-floating particle system.

In the case of molten iron, an alumina crucible was used as a container. In the water model and the lead model, a pyrex beaker and an alumina crucible were used respectively. The dimensions of these vessels are shown in Fig. 4-1. The experimental set-up for each system is shown in Fig. 4-2.

Quantitative observations were made on the water model; qualitative observations on the lead model were made employing close to optimum conditions derived from the water model.

The dimensions of the water model were selected to be as close to values in case (a) in Fig. 4-1 as possible. The effect of vessel diameter was negligible comparing the results of two vessels whose diameters were 76mm and 95mm.

The effects of the following parameters on the critical rate of rotation^{*} were investigated :

(1) the stirrer profile : five types of stirrer profile were chosen. They are shown in Fig. 4-3.

- i) diameter of the stirrer(A), (D), (E).
- ii) height of the stirrer Fig. 4-5,
- iii) pitch of the blade(A), (B).
- iv) efficiency of sweeping out the liquid(A), (C).

The stirrer sweeps out the liquid as shown in Fig. 4-4, ideally. Practically, as the liquid is also rotating, the relative revolution rate between the stirrer and the liquid determines the sweeping rate of the liquid. It depends also on the shape of the stirrer.

* The critical revolution rate is defined as rate at which a particle placed on the surface of the liquid was drawn down into the liquid.

(mm)

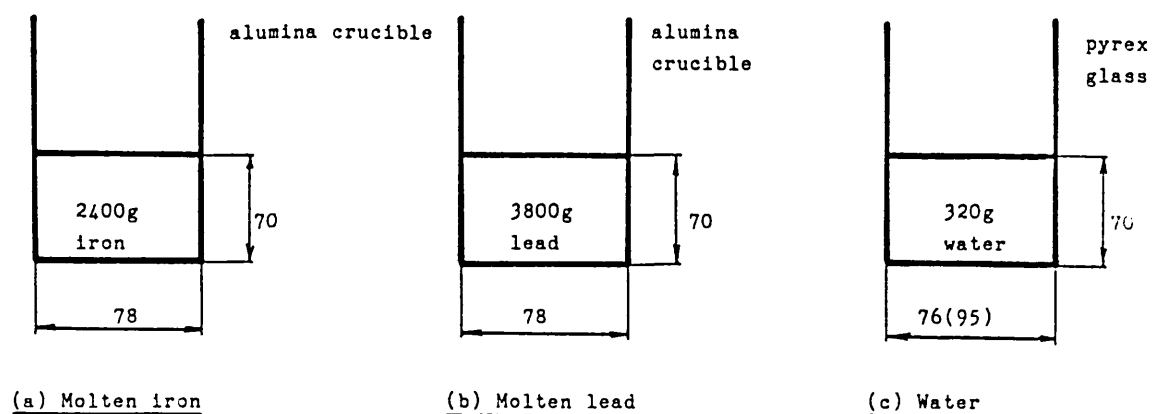
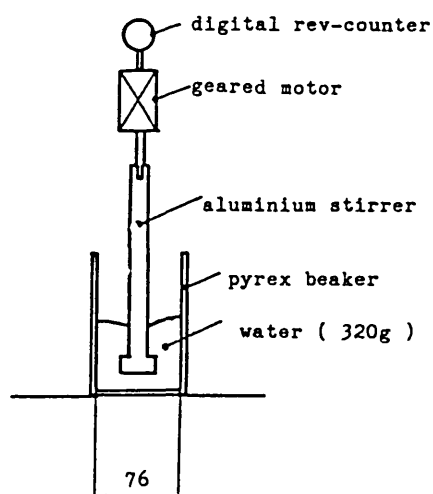
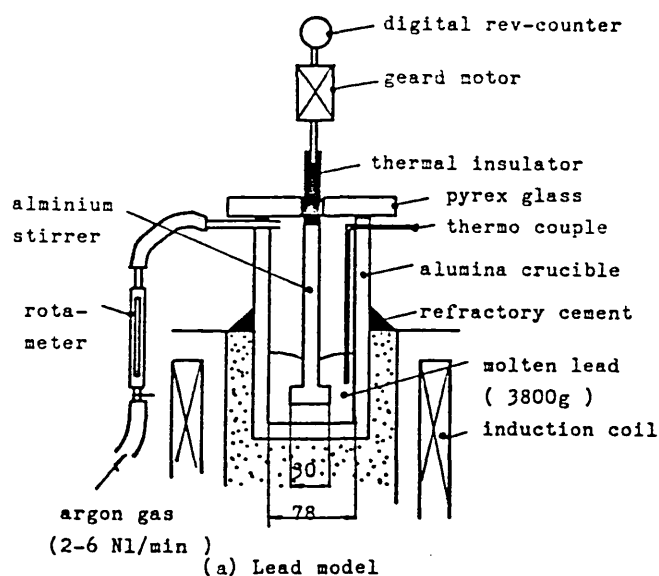


Fig.4-1 Dimensional comparison of three systems.



(mm)

Fig.4-2 Schematic view of the lead and water model

interfacial tension:

(2) the position of the stirrer

- i) horizontal position δ in Fig. 4-5.
- ii) vertical position h_3 in Fig. 4-5.

The depth below the surface is given by $h_1 = H - h_2 - h_3$.

(3) others

- i) baffles qualitative observation.
- ii) combination of the stirrer and gas injection
qualitative observation.
- iii) diameter of the vessel basically
 $D = 76\text{mm}$ is used, comparison is between $D = 76\text{mm}$ and 95mm .

The surface profile of the liquid, the surface rotation velocity and the critical rate were measured under the various stirring conditions.

Two values, e.g. $H_{\min}$ and $H_{\max}$ in Fig. 4-5 were measured as the representative quantities for the surface profile. The surface rotation velocity was measured by tracing one point on the surface. The critical revolution rate was measured by a digital revolution counter. This rate was determined by the following procedures:

- 1) increasing the revolution rate gradually.
- 2) gently pushing down the particles beneath the surface of the liquid in order to get rid of the effect of the surface tension on the entrainment.
- 3) reading the value displayed on the revolution counter just at the time when particle entrainment commences. This value was used as the critical revolution rate.
- 4) further increasing the revolution rate until all particles are fully entrained.
- 5) decreasing the revolution rate gradually.
- 6) reading the value displayed at the time when the particles cease to be entrained.

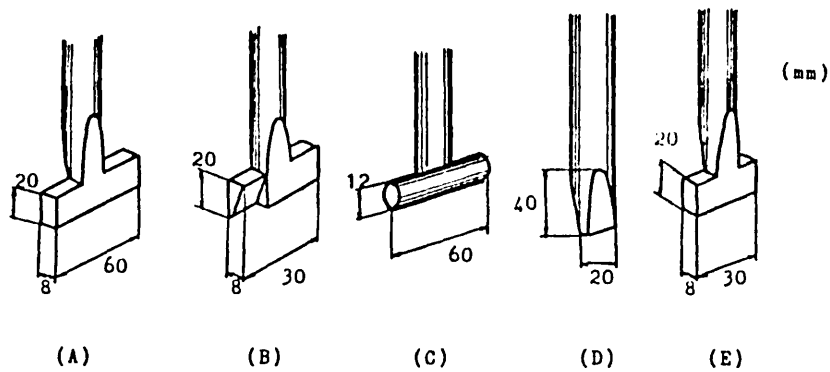


Fig.4-3 Stirrer profiles (stirrer' name (A)-(E)).

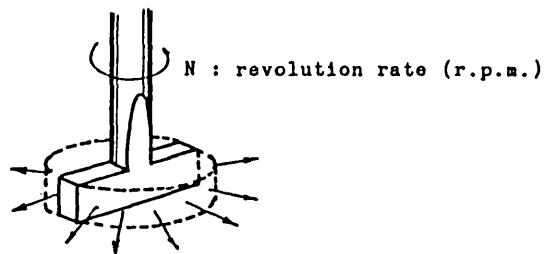


Fig.4-4 Liquid swept out by the stirrer.

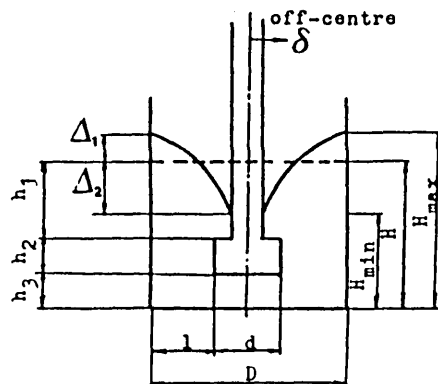


Fig.4-5 Dimensions of a mechanical stirring system.

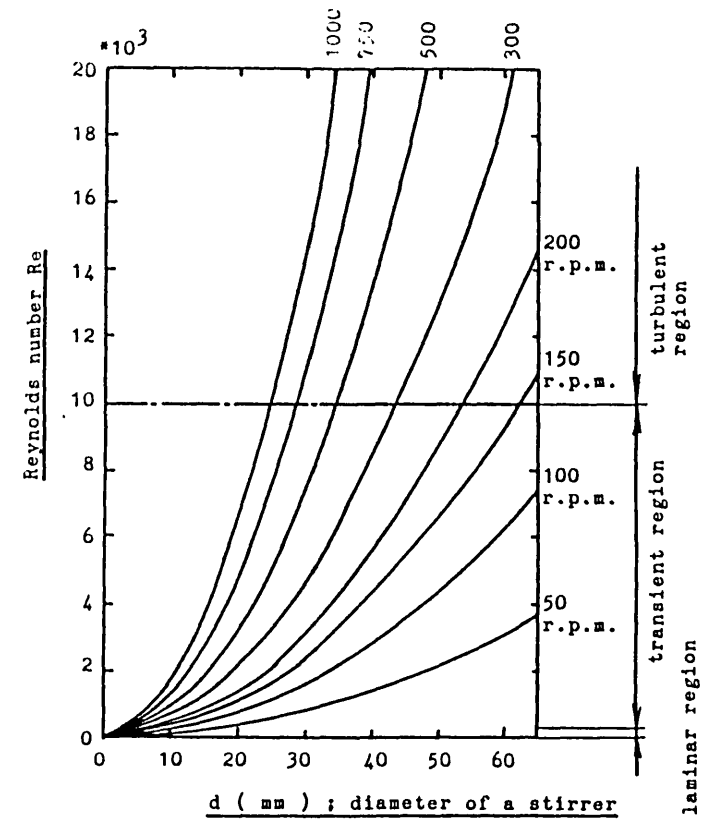


Fig.4-6 Reynolds number for experimental conditions.

The range of Reynolds numbers investigated is shown in Fig. 4-6. There are three regions. The critical values for each region are quoted from the Chemical Engineer's Handbook^[7].

- 1) Laminar region..... $Re \leq \sim 10$
- 2) Transient region .. $10 < Re < 10^4$
- 3) Turbulent region .. $10^4 \leq Re$

4-2 Results

1) Effect of the profile of the stirrer on particle entrainment

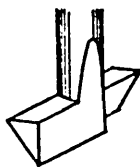
The results are summarised in Table 4-1.

- i) The results of stirrer (B) were not significantly different from those of stirrer (A). The pitch did not have any effect. But the results of stirrer (B) were different from the fully inclined-blade stirrer (see Fig. 4-7).
- ii) The diameter of the stirrer affected the results. Compare (A) with (D) and (E).
- iii) The tangential cross sectional shape of the stirrer affected the results to some extent. Compare (A) with (C) (see Fig. 4-8).

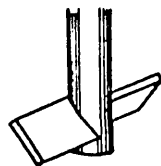
2) Effect of the horizontal position of the stirrer on particle entrainment.

The results are shown in Fig. 4-9.

- i) At a lower revolution rate (~ 300 r.p.m.) the deviation of the centre of the stirrer from the centre of the vessel, δ , did not affect the Δ -value.
- ii) At a higher revolution rate, say ~ 700 r.p.m., δ affected Δ significantly. In the region $0 \leq \delta \leq 5\text{mm}$, there was no significant change in Δ . At $\delta \sim 8\text{mm}$, which was observed by continuous change of δ , the value of Δ changes dramatically.

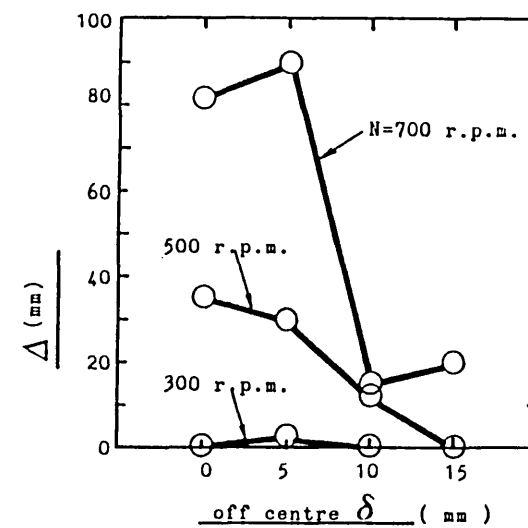


(a) Stirrer (B).



(b) Stirrer with fully inclined blades.

Fig.4-7 Shape of stirrers with pitch.



(a) Stirrer (A).



(b) Stirrer (C).

Fig.4-8 Cross sections of stirrers (A) and (C).

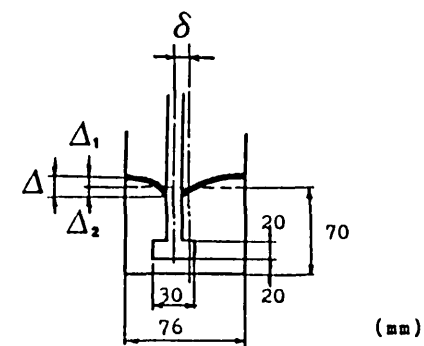


Fig.4-9 Surface profile in the case of off-centre stirring

- iii) As shown in Table 4-1, the critical revolution rate increased with increasing δ .
- iv) The semi-quantitative results of the observations are shown in Fig. 4-10.

3) Effect of the vertical position of the stirrer on particle entrainment.

The results are shown in Fig. 4-11.

- i) For the stirrer (E) in Table 4-1, the deeper stirring required a higher revolution rate for particle entrainment.
- ii) For the stirrer (E), the surface profile was flattened to some extent by increasing the depth of the stirrer at $N = 500$ r.p.m.
- iii) For the stirrer (A), the surface profile was not flattened. Δ value was increased by increasing the depth of the stirrer at $N = 500$ r.p.m.

4) Effect of the baffle on the surface profile.

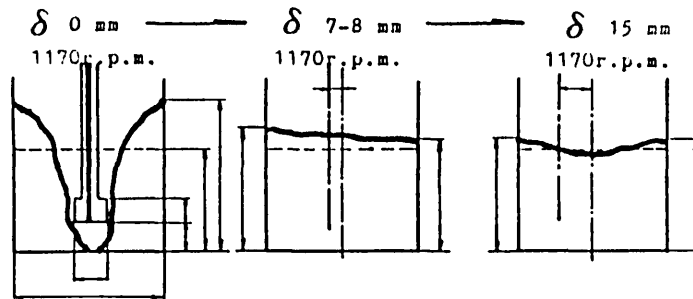
The results of qualitative observation are depicted in Fig. 4-12.

5) Effect of the diameter of the vessel on the surface profile.

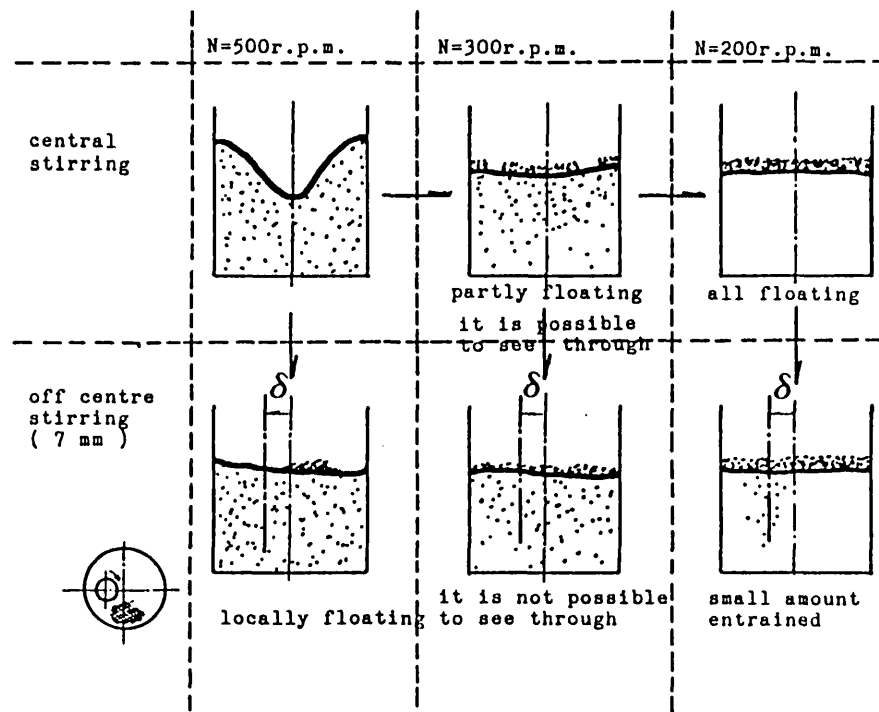
The quantitative results are shown in Table 4-1.

Comparing $D = 76\text{mm}$ ($d/D = 60/76 = 0.79$) with $D = 95\text{mm}$ ($d/D = 60/95 = 0.63$), there was no significant difference in the surface profile of the liquid.

(cf. for the stirrer (E) $d/D = 30/76 = 0.39$,
for the stirrer (D) $d/D = 20/76 = 0.26$.)



(a) Critical value of δ for the surface flattening in case the case where $N=1170$ r.p.m.



(b) Behaviour of the powder (hollowglass : size= $45-90 \mu\text{m}$, density= 300 kg/m^3 , contact angle 30° , terminal velocity in water= 0.09 cm/s).

Fig.4-10 Observation of off centre stirring.

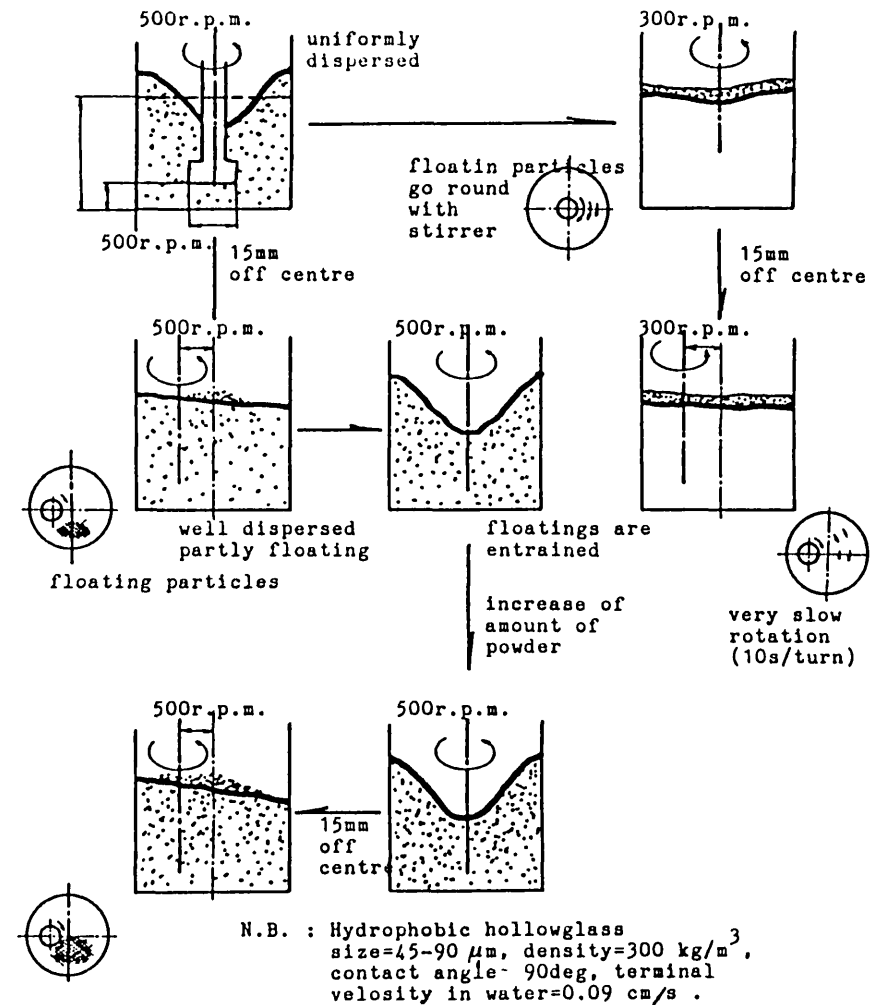


Fig.4-10 (c) Observation of off centre stirring (behaviour of hydrophobic powder).

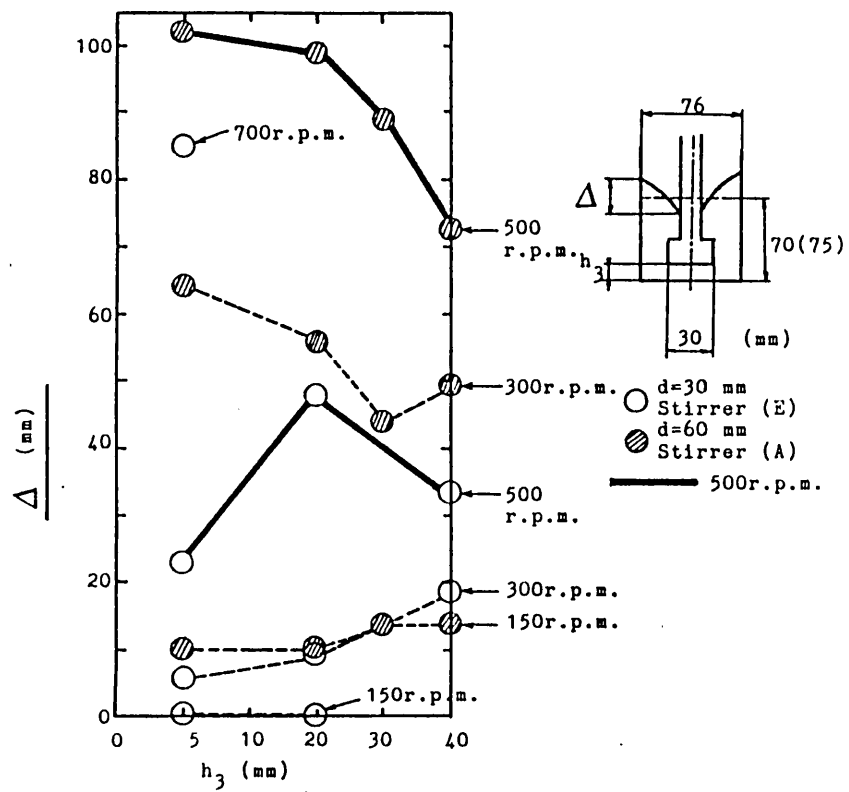


Fig.4-11 Effect of the vertical position of the stirrer on the surface level difference.

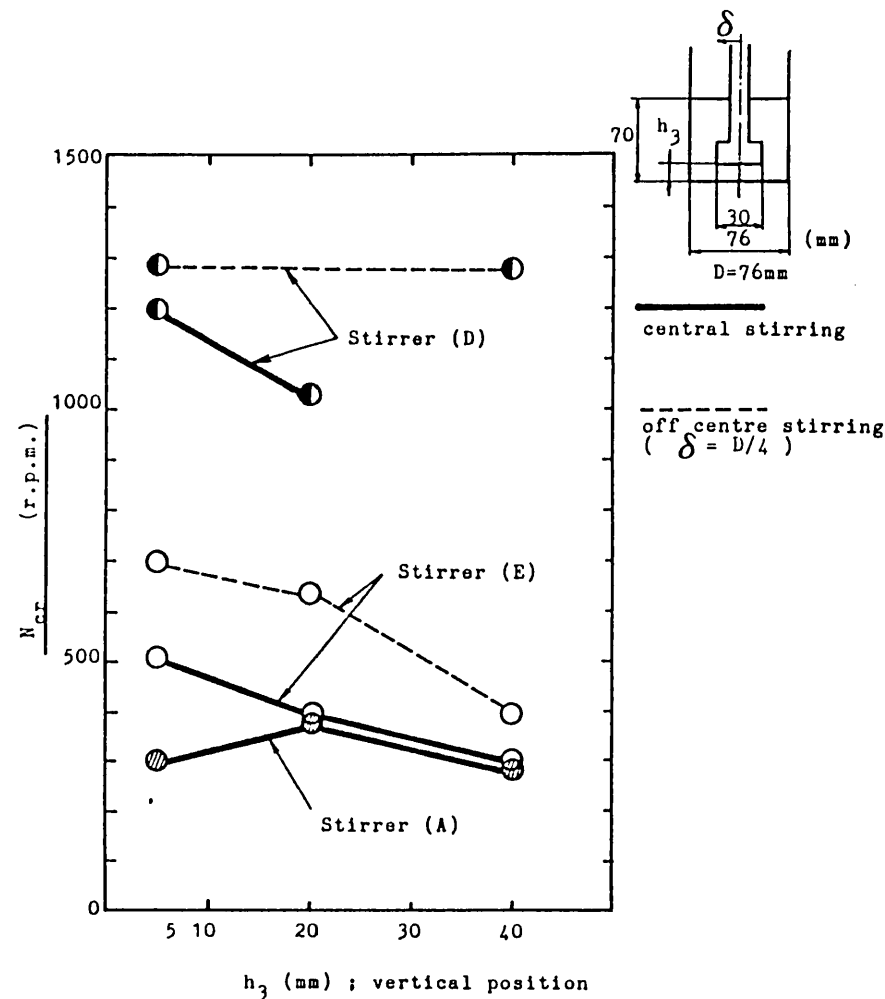


Fig.4-11 (b) Effect of vertical position of the stirrer on the critical revolution rate N_{cr} (polystyrene foam is used, terminal velocity in water = -20cm/s).

6) Effect of the combination of stirrer and gas injection on the results.

Only qualitative observations were made on the surface profile and behaviour of bubbles, as shown in Fig. 4-13. At the higher revolution rate ($\geq \sim 450$ r.p.m.), the bubbles were greatly affected by the rotating motion of the stirrer and rose in a helical path close to the stirrer shaft.

7) The results of the lead model.

The temperature of the molten lead was carefully controlled to maintain its vapour pressure well under the poisonous level. (TLV Pb 0.2 mg/m^3 ; 500°C).

- i) In the case of centre-stirring, there was no splashing of lead. In the case of off-centre or off-perpendicular stirring, however, there was some splashing (not vigorous).
- ii) The surface profile was very sensitive to the horizontal position of the stirrer. 5-8mm off-centre caused a complete difference from that of centre stirring. (vortex flattened-profile).
- iii) Because a reducing atmosphere was not used, solid PbO formed on the surface. At lower revolution rates than 500 r.p.m., it was not possible to see a fresh metal surface and the oxide did not rotate, but remained stationary on the liquid. At higher revolution rates (~ 700 r.p.m.), the molten lead was stirred vigorously enough to break up the solid oxide layer.
- iv) Powder with the properties given below was added to the surface of the molten lead.

10g. of glass ballotini (large) + 10g. of glass ballotini (small)

	size (μm)	density (Kg/m^3)	contact angle
glass ballotini (small)	74 - 150	2450	< 30 deg.
glass ballotini (large)	420 - 840	2450	< 30 deg.

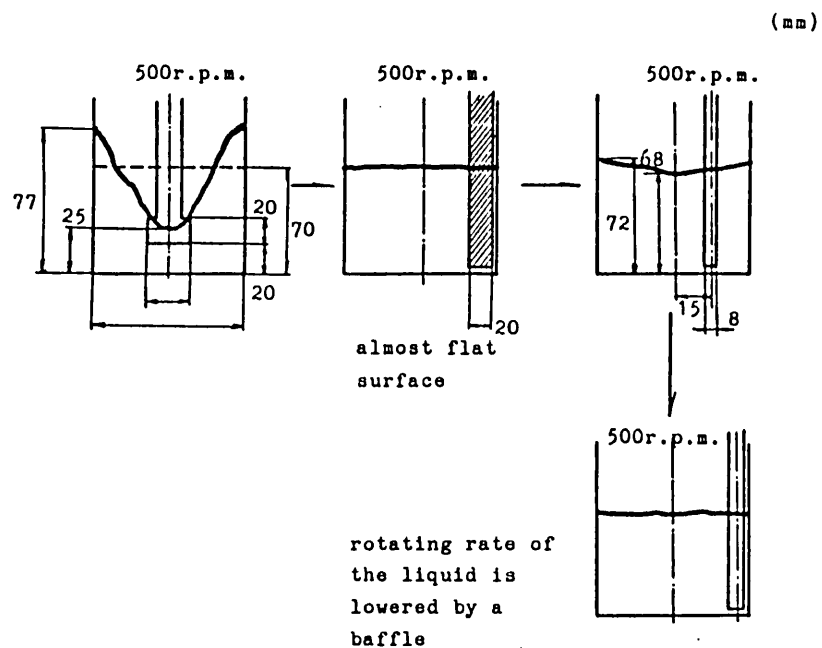
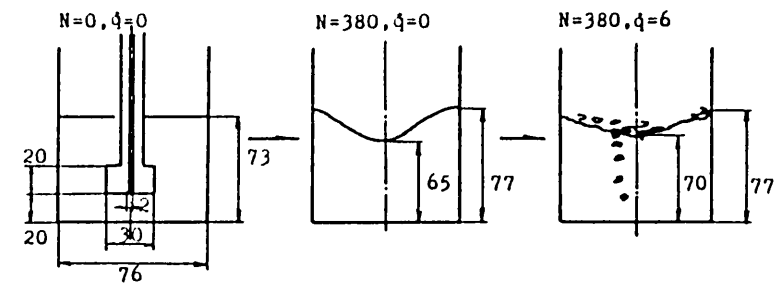
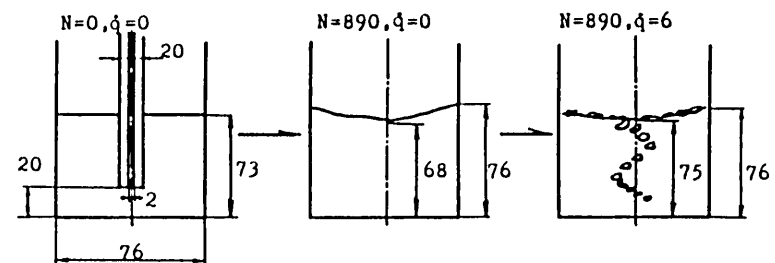


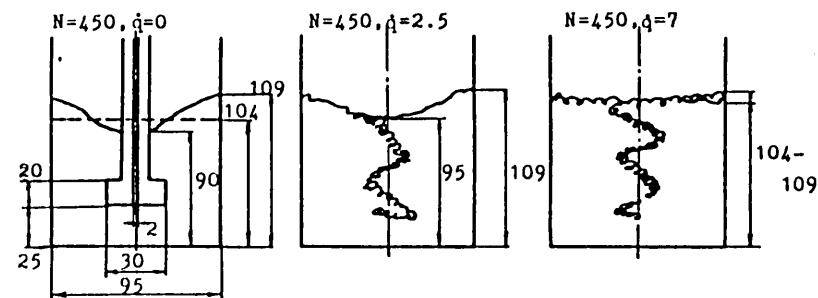
Fig.4-12 Effect of a baffle on the surface profile.



(a) Stirrer (E) (see Table 3-1).



(b) Stirrer (D).



(c) Stirrer (E) with a larger vessel (mm)

N.B. N =r.p.m. , $\dot{q}$ =Nl/min ; argon gas flow rate

Fig.4-13 Observation on combined operations of a stirrer and gas injection.

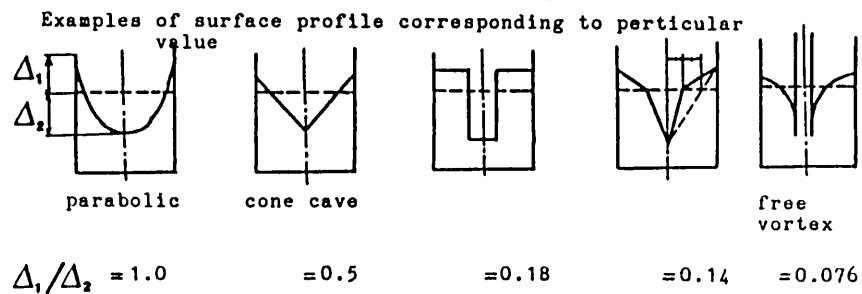
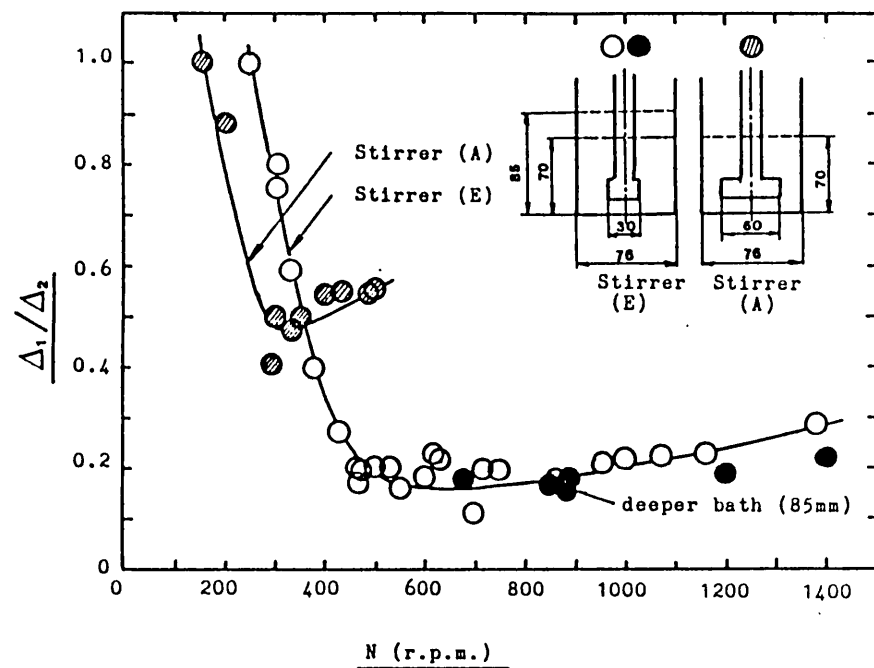


Fig.4-14 Surface profile characteristics of a mechanical stirring system.

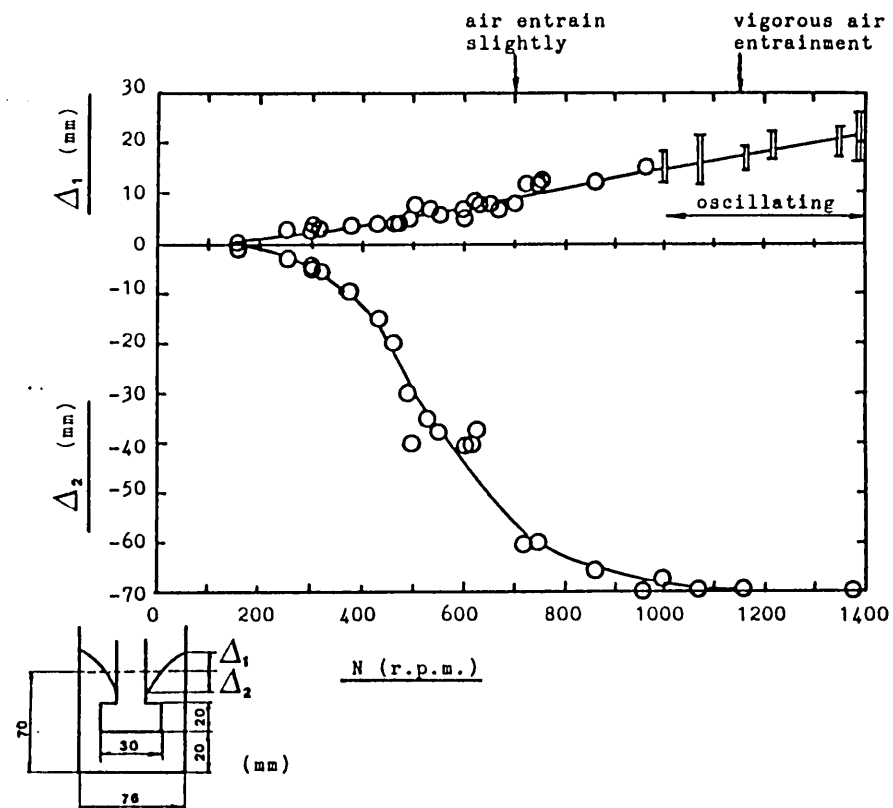


Fig.4-15 Surface profile measurement.

The volume ratio of added powder to the molten lead was approximately 2.4%. At revolution rates below 600 r.p.m., there was no significant powder entrainment. At revolution rates above 600 r.p.m., say 770-850 r.p.m., there was fairly good entrainment and powder was circulated through the liquid.

8) Surface profile measured

The results are plotted in Figs. 4-14 and 4-15

Free vortex in the system investigated had the value of 0.076 for Δ_1/Δ_2 - this value is explained in the next section. The stirrer (E) in Table 4-1 had a lower Δ_1/Δ_2 - value than that of the stirrer (A).

for stirrer (E)..... $\Delta_1/\Delta_2 \simeq 0.15$

for stirrer (A)..... $\Delta_1/\Delta_2 \simeq 0.5$

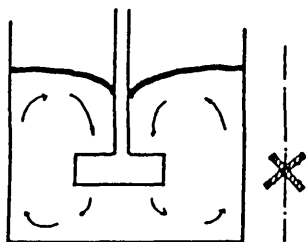
4-3 Interpretation and discussion of results

1) Evaluation of the effect of stirrer shape.

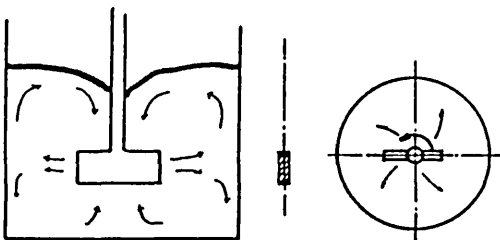
The main function of the stirrer was to create effective downward flow for entraining the particles or powder supplied on the surface of the liquid. The inclined blade stirrer created the circulation flow illustrated in Fig. 4-16 (a). The flat stirrer created the circulation flow illustrated in Fig. 4-16 (b). Both types provide downward flow in the centre of the region above the stirrer. The inclined blade stirrer showed a slightly better entraining performance than the flat one. The inclined blade stirrer is not, however, attractive enough to be chosen for the molten iron system, because of the erosion and complexity in machining.

2) The forced vortex and the free vortex

There are two limiting types of motion in the rotating system of liquid in an axisymmetric cylindrical vessel. They are the forced vortex and the free vortex drawn in Fig. 4-17. Surface profiles for each vortex are calculated in Appendix-1. The results are shown in Fig. 4-18. There are several fluid dynamic characteristics in these two types of motion.

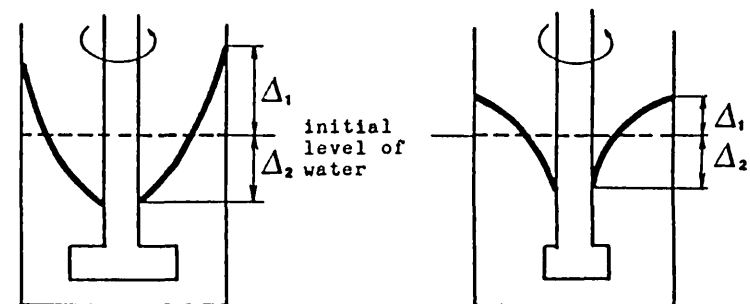


(a) Flow created by a stirrer with inclined blades.



(b) Flow created by a stirrer with flat blades.

Fig.4-16 The flow pattern created by stirrers.



(a) Forced vortex.

(b) Free vortex.

Fig.4-17 Surface profile of rotating liquid in the cylindrical vessel.

i) the velocity distribution. ?

It is drawn in Fig. 4-19(b) by equations (A1-1) and (A1-9). In the case of the forced vortex, the velocity is proportional to the radius.

It means that all liquid rotates around the z-axis at the same revolution rate.

ii) the surface profile of the fluid.

The Δ_1/Δ_2 value does not necessarily determine one particular surface profile, but this parameter is a fairly good index for roughly understanding the surface profile. Typical surface profiles and their Δ_1/Δ_2 values are drawn in Fig. 4-14. In the case of the forced vortex, the Δ_1/Δ_2 - value is 1.0. In the case of the free vortex, the Δ_1/Δ_2 value is 0.076, depending on the dimensions of the system. Other typical profiles have the Δ_1/Δ_2 values between that of the forced vortex and that of the free vortex. The Δ -value is drawn in Fig. 4-19(a).

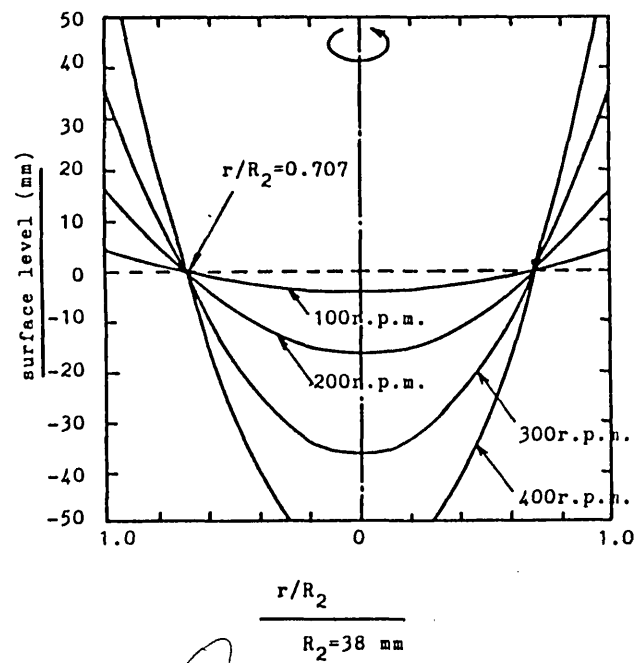
3) Evaluation of the effect of the diameter of the stirrer
(comparing the stirrers type (A), (D), (E) in Table 4-1)

i) According to Fig. 4-19 (b), the stirrer (A) has the characteristics of the forced vortex. The stirrers (D) and (E) have those of the free vortex.

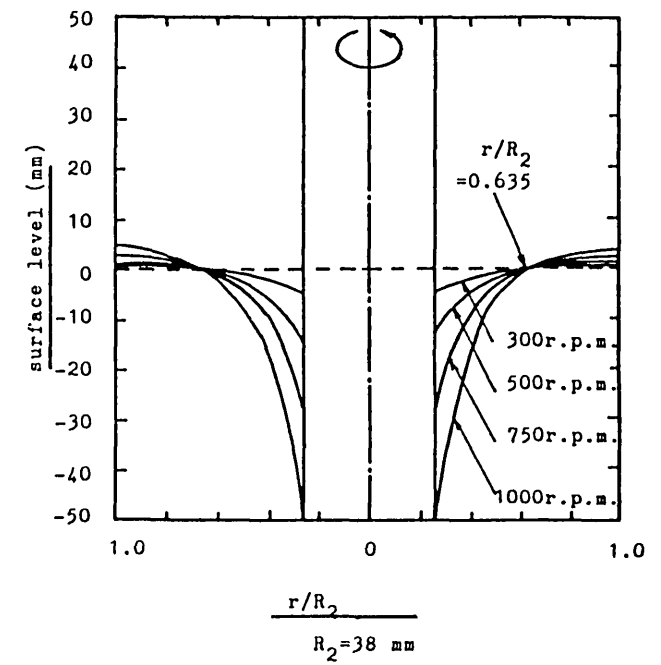
ii) According to Fig. 4-19(a), the surface profile caused by the stirrer (A) is almost equal to the forced vortex. That caused by the stirrer (E) is almost equal to the free vortex for revolution rates less than ~ 300 r.p.m. In the region of the higher revolution rate, the Δ value is greater than that of a free vortex.

iii) According to Fig. 4-20 the stirrer (E) was closer to the stirrer (A) than the stirrer (D) as far as the entrainment performance was concerned.

In order to obtain the same entrainment performance, the stirrer (E) required somewhat higher revolution rates than the stirrer (A), but even in the higher revolution rate the Δ -value for the stirrer (E) was much less than that for the

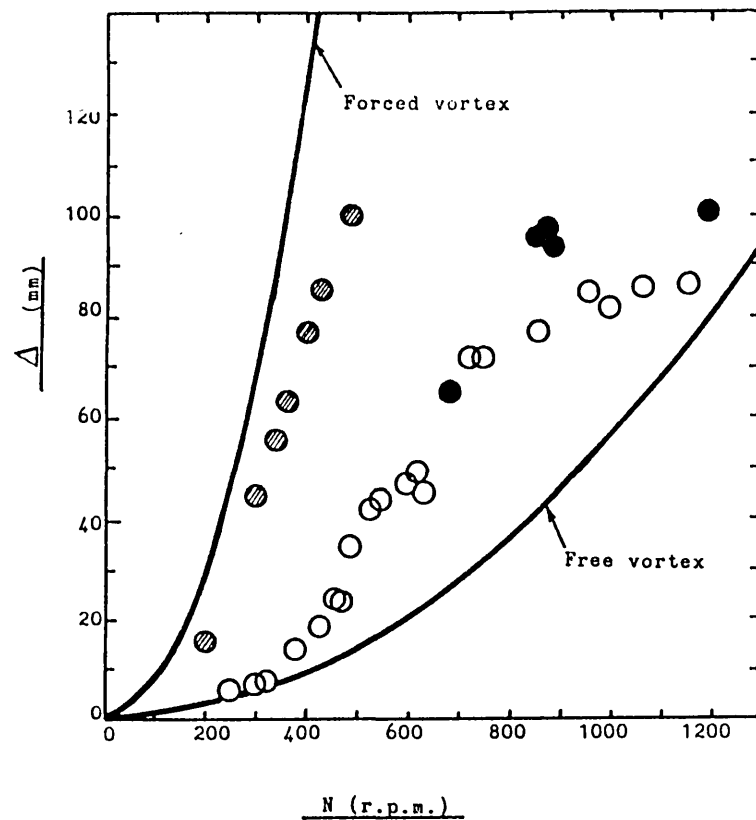


(a) Forced vortex.



(b) Free vortex.

Fig.4-18 Surface profile of liquid in the cylindrical vessel.



- Stirrer (E)
- Stirrer (E) with deep water
- Stirrer (A)

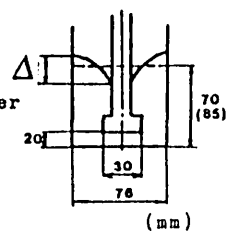


Fig.4-19 (a) Surface profile characteristics of forced and free vortex.

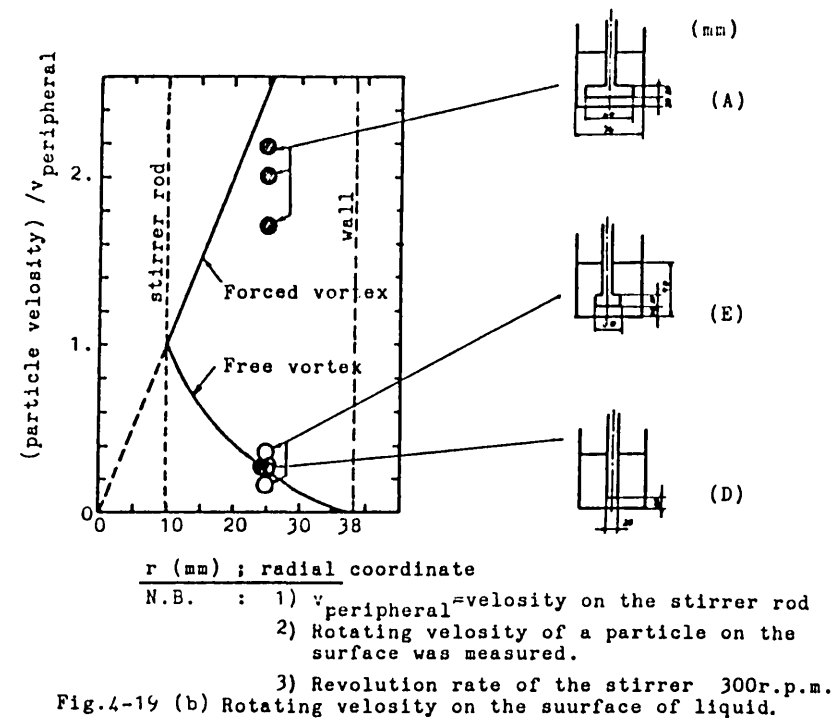


Fig.4-19 (b) Rotating velocity on the suurface of liquid.

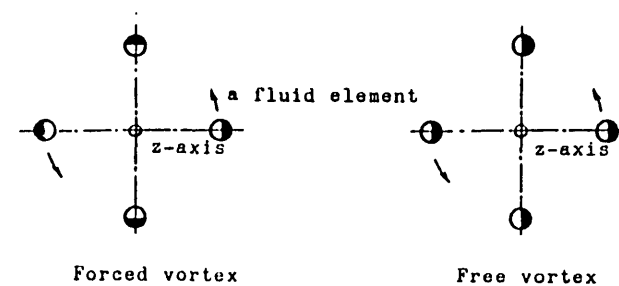


Fig.4-19 (c) Motion of a fluid element.

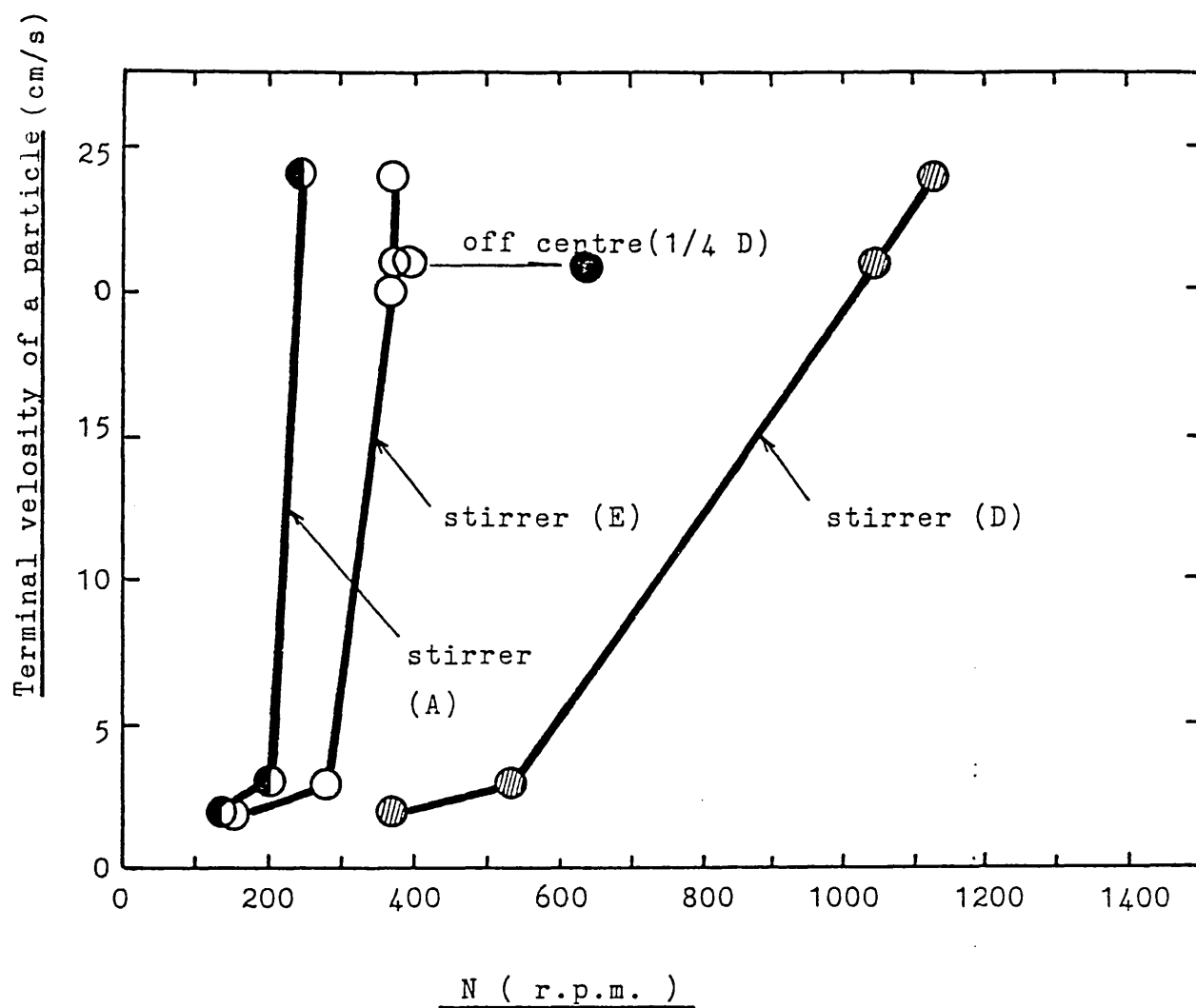


Fig.4-20 Critical revolution rate of stirrers.

stirrer (A) mainly because of the different type of vortex.

4) Dimensional Analysis

The governing equations for the rotating system of the fluid are the equation of continuity (4-1) and the equation of motion (4-2).

$$\nabla \cdot \mathbf{v} = 0 \quad (4-1)$$

$$\rho \frac{D\mathbf{v}}{Dt} = -\nabla \cdot \mathbf{p} + \mu \nabla^2 \mathbf{v} + \rho \mathbf{g} \quad (4-2)$$

Using the characteristic velocity V_0 , time t_0 and length d which denotes the diameter of the stirrer, these equations are rewritten in the dimensionless terms. The symbol $*$ denotes dimensionless variables or derivatives.

$$\mathbf{v} = \mathbf{v}^* V_0$$

$$p - p_0 = p^* \rho V_0^2$$

$$\nabla = d \cdot \nabla^*$$

$$t = t^* \cdot t_0$$

$$t_0 = d/V_0, \quad \mathbf{g}^* \mathbf{g} = \mathbf{g}$$

$$\therefore \nabla^* \cdot \mathbf{v}^* = 0 \quad (4-3)$$

$$\frac{D\mathbf{v}^*}{Dt^*} = -\nabla^* \cdot \mathbf{p}^* + \frac{\mu/\rho}{V_0 d} \cdot \nabla^{*2} \mathbf{v}^* + \frac{d \cdot \mathbf{g}}{V_0^2} \mathbf{g}^* \quad (4-4)$$

If these equations are solved with the appropriate set of the dimensionless initial and boundary conditions, it is possible to obtain similar solutions for two different systems which have different dimensions. Two dimensionless parameters in equation (4-4), $\frac{\mu/\rho}{V_0 d}$ and $\frac{dg}{V_0^2}$ are important. These parameters are known as the following forms:

$$\text{Reynolds number} \quad \text{Re} = \frac{\bar{V}_0 d}{\mu/\rho} \quad (4-5)$$

$$\text{Froude number} \quad \text{Fr} = \frac{\bar{V}_0^2}{dg} \quad (4-6)$$

e.g. in order to set these two dimensionless parameters exactly the same in the two systems, the following conditions are required :

$$\text{Re : } \frac{N_1 d_1^2}{\mu_1/\rho_1} = \frac{N_2 d_2^2}{\mu_2/\rho_2} \quad (4-7)$$

$$\text{Fr : } N_1^2 d_1 = N_2^2 d_2 \quad (4-8)$$

$$N_1 = N_2 \cdot (d_2/d_1)^{\frac{1}{2}} \quad (4-9)$$

This equation (4-9) means that in order to obtain similar characteristics in a 10 times larger system, the revolution rate should be chosen $1/\sqrt{10} \approx 1/3$ of the original system. The kinematic viscosity in the larger system should be thirty times greater than that in the original system. This means that it is impossible to model large scale liquid metal systems on the same scale, since liquid metals have very low kinematic viscosities.

Re and Fr are summarised for three systems (water, lead, iron) in Table 4-2.

Table 4-2 Physical characteristics of systems.

	(1) Water model	(2) Lead model	(3) Molten iron	remarks
kinematic viscosity m^2/s	$1.13 \cdot 10^{-6}$ (16° C) $0.70 \cdot 10^{-6}$ (38° C)	$0.21 \cdot 10^{-6}$ (400° C)	$1.20 \cdot 10^{-6}$ (1300° C) $0.95 \cdot 10^{-6}$ (1550° C)	
stirrer diameter d mm	30	30	30	
revolution rate N r.p.m.	750	750	750	
Reynolds number Re	$1.0 \cdot 10^4$	$5.4 \cdot 10^4$	$0.94 \cdot 10^4$	
Froude number Fr	0.48	0.48	0.48	

$$1) \text{Re} = (d/1000)^2 (N/60) / \nu$$

$$2) \text{Fr} = (d/1000) (N/60)^2 / g \quad ; \quad g = 9.8 \text{ m/s}^2$$

CHAPTER-5

CHEMISTRY AND KINETICS OF DECOPPERISING AND DETINNING FROM CARBON SATURATED IRON AND STEEL (de-Cu/de-Sn)

5-1 Experimental techniques.

Copper and tin removal from carbon saturated iron and steel were studied by varying the metal composition, the slag composition, temperature and bath stirring conditions. The apparatus for these experiments is shown in Fig. 5-1. This consisted of a vacuum induction furnace, which was the main item of equipment, an argon gas bubbling train, equipment for temperature measurement and sampling equipment. Experimental conditions are shown in Table 5-1. Characteristics of these conditions are :

- (1) The carbon content in the metal phase was less than 0.1 wt% for steel and approximately 4.5 wt% for carbon saturated iron.
- (2) Four types of slag were chosen as reagents -
 - $\text{NaS}_{0.5}$ which was thought to be the best reagent for copper removal in the small scale experiments.
 - $\text{NaS}_{0.5}$ -FeS mixtures.
 - CaF_2 - FeS mixtures. The CaF_2 was added as a neutral flux to absorb $\text{CuS}_{0.5}$ and SnS and the FeS to supply sulphur.
 - CaS-CaO-FeS-FeO reciprocal mixture which is more stable than $\text{NaS}_{0.5}$ at the high temperatures of steel making and which is a common type of slag in industrial processes.
- (3) The slag compositions are shown in Table 5-1. The slag weight was 10% of the metal weight. (The metal weight was 3000g or 1000g).
- (4) Three stirring regimes were used, mechanical stirring argon gas bubbling and only electromagnetic. In the case of mechanical stirring, the stirring conditions were selected according to the results of the water model experiments, e.g. the revolution rate of the stirrer was selected so as to be high enough to entrain the slag supplied onto the surface of the metal bath.

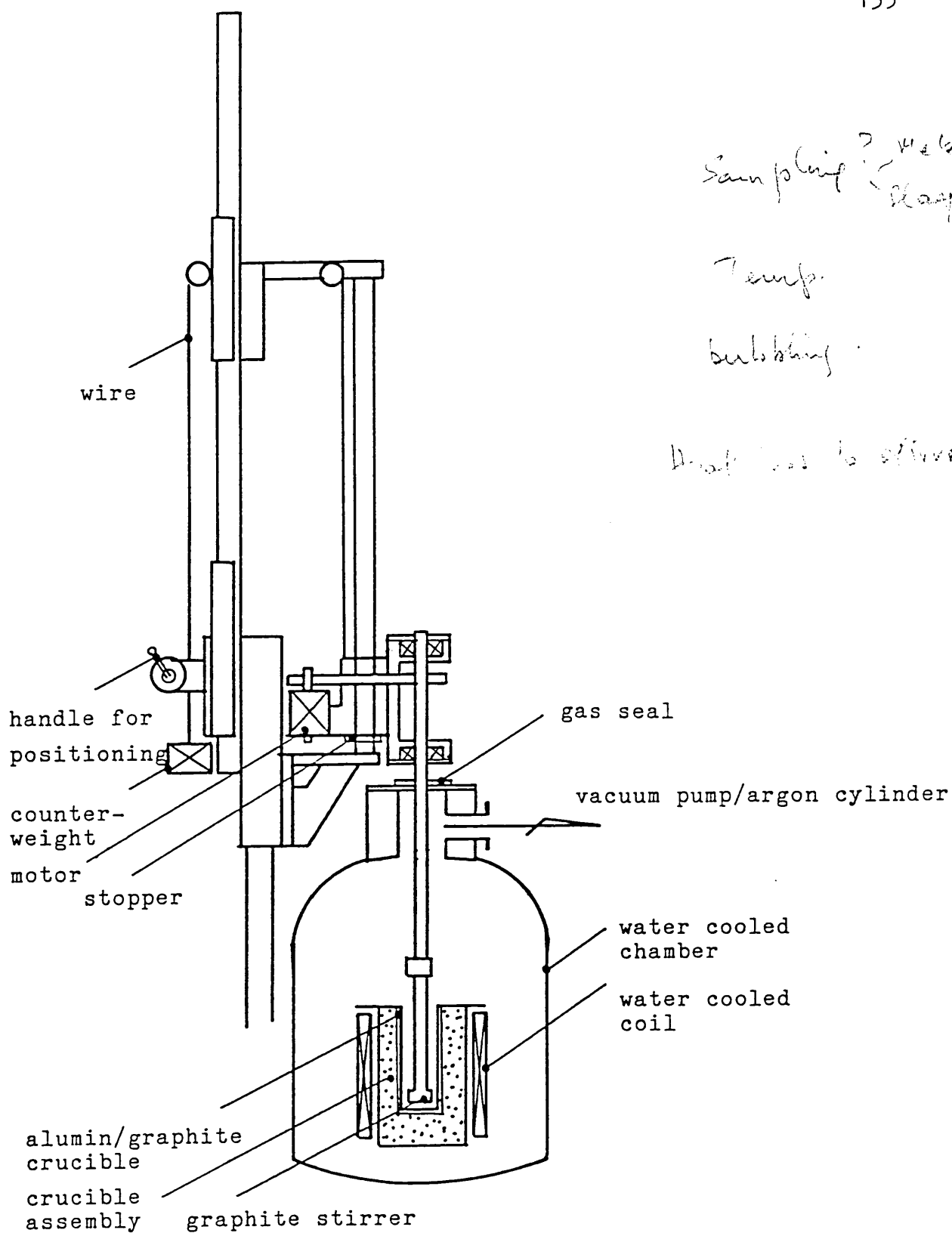


Fig.5-1 Schematic view of the apparatus for experiment.

Table 5-1 (a) Experimental conditions.

	TEMPERATURE
RUN	CRUCIBLE(Graphite,Alumina)
NUMBER	MIXING,METAL

slag type	slag composition	metal mixing	carbon saturated iron			steel argon bubbling	remarks
			no bubbling	argon	bubbling		
NaS _{0.5} FeS	100NaS _{0.5}		1250°C 13 G-3-2 1043g	1250°C 18 G-6-1 BB5,1063	1250°C 6 G-1-5 BB2,1024		BB=bubbling Bl=blowing
	80NaS _{0.5} -20FeS		1275°C 3 G-1-2 919g	1250°C 2 G-1-1 BB2,963	1225°C 11 G-3-1 BB2,2880	1250°C 14 G-4-1 700r.p.m.	revolution rate r.p.m.
	50NaS _{0.5} -50FeS			1275°C 4 G-1-3 BB2,1326		3076g	G-1-2 seq.no. of crucible seq.no.usage
	20NaS _{0.5} -80FeS			1275°C 5 G-1-4 BB2,3019			
CaF ₂ FeS	50CaF ₂ -50FeS			1600°C 25 G-8-3 BB2,2924		1300°C 1 A-1-1 700r.p.m.	1575°C 20 A-6-1 BL4,2040
CaS FeS FeO	37CaS -63FeS			1250°C 21 G-6-2 BB2,2924	run-23 1250°C G-8-1 BB2,3519 pure FeS run-24 1250°C G-8-2 BB2,3496 40NaS_{0.5}- 40FeS-20CaS	1590°C 7 A-2-1 BB2,1019	slag A
	40CaS-47FeS -13FeO _n			1250°C 22 G-6-3 BB2,3141		1575°C 8 A-2-2 BB2,1027	slag B
	43CaS-29FeS -28FeO _n			1250°C 19 G-7-1 BB2,3048		1590°C 9 A-3-1 BB2,1020	slag C
	46CaS-11FeS -43FeO					1600°C 15 A-5-1 BB2,1020	slag D
	15CaS-39FeS -46FeO			1255°C 17 G-5-1 BB2,1039		1605°C 16 A-5-2 BL4,1021	slag E
	18CaS-82FeS			1260°C 10 G-2-1 BB2,1066		1600°C 26 A-7-1 BL8,2094	slag F (modified F)

Table 5-1 (b) Analysed results of samples (de-Cu/de-Sn
from carbon saturated iron/steel).

RUN	METAL PHASE					SLAG PHASE WEIGHT (g)
	WEIGHT (g)	TIME (min)	Cu (wt%)	Sn (wt%)	S (wt%)	
pre-1	961	0	0.79	0.16	0	60.3(100wt%NaS _{0.5})
		8	0.70	0.17	-	
		10	0.65	0.15	-	
		45	0.58	0.20	-	
		70	0.57	0.20	-	
		80	-	-	0.04	
		100	0.54	0.18	-	
pre-2	813	0	0.95	0.19	0	61.5(50wt%FeS-50wt% NaS _{0.5})
		42	0.59	0.18	-	
		50	0.59	0.17	-	
		60	0.61	0.18	-	
		80	0.62	0.15	-	
		90	-	-	0.22	
		120	0.64	0.17	-	
pre-3	1225	0	0.70	0.14	0	60(50wt%FeS-50wt% CaF ₂)
		6	0.64	0.10	0.54	
		9	0.67	0.11	-	
		11	0.67	0.10	-	
		20	0.65	0.10	-	
		30	0.66	0.09	0.51	
		35	0.66	0.10	-	
		45	0.67	0.09	-	
		60	0.64	0.10	-	
		80	0.66	0.09	-	
		91	0.66	0.10	-	
		100	0.63	0.08	0.47	
		120	0.66	0.09	-	
pre-4	1168	0	1.03	0.16	0	180(50wt%FeS-50wt% CaF ₂)
		26	-	-	1.06	
		38	0.82	0.12	-	
		53	0.79	0.11	-	
		71	0.74	0.11	-	
		80	-	-	1.23	
		90	0.72	0.11	-	
		110	0.71	0.10	-	

RUN	METAL PHASE					SLAG PHASE WEIGHT (g)
	WEIGHT (g)	TIME (min)	Cu (wt%)	Sn (wt%)	S (wt%)	
1	3006	3.5	1.01	0.91	0.34	301(50wt%FeS-50wt% CaF ₂)
		10	0.99	0.91	-	
		21	0.95	0.89	-	
		30	-	-	0.99	
					1.04	
2	963	37	0.98	0.89	1.11	100(20wt%FeS-80wt% NaS _{0.5})
					-	
		0	1.05	0.92	0	
		3	-	-	0.042	
					0.075	
3	919	5	0.55	0.92	0.079	92.1(20wt%FeS-80wt% NaS _{0.5})
		10	0.51	0.89	-	
		30	0.47	0.86	0.03	
					-	
					-	
4	1326	0	0.81	0.88	0	133(50wt%FeS-50wt% NaS _{0.5})
		2.5	0.52	0.90	-	
		5	-	-	0.062	
					0.074	
					0.099	
5	3019	15.5	0.46	0.90	-	(0.0586,0.00198, 0.216,0.728,0)
		30	-	-	0.11	
		31	0.44	0.89	-	
					-	
					-	
6	1024	0	0.89	0.85	0	302(80wt%FeS-20wt% NaS _{0.5})
		5	0.44	0.88	-	
		9	0.44	0.90	-	
		30	0.45	0.88	-	
		48	-	-	0.16	
7	3019	53	0.44	0.87	-	(0.0807,0.00321, 0.354,0.562,0)
		0	0.82	0.82	0	
		5.5	0.58	0.88	0.32	
		11	0.52	0.87	-	
		27	0.56	0.89	-	
8	1024	60	0.52	0.87	0.36	98.9(100wt%NaS _{0.5})
					0.38	
					0.45	
					0.54	
					-	
9	1024	0	1.09	0.91	0	
		1.7	0.99	0.91	-	
		3.5	-	-	0.084	
		5	0.54	0.86	-	
		12	0.49	0.89	0.009	
10	1024	30	-	-	0.019	
					-	
		50	0.52	0.86	-	

RUN	METAL PHASE					SLAG PHASE	
	WEIGHT (g)	TIME (min)	Cu (wt%)	Sn (wt%)	S (wt%)	weight (g)	
7	1019	0	-	0.91	0	102(63wt%FeS-37wt% CaS)	
		2.5	1.12	0.88	1.97		
		6	1.11	0.86	-		
		20	1.06	0.76	-		
		30	1.05	0.74	-		
		40	1.05	0.68	1.88		
					2.18		
8	1027				2.22	103(47wt%FeS-14wt% FeO _n -39wt%CaS)	
		-18	1.32	1.07	-		
		0	1.27	1.06	0		
		1	1.23	0.94	-		
		5	1.15	0.93	-		
		15	1.12	0.88	2.24		
					2.29		
9	1020				2.52	102(29wt%FeS-28wt% FeO _n -43wt%CaS)	
					2.64		
		25	1.17	0.88	-		
		30	1.24	0.86	2.12		
		0	1.16	1.16	0		
		3	1.14	1.12	-		
		7	1.13	1.09	-		
10	1066	12	1.09	1.06	-	106(82wt%FeS-18wt% CaS)	
		15	1.11	1.06	1.83		
		25	1.11	1.04	-		
		40	1.10	0.92	-		
		50	1.08	0.76	1.76		
		0	0.95	0.89	0		
		1	0.69	0.89	-		
11	2880	3	0.67	0.88	0.63	274(20wt%FeS-80wt% NaS _{0.5} ⁰)	
		10	0.47	0.84	0.52		
		16	0.46	0.84	-		
		35	0.44	0.82	0.49		
		0	1.07	0.92	0		
		4	0.64	0.88	-		
		8	-	-	0.033		
12	1017				0.042	102(50wt%FeS-50wt% CaF ₂)	
					0.049		
		9.7	0.58	0.91	-		
		21	-	-	0.048		
					0.064		
					0.070		
		38	0.49	0.89	-		
13	2040	60	0.54	0.86	0.11	200(50wt%FeS-50wt% CaF ₂)	
					0.15		
					0.17		
		-15	-	1.01	-		
		0	-	1.00	0		
		2	0.98	0.98	-		
		5	0.96	0.95	-		
14	1043	10	0.97	0.95	1.42	106(100wt%NaS _{0.5})	
		30	-	0.92	1.06		
		0	0.99	0.88	0		
		4	-	-	0.099		
		6	0.59	0.86	-		
		10	0.56	0.90	-		
		20	0.54	0.91	0.006		
15	3076	49	0.46	0.90	0.071	301(20wt%FeS-80wt% NaS _{0.5})	
					0.092		
					0.094		
		0	0.98	0.91	0		
		18.3	0.50	0.84	-		
		28	0.50	0.88	-		
		60	0.48	0.90	0.030		
16	1020				0.045	100(11wt%FeS-43wt% FeO _n -46wt%CaS)	
					0.072		
		0	1.29	1.09	0		
		2.5	1.06	0.94	-		
		4	1.22	0.98	-		
		7	1.18	0.97	1.33		
		10	1.24	0.97	-		
17	1021	20	1.22	0.95	-	100(39wt%FeS-46wt% FeO _n -15wt%CaS)	
		30	1.23	0.91	-		
		40	1.23	0.86	1.34		
		0	1.27	1.06	0		
		5	1.22	1.01	1.38		
		10	1.15	0.93	-		
		16	1.24	0.99	-		
18	1021	40	1.29	0.97	1.39	100(39wt%FeS-46wt% FeO _n -15wt%CaS)	

RUN	METAL PHASE					SLAG PHASE	
	WEIGHT (g)	TIME (min)	Cu (wt%)	Sn (wt%)	S (wt%)	WEIGHT (g)	
12	1017	0	1.41	1.42	0	102(50wt%FeS-50wt% CaF ₂)	
		3	1.30	1.22	-		
		5	1.33	1.27	-		
		8	-	-	1.59		
		11	1.13	1.20	-		
		19	1.30	1.20	-		
		36	1.02	1.12	1.64		
20	2040					200(50wt%FeS-50wt% CaF ₂)	
		-15	-	1.01	-		
		0	-	1.00	0		
		2	0.98	0.98	-		
		5	0.96	0.95	-		
		10	0.97	0.95	1.42		
		30	-	0.92	1.06		
13	1043	0	0.99	0.88	0	106(100wt%NaS _{0.5})	
		4	-	-	0.099		
		6	0.59	0.86	-		
		10	0.56	0.90	-		
		20	0.54	0.91	0.006		
		49	0.46	0.90	0.071		
					0.092		
14	3076				0.094	301(20wt%FeS-80wt% NaS _{0.5})	
		0	0.98	0.91	0		
		18.3	0.50	0.84	-		
		28	0.50	0.88	-		
		60	0.48	0.90	0.030		
					0.045		
					0.072		
15	1020	0	1.29	1.09	0	100(11wt%FeS-43wt% FeO _n -46wt%CaS)	
		2.5	1.06	0.94	-		
		4	1.22	0.98	-		
		7	1.18	0.97	1.33		
		10	1.24	0.97	-		
		20	1.22	0.95	-		
		30	1.23	0.91	-		
16	1021	40	1.23	0.86	1.34	100(39wt%FeS-46wt% FeO _n -15wt%CaS)	
		0	1.27	1.06	0		
		5	1.22	1.01	1.38		
		10	1.15	0.93	-		
		16	1.24	0.99	-		
		40	1.29	0.97	1.39		

RUN	METAL PHASE					SLAG PHASE	
	WEIGHT (g)	TIME (min)	Cu (wt%)	Sn (wt%)	S (wt%)	WEIGHT (g)	
17	1039	0	0.96	0.86	0	100(39wt%FeS-46wt%FeO _n -15wt%CaS)	
		5	0.83	0.87	-		
		6.5	-	-	0.57		
		10	0.83	0.89	-		
		25	-	-	0.65		
		35	0.84	0.82	-		
		38	-	-	0.54		
18	1063	0	1.00	0.83	0	98.6(100wt%NaS _{0.5})	
		5	0.49	0.82	-		
		9	0.50	0.90	0.007		
		14	0.42	0.87	-		
		40	0.43	0.87	0.03		
19	3048	0	0.88	0.91	0	299(29wt%FeS-28wt%FeO _n -15wt%CaS)	
		2.5	0.83	0.91	0.24		
		5	0.82	0.93	-		
		10	0.84	0.93	-		
		20	0.87	0.91	-		
21	2924	0	0.91	0.93	0	300(63wt%FeS-37wt%CaS)	
		5	0.69	0.92	-		
		10	0.66	0.90	0.64		
		20	0.64	0.91	-		
		40	0.64	0.90	0.74		
22	3141	0	0.97	0.93	0	310(47wt%FeS-13wt%FeO _n -40wt%CaS)	
		2	0.82	0.92	-		
		5	0.79	0.90	-		
		30	0.83	0.88	0.63		
		35	0.84	0.87	-		
		45	0.84	0.86	0.44		
		53	0.84	0.86	0.35		
23	3519	0	0.91	0.89	-	355(100wt%FeS)	
		26	0.63	0.92	1.26		
		30	0.73	0.86	1.62		
		60	0.82	0.86	1.33		
					1.45		
24	3496	0	0.85	0.93	0	350(40wt%FeS-40wt%NaS _{0.5} -20wt%CaS) (0.0696,0.00267, 0.297,0.507, 0.124)	
		2	0.59	0.87	-		
		10	0.56	0.88	0.12		
		40	0.50	0.96	0.084		

RUN	METAL PHASE					SLAG PHASE	
	WEIGHT (g)	TIME (min)	Cu (wt%)	Sn (wt%)	S (wt%)	WEIGHT (g)	
25	2427	-10	0.99	0.99	-	250(50wt%FeS-50wt%CaF ₂)	
		0	1.02	0.99	0		
		5	0.94	0.93	1.28		
		15	0.97	0.91	1.15		
		25	0.95	0.89	-		
26	2094	40	0.97	0.89	1.17	210(61wt%FeS-26wt%CaF ₂ -13wt%CaS)	
		0	1.15	0.99	0		
		5	0.90	0.90	-		
		10	0.93	0.89	1.82		
					1.94		
					2.00		
					2.04		
		15	0.88	0.84	-		
		20	0.92	0.80	-		
		30	-	-	1.78		
		40	0.85	0.66	-		

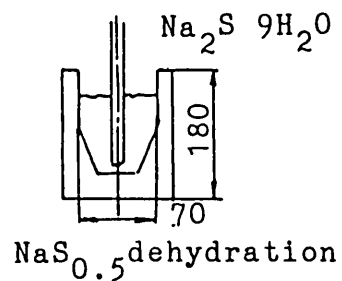
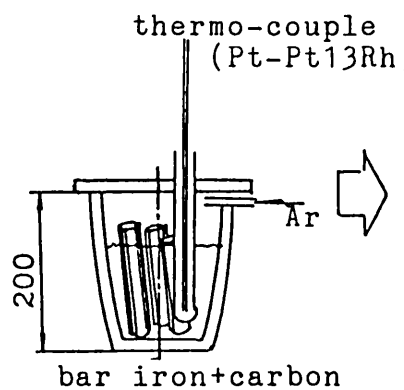
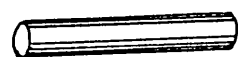
1) slag sample : expressed in mole fractions
 (CuS_{0.5}, SnS, FeS, NaS_{0.5}, CaS)
 calculated from wt% data (
 assuming CuS_{0.5}-SnS-FeS-
 NaS_{0.5}-CaS mixture).

- (5) Atmospheric conditions were 1 atm of argon gas or partial vacuum (approximately 1/10 atm of argon gas).
- (6) Temperature of carbon saturated iron 1250°C or 1600°C and temperature of steel, 1600°C. *control?*
- (7) In the case of CaS-based slags, the compositions were chosen on the line 1 in Fig. 5-5, which shows CaS-CaO-FeS-FeO reciprocal mixture. These slag compositions are saturated with CaS both at 1600°C and at 1250°C. Experiments were carried out using the procedure depicted in Fig. 5-2.

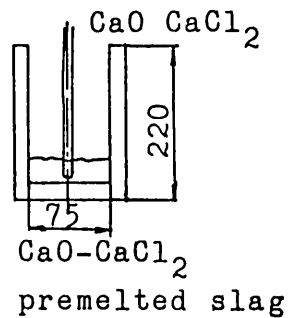
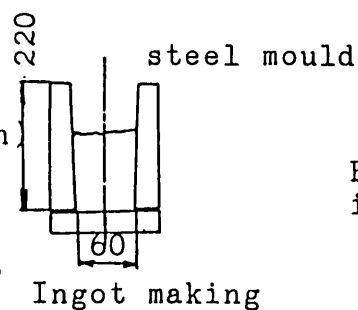
Preparation of materials

- Carbon saturated iron. Bar iron and pure graphite (99.9 wt% C) were melted in a crucible (MORGAN super-crucible A SALAMANDER-A16) under an argon gas atmosphere. Metal melts weighing between 3 and 9 kg, were cast into 3 kg or 1 kg ingots. C content was confirmed by checking the temperatures for solidification and re-melting. Typical results of temperature measurements are shown in Fig. 5-3.
- Steel. Electrolytic iron powder was used.
- Slag. NaS_{0.5} slag was dehydrated from Na₂S·9H₂O (Anala R sodium sulphide Na₂S · xH₂O produced by BDH Chemicals Ltd. Minimum assay is 31 wt% Na₂S and x is about nine.), which is commercially available, in a graphite crucible under reduced pressure (20 - 30 mmHg). A heat cycle used is shown in Fig. 5-4. This compound is very hygroscopic and was kept in a dessicator. Other slags, e.g. CaS, CaF₂, FeS, and CaCl₂ (produced by BDH Chemicals Ltd.), FeO, (iron ore FeO_n), CaO (made from CaCO₃ in recrystallised alumina crucible at 950°C overnight in the PHOENIX furnace) mixture were mixed.

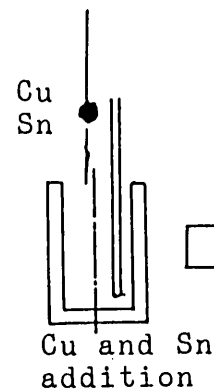
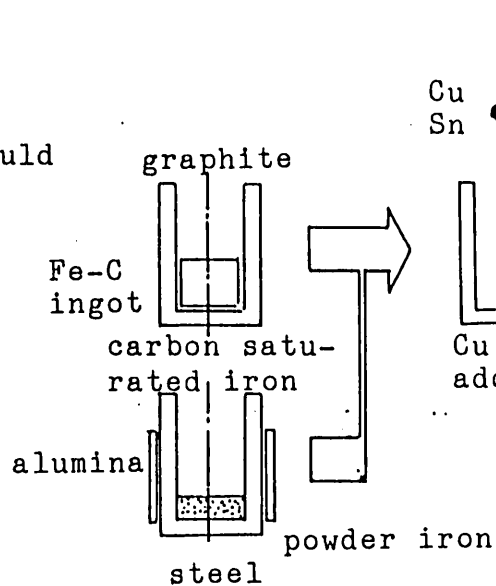
PREPARATION



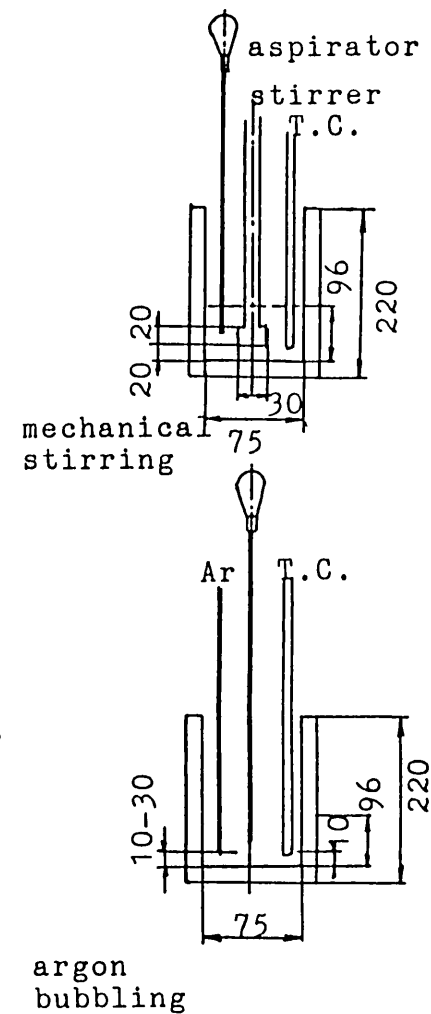
(mm)



MELTING



REACTION



ANALYSIS

Fig.5-2 Procedures for experiment.

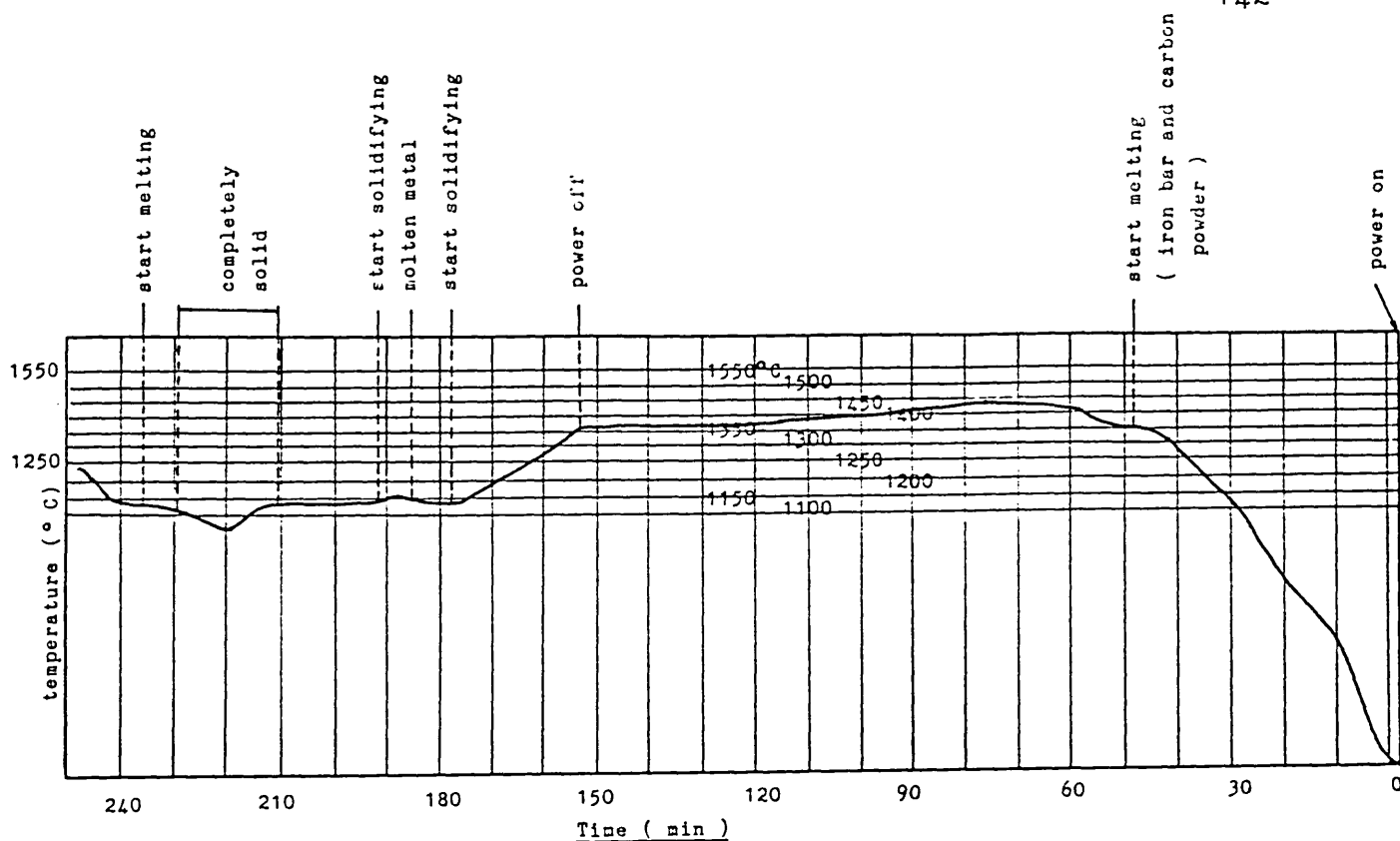


Fig.5-3 Typical temperature data for carbon saturated iron.

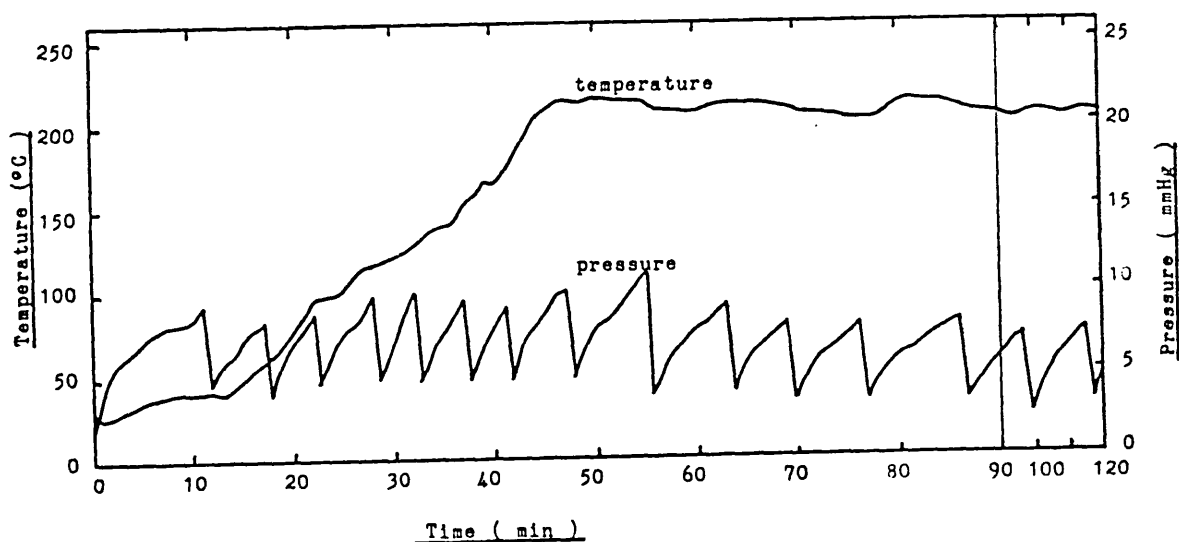


Fig.5-4 $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ dehydration.

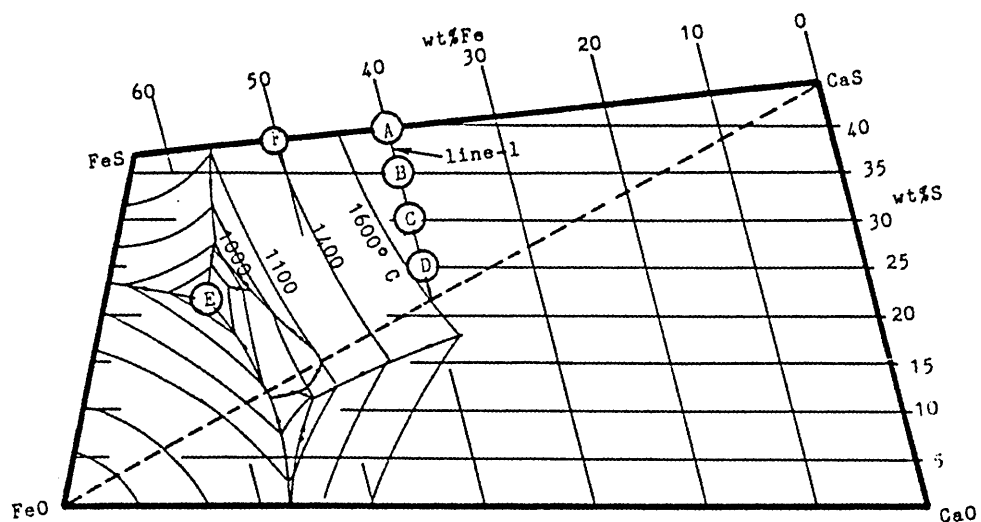


Fig.5-5(27) Choice of slag composition in the $\text{FeO}_n\text{-CaO-CaS-FeS}$ reciprocal system (iso-temperature lines by reference (45)).

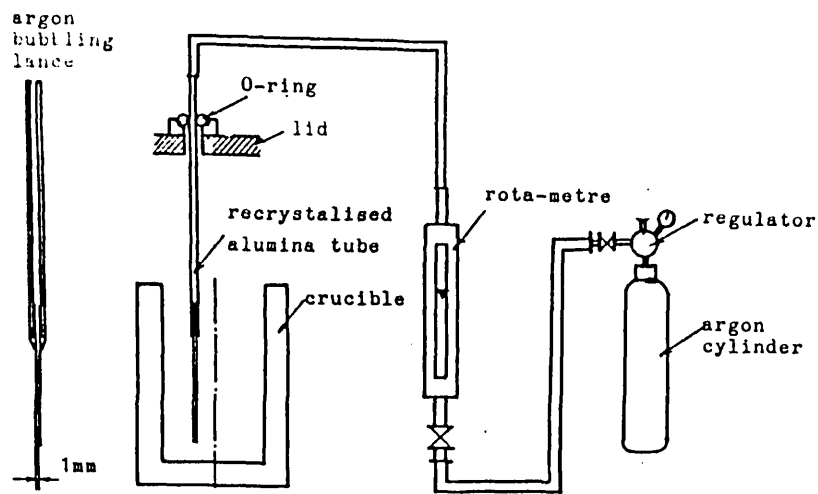


Fig.5-6 Equipment for argon bubbling.

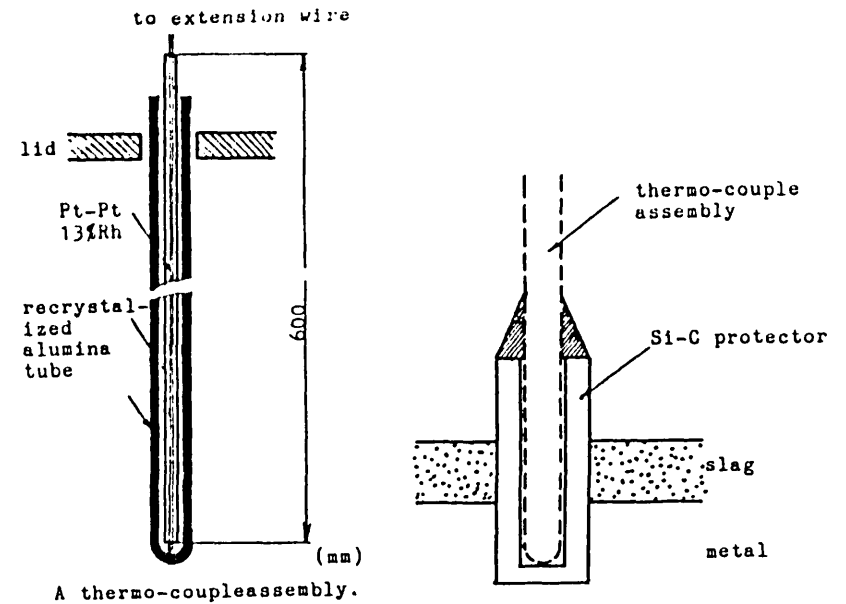
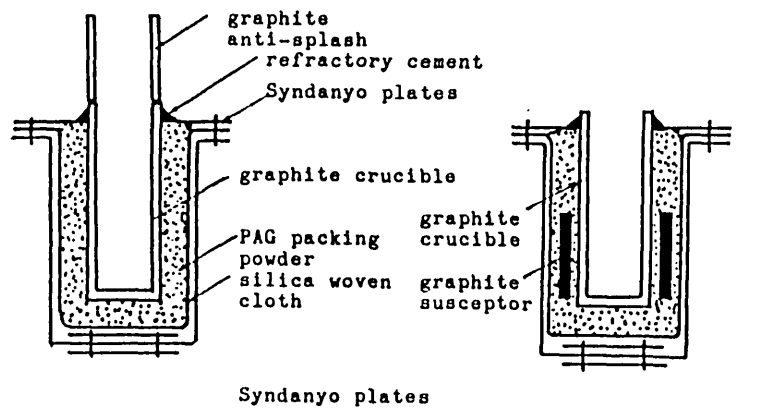


Fig.5-8 Thermo-couple.



(a) Crucible assembly (graphite crucible).
(b) Crucible assembly (alumina crucible).

Fig.5-7 Crucible assemblies.

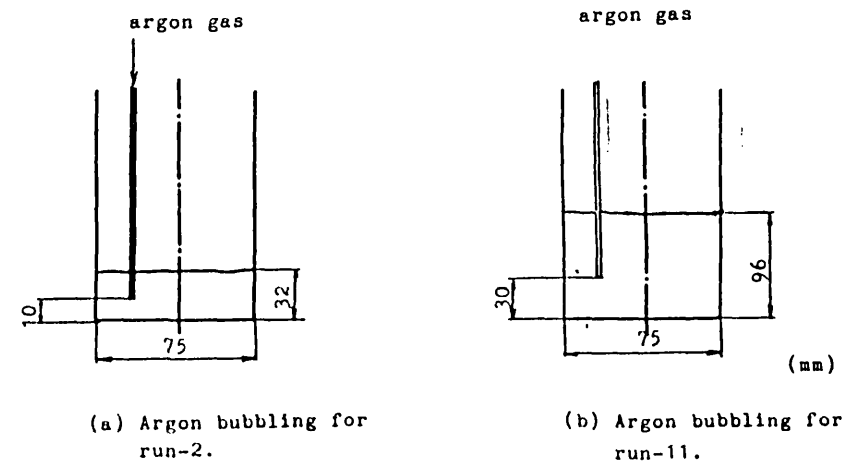


Fig.5-11 Geometry for argon bubbling.

CaO - CaCl₂ mixture was used for the investigation of S behaviour. This slag was premelted and crushed into powder.

Experiment.

Ingots of carbon saturated iron were melted in an alumina crucible or a graphite crucible. Iron powder was melted in an alumina crucible for steel experiment. The required amount of thin copper foil and granulated tin was added to molten metal under an argon atmosphere. After a given period, which was long enough for copper and tin added to be mixed uniformly in the metal bath, a sample was taken from the metal phase and another sample taken five minutes later. The alloy was kept at a particular temperature. Slag was dropped on the surface of the metal bath with a simultaneous increase of electric power of the furnace to compensate heat loss for making molten slag.

After addition of the slag, the temperature of bath was controlled manually by electric power and metal samples taken. Finally a slag sample was taken and the molten metal poured into the steel mould.

Analysis

Cu and Sn in the metal phase were analysed by the author using atomic absorption spectrophotometry. Samples for S analysis in the metal phase are sent to BSC. Samples for Cu, Na, Sn, Fe, Ca analysis in the slag phase were sent to Metallurgie Hoboken-Overpelt.

A vacuum furnace with a power unit was used. LEYBOLD-HERAEUS Type IS 1/III and RADTNE TS generator, 3 k Hz. There were some problems arising from the cooling water system and from deformation of the induction coil which physically supports the crucible assembly. These problems have been overcome. The mechanical agitator consists of a long shafted stirrer (graphite), positioning equipment (vertical stroke = 700mm) and driving mechanism (0-1500 r.p.m.). The operating conditions of the stirrer were determined from the water model and molten lead model simulations.

Stirring conditions were chosen for the entrainment of floating particles on the surface. They were determined under no baffle conditions. In the case of experiments with molten iron, a thermocouple tube was immersed into the bath and this acted as a baffle. It was claimed by Ando et al [3] that the system with a baffle is better than without in the sense of entrainment characteristics.

Equipment for argon bubbling is shown in Fig. 5-6. Alumina tube was found to be satisfactory at the high temperature. It tends to crack easily with sudden changes of temperature with time or/and space. The tip of this tube was set to 10mm above the bottom and off-centred by a quarter of the diameter of crucible.

2Nl/min. of argon gas was usually blown. Crucible assemblies are shown in Fig. 5-7. In the case of the higher argon gas flow rate (5 Nl/min), an anti-splash tube was used on the top of the crucible.

Thermo-couples are shown in Fig. 5-8. Graphite tubes are satisfactory for thermocouple protection. This can only be used for carbon saturated metal melts.

5-2 Results.

In this section, the results obtained are presented in tabular and graphical forms.

(1) Effect of argon bubbling gas flow rate.

Three cases were carried out at varying argon gas flow rates. (0, 2 and 5 Nl/min.). Comparison may be done between runs -13 -6 and -18 for pure $\text{NaS}_{0.5}$ slag and between runs -3 and -2 for 80 wt% $\text{NaS}_{0.5}$ - 20 wt% FeS mixed slag. These results are summarised in Table 5-2 and Fig. 5-9. Without argon bubbling, de-Sn does not occur but the concentration of Cu in the metal phase was still decreasing about 30 minutes after slag addition. On the other hand, with argon bubbling, the concentration of Cu in the metal phase reached steady state around the same time. In run-18 (5 Nl/min. argon bubbling gas flow), a large amount of splash, say 15-20% of the total molten metal, was observed.

Table 5-2 Effect of argon bubbling gas flow rate.

RUN	argon gas flow rate (Nl/min)	$-d(\text{wt}\% \text{Cu})/dt$ (wt%/min)	$-d(\text{wt}\% \text{Sn})/dt$ (wt%/min)	η_{Cu}	η_{Sn}	remarks
13	0	0.067	0	53%	0%	
6	2	0.110	0.01	52%	5%	
18	5	0.102	0	57%	0%	
		mean value	mean value			
		0-5min	0-40min			

1) Slag composition=pure $\text{NaS}_{0.5}$ (100g).

2) Metal=1000g at 1250° C.

Table 5-3 Comparison between argon bubbling and mechanical stirring.

RUN	mixing condition	η_{Cu}	η_{Sn}	remarks
11	argon bubbling 2 Nl/min	50%	7%	1225° C
14	mechanical stirring 700 r.p.m.	51%	1%	1250° C

1) Slag composition= 80wt% $\text{NaS}_{0.5}$ -20wt%FeS (300g).

2) Metal=3000g.

Table 5-4 Effect of mass.

RUN	mass (g) metal slag	$-d(\text{wt}\% \text{Cu})/dt$ (wt%/min)*	$-d(\text{wt}\% \text{Sn})/dt$ (wt%/min)**	η_{Cu} η_{Sn}	remarks
2	1000 100	0.100	0.0020	55% 7%	1275° C
11	3000 300	0.108	0.0008	54% 3%	2 Nl/min argon bubbling 1225° C 2 Nl/min argon bubbling

1) Slag composition= 80wt% $\text{NaS}_{0.5}$ -20wt%FeS.

2) Metal= carbon saturated iron.

3) Graphite crucible (75 mm I.D.)

4) * : mean value of t=0-5min, ** : mean value of t=0-30min.

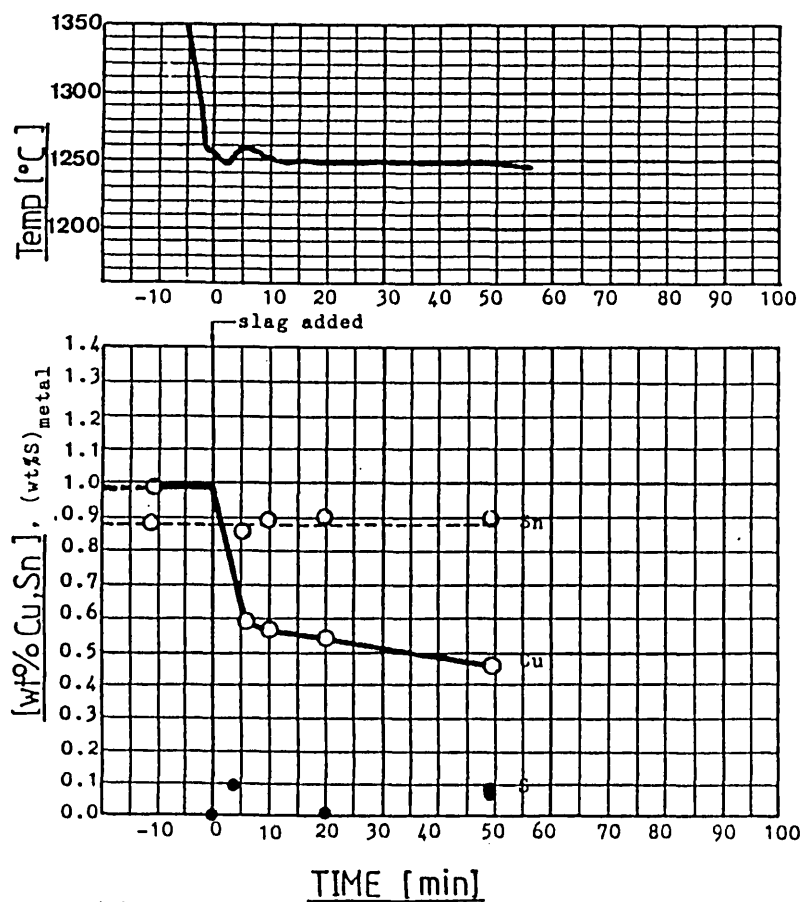
Table 5-5 Effect of slag composition ($\text{NaS}_{0.5}$ -FeS mixed slag for carbon saturated iron).

RUN	slag composition $\text{NaS}_{0.5}$ FeS (wt%)	weight metal slag (g)	t (min)	η_{Cu} η_{Sn}	(wt% S)	remarks
6	100 0	1000 100	50	52% 5%	0.019	
2	80 20	1000 100	30	55% 7%	0.03	
4	50 50	1000 100	53	51% 0%	0.16	
5	20 80	3000 300	60	37% 0%	0.43	
23	0 100	3000 300 (nominal)	6	31% 3%	1.50	

1) Argon bubbling=2 Nl/min.

RUN number	slag pure $\text{NaS}_{0.5}$ (106g)
13	metal carbon saturated iron (1043g)

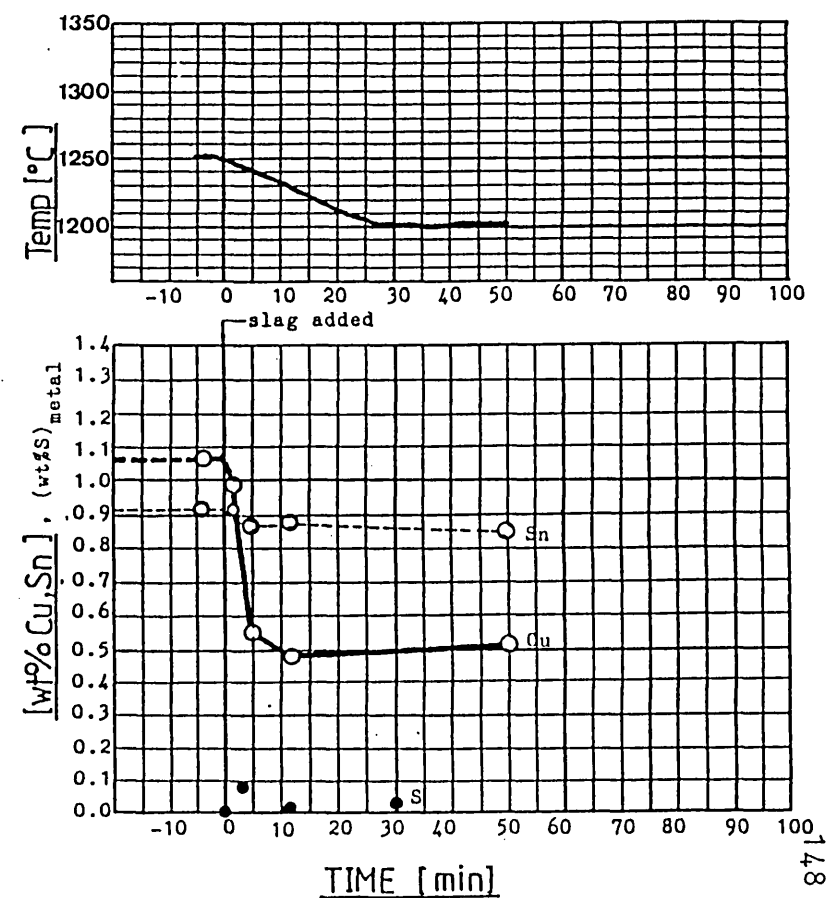
1) no argon bubbling (except for 2 Nl/min from t=44 to 55 minutes).



(a) Run-13.
Fig.5-9 De-Cu/de-Sn experiment.

RUN number	slag pure $\text{NaS}_{0.5}$ (98.9g)
6	metal carbon saturated iron (1023 g)

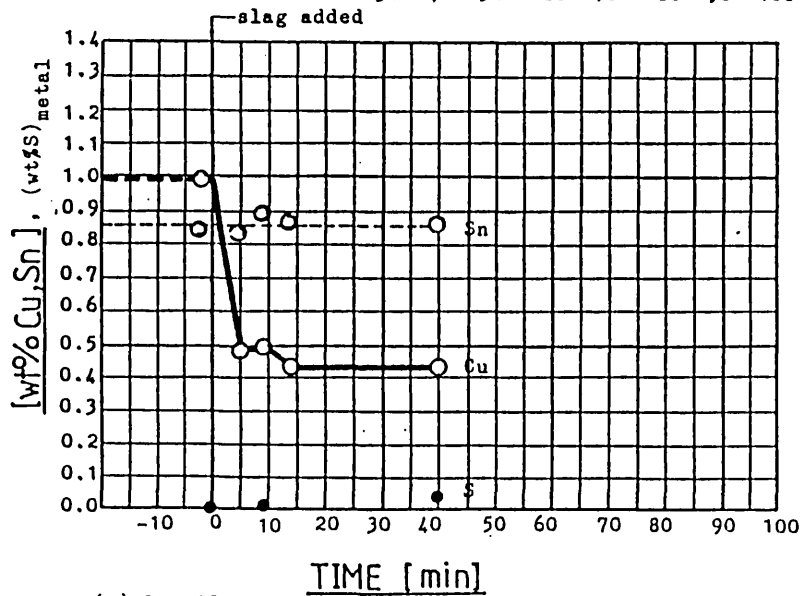
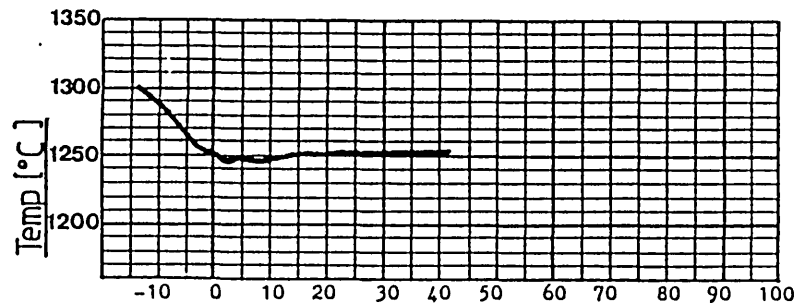
1) argon bubbling=2 Nl/min.



(b) Run-6.

RUN number 18	slag pure $\text{NaS}_{0.5}$ (98.6g)
	metal carbon saturated iron (1063g)

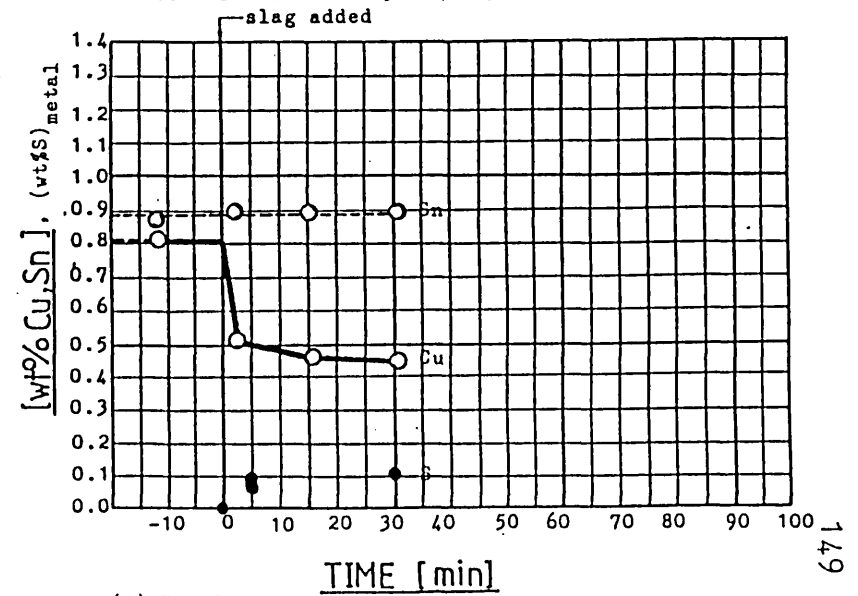
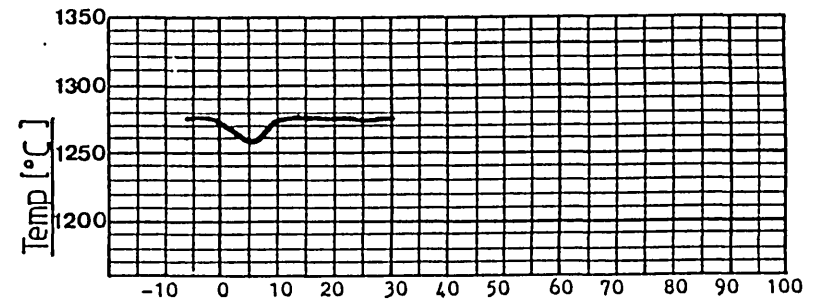
1) argon bubbling = 5 Nl/min.



(c) Run-18.
Fig.5-9 De-Cu/de-Sn experiment.

RUN number 3	slag 80wt% $\text{NaS}_{0.5}$ -20wt%FeS (92.1g)
	metal carbon saturated iron (919g)

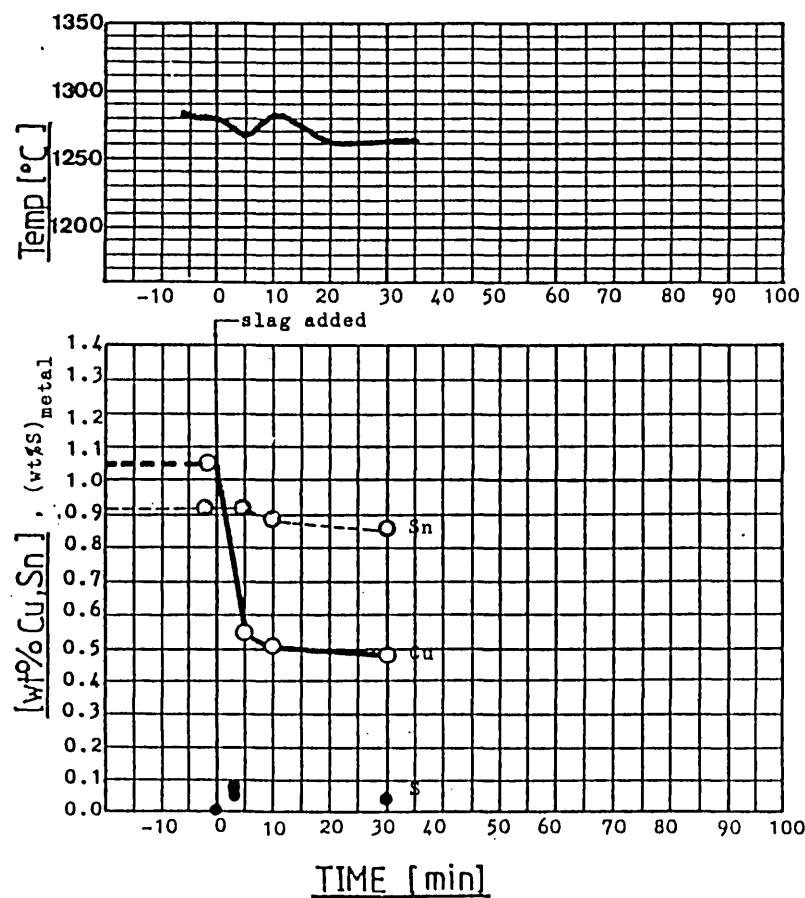
1) no argon bubbling.



(d) Run-3.

RUN number	slag 80wt%NaS _{0.5} -20wt%FeS (100g)
2	metal carbon saturated iron (963g)

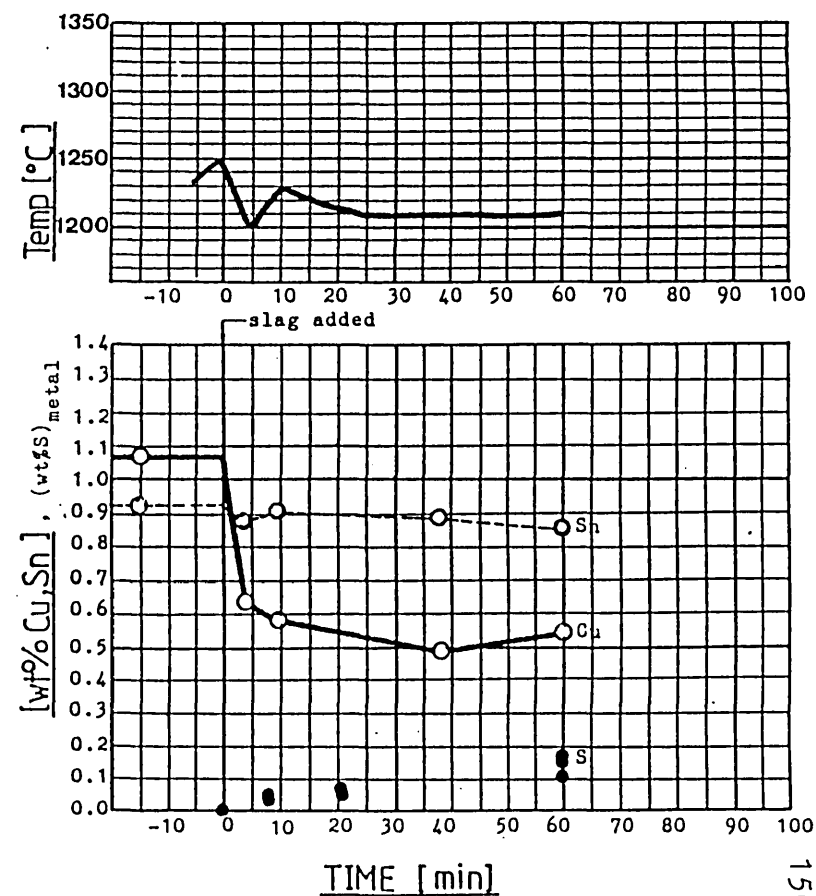
1) argon bubbling = 2 Nl/min.



(e) Run-2.
Fig.5-9 De-Cu/de-Sn experiment.

RUN number	slag 80wt%NaS _{0.5} -20wt%FeS (274g)
11	metal carbon saturated iron (2880g)

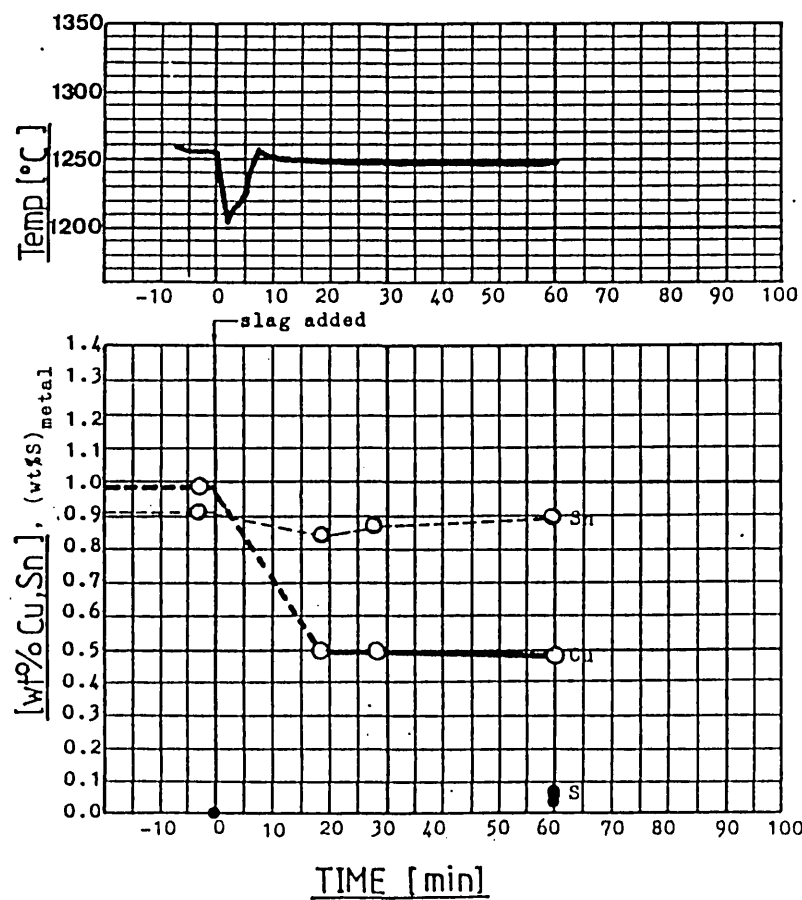
1) argon bubbling = 2 Nl/min.



(a) Run-11.
Fig.5-10 De-Cu/de-Sn experiment.

RUN number	slag 80wt%NaS _{0.5} -20wt%FeS (301g)
14	metal carbon saturated iron (3076g)

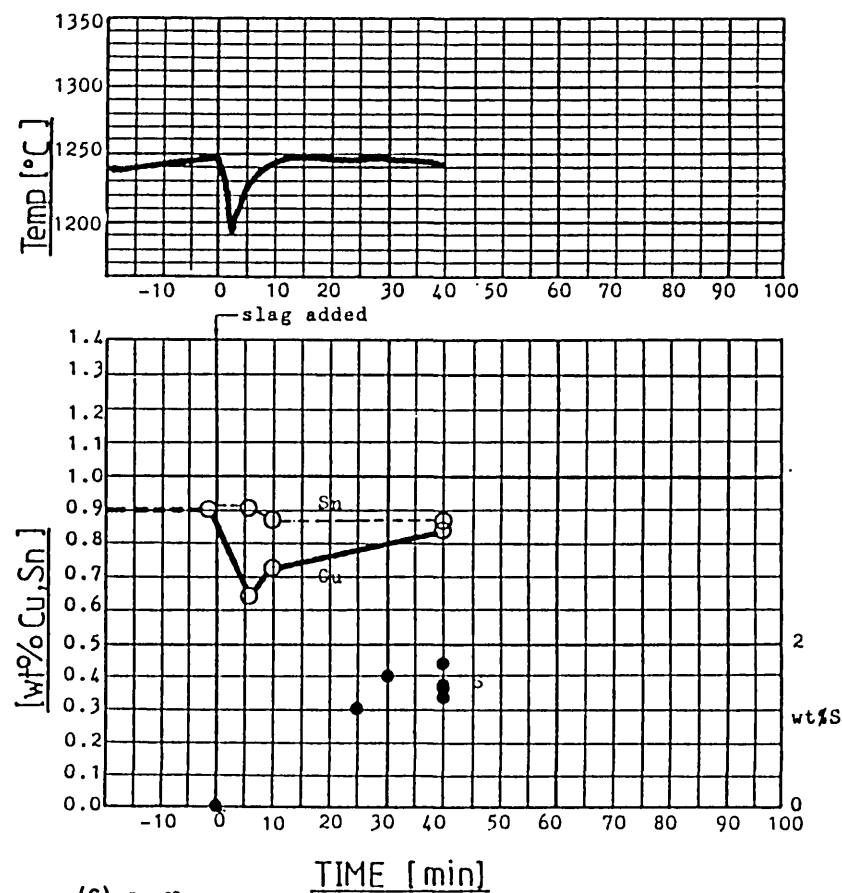
1) mechanical stirring (revolution rate = 700r.p.m.).



(b) Run-14.
Fig.5-10 De-Cu/de-Sn experiment.

RUN number	slag pure FeS (355g)
23	metal carbon saturated iron (3519g)

1) argon bubbling = 2 Nl/min.



(c) Run 23.
De-Cu/de-Sn experiment.

(2) Comparison between argon bubbling and mechanical stirring.

Comparison, which is summarised in Table 5-3 and Fig. 5-10 can be made between run -11 for argon bubbling and run -14 for mechanical stirring. De-Sn is a much slower process than de-Cu. De-Sn with argon bubbling is more efficient than with mechanical stirring. A thermo-couple which was immersed in the molten iron worked as a baffle in the case of mechanical stirring.

(3) Effect of mass

Run -2 in Fig. 5-9(e) was carried out with 1 kg metal and run -11 in Fig. 5-10(a) with 3 kg metal using a 80 wt% $\text{NaS}_{0.5}$ - 20 wt% FeS mixed slag. These two runs were carried in the crucibles with the same inner diameter. The smaller scale seemed to be advantageous in the sense of kinetics as is summarised in Table 5-4. Argon gas flow rate was 2 Nl/min. for both runs. Geometries for bubbling which are shown in Fig. 5-11 were somewhat different in these two cases.

(4) Effect of slag composition in $\text{NaS}_{0.5}$ -FeS mixed slag for carbon saturated iron.

Run -6, -2, -4, in Fig. 5-12, -5 in Fig. 5-13 and -23 were carried out in the order of increasing FeS content in the initial slag phase. Run -2 (80 wt% $\text{NaS}_{0.5}$ - 20 wt% FeS mixed slag) has the highest η_{Cu} value of these slags (see Table 5-5).

(5) Effect of vacuum

Comprehensive investigations on the effect of vacuum on de-Cu/de-Sn have not been carried out. In run-pre 2 in Fig. 5-14 vacuum was exerted in the latter half of the experiment. Under the vacuum condition, some de-Sn occurred, though no de-Sn occurred without argon bubbling on vacuum.

RUN number	slag 50wt%NaS _{0.5} -50wt%FeS (133g)
4	metal carbon saturated iron (1326g)

1) argon bubbling = 2 Nl/min.

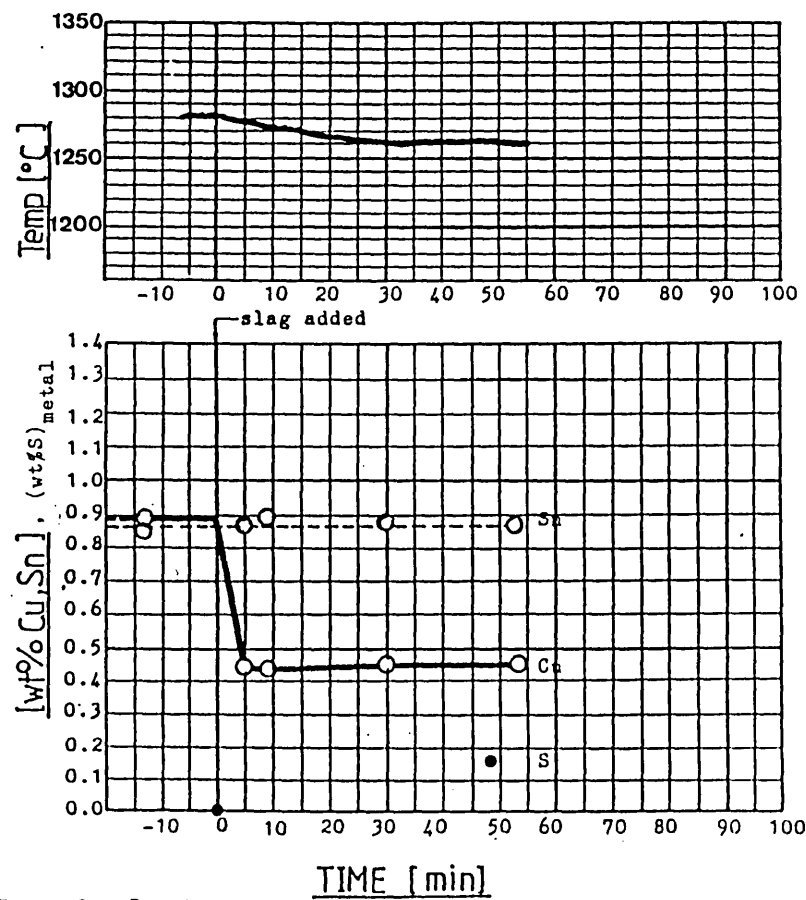


Fig 5-12 Run-4.

RUN number 5	slag 20wt%NaS _{0.5} -80wt%FeS (302g)
	metal carbon saturated iron (3019g)

1) argon bubbling = 2 Nl/min.

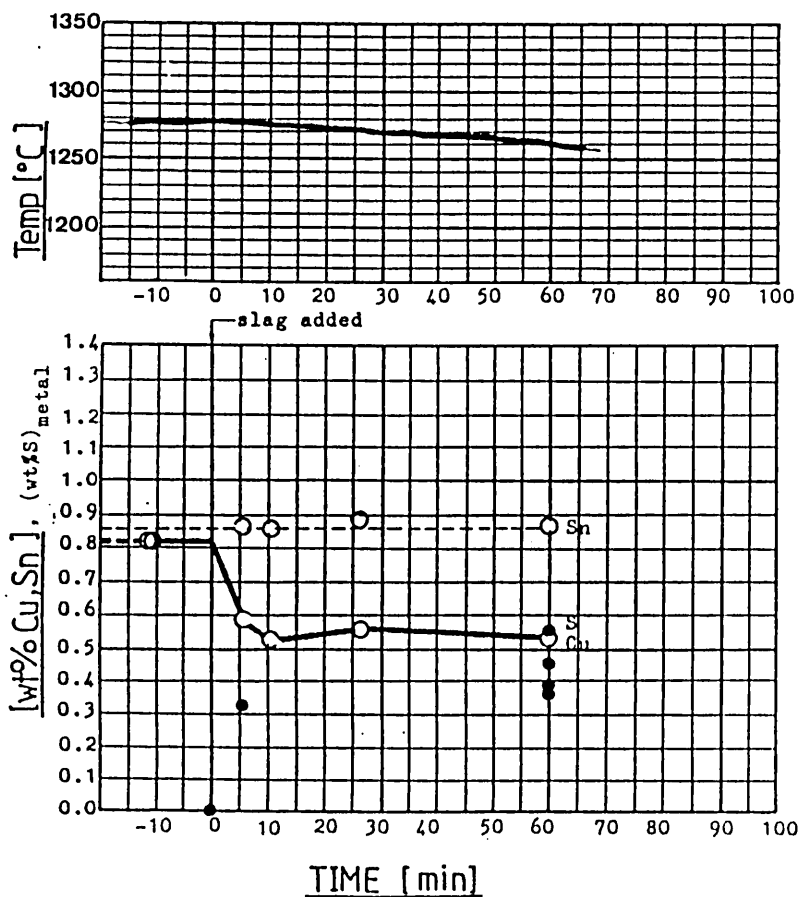


Fig.5-13 De-Cu/de-Sn experiment.

RUN number pre-2	slag 50wt%NaS _{0.5} -50wt%FeS (60.3g)
	metal carbon saturated iron (813g)

1) argon bubbling = 1.2 Nl/min.

2) vacuum (approx. 1/10 atm) was introduced after 120 minutes.

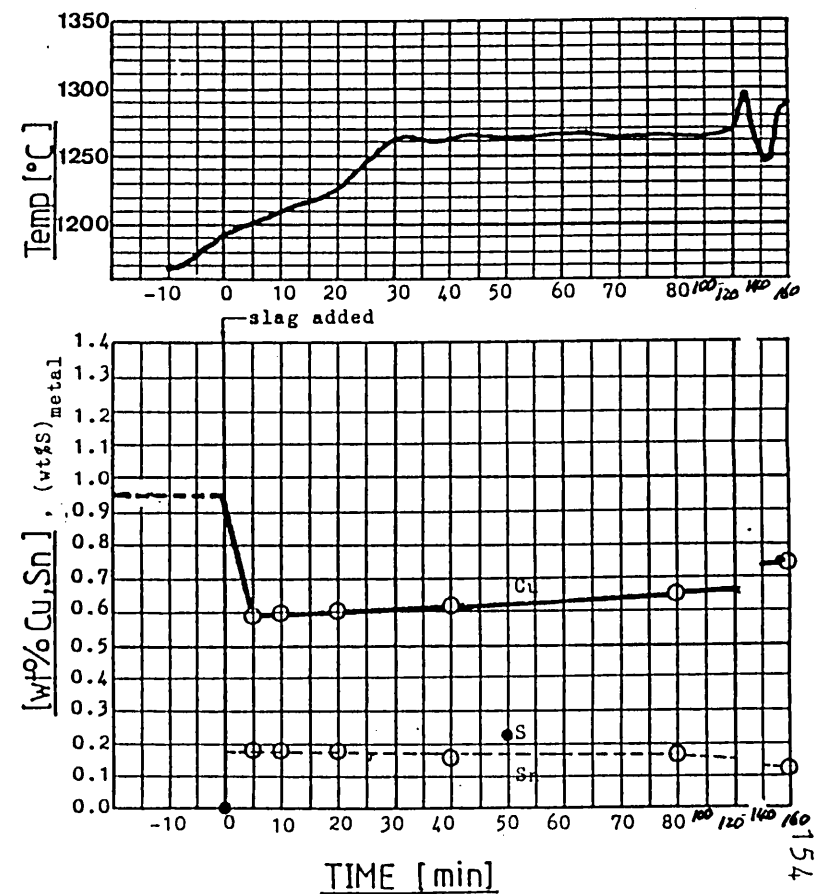


Fig.5-14 De-Cu/de-Sn experiment.

(6) Effect of slag composition in CaS-FeS-FeO mixed slag for carbon saturated iron.

As is shown in Table 5-6, the sulphur content of the metal phase treated with CaS-FeS-FeO mixed slag is generally higher than with $\text{NaS}_{0.5}$ -FeS mixed slag. These results are shown in Fig. 5-15.

In run-17, CaO-CaCl_2 mixed slag was added in the later stage of the de-Cu reaction. Cu reversion and de-S occurred in this run after this CaO-CaCl_2 mixture addition.

(7) Comparison between $\text{NaS}_{0.5}$ -FeS, CaS-FeS and $\text{NaS}_{0.5}$ -CaS-FeS mixed slags.

$\text{NaS}_{0.5}$ -FeS mixture in run -4, CaS-FeS mixture in run -21 and $\text{NaS}_{0.5}$ -CaS-FeS mixture in run -24 which is shown in Fig. 5-16, can be compared for evaluating the characteristics of $\text{NaS}_{0.5}$ and CaS (see Table 5-7).

(8) CaF_2 - FeS mixed slag for carbon saturated iron.

CaF_2 -FeS mixed slag was used in run -pre 3, -pre 4, -1 and -25. Results are shown in Fig. 5-17 and Table 5-8. Slag phase was observed to be partly solid.

(9) Comparison between CaF_2 -FeS mixed slag and CaS-FeS mixed slag for steel

Run -12 in Fig. 5-18 was for CaF_2 - FeS mixed slag and run -7 for CaS-FeS mixed slag. Results are shown in Table 5-8. The sulphur content in the metal phase of run -7 is higher than that of run -12. Run -12 gave better η_{Cu} - values than run -7 (see Table 5-9).

Table 5-6 Effect of slag composition (CaS-FeS-FeO mixed slag for carbon saturated iron).

RUN	TEMPERATURE (°C)	SLAG COMPOSITION			time (min)	η_{Cu}	η_{Sn}	time (min)	wt% S	remarks
		CaS	FeS	FeO						
21	1250	37	63	0	40	29%	3%	40	0.74	slag-A (see Fig.5-5
22*	1250	40	47	13	45	13%	8%	45	0.44	slag-B
								53	0.35	after CaO addition
19	1250	43	29	28	40	0%	0%	40	0.38	slag-C
17**	1255	15	39	46	35	13%	5%	25	0.65	slag-E
								60	0.34	after CaO addition
10	1260	18	82	0	35	54%	8%	35	0.49	slag-F
		wt%								

1) * : at t=45.5min 70g(60wt%CaO-40wt%CaCl₂) added.2) **: at t=36min 50g(60wt%CaO-40wt%CaCl₂) added.3) (slag/metal)_{weight}=0.10

4) Argon bubbling=2 Nl/min.

Table 5-7 Comparison between NaS_{0.5} and CaS for de-Cu/de-Sn from carbon saturated iron.

RUN	SLAG COMPOSITION			time (min)	η_{Cu}	η_{Sn}	time (min)	wt% S	remarks
	NaS _{0.5}	FeS	CaS						
4	50	50	0	53	51%	0%	48	0.16	1275° C
21	0	63	37	40	30%	3%	40	0.74	1250° C
24	40	40	20	40	41%	0%	40	0.088	1250° C

1) Argon bubbling+2 Nl/min.

2) Metal(3000g)-slag(300g) /nominal.

Table 5-8 CaF₂-FeS mixed slag for carbon saturated iron.

RUN	TEMPERATURE (°C)	WEIGHT		time (min)	η_{Cu}	(wt%sn)	time (min)	wt% S	remarks
		METAL (g)	SLAG (g)						
pre-3	1260	1225	80	120	6%	0.05	100	0.47	argon bubbling
pre-4	1315	1168	180	110	31%	0.06	80	1.23	1.2 Nl/min.
1	1300	2924	301	37	3%	0.03	30	1.05	argon bubbling
25	1600	2427	250	40	2%	0.10	40	1.17	1.4 Nl/min.
									mechanical
									stirring 700r.p.m.
									argon bubbling
									2 Nl/min (initial
									10min., afterwards
									argon surface
									blowing).

1) Slag composition= 50wt%CaF₂-50wt%FeS.Table 5-9 Comparison of CaF₂-FeS and CaS-FeS mixed slag for steel.

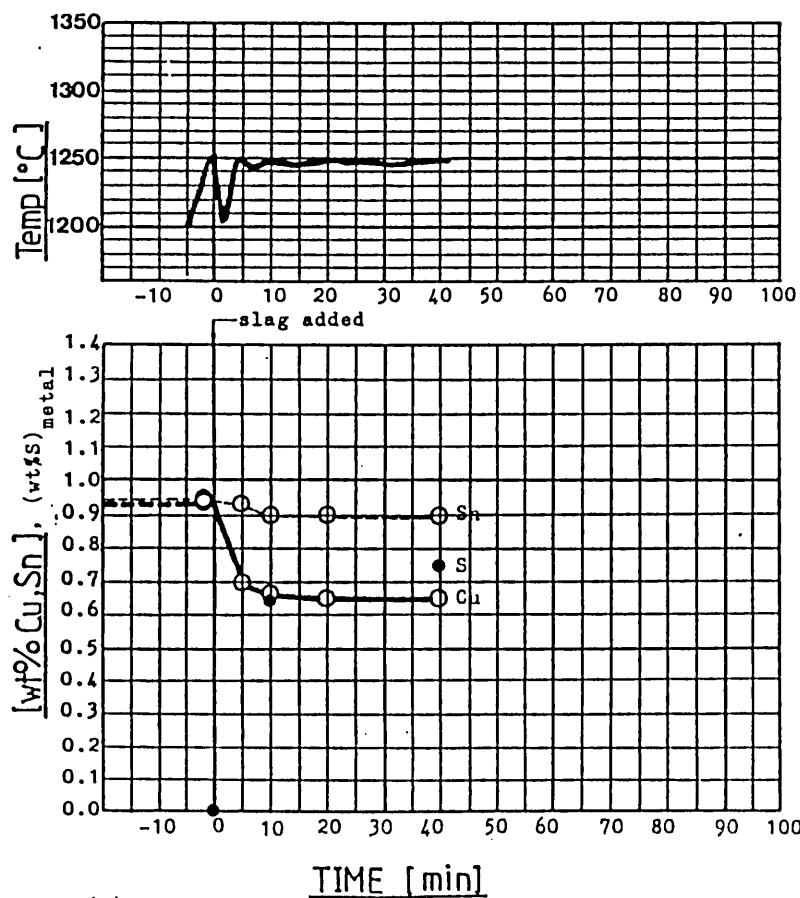
RUN	TEMPERATURE (°C)	SLAG COMPOSITION			time (min)	η_{Cu}	η_{Sn}	time (min)	wt% S	remarks
		CaF ₂	FeS	CaS						
12	1600	50	50	0	36	28%	21%	36	1.64	
7	1590	0	63	37	40	6%	25%	40	2.09	

1) Argon bubbling=2 Nl/min.

2) Metal(1000g)-slag(100g)/nominal.

RUN number 21	slag	37wt%CaS-63wt%FeS (300g)
	metal	carbon saturated iron (2924g)

1) argon bubbling = 2 Nl/min.



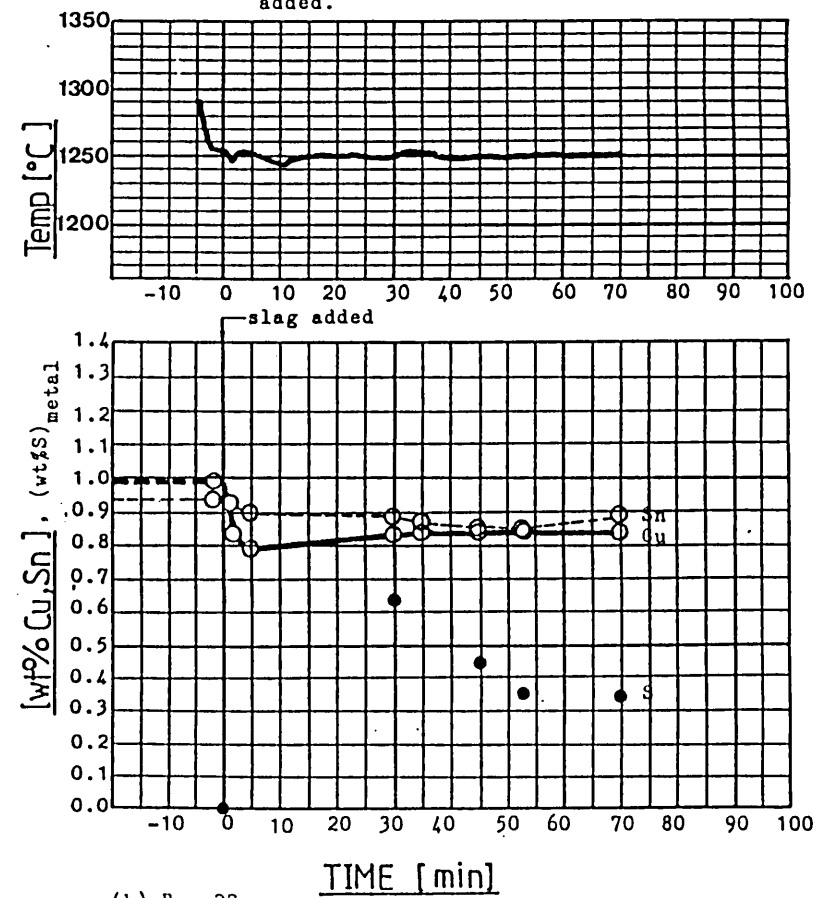
(a) Run-21.
Fig.5-15 De-Cu/de-Sn experiment.

RUN number 22	slag	40wt%CaS-47wt%FeS-13wt%FeO (310g)
	metal	carbon saturated iron (3141g)

1) argon bubbling = 2 Nl/min.

2) at t=31 min. 10g of Al added.

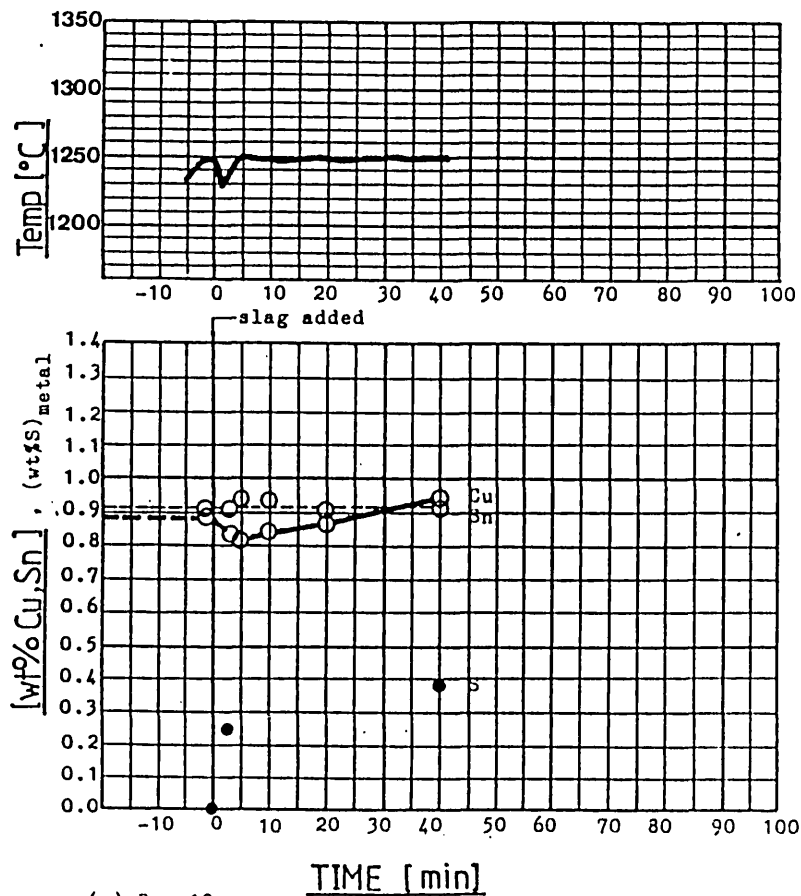
3) at t=45.5 min. 70g of 60wt%CaO-40wt%CaCl₂ added.



(b) Run-22.

RUN number	slag 43wt%CaS-29wt%FeS-28wt%FeO (299g)
19	metal carbon saturated iron (3048g)

1) argon bubbling = 2 Nl/min.

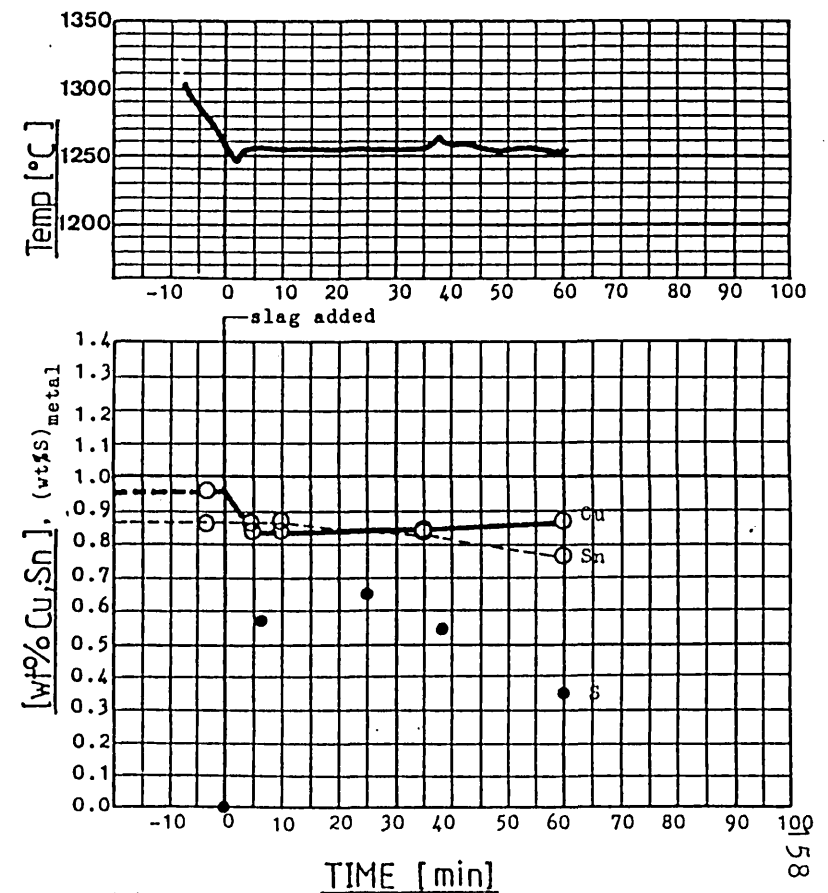


(c) Run-19.
Fig.5-15 De-Cu/de-Sn experiment.

RUN number	slag 15wt%CaS-39wt%FeS-46wt%FeO (100g)
17	metal carbon saturated iron (1039g)

1) argon bubbling = 2 Nl/min.

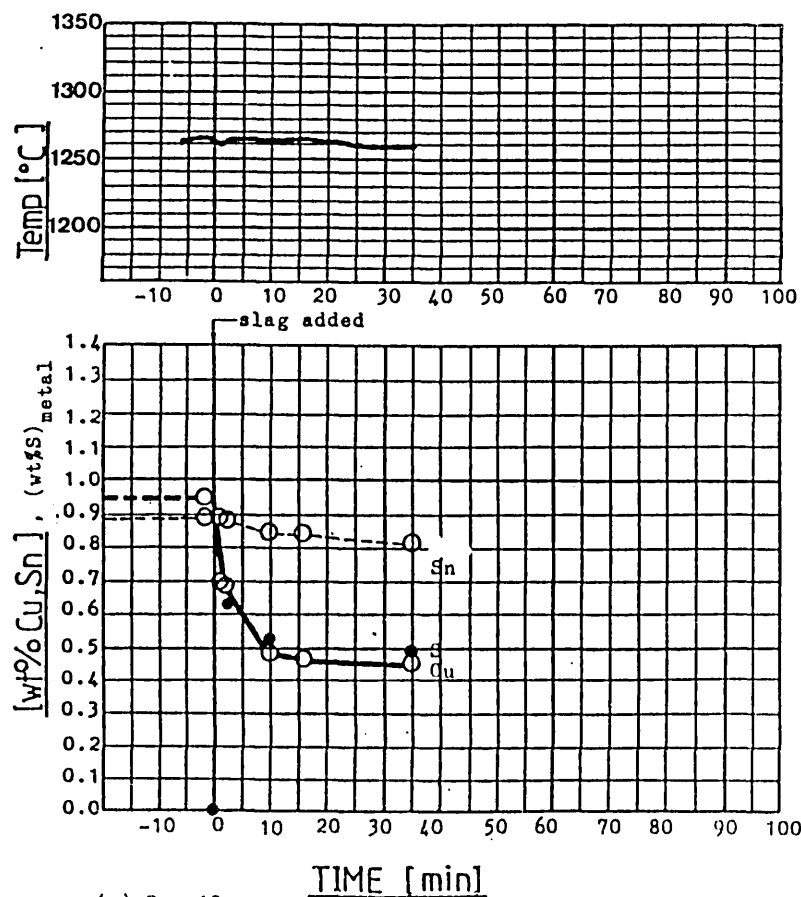
2) at t=36 min. 50g of 60wt%CaO-40wt%CaCl₂ added.



(d) Run-17.

RUN number	slag 18wt%CaS-82wt%FeS (106g)
10	metal carbon saturated iron (1066g)

1) argon bubbling = 2 Nl/min.



(e) Run-10.
Fig.5-15 De-Cu/de-Sn experiment.

RUN number	slag 40wt%NaS _{0.5} -40wt%FeS-20wt%CaS(350g)
24	metal carbon saturated iron (3496g)

1) argon bubbling = 2 Nl/min.

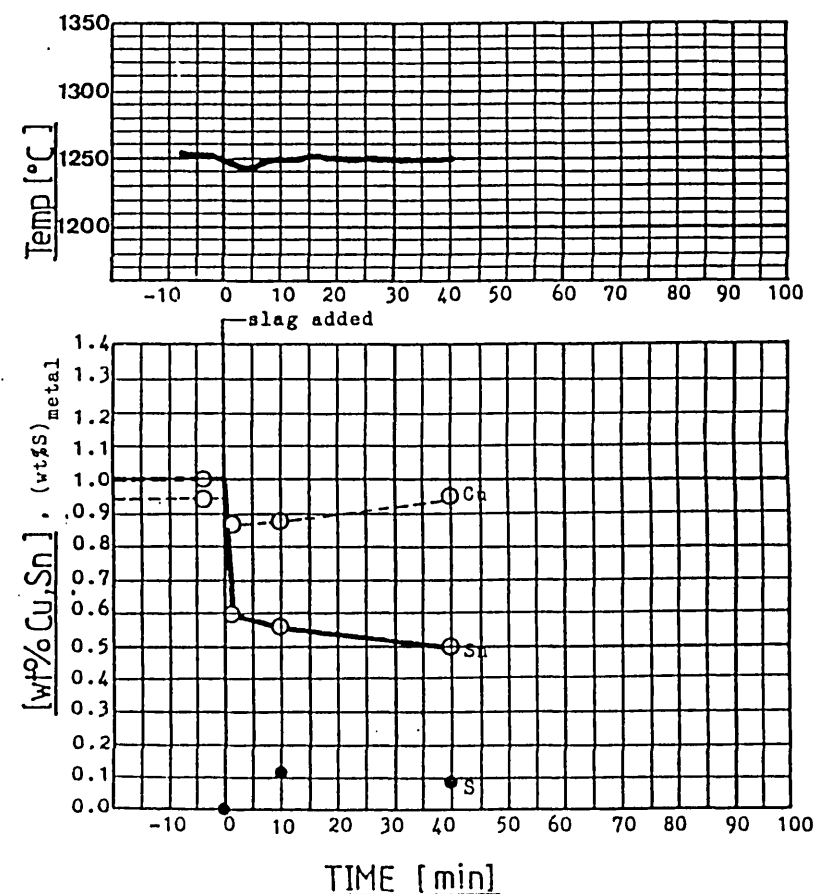
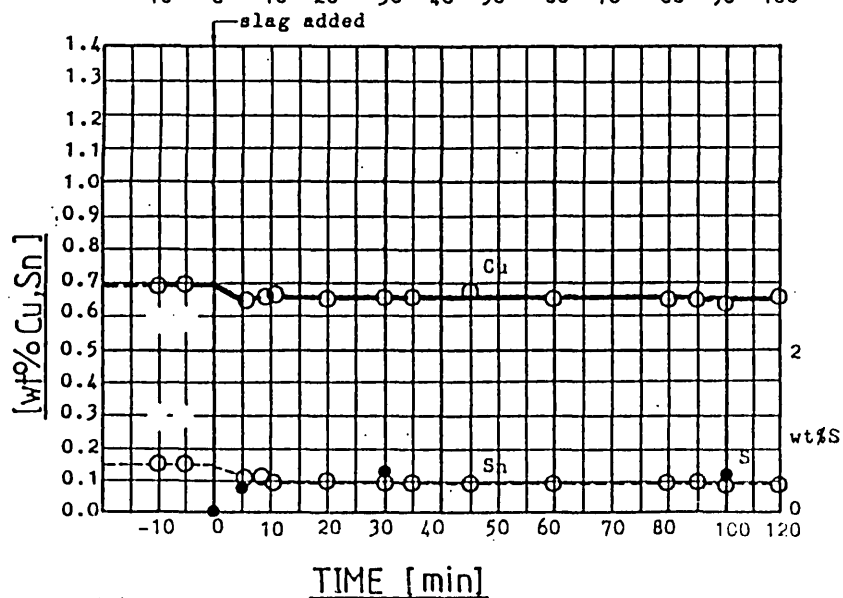
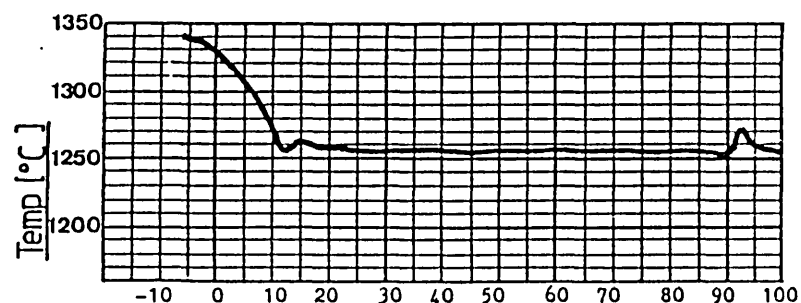


Fig.5-16 De-Cu/de-Sn experiment.

RUN number	slag 50wt%CaF ₂ -50wt%FeS (60g)
pre-3	metal carbon saturated iron (1225g)

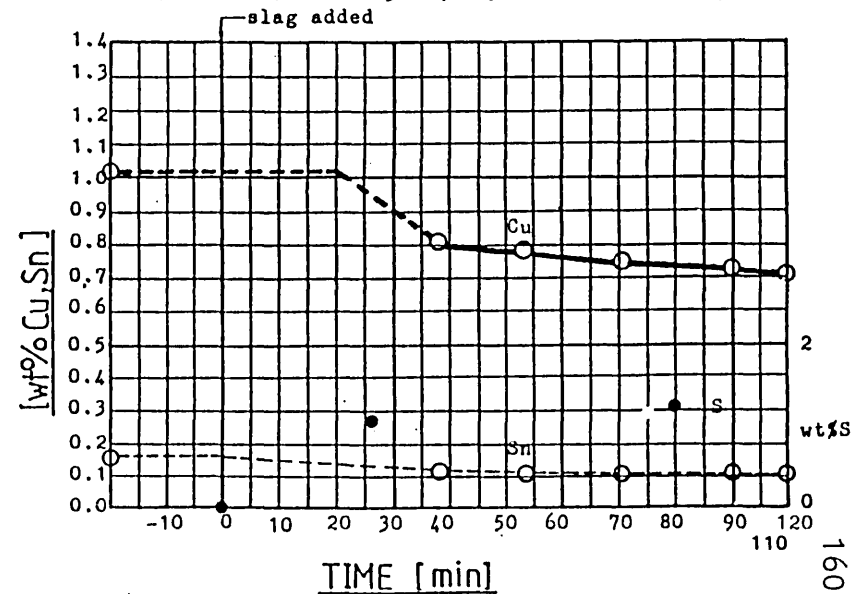
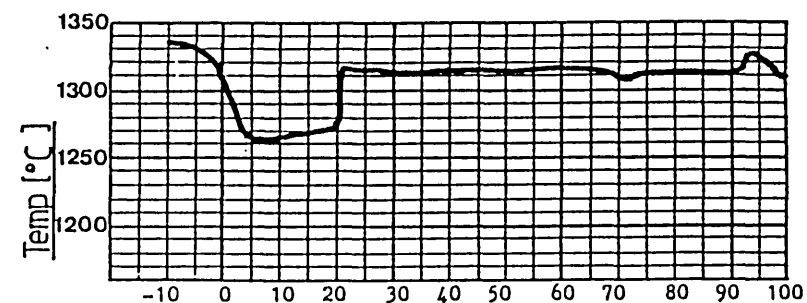
- 1) argon bubbling = 1.2 Nl/min.
- 2) vacuum (approx. 1/10 atm) was introduced after 100 min.



(a) Run-pre-3.
Fig.5-17 De-Cu/de-Sn experiment.

RUN number	slag 50wt%CaF ₂ -50wt%FeS (180g)
pre-4	metal carbon saturated iron (1168g)

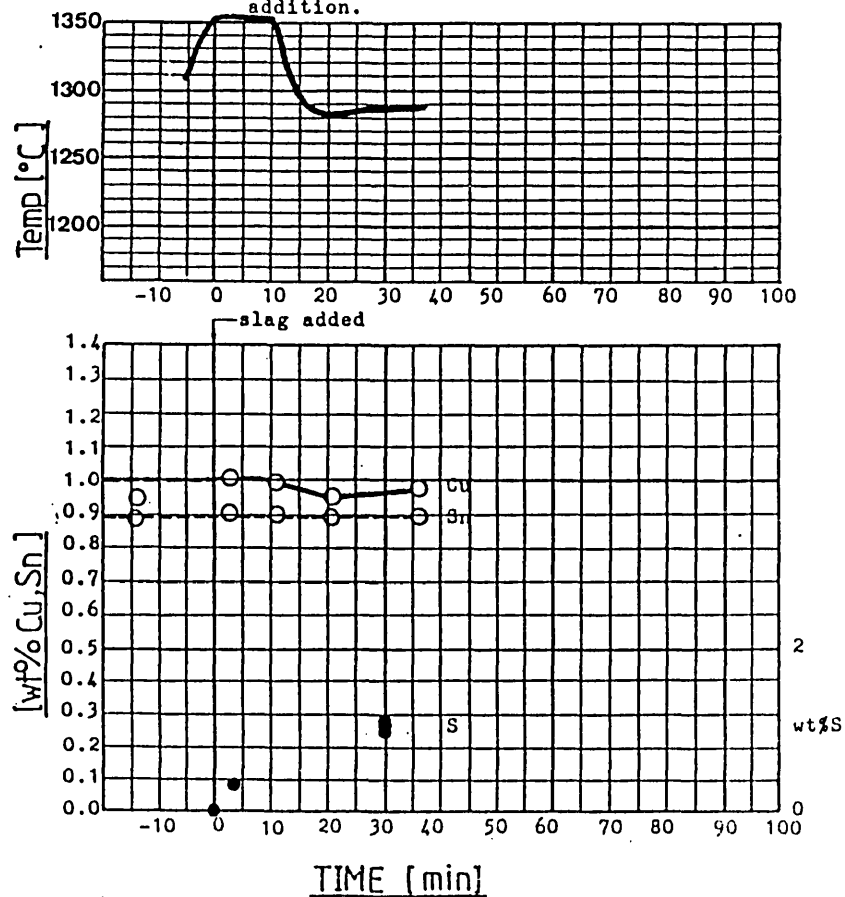
- 1) argon bubbling = 1.4 Nl/min.
- 2) vacuum (approx. 1/10 atm) was introduced after 90 min.



(b) Run-pre-4

RUN number	slag 50wt%CaF ₂ -50wt%FeS (301g)
1	metal carbon saturated iron (3006g)

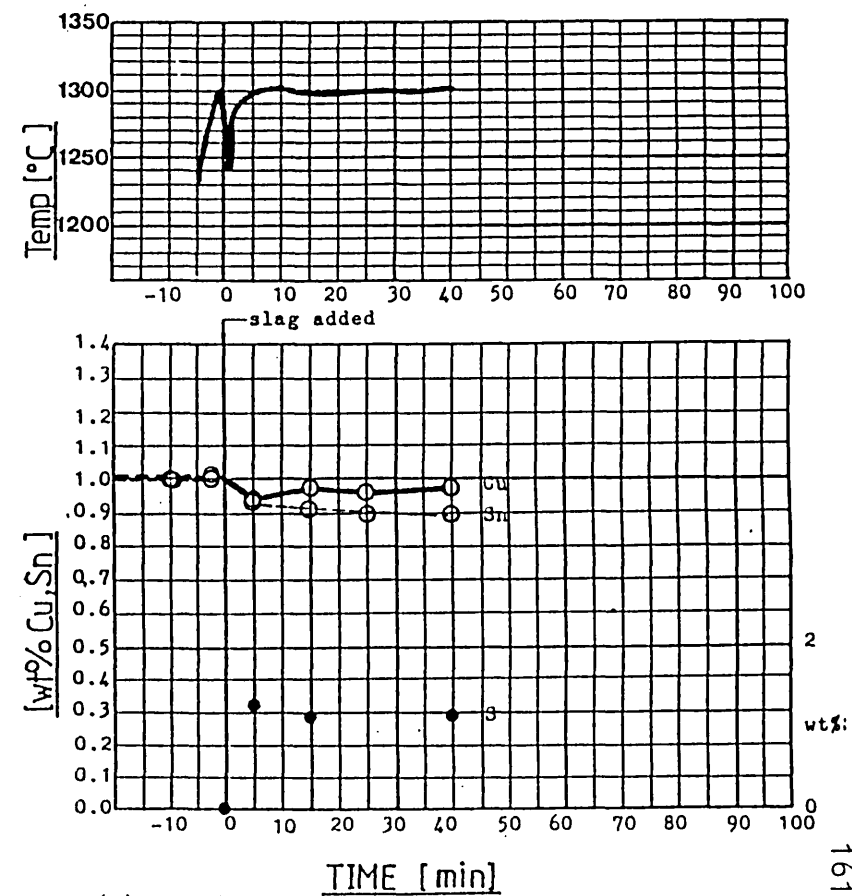
- 1) mechanical stirring (revolution rate = 700r.p.m.).
- 2) 75.2g (slag)*four times (every 5 minutes) addition.



(c) Run-1.
Fig. 5-17 De-Cu/de-Sn experiment.

RUN number	slag 50wt%CaF ₂ -50wt%FeS (250g)
25	metal carbon saturated iron (2427g)

- 1) argon bubbling = 2 Nl/min (t=0 - 10 min.) afterwards argon surface blowing.



(d) Run-25.

Table 5-10 Effect of slag composition (CaS-FeS-FeO mixed slag for steel).

RUN	TEMPERATURE (° C)	SLAG COMPOSITION			time (min)	η_{Cu} η_{Sn}		time (min)	wt% S	remarks
		CaS	FeS	FeO _n						
7	1590	37	63	0	40	6%	25%	40	2.09	slag-A
8	1575	40	47	13	30	2%	22%	30	2.12	slag-B
9	1590	43	29	28	40	5%	21%	50	1.76	slag-C
15	1600	46	11	43	40	5%	21%	40	1.34	slag-D
16	1605	15	39	46	40	0%	8%	40	1.39	slag-E

- 1) Argon bubbling=2 Nl/min, except for run-16 in which 4 Nl/min argon surface blowing was used.
 2) Metal(1000g)-slag(100g)/nominal.

Table 5-11 Comparison of CaS and CaF₂ for steel.

RUN	TEMPERATURE (° C)	SLAG COMPOSITION			time (min)	η_{Cu} η_{Sn}		remarks
		CaF ₂	FeS	CaS				
12	1600	50	50	0	36	28%	21%	
7	1590	0	63	37	40	6%	25%	
26	1600	26	61	13	40	26%	33%	modified slag-F wt% S=1.78 at t=30min.

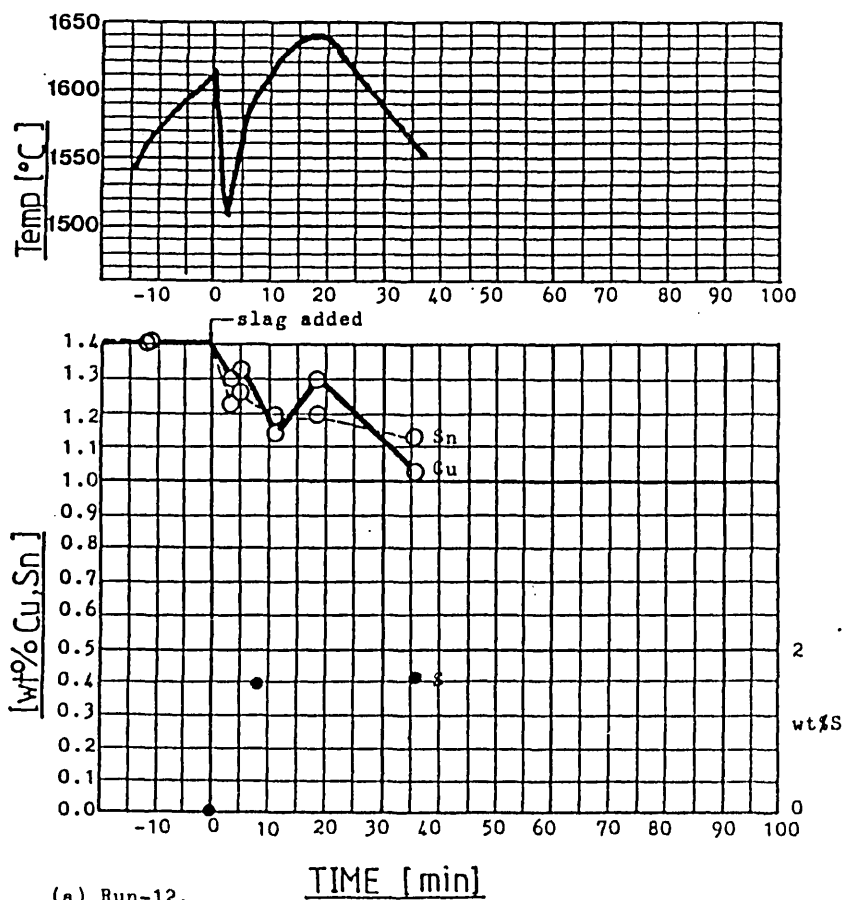
- 1) Run-26 : slag-F + CaF₂ (half of CaS weight), argon surface blowing =3 Nl/min.
 2) (slag/metal)_{weight}=0.10.

Table 5-12 Effect of partial vacuum.

- In Run-pre-2, {
- 1) t=50-80min --- argon bubbling(1.2 Nl/min)
 Sn concentration : 0.172wt% — 0.15 wt%
 (rate=7*10⁻⁴ wt%/min)
 - 2) t=80-120min -- no bubbling
 Sn concentration : 0.151wt% — 0.165wt%
 (rate=-4*10⁻⁴ wt%/min)
 - 3) t=120-180min - partial vacuum
 Sn concentration : 0.165wt% — 0.123wt%
 (rate=1.6*10⁻⁴ wt%/min)

RUN number	slag	50wt%CaF ₂ -50wt%FeS (102g)
12	metal	steel (1017g)

1) argon bubbling = 2 Nl/min.

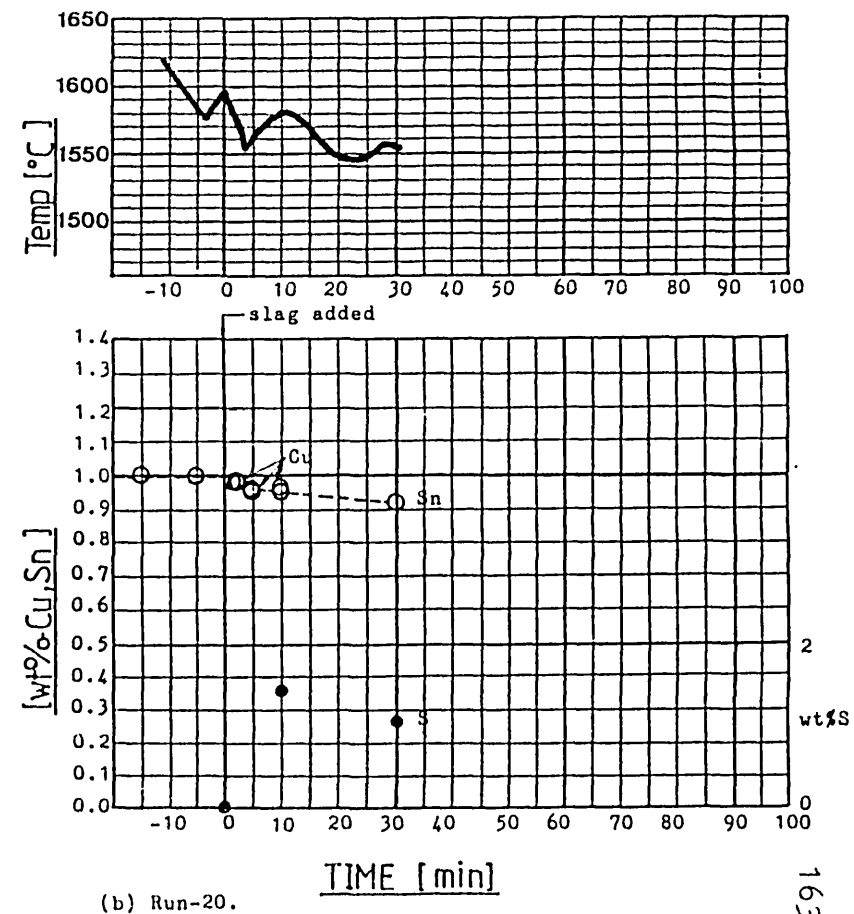


(a) Run-12.

Fig.5-18 De-Cu/de-Sn experiment.

RUN number	slag	50wt%CaF ₂ -50wt%FeS (200g)
20	metal	steel (2040g)

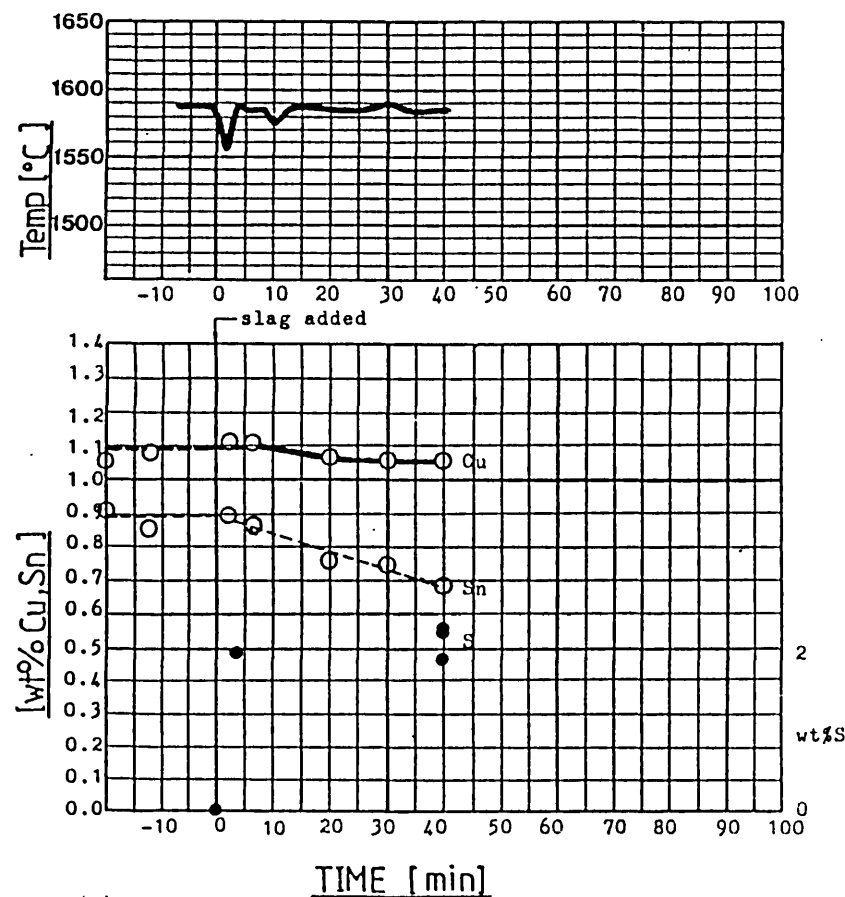
1) argon surface blowing = 4 Nl/min.



(b) Run-20.

RUN number	slag 37wt%CaS-63wt%FeS (102g)
7	metal steel (1019g)

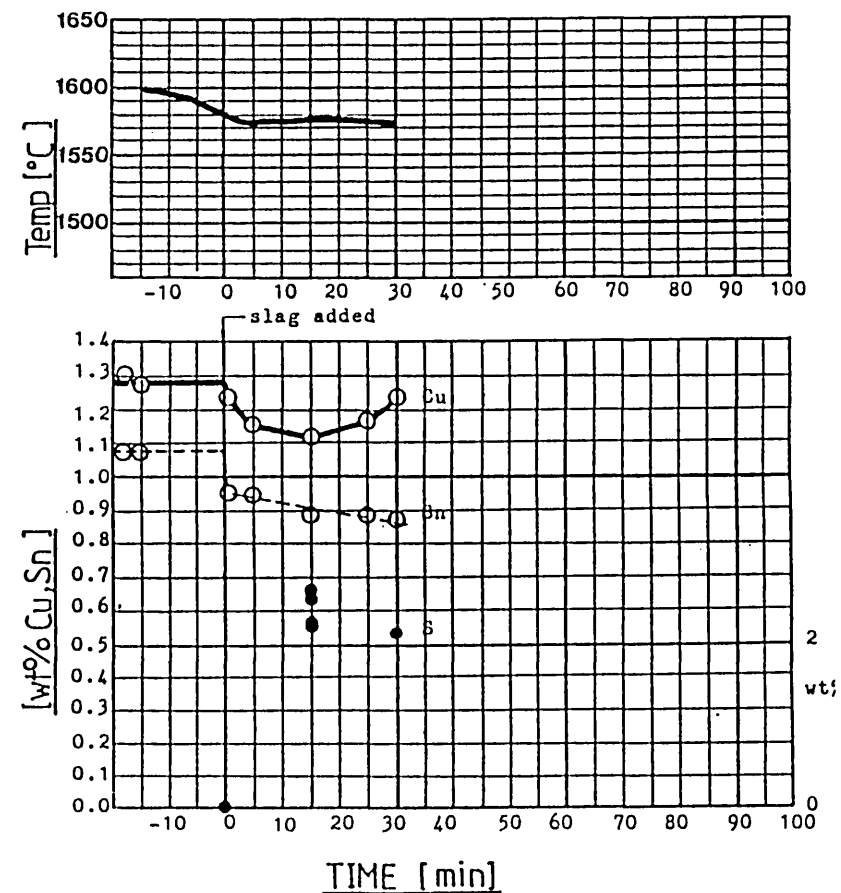
1) argon bubbling = 2 Nl/min.



(a) Run-7.
Fig. 5-19 De-Cu/de-Sn experiment.

RUN number	slag 40wt%CaS-47wt%FeS-13wt%FeO (103g)
8	metal steel (1027g)

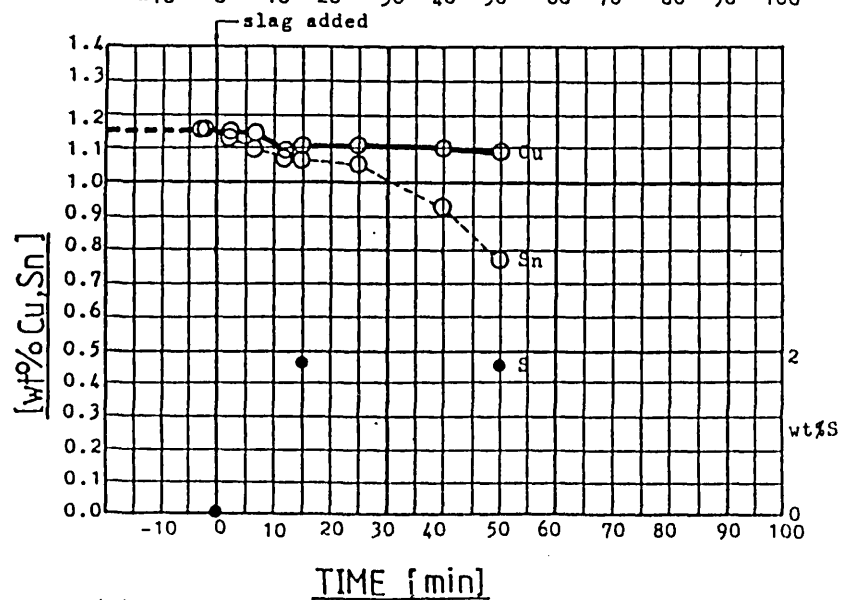
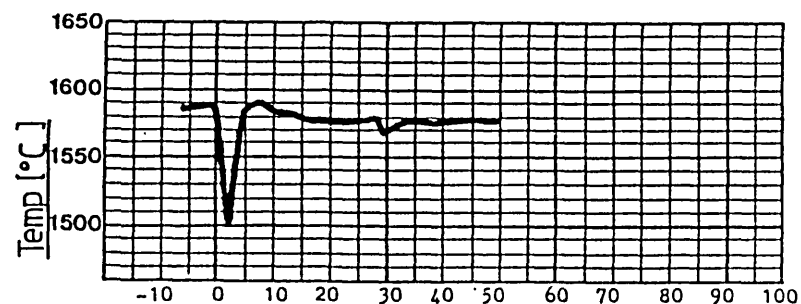
1) argon bubbling = 2 Nl/min.



(b) Run-8.

RUN number	slag 43wt%CaS-29wt%FeS-28wt%FeO (102g)
9	metal steel (1020g)

1) argon bubbling = 2 Nl/min.

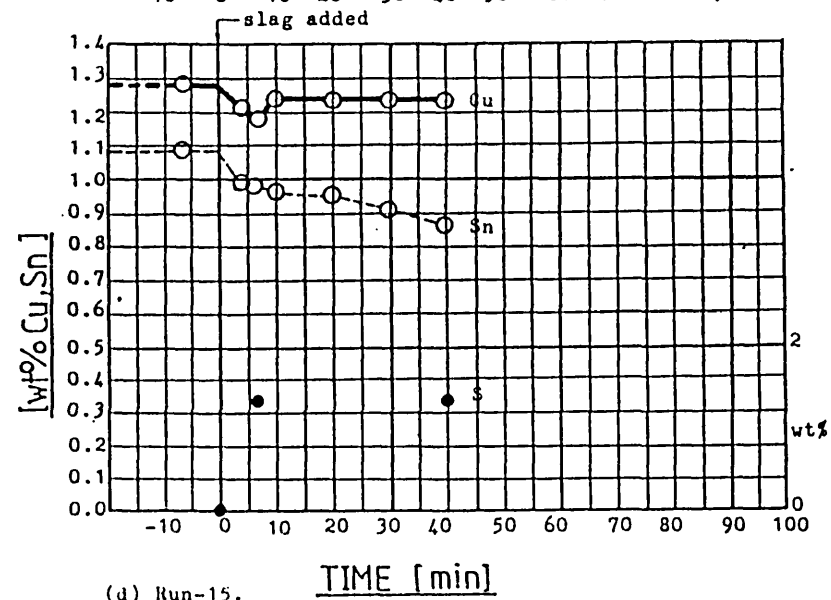
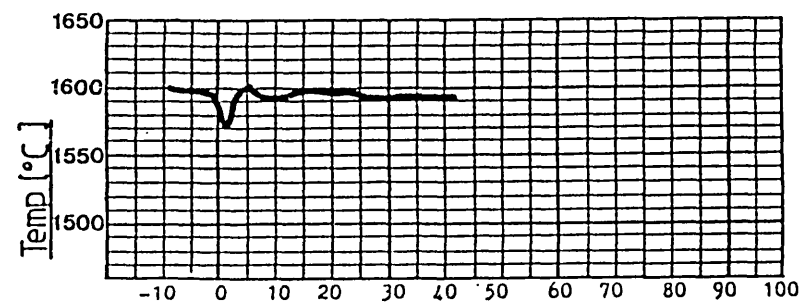


(c) Run-9.

Fig:5-19 De-Cu/de-Sn experiment.

RUN number	slag 46wt%CaS-11wt%FeS-43wt%FeO (100g)
15	metal steel (1020g)

1) argon bubbling = 2 Nl/min.



(d) Run-15.

(10) Effect of slag composition (CaS-FeS-FeO mixed slag for steel)
 Comparisons can be made between runs -7, -8, -9, -15, -16 and -26. The results are summarised in Table 5-10 and Fig. 5-19. De-Sn from steel is generally better than that from carbon saturated iron. Run -16 did not show good de-Sn. This run -16 used argon blown onto the surface of the melt as opposed to bubbling through it.

(11) Effect of CaS and CaF₂ for steel

Comparison can be made between runs -12, -7 and -26. Results are summarised in Table 5-11.

(12) Comparison of de-Cu/de-Sn between carbon saturated iron and steel

Comparison can be made between run -21 and -7, run -22 and -8, run -19 and -9, run -17 and -16, and run -25 and -12.
 η_{Cu} of carbon saturated iron is higher than that of steel, except for run -25 and -12.

5-3 Interpretation of results

(1) The effect of argon bubbling.

When pure NaS_{0.5} slag is used for de-Cu/de-Sn from carbon saturated iron, S for CuS_{0.5} and SnS formation has to be supplied by NaS_{0.5} decomposition. It has been pointed out by Topkaya [18] and Liu [41], that Na volatilisation is a mechanism for sulphur supply.

The boiling point of SnS is 1276°C (1549K). The vapour pressure of SnS is thus high in the range of temperature studied (1250 - 1600°C). In order to promote these reactions, i.e. Na vaporization and SnS formation and vaporization, it is important to devise some mechanism for the increase of the transport rates of these products. Argon bubbling or argon blowing on the surface and introduction of partial vacuum are possible ways to enhance the mass transfer coefficients of these products. Although run -13 was carried out without agitation from argon gas-flow, de-Cu occurred to the same extent as run -6 or run -18, (where Ar flow was employed).

There is some difference in the rate of de-Cu between runs -13, -6 and -18 as shown in Table 5-2.

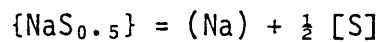
In the case where 1 kg of metal and 0.1 kg of slag were used, flow induced by the induction coil was vigorous enough to create a metal/gas interface. The observed results are shown in Fig. 5-20. This interface would be a good site for Na vaporization. Sn can be removed both to the slag phase as {SnS} where { } denotes liquid state and to the gas phase as (SnS) where () denotes gaseous state. Under the conditions investigated, (SnS) appeared to be dominant as discussed in 6-3.

In run-18, high argon gas flow rate which enhances (SnS) transport and low sulphur content which produces lower SnS vapour pressure lead to inefficient de-Sn.

(2) Comparison between argon bubbling and mechanical stirring

Some de-Sn in the case of argon bubbling, run -11, can be explained by the formation of SnS vapour carried away by the argon gas flow. In the case of mechanical stirring, run -14, de-Cu occurred to the same extent as in run -11. Assuming that the dominant mechanism for transport of Na vapour is the transport induced by the argon gas flow, one can roughly estimate the total moles of sulphur released by $\text{NaS}_{0.5}$ decomposition.

i) The chemical equilibrium at the metal/slag interface is:



$$\Delta G^0 = 57430 - 28.87 T \text{ [cal/mol] } \text{ (see Appendix -5)}$$

ii) Vapour pressure of sodium, P_{Na} , is

$$P_{\text{Na}} = a_{\text{NaS}_{0.5}} \cdot a_{\text{S}}^{-\frac{1}{2}} \cdot \exp \left(\frac{-57430 + 28.87T}{1.986T} \right) \quad (5-1)$$

If $a_{\text{NaS}_{0.5}}$ is assumed to be unity,

$$f_{\text{S}} = 3.35,$$

and $x_{\text{S}} = 6.2 \times 10^{-4}$ mole fraction (at 8 minutes in run -11),

P_{Na} is then calculated for 1250°C :-

$$P_{\text{Na}} = 0.26 \text{ [atm]}$$

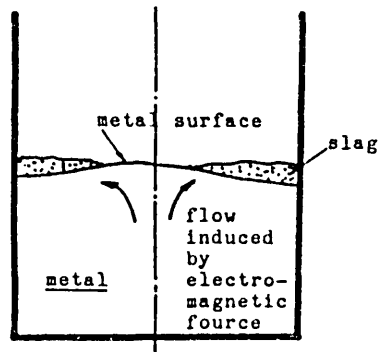


Fig.5-20 Metal/gas interface created
by flow induced by electro-
magnetic force.

iii) The total moles of Na carried away by the argon gas flow rate $\dot{q}$ [m^3/s] at time t is $C_{\text{Na}} \equiv \int_0^t (P_{\text{Na}} \cdot \dot{q} / RT) dt$ [mol]

$$(5-2)$$

where $\dot{q} = 1.7 \times 10^{-4} \text{ m}^3/\text{s}$ for $\dot{q}_N = 2 \text{ NI/min.}$

iv) Assuming that the sulphur concentration in the metal phase increases linearly with time, one can obtain the total moles of Na vaporised C_{Na} .

$$C_{\text{Na}} = 1.6 \times 10^{-2} t^{\frac{1}{2}} \quad [\text{mol}] \quad (5-3)$$

where t has a unit [sec.]

After 60 minutes ($t = 3600$), $C_{\text{Na}} = 0.96$ moles. This is equivalent to 0.48 moles of S (15.4g of S). This corresponds to {0.15 wt% S in the metal phase (1.5g of S) + 0.5 wt% loss of Cu in the metal phase (1.3 g of S) + 35g of FeS formation (12.6g of S)}.

In the case of mechanical stirring, $\dot{q} = 0$. The mechanism explained above for argon bubbling cannot be applied. Enough sulphur for de-Sn could arise from FeS decomposition in this case (run -14).

(3) Effect of mass

The mixing powers of the argon gas flow which were used in run -2 (1 kg metal) and run -11 (3 kg metal) are calculated using the equation below (after Nakanishi et al [48]).

$$\dot{\epsilon} \simeq 6.18 \bar{V}_G \cdot T_m \cdot \ln (1 + \rho_L gH / 1.01 \times 10^5 p_T) \quad [\text{w}]; \quad \text{for cylindrical vessel} \quad (5-4)$$

Here

$\bar{V}_G$: gas flow rate [$\text{Nm}^3/\text{min.}$]

T_m : melt temperature [K]

ρ_L : melt density [kg/m^3]

g : gravity acceleration [m/s^2]

H : depth of gas inlet [m]

p_T : atmospheric pressure [atm]

In both runs, 2Nl/min of argon gas flow was used and the position of bubbling was set $10^{mm}_{(30)}$ above the bottom of the crucible. Depths of the melt bath were 0.032m and 0.096m for runs -2 and -11 respectively. Calculation leads to the results:

$$\dot{\epsilon} \text{ (run -2)} = 0.28 \text{ [W]} \quad (\dot{\epsilon}' = 0.28 \text{ w/kg-melt})$$

$$\dot{\epsilon} \text{ (run -11)} = 0.84 \text{ [W]} \quad (\dot{\epsilon}' = 0.28 \text{ w/kg-melt})$$

Where $\dot{\epsilon}'$ denotes the mixing power per unit weight of melt [W/kg].

According to Qu et al [49] studied the relation between the volumetric mass transfer coefficient k_V and $\dot{\epsilon}'$.

They used pure water ($\nu = 1 \times 10^{-6} \text{ m}^2/\text{s}$ at 293K) and mineral oil ($\nu = 3.5 \times 10^{-5} \text{ m}^2/\text{s}$ at 293 K) to simulate a steel ($\nu = 1 \times 10^{-6} \text{ m}^2/\text{s}$ at 1823 K) - slag ($\nu = 1.0 - 3.3 \times 10^{-5} \text{ m}^2/\text{s}$ at 1868K) system. Volumetric mass transfer coefficient k_V defined by $k_V = k.S/V$ was determined by their water-oil model.

$$k_V = 0.0125 \cdot (\dot{\epsilon}')^{0.817}$$

Kikuchi et al [37] determined relation between $\dot{\epsilon}'$ and volumetric mass transfer coefficient, k_V , for de-P from experimental data of wide range of conditions, e.g. i) 1000g 1600°C small-scale tests
ii) 250 ton-scale tests.

They found that k_V was roughly proportional to $\dot{\epsilon}'$.

Using relation derived by Qu et al [49], one can obtain the ratio of the volumetric mass transfer coefficient k_V [1/s], for two runs below.

$$k_V \text{ (run -2)} / k_V \text{ (run -11)} = 1.0$$

The characteristic time of reaction for each run, t_{ref} , is given by $V_m / (k.V)$ [sec], which is equal to an inverse of k_V .

$$t_{\text{ref}}(\text{run -2}) / t_{\text{ref}}(\text{run -11}) = 1.0$$

Experimental results of this value are roughly evaluated by $t_{\text{ref}}(\text{run -2}) / t_{\text{ref}}(\text{run -11}) \approx 1.1$. This discrepancy between the simply calculated value 1.0, and experimental result, ~ 1.1 , is not surprising in view of the nature of the system which has mass transfer of multicomponents, e.g. Fe, Cu and so on is affected by differences between the actual interfacial area for reaction and the nominal area S and is affected by induced mixing whose effect on k_V could depend on the scale of the system.

(4) Effect of slag composition ($\text{NaS}_{0.5}$ - FeS mixed slag for carbon saturated iron).

Activity coefficients of $\text{CuS}_{0.5}$ and FeS in the slag phase are determined by the help of mathematical models from experimental results η_{Cu} VS. initial wt% FeS is shown in Fig. 5-21(a) with varying γ_{FeS} and $\gamma_{\text{CuS}_{0.5}}$. The final wt% in the metal phase is shown in Fig. 5-21(b) with varying γ_{FeS} and $\gamma_{\text{CuS}_{0.5}}$. Experimental results are also plotted on these figures. η_{Cu} is strongly dependent on $\gamma_{\text{CuS}_{0.5}}$ and weakly on γ_{FeS} . The same results are also shown on the $\gamma_{\text{CuS}_{0.5}}$ and γ_{FeS} plot in Fig. 5-22 for $\text{NaS}_{0.5}$ - FeS mixed slag.

$\gamma_{\text{CuS}_{0.5}}$ and γ_{FeS} are dependent on the initial slag composition.

The estimated values of γ_{FeS} and $\gamma_{\text{CuS}_{0.5}}$ for each initial slag composition are:

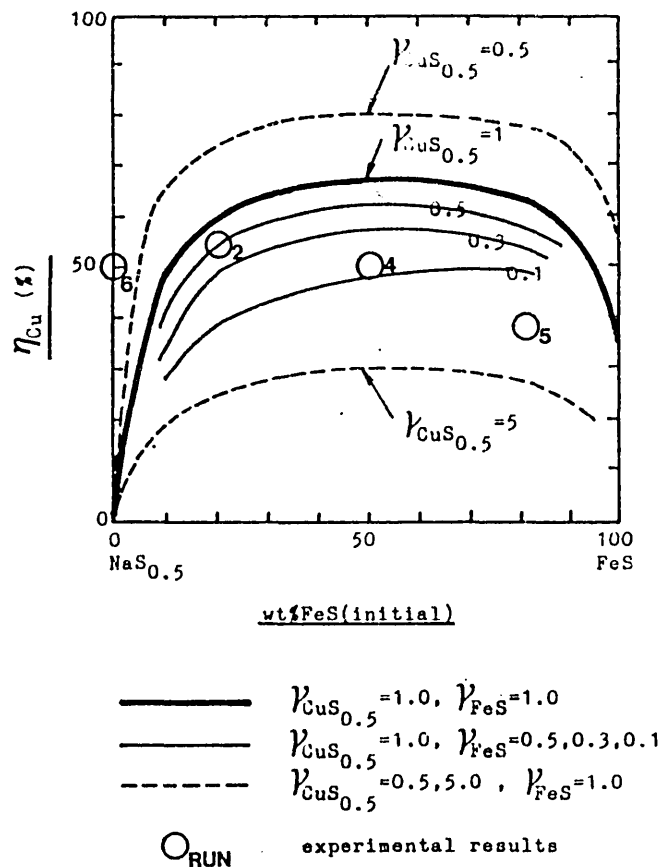
- | | |
|---|--|
| i) <u>80 wt% $\text{NaS}_{0.5}$ - 20 wt% FeS</u> | $\gamma_{\text{FeS}} = 0.1 \sim 0.4$ |
| | $\gamma_{\text{CuS}_{0.5}} = \sim 1.0$ |
| ii) <u>50 wt% $\text{NaS}_{0.5}$ - 50 wt% FeS</u> | $\gamma_{\text{FeS}} = \sim 0.15$ |
| | $\gamma_{\text{CuS}_{0.5}} = \sim 1.0$ |
| iii) <u>20 wt% $\text{NaS}_{0.5}$ - 80 wt% FeS</u> | $\gamma_{\text{FeS}} = \sim 0.2$ |
| | $\gamma_{\text{CuS}_{0.5}} = \sim 1.3$ |

These values are confirmed by Fig. 5-23 which shows the distribution coefficient of Cu between the metal and slag phases.

With increasing FeS content in the initial slag, the final S content in the metal phase which is mainly supplied by FeS decomposition, increases. This leads to favourable condition for de-Cu/de-Sn.

On the other hand decomposition of FeS causes reduction of the weight of slag phase. This leads to unfavourable conditions for de-Cu.

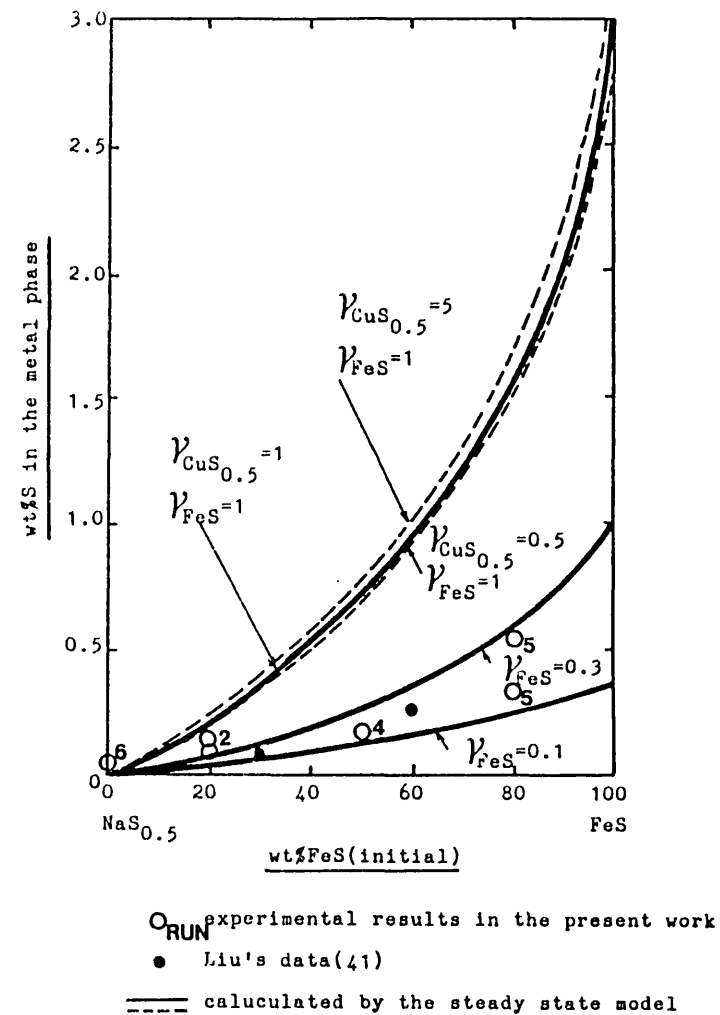
If the main mechanism of de-Sn is SnS vaporisation, this reduction



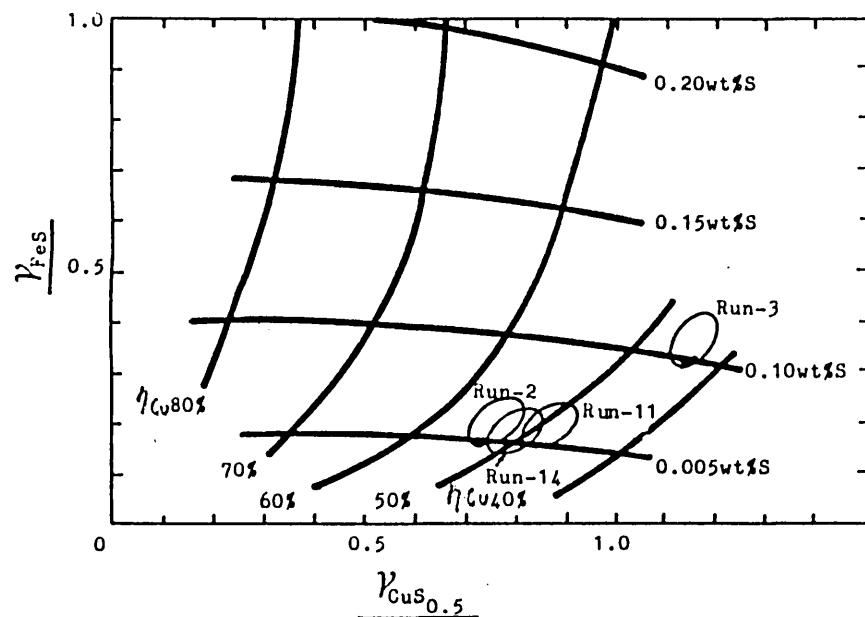
(a) De-Cu using $NaS_{0.5}$ -FeS mixed slag.

Fig.5-21 $\gamma_{CuS_{0.5}}$ and γ_{FeS} for $NaS_{0.5}$ -FeS mixed slag

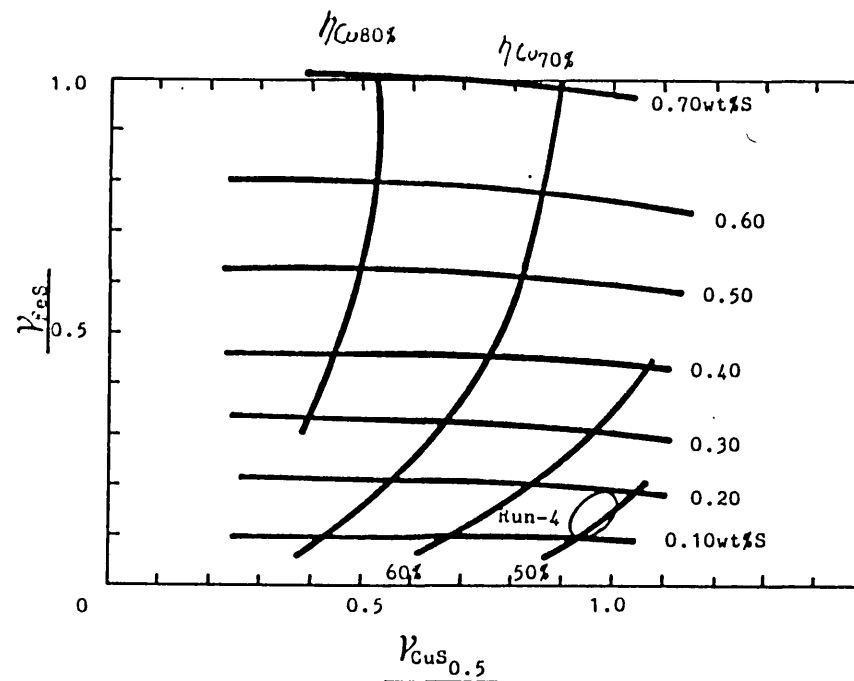
(metal=1000g carbon saturated slag with 1wt%Cu, slag=100g, 1250° C, no Na vaporization).



(b) Sulphur concentration in the metal phase.

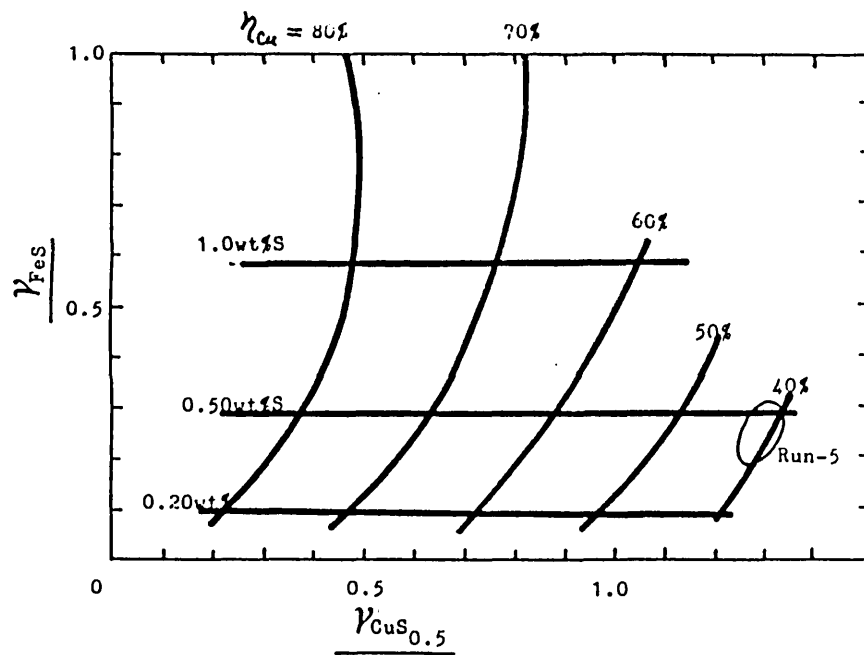


(a) 80wt%NaS_{0.5}-20wt%FeS mixed slag for carbon saturated iron at 1250° C (calculation and experimental result).



(b) 50wt%NaS_{0.5}-50wt%FeS mixed slag for carbon saturated iron at 1250° C (calculation and experimental result).

Fig.5-22 Experimental data plotted on $p_{\text{CuS}_{0.5}}$ - p_{FeS} plain
(1000g carbon saturated iron-100g slag at 1250° C).



(c) 20wt%NaS_{0.5}-80wt%FeS mixed slag for carbon saturated iron at 1250° C (calculation and experimental result).

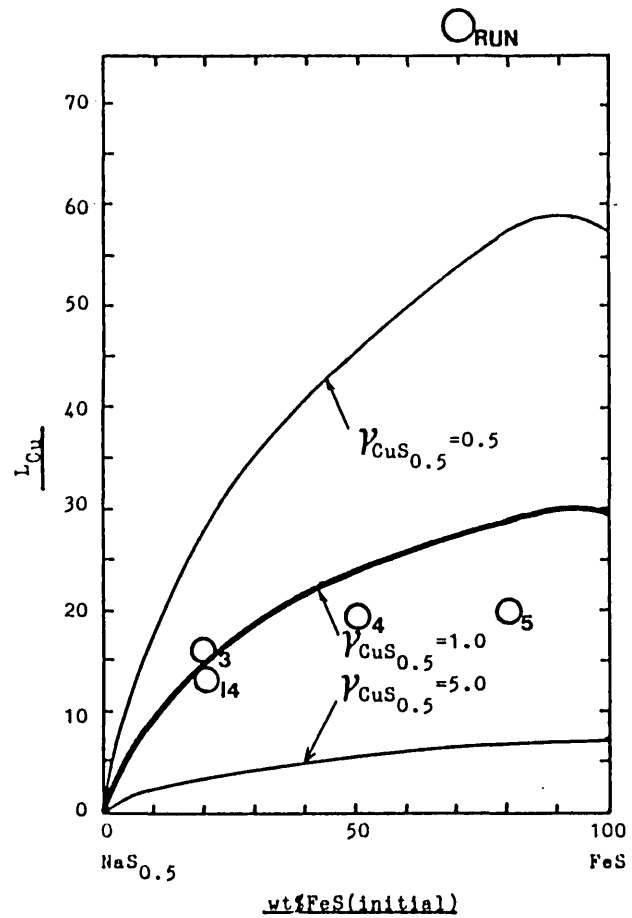
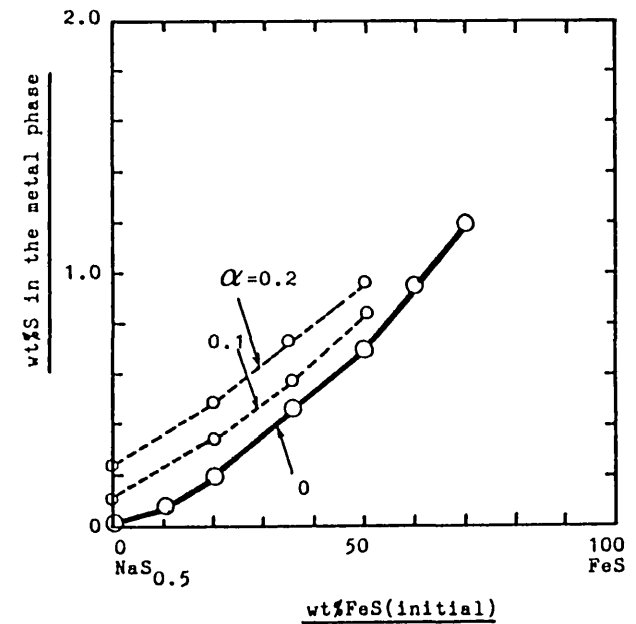


Fig.5-23 Distribution coefficient of Cu, L_{Cu}
 (= $wt\%Cu$ in the slag phase / $wt\%Cu$ in the metal
 phase) for carbon saturated iron/ $NaS_{0.5}$ -
 FeS mixed slag.



(b) Sulphur concentration in the metal phase.

of slag weight does not lead to unfavourable condition for de-Sn.

In the case of pure $\text{NaS}_{0.5}$ (runs -13, -18 and -6), a model, which includes only metal and slag phase, cannot predict experimental results satisfactorily as was explained in 3-2-2.

In Fig. 5-24, α -value, which denotes a fraction of Na decomposed, is evaluated.

$$\alpha \approx 0.12$$

This value corresponds to approximately 1.2 Nl/min. of argon gas flow rate.

(5) Effect of vacuum.

In run -pre 2, de-Sn seemed to be influenced by vacuum.

In this run:

$t = 50 - 80$ min. (1.2 Nl/min argon bubbling)

Sn content changes from 0.172 wt% 0.15 wt%
rate 7×10^{-4} wt%/min.

$t = 80$ min. - 120 min. (no bubbling)

Sn content changes from 0.151 0.165 wt%
rate $- 4 \times 10^{-4}$ wt% min.

$t = 120$ min. - 180 min. (partial vacuum)

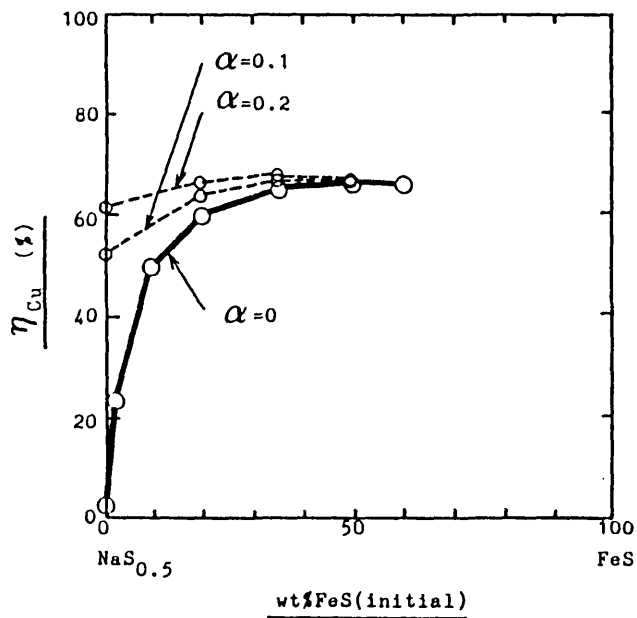
Sn content changes from 0.165 0.12 wt%
rate 1.6×10^{-1} wt%/min.

The rates of de-Sn are compared in Table 5-12 for three types of gas phase conditions.

Under partial vacuum condition, Na vapour could nucleate without argon gas flow. P_{Na} is approximately 0.04 - 0.5 under the conditions in this work which is shown in Fig. 5-25. Partial vacuum (~ 0.1 atm) used in this work could affect the behaviour of Na.

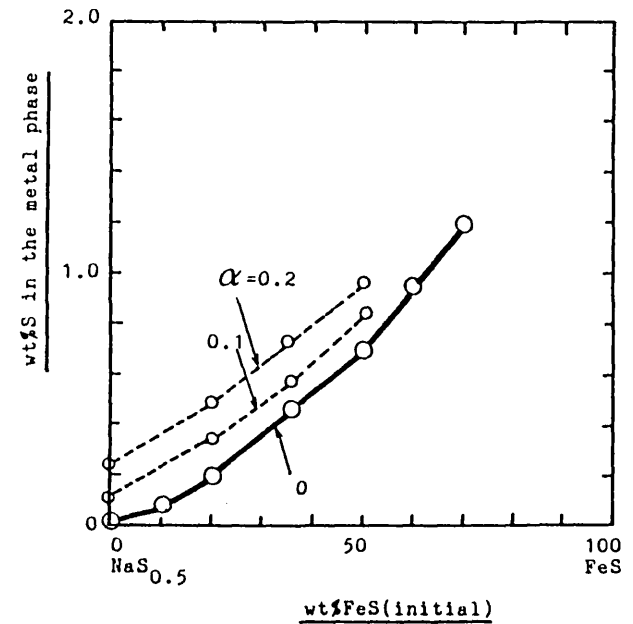
(6) Effect of initial slag weight ($NaS_{0.5}$ - FeS mixed slag).

Effect of initial slag weight on η_{Cu} , which is predicted by the steady state model and shown in Fig. 5-26, agrees well with the experimental results. This figure includes some results of Liu [41].



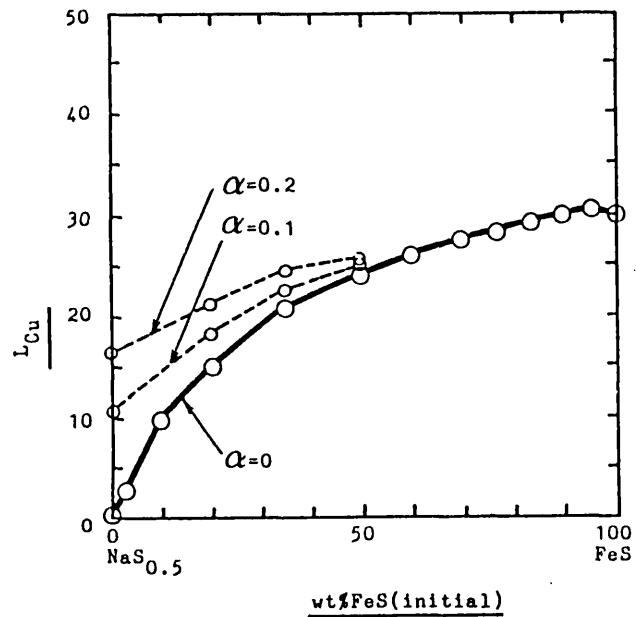
- 1) 1000g metal-100g slag
- 2) $\gamma_{\text{CuS}_{0.5}} = 1$
- 3) carbon saturated iron at 1250° C
- 4) $x_{\text{Cu}}^0 = 0.01$, $x_{\text{S}}^0 = 0$

(a) Effect of α on η_{Cu} .

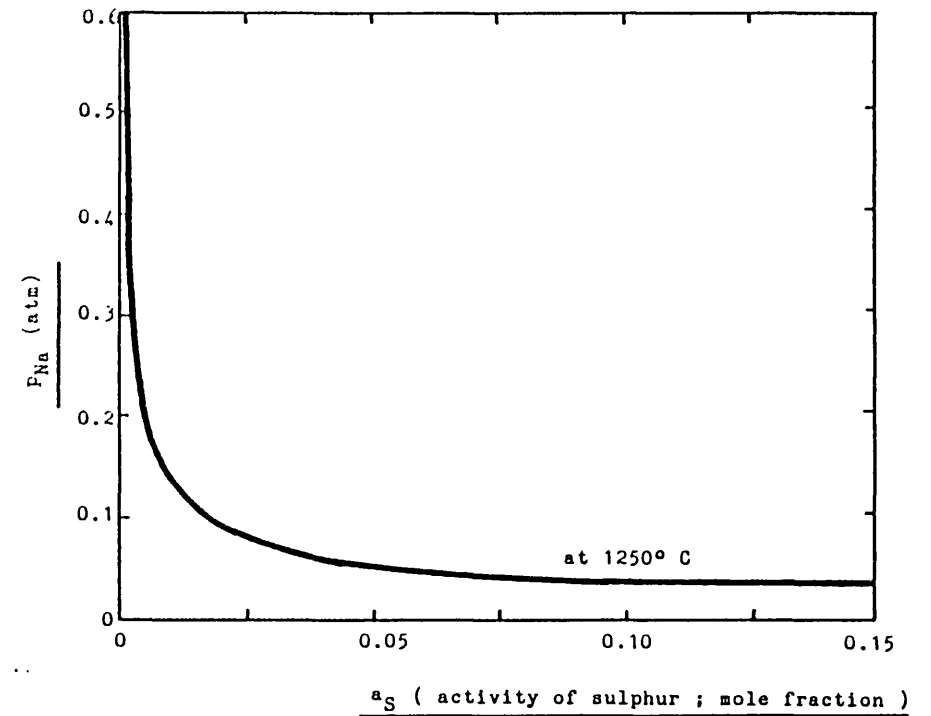


(b) Sulphur concentration in the metal phase.

Fig.5-24 Effect of the fraction of Na vaporised on η_{Cu} , sulphur concentration in the metal phase and distribution coefficient (calculated by the steady state model).



(c) Effect of α on distribution coefficient,
 $L_{Cu} = (\text{wt}\%Cu)_{\text{slag}} / (\text{wt}\%Cu)_{\text{metal}}$.



$$P_{Na} = a_{NaS_{0.5}} a_S^{-1/2} \exp((-57430 + 28.87T)/1.986T)$$

Fig.5-25 Na vapour pressure at the metal/slag interface.

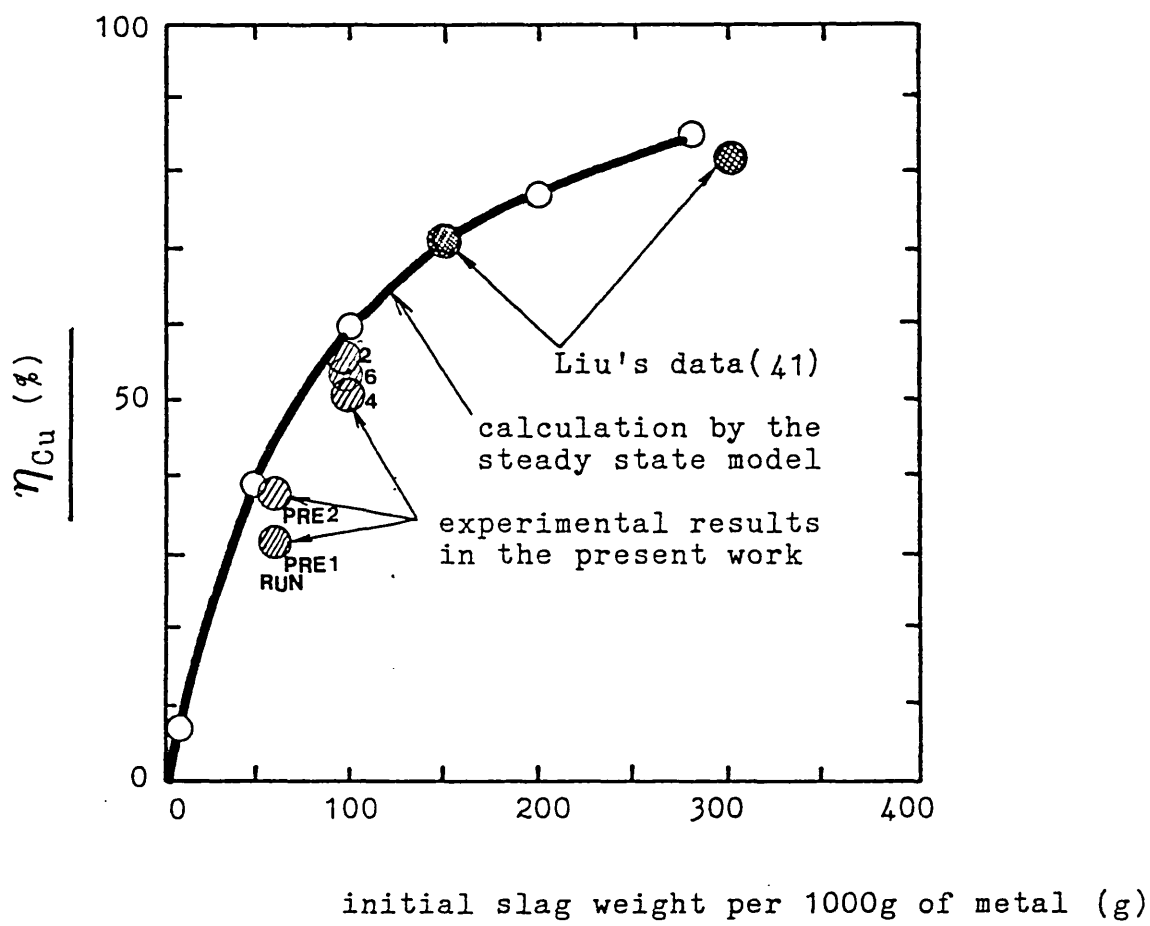


Fig.5-26 Initial slag weight vs η_{Cu} ($NaS_{0.5}$ -
 FeS mixed slag, no Na vaporization,
 $\gamma_{CuS_{0.5}} = 1.0$, carbon saturated iron at
 $1250^{\circ}C$, $x_{Cu}^0 = 0.01, x_S^0 = 0$).

(7) Effect of slag composition (CaS-FeS-FeO mixed slag for carbon saturated iron).

As is shown in Fig. 5-27 (slags A to F), slag compositions used in experimental work were initially all CaS saturated slag except for slag E in this figure. Ignoring this CaS saturation and assuming liquid slag for all ranges of slag compositions, one can obtain fairly good de-Cu(simulated by the steady state model) which is shown in Fig. 5-27. Taking CaS saturation into account in calculation, one can obtain fairly good agreement between calculated results and experimental results.

FeO contained in the slag phase is reduced by carbon to form CO gas. The total weight of slag is also reduced, which leads to unfavourable condition for de-Cu.

(8) De-S by CaO - CaCl₂ mixed slag on the later stage of de-Cu/de-Sn reaction.

In runs -22 and -17, CaO-CaCl₂ mixture was used.

run -22 (slag weight is 2.3% of the metal weight)

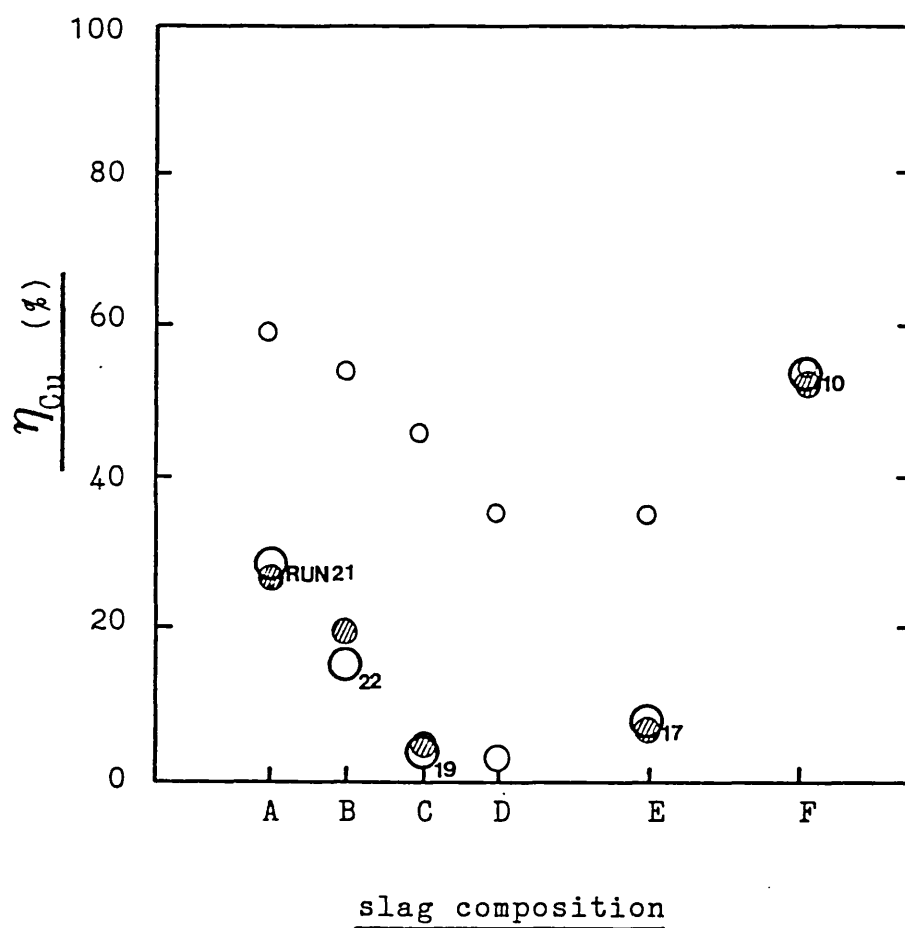
0.44 wt%S $\longrightarrow$ 0.34 wt%S
after 25 minutes

run -17 (slag weight is 5% of the metal weight)

0.65 wt%S $\longrightarrow$ 0.34 wt% S
after 25 minutes

In run -22, 10g of Al was added to 3140g of metal. S decreased from 0.63 wt% to 0.44 wt% after 14 minutes (run -22). Assuming the exchange reaction of O⁼ in the slag and S in the metal, one can obtain 0.57 wt% of S decrease by 10g of Al addition to 3140g of the metal in this case without any other reactions.

This means that Al is partially consumed in other mechanisms, e.g. Al dissolution into the metal phase.



○ CaS saturation neglect

▨ CaS saturation taken into account

○ Experimental data

(a) η_{Cu} vs slag composition.

Fig.5-27 Relation between η_{Cu} and slag composition
(CaS-FeS-FeO mixture for carbon saturated
iron at 1250° C).

(Fig.5-28 is vacant.)

(9) CaF₂ - FeS mixed slag for carbon saturated iron

50 wt% CaF₂ - 50 wt% FeS mixtures were used in runs - pre 3, - pre 4, -1 and -25. As is shown in Fig. 5-29, 40-60% of FeS in the initial slag phase is decomposed. The melting point of CaF₂ is 1418°C. A large portion of slag was observed to be solid which led to poor de-Cu.

In run-25, which was carried out at the higher temperature, 1600°C, de-Cu is very poor, although slag was liquid and sulphur content in the metal phase was fairly high, 1.15 - 1.28 wt% S. It is due to high $\gamma_{\text{CuS}_{0.5}}$ in the slag phase.

In this run, de-Sn is better than other runs. High temperature creates high SnS vapour pressure which leads to high mass transfer rate of Sn.

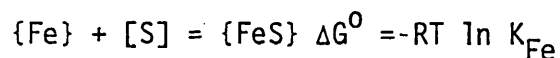
(10) Pure FeS addition to carbon saturated iron

In the case of pure FeS addition in run -23, approximately half of FeS added was decomposed, as is shown in Fig. 5-30.

Main components in the slag phase are FeS and CuS_{0.5} in the final stage.

Fig. 5-30 can be transformed to Fig. 5-31 which shows relation between γ_{FeS} , [wt%S] and θ . Where θ denotes the fraction of FeS decomposed. This transformation was done by the following procedure and assumptions.

i) Chemical equilibrium (5-5) is assumed to be established

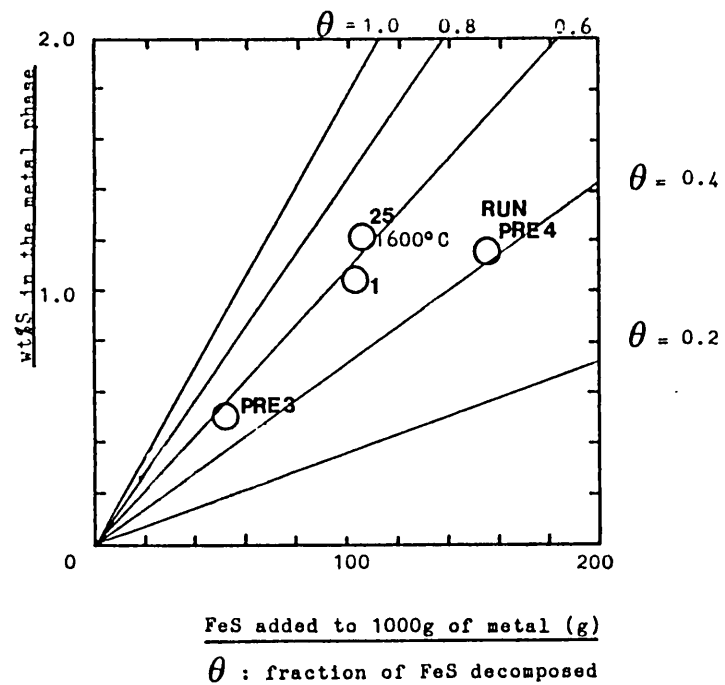


$$K_{\text{Fe}} = a_{\text{FeS}} / a_{\text{Fe}} \cdot a_{\text{S}} \quad (5-5)$$

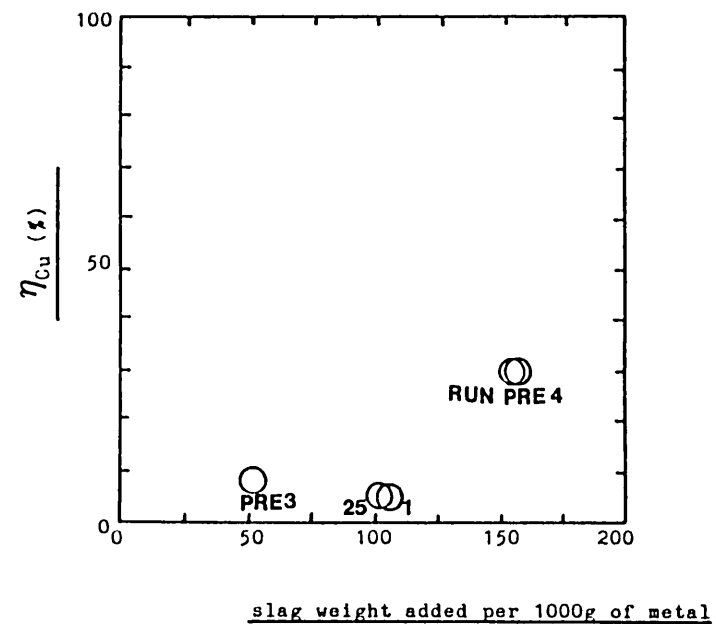
ii) Initial slag is composed of two compounds, (100-w_{FeS}⁰)% of XY and w_{FeS}⁰% of FeS compound XY is assumed to be inert.

A proportion θ of FeS is decomposed. Final slag composition is assumed to be

$$x_{\text{FeS}} = \frac{(1-\theta)w_{\text{FeS}}^0 / M_{\text{FeS}}}{(100-w_{\text{FeS}}^0)/M_{\text{XY}} + (1-\theta)w_{\text{FeS}}^0/M_{\text{FeS}}} \quad (5-6)$$

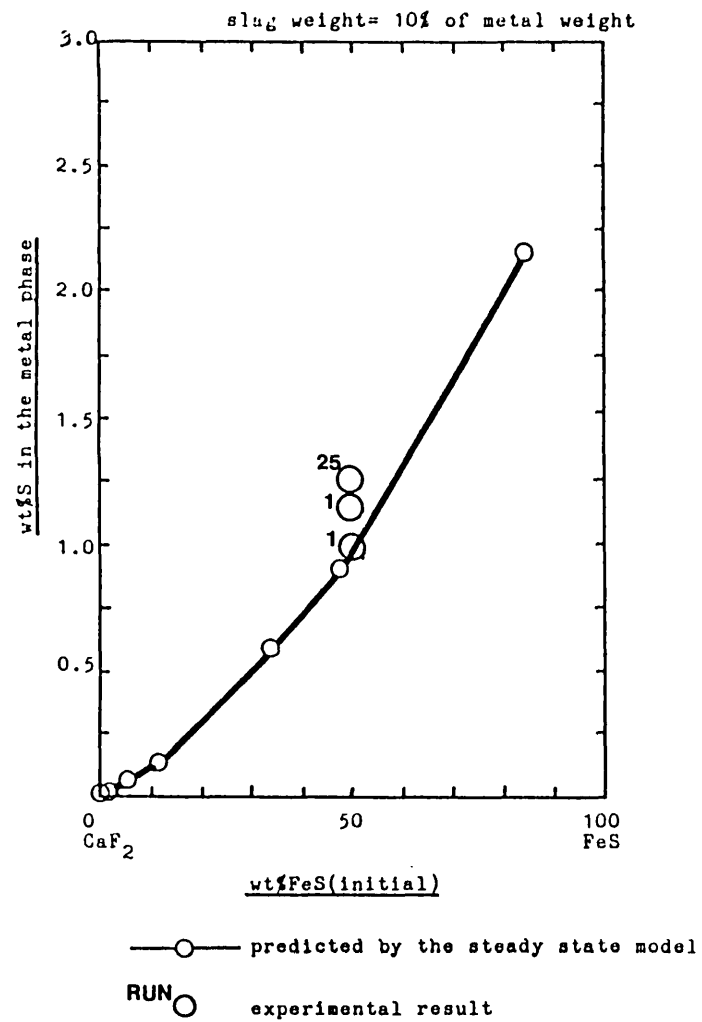


(a) FeS added vs sulphur concentration in the metal phase.

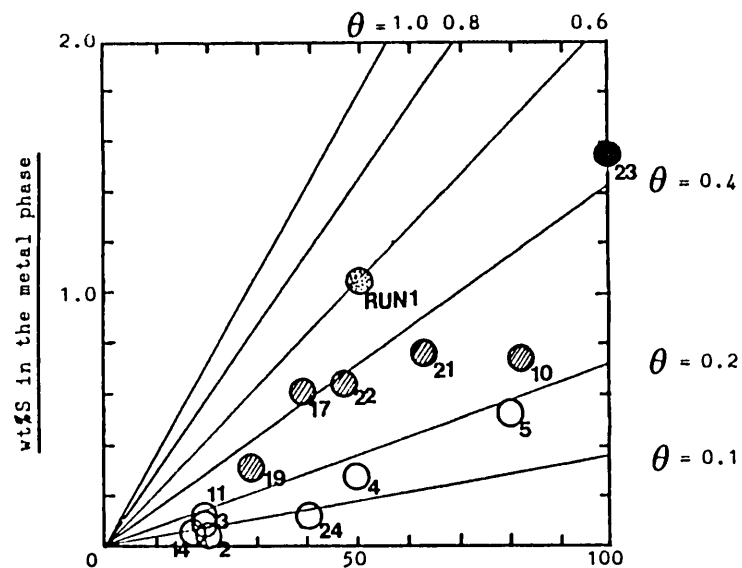


(b) Effect of the amount of slag added on η_{Cu} .

Fig.5-29 Characteristics of CaF_2 -FeS mixed slag.



(c) Sulphur pick-up in carbon saturated iron
at 1250° C (CaF₂-FeS mixed slag).



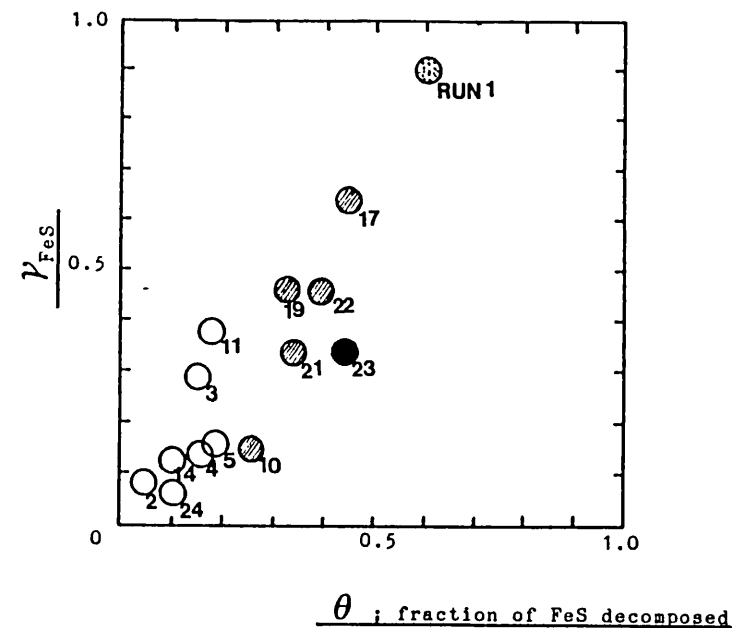
FeS added to 1000g of metal (g)

θ : fraction of FeS decomposed

- | | | |
|---|---------------------------------|------------------------|
| ○ | NaS _{0.5} -FeS mixture | } experimental results |
| ▨ | CaS-FeS-FeO mixture | |
| ⊗ | CaF ₂ -FeS mixture | |
| ● | pure FeS | |

carbon saturated iron at about 1250° C

Fig.5-30 Fraction of FeS decomposed.



- | | |
|---|---------------------------------|
| ○ | NaS _{0.5} -FeS mixture |
| ▨ | CaS-FeS-FeO mixture |
| ⊗ | CaF ₂ -FeS mixture |
| ● | pure FeS |

carbon saturated iron at about 1250° C

Fig.5-31 Converted form of Fig.5-30.

- i.ii) Decomposed FeS is assumed to be all dissolved into the metal phase to raise sulphur content from zero to [wt%S]. 1000g of metal and 100g of initial slag are also assumed.

$$[\text{wt}\% \text{S}] = \theta W_{\text{FeS}}^0 \cdot M_{\text{S}}/10 \cdot M_{\text{FeS}} \quad (5-7)$$

- iv) Using equations (5-5), (5-6) and (5-7), one can obtain a relation between γ_{FeS} and θ .

$$\gamma_{\text{FeS}} = K_{\text{Fe}} \cdot a_{\text{Fe}} \cdot 0.161 \cdot \theta \cdot \{ (100 - W_{\text{FeS}}^0)/M_{\text{XY}} + (1 - \theta) \cdot W_{\text{FeS}}^0/88 \} / (1 - \theta) \quad (5-8)$$

11) NaS_{0.5}-FeS-CaS mixed slag for carbon saturated iron.

FeS-CaS binary system has rather high melting points, higher than 1100°C. Especially in the case where a large proportion of FeS decomposes, the CaS-rich slag has a high melting point, e.g. 1600°C for 30 wt% CaS-70 wt% FeS mixture. NaS_{0.5} has reasonably low m.p. (1180°C). NaS_{0.5}-FeS-CaS mixture (40 wt% NaS_{0.5} - 40 wt% FeS - 20 wt% CaS) is supposed to be a liquid slag at 1250°C, even if some portion of FeS decomposes. This slag has moderately high η_{Cu} - value between η_{Cu} of 50 wt% NaS_{0.5} - 50 wt% FeS mixed slag and η_{Cu} of 37 wt% CaS - 63 wt% FeS mixed slag.

Surface of the slag phase was observed in run-24 :

- i) At $t = 2.5$ [min.], the slag was a nice liquid phase.
- ii) At $t = 6$ [min.], the surface was partly dark where small solid particles were observed. This was located near a thermocouple tube immersed where mixing of the bath was poor.
- iii) Area of this dark surface spread until $t \approx 15$ [min.]. (At $t = 12$ [min.], the dark area was approximately one fifth of the whole surface area.)
- iv) Then this dark area decreased and disappeared at $t = 30$ [min.]. Solid particles could be CaS. Phenomena described above were not fully understood.

(12) CaS-FeS-FeO mixed slag for steel.

Taking CaS saturation into account, one can obtain reasonably good agreement between predicted results and experimental results (see Fig. 5-32). The sulphur pick-up in steel is much more than that in carbon saturated iron (see Fig. 5-33). As is discussed in 6-6, solubility of S in carbon saturated iron at 1250°C is approximately 1.8 wt%. On the other hand, there is no mixibility gap between Fe and FeS without carbon.

The interaction coefficient $e_S^{(C)}$ is positive. Activity coefficients of sulphur calculated are:

$$f_S = 1.0 \quad \text{for steel.}$$

$$f_S = 3.4 \quad \text{for carbon saturated iron.}$$

High temperature and high S content in the metal phase creates high SnS vapour pressure which leads to de-Sn. The calculated vapour pressure of SnS is $2.71 \times 10^{-3} \times [\text{wt}\% \text{S}] \cdot [\text{wt}\% \text{Sn}] \text{ [atm]}$. In the case of run -7, $p_{\text{SnS}} = 5.2 \times 10^{-3} \text{ [atm]}$. After 1 hr, the total weight of Sn removed could be 3.1g under the conditions of argon bubbling (2 Nl/min) which is corresponding to 0.3 wt% Sn for 1000g of steel. This shows good agreement with the experimental results of 0.22 wt% of Sn removal over 40 minutes.

(13) CaF₂ - FeS and CaF₂ - CaS-FeS mixed slags for steel.

CaS-FeS (and CaS-FeS-FeO) mixture have low η_{Cu} values, less than 20% (see Fig. 5-34). In run -26, CaF₂ was added to the slag F in Fig. 5-27. This CaF₂ - CaS-FeS mixture showed better performance than the CaS - FeS mixture. This can be explained by the melting point of the slag phase.

The melting point of the initial slag composition is less than 1600°C if wt% FeS is greater than 30. Some portion of FeS is decomposed so that wt% FeS could be much less than that of initial value. The final slag phase contains CuS_{0.5} and SnS. This causes lowering the melting point of the final slag phase. Neglecting this effect and assuming simply a CaS-FeS binary slag as a final slag,

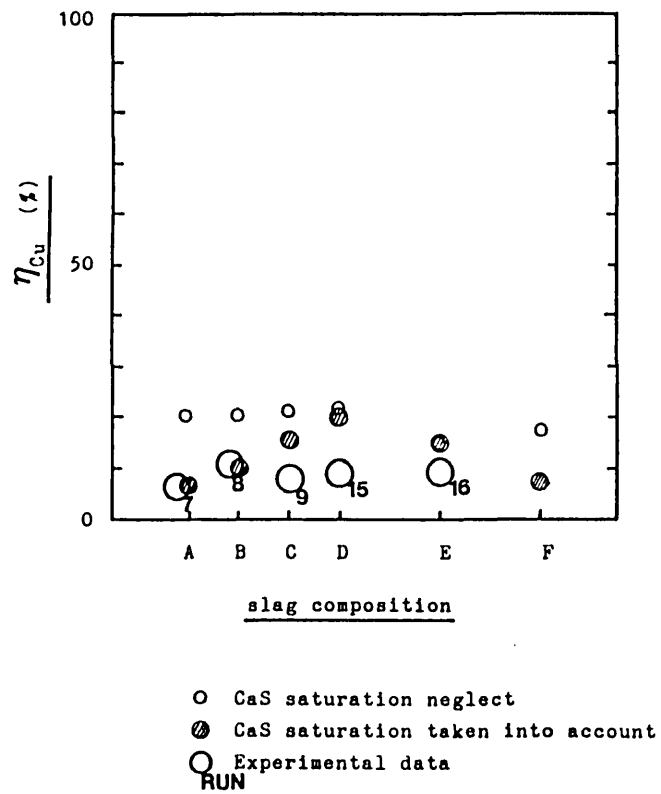


Fig.5-32 Relation between η_{Cu} and slag composition (CaS-FeS-FeO mixture for steel at 1600° C).

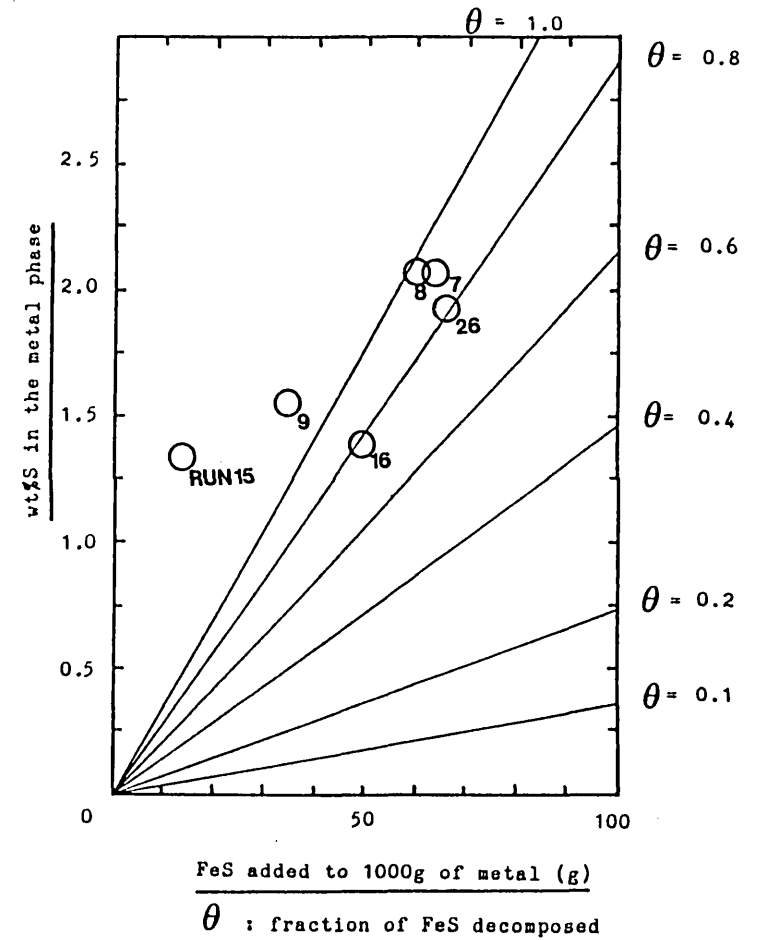
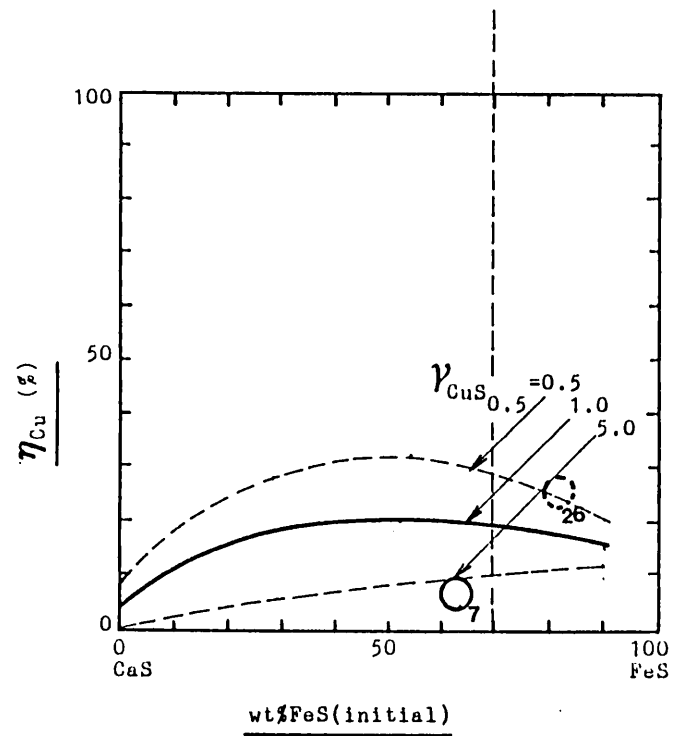
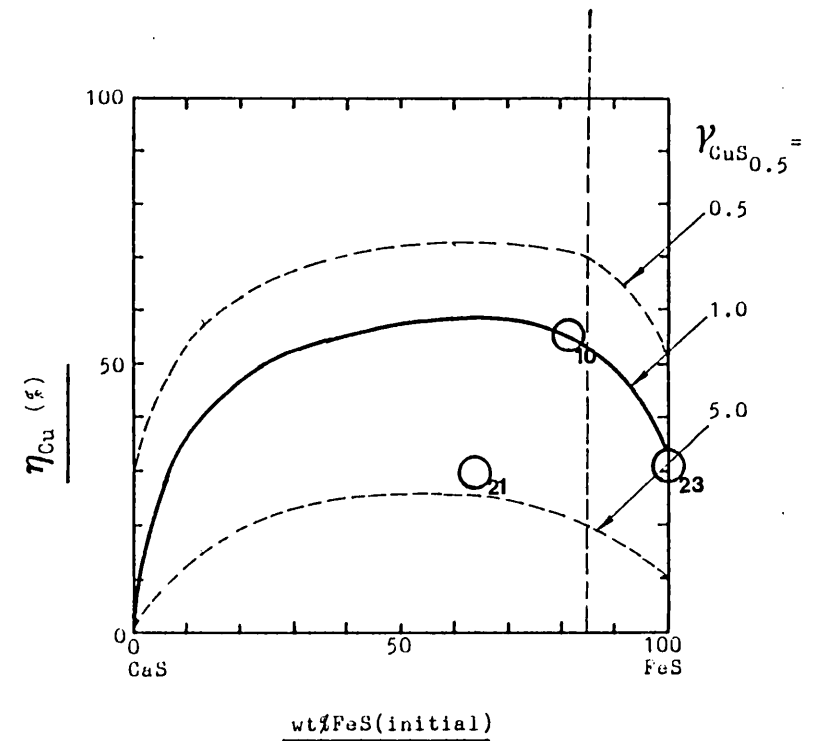


Fig.5-33 Characteristics of CaS-FeS-FeO mixed slag (steel).

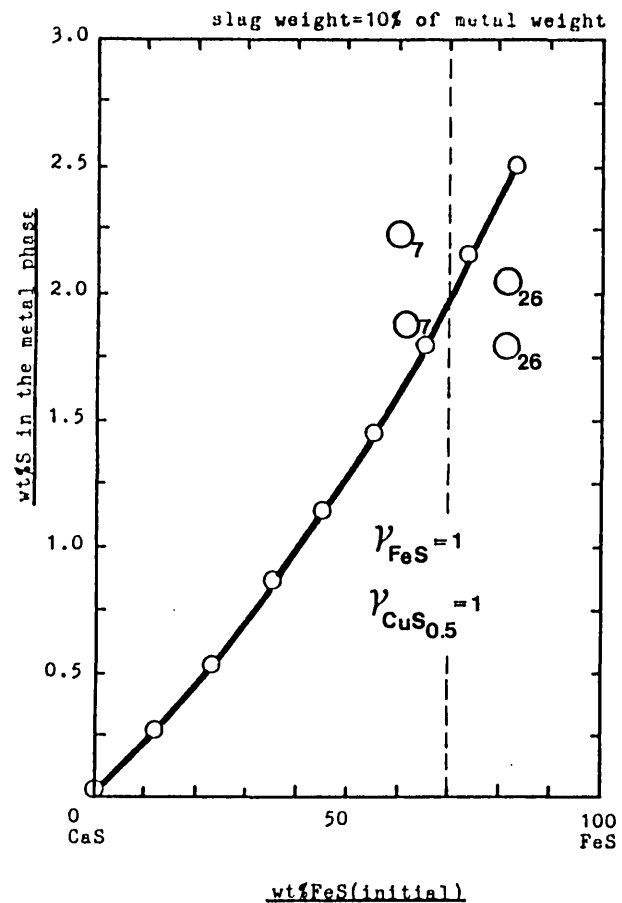


○_{RUN} experiment
 — calculation (steady state model)
 (a) η_{Cu} vs initial slag composition.

Fig.5-34 CaS-FeS mixed slag for steel (at 1600° C,
 1000gmetal-100gslag, initial Cu=1wt%).



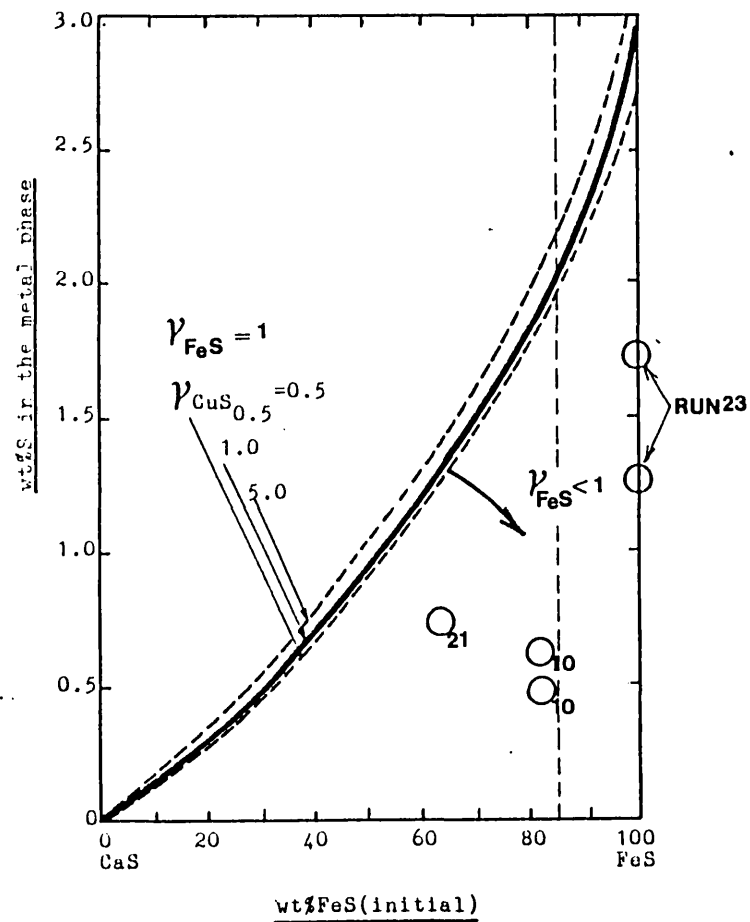
○_{RUN} experiment
 — calculation (steady state model)
 (b) η_{Cu} vs initial slag composition.
 (carbon saturated iron at 1250° C, 1000gmetal-
 100gslag).



○—○ predicted by the steady state model

○_{RUN} experiment

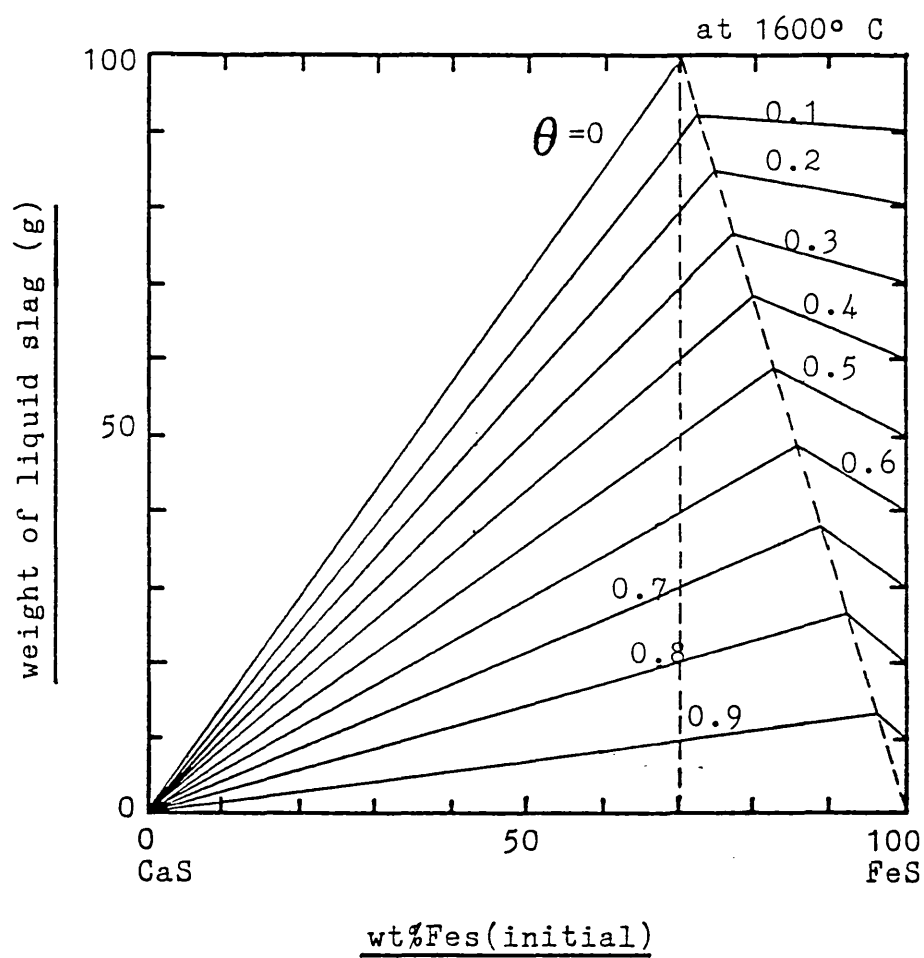
(c) Sulphur pick up in steel at 1600° C
(CaS-FeS mixed slag).



○_{RUN} experimental results

(d) Sulphur concentration in the metal phase.

one can obtain the maximum content of CaS in the initial slag which is still liquid in the final stage at 1600°C . Nice liquid slag was observed in run - 26 during reaction. The calculated results are plotted in Fig. 5-35.



θ : fraction of FeS decomposed.

Fig.5-35 Amount of liquid slag (total amount of slag=100g at 1600° C).

CHAPTER 6 DISCUSSION

6-1 Overall aspects of the full model

Two mathematical models have been developed in the present work. The steady state model is a simplified version of the full model and deals with steady state, and has been developed as a model of restricted applicability to simulate de-Cu/de-Sn from carbon saturated iron/steel using various kinds of slags. It is an efficient model in the sense of cost of computing but it has lost some generality of application. On the other hand the full model is generally applicable and is comprehensive. The main features of this model are summarised in Table 6-1.

All functions in the model are separately formulated and coded into separate sub-programmes. This allows the easy modifications of each function.

In the case of de-Cu/de-Sn, the chemistry was mainly studied by the steady state model and kinetics studied by the full model using the appropriate thermodynamic data, e.g. $\gamma_{\text{CuS}_{0.5}}$, γ_{FeS} etc., which were evaluated by the steady state model and experimental results. These kinetics are discussed in 6-2 and 6-3. In the present section, the features of sub-programme "BUBBLE" is discussed. This was developed for simulation of a gas bubble rising in the metal phase. The formulations are explained in 3-2-2. Some computed results are shown in Fig. 6-1.

Table 6-1 Characteristics of the full model.

	(1) available functions	(2) functions which require minor modifications	(3) functions which require structural modifications
(a) components	* multi-component (20-element and 40-compound) * two types of compounds e.g. oxide & sulphide	* further multi-component	* more than two types of compounds e.g. oxide, sulphide & chloride 9simultaneously)
(b) phases	* metal/slag/gas (incl. gas bubble) * interfacial reactions (metal/slag, slag/gas, metal/gas, metal/gas bubble & metal/crucible)		* slag/crucible reaction * homogeneous reaction
(c) temperature	* constant with time * spatial distribution	* thermal balance by " HEAT "	
(d) transport	* mass transfer in the boundary layers	* bulk mixing * bulk gas flow	
(e) activity coefficient	* constant with time	* temperature & composition dependency	
(f) type of the system	* open gas phase(bulk composition is constant) * dumping and/or continuous feeding of slag	* closed gas phase * continuous metallic component feeding	
(g) solving method of eqs.	* Powell's nonlinear method (library programme)	* original programme	
(h) others			* chemical reaction rate controlling

Table 6-2 Chemical equilibria for Sn.

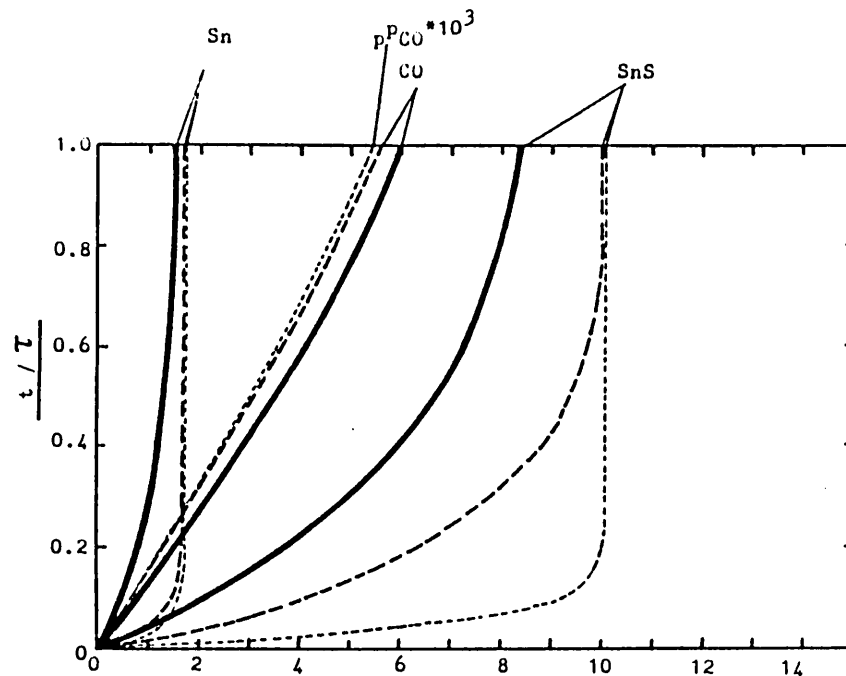
- 1) $\text{Sn} = (\text{Sn}) \quad \Delta G^0 = 66940 - 24.59T \text{ (cal/mol)}$
 $= -RT \ln K_{(\text{Sn})}$
- 2) $\text{Sn} + \text{S} = (\text{SnS}) \quad \Delta G^0 = 34680 - 25.44T \text{ (cal/mol)}$
 $= -RT \ln K_{(\text{SnS})}$
- 3) $\text{Sn} + \text{S} = \text{SnS} \quad \Delta G^0 = 680 - 3.44T \text{ (cal/mol)}$
 $= -RT \ln K_{\text{SnS}}$

Equilibrium constant : $K_{(\text{Sn})} = p_{\text{Sn}}/a_{\text{Sn}} = \begin{cases} 5.83 \times 10^{-5} & \text{for carbon saturated iron at } 1250^\circ \text{C} \\ 3.65 \times 10^{-3} & \text{for steel at } 1600^\circ \text{C} \end{cases}$

$K_{(\text{SnS})} = p_{\text{SnS}}/a_{\text{Sn}} a_{\text{S}} = \begin{cases} 3.83 & \text{for carbon saturated iron at } 1250^\circ \text{C} \\ 32.7 & \text{for steel at } 1600^\circ \text{C} \end{cases}$

$K_{\text{SnS}} = a_{\text{SnS}}/a_{\text{Sn}} a_{\text{S}} = \begin{cases} 4.52 & \text{for carbon saturated iron at } 1250^\circ \text{C} \\ 4.71 & \text{for steel at } 1600^\circ \text{C} \end{cases}$

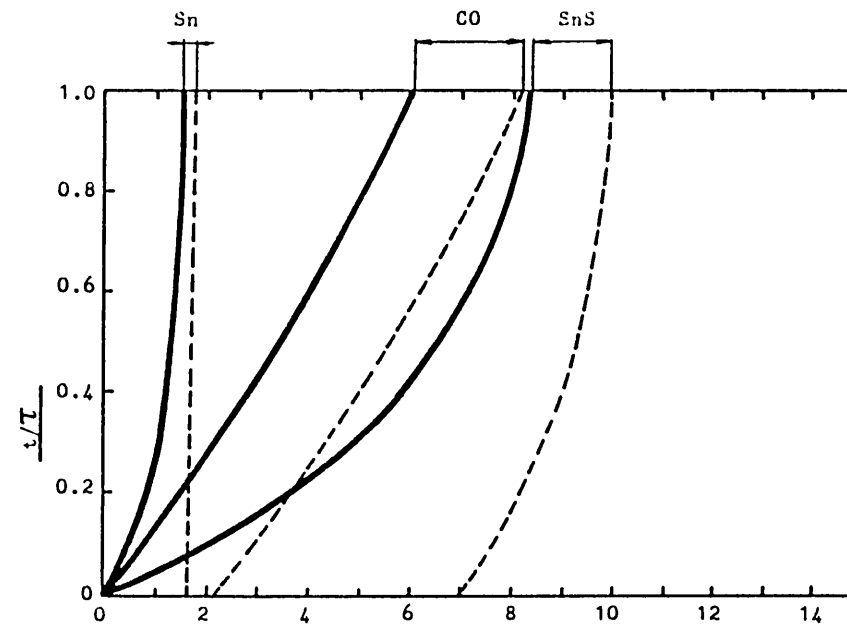
	carbon saturated iron at 1250° C	steel at 1600° C
p_{Sn} (atm)	4.73×10^{-7} wt%Sn	1.73×10^{-7} wt%Sn
p_{SnS} (atm)	1.56×10^{-3} wt%Sn wt%S	2.71×10^{-3} wt%Sn wt%S
x_{SnS} (mole fraction)	1.84×10^{-3} wt%Sn wt%S	3.90×10^{-4} wt%Sn wt%S
remarks	$f_{\text{Sn}}=2.0, f_{\text{S}}=3.35$	$f_{\text{Sn}}=1.0, f_{\text{S}}=1.0$



$P_{Sn} \cdot 10^5, P_{CO} \cdot 10^4, P_{SnS} \cdot 10^5$ (atm)
 partial pressure in the bulk phase.
 temperature = 1600°C (1873K).
 $\tau = 0.14$ (s) : rising time of a bubble.
 $x_0 = 7 \cdot 10^{-4}, x_S = 7 \cdot 10^{-4}, x_C = 0.00467, x_{Sn} = 0.00473$

————— $k_m = 4 \cdot 10^{-4} (\text{m/s}), k_g = 2 \cdot 10^{-2} (\text{m/s})$
 - - - - - $k_m = 4 \cdot 10^{-4} (\text{m/s}), k_g = 2 \cdot 10^{-1} (\text{m/s})$
 - - - - - $k_m = 4 \cdot 10^{-3} (\text{m/s}), k_g = 2 \cdot 10^{-1} (\text{m/s})$

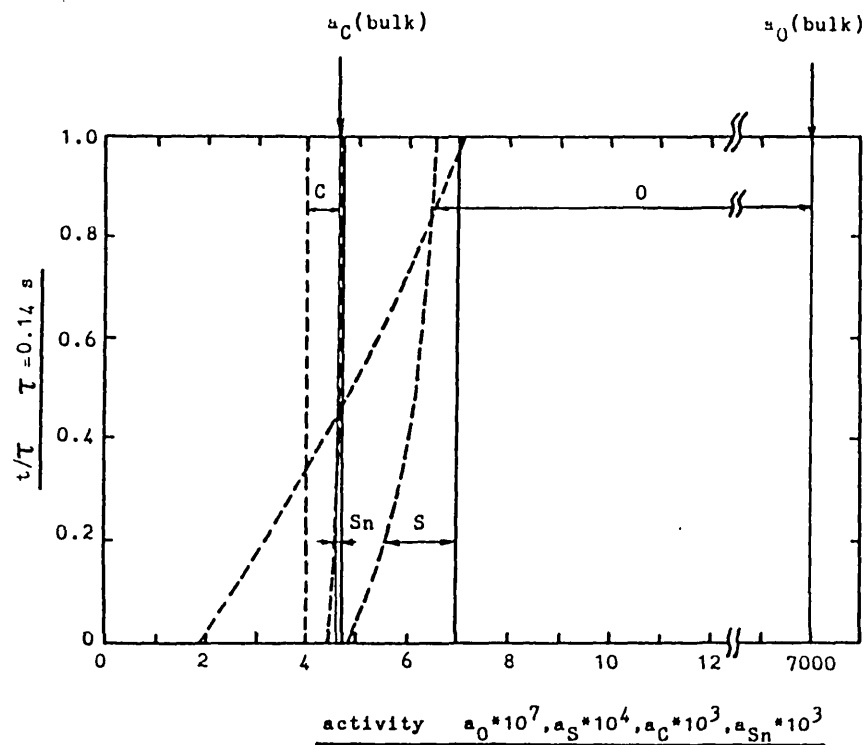
(a) Effect of mass transfer coefficient on the change of composition in a bubble with time (steel at 1600°C).
 Fig.6-1 Behaviour of a gas bubble which rises in the metal phase.



$P_{Sn} \cdot 10^5, P_{CO} \cdot 10^4, P_{SnS} \cdot 10^5$ (atm)
 partial pressure
 temperature = 1600°C (1873K)
 $k_m = 4 \cdot 10^{-4} (\text{m/s})$
 $k_g = 2 \cdot 10^{-2} (\text{m/s})$
 $\tau = 0.14$ (s)

————— pressure in the bulk phase
 - - - - - interfacial pressure

(b) Driving source in the gas phase (steel).



temperature = 1600°C (1873K)

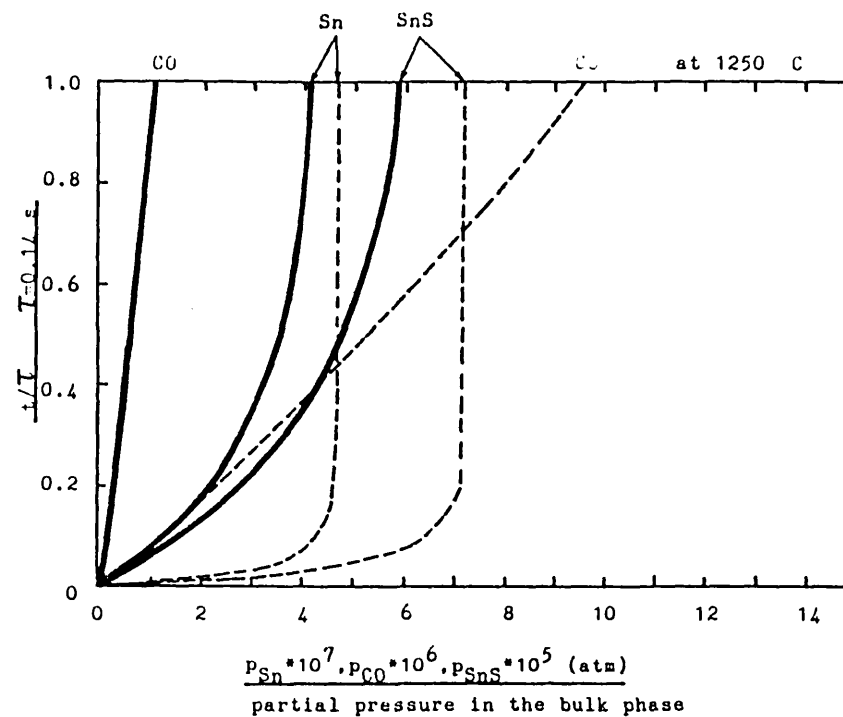
$k_m = 4 \cdot 10^{-4} \text{ (m/s)}$

$k_g = 2 \cdot 10^{-2} \text{ (m/s)}$

———— activity in the bulk phase

----- interfacial activity

(c) Driving force in the metal phase (steel).



———— $k_m = 4 \cdot 10^{-4} \text{ (m/s)}, k_g = 2 \cdot 10^{-2} \text{ (m/s)}$

----- $k_m = 4 \cdot 10^{-3} \text{ (m/s)}, k_g = 2 \cdot 10^{-1} \text{ (m/s)}$

Metal composition : $x_O = 1.21 \cdot 10^{-6}$

$x_C = 0.181$

$x_S = 7 \cdot 10^{-4}$

$x_{Sn} = 4.07 \cdot 10^{-3} \text{ (mole fraction)}$

(d) Effect of mass transfer coefficient on the change of composition in a bubble with time (carbon saturated iron at 1250°C).

Behaviours of rising bubble (volume = $1.0 \times 10^{-7} \text{ m}^3$, diameter = 5.76 mm, argon gas ; initially) in carbon saturated iron (at 1250°C) and in steel (at 1600°C) were simulated under the conditions described in Fig. 6-1. Reactions involved were Sn vaporization, $(\text{SnS})_{\text{gas}}$ formation and CO formation. Partial pressures of these species increased while a argon bubble rose in the molten metal. The results lead to the following discussions.

- 1) Due to a large equilibrium constant for CO reaction, $[\text{C}] + [\text{O}] = (\text{CO})$, partial pressure of CO in a bubble was far from equilibrium at $t_B = 1$, where t_B denotes dimensionless time which is normalised by a rising period. On the other hand, partial pressures of (Sn) and (SnS) were closer to equilibrium conditions.
- 2) The rate of mass transfer is affected by mass transfer coefficients of the metal and gas phase and equilibrium constant.
e.g. CO formation: flux density of CO, N_{CO} , is derived as follows:

i) Chemical equilibrium (effective).

$$K_{\text{CO}}^{\text{eff}} = p_{\text{CO}}^i / x_{\text{C}}^i \cdot x_{\text{O}}^i$$

ii) Flux density continuity.

$$\begin{aligned} N_{\text{CO}} &= k_m \cdot C_m \cdot (x_{\text{C}}^b - x_{\text{C}}^i) \\ &= k_g \cdot C_g \cdot (p_{\text{CO}}^i - p_{\text{CO}}^b) / p_T \end{aligned}$$

- iii) Using equations above, one can obtain N_{CO} expressed only by bulk concentrations. For convenience, superfix "b" is neglected below.

$$N_{CO} = k_g \cdot C_g \cdot \left[\{1 + K_{CO}^{eff} \cdot \epsilon \cdot (x_C + x_O)\} + \sqrt{\{1 + K_{CO}^{eff} \cdot \epsilon (x_C + x_O)\}^2 - 4 \cdot K_{CO}^{eff} \cdot \epsilon^2 \cdot (K_{CO}^{eff} \cdot x_C \cdot x_O - p_{CO})} \right] / 2 \cdot K_{CO}^{eff} \cdot \epsilon^2 \cdot p_T$$

$$\text{where } \epsilon = k_g \cdot C_g / k_m \cdot C_m \cdot p_T$$

$$\text{iv) Assuming } 4K_{CO}^{eff} \cdot \epsilon^2 \cdot (K_{CO}^{eff} \cdot x_C \cdot x_O - p_{CO}) \ll \{1 + K_{CO}^{eff} \cdot \epsilon (x_C + x_O)\}^{2*1},$$

one can obtain N_{CO} in a simple form.

$$N_{CO} \simeq \frac{k_g \cdot C_g}{p_T} \cdot \frac{K_{CO}^{eff} \cdot x_C \cdot x_O - p_{CO}}{1 + K_{CO}^{eff} \cdot \epsilon \cdot (x_C + x_O)}$$

In case $K_{CO}^{eff} \cdot \epsilon (x_C + x_O) \gg 1^{*2}$ and

$$K_{CO}^{eff} \cdot x_C \cdot x_O \gg p_{CO},$$

$$N_{CO} \simeq k_m C_m x_C \cdot x_O / (x_C + x_O)$$

N.B. *1 Under the simulated conditions,

$$4 \cdot K_{CO}^{eff} \cdot \epsilon^2 \cdot (K_{CO}^{eff} \cdot x_C \cdot x_O - p_{CO}) \sim 10$$

$$\{1 + K_{CO}^{eff} \cdot \epsilon \cdot (x_C + x_O)\}^2 \sim 30$$

An assumption above is valid for rough estimation.

*2 Under the simulated conditions,

$$K_{CO}^{eff} \cdot \epsilon (x_C + x_O) \sim 4$$

An assumption above is valid for rough estimation.

The expression for N_{CO} above means that the rate of CO transport is controlled by mass transfer coefficient in the metal phase under the conditions simulated in the present work.

The simulated results are shown in Fig. 6-1(a). Change of k_g from 2×10^{-2} to 2×10^{-1} [m/s] does not affect a rate of CO evolution. Change of k_m from 4×10^{-4} to 4×10^{-3} [m/s] causes ten times difference in partial pressure of CO in a bubble.

On the other hand, change of partial pressure of $(Sn)_{gas}$ with time is not affected by k_m . It is influenced by k_g .

Change of partial pressure of $(SnS)_{gas}$ with time is affected by both k_m and k_g .

Driving forces expressed by difference of activity or partial pressures between the interface and the bulk are shown in Fig. 6-1 (b), (c).

3) There are some applications of "BUBBLE" and further work.

e.g.

i) combining metal/slag model, one can simulate a behaviour of powder injected with gas into the molten metal.

ii) Modelling work for AOD process was reported by Yoshii et al [73]. The present model can be applied to AOD process by inclusion of other elements, e.g. Cr.

6-2 Kinetics of decopperisation(de-Cu)

Comparison between the experimental results and the computed results leads to information on rate phenomena. Rate phenomena in the experimental and mathematical work are controlled by the following parameters:-

- i) Mass transfer coefficients, k [m/s]
- ii) Argon gas flow rate for bubbling, $\dot{q}_N$ [Nl/min]
- iii) Mass transfer rate constant for CO,
 G_{CO} [mol /m²-s].

G_{CO} is not important in the case of de-Cu using sulphide slags. G_{CO} plays an important role when oxide slags are used with higher contents of carbon in the metal phase which makes p_{CO} high enough to nucleate CO bubbles.

When the initial slag contains enough FeS to supply S to the system, the argon gas flow is not very important for de-Cu. Under the circumstances described above, the rate phenomena are simply determined by mass transfer coefficients.

Equation for mass conservation of each species are of the type:-

$$V_m C_m \cdot \frac{dx}{dt} = - S \cdot k_m \cdot C_m (x - x^i) \quad (6-1)$$

where superscript i denotes interfacial value

x denotes mole fraction of each species.

Subscript m denotes the metal phase.

This equation can be expressed in dimensionless form.

$$\frac{dx}{dt^*} = - (x - x^i) \quad (6-2)$$

where $t^* = t/t_{ref}$

and $t_{ref} = V_m/k_m S$ [sec].

Equation (6-2) indicates that the rate phenomena are determined simply by t_{ref} .

In Fig. 6-2, experimental results of run-11 (which used a 80wt% $\text{NaS}_{0.5}$ - 20wt% FeS slag) and computed results are compared.

Computed results using, $\gamma_{\text{FeS}} = 0.14$ and $\gamma_{\text{CuS}_{0.5}} = 0.9$, which are determined from Fig. 5-22(a), represent the experimental results excellently. There are three lines in Fig. 6-2(a) which represent t_{ref} - values of 150, 185 and 220 sec respectively. Experimental results fall between the lines of $t_{ref} = 150$ sec and $t_{ref} = 220$ sec.

$$t_{ref} = 185 \pm 35 \text{ [sec]} \quad (6-3)$$

This means that:

$$\begin{aligned} S.k_m &= V_m / t_{ref} \\ &= (2.3 \pm 0.5) \times 10^{-6} \text{ [m}^3/\text{s]} \end{aligned} \quad (6-4)$$

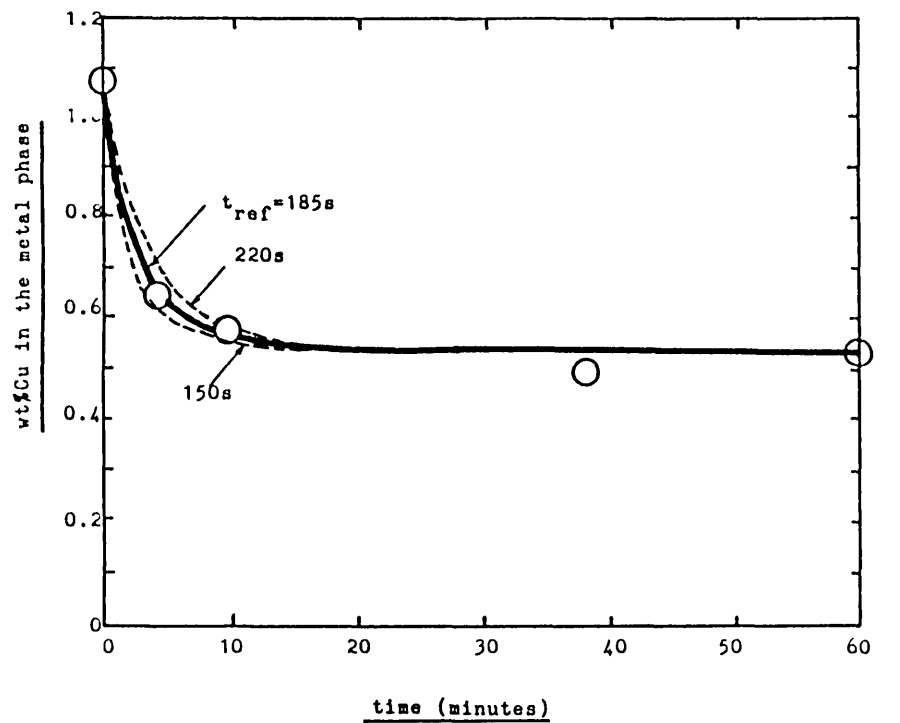
Assuming a nominal interfacial area of the metal/slag interface ($S = 4.42 \times 10^{-3} \text{ [m}^2\text{]}$) one can obtain a mass transfer coefficient, k_m .

$$k_m = (5.2 \pm 1.1) \times 10^{-4} \text{ [m/s]} \quad (6-5)$$

The driving force, which is determined by the mole fraction difference between the bulk and interface, are shown in Fig. 6-2 (c) and (d) for Cu and S respectively. S content in the metal phase increases with time due to $\text{NaS}_{0.5}$ decomposition. Increase of S content is favourable for de-Cu but simultaneously the total slag weight decreases with time. As a result de-Cu continues very slowly toward the end of the simulation ($t^* = 10$).

In the case of pure $\text{NaS}_{0.5}$ slag, the transport mechanism of Na vapour, which is by argon bubbling in the mathematical model, affects the rate phenomena importantly. The effect of the argon bubbling gas flow rate on de-Cu is summarised in Fig. 6-3.

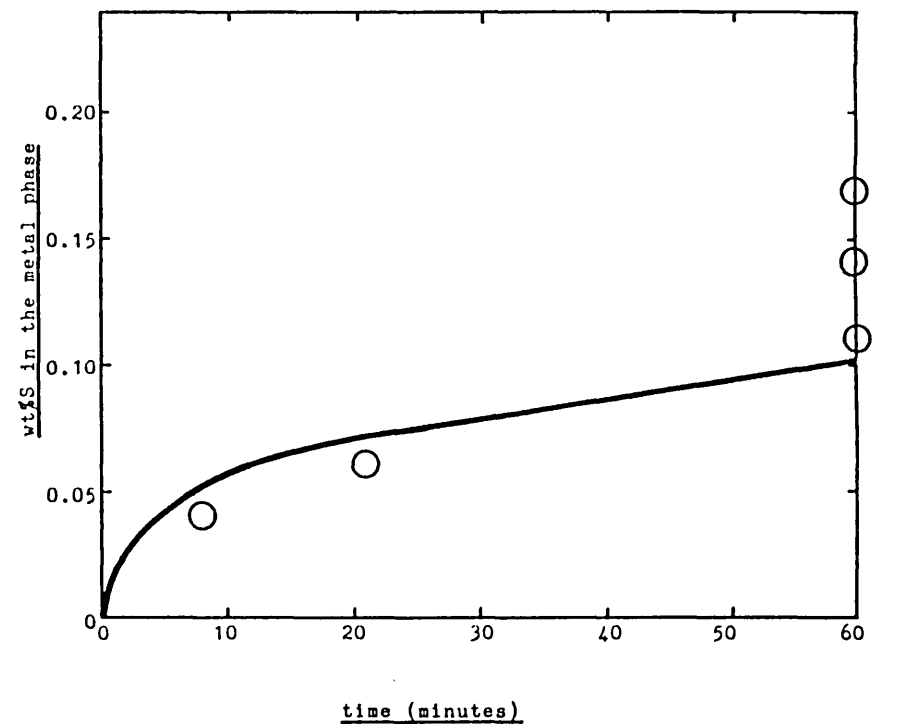
100 Nl/min of argon gas flow rate is an unrealistically high rate for the 3 kg metal/0.3 kg slag system. In this case, a high rate of de-Cu is obtained in the initial stage of reaction and later re-copperising occurs due to decrease of the slag weight.



— $t_{ref}=185s$
 - - - $t_{ref}=150s, 220s$ } (by the full model)

○ experimental results (run-11)

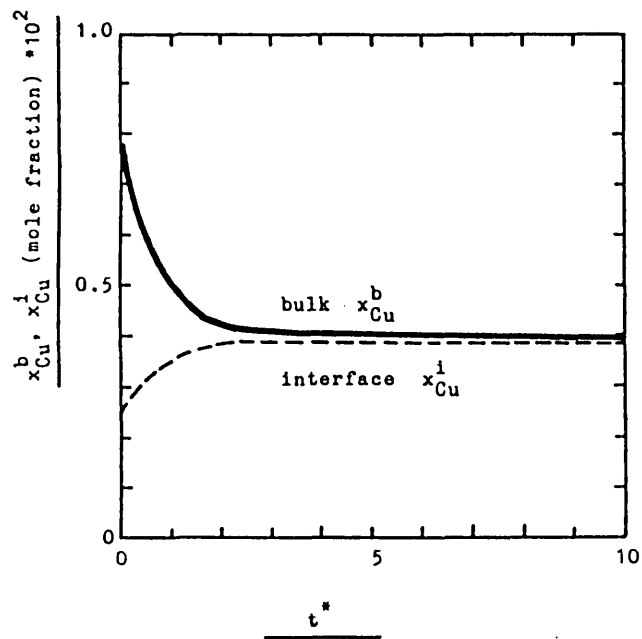
(a) Kinetics of de-Cu.



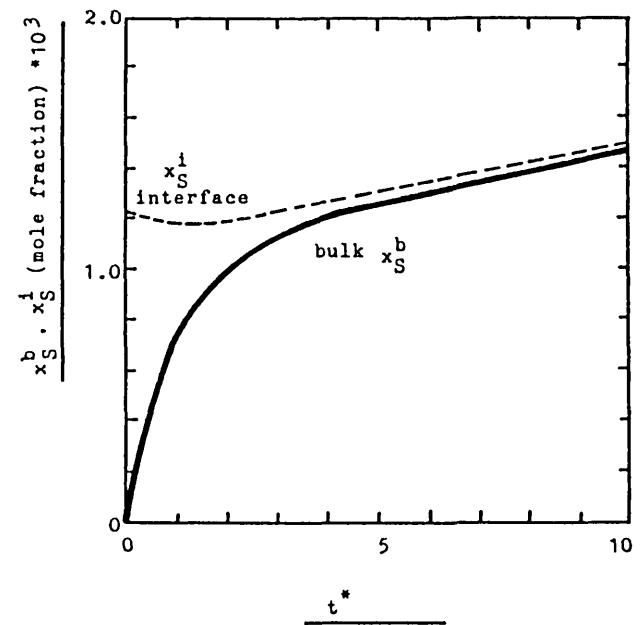
○ experimental results
 — calculated results by the full model

(b) Change of the sulphur concentration in the metal phase with time.

Fig.6-2 Comparison between experimental and calculated result (by the full model, carbon saturated iron, 80wt%NaS_{0.5}-20wt%FeS slag (slag/metal)_{weight}=0.10, γ_{FeS} =0.14 and $\gamma_{CuS_{0.5}}$ =1.0, argon bubbling gas flow rate=2 Nl/min , at 1250° C).



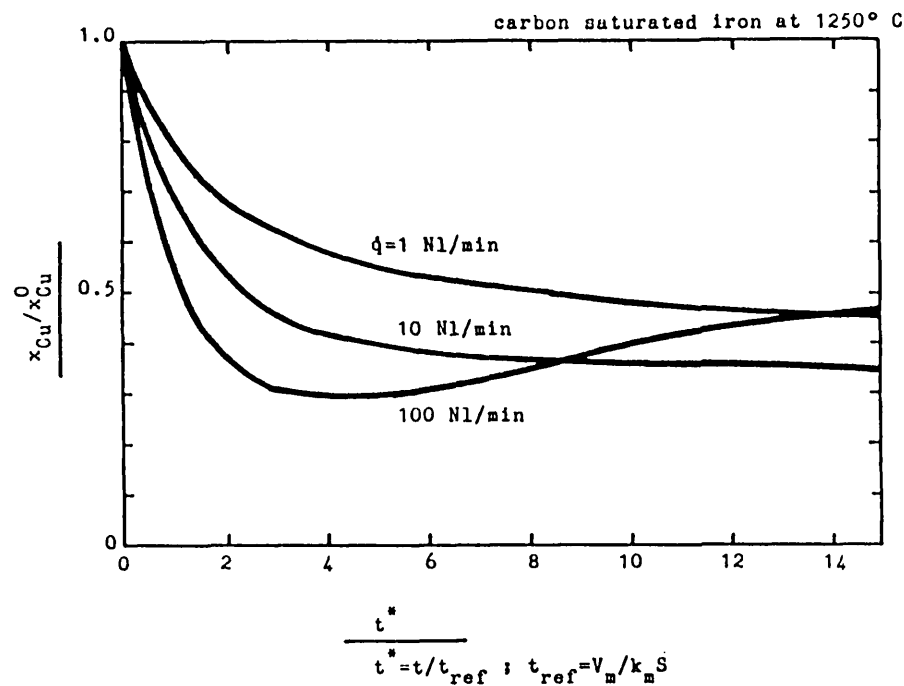
(c) Driving force for Cu transport.



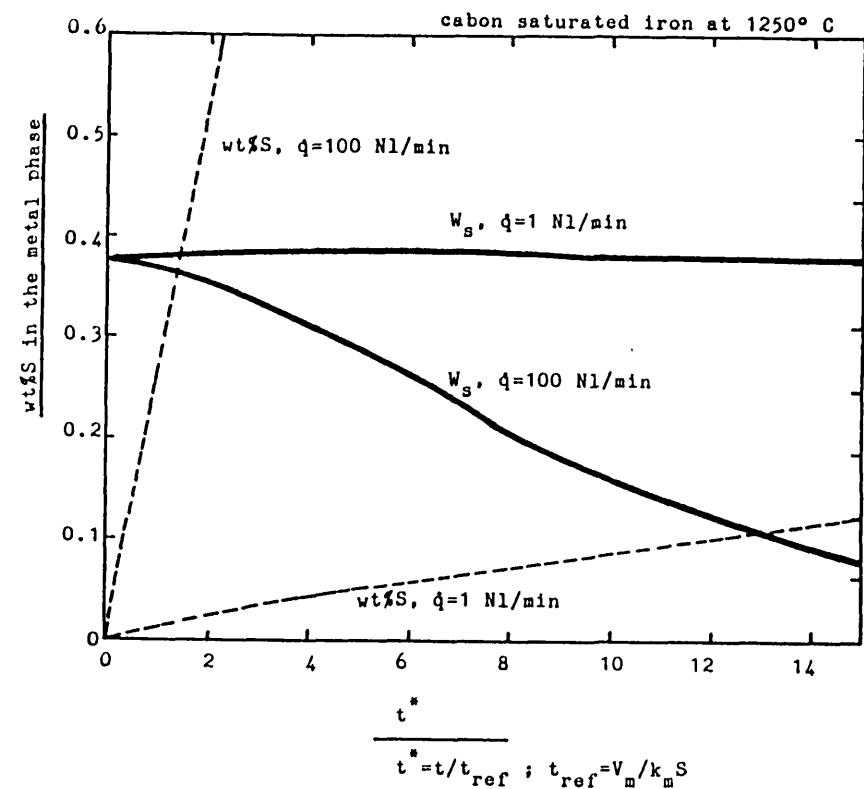
$$t^* = t/t_{\text{ref}} ; t_{\text{ref}} = V_m/k_m S$$

where V_m = volume of the metal phase
 k_m = mass transfer coefficient
in the metal phase
 S = interfacial area

(d) Driving force for sulphur transport.

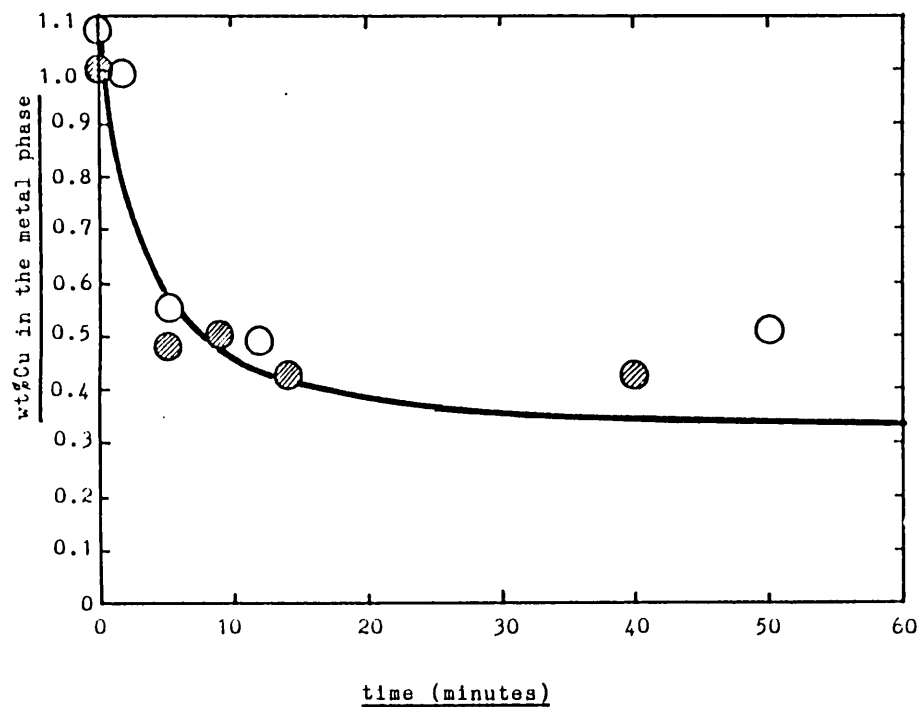


(a) Copper concentration in the metal phase.



(b) Sulphur concentration in the metal phase.

Fig.6-3 Effect of argon bubbling gas flow rate q on de-Cu
(pure $\text{NaS}_{0.5}$ slag (slag/metal)_{weight} =0.10,
 $\gamma=1.0$ for sulphides, carbon saturated iron at
1250° C, $x_{\text{Cu}}^0=0.01$ and $x_{\text{S}}^0=0$, calculated by the full
model).

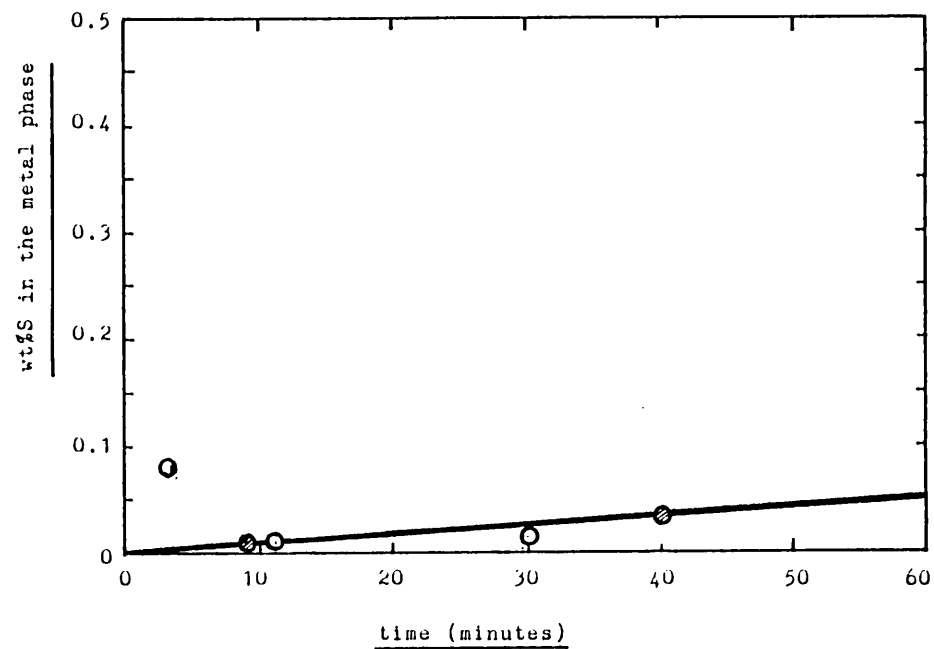


○ experiment (run-6)

● experiment (run-18)

— calculation (by the full model)
with argon bubbling (2 Nl/min)

(carbon saturated iron at 1250° C, pure $\text{NaS}_{0.5}$ slag).



Sulphur concentration in the metal phase.

Fig.6-3 (c) Experimental and calculated results.

6-3 Kinetics of detinning (de-Sn)

There are three possible ways in which tin removal can occur:

- i) (Sn) vapour carried away by argon gas flow.
- ii) (SnS) vapour carried away by argon gas flow.
- iii) {SnS} dissolved into the slag phase.

The chemical equilibria corresponding to the mechanisms above are summarised in Table 6-2. The dominant mechanism can be estimated from Table 6-3 under particular conditions. The experimental results on the behaviour of Sn can be explained by the dominance of (SnS) vaporization. Comparison between the experimental results and de-Sn caused by SnS vaporization is shown in Figs . 6-4 and 6-5 for carbon saturated iron at 1250⁰C and for steel at 1600⁰C respectively.

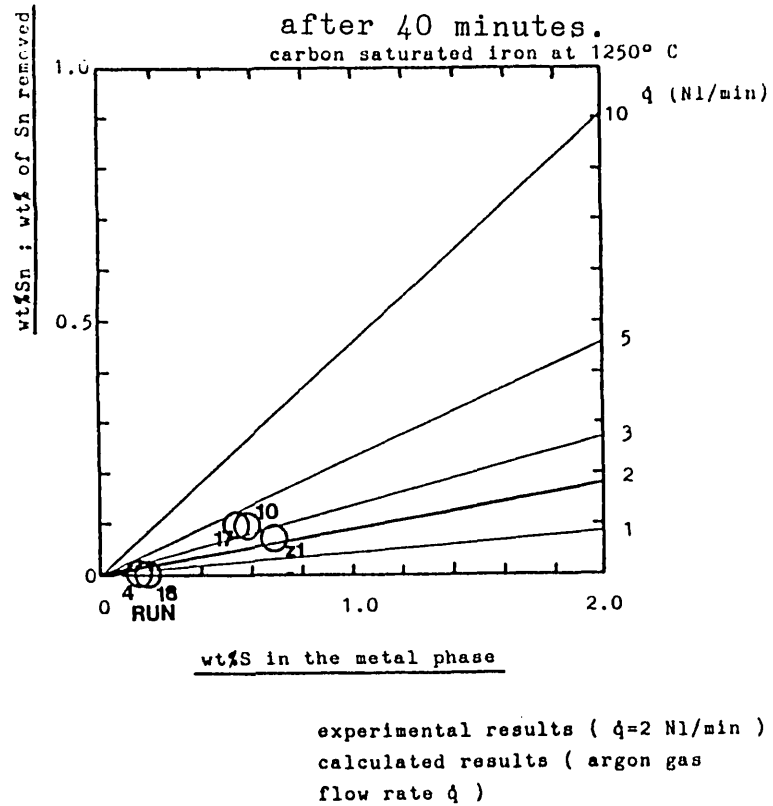


Fig.6-4 De-Cu by argon gas flow (carbon saturated iron at 1250° C).

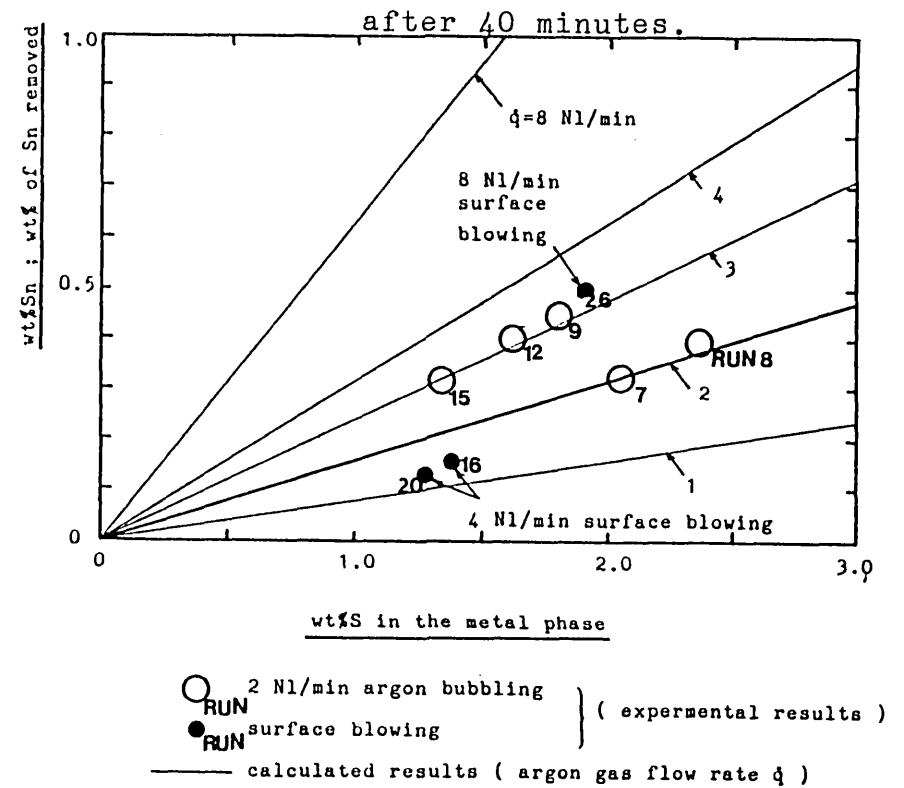


Fig.6-5 De-Sn by argon gas flow (steel at 1600° C).

In Fig. 6-5, there are three points for the runs in which surface argon blowing was used instead of argon bubbling. In these cases, de-Sn is much less effective than de-Sn expected by calculation for argon bubbling.

A local mathematical model was developed for the behaviour of Sn under the assumption that (SnS) vaporization is the dominant process for de-Sn and that no reaction occurred without argon gas flow.

The configuration of the system and governing equations are summarised in Fig. 6-6. The governing equations lead to equation (6-6).

$$x_{\text{Sn}} = x_{\text{Sn}}^0 / (1 + \varepsilon \cdot x_{\text{Sn}}^0 \cdot t^*) \quad (6-6)$$

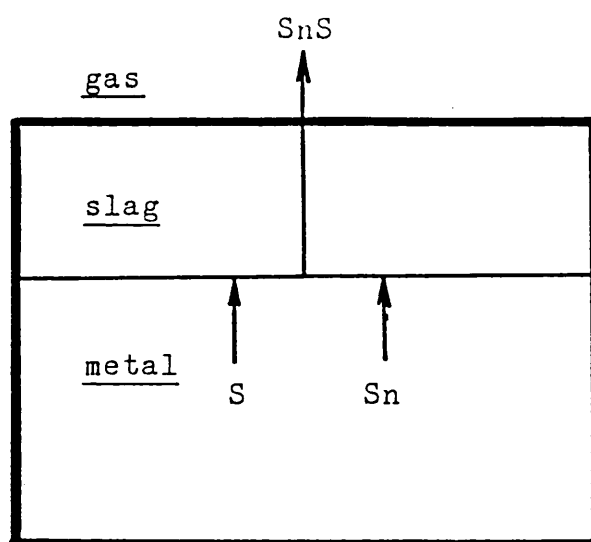
$$\text{where } t^* = t/t_{\text{ref}}$$

$$t_{\text{ref}} = V_m / k_m \cdot S$$

$$\varepsilon = \dot{q} \cdot K_{\text{SnS}} \cdot f_{\text{Sn}} \cdot f_S / (\text{R.T.S.} \cdot k_m \cdot C_m)$$

The ways in which x_{Sn} changes with time is shown in Fig. 6-7. The parameter ε for steel at 1600°C is 0.17.

t_{ref} represents the characteristic time of metal/slag reactions, e.g. sulphurisation by FeS. Under the conditions investigated, de-Sn has a much longer characteristic time than t_{ref} .



1) Chemical equilibrium : $\text{Sn} + \text{S} = (\text{SnS})$

$$K_{\text{SnS}} = p_{\text{SnS}}^i / a_{\text{Sn}}^i a_{\text{S}}^i$$

2) Flux density continuity :

$$\text{Sn} : k_m C_m (x_{\text{Sn}} - x_{\text{Sn}}^i) = p_{\text{SnS}}^i \dot{q} / RTS$$

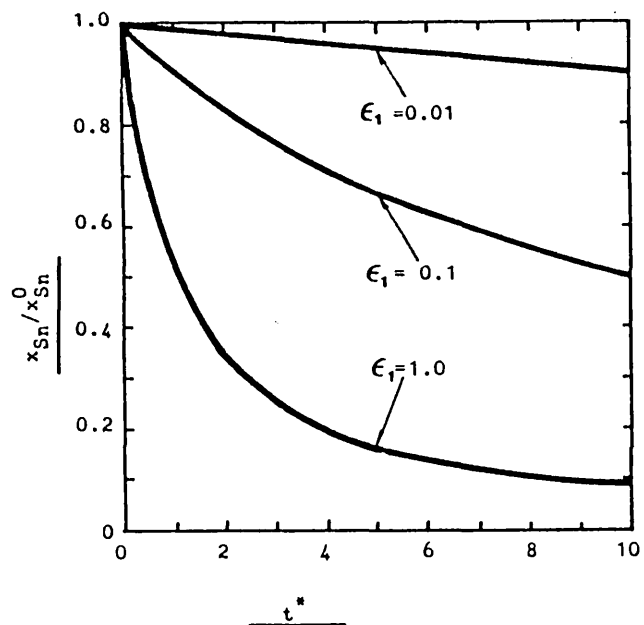
$$\text{S} : k_m C_m (x_{\text{S}} - x_{\text{S}}^i) = p_{\text{SnS}}^i \dot{q} / RTS$$

3) Mass conservation :

$$\text{Sn} : -V_m C_m dx_{\text{Sn}} / dt = S k_m C_m (x_{\text{Sn}} - x_{\text{Sn}}^i)$$

$$\text{S} : -V_m C_m dx_{\text{S}} / dt = S k_m C_m (x_{\text{S}} - x_{\text{S}}^i)$$

Fig.6-6 A mathematical model for de-Sn.

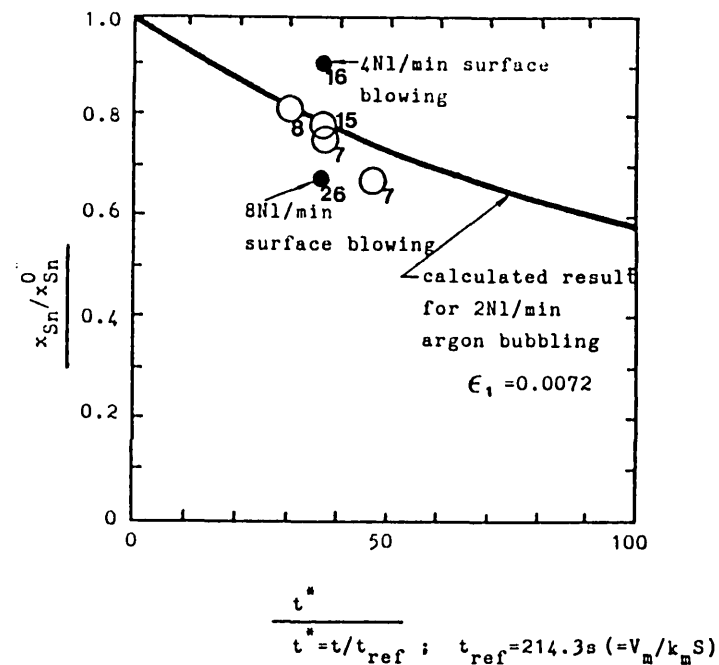


N.B. : x_{Sn} denotes mole fraction of tin in the metal phase. x_{Sn}^0 is an initial value of it.

$$\epsilon_1 : x_{Sn}/x_{Sn}^0 = 1/(1 + \epsilon_1 t^*)$$

(a) Calculation.

Fig.6-7 Change of tin concentration in the metal phase with time (predicted by a mathematical model).



○ 2Nl/min argon bubbling
● argon surface blowing
RUN

(experimental result)

(b) Experimental results.

Table 6-3 Total amount of Sn removed as (Sn)_{vapour},
(SnS)_{vapour} and (SnS)_{slag,liquid}.

(1) Weight of Sn removed as each species.

	carbon saturated iron at 1250° C	steel at 1600° C (g)
Sn vapour	$1.4 \cdot 10^{-4} (\text{wt}\% \text{Sn}) \dot{q}$	$5.1 \cdot 10^{-3} (\text{wt}\% \text{Sn}) \dot{q}$
SnS vapour	$0.46 (\text{wt}\% \text{Sn}) (\text{wt}\% \text{S}) \dot{q}$	$0.80 (\text{wt}\% \text{Sn}) (\text{wt}\% \text{S}) \dot{q}$
SnS liquid	$0.22 (\text{wt}\% \text{Sn}) (\text{wt}\% \text{S}) M_s$	$0.046 (\text{wt}\% \text{Sn}) (\text{wt}\% \text{S}) M_s$

- 1) Gaseous species are assumed to be carried away by argon gas flow (gas flow rate $\dot{q}$ Nl/min).
- 2) Flux of gaseous species :
(flux of Sn) = $p_{\text{Sn}} \dot{q} / RT$ mol/s
(flux of SnS) = $p_{\text{SnS}} \dot{q} / RT$ mol/s
- 3) Tabulated values above are the total amount removed after 60 minutes (expressed in grams).
- 4) M_s = total moles of the slag phase.

(2) Weight of Sn removed (normalised by weight of Sn removed as (SnS)_{vapour}).

	carbon saturated iron at 1250° C	steel at 1600° C
Sn vapour	0.003 (wt%S=0.1) 0.03 (wt%S=0.01)	0.06 (wt%S=0.1) 0.63 (wt%S=0.01)
SnS vapour	1.00*	1.00*
SnS liquid	0.31	0.04

- 1) Argon gas flow rate $\dot{q} = 2$ Nl/min (60 minutes).
- 2) Metal(1000g)-slag(100g, pure NaS_{0.5}).
- 3) wt%Sn=1.
- 4) * : tabulated values above are normalised by weight of Sn removed as (SnS)_{vapour}.
- 5) (SnS) vaporization is dominant under the conditions studied.

Table 6-4 Simulation conditions for de-S.

- (1) Initial metal = 3.0kg (carbon saturated iron with $x_{\text{Cu}}^0 = 0.01$, $x_{\text{Sn}}^0 = 0.002$ and $x_{\text{S}}^0 = 0$ in mole fraction).
- (2) Initial slag = 0.450kg (80wt%NaS_{0.5}-20wt%FeS).
- (3) Temperature = 1250° C.
- (4) CaO addition.
CASE-I : no CaO addition.
CASE-II : continuous CaO addition between $t=7\text{min}$ and $t=12\text{min}$ (amount of CaO added = $36 \text{ G/min} \cdot 5 \text{ min} = 180\text{g}$).
CASE-III: continuous CaO addition between $t=7\text{min}$ and $t=12\text{min}$ (amount of CaO added = 180g). at $t=7\text{min}$, slag used for de-Cu/de-Sn is partly removed (deslagging, residuals = 180g).

6-4 Desulphurisation (de-S) after decopperising (de-Cu)

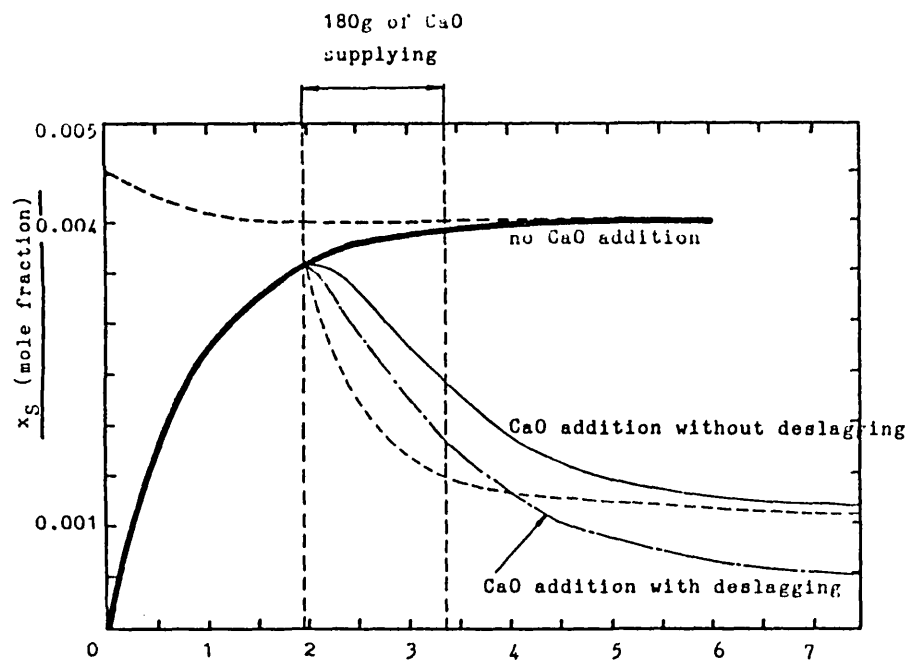
Simulations were made by the full model under the conditions summarised in Table 6-4.

The effect of CaO on de-S is shown in Fig. 6-8. There is no sulphur in the initial metal phase. The sulphur is picked up by the metal phase with the driving force shown in Fig. 6-8. De-S occurs in the case of CaO addition. The amount of sulphur removed is larger with deslagging than without deslagging. The behaviour of Cu is shown in Fig. 6-9. Cu reversion occurs after CaO addition. This reversion process is slower than the de-Cu process in the initial stage due to lower driving force for the reaction. In the deslagging case (residual slag 180g) slightly larger reversion occurs than in the no deslagging case. This is because deslagging leads to the lower sulphur content in the metal phase which is unfavourable condition for de-Cu ($[Cu] + \frac{1}{2} [S] = \{CuS_{0.5}\}$ equilibrium). It is obvious that perfect deslagging must result in no reversion.

6-5 Behaviour of other elements during decopperisation and detinning (de-Cu/de-Sn)

The sulphur activity should be kept high enough to promote $CuS_{0.5}/SnS$ formation during de-Cu/de-Sn. This sulphur would react with Mn in the metal. Computed results are shown in Fig. 6-10.

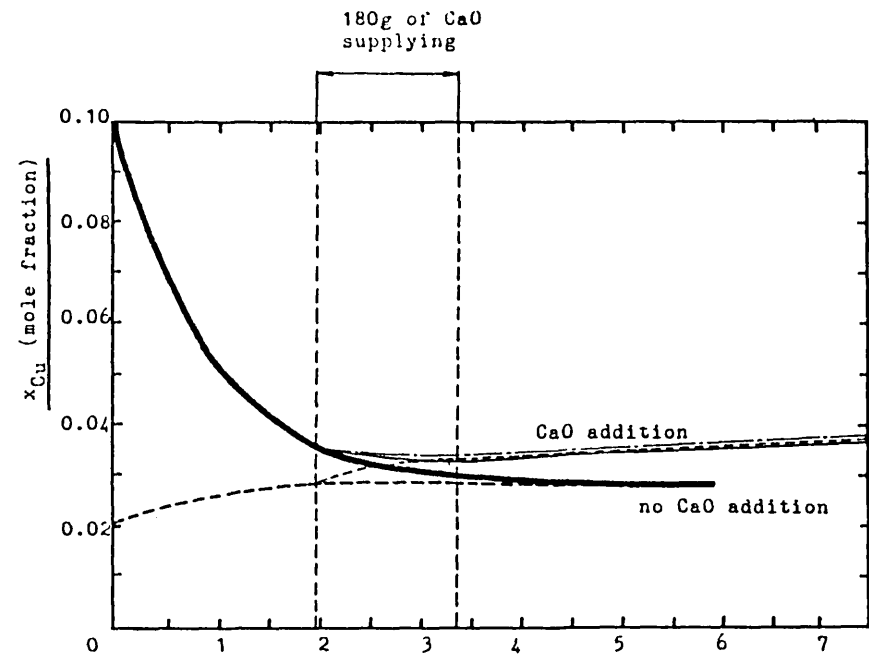
n_{Cu} decreases from 50% to 43% by addition of 0.01 mole fraction of Mn (at $t^* = 15$). 85% of Mn was removed without MnS addition, 70% of Mn was removed with 0.1 mole fraction of MnS addition.



t^*
 $t_{ref}=214.3 \text{ s}, x_S^0=0, x_{Cu}^0=0.01$

— sulphur concentration in the bulk phase
 - - - interfacial sulphur concentration
 no CaO addition
 — sulphur concentration in the bulk phase
 - - - interfacial sulphur concentration
 CaO addition without deslagging
 - - - sulphur concentration in the bulk phase
 CaO addition with deslagging
 (residual slag weight = 180g)

Fig.6-8 Behaviour of sulphur in the metal phase with/without CaO addition and effect of deslagging (80wt%Na₂O₅-20wt%FeS slag 450g, carbon saturated iron at 1250°C).



t^*
 $t_{ref}=214.3 \text{ s}$

— $x_{Cu}(\text{bulk})$, no CaO addition
 - - - $x_{Cu}(\text{interface})$, no CaO addition
 — $x_{Cu}(\text{bulk})$, CaO addition without deslagging
 - - - $x_{Cu}(\text{interface})$, CaO addition with deslagging
 - - - $x_{Cu}(\text{bulk})$, CaO addition with deslagging
 (residual slag weight=180g)

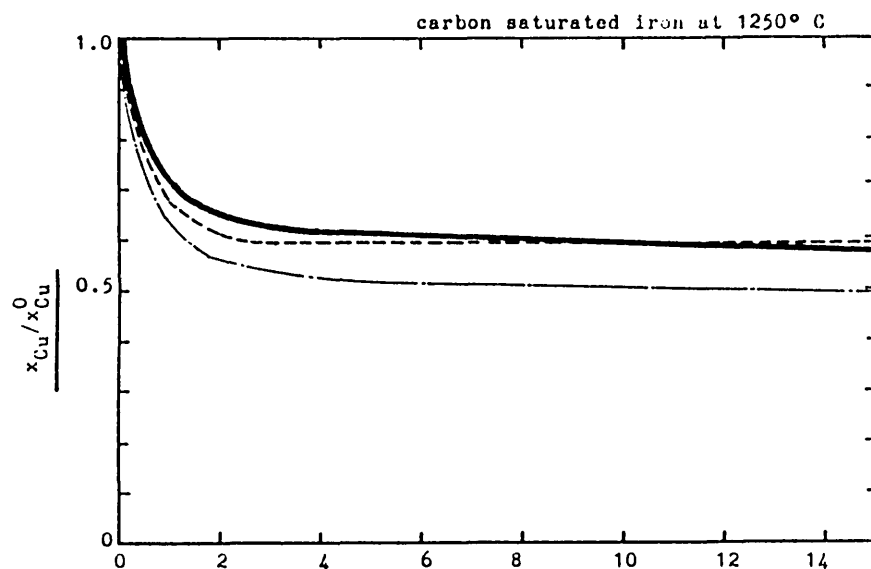
Fig.6-9 Behaviour of Cu with/without CaO addition and effect of deslagging (same simulation conditions as those of Fig.6-8).

With presence of Mn in the metal phase, de-Cu was less effective because sulphur was partly consumed by MnS formation. 85% of Mn ($x_{\text{Mn}}^0 = 0.01$) was removed at $t^* = 15$ with 80wt% $\text{NaS}_{0.5}$ - 20 wt% FeS slag (at 1250°C). Mn removal was slightly suppressed by addition of MnS in the initial slag, e.g. in case $x_{\text{MnS}}^0 = 0.10$, 70% of Mn ($x_{\text{Mn}}^0 = 0.01$) was removed.

MnO added in the initial slag caused increase of Mn in the metal phase, e.g. in case $x_{\text{MnO}}^0 = 0.10$ and $x_{\text{Mn}}^0 = 0.0$, $x_{\text{Mn}} = 1.4 \times 10^{-3}$, as shown in Fig. 6-10(b).

Simulations above were carried out under the assumption of $\gamma_{\text{MnS}} = 1.0$. These simulated results should be compared with the experimental results. This is a further work in this field.

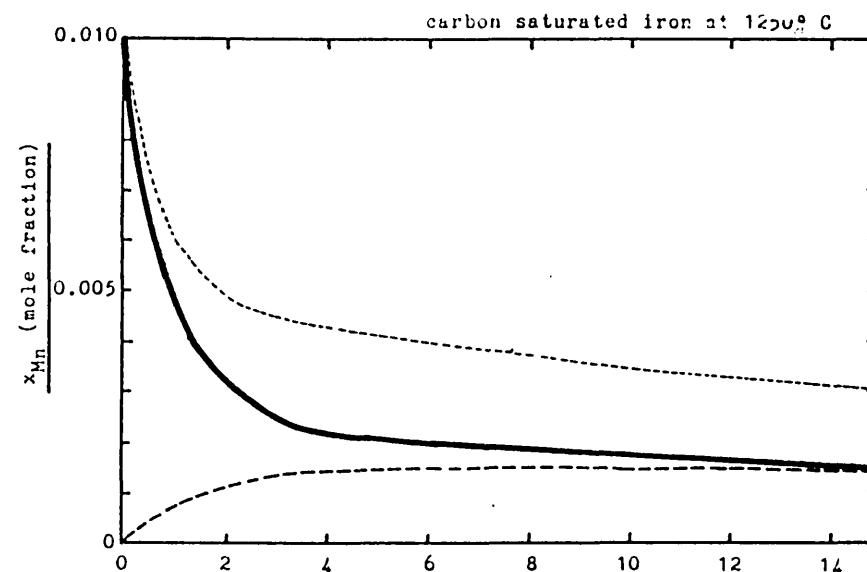
In the experimental work for de-Cu/de-Sn from steel, alumina crucibles were used. After slag addition, some erosion of crucible was observed. The effects of $\text{AlO}_{1.5}$ addition and metallic Al addition on de-Cu were studied by the full model. As is shown in Fig. 6-19(c)-(e), $\text{AlO}_{1.5}$ addition ($x_{\text{AlO}_{1.5}}^0 = 0.20$) led to slightly better de-Cu and lower sulphurisation. Al addition in the metal phase ($x_{\text{Al}}^0 = 0.001$) did not cause any significant effect on η_{Cu} or x_{S} (in this case oxygen activity was very low and oxidic component was not involved in the system simulated.)



$$t^* = t/t_{ref} ; t_{ref} = V_m/k_m S$$

	x_{Mn}^0	$x_{NaS_{0.5}}^0$	x_{FeS}^0	x_{MnS}^0	x_{MnO}^0
—	0.01	0.889	0.11	0	0
- - -	0	0.789	0.11	0	0.10
· · ·	0.01	0.789	0.11	0.10	0
- · -	0	0.889	0.11	0	0

(a) Effect of the manganese on de-Cu (metal=1000g carbon saturated iron with $x_{Cu}^0=0.01$ and $x_S^0=0$, slag=100g, $\gamma_{FeS}=0.2$, $\gamma_{CuS_{0.5}}=1.0$, $\gamma_{MnS}=1.0$, $\gamma_{MnO}=1.0$)

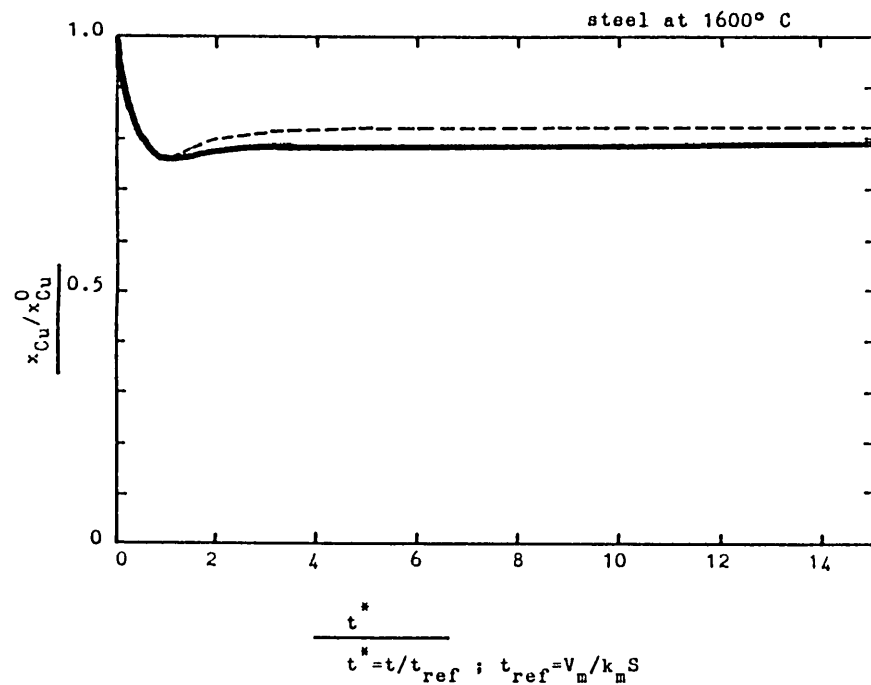


$$t^* = t/t_{ref} ; t_{ref} = V_m/k_m S$$

	x_{Mn}^0	$x_{NaS_{0.5}}^0$	x_{FeS}^0	x_{MnS}^0	x_{MnO}^0
—	0.01	0.889	0.11	0	0
- - -	0	0.789	0.11	0	0.10
· · ·	0.01	0.789	0.11	0.10	0

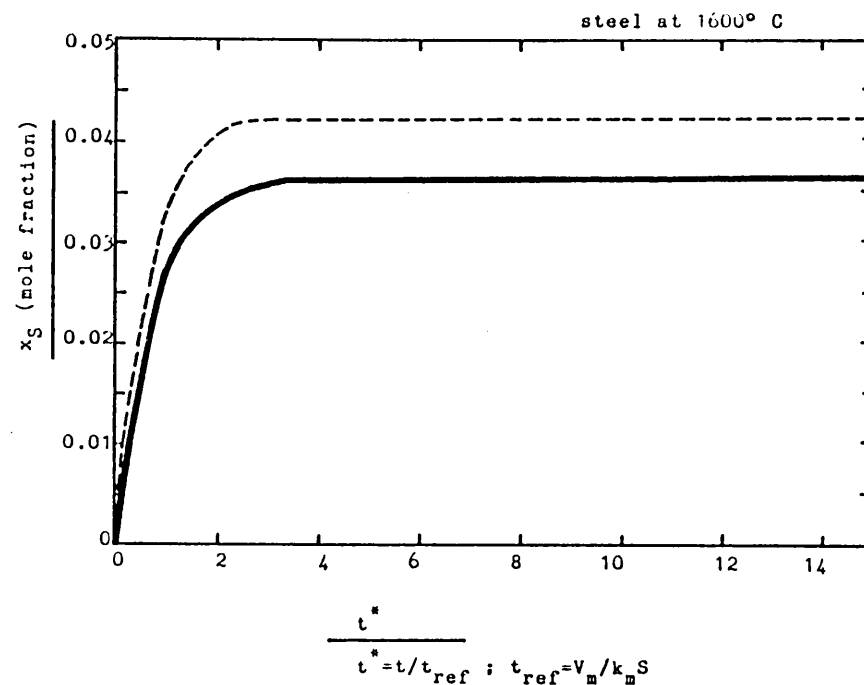
(b) Behaviour of Mn in the metal phase (same conditions as Fig.6-10 (a)).

Fig.6-10 Effect of Mn and Al on de-Cu (calculated by the full model).



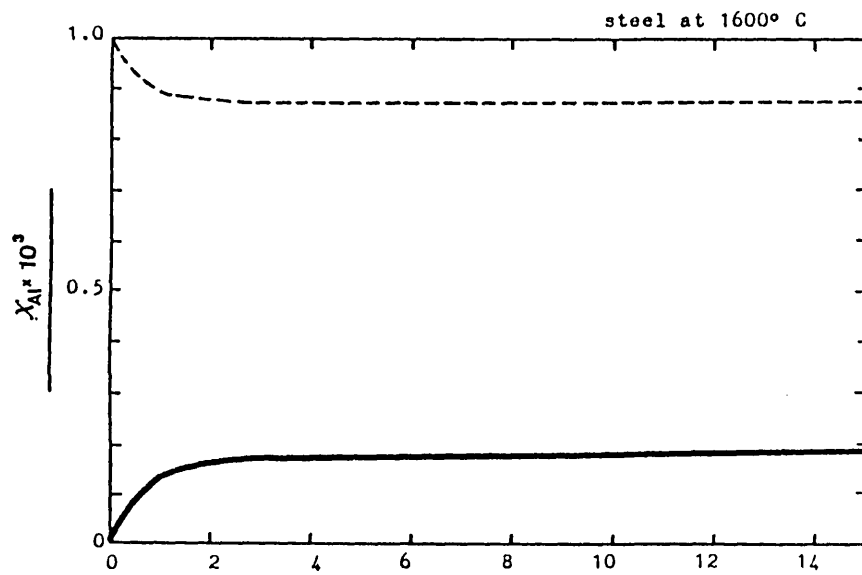
	x_{Al}^0	x_{Cu}^0	x_S^0	x_{CaS}^0	x_{FeS}^0	$x_{AlO_{1.5}}^0$
-----	0.001	0.01	0	0.21	0.79	0
————	0	0.01	0	0.17	0.63	0.20
————	0	0.01	0	0.21	0.79	0

(c) Effect of the Al and $AlO_{1.5}$ on de-Cu (metal=3000g steel at 1600° C, slag=300g, $\gamma^0=1$ for sulphides and oxides).



	x_{Al}^0	x_{Cu}^0	x_S^0	x_{CaS}^0	x_{FeS}^0	$x_{AlO_{1.5}}^0$
-----	0.001	0.01	0	0.21	0.79	0
————	0	0.01	0	0.17	0.63	0.20
————	0	0.01	0	0.21	0.79	0

(d) Effect of Al and $AlO_{1.5}$ on the sulphur concentration in the metal phase (same conditions as Fig.6-10 (c)).



t^*
 $t^* = t/t_{ref} ; t_{ref} = V_m/k_m S$

	x_{Al}^0	x_{CaS}^0	x_{FeS}^0	$x_{Al_{1.5}}^0$
-----	0.001	0.21	0.79	0
————	0	0.17	0.63	0.20

(e) Behaviour of Al in the metal phase (same conditions as Fig.6-10 (c)).

6-6 Differences between carbon saturated iron and steel on decopperisation and detinning(de-Cu/de-Sn)using sulphide slags.

Due to the very different concentration of C between carbon saturated iron and steel, the activity coefficients of Cu, Sn and S are different and the solubility of S is different. Activity coefficients are summarised in Table 3-2. These activity coefficients affect distribution coefficients of Cu in a manner described by equation (6-7), which is a modified form of equation (3-50).

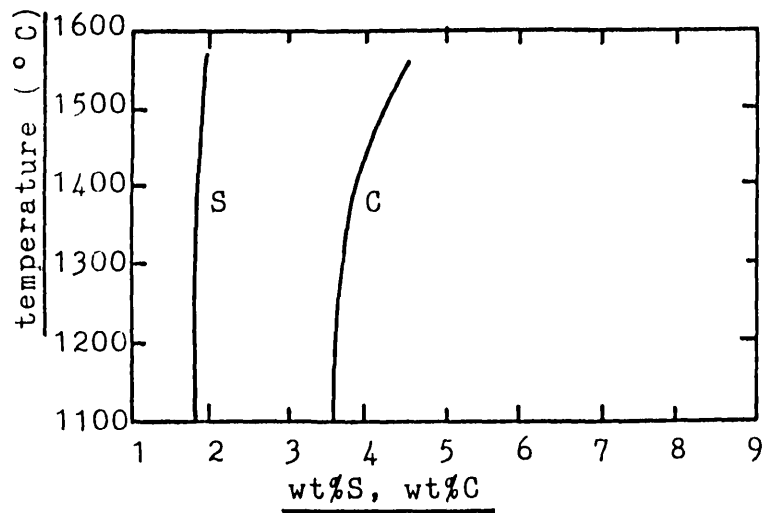
$$x_{\text{CuS}_{0.5}} / x_{\text{Cu}} \propto f_{\text{Cu}} f_{\text{S}}^{\frac{1}{2}} x_{\text{S}}^{\frac{1}{2}} \quad (6-7)$$

For Sn, according to Table 6-2,

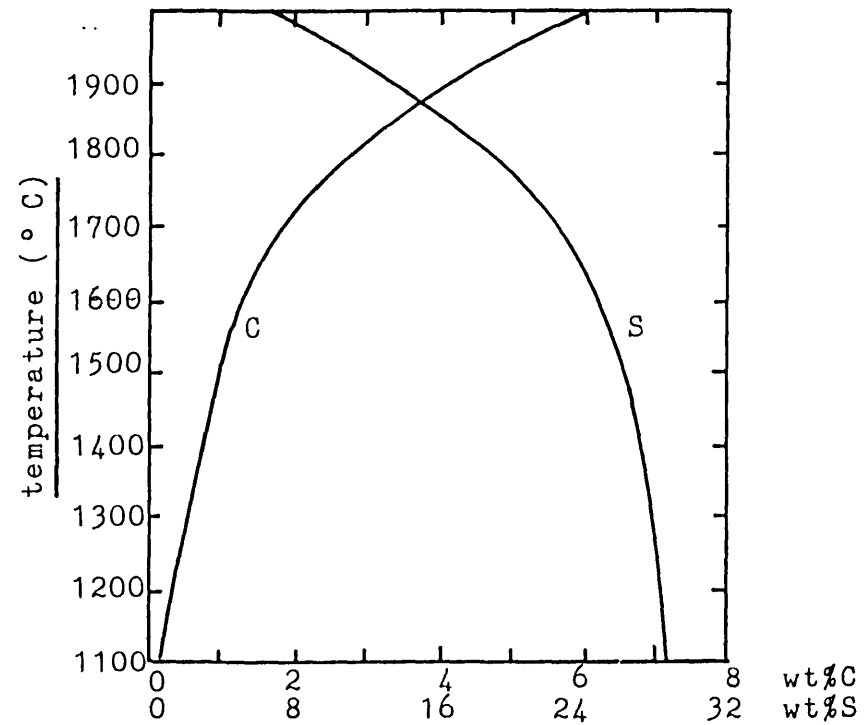
$$p_{\text{SnS}} / x_{\text{Sn}} \propto f_{\text{Sn}} \cdot f_{\text{S}} \cdot x_{\text{S}} \quad (6-8)$$

Higher f_{Cu} and f_{Sn} are advantageous condition for de-Cu and de-Sn respectively.

In the case of carbon saturated iron, S solubility was studied by Turkdogan [47], whose results are illustrated in Fig. 6-11. At 1250°C, the S solubility is approximately 1.8 wt%. In the case of steel, there is no solubility limit of S, according to Hansen [30]. As is shown in Table 6-6, 49.5g of FeS can decompose to make 1.8 wt% of S in 1000g of carbon saturated iron at 1250°C. If 100g of FeS is added to carbon saturated iron (similar condition to run - 23), some FeS would remain in the slag phase. In the case of steel, however, almost all of FeS could decompose under similar conditions (except for temperature). In this case, the sulphur content in the steel becomes fairly high, about 3 wt%S, but there remains a very small amount of slag. This could lead to poor results of de-Cu. De-Sn is not spoiled by this as long as SnS vaporization remains the dominant mechanism for de-Sn.



(a) Composition/temperature relation in carbon-rich layer of two immiscible liquids in Fe-S-C melts.



(b) Composition/temperature relation in sulphur-rich layer of two immiscible liquids in Fe-S-C melts.

Fig.6-11 Solubility of the sulphur in the carbon saturated iron after Turkdogan(47).

Table 6-5 Solubility of S in the molten iron (47).

	carbon saturated iron	steel
1250° C	1.8wt%S*	-
1350° C	1.9wt%S	-
1600° C	2.0wt%S	-

1) * : FeS decomposition limit into 1000g of metal is approximately 49.5g (carbon saturated iron at 1250 C).

Table 6-6 Simulation conditions for de-Cu/de-Sn.

	carbon saturated iron	steel
1) Initial weight.		
-metal	3.0kg	3.0kg
-slag	0.3kg	0.3kg
2) Mass transfer coefficient.		
-metal	$k_m = 4 \times 10^{-4}$ m/s	
-slag	$k_s = 2 \times 10^{-4}$ m/s	
-gas	$k_g = 2 \times 10^{-2}$ m/s	
-CO	$G_{CO}^g = 3 \times 10^{-3}$ mol/m ² s	
3) Initial composition in the		metal phase.
-S	0	0
-C	0.181(4.5wt%)	0.0047(0.10wt%)
-Cu	0.0076(1.0wt%)	0.0088(1.0wt%)
-Sn	0.0041(1.0wt%)	0.0047(1.0wt%)
	mole fraction	mole fraction
4) Initial composition in the slag phase.		
	NaS _{0.5} , CaS, CaF ₂ , FeS, FeO, MnS, MnO and AlO _{1.5} .	
5) Activity coefficient.		
	(given in Table 6-2).	
6) Temperature.		
	1523 K	1873 K
7) Total pressure in the gas phase.		
	1.0 atm	a.0 atm

6-7 Evaluation of activity coefficients of sulphides in the slag phase

According to equation (3-50), $\gamma_{\text{CuS}_{0.5}}$ is an important parameter which directly affects distribution coefficients of Cu between the slag and metal phase. γ_{FeS} plays an important role in de-Cu through sulphur content in the metal phase. $\gamma_{\text{CuS}_{0.5}}$ and γ_{FeS} evaluated in different ways are shown in Fig. 6-12 and Fig. 6-13 respectively. Both are plotted with the initial slag composition as the horizontal axis.

6-8 Performance of mechanical stirrer

Physical modelling leads useful conclusions for designing and for operating conditions of a mechanical stirrer fitted to the experimental apparatus for molten iron/steel used in the present work.

There are some deficiencies in this part of the work which can be subject of further studies in this field.

- i.e. i) Hysteresis of entraining efficiency under various kinds of stirring conditions. The critical revolution rate was determined by increasing revolution rate. It would be best to determine the critical revolution rates by both increasing and decreasing revolution rate. These two critical revolution rates could have significantly different values.
- ii) Full description of dimensional analysis. Experimental work was held with two sizes of vessels, i.e. 76 mm ID and 95 mm ID. This was not enough to find exact dependency of the system on size.
- iii) The physical properties of floating particles, especially the wetting angle, are important for entrainment. The effect of wetting angles was just qualitatively observed in this work.

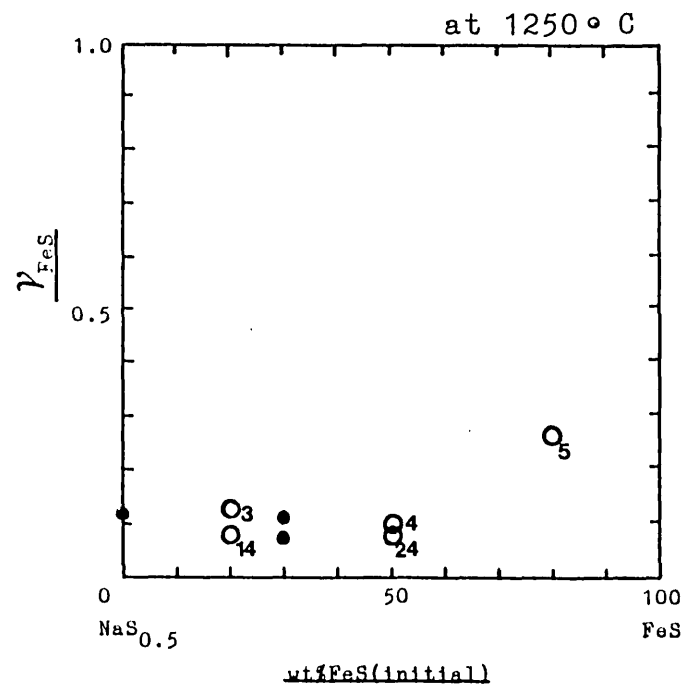


Fig.6-12 wt% FeS vs γ_{FeS}

- _{RUN} present work (1000gmetal-100gslag
or 3000gmetal-300gslag).
- * Liu's data(41) (20gmetal-3gslag).
- * : some caluculation were carried out by
the present author.

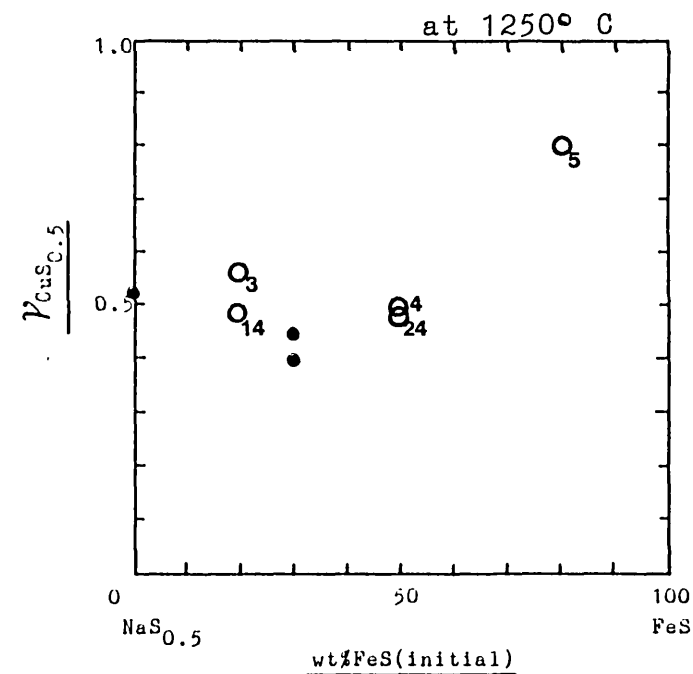


Fig.6-13 wt% FeS vs $\gamma_{\text{CuS}_{0.5}}$

- _{RUN} present work.
- Liu's data(41).

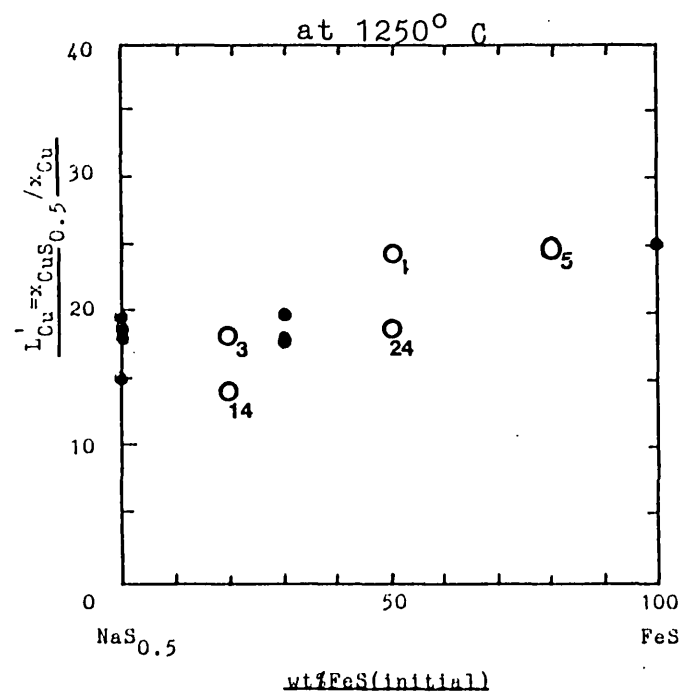


Fig.6-14 wt%FeS vs distribution coefficient of Cu.

O_{RUN} present work.

• Liu's data(41).

CHAPTER 7

CONCLUSIONS

A comprehensive mathematical model (the full model), which includes multiphases and multicomponents, and a simplified version of this model (the steady state model) have been developed in the present work. The following conclusions are obtained from the mathematical modelling work.

- 1) The validity of the full model was confirmed by the previous model of Ohguchi [10] in the case of simultaneous de-P/de-S from carbon saturated iron.
- 2) As these models can simulate the effect of argon bubbling on the transport of Na vapour and SnS vapour, copper and tin removal from molten iron by $\text{NaS}_{0.5}$ slag which essentially involves three phase such as metal, slag and gas phase can be properly simulated.
- 3) As the full model is based on general governing equations, i.e. local chemical equilibria and flux density continuity at the interfaces and mass conservation in the bulk phase, it is possible to apply this model to various kinds of pyrometallurgical problems, i.e. refining of molten iron and steel, Cr - slag cleaning etc.

The characteristics, especially about the entrainment of the particle, of the flat blade stirrer without baffles are investigated by the water model and the molten lead model. This physical modelling lead to the following conditions for the stirrer in order to obtain the good entrainment. These conditions were used in experimental work with carbon saturated iron.

For $D = 76\text{mm}$, here D denotes diameter of the container.

- 1) $N \sim 750$ r.p.m., here N denotes the rate of rotation of the stirrer.
- 2) $d = 30\text{mm}$, where d denotes diameter of the stirrer.
- 3) central stirring $\delta < \sim 5\text{mm}$, here δ denotes horizontal deviation of stirrer from the centre of the crucible.
- 4) $h_3 \sim 20\text{mm}$, here h_3 denotes height of the stirrer from the bottom of the crucible.

The chemistry and kinetics of de-Cu/de-Sn were studied by combining experimental work and mathematical modelling. Conclusions obtained in this investigation are summarised below:

- 1) $\text{NaS}_{0.5}$ - FeS mixed slag is confirmed to be fairly good slag for de-Cu from carbon saturated iron the laboratory scale experiment. This slag has a low γ_{FeS} (~ 0.2) and $\gamma_{\text{CuS}_{0.5}}$ (~ 0.9) which lead to low sulphur and copper contents of the metal phase.
 $\eta_{\text{Cu}} \geq 50\%$ is achieved with 10% of slag weight to the metal weight where pure $\text{NaS}_{0.5}$ or 80% $\text{NaS}_{0.5}$ - 20% FeS is used.
- 2) CaS - FeS mixed slag and CaS - $\text{NaS}_{0.5}$ FeS mixed slag are slightly less efficient than $\text{NaS}_{0.5}$ - FeS mixture for carbon saturated iron.

In the case of CaS-FeS mixture, it is important to choose a slag composition which has melting point low enough to maintain liquid state under the given conditions. At 1250°C , η_{Cu} obtained for each slag is:

- i) $\eta_{\text{Cu}} \cong 55$ % by $\text{NaS}_{0.5}$ - FeS mixture
- ii) $\eta_{\text{Cu}} \cong 54$ % by 18 wt% CaS - 82 wt% FeS mixture
 (29) (37 wt% CaS - 63 wt% FeS)
- iii) $\eta_{\text{Cu}} \cong 41$ % by 40 wt% $\text{NaS}_{0.5}$ 20 wt% CaS - 40 wt% FeS mixture

Other conditions are : 1000g metal (1 wt% Cu, 1 wt% Sn)
 100g slag

- 3) CaF_2 - FeS or CaF_2 - CaS-FeS slag can be used for de-Cu/de-Sn from steel. De-Cu from steel is less effective than from carbon saturated iron.
- i) $\eta_{\text{Cu}} \cong 28$ % by 50 wt% CaF_2 - 50 wt% FeS mixture
- ii) $\eta_{\text{Cu}} \cong 26$ % by 26 wt% CaF_2 - 61 wt% FeS - 13 wt% CaS mixture

Other conditions are : 1600°C
 1000g metal (1 wt% Cu, 1 wt% Sn)
 100g slag

- 4) The dominant feature of the mechanism for de-Sn is theoretically estimated to be SnS vaporization from the possibilities of Sn vaporisation, SnS vaporization and {SnS} slag formation. This was confirmed by experimental data. Argon bubbling helps transport of SnS vapour. Argon gas blown onto the surface of bath helps this but is less effective than bubbling at the same rate of gas flow.

As further work the following items are suggested:

- 1) CaF_2 - CaS - FeS mixture can be good reagent for de-Cu/de-Sn from steel. This mixture is worth investigating further.

This mixture is more conventional than $\text{NaS}_{0.5}$ slag in industrial processes and is easy to deal with. The melting point of CaS-FeS mixtures are higher than 1600°C if the CaS content is higher than 30 wt% which easily occurs with decomposition of FeS. In this case, CaF_2 additions can keep this mixture in a liquid state.

- 2) Applications of the full model could be carried out on various other kinds of pyrometallurgical problems.
- 3) Some further functions could be added to the full model i.e. version up of subroutine "HEAT" which enables to simulate changes of temperature.

APPENDIX-1

SURFACE PROFILES OF THE FORCED VORTEX AND FREE VORTEX(1) The forced vortex

The liquid rotates as if it were one rigid body. Shear force distribution is constant everywhere. The velocity distribution in the radial co-ordinate is :

$$v(r) = 2\pi \frac{N}{60} \times r \quad (A1-1)$$

At the wall $v(r) = 0$ and in the very thin layer near the wall the velocity distribution is not expressed by the equation (A1-1). This is not, however, important in the current problem. According to Bernoulli's equation,

$$z + \frac{(2\pi \frac{N}{60})^2}{2g} r^2 = \text{constant}$$

at $r = 0$, velocity = 0, $z = z_0$

$$\therefore z + \frac{(2\pi \frac{N}{60})^2}{2g} r^2 = z_0 \quad (A1-2)$$

(2) The free vortex

Navier-Stokes equations in the cylindrical system (refer to [52]) are:

$$\text{r-component} \quad \frac{\rho v_\phi^2}{r} = \frac{\partial p}{\partial r} \quad (A1-3)$$

$$\phi\text{-component} \quad \frac{\partial}{\partial r} \left\{ \frac{1}{r} \frac{\partial}{\partial r} (r v_\phi) \right\} = 0 \quad (A1-4)$$

Equation (A1-4) is solved for the following cases:

1) Case 1 (infinite space)

boundary condition : $r \rightarrow \infty \quad v_\phi \rightarrow \text{finite or zero}$

$$\text{integral (A1-4)} \quad \frac{1}{r} \frac{\partial}{\partial r} (r v_\phi) = \text{constant} \\ \equiv 2c_1$$

integral $r \cdot v_\varphi = c_1 r^2 + c_2$

divided by $r \therefore v_\varphi = c_1 r + \frac{c_2}{r}$

according to the boundary condition $c_1 = 0$

In this case, the solution of equation (A1-4) is

$$v_\varphi = \frac{c_2}{r} \quad (\text{A1-5})$$

Circulation Γ can be calculated

$$\begin{aligned} \Gamma &\equiv \oint v \, d\ell \\ &= 2\pi r v_\varphi \\ &= 2\pi r c_2 \end{aligned} \quad (\text{A1-6})$$

Using this expression for circulation, one can obtain

$$v_\varphi = \frac{\Gamma}{2\pi r} \quad (\text{A1-7})$$

In this case, z component of vorticity ω_z is

$$\begin{aligned} \omega_z &\equiv \frac{1}{r} \frac{\partial}{\partial r} (r v_\varphi) - \frac{1}{r} \frac{\partial v_r}{\partial \varphi} \\ &= 0 - 0 \\ \therefore \omega_z &= 0 \end{aligned} \quad (\text{A1-8})$$

2) Case 2 (cylindrical vessel)

boundary condition : $r = R_2$ $v_\varphi = 0$ (wall condition)

$r = R_1$, $v_\varphi = v_{\text{peripheral}}$ (axis of the stirrer)

$$\frac{v_\varphi}{v_{\text{peripheral}}} = \frac{R_2/R_1}{(R_2/R_1)^2 - 1} \left(\frac{1}{r/R_2} - r/R_2 \right) \quad (\text{A1-9})$$

In this case, vorticity ω_z is

$$\omega_z = \text{constant} (=0) \quad (\text{A1-10})$$

The surface profile is expressed by Bernoulli's equation (this is the approximation method, see note below) combined with equation (A1-5).

$$z = z_1 - \frac{v_{\text{peripheral}}}{2g} \left[\left\{ \frac{R_2/R_1}{R_2/R_1} \left(\frac{1}{r/R_2} - r/R_2 \right) \right\}^2 - \frac{2(R_1/R_2)^2}{\{1-(R_1/R_2)^2\}^3} \left\{ \frac{2}{3} - \frac{R_1}{R_2} + \frac{1}{3} \left(\frac{R_1}{R_2} \right)^3 \right\} \right] \quad (\text{A1-11})$$

here z_1 is the surface level in the case of no stirring. This is plotted in Fig. 4-18(b). Equation (A1-11) is rewritten as equation (A1-12).

$$z = z_2 - \frac{v_{\text{peripheral}}}{2g} \left\{ \frac{R_1/R_2}{1-(R_1/R_2)^2} \right\}^2 \left\{ \frac{1}{r/R_2} - r/R_2 \right\}^2 \quad (\text{A1-12})$$

Note The surface profile should be calculated from equation (A1-3) and equation (A1-9) in the case of a cylindrical vessel.

$$\begin{aligned} p &= \int \frac{\rho v_{\phi}^2}{r} dr \\ &= \int \frac{1}{r} \left(\frac{C_2}{r} + C_1 r \right)^2 dr \\ &= \left[\frac{C_1^2}{2} r^2 + 2 C_1 C_2 \ln \frac{r}{r_0} - \frac{C_2^2}{2r^2} \right] \quad (\text{A1-13}) \end{aligned}$$

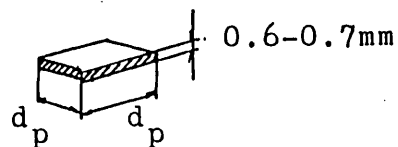
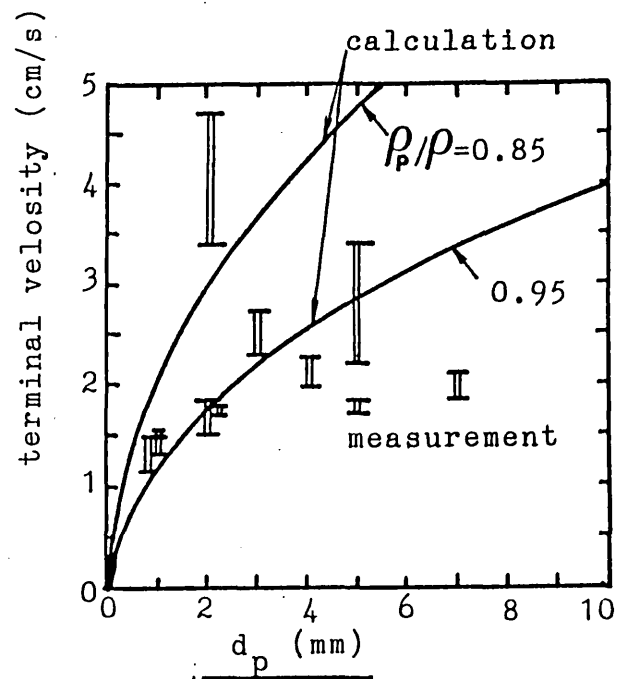
p can be replaced by $\rho g z$ in equation (A1-13).

APPENDIX-2

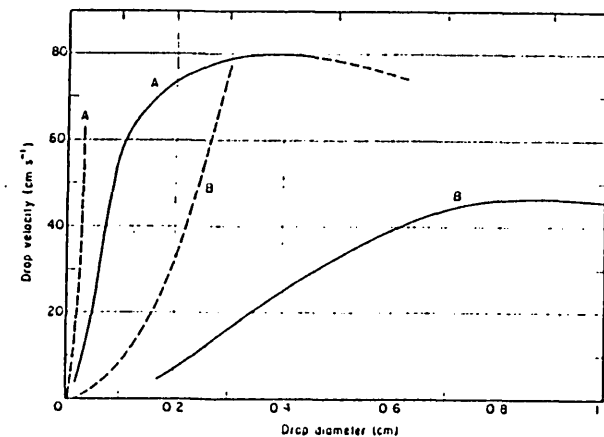
TERMINAL VELOCITY

The terminal velocities of polystyrene foams and plastic plates which were used in the physical modelling were measured in water and plotted in Figs. A2-1 and A2-2. For the polystyrene foams, Stokes' law predicts the terminal velocities very well. For plastic plates, Stokes' law cannot be applied for the larger plates, say $d_p > 5\text{mm}$. This phenomenon is explained in ref.[6] for falling liquid drops which tend to be flattened in case of larger diameters.

In order to evaluate the effect of particles' properties, e.g. wettability, terminal velocity, on entrainment, it may be helpful to use device depicted in Fig. A2-3. This is a further work.

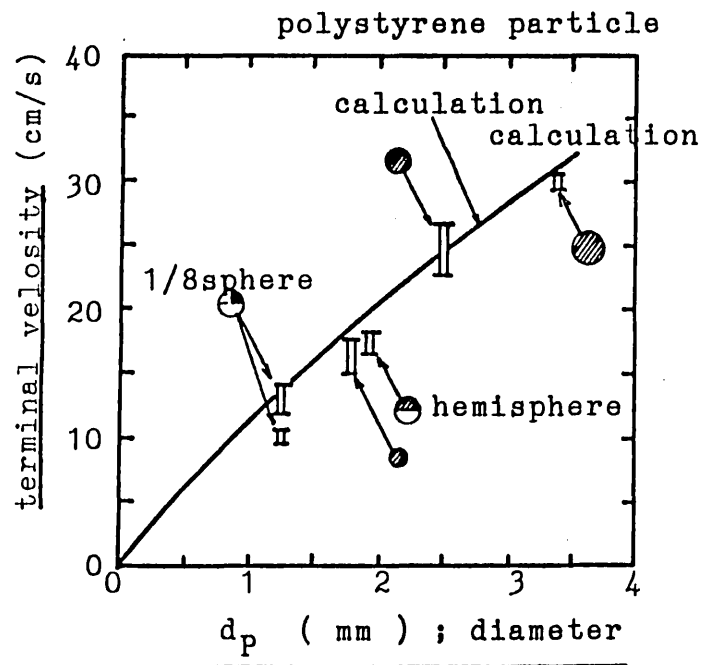


(c) Terminal velocity of solid plates measured in the water and calculated.



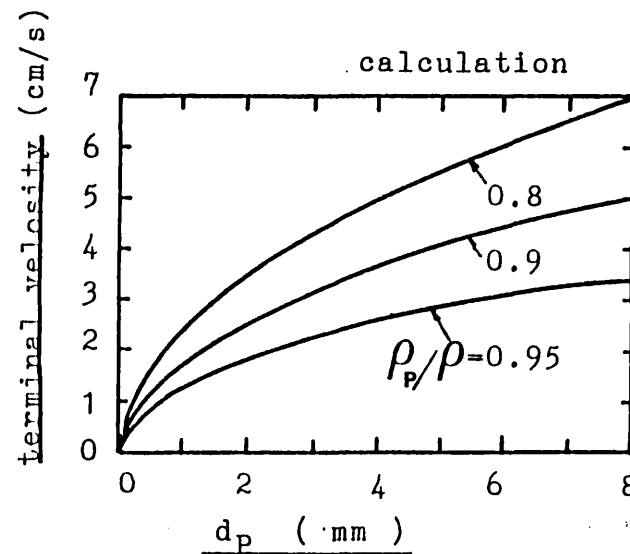
(d) Drop velocity (6).

Fig.A2-2 Terminal velocity.



Note : polystyrene
 1) density = 54 kg/m^3
 2) contact angle = 50°

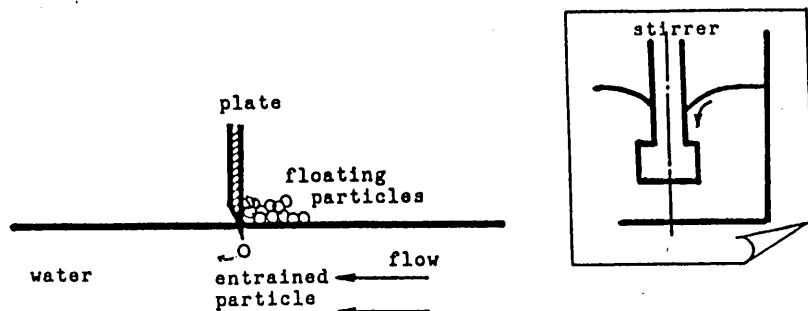
(a) Polystyrene foam.



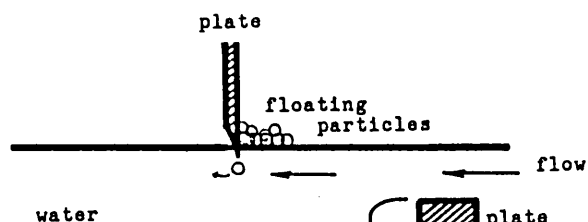
Note : plastic plate is
 shown in Fig.A2-2(c).
 ρ_p : density of a particle.
 ρ : density of liquid.

(b) Plastic plate (square).

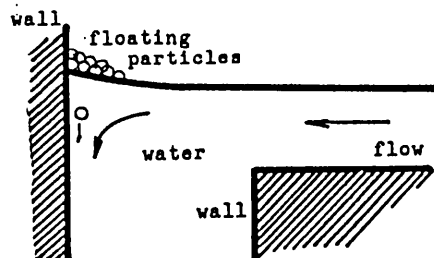
Fig.A2-2 Terminal velocity



(a) Horizontal flow.

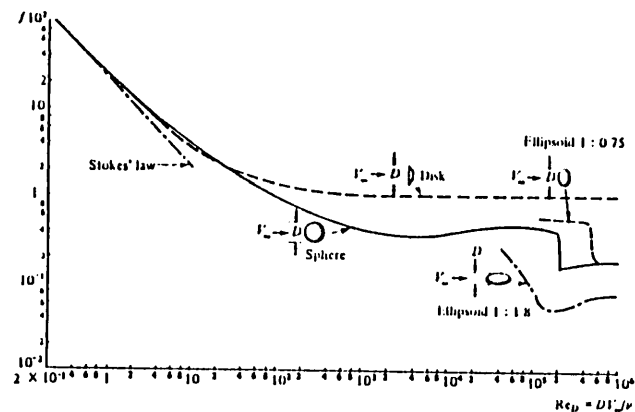


(b) Disturbed horizontal flow.



(c) Horizontal-vertical flow.

Fig.A2-3 Some idea to evaluate the effect of particles' properties on entrainment.



Friction factors for submerged bodies. (Adapted from F. Eisner, *Proc. 3rd Intern. Congr. Appl. Mech.*, 1930, page 32.)

Fig. A2-1. Friction factors(12).

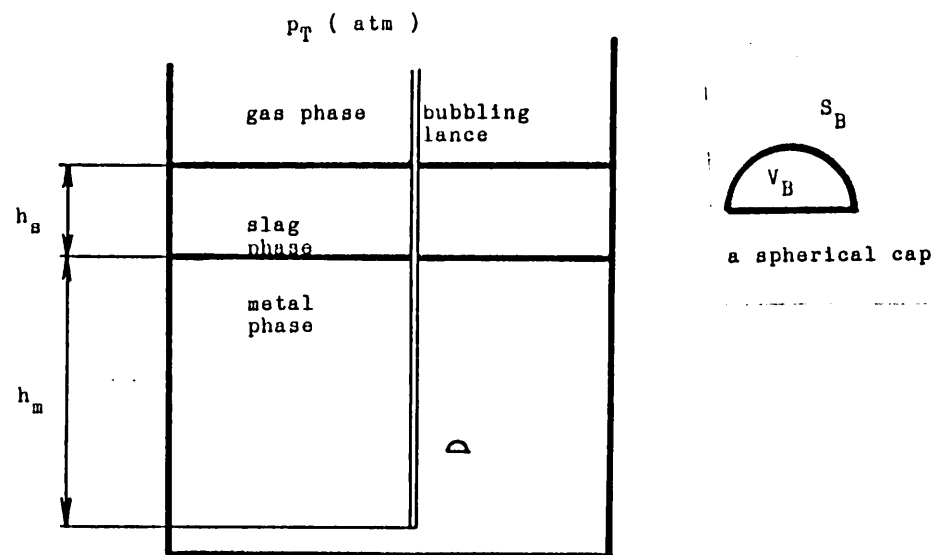


Fig.A3-1 Configuration of rising bubble.

APPENDIX-3

DERIVATION OF THE FULL MODEL

The flow chart for computation is i) defining the initial bulk activities - ii) solving simultaneous equations for the interfacial activities - iii) calculating all flux densities - iv) calculating new bulk activities - go to ii).

Step ii) is the most important procedure in the model. These are a large number of equations corresponding to the number of species involved. All interfacial activities can be expressed explicitly by the interfacial activities of oxygen and sulphur and flux density of metal reduced at the slag/gas interface NT_m which appears only in the case of a reducing gas phase. The derivation of these simultaneous equations is explained below.

1) The metal/slag interface.

The activities of oxide and sulphide at the metal/slag interface, $a(i + 20i_o, 2, 1)$, are expressed by the activities of metal and oxygen or sulphur according to the equation (3-4).

$$a(i + 20i_o, 2, 1) = E(i + 20i_o, 1, 2) a(i, 1, 2) \cdot a(i_o, 1, 2)^{\sigma(i_o, i)}$$

$$\text{where } i \geq 3 \quad (A3-1)$$

$$i_o = \begin{cases} 1 & \text{for oxide} \\ 2 & \text{for sulphide} \end{cases}$$

Substituting $a(i + 20i_o, 2, 1)$ from equation (A3-1) into equation (3-4) one can obtain interfacial activities of elements at the metal/slag interface $a(i, 1, 2)$ expressed by interfacial oxygen activity $a(i, 1, 2)$, interfacial sulphur activity and the bulk activities of metallic elements and compounds.

$$\begin{aligned} & a(i, 1, 2) \\ & \quad k(i, 1) \cdot C(1) \cdot a(i, 1, 1) / \gamma(i, 1) + C(2) \cdot \sum_{i_o=1}^2 \{ k(i + 20i_o, 2) \cdot a(i + 20i_o, 2, 2) / \gamma(i + 20i_o, 2) \} \\ = & \frac{a(i, 1, 2)}{k(i, 1) \cdot C(1) \gamma(i, 1) + C(2) \cdot \sum_{i_o=1}^2 \{ k(i + 20i_o, 2) E(i + 20i_o, 1, 2) \cdot a(i_o, 1, 2)^{\sigma(i_o, 1)} / \gamma(i + 20i_o, 2) \}} \\ & \equiv h(i ; a(1, 1, 2), a(2, 1, 2)) \\ & \text{where } i \geq 7 \quad (A3-2) \end{aligned}$$

$a(i+20i_0, 2, 1)$ is also expressed uniquely by $a(1, 1, 2)$, $a(2, 1, 2)$ and the bulk activities using equation (A3-1) and (A3-2).

$$a(i+20i_0, 2, 1) = E(i+20i_0, 1, 2) \cdot a(i_0, 1, 2)^{\sigma(i_0, i)} \times h(i; a(1, 1, 2), a(2, 1, 2)) \quad (\text{A3-3})$$

For the special species ($i \leq 6$, $i=8, 9$).

$i=9$ (Sn) According to the equation (3-22) and (A3-1),

$$\begin{aligned} & a(9, 1, 2) \\ & k(9, 1) \cdot C(1) \cdot a(9, 1, 1) / \gamma(9, 1) + C(2) \cdot \sum_{i_0=1}^2 \{k(9+20i_0, 2) \cdot a(9+20i_0, 2, 2) / \gamma(9+20i_0, 2)\} \\ & = \frac{k(9, 1) \cdot C(1) / \gamma(9, 1) + C(2) \cdot \sum_{i_0=1}^2 \{k(9+20i_0, 2) \cdot E(9+20i_0, 1, 2) \cdot a(i_0, 1, 2)^{\sigma(i_0, 9)} / \gamma(9+20i_0, 2)\} + E(49, 1, 2)}{E(49, 3, 2) \cdot a(2, 1, 2) \cdot \dot{q} / \text{RTS}(1, 2)} \\ & \equiv h(9; a(1, 1, 2), a(2, 1, 2)) \end{aligned}$$

$i=8$ (Na) According to the equation (3-5) and (A3-1),

$$\begin{aligned} & a(8, 1, 2) \\ & k(8, 1) \cdot C(1) \cdot a(8, 1, 1) / \gamma(8, 1) + C(2) \cdot \sum_{i_0=1}^2 \{k(8+20i_0, 2) \cdot a(8+20i_0, 2, 2) / \gamma(8+20i_0, 2)\} \\ & = \frac{k(8, 1) \cdot C(1) / \gamma(8, 1) + C(2) \cdot \sum_{i_0=1}^2 \{k(8+20i_0, 2) \cdot E(8+20i_0, 1, 2) \cdot a(i_0, 1, 2)^{\sigma(i_0, 8)} / \gamma(8+20i_0, 2)\} + E(8, 3, 2) \cdot \dot{q} / \text{R.T.S}(1, 2)}{E(8, 3, 2) \cdot a(2, 1, 2) \cdot \dot{q} / \text{R.T.S}(1, 2)} \\ & \equiv h(8; a(1, 1, 2), a(2, 1, 2)) \quad (\text{A3-4}) \end{aligned}$$

$a(8, 2, 1)$ is calculated by $a(8, 2, 1) = E(8, 3, 2) \cdot a(8, 1, 2)$.

$i=5, 6$ (Fe) According to the equation (3-19) and (A3-1)

$$\begin{aligned} & a(5, 1, 2) \\ & (=a(6, 1, 2)) \\ & k(5, 1) \cdot C(1) \cdot a(5, 1, 1) / \gamma(5, 1) + C(2) \cdot \sum_{i_0=1}^2 \sum_{i=5}^6 \{k(i+20i_0, 2) \cdot a(i+20i_0, 2, 2) / \gamma(i+20i_0, 2)\} \\ & = \frac{k(5, 1) \cdot C(1) / \gamma(5, 1) + C(2) \cdot \sum_{i_0=1}^2 \sum_{i=5}^6 \{k(i+20i_0, 1, 2) \cdot a(i_0, 1, 2)^{\sigma(i_0, i)} / \gamma(i+20i_0, 2)\} + E(5, 3, 2) \cdot \dot{q} / \text{R.T.S}(1, 2)}{E(5, 3, 2) \cdot a(2, 1, 2) \cdot \dot{q} / \text{R.T.S}(1, 2)} \\ & \equiv h(5; a(1, 1, 2), a(2, 1, 2)) \\ & \equiv h(6; a(1, 1, 2), a(2, 1, 2)) \quad (\text{A3-5}) \end{aligned}$$

i=3,4 (C) According to the equation (3-20) and (A3-1),

$$\begin{aligned}
 & \therefore a(3,1,2) (\equiv a(4,1,2)) \\
 & = \frac{k(3,1) \cdot C(1) \cdot a(3,1,1) / \gamma(3,1) + G_{CO}}{k(3,1) \cdot C(1) / \gamma(3,1) + G_{CO} \cdot E(23,1,2) \cdot a(1,1,2) / P_T} \\
 & \equiv h(3 ; a(1,1,2)) \quad (A3-6) \\
 & \equiv h(4 ; a(1,1,2))
 \end{aligned}$$

i=1(0), 2(S) According to the equation (3-23) and (3-24)

$$\begin{aligned}
 & \therefore \{k(i_0,1) \cdot C(1) / \gamma(i_0,1) + \delta_{i_0 1} G_{CO} \cdot E(23,1,2) \cdot h(3; a(1,1,2) / P_T) a(i_0,1,2) \\
 & + C(2) \cdot \sum_{i=5} \{\sigma(i_0,i) \cdot k(i+20i_0,2) \cdot E(i+20i_0,1) \cdot h(i ; a(1,1,2), \\
 & a(2,1,2)) \cdot a(1,1,2)^{\sigma(1,i)} / \gamma(i+20i_0,2)\} \\
 & = k(i_0,1) \cdot C(1) \cdot a(i_0,1,1) / \gamma(i_0,1) + \delta_{i_0 1} G_{CO} + C(2) \cdot \sum_{i=5} \{\sigma(i_0,i) \\
 & k(i+20i_0,2) \cdot a(i+20i_0,2,2) / \gamma(i+20i_0,2)\} \\
 & \quad \begin{cases} i_0=1 & (A3-7) \\ i_0=2 & (A3-8) \end{cases}
 \end{aligned}$$

Where δ_{ij} denotes Kronecker's delta function.

The right hand sides of equations (A3-7) and (A3-8) include only bulk activities and the left hand sides include two variables $a(1,1,2)$ and $a(2,1,2)$. These two can be obtained by solving the simultaneous equations (A3-7) and (A3-8). The activities of oxygen and sulphur can be expressed by the activities of bulk phases. These equations can be solved by numerical techniques.

2) The slag/gas interface.

The activities of all species in the gas phase, $a(i + 20i_o, 3, 2)$ $i_o = 0, 1, 2$, are expressed by the activities of corresponding species in the slag phase according to equation (3-6).

$$a(i + 20i_o, 3, 2) = E(i + 20i_o, 3, 2) a(i + 20i_o, 2, 3)$$

$$\text{Where } i_o = 0, 1, 2 \quad (A3-9)$$

$$i \geq 5$$

According to equation (3-7),

$$a(i, 3, 2) = E(i, 3, 2)^2 a(i, 2, 3)^2 \quad (A3-10)$$

$$\text{Where } i = \begin{cases} 1 & \text{for oxygen} \\ 2 & \text{for sulphur} \end{cases}$$

According to equation (3-10),

$$a(22, 3, 2) = E(22, 2, 3) \cdot a(1, 2, 3)^2 a(2, 2, 3)$$

$$\text{According to equation (3-9)} \quad (A3-11)$$

$$a(24, 3, 2) = E(24, 2, 3) \cdot a(1, 2, 3) \cdot a(23, 3, 2) \quad (A3-12)$$

In the slag phase, all activities of oxides and sulphides at the slag/gas interface $a(i + 20i_o, 2, 3)$ can be expressed by the activity of elements at the slag/metal interface $a(i, 2, 3)$. According to equation (3-6).

$$a(i + 20i_o, 2, 3) = E(i + 20i_o, 2, 3) \cdot a(i, 2, 3) \cdot a(i_o, 2, 3)^{\sigma(i_o, i)}$$

$$\text{Where } i \geq 5, i_o = 1, 2 \quad (A3-13)$$

As a result all $a(i + 20i_o, 3, 2)$ and $a(i + 20i_o, 2, 3)$ can be expressed in terms of $a(i, 2, 3)$.

According to equations (A3-9) and (A3-13),

$$a(i + 20i_o, 3, 2) = E(i + 20i_o, 3, 2) \cdot E(i + 20i_o, 2, 3) \times a(i, 2, 3) \cdot a(i_o, 2, 3)^{\sigma(i_o, i)}$$

$$\text{Where } i \geq 5, i_o = 1, 2 \quad (A3-14)$$

Substituting $a(i + 20i_o, 3, 2)$ and $a(i + 20i_o, 2, 3)$ into equation (3-25) from the equations (A3-14) and (A3-13) respectively, one can obtain $a(i, 2, 3)$ expressed by only three key variables, i.e. $a(1, 2, 3)$, $a(2, 2, 3)$ and NT_m .

$$\begin{aligned}
 & \therefore a(i, 2, 3) \\
 & = \sum_{i_o=1}^2 [C(2) \cdot k(i + 20i_o, 2) a(i + 20i_o, 2, 2) / \gamma(i + 20i_o, 2) + C(3) \cdot p_T^{-1} \cdot k(i + 20i_o, 3) \cdot \\
 & \quad a(i + 20i_o, 3, 3) + C(3) p_T^{-1} \cdot k(i, 3) \cdot a(i, 3, 3)] \\
 & \quad \frac{\sum_{i_o=1}^2 \{ [C(2) \cdot k(i + 20i_o, 2) / \gamma(i + 20i_o, 2) + C(3) \cdot p_T^{-1} \cdot k(i + 20i_o, 3) \cdot E(i + 20i_o, 3, 2)] \times E(i + 20i_o, 2, 3) \cdot \\
 & \quad a(i_o, 2, 3)^{\sigma(i_o, i)} \} + C(3) p_T^{-1} \cdot k(i, 3) \cdot E(i, 3, 2) + NT_m / \gamma(i, 2, 3)}{ } \\
 & \equiv f(i ; a(1, 2, 3), a(2, 2, 3), NT_m) \quad (A3-15)
 \end{aligned}$$

Where $i \geq 7$.

For $i=5, 6(Fe)$, according to the equation (3-26),

$$\begin{aligned}
 & a(5, 2, 3) \\
 & = \frac{\sum_{i_o=1}^2 \sum_{i=5}^6 [C(2) \cdot k(i + 20i_o, 2) \cdot a(i + 20i_o, 2, 2) / \gamma(i + 20i_o, 2) + C(3) p_T^{-1} \cdot k(i + 20i_o, 3) \cdot a(i + 20i_o, 3, 3) + C(3) p_T^{-1} \cdot k(5, 3) \cdot a(5, 3, 3)]}{\sum_{i_o=1}^2 \sum_{i=5}^6 \{ [C(2) \cdot k(i + 20i_o, 2) / \gamma(i + 20i_o, 2) + C(3) \cdot p_T^{-1} \cdot k(i + 20i_o, 3) \times E(i + 20i_o, 3, 2)] \times E(i + 20i_o, 2, 3) \cdot a(i_o, 2, 3)^{\sigma(i_o, i)} + C(3) \cdot p_T^{-1} \cdot k(5, 3) \cdot E(5, 3, 2) + NT_m / \gamma(5, 2, 3) \}} \\
 & \equiv f(5; a(1, 2, 3), a(2, 2, 3), NT_m) \quad (A3-16) \\
 & \equiv f(6; a(1, 2, 3), a(2, 2, 3), NT_m)
 \end{aligned}$$

For $i = 3, 4(C)$, according to the equation (3-27),

$$\therefore a(3,2,3)$$

$$\begin{aligned}
 &= \frac{k(23,3).a(23,3,3) + k(24,3) : a(24,3,3)}{\{k(23,3) + k(24,3). E(24,2,3). a(1,2,3)\}E(23,2,3).a(1,2,3)} \\
 &\equiv f(3 ; a(1,2,3)) \\
 &\equiv f(4 ; a(1,2,3)) \quad (A3-17)
 \end{aligned}$$

As a result, all interfacial activities have been expressed explicitly by three main variables. According to the equation (A3-9),

$$a(i,3,2) = E(i,3,2).f(i ; a(1,2,3), a(2,2,3), NT_m)$$

$$\text{Where } i \geq 5 \quad (A3-18)$$

$$a(i,3,2) = E(i,3,2)^2 . a(i,2,3)^2 \quad (A3-10)$$

$$\text{Where } i = 1,2$$

$$a(i,3,2) = 0 \quad (A3-19)$$

$$\text{Where } i = 3,4$$

According to the equation (A3-13)

$$a(i + 20i_o,2,3) = E(i + 20i_o, 2,3) . a(i_o,2,3)^{\sigma(i_o,i)} f$$

$$\text{Where } i \geq 5. \quad (A3-20)$$

According to equation (A3-9),

$$\begin{aligned}
 a(i+20i_o,3,2) &= E(i+20i_o,3,2) E(i+20i_o,2,3).a(i_o,2,3)^{\sigma(i_o,i)} \\
 &\quad \times f(i ; a(1,2,3), a(2,2,3), NT_m)
 \end{aligned}$$

$$\text{Where } i \geq 5 \quad (A3-21)$$

Substituting all these interfacial activities into equations (3-28), (3-29) and (A3-22).

$$\sum_i NT_m a(i,2,3)/\gamma(i,2,3) = NT_m \quad (A3-22)$$

This is the additional equation for NT_m which is only non zero in the case of a reducing gas phase.

If $NT_m = 0$, equation (A3-22) is satisfied but trivial.

According to the equations (3-28) and (3-29),

$$\begin{aligned}
 & C(2) \cdot \sum_{i=5} [\sigma(i_0, i) \cdot k(i+20i_0, 2) \{a(i+20i_0, 2, 2) - E(i+20i_0, 2, 3) \\
 & \quad \times a(i_0, 2, 3)^{\sigma(i_0, i)} f(i; a(1, 2, 3), a(2, 2, 3), NT_m)\} / \gamma(i+20i_0, 2)] \\
 & = C(3) p_T^{-1} \sum [\sigma(i_0, i) \cdot k(i + 20i_0, 3) \cdot \{E(i+20i_0, 3, 2) \cdot E(i+20i_0, 2, 3) \\
 & \quad \cdot a(2, 2, 3) \\
 & \quad \times a(i_0, 2, 3)^{\sigma(i_0, i)} \cdot f(i; a(1, 2, 3), NT_m) - a(i+20i_0, 3, 3)\}] \\
 & + \epsilon(i_0) \cdot C(3) \cdot p_T^{-1} \quad i_0 = 1 \quad (A3-23) \\
 & \quad \quad \quad i_0 = 2 \quad (A3-24)
 \end{aligned}$$

Where

$$\begin{aligned}
 \epsilon(1) &= 2 \cdot k(1, 3) \cdot \{E(1, 3, 2)^2 \cdot a(1, 2, 3)^2 - a(1, 3, 3)\} \\
 &+ 2 \cdot k(22, 3) \cdot \{E(22, 2, 3) \cdot a(1, 2, 3)^2 \cdot a(2, 2, 3) \\
 &- a(22, 3, 3)\} - k(23, 3) \cdot \{E(23, 2, 3) \cdot a(1, 2, 3) \\
 &\times f(3; a(1, 2, 3)) - a(23, 3, 3)\} \\
 \epsilon(2) &= 2 \cdot k(2, 3) \cdot \{E(2, 3, 2)^2 \cdot a(2, 2, 3)^2 - a(2, 3, 3)\} \\
 &+ k(22, 3) \cdot \{E(22, 2, 3) \cdot a(1, 2, 3)^2 \cdot a(2, 2, 3) \\
 &- a(22, 3, 3)\} + NT_m \cdot a(2, 2, 3) / \gamma(2, 2)
 \end{aligned}$$

$$i_0 = 1, 2$$

According to the equation (A3-22), in case $NT_m = 0$,

$$\begin{aligned}
 & \sum_{i=5} \{f(i; a(1, 2, 3), a(2, 2, 3), NT_m) / \gamma(i, 2)\} \\
 & \quad (excl. i=6) \\
 & + a(2, 2, 3) / \gamma(2, 2) = 1 \quad (A3-25)
 \end{aligned}$$

Three equations, (A3-23), (A3-24) and (A3-25), are the simultaneous equations for three variables, $a(1,2,3)$, $a(2,2,3)$ and NT_m .

3) The metal/gas interface.

All interfacial partial pressures at the gas/metal interface $a(i,3,1)$ can be expressed in terms of interfacial activities at the metal/gas interface $a(i,1,3)$ according to equation (3-48), (3-49), (3-50) and (3-51).

$$a(i,3,1) = E(i,3,1)^2 \cdot a(i,1,3)^2 \text{ for } i=1,2 \quad (\text{A3-26})$$

$$a(i,3,1) = E(i,3,1) \cdot a(i,1,3) \text{ for } i \geq 5 \quad (\text{A3-27})$$

except for

$$a(23,3,1) = E(23,1,3) \cdot a(3,1,3) \cdot a(1,1,3) \quad (\text{A3-28})$$

CO

$$a(49,3,1) = E(49,1,3) \cdot a(9,1,3) \cdot a(2,1,3) \quad (\text{A3-29})$$

SnS vapour

Combining these equations for equilibria and equations for continuity of flux density (3-30), (3-31) and (3-32), one can obtain $a(i,1,3)$ explicitly expressed below in terms of the interfacial activities of oxygen and sulphur and bulk activities.

$$a(i,1,3) = a(i,1,1) / \{1 + k(i,3) \cdot C(3) \cdot \gamma(i,1) \cdot E(i,3,1) / k(i,1) \cdot C(1) \cdot p_T\} \quad \text{for } i \geq 5 \text{ (i = 9)} \quad (\text{A3-30})$$

$$a(3,1,3) = a(3,1,1) / \{1 + k(3,3) \cdot C(3) \cdot \gamma(3,1) \cdot E(23,1,3) \cdot a(1,1,3) / k(3,1) \cdot C(1) \cdot p_T\} \quad (\text{A3-31})$$

$$a(9,1,3) = a(9,1,1) / [1 + k(9,3) \cdot C(3) \cdot \gamma(9,1) \cdot \{E(9,3,1) + E(49,1,3) \cdot a(2,1,3)\} / k(3,1) \cdot C(1) \cdot p_T] \quad (\text{A3-32})$$

Interfacial activities of oxygen and sulphur at the metal/gas interface should satisfy the equations for continuity of flux density (3-33) and (3-34). These two equations lead to the equations below for two unknowns in the case where all species have a common mass transfer coefficient in a particular phase.

$$-a_1(i) + a_2(i) \cdot x(i) + x(i)^2 + a_3(i) \cdot x(i) / \{a_4(i) + x(i)\}$$

Where $x(i)$ is $a(i,1,3)$, $i=1$ or 2 , and $a_4(i)$ is constant. (A3-33)

$$a_1(i) = a(i,1,1) / 2\gamma(i,1) \cdot z_0 E(i,3,1)^2$$

$$a_2(i) = 1 / 2\gamma(i,1) \cdot z_0 E(i,3,1)^2$$

$$a_3(1) = a(3,1,1) / 2\gamma(3,1) \cdot z_0 E(1,3,1)^2$$

$$a_3(2) = a(9,1,1) / 2\gamma(9,1) \cdot z_0 \cdot E(2,3,1)^2$$

$$a_4(1) = 1 / \gamma(3,1) \cdot z_0 E(23,1,3)$$

$$a_4(2) = \{1 + \gamma(9,1) \cdot z_0 \cdot E(9,3,1)\} / \gamma(9,1) \cdot z_0 \cdot E(49,1,3)$$

Where $z_0 = k(\text{gas}) C(3) / k(\text{metal}) \cdot C(1) \cdot p_T$

After solving these simultaneous equations for $a(1,1,3)$ and $a(2,1,3)$, one can obtain other interfacial activities by using equations (A3-26) to (A3-32).

4) The metal/gas bubble interface.

The change with time of variables relevant to one particular bubble can be calculated by means of the quasi-steady state approximation:-

Bulk composition of the metal phase does not change while one particular bubble rises from the tip of bubbling lance to the gas phase. Constituents of the bubble atmosphere are CO gas (P_{CO}), Sn vapour (P_{Sn}), SnS vapour (P_{SnS}) and inert gas.

Equations for chemical equilibrium and continuity of flux density at the metal/gas bubble interface lead to solutions of interfacial activities expressed in terms of bulk activities.

$$a(3,1,3) = (-a_2 + \sqrt{a_2^2 + 4a_1 a_3}) / 2a_1 \quad (A3-34)$$

$$a(9,1,3) = (-a_5 + \sqrt{a_5^2 + 4a_4 a_6}) / 2a_4 \quad (A3-35)$$

Where

$$a_1 = z_0 \cdot \gamma(1,1) E(23,1,3)$$

$$a_2 = 1 + z_0 \cdot E(23,1,3) \cdot \{\gamma(3,1) \cdot a(1,1,1) - \gamma(1,1) \cdot a(3,1,1)\}$$

$$a_3 = a(3,1,1) + \gamma(3,1) \cdot z_0 P_{CO}$$

$$a_4 = \{1 + \gamma(9,1) \cdot z_0 \cdot E(9,3,1)\} \gamma(2,1) z_0 E(49,1,3)$$

$$a_5 = 1 + z_0 E(49,1,3) \{\gamma(9,1) \cdot a(2,1,1) - \gamma(2,1) \cdot a(9,1,1) - \gamma(2,1) \cdot \gamma(9,1) z_0 P_{Sn}\} + \gamma(9,1) \cdot z_0 \cdot E(9,3,1)$$

$$a_6 = a(9,1,1) + \gamma(9,1) \cdot z_0 \cdot (P_{Sn} + P_{SnS})$$

Using these interfacial activities of carbon, $a(3,1,3)$, and tin, $a(i,1,3)$, one can obtain the interfacial activities of other constituents from the following equations which are derived from chemical equilibria and continuity of flux densities.

$$a(1,1,3) = \frac{a(1,1,1) + \gamma(1,1) \cdot z_0 P_{CO}}{1 + \gamma(1,1) \cdot z_0 E(23,1,3) \cdot a(3,1,3)} \quad (A3-36)$$

$$a(2,1,3) = \frac{a(2,1,1) + \gamma(2,1) \cdot z_0 P_{SnS}}{1 + \gamma(2,1) \cdot z_0 E(49,1,3) \cdot a(9,1,3)} \quad (A3-37)$$

$$a(9,3,1) = E(9,3,1) \cdot a(9,1,3) ; \text{ interfacial pressure of tin at the gas bubble/metal interface} \quad (\text{A3-38})$$

$$a(23,3,1) = E(23,1,3) \cdot a(3,1,3) \cdot a(1,1,3) ; \text{ interfacial pressure of CO} \quad (\text{A3-39})$$

$$a(49,3,1) = E(49,1,3) \cdot a(9,1,3) \cdot a(2,1,3) ; \text{ interfacial pressure of SnS vapour} \quad (\text{A3-40})$$

The following assumptions are made:-

- i) Rising velocity of a bubble, U_B [m/s], is constant.
- ii) Total pressure in a bubble P [atm] is equal to the static pressure.

$$P_B = P_T + \{ \rho_m (h_m - h) + \rho_s h_s \} g / 1.0133 \times 10^5 \quad (\text{A3-41})$$

Where p_T : atmospheric pressure [atm]

ρ_m : density of metal [kg/m^3]

ρ_s : density of slag [kg/m^3]

h_m, h_s : see Fig. A3-1

g : gravitational acceleration [m/s^2]

- iii) Shape of bubble is hemisphere. The relation between volume, V_B [m^3], and surface area, S_B [m^2], of a bubble is:

$$S_B = 5.757 V_B^{2/3} \quad (\text{A-42})$$

Mass balance of each species leads to the following set of equations :-

$$\frac{d(p_{\text{Sn}} V_B)}{dt} = S_B \cdot k_g \cdot \{a.(9,3,1) - p_{\text{Sn}}\} \quad (\text{A-43})$$

$$\frac{d(p_{\text{CO}} V_B)}{dt} = S_B \cdot k_g \cdot \{a(23,3,1) - p_{\text{CO}}\} \quad (\text{A-44})$$

$$\frac{d(p_{\text{SnS}} V_B)}{dt} = S_B \cdot k_g \cdot \{a(49,3,1) - p_{\text{SnS}}\} \quad (\text{A-45})$$

$$p_B = p_B^0 + p_{\text{Sn}} + p_{\text{CO}} + p_{\text{SnS}} \quad (\text{A-46})$$

p_B^0 : initial pressure of a bubble

After normalisation, a set of differential equations can be solved by the optimised Runge-Kutta method.

APPENDIX-4 DOCUMENTATION OF THE FULL MODEL

A4-1 Flow chart

The procedure of computation is shown in Fig. A4-1.

- 1) The parameters, which control the procedures of computation and characterise the general features of the model, are read from the data-file.
- 2) General constants are read.
e.g. atomic weight stoichiometric factors.
- 3) The characteristics of the system to be simulated are read.
e.g. initial weight of each phase, temperature, powder supplying conditions, initial composition of each phase.
- 4) The equilibrium constants are calculated.
- 5) The activity coefficients are evaluated.
- 6) Constants used in the simultaneous equations are introduced.
- 7) The interfacial activity of each species is calculated from the known bulk phase activity, non-linear simultaneous equations are solved.
- 8) The flux density of each species at the interface is calculated.
- 9) New bulk activities are calculated.
- 10) "time step control".

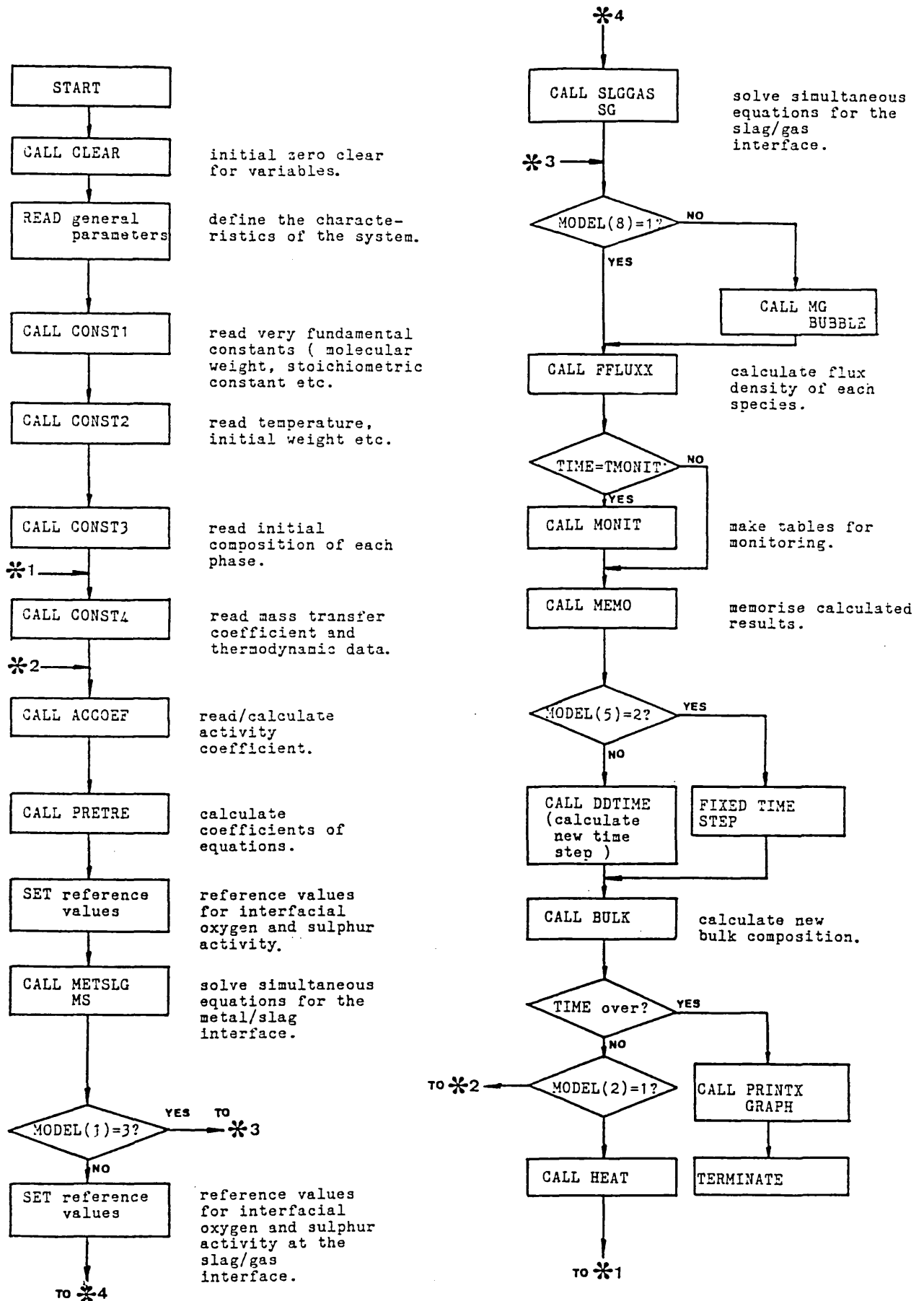


Fig.A4-1 Flow chart of the full model.

A4-2 Structure of coded programme

This programme was coded according to the following general scheme:-

- 1) The whole programme is divided into an appropriate number of subroutines which have their own individual functions.
- 2) The main programme is kept as simple as possible. It merely controls the flow of computation.
- 3) Some important functions can be added very easily by the inclusion of particular subroutines for which calls etc. are already included, e.g. subroutine "HEAT" for a calculation of the evolution of temperature.
- 4) Other information. Arrays are used for generality. Some parts of arrays may be redundant. This does not cause any trouble, as long as a computer with sufficient storage is used. Statement numbers are characterised as follows:

integer * 100 = FORMAT - statement
(i.e. 100, 200, 1100, etc.)

integer * 10 = closing line for DO-statement
(but not integer * 100) (i.e. 10, 20, 110, 1110, etc.)

integer = CONTINUE statement for the order of computation
(but not integer * 10,*100) (i.e. 1, 2, 111, 1111 etc.)

The whole coded programme consists of one main programme and 26 sub-programmes. Features of each programme are summarised in Table A4-1. Detailed programme lists are available in a separate report [46].

Table A4-1 Main and sub-programmes of the full model.

PROGRAMME'S NAME	CHARACTERISTICS	STEPS
MSG1(main)	computing flow control	426
CONST1		27
CONST2	kinetic and thermodynamic	68
CONST3	data are read from data	23
CONST4	file	104
PRETRE	pretreatment of coefficients in equations	62
ACCOEF	set activity coefficient	51
METSLG	solution of interfacial activity of oxygen and sulphur at the metal/slag interface	34
MS	calculation for interfacial activities of other species	62
SLGGAS	solution of interfacial activity of oxygen and sulphur and flux density of metal reduced at the slag/gas interface	41
SG	calculation for interfacial activities of other species	69
MG	solution of interfacial activities at the metal/gas interface	46
BUBBLE	solution of change of composition in a bubble injected during rising in the metal phase	119
TOTAL	calculation for coefficient in equations during iteration	75
POPS		55
RESID	calculation for residuals (for solution of simultaneous equations)	157
BULK	calculation of new bulk activities of species after a finite time interval	187
HEAT	calculation of thermal balance (vacant)	5
DDTIME	calculation of optimum time interval for unsteady calculation	31
FFLUXX	calculation of flux density	37
GUESS	guess for initial values for iteration (vacant)	3
MEMO		80
PRINTX		97
GRAPH	making tabular and graphical	356
MONITO	forms of calculated results	114
CLEAR	initial zero clear	56
FUNC	function programme for BUBBLE	17

A4-3 Input data

Table A4-2 is a complete set of datafile for the full model. A users' manual is available in the separate short report [46]. Characteristics of this data file are as follows:-

- 1) Any elements and compounds can be included as long as proper data are used for atomic weights (line 19-24 in the datafile), stoichiometric factors (line 25-29), changes of enthalpy and entropy for formation of compound (line 57-88) and activity coefficients (line 89-96).

- 2) In the present work, one commonfile was used in simulations for de-P/de-S, de-Cu/de-Sn and Cr slag cleaning.

Element identification numbers are:

i	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
element	0	S	C	C	Fe	Fe	Cu	Na	Sn	Ca	Mn	Si	P	Mg	Al	Cr

The number of elements involved in a particular simulation is set by the variable $i_{\max}$ which is indicated in Table A4-2.

- 3) General features of the system simulated are set by ten variables, MODEL (1) ~ (10), which are indicated in Table A4-2.

i) MODEL (1) defines gas phase characteristics.

- = 1 : oxidising gas phase.
- = 2 : reducing gas phase.
- = 3 : no gas phase except for CO formation.

ii) MODEL (2) defines temperature conditions:-

- = 1 : isothermal.
- = 2 : temperature change is calculated.

iii) MODEL (3) defines the characteristics of the activity coefficients.

- = 1 : constant activity coefficients.
- = 2 : varying with temperature and bulk composition.

iv) MODEL (6) and MODEL (9) define SnS and Na vaporization at the metal/slag interface respectively.

v) MODEL (7) defines behaviour of carbon content in the metal phase.

= 1 : no auxiliary carbon supply.

= 2 : carbon is supplied through erosion of graphite crucible to maintain carbon saturation.

vi) MODEL (8) defines the existence of a metal/gas interface.

= 1 : no metal/gas interface except for CO formation and/or SnS vapour, Na vapour formation.

= 2 : a metal/gas interface which has $S(1,3) [m^2]$ interfacial area.

= 3 : metal/gas bubble (argon) interfaces which have characteristics defined by gas flow rate $\dot{q}_N$ [Nl/min], gas temperature T_{gas} [K], dwell time t_B [S], initial volume of a bubble $V_B [m^3]$, vertical position of tip of bubbling lance [m] atmospheric pressure p_T [atm], which are indicated in Table A4-2.

A4-4 Output results

Results can be obtained in tabular forms and figures from a line printer. Features of outputs are outlined below.

- 1) Characteristics of system simulated are printed out first of all, as shown in Table A4-3.
- 2) Changes with time of concentrations of all phases and flux densities are printed out in a special arrangement which is explained in Table A4-4. In this arrangement it is easy to see both bulk and interfacial concentrations and flux densities caused by the concentration difference between bulk and interface.
- 3) Some graphic forms of changes of essential parameters in the system are available.

e.g. i) changes of the bulk concentrations in the metal phase (see Fig. A4-2).

ii) changes of interfacial oxygen and sulphur activities etcetera.

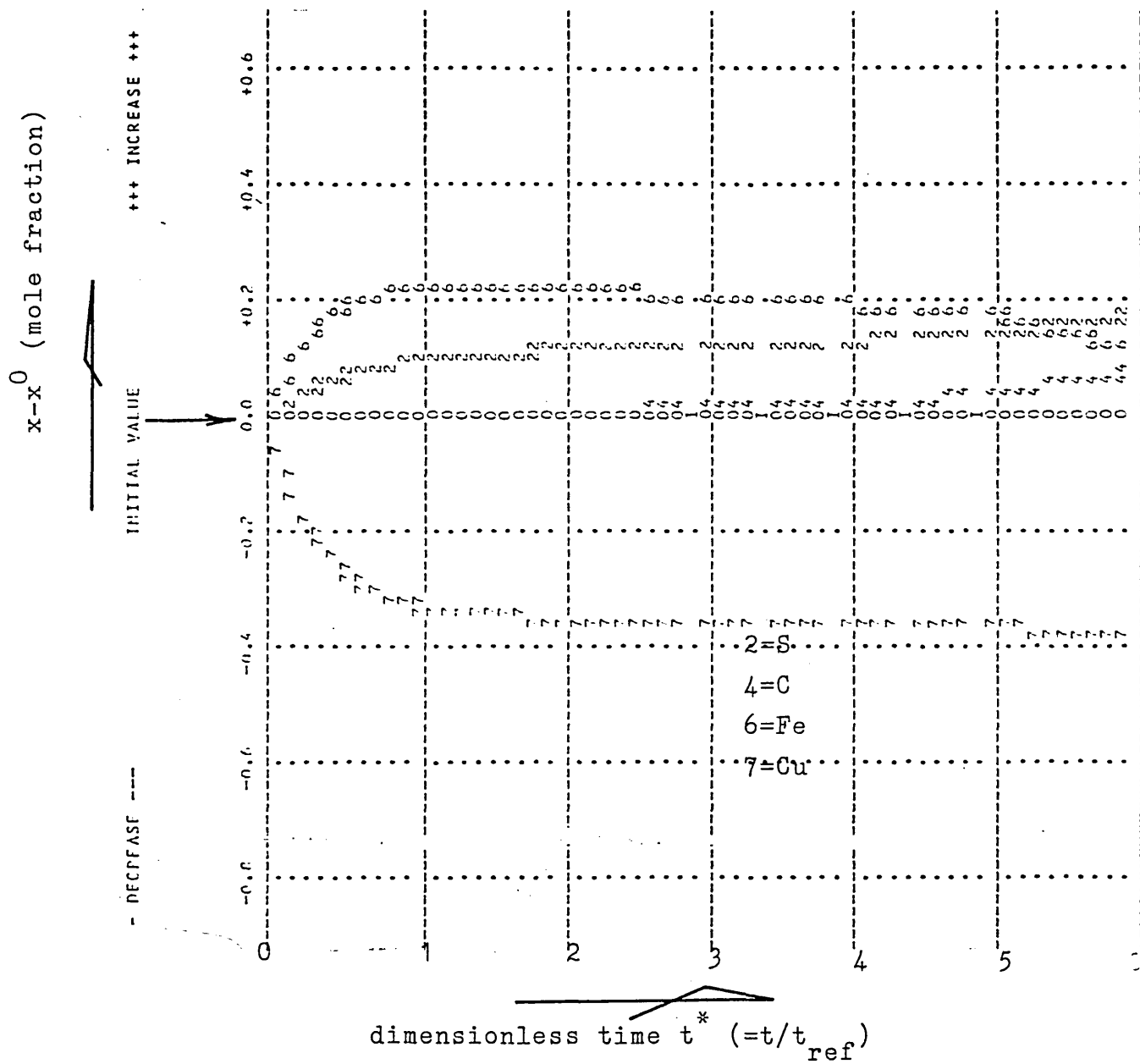


Fig.A4-2 Change of composition of the metal phase with time (a graphical out put of the full model).

Table A4-3 Characteristics of the system simulated (a
output of the full model).

```

+++++ MODEL(1) - MODEL(10) +++++
      2 1 1 1 1 1 2 1 1 1
MODEL(1) REDUCING GAS PHASE
MODEL(5) FIXED TIMESTEP
MODEL(6) NO SHS VOLATILISATION (MET/SLG)
MODEL(7) CONSTANT CARBON CONCENTRATION
MODEL(8) NO GAS/MET DIRECT CONTACT
MODEL(9) NO MA VOLATILISATION (MET/SLG)
MODEL(10) INITIAL GUESSE BY DATAFILE
ALPHA= 1.000
BETA= 1.000
+++++ INITIAL-PARAMETERS +++++
(1) VOLUME ( M**3 )
METAL-PHASE= 1.429E-04 SLAG-PHASE= 3.333E-05 GAS-PHASE= 1.000E+00
(2) WEIGHT ( KG )
METAL-PHASE= 1.000E+00 SLAG-PHASE= 1.000E-01 GAS-PHASE= 1.000E+00
(3) DENSITY ( KG/H**3 )
METAL-PHASE= 7.000E+03 SLAG-PHASE= 3.000E+03 GAS-PHASE= 1.000E+00
(4) INTERFACIAL-AREA ( M**2 )
1.230E-02
(5) TOTAL-PRESSURE ( ATM )
1.000
(6) PARAMETERS FOR POWDER-SUPPLYING
START-TIME= .00 ( SEC )
STOP-TIME= 1800.00 ( SEC )
SUPPLYING-RATE= 2.780E-03 ( KG/S )
SUPPLYING-RATE= 4.530E-02 ( MOL/S )
POWDER-INCRCD-X( 25 ) = 1.250E-01
POWDER-INCRCD-X( 32 ) = 3.600E-02
POWDER-INCRCD-X( 34 ) = 2.550E-01
POWDER-INCRCD-X( 35 ) = 1.120E-01
POWDER-INCRCD-X( 36 ) = 4.720E-01
(7) TEMPERATURE
TEMP= 2123.0 ( K )
+++++ EQUILIBRIUM-CONSTANT +++++
(1) OXIDE (MET/SLG)
.000E+00 .000E+00 2.510E+05 .000E+00 8.310E+01 1.103E+01 2.919E+00
9.363E+03 1.877E+07 2.272E-01 1.262E+08 2.593E+08 6.686E+04 .000E+00
(2) SULPHIDE (MET/SLG)
.000E+00 .000E+00 .000E+00 .000E+00 7.220E+00 .000E+00 2.221E+01
1.103E+02 2.255E-03 .000E+00 4.347E+04 .000E+00 .000E+00 .000E+00

```

Table A4-4 Current situation of three phases (metal-slag-gas) at a particular time (a output of the full model). interfacial mole fraction

		 MONITOR OF SITUATION AT TIME 1300.402 (SEC)		 MONITOR OF SITUATION AT TIME 32.005 (DIMENSIONLESS)	
		(1) METAL		(2) SLAG	
		TOTAL-WEIGHT (KG)		TOTAL-WEIGHT (KG)	
		MOLAL-COMCENT. (MOL/PPM)		MOLAL-COMCENT. (MOL/PPM)	
		VOLUME (M=3)		VOLUME (M=3)	
		BULK		BULK	
		BULK		BULK	
		BULK		BULK	
		BULK		BULK	
		BULK		BULK	
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		BULK		B	

APPENDIX-5

THERMODYNAMIC AND KINETIC DATA

The mathematical model requires a complete set of thermodynamic and kinetic data.

This model is governed by equations for i) chemical equilibrium, ii) flux density continuity and iii) mass conservation. Equations for chemical equilibrium require Gibbs free energy change, ΔG^0 , as thermodynamic data co-responding to the standard states of activities defined in the model. Equations for ii) and iii) require activity coefficients for all species, (since concentrations are used in these equations,) also mass transfer coefficients for each species in each phase.

- 1) Gibbs free energy changes for compound formation, ΔG^0 .

Data are mainly quoted from the compilations of Kubaschewski and Alcock [15] and Turkdogan [13]. Data used in this work are summarised in Table A5-1.

- 2) Activity coefficients of elements in the metal phase.

Activity coefficients f_i are calculated for particular metal compositions by using interaction parameters $e_i^{(j)}$ which are summarised in Table 3-1. The activity coefficient for iron is calculated by Gibbs-Duhem integration of the activities of solutes (A5-1)

$$x_{Fe}^d \ln a_{Fe} + x_C^d \ln a_C = 0 \quad (A5-1)$$

Using $e_C^{(C)} = 0.14$, one can obtain

$$\begin{aligned} \ln \gamma_{Fe} &= 6.93 (\ln \{1 - 4.65 [\text{wt}\%C]/100\} \\ &+ 4.65 [\text{wt}\%C]/100) \end{aligned} \quad (A5-2)$$

γ_{Fe} is plotted against [wt%C] in Fig. A5-1.

- 3) Activity coefficients of compounds in the slag phase.

For $\text{Na}_{0.5}\text{-FeS}$ mixed slag for de-Cu/de-Sn activity coefficients are summarised in Appendix-6 [17], [24], [29], [43].

For de-P/d-S, the activity coefficients used are those of Ohguchi [10].

Table A5-1 Thermodynamic data (Gibbs free energy change, cal/mol).

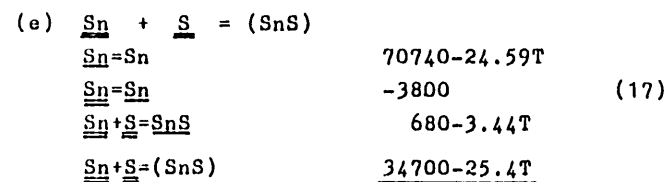
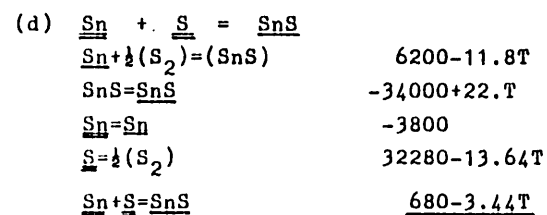
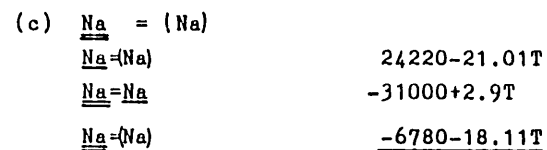
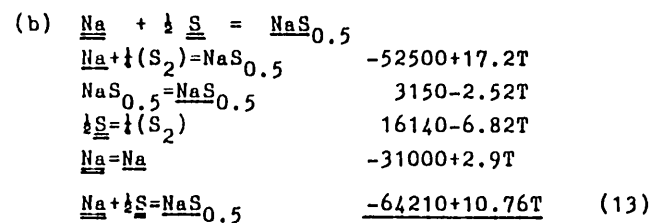
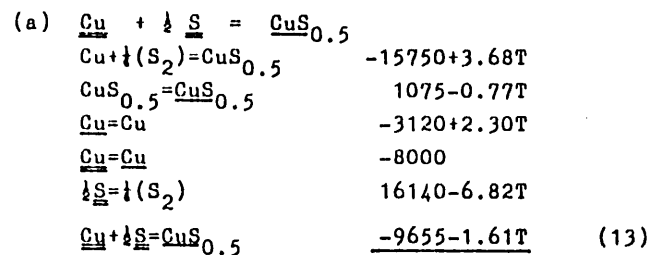
(1) Comparison of thermodynamic data relevant to de-Cu.

REACTION	reference(15)	reference(13)
(a) $\text{Cu} + \text{NaS}_{0.5} = \text{CuS}_{0.5} + (\text{Na})$; overall. $\text{Cu} + \frac{1}{2}\text{S} = \text{CuS}_{0.5}$ $\text{Cu} + \frac{1}{2}(\text{S}_2) = \text{CuS}_{0.5}$ $\text{CuS}_{0.5} = \text{CuS}_{0.5}$ $\text{Cu} = \text{Cu}$ $\text{NaS}_{0.5} = \text{Na} + \frac{1}{2}\text{S}$ $\text{NaS}_{0.5} = \text{NaS}_{0.5}$ $\text{NaS}_{0.5} = \text{Na} + \frac{1}{2}(\text{S}_2)$ $\text{Na} = \text{Na}$ $\text{Na} = \text{Na}$ $\text{Na} = (\text{Na})$ $\text{Cu} + \text{NaS}_{0.5} = \text{CuS}_{0.5} + (\text{Na})$	-9500-2.72T 1300-0.93T -3100+2.29T 44750-6.56T -3150+2.52T 52500-17.2T 620-1.67T 24200-21.01T 26000-24.45T 56300-29.85T	-15800+3.68T 1100-0.77T -3100+2.30T -3150+2.52T 52500-17.2T 620-1.67T 24200-21.01T 55750-30.48T
(b) $2\text{Cu} + \text{CaCl}_2 = 2\text{CuCl} + (\text{Ca})$; overall. $\text{Cu} + \frac{1}{2}(\text{Cl}_2) = \text{CuCl}$ $\text{Cu} + \frac{1}{2}(\text{Cl}_2) = (\text{CuCl})$ $(\text{CuCl}) = \text{CuCl}$ $\text{Cu} = \text{Cu}$ $\text{CaCl}_2 = \text{Ca} + (\text{Cl}_2)$ $\text{CaCl}_2 = \text{Ca} + (\text{Cl}_2)$ $\text{CaCl}_2 = \text{CaCl}_2$ $\text{Ca} = (\text{Ca})$ $\text{Ca} = (\text{Ca})$ $2\text{Cu} + \text{CaCl}_2 = 2\text{CuCl} + (\text{Ca})$	-32800+13.97T 15120-15.96T -46500+23.60T -3100+2.29T 190200-38.24T 190900-34.89T -6820+6.53T 42600-27.04T 157680-31.07T	15120-15.96T -46500+23.60T -3100+2.29T 190900-34.89T -6820+6.53T 37720-20.82T 165860-40.43T
(c) $2\text{Cu} + \text{CaF}_2 = 2(\text{CuF}) + (\text{Ca})$; overall. $\text{Cu} + \frac{1}{2}(\text{F}_2) = \text{CuF}$ $\text{Cu} + \frac{1}{2}(\text{F}_2) = (\text{CuF})$ $\text{CaF}_2 = \text{Ca} + (\text{F}_2)$ $\text{Ca} = (\text{Ca})$ $\text{CaF}_2 = \text{CaF}_2$ $2\text{Cu} + \text{CaF}_2 = 2(\text{CuF}) + (\text{Ca})$	not sufficient data	5000-15.8T 285000-35.0T 37720-20.82T -7100+4.20T 325600-83.22T

REACTION	reference(15)	reference(13)
(d) $\text{Cu} + \text{KF} = (\text{CuF}) + (\text{K})$; overall. $\text{Cu} + \frac{1}{2}(\text{F}_2) = (\text{CuF})$ $\text{KF} = \frac{1}{2}(\text{F}_2) + (\text{K})$ $\text{Cu} + \text{KF} = (\text{CuF}) + (\text{K})$		5000-15.8T 145190-33.97T 150190-49.77T
(e) $\text{Cu} + \text{MnS} = 2\text{CuS}_{0.5} + (\text{Mn})$; overall. $\text{Cu} + \frac{1}{2}(\text{S}_2) = \text{CuS}_{0.5}$ $\text{MnS} = \text{Mn} + \frac{1}{2}(\text{S}_2)$ $\text{Mn} = (\text{Mn})$ $2\text{Cu} + \text{MnS} = 2\text{CuS}_{0.5} + (\text{Mn})$	62770-15.40T	-17800+5.21T 56350-24.18T 83520-29.16T
(f) $2\text{Cu} + \text{MgS} = 2\text{CuS}_{0.5} + (\text{Mg})$; overall. $\text{Cu} + \frac{1}{2}(\text{S}_2) = \text{CuS}_{0.5}$ $\text{MgS} = (\text{Mg}) + \frac{1}{2}(\text{S}_2)$ $2\text{Cu} + \text{MgS} = 2\text{CuS}_{0.5} + (\text{Mg})$	134350-48.75T	-17800+5.21T 98750-38.33T
(g) $2\text{Cu} + \text{CaS} = 2\text{CuS}_{0.5} + (\text{Ca})$; overall. $\text{Cu} + \frac{1}{2}(\text{S}_2) = \text{CuS}_{0.5}$ $\text{CaS} = (\text{Ca}) + \frac{1}{2}(\text{S}_2)$ $2\text{Cu} + \text{CaS} = 2\text{CuS}_{0.5} + (\text{Ca})$	168360-45.72T	-17800+5.21T 132760-35.3T
(h) $2\text{Cu} + \text{FeS} = 2\text{CuS}_{0.5} + \text{Fe}$; overall. $\text{Cu} + \frac{1}{2}(\text{S}_2) = \text{CuS}_{0.5}$ $\text{FeS} = \text{Fe} + \frac{1}{2}(\text{S}_2)$ $\text{FeS} = \text{FeS}$ $2\text{Cu} + \text{FeS} = 2\text{CuS}_{0.5} + \text{Fe}$	-7730+5.27T	-17800+5.21T 39200-14.6T -4130+1.09T

(2) Thermodynamic data for the full model.

reference



= dissolved in iron
 - liquid

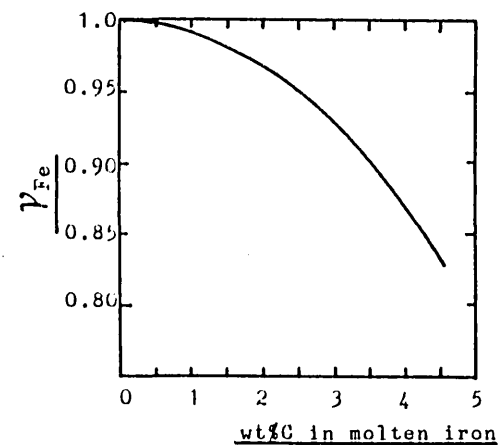


Fig. A5-1 Activity coefficient of iron in the Fe-C system (calculation).

4) Mass transfer coefficients, k [m/s] [11], [12], [14].

It is assumed that mass transfer coefficients for all species have a common value in each phase.

Rate phenomena are characterised by a reference time,

t_{ref} [sec].

$$t_{\text{ref}} = V_m / k_m S$$

t_{ref} can be determined by experiment.

$$\text{Using } k_m/k_s = \sqrt{D_m/D_s}$$

subscript m denotes metal phase.

s denotes slag phase.

D denotes diffusion coefficients.

one can obtain k_m and k_s values.

APPENDIX-6

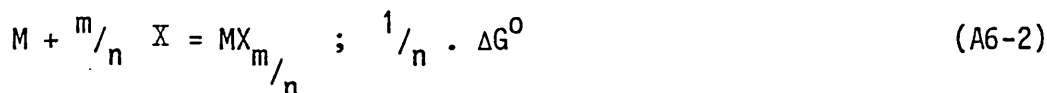
ACTIVITY AND ACTIVITY COEFFICIENT IN THE SLAG PHASE.

In both the steady state model and the full model, all compounds in the slag phase are expressed as a form MX_σ , here M is a metallic element and X is usually selected as the Raoultian standard state for the compounds in the slag phase.

An important region for $CuS_{0.5}$ is between $x_{CuS_{0.5}} = 0$ and $x_{CuS_{0.5}} \sim 0.1$. In this region γ is dependent on the components chosen for the analysis, e.g. Cu_2S-Na_2S or $CuS_{0.5} - NaS_{0.5}$. It is possible to calculate the dependency of activity coefficient on a slag composition which is changing with time. The choice of components which give constant activity coefficients convenient for analysis. The form MX_σ is chosen because it displays this convenient behaviour and also because the equilibrium of this system is described in the linear equation as far as metallic element M is concerned. Generally the reactions concerned are written using the formula (A6-1) or (A6-2).



where n and m are integers



An equilibrium constant, K_1 , for the formula (A6-1) is

$$K_1 = a_{M_n X_m} / a_M^n \cdot a_X^m \quad (A6-3)$$

An equilibrium constant, K_2 , for the formula (A6-2) is

$$K_2 = a_{MX_{m/n}} / a_M \cdot a_X^{m/n} (\equiv K_1^{1/n}) \quad (A6-4)$$

a_M and $a_{MX_{m/n}}$ have a linear relation from the equation (A6-4) but a_M and $a_{M_n X_m}$ have a non-linear relations.

Activity coefficients in the $\text{CuS}_{0.5}\text{-FeS}$ system are obtained as follows:-

The relation between activity and composition in the $\text{Cu}_2\text{S-FeS}$ binary system was derived by Topkaya [18].

This relationship can be transformed to the $\text{CuS}_{0.5}\text{-FeS}$ system in the following way. The relation of these two binary systems are described by the equations:-

$$x_{\text{FeS}}^{\text{B}} = x_{\text{FeS}}^{\text{A}} / (2 - x_{\text{FeS}}^{\text{A}}) \quad (\text{A6-5})$$

$$x_{\text{CuS}_{0.5}} = 2x_{\text{Cu}_2\text{S}} / (1 + x_{\text{Cu}_2\text{S}}) \quad (\text{A6-6})$$

where superscript A denotes $\text{Cu}_2\text{S-FeS}$ system.

superscript B denotes $\text{CuS}_{0.5}\text{-FeS}$ system.

i.e. $x_{\text{FeS}}^{\text{A}}$ is mole fraction of FeS defined in $\text{Cu}_2\text{S-FeS}$ system.

Activity coefficients in $\text{CuS}_{0.5}\text{-FeS}$ system are expressed by activity coefficients in $\text{Cu}_2\text{S-FeS}$ system.

$$\gamma_{\text{CuS}_{0.5}} = (1 - 1/2x_{\text{FeS}}^{\text{A}}) \cdot \sqrt{\gamma_{\text{Cu}_2\text{S}} / (1 - x_{\text{FeS}}^{\text{A}})} \quad (\text{A6-7})$$

$$\gamma_{\text{FeS}}^{\text{B}} = 2 \cdot \gamma_{\text{FeS}}^{\text{A}} (1 - 1/2x_{\text{FeS}}^{\text{A}}) \quad (\text{A6-8})$$

Calculated results are summarised in Table A6-1. In $\text{CuS}_{0.5}\text{-Fe}_{0.5}\text{S}_{0.5}$ system(c), activity coefficients are transformed from $\text{Cu}_2\text{S-FeS}$ system (A).

$$x_{\text{Fe}_{0.5}\text{S}_{0.5}} = x_{\text{FeS}} \quad (\text{A6-9})$$

$$x_{\text{CuS}_{0.5}} = x_{\text{Cu}_2\text{S}} \quad (\text{A6-10})$$

$$\gamma_{\text{Fe}_{0.5}\text{S}_{0.5}} = \sqrt{\gamma_{\text{FeS}} / x_{\text{FeS}}} \quad (\text{A6-11})$$

$$\gamma_{\text{CuS}_{0.5}} = \sqrt{\gamma_{\text{Cu}_2\text{S}} / x_{\text{Cu}_2\text{S}}} \quad (\text{A6-12})$$

Activity - composition relations in these three systems are shown in Fig. A6-1 .

Table A6-1 Transformation of activity coefficients from the Cu_2S -FeS system to the $\text{CuS}_{0.5}$ -FeS system (in the lower concentration region of Cu_2S ; $x_{\text{Cu}_2\text{S}} < 0.10$).

(A) Cu_2S -FeS system (system-A) (B) $\text{CuS}_{0.5}$ -FeS system (system-B)

x_{FeS}	$x_{\text{Cu}_2\text{S}}$	$\gamma_{\text{Cu}_2\text{S}}^*$	x_{FeS}	$x_{\text{CuS}_{0.5}}$	$\gamma_{\text{CuS}_{0.5}}$
1.0000	0	0.0696	1.0000	0	-
0.9899	0.0101	0.0722	0.980	0.020	1.34
0.9796	0.0204	0.0749	0.960	0.040	0.97
0.9691	0.0309	0.0778	0.940	0.060	0.81
0.9583	0.0417	0.0809	0.920	0.080	0.71
0.9474	0.0526	0.0841	0.900	0.100	0.65

1) * : $\gamma_{\text{Cu}_2\text{S}} = \exp(3.595x_{\text{Cu}_2\text{S}} - 2.665)$ by Topkaya(18).

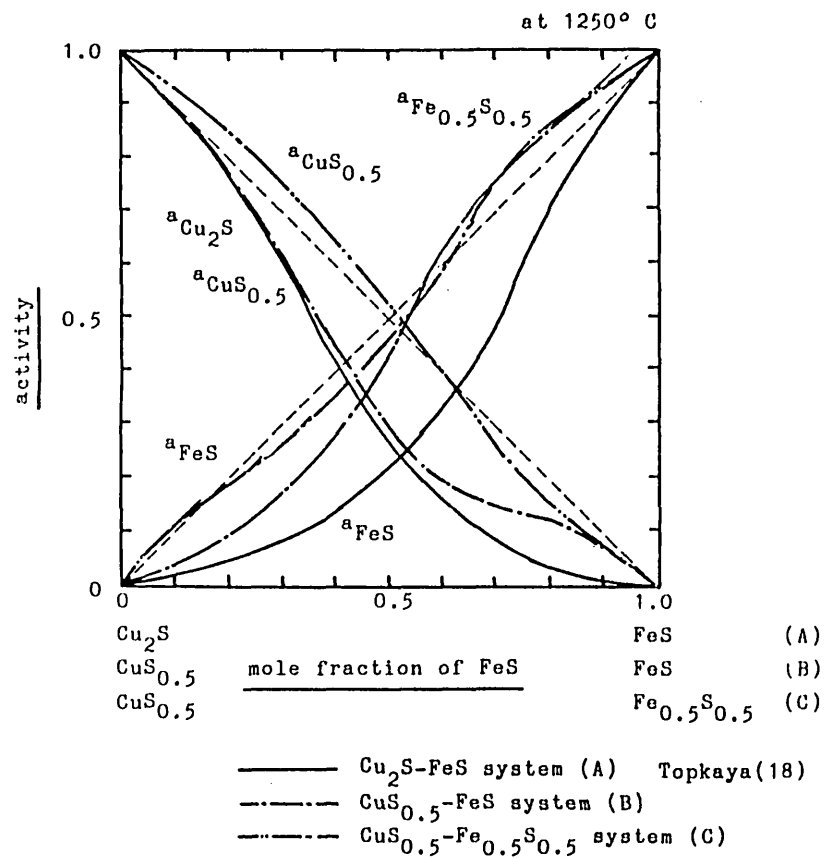
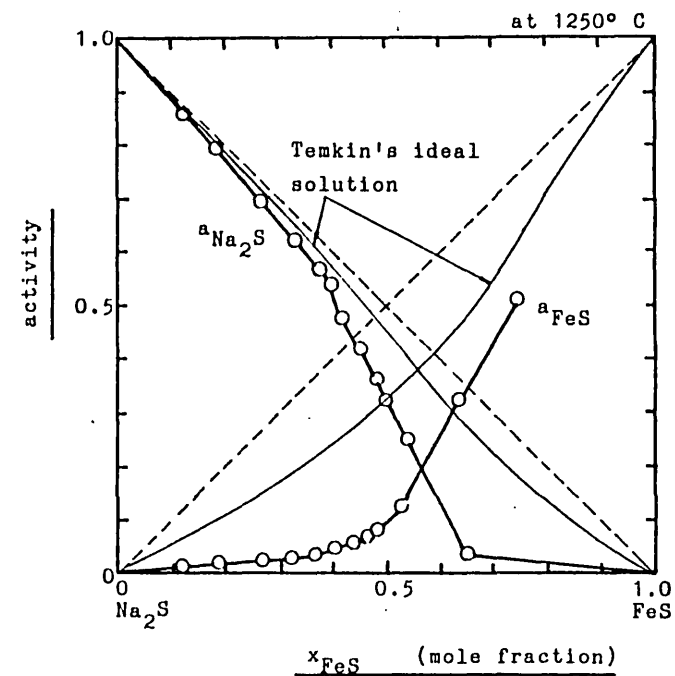
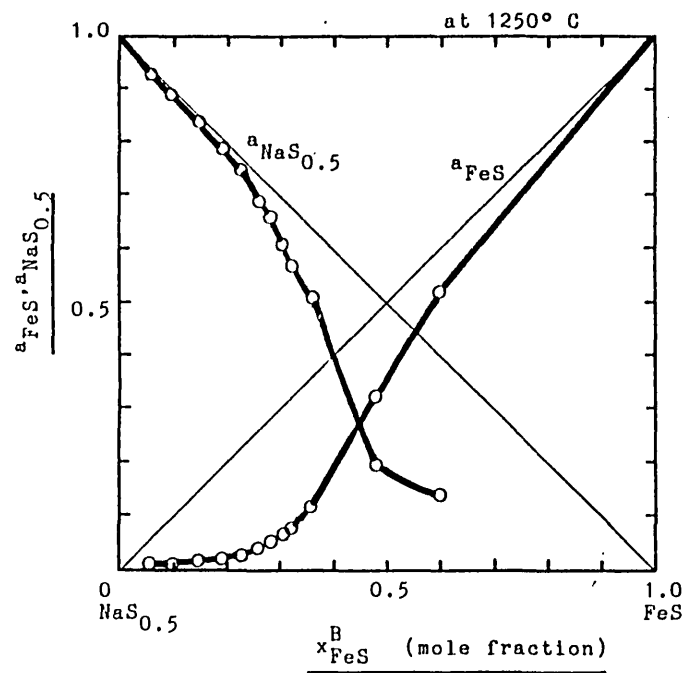


Fig.A6-1 Activity-composition relations in the three systems.



(a) Na_2S -FeS system (A), Topkaya (18).

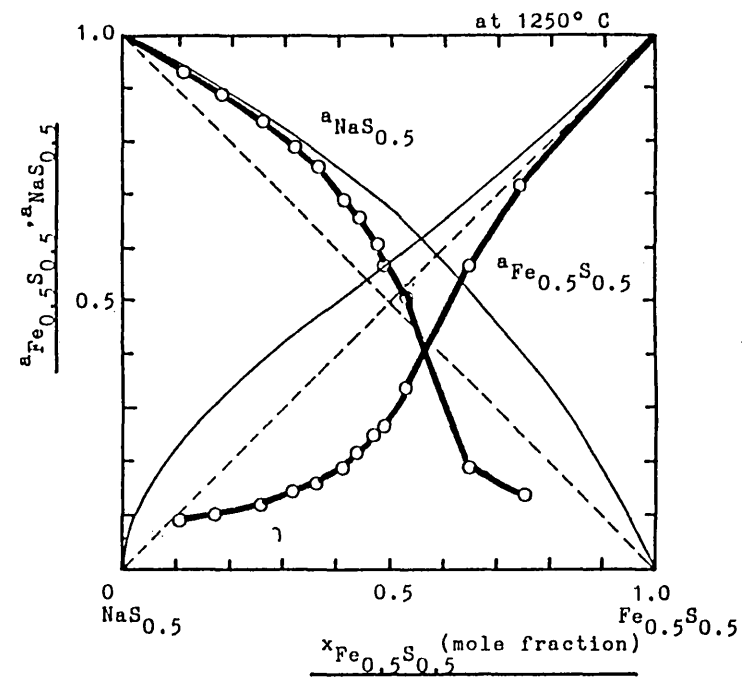
Fig.A6-2 Activity-composition relations.



○—○ Topkaya(18) data converted to the system (B)

— Temkin's ideal solution

(b) $\text{NaS}_{0.5}$ -FeS system (B).



— Topkaya(18) data converted to the system (C)

— Temkin's ideal solution

(c) $\text{NaS}_{0.5}$ - $\text{Fe}_{0.5}\text{S}_{0.5}$ system (C).

Activity coefficients in $\text{NaS}_{0.5}$ -FeS system, (B), can be derived from those in Na_2S - FeS system, (A), which are available from Tapkaya [18].

$$x_{\text{FeS}}^{\text{B}} = x_{\text{FeS}}^{\text{A}} / (2 - x_{\text{FeS}}^{\text{A}}) \quad (\text{A6-13})$$

$$x_{\text{NaS}_{0.5}} = (1 - x_{\text{FeS}}^{\text{A}}) / (1 - 1/2 x_{\text{FeS}}^{\text{A}}) \quad (\text{A6-14})$$

$$\gamma_{\text{FeS}}^{\text{B}} = 2 \cdot \gamma_{\text{FeS}}^{\text{A}} (1 - 1/2 x_{\text{FeS}}^{\text{A}}) \quad (\text{A6-15})$$

$$\gamma_{\text{NaS}_{0.5}} = (1 - 1/2 x_{\text{FeS}}^{\text{A}}) \sqrt{\gamma_{\text{Na}_2\text{S}} / (1 - x_{\text{FeS}}^{\text{A}})} \quad (\text{A6-16})$$

Calculated results are shown in Fig. A6-2.

For $\text{NaS}_{0.5}$ - $\text{CuS}_{0.5}$ system,

$$\gamma_{\text{NaS}_{0.5}} = \sqrt{\gamma_{\text{Na}_2\text{S}} / x_{\text{Na}_2\text{S}}} \quad (\text{A6-17})$$

$$\gamma_{\text{CuS}_{0.5}} = \sqrt{\gamma_{\text{Cu}_2\text{S}} / (1 - x_{\text{Na}_2\text{S}})} \quad (\text{A6-18})$$

Calculated results are shown in Fig. A6-3.

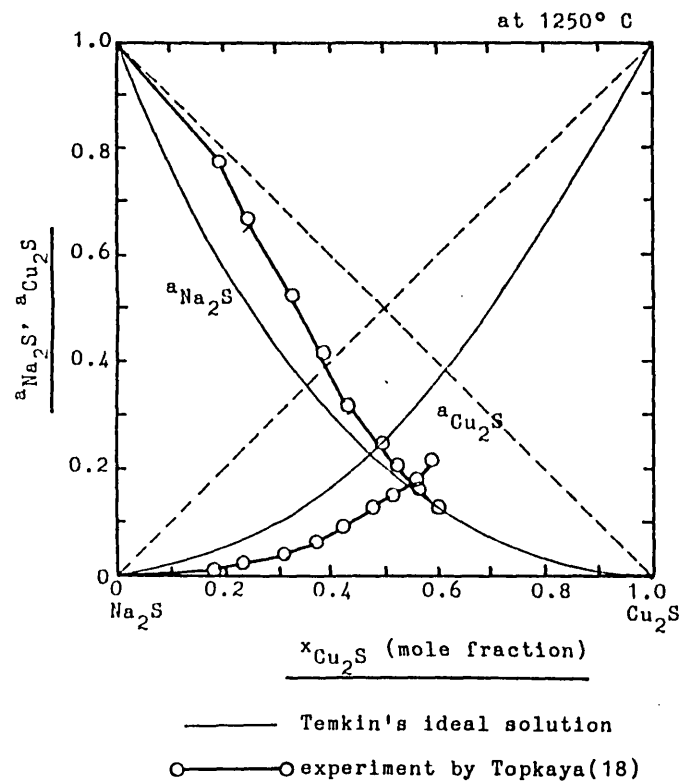
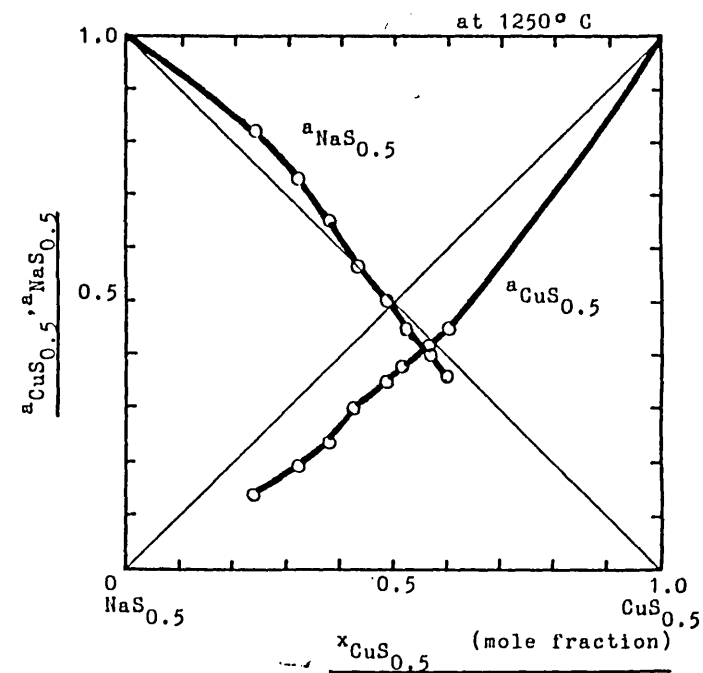


Fig.A6-3 Activity-composition relations.



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