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Expert Group Meeting on Lead and Zinc Production
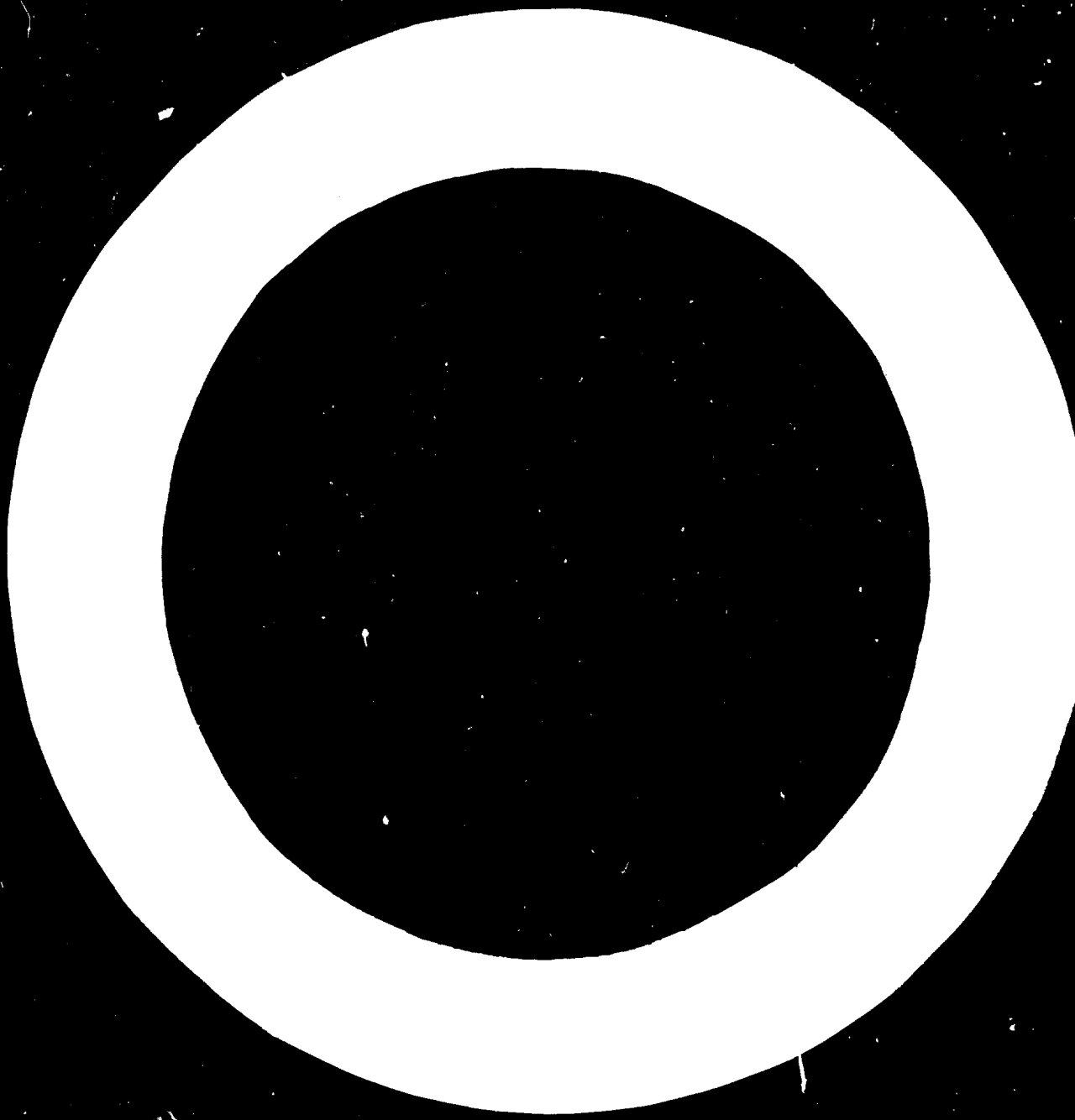
London, England, 28 April - 2 May 1969

THE IMPERIAL SMELTING PROCESS FOR THE

SIMULTANEOUS PRODUCTION OF ZINC AND LEAD

AT THE HARIMA WORKS OF SUMIKO [1]

by

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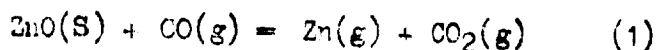Chief Metallurgist
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SUMMARY

The most basic problem in the I.S. Furnace is the reducing condition in the shaft, namely CO_2/CO ratio. This report compares the theoretical calculations for equation (1) and the actual operational data

$$ZnO(S) + CO(g) = Zn(g) + CO_2(g) \qquad (1)$$

CO_2/CO ratio in the shaft dominates the zinc oxide reduction reaction and, especially, is the most important factor together with temperature in condensing zinc vapour in the gas which leaves the furnace. CO_2/CO ratio also has a considerable effect on the production rate of zinc in the I.S. Furnace and smelting costs, especially fuel cost.

The reactivity of coke is considered as most important from this point of view, so at Befu it is specified as 25 to 32 percent in order to get a CO_2/CO ratio of 0.3 to 0.6 and an iron activity, a_{Fe}, of 0.3–0.5 in equation (2) at the minimum theoretical equilibrium temperature 1000 to 1020°C, assuming the activity of FeO in slag to be 0.4 to 0.5 and Pzn to be 0.06.

$$FeO(s) + CO(g) = Fe(\gamma) + CO_2(g) \qquad (2)$$
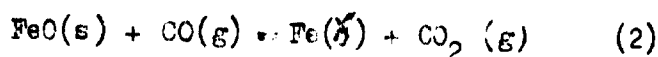
A theoretical value of condensation efficiency has been deduced as 93%, and the actual value achieved in Sumiko has been 90 to 92%.

When the temperature is kept constant, a_{ZnO} in slag drops as a_{FeO} in slag does. (The coefficient of correlation is given as 0.76 by statistical analysis of slags at Befu.) Using this and a P_{CO_2}/P_{CO} of 0.3–0.4 which is obtained from actual operation data at Sumiko, the composition of matte and the equilibrium in equation (10) is obtained, given an iron activity of 0.2 to 0.5.

Equation (10) also shows that the higher the activity a_{Fe} the higher the copper activity a_{Cu} at a constant value of Cu_2S/FeS. Since a_{Cu} increases as PCO_2/PCO decreases, it is more economic for copper to be recovered in lead bullion in a furnace which has strongly reducing conditions as has the I.S. Furnace.

There are a number of economic advantages arising from the presence of lead in the charge to the I.S. Furnace and the production of lead bullion. These are not only the ability to smelt lead and zinc simultaneously but also the ability to recover valuable metals in the bullion. Lead has another merit, giving good hardness of sinter instead of adding SiO_2, which results in a smaller slag quantity.

However, the behaviour of lead charged to the I.S.F. should be carefully considered from a different viewpoint as having some effect on the elimination of sulphur in sintering and the formation of accretion in the furnace shaft.
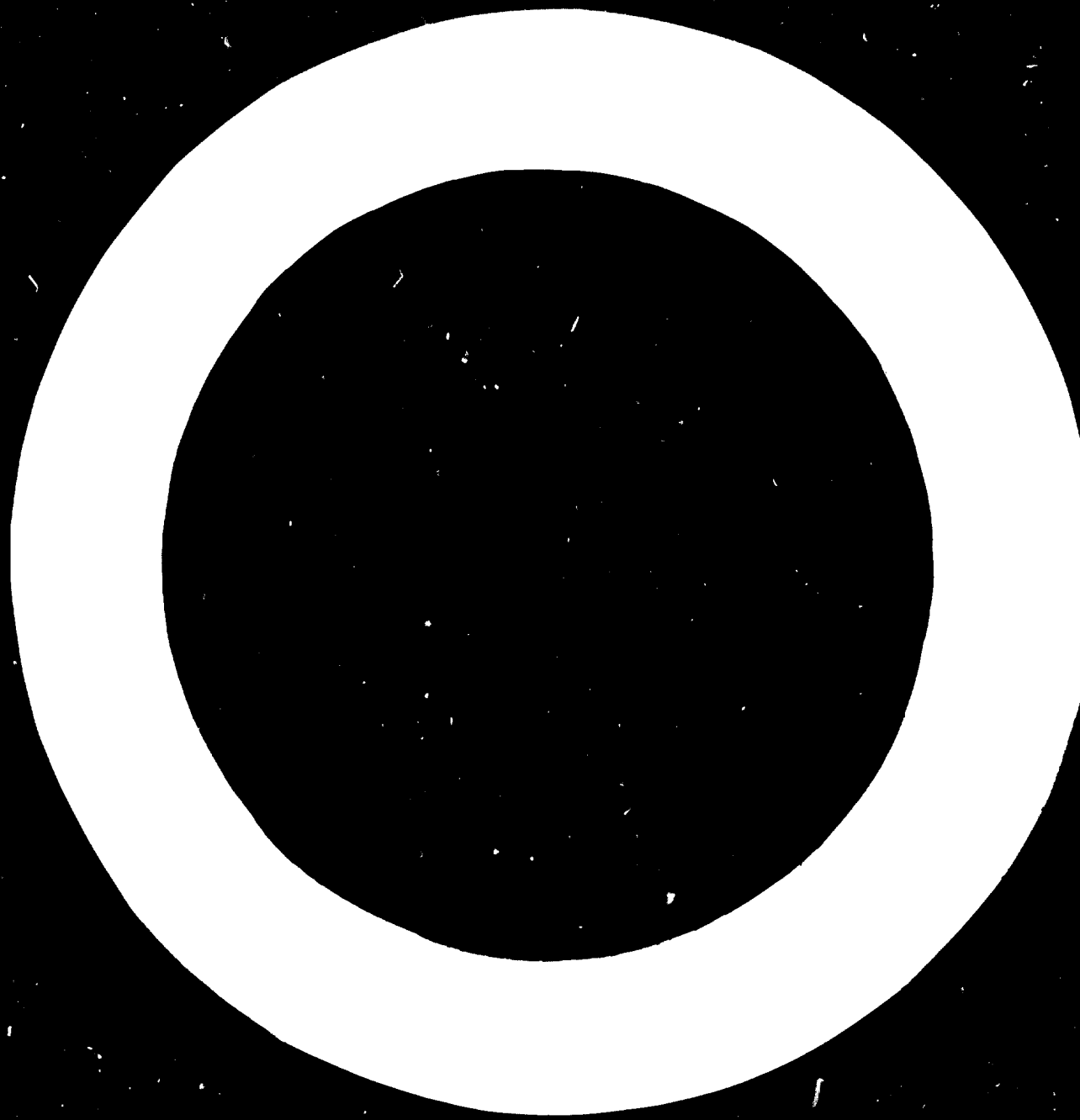
INTRODUCTION

Zinc smelting made a great advance in the past ten years. Originally smelting began with pot-distillation, followed by the introduction of horizontal retorts. These have been used for a long time until progressively replaced by continuous vertical retorts.

In the meantime, the St. Joseph electrothermic process and the Starling furnace process have also been developed. On the other hand, the electrolytic process had been developed and the majority of zinc production in the world is now by this process.

After extensive research and development a new process, the Imperial Smelting Process, was developed by I.S.C. (N.S.C.) of Avonmouth, U.K., for the blast furnace production of zinc. In 1960 the first full-size furnace using this process was started up at their Swansea Vale Works where it replaced the horizontal retort process.

This was of great interest to zinc producers throughout the world and many plants subsequently introduced this process. Zinc output from I.S. Furnaces at present has reached 10% of world zinc production.

This process has the following specific characteristics:-

(1)   As a zinc blast furnace is similar to a conventional lead blast furnace, it is capable of smelting lead simultaneously with zinc. This gives it the ability to recover copper, gold, silver and bismuth as a lead blast furnace does. Harima Works recovers silver, bismuth, gold, copper, antimony and arsenic on a commercial basis.

Another merit of a zinc blast furnace is that it gives great flexibility in the selection of raw materials to be treated compared with alternative processes. For example, the retort distillation process requires the minimisation of iron in concentrates because of corrosion problems. Also in the electrolytic process lead has to be maintained at less than 3% in the roasting process before leaching, and in addition it is well known that iron causes formation of zinc ferrite in roasting, which lowers zinc recovery in leaching. On the other hand in the lead blast furnace zinc is deleterious, since it gives a high melting point sticky slag. The zinc in a lead blast furnace slag is not usually recovered except as oxide, where a slag fuming process can be economically justified.

Zinc and lead nearly always co-exist in their ores, and conventionally they have been separated by differential flotation and treated by separate metallurgical processes. However, efficient separation is impossible with some ores and thus the ability of the I.S. Furnace to treat readily sintered bulk concentrates is particularly important.

Thus the I.S. Furnace has brought a new concept to zinc and lead smelting in that it is able to treat economically varied raw materials containing zinc, lead and other metals such as copper, bismuth, antimony and precious metals. The combination of ore concentration and metal smelting processes can now be considered from a new point of view.

TABLE 1

OPERATIONS AND SERVICES PER TON OF ZINC

		Standard* I.S.P.	Horizontal** Retort	Vertical** Retort	Electrothermic** Process	Electrolytic Process		
						KAMIOKA	IBUKA	HOSOKURA
Zinc Extraction	%	84.5		93.0		92.5	91.0	93.5
Lead Extraction	%							
Labour	Number	4.0	21.6	9.6	4.8	8.0	16.0	15.4
Electrical Power	kWh	275	70	259	4,875	3,756	4,980	4,065
Raw Water	t	73.5 (with some recirculation)	2.1	6.7		45	55	130
Steam	kg	72	0.3 used / 2.4 recovered			Minus 1.0	1.4 / 1.8	0.8 / 1.1
Sodium	kg	0.225				Minus 7.0	23.6	15.6
Ammonium Chloride	kg	Zn-Mn.Cl. 5.65				0.9	0.7	1.3
Oxygen	m³	1.04				Zinc dust 21.7	39.3	18.0
Lime rock	kg	1.3						
Other Heating Fuels	Million Kcal	0.35	Heavy Oil 1,005		Heavy Oil 8.8 L	Heavy Oil 28.6		Heavy Oil 54.5
						H_2SO_4 11 L		30
Coke	t	0.95	0.40	0.12	0.47	Glue 0.1 kg / Latex – kg	0.42 / 97.7	0.45 / 27.5
Coal (lump)	t				Graphite E-pol. 1.2 kg	Aluminium 2.2 kg / Filter cloth 0.3 m²		
Coal (fine)	t		Retort 0.2 / Condenser 3.9	0.9	0.06		1.1	1.5
Miscellaneous Process Items	$	1.00						0.1
Zn Production	t/year	60,000	24,000	66,000	90,000	60,000	18,000	22,000
Pb Production	t/year	Up to 45,000						
Maintenance								
Labour	Man-hrs	3.0						
Materials	%	5.00						
Construction Cost	$/t	122,000 Includes H_2SO_4 Plant, Sinter Plant, 18¢ sq.ft ISP, 35,000 T.Refinery						

* Ref. S.W.K. MORGAN and D.A. TEMPLE, Jnl. of Metals, August 1961, p.139. These figures assume all the consumptions and services to be carried by the zinc production of a standard (105 ft² hearth area × 6 vans) and then by the lead production.

** Ref. Statistics of Japan Mining and Metallurgical Association.

(2) It is generally considered that a blast furnace has a high productivity and low labour and capital costs (1). When zinc and lead are produced together, these factors should be improved further. Table 1 gives a comparison of these costs for several zinc smelting processes in Japan.

The data for the standard I.S.F., in Table 1, is as reported by S.W.K. Morgan and D.A. Temple on the basis of recent operations (1).

It is to be noted that there has been great progress in the performance of the standard sized furnace since 1960.

Some operational data for 1960 and 1968 is compared in Table 2.

TABLE 2. I.S.F. Operational Data

	1960	1968
Carbon burning rate	94 t/day	154 t/day
Carbon consumption/t.Zinc	0.98	0.85
Zinc production	3000 t/month	5000-6000 t/month

(3) As mentioned above, since the process by which lead is recovered together with zinc is the same as in a lead blast furnace, precious metals in raw materials are recovered by solution in lead bullion. Up to now valuable metals in zinc concentrates except cadmium have remained in residues when treated pyrometallurgically. Recovery has been by a subsequent treatment when economically justifiable. On the other hand, in the hydrometallurgical process for zinc, valuable metals except cadmium and a part of the copper remain in leach residues which also contain some of the zinc.

For treatment of these residues in Japan several processes are used which have been most suitable for the smelters concerned. For example, residues are treated by a combination of the copper blast furnace and a fuming process for the recovery of copper, gold, silver and zinc, by the St. Joseph process for zinc combined with the copper converter for copper, zinc oxide, gold and silver from zinc residue, and the copper reverberatory furnace for copper, gold and silver.

As the I.S.F. is capable of simultaneous recovery of these valuable metals in one unit, a great simplification of equipment and process is possible. In certain cases the I.S.F. is suitable for complex ores which contain valuable metals and which are unsuitable for conventional processes.

SLAG COMPOSITION

The desired characteristics of slag are:-

(1) It should be small in quantity

(2) It should contain as little zinc as possible

(3) It should be fluid in order to gain higher zinc recovery.

These are effected by the following factors:-

(1) Activity of FeO in slag

(2) Activity of ZnO in slag

(3) The reducing atmosphere (CO_2:CO ratio) in the shaft.

The reducing atmosphere has to be controlled for zinc oxide to be reduced and for iron oxide to be reduced as far as ferrous oxide which is removed into the slag.

The reduction of iron oxide is determined by activity of FeO in slag and CO_2:CO ratio in the shaft. When the activity of FeO in slag is fixed, the activity of ZnO in slag is fixed for a constant value of CO_2:CO and limits the reduction of zinc oxide.

As calculated by T. Azagami and M. Yazawa (3), the activity of zinc oxide is 0.02 to 0.03, assuming 0.06 for the partial pressure of zinc, Pzn, and of 0.3 to 0.4 for the activity a_{FeO} in slag.

If coefficient of activity of ZnO is assumed as 3 (4), then theoretically the zinc content of slag could be reduced to 1.0-1.5%. This was shown experimentally by S. Goto (4) and also supported by statistical analysis of slag composition at Bofu plant, Sumiko, which showed a good correlation between zinc and FeO in slag. Table 3 shows correlation coefficients obtained at Bofu between zinc and other slag constituents.

TABLE 3.

Constituent		Correlation Coefficient
FeO	(zinc free)	0.766 .
CaO	(" ")	-0.694
SiO_2	(" ")	-0.750
Al_2O_3	(" ")	-0.800

At Befu it has been found that the total slag weight can be reduced to a minimum at the prevailing Al_2O_3 levels with low CaO and SiO_2. This produces a slag of the Melilite type ($FeO-CaO-SiO_2-Al_2O_3$) and eliminates the need to add hard burnt lime which is often the practice on other I.S. Furnaces. A typical Befu slag composition is given in Table 4. Table 5 shows current slag/zinc ratios at Befu.

TABLE 4. Standard composition of slag

SiO_2	CaO	FeO	Al_2O_3	Zn	Cu	S
20%	20%	36.5%	9-10%	7.0%	0.38 - 0.4%	2.5 - 3.5%

TABLE 5. Zinc and slag production

	Zinc Production	Slag	Slag/Zinc Ratio
Nov. 1968	4198 t*	2087 t.	0.641
Dec. 1968	4595 t.	2914 t.	0.639

* Metric tons

SHAFT GAS ANALYSIS

As mentioned above, in I.S.F. iron oxides in the charge are reduced to ferrous oxide and removed into the slag but not reduced to metallic iron. On the other hand, zinc oxide is reduced to zinc vapour. The reducing conditions in the shaft must be decided with this aim. The reactions involved are:-

$$ZnO(s) + CO(g) = Zn(g) + CO_2 (g) \qquad (1)$$

$$K_1 = Pzn . PCO_2/PZnO . Poo \qquad (2)$$
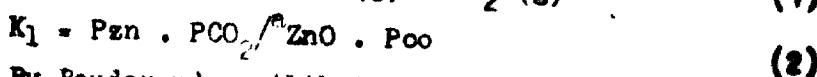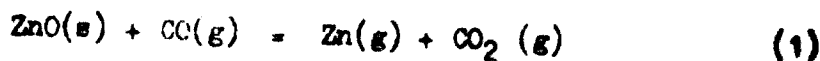
By Boudouard equilibrium and other reactions

$$C(s) + CO_2(g) = 2 CO(g) \qquad (3)$$

$$K_2 = P^2co/Pco., \qquad aC = 1.$$

$$Fe_3O_4 (\alpha) + 4 CO(g) = 3 Fe (\gamma) + 4 CO_2(g) \qquad (4)$$

$$FeO (s) + CO(g) = Fe (\gamma) + CO_2(g) \qquad (5)$$

$$Fe_3O_4 (\alpha) + CO(g) = 3 FeO (s) + CO_2(g) \qquad (6)$$
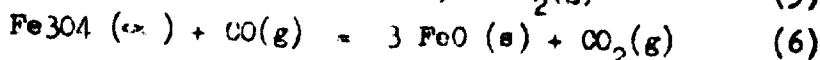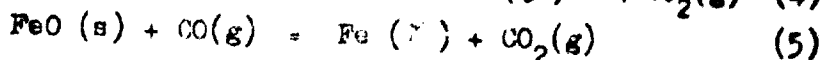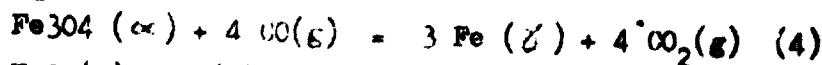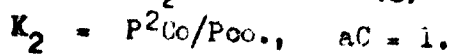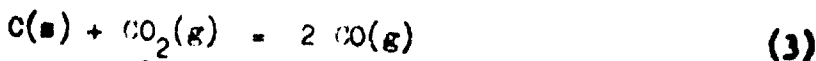
The equilibria for these equations at various Pco_2/Pco ratios and temperatures are plotted on Fig. I for the conditions shown in the table below Fig. 1. The stable co-existent area of FeO and zinc vapour is shown with oblique lines.

(1) $ZnO\ (s) + CO\ (g) = Zn\ (g) + C$
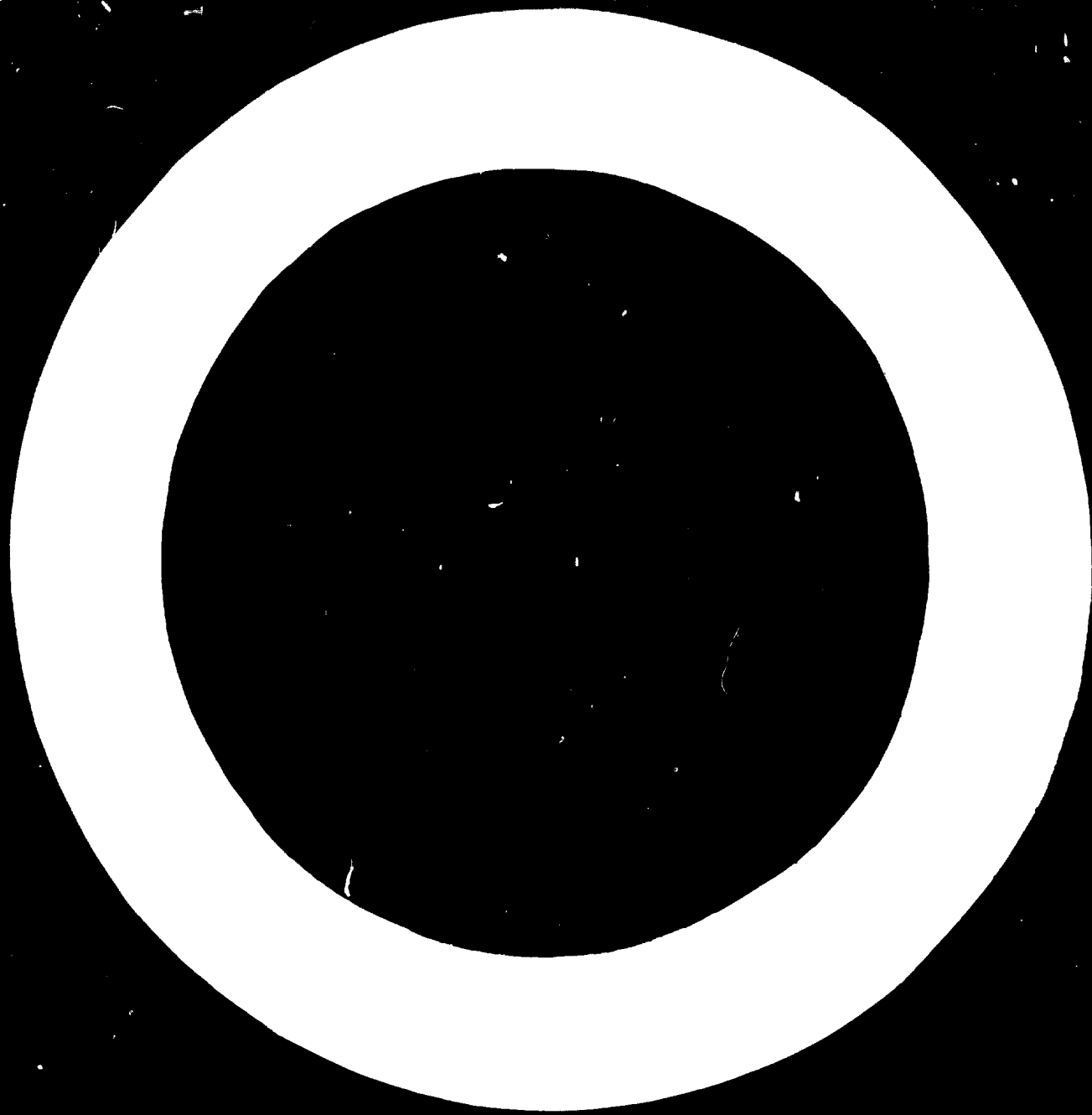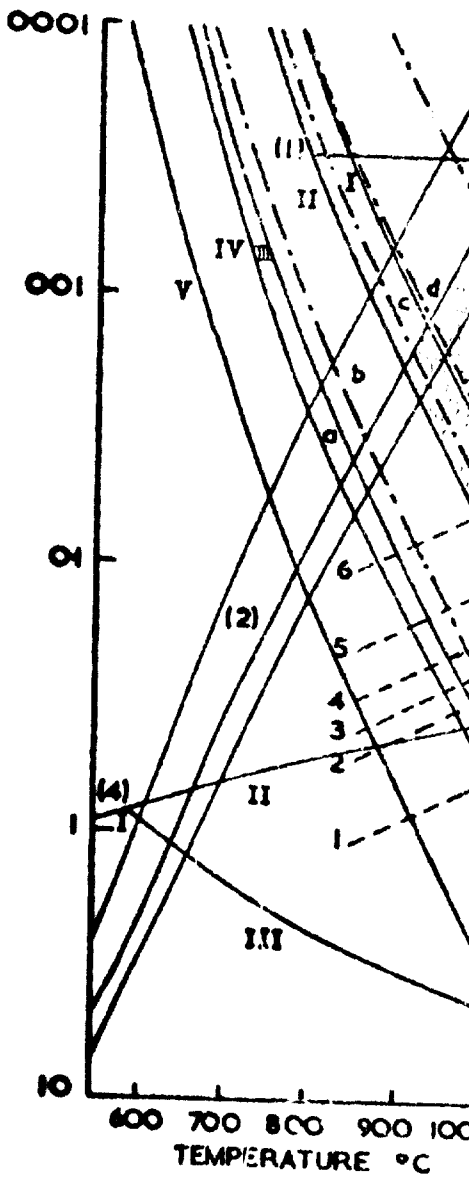
	I	II	II	IV	V
a ZnO	1	1	1	1	1
p Zn	1·0	0·45	0·1	0·06	0·0

(2) $C\ (s) + CO_2\ (g) = 2\ CO$

	A	B
p CO$_2$ + p CO	1·0	0·6

(3) $FeO\ (l) + CO\ (g) = Fe\ (r) + CO$

	1	2	3
a FeO	1·0	0·5	0·4

(4) EQUILIBRIUM OF REDUCTION

   I $Fe_3O_4\ (a) + 4\ CO\ (g) = 3$

  II $FeO\ (s) + CO\ (g) = Fe\ (r)$

 III $Fe_3O_4\ (a) + CO\ (g) = 3F$

Fig. 1

EDUCTION FOR ZINC AND
OXIDES

REDUCTION FOR ZINC AND OXIDES

Axis labels: 1000 1100 1200 1300
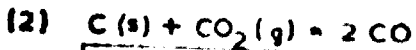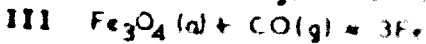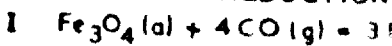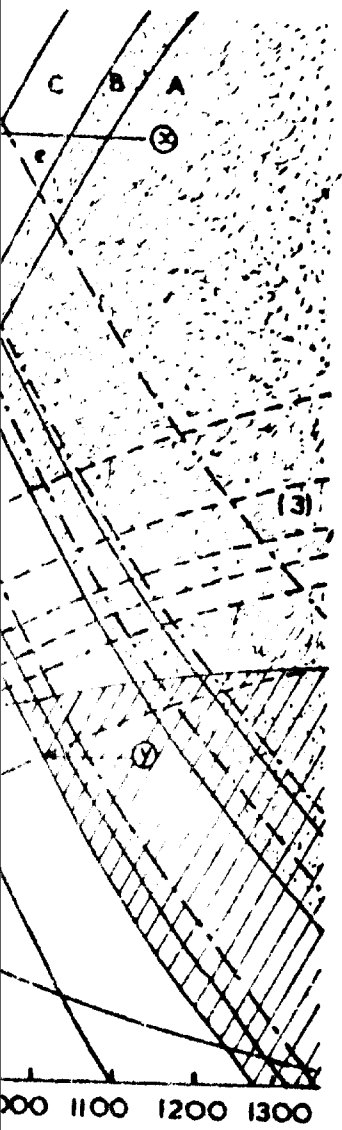
$CO_2(g)$

V	a	b	c	d	e
1	1·0	0·5	0·1	0·05	0·01
0·01	0·06	0·06	0·06	0·06	0·06

	C
6	0·2

$O_2(g)$

	4	5	6
	0·3	0·2	0·1

N FOR IRON OXIDE

$3Fe(\gamma) + 4CO_2(g)$

$(\gamma) + CO_2(g)$

$+ O(s) + CO_2(g)$
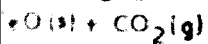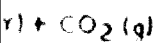
It is desirable to obtain conditions where after top air addition
the temperature is more than $1000^{\circ}C$ and P_{CO_2} is 0.3 to 0.6 at the furnace
top. This means that no reverse reaction of equation (1) occurs at the
furnace top and FeO is stable in the shaft. It is, however, normal that
the partial pressures of CO_2 and CO vary at the tuyere zone, in the
reaction zone and in the preheating zone of the shaft. Befu I.S.F. has
been examining $CO_2:CO$ ratios by oxygen balances, and the effect on these
of coke reactivity, and have concluded that a reactivity from 20-30% is
required. Almost all the carbon burns to CO at a tuyere zone and the
$CO_2:CO$ ratio then increases up to 1.0 at the reaction zone, but with
coke of this reactivity the Boudouard reaction reduces this ratio to
0.3-0.6 at charge level.

Works trials gave satisfactory results at Befu plant where cokes of
different reactivity were used in a number of trials.

As it will be mentioned later, $CO_2:CO$ ratio is an important factor
for formation of matte and speiss.

BLAST TEMPERATURE

Sumiko adopted Cowper stoves with a separate combustion chamber for
preheating blast air, in view of the low calorific value of the exhaust
gas from the I.S.F. The stoves have been definitely satisfactory in
operation. Blast temperature is maintained at $800^{\circ}C$ at the bustle main.
The dome temperature of the combustion chamber is kept below $1100^{\circ}C$ to
protect the refractories. This temperature could be increased if the
cleaning of the gas was improved.

Heat input into the furnace is that generated from combustion of
coke, the sensible heats of charge and hot blast. Besides being a source
of heat, the hot blast has an important metallurgical role in the furnace;
it increases reactivity of coke and accelerates oxide reducing reactions.

Temperature distribution in the shaft is considered to be as follows:-

The highest temperature, $1400-1450^{\circ}C$ is attained in the coke combustion
zone at tuyere level and at the reaction zone, the temperature should have
been reduced to about $750^{\circ}C$ according to our calculations, because of
endothermic reduction reactions. Above charge level a temperature of
$1020-1050^{\circ}C$ is maintained by combustion of furnace gas to prevent the
reverse reaction of oxide formation from zinc vapour.

TABLE 6.   I.S.F. Gas Analyses

	Gas in furnace top	Gas leaving the charge level
CO	21.38 *	23.84
CO_2	11.43	8.68
N_2	61.00	60.67
Zn	6.39	6.71
Pb(s)	-	0.14

* 21.1% is measured by analysis

TABLE 7.   I.S.F. Heat Input

	%
C → CO) Up to charge level	26.9
C → CO₂)	38.5
Sensible heat of sinter	1.6
" " " coke	5.7
Hot blast (tuyere)	18.2
" " (top air)	1.4
CO → CO₂ in a furnace top	7.7

Heat supplied from hot blast accounts for nearly 20% of the total air. Increase in this heat increases the combustion rate of carbon and the smelting rate and thus gives the possibility of an increase in production.

CONDENSATION EFFICIENCY

The partial pressure of zinc vapour is low as it leaves the furnace. Also the $CO_2 : CO$ ratio in this gas is high, so that it would be very difficult to recover zinc in a conventional type of condenser as is used in other zinc smelting processes. In the Imperial Smelting Process zinc is adsorbed in lead as the vapour goes through a condenser where a shower of lead droplets is maintained. Zinc is separated from the zincy lead by cooling. Usually the zincy lead is taken out of the condenser with 2.26% of zinc at a temperature of $560^{\circ}C$ and returned to the condenser with 2.02% of zinc at a temperature of $440^{\circ}C$.

The condensation efficiency can be calculated theoretically by applying the activity of zinc (5). Although the theoretical efficiency suggested by Azagami (4), (6), was 93%, the actual result might be somewhat lower because it is influenced by variations in the composition and temperature of the gas, furnace condition and technique of condensation.

In Fig. 2, condensation efficiency, carbon consumption and zinc production at Befu plant are shown.

RECOVERY OF LEAD

The recovery of lead in I.S.F. has great metallurgical significance other than the economic advantage of simultaneous smelting.

Lead oxide in charge can be easily reduced in an exothermic reaction

$$PbO(s) + CO(g) = Pb(l) + CO_2(g) \qquad (7)$$
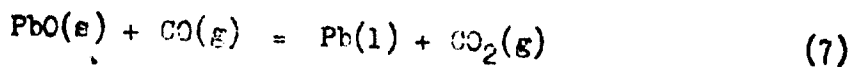
$$\Delta G = -15,600 - 2.38T$$

$$K = a_{Pb} \, P_{CO2} / a_{PbO} . P_{CO}$$

As the value of K is obtained as 2.32 at $1200^{\circ}C$, it is clearly appreciated that this reduction reaction proceeds with ease.
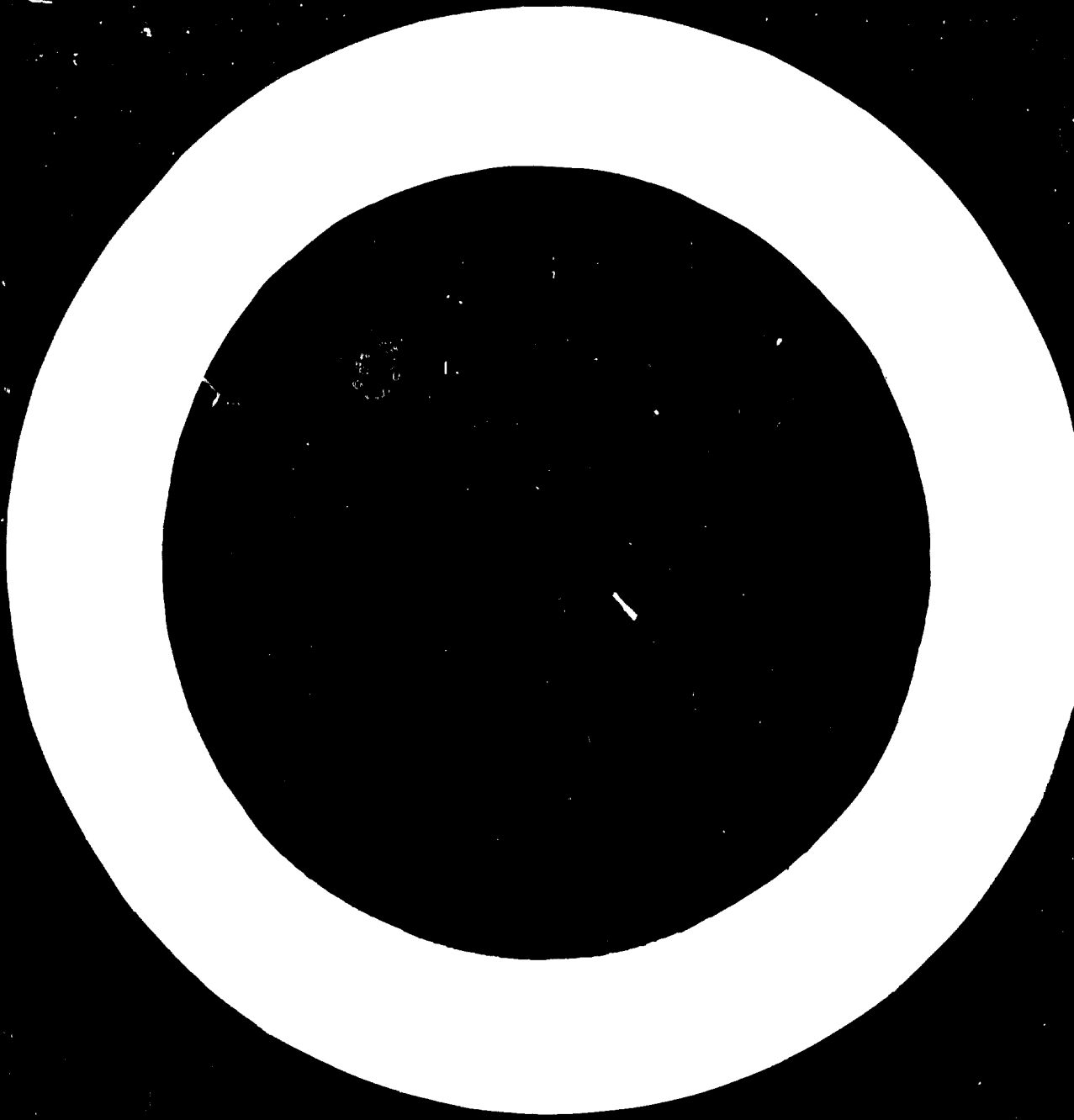
Fig. 2
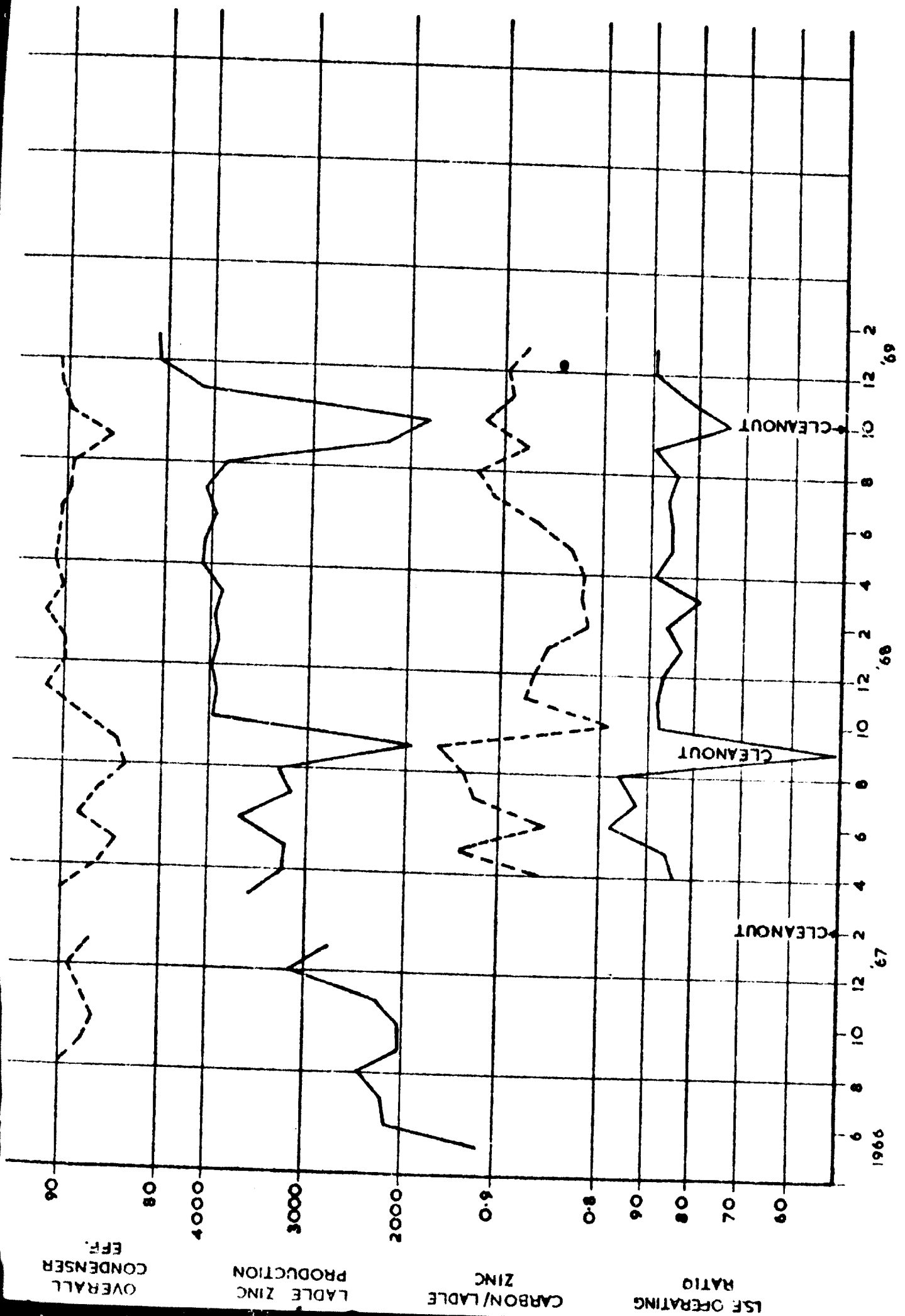
Most of the lead in charge, therefore, is reduced at the upper part of the shaft. Part of the lead sulphide and oxide reacts with zinc to form zinc sulphide which forms accretion on the walls of the shaft -

$$PbS + Zn(g) = Pb(l) + ZnS \qquad (8)$$

$$PbO + ZnS = PbS + ZnO \qquad (9)$$
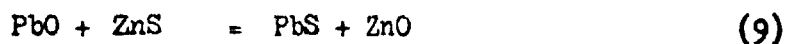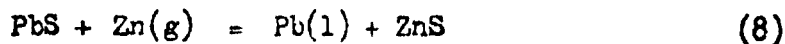
These reactions are carried out a little above the reducing zone for zinc oxide and sulphur is recirculated in some degree in the shaft. Analysis of accretion can indicate this region.

TABLE 8.   I.S.F. Accretion Composition

Distance from Roof	Zn	Pb	S	As	Fe	$Al_2O_3 + CaO = SiO_2$
3 M	60.0	12.8	0.98	0.06	2.57	3.22
4 "	61.6	16.0	0.72	0.04	2.29	2.77
5 "	58.0	17.6	0.71	0.04	2.40	4.11
6 "	29.6	12.4	3.75	0.18	3.80	17.69
7 "	27.7	14.2	6.65	0.15	15.1	20.73
8 "	38.1	14.2	2.86	0.46	9.4	16.43

(Accretion analysis in No. 1 campaign at Befu)

As shown in Table 8, there is a clear difference in the analysis of accretion above and below the 5 meter level. Thus one deduces that the reaction zone might be at the 6 to 7 meter level.

Fig. 3 shows the equations for the reactions in the shaft and factors such as Pco_2/Poo and temperature.

Metallic lead, which is reduced in the upper part of the shaft, acts as collector for copper, gold, silver, antimony and bismuth.

Another metallurgical advantage of lead in the charge is that it can increase the hardness of sinter instead of silica. Silica content in sinter can be decreased from 4% to 2.5% when lead in sinter is raised from up to 20%. This leads to a decreased slag volume, which results in decreased fuel cost and zinc loss in the slag.

A typical analysis of sinter is 19% lead, 45% zinc, 2.5% silica, 4% lime and a hardness of 80 rattler index at Befu plant.

Distribution of new lead in the I.S.F. is shown in Table 9, from recent operating results at Befu.

TABLE 9.   Lead Distribution

	Oct. 1968	Nov. 1968	Dec. 1968
Ladle zinc	3.2	3.1	3.4
Bullion	84.6	87.6	87.0
Cu Dross	9.2	6.6	6.5
Slag	0.7	0.6	0.8
Matte & Speiss	-	-	-
Unaccounted Loss	2.3	2.1	2.3

FIG. 3

Furnace Roof

Furnace Offtake

— Zn (Vapor)

Temperature

1 M 1020 - 1050°C
$PCO_2/PCO = 0.4 \sim 0.6$

2 M Top Tuyere Level
$CO + \frac{1}{2}O_2 = CO_2$
$(Zn_{(v)} + \frac{1}{2}O_2 = ZnO)$

Accretion
Constituent

3 M Tuyere Level   Fe = 2.57
$S = 0.98$ $Zn = 60.0$ 740 ~ 800°C

$PCO_2/PCO = 0.3 \sim 0.4$ $(d = Al_2O_3 \cdot CaO \cdot SiO_2)$
= 3.22

4 M Fe = 2.29 $Zn = 61.6$
$(d = 2.77)$

$RO + CO_{(g)} = Fe_{(s)} + CO_{2(g)}$

5 M Fe = 2.40 $Zn = 58.8$
$(d = 4.11)$
$800 \sim 1000°C$ $Zn_{(v)} + CO_2 = ZnO + D + CO$

$RSO_4 + CO \rightarrow RS + CO_2$
$CaSO_4 + 3CO = R + CaO + RS + 3CO_2$
$CaSO_4 + 3Zn + R = CaO + RS + 3ZnO$
$RSiO_3 == RaO + SiO_2$
$R_2C + ZnS = ZnO + RS$
$FeS + Zn_{(v)} = Fe + ZnS$

6 M Fe = 3.86 $Zn = 26.9$
$(d = 17.69)$

$PCO_2/CO = 0.6$

7 M Fe = 15.1 $Zn = 27.7$
$(d = 20.73)$

$2CO$
$ZnO_3 + CO = Zn_{(g)} + CO_2$

PCO_2 $PCO = 1.0$ 1200°C

8 M Fe = 24 $Zn = 32.1$
$(d = 6.43)$

$C + \frac{1}{2}O_2 = CO$

$PCO_2/PCO = \frac{1}{12}$ ~1400°C

Tuyere Level

9 M Tap Hole $1250 \sim 1280°C \rightarrow$ Slag

$Fe_3O_4 + CO_2 \rightarrow 3Fe_2O_3 + CO_{(g)}$
$Fe_3O_4 + 4CO_{(g)} \rightarrow 3Fe + 4CO_2$
$Fe_3O_4 + CO_{(g)} \rightarrow Fe + CO_{(g)}$

$Al_2O_3 + SiO_2 \rightarrow Al_2SiO_5$
$2CaO \cdot SiO_2 \rightarrow Ca_2SiO_4$
$2CaO \cdot SiO_2 + Al_2O_3 \rightarrow Ca_2Al_2SiO_7$
$CaO \cdot SiO_2 \rightarrow CaSiO_3$
$2FeO + 2Fe + SiO_2 \rightarrow 2FeO \cdot SiO_2$

$RSiO_3 + Fe_{(s)} \rightarrow Po_{(s)} + FeS(\ell)$
$CaS + Fe_{(s)} \rightarrow FeS$

Reaction Zone

Zinc Oxidizing Zone
Lead Oxide Reducing Zone
Sulphide Reducing
Iron Oxide Reducing
Zinc Oxide Reducing
Slag Formation
Melting Zone

Some matte and speiss are produced, but as they are not separated in the forehearth they are included in slag. Lead content in slag at Befu is found to be much less than that of the lead blast furnace.

TABLE 10.   Lead in Slag

	Oct. 1968	Nov. 1968	Dec. 1968
Pb in slag	0.43	0.33	0.43

The upper limit of lead in sinter has not been clearly determined yet, although S.E. Woods and D.A. Temple estimated it as 28% (7).

BEHAVIOUR OF SULPHUR AND COPPER

Most of the sulphur is brought into the I.S.F. from sinter and coke. These usually have sulphur contents of less than 0.8 and 0.7 respectively.

Table 11 shows sulphur distribution in No. 3 campaign of Befu I.S.F. Most of the sulphur was rejected into slag.

TABLE 11.   Sulphur Distribution during No. 3 Campaign at Befu

	Performance Period	
	High S Cokes	
	8th Apr.-1st May	28th Feb.-31st Mar.
INPUT		
Sinter Cake	59.1	61.5
Flux Bath Dross	0.1	
Slag from Rev. Furnace		6.4
Coke No. 1	40.4	
Coke No. 2	0.4	32.1
Total	100.0	100.0
OUTPUT		
Dross from bullion	2.3	2.6
Blue Powder	13.6	5.1
I.S.F. Dross	3.4	2.6
Flux Bath Dross	0.3	
Slag	67.0	71.8
Matte and Speiss	10.0	11.5
Total	96.6	93.6
Loss	3.4	6.4

* High sulphur coke   S:1.3%

TABLE 12.   Sulphur in Slag

	No. 1 Campaign	No. 2 Campaign	No. 3 Campaign
S in Slag %	3.29	2.53	2.54

Sulphur in slag is inferred to exist in solution with $Fe_{(1-x)}O$, because the reducing atmosphere in the shaft is very strong.

Some sulphur is combined with matte, the analysis of which is as shown in Table 13.

TABLE 13. Speiss and Matte Analysis during No. 1 Campaign at Befu

	Cu	Fe	Zn	S	Pb	As	Co	Au g/t	Ag g/t
Speiss	2-4	60	4-5	2	1-5	18-23	4-7	0.3-0.5	60-260
Matte	3-5	50	4-7	15	2-5	0.n-1	0.7	0.3-0.5	60-360

Assuming that matte is in equilibrium with molten lead, the composition of matte is obtained by calculation as shown in Table 14.

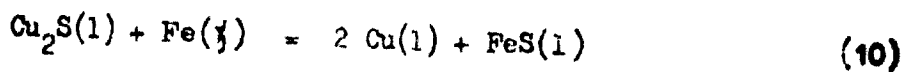TABLE 14.   Calculated Matte Composition

Cu_2S	PbS	ZnS	FeS	FeO
3.75-6.28	2.3-5.7	5.96-10.51	32.89-28.88	37.2-39.8

Table 15 shows the calculated copper content of lead bullion which is in equilibrium with the matte.

TABLE 15.   Copper in Lead Bullion

No. 1 Campaign	No. 2 Campaign	No. 3 Campaign
2.07%	2.15%	1.87%

Value of activity of iron can be obtained as follows:-

$$Cu_2S(l) + Fe(\mathfrak{z}) = 2 Cu(l) + FeS(l) \qquad (10)$$

$$\Delta G = -10,610 + 9.74T \quad (8)$$

$$K_1 = a^2_{Cu} \cdot a_{FeS}/a_{Cu_2S} \cdot a_{Fe}$$

$$FeO(l) + CO(g) = Fe(\mathfrak{z}) + CO_2 (g)$$

$$\Delta G = -10,430 + 9.11T$$

$$K_2 = a_{Fe} \cdot P_{CO_2}/a_{FeO} \cdot P_{CO}$$
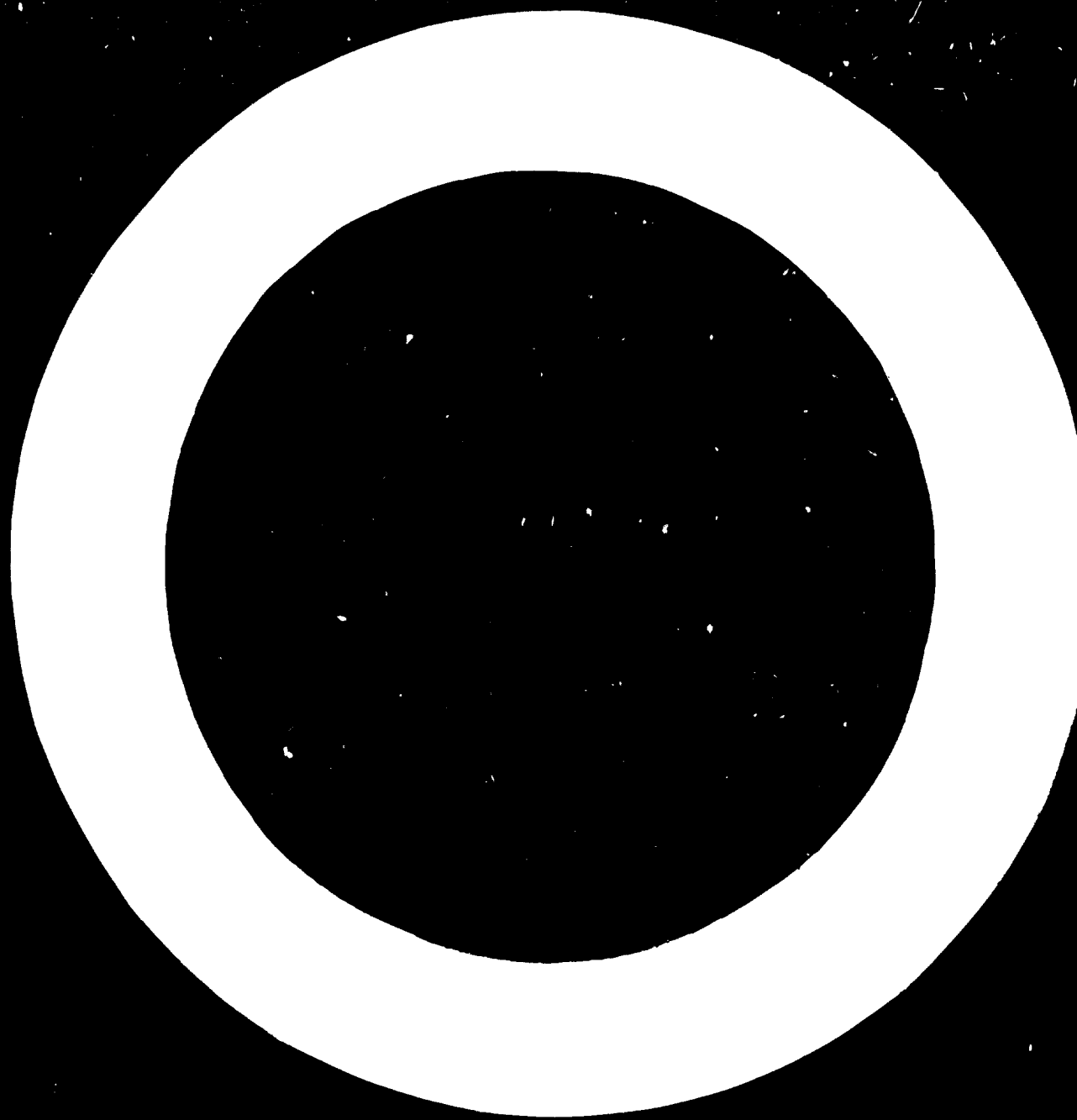
Taking the value of activity of copper as 0.025 from the solution activity curve for the Cu-Pb system and the value of K_1 as 0.28 in equation (10), then a value for the activity of iron of 0.3 is obtained. A satisfactory correlation between this theoretically determined activity and the activity determined from practical considerations is obtained as indicated below.

Since the value of the activity of FeO is estimated to be approximately 0.4 in the I.S.F., the relation between value of the activity of iron and the partial pressure ratio of $CO_2:CO$ is as shown in Table 16.

TABLE 16. Relationship between a_{Fe} and Pco_2/Pco

a_{Fe}	1	0.8	0.5	0.3	0.1
Pco_2/Pco	0.114	0.143	0.228	0.38	1.14

In actual operation as $Pco_2:Pco$ is estimated to be 0.3 to 0.4, a_{Fe} will be 0.3 to 0.5.

Kaneta and Yazawa [6] determined copper in lead and lead in matte at various values of Pco_2/Pco at $1200°C$. The copper content in lead is about 2% at a Pco_2/Pco ratio of 0.28 ($a_{Fe} = 0.3$). As Pco_2/Pco goes down, copper in lead increases much more and lead in matte goes down.

The above shows that in the I.S.F. copper cannot be completely reduced into matte but must be dissolved in bullion to be recovered.

TABLE 17. Copper Distribution at Befu

	No. 1 Campaign	No. 2 Campaign	No. 3 Campaign
Ladle Zinc	-	-	-
Bullion	6.8	0.5	9.3
Speiss and Matte	8.2	10.0	3.2
Slag	21.3	20.1	22.2
Copper Dross	68.2	61.5	62.0
Blue Powder	2.6	0.3	1.3
Others	0.7	0.2	
Loss	-7.8	7.4	2.0
Total	100.0	100.0	100.0

Sulphur, which is charged in the furnace, recirculates inside the shaft and causes accretion formation. It is clear from Table 11 that sulphur is brought in by sinter and coke. The analysis in Table 8 indicates that sulphur plays some part in accretion formation. As shown in Fig. 5, increasing sulphur in sinter has a deleterious effect on the furnace such as increase of blast pressure by accretion formation, high carbon consumption and higher zinc loss.

According to P.M.J. Gray [9], matte is expected to form with low content of copper, only when sulphur in sinter is more than 1.5%. This depends upon the activity of FeO in slag. In order to obtain matte with high content of copper, activity of FeO in slag has to be decreased as much as possible [8].
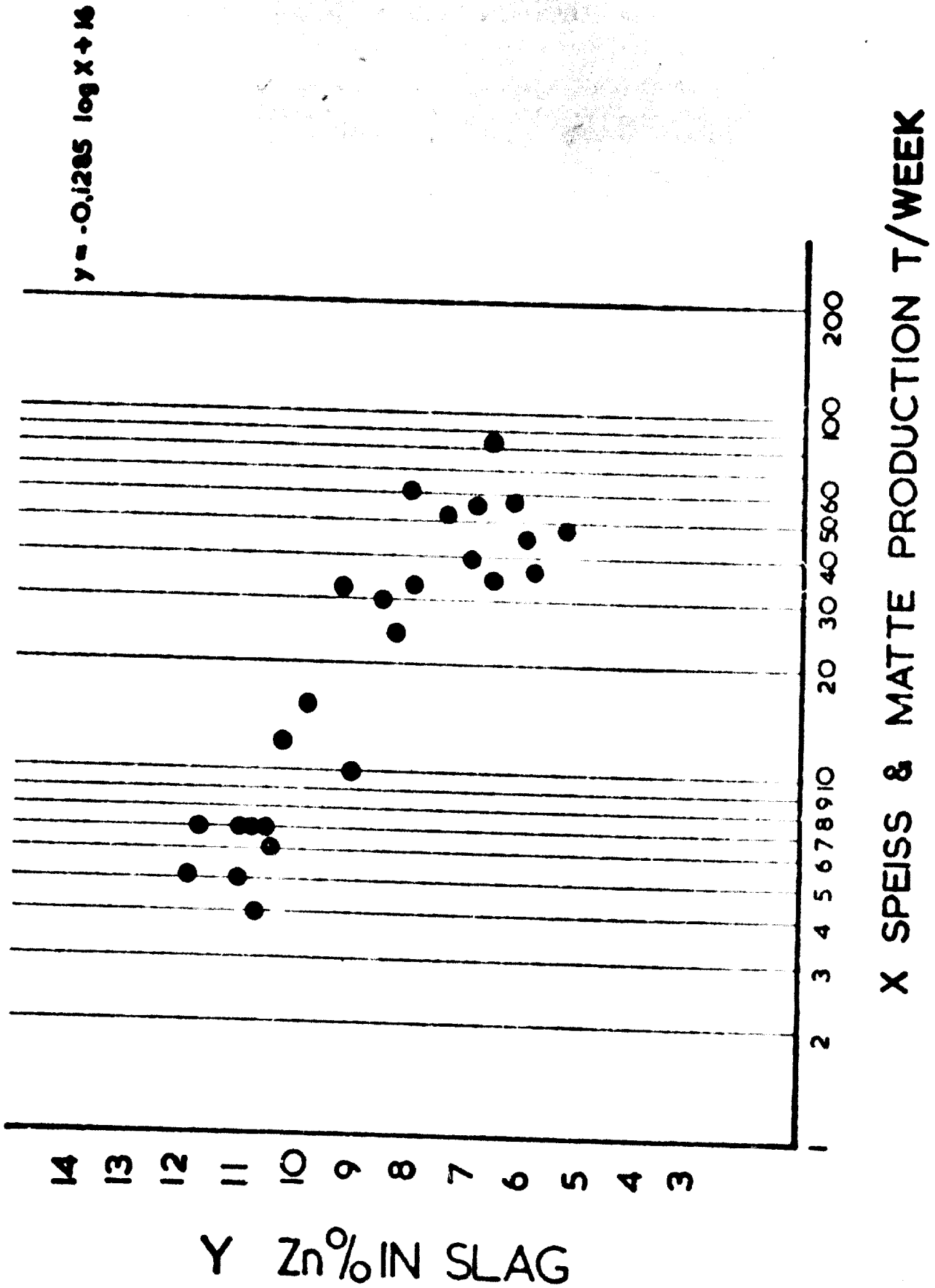
Fig. 4

y = -0.1285 log x + 16

X SPEISS & MATTE PRODUCTION T/WEEK

Y   Zn% IN SLAG

Fig. 5

Sinter in Sinter — Bustle Main Pressure, Carbon Consumption and Zinc in Slag

Fig. 4

$y = -0.1285 \log x + 16$
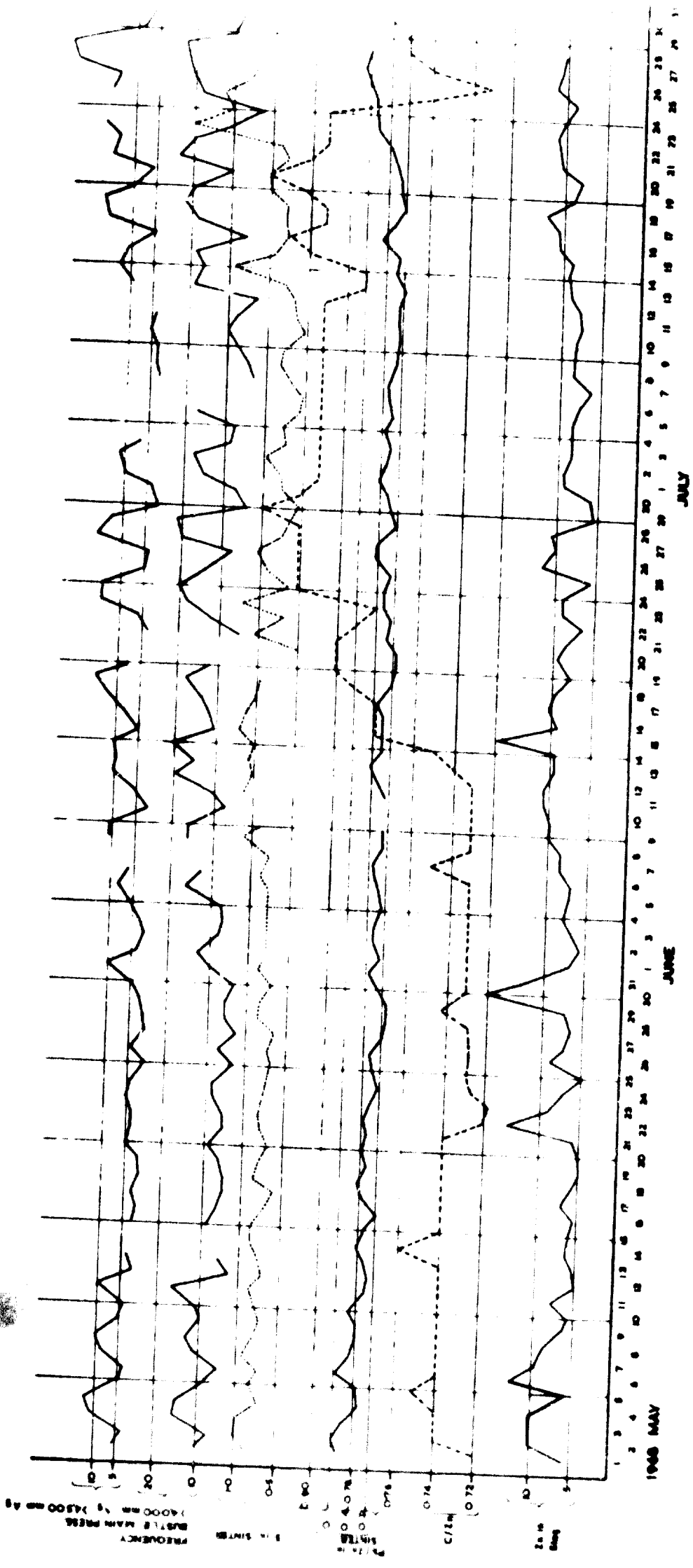
Y Zn% IN SLAG
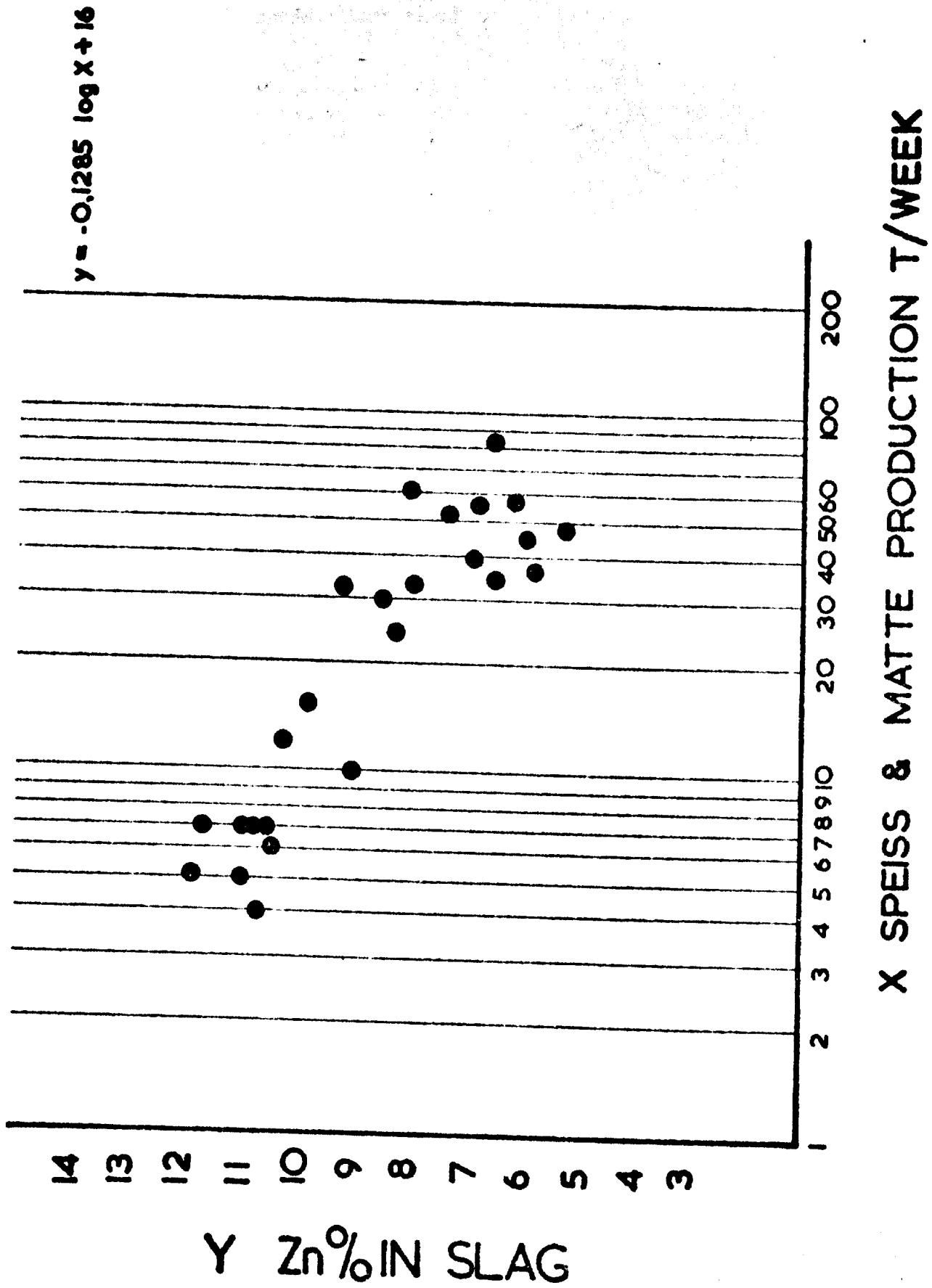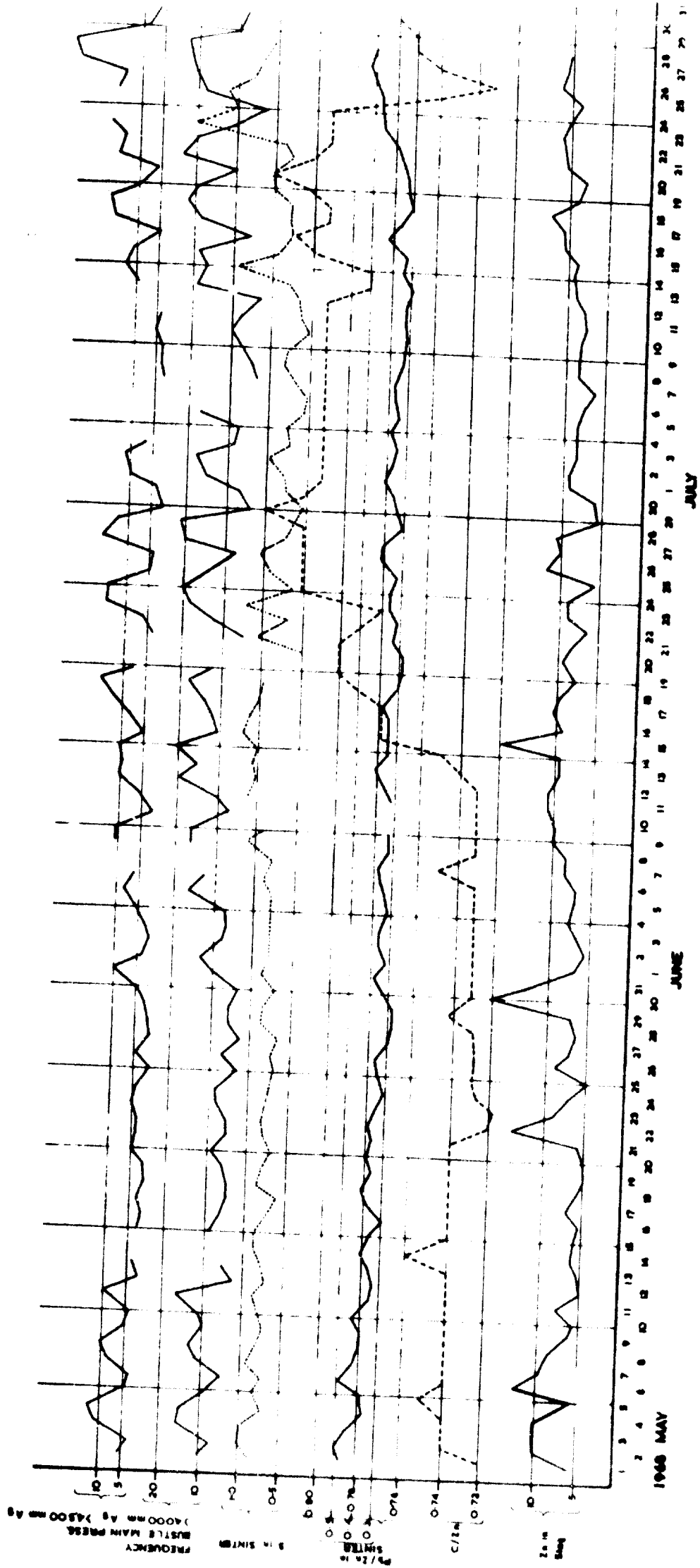
X SPEISS & MATTE PRODUCTION T/WEEK

Fig. 5

Sulpher in Sinter — Bustle Main Pressure, Carbon Consumption and Zinc in Slag

BEHAVIOUR OF IRON

The behaviour of iron in the I.S.F. is very important when discussing slag and matte formation. As mentioned before, it is controlled by the reducing conditions, i.e. Pco_2/Pco, in the shaft. Ferrous oxide, made in the lower part of the shaft, in combination with silica, forms fayalite. Some goes into matte.

Another important consideration is the removal of arsenic as speiss.

TABLE 18.   Distribution of New Arsenic

	%
Matte and Speiss	61.5
Slag	5.7
Ladle Zinc	1.3
Cu dross	18.2
Bullion (after drossing)	10.1
Others	3.2
Total	100.0

When speiss exists as a third layer between slag and bullion, it can be taken out via the forehearth. It is noticeable that cobalt and nickel are concentrated into speiss.

Zinc content in slag has a positive correlation with FeO content in slag and a negative correlation with matte and speiss formation (see Fig. 4). This means that the stronger the reducing atmosphere, more FeO in slag decreases and matte and/or speiss formation increases.

Although it is desirable to keep FeO content and amount of slag as low as possible, a target of FeO content is stipulated of 36% because the slag from our plants is supplied to a producer of Portland cement as a source of iron.

FLUORINE AND CHLORINE BALANCE

Fluorine and chlorine in ores and fluxes are often problems in the Imperial Smelting Process. Fluorine particularly would attack the lead-lined venturi scrubber in our Sinter Plant and silicon carbide in I.S.F.

Most of the chlorine is put into I.S.F. from raw materials, flux bath dross and chlorine gas at the effluent treatment plant. Chlorine balances for our plant in No. 2 and No. 3 campaigns were made. Though it has been stated that chlorine could improve condensation efficiency, this relation is not clear yet.

Fluorine is mainly introduced into the I.S.F. from sinter, and most of it is returned to the sinter plant in blue powder, as shown in Table 22, although 22% of it is rejected with slag. The behaviour of fluorine is a clear contrast with that of chlorine which is removed in solution in effluent discharge.

In Table 19 the fluorine balance for the Sumiko I.S.F. is shown.
Tables 20 and 21 show chlorine balances for the works and for the I.S.F.
respectively.

TABLE 19. I.S.F. Fluorine Balance (Jan. 1968)

	Distribution %
INPUT	
Sinter Cake	99.53
Flux Bath Dross	0.47
Total	100.00
OUTPUT	
Slag	21.73
I.S.F. Dross	9.12
Flux Bath Dross	0.47
I.S.F. -- Hygiene	0.77
Blue Powder	63.14
I.S.F. - Loss	4.77
Total	100.00

TABLE 20.   Works Chlorine Balance (Dec. 1968)

	Distribution %
INPUT	
Sinter Cake	3.9
Hygiene Dust	6.6
Flux (NH_4Cl)	32.6
Cd-spent solution	55.3
Cl_2 gas	1.4
New water	0.2
Total	100.0
OUTPUT	
Overflow from Neutralisation Thickener to sea	84.1
Blue Powder and gondola	0.9 + 0.1 = 1.0
Slag	0.3
I.S.F. Dross	5.6
Sludge to sinter plant	4.2
Evaporation loss from cooling tower	3.7
Venturi loss	0.5
Unaccounted loss	0.6
Total	100.0

TABLE 21.   I.S.F. Chlorine Balance

	Distribution %
INPUT	
Sinter Cake	7.1
Flux Bath dross	34.5
Ammonium chloride	58.4
Total	100.0
OUTPUT	
I.S.F. Dross	10.0
Slag	0.6
Flux Bath dross	34.5
Condenser exhaust gas & hygiene dust	41.3
Washing & hygiene gas and dust	12.5
Unaccounted loss	1.1
Total	100.0

11/RWL/IMO
10.4.1969

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