

STUDIES ON DESULPHURISATION OF PIG IRON WITH SODIUM,  
RARE EARTH METALS AND SLAGS RICH IN CERIUM OXIDE

STUDIES ON DESULPHURISATION OF PIG IRON WITH SODIUM,

RARE EARTH METALS AND SLAGS RICH IN CERIUM OXIDE

By

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A Thesis

Submitted to the Faculty of Graduate Studies

in Partial Fulfilment of the Requirements

for the Degree

Master of Engineering

McMaster University

September 1969

MASTER OF ENGINEERING  
(Metallurgy)

McMASTER UNIVERSITY  
Hamilton, Ontario

TITLE: Studies on Desulphurisation of Pig Iron with Sodium,  
Rare Earth Metals and Slags Rich in Cerium Oxide

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NUMBER OF PAGES: ix, 28

SCOPE AND CONTENT:

An experimental evaluation of three desulphurisers for pig iron has been conducted. Sodium vapor, blast furnace slag enriched with cerium oxide and a rare earth alloy named misch metal have been used.

### ACKNOWLEDGEMENTS

The author is indebted to Professor W-K. Lu for his supervision and advice during the progression of this work and to Dr. B. Strathdee of Dominion Foundries and Steel Ltd. for his assistance.

The author wishes to express his appreciation of the financial support which was provided by an N.R.C. postgraduate scholarship.

Grateful acknowledgements are given to the staff and graduate students of the Department of Metallurgy and Materials Science, McMaster University.

The cooperation of the staff of Dominion Foundries and Steel Ltd., in particular of Mr. S. Smith for his probe work and of Mr. W. Van de Vrande for his chemical analysis, is gratefully appreciated.

Many thanks are given to Dr. R. Meadowcroft of the Steel Company of Canada and to Mr. W. Wilson of Molybdenum Corporation of America for respectively supplying the Ceralloy and the rare earth silicide.

Finally the author wishes to express his appreciation for the understanding given to him by his wife.

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## CHAPTER 1

### INTRODUCTION

With the exception of a few grades of free cutting steels where it is deliberately added, sulphur is considered as an undesirable impurity of steel because it lowers the mechanical properties and contributes to many defects. The sulphur level in steel depends on its level in raw materials and on its removal from the metal before or during the steelmaking operation. The present trend is for the user to demand lower sulphur levels while the blast furnace uses coke of increasing sulphur content. In the coming years more steel producers will rely on the basic oxygen process which has limited capacity in removing sulphur from the metal phase in its standard operation. The fluctuations in the sulphur content of blast furnace iron from one cast to another is also a problem that requires some form of sulphur control. For the purpose of lowering the sulphur level in hot metal for steelmaking, it is desirable to study various methods of desulphurisation of pig iron outside the blast furnace.

As indicated in Figure 1, rare earth sulphides are thermodynamically very stable and are solid at  $1600^{\circ}\text{C}$ ; hence, it may be expected that, following the addition of rare earth elements, sulphides can be readily formed and separated, leaving a low sulphur level in the melt. The residual rare earth metals will be easily removed from the melt in any subsequent oxidation process.

According to the thermodynamic properties of sodium sulphide, sodium can desulphurise a pig iron melt. Because of its low cost, sodium could be an attractive industrial desulphuriser.

During preliminary experiments reported in Appendix 2, a loss of sulphur from the slag and the formation of  $\text{SO}_2$  were observed as the rare earth sulphides contained in the slag reacted with the oxygen from the atmosphere. Based on this, it was thought that rare earth oxides could act as carriers taking the sulphur from the metal to the slag and subsequently to the atmosphere.

The aim of this project is to study the engineering practicality of the following methods for desulphurisation:

- I) bubbling sodium vapor through a pig iron melt with and without a slag cover.
- II) adding rare earth metals to a pig iron melt covered with blast furnace slag.
- III) adding one part of cerium oxide to three parts of blast furnace slag and using this slag to desulphurise a pig iron melt.

Although many desulphurisation techniques are available, the final choice is always a matter of cost and particular requirements of each individual steel producer.

## CHAPTER 2

### LITERATURE REVIEW

Many investigations on desulphurisation of pig iron outside the blast furnace have been reported. Schulz (1969) summarized all the previous work indicating the methods for which there was industrial experience in treating at least 100 tons at a time to a sulphur level below 0.015 wt%. The use of  $\text{CaO}$ ,  $\text{CaC}_2$ ,  $\text{Na}_2\text{CO}_3$  and the description of the techniques involved are thus included. Typical results, taken from Schulz's work, indicate a reduction from 0.050 wt% to 0.008 wt% in pig iron sulphur content with the addition of 13 lbs/ton or about \$1 worth of calcium carbide; the  $\text{CaC}_2$  injection in the melt takes about 15 min. Gruver (1969) reports the rate of desulphurisation obtained with nitrogen stirring of calcium carbide in pig iron; the sulphur content is reduced from 0.100 wt% to 0.008 wt% in less than 3 min. with a 1 wt% addition and in less than 1.5 min. with a 2 wt% addition of  $\text{CaC}_2$ . Low sulphur iron for the foundry is thus prepared at a cost of \$2 to \$3/ton and used for the production of nodular cast iron.

A few investigations concerning the desulphurisation of steel with calcium, lithium, magnesium and rare earth metals are reported: Barnard (1967), Beaulieu, Chaillou and Olette (1963), Berger and Snellman (1954) and Colling (1962).

No reference to the use of sodium in iron or steelmaking was found, but Beaulieu (1963) in his work with lithium in steel has found that lithium is a very good deoxidiser and desulphuriser. Starting with

0.100 wt% oxygen and 0.020 wt% sulphur, he obtained 0.002 wt% oxygen and 0.005 wt% sulphur with a 0.5 wt% addition of lithium. This author also mentioned the volatility of lithium at steelmaking temperatures and the difficulties encountered in adding it to a melt.

The use of magnesium to desulphurise pig iron is reported by Polochenko (1964) while the use of rare earth metals is reported by Vashukov (1962).

Pokhvisnev, Sharov and Inozemtsev (1962) mentioned the possibility of blowing blast furnace slag with air or oxygen and to reuse it as a desulphuriser while Chuchmarev, Esin and Dobryden (1961) studied the kinetics of sulphur oxidation during oxygen blowing of the slag.

Concerning the use of rare earth metals, Richerd (1962) calculated that 0.0003 wt% lanthanum would be in equilibrium with 0.001 wt% sulphur at 1600°C while 0.12 wt% cerium was experimentally found to be in equilibrium with the same level of sulphur. The value of 0.12 wt% cerium is taken from the work of Langenberg and Chipman (1958) who found the value of  $1.5 \pm 0.5 \times 10^{-3}$  for the solubility product wt% Ce x wt% S at 1600°C. This last result was confirmed by the work of Schindlerova and Buzek (1965).

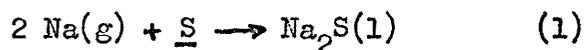
Chipman (1952) mentioned that the activity coefficient of sulphur in pig iron is 5 to 6 times that of sulphur in steel. Richardson and Jeffes (1948, 1952) made available the standard free energy of formation of CeS and CeO<sub>2</sub> as a function of temperature.

## CHAPTER 3

### THERMODYNAMIC CALCULATIONS

#### 3.1 Sodium Vapor as a Desulphuriser

The desulphurisation of pig iron by sodium vapor can be described by the following reaction.



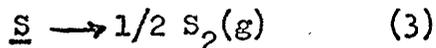
Where  $\underline{\text{S}}$  represents sulphur dissolved in iron.

Thermodynamic properties of reaction (1) can be obtained from the data on standard free energy of formation of sodium sulphide and the free energy of solution of sulphur in iron.



By extrapolation of the data of Richardson and Jeffes (1952) by about  $300^\circ\text{K}$ ,  
at  $1773^\circ\text{K}$ ,  $\Delta G_2^\circ = -29,000 \pm 5,000$  cal.

Where the standard state for  $\text{Na}_2\text{S}$  is the pure liquid phase. The standard free energy change of the following reaction was reported by Ban-ya and Chipman (1968)



at  $1773^\circ\text{K}$ ,  $\Delta G_3^\circ = 22,350 \pm 1,000$  cal.

Where the standard state for sulphur in solution is 1 wt%  $\underline{\text{S}}$ .

The standard free energy change of reaction (1) is the sum of the corresponding values for reactions (2) and (3).  
at  $1773^\circ\text{K}$ ,  $\Delta G_1^\circ = -6,650 \pm 6,000$  cal.

$$\text{Then, } K_1 = \frac{a_{\text{Na}_2\text{S}}}{p_{\text{Na}}^2 \cdot a_{\text{S}}} = e^{-\frac{\Delta G^\circ}{RT}}$$

As pure  $\text{Na}_2\text{S}$  always forms at the gas-liquid interface,  $a_{\text{Na}_2\text{S}} = 1$  and the activity coefficient of sulphur in hot metal may be taken as 5.5 as reported by Chipman(1952). The above expression is thus simplified to:

$$p_{\text{Na}}^2 \times \text{wt\% S} = 1/5.5 \times e^{-\frac{\Delta G^\circ}{RT}}$$

Taking  $\Delta G_1^\circ$  by its mean value of  $-6,650$  cal.,

$$p_{\text{Na}}^2 \times \text{wt\% S} = 0.028$$

By introducing the temperature dependence of the standard energy of formation of  $\text{Na}_2\text{S}$  and of the free energy of solution of sulphur in iron, it is possible to obtain equilibrium values for other temperatures. Some results for different temperatures and different  $p_{\text{Na}}$  are reported below:

Pig Iron Temperature in °C	Sodium Pressure in atm.	Equilibrium Sulphur in wt%
1400	1	0.004
1400	3	0.00044
1500	1	0.0275
1500	3	0.003
1600	1	0.154
1600	3	0.017

### 3.2 The Solubility Product wt% Ce x wt% S

Langenberg and Chipman (1958) melted electrolytic iron in CeS crucibles and sampled the melt after different times. At first neither cerium nor sulphur was added to the melt and they observed little pickup of either elements from the crucible. In order to obtain their solubility product, they relied on experiments with cerium added to melts held in CeS, Al<sub>2</sub>O<sub>3</sub> and MgO crucibles.

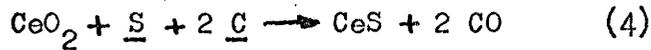
Taking the value of  $1.5 \pm 0.5 \times 10^{-3}$  they obtained for the solubility product wt% Ce x wt% S in pure iron at 1600°C and considering the activity coefficient of sulphur in pig iron to be 5.5, one finds:

$$\text{wt\% Ce x wt\% S (at 1600}^\circ\text{C in pig iron)} = 0.3 \pm 0.1 \times 10^{-3}$$

### 3.3 Approximate Stoichiometry of Rare Earth Sulphides

Appendix 1 gives the atomic weight of the rare earth elements and the average atomic weight of misch metal. It also gives the sulphur content of the three possible cerium sulphides. From this data, in the light of the uncertainty about the reaction products, it is assumed that the sulphides contain on the average 80 wt% REM and 20 wt% S. In absence of accurate information, such composition of sulphides will be used as a guide line in further calculations.

### 3.4 The Relative Strength of CeO<sub>2</sub> and CaO as Desulphurisers



Where the standard state for sulphur in solution is a 1wt% solution and where the standard state for C is pure C.

$$\Delta G_4^\circ \text{ at } 1700^\circ\text{K} = -42,500 \text{ cal.}$$

$$\Delta G_4 = RT \ln K_4^* + \Delta G_4^\circ$$

$$\text{with } K_4^* = \frac{(p_{\text{CO}})^2 \cdot a_{\text{CeS}}}{a_{\text{CeO}_2} \cdot a_{\underline{\text{S}}} \cdot (a_{\underline{\text{C}}})^2} \approx \frac{a_{\text{CeS}}}{a_{\text{CeO}_2} \cdot a_{\underline{\text{S}}}}$$


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Where the standard state for sulphur in solution is 1 wt% S and where the standard state for C is pure C.

$$\Delta G_5^\circ \text{ at } 1700^\circ\text{K} = -18,680 \text{ cal.}$$

$$\Delta G_5 = RT \ln K_5^* + \Delta G_5^\circ$$

$$\text{with } K_5^* = \frac{p_{\text{CO}} \cdot a_{\text{CaS}}}{a_{\text{CaO}} \cdot a_{\underline{\text{S}}} \cdot a_{\underline{\text{C}}}} \approx \frac{a_{\text{CaS}}}{a_{\text{CaO}} \cdot a_{\underline{\text{S}}}}$$

Taking a<sub>S</sub> as being the same in both cases and choosing a<sub>CeS</sub>/a<sub>CeO<sub>2</sub></sub> equal to a<sub>CaS</sub>/a<sub>CaO</sub>, CeO<sub>2</sub> would be a better desulphuriser than CaO because  $\Delta G_4$  would be more negative than  $\Delta G_5$ .

## CHAPTER 4

### EXPERIMENTAL CONSIDERATIONS

#### 4.1 Description of Apparatus

All experiments were carried out in induction furnaces. Figure 2 shows the essential features of the apparatus. For the three types of experiments described in Chapter 1, the setup is essentially the same and consists of:

- I) a graphite crucible or a magnesia lining of equal capacity surrounded by an induction coil not shown in Fig. 2
- II) a graphite thermocouple sheath containing a mullite sheath and a Pt/Pt-13pct Rh thermocouple.
- III) a graphite tube to bubble argon through the melt.

For an experiment with a cerium oxide rich slag, one simply replaces the misch holder (item 7) in Fig. 2 by cerium oxide. Fig. 3 shows the purification train which goes on the argon line before the argon bubbler (item 1) in Fig. 2. Figures 4 and 5 show the stainless steel vessel that is placed in the argon line before the graphite tube in the case of sodium experiments. To use the apparatus shown in Fig. 2 for a sodium experiment, one removes the slag and the misch holder (items 6 and 7) and adds the stainless steel vessel shown in Fig. 4 on the argon line before the argon bubbler.

Figure 6 shows the sampling instruments and the samples taken from a run. The instruments for temperature measurement are shown

in Figure 7.

#### 4.1.1 Power Source

Power was supplied from a 30 KVA, 3,000 C.P.S. Tocco generator to an 8" O.D. water-cooled induction coil made up from 0.5" diameter copper tubing. At Dominion Foundries and Steel Ltd., the unit used was a 100 KVA generator.

#### 4.1.2 Crucibles

The metal-slag system was contained in a graphite crucible machined from Union Carbide grade CS graphite rod. One size of crucible was used; the outside dimensions were 5" dia. by 7" high and the inside dimensions were 4" dia. by 6" deep. Some experiments where little or no slag was used were done in a magnesia lining; such a furnace lining was used at Dofasco\*.

#### 4.1.3 Argon Supply

The argon used was purified by passing it through Drierite, silica gel and magnesium perchlorate for water removal and through titanium chips at 875°C for oxygen removal. The gas train used is shown in Fig. 3. At Dofasco a commercial grade of argon was used.

#### 4.1.4 Furnace Atmosphere

No cover was used on the crucible so the atmosphere above the melt was mainly air with some CO and CO<sub>2</sub> due to the oxidation of the graphite components used.

\*Dofasco stands for Dominion Foundries and Steel Ltd.

## 4.2 Experimental Techniques

### 4.2.1 Temperature Measurements

In all cases a Pt/Pt-13pct Rh thermocouple was used; it was encased in a mullite sheath which in turn was protected from the melt by a graphite sheath. The thermocouple was connected to a chart recorder. The only reliable temperature measurements were obtained when the power to the coil was momentarily turned off.

### 4.3 Materials

#### 4.3.1 Metal Charge

In all cases pig iron supplied by Dofasco was melted. The analysis of this pig iron was: 3.8-4.0 wt% C, 0.75-0.84 wt% Si, 1.11-1.21 wt% Mn, 0.013-0.015 wt% S. Between 3 and 7 Kg of iron were used in McMaster experiments while 300 lbs. was charged at Dofasco for the D-1, D-2 and D-3 experiments.

#### 4.3.2 Slags

One large sample of crushed blast furnace slag was obtained from Dofasco and used throughout this work. This slag had the following composition: 33.8 wt% CaO, 35.9 wt% SiO<sub>2</sub>, 13.4 wt% MgO, 8.5 wt% Al<sub>2</sub>O<sub>3</sub>, 0.2 wt% Mn and 0.2 wt% Fe. In most cases the slag was simply remelted over the iron, but in some cases cerium oxide was added to it. In those cases Fisher Scientific C-257 purified ceric oxide (CeO<sub>2</sub>) was used. In experiment S-6 an addition of silica sand was made to the slag. The slag weight was from 4 wt% to 8 wt% of the metal charge.

### 4.3.3 Additions

Two rare earth alloys were added to pig iron melts. The first one has the technical name misch metal and the commercial name Ceralloy. It is manufactured by Cerium Metals and Alloys Division of Ronson Metals Corporation and given to us by the Research Dept. of the Steel Company of Canada. The composition of this alloy is: 45-50 wt% Ce, 22-25 wt% La, 18 wt% Nd and 5 wt% Pr for a total of 94-98 wt% rare earth metals. At the present time, it sells for \$3/lb. The other alloy is a rare earth silicide supplied by Molybdenum Corporation of America and has the following composition: 0.26 wt% C, 29.48 wt% Si, 35.22 wt% Fe and 33.60 wt% rare earth metals. The rare earth fraction of the silicide has the analysis of misch metal. The price per pound of silicide is \$0.5 in the present conditions of the market.

For the sodium experiments, a laboratory grade of sodium was used. The industrial price for sodium is about \$0.25/lb.

## 4.4 Sampling

### 4.4.1 Metal Samples

A suction sampling technique was employed which involved the use of 2mm I.D.-3mm O.D. silica tube attached to an aspirator bulb. Metal samples in the form of thin rods were obtained and checked for sulphur segregation as shown in Appendix 4.

### 4.4.2 Slag Samples

Slag samples were obtained by dipping the end of a cold copper rod 1/2" dia. in the liquid slag for a few seconds. Very good slag

buttons were obtained and were used for sulphur determination and in some cases for slag analysis. The slag buttons were always used in the powdered form, the entire sample being crushed and grounded in a mortar.

#### 4.5 Analysis

##### 4.5.1 Sulphur Analysis

The sulphur analysis was carried out in a Leco 518 titrator by a combustion-iodometric method. Details of the procedure can be found under A.S.T.M. method E 30-47. Solutions of approximately 0.15 grams/litre and 1.2 grams/litre of potassium iodate were used for metal and slag analysis respectively. National Bureau of Standards samples 14-D, 16-D and 8i were used to standardize the titrating solution. Appendix 3 shows the deviation obtained by analysing 7 samples of standard 16-D.

##### 4.5.2 Slag Analysis.

The slags were analysed by Mr. W. Van de Vrande of Dofasco on an atomic absorption spectrophotometer using Dofasco methods and standard samples.

#### 4.6 Experimental Procedure

##### 4.6.1 Melting of Pig Iron Charge

In all cases the pig iron was charged in the cold crucible before the power was turned on. The charge was melted in about 30 minutes and was then skimmed of all the non-metallic released during melting.

#### 4.6.2 Introduction of the Thermocouple

After the charge melted, the graphite sheath containing the mullite sheath and the thermocouple was lowered into the melt.

#### 4.6.3 Argon Bubbling and Misch Metal Addition

When the thermocouple was in place, the graphite tube was introduced in the melt and the argon bubbling started. In the experiments D-1, D-2 and D-3, a porous plug located in the bottom of the lining was used to bubble argon. The slag was then charged and melted. To add the misch metal, a special graphite holder was made by drilling an 1/2" dia. axial hole in a 1" dia. graphite rod; smaller holes were drilled so as to make openings all around the top of the cavity. At the time of addition, the holder was lowered rapidly into the melt and held there so that the misch metal would melt, escape through the top and bottom of the cavity and dissolve in the pig iron melt. The oxidation of rare earth metals at the surface of the melt was always observed at the time of addition.

#### 4.6.4 Argon Bubbling and Sodium Addition

For the experiments where sodium was used, the vessel shown in Fig. 5 was washed with alcohol, dried and kept in an air conditioned room. The sodium charge was cut from a large ingot using a steel knife, weighed and transferred to the vessel. The cap was then replaced and tightened. The vessel was then taken to the furnace room, connected to the argon line and kept with its graphite snorkel submerged in a pool of dibutyl phthalate. It was later intro-

duced in the heating furnace located above the melt; as soon as it was in position, the argon started to bubble through the melt. The heating of the vessel was then started so as to obtain the temperature required for the sodium to vaporize and be carried to the melt by the argon flow. The vapor pressure of sodium as a function of temperature is given in Appendix 5 while the temperature of sodium as a function of time is shown in Fig. 13.

#### 4.6.5 Argon Bubbling and Addition of Slags Rich in $\text{CeO}_2$

In these experiments the procedure was the same as that for the misch metal experiments except that after charging the slag, no other addition was made. Details of run J-22 found in Table 19 show that the slag-air interface was blown with air during periods of that experiment.

## CHAPTER 5

### RESULTS OF EXPERIMENTS

#### 5.1 Introduction

Three experiments using sodium as a desulphuriser were carried out which were designated S-4, S-5 and S-6. The results of preliminary experiments using cerium, misch metal and misch metal silicide additions were erratic because no argon bubbling was used and are summarized in Appendix 2. In Section 5.3, only the experiments with argon bubbling are reported (J-30, J-31, A-4, D-1, D-2 and D-3). The first three experiments were carried out at McMaster University with graphite crucibles containing from 3 to 6 Kg of pig iron. The last three experiments were carried out at Dofasco using a rammed magnesia lining and 300 lbs. of pig iron; the three experiments actually were the results of three sequential additions of misch metal to the same melt. The relative effectiveness of ordinary blast furnace and  $\text{CeO}_2$  rich slag for desulphurisation are studied by comparing experiments A-3 and A-5, A-3 being a reference experiment where only blast furnace slag was used. The results of experiment J-22 with soft air blowing of the  $\text{CeO}_2$  slag are also reported.

#### 5.2 Sodium as a Desulphuriser

In these experiments sodium vapor was carried by argon and bubbled through a pig iron melt. Tables 1 to 4 give the details of each of these runs. The results are also presented in Figures 12 and 15 and summarized below:

Experiment No.:	S-4	S-5	S-6
Initial Sulphur in wt%:	0.036	0.041	0.140
Final Sulphur in wt%:	0.030	0.031	0.030
Sodium Added in lbs./ton:	6.98	7.10	11.3
Temperature of Pig Iron in °C:	1350-1450	1350-1450	1450-1550

Figure 13 gives the sodium temperature as a function of time, the time zero corresponding to the introduction of the graphite snorkel in the melt. Figure 14 gives the pig iron temperature as a function of time for experiment S-5; as shown in this Figure, a pig iron temperature of 1350-1450°C is maintained throughout experiment S-5 and similar results were obtained for the other experiments.

The sodium vessel shown in Figure 4, with a threaded cap, was used in experiments S-1 and S-2 but was found to leak sodium vapor. It was therefore replaced, for experiments S-4, S-5 and S-6, by a vessel with a flanged cap, sealed with a Pt O-ring, and with a Swagelok fitting for fixing the graphite snorkel. Ingots S-1 and S-2 were, however, taken for metallographic examination because the desulphurisation was similar to that found in S-4 and S-5.

Specimens taken from the top centre and the bottom centre of ingots S-1 and S-2 were mounted and polished. The various phases present were identified by electron probe microanalysis, no phase containing sodium being found. Grey angular inclusions were identified as MnS, yellow angular inclusions as TiN and Fe<sub>3</sub>C was found next to the graphite flakes.

### 5.3 Misch Metal as a Desulphuriser

Six experiments were performed using misch, the details of which are given in Tables 5 to 15. The change in metal and slag sulphur for each experiment are shown in Figures 16 to 20. The experimental results can be summarized as:

Experiment No.	Initial Sulphur in wt%	Final Sulphur in wt%	Misch Metal Added in wt%
J-30	0.019	0.0045	0.291
j-31	0.0155	0.0074	0.146
A-4	0.028	0.0125	0.220
D-1	0.036	0.0225	0.078
D-2	0.0225	0.0105	0.148
D-3	0.0105	0.0030	0.333

As one can see in the Figures 16 to 20, the rate of desulphurisation obtained with misch metal is very high.

Microscopic examination and probe work done on the ingot produced in experiment A-4 showed no phase containing cerium or lanthanum. This is due to the fact that the residual rare earth metals which are in the melt after the addition are continuously forming sulphides and oxides with the sulphur and oxygen coming from the slag and are thus eliminated from the melt. An ingot obtained by adding cerium to a pig iron melt without using argon bubbling and without adding a slag was also studied and was found to contain cerium sulphide and cerium oxide inclusions. Figure 8 shows some inclusions, orange in color under the microscope, which were identified as cerium

sulphide with the electron probe; an X-ray image for carbon radiation is shown in the same Figure while the X-ray images for cerium and sulphur radiations are given in Figure 9. As cerium is a better deoxidiser than C, Mn and Si, cerium oxide inclusions can be expected. Inclusions located near the upper face of the ingot were found, by electron probe microanalysis, to contain oxygen and cerium as shown in Figures 10 and 11.

#### 5.4 Experiments with Slags Rich in Cerium Oxide

Details of experiments A-5 and J-22 are given in Tables 16 to 19 and in Figures 21 and 22. Figure 21 compares the desulphurising power of a slag rich in cerium oxide (curve A-5) to that of a normal blast furnace slag (curve A-3), all other parameters being equal. Figure 22 shows the slag and metal desulphurisation curves of exp. J-22; here the pig iron had an initial sulphur level of 0.55 wt% and was covered by a modified blast furnace slag containing 28 wt%  $\text{CeO}_2$ . Table 19 gives the details of this run featuring air blowing of the surface of the slag.

#### 5.5 Oxygen Bubbling in Blast Furnace Slag

This experiment involves only liquid slag and was designed to supply a very low sulphur slag usable in other experiments. Fig. 23 gives the desulphurisation curve for this experiment where 330 grams of slag were treated by bubbling 1 litre of oxygen per minute through a Pt-Rh tube of I.D. 3mm submerged in the slag.

## CHAPTER 6

### DISCUSSION

#### 6.1 Sodium as a Desulphuriser

A final level of 0.030 wt% sulphur in pig iron was obtained in all experiments where sodium was boiled under normal atmospheric pressure and the vapor carried through the melt. These results agree with the thermodynamic calculations given in Chapter 3. Such results were needed because of the large imprecision on the value of  $\Delta G_1^0$  given in Section 3.1.

Figure 15 shows sulphur reversion occurring after the end of the sodium addition. This reversion happens as soon as the melt is no longer in contact with sodium vapor; then the dissociation of  $\text{Na}_2\text{S}$  becomes important. A slag could be used to slow down this reversion by decreasing the activity of  $\text{Na}_2\text{S}$ . In experiment S-6, a slag was used but, as a very large amount of sulphide was formed, the reversion cannot be taken as an evidence that the slag is ineffective.

It is very likely to be true that the product  $p_{\text{Na}}^2 \times \text{wt\% S}$  is a constant for a pig iron melt at a given temperature. If the hot metal is treated in a pressurized vessel under three atmospheres, the final sulphur could be as low as 0.003 wt%.

#### 6.2 Misch Metal as a Desulphuriser

The experiments described in Section 5.3 show that misch metal is an effective desulphuriser for pig iron. It can remove sulphur at a very high rate and leave the melt with a very low sulphur

level. To establish an engineering correlation between the amount of misch metal added and the reduction in sulphur content of the melt, it is necessary to obtain the product  $\text{wt}\% \text{ REM} \times \text{wt}\% \text{ S}$ , where REM stands for rare earth metals, by calculating the residual amount of REM after desulphurisation and multiplying it by the final sulphur level.

Exp. No.	Misch Added in wt%	Misch Used to Form Sulphide in wt%	Residual Misch by Difference in wt%
J-30	0.291	0.058	0.233
J-31	0.146	0.032	0.114
A-4	0.221	0.062	0.159
D-1	0.078	0.054	0.024
D-2	0.148	0.048	0.124
D-3	0.333	0.030	0.427

The residual amounts of REM were considered as cumulative in experiments D-1, D-2 and D-3. The calculation of the amount of misch metal used is based on the approximate stoichiometry of rare earth sulphides as discussed in Section 3.3.

Exp. No.	Residual Misch in wt%	Final Sulphur in wt%	Temperature in °C	Product
J-30	0.233	0.0045	1500-1600	$1.05 \times 10^{-3}$
J-31	0.114	0.0074	1450-1550	$0.84 \times 10^{-3}$
A-4	0.159	0.0125	1450-1550	$1.94 \times 10^{-3}$
D-1	0.024	0.0225	1450-1550	$0.54 \times 10^{-3}$
D-2	0.124	0.0105	1450-1550	$1.30 \times 10^{-3}$
D-3	0.427	0.0030	1450-1550	$1.28 \times 10^{-3}$

The products can be compared with the value of  $0.3 \times 10^{-3}$  for the product  $\text{wt}\% \text{ Ce} \times \text{wt}\% \text{ S}$ . This value was obtained in Section 3.2 by correcting the equilibrium results of Langenberg (1958), for steel at  $1600^{\circ}\text{C}$ , to refer to pig iron. The values calculated above are not expected to be equal to equilibrium results because the physical losses, the deoxidation losses and the misch metal retained as sulphide inclusions were not taken into account in the calculations. Vaporization and deoxidation losses cause an over estimation of the residual REM while incomplete separation of the sulphide inclusions would give a higher sulphur analysis.

On the other hand, it is possible to explain part of the disparity between the results of this work by considering the effect of the slag as a source of sulphur and oxygen and as a sink for REM. Figure 20 indicates that the slag can sulphurise as well as desulphurise; the reversion of sulphur together with the transfer of oxygen from the slag will eliminate the residual REM by forming solid oxide and sulphide inclusions.

At the time of the misch metal addition in experiment A-4, the slag was very high in sulphur and certainly the sulphur level reached after the misch metal addition was affected by the reversion so that the product would be lower than  $1.94 \times 10^{-3}$  if the reversion had been less important.

The D-2 misch metal addition was made without using the special holder so the true input is not as high as the one used in the calculations; also after considering the effect of the slag as a

source of sulphur and oxygen, it is reasonable to assume that part of the residual REM from addition D-1 were eliminated from the melt before the D-2 addition was made. This last remark also applies for the residual of D-2 present at the time of the D-3 addition.

In all experiments, the sulphur level reported as final sulphur has been taken less than 10 minutes after the misch metal addition, but it could very well have been taken later in the experiment because any desulphurisation done at the 0.005 wt% level cannot be the effect of the slag alone. Applying this last remark to experiments D-3 and J-31, the product could be lowered in both cases.

A practical value for the product wt% REM x wt% S will thus be:  $1.0 \pm 0.5 \times 10^{-3}$ .

From this one can calculate the cost of desulphurisation of pig iron with misch metal. Typical costs are given below, the present price of misch metal being \$3/lb.

Sulphur Levels in wt%	Misch Needed in wt%	Cost per Ton Treated in \$
From To		
0.040 0.020	0.130 $\pm$ 0.025	7.80 $\pm$ 1.50
0.030 0.015	0.127 $\pm$ 0.033	7.60 $\pm$ 2.00
0.020 0.005	0.260 $\pm$ 0.100	15.60 $\pm$ 6.00
0.040 0.005	0.340 $\pm$ 0.100	20.40 $\pm$ 6.00

A 50% reduction in cost and an increase of the silicon level in the pig iron could be obtained by using rare earth silicide as a replacement for misch metal. According to results obtained in preliminary work, rare earth silicide is as effective as misch metal.

The work with the rare earth silicide was done at 1500 to 1600°C and this could well be a factor responsible for the rapid dissolution of the addition. If this is the case, a change in the composition of the silicide could facilitate its use at lower temperatures.

The microscopic examination of the pig iron structure showed that cerium sulphides and cerium oxides were formed when cerium was added to a pig iron melt. More data on the distribution of cerium in pig iron is already available from the work of Lev (1965). This author found that spheroidal graphite inclusions growing in contact with the liquid phase were enriched in cerium, and that this was also the case for the colonies of austenite-graphite eutectic. In the carbide phase and the spheroidal graphite formed by diffusion of the eutectic graphite, there was no sign of cerium.

### 6.3 Experiments with Slags Rich in Cerium Oxide

As it is shown in Figure 21, the metal desulphurisation curve obtained with the modified blast furnace slag containing 25 wt% of cerium oxide is close to the reference curve for which normal blast furnace slag was used. The slopes of the linear portions, obtained after 17 min. of metal desulphurisation, are equal indicating that no increase in the rate of desulphurisation can be attributed to the presence of the cerium oxide. The difference of 0.005 wt% S between these two parallel portions can be explained by the lower initial sulphur content of the CeO<sub>2</sub> bearing slag. This is due to the addition of 75 grams of sulphur free CeO<sub>2</sub> to 225 grams of blast furnace slag containing 1.2 wt% S.

The two slag sulphur curves of Figure 21 indicate a rapid loss of sulphur from the slag to the atmosphere. The results shown in Figure 22 point out the importance of the sulphur loss from the metal-slag system in an experiment where the pig iron initially contained 0.55 wt% S. A calculation has shown that 76% of the initial sulphur was lost during the 85 minutes experiment.

## CHAPTER 7

### CONCLUSIONS

#### 7.1 Sodium as a Desulphuriser

Sodium has been found to be capable of removing sulphur from pig iron; the desulphurisation proceeds at a high rate. The sulphur level in the treated melt depends on the partial pressure of the sodium vapor in the bubbles. At one atmosphere pressure of sodium vapor, the final sulphur was found to be around 0.030 wt% for experiment done at 1400-1500°C. A thermodynamic calculation shows that a melt containing 0.003 wt% S could be obtained by using a partial pressure of sodium of three atmospheres at about 1500°C.

#### 7.2 Misch Metal as a Desulphuriser

Misch metal was found to be a very good desulphuriser. The rate of desulphurisation, starting at a level of 0.030 wt% sulphur, is greater than 0.010 wt% sulphur per minute and the final level depends only on the amount of misch metal added. An apparent solubility product for misch metal and sulphur in pig iron was obtained and is equal to:  $1.0 \pm 0.5 \times 10^{-3}$

Using this product and the approximate stoichiometry for the REM sulphides, one can estimate the amount in wt% of misch metal needed to desulphurise pig iron from  $S_{\text{initial}}$  in wt% to  $S_{\text{final}}$  in wt%.

$$\text{Misch Metal Needed} = 4 (S_{\text{initial}} - S_{\text{final}}) + \frac{1.0 \pm 0.5 \times 10^{-3}}{S_{\text{final}}}$$

### 7.3 Experiments with Slags Rich in Cerium Oxide

The addition of 75 grams of cerium oxide to 225 grams of blast furnace slag does not make the blast furnace slag a better desulphurising slag in the experimental conditions of this work.

### 7.4 Suggestions for Future Work

For different sulphur levels in pig iron, further experiments are required to establish reliable thermodynamic data and to evaluate the efficiency of the sodium addition. This efficiency depends on the following parameters:

- I) Bubbles size
- II) Bath depth
- III) Sodium vapor pressure
- IV) Temperature of the bath

Decreasing the bubble size will aid desulphurisation by increasing the dwell time as well as the gas-metal interface area per unit gas volume. Increasing the bath depth will also increase the dwell time while increasing the sodium pressure and/or decreasing the temperature as shown in Section 3.1 will increase the driving force for desulphurisation and will result in a lower sulphur level in the treated melt.

Making use of all what has been found throughout this work on desulphurisation of pig iron, two possible methods for desulphurising blast furnace iron, without the addition of reactive metals, will be mentioned. It is believed that the cost for treating iron by these processes could be low.

It has been found:

1) that argon bubbling through a pig iron melt covered with blast furnace slag and held in air will desulphurise the melt and the slag. The calcium acts as a carrier for the sulphur and takes it from the melt to the atmosphere. From this point of view the sulphur capacity as defined by Richardson and Fincham (1954) is not a limitation to the total possible desulphurisation.

2) that sulphur can be removed from blast furnace slag by bubbling oxygen through it. The reaction is exothermic and the slag produced is a good desulphuriser.

The following large scale trials are thus suggested:

1) 10 to 15 tons of blast furnace slag should be poured in a ladle and then 100 tons of iron poured through it; argon bubbling should be used at all time to increase the mixing. At the end of the tap, air or oxygen lancing should be started at the slag-air interface and the operation continued for as long as possible.

2) a second possibility is to tap the slag in the ladle bubble oxygen through the slag to desulphurise it, then tap the metal through the slag while bubbling argon and continue the argon bubbling past the end of the tap to further desulphurise.

APPENDIX 1

Atomic Weight of Rare Earth Elements in Misch Metal, Average

Atomic Weight of Misch Metal and Sulphur Content of Cerium Sulphides

Element	wt% of total	Atomic Weight
Ce	50	140.13
La	20	138.92
Nd	10	144.27
Pr	10	140.92
Others	10	145.00
	100	Average 140.9

CeS : 18.6 wt% Sulphur

Ce<sub>2</sub>S<sub>3</sub> : 25.5 wt% Sulphur

Ce<sub>3</sub>S<sub>4</sub> : 23.3 wt% Sulphur

APPENDIX 2

Results of Preliminary Experiments with Cerium, Misch Metal  
and Misch Metal Silicide

These experiments were done on 250 to 425 grams melts and did  
not have argon bubbling. The metal temp. was between 1450°C and 1600°C.

Exp. No.	Addition	Crucible Material	Slag Used
1-B	Cerium	Alumina	No
2-A	Cerium	Graphite	No
5-B	Misch Metal	Alumina	Blast Furnace
6-B	Misch Metal	Alumina	No
7-B	Misch Metal	Alumina	No
8-B	Misch Metal	Graphite	No
9-B	Misch Metal Silicide	Graphite	No
10-B	Misch Metal Silicide	Alumina	No
14-B	Misch Metal Silicide	Alumina	Blast Furnace
15-B	Misch Metal Silicide	Alumina	Blast Furnace

Exp. No.	REM Added in wt%	Initial Sulphur in wt%	Final Sulphur in wt%	Remarks
1-B	2.74	0.68	0.13	Heavy Corrosion
2-A	0.35	0.013	0.003	--
5-B	2.82	0.44	0.04	Light Corrosion
6-B	2.10	0.38	0.11	--
7-B	4.7	0.36	0.01	Light Corrosion

## APPENDIX 2 (continued)

Exp. No.	REM Added in wt%	Initial Sulphur in wt%	Final Sulphur in wt%	Remarks
8-B	4.0	0.35	0.01	-
9-B	4.0	0.35	0.003	-
10-B	2.0	0.43	0.13	No Corrosion
14-B	3.3	0.67	0.016	-
15-B	0.2	0.046	0.031	-

### APPENDIX 3

#### Standardization of the Potassium Iodate Titrating Solution with N.B.S. Standard 16-D

This standard has a sulphur content of  $0.033 \text{ wt}\% \pm 0.001 \text{ wt}\%$ .

Analysing seven samples of this steel with the same titrating solution, one finds:

Sample No.	Weight in grams	Reading in Divisions	Corrected Reading in div.	Reading for a 1 gram Sample
1	0.6790	70.6	66.6	98.08
2	0.7194	75.5	71.5	99.38
3	0.7484	77.8	73.8	98.61
4	1.0011	102.4	98.4	98.29
5	0.8447	87.9	83.9	99.43
6	0.9435	97.0	93.0	98.56
7	0.6722	72.0	68.0	<u>101.16</u>
			Average	99.07
			Deviation	2%

The corrected reading takes into account the small amount of sulphur present in the iron and tin powders added to the steel sample for analytical purposes.

APPENDIX 4

Reproducibility of Sulphur Analysis on a Suction Sample  
of Pig Iron

The suction samples used were 2mm in dia. and from 4" to 7" long. Their weight per inch is 0.6 grams. The cold or upper end of the stick was always oxidized and 1/2" was always discarded before any samples were taken for analysis.

To evaluate the segregation of results, five samples were taken from the same stick and analysed for sulphur. The results are given below:

Sample No.	Weight in grams	Reading in Divisions	Corrected Reading in Divisions	Reading for 1 gram sample
1	0.4275	50.0	46.0	107.6
2	0.4283	49.0	45.0	105.1
3	0.2862	34.0	30.0	104.8
4	0.3769	42.0	38.0	100.8
5	0.3165	38.0	34.0	107.4
			Average	<u>105.1</u>
			Deviation	4%

The corrected reading takes into account the small amount of sulphur present in the iron and tin powders added to the pig iron sample for analytical purposes. The average reading of 105.1 correspond to a sulphur level of 0.035 wt% and the precision is 0.003 wt%.

APPENDIX 5

Physical Properties of Sodium and Melting Point of  $\text{Na}_2\text{S}$

Atomic Weight: 22.997

\*Melting Point: 97.8 °C

Boiling Point: 881 °C

\*\*Vapor Pressure as a Function of Temperature:

°C	mm Hg
97.8	$9.839 \times 10^{-8}$
100	$1.199 \times 10^{-7}$
200	$1.481 \times 10^{-4}$
300	$1.474 \times 10^{-2}$
400	$3.678 \times 10^{-1}$
500	3.958
600	24.58
700	104.4
800	336.7
900	885.2
1000	1988

\*\*\* Melting point of  $\text{Na}_2\text{S}$ : 1,223 °K

\*Atomic Energy Commission (1955)

\*\*Sittig (1956)

\*\*\*Rossini and Wagman (1952)

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Table 1

Results of Experiment S-6

Initial Pig Iron Weight:	4250 grams
FeS Addition:	22 grams
Sodium Addition in lbs./ton:	11.3
Initial Blast Furnace Slag Weight:	210 grams
SiO <sub>2</sub> Addition to Blast Furnace Slag:	40 grams
Pig Iron Temperature:	1450-1550°C

Table 2

## Results of Experiment S-6

Time min.	Metal Sulphur	Remarks
0	0.163 wt%	Argon on
1	-	Slag in
21.2	0.153 wt%	-
45.0	-	Sodium Vessel in
47.5	0.142 wt%	T <sub>Na</sub> 400°C
51.6	0.136 wt%	T <sub>Na</sub> 670°C
55.8	0.108 wt%	T <sub>Na</sub> 810°C
60.3	0.099 wt%	T <sub>Na</sub> 810°C
67.5	0.094 wt%	T <sub>Na</sub> 860°C
68.5	0.090 wt%	T <sub>Na</sub> 880°C
69.6	0.084 wt%	T <sub>Na</sub> 900°C
70.9	0.052 wt%	T <sub>Na</sub> 900°C
71.6	0.041 wt%	T <sub>Na</sub> 900°C
73.0	0.028 wt%	T <sub>Na</sub> 900°C
74.0	-	End of Sodium
78.2	0.037 wt%	Argon Only

Table 3

Data from Experiment S-4

Initial Pig Iron Weight:	6020 grams
FeS Addition:	4.2 grams
Sodium Addition:	21 grams
Crucible Material (not standard):	Magnesia
Sodium Addition in lbs./ton:	6.98
Pig Iron Temperature:	1350-1450 °C

Time min.	Metal Sulphur	Remarks
0	0.036 wt%	Sodium vessel in
15	0.035 wt%	-
26	0.033 wt%	-
33	0.031 wt%	-
37	0.028 wt%	-
38	0.027 wt%	-
40	-	Snorkel broken
43	0.030 wt%	-
45	0.031 wt%	End of experiment

Table 4

## Data from Experiment S-5

Initial Pig Iron Weight:	6200 grams
FeS Addition:	4.13 grams
Sodium Addition:	22 grams
Blast Furnace Slag Addition:	100 grams
Crucible Material ( not standard):	Magnesia
Sodium Addition in lbs./ton:	7.10
Pig Iron Temperature:	1350-1450 °C

Time min.	Metal Sulphur	Remarks
0	0.037 wt%	Sodium vessel in
13	-	Slag in
15	0.036 wt%	-
20	0.041 wt%	-
25	0.040 wt%	-
30	0.041 wt%	-
35	0.035 wt%	-
40	0.028 wt%	-
45	0.031 wt%	-
49	0.030 wt%	End of sodium
52	0.033 wt%	-
55	0.034 wt%	-
65	0.032 wt%	End of experiment

Table 5

Data from Experiment J-30

Initial Pig Iron Weight:	2810 grams
Initial Blast Furnace Slag Weight:	275 grams
Misch Metal Addition:	6.87 grams
FeS Addition:	3.6 grams
CeO <sub>2</sub> Addition:	30 grams
Final Pig Iron Weight:	1910 grams
Average Pig Iron Weight:	2360 grams
Misch Metal Addition in wt%:	0.291
Pig Iron Temperature:	1500-1600 °C

Table 6

Data from Experiment J-30

Time min.	Metal Sulphur	Slag Sulphur	Remarks
0	0.059 wt%	-	Argon on
10	-	-	-
20	0.057 wt%	-	-
22	-	-	Slag in
27	0.033 wt%	1.21 wt%	-
45	0.025 wt%	0.96 wt%	-
54	0.019 wt%	0.68 wt%	-
62	0.019 wt%	-	-
63	-	-	Misch Metal in
65	0.006 wt%	0.52 wt%	-
75	0.005 wt%	-	-
75-100	-	-	CeO <sub>2</sub> in
100	-	-	End of experiment

Table 7

Data from Experiment J-31

Initial Pig Iron Weight:	4700 grams
Initial Blast Furnace Slag Weight:	275 grams
Misch Metal Weight:	6.04 grams
FeS Addition:	5 grams
Final Pig Iron Weight:	3570 grams
Final Blast Furnace Slag Weight:	-
Average Pig Iron Weight:	4135 grams
Misch Metal Addition in wt%:	0.146
Pig Iron Temperature:	1450-1550 °C

Table 8

Data from Experiment J-31

Time min.	Metal Sulphur	Slag Sulphur	Remarks
-5	-	-	FeS in
0	0.052 wt%	-	Argon on
2	-	-	Slag in
7	0.044 wt%	-	-
15	0.033 wt%	-	-
35	0.025 wt%	0.85 wt%	-
36	-	-	More FeS
60	-	-	-
65	0.023 wt%	-	-
75	0.021 wt%	-	-
90	0.016 wt%	0.36 wt%	-
94	-	-	Misch Metal in
95	0.007 wt%	-	-
98	0.008 wt%	-	-
100	0.0038 wt%	0.36 wt%	-
105	-	-	-
120	0.0037 wt%	0.21 wt%	End of experiment

Table 9

Data from Experiment A-3

Initial Pig Iron Weight:	4100 grams
Initial Blast Furnace Slag Weight:	300 grams
FeS Addition:	4.05 grams
Calculated Final Pig Iron Weight:	3775 grams
Final Blast Furnace Slag Weight:	165 grams
Pig Iron Temperature:	1450-1550 °C

Table 10

Data from Experiment A-3

Time min.	Metal Sulphur	Slag Sulphur
0	0.049 wt%	-
5.58	0.041 wt%	-
7.91	0.035 wt%	-
9.83	0.031 wt%	1.40 wt%
11.83	0.031 wt%	-
13.83	0.026 wt%	-
15.88	0.025 wt%	-
17.88	0.025 wt%	-
19.88	0.025 wt%	1.26 wt%
21.90	0.024 wt%	-
23.90	0.025 wt%	-
25.90	0.021 wt%	-
28.00	0.022 wt%	-
30.00	0.021 wt%	1.00 wt%
32.00	0.019 wt%	-
34.00	0.021 wt%	-
36.00	-	-
38.00	0.019 wt%	-
40.00	-	0.64 wt%

Table 11

Data from Experiment A-3

Time min.	Metal Sulphur	Slag Sulphur
42.16	0.017 wt%	-
44.16	0.019 wt%	-
46.16	-	-
48.15	0.016 wt%	-
50.15	-	-
52.15	0.016 wt%	0.61 wt%
54.15	-	-
56.15	0.015 wt%	-
58.15	-	-
60.00	0.016 wt%	0.49 wt%
End of experiment		

Table 12

Data from Experiment A-4

Initial Pig Iron Weight:	3775 grams
Initial Blast Furnace Slag Weight:	300 grams
FeS Addition:	4.05 grams
Misch Metal Addition:	8.0 grams
Final Pig Iron Weight:	3450 grams
Final Blast Furnace Slag Weight:	-
Misch Metal Addition in wt%:	0.221
Pig Iron Temperature:	1450-1550 °C

Table 13

Data from Experiment A-4

Time min.	Metal Sulphur	Slag Sulphur
0	0.051 wt%	-
4.16	0.042 wt%	-
6.15	0.035 wt%	1.46 wt%
8.15	0.031 wt%	-
9.17	0.032 wt%	-
10.0	Misch in	
10.88	0.014 wt%	-
11.32	0.013 wt%	-
12.13	0.013 wt%	-
12.82	0.0125 wt%	1.53 wt%
13.93	0.016 wt%	-
15.05	0.0145 wt%	-
17.05	0.018 wt%	-
19.10	0.018 wt%	-
21.10	0.017 wt%	-
23.00	0.017 wt%	1.18 wt%
25.00	0.018 wt%	-
27.00	0.018 wt%	-
28.98	0.017 wt%	-
31.00	0.016 wt%	0.80 wt%

End of experiment

Table 14

Data from Experiments D-1, D-2 and D-3

Initial Pig Iron Weight:		300 lbs.
Initial Blast Furnace Slag Weight:		12-13 lbs.
FeS Addition:		130 grams
Misch Metal Addition:	D-1	106 grams
	D-2	200 grams
	D-3	451 grams
Misch Metal Addition in wt%:	D-1	0.078
	D-2	0.148
	D-3	0.333
Pig Iron Temperature:		1450-1550 °C

Table 15

Data from Experiments D-1, D-2 and D-3

Time min.	Metal Sulphur	Slag Sulphur	Remarks
0	0.041 wt%	-	Argon on
10	-	-	Slag in
25	0.037 wt%	1.17 wt%	-
35	0.0365 wt%	1.18 wt%	-
45	0.036 wt%	1.04 wt%	-
50	-	-	Misch 106 grams
53	0.024 wt%	1.05 wt%	-
57	0.0225 wt%	1.01 wt%	-
75	0.0225 wt%	0.75 wt%	End of D-1
77	-	-	Misch 200 grams
90	0.010 wt%	-	-
95	0.011 wt%	0.55 wt%	End of D-2
96	-	-	Misch 451 grams
100	0.004 wt%	-	-
105	0.003 wt%	0.54 wt%	-
115	0.003 wt%	0.28 wt%	-
125	0.002 wt%	-	End of D-3

Table 16

Data from Experiment A-5

Initial Pig Iron Weight:	4100 grams
Initial Blast Furnace Slag Weight:	225 grams
Initial Cerium Oxide Weight:	75 grams
FeS Addition:	4.05 grams
Final Pig Iron Weight:	3840 grams
Final Slag Weight:	250 grams
Cerium Oxide in wt% of Slag:	25
Pig Iron Temperature:	1450-1550 °C

Table 17

Data from Experiment A-5

Time min.	Metal Sulphur	Slag Sulphur
0	0.048 wt%	-
5.76	0.038 wt%	-
7.75	0.034 wt%	-
9.73	0.031 wt%	-
11.73	0.024 wt%	-
13.73	0.018 wt%	1.32 wt%
15.76	0.020 wt%	-
17.70	0.019 wt%	-
19.70	0.019 wt%	-
21.70	0.018 wt%	1.24 wt%
23.80	0.017 wt%	-
25.80	0.015 wt%	-
27.80	0.018 wt%	-
29.88	0.016 wt%	-
31.90	0.014 wt%	0.89 wt%
33.95	0.013 wt%	-
35.91	0.015 wt%	-
37.93	0.015 wt%	-
40.06	0.013 wt%	-

Table 18

Data from Experiment A-5

Time min.	Metal Sulphur	Slag Sulphur
44.08	-	-
46.08	0.014 wt%	0.55 wt%
48.08	0.011 wt%	-
50.10	0.012 wt%	-
52.40	0.010 wt%	-
54.40	0.011 wt%	-
56.40	-	0.40 wt%
58.46	0.011 wt%	-
60.45	0.009 wt%	-
62.45	0.010 wt%	-
64.90	0.0095 wt%	0.34 wt%
66.16	0.009 wt%	0.33 wt%

End of Experiment

Table 19

Data from Experiment J-22

Initial Pig Iron Weight: 4000 grams  
 Initial Slag Weight: 300 grams  
 Cerium Oxide in wt% of Slag: 28  
 FeS Addition: 90 grams

Time min.	Metal Sulphur	Slag Sulphur	Remarks
0	0.605 wt%	0.850 wt%	Argon on
1	-	-	Slag Added
3	-	-	Slag Liquid
5	-	-	-
13	0.450 wt%	3.410 wt%	-
28	0.350 wt%	3.250 wt%	-
28-43	-	-	Air Blowing of Surface of Slag
43	0.280 wt%	-	-
44-50	-	-	Air Blowing
58	0.185 wt%	-	-
64-75	-	-	Air Blowing
75	0.130 wt%	-	-
80	-	0.450 wt%	-
85	-	0.380 wt%	-
88	0.130 wt%	-	End of experiment

Table 20

## Slag and Metal Analysis

## Experiments D-1, D-2 and D-3

Slag at 45 min.	34.5 wt% CaO, 33.95 wt% SiO <sub>2</sub> , 17.6 wt% MgO, 6.69 wt% Al <sub>2</sub> O <sub>3</sub> , 0.75 wt% Mn and 0.54 wt% Fe.
Metal at 53 min.	3.65 wt% C, 0.77 wt% Si, 1.21 wt% Mn and 0.024 wt% S
Slag at 95 min.	28.6 wt% CaO, 33.4 wt% SiO <sub>2</sub> , 24.6 wt% MgO, 5.70 wt% Al <sub>2</sub> O <sub>3</sub> , 0.33 wt% Mn and 0.57 wt% Fe.
Metal at 125 min.	3.79 wt% C, 0.76 wt% Si, 1.21 wt% Mn and 0.006 wt% S

## Experiment A-3

Slag at 60 min.	33.3 wt% CaO, 37.8 wt% SiO <sub>2</sub> , 13.1 wt% MgO, 8.1 wt% Al <sub>2</sub> O <sub>3</sub> , 0.3 wt% Mn and 0.2 wt% Fe.
-----------------	--

## Experiment A-4

Slag at 31 min.	32.6 wt% CaO, 37.8 wt% SiO <sub>2</sub> , 12.9 wt% MgO, 7.7 wt% Al <sub>2</sub> O <sub>3</sub> , 0.3 wt% Mn and 0.7 wt% Fe.
-----------------	--

## Experiment A-5

Slag at 66 min.	23.6 wt% CaO, 31.4 wt% SiO <sub>2</sub> , 10.65 wt% MgO, 6.7 wt% Al <sub>2</sub> O <sub>3</sub> , 0.3 wt% Mn and 0.7 wt% Fe.
-----------------	---

## Initial Blast Furnace Slag

	33.8 wt% CaO, 35.9 wt% SiO <sub>2</sub> , 13.4 wt% MgO, 8.5 wt% Al <sub>2</sub> O <sub>3</sub> , 0.2 wt% Mn and 0.2 wt% Fe.
--	--

Figure 1

Standard Free Energy of Formation  
of Some Oxides and Sulphides as a  
Function of Temperature.

From Richardson and Jeffes (1948,1952)

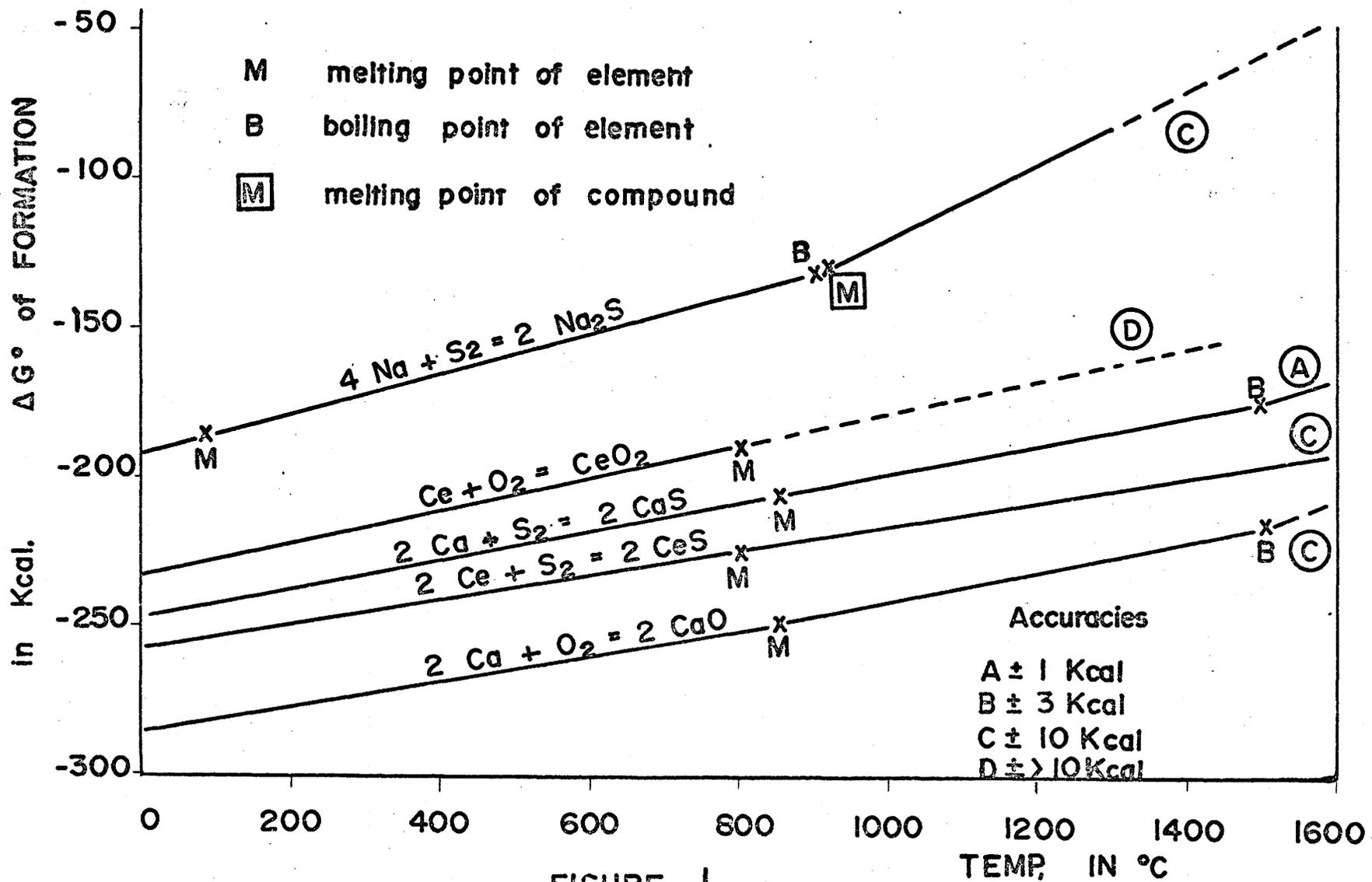


FIGURE 1

Figure 2      Apparatus and Input for a  
Misch Metal Experiment

- (1) Graphite Tube for Argon Bubbling
- (2) Mullite Sheath for Thermocouple
- (3) Graphite Sheath for Thermocouple
- (4) Graphite Crucible, 5" O.D. by 7" High
- (5) Pig Iron Ingot
- (6) Crushed Blast Furnace Slag
- (7) Misch Metal Addition and Holder

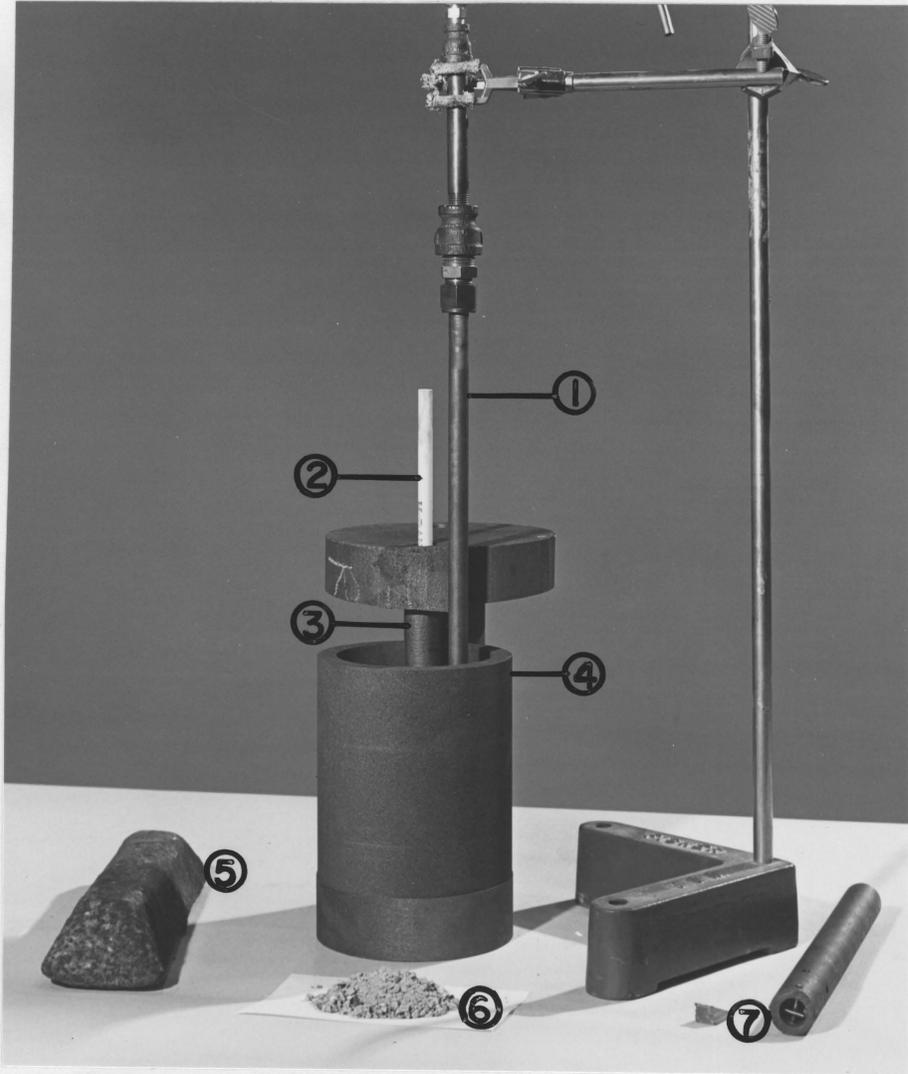
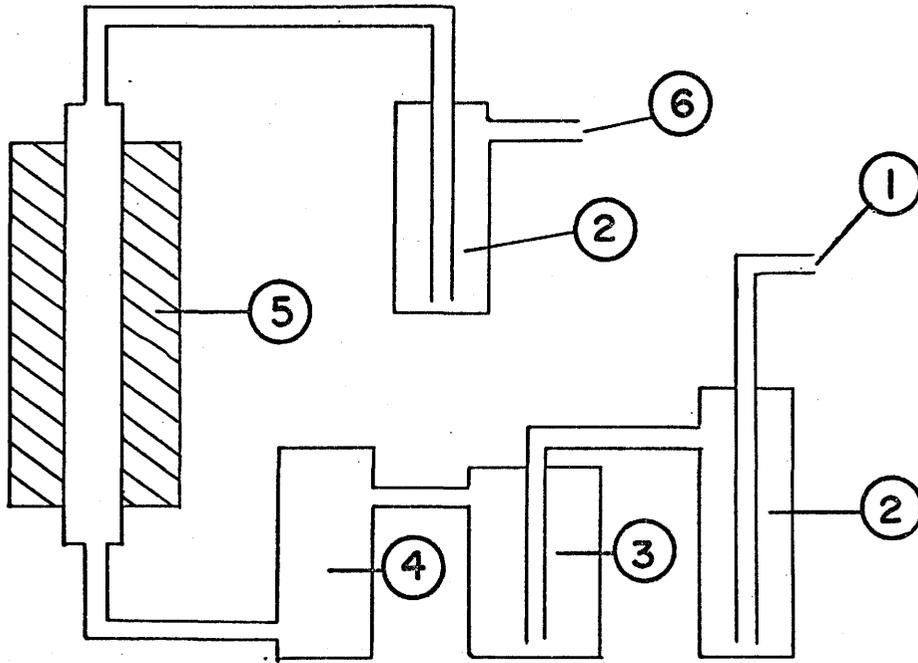


Figure 2

## PURIFICATION TRAIN FOR ARGON



- ① ARGON INLET
- ② DIBUTYL PHTHALATE BUBBLER
- ③ DRIERITE AND SILICA GEL
- ④ MAGNESIUM PERCHLORATE
- ⑤ TITANIUM AT 875 °C
- ⑥ ARGON OUTLET

FIGURE 3

- (1) Body of Stainless Steel Sodium Vessel
- (2) Cap of Stainless Steel Sodium Vessel
- (3) Kanthal Resistance Heating Element
- (4) Graphite Snorkel
- (5) Thermocouple in Position

Figure 4 Sodium Vessel Taken Apart and in Position

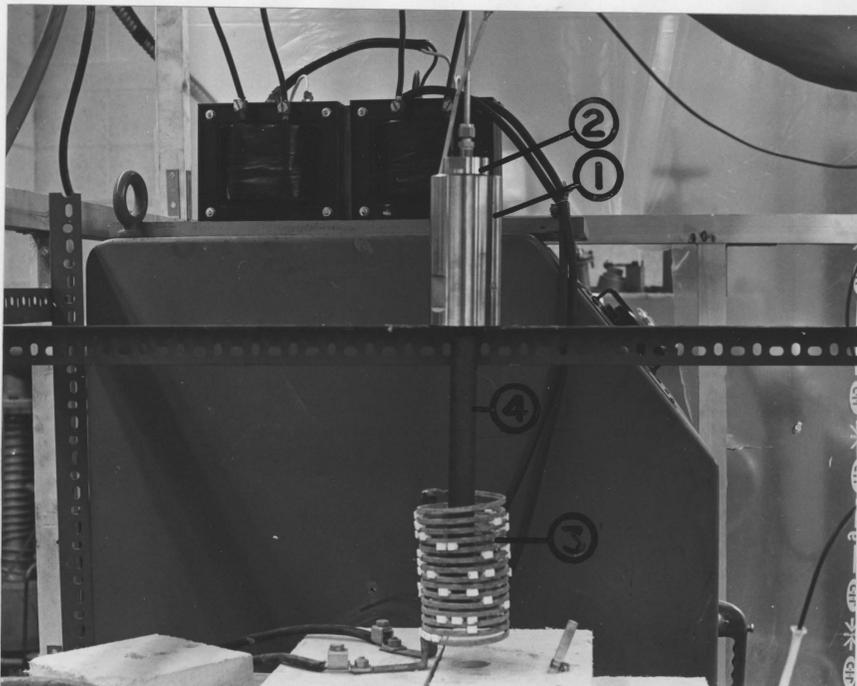
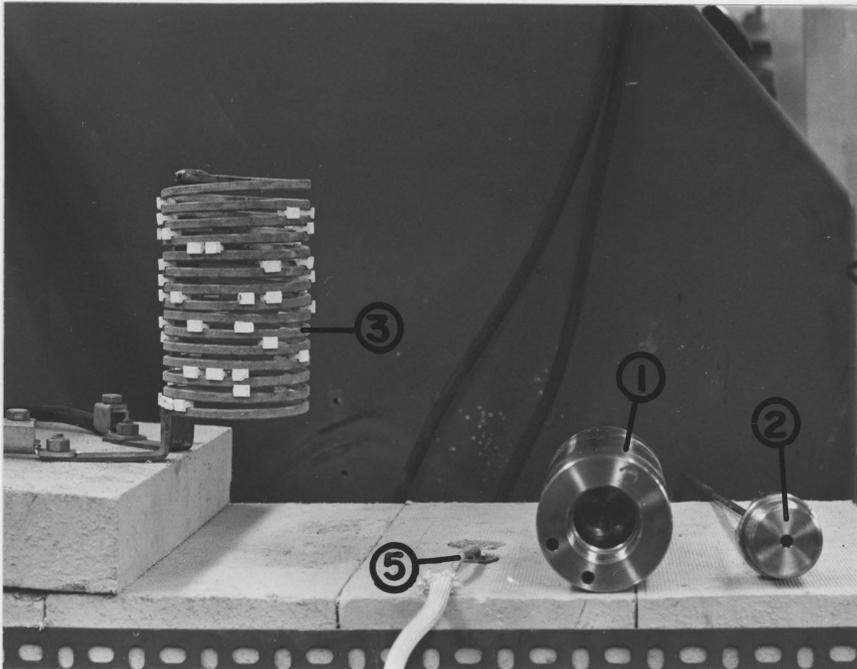


Figure 4

Figure 5

Apparatus for Sodium Experiments

- (1) Stainless Steel Argon Inlet
- (2) Hole Through (3) for Chromel-Alumel Thermocouple Fitting in Well (6)
- (3) Pressed Asbestos Cover
- (4) ~~Bottomless Clay Graphite Crucible~~ <sup>tube</sup>
- (5) Stainless Steel Sodium Vessel
- (6) Thermocouple Well
- (7) Kanthal Resistance Heating Element  
Maximum Input of 2500 Watts
- (8) Threaded Graphite Snorkel
- (9) Pressed Asbestos Insulation
- (10) Graphite Thermocouple Sheath
- (11) Graphite Crucible 4" I.D. by 6" Deep
- (12) Induction Coil

APPARATUS FOR SODIUM RUNS

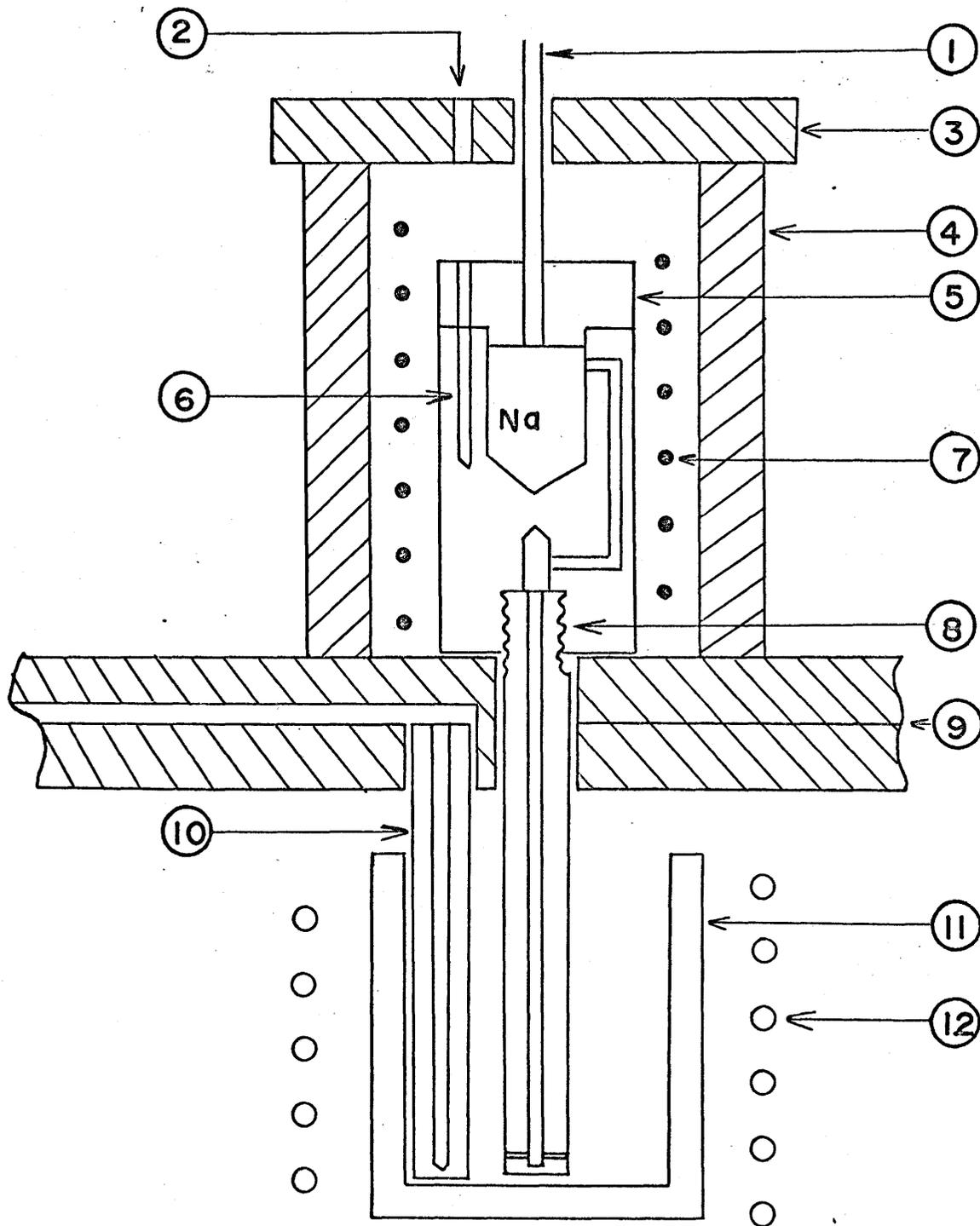
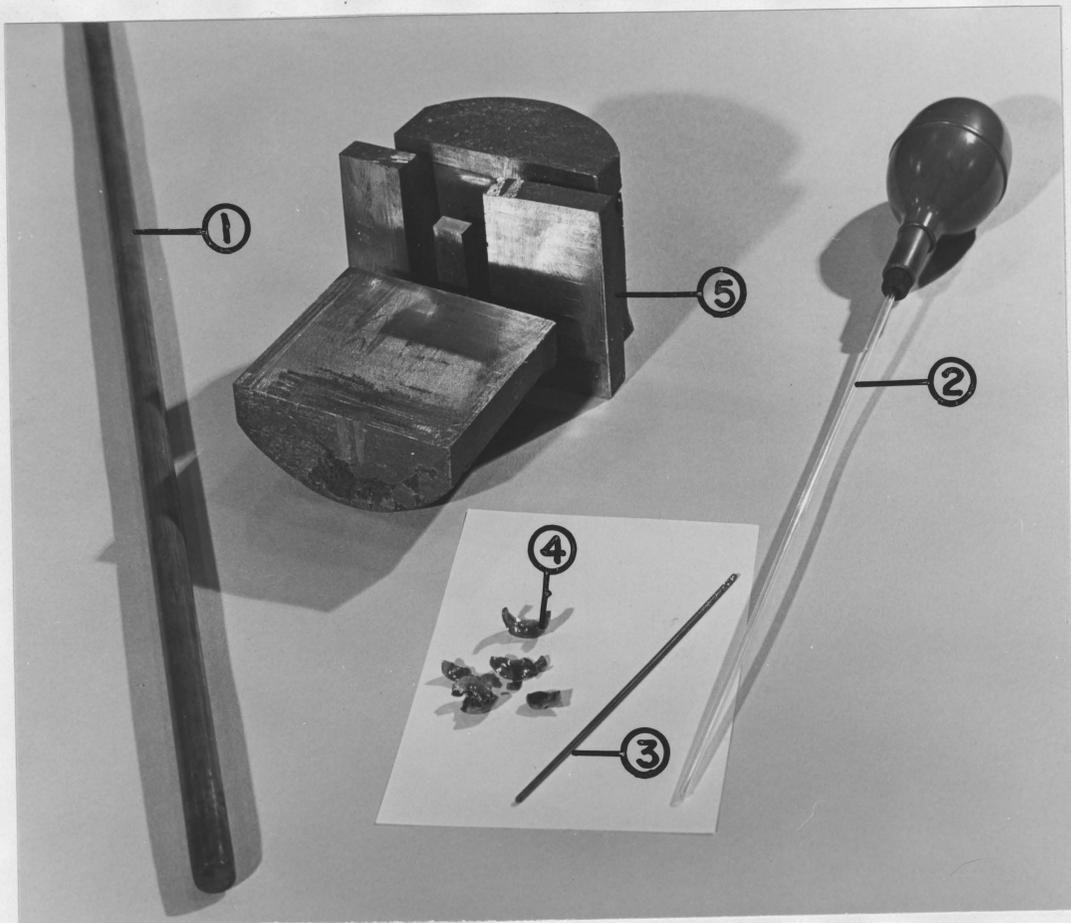
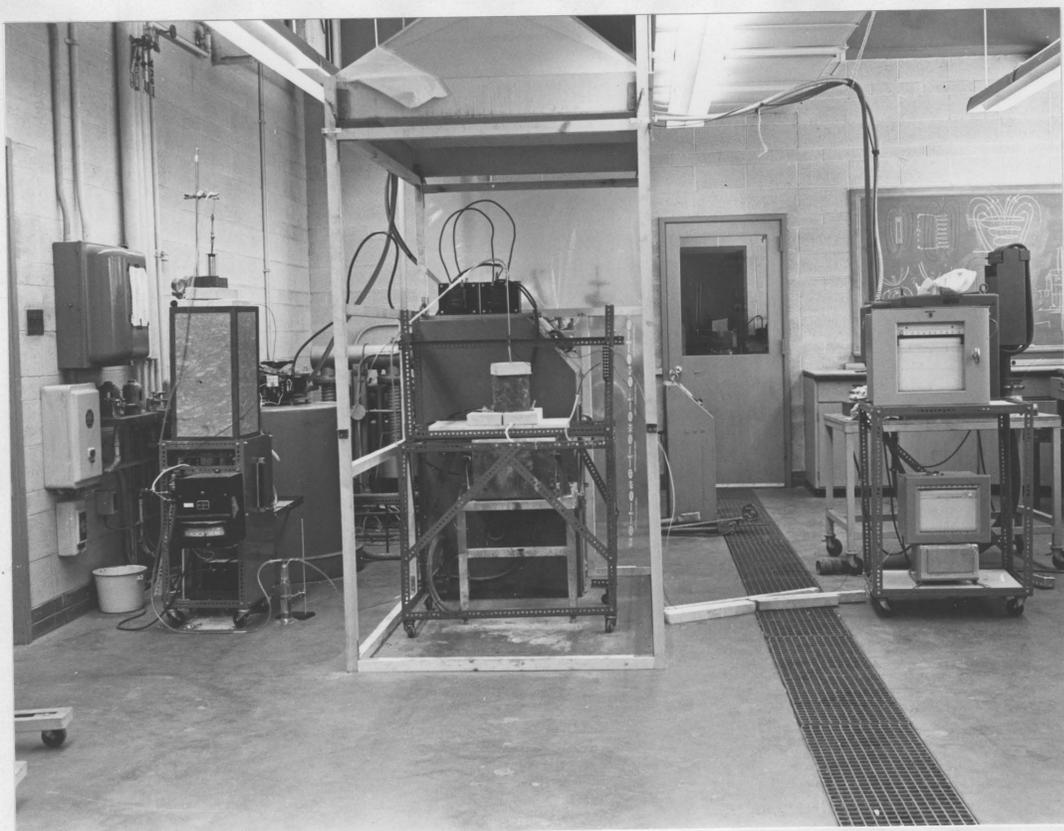


FIGURE 5



- (1) 1/2" dia. Copper Rod for Sampling the Slag
- (2) Aspirator and Silica Tube for Sampling the Metal
- (3) Metal Sample
- (4) Slag Sample
- (5) Expanded View of Sectioned Ingot

Figure 6 Samples Taken During a Run and on the Ingot



- (1) Right, the Temperature Recorders
- (2) Centre, the Furnaces as Shown in Fig. 5
- (3) Left, the Gas Purification Train

Overall View of the Apparatus Used for a Sodium Experiment

Figure 7

Figure 8

Top: Photomicrograph Showing Cerium Sulphide  
Inclusions in Pig Iron.

Magnification: 500X

Bot: Electron Microanalysis of the Field Shown  
in the Top Photo; X-ray Image for Carbon  
Radiation.

Magnification: 500X

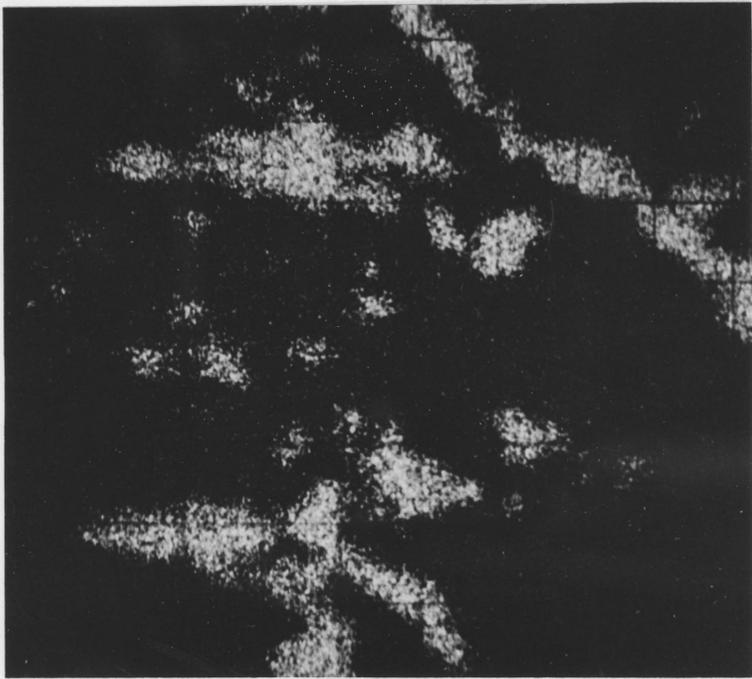
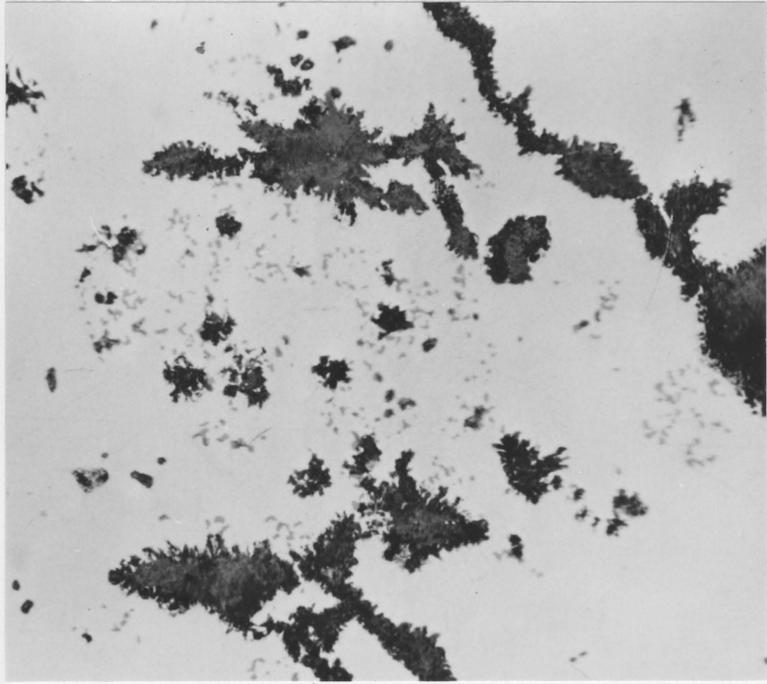


Figure 8

Figure 9

Top: Electron Microanalysis of the Field Shown  
in Figure 8. X-ray Image for Cerium Radiation.

Magnification: 500X

Bot: Electron Microanalysis of the Field Shown  
in Figure 8. X-ray Image for Sulphur Radiation.

Magnification: 500X

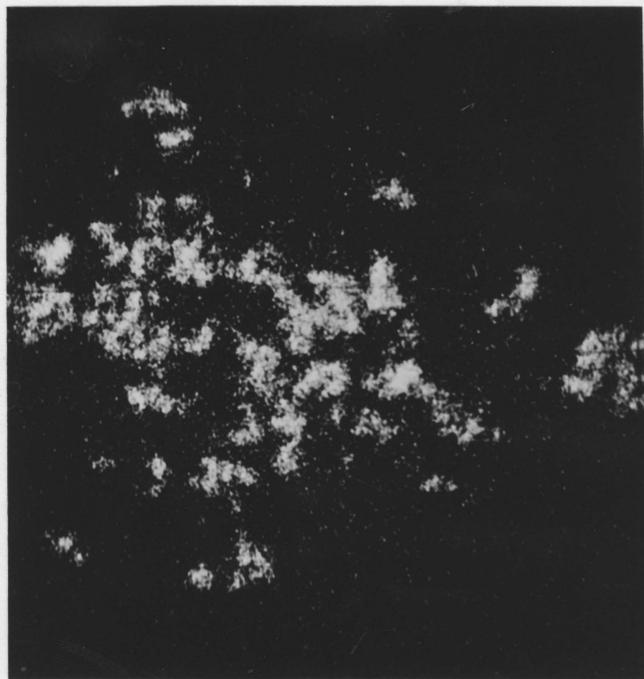
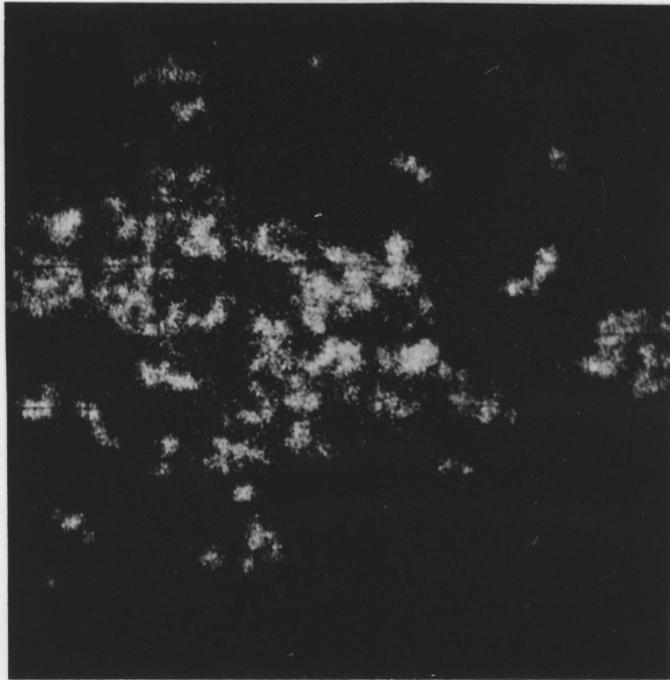


Figure 9

Figure 10

Top: Photomicrograph Showing Cerium Oxide  
Inclusions in Pig Iron.

Magnification: 500X

Bot: Electron Microanalysis of the Field Shown  
in the Top Photo; X-ray Image for Carbon  
Radiation.

Magnification: 500X

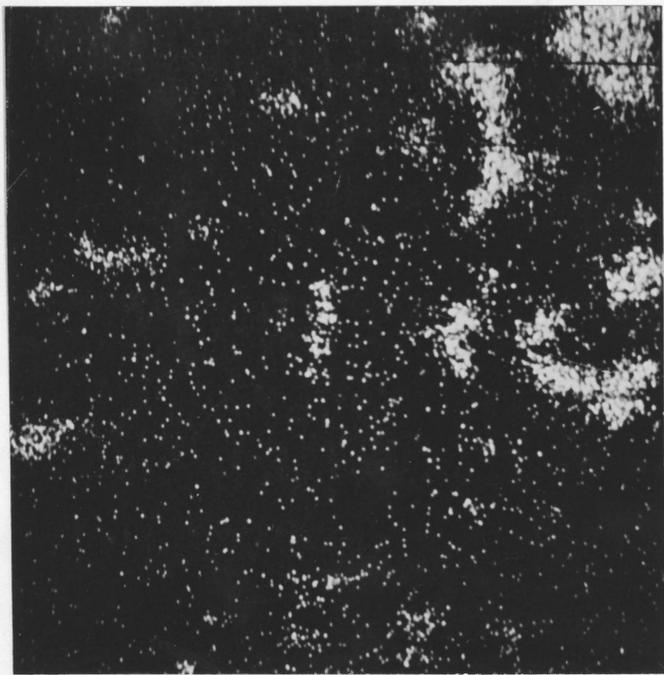
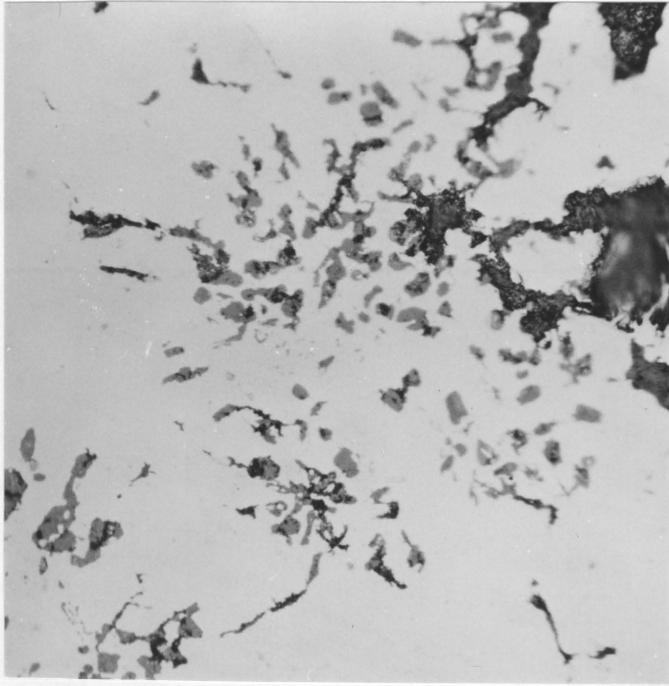


Figure 10

Figure 11

Top: Electron Microanalysis of the Field Shown  
in Figure 10. X-ray Image for Cerium Radiation.

Magnification: 500X

Bot: Electron Microanalysis of the Field Shown  
in Figure 10. X-ray Image for Oxygen Radiation.

Magnification: 500X

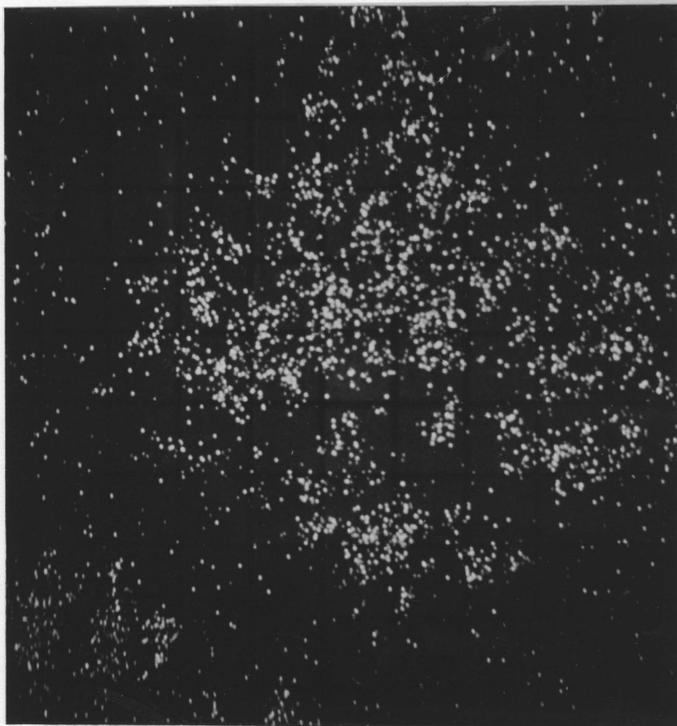
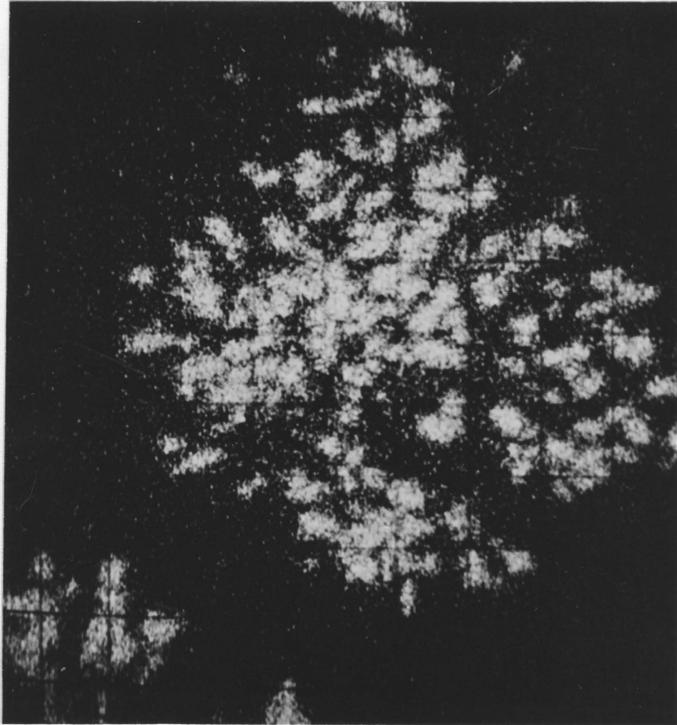


Figure 11

Figure 12

Desulphurisation with Sodium Vapor

Metal Sulphur as a Function of Time  
for Experiment S-6

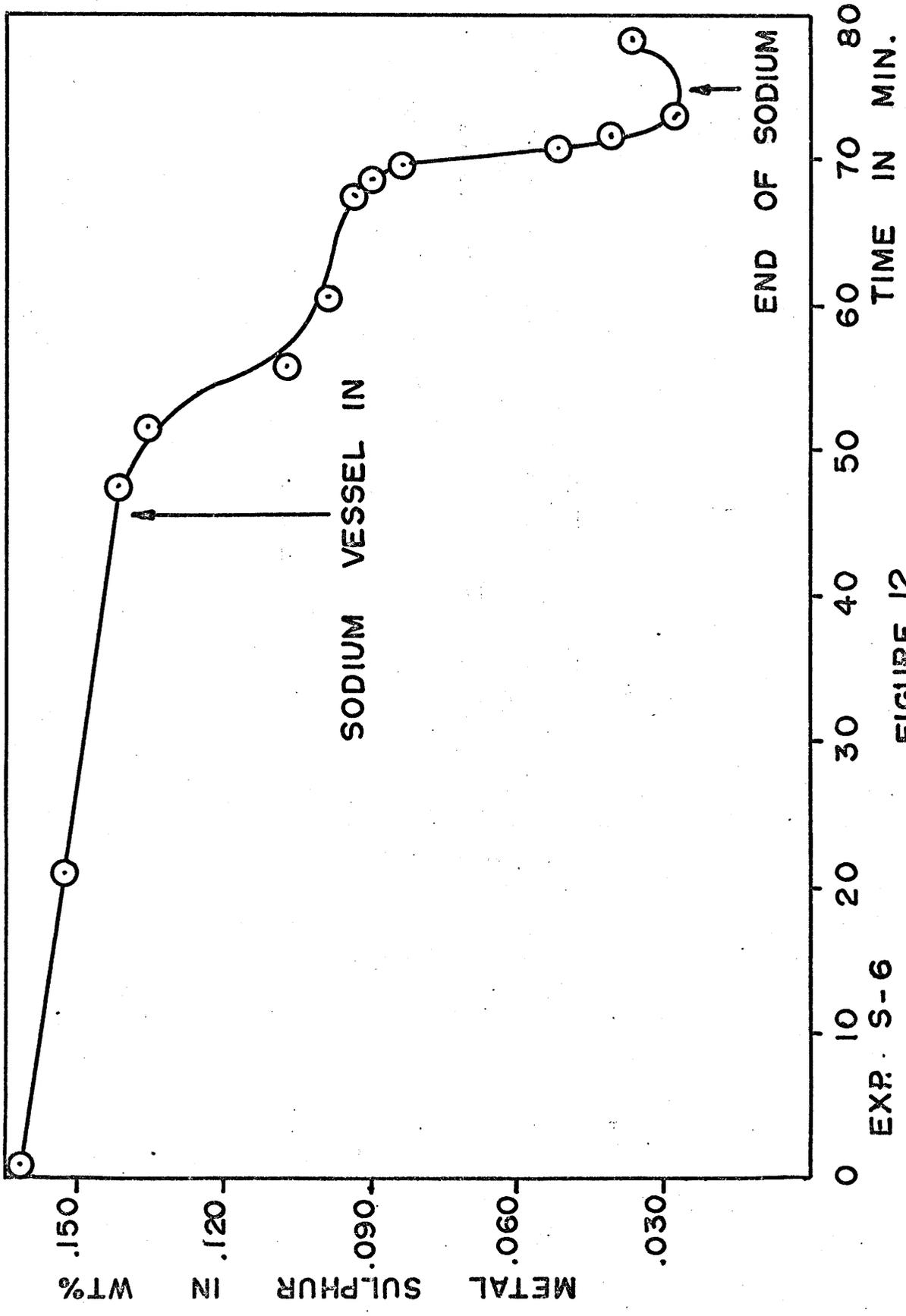
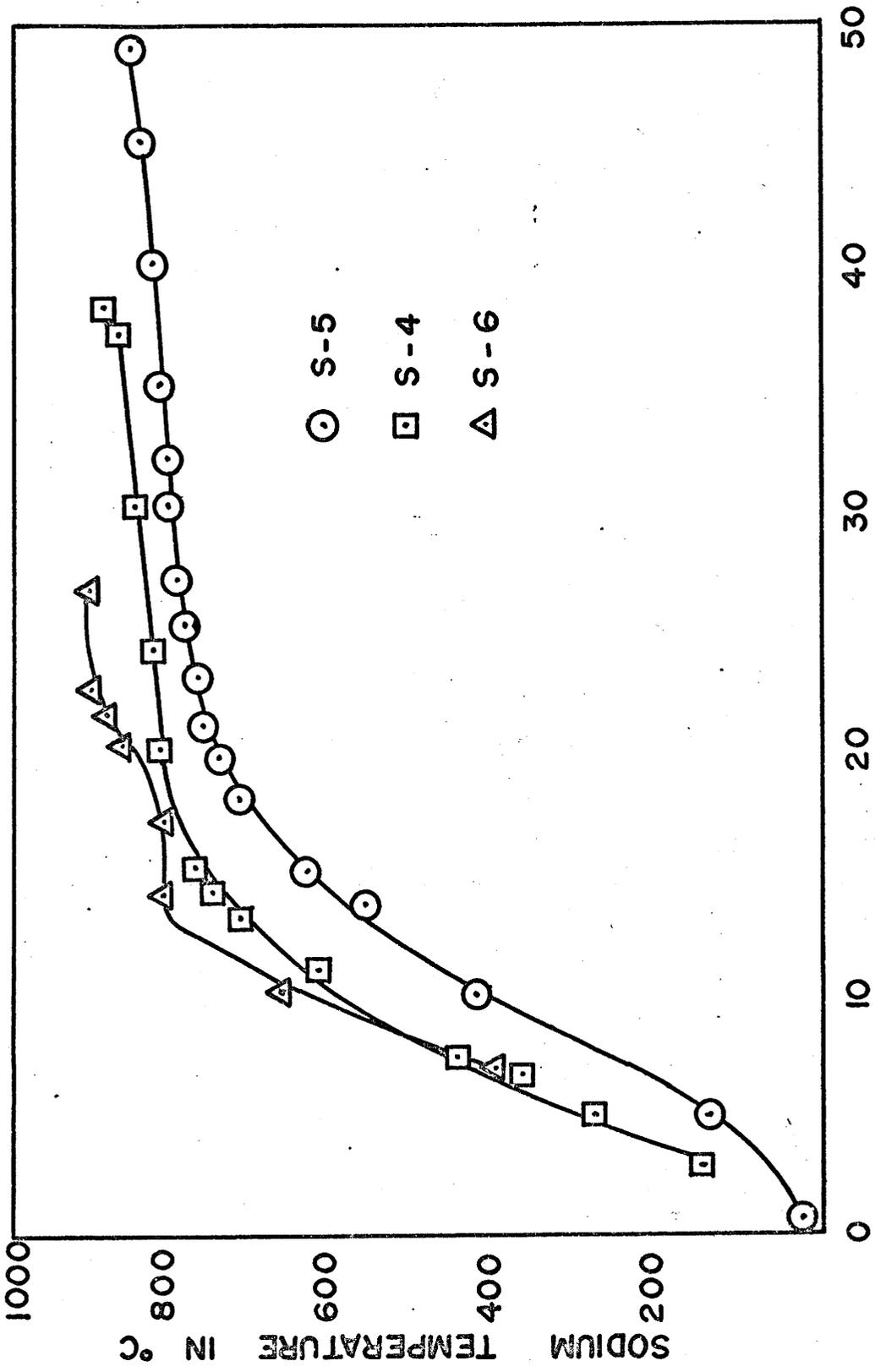


FIGURE 12

EXP. S-6

Figure 13

Sodium Temperature as a Function of  
Time for Experiments S-4, S-5 and S-6

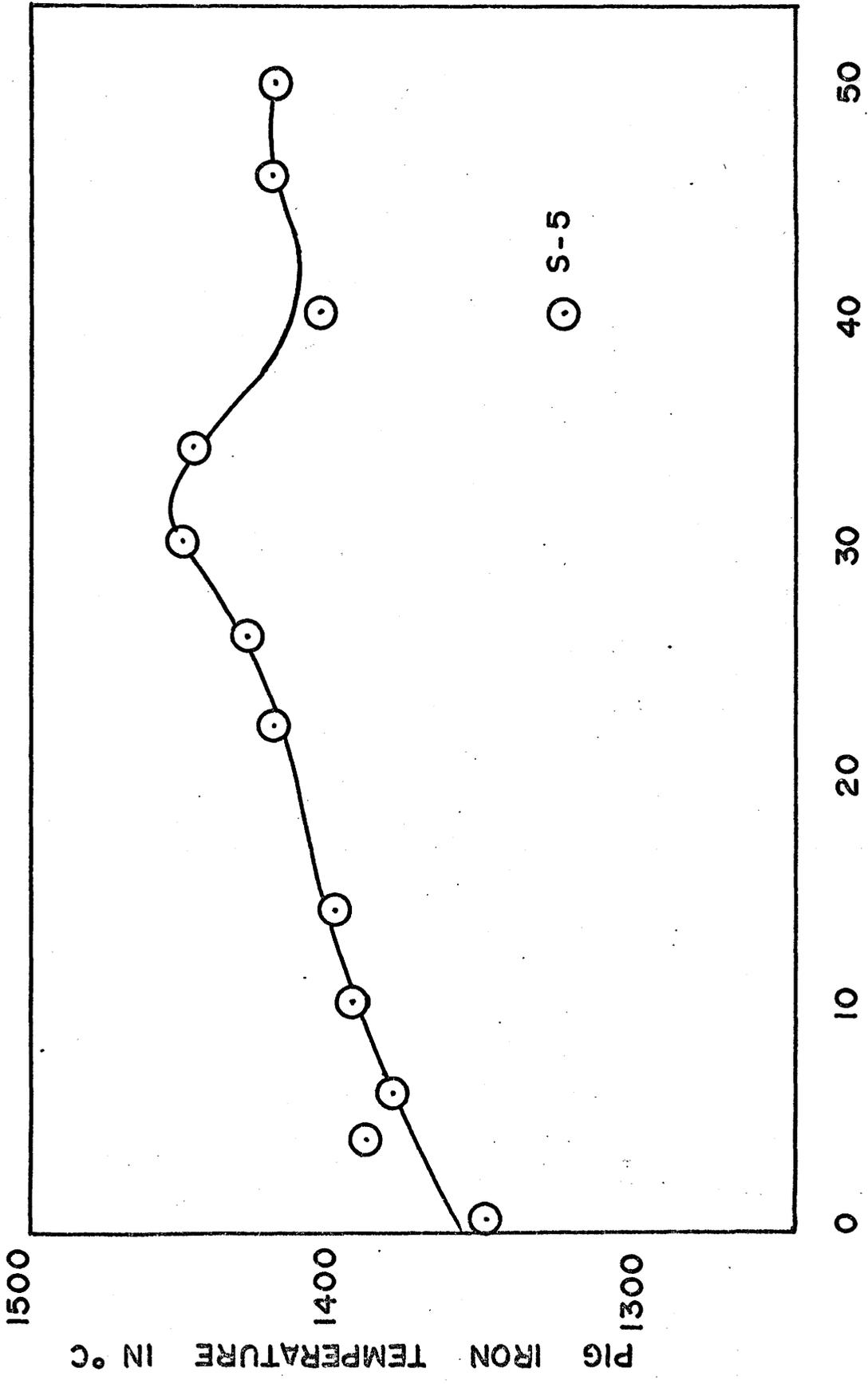


TIME IN MIN.

FIGURE 13

Figure 14

Pig Iron Temperature as a Function  
of Time for Sodium Experiment S-5



○ S-5

**FIGURE 14**

Figure 15

Desulphurisation with Sodium Vapor

Metal Sulphur as a Function of Time  
for Experiments S-4 and S-5

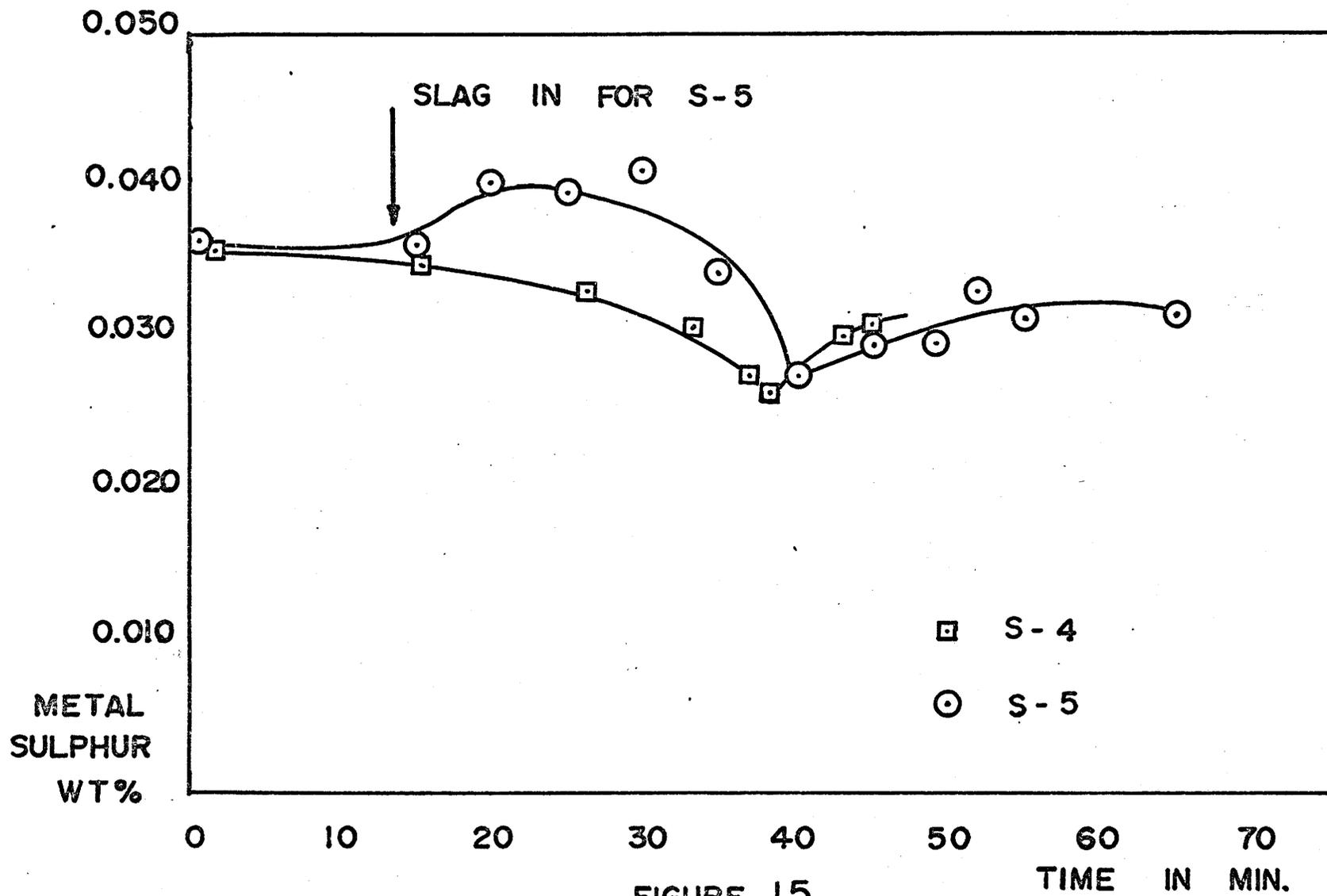


FIGURE 15

Figure 16

Desulphurisation with Misch Metal

Metal Sulphur and Slag Sulphur as a  
Function of Time for Experiment D-1

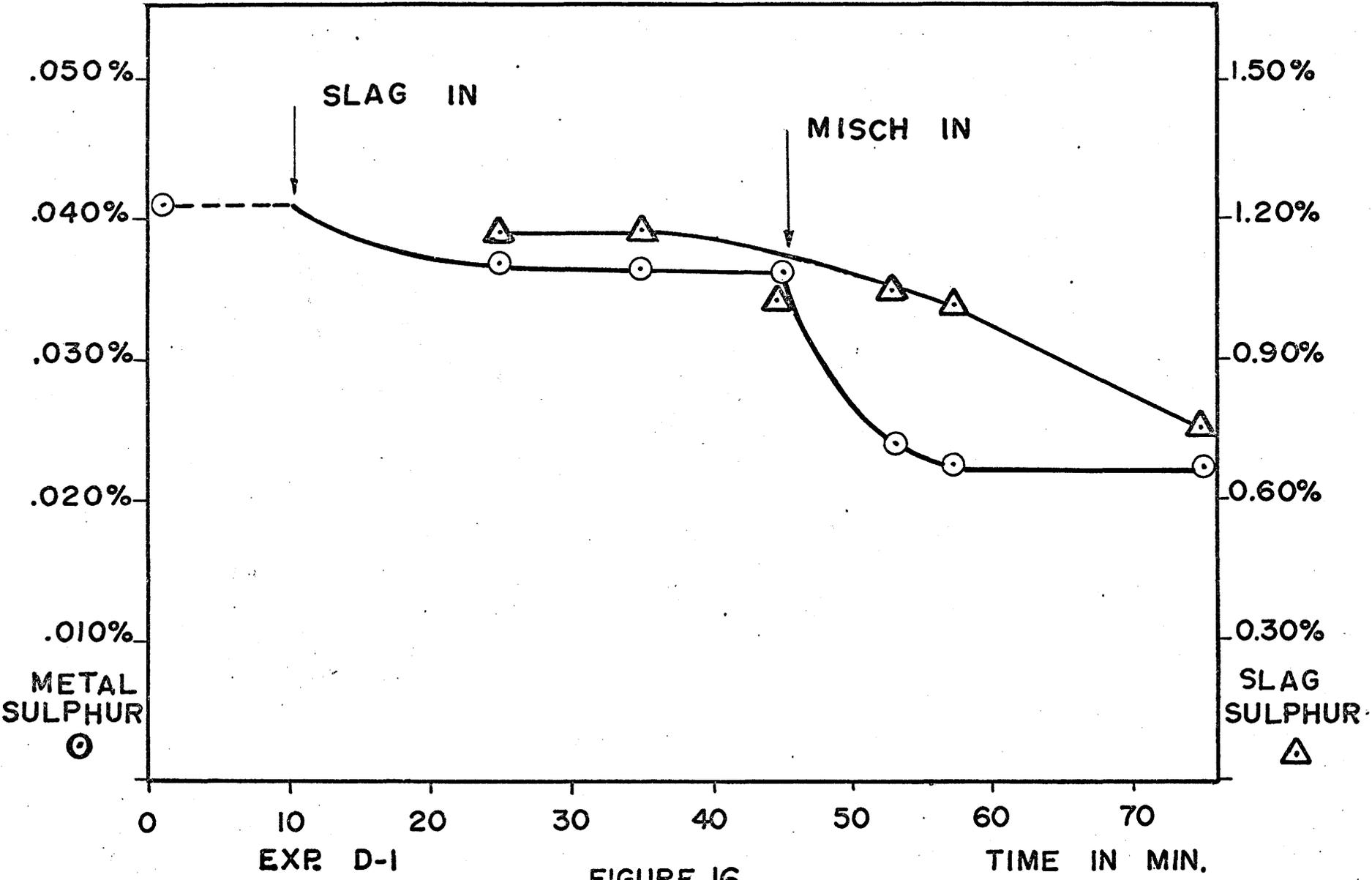


FIGURE 16

EXP. D-1

TIME IN MIN.

Figure 17

Desulphurisation with Misch Metal

Metal Sulphur and Slag Sulphur as a Function  
of Time for Experiments D-2 and D-3

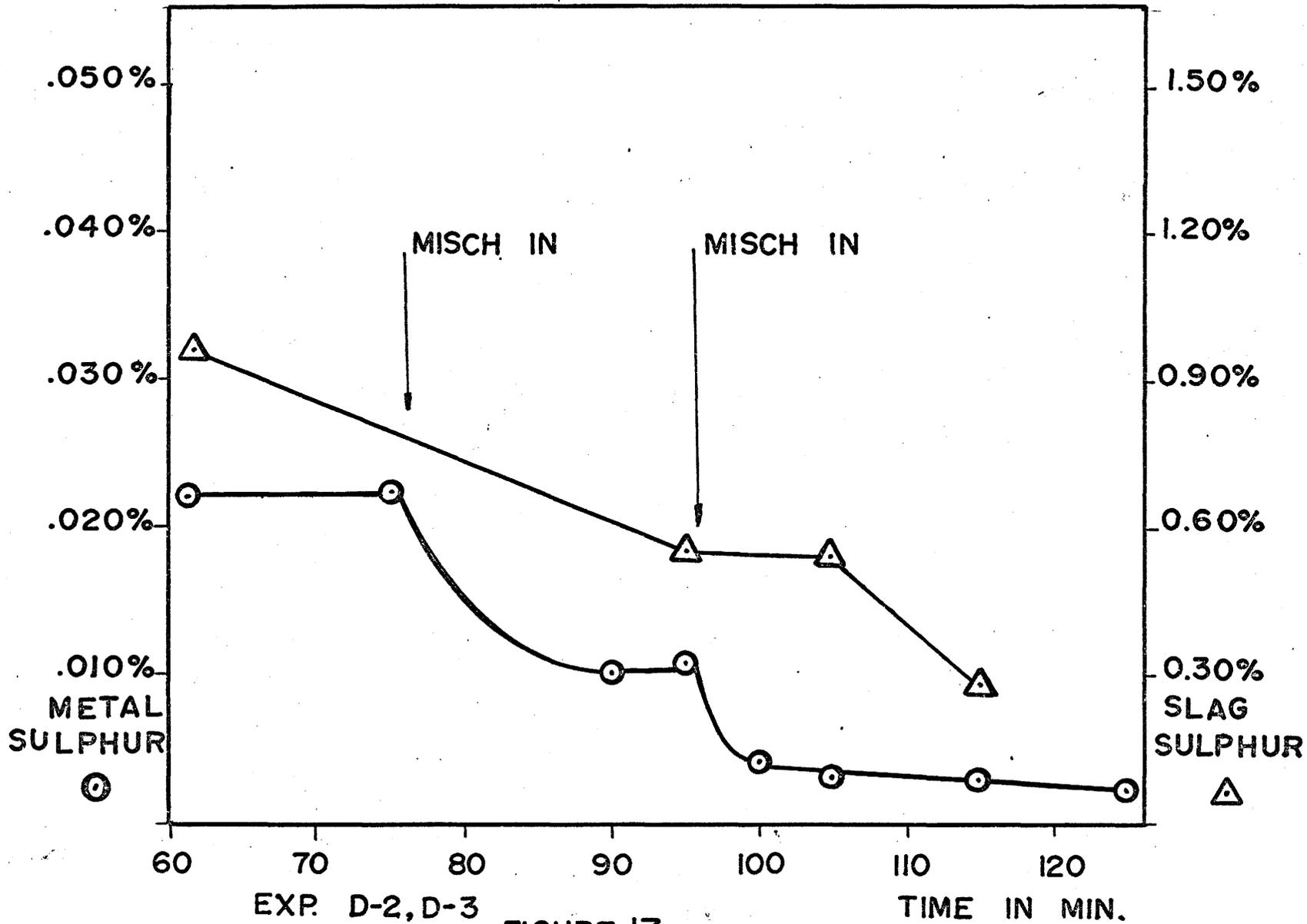


FIGURE 17

Figure 18

Desulphurisation with Misch Metal

Metal Sulphur and Slag Sulphur as a  
Function of Time for Experiment J-30

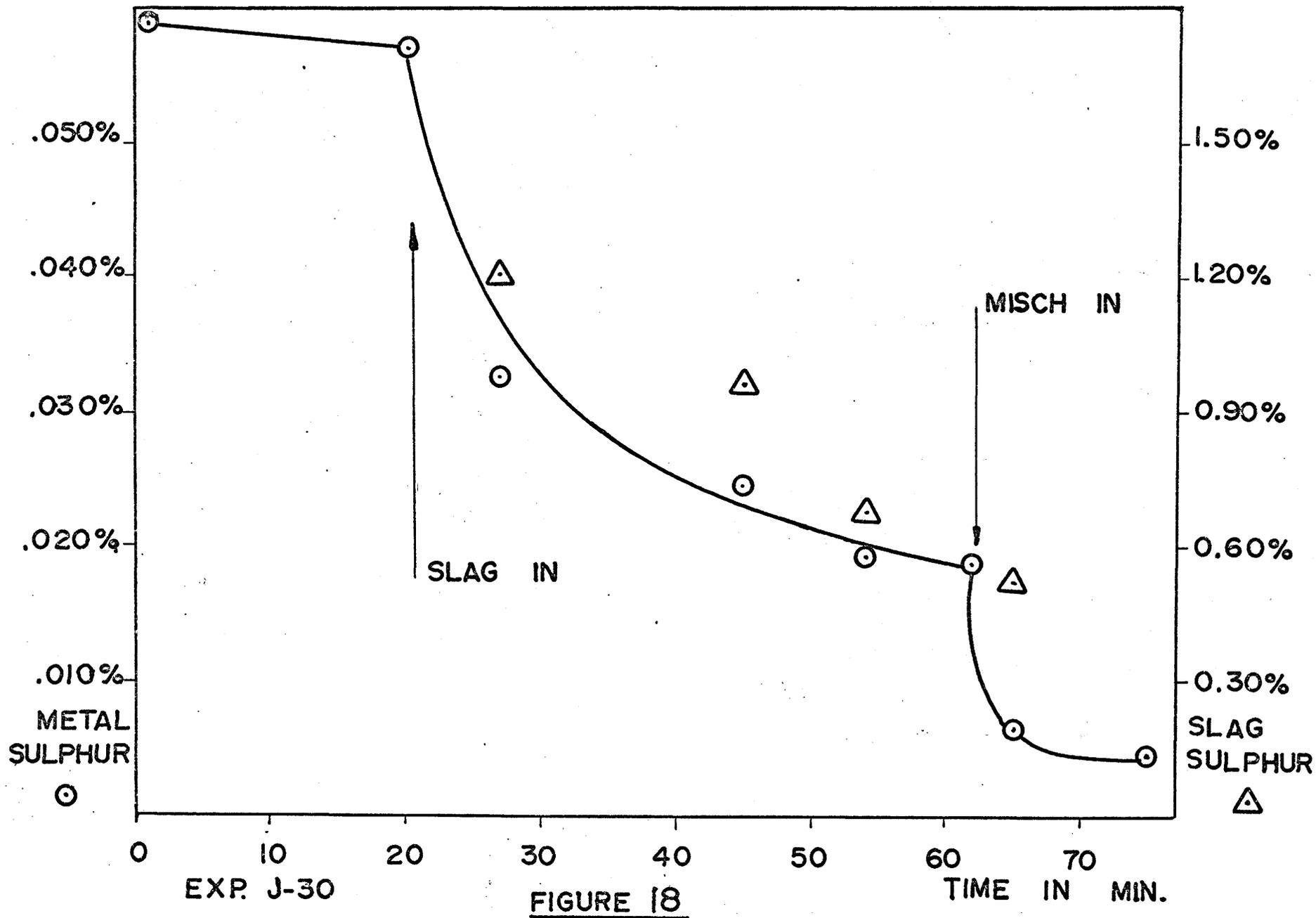
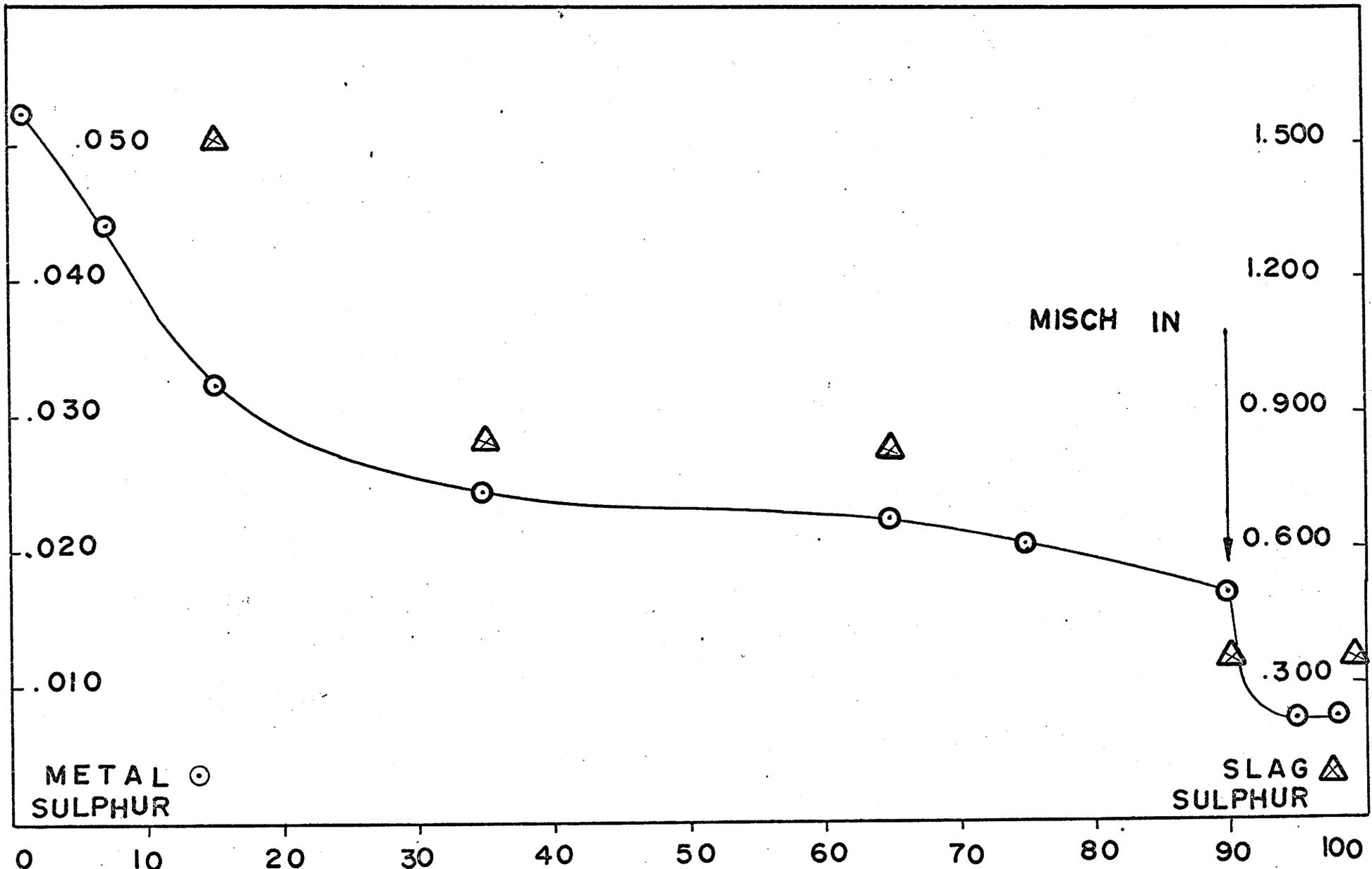


Figure 19

Desulphurisation with Misch Metal

Metal Sulphur and Slag Sulphur as a  
Function of Time for Experiment J-31



EXP. J-31

FIGURE 19

TIME IN MIN.

Figure 20

Desulphurisation with Misch Metal

- I) Experiment A-3: Desulphurisation with Blast  
Furnace Slag Only
- II) Experiment A-4: Desulphurisation of a Melt  
Covered with Blast Furnace  
Slag Using Misch Metal

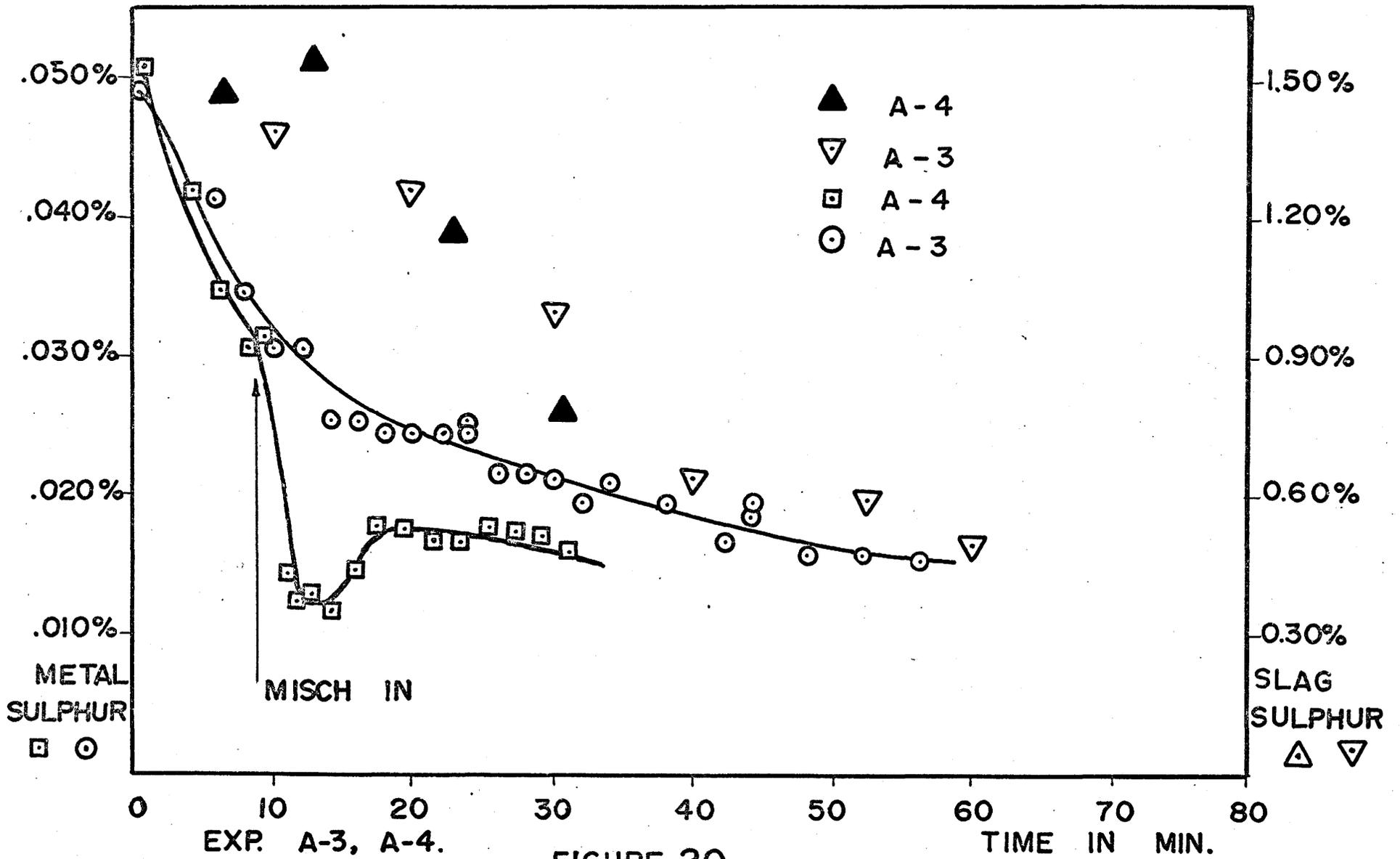


FIGURE 20

Figure 21

Desulphurisation with Slags

I) Experiment A-3: Desulphurisation with Blast  
Furnace Slag

II) Experiment A-5: Desulphurisation with a Slag  
Rich in Cerium Oxide

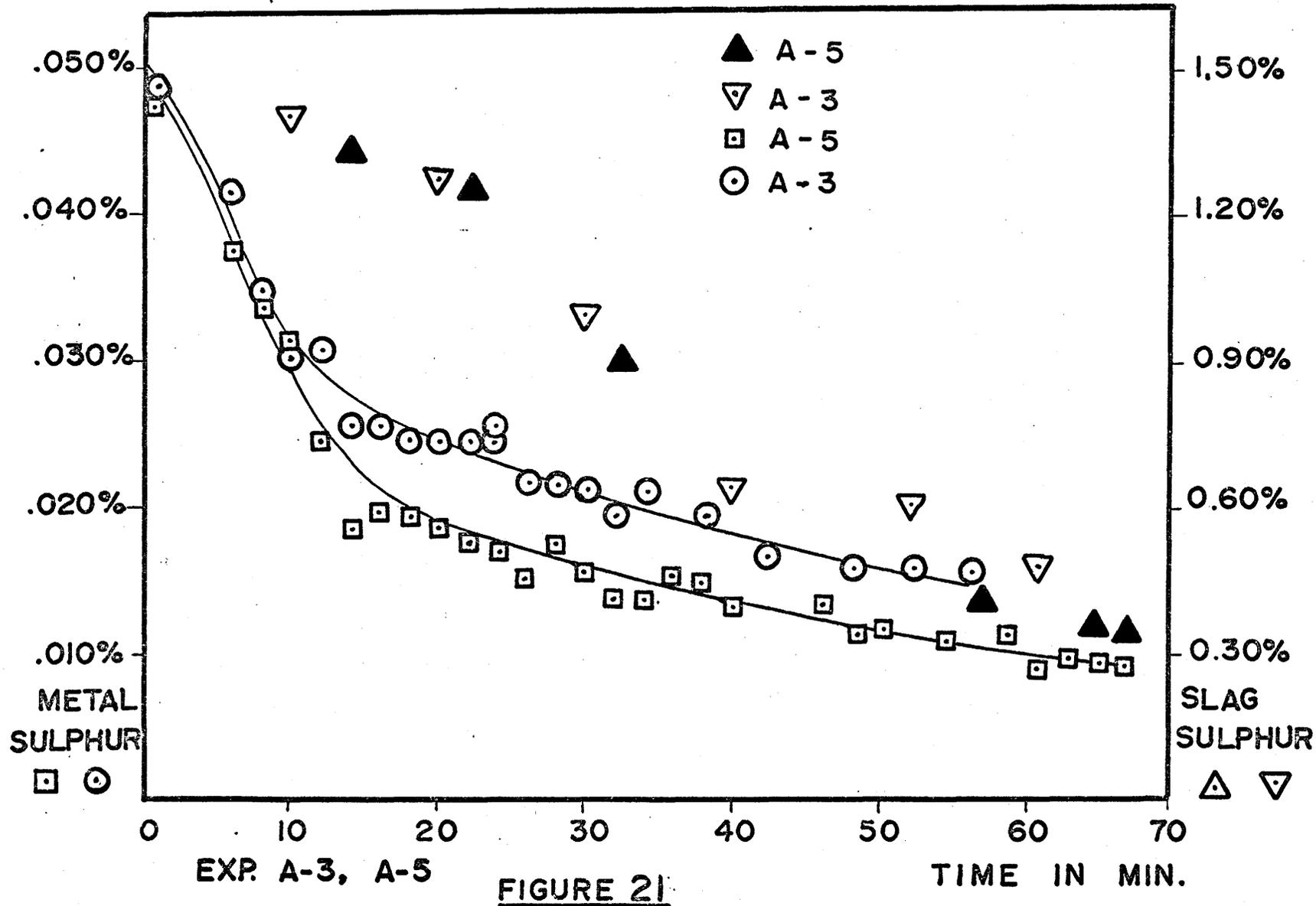
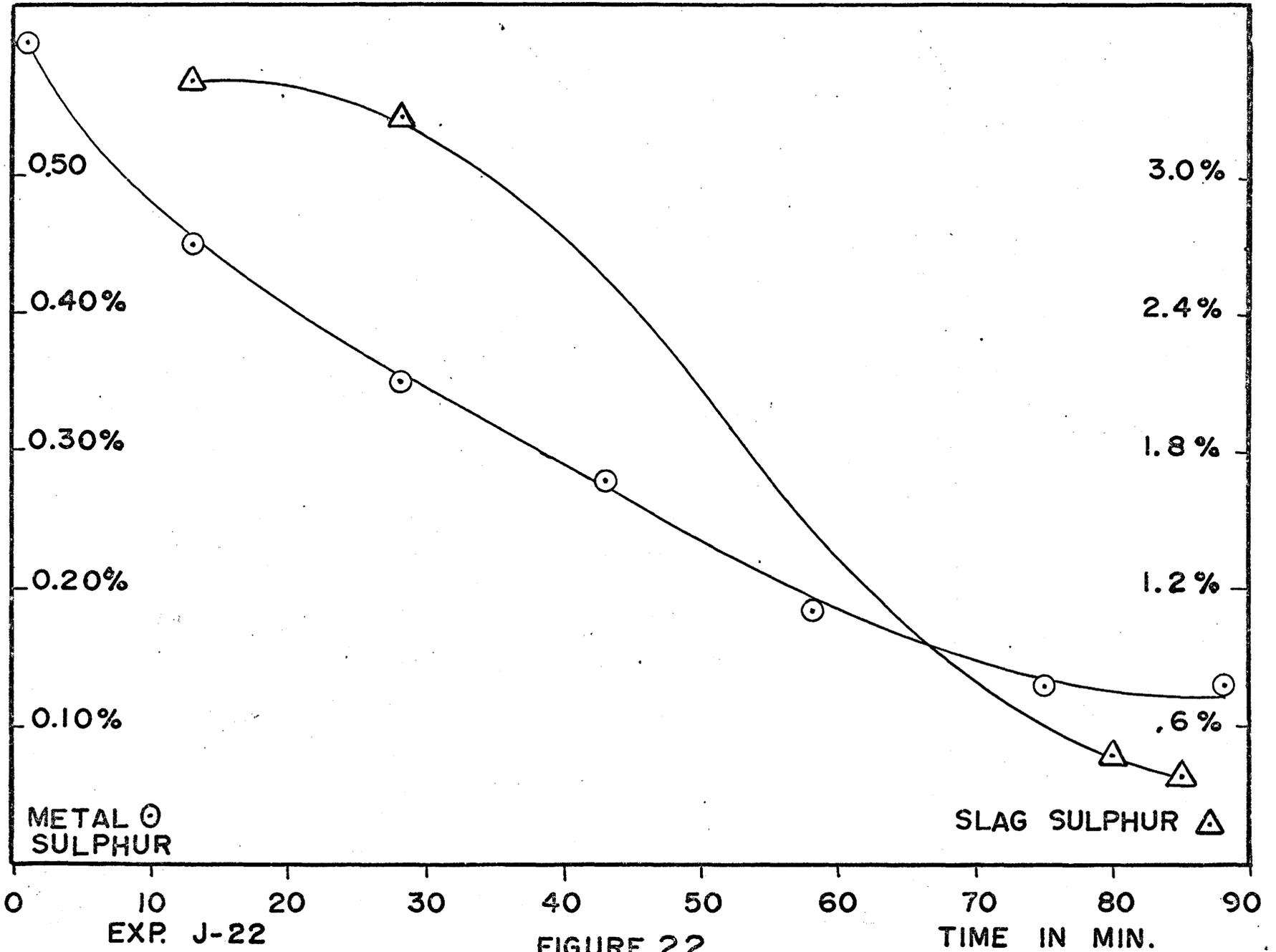
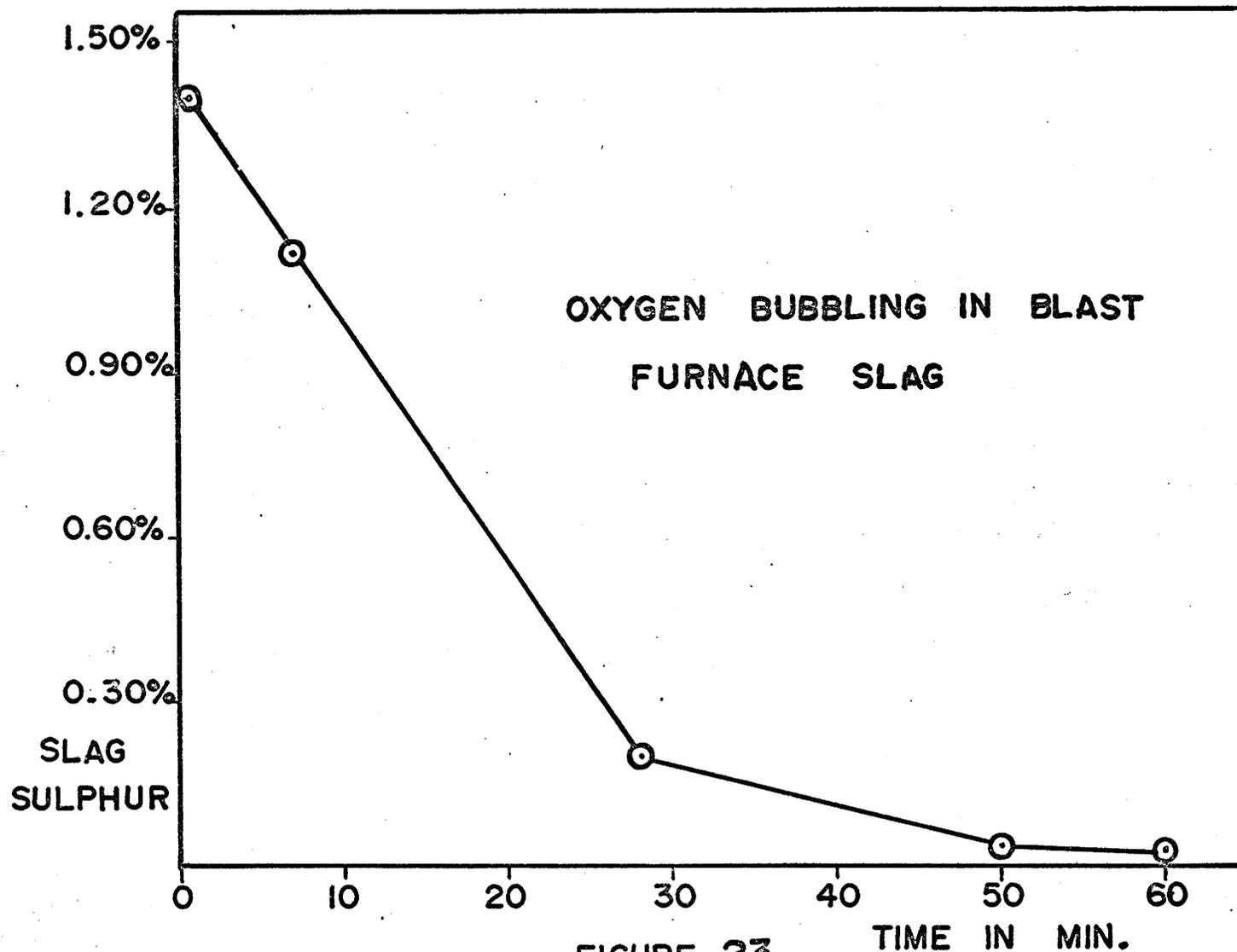


Figure 22

Desulphurisation with Cerium Oxide Rich Slag

Metal Sulphur and Slag Sulphur as a Function  
of Time for Experiment J-22





**FIGURE 23**