

ON THE FORMATION AND DECOMPOSITION
OF ZINC FERRITE UNDER SINTERING
CONDITIONS

by

JOHN ROUGHLEY RAWLING

A THESIS SUBMITTED IN PARTIAL FULFILMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF APPLIED SCIENCE

in the Department
of
Mining and Metallurgy

We accept this thesis as conforming to the standard
required from candidates for the degree of
MASTER OF APPLIED SCIENCE

Members of the Department of Mining and Metallurgy

THE UNIVERSITY OF BRITISH COLUMBIA

August 1956

Acknowledgements

The author is indebted to the National Research Council of Canada for the financial assistance which was needed to complete this project. He is grateful to the members of the Department of Mining and Metallurgy at the University of British Columbia for their advice and assistance, particularly to Professor F. A. Forward, Dr. E. Peters and Mr. J. P. Warner who co-directed the work.

Abstract

The formation of zinc ferrite from zinc and iron compounds, which reacted under sintering conditions, has been investigated. A mechanism of ferrite formation controlled by cation diffusion has been suggested and it has been shown that the nature of the reagents affects the rate of ferrite formation.

The decomposition of zinc ferrite by alkaline earth compounds, which reacted under sintering conditions, has also been studied. Calcium ferrite was found to be more stable than zinc ferrite but, for kinetic reasons a metastable phase of zinc ferrite was formed more readily.

Table of Contents

<u>Introduction</u>	<u>Page Nos.</u>
The constitution of zinc ferrite	1
Review of previous work	2
The crystal structure of spirals and ferrites	4
General properties of zinc ferrite	5
Scope and object of the present investigation	6
 <u>Experimental Procedure</u>	
Materials used	7
Preparation of mixtures for sintering	7
Method of sintering samples	8
Methods of analysis	10
Recording of Results	11
 <u>Results and Discussion</u>	
Physical Variables	11
The formation of zinc ferrite under sintering conditions	14
The decomposition of zinc ferrite under sintering conditions	26
 <u>Summary and Conclusions</u>	35
 <u>Suggestions for further Work</u>	38
 <u>Appendix A.</u>	
Microphotographs of powdered reagent mixtures prepared for sintering	39
 <u>Appendix B.</u>	
Analytical Methods	41
 <u>Appendix C.</u>	
Experimental Data	46

Appendix D.

Debye-Scherrer diagrams of reagents
used and sinter products obtained

65

Bibliography

67

List of Figures

	<u>Page Nos.</u>
Fig. 1 Sectional view of sintering furnace	9
Fig. 2 Effect of sintering mixture I at various temperatures for periods ranging between 30 minutes and 24 hours.	16
Fig. 3 Effect of sintering mixture II at various temperatures for periods ranging between 30 minutes and 24 hours.	17
Fig. 4 Effect of sintering mixture III at various temperatures for periods ranging between 30 minutes and 24 hours.	18
Fig. 5 Arrhenius plots.	21
Fig. 6 Effect of temperature variations on the sintering of different starting mixtures of zinc and iron compounds.	24
Fig. 7 Arrhenius plots.	25
Fig. 8 The effect of composition, sintering time and temperature upon the decomposition of zinc ferrite by calcium oxide.	29
Fig. 9 The effects of temperature and calcium oxide content upon sinter products.	32
Fig. 10 The effect of sintering time upon the composition of sinter products from a $\text{CaO-ZnO-Fe}_2\text{O}_3$ ternary mixture.	34

ON THE FORMATION AND DECOMPOSITION OF ZINC FERRITE UNDER SINTERING CONDITIONS

INTRODUCTION

During the early development period of a hydrometallurgical process for the extraction of zinc, which took place towards the end of the nineteenth century, it was noticed that, while most of the zinc present in the calcined ore could be leached using cold dilute sulphuric acid, there remained a residue which could only be extracted by prolonged boiling. (1) It was recorded (2) that the solution formed by leaching the insoluble residue in boiling acid invariably contained zinc and iron in the atomic ratio of one to two, with the conclusion that the iron present in the ore combined with the zinc to form a refractory compound. That this compound is the result of the combination of zinc and ferric oxides during the dead roasting of sulphide ores and concentrates was suggested by Prost (3) and has been considered as probably by others (1, 4, 5).

The Constitution of Zinc Ferrite

The compound formed by the reaction of zinc and ferric oxides has been placed in a general class of many such products which are known as ferrites. In 1847 Ebelman (6) succeeded in synthesising a number of spinels by fusing the component oxides in boric acid; among these was zinc ferrite which was obtained as small black octahedral crystals. Their general properties were as follows:-

Streak: dark brown

Hardness: scratched felspar with difficulty

Specific Gravity: 5.13.

Solubility: insoluble in dilute hydrochloric acid
Slightly magnetic.

Upon analysis, the compound was found to contain 66.5% Fe_2O_3 and 33.8% ZnO , corresponding to the formula ZnFe_2O_4 . The synthetic compound was found to be similar in all respects to naturally occurring Franklinite. Subsequent investigations into the constitution of zinc ferrite made by other workers have contributed a variety of results; some have claimed that more basic compounds than Ebelman's occur while others claim that this is not possible. Similar disagreement is found in the observation of magnetic properties. Recently Kushima and Amanuma (7) have concluded that zinc ferrite is a stoichiometric compound having the formula ZnFe_2O_4 and is normally non magnetic. They found that, above 1025°C , solid solutions of both ferric and zinc oxides in zinc ferrite were formed and that, when heated to higher temperatures the dissolved ferric oxide lost oxygen, forming magnetite, and the specimen became ferromagnetic.

Review of Previous Work

Most of the work done in investigating the chemical properties of zinc ferrite (2, 4, 8, 9, 10, 11, 12) has been directed towards the extraction of its zinc content or the suppression of its formation during industrial roasting operations. Some work has been done in the investigation of the reactivities of reagents in solid state reactions (13) although the knowledge of reaction mechanisms is limited.

The physical condition of reagents in solid state reactions is of major importance when the rate of reaction is being considered. Clearly the surface area of components and the degree of mixing and

packing are important but the crystalline structure of reagents and products may also affect the rate of reaction profoundly. In the formation of ferrites it has been shown (13) that the ferric oxide used has a widely varying reactivity depending on its physical form. (14, 15, 16) There are two principal forms of ferric oxide. The more stable form, α Fe_2O_3 , has a corundum structure and is formed by such processes as the oxidation of ferrous sulphate at high temperatures (about 800°C). The other form, γ Fe_2O_3 , has a spinel structure and x-ray analysis shows that its lattice spacing is almost identical to that of magnetite. It is formed by carefully oxidizing magnetite at 200°C or by precipitating ferric hydroxide from aqueous solution and calcining the precipitate at about 200°C . At 550°C γ Fe_2O_3 changes, non-reversibly, to α Fe_2O_3 . It has been shown (9, 17) that the form of the ferric oxide and the number of its lattice imperfections have a marked effect upon its reactivity during the formation of ferrites, the γ ferric oxide being the most reactive.

Methods of mixing reagents for the preparation of ferrites in the laboratory are of three main types. Ebelman (6) used a method in which the reagents were fused in borax; other workers have prepared mixtures of solid reagents by mechanical means (7, 18) or by precipitating them as carbonates or hydroxides from aqueous solution (7, 18). Again, some investigators have isolated ferrites from the leach residues of industrial extraction processes (2, 10). The rate and mechanism of ferrite formation will therefore be controlled by the method by which reagents are prepared.

The preparation of ferrites from mixtures of solid reagents has generally been done by sintering in furnaces whose temperatures were controlled within the limits of $\pm 5^\circ\text{C}$ or less. In most cases furnace atmosphere was not controlled except where ferrimagnetic ferrites were being formed for magnetic measurements(18).

The Crystal Structure of Spinel and Ferrites

The spinel structure is one in which the oxygen ions are arranged in cubic close-packing and which contains two species of cations, A and B, having tetrahedral and octahedral coordination with the oxygens. The crystallographic unit cell contains thirty two oxygen atoms; there are equivalent positions for eight metal atoms, of species A, surrounded tetrahedrally by four oxygen atoms and for sixteen metal atoms, of species B, surrounded octahedrally by six oxygens. The unit cell may be considered as containing eight AB_2O_4 units.

Where A is a divalent cation and B is a trivalent cation it has been calculated (19, 20) that the normal structure, as described above, is the stable one, - assuming that the crystals are completely ionic. It is concluded that M^{+++} cations prefer octahedral sites with the exception of Fe^{+++} , In^{+++} and Ga^{+++} which prefer a coordination of four. Some divalent cations also show a strong preference for the tetrahedral sites and of these Zn^{++} is one. Therefore while most ferrites are 'inverted' (i.e. some Fe^{+++} replaces M^{++} in the tetrahedral sites e.g. $\text{Fe}^{+++}(\text{Mg}^{++} \text{Fe}^{+++}) \text{O}_4$) zinc ferrite is a normal spinel having the Zn^{++} coordinated with four oxygens.

Bearing in mind the nature of the spinel structure and the energies of the ions associated with it, it is not difficult to believe that Fe_3O_4 , $(\text{Fe}^{+++} (\text{Fe}^{++} \text{Fe}^{+++}) \text{O}_4)$ can easily be converted to γ Fe_2O_3 which retains the cubic close packing of the spinel but which contains only $21\frac{1}{3}$ iron atoms per unit cell. In considering the ferrites of certain alkaline and alkaline earth elements it is found that, owing to the size of the cations, complex oxide structures prevail.(21) Thus calcium aluminate has the formula $3\text{CaO} \cdot 16\text{Al}_2\text{O}_3$ and it seems likely that calcium ferrite will also be of complex form.(10) It should be noted that in many of these complex oxides x-ray analysis shows that they are closely related to the spinel structure.(20)

General Properties of Zinc Ferrite

The general chemical properties of zinc ferrite have been studied by a number of investigators in an attempt to find suitable methods by which this compound can be decomposed. It has been found that, when the compound is heated above 560°C in a retort with carbon, it dissociates giving zinc oxide and ferric oxide.(9, 12) In an atmosphere containing 7.5% sulphur dioxide it was found that zinc ferrite was decomposed at 450°C giving zinc sulphate and ferric oxide (11, 12) The reaction was slow, however, and though it has been tried on an industrial scale in sulphating roasts it was not successful. A more promising method of decomposition was indicated by Schwartz and Krauskopf (10) who showed that zinc ferrite was decomposed by sintering with oxides of the alkaline earth elements. When magnesium oxide was used, no more than 37% of the available zinc was rendered soluble no matter how great an excess of

magnesium oxide was added. Using calcium oxide in the ratio of $3\text{CaO}:1\text{ZnFe}_2\text{O}_4$ as much as 87% of the available zinc was rendered soluble. From x-ray diffraction studies it appeared that magnesium oxide replaced the zinc oxide in the spinel lattice while in the case of the calcium oxide a new structure was developed.

The properties of zinc ferrite have been summarised as follows:(8)

Colour: Deep orange brown

Specific Gravity: 5.09 to 5.29 (5.322 and 5.349 calculated from lattice parameters)

Hardness: 5.5 (mohr's Scale)

Unit lattice: $a_0 = 8.42 \pm 0.01 \text{ \AA}$ (mean of 7 values)

Melting Point: 159°C

Crystal Form: Cubic - octahedral

Scope and Object of the Present Investigation

The present investigation has been made with the object of expanding the existing knowledge of the mechanisms by which zinc ferrite is formed and the conditions which favour its formation and decomposition during sintering. At the outset, a study of physical variables affecting solid state reactions was made in order to select an experimental procedure which yielded reproducible results. Following this preliminary investigation, the study was continued in three major sections, namely:-

1. Factors affecting the formation of zinc ferrite from various starting mixtures.

2. Factors affecting the decomposition of zinc ferrite by the addition of calcium and magnesium salts.

3. Factors affecting the formation and decomposition of zinc ferrite on sintering ternary mixtures of zinc oxide, ferric oxide and calcium oxide.

EXPERIMENTAL PROCEDURE

Materials Used

All materials used in this investigation were of reagent grade with the exception of calcium and magnesium compounds which were all chemically pure. The ferric oxide used was prepared by the thermal decomposition of ferrous sulphate under controlled oxidising conditions at temperatures lying between 760°C and 930°C.

Preparation of Mixtures for Sintering

Three methods were used to prepare mixtures for sintering:-

(a) Mechanical Mixing

Mixtures of zinc and ferric oxides were prepared by weighing the required amounts of the constituents and rolling them together in a bottle for twenty four hours.

(b) Co-precipitation

Zinc and ferric hydroxides and carbonates were co-precipitated from an aqueous nitrate solution by the rapid addition of a strong solution of sodium carbonate. The precipitate was washed, filtered and calcined at 500°C to decompose hydroxides and carbonates present.

(c) Ball Milling

The desired components were mixed by grinding them in a quartz pebble mill with a grinding fluid in which they were insoluble.

Usually water satisfied this requirement but in one case, where zinc sulphate was being mixed, ethanol was used.

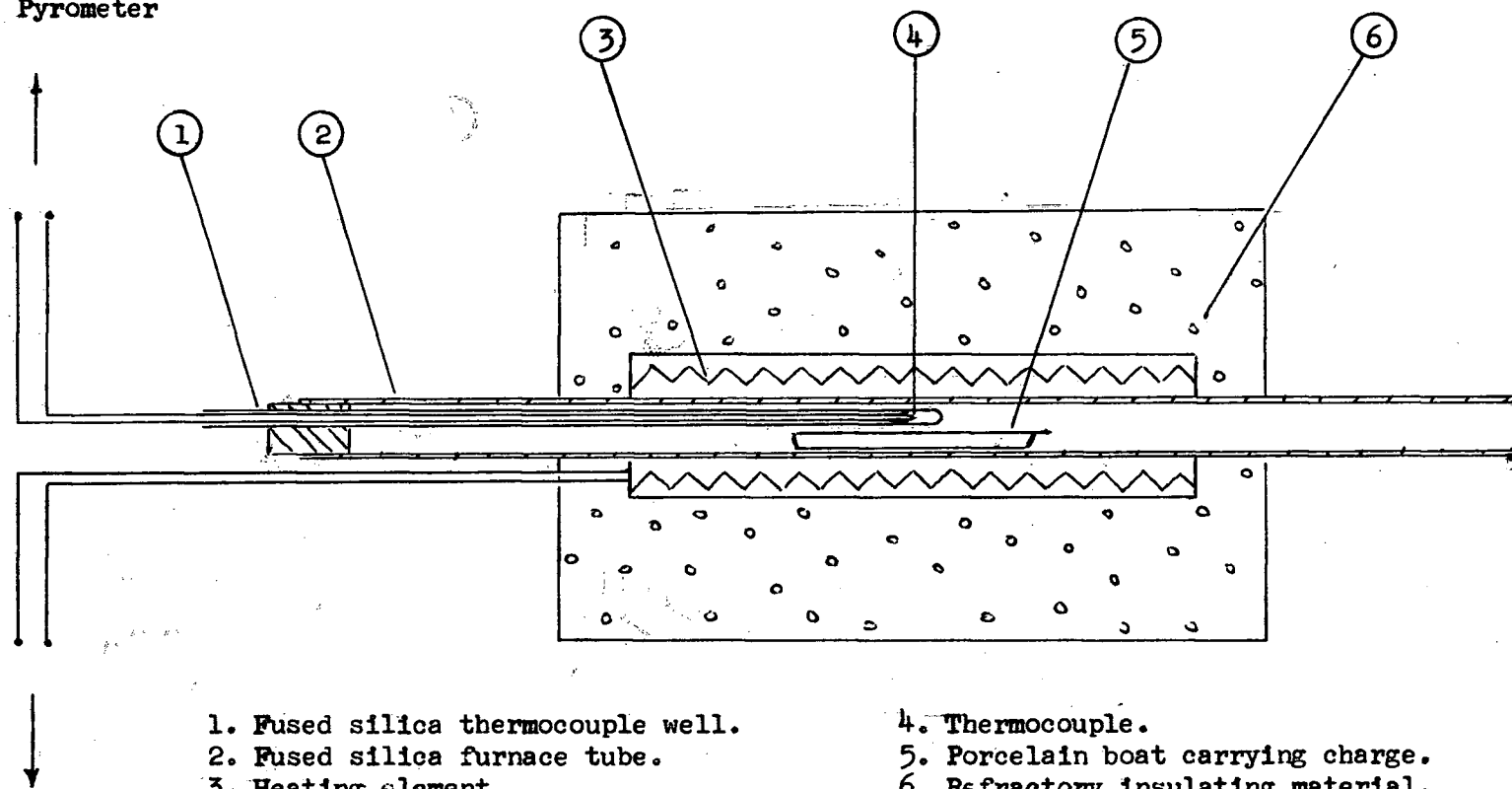
The procedure for mixing was as follows:-

The charge, which varied from 120 to 350 grams of solids, was placed in the mill together with 1000 to 1250 ml. of grinding fluid, the amount depending upon the size of the charge. The mixture was then ground for two hours, washed from the mill, filtered and dried in readiness for sintering. Mixtures thus produced were studied under the microscope; components appeared to be evenly distributed through the mixture and had an average particle diameter of about half a micron (see Appendix A).

Method of Sintering Samples

Two identical furnaces were used for sintering (see fig. 1). Each consisted of a fused silica tube 26 inches long and 1 inch l.d. surrounded by a 600 watt heating element itself contained in a fire-brick block 15" x 9" x 9" in overall dimensions. The element was connected in series with the secondary of a variable transformer and, by suitably adjusting the latter, the power output could be adjusted until a minimum temperature fluctuation of the furnace was obtained. Temperature control was effected by a chromel-alumel thermocouple which was placed in the centre of the furnace tube and was protected by a fused silica well. The thermocouple was connected to a Wheelco pyrometer which was capable of controlling the temperature to within $\pm 5^{\circ}\text{C}$ at 100°C ; the pyrometer was calibrated by means of a potentiometer before each experiment.

To
Pyrometer



To
Variable
Transformer.

Fig. 1 Sectional view of sintering furnace.

The furnace atmosphere, which was not controlled, consisted of a mixture of air and any gaseous products of calcination which were formed during sintering.

Sintering operations were carried out as follows: The furnace was first run up to the required temperature and allowed to stand for about an hour until temperature fluctuations had decreased to less than $\pm 5^{\circ}\text{C}$. The sample to be sintered (about 10 grams) was placed in a glazed porcelain boat (2 x 10 x 1.5 cm. in overall dimensions) which was then pushed into the centre of the furnace. After sintering, the boat was removed from the furnace and allowed to cool in air. In cases where the sintering period was only thirty minutes in length, boats were preheated in the furnaces and small samples (3 or 4 grams) were added to reduce the time needed to bring them to temperature.

Methods of Analysis

Samples for analysis were prepared by grinding the sinters with pestle and mortar and then rolling them prior to weighing. They were then analysed by conventional chemical methods (see Appendix B.) in order to determine the total amounts of zinc and iron present and also the amounts of zinc which had not combined with ferric oxide to form zinc ferrite.

Since the zinc present as zinc ferrite is relatively refractory, it is not difficult to separate it from the zinc remaining as uncombined zinc oxide, carbonate or sulphate, hereafter referred to as soluble zinc. The solvent used was an ammonia-ammonium chloride solution as used by

Hopkins (8) and by many of the other investigators in this field. By this means 'soluble' zinc was dissolved as an ammine leaving behind a residue of zinc ferrite and ferric oxide. Soluble ferrous ion was not detected.

Recording of Results

The results obtained by chemical analysis were recorded and from them the amounts of zinc ferrite in sintered samples were calculated. In order to compare the ferrite yields of mixtures containing different zinc-iron ratios the atomic ratio of the zinc present as ferrite to total iron was taken as the absolute yield of ferrite.

RESULTS AND DISCUSSION

Physical Variables

Physical variables such as particle size, degree of packing and mixing technique were investigated in order to find methods for their control in subsequent experiments. Their effects upon ferrite formation were not studied further.

(a) Methods of Mixing

The various techniques employed for mixing reagents prior to sintering have been described above. Mixtures of zinc and ferric oxides were prepared by each of these methods and samples were then sintered over a range of temperatures for four hour periods. Sinter products were analysed and compared on the basis of their ferrite yield (Table I).

TABLE I Results of Sintering Mixtures of Zinc and Ferric Oxides
(approx molar ratio 1:1) prepared by Dry Rolling, Co-
precipitation and Wet Grinding Methods.

Prepared by Dry Rolling - mixtures A and B
 Prepared by Co-Precipitation - mixture C
 Prepared by Wet Grinding - mixtures D, E, F and G.

Sintering Time - 4 hours

Sintering	Ratio -Zn combined as ferrite: Total Fe.						
Temp. °C.	A	B	C	D	E	F	G
650	.050	-	-	-	-	-	-
700	.050	-	.466	.479	.469	-	-
750	.161	-	.458	.479	.481	-	-
800	-	.302	.446	.486	.487	.487	.488
850	.212	-	.464	-	-	-	-
Calcine	-	-	.372	-	-	-	-

All mixtures prepared contained 1 gram molecule of zinc oxide and 1 gram molecule of ferric oxide except mixtures F and G which contained half a gram molecule each.

Results showed that mixtures prepared by dry rolling (A and B) did not sinter uniformly and gave a low yield of ferrite. Sinters of the co-precipitated mixture were found to be uniform and a high yield of ferrite was obtained. However an anomalously large yield of ferrite was formed during the calcining process prior to sintering. It was concluded, from comparing the results with those subsequently obtained by sintering a mechanical mixture of zinc carbonate and ferric oxide, that the ferric oxide produced by the coprecipitation method was highly reactive and did not resemble the form produced by roasting ferrous sulphate. Sinners produced from mixtures prepared by the wet grinding method yielded large amounts of ferrite and results were found to be reasonably reproducible even when the size of the ball mill charge was reduced by half. Contamination of the charge with silica from the mill was not great and averaged 0.5% of the total charge, plus or minus 0.1%.

Preparation of mixtures by dry rolling was discarded in favour of one of the others since the results of sintering were not reproducible. Of the remaining two methods the wet grinding method had the advantages in that the components of the mixture could be chosen more freely, that mixtures were prepared more simply and the results of sintering them were reproducible. It was therefore used in all subsequent experiments.

(b) Effects of Packing

Several tests were run in order to discover the effect of packing on sintering. Samples were prepared as loose powder and as bars compressed at 57000 psi. Results are tabulated in Table 2 and show that the variation in sinter product was small.

TABLE II Effect of Packing upon Sinter Product

Samples prepared by wet grinding

Sintering time:- 4 hours

Types of Packing: (1) Powder

(2) Powder compressed into bars at 57000 psi.

Sintering Temp. °C	Atomic Ratio - Zn combined as ferrite: Total Fe.	
	(i)	(ii)
800	0.485	0.485
660	0.410	0.401
640	0.270	0.261
620	0.110	0.102

THE FORMATION OF ZINC FERRITE UNDER SINTERING CONDITIONS

(a) The Effects of Sintering Time on the Composition of Sinter Products obtained from mixtures of Zinc and Ferric Oxides.

The rate of formation of zinc ferrite from sintered mixtures of zinc and ferric oxides was investigated in an attempt to establish the controlling mechanism of ferrite formation. Mixtures of varying proportions were used to observe their effect on the rate of formation of ferrite and to establish the solubility limit of zinc oxide in zinc ferrite at the sintering temperatures selected.

The following mixtures were prepared for sintering

I. $\text{ZnO-Fe}_2\text{O}_3$ (atomic ratio Zn:Fe 0.474:1 ^{*})

^{*} Exact atomic ratios of Zn:Fe were determined by analysis of the mixtures.

II. $\text{ZnO-Fe}_2\text{O}_3$ (atomic ratio Zn:Fe 0.466:1)

III. 2 $\text{ZnO-Fe}_2\text{O}_3$ (atomic ratio Zn:Fe 0.940:1)

Samples of these mixtures were sintered at selected temperatures between 600°C and 1050°C for periods ranging from 30 minutes to 24 hours in length.

The results^{*} of these experiments are summarised in figs. 2, 3, and 4. They show that the relationship between the yield of ferrite and the square root of the sintering time is approximately linear until the reaction approaches completion, when the rate gradually decreases. The plots fail to intersect the time axis at the origin, the length of the intercept being some inverse function of temperature. This is suggestive of an induction period in which nucleation takes place. In the first two series it was noted that at the conclusion of the reaction all the available zinc was converted into ferrite. In the third series, where excess zinc oxide was added, the atomic ratio of insoluble zinc to total iron, in the equilibrium condition, was rather greater than 0.5 and appeared to increase slightly with temperature. This indicated that there is limited solid solubility of zinc oxide in zinc ferrite.

An explanation of the linear portion of the graphs obtained may be made by considering a diffusion controlled mechanism of ferrite formation which is analogous to that developed by Mott (23) to explain the formation of thin oxide films on certain metal surfaces. In the present case, where zinc and ferric oxides are in contact, it is suggested that zinc ferrite is formed at the interface and the rate of growth of the ferrite film

* see Appendix C for experimental data.

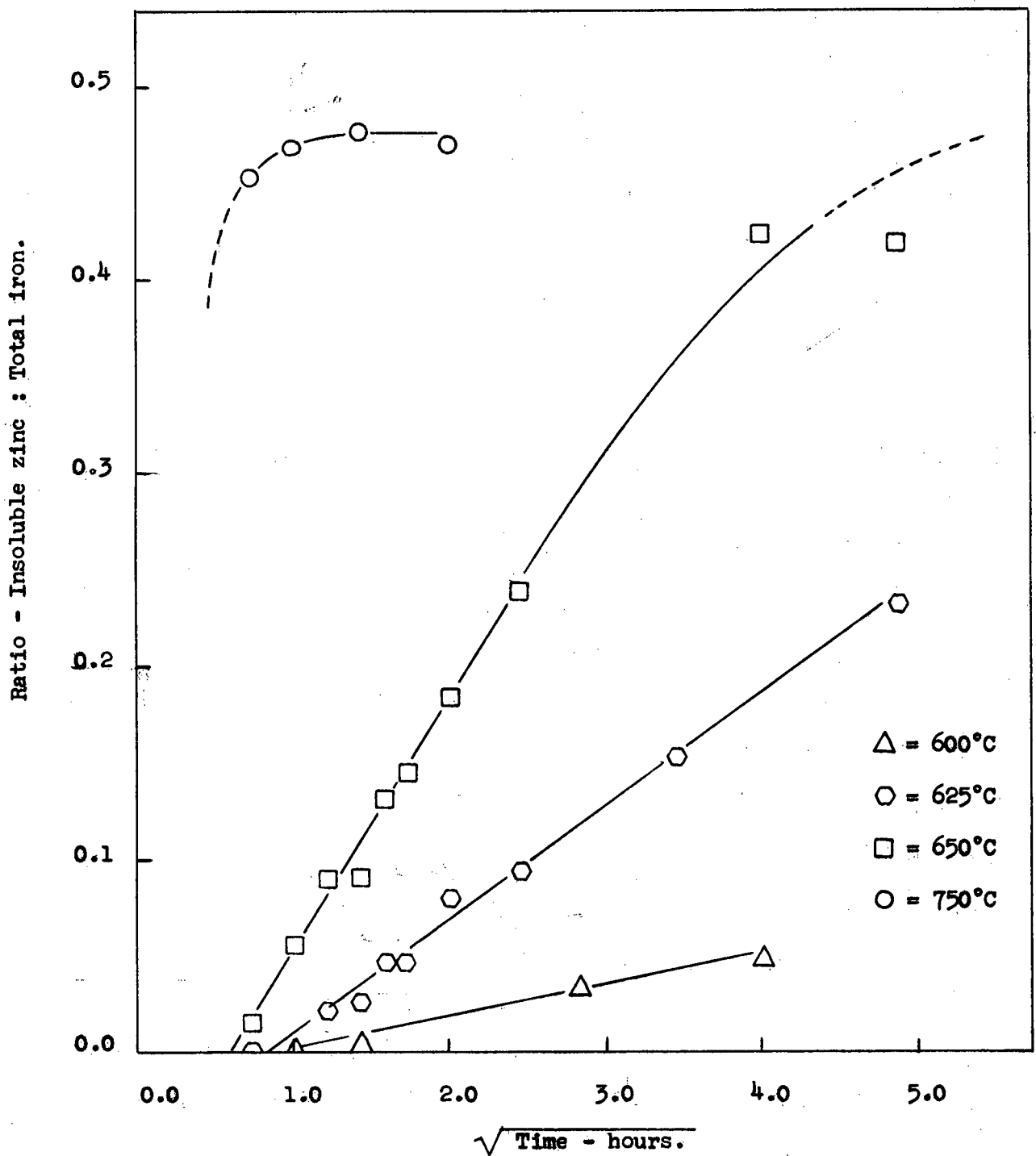


Fig. 2 - Effect of sintering mixture I at various temperatures for periods ranging between 30 minutes and 24 hours.

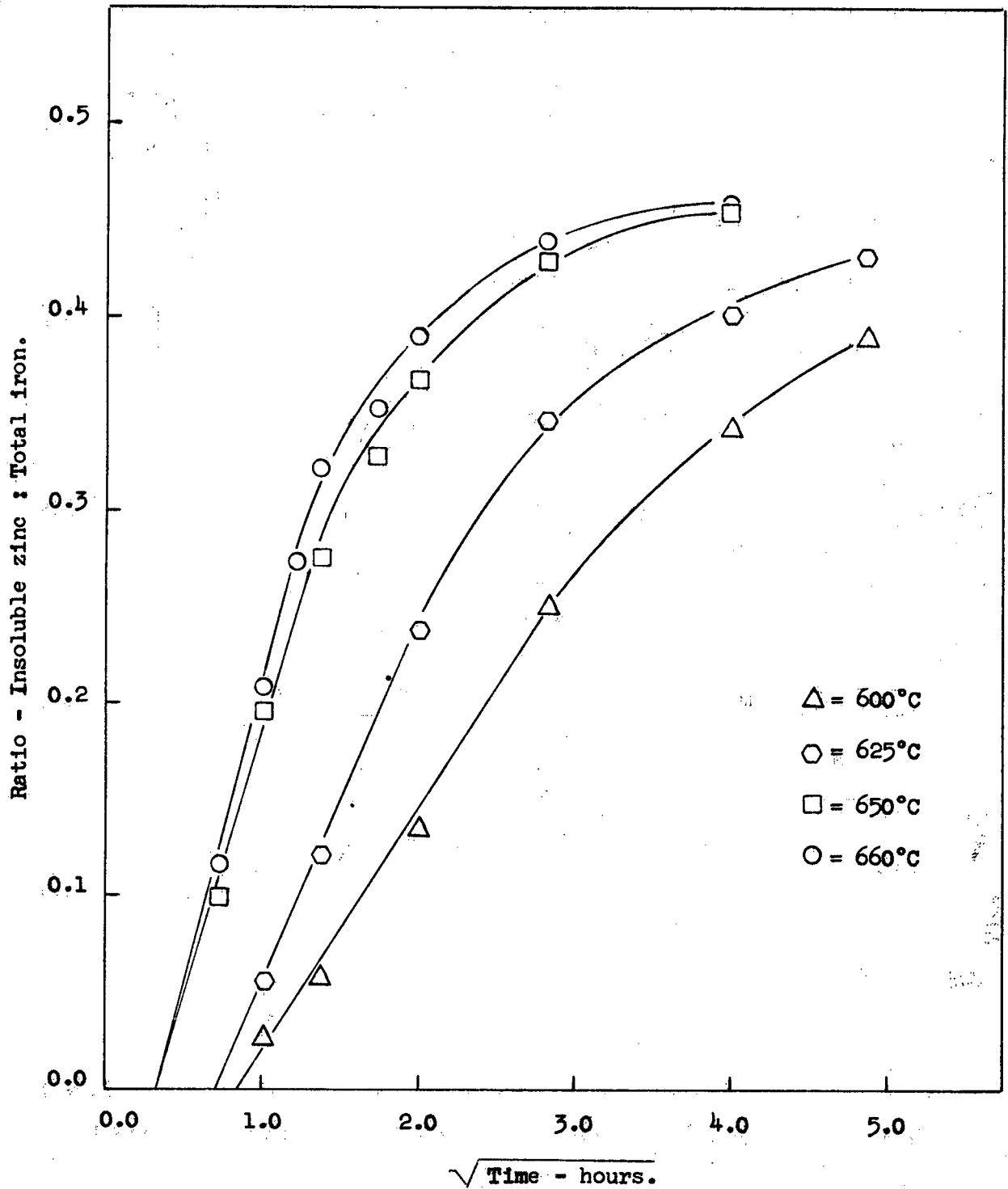


Fig. 3 - Effect of sintering mixture II at various temperatures for periods ranging between 30 minutes and 24 hours.

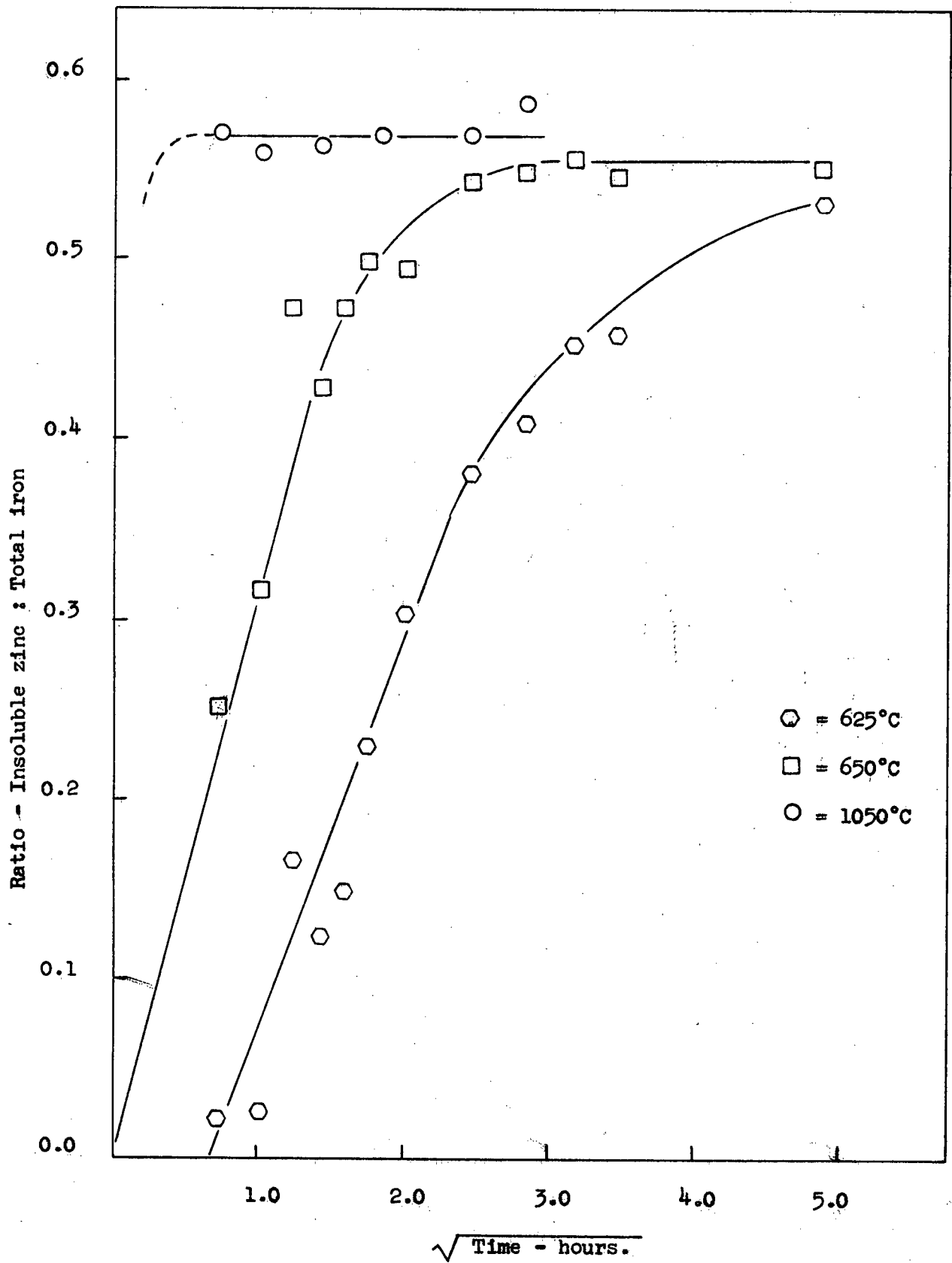


Fig. 4 - Effect of sintering mixture III at various temperatures for periods ranging between 30 minutes and 24 hours.

is determined by the rate of diffusion of the cations^{*} through the film.

The diffusion of one species of cation, say Zn^{++} , in zinc ferrite is now considered. If $n(x)$ is the number of zinc ions per unit volume at a distance x from the zinc oxide-ferrite interface, the flow of ions is given by

$$J = \frac{\partial n}{\partial x} D_i \quad (1)$$

where J is the number of ions diffused per unit area per unit time and D_i is the diffusivity.

It is assumed that $n=0$ at the ferrite-ferric oxide interface. If n_0 is the concentration of zinc ions in the ferrite in equilibrium with zinc oxide then

$$J = \frac{n_0 D_i}{x} \quad (2)$$

The rate of growth of the ferrite film is given by the expression

$$\frac{dx}{dt} = J \Omega \quad (3)$$

where Ω is the volume of ferrite per metal ion.

Substituting in equation (2) we have

$$\frac{dx}{dt} = \frac{n_0 \Omega D_i}{x} \quad (4)$$

and by rearranging and integrating

$$x^2 = 2 n_0 \Omega D_i t \quad (5)$$

$$\text{or } x = \sqrt{2 n_0 \Omega D_i t} \quad (6)$$

where x , being a measure of the thickness of the ferrite film is also proportional to the ferrite yield.

* Mott assumes that oxygen ions cannot diffuse interstitially in such films owing to their relatively large size.

Arrhenius plots (see fig. 5) were constructed from the series of experimental data obtained from sintering mixtures I, II and III as described above. The plots were rather indefinite since the amount of data available was small. However, a linear plot was obtained from the results of series II (mixture II) and the points obtained from the other series appeared to belong to parallel but not coincident plots. The fact that the plots do not coincide indicates that different frequency factors were obtained for different mixes owing to variables which were beyond the experimental control adopted.

The activation energies obtained from the Arrhenius plots are given in Table III below:

TABLE III Activation energies for the Formation of Zinc Ferrite
from Zinc and Ferric Oxides

Experimental Series	Activation Energy
Series I	36 K Cal.
Series II	25 K Cal.
Series III	26 K Cal.

These values are of the order which might be expected for a diffusion mechanism.

Lindner (24) has measured the diffusivities of both zinc and iron in zinc ferrite and found them to have approximately equal values. The activation energies of both processes, measured by him, are given below.

Diffusion of Zinc in Zinc ferrite; Activation Energy 86 K Cal.

Diffusion of Iron in Zinc ferrite; Activation Energy 82 K Cal.

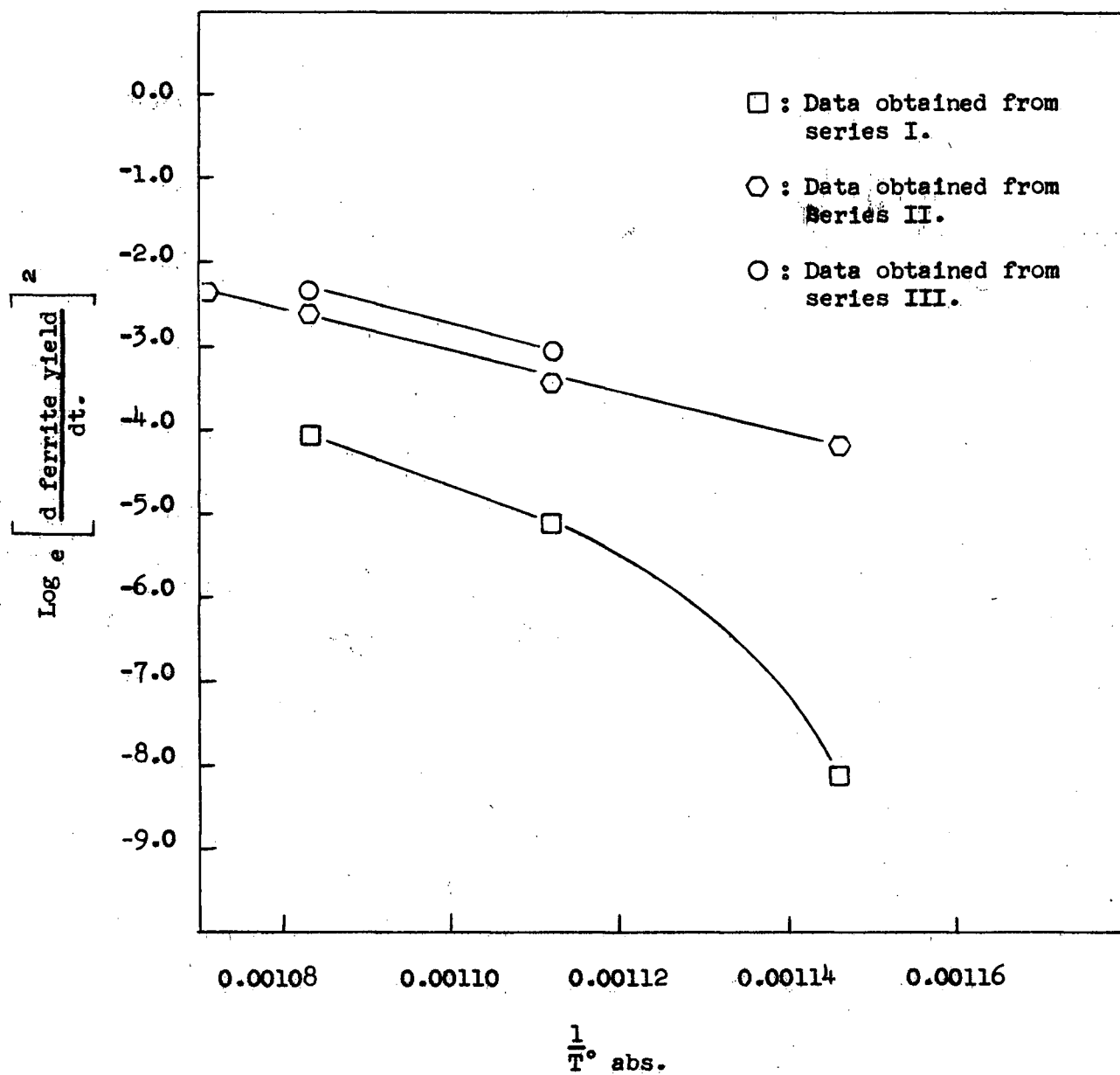


Fig. 5 - Arrhenius plots.

These values are high in comparison with the ones obtained in the present work. However results obtained by the radio tracer technique, as used by Lindner, were subsequently shown to give erroneously high values in similar systems (25). There is, therefore, the possibility that Lindner's work is in error.

(b) The Effect of Temperature Variations on the Sintering of Different Starting Mixtures.

The object of the following series of experiments was to discover the effect of reacting mixtures of different reagents, containing zinc and iron, upon temperature of formation of zinc ferrite, and if possible, to determine the mechanisms of ferrite formation.

The following mixtures were prepared for sintering:-

$\text{Zn(OH)}_2 - \text{Fe}_2\text{O}_3$ (atomic ratio Zn:Fe 0.530:1)

$\text{Zn CO}_3 - \text{Fe}_2\text{O}_3$ (atomic ratio Zn:Fe 0.530:1)

$\text{ZnO} - \text{Fe}_2\text{O}_3$ (atomic ratio Zn:Fe 0.482:1)

$\text{ZnSO}_4 - \text{Fe}_2\text{O}_3$ (atomic ratio Zn:Fe 0.510:1)

Samples of these mixtures were sintered for four hours at constant temperatures which ranged from 300°C to 1000°C.

The results, summarised in Fig. (6), were similar for each series excepting that the temperatures of ferrite formation were different in each case. In the case of the zinc oxide-ferric oxide series, ferrite was formed in the temperature range 575°C - 675°C, whilst for the zinc carbonate-ferric oxide series this temperature range was lowered by some 30°C and for the zinhydroxide-ferric oxide series by about 75°C.

The results do not afford a satisfactory explanation of these phenomena; in both the latter cases the zinc compounds could have been decomposed, forming a gaseous product and zinc oxide, below the temperatures at which ferrite formation occurred and it is considered that the lowering of the temperature of ferrite formation could be due to the presence of a more highly disordered and, consequently, more active form of zinc oxide than was present in the zinc oxide-ferric oxide mixture.

In the case of the zinc sulphate-ferric oxide series it was noticed that little ferrite was formed until the temperature of decomposition of zinc sulphate was reached, with the inference that, when zinc ferrite is formed from zinc sulphate and ferric oxide, the reaction goes in two steps:

1. $\text{ZnSO}_4 \rightarrow \text{ZnO} + \text{SO}_3$
2. $\text{ZnO} + \text{Fe}_2\text{O}_3 \rightarrow \text{Zn Fe}_2\text{O}_4$

Therefore it appears that the temperature of ferrite formation depends upon the thermodynamic properties of zinc sulphate. The reverse reaction, namely the formation of zinc sulphate from zinc ferrite by the action of an oxidising atmosphere containing sulphur dioxide has been observed at 450°C.(25)

Arrhenius plots, constructed for each series of experimental data, are shown in fig. 7. They were found to be approximately linear except at low temperatures when their gradients were found to increase. This suggests that the activation energy for the formation of zinc ferrite decreases with an increase in temperature. Activation energies

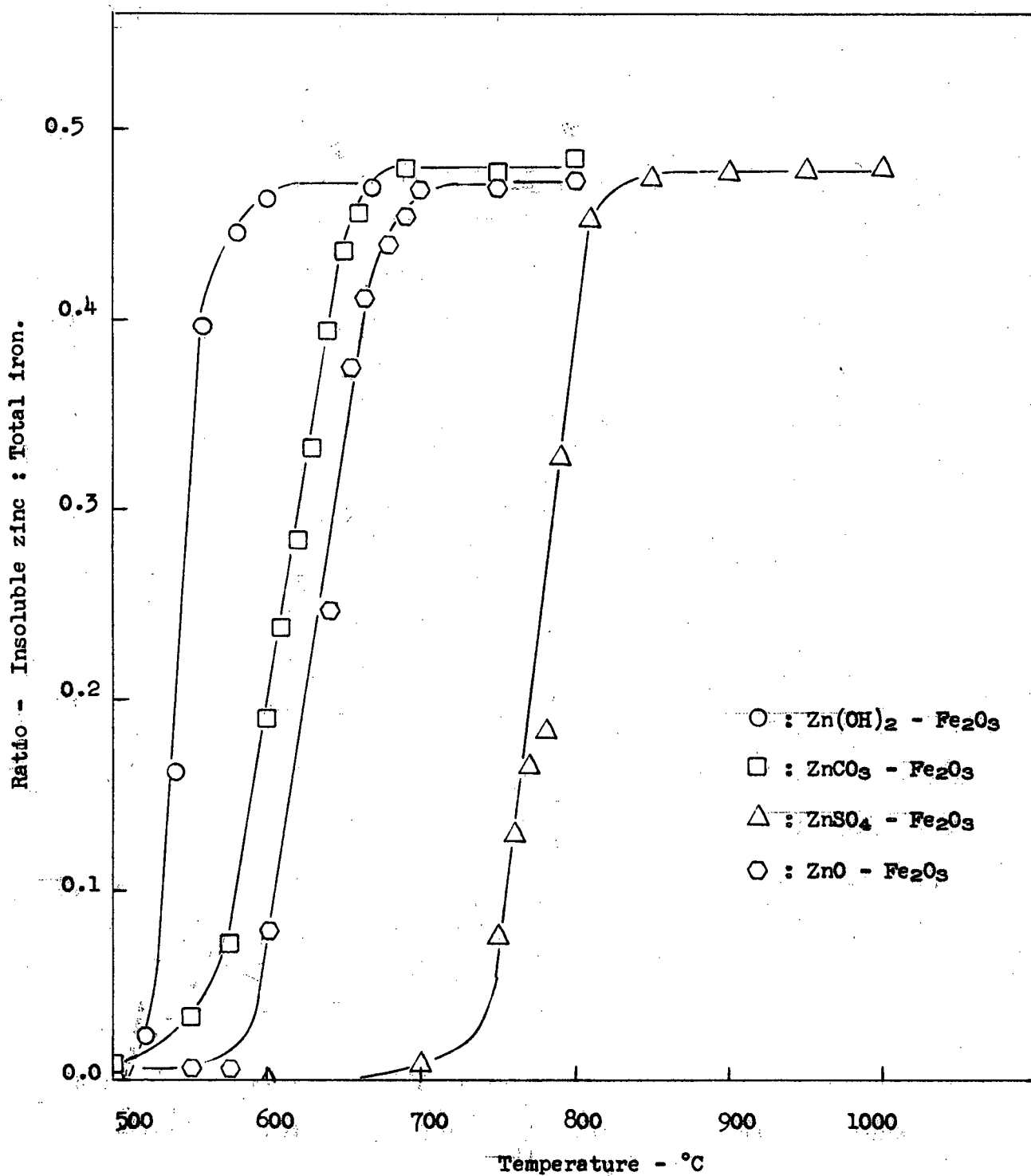


Fig. 6 - Effect of temperature variations on the sintering of different starting mixtures of zinc and iron compounds.

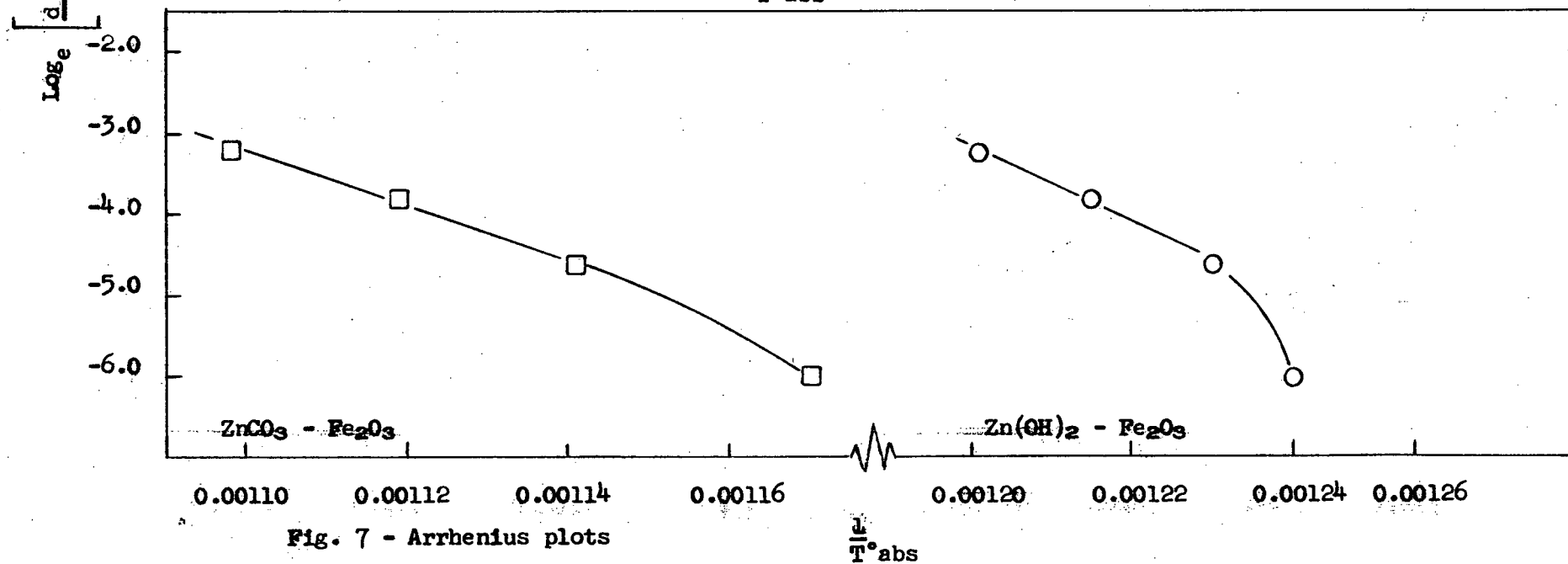
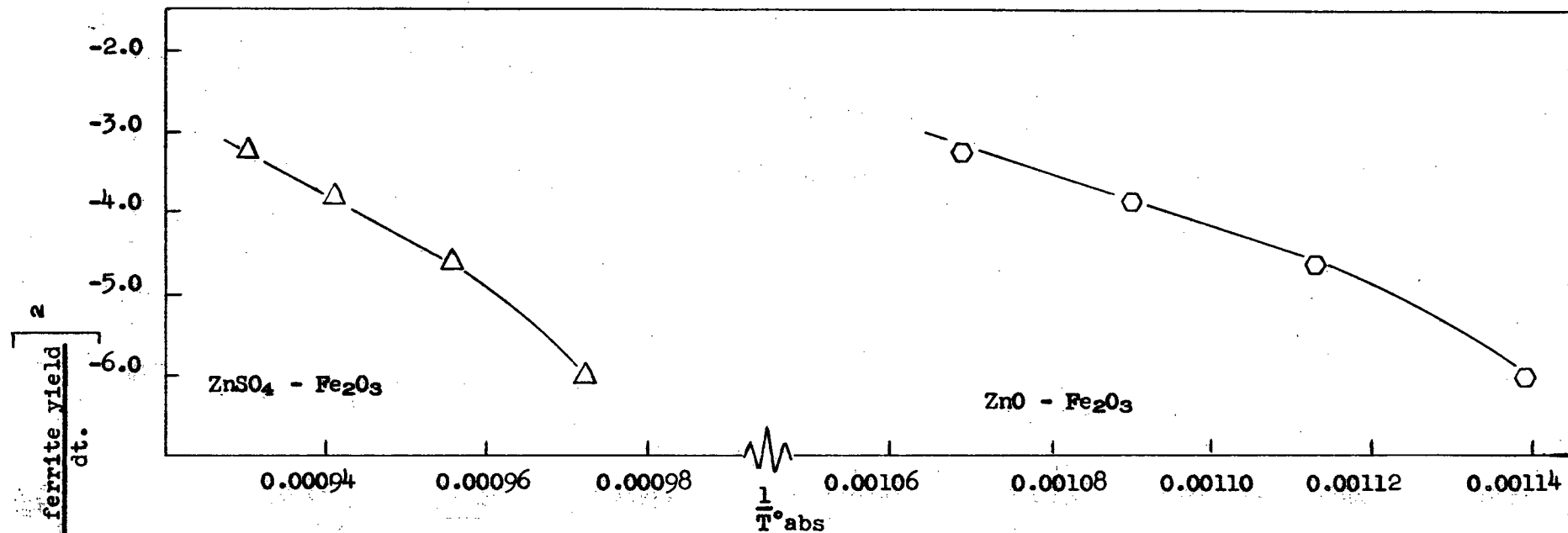


Fig. 7 - Arrhenius plots

were calculated from the straightest portion of the Arrhenius plots and are tabulated in Table IV below:

TABLE IV Activation Energies for the Formation of Zinc Ferrite from various starting mixtures.

Starting Mixture	Activation Energy
Zn(OH) ₂ - Fe ₂ O ₃	49 K Cal.
Zn CO ₃ - Fe ₂ O ₃	34 K Cal.
ZnO - Fe ₂ O ₃	32 K Cal.
ZnSO ₄ - Fe ₂ O ₃	54 K Cal.

THE DECOMPOSITION OF ZINC FERRITE UNDER SINTERING CONDITIONS

(a) The Effect of Temperature on the Decomposition of Zinc Ferrite by several Calcium and Magnesium Salts.

In considering the decomposition of Zinc ferrite, it was thought that zinc might be replaced in the spinel structure by more basic elements such as the alkaline earths. Swartz and Krauskopf (9) have already indicated that this is possible, at least to some extent, and it was decided to extend their study by discovering the effect of sintering different calcium and magnesium salts with samples of zinc ferrite.

Zinc ferrite was prepared by sintering an equimolecular mixture of zinc and ferric oxides at 850°C for six hours. Samples of ferrite were then mixed with one of the following compounds in approximately one to one molar ratio:-

Calcium oxide; Calcium Carbonate; Calcium Sulphate; Magnesium oxide; Magnesium Sulphate.

Samples of the mixtures obtained were sintered for two hours at 750°C, 850°C, 950°C and 1050°C and then were analysed.

The results, given in Table V, show that zinc ferrite was decomposed by all the compounds added with the exception of calcium sulphate.

TABLE V Effect of Temperature on the Decomposition of Zinc Ferrite by several Calcium and Magnesium salts.

Added Compound	Ratio:- Insoluble Zinc/Total hon.			
	750°C	850°C	950°C	1050°C
CaO	0.462	0.451	0.410	0.324
CaCO ₃	0.457	0.431	0.378	0.289
CaSO ₄	0.454	0.453	0.448	0.444
MgO	0.448	0.398	0.354	0.361
MgSO ₄	0.442	0.419	0.239	0.299

Atomic Ratio Total Zn/Total Fe - 0.466:1

(b) The Effects of Composition, Sintering Time and Temperature upon the Decomposition of Zinc Ferrite by Calcium Oxide.

An attempt was now made to explain the mechanism by which zinc is replaced in zinc ferrite by calcium and magnesium when mixtures of zinc ferrite and a compound of calcium or magnesium are sintered together. Calcium oxide was chosen as the added compound since the reaction between oxides in ferrite formation is probably simpler than those which occur between other salts and since calcium was found to react more favourably than magnesium by previous investigators (10).

Zinc ferrite was prepared by sintering an equimolecular mixture of zinc and iron oxides for eight hours at 850°C. Three samples of zinc ferrite were then mixed with calcium oxide in the approximate molar ratios ($\text{ZnFe}_2\text{O}_4:\text{CaO}$) 1:1, 1:2, and 1:4 respectively. Samples of each of these mixtures were then sintered at 850°C, 950°C and 1050°C for periods varying from one to eight hours.

The results show that zinc previously combined as ferrite is rendered soluble in varying amounts. Zinc oxide was identified in the sinter product by the comparison of x-ray diffraction patterns^{*} of pure zinc oxide and of the sinter product.

Rate curves were plotted (see fig. 8) for the decomposition of zinc ferrite by calcium oxide. The amount of zinc rendered soluble, being proportional to the amount of calcium reacted, was plotted against a time base. It was noted that the reaction went very quickly at the start but approached equilibrium very slowly. The amount of zinc rendered soluble increased with the lime content until 90% of the zinc could be rendered soluble in a mixture of $4\text{CaO}:1\text{ZnFe}_2\text{O}_4$. No explanation for the mechanism of the reaction was apparent.

Soluble zinc present in sinters formed at 1050°C was found difficult to extract. Resampling and redetermining soluble zinc in these sinters after further grinding showed an increase in the yield obtained. This indicates that soluble zinc determinations made on sinters produced at 1050°C are unreliable and results have therefore

* See Appendix D.

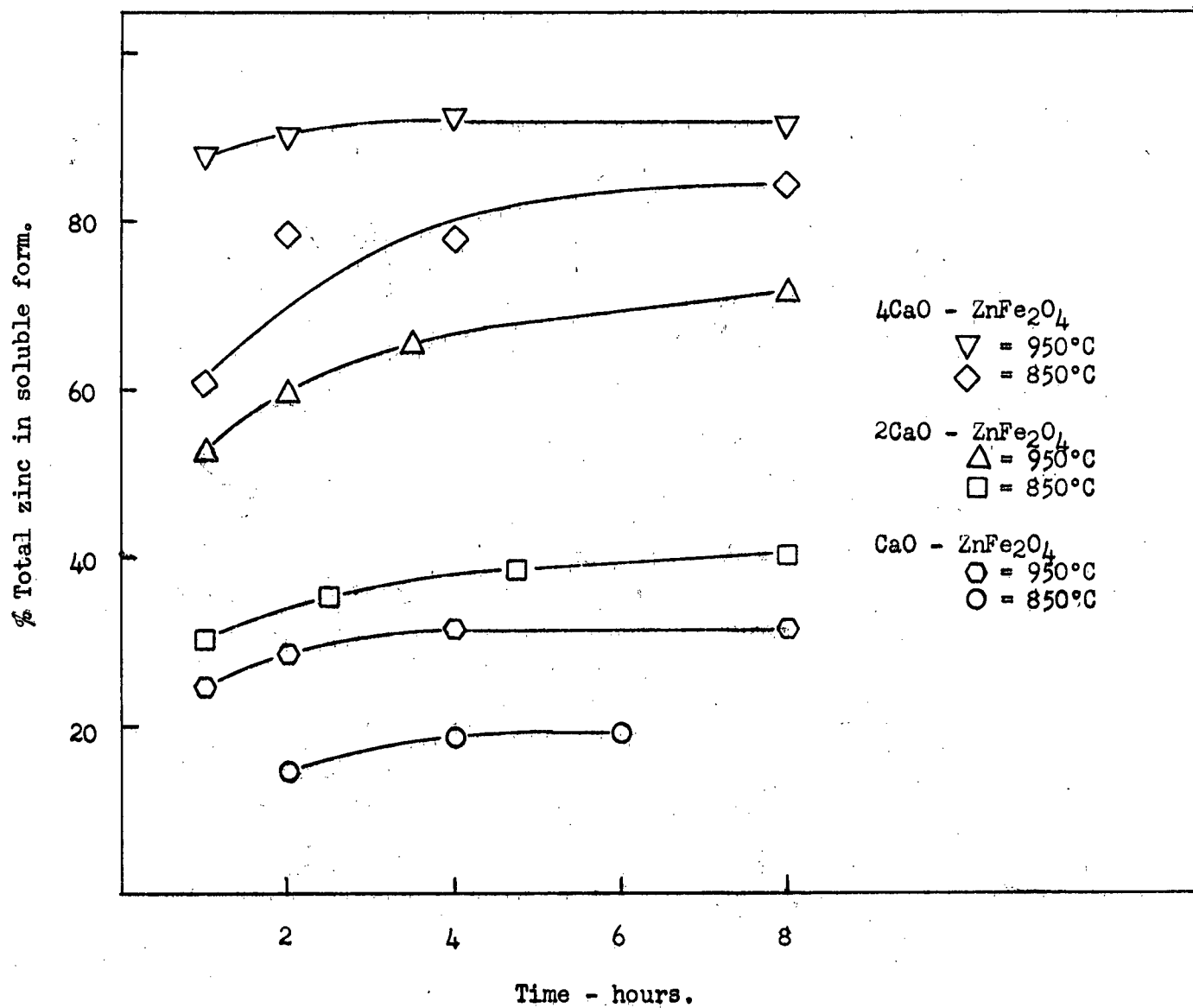


Fig.8 - The effect of composition, sintering time and temperature upon the decomposition of zinc ferrite by calcium oxide.

been discarded. Similar treatment of lower temperature sinters produced no variation in soluble zinc content.

The sinter products obtained at 1050°C were found to be much more strongly cemented than those produced at lower temperatures. This observation together with those of the previous paragraph suggests that incipient fusion took place at about 1050°C.

THE FORMATION AND DECOMPOSITION OF ZINC FERRITE ON SINTERING TERNARY MIXTURES OF ZINC OXIDE, FERRIC OXIDE AND CALCIUM OXIDE.

Having shown that zinc ferrite is decomposed by sintering with calcium oxide, it was decided to investigate the possibility of using calcium oxide to inhibit the formation of zinc ferrite during the sintering of mixtures containing zinc and ferric oxides:-

(a) The Effects of Temperature and Calcium Oxide content upon Sinter Products

Mixtures of the three component oxides were prepared using the molar proportions $\text{CaO}:\text{ZnO}:\text{Fe}_2\text{O}_3$ of 1:1:1 and 3:1:1 respectively. Samples were sintered for four hour periods at constant temperatures which ranged from 600°C to 1050°C.

The results of these experiments are shown in fig. 9. They show that, in the sintering period chosen, little zinc was rendered insoluble until a sintering temperature of 650°C was reached and that a maximum yield of insoluble zinc was obtained at 750°C. In comparing the results obtained from the Zinc oxide-ferric oxide binary system, (see fig. 6) it can be seen that the temperature at which an appreciable

amount of zinc ferrite was formed under the selected sintering conditions was increased by some sixty degrees. It seems probable that this is due to the calcium oxide acting as a comparatively inert diluent in the lower range of sintering temperatures. About 750°C the amount of insoluble zinc was found to decrease slowly in the case of the lean calcium oxide ternary and more rapidly in the case of the richer mix with the inference that, between 750°C and 1050°C, calcium ferrite is more stable than zinc ferrite.

The experiments show that calcium oxide may inhibit the formation of zinc ferrite during the sintering of $\text{CaO-ZnO-Fe}_2\text{O}_3$ systems by one or more of three mechanisms:-

1. By acting as a diluent which makes zinc ferrite formation less rapid.
2. By combining with ferric oxide to form calcium ferrite.
3. By displacing zinc oxide in zinc ferrite to form calcium ferrite.

(b) The Effect of Sintering Time on the composition of Sinter Products

The maxima shown in fig. 9 have not been explained. They may be caused by one of two conditions:

1. Zinc ferrite may be thermodynamically more stable than calcium ferrite below 750°C whilst the reverse may be the case above that temperature.
2. Calcium ferrite may be thermodynamically more stable than zinc ferrite over the whole temperature range considered, but, owing to the large kinetic barrier involved in the formation of calcium

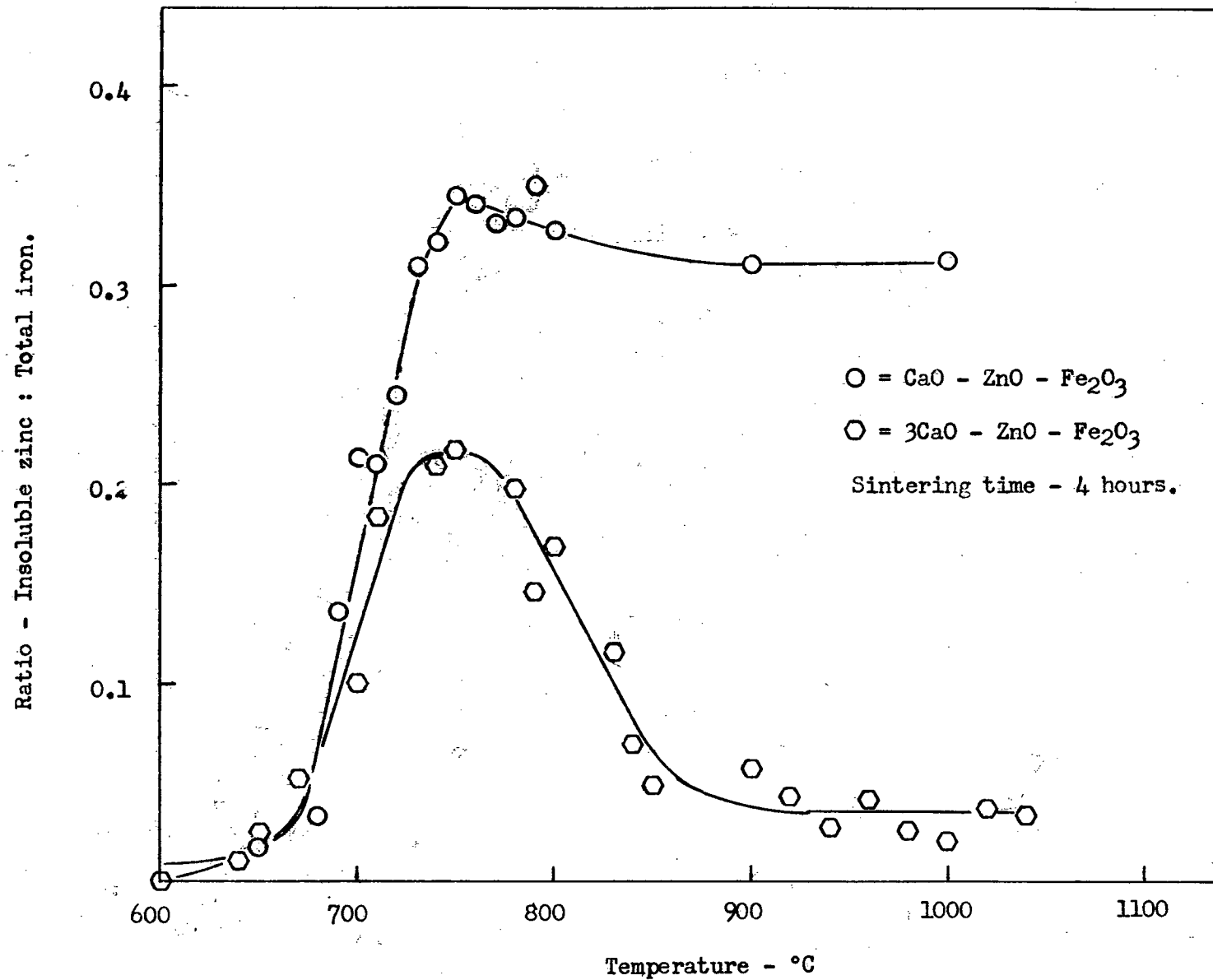


Fig.9 - The effects of temperature and calcium oxide content upon sinter products.

ferrite, zinc ferrite is formed as a metastable phase before equilibrium is reached.

A rate study of the sintering process of the $3\text{CaO-Fe}_2\text{O}_3\text{-ZnO}$ system was therefore made in order to explain the phenomenon.

Samples of the mixture $3\text{CaO-Fe}_2\text{O}_3\text{-ZnO}$ as used in part (a) of this section were sintered for periods varying from 30 minutes to 16 hours at 700°C , 750°C and 800°C .

The results of the study are given in fig. 10. They show that, when ternary mixtures, $\text{CaO-Fe}_2\text{O}_3\text{-ZnO}$, were sintered at temperatures varying 700°C to 800°C , zinc ferrite tended to form at first. This was later decomposed by the action of calcium oxide which combined with ferric oxide to form calcium ferrite. As the sintering temperature was increased the maximum zinc ferrite yield appeared after progressively shorter sintering periods indicating that the rate of both reactions was increased and, since the maximum yield of zinc ferrite did not vary greatly with temperature, the corresponding increases in the reaction rates were estimated to be approximately equal to each other.

It is concluded that, whilst calcium ferrite is thermodynamically more stable than zinc ferrite, the rate at which zinc ferrite is formed is greater than that at which calcium ferrite forms and, as a result, a metastable zinc ferrite phase is produced before the equilibrium condition is approached. The composition of the sinter product is, therefore kinetically controlled.

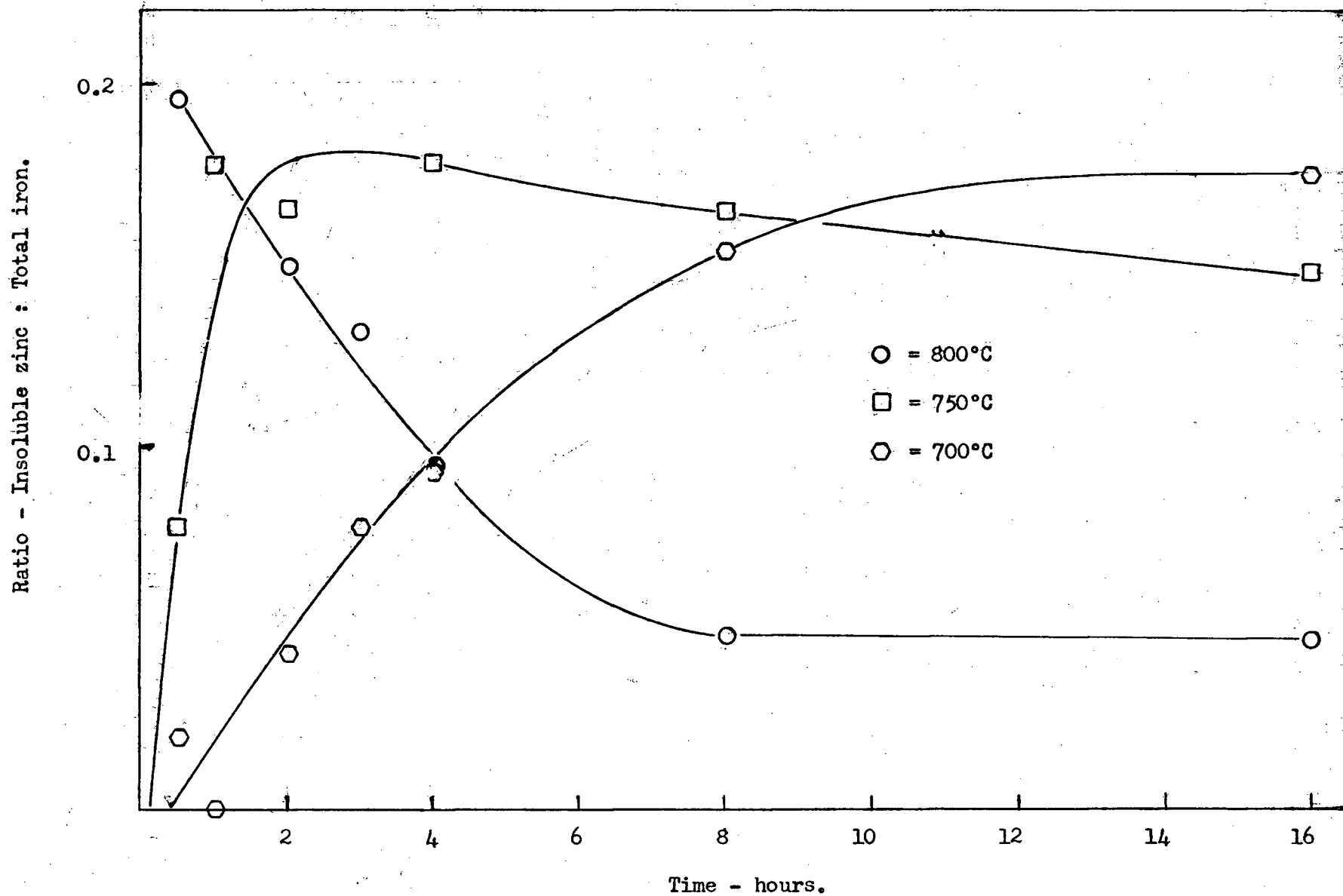


Fig.10 - The effect of sintering time upon the composition of sinter products from a $\text{CaO} - \text{ZnO} - \text{Fe}_2\text{O}_3$ ternary mixture.

SUMMARY AND CONCLUSIONS

The formation and decomposition of zinc ferrite by sintering mixtures of powdered reagents has been studied. Mechanisms for the various reactions encountered were sought but the limitations of the experimental procedures adopted prevented these from being clearly shown; the effects of some form of nucleation process encountered and of the small particles used masked the true reaction mechanisms. Mechanical variables such as particle size and packing of particles were controlled to obtain reproducible mixtures, however other variables, such as crystalline perfection of reagents were not controlled but were thought to affect reaction rates.

In the formation of zinc ferrite from zinc and ferric oxides, reaction took place following an induction period which varied as some inverse function of temperature. The amount of ferrite produced was found to be proportional to the square root of the sintering time. It is suggested that the reaction was diffusion controlled as the activation energy for the reaction was found to be of the order expected for such a mechanism. It was found that the maximum amount of zinc oxide rendered insoluble during sintering increased slightly with temperature indicating that a limited range of solid solubility of zinc oxide in zinc ferrite exists.

When different zinc compounds were sintered with ferric oxide, it was found that the rates of ferrite formation were varied. Thus compounds which decompose below the temperature range of ferrite formation (e.g. zinc hydroxide and zinc carbonate) formed ferrite at

lower sintering temperatures than did zinc oxide-ferric oxide mixtures in equal sintering periods. On the other hand those compounds which decomposed above the normal temperature range of ferrite formation (e.g. zinc sulphate) retarded the formation of zinc ferrite. It is concluded that as zinc ferrite forms only from zinc oxide and ferric oxide other compounds must be decomposed prior to ferrite formation. However, such decompositions may produce highly active forms of the oxides required and therefore the rate of ferrite formation may be increased in the case of easily decomposed compounds but is retarded when compounds are decomposed at high temperatures.

Zinc ferrite was found to be decomposed by various calcium and magnesium compounds and zinc oxide was liberated. Of the compounds selected all except calcium sulphate appeared to have an effect upon zinc ferrite. This may be due to the fact that calcium sulphate is decomposed at a temperature far above the sintering temperatures selected and behaves in accordance with the theory developed in the previous paragraph. Replacement of zinc oxide by calcium oxide in zinc ferrite was found not to be a simple molecule for molecule substitution; about four molecules of calcium oxide were found to replace one of zinc oxide.

In sintering ternary mixtures of zinc oxide, calcium oxide and ferric oxide, it was found that, though calcium ferrite is more stable than zinc ferrite, the rate of formation of zinc ferrite is more rapid and a metastable zinc ferrite phase tends to form before

an equilibrium condition is reached. Therefore, the composition of the sinter product obtained is controlled kinetically rather than thermodynamically. It is thought that the use of calcium oxide as a ferrite inhibitor in zinc roasting operations would be of doubtful value for two main reasons:

1. The kinetics of the process favour the formation of zinc ferrite rather than calcium ferrite: this would be accentuated by the close association of iron and zinc in marmatite ores.

2. In order to free the zinc combined as ferrite, calcium oxide would be consumed in quantities of the order of one ton per ton of ferrite treated.

Suggestions for Further Work

While the results may suggest that a parabolic diffusion law controls the formation of zinc ferrite this hypothesis has not been conclusively proved. It could possibly be done by comparing the activation energies associated with diffusion of cations in samples of ferrite and with the diffusion of cations during the formation of zinc ferrite. If the activation energies of the two processes were found to be of the same order then the parabolic diffusion law would be established as the controlling mechanism. The experimental method suggested is one using labelled isotopes to determine reaction rates by sectioning or possibly by the decrease in surface activity method.(25)

APPENDIX A

Microphotographs of powdered reagent
mixtures prepared for sintering.

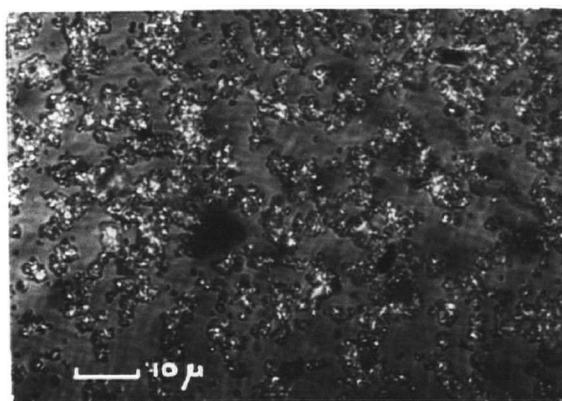


Plate I. $\text{ZnO} - \text{Fe}_2\text{O}_3$

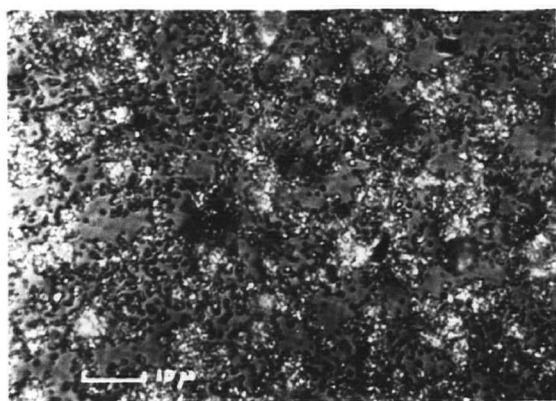


Plate II. $\text{ZnCO}_3 - \text{Fe}_2\text{O}_3$

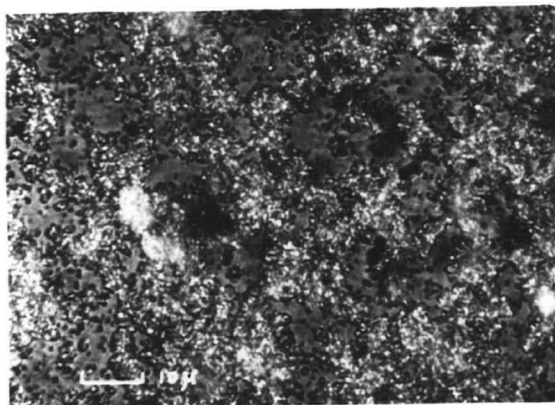


Plate III $\text{Zn}(\text{OH})_2 - \text{Fe}_2\text{O}_3$

APPENDIX B

Analytical Methods

1. Volumetric Determination of Zinc

(a) Solutions

Potassium Ferrocyanide 21.63 gm/litre.

Potassium Ferricyanide 10 gm/litre.

(b) Standardisation

0.2 gm of granulated zinc were accurately weighed and dissolved in 5 ml of hydrochloric acid. The solution was diluted to about 100 ml with distilled water and a few drops of potassium ferricyanide solution were added. It was then titrated against the potassium ferrocyanide solution to a potentiometrically determined end point. A mean of three such standardisations was taken.

(c) Determination of the Total Zinc Content of Sinter Products

A 0.5 gm sample was weighed and dissolved in 5 ml. hydrochloric acid. 20 ml distilled water was added followed by excess ammonium hydroxide to precipitate the iron. The mixture was brought to the boil and the precipitate filtered off and washed thoroughly. Both filtrate and washings were collected and evaporated to a convenient bulk. The residue was dissolved in a little hot concentrated hydrochloric acid and then reprecipitated with ammonium hydroxide. The mixture was treated as before, the filtrates from each cycle being added together. The cycle was repeated a third time.

The collected filtrate was neutralised with hydrochloric acid in slight excess and a few drops of potassium ferricyanide were added. The sample was filtrated against standardised potassium ferrocyanide solution.

(d) Determination of the Soluble Zinc Content of Sinter Products

1. Ammonia - Ammonium chloride leach solution:-

NH_4Cl	160 gm.
aq. NH_4OH (SpGr. 0.88)	100 ml.
Distilled water	900 ml.

2. Determination.

A sample of sinter product was weighed and leached in 50 ml of ammonia-ammonium chloride leach solution for sixteen hours. The size of the sample used depended upon its estimated soluble zinc content; for sinters containing less than 5% soluble zinc 2.5 gm samples were needed while for those containing greater amounts 0.5 gm samples were sufficient. Following leaching, the residue was filtered off and the filtrate was neutralised with hydrochloric acid in excess. A few drops of potassium ferricyanide were added and the sample was titrated against standard potassium ferrocyanide solution.

3. Limitations of the Method

When free calcium oxide was present in the samples it was dissolved by the leach solution together with the zinc. During titration it was complexed by the ferrocyanide and erroneous zinc determinations resulted. Therefore a polarographic method was developed for soluble zinc in samples which contained lime.

2. Polarographic Determination of Zinc(a) Standard Zinc Solution

0.500 gm of granulated zinc were weighed out and dissolved in 5 ml. hydrochloric acid. The solution was made up to 1.0 litre with distilled water in a volumetric flask.

(b) Calibration of the Polarograph

50 ml. of the standard zinc solution was placed in a 500 ml volumetric flask together with 50 ml of ammonia-ammonium chloride leach solution^{*} and 6 ml of hydrochloric acid. The solution was diluted to volume with distilled water. A portion of the solution was now placed in a 5 ml Heyrovsky electrolysis vessel and bubbled with nitrogen for five minutes to remove any dissolved oxygen.

Mercury, for the electrode, was added to the cell and nitrogen was bubbled for a further five minutes. The sample was then electrolysed on the polarograph and the zinc wave height was measured. The procedure was then repeated using 100 ml and 150 ml aliquots of standard zinc solution. A calibration curve was drawn plotting zinc wave height on the ordinate and zinc concentration on the abscissa. Calibrations were made immediately before and after each series of determinations.

(c) Determination of soluble zinc in sinter products

A 0.5 gm sample of sinter product was leached in 50 ml of ammonia-ammonium chloride solution for sixteen hours. The residue was then filtered off and washed with distilled water, the filtrate and washings being caught in a 500 ml volumetric flask. The solution was neutralised by adding 6.0 ml hydrochloric acid and diluted to volume. The sample was then prepared for electrolysis on the polarograph in the manner described in section (b) above. The zinc waves obtained from the polarograph were measured and the zinc content.

* See Method 1(d).

determined by interpolation on the calibration curve. The limiting error of the method was estimated as $\pm 2\%$.

3. Volumetric Determination of Iron

(a) Potassium Dichromate: 4.4 g/l

Indicator: 1% Solution of diphenylamine in conc H_2SO_4 .

Buffer Solution: 30% H_2SO_4 ; 30% H_3PO_4

40% H_2O - by vol.

(b) Standardisation

0.2 gm of iron wire was weighed out and dissolved in 10 ml. HCl . The solution was diluted with distilled water and boiled with test lead until colourless. Boiling was continued for a further five minutes. The solution was then cooled and decanted off the test lead, the latter being washed free of all solution. 20 ml of Buffer solution were added together with six drops of indicator. The solution was titrated against potassium dichromate solution to the first permanent blue colour. 0.1 ml was subtracted as blank. A mean of three such standards was taken.

(c) Determination of Iron in Sinter Products

0.5 gm samples were weighed out and dissolved in 10 ml. hydrochloric acid. Procedure then followed that used in the standardisation method above.

APPENDIX C

Experimental Data

The Effect of Sintering Time on the Formation of Zinc Ferrite From Zinc and Ferric Oxides

Series I

Mixture:- ZnO - Fe₂O₃ Atomic Ratio, Zn:Fe 0.474:1.

Table 1.1

Sintering Temperature 600°C

Sintering Time (hours)	Assays %			
	Total Iron	Total Zinc	Soluble Zinc	<u>Insoluble Zn</u> Total Fe.
0.5	46.0	25.9	25.9	Tr.
1.0	46.0	25.9	25.8	0.002
2.0	46.2	26.1	25.6	0.006
8.0	47.1	26.0	24.3	0.034
16.0	47.1	25.9	23.3	0.048

Table 1.2

Sintering Temperature 625°C

Sintering Time (hours)	Assays %			
	Total Iron	Total Zinc	Soluble Zinc	<u>Insoluble Zn</u> Total Fe
0.5	46.2	25.6	26.1	Tr.
1.0	46.5	25.7	25.8	Tr.
1.5	46.2	25.7	24.6	0.022
2.0	46.5	25.7	24.5	0.026
2.5	46.5	25.7	23.5	0.047
3.0	46.2	25.6	23.4	0.048
4.0	46.4	25.6	21.9	0.081
6.0	46.5	25.6	21.2	0.095
12.0	46.6	25.7	18.6	0.153
24.0	46.6	25.7	14.9	0.232

Table 1.3

Sintering Temperature. 650°C.

Sintering Time (hours)	Assays %			
	Total Iron	Total Zinc	Soluble Zinc	<u>Insoluble Zn</u> Total Fe
0.5	46.7	26.0	25.1	0.015
1.0	46.5	25.9	22.9	0.055
1.5	46.4	25.9	20.9	0.091
2.0	46.6	26.0	21.1	0.090
2.5	46.5	25.9	18.7	0.132
3.0	46.6	26.0	18.1	0.145
4.0	46.6	26.0	15.3	0.194
6.0	46.5	25.9	12.8	0.240
16.0	47.2	26.2	2.6	0.426
24.0	46.5	26.0	5.4	0.420

Table 1.4

Sintering Temperature 750°C.

Sintering Time (hours)	Assays %			
	Total Iron	Total Zinc	Soluble Zinc	<u>Insoluble Zn</u> Total Fe
0.5	45.9	25.9	1.5	0.455
1.0	45.9	25.9	0.6	0.470
2.0	45.9	25.9	0.4	0.474
4.0	45.9	25.9	0.6	0.471

Series IIMixture: ZnO - Fe₂O₃ Atomic Ratio, Zn:Fe 0.466:1Table 2.1

Sintering Temperature 600°C

Sintering Time (hours)	Assays %			
	Total Iron	Total Zinc	Soluble Zinc	<u>Insoluble Zn</u> Total Fe
1.0	47.5	25.9	24.3	0.027
2.0	47.8	26.1	22.8	0.059
4.0	47.5	25.9	18.3	0.135
8.0	47.6	26.0	12.0	0.250
16.0	47.8	26.1	6.9	0.342
24.0	47.5	25.9	4.2	0.389

Table 2.2

Sintering Temperature 625°C

Sintering Time (hours)	Assays %			
	Total Iron	Total Zinc	Soluble Zinc	<u>Insoluble Zn</u> Total Fe
1.0	47.4	25.9	22.7	0.056
2.0	47.5	25.9	19.1	0.122
4.0	47.2	25.8	12.6	0.238
8.0	47.9	26.2	6.7	0.347
16.0	47.8	26.1	3.6	0.401
24.0	47.4	25.9	1.9	0.432

Table 2.3

Sintering Temperature: 650°C

Sintering Time (hours)	Total Iron	Assays %		
		Total Zinc	Soluble Zinc	<u>Insoluble Zn</u> Total Fe
0.5	47.0	25.7	20.1	0.101
1.0	47.3	25.8	14.9	0.196
1.5	47.3	25.8	12.3	0.233
2.0	47.1	25.8	9.6	0.276
3.0	47.3	25.8	6.6	0.328
4.0	47.5	26.0	4.3	0.369
8.0	47.3	25.8	2.0	0.430
16.0	47.5	25.9	0.6	0.454

Table 2.4

Sintering Temperature 660°C

Sintering Time (hours)	Total Iron	Assays %		
		Total Zinc	Soluble Zinc	<u>Insoluble Zn</u> Total Fe
0.5	47.4	25.9	19.3	0.118
1.0	47.4	25.9	14.3	0.208
1.5	47.3	25.8	10.6	0.274
2.0	47.3	25.8	7.9	0.323
3.0	47.5	26.0	6.3	0.353
4.0	47.3	25.8	4.3	0.390
8.0	47.1	25.8	2.0	0.440
16.0	47.2	25.8	0.5	0.456

Series IIIMixture:- $\text{ZnO-Fe}_2\text{O}_3$ Atomic Ratio Zn:Fe 0.94:1Table 3.1Sintering Temperature 625°C

Sintering Time (hours)	Assays %			
	Total Iron	Total Zinc	Soluble Zinc	<u>Insoluble Zn</u> Total Fe
0.5	34.6	38.3	37.6	0.022
1.0	34.6	38.1	37.2	0.027
1.5	34.8	38.4	32.6	0.166
2.0	35.1	38.7	34.3	0.124
2.5	34.8	38.4	33.2	0.149
3.0	34.6	38.3	30.4	0.230
4.0	35.1	38.7	28.0	0.304
6.0	35.4	39.0	25.5	0.382
8.0	34.9	38.5	24.2	0.410
10.0	34.9	38.5	22.7	0.454
12.0	35.4	39.0	22.8	0.459
24.0	35.4	38.6	19.7	0.532

Table 3.2

Sintering Temperature - 650°C

Sintering Time (hours)	Assays %			
	Total Iron	Total Zinc	Soluble Zinc	<u>Insoluble Zn</u> Total Fe
0.5	35.7	39.2	30.2	0.252
1.0	35.8	38.9	27.6	0.316
1.5	35.9	39.0	22.0	0.474
2.0	36.1	39.2	23.7	0.429
2.5	35.8	38.9	21.9	0.475
3.0	35.8	39.0	21.2	0.499
4.0	36.1	39.2	21.3	0.496
6.0	36.1	39.2	19.5	0.545
8.0	36.0	39.1	19.3	0.550
10.0	36.2	39.2	19.1	0.558
12.0	35.8	38.9	19.1	0.548
24.0	36.2	38.5	18.6	0.552

Table 3.3

Sintering Temperature 1050°C

Sintering Time (hours)	Assays %			
	Total Iron	Total Zinc	Soluble Zinc	<u>Insoluble Zn</u> Total Fe
0.5	36.1	39.0	18.4	0.572
1.0	35.6	38.5	18.5	0.560
1.5	35.9	38.8	18.4	0.566
2.0	35.6	38.5	18.3	0.565
2.5	36.1	39.0	18.9	0.559
3.5	35.6	38.5	18.2	0.570
6.0	35.6	38.5	18.2	0.570
8.0	35.9	39.0	17.9	0.588

The Effect of Sintering Temperature on the Formation of Zinc Ferrite
From Mixtures Containing Various Compounds of Zinc and Ferric Oxides

Series IV

Mixture: $\text{Zn}(\text{OH})_2 - \text{Fe}_2\text{O}_3$ Atomix Ratio Zn:Fe - 0.53:1

Sintering Time:- 4 hours

Table 4.1

Sintering Temp. °C	Total Iron	Assays %		
		Total Zinc	Soluble Zinc	<u>Insoluble Zn</u> Total Fe
500	44.9	27.9	27.8	-
520	44.9	27.9	26.7	0.024
540	44.9	27.9	19.4	0.162
563	44.9	27.9	7.0	0.396
580	44.9	27.9	4.4	0.446
600	44.9	27.9	3.5	0.464
668	44.9	27.9	3.2	0.470

Series VMixture: $\text{ZnCO}_3 - \text{Fe}_2\text{O}_3$ Atomic Ratio, Zn:Fe 0.53:1

Sintering Time: - 4 hours

Table 5.1

Sintering Temp °C	Assays %			
	Total Iron	Total Zinc	Soluble Zinc	<u>Insoluble Zn</u> Total Fe
300	44.1	27.3	27.3	-
500	44.8	27.7	27.3	0.009
550	44.6	27.6	25.8	0.034
575	45.3	28.0	23.1	0.093
600	44.8	27.8	17.8	0.191
610	44.9	27.7	15.1	0.239
620	44.7	27.7	12.9	0.284
630	44.8	27.8	9.2	0.333
640	44.8	27.7	7.0	0.394
650	44.8	27.7	4.8	0.436
660	45.0	27.8	3.9	0.454
670	45.0	27.8	3.1	0.468
680	45.4	28.0	2.9	0.471
690	45.6	28.2	2.8	0.470
700	45.7	28.2	2.7	0.464
750	46.3	28.6	2.6	0.478
800	45.3	28.1	2.5	0.484

Series VIMixture ZnO - Fe₂O₃ Atomib Ratio Zn:Fe 0.48:1

Sintering Time:- 4 hours

Table 6.1

Sintering Temp. °C	Assays %			
	Total Iron.	Total Zinc	Soluble Zinc	<u>Insoluble Zn</u> Total Fe
500	46.0	25.9	25.5	0.007
550	46.0	25.9	25.5	0.007
575	46.0	25.9	25.5	0.007
600	46.0	25.9	21.7	0.079
640	46.0	25.9	12.6	0.247
655	46.0	25.9	5.7	0.375
664	46.0	25.9	3.7	0.412
679	46.0	25.9	2.2	0.440
690	45.0	25.8	1.3	0.454
700	45.0	25.8	0.5	0.470
750	45.0	25.8	0.5	0.470
800	45.0	25.8	0.3	0.474
850	45.0	25.8	0.3	0.474
900	45.0	25.8	0.3	0.474
950	45.0	25.8	0.3	0.474
1000	45.6	25.8	0.2	0.475

Series VIIMixture $\text{ZnSO}_4 - \text{Fe}_2\text{O}_3$ Atomic Ratio Zn:Fe 0.51:1

Sintering Time: 4 hours

Table 7.1

Sintering Temp. °C	Assays %			
	Total Fe	Total Zn	Soluble Zn	<u>Insoluble Zn</u> Total Fe
600	32.4	18.7	18.7	0.000
700	32.2	18.6	18.3	0.009
750	33.5	19.7	16.8	0.075
760	34.5	19.5	14.3	0.129
770	34.5	19.8	13.2	0.164
780	39.1	20.2	11.8	0.184
790	41.7	23.1	7.1	0.327
800	44.4	26.2	1.6	0.475
810	45.0	25.9	2.1	0.452
850	46.4	27.0	1.2	0.474
900	46.4	26.6	1.2	0.477
950	46.4	27.2	1.3	0.478
1000	46.4	27.1	1.2	0.478

The Effect of Composition, Sintering Time and Temperature upon the
Decomposition of Zinc Ferrite by Calcium Oxide

Series VIII

Approximate Ratio $\text{CaO}:\text{ZnFe}_2\text{O}_4$ 1:1

Table 8.1

Sintering Temperature 850°C

Sintering Time -hrs	Assays			
	Total Fe %	Total Zn %	Soluble Zn %	% Total Zn In soluble Form
2	38.6	21.2	3.2	14.8
4	38.1	20.9	3.9	18.8
6	38.1	20.9	4.0	19.1

Table 8.2

Sintering Temperature 950°C

Sintering Time -hrs	Assays			
	Total Fe %	Total Zn %	Soluble Zn %	% Total Zn In soluble form
1	39.4	21.6	5.4	24.9
2	39.2	21.5	6.2	28.8
4	39.2	21.8	6.8	31.4
8	39.0	21.4	6.7	31.4

Series IXApproximate ratio $\text{CaO}:\text{ZnFe}_2\text{O}_4$ 2:1Table 9.1Sintering Temperature 850°C

Sintering Time -hrs	Assays			
	Total Fe %	Total Zn %	Soluble Zn %	% Total Zn In Soluble form
1.0	31.9	17.3	5.4	30.1
2.5	31.9	17.4	6.3	35.3
4.75	32.1	17.3	6.9	38.8
8.0	31.9	17.3	7.4	40.4

Table 9.2Sintering Temperature 950°C

Sintering Time -hrs	Assays			
	Total Fe %	Total Zn %	Soluble Zn %	% Total Zn In soluble form
1.0	32.9	17.8	9.3	52.6
2.0	33.2	18.0	10.8	59.6
4.0	33.3	18.0	11.8	65.2
8.0	33.2	18.0	12.9	71.7

Series XApproximate ratio of $\text{CaO}:\text{ZnFe}_2\text{O}_4$ 4:1Table 10.1

Sintering Temperature 850°C

Sintering Time -hrs	Assays			
	Total Fe %	Total Zn %	Soluble Zn %	% Total Zn In soluble form
1.0	26.0	13.6	8.3	61.0
2.0	25.7	13.5	10.6	78.5
4.0	26.3	13.8	10.7	78.0
8.0	26.5	13.9	11.8	84.7

Table 10.2

Sintering Temperature 950°C

Sintering Time -hrs	Assays			
	Total Fe %	Total Zn %	Soluble Zn %	% Total Zn In soluble form
1.0	26.3	13.8	12.1	88.0
2.0	26.3	13.8	12.4	90.2
4.0	25.8	13.5	12.5	92.6
8.0	26.3	13.8	12.6	91.6

The Effects of Temperature and Calcium Oxide Content upon Sinter Products
of ZnO-Fe₂O₃-CaO Mixtures

Series XI

Approximate Ratio ZnO-Fe₂O₃-CaO 1:1:1

Table 11.1

Sintering Time 4 hours

Sintering Temp - °C	Total Fe	Assays %		
		Total Zn	Soluble Zn	<u>Insoluble Zn</u> Total Fe
500	36.7	19.6	18.3	0.035
650	37.4	20.2	19.5	0.019
660	36.7	19.9	19.1	0.022
680	37.6	19.5	18.3	0.034
690	37.9	20.0	14.8	0.137
700	37.8	20.6	12.5	0.214
710	37.9	19.7	11.6	0.211
720	37.9	19.8	10.5	0.246
730	37.4	20.1	8.5	0.310
740	37.1	19.9	7.9	0.323
750	37.6	20.5	7.5	0.346
760	37.4	20.2	7.4	0.342
770	37.9	20.4	7.8	0.332
780	37.9	20.5	7.8	0.335
790	37.6	20.9	7.8	0.351
800	37.6	19.1	6.8	0.328
900	38.1	21.2	9.3	0.312
1000	37.9	21.0	9.1	0.314

Series XIIApproximate Ratio ZnO-Fe₂O₃-CaO 1:1:3Table 12.1

Sintering Time 4 hours

Sintering Temp - °C	Assays %			
	Total Fe	Total Zn	Soluble Zn	<u>Insoluble Zn</u> Total Fe
600	25.2	13.9	13.8	0.009
650	26.2	14.5	14.2	0.011
660	26.3	14.4	13.7	0.027
670	26.5	14.5	13.1	0.053
700	26.5	14.5	11.8	0.102
710	27.0	14.8	9.8	0.185
740	28.0	15.1	9.3	0.210
750	27.2	14.9	9.0	0.218
780	28.7	15.7	10.0	0.198
790	28.4	15.5	11.4	0.146
800	27.5	15.1	10.4	0.170
830	28.5	15.9	12.6	0.116
840	28.5	15.6	13.7	0.069
850	28.3	15.5	14.1	0.049
900	28.4	15.5	13.9	0.058
910	28.8	15.8	14.7	0.036
920	28.8	15.8	14.5	0.044
930	28.5	15.6	14.9	0.024
940	28.5	15.7	14.9	0.028
950	28.8	15.8	14.9	0.031
960	28.6	15.7	13.5	0.042

Table 12.1 continued

Sintering Temp - °C	Total Fe	Total Zn	Soluble Zn	<u>Insoluble Zn</u> Total Fe
970	28.8	15.8	14.9	0.031
980	28.8	15.8	15.0	0.027
990	28.8	15.8	13.4	0.083
1000	28.8	15.6	15.0	0.021
1010	29.2	16.0	15.0	0.034
1020	29.2	16.0	14.9	0.038
1030	28.9	15.8	15.0	0.029
1040	29.1	15.9	15.0	0.033
1050	29.1	15.8	15.2	0.024

The Effect of Sintering Time upon the Composition of Sinter Products
from CaO-Fe₂O₃-ZnO Ternary Mixtures

Series XIII

Approximate Ratio CaO-Fe₂O₃-ZnO:3:1:1

Table 13.1

Sintering Temperature 700°C

Sintering Time -hrs	Assays			
	Total Iron %	Total Zinc %	Soluble Zinc %	<u>Insoluble Zn</u> Total Fe
0.5	26.0	14.3	13.4	0.020
1.0	26.0	14.3	14.9	0.000
2.0	26.0	14.3	13.0	0.043
3.0	26.3	14.4	12.0	0.078
4.0	26.5	14.5	11.6	0.093
8.0	27.2	14.9	10.0	0.154
16.0	26.3	14.4	9.0	0.175

Table 13.2

Sintering Temperature 750°C

Sintering Time -hrs	Assays			
	Total Iron %	Total Zinc %	Soluble Zinc %	<u>Insoluble Zn</u> Total Fe
0.5	26.3	14.4	12.0	0.078
1.0	26.5	14.5	9.0	0.178
2.0	28.0	15.3	9.8	0.165
4.0	28.3	15.5	9.6	0.178
8.0	28.3	15.5	10.1	0.163
16.0	28.8	15.8	10.8	0.148

Table 13.3

Sintering Temperature 800°C

Sintering Time -hrs	Assays			
	Total Iron %	Total Zinc %	Soluble Zinc %	<u>Insoluble Zn</u> Total Fe
0.5	28.3	15.6	9.0	0.196
1.0	27.8	15.3	9.5	0.178
2.0	28.5	15.6	10.6	0.150
3.0	29.0	15.9	11.4	0.132
4.0	28.3	15.5	12.4	0.094
8.0	28.3	15.5	13.9	0.048
16.0	31.0	17.0	15.3	0.047

APPENDIX D

Debye Scherrer diagrams of
the reagents used and sinter
products obtained

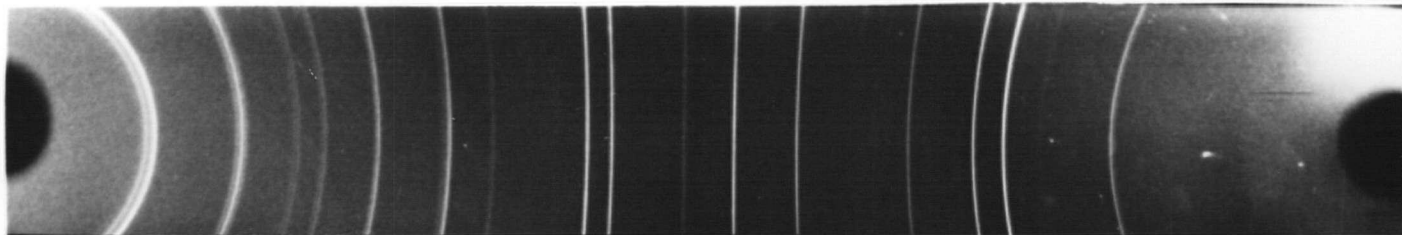


Plate IV \propto Ferric Oxide

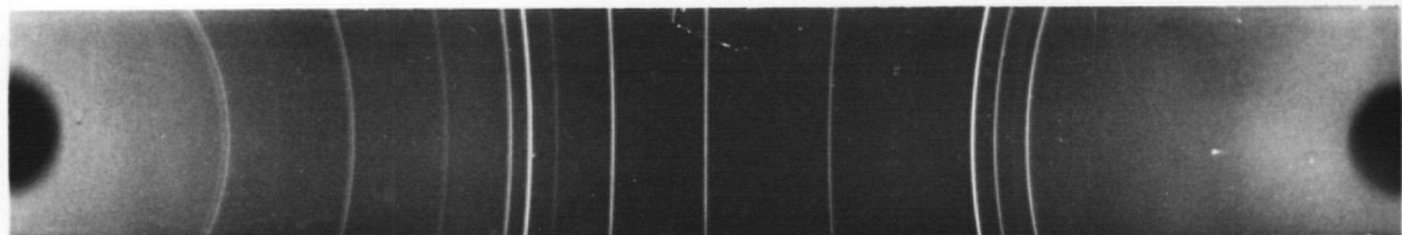


Plate V Zinc Oxide

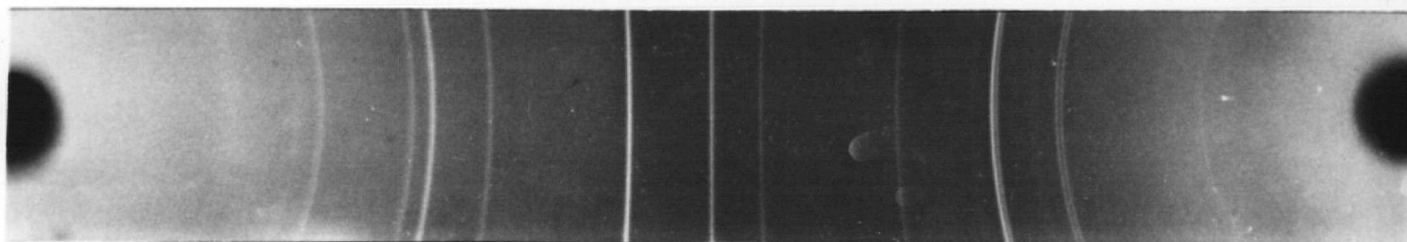


Plate VI Zinc Ferrite

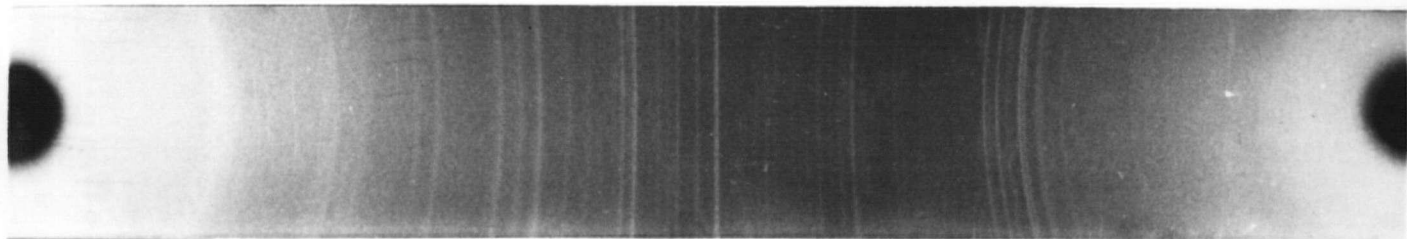


Plate VII Sinter Product obtained from a mixture of zinc ferrite and calcium oxide

BIBLIOGRAPHY

1. Ingalls W. R. Metallurgy of Zinc and Cadmium p. 6, 32.
Eng. Mining J. Press. (1903)
2. Tainton and Leyson. Trans. Am. Inst. Mining. Met. Engrs.
70 p. 486 (1924)
3. Prost. Bull. Assoc. Belge. Chim. 10 p. 246 - 263
4. Wells J. S. C. Eng. Mining J. 86 p. 420 - 422
5. Hofman. Trans. Am. Inst. Mining. Met. Engrs. 35 p. 811 (1905)
6. Ebelman. Ann. Chim (Phys.) Ser 3. 33 p. 53 (1851)
7. Kushima, I and Amanuma I. Mem Fac. Kyoto Univ. 16 p. 191 (1954)
8. Hopkins D. W. Bull Inst. Mining Met. 59 p. 219 (1949)
9. Hopkins D. W. and Adlington A. G. Bull Inst. Mining Met. 60 p.117
(1950)
10. Swartz and Krauskopf. Trans. Am. Inst. Mining. Met Engrs. T.P. 40
(1928)
11. Guilleissen and Van Rysselberghe, P. Trans. Am. Electrochem. Sec.
59 p. 95. (1931)
12. Ralston O.C. U. S. Bur. Mines Bull. 296 (1929)
13. Huckel W. Structural Chemistry of Inorganic Compounds. Elsevier (1951)
14. Sidgewick N.V. Chemical Elements and their compounds. Oxford. Univ.
Press.
15. Welo and Baudisch, Phys Rev. 25 p. 587 (1925)
16. Welo and Baudisch. Phil Mag. 50 (6) p. 399 (1925)
17. Huttig and Kittel Z. Anorg. Chem. 26 p. 210 (1933)
18. Gorter. E. W. Phillips Res. Rep. 9 pp 295-320 (1954)
19. Verwey E.J.W. J. Chem Phys. 15 p. 174 (1947)
20. Verwey E. J. W. Ibid. p. 181
21. Forestier H. Comptes Rend. 192 p. 842 (1931)
22. Wells A. F. Structural Inorganic Chemistry Oxford Univ. Press. (1950)

23. Mott. N. F. Trans. Faraday Soc. 36 p. 472 (1940)
24. Lindner R. Proc. Intern. Symposium on Reactive Solids. Gothenburg 1952
Ptl. p. 195 (pub 1954)
25. Carter R. E. and Richardson F. D. J. Metals 6 p. 1244 (1954)