

THE S I S F O R D E G R E E O F Ph. D.

O F T H E

U N I V E R S I T Y O F G L A S G O W.

Presented By

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This research was carried out under the direction of Professor J. H. Andrew, D. Sc., over the period extending from September 1925 until June 1928, at the Royal Technical College, Glasgow.

The author desires to express his appreciation and indebtedness to Professor Andrew for his continuous interest and guidance, and for the generous manner in which complete facilities were placed at the author's disposal during the course of the work.

THE CONTROL OF BASIC OPEN-HEARTH FURNACE

REACTIONS.

FURNACE REACTION PRODUCTS.

It is the general belief that in the steel making processes the elimination of metalloids is effected by ferrous oxide in the molten bath, whilst the ferrous oxide in the bath is a function of the ferrous oxide content of the slag. Considerable divergence of opinion arises with respect to the amount of iron which should be considered as affording available ferrous oxide in the slag.

(1) Field stresses the necessity of calculating to FeO all iron found by analysis in the slag.

(2) McNair regards all the FeO as free and ignores the existence of ferric oxide.

(3) Colcough assumed the ferric oxide present to be stabilized by the lime and considers the whole of the FeO to be free.

(4) McCance states that only free FeO should be considered as being available for the bath and emphasises the lack of experimental data in this connection.

(5) Styri has stated that "only FeO not bound chemically to any other slag constituent" should be considered.

(6) Whiteley on the other hand has advanced the view that an important part of the oxidation of bath metalloids is due to the ferric oxide content of the slag.

In the case of the basic open-hearth process therefore, the lack of fundamental data regarding the constitution of the process slags renders recent applications of chemical kinetics to the consideration of metalloid elimination somewhat obscure. Further, the/

the conclusions arrived at by different workers appear largely speculative.

In this thesis the results of experiments made upon the products of the reactions occurring in the basic open-hearth furnace are described. Special attention has been given to the changes which take place in slag constitution during the refining stages. Such experimental investigations it is believed form an essential preliminary towards an exact knowledge of the reactions which occur at steel making temperatures and concerning which very little quantitative data exists.

The objects of the investigations were: -

- (1) To ascertain the nature of non-phosphoric constituents in basic slags.
- (2) To observe the alterations in constitution which take place in the slag during the refining stages.
- (3) To determine the practical basis of the furnace reaction control during process operations.

Microscopic examinations of the bath metal corresponding to differences in slag constitution were made. Some investigations were also made upon the structure of the furnace hearth.

Previous investigations of basic slags have been confined almost entirely to the phosphoric constituents in view of the importance of these compounds to the agriculturist. Such constituents are not however of first importance in the processes using a high percentage of steel scrap, the reactions being primarily dependent on the oxides of Calcium, Iron and Manganese.

In 1887 Stead and Redsdale⁽⁷⁾ published analyses of crystals and crystallites isolated from basic bessemer slags. No optical data was given and analogous constituents have not hitherto been isolated from open-hearth slags.

In 1911 Kroll⁽⁸⁾ in an exhaustive paper on Basic Slag Phosphates

States:- "Besides the phosphates there exist crystals of metallic oxides of great interest but beyond the scope/

scope of the present investigation".

These researches are confined to basic bessemer slags, and in conclusion he states - "It would be interesting to investigate the basic slag crystals from the open-hearth, their composition differing sufficiently from converter slags to be interesting.

In 1920 Bainbridge ⁽⁹⁾ noted the existence of magnetic material in basic open hearth slags and suggested the existence of combinations of ferric oxide and lime.

In 1922 Scott and McArthur ⁽¹⁰⁾ published the results of their applications of petrographic methods to the examination of open-hearth finishing slags from the basic process. Their slags were obtained from different sources and unfortunately their work, apart from general slag analyses is confined to microscopic examination only. No isolation or analysis of individual constituents was secured and little optical data was given. They however identified several of the slag constituents with the analyses given by Stead and Ridsdale ⁽⁷⁾ and their research is the only contribution of its kind.

Published researches ⁽¹¹⁾ on basic slags reveal a mass of evidence of the occurrence of phosphate and silica-phosphate compounds in a free state. Morrison ⁽¹²⁾ found a silico-phosphate of iron and lime approximating in composition to the formula $FeO \cdot 5CaO \cdot P_2O_5 \cdot SiO_2$. The existence of this compound has not been confirmed by other workers and in view of the difficulties experienced in isolating slag constituents in the pure state it is probable that the FeO existed as an impurity.

In this thesis an account is given of the methods used to isolate the basic slag constituents other than those containing phosphorus, referred to by Kroll ⁽⁸⁾.

Special facilities were available to the writer to prepare open-hearth charges on the manufacturing scale whereby the formation of non-phosphoric constituents could be augmented in sufficient quantity for optical examination and analysis.

The optical data thus secured was employed to observe the progressive/

progressive changes which occur in process slags.

The work described can be divided into the following parts:-

- (1) Basic Slag constituents.
- (2) Examination of the process slags.
- (3) Examination of the bath metal.
- (4) Examination of the structure of the basic hearth.

A series of open-hearth charges was prepared and slags obtained under observed conditions with a phosphoric oxide content not exceeding about 3%. These slags were subjected to treatment and examination as described later. Photographs of the constituents noted together with the results of chemical analysis are given. wherever possible the constituents were examined by petrographical methods and the optical data obtained is also given.

ISOLATION OF SLAG CONSTITUENTS.

(10)

Scott and McArthur have drawn attention to the closeness of the analogy between certain igneous rocks and basic slags. They also pointed out the existence of certain constituents which correspond to mineralisers in these rocks. Basic furnace slags differ from many igneous rocks and from slags of the acid process in their complete freedom from glass.

These two facts were utilised in the isolation and subsequent identification of the slag constituents here described. The essentially halocrystalline nature of the slag minerals facilitated their separation.

When a slag magma solidifies it exhibits similar characteristics to those observed in the cooling of igneous rocks. The character of the product depends upon the cooling conditions. Crystallisation occurs to a degree dependent on the time available for the atomic groups which form the crystals to move towards the centres at which crystallisation begins. It also depends upon the mobility of these atomic groups which in turn largely depends upon the viscosity of the slag.

The occlusion or solution of gases in the liquid causes an increase in mobility with consequent decrease in viscosity, and during cooling this action results in a more effective diffusion and augmented crystallisation.

It was found by experiment that the amount of occluded gases in the slag could be largely increased by the addition of small amounts of moist slag of the same general composition as the molten magma. The use of this gaseous or "volatile flux" did not affect the slag composition.

It was possible by this means to increase effectively the mobility of the slag when slowly cooled in large masses so that an improved degree of crystallisation was obtained. The slag masses weighed about 12 tons and were allowed to cool for 96 hours.

When/

When such masses cool slowly the possibility exists that each crystal separation may modify to some extent the composition of the residual magma and the effects of these changes might alter to some degree the composition of the final products. That this action is apparently not of great importance is deduced by comparison of slowly cooled with those of quickly cooled slags described later.

The slowly cooled slag masses were broken into lumps which were separately examined. Suitable pieces were crushed without grinding into a powder. Dust and cryptocry stalline slag aggregates were removed with sieves. At each stage the larger euhedral and subhedral crystals were picked out. The slag powder thus roughly purified was subjected to further treatment. The powder was examined under a low power in a binocular microscope and euhedral crystals removed with a moistened splinter of soft wood. It was then subjected to magnetic separation.

An electro-magnetic field of variable intensity was used. The magnet consisted of a cylindrical core of soft iron bent to a U shape. Each limb was tapered at its end and fitted with an adjustable sharp pointed soft iron shoe. A variable resistance was connected in series with the battery and the field coils. The magnet was mounted below an ebonite plate supported by side-brackets. An adjustable table below the magnet allowed a glass tray containing a thin layer of powder to be passed at fixed distances beneath the magnet shoes. For the first separation the minimum field was used so that the most strongly magnetic minerals were just attracted. The tray was withdrawn and a glass plate substituted. Typical crystals were abstracted from the crop with a moistened wood splinter.

Magnetic separation is an essential preliminary step in basic slag crystal powder examination, as it eliminates metallic shot which would interfere with subsequent analysis.

The use of high specific gravity liquids for crystal separation/

separation is limited to those media having a density of over 3.1

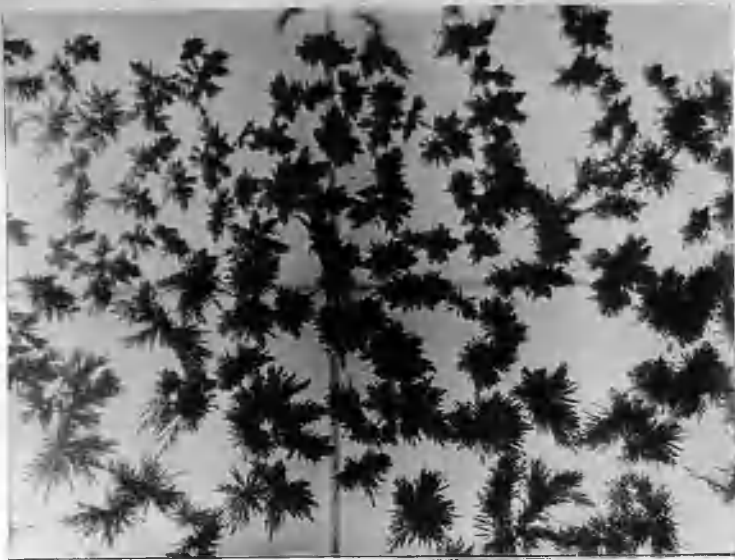
Thoulet Solution was prepared by stirring 270 grms. Mercuric Iodide with 230 grms. Potassium Iodide in 80 cc. distilled water. A flat basin was used and the solution evaporated until a crystalline film formed. It was cooled and water added drop by drop to dissolve crystals formed during cooling. A crystal of Fluor Spar (Spec. Gr. 3.18) floats on the concentrated solution. This liquid is mobile and conveniently miscible with water in any proportion. It is reconcentrated by evaporation or a waterbath. Any iodine separating out through decomposition can be restored by addition of mercury.

This solution was used to separate the long needle-like clear crystals subsequently identified as Fluorapatite. The crystal crop from the magnetic separator was introduced and the liquid allowed to stand until a clear layer showed beneath the suspended matter. A conical vessel was then introduced into the cylinder containing the solution until the contents overflowed and the suspension washed into a containing basin. The suspended material was filtered, washed with diluted potassium iodide and finally with hot water. The residue was then dried.

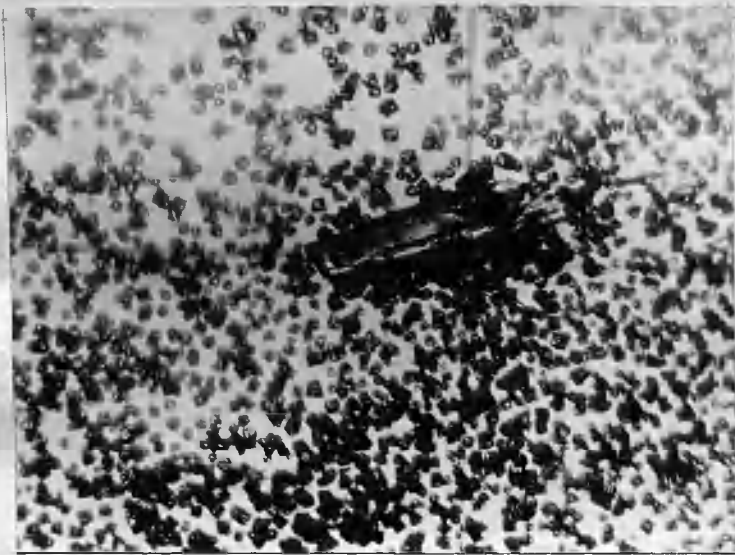
Molten Mercurous Nitrate (Sp. Gr. 4.3) was found to be exceedingly troublesome to work with owing to the formation of a white basic salt of higher melting point which separated out soon after fusion, which occurred at 70 C.

A fair degree of separation of crystals of Tricalcic Ferrite was obtained when the powder was preheated to about 70 C and rapidly plunged into the nitrate immediately upon fusion. The tube containing the mixture was cooled and the solidified mass divided. The nitrate was dissolved off, the crystals dried and hand picked under the microscope.

It was occasionally difficult to obtain enough material for a chemical analysis. In such cases certain microchemical tests/



No. 1
TRANS. LT. 60-M
GYPSUM CRYSTALLINE AGGREGATES.



No. 2
TRANS. 60-M
AMMONIUM-PHOSPHO-MOLYBDATE
OCTAHEDRA FROM FLUORAPATITE
BASIC SLAG CRYSTAL.



No. 3
TRANS. LT. 60-M
MAGNESIUM - AMMONIUM - PHOSPHATE.
AGGREGATES.

8

tests were found of value in the approximate determination of chemical composition. For this purpose crystals and crystal fragments optically free from inclusions and extraneous matter were selected. This was usually possible where difficulty was experienced in obtaining larger quantities necessary for full analysis.

A number of glass rods about 10 cm. long were prepared by heating and drawing their extremities to a fine point. These ends were rounded by heating momentarily in a bunsen flame. The rods were used in the manipulation of the reagents. The crystal under examination was put on a slide and a drop of the reagent placed upon it. In some cases slow evaporation of this solution formed the crystals which characterised the reaction. In others a drop of an additional reagent was placed alongside the first and the two liquids caused to merge gradually. In each case the precipitate could be recognised by its optical properties.

The following tests which can be rapidly performed upon small quantities of material were utilised in the course of this work.

CALCIUM: - The crystal was dissolved in a drop of hydrochloric Acid. A drop of Sulphuric Acid was placed adjacent to this solution and merged therein by means of a fine glass rod. Characteristic radial groups and needles of Gypsum appear on gradual evaporation. These needles unite in star shaped aggregates as shown in photograph No. 1. They have a maximum extinction angle between crossed nicols of 37° and terminate obliquely at an angle of 65° .

PHOSPHORUS - The crystal was dissolved in Nitric Acid, the slide was placed upon a hot plate over a bunsen burner and the solution evaporated to dryness. It was heated to render any silica present insoluble. The material was taken up in nitric acid and treated with a drop of ammonium molybdate. The yellow precipitate of ammonium-phospho-molybdate appears as rounded octa hedral forms and aggregates of globular outline/

outline illustrated in photograph No. 2. In this photograph the results of the application of this test to a crystal of apatite (ex basic slag) are shewn.

CHROMIUM - Chromium was detected in an inclusion in a silicate of lime crystal. The silicate crystals were treated with Hydrofluoric Acid, then fused with Sodium Carbonate and Saltpetre on platinum foil. The fused mixture was dissolved in hot water acidified with Nitric Acid. The addition of a drop of Silver Nitrate caused a deep red colouration. On gentle evaporation of some of this solution on a glass slide red rhombohedral crystals of Silver Chromate were formed.

IRON - To distinguish between ferrous and ferric iron under the microscope the crystal was dissolved in Hydrochloric Acid. The addition of a dilute solution of potassium ferricyanide caused the characteristic blue colouration in presence of ferrous iron. Potassium Thiocyanate gave a red colouration in presence of ferric iron. Occasionally metallic Iron shot is found in the Slag. Its existence was proved by the addition of copper sulphate solution in which case it became coated with metallic copper.

SILICATES - An adaptation of the method described by Dr. Scott (13) was utilised in the examination of basic slags in reflected light. The polished slag section was etched with dilute Hydrochloric Acid and washed free from acid with water. The section was allowed to remain in a solution of malachite green or congo red until the gelatinous silica formed by the etch had become impregnated with the dye. The surface was again washed, dried, and after warming covered with Canada Balsam to prevent alteration. The acid must first be removed to obtain satisfactory results with the dye.

MAGNESIUM - Certain crystals from the basic hearth were placed in/

in hydrochloric acid. The solution was taken to dryness, heated, taken up in acid and decanted. Iron and any Manganese Salts present were precipitated in slightly ammoniacal solution to which ammonium chloride had been added. The solution was filtered, diluted and sodium phosphate added. In presence of magnesium salts crystals of magnesium-ammonium phosphate were precipitated. These crystals, which are shown in photograph No. 3 have a very low double refraction and their refractive index is lower than that of Canada Balsam.

For the microscopic identification of constituents isolated from slags the determination of their optical properties is essential. This necessitates the preparation of crystals and crystallites in sections of thickness approximating 0.03 to 0.05 m.m. It is desirable to obtain sufficient transparency in order to avoid overlapping of adjacent crystals and to prevent the study of their inner texture.

The following method gave satisfactory results:-

A quantity of Zinc Oxide was found to a fine powder. Approximately 5 grams were taken and gently mixed with a small quantity of the crystals to be examined. Enough potassium waterglass was added to give the mixture the consistency of a stiff paste. Too much of the waterglass causes the mixture to crack, while if too little be used the mixture lacks coherence and breaks up on the grinding later. The paste was pressed into a mould formed by $\frac{1}{2}$ " dia. glass tube about $\frac{1}{2}$ " long and resting upon a glass slide. It was found advantageous to moisten the inside of the tube with potassium silicate. The mixture was left at a temperature of about 50^o C for several days. The tube was broken off and the cement subjected to the usual/

usual grinding and polishing to thin section. Under the microscope in transmitted light Zinc Oxide has a dullish-green non-crystalline appearance distinguishable from any slag constituent. This method permits of approximately accurate orientation of the larger slag crystals in the cement with reference to their crystallographic axes.

MICROSCOPIC METHODS:-

Thickness of section - The method used was a modification of that of Duke & Chaulnes for refractive index measurement. It was applied in the reverse manner. The Canada Balsam of the mount was taken as of similar thickness to that of the section. Any fine dust particle occurring between the coverglass and the Balsam was first focussed, then the tube of the microscope was lowered until the same was seen reflected from the under side of the slide.

Then when

- t = Thickness of section.
- d = Distance of lowering the tube
- n = Index of refraction of Canada Balsam (n = 1.54

$$t = dn$$

The change of objective focus was read from the drum of the micrometer screw.

REFRACTIVE INDEX:

The Becke and Schroeder Van der Kolk⁽¹⁴⁾ methods of determination were used. Use was made of Thoulet solution as the immersion medium.

ADJUSTMENT:

For crossed nicol observations etc. the ocular cross-hairs were adjusted exactly parallel to the vibrational directions of the nicols by use of known crystals of quartz in thin section mounted in/

in Canada Balsam. These crystals showed needle growth and straight extinction whilst the refractive index of quartz is close to that of the Balsam. The long edge of a quartz crystal was placed exactly parallel to one of the ocular cross-hairs. The bottom nicol was rotated until its vibrational direction was exactly similar when light passes through the quartz unaltered and no interference colours resulted when the analyser was rotated through 90° .

EXTINCTION ANGLES:

The Bertrand Plate was used for accurate determinations of extinction angles between crossed nicols. The tube analyser was withdrawn from the polarising microscope and a cap nicol fitted over the eyepiece. The Bertrand Plate was placed in the ocular. This device consisted of four sections of alternating right and left rotating quartz plates 2.5 mm. thick cut perpendicularly to the optic axes. The dextro-rotary and levo-rotary quartz sections lie in opposite segments. When the nicols are accurately crossed the quadrants have a uniformly pale blue tint. The introduction of a doubly refracting crystal upon the stage allows these quadrants to add to or subtract from its retardation except when it is on the position of extinction when the whitish blue tint is uniform throughout the field.

Incidentally this device was used to check the adjustment of the ocular cross-hairs as determined by means of quartz crystals.

INTERFERENCE COLOURS:

The interference colour for a given section thickness in the 45° position between crossed nicols was used as a measure of the relative retardation of the slow ray behind the fast ray of the section. This colour is the result of the sum of the effects produced by interference between/

between these two rays for each wave length.

When the relative retardation is thus determined then the Bifringence is also known since

$$\text{Bifringence} = \frac{\text{Retardation}}{\text{Thickness}}$$

Thus where

- d = Thickness of Section.
- t_1 = Time taken by the slow ray to traverse this thickness.
- t_2 = Time taken by the fast ray to traverse this thickness.
- s = Maximum refractive index corresponding with the slow ray.
- f = Minimum refractive index corresponding with the fast ray.
- L = Velocity of light in vacuo.

Then

$$\text{Velocity of slow ray} = \frac{d}{t_1} = \frac{L}{s}$$

$$\text{Velocity of fast ray} = \frac{d}{t_2} = \frac{L}{f}$$

$$\text{Hence } t_1 = s \frac{d}{L} \text{ and } t_2 = \frac{fd}{L}$$

And

$$t_1 - t_2 = (s-f) \frac{d}{L} = \text{Retardation in time.}$$

Retardation can be expressed in terms of distance if time retardation be multiplied by the velocity of light in vacuo.

$$\text{Hence Retardation (in distance)} = L(t_1 - t_2) = (S-F)d$$

$$R = \text{Bifringence} \times \text{Thickness of Section.}$$

Since R is always expressed in micromillimeters and the thickness in microns the thickness of the section must be multiplied by 1000 to give the retardation in micromillimeters. Hence

$$R \mu\mu = 1000(S-F)d$$

The relative retardation can therefore be approximately determined by observation of the interference colour. The variations in intensity and tone from the deep hard colours of the first order to the faint pinks, greens and whites are sufficiently marked to render/

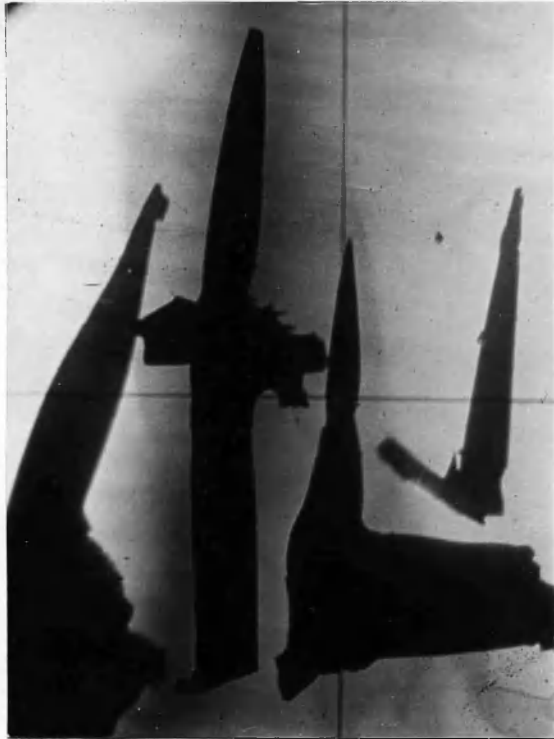
render this convenient method sufficiently accurate for most purposes of identification in slag sections.

For the actual determinations of relative retardation and maximum birefringence values of unknown minerals the Quartz Wedge device in common use in petrography was used. This compensator was also used for the determination of crystal character (i.e. positive or negative) by the usual methods.

In addition to the ordinary convergent polarised light tests the method recommended by Johansen (15) was used when small grains were under observation, for the determination of the number of axes of no double refraction (i.e. uniaxial or biaxial nature). The figures in such grains are otherwise difficult to observe. By use of this method they are small but well defined.

A glass rod was heated in a bunsen flame and drawn to a fine thread. The extremity of the thread was fused and a spherical glass globule formed. The rod carrying this spherical glass lens was clamped in position just over the section but independent of the stage. The microscope was focussed upon the sphere and slightly raised.

TRICALCIC FERRITE CRYSTALS
(MONOCLINIC)
EX BASIC SLAG.



No. 4
TRNS. LT. 60-M

NEEDLE CRYSTALLITES.



No. 5
OBLIQUE LT. 50-M

CRYSTALS AND CRYSTALLITES.

TRI-BASIC FERRITE CRYSTALS.

Photograph No.4 shows the appearance in transmitted light at 60 Mags. of needle-like crystals isolated from basic finishing slags. Their appearance in oblique light at 50 Mags. is illustrated in photograph No.5.

These crystals were of quite common occurrence in certain slags and were isolated from the slag powder by careful hand-picking with a sharp splinter of moistened wood under low powers in a binocular microscope.

In reflected light they were characterised by a brilliant metallic lustre and appeared black in colour.

The crystals were elongated parallel to the vertical axis, one of the lateral ^{axes} appeared inclined to the principal axis, while the other was at 90° to it.

Where development had been incomplete the crystals had developed a flat needle form with occasionally a barrel-shaped outline as shown in photograph No.4.

This characteristic needle growth was frequently seen to be the result of incomplete crystallisation along a secondary axis at 90° to the primary axis of a larger crystal.

The crystals were hard and nonmagnetic; they varied in size from minute individuals up to a length of 7 m.m. They were isolated from the slag vesicles in a high degree of purity.

The chemical analysis showed:-

Analysis No.1.	%	Molecular Comportion.						
SiO ₂	1.08	0.0180						
Al ₂ O ₃	1.36	0.0333	Recalculation.					
Fe ₂ O ₃	44.04	0.2753						
FeO	Nil	-	RO	R ₂ O ₃	Acids.			
MnO	4.43	0.0624						
CaO	44.16	0.7884	CaO	0.8201	Fe ₂ O ₃	0.2864	SiO ₂	0.019
MgO	4.48	0.1106	MgO	0.1150	AP ₂ O ₃	0.0346		
P ₂ O ₅	-		MnO	0.0649				
	<u>99.55</u>			<u>1.000</u>		<u>0.3210</u>		<u>0.019</u>

It consists essentially of a Calcic-Ferrite compound of the approximate formula - $3 \text{CaO-Fe}_2\text{O}_3$ - where MgO can apparently replace CaO.

The completely developed crystals appeared opaque in transmitted light under high magnifications. The flat needles were faintly translucent, had a deep ruby-red colour and were doubly refracting between crossed nicols.

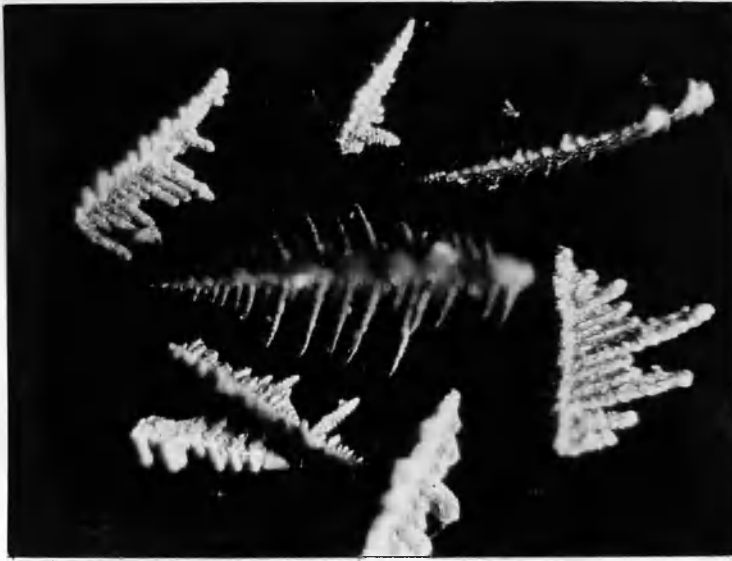
Crystal fragments and sections of crystals had a reddish rust colour. They showed high relief and roughness when the condenser of the microscope was raised. The refractive index exceeded 1.73. Cleavage was indistinct and imperfect parallel to the (c) axis. The fracture was uneven.

These crystals were characteristically free from inclusions thus indicating formation at an early stage in the solidification of the slag. In a section 0.04 m.m. thick the colour was yellowish rust. Between crossed nicols when the direction of the principal zone was parallel to the slow direction of the quartz wedge the interference colours were additive. This direction was therefore that of least velocity and the character of the principal zone was positive. When the combination was subtractive compensation occurred with second order greenish blue. This corresponds to a relative retardation of approx: 670 micromillimeters. The maximum birefringence measured was therefore about 0.017.

The extinction angle of some of the grains was straight, in others it was inclined to the principal direction of elongation indicating that the crystal system is probably monoclinic. The crystal form supports this conclusion although the nature of the figure in convergent polarised light was not definitely ascertained

Similar crystals were obtained in the course of this work from investigations upon the basic hearth. In this latter case, however, they contained 9.4% FeO .

MAGNETIC CONSTITUENT (CUBIC)
EX BASIC SLAG.



OBLIQUE LT.

No. 6

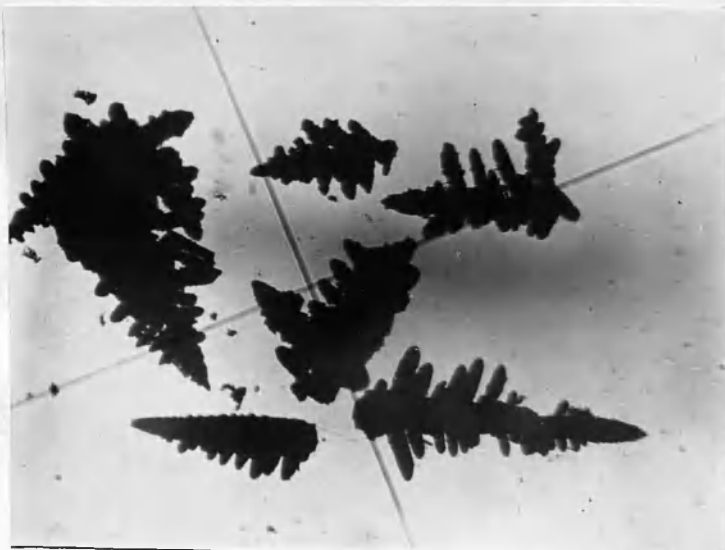
50-M



TRANS. LT.

No. 7

50-M



TRANS. LT.

No. 8

35-M.

MAGNETIC CONSTITUENT.

Photograph No. 6 shows at 50 Mags. the appearance of typical crystalline skeleton formations of this substance in oblique light. Photographs Nos. 7 and 8 exhibit their appearance in transmitted light.

These crystallites were strongly magnetic and the first separations were made from the slag powder by use of a bar magnet. These separations were exposed to weak electromagnetic fields and further division effected in the manner already described.

The appearance of this substance is most easily observed in oblique light. Well developed specimens showed growth to have taken place along six directions at 60° to each other, forming a secondary axial system simultaneously with the elongation of the primary crystal axis perpendicular to the plane of the secondary axes. These secondary lines of growth in turn showed development ternary and quaternary axial systems, etc.

In all cases the axes of the higher orders exhibited the same development as those of the lower orders and the material showed a characteristic dendritic structure.

The chemical analysis showed:-

Analyses No. <u>11</u>			Analyses No. <u>111</u>		
	%	Molecular Composition.		%	Molecular Composition
SiO ₂	8.00	0.1333	SiO ₂	5.18	0.0863
Al ₂ O ₃	4.79	0.0470	Al ₂ O ₃	4.27	0.0486
Fe ₂ O ₃	32.04	0.2002	Fe ₂ O ₃	34.10	0.2131
FeO	4.86	0.0675	FeO	6.36	0.0884
MnO	13.65	0.1923	MnO	14.53	0.2046
CaO	32.20	0.5750	CaO	29.66	0.5297
MgO	<u>5.00</u>	0.1234	MgO	<u>5.25</u>	0.1296
	100.54			99.35	

No. 11 is the analysis of the material as separated from the Slag, No. 111. was after grinding and further electro-magnetic cleaning. At higher powers the structure was seen to consist of purely crystalline material; the formation was the result of parallel intergrowth along the common axis of development. The constituent crystals were piled one on top of the other.

In ordinary light the crystallites appear grayish black in colour; they were highly reflecting and showed a hard metallic lustre.

This constituent was obtained from slags where the iron content exceeded about 14%. It was not noticed in slags where the iron content was known to be low.

Its formation made it troublesome to obtain free from extraneous matter; electro-magnetic separation did not overcome this difficulty. It was observed as an inclusion in certain of the tribasic silicate of lime crystals described elsewhere.

Under the microscope at high powers the crystallites at the tips of the dendrites exhibited octahedral faces while certain facets showed a deep blood red colour in oblique light.

These crystals are the result of growth at the most sharply pointed angles, diffusion in the supersaturated solution being greatest at these angles. The formation of the secondary axes was the result of growth occurring at some of the solid angles produced. This ~~was~~ repeated for each of the higher axial systems.

The crystals ~~were~~ quite free from inclusions but there was a great tendency for impurities to be entrapped amongst the dendrites. This foreign matter can be readily distinguished in transmitted light. It consisted partly of the silicate of lime crystals described later. The material analysed was therefore/

MAGNETIC CONSTITUENT (CUBIC)

EX BASIC SLAG



No. 9

TRANS. LT.

150-M

THIN SECTION IN ZINC
OXIDE CEMENT.



No. 10

TRANS. LT.

150-M

THIN SECTION IN ZINC
OXIDE CEMENT.

FLUORAPATITE CRYSTALS (HEXAGONAL)

EX BASIC SLAG.



No. 11

TRANS. LT.

35-M



No. 12

TRANS. LT.

35-M

therefore not quite pure.

Thin sections of this constituent were prepared by use of the Zinc Oxide cement in the manner already described.

Photographs 9 and 10 show its appearance in parallel transmitted light at 150 Mags. In the photographs of the thin sections this constituent appears dead black, the half-tone and lighter coloured groundmass is the zinc oxide cement which shows a dull green colour under the microscope.

In thin sections the crystals were homogeneous. They were often almost opaque but frequently showed the deep blood red colour with imperfect cleavage. They were distinctly octahedral in form in suitably oriently sections. The fracture was even. The refracture index exceeded 1.9. The crystal junctions with the balsam were rough and the surface uneven with the condenser of the microscope raised as high as possible.

In parallel polarised light using the bottom nicol the crystals were non-pleochroic. Between crossed nicols they remained dark or showed no regular double refraction. A few of the grains appeared faintly translucent and did not exhibit extinction in any position of rotation between the nicols.

This phenomena is of the nature of an optical anomaly not uncommon in cubic minerals and may be the result of strain produced during the cooling of the dendrites.

This magnetic constituent belongs to the octahedral group of the cubic system.

Previously published analyses of magnetic material isolated from basic slags are of interest.

Analyses No. IV is by Stead (7) from basic bessemer slags. Analyses No. V is given by Bainbridge (9) from hearth slags.

In each case the corresponding molecular composition has been calculated.

	Analyses No. <u>IV</u> Steam		Analyses No. <u>V</u> Mainbridge.		
	%	Mol. Comp.	%	Mol. Comp.	
CaO	18.73	0.3344	CaO	7.40	0.1312
MgO	11.46	.2830	MgO	24.90	.6148
Al ₂ O ₃	1.80	.0177	Al ₂ O ₃	1.84	.0180
Fe ₂ O ₃	16.14	.1009	Fe ₂ O ₃	23.29	.1455
FeO	38.06	.5286	FeO	26.23	.3643
MnO	9.58	.1349	MnO	14.04	.1977
SiO ₂	0.80	.0134	SiO ₂	1.30	.0216
P ₂ O ₅	<u>1.66</u>	.0117	P ₂ O ₅	<u>1.03</u>	.0073
	98.23			100.03	

The composition of the material separated by the author differs from these analyses in being lower in ferrous oxide and magnesia while the ferric oxide and the silica are higher.

A feature of each analysis is the relatively high content of Manganese Oxide. The possibility exists that under the oxidising conditions which frequently occur towards the end of the process, the Manganese oxide may act as a base towards the ferric oxide which in the absence of lime may combine to form constituents of complex constitution. Crystals of Magnetite have never been observed in basic slags and its formation as a separate basic slag constituent appears unlikely.

The amount of magnetic material in basic slags is normally very low, at least until the finishing stages are reached. This constituent consequently cannot be of great importance as a refining agent. Its origin is apparently of a secondary nature and appears the result of complex combinations when the slag assumes a more strongly oxidising character towards the finishing stages of the process.

HEXAGONAL COLUMN CRYSTALS.

These crystals are illustrated in photographs Nos. 11 and 12 at 35 Mags. in ordinary transmitted light.

Their separation was effected from the slag powder after Tricalcic Ferrite crystals and the magnetic material had been removed.

A quantity of the concentrated **Thoulet** solution (sp. GR 3.17) was placed in a narrow beaker and the slag powder introduced into the solution. The beaker was set in a basin and allowed to stand until a layer of clear liquid showed between the suspended matter and that at the bottom of the beaker.

A conical vessel was gradually introduced until the contents of the beaker overflowed. The suspension was thus worked into the basin, the contents of which were diluted with water and filtered. This process was repeated until a small quantity was collected.

The crop was dried, gently crushed between two watch glasses and the process of separation in the potassium-mercuric iodide solution repeated. Finally the solution containing the suspended matter was diluted drop by drop with water until only pure crystals remained suspended. The specific gravity at this stage was determined as 3.105. These crystals were collected, washed and dried.

This process was extremely tedious as the amount of this constituent in the slag was very small. Insufficient material was collected for a chemical analyses, but the amount obtained was sufficient for optical and microchemical determinations.

In reflected and in oblique light the crystals appear as colourless hexagonal columns which show considerable elongation in the direction of the principal axis. They ranged in size up to 10 m.m. in length. In ordinary light they showed a vitreous lustre, imperfect cleavage and **conchoidal** fracture.

Determination of the refracture index in the direction perpendicular/

perpendicular to the principal axis by the Schroder van der Kolk method using Thoulet solution as indicator gave the value of 1.64.

The crystals were transparent and brittle. They were free from inclusions. In thin sections when rotated over the polariser the crystals were slightly deeper in colour when the long edge of the crystal was parallel to the vibrational direction of the nicol prism thus showing stronger absorption parallel to the principal zone. They were therefore faintly dichroic. In sections parallel to the principal zone they were doubly refractive and showed straight extinction between crossed nicols.

The long edge of the crystal was placed at 45° from its position of extinction. The quartz wedge cut with its length parallel to its optic axis, thus having its length the slow direction, was introduced between the nicols so that its length was also at 45° to the vibrational direction of the nicols. Compensation occurred on a section 0.05 m.m. thick with first order greyish white. The relative retardation is therefore very low at about 200 u.u. The corresponding birefringence value is 0.004 u.u.

The slow direction of the wedge was, in the position given, parallel to the fast direction of the crystal. The combination was therefore subtractive and the sign of the principal zone was negative.

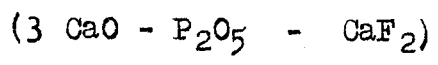
In hexagonal cross-sections, i.e. at 90° to the direction of the principal zone, the interference figure in convergent polarised light could not be distinguished on account of the low double refraction. In these sections the crystals remained dark between crossed nicols in parallel light.

The uniaxial nature and the crystal form indicated that this constituent belongs to the hexagonal system.

The material was subjected to the following microchemical tests/

- (1) The solution containing the crystals in nitric acid was evaporated to dryness on a glass slide, then heated. The deposit was taken up in dilute nitric acid and tested with a drop of ammonium molybdate. The small yellow "rounded" octahedra appeared as globular aggregates recognisable as ammonium phospho-molybdate. The presence of phosphorus was therefore indicated. Photograph No.2 shows the results of the application of this test to a crystal in partial solution.
- (2) The addition of Sulphuric Acid to a Hydrochloric Acid solution of the crystals caused the precipitation of gypsum needles and indicated the presence of lime.
- (3) No traces of iron in pure crystal fragments were observed.
- (4) Some crystals were dissolved on a glass slide in a solution of concentrated sulphuric acid containing Sodium Silicate. A drop of this solution was transferred to another slide which had been gently heated. Rosettes and Stars of faintly rose tinted crystals hexagonal in form gradually appeared. These coloured crystals of Sodium Fluosilicate indicated the presence of Fluorine.

The microchemical tests proved the existence of Fluorine, Lime and Phosphorus. The hexagonal crystals form and optical tests agreed with those of the mineral Fluorapatite



The calculated percentage of Phosphoric Acid in this substance is about 42.3%. The amount of this mineral in a slag containing 3% P₂O₅ will therefore be about 7%

STAR-SHAPED CRYSTALLITES

of FLUORAPATITE

EX BASIC SLAG



TRANS. LT. No. 13 50-M



OBLIQUE LT. No. 14 50-M



TRANS. LT. No. 15 35-M

FLUORAPATITE CRYSTALLITES
BETWEEN CROSSED NICOLS.

STAR - SHAPED CRYSTALLITES.

Photographs Nos. 13 & 14 show crystallites which were separated from the slag powder along with the euhedral Fluorapatite crystals by use of the methods described. The amount collected was insufficient for chemical analysis.

The crystallite development indicated that growth had occurred along three horizontal axes and thus conferred a six-pointed star shaped appearance upon the formation. The points lie at 60° to each other along the horizontal plane. Development was also noticed to have occurred, as can be observed in the photograph, at a reduced rate along the normal principal axis at 90° to the three horizontal axes. Growth along this normal principal axis frequently resulted in the formation of hexagonal columns similar to those of Fluosapatite crystals as already described.

Microchemical tests showed the presence of Fluorine, Phosphorus and Lime. The crystallites had the same index of refraction as the Apatite Crystals while the density was also identical. The crystallites also showed similar optical properties. In photograph No. 15 taken between crossed Nicols a crystal and a crystallite are shown along the same plane. The crystal is in the 45° position between the nicols. In this position the crystallites remained dark during rotation of the stage through 360° and their optical behaviour was identical with that of the hexagonal cross-section of the Fluorapatite crystals.

It was concluded therefore that these crystallites were the result of incomplete or interrupted crystallisation of Fluorapatite, their formation being the result of development of the axes of binary symmetry.

TRICALCIC SILICATE CRYSTALS (ORTHORHOMBIC)

EX BASIC SLAG.



No. 16

TRANS. LT.

18 -M

TYPICAL CRYSTALS OF
TRICALCIC SILICATE.



No. 17

TRANS. LT.

30-M

TRICALCIC SILICATE CRYSTALS
SHOWING INCLUSIONS.

TRICALCIC SILICATE CRYSTALS

A commonly occurring euhedral crystal constituent of the slags examined is illustrated in photograph No. 16 taken at 18 Magnifications.

The crystals vary in size from minute individuals up to a length of 7 m.m. They were readily picked out by means of a moistened splinter of soft wood with the use of low powers under a binocular microscope.

It occurred in the slag in masses, as flat plates occasionally elongated with domatic terminations. The colour of the crystals varied from olive green, through citron yellow to brownish green. The dominant and characteristic colour was olive green. The crystals exhibited vitreous lustre and showed conchoidal to uneven fracture. Cleavage was indistinct. Typical crystal forms are shown in the photographs Nos. 16 & 17.

The crystals of this substance frequently contained abundant inclusions, mostly identified as Tricalcic Ferrite, the Magnetic Constituent and crystals of Fluorapatite. Photograph No. 17 (30 Magnifications) shows those inclusions by transmitted light. The symmetrical arrangement of the inclusions with reference to the crystal faces can be observed in the photograph and indicates that this silicate has been amongst the last of the slag constituents to solidify.

The euhedral development of the material in large crystals facilitated observation of the crystal form at low powers. Development had taken place along three unequal axes. Two of these axes were at right angles to each other. Microscopic measurement showed they were at 90° to the principal axis. No goniometrical measurements were made however. The transparency of the material enables the crystal symmetry to be observed in the photographs.

In their place of origin in the slag they occasionally showed/

showed parallel growth where the corresponding axes, edges and faces of different individuals were parallel. This type of composite crystallisation differs from that resulting in twin crystals since there is no symmetrical union along a common plane or axis between adjacent crystals.

The chemical composition was:-

	Analyses No. <u>VI</u>			Analyses No. <u>VII</u>	
	%	Mol. Comp.		%	Molecular Composition.
CaO	57.40	1.0250	CaO	57.50	1.027
MgO	2.50	0.0619	MgO	2.70	0.067
Al ₂ O ₃	3.66	0.0359	Al ₂ O ₃	3.41	0.033
Fe ₂ O ₃	7.74	0.0484	Fe ₂ O ₃	7.39	0.046
FeO	8.10	0.1123	FeO	7.50	0.104
MnO	5.58	0.0786	MnO	5.15	0.072
SiO ₂	15.20	0.2533	SiO ₂	15.60	0.260
P ₂ O ₅	-	-	P ₂ O ₅	-	-
	100.18			99.25	

Analysis No. VI was made upon the crystals as picked from the slag. Analysis No. VII was upon this material after crushing and treating with a bar magnet, whereby the amount of iron oxide bearing inclusions was slightly reduced.

This substance has a strongly vitreous lustre by incident light. Strong total reflections from the crystal faces inclined to the axis of the microscope together with high "relief" and rough surfaces in Canada Balsam indicated a high index of refraction. In section parallel to the principal zone determination by the Van der Kolk method gave the value of 1.707. Convergent polarised light on certain of the crystal grains showed a biaxial figure with relatively low optic angle.

Approximately accurate orientation of the grains with reference to the three axes was secured by setting several of the crystals in zinc oxide cement before polishing to thin section by the usual methods.

TRICALCIC SILICATE CRYSTALS IN THIN
SECTION - 45° POSITION - BETWEEN
CROSSED NICOLS.



No. 18
TRANS. LT. 100-M

PARALLEL TO ZONE OF
PRINCIPAL AXIS.



No. 19
TRANS. LT. 100-M

PARALLEL TO ZONE OF
(b) AXIS.



No. 20
TRANS. LT. 100-M.

PARALLEL TO ZONE OF
(c) AXIS.

Photograph No.18 is that of the thin section approximately parallel to the zone of the principal axis. In ordinary light the section was colourless. Cleavage was imperfect. In polarised light it was nonpleochroic. Between crossed nicols the extinction was straight. On the insertion of the quartz wedge with the crystal in the 45° position to the direction of the nicols the colour combination was subtractive and compensation occurred with first order white of the compensator.

The thickness of the section was 0.05 m.m. The relative retardation was 230 u.u. The corresponding birefringence value was therefore about 0.0046.

In Photograph No.19 is shown the crystal at approximately 90° to the principal zone, i.e. parallel to the zone of the (b) axis. Photograph No.20 shows the section parallel to the zone of the (a) axis.

In each of these three sections the extinction, with reference to the respective crystallographic axis, was straight.

In convergent polarised light the character of the interference figure was indistinct in thin section. In thick sections it was biaxial and on the introduction of the quartz wedge with its slow direction parallel to the direction of traces of the optic axial plane as indicated by the hyperbolae of the interference figure (i.e. when the plane of the optic axes was also at 45° to the nicols) there was a decrease of colour on the inside and an increase on the outside of the hyperbolae. The dark bar produced by an oblique axis is curved with the convex side towards the acute bisectrix. The increase of colour takes place when the wedge and the section are additive. In this case it coincided with the direction of the acute Bisectrix so that the character of these crystals was negative since the direction of the acute Bisectrix was slow.

The biaxial nature, straight extinction and crystal form indicate/

indicate that these crystals belong to the Orthorhombic System.

The chemical composition approximates to that of the Tricalcic Silicate, $3 \text{ CaO} - \text{SiO}_2$, if allowance be made for the composition of the inclusions illustrated in Photograph No.17. These inclusions must contain the bulk of the R_2O_3 oxides shown in the analysis in combination chiefly with lime. The relative amounts of each type of inclusion could not be ascertained with certainty but they consist mostly of Tricalcic Ferrite needles.

The optical properties of this silicate differ from those of dicalcic silicate which were characteristic of basic slags of a higher silica content. The latter were frequently obtained from earlier stages of the process and are described later. Dicalcic silicate crystals in thin section were always yellowish to bluish yellow in colour, they showed inclined extinction, higher double refraction and higher refractive index.

These tribasic silicate crystals were always associated with inclusions containing ferric iron; in slags containing dicalcic silicate the amount of ferric iron was relatively low.

NO. 22 ET. SEQ.- SHOWS MICRO-STRUCTURE OF RAPIDLY
COOLED BASIC FURNACE BATH SLAGS FROM
THE INITIAL STAGES OF THE MELT.



REF.LT. No. 21 100-M

REF.LT. No. 22 300-M

CHROMITE CRYSTALS AS
INCLUSIONS IN SUBHEDRAL
TRICALCIC SILICATE MASSES.
EX BASIC SLAG.

DARK AREAS ARE CONSISTED OF A
SILICATE OF LIME, HALF TONE
AREAS CONTAIN "SPINELLOIDS"
WHITE AREAS-THE FREE OXIDES.
BATH SLAG 4^S
(ETCHED IN STRONG ACETIC ACID).



REF.LT. No. 23 150-M

REF.LT. No. 24 80-M

LATH CRYSTALS OF DICALCIC
SILICATE, WHITE MASS CONSIST
OF FREE OXIDES.
BATH SLAGS 6^S
(ETCHED IN STRONG ACETIC ACID).

DICALCIC SILICATE CRYSTALS
IN COMPOSITE GROUNDMASS
BATH SLAG 7^S
(ETCHED IN DILUTE ACETIC ACID).

CHROMITE CRYSTAL INCLUSIONS.

Photograph No. 21 taken at 100 Magnifications in reflected light shows the appearance of minute crystals occasionally noticed as inclusions in crystals of Tricalcic Silicate, obtained in subhedral form from slowly cooled slag masses. These silicate crystals had partially developed certain faces during solidification and the inclusions were observed upon these faces.

They were placed upon a celluloid plate and treated with hydrofluoric acid. The inclusions were partially isolated and were fused with sodium carbonate and saltpetre on platinum foil. The fusion was dissolved in hot water. The tests described on page 6 shewed presence of chromium.

The crystals were non-magnetic, very hard and almost insoluble in acids. They occurred as sharp definitely outlined crystals in various forms of the cube. They exhibited medium lustre in reflected light and were black in colour.

In nature Chromite is universally associated with rocks of the olivine group where it occurs as well formed sharp crystal inclusions similar in appearance to those illustrated in the photograph .

It was included that these minute crystals consisted essentially of the oxide of Chromium Cr_2O_3 probably introduced as an impurity in the steel scrap. Its existence within the silicate crystals indicates that it must be one of the earliest products of crystallisation from the slag magma. The possibility exists that the Chromic oxide is in combination with CaO in these cubic crystals although this was not definitely ascertained.

EXAMINATION OF PROCESS SLAGS.

With the exception of Fluorapatite the constituents described in the preceding section have not previously been observed in basic open hearth slags. These slag minerals were obtained from finishing slags where the cooling conditions allowed the maximum degree of crystallisation of their components. A knowledge of the constitution of the molten slag must be the ultimate practical object of metallurgical investigations, It was desirable to ascertain if the occurrence of these constituents in slowly cooled slags had significance in the constitution of the liquid slag.

Small rapidly chilled slag samples were taken from a furnace bath. Microscope examination of polished sections in reflected light revealed the existence of crystalline constituents. This proved therefore, that reaction must have taken place in the liquid state between the components of these crystals and that saturation with the corresponding molecules must have occurred just before solidification of the specimen. The crystal form preserved by the rapid chill would be characteristic of the temperature at which the specimen was obtained. Where no constituent formation in the chilled slag was noticeable then either no reaction had occurred in the liquid phase or the concentration of any new combinations must have failed to reach saturation point on cooling.

The examination of small rapidly chilled specimens of slags taken at different stages of the process was systematically undertaken.

A representative series of slag samples was obtained from a typical cold metal charge using low-phosphorus pig iron. The specimens were drawn at regular intervals under uniform sampling conditions.

Table No. 1 gives the composition and amount of the materials charged.

The slag specimens were taken, $4\frac{1}{2}$ ft. from the dolomite banks. The weight of the samples was approximately $\frac{1}{2}$ kilogram.

Table No. 2 gives the time intervals of sampling during the working of the charge with notes upon the bath conditions.

Table No. 3 shows the analyses of the slags.

Table No. 4 gives the composition of the metal when the slags were obtained.

MICROSCOPIC EXAMINATION: For reflected light examination the specimens were ground to a size approximately $\frac{3}{4}$ " x $\frac{1}{2}$ " x $\frac{1}{2}$ ". Slags containing over 8% iron were ground on a carborundum wheel. Where the iron content was lower the slags were fragile and were shaped with a fine file.

Further grinding was done by hand, using ordinary polishing papers. Polishing in the usual sense was impossible. The use of water or oil in the final stages formed a cement-like layer very difficult to remove. After the finest paper the sections were gently rubbed on a dry "Selvet" cloth and finished on a silk pad.

The finished slag surfaces frequently showed certain constituents in relief owing to relative differences in hardness but for satisfactory definition the use of an etching reagent was essential. The correct strength of this reagent varied with the type of slag since marked differences were found to occur during the melt. Experiments were made to determine the most suitable solutions.

HYDROCHLORIC ACID: A 2% Solution, used as recommended (13) (10) distinguishes between ferrous and ferric iron. Compounds containing Fe_2O_3 are not at once attacked as can be proved by testing the solution used for the etch with potassium thiocyanate, only when the solution is oxidised is a red colouration.

colouration noticed. The application of this test requires care and it was found unsuitable for slags containing much ferrous oxide. In such cases the ferric oxide was also attacked.

LACTIC ACID: A 2½% solution attacked silicates and phosphates but had little action on material containing iron compounds.

OXALIC ACID: A 2½% Solution had little differential effect. Its action on the slags was slight.

CITRIC AND MALIC ACIDS: These were found to have similar effects but had not marked differential action. Scott and McArthur (10) recommended a 0.2% Solution of citric acid to differentiate between apatite and silico phosphates, the latter shewing phosphorus to be dissolved when the solution used was tested with ammonium molybdate. The delicacy of this test was increased by carrying out the precipitation of the crystals upon a glass slide under the microscope in the manner already described.

ACETIC ACID: This acid was found to give the best results in differential etching. A rapid etch in strong acid quickly attacks silicate compounds. Phosphates are less readily attacked. Ferrous oxide is attacked least while spinelloid materials appear greyish in colour. A 2½% solution was found most convenient and was extensively used in the course of this work.

After etching the slag sections were rapidly washed in a stream of water, then dried in alcohol.

The preparation and reflected light examination of basic slag samples can be quickly performed. The normal variations in the amounts of essential constituents was found to be small with in the usual range of an established practice in an open-hearth melting shop. Where positive determinations of the usual components in the slag have first been established for a particular range of slag compositions their subsequent recognition by reflected/

reflected light was found easily possible.

This latter method offered a method of process control which can supplement if not replace the usual bath tests during the working of the heat. The physical differences of basic slags would seem to bear little relation to their chemical composition. This fact is well known to the experienced steel-furnace man. The use of the microscope has been found of service by the author in the control of slag formation during furnace operations on an extensive scale.

In the scheme adopted for this work the slags were first examined by reflected light. Sections were also prepared for transmitted light examination and comparison made of the constituents observed by these two methods.

The nature of the slags was found to vary considerably at different stages of the process, hence the method adopted is based on their ultimate composition.

The molecular composition corresponding to the chemical analysis was calculated. The sum of the oxides of the potential bases viz - Calcium, Magnesium, Ferrous Iron and Manganese was recalculated to unity.

The sesquioxides of Iron and Aluminium were recalculated to their corresponding proportionate weights. The acidic oxides of Silicon and Phosphorus were likewise recalculated and shown separately.

This method serves for the range of slag compositions examined although from the purely metallurgical viewpoint the most desirable classification of steel process slags would be to separate the "active" refining agents i.e. the oxide of iron and possibly also of manganese from lime and magnesia. In practice this latter method is usually adopted within the normal ranges of finishing slags.

It has been shewn ⁽⁴⁾ however, that there exists the possibility in the case of the earlier slags that the ferrous oxide and the oxide of manganese may function as true bases.

In/

4

In certain finishing slags deficient in lime it is here shown that FeO and MnO act as bases towards the R_2O_3 oxides since such slags where the iron content is high, become distinctly more magnetic towards the end.

The method proposed by Whiteley (16) has little metallurgical significance. This writer has obtained a "Basicity Index" by dividing the summation of the molecular ratios of ferrous, manganous, calcium and magnesium oxides less that of three times the phosphorus pentoxide by the molecular ratio of the Silica present. This figure, together with that of a "Distribution Factor" got by dividing the phosphorus content of the slag by that of the metal - is suggested as being indicative of the nature of the slag.

Consideration shews that, although Whiteleys method of calculation holds approximately for a certain range of Phosphorus-Silica Slags, with higher Silica slags such as those examined in the course of this work there may be a high "Distribution Factor" with a "Basicity Index" of normal value only. Whiteleys method of expression for comparative slag classification is therefore not generally applicable.

SLAG S1

This sample was obtained from the first formed slag in the bath before the pig iron had been completely charged.

Chemical Analysis and recalculation of the molecular composition from Table No. 3 shews:-

		Molecular % Composition.							
SiO ₂	2.80	0.047	Recalculation						
Al ₂ O ₃	1.00	0.050							
P ₂ O ₅									
				RO		R ₂ O ₃	Acids		
CaO	24.50	0.438							
MgO	3.82	0.094	FeO	0.545	Fe ₂ O ₃	0.067	SiO ₂	0.037	
MnO	3.82	0.049	CaO	0.343	Al ₂ O ₃	0.004	P ₂ O ₅	0.003	
Fe ₂ O ₃	13.60	0.085	MnO	0.038					
FeO	<u>50.14</u>	0.695	MgO	<u>0.074</u>					
	99.68			1.000		0.071		0.040	

This cinder was very strongly magnetic. In reflected light the polished section shewed a strongly reflecting surface without definite structure. When etched with strong HCL irregular areas were attacked throughout the matrix which remained brilliantly white. Prolonged annealing for 170 Hours at 1050 C resulted only in a slightly greater solution in etching reagents.

The thin section in transmitted light shewed that this cinder was not homogeneous. The field consisted of opaque masses around which were boundary lines of a red translucent constituent. Rounded groups, indefinitely arranged, of the same constituent were also observed. These small crystals shewed no cleavage traces. Their refractive index was high since they shewed "roughness" and relief". They are doubly refracting between crossed nicols. Their small size prevented definite identification though their optical properties are generally similar to those of the Tricalcic Ferrite crystals already described.

The opaque masses are not homogeneous as they vary somewhat in/

in colour by light incident to the surface of the section.

The constitution of this cinder is complex. Micro-chemical tests indicate free Ferrous Oxide. The magnetic nature of the material points to further combinations which were not defined. They probably consist of free ferrous oxide in solid solution with a substance similar to the magnetic constituent isolated from finishing slags. The existence of free Magnetite - although easily optically recognisable - has not been observed in this or any other basic slags examined. It appears unlikely that it can exist separately in presence of sufficient lime but may form either of the "spinelloid" constituents already described.

This slag is typical of the earliest non-metallic material to reach the basic furnace hearth and banks, during the operation of the scrap and pig process. It can be regarded as the reception slag for the molten pig iron. A feature is its highly basic nature. Its oxidising character will also promote rapid reaction with the non-metallic impurities in the iron. This reaction is specially marked on the introduction of molten iron in the hot-metal scrap process.

The existence of a compound of lime and ferric-oxide indicates that due care must be taken during charging operations to provide the lime necessary for this combination. Otherwise damage to the hearth is liable to occur during the softening down of the steel scrap owing to the combination of the lime in the hearth-dolomite with the ferric oxide formed.

SLAG S2

This was taken from the first slag formation after the charge had been completed.

		Molecular Composition.						
%								
SiO ₂	7.00	0.12	Recalculation					
Al ₂ O ₃	} 2.40	0.012						
P ₂ O ₅		0.008	RO	Fe ₂ O ₃	Acids			
CaO	34.20	0.61						
MgO	4.69	0.12	CaO	0.477	Fe ₂ O ₃	0.063	SiO ₂	0.09
MnO	6.62	0.09	MgO	.094	Al ₂ O ₃	.009	P ₂ O ₅	.006
Fe ₂ O ₃	12.50	0.08	MnO	.070				
FeO	<u>32.79</u>	0.46	FeO	<u>.477</u>				
	100.20			1.000		0.072		0.096

This slag was magnetic and lustrous in reflected light. Etching solutions showed a reduction in the irregularly attacked areas when compared with S1 but otherwise it was similar in appearance. The annealing treatment of slag material to develop structure recommended by McCance (17) was tried with this and other slags. In this case the slag was annealed for 60 Hours at 1050 C to 1100 C. In the case of the authors basic slags no deposition of Fe₂O₃ in the form of Magnetite took place. This treatment although successful with acid slags which are of a glassy nature is apparently not applicable to basic slags. The possibility also exists that such treatment may result in the formation of low temperature forms or combinations of the components, this method of developing slag structure was therefore discontinued.

SLAG S3

The bath at this stage contained pools of slag in separate areas. The pig iron had commenced to soften and melt.

		Molecular Composition.						
%								
SiO ₂	11.00	0.18	Recalculation					
Al ₂ O ₃	5.29	.026						
P ₂ O ₅			.019	RO	R ₂ O ₃	Acids		
CaO	40.80	.73						
MgO	5.62	.14	CaO	0.584	Fe ₂ O ₃	0.045	SiO ₂	0.144
MnO	3.72	.05	MgO	.112	Al ₂ O ₃	.021	P ₂ O ₅	.015
Fe ₂ O ₃	9.00	.056	MnO	.040				
FeO	23.60	.33	FeO	.264				
	<u>99.03</u>			<u>1.000</u>		<u>0.066</u>		<u>0.159</u>

The specimen was faintly magnetic. Polished and etched with 2½% HCL the matrix had a greenish white tinge. Deeply etched areas showed the presence of silicate when stained with malachite green. The structure was, however, indefinite, and the constitution of this slag is complex. No examination was made by transmitted light.

The appearance of the three earliest slags under the microscope suggests that they can be regarded as consisting largely as solid solutions of FeO containing CaO-Fe₂O₃ combinations. Apparently FeO can dissolve considerable amounts of Spinelloids although it was not found possible to secure their deposition by heat treatment. Slag S3 is evidently the product of a transition stage. The effect of silica increment seems to split up the CaO-Fe₂O₃ combinations with the formation of lime Silicates Examination of succeeding slags shows that as the amount of Silicate increased the amount of Spinelloid material in the slag rapidly decreased. The early slags appeared dead white in reflected light under the microscope. They were almost entirely without structure.

The/

The change in appearance which accompanies the reduction in iron oxides and the increase in Silica content was very marked. The slags become crystalline even to the eye, their brittleness increased while differentiation of their structure could be secured by means of suitable etching solutions.

SLAG S4

The slag sample was brittle and contained many blow-holes. The slag in the furnace bath was viscous and thickly adhered to a stirring rod. It contained much undissolved lime. A slag "scum" was observed around the furnace banks. This occurrence is not uncommon in the early stages but its cause had not been determined.

	%	Molecular Composition.						
SiO ₂	12.40	0.2066	Recalculation					
Al ₂ O ₃	2.75	.0270						
P ₂ O ₅	1.28	.0090	RO		R ₂ O ₃	Acids		
CaO	46.50	.8305						
MgO	5.77	.1424	CaO	0.63	Fe ₂ O ₃	0.0339	SiO ₂	0.1587
MnO	5.09	.0717	MgO	0.11	Al ₂ O ₃	.0207	P ₂ O ₅	0.0069
Fe ₂ O ₃	7.50	.0441	MnO	0.06				
FeO	<u>18.50</u>	.2569	FeO	<u>0.20</u>				
	99.79			1.00		0.0546		0.1646

The structure of this slag in reflected light deeply etched with acetic acid is shown in photograph No.22 taken at 300 Magnifications. The dark areas are masses of a lime silicate which do not stain deeply with the dye when treated by Scotts method. The half tone areas contain "Spinelloid" material while free oxides, mostly ferrous oxide appear as dead white highly reflecting globules in this matrix. This slag was not examined by transmitted light.

The amount of magnetic material in this slag was small. It is likely that the reduction in the amount of the solvent FeO has caused some deposition of the spinelloids from the solid solution during cooling. At higher magnifications the white globules of FeO appeared occasionally surrounded with dully white fringes lightly stained by the etch.

SLAG 5S

The effect of an addition of 5½ cwts Spar to the bath at this stage was very noticeable. The "slag scum" disappeared and the fluidity was increased. The powerful fluxing action of Fluor Spar upon lime is well known. It seems likely that the lime rendered available in the slag had combined with the material around the slag wash. The analysis of the slag suggests that this substance was probably free Silica from the iron although attempts to isolate it were unsuccessful.

	%	Molecular Composition.						
SiO ₂	26.40	0.44	Recalculation.					
Al ₂ O ₃	2.72	0.027						
P ₂ O ₅	1.28	0.012	RO	R ₂ O ₃		ACIDS.		
CaO	41.20	0.74	CaO	0.66	Fe ₂ O ₃	0.02	SiO ₂	0.38
MgO	5.47	0.14	MgO	0.12	Al ₂ O ₃	0.024	P ₂ O ₅	0.01
MnO	5.95	0.08	MnO	0.07				
Fe ₂ O ₃	3.67	0.023	FeO	0.15				
FeO	<u>12.15</u>	0.17						
	98.84			1.00		0.044		0.39

The slag section etched in acetic acid showed in reflected light large masses of silicate less deeply attacked by the solution than long bath shaped crystals of a darker etched silicate. The appearance of this section closely resembles that of the following member of the series. The globules of free oxides and spinelloids were of less frequent occurrence than in the previous section,

SLAG 63

The slag in the bath had become more viscous and contained undissolved free lime. Photograph No. 23 shows the specimen in reflected light etched with strong acetic acid. The magnification is 150

		Molecular Composition					
SiO ₂	^g 27.20	0.4533	RECALCULATION				
Al ₂ O ₃	2.57	.0252					
P ₂ O ₅	1.79	.0126	RO		R ₂ O ₃		Acids
CaO	46.00	.8215	CaO	0.7206	Fl ₂ O ₃	0.0132	SiO ₂ 0.3977
MgO	5.48	.1353	MgO	0.1187	Al ₂ O ₃	0.0221	P ₂ O ₅ 0.0111
MnO.	7.81	.1100	MnO	0.0965			
Fe ₂ O ₃	2.40	.0150	FeO	0.0641			
FeO	<u>5.26</u>	.0731					
	98.51			1.0000		0.0352	0.4088

The needle crystals were identified later as the α -form of Dicalcic Silicate. The amount of free oxides and spinelloids was considerably reduced. As shewn in the photograph these substances occurred in segregated areas throughout the section. The matrix between the needle crystals was composite.

MICRO-STRUCTURE OF RAPIDLY COOLED BASIC FURNACE

BATH SLAGS - FROM INITIAL STAGES OF LIME-SILICA

SLAG FORMATION.



No. 25

TRANS.LT. 60-M.
DICALCIC SILICATE LATH CRYSTALS
IN OPAQUE-GROUNDMASS OF FREE
OXIDES.
BATH SLAGS 7^S IN THIN SECTION.



No. 26

TRANS.LT. 300-M.
BATH SLAGS 7^S IN THIN SECTION.



No. 27

TRANS.LT. 300-M.
DICALCIC SILICATE CRYSTALS
IN NO. 26 BETWEEN X-NICOLS.
BATH SLAG 7^S IN THIN SECTION.



No. 28

REF.LT. 80-M.
DICALCIC SILICATE CRYSTALS
IN COMPOSITE GROUNDMASS.
BATH SLAG 8^S.
(ETCHED IN DIL. ACETIC ACID.)

spinel or spinelloids were not observed.

Photograph No. 25 shows this slag in thin section at 60 magnifications in transmitted light. Individual crystal grains at 300 magnifications are shown in photograph No. 26, while photograph No. 27 shows the same crystal section at 45° to crossed nicols.

The dark groundmass between the crystals in these photographs is opaque. No resolution was effected at higher powers. By incident light the colour of these opaque areas varied from green to black, so they probably contain the whole of the Manganese and Iron oxides.

In thin section the elongated crystals formed a system of interwoven laths giving occasionally a lattice structure. Complicated twinning was characteristic. The intersection of the crystals at various angles to each other produces the complicated crystal arrangements illustrated in the photograph.

The crystals were distinctly yellowish to lavender yellow in colour. They were free from inclusions. The average refractive index was 1.72. When rotated over the bottom nicol they showed no difference in absorption for any orientation of the grains, they are therefore non-pleochroic.

Between crossed nicols they were doubly refracting. Extinction was inclined to the direction of the greatest elongation. The maximum angle measured was 12°.

When the quartz wedge was introduced with its slow direction parallel to the principal axes of these crystals in the 45° position between the nicols the interference colours ascended. The character of the principal zone was positive.

When the section thickness was approximately 0.03 m.m. maximum compensation occurred with second order green. The relative retardation was therefore about 750 u.u. so that the maximum birefringence value measured was approximately 0.025.

In convergent polarised light the figure was biaxial with/

with a large optic angle. On the introduction of the wedge the colours increased on the side of the hyperbolac. This corresponds to the direction of the acute bisectric; the crystal character was therefore positive.

The amount of magnesia in this slag was about 6% but the optical properties of the numerous crystal grains were perfectly uniform throughout the section, all these grains therefore consisted of the same substance. Any Magnesium Silicate (Fosterite) $2MgO.SiO_2$ present must be in solid solution in the crystals described which are apparently those of a high temperature form of Dicalcic Silicate.

No traces of the intermediate compound Monticellite $(CaO.MgO)SiO_2$ were observed in this or any of the subsequent specimens examined.

SLAG 88

The sample was solid, free from blowholes, nonmagnetic and with vitreous fracture.

	%	Molecular Composition.						
SiO ₂	28.80	0.4799						
Al ₂ O ₃	4.00	0.0392	Recalculation					
P ₂ O ₅	1.98	0.0139						
CaO	46.50	0.8305			R ₂ O ₃	ACIDS.		
MgO	5.77	0.1424	CaO	0.741	Fe ₂ O ₃	0.005	SiO ₂	0.4282
MnO	7.63	0.1074	MgO	0.127	Al ₂ O ₃	0.039	P ₂ O ₅	0.0124
Fe ₂ O ₃	0.90	0.0056	MnO	0.096				
FeO	<u>2.91</u>	0.0404	FeO	<u>0.036</u>				
	98.49			1.000		<u>0.044</u>		<u>0.4406</u>

Photograph No.28 is of this slag at 60 Mags. in reflected light after acetic acid etch.

It was identical with that of the preceding specimen and confirmed the observations made thereon.

MICRO-STRUCTURE OF RAPIDLY COOLED BASIC FURNACE BATH
SLAGS - FROM THE EARLY STAGES - SHOWING THE
EFFECT OF INCREASE OF IRON OXIDES.



No. 29

REF. IT. 150-H
DICALCIC SILICATE LATHS
AND FREE OXIDES (WHITE)
BATH SLAG 9^S
(ETCHED IN DIL. ACETIC ACID.)



No. 30

REF. IT. 150-H
DICALCIC SILICATE MASSES
AND FREE OXIDES.
BATH SLAG 10^S
(ETCHED IN DIL. ACETIC ACID.)



No. 31

REF. IT. 150-H
DICALCIC SILICATE MASSES
AND FREE OXIDES.
BATH SLAGS 11^S
(ETCHED IN DIL. ACETIC ACID.)



No. 32

REF. IT. 150-H
DICALCIC SILICATE MASSES
AND FREE OXIDES.
BATH SLAGS 12^S
(ETCHED IN DIL. ACETIC ACID.)

Slag 98

The sample was take 2 mins. after 470 lbs. Fluor spar had been fed.

Molecular

Molecular			Recalculation					
			RO	R ₂ O ₃	ACIDS			
SiO ₂	26.6	0.4433						
Al ₂ O ₃	2.77	0.0272						
P ₂ O ₅	1.90	0.0133						
CaO	49.50	0.8839						
MgO	5.70	0.1408	CaO	0.7502	Fe ₂ O ₃	0.0081	SiO ₂	0.3780
MnO	6.88	0.0969	MgO	0.1195	Al ₂ O ₃	0.0220	P ₂ O ₅	0.0114
Fe ₂ O ₃	1.53	0.0096	MnO	0.0825				
FeO	<u>4.05</u>	0.0563	FeO	<u>0.0478</u>				
	98.93			1.0000		<u>0.0301</u>		<u>0.3894</u>

The acetic acid etched structure is shewn in photograph 29 at 150 Mags. It consisted of twinned crystals of dicalae silicate set in a highly reflecting mateox of free oxides containing the spinelloids. The peculiar "balled" form of the oxide is illustrated. Apparently the reduced concentration of the Silicate had diminished the idiomorphic nature of the crysrals and resulted in the formation of irregular masses of the same substance as shewn in the phtograph. This tendency became increasingly marked in subsequent slags.

Bath metal incompletely melted. The chemical analysis shows a marked increase in lime content of the slag.

	%	Molecular Composition.						
SiO ₂	22.00	0.3666						
Al ₂ O ₃	2.23	0.0219	Recalculation					
P ₂ O ₅	2.04	0.0144		RO	R ₂ O ₃		Acids	
CaO	53.34	0.9517						
MgO	5.33	0.1316	CaO	0.7567	Fe ₂ O ₃	0.0144	SiO ₂	0.2915
MnO	5.58	0.0786	MgO	0.1046	Al ₂ O ₃	0.0174	P ₂ O ₅	0.0114
Fe ₂ O ₃	2.87	0.0179	MnO	0.0625				
FeO	<u>6.89</u>	0.0957	FeO	<u>0.0762</u>				
	100.24			1.0000		0.0318		0.3029

The alteration in appearance of the micro-section is shown in photograph No. 30, taken in reflected light at 150 Mags. The idiomorphic nature of the crystals of dicalcic silicate had disappeared. They occurred as irregular masses of indefinite shape. The free oxides & spinelloids shew dead white in the photograph.

11 S

Bath incompletely melted.

	%	Molecular Composition.						
SiO ₂	21.40	0.3567	Recalculation					
Al ₂ O ₃	2.00	0.0197						
P ₂ O ₅	2.00	0.0141	RO	Fe ₂ O ₃	ACIDS			
CaO	53.25	0.9510						
MgO	5.12	0.1264	CaO	0.7598	Fe ₂ O ₃	0.0148	AlO ₂	0.2848
MnO	5.58	0.0786	MgO	0.1009	Al ₂ O ₃	0.0157	P ₂ O ₅	0.0113
Fe ₂ O ₃	2.96	0.0186	MnO	0.0628				
FeO	<u>6.89</u>	0.0957	FeO	<u>0.0765</u>				
	99.20			1,0000		<u>0.0305</u>		<u>0.2961</u>

The structure in reflected light is shown at 150 Mags. after acetic acid etch in photograph No. 31. It was similar to that of the preceding specimen.

12 3

Bath metal incompletely melted.

	%	Molecular Composition						
SiO ₂	21.00	0.3499						
Al ₂ O ₃	1.95	0.0191	Recalculation					
P ₂ O ₅	1.95	0.0137	Ro		R ₂ O ₃		ACIDS.	
CaO	52.75	0.9417						
MgO	5.33	0.1308	CaO	0.7489	Fe ₂ O ₃	0.0134	SiO ₂	0.2783
MnO	5.95	0.0838	MgO	0.1040	Al ₂ O ₃	0.0152	P ₂ O ₅	0.0109
Fe ₂ O ₅	2.70	0.0169	MnO	0.0667				
FeO	<u>7.29</u>	0.1013	FeO	<u>0.0805</u>				
	98.92		1.0000		0.0286		0.2892	

The effect of the increased iron content upon the structure of the slag is shown in photograph No. 32. The reduced concentration of the silicate had resulted in the gradual reduction in size of the crystal masses which frequently appeared in a state of fine division in the matrix of free oxides and spinelloids.

13 S

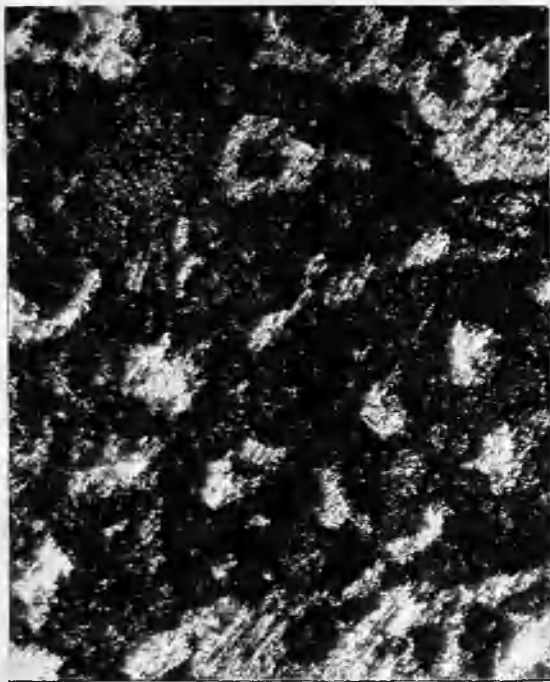
Bath metal incompletely melted.

		Molecular Composition.					
%							
SiO ₂	20.8	0.3466					
Al ₂ O ₃	1.95	0.0191	Recalculation				
P ₂ O ₅	1.95	0.0137					
CaO	52.60	0.9393		RO	R ₂ O ₃	ACIDS	
MgO	5.12	0.1264	CaO	0.7580	Fe ₂ O ₃	0.0173	SiO ₂ 0.2798
MnO	5.77	0.0813	MgO	0.1021	Al ₂ O ₃	0.0154	P ₂ O ₅ 0.0111
Fe ₂ O ₃	3.43	0.0214	MnO	0.0656			
FeO	6.43	0.0922	FeO	0.0743			
	<u>98.26</u>			<u>1.0000</u>		<u>0.0327</u>	<u>0.2909</u>

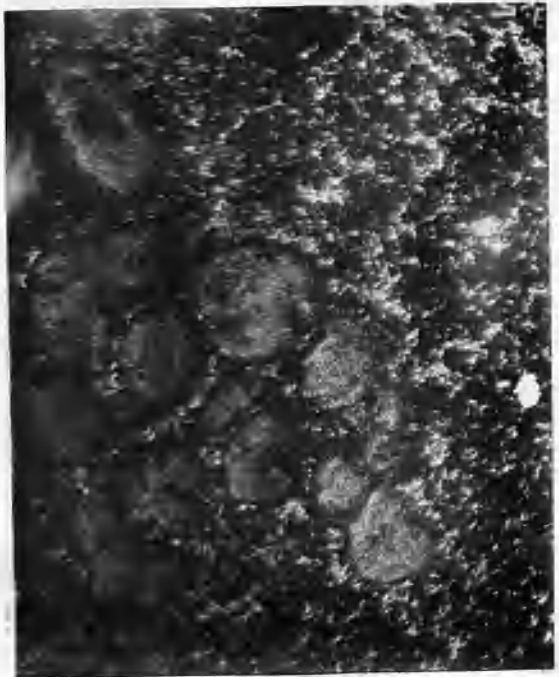
Microscopically this slag was identical with the preceding specimen of the series. The photographs Nos. 28, 29, 30, 32 illustrate the effect of the gradual increase of iron oxides upon the microscopic appearance of dicalcic silicate in the slag. In Slags 7^S and 9^S the crystals of this substance are subhedral in form. The progressive reduction in concentration which takes place owing to the increase in iron and lime content of the slag caused the crystals to gradually assume the anhedral form, they finally appeared in the chilled bath samples mostly in a state of fine division throughout the structure of the slag. On the other hand the free oxides which have globular form in the earlier slags coalesce and merge into large irregular masses apparently surrounding and occasionally appearing amongst the disilicate masses in the slags of higher iron content.

The cooling conditions in each case were uniform, hence these photographs illustrate the effect of the reduced saturation of the melt with the molecules of the ortho silicate of lime, and those of the solid solution of FeO containing the spinelloids.

MICRO-STRUCTURE OF RAPIDLY COOLED BASIC FURNACE
BATH SLAGS FROM INTERMEDIATE STAGES-SHOWING
EFFECT OF INCREASE OF LIME AND IRON OXIDES.



No. 33
Ref.Lt. 150-M
DICALCIC SILICATE MASSES IN
GROUND MASS CONSISTING MOSTLY
OF FREE OXIDES.
BATH SLAG 14^S
(ETCHED IN DIL.ACETIC ACID).



No. 34
Ref.Lt. 150-M
TRICALCIC SILICATE CRYSTAL MASSES
IN COMPOSITE GROUNDMASS CONTAINING
FREE OXIDES.
BATH SLAG 14^S
(ETCHED IN DIL.ACETIC ACID).



No. 35
REF.LT. 150-M
TRICALCIC SILICATE CRYSTAL
BATH SLAG 15^S
(ETCHED IN DIL.ACETIC ACID.)



No. 36
TRANS.LT. 200-M
1 - TRICALCIC SILICATE CRYSTAL
2 - FREE LIME CRYSTAL.
BATH SLAG 15^S IN THIN SOLUTION.

14 S

This was the first slag taken after the metallic bath was completely melted.

		Molecular % Composition						
SiO ₂	20.2	0.3367						
Al ₂ O ₃	1.95	0.0191	Recalculation					
P ₂ O ₅	1.95	0.0137	RO		R ₂ O ₃		ACIDS	
CaO	51.60	0.9212						
MgO	5.05	0.1247	CaO	0.7375	F ₃ O ₃	0.0144	SiO ₂	0.2696
MnO	5.77	0.0813	MgO	0.0999	Al ₂ O ₃	0.0153	P ₂ O ₅	0.0110
Fe ₂ O ₃	2.88	0.0180	MnO	0.0654				
FeO	<u>8.74</u>	0.1213	FeO	<u>0.0972</u>				
	98.14			1.0000		0.0297		0.2806

The slag structure was not homogenous. Two distinct types of structure were observed. Photograph No. 33 illustrates the appearance of the first which is identical with that of the preceding specimens.

Photograph No. 34 shews the appearance of large crystals of rounded outline which have separated from the groundmass of finely diffused more deeply etched silicate. These large crystals were less deeply attacked by the reagent and did not stain as strongly with dye. They apparently consisted of crystals of the Tricalcic Silicate identified in later slags.

Slag 15 S

This sample was drawn 10 Minutes after about 19 Cwts of Mill Scale had been fed into the bath. The composition of the scale was: -

FeO	-	61.58
Fe ₂ O ₃	-	36.54
SiO ₂	-	0.80
MnO	-	0.93

The slag analyses shew: -

	%	Molecules	Composition.					
SiO ₂	16.50	0.2750	Recalculation					
Al ₂ O ₃	2.70	0.0265						
P ₂ O ₅	2.70	0.0150	RO	R ₂ O ₃	ACIDS			
CaO	47.80	0.8535						
MgO	4.32	0.1067	CaO	0.6961	Fe ₂ O ₃	0.0275	SiO ₂	0.2243
MnO	6.12	0.0862	MgO	0.0870	Al ₂ O ₃	0.0216	P ₂ O ₅	0.0120
Fe ₂ O ₃	5.40	0.0338	MnO	0.0703				
FeO	<u>12.96</u>	0.1800	FeO	<u>0.1466</u>				
	98.50			1.0000		0.0491		0.2363

The slag was non magnetic but contained some metal shot.

The polished surface in reflected light shewed the existence of large crystals of the lighter etched silicate. The structure containing these massive crystals is shewn in photograph No. 35 taken at 150 Mags. The surrounding groundmass consisted free oxides and spinelloids which have considerably increased in this specimen. A peculiarity of these large crystals is that their edges shew in sharp detail under the microscope and are surrounded by a dark border in these specimens.

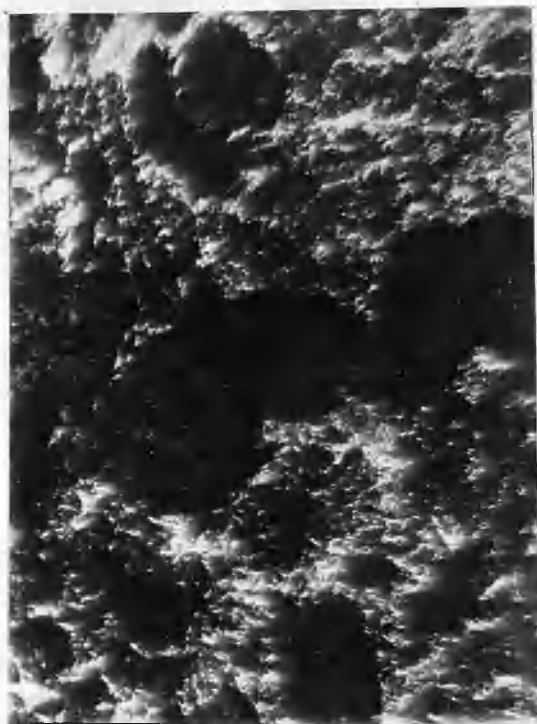
Photograph No. 36 is of this slag in thin section in transmitted light. It shewed two distinct crystalline constituents marked 1 and 2 in the micrograph. No. 1 consisted of crystals white in colour in ordinary transmitted light. These shewed no cleavage/

MICRO-STRUCTURE OF RAPIDLY COOLED BASIC FURNACE

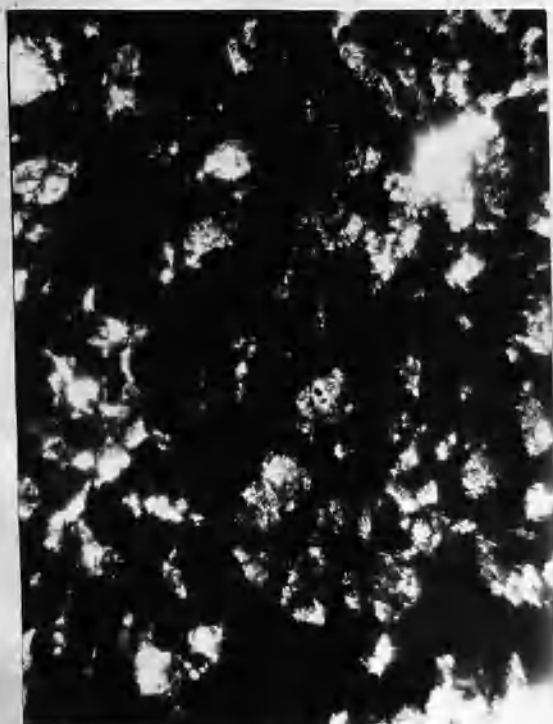
BATH SLAGS - FROM FINISHING STAGES OF THE PROCESS.



TRANS.LT. No. 37 50-M
 (1) WHITE CRYSTALS ARE TRICALCIC SILICATE.
 (2) THE ISOTROPIC CRYSTALS OF LIME APPEAR DARY GREY.—BLACK GROUND MASS CONTAINS OPAQUE OXIDES & RED COLOURED SPINELLICIDS.
 BATH SLAG 15⁸IN THIN SECTION. BETWEEN CROSSED NICOLS.



REF.LT. No. 38 100-M
 TRICALCIC SILICATE MASSES IN COMPOSITE GROUNDMASS OF FREE OXIDES AND SPINELLOIDS.
 BATH SLAG 17⁸
 (ETCHED IN DIL.ACETIC ACID).



TRANS.LT. No.39 50-M
 WHITE CRYSTALS OF TRICALCIC SILICATE. DARK AREAS CONTAIN
 (a) APHANIC MATERIAL CONSISTING OF FREE FeO and MnO.
 (b) BROWNISH RED GLOBULES OF TRICALCIC FERRITE.
 (c) ISOTROPIC BLOOD-RED GRAINS
 BATH SLAGS 19⁸IN THIN SECTION.



TRANS.LT. No.40 20-M
 TRICALCIC SILICATE CRYSTALS IN SLOWLY COOLED SLAG MASS. SHOWING EFFECT OF SLOW COOLING IN PROMOTING CRYSTAL GROWTH.
 SLOWLY COOLED SLAG MASS IN THIN SECTION

cleavage traces, very low double refraction and straight extinction. Their optical behaviour corresponds with that of the crystals of Tricalcic Silicate separated from finishing slags.

No. 2 Crystals in ordinary transmitted light were brownish yellow in colour, shewed two fairly good cleavages. They exhibited very ^{high} "relief" and "roughness" indicative of very high refractive index. The value of the refractive index considerably exceeded that of concentrated Thoulet Solution (1.73). These grains are usually rounded in outline but several shewed a distinctly cubic form. They were non-pleochroic and were isotropic between crossed-nicols. They belonged to the cubic system.

These crystals were irregularly distributed in the section. They were noticeably different from other slag constituents. Their optical properties identify them as crystals of free lime.

In this section the free oxides were opaque. Red translucent crystals of spinelloid constituents were noticed but these were minute in size. They correspond to similar crystals which were more abundant and consequently more completely observed in later slags.

Photograph No. 37 is of the same section taken at 50 Mags. between crossed nicols. IT shews the Tricalcic Silicate Crystals dead white in colour, the isotropic lime crystals shew a dark gray while the groundmass of opaque oxides and red coloured spinelloids appear dead black in the photograph.

No traces of free magnetite were observed although the sample was drawn soon after heavy additions of Mill Scale.

SLAG 16 S

Bath boiling briskly. Sample taken 20 Minutes after 4½ Cwts Scale had been fed.

		% Molecular Composition					
SiO ₂	16.30	0.2718					
Al ₂ O ₃	2.50	0.0245	Recalculation				
P ₂ O ₅	2.50	0.0176					
CaO	50.00	0.8930	RO		R ₂ O ₃		ACIDS
MgO	5.04	0.1245	CaO	0.7016	Fe ₂ O ₃	0.0221	SiO ₂ 0.2134
MnO	6.12	0.0862	MgO	0.0977	Al ₂ O ₃	0.0193	P ₂ O ₅ 0.0138
Fe ₂ O ₃	4.50	0.0281	MnO	0.0678			
FeO	<u>12.15</u>	0.1688	FeO	<u>0.1329</u>			
	99.10		1.0000		0.0414		0.2272

In reflected light this specimen was generally similar in structure to the preceding specimen.

slag 17 S

Additional Mill Scale was fed to bath beyond the normal requirements so that the effect of these additions upon the slag structure could be examined. This sample was taken 12 minutes, after about 12 cwts had been fed.

		% Molecular composition					
SiO ₂	15.80	0.2633					
Al ₂ O ₃	2.00	0.0201	Recalculation				
P ₂ O ₅	2.00	0.0144					
CaO	49.70	0.8876	RO		R ₂ O ₃		ACIDS
MgO	5.50	0.1371	CaO	0.6797	Fe ₂ O ₃	0.0215	SiO ₂ 0.2017
MnO	5.97	0.0841	MgO	0.1049	Al ₂ O ₃	0.0154	P ₂ O ₅ 0.0111
Fe ₂ O ₃	4.50	0.0281	MnO	0.0644			
FeO	<u>14.41</u>	0.1968	FeO	<u>0.1510</u>			
	99.81		1.0000		0.0369		0.2128

This/

This slag examined in reflected light consists of large Silicate crystals in a composite groundness. Its appearance is shown in photograph No. 38 at 100 Mags. The groundmass was similar to the of slag 19 S which shewed the highest iron content of the series of finishing slags and which is described in detail later.

SLAG 18 S

At this stage boiling action had almost ceased.

		Molecular Composition.						
%								
SiO ₂	15.80	0.2633						
Al ₂ O ₃	2.00	0.0196	Recalculation					
P ₂ O ₅	2.00	0.0141						
CaO	49.40	0.8839	RO	R ₂ O ₃		ACIDS		
MgO	5.33	0.1316	CaO	0.6795	Fe ₂ O ₃	0.0203	SiO ₂	0.2024
MnO	6.04	0.0851	MgO	0.1012	Al ₂ O ₃	0.0151	P ₂ O ₅	0.0108
Fe ₂ O ₃	4.23	0.0264	MnO	0.0654				
FeO	<u>14.41</u>	0.2000	FeO	<u>0.1540</u>				
	99.21			1.0000		0.0354		0.2132

In reflected light the microstructure of this slag was identical with 17 S and 19 S.

SLAG 19 S

Boiling action had almost completely stopped. The carbon content of the bath metal was 0.05%. The analysis of this slag shewed an increase in iron oxides and magnesia. The amount of Silica had been reduced by dilution while the lime content was maintained by increment from the dolomite of the hearth and banks since no additions were made to the bath.

Molecular % Composition.								
SiO ₂	14.00	0.2333						
Al ₂ O ₃	1.72	0.0169	Recalculation					
P ₂ O ₅	1.72	0.0121	RO		R ₂ O ₃		ACIDS	
CaO	49.70	0.8876						
MgO	6.42	0.1585	CaO	0.6659	Fe ₂ O ₃	0.0249	SiO ₂	0.1750
MnO	5.58	0.0786	MgO	0.1189	Al ₂ O ₃	0.0127	P ₂ O ₅	0.0090
Fe ₂ O ₃	5.31	0.0332	MnO	0.0589				
FeO	<u>15.00</u>	0.2084	FeO	<u>0.1563</u>				
	99.45			1.0000		0.0376		0.1840

Photograph No. 38 illustrates the appearance of the last three slags in reflected light. The crystals of tricalcic silicate were of large size, but the groundmass was complex and little resolution could be effected by this examination.

The appearance of a thin section of basic slag in transmitted light is most inadequately shown in a photograph because of the differences in diaphaneity of the constituents.

Photograph No. 39 is of this slag in thin section at 50 Mags. The crystals of Tricalcic Silicate shew white in colour. The groundmass appears dead black in the photograph but exhibited a heterogeneous appearance under the microscope in transmitted light. It was cryptocrystalline, while aphanic components were also discernible.

(1) APHANIC MATERIAL: This existed in irregular masses unevenly distributed between the crystalline components of the section. Its nature did not appear to be that of a cement as it did not form a boundary between the grains. It increased in amount to an extent which corresponded to the percentage increase of FeO in the slags of the series, and to the dead white material appearing in sections examined after etching by reflected light.

In finishing slags this opaque ^{substance} was quite black in colour by incident light and resembled that noticed in 1^S which contained

50% FeO. In slags 7^S and 8^S where the percentage MnO exceeded that of FeO, similar material had a distinctly greenish tinge.

It was concluded that these opaque masses contained most of the FeO and the MnO in the slag. The magnetic nature of the early cinders suggested that certain spinelloids must also exist therein in a state of solid solution.

(2) CRYPTO CRYSTALLINE COMPONENTS:

(a) Reddish to brownish red globules were observed. Occasionally the same material had an irregular shred-like appearance. This substance was doubly refracting and showed refractive index and birefringence values which correspond to those of the constituent identified as Tricalcic Ferrite.

In some cases the colour of these globules varied through brownish red to a subtranslucent red approaching black. Apparently they were not uniform in composition and the variation was probably due to the presence of FeO.

This constituent was quite absent in the case of slag 7S. It had increased in amount in the more highly basic finishing slags.

(b) Very dark subtranslucent blood-red grains occasionally showing octahedral cleavage traces were observed. These crystals were isotropic between crossed nicols, and were thus distinguished from those just described. These grains were minute and evenly distributed. Their small size prevented further discrimination.

They were not noticed in any of the earlier slags.

SLOWLY COOLED SLAG 22^S

The slag from this charge was allowed to cool slowly in a large block. Sections of this slag were examined by reflected and transmitted light. The thin section at 20 Mags. is shown in photograph No. 40. The chief difference between the quickly cooled bath slag and this section was in the increased size of the/

the crystalline constituents. Optically the components were identical with those observed and described in the case of the finishing slags. The slower cooling did not produce any alterations in the constituents observed in the rapidly chilled slags and no new forms were noticed.

EXAMINATION OF THE BASIC HEARTH.

The analyses of Slags 17^S, 18^S, 19^S shew that although dilution had occurred as a result of the increase in iron oxide content of the slag, the percentage of lime was maintained while the magnesia content had increased.

No additions were made so these increases had come from the Basic Hearth.

In practice the Slag make depends upon the quality and amount of the pig iron in the charge. The minimum amount necessary is usually about 12% of the weight of the charge. The consumpt of the dolomite fettling varies with the working conditions from about 50 to 70 lbs. per ton of steel produced. The nature of the hearth therefore must exercise a considerable influence upon the slag.

The durability of the hearth depends upon the corrosive actions to which it is subjected and the temperature maintained while these actions are in progress. The campaign may extend to upwards of 14 weeks, during which time hearth temperatures seldom fall below 1000 °C. The normal working temperature is in the neighbourhood of 1500 °C while the maximum exceeds 1800 °C. During the campaign the slag is in intimate contact with the hearth. In periods of activity the viscosity of the slag will tend to increase at the expense of the hearth, while wear of the silicious portions of the furnace structure due to attack by hot ferrous fume must also react upon the hearth.

At working temperatures the hearth exhibits the characteristics of an extremely viscous fluid. This can be observed by examination of the "lines of flow" on samples obtained by forcing a hollow tube about 1½" Dia. into the banks or bottom before fettling begins. The specimen, usually about 3" long, can be withdrawn when cool.

The chemical analyses of these tests shewed considerable variation in composition although the principal components were/

were Magnesia and Ferric Oxide. The lime content was low.

Specimens obtained in this way were examined in reflected light. The structure resembled that of an intensely hard cinder and no crystalline components were observed.

Examination of the hearth when cold shewed that high temperatures maintained over periods of 2000 hours had resulted in the formation and segregation of constituents in crystal "pockets" throughout the hearth. The time factor had replaced that of nobility in securing crystallisation in the viscous media. Crystallisation was most complete at depths exceeding 4 inches from the working hearth surface.

The constituents described were obtained from uniform crystal masses in the basic furnace bottom, the original composition of which consisted extirely of high grade English Dolomite.

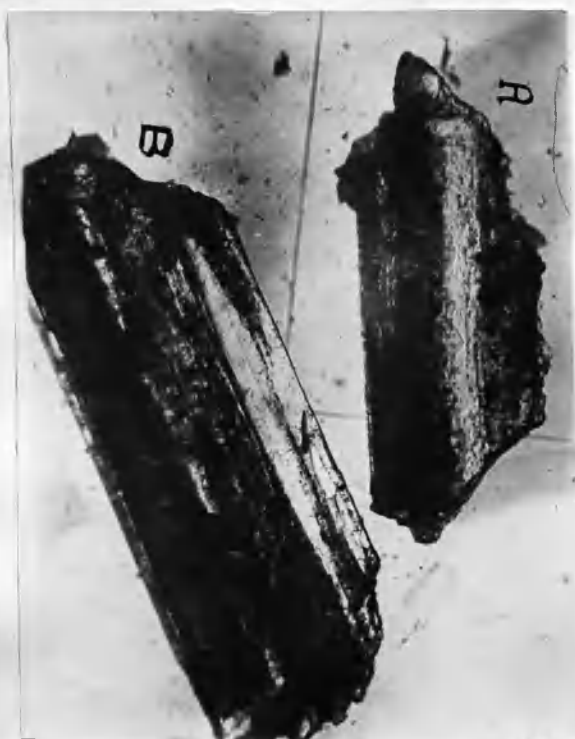
STRUCTURE OF THE BASIC BASIC FURNACE HEARTH



No. 41
 OBLIQUE LT. 50-M
 COLUMNULAR BLACK CRYSTALS.
 EX BASIC FURNACE HEARTH.



No. 42
 OBLIQUE LT. 50-M
 COLUMNULAR BLACK CRYSTALS
 EX BASIC FURNACE HEARTH.



No. 43
 TRANS. LT. 150-M
 TRANSPARENT COLUMNULAR
 MAGNESIUM-META-SILICATE-CRYSTALS.
 (ORTHORHOMBIC)
 (EX BASIC FURNACE HEARTH.)



No. 44
 TRANS. LT. 150-M.
 GOLDEN YELLOW CRYSTALS (C)
 OCCASIONALLY ASSOCIATED WITH
 MAGNESIUM-META-SILICATE (B)
 (EX BASIC FURNACE HEARTH.)

BLACK COLUMNULAR HEARTH CRYSTALS.

Photographs No. 41 and 42 show their appearance in oblique light at 50 Mags. They varied in size up to about 10 m.m. long.

In reflected light they showed a brilliant lustre and were jet black in colour. They were hard and faintly magnetic. They commonly showed parallel growth where corresponding edges, faces and axes were parallel. They were normally well developed and almost free from extraneous matter.

The chemical analyses showed:-

Analysis No. VII

	%	Molecular Composition
SiO ₂	3.60	0.0586
Al ₂ O ₃	2.43	0.0238
Fe ₂ O ₃	34.39	0.2146
FeO	9.48	0.1316
MnO	1.50	0.0211
CaO	41.30	0.7375
MgO	6.84	0.1689

The composition approximately corresponds to the formula $3RO.R_2O_3$ where RO is chiefly lime and magnesia, and R_2O_3 chiefly ferric oxide.

In transmitted light the crystals were opaque. Crystal fragments in thin section were reddish in colour. The refractive index was high. They were doubly refracting between crossed nicols.

In the direction of the principal axes the extinction angle was straight but was inclined with certain orientations not exactly defined. The maximum birefringence value observed was 0.02

These crystals differed somewhat from those of Tricalcic Ferrite obtained from the Slags. They were slightly magnetic and contained 9.5% FeO. Their optical properties were however generally similar and they apparently consist of an impure form of the same constituent/

This substance was quite frequently observed in the examination of the hearth. Its composition indicates the selective action which ferrogeneous slags must exercise upon the dolomite. The relatively low MgO content explains the superiority of the purely magnesite hearth in resisting the destructive action of slags of high iron content.

TRANSPARENT COLUMENULAR HEARTH CRYSTALS.

Photograph No. 43 taken by transmitted light at 150 Mags. shows crystals obtained in the hearth at a depth of about 12 inches below the normal slag contact face.

They varied in colour from a clear to a very faint yellowish white. They were transparent and exhibited a characteristic pearly lustre and fibrous cleavage.

They sank slowly in concentrated Thoulet Solution (Sp.Gr.3.17) They were free from inclusions and extraneous hearth material.

The Chemical Analysis shewed:-

Analysis No. VIII:-

		Molecular Composition.						
SiO ₂	52.50	0.8750						
Al ₂ O ₃	0.20	0.0020	Recalculation					
Fe ₂ O ₃	10.80	0.0675						
FeO	-	-	RO	R ₂ O ₃	ACIDS			
MnO	1.40	0.0197	CaO	0.0599	Al ₂ O ₃	0.0023	SiO ₂	1.013
CaO	2.90	0.0518	MgO	0.9173	Fe ₂ O ₃	0.0781		
MgO	<u>32.10</u>	0.7925	MnO	<u>0.0228</u>				
	99.10			1.0000		0.0804		1.013

Most of the crystals shewed incomplete development as in "A" of the photograph. Certain of the crystals exhibited roughly elongated prismatic development with partial striation along the prism faces.

The refractive index was 1.65 In polarised light they were pleochroic. Between crossed nicols the extinction was straight for all the orientations examined. The double refraction was low.

The figure in convergent polarised light was biaxial. These tests indicated that these crystals belonged to the orthorhombic system.

The chemical analysis shew that this substance is a magnesium meta-silicate containing ferric oxide.

It/

It is apparently formed as the result of the action between silicious material from the furnace structure and the Magnesia of the hearth.

YELLOW-HEARTH CRYSTALS.

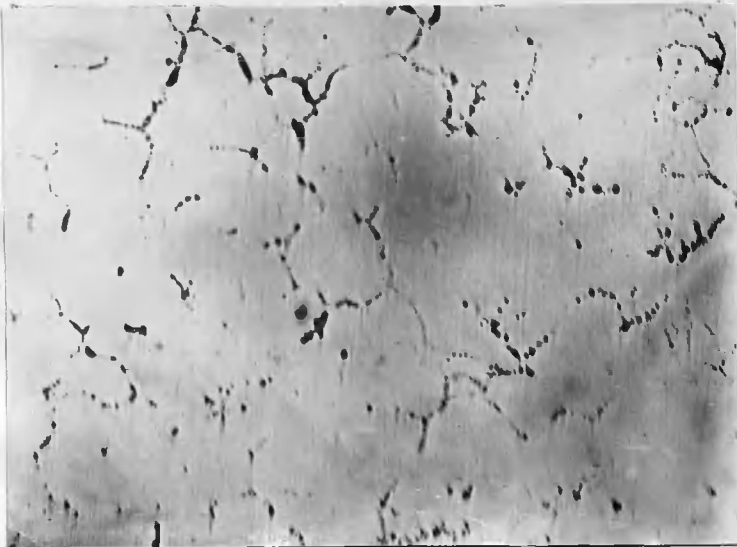
In photograph No. 44 taken at 150 Mags. by transmitted light the appearance of golden-yellow coloured crystals is illustrated in the specimen marked D.

When observed they were associated with the transparent columnular crystals C previously described. They were not obtained in sufficient quantity for analysis.

The colour was characteristic. They shewed perfect cleavage and very marked difference in absorption or polarised light along the principal zone. Microchemical tests shewed the presence of Silica and Magnesia in large quantities.

This substance was not identified but its occurrence along with the magnesium meta-silicate described, suggests that it is probably a modified form of the same substance.

MICRO-STRUCTURE OF BATH METAL.



No. 45

REF. LT. 100 M.

1% C - 0.045%
Mn - 0.02 %

TAKEN FROM FIRST FORMED LIQUID STEEL
SCRAP IN BATH AND SLOWLY COOLED.

SHOWING CONCENTRATION OF IRON OXIDES
AROUND GRAIN BOUNDARIES.
UNETCHED.

Edge



No. 46

REF. LT. 60-M

2% C 0.31 %
Mn. C. 21 %

SAMPLE SLOWLY COOLED.
EDGE OF SPECIMEN SHOWING.
REDUCED CONCENTRATION OF
THE PEARLITE.
(ETCHED 1% NITRIC ACID).



No. 47

REF. LT. 60-M

INTERICE OF SPECIMEN
SHOWN IN MICROGRAPH.

No. 45 ABOUT 1/4" FROM
EDGE OF SAMPLE.
(ETCHED 1% NITRIC ACID)

Note on the Microscopic Examination of Steel Bath Samples.

A series of metal bath samples was taken concurrently with the series of slag samples already described.

Experience had shown that the rolling quality of the steel apparently depended more upon the composition or constitution of the slag than upon the chemical composition of the steel indicated by analyses.

An attempt was made to trace the effect of the gradual change in slag constitution upon the microstructure of the steel during the progress of the refining reactions.

In photograph No. 45 the unetched structure of bath samples 1^m (CO.045 - Mn0.02) at 100 Mags. is shown. This sample was taken from the first formed liquid scrap in the bath.

It contains numerous specks situated mostly along the grain boundaries. In appearance it resembled closely the sections illustrated by Tritton and Thomson (18) in Plate V - photographs Nos. 12 and 14 of their paper.

Bath samples are seldom wholly free from such inclusions. In colour these specks were dark blue in reflected light. They were treated with 2% Hydrofluoric Acid in alcohol since sulphides and silicates are darkened by this treatment. The method recommended by Comstock for the differential etch of MnS by means of boiling sodium picrate was also used. Neither of these treatments gave distinctive results.

McCance (17) has noticed that in soft basic steel the composition of hard black inclusions consisted of 94.5 Manganous and Ferrous Oxides. In this case the Mn. was only 0.02%. It was concluded that these inclusions must consist mostly of an oxide of iron.

Tritton and Thomson (18) have shown that the solubility of Oxygen in pure iron at 1530° C. is 0.21% while evidence of liquid immiscibility of oxide of iron and iron beyond 0.21% oxygen is also given in the paper.

In the steel bath, however, the liquid metal contains carbon and manganese. The solubility of oxygen in iron containing these elements is not known.

In the specimens taken from the steel bath therefore, the oxide noticed may consist partly of material deposited from solution on the cooling of the specimen and partly from oxidised material occluded but immiscible in the molten metal.

The slowly cooled samples of analyses given in Table No.4 were cut and sectioned so that the effect of chill on the edge of the specimen could be examined. The microstructures divided the specimens into three groups.

Group I - Consisted of Nos. 14^m to 19^m together with those of 1^m and 3^m taken during the early stages. In this group the ferrite constituted the greatest mass and enclosed the pearlite. In specimens containing less than 0.13 Carbon the pearlite occurred along the grain boundaries.

Group II - Comprised specimens 9^m to 13^m. Where pearlite formed the greatest mass and ferrite formed the surrounding network.

Group III.- In specimens 4^m to 8^m the grains consisted of eutectoid pearlite surrounded by a network of free cementite. This group all showed needles of Martensite, well developed near the edge of the samples.

Certain features were common to each group. The inclusions noticed in the case of 1^m persisted in somewhat reduced amount up to 12^m. Although the carbon content in the bath metal reached a maximum 1.35% in 6^m no marked reduction in the amount of the inclusions was noticed until the steel bath reached the completely melted stage. The FeO content of the slag had fallen from 50.14% in the case of 1^s to 2.91% in the case of 8^s and again risen to 7.29% in 12^s before any reduction in the amount of the inclusions in the metal was discernable.

In specimens 13^m to 18^m the number of oxide specks was greatly reduced. In 19^m they again appreciably increased in number.

In all specimens most of these inclusions were situated

situated along the grain boundaries. Their occurrence did not appear directly related to either metal or slag composition in the incompletely melted bath. Their elimination from the metal however coincides with the decrease in slag acidity in the completely melted bath which accompanied the increase in lime content in slags 14^s, 15^s, etc.

The increase in the number of inclusions noticed in 19^m can be accounted for by the increase in metal oxidation which occurred in the almost completely decarbonised bath.

In the case of 8^s the slag contained only about 3% FeO and over 1% Carbon existed in the metal. It was evident that the existence of Carbon in the bath metal when the slag is relatively acidic in character had little action upon their elimination.

It follows therefore that since the Carbon of the bath metal did not appreciably reduce the extent of the occurrence of this substance the latter cannot wholly exist in solution in the molten metal. These oxides existed largely in the "free" state in excess of that solution saturation which the metal possesses at the bath temperature

To investigate the reasons for the occurrence of these oxide specks at the grain boundaries samples were taken from different charges of similar composition at the finishing stages of the melt.

Table No. 5 gives the composition and treatments in each case:-

TABLE No. 5

<u>Mark.</u>	<u>Carbon.</u>	<u>Manganese.</u>	<u>Remarks.</u>
A W	0.05	0.15	Water quenched while steel liquid.
B W	0.05	0.15	Slowly cooled under slag.
A X	0.09	0.15	Water quenched while steel liquid.
B X	0.09	0.15	Slowly cooled under slag.
A U	0.08	0.18	Water quenched while steel liquid.
B U	0.08	0.18	Slowly cooled under slag.
A T	0.08	0.21	Water quenched while steel liquid.
B T	0.08	0.21	Slowly cooled under slag.
A J	0.08	0.24	Water quenched while steel liquid.
B J	0.08	0.24	Slowly cooled under slag.
L G	0.31	0.21	Water quenched while steel liquid.
2 G	0.31	0.21	Slowly cooled under slag.
3 G	0.31	0.21	Metal shaken while liquid and water quenched.

In the water quenched specimens the oxide specks in each case existed in reduced amount and were evenly distributed throughout the crystal grains. In the specimens slowly cooled under the slag the specks occurred mostly around the grain boundaries.

No difference in the amount of inclusions was noticed with the slightly higher Manganese content.

The distribution of this material along the grain boundaries was apparently the result of the mode of cooling. Tritton and Thomson (18) have shown that the solubility of FeO in molten iron is appreciably greater than in the solid state. On cooling therefore, that portion of the FeO content which is not in solution will increase with a corresponding reduction in the amount/

MICRO-STRUCTURE OF BATH METAL

Edge.



No. 48

REF.LT.

60-M

1^G - C 0.31%
Mn. 0.21%

SAMPLE TAKEN SIMULTANEOUSLY FROM BATH WITH 2^G (MICROGRAPHS NOS. 46 and 47) BUT QUENCHED WHILE LIQUID.

GRAINS SORBITIC IN CHARACTER WITH TROOSTITIC AREAS ALONG CERTAIN OF THE EDGES OF THE GRAINS.

(ETCHED 1% NITRIC ACID.)



No. 49

REF.LT.

56-M

17^M C - 0.13 %
Mn. - 0.09 %

SHOWING EFFECT PRODUCED UPON SURROUNDING STRUCTURE BY INTERIOR BLOW HOLES.

(ETCHED IN 1% NITRIC ACID.)

amount of dissolved oxide. The concentration of the oxide at the grain surface must reach the stage of super-saturation before that of the interior of the grain. The first formed neuclei would tend to form the basis of further deposition in the case of the slowly cooled specimens so that deposition tended to accumulate around the grain boundaries.

Certain differences in structure, the result of different cooling conditions, were noticed in the etched specimens.

In photograph No.46 taken at 60 Mags. the appearance of the edge of the slowly cooled specimen 2 G is shown. Photograph No.47 is of the interior of the same specimen about 1/4" from the edge.

Pronounced segregation had taken place. The effects of chill from the sample spoon upon the liquid metal resulted in the formation of "chill crystals" of ferrite and reduced pearlite concentration at the edge of the specimen.

In photograph No.48 is shown the sample 1 G taken from the bath at the same time as the previous specimen and similarly etched. The water quench of the liquid steel had produced a marked difference in structure. Segregation was practically absent. The grains were uniformly sorbitic in character. Along certain of the edges of the grains dark areas apparently troostitic in nature were observed.

The bath samples examined commonly showed numerous blowholes. The distortion produced upon the surrounding structure was particularly marked. This effect is illustrated in photograph No. 49 which shows sample 17^m taken at 56 Magnifications. The deep seated nature of the effects produced upon the steel structure is evident. It seems questionable if such effects caused by interior blowholes can be removed by subsequent heat treatment, as has been frequently suggested.

CONCLUSIONS

In these slags the phosphorus existed wholly as fluorapatite; no traces of silico-phosphate combinations were observed.

Other crystalline constituents consisted principally of the oxides CaO, Fe₂O₃ and SiO₂; in certain cases MgO apparently partially replaced lime.

The earliest combinations resulted from the oxidation products of the scrap and their combinations with lime.

The existence of lime-iron oxide compounds in basic bessemer slags was noticed by Stead (7) but the isolation and identification of a compound approximating in composition to 3 CaO-Fe₂O₃ has not hitherto been secured from open-hearth slags.

Hilpert and Kohlmeier (19) identified a substance of this composition in their examination of the system CaO - Fe₂O₃. On the other hand the most basic calcium ferrite found by Sosman and Merwin (20) had the composition 2 CaO - Fe₂O₃.

This tribasic ferrite was observed in both samples where the slag was strongly basic in character, viz: at the beginning and towards the end of the refining stages.

It was not noticed in slags taken during the intermediate stages when the character of the slag was relatively acidic.

Its appearance in finishing slags coincided with that of tricalcic silicate. Its formation apparently depended upon the availability of the lime essential to its formation, i.e. upon the order of the slag basicity.

In this connection definition of the terms used here in the consideration of slag constitution, is desirable.

(1) Slag basicity is the expression of the value obtained by dividing the sum of the molecular ratios of the bases CaO and MgO present, by that of the components with which these bases were found to enter into an appreciable combination viz, P₂O₅ SiO₂ and Fe₂O₃.

(2)/

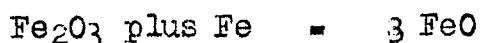
- (2) At 1350° C Fe_2O_3 changes to a magnetic oxide with a lower oxygen content. Magnetite was not observed in the slags, therefore the combination of iron oxides which exists at steel making temperatures should be designated $\text{Fe}_2\text{O}_3 \times \text{FeO}$. It is the Fe_2O_3 in this combination which is referred to as "free" in order to distinguish it from the ferric-oxide found to be in combination with lime.

GAS OXIDATION -

The analyses of the slag series on Table No.3 shows that the amount of ferric oxide was reduced from 13.6% in slag 1^S to a minimum of 0.9% in 8^S; thereafter it rose to 5.3% in 19^S the last slag of the series.

This variation corresponds with that of the slag basicity. The oxidising effect of the furnace gases had formed $\text{Fe}_2\text{O}_3 \times \text{FeO}$ from the bath metal through the medium of the slag, since little direct oxidation was possible except during a vigorous boil, and the variation does not directly correspond with the oxide additions.

Tritton and Hanson (18) have shown that $\text{Fe}_2\text{O}_3 \times \text{FeO}$ in the presence of iron at 1530° C results in the formation of FeO according to the equation.



This reaction does not proceed to completion although the equilibrium constant increases with the temperature.

At steel making temperatures the oxidising effect of the gases which results in the formation of further Fe_2O_3 must be checked when lime is available for the stabilisation of the ferric oxide, with the formation of the calcic ferrite compound observed in the slag.

When lime is not available for this combination then oxidation of the impurities in the bath and the iron of the bath will proceed by the reduction of the ferric oxide.
It/

It appears certain that the lack of requisite basicity is the prime cause of gas oxidation, apart from the similar effects produced by low temperatures.

Gas oxidation of the charge is the source of many of the practical difficulties experienced in the control of the process. No explanation has hitherto been advanced which satisfactorily meets the apparently anomalous results which occur under working conditions.

Whiteley ⁽⁶⁾ has stated that "Gas oxidation should increase with the basicity" of the slag. This view appears erroneous and is not in accordance with the observed facts of practice.

Thus, a deficiency of lime in the slag is followed by the commencement of the boil without ore additions or by a "soft melt" where the carbon has almost disappeared from the metal before the bath is completely melted.

Steel made under such conditions shows large amount of non-metallic inclusions and is frequently "red short" when rolled.

An increase in slag acidity from any source - hearth structure, impure ore, etc, will therefore tend to increase the gas-slag reaction because of the reduction in basicity. It follows also that in normal keenly working furnaces, the extent of the losses which occur from gas oxidation can be controlled by adjustment of the lime content of the slag. The realisation of this fact is of considerable importance in practice since the losses incurred through gas oxidation increase with surprising rapidity and may account for an appreciable percentage of the charged weight of metal.

Fe₂O₃ in Basic Slag:

Whiteley ⁽⁶⁾ had suggested that Fe₂O₃ plays an important part in the oxidation of the bath impurities. These investigations show however that in a slag of correctly adjusted basicity the Fe₂O₃ is in combination with the lime.

The/

The experiment upon which the conclusions of Whiteley are based was repeated.

Two bath slags were drawn simultaneously from a normal charge. No. 1 was taken near the door where the bath was perfectly quiet owing to breast erosion.

No. 2 was taken in the interior of the furnace where a little boiling action was in progress.

The analysis of the two samples was as follows:

Analysis No. <u>LX</u>			Analysis No. <u>X</u>		
Near Door.			4½ Ft. within Door.		
	%	Molecular Composition.		%	Molecular Composition.
SiO ₂	14.40	0.2400	SiO ₂	14.60	0.2433
FeO	12.31	0.1710	FeO	13.11	0.1821
Fe ₂ O ₃	5.04	0.0318	Fe ₂ O ₃	3.77	0.0236
Al ₂ O ₃	2.15	0.0211	Al ₂ O ₃	2.10	0.0206
MnO	6.50	0.0727	MnO	6.50	0.0915
CaO	44.20	0.7893	CaO	43.90	0.7839
MgO	7.80	0.1926	MgO	8.06	0.1990
P ₂ O ₅	<u>6.14</u>	0.0432	P ₂ O ₅	<u>6.14</u>	0.0432
	98.54			98.18	

$$\text{Ratio: } \frac{\text{CaO plus MgO}}{\text{P}_2\text{O}_5 \text{ plus SiO}_2} = 3.47$$

$$\text{Ratio: } \frac{\text{CaO plus MgO}}{\text{P}_2\text{O}_5 \text{ plus SiO}_2} = 3.41$$

The analyses corroborate those from the same experiment made by Whiteley, viz; the Fe₂O₃ in the sample taken nearer the door was higher than that taken from the interior of the bath. Whiteley attributed the lower ferric oxide in the second sample to the activity of the Carbon reaction within the bath.

In the writer's experiment a sample of bath metal was also taken within the bath. The Carbon content was 0.05%. It is not possible in the basic furnace to obtain a perfectly quiet bath/

bath even although in this case the metal was almost completely decarbonised and the elimination of carbon had ceased.

The increased amount of Fe_2O_3 shown by the analyses of the first sample must therefore be attributed to the stabilisation of the ferric oxide which results from the increased basicity of the slag adjacent to the furnace breast.

Recalculation of the analyses given in Whiteley's paper also confirms this explanation. Such evidence offered to support the view that Fe_2O_3 in a normal slag plays an essential part in the oxidation of impurities, is therefore inconclusive.

Influence of Temperature:

The influence of atmospheric oxidation on basic slags at different low temperatures is indicated by the following experiments.

A quantity was ground to a fine powder and analysed.

Its analysis showed:-

Analysis No. <u>X1</u>	
	%
SiO_2	11.40
Al_2O_3 plus P_2O_5	4.22
Fe O	23.91
Fe_2O_3	7.50
MnO	6.50
CaO	40.00
MgO	<u>5.33</u>
	98.86

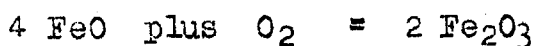
Quantities each consisting of 2.5 grms. were spread in a thin layer in an open container. This was placed in an open electric furnace and heated for 30 mins. Successively increasing temperatures up to 1250°C were employed. The increase/

increase in weight was measured after each treatment. The results are given in Table:-

<u>Specimen.</u>	<u>Temperature.</u>	<u>Weight increase in grms.</u>	<u>% increase in Weight.</u>	<u>Calculated % FeO oxidised.</u>	<u>Residual FeO found by analyses.</u>
H 1	400°C	0.0014	0.056	0.504	22.51
H 2	520	0.0125	.500	4.500	19.49
H 3	540	0.0168	.672	6.048	17.37
H 4	600	0.0404	1.616	14.544	10.29
H 5	700	0.0760	3.040	27.360 ?	Nil
H 6	800	0.0908	3.632	32.688 ?	-
H 7	900	0.0964	3.856	34.704 ?	-
H 8	1000	0.0980	3.920	35.280 ?	-
H 9	1100	0.0974	3.896	35.064 ?	-
H 10	1150	0.0950	3.800	34.200 ?	-
H 11	1200	0.0938	3.748	33.74 ?	-
H 12	1250	0.0916	3.664	32.98 ?	-

The total FeO content of the original slag was 23.91%.

Agreement exists between the calculated amount of FeO oxidised to Fe_2O_3 and the residual amount found by analyses up to a temperature of about 540°C. Above this temperature the increase is greater than can be accounted for by the reaction.



The amount of oxygen required to oxidise 23.91% FeO to Fe_2O_3 is 2.657%. The maximum increase in weight was 3.92% so that 1.263% oxygen remains unaccounted for.

The slag contained 6.5% MnO. This excess gain in oxygen by the slag approximates that required for the formation of MnO_2 .

Above 1100°C. the slag became distinctly magnetic and this change was accompanied by a decrease in weight up to 1250° C. the highest temperature reached.

It is apparent therefore that the amount of ferric oxide found by/

by chemical analysis must depend to some extent upon the conditions under which the slag cools. In normal bath slag samples the time-temperature gradient is usually steep, above 540°C , so that ferric oxide is not formed to an appreciable extent in this way.

In rapidly chilled slags FeO is the oxide of iron which occurs in the greater amount. The dissociation pressure of FeO is less than that of Fe_3O_4 and the dissociation pressure of Fe_3O_4 less than that of Fe_2O_3 consequently, as the slag-heating experiments indicate, when the bath temperature increases the less will be the tendency for the oxide with the higher dissociation pressure to exist, since the most stable oxide will be that with the lowest dissociation pressure.

LOW BATH TEMPERATURES:

It is well known to the furnaceman that low bath temperature promotes increased gas oxidation at all stages of the process and results in an increase in the FeO content of the slag.

In practice this increase is always checked by lime additions; if possible the bath temperature is raised and recarburising agents added. The avidity with which slags formed under low temperature conditions can absorb large quantities of lime is explained by the formation of the CaO - Fe_2O_3 constituents described.

It also supports the belief that in such slags Fe_2O_3 unless in combination with lime must be the medium for the oxidation of the bath metal. No other reaction which would account for the loss of iron seems possible.

HIGH BATH TEMPERATURES:

On the other hand at the higher temperatures of steel-making the tendency for the formation of Fe_2O_3 must be reduced owing to the instability of the oxides of the higher dissociation pressure as the temperature rises.

At higher temperatures with the normal limey slag any Fe_2O_3 formed will combine with lime; consequently the losses incurred by the gas-slag reaction must be reduced as the result of high temperature high slag basicity.

Under these conditions the control of the reactions which determine the elimination of impurities will depend, apart from the time factor, directly upon the oxide additions made to the bath by the operator. This elimination under these conditions must then depend entirely upon the FeO content of the slag.

The diversity of opinion, commented upon earlier, which exists regarding the nature of the medium of oxidising action in the steel bath, is explained by the fact that this must vary according to the prevailing conditions of slag composition and bath temperature.

These conclusions based upon the foregoing experimental investigations permit the conditions to be thus defined -

- (1) In a slag of sufficient basicity at normal high bath temperatures the elimination of impurities must depend entirely upon the FeO content of the slag.
- (2) Fe_2O_3 can also function as an oxidising medium when the basicity of the slag is insufficient to meet the requirements of the acids. Low bath temperatures promote this action by increased formation of Fe_2O_3 with consequently increased demands for lime.

The control of the reactions which govern the elimination of impurities therefore depends upon the operator securing the conditions of correct basicity and of high temperature.

Correct slag basicity necessitates lime in slight excess to what-ever amount may be required to satisfy the requirements of those components with which it enters into combination.

The determination of the relationships which exist in the slags between the components is therefore of prime importance in/

in this connection.

The data obtained regarding the nature of these combinations is detailed earlier in this thesis. It supplies evidence which permits the approximate definition of that degree of slag basicity essential to the accurate control of the refining reactions.

In slags 7^S and 8^S crystals of a substance corresponding in composition to the compound $2 \text{CaO} \cdot \text{SiO}_2$ were observed. Its optical properties identify this substance with the high temperature form of the orthosilicate of lime noticed by Messrs Ranken and Wright (21) in their examination of the CaO-SiO_2 system.

According to these writers this α -form exists above 1420°C , below this temperature it changes reversibly to the β -form, which also passes reversibly at 650° to the γ -form accompanied by a change in volume which shatters the compound to a fine dust.

The α -form is characterised by intricate twining which is absent from the β -form. In the rapidly chilled bath samples it was this α -form which was observed. The slag analyses indicates that the crystals may contain some magnesium replacing the calcium.

No traces of the double compound Monticellite (CaO-MgO)- SiO_2 were observed in any of the slags examined. In magnesium silicate crystals obtained from the basic hearth the lime content was surprisingly low. It seems unlikely that the double salt exists at steel-bath temperatures.

The degree to which the orthosilicate of lime can hold the analogous magnesium silicate in solid solution is not known. The crystals in these slags were optically uniform and no trace of the compound Fosterite ($2 \text{MgO} - \text{SiO}_2$) was observed.

(22)
Niggli has pointed out in connection with the melt diagrams of CaO and MgO with SiO_2 that when the orthosilicate in each case/

case separates out from a melt of its own composition the addition of small quantities of lime and silica suffices to produce marked alterations in the melting point. The reaction is almost quantitative in the liquid phase and it is certain that the new compound is very sparingly dissociated into its component parts.

In these slags therefore the orthosilicate of lime can be regarded as a fundamental compound.

The orthosilicates of Iron and Manganese on the other hand differ from those of lime and magnesia when thus examined. The addition of their components produces no great variation in melting point, so it is probable in these cases that the reactions are incomplete when equilibrium sets in, and that certain percentages of the original substances remain.

McCance (4) has suggested, on physico-chemical grounds, that where no dissociation occurs a slag containing CaO , FeO , MnO and SiO_2 should contain that amount of each silicate which is proportional to the square of the concentration of the respective oxide.

The considerations outlined above, however, indicate that it is improbable that any appreciable amount of the silicates of Iron or Manganese can exist in rapidly cooled basic slags owing to the dissociation which occurs at steel making temperatures.

The existence of a substance approximating in composition to $3\text{CaO} \cdot \text{SiO}_2$ has not previously been observed in basic slags. Its occurrence must modify the views commonly accepted regarding the amount of lime necessary to satisfy the requirements of the Silica.

The optical data of the slag constituent agrees with that of the synthetically prepared compound of Messrs Rankin and Wright (21) except that in this case the extinction angle was straight and the small angles noticed in the synthetic crystal were not observed. The results obtained also indicate/

indicate that this slag crystal belongs to the orthorhombic system.

The appearance of tricalcic silicate in slag 15^S was accompanied by an increase in the ferric oxide found by analyses, evidently the result of an increase in the lime available for the stabilisation of this oxide.

Slag 14^S suggests that apparently $2 \text{CaO} \cdot \text{SiO}_2$ and the compound $3 \text{CaO} \cdot \text{SiO}_2$ can exist together in the same slag.

It is probable that in basic slags the formation of the orthosilicate precedes that of the tribasic silicate. The early slags in which the orthosilicate was characteristic, were viscous and thick, while they absorbed lime with difficulty. Slags which contained tricalcic silicate were relatively more fluid in the bath.

The exact action of fluorspar is not definitely known. Its effect is to hasten the solution of undissolved lime and thus promote combination. When added in excess to the slag gas oxidation increases, the slag loses basicity and further lime additions are necessary. Observations suggest that the fluorine gradually becomes dissociated as later on the slag becomes thicker and further spar additions may be necessary to maintain fluidity.

The addition of fluorspar to the bath in these experiments was followed, first by the formation of dicalcic silicate, and later by the formation of tricalcic silicate and tricalcic ferrite. The mineral Apatite was also observed.

It therefore appears certain that the requisite degree of basicity essential for satisfactory control of the process is not reached until the slag assumed an essentially tribasic character towards the acidic oxides it contains.

The accuracy of this conclusion has since been conclusively proved by the improvement in practice which ensued from the applications of these considerations to the control of open-hearth furnaces under/

under the charge of the writer.

The study of low phosphorus slags containing fluorspar was gradually found to consist largely of the examination of the system $\text{CaO} - \text{Fe}_2\text{O}_3$ and SiO_2 since FeO is "free" and the phosphorus exists independently as apatite.

No work has been done on this system. The existence of compounds approximating in composition to $3\text{CaO} \cdot \text{SiO}_2$ and $3\text{CaO} \cdot \text{Fe}_2\text{O}_3$ together with the fact that $2\text{CaO} \cdot \text{SiO}_2$ can also exist in these slags suggests that this system is closely analogous to that of the system $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ investigated by Ranken and Wright.

Comprehensive examinations showed that pure CaO , Al_2O_3 and SiO_2 heated at a high enough temperature for a sufficiently long time resulted in equilibrium being reached with the formation of the three compounds, $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{SiO}_2$ and $3\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$.

They found that if equilibrium were approached but not reached either free CaO or the compound $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ or both would be obtained in addition to these three compounds.

These predictions were subsequently confirmed by the Pittsburg Bureau of Standards in their investigations on Portland Cement clinkers which consist essentially of $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$.

The tribasic compounds here described can be regarded as two of the final slag products when equilibrium conditions have been approached. In the almost carbonless metal bath however, the conditions will rapidly tend to become more complex unless basicity and high temperatures are maintained, owing to the instability of ferric oxide at high temperature.

If the time factor be sufficiently increased any normal charge can be worked out to a finish without ore additions from a high carbon content even where the bath temperature is high.

This/

This shows that at steel making temperatures some Fe_2O_3 is always formed. This gas-slag reaction will therefore continuously tend to diminish the basicity of the slag.

In normal slags the amount of material which can be magnetically separated is very low; it, however, increases rapidly when the lime content of the slag is low and the carbon in the bath metal approaches 0.045%, this value being the usual minimum observed.

Consequently the magnetic constituent noticed in the finishing bath slags and isolated from the slowly cooled slags cannot be of importance as a refining agent. Its origin appears of a secondary nature and to be the result of combinations when the slag assumes a strongly oxidising character towards the end of the process.

S U M M A R Y

- (1) A description is given of several constituents not previously isolated, which were obtained from open-hearth basic slags and from the basic furnace hearth. Their chemical composition and their optical data are detailed.
- (2) The results obtained from the chemical and microscopical examination of a series of rapidly chilled bath slags are described and discussed.
- (3) Data are given to show that the amount of Fe_2O_3 formed by atmospheric oxidation on basic slag increases with decrease of temperature.
- (4) Data are given to show, that in a slag of sufficient basicity the Fe_2O_3 combined with CaO . When the basicity was low such combinations were not observed and the Fe_2O_3 then functioned as an oxygen carrier to the bath.
- (5) The importance of the effects which resulted from oxidation due to the furnace gases, upon the operation of the basic process, is considered. Control of the refining reactions by the operator is shown to be opposed by the effects of gas-oxidation upon the slag and metal.
- (6) The extent to which gas oxidation will occur is shown to depend upon the prevailing bath conditions of slag basicity and temperature.
 - (a) Gas oxidation losses decrease with high slag-basicity and high bath temperatures.
 - (b) Conversely - Gas oxidation losses increase with slag acidity and low bath temperatures.
- (7) The bath conditions essential to the effective control of refining action are defined
 - (a) The combinations which occur in the slag between the/

the bases (CaO and MgO) and the acids (P₂O₅, SiO₂ and Fe₂O₃) must be tribasic in character, i.e. the slag basicity must be of a tribasic order.

(b) Control is increased by high bath temperatures.

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APPENDIX - BTABLE No. 2SLAG AND METAL BATH SAMPLES.

SLAG			METAL.
No.	Time taken after Charging.	NOTES, ETC.	No.
	<u>Min.</u>		
1 S	-	1st Slag noticed in furnace 9 Mins. before pig iron completely charged.	1 M
2 S	25	Pig iron beginning to melt. No metal sample obtained.	2 M
3 S	52	Pig iron melting.	3 M
4 S	82	Bath incompletely melted. Slag gaseous. Much undissolved Lime.	4 M
5 S	105	Do. 20 Mins. after 5½ cwts Spar fed. No metal sample obtained.	5 M
6 S	107	Do. Slag thick. much undissolved Lime. Iron melted.	6 M
7 S	130	Do. After 1 cwt Spar. Slag opening out. Bath level.	7 M
8 S	150	Do. Slag more fluid. Contains undissolved lime.	8 M
9 S	175	Do. After 4½ cwts. Fluorspar.	9 M
10 S	195	Do. Contains undissolved Lime. Metal gaseous.	10 M
11 S	207	Do. Contains undissolved lime. Slag opening out.	11 M
12 S	234	Do. Do. Boil commencing.	12 M
13 S	255	Bath completely melted. Slag contains undissolved lime.	13 M
14 S	274	Do. Slag opening out and boil increasing.	14 M
15 S	295	Do. After 19 cwts. Scale fed.	15 M
16 S	318	Do. Bath boiling briskly.	16 M
17 S	337	Do. After 12 cwts. Scale fed. Strong boil. Active slag.	17 M
18 S	358	Do. Boil slackening. Slag fluid.	18 M
19 S	381	Do. Furnace tapping.	19 M

BASIC OPEN HEARTH CHARGE.

TABLE NO. 3

ANALYSES OF BATH SIAC SAMPLES.

	1 ^s	2 ^s	3 ^s	4 ^s	5 ^s	6 ^s	7 ^s	8 ^s	9 ^s	10 ^s	11 ^s	12 ^s	13 ^s	14 ^s	15 ^s	16 ^s	17 ^s	18 ^s	19 ^s
SiO ₂	2.8	7.0	11.0	12.4	26.4	27.2	28.4	28.8	26.6	22.0	21.4	21.0	20.8	20.2	16.5	16.3	15.8	15.8	14.0
Al ₂ O ₃	1.0	2.4	5.29	2.75	2.72	2.57	4.28	4.0	2.77	2.23	4.0	3.8	3.80	3.80	2.7	2.5	2.05	2.0	1.72
P ₂ O ₅				1.28	1.28	1.79	1.92	1.98	1.90	2.04					2.7	2.5	2.05	2.0	1.72
CaO	24.5	34.2	40.8	46.5	41.2	46.0	45.0	46.5	49.5	53.3	53.25	52.75	52.6	51.6	47.8	50.0	49.70	49.4	49.7
MgO	3.82	4.69	5.62	5.77	5.47	5.48	5.91	5.77	5.70	5.33	5.12	5.33	5.12	5.05	4.32	5.04	5.50	5.33	6.42
MnO	3.82	6.62	3.72	5.09	5.95	7.81	7.81	7.63	6.88	5.58	5.58	5.95	5.77	5.77	6.12	6.12	5.97	6.04	5.58
Fe ₂ O ₃	13.60	12.50	9.0	7.50	3.67	2.40	1.61	0.90	1.53	2.87	2.96	2.70	3.43	2.88	5.40	4.50	4.50	4.23	5.31
FeO	50.14	32.79	23.6	18.5	12.15	5.26	3.40	2.91	4.05	6.89	6.89	7.29	6.64	8.74	12.96	12.15	14.17	14.41	15.0
	99.68	100.20	99.03	99.79	98.84	98.51	98.53	98.49	98.93	100.24	99.20	98.42	98.26	98.14	98.50	99.11	99.98	99.21	99.45

APPENDIX E

TABLE NO. 5

BASIC OPEN HEARTH CHARGE.

CALCULATED MOLECULAR PERCENTAGE SLAG COMPOSITION.									
Slag No.	Time Mins.	CaO	MgO	Fe ₂ O ₃	SiO ₂	P ₂ O ₅	CaO plus MgO	SiO ₂ plus P ₂ O ₅	Ratio CaO plus MgO / SiO ₂ plus P ₂ O ₅
S1	0	30.87	6.66	6.03	3.33	0.27	37.53	3.60	10.42
S2	25	40.83	8.05	5.39	7.70	0.51	48.88	8.21	5.95
S3	52	47.71	9.14	3.68	11.77	1.23	56.85	13.00	4.37
S4	82	52.20	8.95	2.95	12.99	0.57	61.15	13.56	4.51
S5	105	46.03	8.37	1.40	26.51	0.70	54.40	27.21	2.00
S6	107	50.02	8.26	0.90	27.62	0.76	58.28	28.38	2.05
S7	130	48.68	9.08	0.61	28.65	0.81	57.76	29.46	1.96
S8	150	48.17	8.26	0.33	27.83	0.78	56.43	28.61	1.97
S9	175	52.82	8.45	0.56	26.62	0.78	61.27	27.40	2.24
S10	195	56.69	7.86	1.05	21.87	0.82	64.55	22.69	2.85
S11	207	57.22	7.60	1.13	21.45	0.83	64.82	22.28	2.91
S12	234	56.83	7.89	0.99	20.64	0.84	64.72	21.48	3.01
S13	255	57.29	7.70	1.28	21.09	0.83	64.99	21.92	2.97
S14	274	56.23	7.62	1.07	20.61	0.84	63.85	21.45	2.98
S15	295	53.99	6.75	2.17	17.38	1.16	60.74	18.54	3.28
S16	318	55.31	7.72	1.75	16.78	1.10	63.03	17.86	3.53
S17	337	54.41	8.40	1.76	16.16	0.88	62.81	17.04	3.69
S18	358	54.44	8.09	1.60	16.17	0.88	62.53	17.05	3.67
S19	381	54.50	9.74	2.05	14.32	0.74	64.24	15.08	4.26
LS	-	43.66	8.73	0.85	24.72	0.85	52.39	25.57	2.05

BASIC OPEN HEARTH CHARGE

GRAPH SHOWING VARIATION OF MOL % OF Fe_2O_3 WITH RATIO OF MOL %
 $\frac{CaO + MgO}{SiO_2 + P_2O_5}$ IN THE SLAG DURING THE REFINING STAGES
 FROM TABLES Nos 2 and 5

MOLECULAR PERCENTAGE Fe_2O_3

