LOW GRADE BASIC SLAG

A STUDY of ITS CONSTITUTION and MANURIAL VALUE

A THESIS

by

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CONSTITUTION OF LOW GRADE BASIC SLAG

The experiments of Snelus in 1872 and of Thomas and Gilchrist in 1878 proved that steel could be manufactured from phosphatic iron ores by using a basic lining in the Bessemer Converter. The introduction of the Basic Bessemer Process of Steel-making resulted in the production of a slag - basic slag - which at first was regarded merely as a waste product. The possibility of using this material as a fertiliser was demonstrated by Wrightson and Munro in 1884 and about the same time Hoyermann and Albert began their research to determine the fertilising value of basic slag in its natural state.(1) The famous trials conducted at Cockle Park near Newcastle-on-Tyne by Somerville, Middleton and Gilchrist have proved that basic slag is a valuable fertiliser.

During the past few years very great changes have taken place in the methods by which the de-phosphorisation of steel is accomplished and attention has been directed to the difference which exists between the fertilising values of the older Bessermer slags and the newer Open Hearth slags produced with, and without, the use of fluorspar.(2) It has always been assumed that the phosphate, which is present in the slag, is the effective constituent and, until recently, the agricultural value of a slag was assumed to be proportional to the solubility of the phosphate, under standard conditions, in two per cent citric acid.

It, however, has been recognised that the solubility of any given slag, quite apart from the agricultural value, is determined by the nature of the constituents.

The 'citric acid test' has been shown to be entirely empirical and numerous trials, with open hearth slags of low solubility, have shown that a so-called insoluble slag, nevertheless, may have a distinct value as a fertiliser.

These facts, in themselves, are sufficient to warrant a thorough investigation into the constitution of basic slag.

When it is remembered, however, that in most of the recorded trials, the history and the constitution of the slags used have been unknown, it must be evident that there is but little upon which to build a theory regarding the relative fertilising values of the constituents.

The object of this research was to determine the constitution of an Open Hearth Fluorspar Slag of known history and to determine the relative fertilising values of the constituents under known soil conditions.

The slag used was one of low phosphorus content made by the Open Hearth Basic Process using fluorspar and was representative of the so-called "low grade slags" which are not used to any great extent because they are regarded as containing insufficient phosphate. It was thought that, by using such a slag, an opinion might be formed regarding the part played by those constituents, other than the phosphates present.

Any information, that is available regarding the nature of the constituents of basic slag, has been derived from investigations made upon various crystals which have been isolated from vesicles occurring in the cooled unground slag. It is known from a study of the constitution of many igneous rocks, that the composition of the crystals isolated from vesicles, does not necessarily indicate the composition of the rock itself. Thus it was realised that a study of the constitution of a slag was a necessary prelude to a study of its agricultural value. An investigation of the constitution of a number of basic slags, obtained in different processes of manufacture of steel, was made by Scott and McArthur and the results have been published elsewhere(3).

The methods used in the above research have been again used in this investigation.

Three distinct problems presented themselves and the results obtained are discussed in three sections. -

Part I. deals with the constitution of the slag.

Part II. deals with the results obtained in a series of field trials made with the slag, the constitution of which had been determined.

Part III. deals with a series of Pot experiments conducted with a view to determine the relative fertilising values of the constituents of the slag.

A summary of the previous literature relative to each problem is given at the beginning of each Part.

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PART I.

"THE CONSTITUTION OF AN OPEN HEARTH FLUORSPAR SLAG"

of their composition, the following may
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and Broeckman,(8) Stead and Ridsdale,(
[illegible](11) Kroll(12),(15) and Morison
[illegible]

An examination of the literature on the constitution of basic slag shows that attention has been confined to an examination of various crystals isolated from cooled slags. The chief compounds, which have been identified, mainly those occurring in Bessemer Slags, are

(a) Tetra - Calcium Phosphate:- $4\ CaO.\ P_2O5$.

(b) A Calcium - Silico - Phosphate:- $4\ Ca_3P_2O_8 \cdot$
$3\ Ca_3SiO_5$.

(c) A Calcium - Silico - Phosphate, containing impurities mainly of the nature of silicate of iron:- $4\ Ca_3P_2O_8.\ Ca_3SiO_5$.

(d) Crystals of the composition:-
$6\ CaO.P_2O_5 + 2\ CaO\ SiO_{\cancel{5}_2}$.

(e) Crystals composed of lime, ferric oxide, and alumina which are not attracted by a magnet.

(f) Crystals composed of lime, ferric oxide, ferrous oxide and alumina which are attracted by a magnet.

(g) Crystals composed of ferrous and ferric oxides, lime and magnesia.

The silicophosphates have received most attention and amongst those, who have contributed to our knowledge of their composition, the following may be mentioned:- Carnot and Richard,(4) Hilgenstock,(5), (6), (7) Groddeck and Broockmann,(8) Stead and Ridsdale, (9), (10) Bucking and Linck,(11) Kroll(12),(13) and Morison(14).

In a recent paper by Scott and McArthur(15) it has been shown, from microscopical investigation of slags that, if those slags to which fluorspar has been added be disregarded, basic slags consist essentially of three types of compounds,

(a) Silicophosphates

(b) 'Spinelloid' [X]Material.

(c) Uncombined Oxides.

Four different silico-phosphates have been recognised.

(1) Brown Crystals described by Stead and Ridsdale. The ratio of the molecular proportions of SiO_2 and P_2O_5 is 1 : 4.

(2) Pleochroic Crystals described by Stead and Ridsdale. The ratio of the molecular proportions of SiO_2 and P_2O_5 is 1 : 1.

(3) The "Octobasic" compound described by Kroll. The ratio of the molecular proportions of SiO_2 and P_2O_5 is 1 : 1.

(4) A new silico-phosphate described by Scott and McArthur. The ratio of the molecular proportions of SiO_2 and P_2O_5 is approximately 3 : 1.

The silico-phosphates are differentiated easily by

[X] The term 'spinel' or 'Spinelloid' material is used to designate the aluminates and ferrites present in the slag.

the method indicated above, namely by using the ratio of the molecular proportions of silica and phosphoric oxide present in the slag. The total molecular proportions of the basic oxides is taken as unity when calculating those of silica and phosphoric oxide.

The slags, however, which are formed during the manufacture of Steel by the Open Hearth Process using fluorspar, are very different from those which have been discussed. Robertson(16) has drawn attention to the fact that the use of fluorspar in the Open Hearth Process results in the production of a slag containing phosphates of very different nature from those present in the older type of slag. He also showed that "the citric acid test gives no true idea of the solubility of the phosphate in fluorspar slags" and that "a phosphatic slag of low citric solubility is completely soluble in citric acid if sufficient time is spent on the extraction".

The phosphate present in fluorspar slag has been identified by Bainbridge(17),(18) as apatite - $3\ Ca_3\ P_2O_8 . CaF_2$. Scott and McArthur(15) confirmed this by another method of examination. They showed that, provided sufficient fluorspar has been added to saturate all the phosphorus present in the slag, apatite was formed and that none of the silico-phosphates could be detected. The other constituents were found to be di-calcium silicate, spinelloid material and uncombined oxides.

History of the Slag.

The slag was obtained from an ordinary charge of Basic Pig Iron and Steel scrap while fluorspar containing 70 per cent Calcium Fluoride, CaF_2, had been to the bath. The amount of fluorspar added was three per cent of the weight of the slag. After the furnace was tipped, the slag was allowed to cool, broken up and specimens selected for microscopical examination.

Thereafter the slag was ground to different degrees of fineness and used in the trials to ascertain its manurial value.

Constitution.

I. MICROSCOPICAL EXAMINATION

Microscopical examinations of the selected specimens were made, using both transmitted and reflected light and the methods adopted were those used by Scott and McArthur in the examination of a number of different slags. So far as they are aware, this manner of examining basic slags is entirely new and there are distinct benefits in using both methods of optical examination.

With transmitted light, the optical properties of the various crystalline constituents were determined and, by comparison with data relating to synthetic silicates and other identified compounds, these constituents were identified.

With reflected light, the opaque materials were studied and the various constituents compared with those identified by transmitted light. The opaque materials were further investigated by etching with several reagents. A higher degree of magnification was possible than in the previous method and the discrimination of fine detail was accordingly easier.

(a) Transmitted Light.

Thin sections, as in the examination of rocks were made from the selected specimens, and these were examined by transmitted light. They showed two distinct types of crystals and a dark matrix of sub-translucent crystals.

(i) Some of the crystals were colourless with fairly well defined crystal faces. These crystals were relatively abundant and many were of large size and of a porphryitic nature. They invariably showed straight extinction and had a low double refraction while the refractive index, compared with that of the Canada Balsam in which the section was mounted, was high. In cross section they appeared to be hexagonal. These properties agree entirely with those of the mineral "apatite". From some of the vesicles of the slag, clear colourless crystals were picked out and mounted in Canada Balsam. Upon examination they were identified as crystals of apatite.

(ii) The other crystals were much smaller and were more abundant than those of apatite. They were frequently present as small laths of irregular outline and had a yellowish colour. They showed straight extinction and had a high double refraction, much higher than that of apatite. Two distinct cleavages, inclined to each other at an angle of almost ninety degrees, were visible. The refractive index was high and, in convergent light, a biaxial figure was obtained. In many cases, twinning and wavy extinction were observed. When these properties are compared with those given for di-calcium silicate(19) it is found that they are probably crystals of alpha-di-calcium silicate.

(iii) The matrix was found to consist of red subtranslucent crystals, which were present in a characteristic rounded form, and of opaque material. The discrimination of these constituents in the section was found to be difficult on account of the opaque nature of the material and in order to investigate the nature of the matrix, another section of the slag was examined by reflected light.

(b) <u>Reflected Light</u>.

The selected specimen of slag was ground to a flat surface and polished as in the preparation of a metallic specimen for examination by reflected light. The preparation of the surface was often a long and tedious process as the slag had a tendency to disintegrate and it was only, with great care, that a suitable polish could be obtained. Two distinct types of crystals were again recognised and these were set in a matrix which was composite and which corresponded to the opaque groundmass of the thin section. The matrix consisted of rounded grains of a dead-white, highly reflecting substance. In order to differentiate between the constituents, the surface was etched with 0.2 per cent citric acid. The lath shaped crystals, indentified above as di-calcium silicate, were found to dissolve. The crystals of apatite were not attacked to any extent, and the groundmass was unaffected. On etching with 2 per cent citric acid the material of dead-white colour was resolved into two constituents which were in intimate intergrowth. By comparison with similar results obtained in the course of investigations with other slags, - to which reference has been made - it was recognised that one constituent was a "spinel" and the other was an isomorphous mixture of the excess of basic oxides of ferrous iron and of manganese, present in the uncombined form.

Microchemical tests were then made, in order to ascertain the nature of these constituents. On etching with hydro-chloric acid the spinelloid material was not attacked but the other constituent was dissolved. The solution obtained after etching was found, by careful analysis, to contain no ferric iron. On oxidising the liquid a distinct colouration was obtained with potassium thiocyanate, thus indicating that the spinelloid material, containing ferric oxide was not attacked but that ferrous iron had been dissolved from the isomorphous mixture of the free oxides.

II. DISCUSSION of MICRO STRUCTURE

The chemical analysis of the slag is given in Table I. together with the molecular proportions of each oxide. The molecular proportions were calculated by dividing the percentage of each oxide by its molecular weight.

TABLE I.

ANALYSIS of SLAG and MOLECULAR PROPORTIONS of OXIDES

	Percentage	Molecular Proportion
P_2O_5	6.48	0.046
SiO_2	12.20	0.203
CaO	38.23	0.683
MgO	3.74	0.093
MnO	5.87	0.082
FeO	23.11	0.320
Fe_2O_3	5.92	0.037
Al_2O_3	4.15	0.041
S	0.17	0.005

The various oxides can be grouped into three classes (a) the basic oxides, (b) the sesquioxides and (c) the oxides of silicon and phosphorus,

(a)		(b)	(c)
38.23 %	CaO		
3.74 %	MgO	5.92 % Fe_2O_3	12.20 % SiO_2
5.87 %	MnO	4.15 % Al_2O_3	6.48 % P_2O_5
23.11 %	FeO		
70.95 %	Total		

The high percentage of basic oxides is noticeable and also the low percentage of phosphoric oxide, so low in fact that such a slag is at present not considered worth grinding.

In order to form some idea of the constitution of the slag the molecular formula was obtained by grouping the molecular proportions in a similar manner to that adopted above and dividing each proportion by the sum of the molecular proportions of the basic oxides. Hence the sum of the basic oxides is always unity.

(a)		(b)	(c)
0.682	CaO		
0.093	MgO	0.037 Fe_2O_3	0.203 SiO_2
0.082	MnO	0.041 Al_2O_3	0.046 P_2O_5
0.320	FeO		
1.177	Total		

The molecular formula therefore is -

(a) R O		(b) R_2O_3	(c)
0.580	CaO		
0.080	MgO	0.032 Fe_2O_3	0.171 SiO_2
0.069	MnO	0.035 Al_2O_3	0.040 P_2O_5
0.271	FeO	0.067 Total	
1.000	Total		

or approximately -

$$R\,O : 0.07\,R_2O_3 : \left(\begin{array}{l} 0.17\ SiO_2 \\ 0.04\ P_2O_5 \end{array} \right.$$

The "Citric Solubility" of the slag was found in the usual way using 2 per cent citric acid but the percentage solubility of each constituent also was determined. The results are given in Table II.

TABLE II.

THE SOLUBILITY of the SLAG in TWO per cent CITRIC ACID

	Percentage Total	Percentage Soluble in 2% Citric Acid	Percentage Solubility
P_2O_5	6.48	2.22	34.26
SiO_2	12.20	11.13	91.20
CaO	38.23	25.59	66.94
MgO	3.74	3.60	96.25
MnO	5.87	0.79	13.46
FeO	23.11	1.92	8.31
Fe_2O_3	5.92	-	-
Al_2O_3	4.15	0.46	11.09
S	0.17	-	-

The molecular formula for the soluble portion is -

$$\left.\begin{array}{ll}0.387 & \mathrm{CaO}\\ 0.076 & \mathrm{MgO}\\ 0.009 & \mathrm{MnO}\\ 0.022 & \mathrm{FeO}\end{array}\right)\quad 0.003\ \mathrm{Al_2O_3}\quad \left(\begin{array}{l}0.159\ \mathrm{SiO_2}\\ 0.013\ \mathrm{P_2O_5}\end{array}\right.$$

or approximately $3\ R\ O : SiO_2$.

The chief oxides soluble in citric acid in a first extraction are therefore those of Calcium, Magnesium and Silicon. If the amount of Calcium oxide required to saturate the phosphoric acid and alumina together with the oxides of iron and manganese, which probably represent dissolved free oxides, be subtracted from the "R O" column the formula becomes $0.315\ R\ O : 0.159\ SiO_2$ plus $0.097\ CaO$. Thus the formula for the soluble portion is $2\ R\ O.\ SiO_2$ where R is five sixths calcium and one sixth magnesium together with a quantity of free calcium oxide amounting to 5 per cent of the total lime in the slag.

This is in agreement with the results of the microchemical tests which showed that the apatite was not dissolved to any extent by citric acid, while the opaque material was only slightly attacked. Of the opaque material, the spinelloid constituent consists of aluminates and ferrites of calcium, of iron (ferrous) and of manganese. The amounts of manganese and ferrous oxides present in combination are probably small. The excess of basic oxides, notably ferrous oxide and manganese oxide, seem to crystallise out in the uncombined state. It was not possible to resolve these constituents by any method of etching and so it must be assumed that a complex group of solid solutions exists and that these oxides crystallised out not as individual oxides but as an isomorphous mixture.

The comparison of the results of the examination of slags obtained with and without the addition of fluorspar shows that, if fluorspar is added in sufficient amount to saturate all the calcium phosphate and so form apatite, the silica is found as di-calcium silicate. This silicate contains some magnesium replacing the calcium and as such is readily soluble in citric acid. It is interesting to note that silico-phosphate is apparently not formed so long as there is sufficient fluorspar to combine with the phosphoric anhydride to give apatite. Further the euhedral nature of the apatite indicates that it crystallised from the molten slag at an early stage in the cooling. This is in agreement with the behaviour of the mineral in igneous rocks where it is one of the earliest secretions from the magma. The chief compounds in the slag under consideration are therefore:-

(a) Apatite:- $3\ Ca_3\ P_2O_8 \cdot CaF_2$ (b) impure di-calcium silicate:- $2\ CaO \cdot SiO_2$ (c) Aluminates and Ferrites (d) Oxides of ferrous iron and of manganese in the free state.

Conclusions.

The constitutional composition of the slag may be expressed:-

Apatite:-	$3\ Ca_3\ P_2O_8\ .\ CaF_2$	15.33 per cent.
Di-calcium Silicate containing Magnesium.	$2\ CaO \cdot SiO_2$	34.97 per cent.
Free Lime	CaO	5.00 per cent.
Spinelloid Material + Uncombined Oxides		44.70 per cent.

PART II.

"A STUDY of the FERTILISING VALUE of a LOW GRADE OPEN-HEARTH FLUORSPAR SLAG of KNOWN CONSTITUTION"

For many years "the citric solubility" of a basic slag was taken as a measure of its agricultural value. Recently, however, as a result of investigations in the laboratory and in the field it has been shown that the citric solubility of a slag, as determined by the old official method does not always indicate its value as a fertiliser. Especially has this been shown to be true of the Open-Hearth Slags.

Basic Slags are now generally valued according to their total content of phosphoric oxide without any reference to their constitution. It appeared to the writer that the only basis which would be satisfactory would be a knowledge of the constitutional composition. It was decided therefore to determine the fertilising value of the slag, whose constitutional composition has been discussed in Part I.

The slag contained about 35 per cent of impure di-calcium silicate and about 15 per cent of the phosphatic mineral apatite. In addition, there was a very large proportion of free oxides and spinelloid material and a small quantity - about 5 per cent - of uncombined calcium oxide.

Comparing this constitutional composition with the solubility of the slag in two per cent citric acid it follows that the calcium silicate is one of the first constituents to dissolve as 91 per cent of the total silica, 96 per cent of the total magnesia and 67 per cent of the total lime CaO, were soluble in the first extraction while only 34 per cent of the phosphoric anhydride had dissolved. (See Table II.)

It was therefore decided to test the fertilising value of the calcium compounds contained in the slag, with special reference to the calcium silicate present, and it was thought that such a slag might have a fertilising value quite apart from any value due to the phosphate which it contained. This has been suggested by Sheldon (20) on purely chemical grounds, and there is a large literature dealing with value of di-calcium silicate as a source of calcium.

In 1909 Hendrick (21)(22) showed by a series of chemical tests, that in basic slag there is a considerable proportion of the lime capable of acting as a base. No attention, however, was paid to the nature of the calcium compounds present in the slag.

In 1914 MacIntyre and Willis (23) demonstrated, in a series of pot experiments, the value of several silicates and carbonates as sources of lime and magnesia when used as soil amendments.

In 1917 Cowles (24) showed that beneficial results were obtained from the application of impure di-calcium silicate. The material used was a bye-product from the manufacture of sodium aluminate and contained a readily decomposable calcium silicate and a water soluble sodium silicate. In the same year, Scheidt(25) also made a comparison of calcium silicate, carbonate and hydrate as fertiliser materials.

In 1920 Hartwell and Pember(26) repeated the work of Cowles and found "that di-calcium silicate was as effective as limestone in counteracting the toxic conditions existing in an acid soil".

In 1921 Conner(27) demonstrated that di-calcium silicate gave better results, in field and pot experiments, than were obtained from the use of lime.

In the same year Schollenberger(28) showed that the base of di-calcium silicate was quite as effective in reducing the lime requirement of soil as that of ground limestone under similar conditions.

The ball slag described in Part I. was ground to two grades of fineness so that one portion passed a sieve of 100 meshes to the linear inch whilst the other portion was composed of particles which passed a sieve of 16 meshes to the linear inch but too coarse to pass the "100" sieve. By using these two grades of fineness, it was possible to compare the effect of fineness of division on the efficacy of the slag as a fertiliser.(29)

Field trials were conducted on swede crops during 1921 at Grange Farm Kilmarnock and during 1922 at Robroyston Farm, Robroyston. The soils and the various other limiting factors at Kilmarnock were very different from those at Robroyston, so that the total yields obtained from the slag used at both centres cannot be compared. These yields however can be considered with reference to the yields from the other plots.

1921 Trials.

Each plot was one-fortieth of an acre in size and each received a dressing of farmyard manure applied to the stubble of the previous crop and ploughed in. The experiments were carried out in duplicate and the results are shown in Table III. expressed as 'yield per acre'. Two plots were reserved as controls and received no artificial fertilizer.

On Plot 2 the Coarse slag was applied in the drill at the rate of 1 ton per acre while on Plot 3 the fine slag was applied at the same rate.

Plot 4 received finely ground limestone so that the weight of lime, as CaO, was the same as that applied in the case of the slag in Plots 2 and 3.

Plot 5 received a mixture of finely ground limestone and finely ground mineral phosphates so that the total weights of lime, as CaO, and phosphorus, as P_2O_5, were the same as those supplied by the slag.

Plot 6 received a mixture of finely ground limestone, mineral phosphates and magnesium carbonate, so that the total weights of CaO, P_2O_5 and MgO were the same of those supplied by the slag.

The chemical composition of the limestone, mineral phosphates and magnesite used had previously been determined.

Mineral phosphate was chosen (30) so that the phosphate applied in Plots 5 and 6 might be comparable to the phosphates contained in the slag.

By such trials, it was possible - while fully realising the limitations imposed - to form an opinion of the relative importance of the lime, phosphate and magnesia contained in the slag.

TABLE III

1921. Yields of the Plots expressed as "Yield per Acre"

Plot	Treatment	Yield per Acre A Tons	 Cwt	 B Tons	 Cwt
1.	Control....................	10	10	11	-
2.	Coarse Slag................	15	5	16	-
3.	Fine Slag..................	19	-	19	5
4.	Finely ground Limestone......	17	15	18	-
5.	Limestone + Mineral Phosphates	19	-	18	15
6.	Limestone + Min. Phos. + Magnesia	19	15	20	-
7.	Control....................	10	-	11	15

("A" and "B" are the results of the duplicate trials)

The beneficial effect of the application of the slag is more clearly shown in Table IV in which are tabulated the various increases over the average controls namely, 10 Tons 5 Cwts in series A and 11 Tons 7.5 Cwts in series B.

TABLE IV

1921 Increased Yields per acre over Control Plots

Plot	Increase	Increased Yield per acre A Tons	 Cwt	 B Tons	 Cwt
2.	Coarse Slag................	5	-	4	13
3.	Fine Slag..................	8	15	7	18
4.	Limestone..................	7	10	6	13
5.	Limestone and Min. Phos......	8	15	7	8
6.	Limestone + Min. Phos. + Magnesia	9	10	8	13

The various data relative to the soil and crop are given in Table V.

TABLE V

Mechanical Analysis of Soil

Fine Gravel.........	above 1mm	8.7
Coarse Sand.........	1-0.2mm	18.8
Fine Sand...........	0.2-0.04mm	19.3
Silt................	0.04-0.01mm	11.6
Fine Silt*	0.01-0.002mm	19.3
Clay................	below 0.002mm	3.4
Moisture............		5.0
Loss on Ignition....		12.9

*	Fine Silt...........	0.01-0.005mm	12.0
	Do..............	0.005-0.002mm	7.3

Lime Requirement................	0.217%
p H value.....................	6.1

Rainfall 1st May to 30th November 1921,

22.75 inches.

Variety of Swede.......	Sutton's "Caledonia"
Date of Sowing.........	14th May 1921.
Date of Harvest........	19th November 1922.

1922 Trials

The trials were conducted in order to corroborate the results of those of the previous year. In order to prove the value of the calcium compounds in the slag, a very impoverished soil was chosen. Successive crops of rhubarb had been taken from the field for many years. No farmyard manure was applied. It was thought that under such conditions a true comparison of the slag with limestone would be possible. Each plot was one-twentieth of an acre in size and in duplicate but in this year's trials the slag was compared with limestone and with the control plot only. The basis of comparison between the plots was similar to that of the previous year and the results are shown in Table VI.

TABLE VI

1922 Yields of Plots expressed as "Yield per acre"

Swedes

		Yield per Acre			
		A		B	
Plot	**Treatment**	**Tons**	**Cwts**	**Tons**	**Cwts**
1.	Control...............	1	10	1	12
2.	Fine Slag.............	4	0	4	19
3.	Finely ground Limestone	2	1	3	2

The beneficial effect of the application of the slag is more clearly shown in Table VII in which are tabulated the various increases over the controls, namely 1 Ton 10 Cwts in series A and 1 Ton 12 Cwts in series B.

TABLE VII

1922 Increased Yields per acre over Control Plot.

		Increased Yield per Acre			
		A		B	
Plot	Increase	Tons	Cwts	Tons	Cwts
2	Fine Slag...........	2	10	3	7
3	Limestone...........	0	11	1	10

Discussion of Results.

1921. The results show that Finely ground Slag has a distinct beneficial effect as reflected in the increased yield and that the returns are better than these obtained from the application of finely ground limestone on the basis of same lime content.

The additional yield from Plot 5 over Plot 4 which may be attributed to the presence of phosphate is small compared with that obtained from the application of limestone, - Plot 4 over Control - being 1 ton and 7 tons respectively. The part played by the magnesia is of a debatable nature and this point is treated in Part III.

Fineness of Grinding.

The importance of fineness of grinding is demonstrated by the results of the trials with the same slag in the coarse and fine state. It is clearly shown that the more finely divided, the more available does the slag become. This question is also further discussed in Part III.

The main feature of these trials is that, considering the increases obtained from the application of limestone, and limestone plus phosphate, the greatest increase was obtained with the limestone, the phosphate only producing a small additional yield. It seems reasonable to conclude that the main benefit derived from the slag under the pertaining soil conditions was due to the calcium content of the slag, namely the di-calcium silicate.

1922. The results of these **trials** again showed that the slag could be compared with limestone as a fertilizer but the abnormal conditions of the soil must also be considered in comparing the results with those of 1921 trials. A comparison is more readily made by comparing the increased yields due to the slag and limestone obtained at both centres.

TABLE/

TABLE VIII

Comparison of Increased Yields obtained at both Centres with Fine Slag and Limestone

		Kilmarnock				Robroyston			
		A		B		A		B	
		Tons	Cwts	Tons	Cwts	Tons	Cwts	Tons	Cwts
X	Increase due to Fine Slag......	8	15	7	18	2	10	3	7
Y	Increase due to Limestone......	7	10	6	13	0	11	1	10

The difference (X-Y) between these increases from the duplicate plots at the two centres agree in a striking manner.

TABLE IX

Increased Yield of Fine Slag over Limestone at both Centres

Kilmarnock				Robroyston			
A		B		A		B	
Tons	Cwts	Tons	Cwts	Tons	Cwts	Tons	Cwts
1	5	1	5	1	19	1	17

Such results must be attributed to the effect of the di-calcium silicate contained in the slag and they are in accordance with results obtained from pot trials by other workers using the pure compound.

Conclusions

(1) Open Hearth Fluorspar Slags, of low phosphate content, have a distinct fertilising value, due to their lime content and could be used to replace ground limestone in agricultural practice.

(2) Their "lime value" is due to the di-calcium silicate which therefore, must now be regarded as an important constituent of these slags and under certain soil conditions more important than the phosphatic "apatite" which they also contain.

PART III.

"A STUDY, BY MEANS OF A SERIES OF POT EXPERIMENTS, of the RELATIVE FERTILISING EFFECTS of the CONSTITUENTS PRESENT in an OPEN HEARTH FLUORSPAR SLAG of KNOWN CONSTITUTION"

From the cultural experiments which were made by Meissl and Defert [31] and by others, it has been assumed rightly or wrongly, that the phosphate present in a basic slag is its principal constituent from the point of view of its use as a fertiliser. The validity of this assumption, under all soil conditions, was questioned on account of the results which were obtained with the Open Hearth Fluorspar Slag previously described, and it was decided to carry out a series of pot experiments with the object of ascertaining the relative fertilising values of the various constituents of this slag. It was fully realised that results obtained could refer only to the special soil conditions under which the experiments were conducted.

Previous Literature.

The literature dealing with the relative fertilising values of the various constituents of basic slag is scanty, and that which is available deals with only a few of the more important constituents. Many trials,(32) however, have been conducted both in culture solutions and in pot experiments, to test the effects of many chemical compounds on plant growth, but the results obtained do not bear directly upon the problem under investigation.

In 1905 The National Society of Agriculture (33) summarised the results of the investigations of Guffoy, Milon and Crepeaux on the efficacy of the compounds of manganese and silicon present in basic slag. These investigators found that the manganese compounds should be regarded as important constituents of slags.

In 1915 Collins and Hall [34] investigated the constituents of secondary importance and showed that the citric solubility of slags is correlated with their constitution provided the arbitrary character of the test is realised.

In 1919 McHargue[35] drew attention to the fact that basic slag contains about 100 lbs of combined manganese to the ton and stated that probably some of the benefit obtained from slag is due to this element.

In 1920, Russell and also Ridsdale[36] referred to the influence of the various constituents of slag - the former laying emphasis on the manganese content, the latter drawing attention to the iron content. Ridsdale also referred to the results obtained from Cleveland iron phosphate and Robertson[37] has made a further investigation on the fertilising value of this material.

In 1920, Vandormal[38] showed that, apart from basic calcium phosphate, slag contains not only essential elements such as calcium, phosphorus and silicon but also diastatic elements, in a soluble form such as manganese and sulphur.

The influence of the silicon content of slag, however, has not received any attention, apart from some experiments on the application of different silicates and the probable effect of the silicophosphates contained in certain types of basic slag.

The pot trials[x] were begun in 1921 and continued during 1922. The soil used was obtained from Grange Farm, Kilmarnock, and was of the same type, and from the same field as that upon which the field trials described in Part II were conducted..Each pot contained equal weights of soil and the slag was applied at the rate of one ton per acre - a similar dressing to that given in the field.

In applying the slag at this rate the following weights, expressed as oxides, are added. (See Table X)

TABLE/

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[x] A separate series of pot experiments was used to determine the part played by the silicon compounds of the slag. See Table XV, Page45.

TABLE X

The Weights of Various Materials expressed as Oxides added to the soil in an application of the slag at the rate of One Ton per Acre

Material Added expressed as Oxide	Lbs per Acre
CaO	825
FeO	563
SiO_2	269
MnO	146
P_2O_5	131
MgO	106
Al_2O_3	98
Fe_2O_3	93

The effect of each of the elements contained in the slag was tested by applying pure compounds to the various pots so that the weights, expressed as oxides, added were equal to those supplied by the slag dressing. The weighed quantities of each dressing were thoroughly mixed with the soil contained in the respective pots. The plan of the experiment is given in Table XI.

TABLE XI

Manurial Treatment of the Various Pots

Pot No.	Treatment	Oxides supplied equal in weight to those contained in the slag dressing of Pots 19 & 20
1.	Control Pot - No treatment given	
2.	Calcium Carbonate	CaO
3.	Tri-Calcium Phosphate	P_2O_5
4.	Calcium Carbonate + Calcium Phosphate	$CaO + P_2O_5$
5.	Magnesium Carbonate	MgO
6.	Calcium Carbonate + Magnesium Carbonate.	$CaO + MgO$
7.	Calcium Carbonate + Calcium Phosphate + Magnesium Carbonate	$CaO + P_2O_5 + MgO$
8.	Ferrous Sulphate	FeO
9.	Calcium Carbonate + Ferrous Sulphate	$CaO + FeO$
10.	Calcium Carbonate + Calcium Phosphate + Ferrous sulphate.	$CaO + P_2O_5 + FeO$
11.	Calcium Carbonate + Calcium Phosphate + Magnesium Carbonate + Ferrous Sulphate	$CaO + P_2O_5 + MgO + FeO$
12.	Manganese Carbonate	MnO
13.	Calcium Carbonate + Manganese Carbonate	$CaO + MnO$
14.	Calcium Carbonate + Calcium Phosphate + Manganese Carbonate	$CaO + P_2O_5 + MnO$
15.	Calcium Carbonate + Calcium Phosphate + Magnesium Carbonate + Manganese Carbonate	$CaO + P_2O_5 + MgO + MnO$

TABLE XI (Continued)

Pot No.	Treatment	Oxides supplied equal in weight to those contained in the slag dressing of Pots 19 & 20
16.	Calcium Carbonate + Calcium Phosphate + Magnesium Carbonate + Ferrous Sulphate + Manganese Carbonate	$CaO + P_2O_5 + MgO + FeO + MnO$
17.	Ferric Sulphate	Fe_2O_3
18.	Calcium Carbonate + Calcium Phosphate + Magnesium Carbonate + Ferrous Sulphate + Manganese Carbonate + Ferric Sulphate	$CaO + P_2O_5 + MgO + FeO + MnO + Fe_2O_3$
19.	Fine Slag	
20.	Coarse Slag	

In 1921 Italian Ryegrass and Clover seeds were sown and each pot was regularly watered with similar quantities of water. At the end of the growing season the pots were photographed and thereafter the crop of each pot was cut close to the surface of the soil, air-dried and weighed. The pots were allowed to stand, during the following winter, exposed to the air.

In the spring of 1922 the soil of each pot was removed, thoroughly mixed and replaced. Barley was then sown but no further manurial treatment was given. By so doing an idea was formed of the residual manurial values of the treatment of the previous year. The subsequent procedure was similar to that of the previous year. Photographs of the growing crops during both years are appended.

Results of 1921 Trials

TABLE XII

Comparison of the Growing Crops

Pot No.	Treatment	Oxides supplied equal in weight to those contained in the slag dressing of Pots 19 & 20.	Observation
1.	Control.	--	Poor
2.	Calcium Carbonate	CaO	More clover than Pot 1
3.	Tri-Calcium Phosphate	P_2O_5	Best of Pots 1, 2 and 3.
4.	Calcium Carbonate + Calcium Phosphate	$CaO + P_2O_5$	Thick growth, leaves broad. Best of Pots 1,2,3 & 4.
5.	Magnesium Carbonate	MgO	Clover good, leaves of ryegrass narrow
6.	Calcium Carbonate + Magnesium Carbonate	$CaO + MgO$	Similar to Pot 5.
7.	Calcium Carbonate + Calcium Phosphate + Magnesium Carbonate	$CaO + P_2O_5 + MgO$	Similar to Pots 5 &6
8.	Ferrous Sulphate	FeO	Thin growth, narrow leaves in comparison to Pot 2.

TABLE XII (Continued)

Pot No.	Treatment	Oxides supplied equal in weight to those contained in the slag dressing of Pots 19 & 20.	Observation
9.	Calcium Carbonate + Ferrous Sulphate	$CaO + FeO$	Better than Pot 8, worse than Pot 2.
10.	Calcium Carbonate + Calcium Phosphate + Ferrous Sulphate	$CaO + P_2O_5 + FeO$	--
11.	Calcium Carbonate + Calcium Phosphate + Magnesium Carbonate + Ferrous Sulphate	$CaO + P_2O_5 + MgO + FeO$	Improvement on Pot 7 worse than Pot 4.
12.	Manganese Carbonate	MnO	Thin leaves and shorter than Pot 2.
13.	Calcium Carbonate + Manganese Carbonate	$CaO + MnO$	Not so good as Pot 2.
14.	Calcium Carbonate + Calcium Phosphate + Manganese Carbonate	$CaO + P_2O_5 + MnO$	Narrower leaves than Pot 4.
15.	Calcium Carbonate + Calcium Phosphate + Magnesium Carbonate + Manganese Carbonate	$CaO + P_2O_5 + MgO + MnO$	Similar to Pot 7.
16.	Calcium Carbonate + Calcium Phosphate + Magnesium Carbonate + Ferrous Sulphate + Manganese Carbonate	$CaO + P_2O_5 + MgO + FeO + MnO$	Similar to Pot 7, but darker green.
17.	Ferric Sulphate	Fe_2O_3	Remarkable growth compared with Pot 8.

18/

TABLE XII (Continued)

Pot No.	Treatment	Oxides supplied equal in weight to those contained in the slag dressing of Pots 19 & 20	Observation
18.	Calcium Carbonate + Calcium Phosphate + Magnesium Carbonate + Ferrous Sulphate + Manganese Carbonate + Ferric Sulphate	$CaO + P_2O_5 + MgO + FeO + MnO + Fe_2O_3$ an "artificial slag"	Better than Pot 16.
19.	Fine Slag	--	Similar to Pot 4.
20.	Coarse Slag	--	Not so good as Pot 19.

Results of 1922 Trials

TABLE XIII

Comparison of the Growing Crops

Pot No.	Treatment of Previous Year	Oxides supplied equal in weight to those contained in Slag dressing of Pots 19 and 20	Observation
1.	Control	--	Very poor
2.	Calcium Carbonate	CaO	Much better than Pot 1.
3.	Tri-Calcium Phosphate	P_2O_5	Little better than Pot 1.
4.	Calcium Carbonate + Calcium Phosphate	$CaO + P_2O_5$	Improvement on Pots 2 and 3.
5.	Magnesium Carbonate	MgO	Poorest of Pots 1,2,3,4 and 5.
8.	Ferrous Sulphate	FeO	Best of all Pots 1,2,3, 4,5 and 8.
12.	Manganese Carbonate	MnO	Similar to Pot 1.
17.	Ferric Sulphate	Fe_2O_3	Poorer than Pot 8, equal to Pot 4.
19.	Fine Slag	--	Similar to Pot 4.
20.	Coarse Slag	--	Better than Pot 19.

Comparison of Results of 1921 and 1922 Trials

TABLE XIV

Weights of Air-Dried Crops in Grammes

Pot No.	Treatment given in 1921	Ryegrass & Clover 1921	Barley 1922
1.	Control	3.2	7.1
2.	Calcium Carbonate	3.4	8.5
3.	Tri-Calcium Phosphate	4.2	8.8
4.	Calcium Carbonate + Calcium Phosphate	4.8	8.8
5.	Magnesium Carbonate	3.4	7.4
6.	Calcium Carbonate + Magnesium Carbonate	3.3	6.6
7.	Calcium Carbonate + Calcium Phosphate + Magnesium Carbonate	3.8	7.0
8.	Ferrous Sulphate	3.1	10.8
9.	Calcium Carbonate + Ferrous Sulphate	3.4	8.1
10.	Calcium Carbonate + Calcium Phosphate + Ferrous Sulphate	4.7	6.9
11.	Calcium Carbonate + Calcium Phosphate + Magnesium Carbonate + Ferrous Sulphate	5.2	8.3
12.	Manganese Carbonate	4.9	-
13.	Calcium Carbonate + Manganese Carbonate	-	8.5

TABLE XIV (Continued)

Pot No.	Treatment given in 1921	Ryegrass & Clover 1921	Barley 1922
14.	Calcium Carbonate + Calcium Phosphate + Manganese Carbonate	4.3	7.2
15.	Calcium Carbonate + Calcium Phosphate + Magnesium Carbonate + Manganese Carbonate	4.1	7.1
16.	Calcium Carbonate + Calcium Phosphate + Magnesium Carbonate + Ferrous Sulphate + Manganese Carbonate	4.2	6.0
17.	Ferric Sulphate	5.0	9.0
18.	Calcium Carbonate + Calcium Phosphate + Magnesium Carbonate + Ferrous Sulphate + Manganese Carbonate + Ferric Sulphate	4.1	6.7
19.	Fine Slag	4.2	7.5
20.	Coarse Slag	3.6	9.1

Discussion of the Results in 1921.

(a) The Effect of Calcium Carbonate, supplying lime, CaO, alone and in various mixtures, was judged by the crops grown on Pots 2,4,6,9 and 13.

The yields of the various pots in order of magnitude, were those of Pots 4, 13, 2, 9 and 6. The best growth was obtained from the application of a mixture of calcium phosphate and calcium carbonate to Pot 4. The addition of magnesium carbonate to the calcium carbonate (Pot 6) caused a distinct depression - an effect which has been previously noticed by other investigators.

The application of manganese carbonate along with calcium carbonate (Pot 13) resulted in a slight increase in crop.

Pot 19, which received the dressing of Fine Slag was much better than Pot 2, calcium carbonate alone, and compared favourably with Pot 4 which received a mixture of calcium carbonate and calcium phosphate.

(b) The Effect of Calcium Phosphate, alone and with the various other compounds added, was observed in Pots 5, 4, 7, 11 and 16.

The mixture, containing calcium carbonate and calcium phosphate (Pot 4) appeared to give the best result while the addition of magnesium carbonate to this mixture (Pot 7) appeared to depress the yield. This depression was obviated, by including in the mixture, either ferrous sulphate (Pot 11) or manganese carbonate (Pot 15) or both (Pot 16).

(c) The Effect of Iron (Ferrous) Sulphate was studied by means of Pots 8, 9, 10, 11 and 16.

In this series it was noticed that ferrous sulphate alone had practically no effect but that it did not depress the yield obtained from calcium carbonate (Pot 4) and calcium phosphate (Pot 9).

(d) The Effect of Manganese Carbonate was observed in Pots 12, 13, 14, 15 and 16.

In this series it was noted that manganese carbonate alone (Pot 12) produced a yield comparable with that obtained from the application of the mixture of calcium carbonate and calcium phosphate (Pot 4), but that, when mixed with the various other compounds, (Pots 14, 15 and 16) smaller yields were obtained.

(e) The Effect of Magnesium Carbonate - to which reference has already been made - was noted in Pot 5, Pot 6, Pot 7, Pot 11 and Pot 16.

(f) The Effect of the Slag in the fine state of division and in the coarse state of division was observed in Pot 19 and Pot 20 and here, as in the field experiment, the fine slag produced distinctly the better crop.

The "artificial slag" (Pot 18) gave a result similar to that of the fine slag (Pot 19)

Discussion of the Results in 1922.

The results of this experiment furnished data regarding the residual values of the materials applied in the previous year.

(a) The outstanding result was that the crop obtained from the application of coarse slag (Pot 20) was better than that from the fine slag (Pot 19). This agrees with results which have previously been obtained showing that fineness of division gives a quicker return but that the coarser material becomes available in succeeding years.

(b) The "artificial slag" (Pot 18) was, however, distinctly inferior to either the fine or coarse slag (Pots 19 and 20).

(c) The residual effect of Ferrous Sulphate (Pot 8) was very marked and also that of the Ferric Sulphate (Pot 17). The effect of the latter substance however was less marked than in 1921.

(d) The depression of the yields, due to the presence of magnesium carbonate was again noticed and the results were similar to those previously described.

The Influence of the Silicon Compounds in the Slag.

A separate series of pot experiments was used to determine the value of the silicon compounds in the slag. It was known from the investigation of the constitution of the slag that the silicon was present as dicalcium silicate and magnesium silicate.

Barley was grown in a number of pots during 1922 and a similar method was adopted to that already described. The soil used was of a sandy nature and had a distinctly "acid" reaction. The weight of silica applied in the slag dressing was calculated and similar weights of combined silica, in the form of calcium silicate (precipitated) and magnesium silicate, were added to other pots. (Pots 2 and 3). As a control upon the weights of combined lime, CaO, and combined magnesia, MgO, supplied by these dressings, two other pots (Pots 4 & 5) were included in the series. These pots received calcium carbonate and magnesium carbonate respectively so that the weights of combined lime, CaO, and combined magnesia, MgO, were equal to those supplied by the calcium silicate and magnesium silicate.

The results of the experiment are given in Table XV.

TABLE XV

The Yields obtained with Various Materials containing Silicon

Pot No.	Treatment	Ingredient supplied	Weight in Grammes of air-dried crop
1.	Sodium Silicate	Same weight of SiO_2 as in Pot 6	5.7
2.	Magnesium Silicate	" " " SiO_2 " " Pot 6	9.0
3.	Calcium Silicate (precipitated)	" " " SiO_2 " " Pot 6	10.4
4.	Calcium Carbonate	" " " CaO " " Pot 3	9.0
5.	Magnesium Carbonate	" " " MgO " " Pot 2	7.6
6.	Fine Slag	---	12.2
7.	Control	---	4.2

Discussion of Results

As was to be expected on account of the additional lime and phosphorous content, the application of the slag (Pot 6) gave the best result.

The calcium silicate (Pot 3) produced a yield comparable with that from the slag (Pot 6) - distinctly better than that obtained with calcium carbonate (Pot 4) supplying the same amount of combined lime, CaO, as the calcium silicate.

Schollenberger [39] concluded that calcium silicate enabled most crops to absorb more phosphorus when the latter element was supplied as rock phosphate.

The peculiar secondary effect of silicon has long been observed at Rothamsted(40) (compare Pot 1) and Hall and Morison(41) have shown that silica increases the absorption of phosphorus. The results of the present trials suggest that the di-calcium silicate in this Open Hearth Slag plays no small part in bringing about the increased yields obtained by its use. The application of <u>magnesium silicate</u> (Pot 2) produced a better crop than magnesium carbonate (Pot 5). The yields are, however, smaller than those obtained with either calcium silicate or calcium carbonate.

Shedd[42] found that where magnesium silicate was applied to the soil the average calcium content of the hay or straw crop of all the crops grown and of the grain of oats was lower than that obtained with calcium silicate.

These results suggest that the magnesium silicate contained in the slag is useful in neutralising the "sour" conditions of a soil.

It may be concluded from these trials that the Open Hearth Fluorspar Slag owes its manurial value, to some extent at least, to the calcium and magnesium silicates which it contains.

CONCLUSIONS FORMED from the RESULTS of the POT EXPERIMENTS

The main conclusions which have been formed, are -

1. That the problem of correlating the relative values of the constituents of each slag is highly complex.
2. That the effect of the application of any one substance, in quantity - expressed as oxide - equivalent to that contained in an Open Hearth Fluorspar Slag, depends upon the substance or substances with which it is associated. (Pots 1 to 18).
3. That the calcium silicate present in an Open Hearth Fluorspar Slag is an important manurial constituent.
4. That the value of an Open Hearth Fluorspar Slag depends not only upon the individual constituents but also upon the proportions in which the constituents are present.

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PLATE 1.

Microphotograph of Open Hearth Fluorspar Slag - Transmitted Light

The large white crystals are apatite, the grey are di-calcium silicate, the black matrix being uncombined oxides and spinelloid material. x 45.

PLATE 2.

Microphotograph of Open Hearth Fluorspar Slag - Transmitted Light

The grey crystals are di-calcium silicate showing two good cleavages inclined to each other x 60.

PLATE 3.

Microphotograph of Open Hearth Fluorspar Slag - Reflected Light

The dead white material is spinelloid material and the dull white is a mixture of free oxides both set in a dark matrix of di-calcium silicate. x 60.

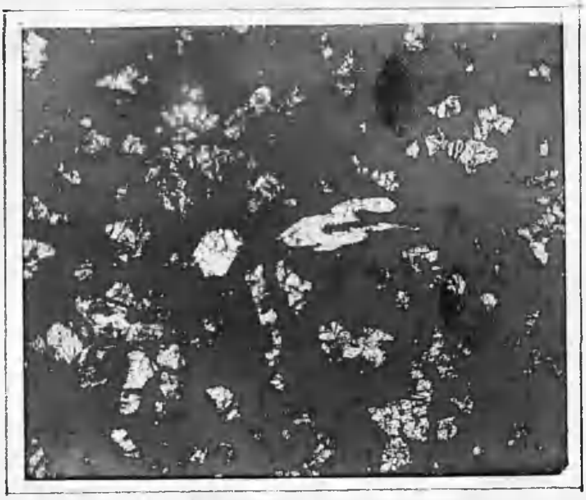


PLATE 1.

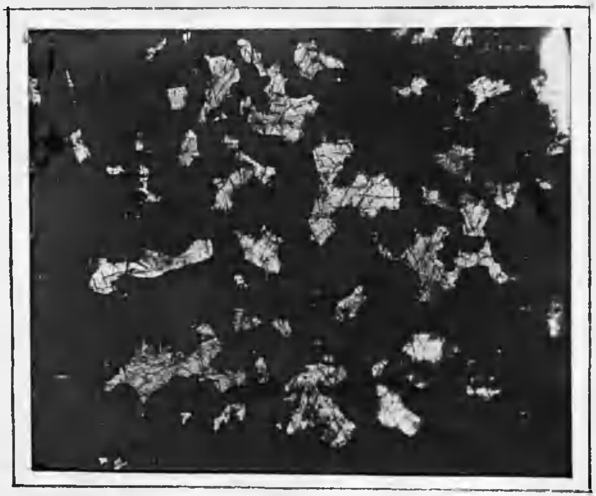


PLATE 2.

PLATE 3.

PLATE 4.

1921 Trials

Pot 1.	Control
Pot 2.	Calcium Carbonate
Pot 3.	Calcium Phosphate

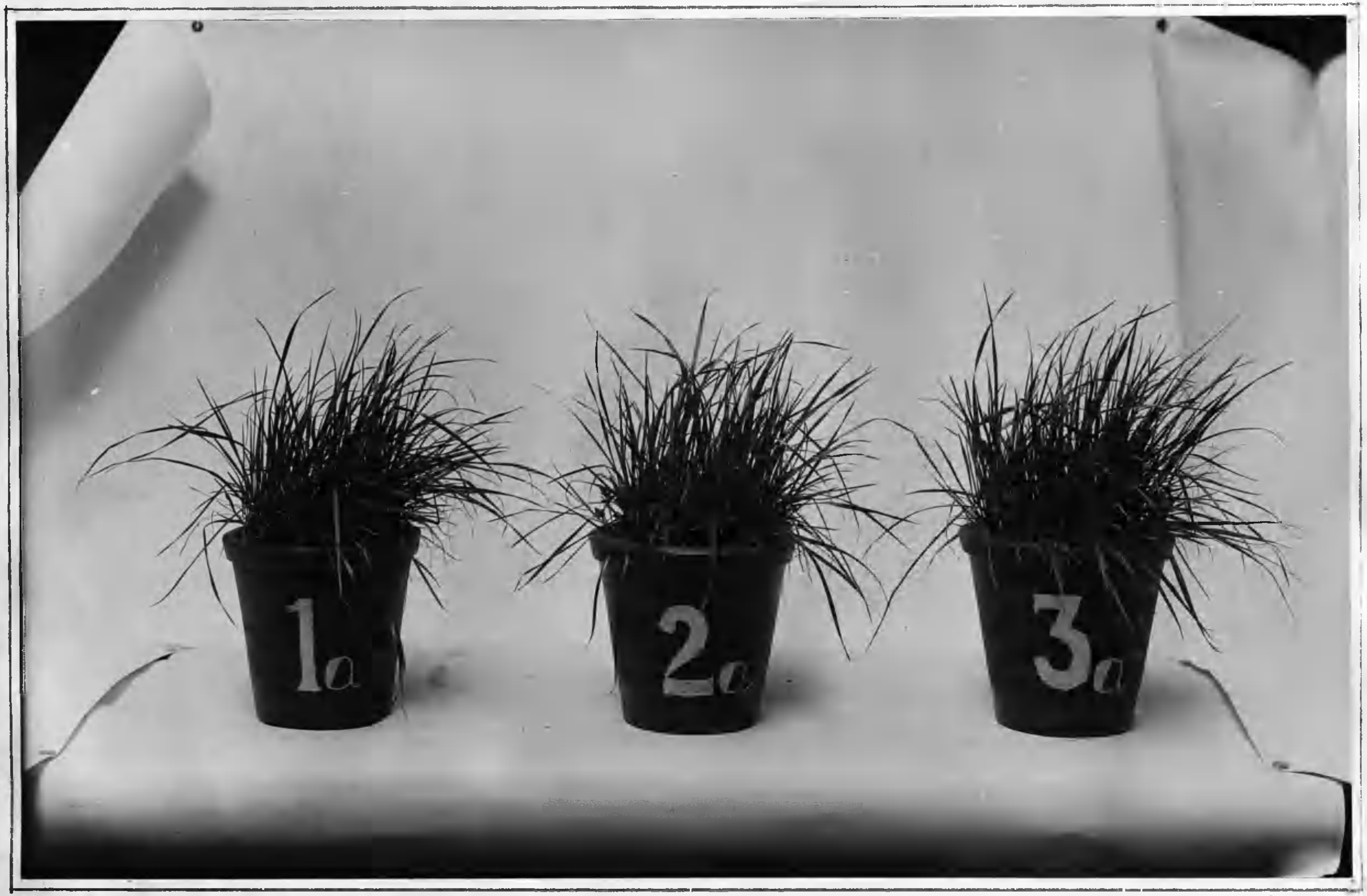

1a
2a
3a

PLATE 5.

1921 Trials

Pot 4.	Calcium Carbonate + Calcium Phosphate
Pot 5.	Magnesium Carbonate
Pot 8.	Ferrous Sulphate.


4a
5a
8a

PLATE 6.

1921 Trials

Pot 12.	Manganese Carbonate
Pot 14.	Calcium Carbonate + Calcium Phosphate + Manganese Carbonate
Pot 17.	Ferric Sulphate

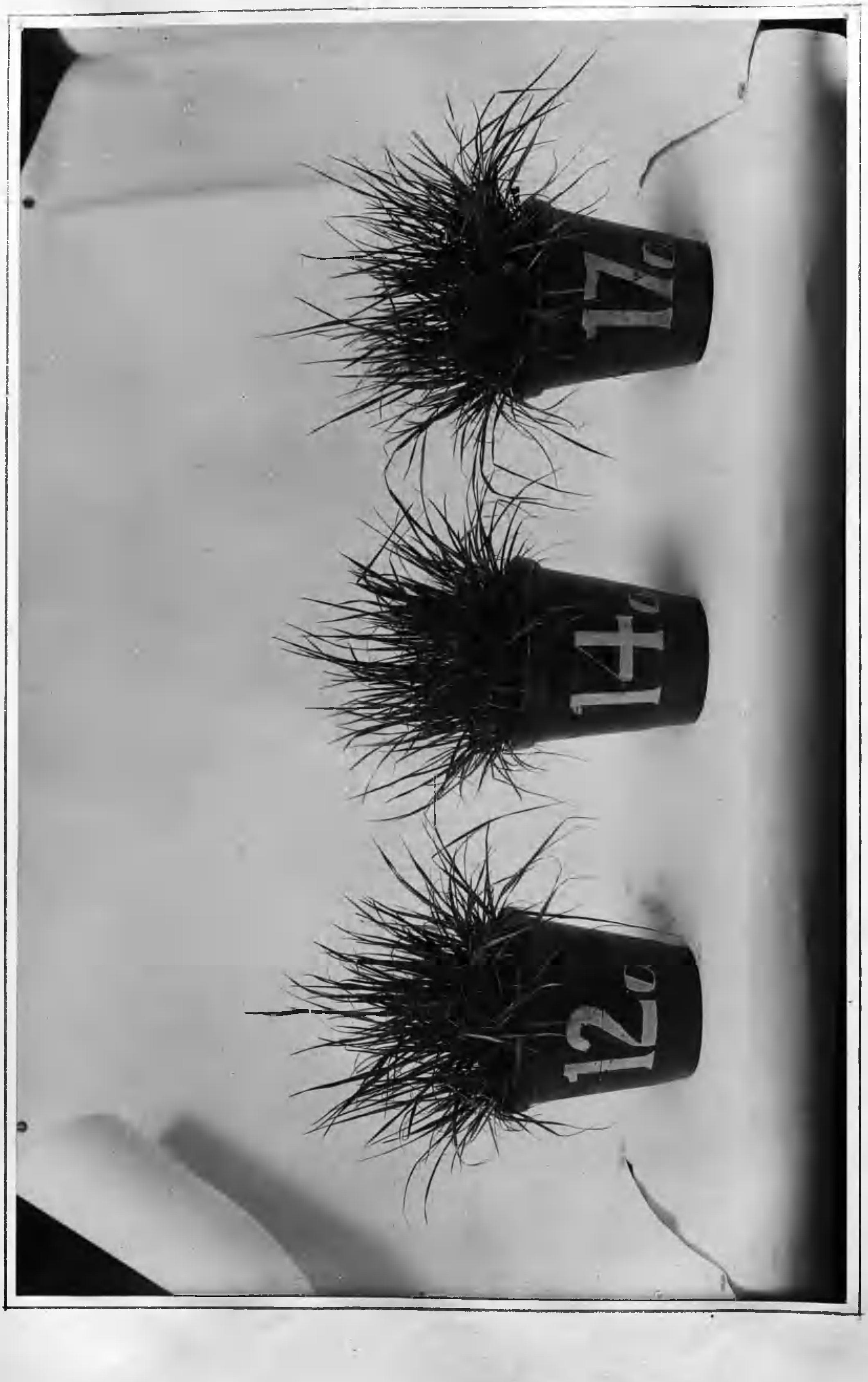

17c
14c
12c

PLATE 7

1921 Trials

Pot 18.	"Artificial Slag"
Pot 19.	'Fine' Open Hearth Fluorspar Slag
Pot 20.	'Coarse' Open Hearth Fluorspar Slag


18a
19a
20a

PLATE 8

1921 Trials

Pot 1.	Control
Pot 2.	Calcium Carbonate
Pot 19.	Fine Slag


1a
2a
19a

PLATE 9

1921 Trials

Pot 1	Control
Pot 3.	Calcium Phosphate
Pot 19.	Fine Slag


10a
3a
1a

PLATE 10.

1921 Trials

Pot 1.	Control
Pot 5.	Magnesium Carbonate
Pot 19.	Fine Slag


1a
5a
19a

PLATE 11.

1921 Trials

Pot 1	Control
Pot 19	Fine Slag
Pot 20	Coarse Slag


1a
19a
20a

PLATE 12.

1922 Trials - Residual Values

Pot 1	Control
Pot 2	Calcium Carbonate
Pot 3	Tri-Calcium Phosphate

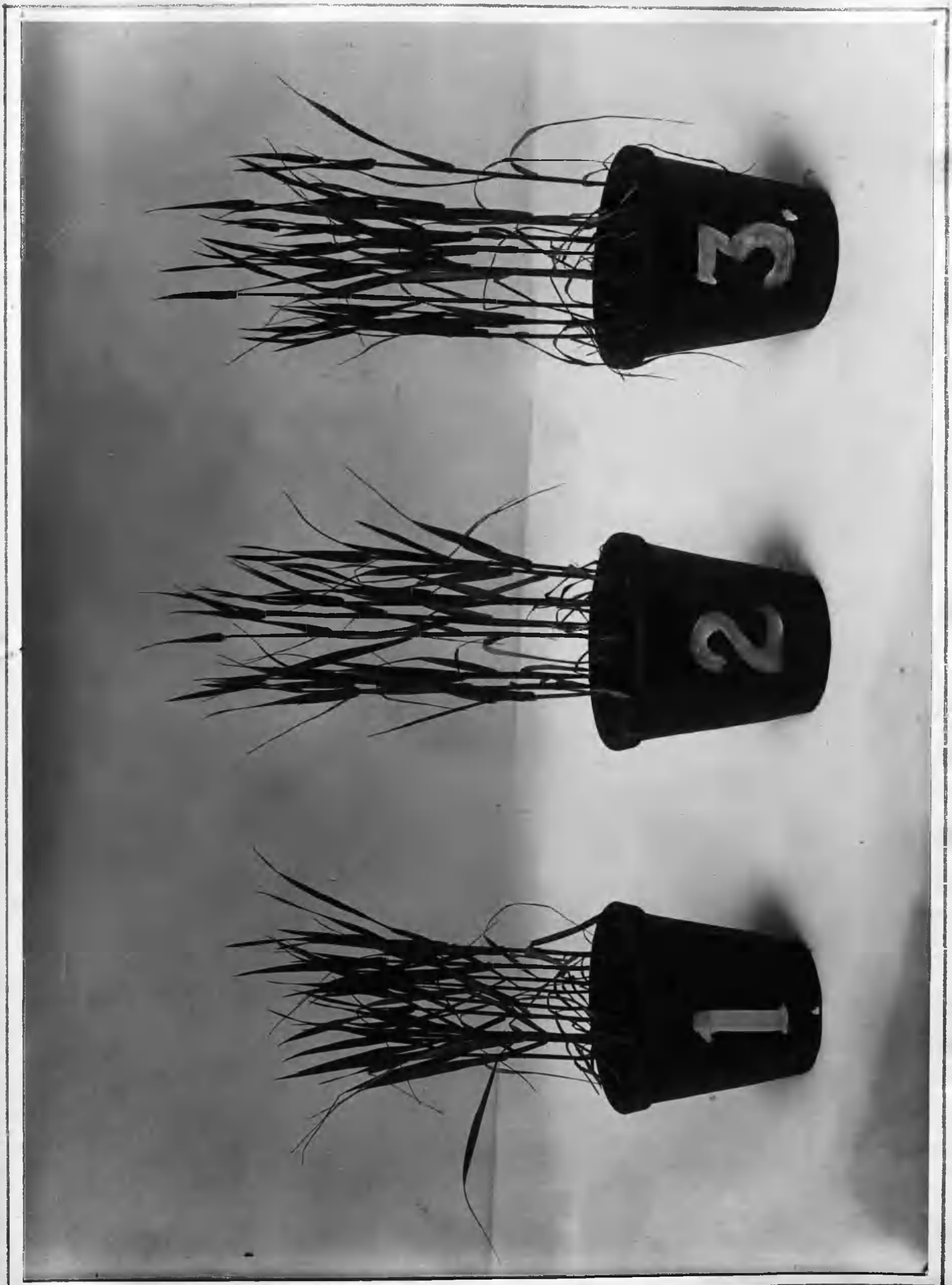

1
2
3

PLATE 13.

1922 Trials - **Residual Values**

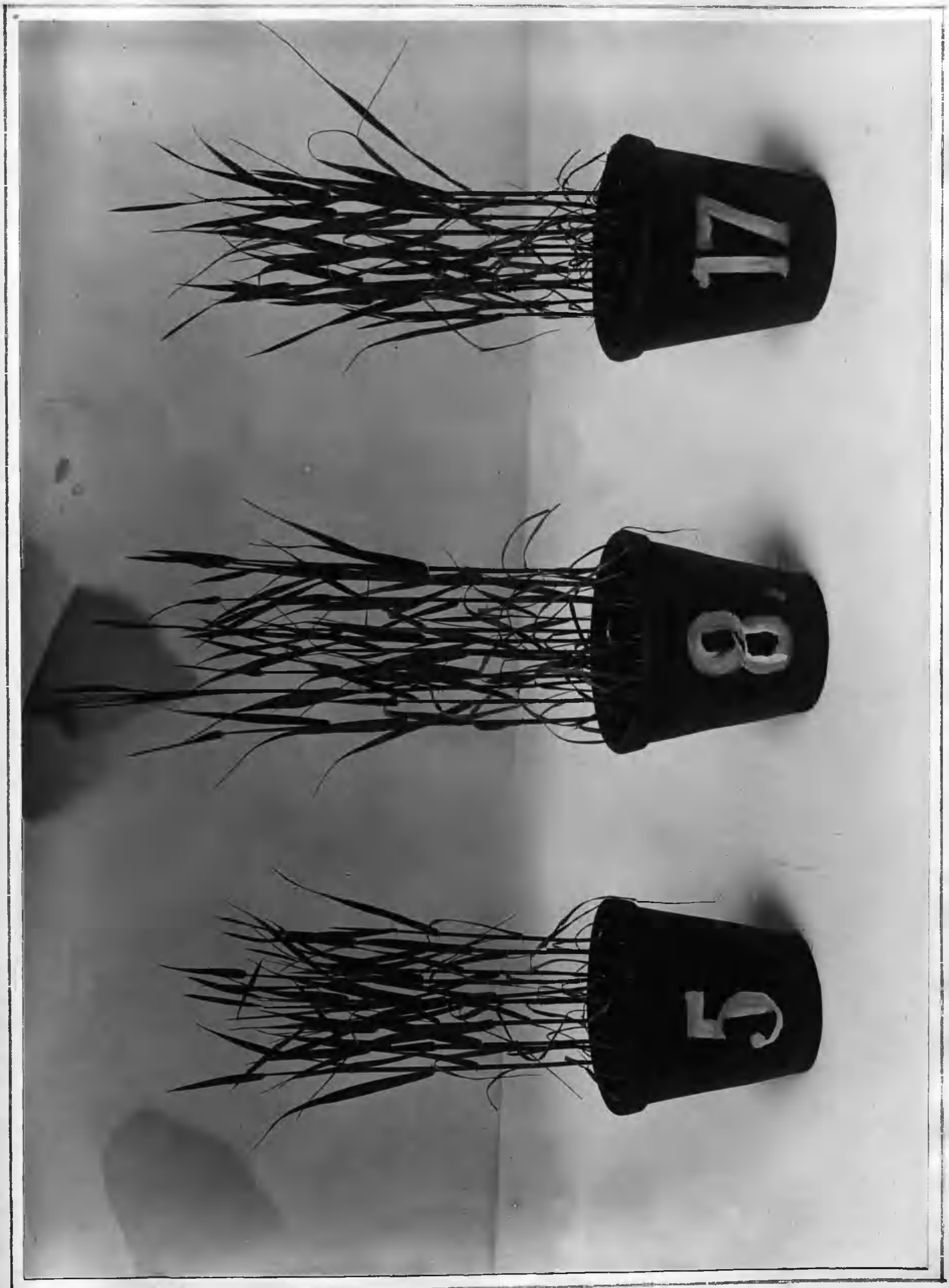
Pot 4	Calcium Carbonate + Calcium Phosphate
Pot 6	Calcium Carbonate + Magnesium Carbonate
Pot 7	Calcium Carbonate + Calcium Phosphate + Magnesium Carbonate


4
6
7

PLATE 14.

1922 Trials - Residual Values

Pot 5	Magnesium Carbonate
Pot 8	Ferrous Sulphate
Pot 17	Ferric Sulphate


5
8
17

P L A T E 15.

<u>1922 Trials</u> - <u>Residual Values</u>

Pot 12	Manganese Carbonate
Pot 16	Calcium Carbonate + Calcium Phosphate + Magnesium Carbonate + Ferrous Sulphate + Manganese Carbonate
Pot 18	Artificial Slag


12
16
18.

PLATE 16.

1922 Trials - Residual Values

Pot 1	Control
Pot 19	Fine Slag
Pot 20	Coarse Slag


1
19
20

PLATE 17

Effect of Silicon Compounds

Pot 1	Sodium Silicate
Pot 2	Magnesium Silicate
Pot 5	Magnesium Carbonate


1
2
5

PLATE 18

Effect of Silicon Compounds

Pot 3	Calcium Silicate
Pot 6	Fine Slag
Pot 7	Control


3
6
7

PLATE 19

Effect of Silicon Compounds

Pot 3	Calcium Silicate
Pot 4	Calcium Carbonate
Pot 6	Fine Slag


3
4
6

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RECOVERY OF POTASH FROM BLAST FURNACE GASES.

By Professor R. A. BERRY, F.I.C., and D. N. McARTHUR, B.Sc.

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RECOVERY OF POTASH FROM BLAST FURNACE GASES

By Prof. R. A. Berry, F.I.C., of the Chemical Department,
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and D. N. McArthur, B.Sc.

In 1913 the world consumption of Potash (K_2O) for all purposes amounted to close upon 1,000,000 tons, and of this Agriculture absorbed almost 90%, the remainder being used in the manufacture of chemicals, soap, glass, &c. During the last thirty years the total annual consumption rose from 58,580 tons to 867,883 tons, and the amount used in manufacturing processes increased from 39,453 tons to 91,299 tons. In the same period the quantity used for manurial purposes has grown rapidly, amounting in 1880 to 40%, in 1890 to 60%, in 1900 to 78%, and in 1910 to 89% of the whole. (1.) Although Agriculture absorbs such a large proportion of the total, the shortage caused by the war was not felt so quickly as it was in other industries. The crops for 1914 were already supplied, while the soil contained unexhausted stocks from previous applications of potash manures.

In addition there is consumed each year in the British Isles a quantity of farmyard manure estimated approximately at 40,000,000 tons, and this, after deducting losses during the making and storing, would yield about 110,000 tons of Potash (K_2O). (2.) While this is still available, the continued shortage seriously affects crop production, more especially the cultivation of the potato, which is peculiarly responsive to and dependent upon supplies of potassium salts.

In 1913 the total Potash consumption in the form of Potash Salts in the United Kingdom was 32,000 tons (3), practically all obtained from German sources, and of this amount agriculture absorbed 23,000 tons. (4.) For many years the extensive and easily worked deposits of the German " Kali-Syndicat " have produced sufficient quantities of Potash at a price which precluded the development of any sources in this and other European countries, with the result that, outside the enemy countries, very limited supplies were available after the outbreak of war. The stoppage of the German supplies has led to the investigation of other possible sources, and a brief account of some of these may be of interest. (5, 6.)

VEGETABLE SOURCES OF SUPPLY.

The value of the Potash salts from vegetable sources has long been known, and of these kelp is the most important. The kelp industry at one time was a flourishing one in Scotland, but in recent years it has been somewhat neglected. In the United States, however, systematic investigation of the Potash content of the Giant Algae has been in progress for several years, (7) with the result that it is estimated that 2,266,000 tons per annum of Potassium Chloride (KCl) could be obtained from the Algae growing on the Pacific Coast, (8) the dried kelp having an average Potash (K_2O) content of 20%. Although the growth of seaweed on the Scottish Coast differs radically from that on the Pacific Coast, it is possible that, even under pre-war conditions, the kelp industry in Scotland could be revived under proper organisation and with the recovery of all possible by-products, and at present the estimated annual production is from 1000 to 2000 tons of Potash (K_2O).

By such a development of the kelp industries local supplies of Potash salts of considerable value might be obtained in Scotland, Ireland, Norway, and Japan. Another local source to which attention has been directed within the last three years, is the ashes from various plants, and analysis shows the Potash (K_2O) content of some of these to be as follows : Hedge clippings, 10% (9); sawdust, 6% (10); banana stems 40-50% (11); bracken, 30-40% (12). The ash of this latter plant when cut in

June contains over 50% of Potash (K_2O), the percentage falling to about 35 in September.

MINERAL SOURCES OF SUPPLY.

There has also been considerable investigation of the various inorganic sources, and methods have been suggested for such Potash-bearing minerals as Alunite (13), Mica (14), Leucite (15), Felspar (16), and other silicate rocks (17-18), with the object of rendering the Potassium soluble. The cost of production has usually been too high to compete with the price of the Stassfurt deposits. Rhodin has, however, claimed to have found a successful process. In 1899 he described a method of rendering the Potash in Felspar soluble in water (19), and in 1911 he patented a process for converting the insoluble residue into white cement. (19.) The process is: " A mixture of about 10 parts of Felspar, with four parts each of lime and common salt, in fine powder, is strongly heated, but below the fusing temperature, for a considerable time. After cooling the mixture, which still remains in a powder, it will be found that the Potassium in the Felspar is in such a state that it can be dissolved in water, and will combine readily with sulphuric acid and other acids to form soluble salts suitable for manurial and manufacturing processes." Preliminary trials of the method (20) carried out in this country with Swedish Felspars proved satisfactory, with the result that it was decided to test the Felspar at Loch Eireboll (22) in Sutherlandshire and at Roche in Cornwall. In the case of the former locality the total Potash (K_2O) content is 8·6%, of which 60% is able to be rendered soluble, while the Cornish mineral contains 8% Potash, of which 75% can be rendered soluble in water. (23.)

Important new sources of Potash salts are the natural deposits which have recently been found.

Near Barcelona fresh borings have been made in a deposit known to exist there with the result that Potash salts were found at depths of 121, 196, 426, and 885 feet, but of these the last was the most important, and it is estimated that 3,675,000 tons of Potash salts can be obtained. (24.)

In Eritrea, on the borders of Abyssinia, a deposit, estimated to contain 1,000,000 tons of 80% Potassium Chloride (KCl) is being worked by a British Syndicate.

Among other well-known sources are the salt deposits of India and Chili, seawater and saline residues.

MISCELLANEOUS SOURCES OF SUPPLY.

The sugar industries and the scouring of wool also furnish small quantities of Potassium salts. From the latter source at least one wool firm in Scotland extract sufficient Potash salts from the wool to meet its own requirements.

INDUSTRIAL BY-PRODUCTS.

That the dust deposited from blast furnaces and kiln gases contained Potash salts (25) is by no means a new discovery. In 1884 a patent was taken out by Hugh Barclay and Robert Simpson, of the Harrington Iron Works, Cumberland, for the recovery of salts, especially Potash salts, from coke-fed furnaces.

References to similar patents occur in American literature. (26.) At the Riverside Portland Cement Company's works in California a Cottrell Electrical Precipitation Plant (27) was installed in 1911 for the purpose of precipitating the dust from the kiln gases, and it was found to contain Potassium salts, the raw material containing ·2% K_2O. Owing to the low price of Potash salts at that time the dust was not considered to be of any value, but it was allowed to accumulate. With the outbreak of war, however, the whole position changed, and this accumulated dust then became a product of considerable value. In 1915 the same Company every twenty-four hours was recovering from five kilns from 20 to 25 tons of dust containing 5 to 20% of water soluble Potash (K_2O). De Beers (28) calculated that 80,000 tons of Potash could be obtained annually from such sources in the United States. Wysor (29) found that the yellowish dust which accumulated at the bottom of the stone chequer work in the stoves and gas-fired boilers contained 15% of water soluble

Potash (K_2O). Since the war started he has gone into the question of the Potash content of the raw material and of its recovery from the furnace gases, and has drawn up a balance-sheet to show the weight of Potash charged into the furnace and the amount recovered and lost. He estimates the greatest loss to be in the primary and secondary washers, amounting to some 56% of the whole, while in the slag some 20% is lost. The amount recovered in the dust from the stoves and boilers is under 1% of the Potash charged. In 1916 an experimental Cottrell plant was installed, being connected to the gas main leaving one of the dust catchers, and he found that practically all the dust entering the plant could be successfully precipitated. This dust contained on an average about 10% of Potash (K_2O), the colour of which varied from a light to a dark grey. The quantity of Potash charged was 22·4 lbs. per ton of pig-iron produced, and deducting the amount of Potash in the slag and dust catcher, namely, 6 lbs., about 15 lbs. per ton of pig-iron appear to be left in the gases, which were then recoverable by the Cottrell process.

According to Burchord's (30) figures the Potash content of the iron ores varies greatly, from ·17% to 2·56% (K_2O), in some American ores the average being ·63%. Grasty (31), however, gives the average as 1·32%, the lowest being ·70% (K_2O) and the highest 2·29%.

The production of pig-iron in the United States in 1916 amounted to over 39,000,000 (32) tons, so that if Wysor's figures are correct then the flue dust from the coke-fed furnaces in the States is a great addition to the Potash supply.

In Scotland, however, the recovery of Potash from blast furnace gases is a rather different problem, as, not only is the Potash content of the iron ores used probably lower, but coal instead of coke is normally used.

In the case of the coal-fed furnaces much tarry matter is produced. With the coke-fed furnaces, as in England, this is absent, so that the gases are not washed but led from the dust catcher direct to the stoves and boilers, the dust being deposited in the dust catchers, tubes, stoves, and at the base of the chimney stalk.

Cranfield (33) states that from one furnace per week 20 tons of a coarse black dust are deposited in the dust catcher, 5 tons of a reddish dust in the stoves and boilers, and 1 ton of a cream-coloured dust at the base of the chimney stalks. The Potash (K_2O) content of each is 2·5%, 7·0%, and 10% respectively, and a total annual yield from the furnaces in Great Britain of 15,000 tons of Potash (K_2O) is estimated. His estimate is, however, too high, as he assumes that the Scottish furnaces are producing dust at the same rate as the English ones. Coke-fed furnaces are driven harder with a blast of 12 lbs. compared with 5 lbs. in the Scottish practice, and consequently more dust is produced in the English works.

As the amount of dust produced in the Scottish practice is relatively very small, the spent liquor, which, according to Wysor, is the main avenue of loss, seems more deserving of attention. So far as we are aware there are no published analyses of the spent liquors; while the analytical data showing the Potash content of the raw materials are almost equally unsatisfactory.

The Potassium is present mostly in combination with silica, and its amount will vary largely.

Probably the silicates of Potassium, at the high temperature reached at the base of the furnace, interact with other components of the charge liberating the Potassium as the oxide which, in turn, reacts with the sulphate and chlorides present to form Potassium salts. Cyanide of Potassium is found at certain regions in the furnace, but is again decomposed, the nitrogen being given off as ammonia and free nitrogen, and the Potassium probably as the oxide or carbonate. The high temperature vapourises the Potassium compounds, and the vapours, as they pass into the cooler parts of the furnace, condense in the form of fine dust particles which are carried over along with the dust from the fuel and ores. The heavier particles are deposited in the dust catcher and form a coarse black powder. Inside the main tube a thick coating of carbonaceous matter is formed, which is periodically cleaned out, and forms, along with the dust from the dust catcher, the "tube cleanings."

The furnace gases contain a large proportion of tarry matter from the coal, which condenses and encrusts much of the mineral matter.

Most of the heavy tarry matter separates in the condensers, and in settling carries down with it a considerable quantity of the fine dust. The rest of the tarry matter, the ammonia and most of the remaining fine dust, are then caught by the water during the cleaning of the gas in the scrubbers. The gases on leaving the scrubbers should only contain a very little mineral matter, and this is caught in the stove and boilers, forming the stove and boiler dust. The spent liquor, from which the bulk of tarry matter and the ammonia have been extracted, is at present allowed to escape except at Messrs Baird & Co.'s Lugar and Muirkirk plants, and at the Dalmellington Iron Co. Works, Dunaskin, where for several years the Potassium salts have been recovered by evaporating the spent liquors. Samples of the spent liquors and of the dusts were received for analysis towards the end of May, 1917, from the different plants in Scotland, and their Potash content were determined with a view to forming an estimate of the quantity of Potash which might possibly be recovered.

Consideration may first be given to the dusts:

FLUE DUSTS. Nine samples were received. The dusts were of a very fine powdery nature, but microscopic examination revealed a large number of minute crystals too small for identification. The colour varied from cream to purple, and some dusts were distinctly alkaline, while others were neutral to litmus paper. The water soluble Potash (K_2O) was first determined in each sample, and subsequently the total Potash in several samples.

TABLE I.

FLUE DUSTS.

Firm No.	Water Sol. Potash percentage	Colour	Action towards Litmus Paper	Yield per annum Tons	Value at 15s per unit of K_2O	Value at 4s per unit of K_2O
					£	£
1	11.06	Grey	Alkaline	21	174.2	46.5
2	19.49	Yellowish Brown	Neutral	10	146.2	40.0
3	6.59	,,	,,	5	25.2	6.6
4	4.59	Greyish White	,,	6	20.7	5.5
7	4.07	Reddish White	,,	2	6.1	1.6
8	8.58	Light Brown	,,	2	12.9	3.2
14	8.05	Purple	Alkaline	20	120.8	32.2
16	8.46	Cream	Neutral	5	31.7	8.5
* 17	3.13	Grey	Alkaline	300	704.3	187.8

* No. 17 Coke Fed Furnace.

Average % Water Sol. Potash in Dust from 8 Coal Fed Furnaces 8.86.
Total Yearly Yield of Flue Dust from 8 Coal Fed Furnaces 71 tons.
Total Yearly Value of Flue Dust at 15/- per unit K_2O £550 approx.
Total Yearly Value of Flue Dust at 4/- per unit K_2O £144 approx.

The water soluble Potash (K_2O) varied from 4·07% to 19·49%, the average being 8·86%. It was not possible to correlate colour and Potash content.

A qualitative examination of the dust usually showed in addition to Potassium the presence of Iron, Aluminium, Calcium, Magnesium, Sodium and Silica, while in many Lead and Zinc were also found. Chlorides, sulphates, and carbonates were the predominating acid radicles.

The highest yield of dust per annum at any one of the plants was 21 tons. The one plant using coke fuel gave a yield of 300 tons per annum, due to a greater blast, but the Potash content was low, namely, 3·13%. Excluding the latter, the total production per annum of flue dust in Scotland from the coal-fed furnaces does not reach 100 tons, and taking the present value of the Potash at 15/- per unit, the estimated total value is £550, whilst the estimated value of dust from the coke-fed furnace amounts to £700 per annum, as against £150 and £190 respectively if valued at the pre-war rate of 4/- per unit of Potash (K_2O).

STOVE DUST. Only three samples were received. The Potash content varied between 6% and 8% water soluble K_2O. With the exception of the plant using coke fuel, the yields are negligible. In this case the yield was 150 tons per annum, the total Potash content being 13·6% K_2O, and the water soluble Potash 7·6%. These values are given in Table II.

TABLE II.

STOVE DUSTS.

Firm No.	Water Sol. Potash percentage	Colour	Yield per annum	Value at 15s per unit of K_2O	Value at 4s per unit of K_2O
			Tons	£	£
3	7.87	Reddish Brown	1	5.9	1.5
14	6.86	Grey	6	30.9	8.2
* 17	7.65	White	150	860.6	229.5

* No. 17 Coke Fed Furnace.

Total Yearly Yield of Dust from 2 Coal Fed Furnaces 7 tons.
„ „ Value „ do. at 15/- per unit K_2O £37 approx.
„ „ „ „ do. at 4/- „ „ „ £10 „

The total Potash was determined in five samples of dust, and the percentage of the total Potash soluble in water ranged from 40 to 89.

TABLE III.

COMPARISON OF WATER SOLUBLE and TOTAL POTASH in DUST.

Firm No.	Dust	Percentage Total Water Sol. Salts	Total Sol. Potash (K_2O) in HCL	Water Sol. Potash K_2O	Percentage Total Potash Water Sol.
2	Flue	56.9	21.96	19.49	88.7
14	,,	25.8	11.13	8.06	72.4
15	Burnt Tube Cleanings	11.5	2.60	1.04	40.0
17	Flue	11.3	6.67	3.13	46.9
17	Stove		13.58	7.65	56.3

In Flue Dust Average% Total Potash (K_2O) Water Soluble 69.3.

TUBE CLEANINGS. Samples from 15 works were received. They were black, and contained a considerable amount of carbonaceous matter. The percentage of ash in the samples analysed varied from 53% to 74%. As the ash contained only a very small percentage of water soluble Potash, the highest being 2·7% and the lowest under 1% only a few samples were analysed. The value of these dusts is, however, high in comparison to the other dusts on account of the great quantities of cleanings annually produced. According to estimates supplied, the total quantity of tube cleanings produced per annum from the Scottish furnaces amounts to nearly 15,000 tons.

SPENT LIQUOR. Fifteen works supplied samples. Two samples were taken from each plant at an interval of one week. The method of sampling consisted in taking a ladleful—about ½ gallon—every hour during the 24 hours, and from the composite sample a further one gallon was drawn for analysis. The specific gravity, total solids, ash and water soluble Potash in the ash were determined in each sample.

TABLE IV.

TUBE CLEANINGS.

Firm No.	Percentage of Ash	Percentage of Water Sol. Potash K_2O in Ash	Yearly Yield Ash (App.) Tons	Yearly Yield of Tube Cleanings Tons	Value at 15s per unit of K_2O	Value at 4s per unit of K_2O
3	60.5	1.1	151	250	124.6	33.0
7	74.4	2.7	350	470	708.75	189.0
9	59.1	.3	236	400	53.1	14.2
12	53.5	2.5	1605	3000	3009.4	802.5
* 17	65.8	1.0	342	520	256.5	68.4

* No. 17 Coke Fed Furnace.

Average% Water Sol. Potash in Ash from 4 Coal Fed Furnaces 1.6.
Total Yearly Yield of Cleanings from 4 Coal Fed Furnaces 4120 tons.
Total Yearly Value of Ash from 4 Coal Fed Furnaces at 15/- per unit K_2O £3900 (approx).
Total Yearly Value of Ash from 4 Coal Fed Furnaces at 4/- per unit K_2O £1040 (approx).

Owing to the presence of the tarry matter evaporation was greatly retarded. The Cottrell processes are employed for precipitating coal tar products. (34.) If the temperature was kept above the vapourising point of the light oils, &c., the heavy tarry matter might be precipitated out with all the dust, and thus produce a partial cleaning of the gas. This pitch might then be burnt. (See later.)

The Potassium was present mainly as sulphate and chloride, except in one or two cases where a fair percentage of carbonate was found.

The ash was usually white or grey. The duplicate analyses varied considerably in many cases, but on the whole the agreement was considered satisfactory. The highest percentage of Potash K_2O found was 55·7% from firm No. 6, and the lowest 20·6% from No. 8, the average being 33·5%. The Potash content of the ash was high, but the yield of ash was disappointing. The highest yield obtained for any one plant was 318 tons at No. 12, and the lowest 17 tons at No. 8, while the total yield of ash was 1696 tons.

TABLE V.

SPENT LIQUOR.

Firm No.	Sp. gr. Average	One Gallon contains in grammes			Ash Yield in Tons Yearly Average	Water Sol. Potash Av. Percentage in Ash	Yearly Value of Potash at 15s per unit £	Yearly Value of Potash at 4s per unit £
		Dry Matter	Ash	Potash K_2O				
1	1.019	9.443	4.721	1.525	257	31.4	6152.4	1614.0
2	1.039	120.58	84.525	30.753	273	36.4	7452.9	1987.4
3	1.320	—	434.952	156.583	125	36.0	3375.0	900.0
4	1.035	9.824	6.773	2.452	58	36.2	1574.7	419.9
5	1.020	7.640	4.843	1.822	148	43.1	4719.5	1275.8
6	1.025	9.198	4.431	2.429	66	55.7	2757.2	735.2
7	1.017	6.065	3.990	0.826	50	20.6	772.5	206.0
8	1.027	4.558	1.587	0.321	17	20.6	262.7	70.0
9	1.013	8.622	5.257	2.029	95	38.2	2837.0	725.8
10	1.018	7.318	2.065	0.573	45	27.2	918.0	244.8
11	1.019	5.663	3.787	1.329	36	33.6	907.2	241.9
12	1.019	18.296	12.712	2.833	318	22.3	5286.8	1418.3
13	1.023	5.401	2.260	0.667	41	28.8	885.6	236.2
14	1.035	9.797	6.405	3.036	69	47.4	3833.0	654.1
15	1.026	10.460	5.448	2.179	98	40.0	2940.0	784.0

Average % Water Soluble Potash 33.5.

Total Yearly Yield of Ash from 15 Coal Fed Furnaces 1696 tons.

Total Yearly Value of Ash from 15 Coal Fed Furnaces at 15/- per unit K_2O £44,575 (Approx.).

Total Yearly Value of Ash from 15 Coal Fed Furnaces at 4/- per unit K_2O £11,513 (Approx.).

The factors which would account for the variation in yield comprise the number of furnaces in blast, the structural differences in individual plants, the efficiency of the washing, and the Potash content of the raw materials. Considerable variation must be expected in the raw materials according to the nature of the coal, the iron ore, and the limestone used. As stated above, published data showing the Potassium content of the raw materials are not available.

The Potassium salts could be extracted with water or the ash without further treatment might be used as a manure. The value of the ash is given in Table V. No. 1 plant yields 257 tons, containing 31·4% K_2O soluble in water, and at the present market price of Potash, namely, 15/- per unit, this quantity is valued at £6052, or at £1614 on the pre-war basis of 4/- per unit K_2O. No. 12 plant yields 318 tons, containing 22·3% K_2O soluble in water, and valued at 15/- per unit of Potash represents £5286, or £1418 on a 4/- per unit basis. The total value of 1677 tons containing an average of 33·5% water soluble Potash (K_2O) is £44,312 on a 15/- per unit basis and £11,500 on a 4/- per unit basis. These data refer to 15 plants using coal fuel and having a total of 72 furnaces in blast. The question of the advisability of evaporating the spent liquor must be decided by each firm for itself. When the yield of ash reaches 100 tons and its value between £2500 and £3000, and when spare heat and exhaust steam are available, the matter is worthy of serious consideration. It is, however, necessary to remember that the price per unit of Potash (K_2O) in pre-war days was about 4/-, and it may again fall to that figure after the war. The erection of evaporating plants at most of the works would be necessary, and, at the present time, the cost of so doing would be high. Preliminary concentration of the liquors where exhaust steam is available is recommended, and owing to the scum of tarry matter which forms on the surface this must be facilitated by mechanical stirring and splashing with furnaces of the Porion type or by other means. According to an estimate supplied to us by Messrs Gillespie & Son, consulting engineers, Glasgow, an evaporating plant of this kind to deal with 20,000 gallons daily would cost £4000, and to deal with 100,000 gallons daily would cost £14,000. If spare heat is available then the capital outlay may be wiped off in a few years. Even if the value of the Potash salts recovered is sufficient only to pay the running expenses of the plant, then evaporation of the spent liquor is perhaps the best way for its disposal.

Sources of Loss. Considering how such relatively small quantities of Potash are recoverable in the dust and spent liquor, the question arises what is the weight of Potassium charged into the furnaces and what are the sources of loss? The principal losses would be in the pitch and the slag.

"*Pitch*" from blast furnaces contains much more mineral matter than that from coke and coal gas plants. According to the conditions of deposition and recovery of the tarry matter, the percentage of the amount of ash in the pitch will vary in different works. Figures which have been supplied to us indicate that the ash content varies from 10% to 25%, the average being about 15%. Devices, such as filtration, centrifugalisation, and so forth are in use to remove the ash. It is also possible that the percentage of Potash in the ash from any one plant may vary. An analysis of the pitch from No. 1 plant shows it to contain 17% of ash and the ash 8·8% of water soluble Potash (K_2O). The yield of pitch per ton of coal burnt varies from 98 lbs. to 140 lbs. at different plants, the average being about 112 lbs. The pitch left after the recovery of the light oils, &c., from the tar also varies at the different works, as, for example, at No. 1 plant it was 70% of the tar, while Gray and Mellamby (36) put the figure at 65%. (36.)

When the ash content is 15% and 8% of this is water soluble Potash it would, with pitch at 12/- per ton, pay to burn the latter as fuel and collect the ash. On the basis of these figures, and ignoring the insoluble Potash, 1 ton of ash could be obtained from 6·6 tons of pitch, and, with the market price of Potash at 15/- per unit (K_2O), would be worth £6 without taking into account the fuel value, while the initial cost of the pitch at 12/- per ton would be approximately £4. At the pre-war rate of 4/- per unit (K_2O) the ash would only be worth £1 12/-. The burning of the pitch might produce difficulties, but these doubtless could be overcome.

The coal consumed in blast furnaces in Scotland in 1915 amounted to 1,478,924 tons, so that on an average production of 112 lbs. pitch per ton of coal, then the total yield of pitch would be about 74,000 tons. If all the pitch were burned 11,092 tons of ash containing 8% Potash (K_2O) would be obtained, and at present prices would be worth £41,596 and at pre-war prices £11,100.

"*Slag.*" The quantity of slag produced per ton of pig-iron varies according to the purity of the iron ore and limestone, and the weight of slag also varies from 9 cwts. to 23 cwts. per ton of pig-iron produced at the different plants. The slag contains Potassium (·24% K_2O was found in slag from firm No. 1), but at present it does not seem feasible to recover this.

BALANCE SHEET. The amounts of Potash in the raw materials—coal, coke, iron ore, and limestone, and in the slag and other by-products from No. 1 plant have been determined, and are as follows:—Spent coal, ·040% K_2O; coke, ·121% K_2O; iron ore, ·128% K_2O; limestone, ·136% K_2O. A balance-sheet was drawn up with the following result:—

TOTAL POTASH CHARGED INTO FURNACE 7.6 lbs. p. ton of pig iron.

POTASH RECOVERED—

In spent Liquor ..	1.4	lbs. p. ton of pig iron
In Flue and Stove Dust	.04	,, ,,
In Pitch	1.7	,, ,,
In Tube Cleanings ..	.2	,, ,,
Acc. in Slag.. ..	2.7	,, ,,
Total ..	6.04	lbs. p. ton of pig iron

Unaccounted 1.6 lbs. p. ton of pig iron.

The deficiency is due to other sources of loss in the furnace and in the running off of the slag, pig-iron, &c.

The iron ore was the principal source of the Potash, while the coal did not supply much more than the limestone. In contradistinction to these results Sir Lothian Bell states in his work on "Chemical Phenomena of Iron Smelting" that the Potash is derived from the coal. (37.)

The balance-sheet is in great contrast to that obtained by Wysor. Too much stress, however, cannot be laid on the fact that our figures are only applicable to the raw materials and to the plant in question. Although it has not been possible in the time at our disposal to obtain similar figures from other works, these figures may be extended generally to those plants using Welsh limestone and a mixture of Spanish ores. Thus taking the production of pig-iron in Scotland for 1916 at 1,144,756 tons and the Potash charged into the furnaces at 7·6 lbs. per ton of pig-iron, the total weight of Potassium would amount to 3884 tons, more than one-half of which is recoverable.

The total quantity of Potash recoverable from the Potash bearing by-products from blast furnaces produced in Scotland from 12 Companies, including 17 works and 102 furnaces, is as follows:—

	Tons K_2O
Spent Liquor 1,694 tons containing 33.5% wat. sol. Potash ..	567.4
Flue and Stove Dust about 100 tons containing 8% wat. sol. Potash ..	8.0
Pitch Ash about 11,092 tons containing 8% wat. sol. Potash	885.8
Tube cleaning Dust about 8,250 tons containing 2.5% wat. sol. Potash	206.0
Total production ..	1667.2

The figure is, relatively, a very small one, but it represents water soluble Potash. It is hardly possible with the data we have to estimate approximately what the total amount of insoluble Potash would be. The insoluble Potash might be rendered soluble by a process similar to that of Rhodin. The heat from burning the pitch and tube cleanings could be utilised for evaporating the spent liquor.

As the total requirements of Potash for the British Isles is estimated to be 32,000 tons per annum, there is good reason to believe that if the different sources of Potassium in this country to which attention has already been drawn were developed to the fullest extent the country's requirements in Potash salts would be more than met.

In any scheme of development of this nature, after war conditions have passed away, it must always be borne in mind that if the Alsatian deposits come into the occupation of their rightful owners, as they must, there will be available an almost unlimited supply irrespective of the deposits in Germany. (37.)

In conclusion, we wish to thank the different Companies for their very sympathetic co-operation in the work, and in particular Mr A. K. McCosh for his help and advice at every stage of the investigation.

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DISCUSSION.

The Chairman (Mr J. McLeod) said that they had all been greatly interested in this most opportune paper by Professor Berry, and he was sure that the greatest compliment they could pay him would be to have a good discussion on it. He would, therefore, now invite those present to express their views on the subject.

Mr Edwin H. Lewis said that there were one or two points he should like to refer to in connection with this most interesting paper, interesting to him as representing one of the blast furnace owners. In the paper written by Mr R. J. Wysor, which appeared in the Bulletin of the American Institute of Mining Engineers for January of this year, he stated that he could not discover any record whatever as to the actual sale or commercial disposal of flue dust for its potash content until this was inaugurated in their plant at Bethlehem. He (Mr Wysor) evidently did not know very much about the Scotch practice, as he (Mr Lewis) understood that, after various attempts, at various works potash had been recovered from the flue dust, or spent liquor, which really came to the same thing. At Wishaw certainly it had been done some years ago, when they had nothing better to do with their waste gas. But they had something better to do with it at the present time. Another point he should like to refer to was with regard to the mention in the early part of the paper of the recovery from cement plants. He should like to know whether the particular cement plant in California was working on the wet or the dry process. He should imagine it would be working on the wet process, where only a small quantity of dust was produced which would be more in the nature of a pure fume, and, consequently, much higher in potash than in the case of a cement plant working on the dry process, where the amount of dust was comparatively large. Professor Berry mentioned that the potash which went into the slag was evidently lost. Personally, he thought this rather a rash statement to make, and he did not see any reason why potash which was carried away in the slag might not—he did not say that it was—be recoverable from the dust from the cement plant using the slag unless it was lost in the atmosphere at the time of running the slag out from the blast furnace. But if the potash was not lost at the moment of blowing the slag out of the furnace, it might conceivably be recovered from the flue dust at the cement plant. He had that morning received the result of an analysis of flue dust taken from the dust chamber close to the chimney. There was no trace of potash at that point, so it was quite possible that the temperature at the base of the chimney would be rather high, and that if there were any potash carried to the cement works in the slag it went up the chimney and was lost. Another question was—Had the writers of the paper any knowledge of any pockets of material high in potash having been found in the lining of a blown-out blast furnace? He believed that something of the kind had been found in some of the American furnaces. Any information on this point would, of course, not be of much value with regard to the recovery of potash, but would be very interesting as throwing light on the reactions due to potash and cyanides. And what was the effect with regard to the reduction of ore? It was believed by some people that a considerable amount of ore was reduced through the action of the cyanides. One reason suggested why the blast furnace did not work up to its full output for some time was because it required some months before the amount of alkalis in the furnace came up to the normal level. One other point—with regard to the spent liquor. Supposing it was possible to remove certain other impurities from that spent liquor, would the presence of potash in solution interfere with the use of that same liquor for the recovery of ammonia? He should like Professor Berry or some other chemist to answer this question. It opened up rather an interesting possibility of concentrating potash in the spent liquor to the point at which it would be profitable to recover the potash by evaporation.

Dr C. H. **Desch** said that he would have liked if Professor Berry could have told them how it was that the Rhodin process, which had been in existence for a considerable time, had not yet given any results worth speaking of. He understood him to say that a good yield of potash had been obtained; but the process was not a new one. He himself had seen Rhodin's white cement more than ten years ago, and, as far as he could say, the process was scarcely changed since then; and, if it were going to give any practical results, one would have expected them to have been attained ere now. The figures shown for recovery seemed in a sense artificial, because the value of the potash was taken at 15/- per unit. This certainly was the present price of potash; but, when the war was over, that would fall very rapidly, because then they would have the competition of the Alsace deposits with the German, and the prospect of these Spanish and other deposits being opened up. They must, therefore, look for a rapid fall in the value of potash. These figures, he took it, applied to Scotch works, and it would be interesting to know if Professor Berry had any figures available from English works. He supposed that, ore being the source of potash, the nature of the ore would make an immense difference. He wondered whether, in the case of the coke-fired furnace, the increased yield there was actually due to the fact the coke was used or to the fact that the ore used was different in character. So far as the paper went, it seemed to show that the prospect of recovering potash profitably in Scotland after the war was very poor indeed. Taking the paper all over, however, it was a most interesting contribution.

Dr **Carrick Anderson** said that he did not intend to make any lengthy remarks on the paper; but he had with him some figures which he thought might be considered as worthy of putting on record just by way of supplementing those given by Professor Berry. On the average his figures deviated very considerably from those stated by Professor Berry, and the results lent more to the American figures quoted by the latter. They tried to find out how much potash went into the furnace, and how much potash went out in different directions; but they did not differentiate as to the directions in which the potash went when it left the top of the furnace. They found out how much went into the slag and how much went away in the metal. This was a point that had not been touched upon by Professor Berry, and at first one was inclined to think that to look in a metal for potash was rather absurd; but, as a matter of fact, very careful analysis showed that it was not entirely free from metallic potassium. In making their calculation they based upon 38 cwts. of iron ore, 37 cwts. of coal, and 6 cwts. of limestone, giving 1 ton of pig-iron and 14 cwts. of slag. The hematite iron ore that was going into the furnace showed 8·02 lbs. of potash per ton, the coal 3·02 lb., and the limestone 1·93 lbs. per ton. Coming out of the furnace, the hematite iron gave potassium equivalent to 0·36 lb. of potash per ton, and in the slag they found 4·39 lbs. of potash. For each ton of iron ore entering the furnace there was found 21·4 lbs., and on the same basis there was found leaving, in the metal and slag, 3·5 lbs., so that apparently there was available for recovery in one form or another 17·9 lbs. of potash per ton. They did not differentiate between the directions in which it went. They also found soda associated with the potash, which rather exceeded the potash in amount. The calculations they had made with regard to the pitch showed very much the same figure as Professor Berry had quoted. One word about the lees water. It was apparently very varied in composition. They found in the lees water in one works as carbonate about 1 grm. per litre; in another works only about one-tenth of this. In the lees water where the larger amount occurred the bulk of the potash was carbonate and a small part only chloride and sulphate. He gave the foregoing figures in supplement to those quoted by Professor Berry in the hope that they would help the paper.

The CHAIRMAN (Mr J. McLeod) said that he felt sure there was a good deal more to be said on this subject. One of the most curious samples of flue dust that he personally came across was at the Provan Gas Works, Glasgow. About ten years ago he found there a most curious sort of cream-coloured deposit, and, on analysis, this proved to be zinc oxide, with, he was speaking from memory, about 1½% of potash. He published the analysis in the Journal of Gas Lighting at the time, and asked if any similar experience had been noted elsewhere; but his query failed to elicit a reply. He looked at the deposit, which was considerable in amount, and thought that it might prove useful as a manure on account of the high percentage of phosphoric acid present in it. He tested it on the grass, but the result was disappointing, for the grass disappeared very rapidly and completely.

The CHAIRMAN said that, if no other members of either body wished to speak on the paper, he should now call upon Mr Cunningham, Vice-President of the West of Scotland Iron and Steel Institute, to move a vote of thanks to Professor Berry for his address.

Mr WM. CUNNINGHAM, Vice-President, West of Scotland Iron and Steel Institute, said that he accepted the invitation of Mr McLeod with pleasure. Before proceeding to move the vote of thanks to Professor Berry, he should like to claim their indulgence for a minute or two, because he thought this a most unique occasion in being the first time, so far as he could recall, that the members of the West of Scotland Iron and Steel Institute had been associated with a kindred Scientific Society in a joint meeting. This was a spirit which he thought ought to be further cultivated, and he felt that he was voicing the feelings of the members of their Institute and of their Council when he said that they should take the earliest opportunity of returning the compliment. He must also thank Mr McLeod for the generous way in which he had explained his position in the chair. He said that the West of Scotland Iron and Steel Institute had waived their right to that; but, as a matter of fact, they had no right. He might explain that one of their members of Council interested in blast furnace recovery from the waste gases suggested that this subject would be a very suitable one for their syllabus. They at once wrote Professor Berry, to learn, however, that they had been forestalled by the Society of Chemical Industry. That Society, however, were good enough to express a desire that they should join with them in hearing Professor Berry, so that they were really present this evening at the invitation of the Society of Chemical Industry, and, therefore, had no right to the chair. Now he came to the main part of the business which had brought him to his feet, and that was to propose a vote of thanks to Professor Berry for his most interesting paper. Professor Berry, of course, represented himself as an individual; but he also represented, as they knew, the Agricultural College, and, further, he in a way made a departure which they all welcomed in that he represented the Ministry of Munitions. He thought there was no question whatever as to the paper being most interesting; but he was inclined, speaking from the commercial side of the matter, to favour the view expressed by Dr Desch that, looking to the fact that there were such enormous natural deposits that would be available after the war, there was very little encouragement for blast furnace proprietors to instal a plant on the 15/- unit basis. That, however, did not detract from the paper being extremely interesting, and had been submitted to them by Professor Berry in a very capable manner. Certainly, like all such papers, it contained a great mass of figures, which were a little bit difficult to digest right away; but, once the paper was in printed form, there would be, at least so far as their Institute was concerned, the usual opportunity for sending in written communications; and he hoped that, with these additions, they should have in the end a most interesting and valuable record of the subject. He would simply ask them now, on behalf of the joint Societies, to accord to Professor Berry a very hearty vote of thanks for the trouble he had taken in preparing and submitting to them this very excellent paper.

The vote of thanks was most cordially given.

Prof. Berry said that, on behalf of Mr McArthur and himself, he had to thank Mr Cunningham for his kind remarks, and the meeting for their cordial vote of thanks. In reply to some of the questions raised, he should first like to say that in the short time at their disposal they had not been able to make anything like the complete or thorough investigation which such a subject required. It meant the carrying out of a large number of analyses to determine the extent of the variation in the potash content of the coal, coke, iron ores, and the limestone; but they had only time to make analyses of the raw materials used at one plant. To obtain the data given in the balance-sheet they took the weight of the material charged into a number of furnaces, and the weight of the by-products obtained from them, and knowing their potash content they were able to calculate the weight of potash passing in and out of the furnaces. In addition, they took into account the conditions under which that particular plant was working as regards by-products produced and as regards the raw materials used. The figures obtained were a great surprise. Knowing the results obtained in the United States, they fully expected to find that the potash charged into the furnace was a very much larger figure than was actually obtained, and it was quite possible that, using coal, coke, and limestone from other sources, they might get figures varying very considerably from those which they had obtained. The ore used was a mixture of Spanish ores principally, and the limestone was Welsh. As regards the price per unit of the potash it was necessary to bear in mind that the present price, namely, 15/- per unit, would in all probability rapidly fall to the pre-war figure, namely, 4/-, after the war, and this would obviously require to be taken into account in deciding whether or not it was worth while putting up an evaporating plant. The current market price would be obtained for the potash contained in the dusts and in the pitch ash, the former by-products they already had and the latter could be procured if it was thought worth while without any additional capital outlay. With regard to the Rhodin process, the only information which he had was that contained in a recent publication of the Journal of the Board of Agriculture, in which it was stated quite clearly that the working on a commercial basis of the deposits of felspar in this country by the Rhodin process was a very promising one. With regard to the question of cyanides, other members of the audience had far greater experience on this subject than he had, and were better qualified to express an opinion as to the functions of cyanides in the blast furnace industry; and as regards the cement process in California he had no information. So far as he knew of developments in England, he was led to believe that there was a scheme in hand for utilising the whole of the flue dust produced from coke-fired furnaces, and he understood that the amount of potash obtainable from that particular source would represent a considerable amount. With regard to the concentration of the spent liquor, he had had no experience on a large scale. They found in the laboratory that there was some difficulty in concentrating the spent liquor, because they got coatings of tarry matter on the surface which retarded evaporation. It had been remarked by one of the speakers that the Ministry of Munitions was interested in the subject matter of his paper; but he would like to point out that it was the Board of Agriculture who brought up the question, and asked him if he would enquire if it were possible to get much potash from blast furnace gases, and it was to answer their enquiry that this work was carried on.

Mr Cunningham proposed a vote of thanks to Mr McLeod for his conduct in the chair, and this was accorded in the usual fashion.

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The Constitution of Basic Slag

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The Constitution of Basic Slag

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THE work which is described on the following pages was commenced with the intention of elucidating certain problems in connection with the utilisation of basic slag for agricultural purposes. At an early stage it was realised that the results of previous observers did not fit in with our examination of certain types of slag; consequently it was decided that the subject of the constitution of basic slag required a further investigation, and it was obvious that such a re-investigation was a necessary prelude to any research on the agricultural side of the problem. The present paper contains the results of microscopic and chemical examinations of a number of slags from basic steel furnaces, both open hearth and Bessemer. In each case the slag examined was material taken from a late stage in the run of the particular furnace and cooled on the slag tip in the ordinary way. Unfortunately no data were available regarding the particular history of each run. Hence, the results must only be regarded as giving an idea of the constitution of the cooled slags. Any deductions from these results which may be made concerning the running of furnaces and so forth have been advisedly postponed until the results of some future work, on which one of us is at present engaged, become available.

In the first part of the paper a summary of previous literature on the subject is given, and this literature discussed briefly. The second part contains a description of the microscopic characters of the various slags examined; while in the third part the constituents and structures are discussed in relation to the chemical analyses of the particular slags.

For samples of the slags and for assistance in various other ways we are indebted to the following firms:—Messrs. Leeds Phosphate Co., Bolckow, Vaughan & Co., Ebbw Vale Iron, Steel and Coal Co., Brymbo Steel Co., North-East Steel Co., Shelton Iron, Steel and Coal Co., Alfred Hickman Ltd., Parkgate Iron and Steel Co., The Lilleshall Co. Ltd., and Stewarts & Lloyds Ltd.

In 1883 A. Carnot and A. Richard[1] examined some prismatic blue crystals from a slag, and found them to consist of a mixture of calcium phosphate and silicate. In the same year G. Hilgenstock[2] isolated large brown crystals, belonging to the orthorhombic system, and having the composition $4CaO.P_2O_5$. These crystals, which were thus tetracalcium phosphate, occurred as thin rectangular scales set in an apparently amorphous groundmass. Two similar types of crystals were observed by A. von Groddeck and K. Broockmann,[3] who concluded that both were forms of calcium tetraphosphate, the silica of the blue crystals being unnoticed, possibly on account of the paucity of the material available for analysis. The blue material which Ahrens thought to be a phosphate of lime was probably Carnot's mixed crystals. In 1886 E. Jensch,[4] on the basis of chemical analyses, indicated a hypothetical constitution for basic slag, the most important compounds, which he assumed to occur being calcium-silicophosphate, tetracalcium phosphate, and calcium ferrite.

In 1887 Stead and Ridsdale[5] published an account of several types of crystals which they had isolated from a basic converter slag; some crystallographic details by H. A. Miers were also included. The crystals so obtained were examined microscopically, and a chemical analysis of each type was made. Although the materials were naturally somewhat contaminated by the adhering slag, the chemical data are sufficient to indicate the essential composition in each case.

The various minerals isolated were:—

(a) *Tetracalcium phosphate.* This occurred in the form of relatively large tabular crystals, rectangular in shape, and having two imperfectly developed cleavages perpendicular to the tabular form. The crystals, which were transparent and of a faint yellow colour, showed slight pleochroism, and appeared to be orthorhombic.

(b) *Calcium silicophosphate.* This material was found in the form of stout prismatic crystals of a blue colour and having well-developed crystal

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[1] A. Carnot and A. Richard, Compt. Rend., 97, 316, 1883; Bull. Soc. Min., 6, 237, 1883.

[2] G. Hilgenstock, Stahl und Eisen, 3, 498, 1883.

[3] A. von Groddeck and K. Broockmann, Stahl und Eisen, 4, 141, 1884.

[4] E. Jensch, Ber., 19, 3093, 1886.

[5] J. T. Stead, C. H. Ridsdale and H. A. Miers, Journ. Iron Steel Inst., i, 222, 1887; Journ. Chem. Soc., 52, 601, 1887.

faces. Goniometrical measurements showed the crystal system to be orthorhombic. The crystals were markedly pleochroic, the colour varying from a faint blue to an intense sapphire tint.

(c) The third type of crystal appeared, on analysis, to be *tetracalcium phosphate*, containing about ten per cent. of impurity, mainly of the nature of silicate of iron, with much of the iron in the ferric condition. These crystals, which were of prismatic habit and had a hexagonal cross-section, showed pyramidal cleavage, and, from their optical properties, apparently belonged to the hexagonal system. They were also markedly dichroic, the colour, in plane polarised light, varying from light to dark brown.

(d) Crystals were also found with a "feathery" or fern-like habit, and on analyses these proved to be composed of ferrous and ferric oxides, lime, and magnesia.

(e) Finally, two varieties of "black, spear-shaped crystals which resembled flakes of graphite" were found, one being attracted by the magnet and the other unattracted. Each consisted mainly of lime, ferric oxide, and alumina, but the magnetic material also contained about eight per cent. of ferrous oxide.

About the same time H. Bucking and G. Linck[6] published the results of a detailed chemical and microscopical examination of similar material. They isolated tetracalcium phosphate, and verified its orthorhombic nature. The blue silicophosphate, however, they showed to belong to the monoclinic system, and not to the orthorhombic, as Miers had indicated. Analyses of the crystals indicated that their composition was approximately

$$4Ca_3P_2O_8,\ 3Ca_3SiO_5,$$

part of the calcium being apparently replaced by ferrous iron. They found a third type of crystal belonging to the hexagonal system, and approximating in composition to

$$4Ca_3P_2O_8,\ Ca_3SiO_5.$$

As the crystals contained both ferrous and ferric iron in small quantities, and had optical properties similar to those of the hexagonal compound described by Stead and Ridsdale, it is probable that the two are identical. According to Bucking and Linck, in cooling the slag from its highest temperatures, the rhombic tabular crystals separate out first, then the hexagonal type, and finally the blue monoclinic material.

These conclusions were vigorously combatted by G. Hilgenstock,[7] who maintained that the silicate in the silicophosphates was present merely as an impurity, and that the various crystals were different forms of the tetrabasic salt, the occurrence of any particular form depending on the conditions prevailing at the time of formation. He endeavoured to synthesize this salt, but owing to the difficulty in obtaining sufficiently high temperatures he invoked the aid of calcium fluoride as a flux. Instead of orthorhombic crystals, the forms he obtained were hexagonal, and there is little doubt but that they corresponded to the mineral *fluorapatite*. An eariler attempt to "synthesize" basic slag from iron phosphate and lime was made by A. Frank.[8]

In 1892 G. Förster[9] investigated the decomposition of the tetrabasic phosphate. In his endeavours to prepare this and some similar compounds he obtained an analogue of apatite with the formula $CaO.3Ca_3P_2O_8$, and stated that the latter is found in the residual material when basic slag is treated with citric acid. Such a mineral, in which the calcium fluoride and chloride of the apatite is replaced by calcium oxide, has been described by A. F. Rogers[10] under the name of *voelckerite*. Further details concerning the crystallography of tetracalcium phosphate were given by Termier and Richard[11] in 1895. In the latter year the whole question of the nature of the compounds in the slag was reviewed by Carnot.[12] He criticised Hilgenstock's views, and maintained the individuality of the two silicophosphates found by himself and Stead. He also deprecated the attempts of various authors to separate the silicophosphates into a phosphate and silicate, and he held to the view that the compound was the calcium salt of a complex acid. Hilgenstock, on the basis of the reaction between metallic iron and the phosphates, had argued that the lime should be apportioned between the silicate and phosphate in a particular way, so that the tetrabasicity of the latter was maintained. This view, however, was controverted by Carnot. J von Jonstorff,[13] from the analyses of basic slags of different types, calculated a hypothetical composition in terms of calcium phosphate, olivine, spinel, and free oxides, but these results bear no relation to the actual constitution.

An elaborate discussion of previous work, together with an account of further investigations on his own part, was given by Kroll[14] in 1910. He admits the existence of the tetrabasic phosphate and of the two silicophosphates, but argues that

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[6] H. Bucking and G. Linck, Stahl und Eisen, 7, 245, 1887.

[7] G. Hilgenstock, Stahl und Eisen, 7, 557, 1887.

[8] A. Frank, Tagebl. Naturfor. Berlin, 118, 1886.

[9] G. Förster, Zeit. angew. Chem., 5, 13, 1892.

[10] A. F. Rogers, Amer. Journ. Sci. (4), 33, 475, 1912.

[11] Termier and A. Richard, Bull. Soc. Min., 18, 391, 1895.

[12] A. Carnot, Ann. Mines (9), 8, 300, 1895.

[13] J. von Jonstorff, Journ. Iron Steel Inst., ii, 276, 1900.

[14] V. A. Kroll, Stahl und Eisen, 28, 675, 1908; Journ. Iron Steel Inst., ii, 126, 1911.

they are decomposition products formed during comparatively slow cooling. According to this author, it is yet another silicophosphate which forms the " mother-mass " of the slag, and which, being invariably present, must be regarded as the most important constituent. This is described as occurring in the form of greenish blue hexagonal crystals, but no optical verification of the crystal system is given, nor were the crystals measured on the goniometer. The absence of optical data is especially unfortunate, as it prevents the microscopical identification of the material in other slags. Chemically, its composition is approximately

$$6CaO.P_2O_5 + 2CaO.SiO_2,$$

and it is considered to be derived from an octophosphate. As much of the author's reasoning is based on analogy with the behaviour of the compounds formed in the system, lead-oxide—phosphoric anhydride, the formulæ suggested carry but little weight. Kroll also mentions the occurrence of compounds of the spinel group, and likewise of free oxides. G. Hilgenstock[15] also argued in favour of the existence of the tetrabasic compound by analogy with the properties of the copper and barium salts.

The system, calcium phosphate ($4CaO.P_2O_5$)—calcium silicate ($2CaO.SiO_2$), has been investigated by H. Blome.[16] He found two maxima on the melting point curve corresponding to the compounds (i) $4CaO.P_2O_5.2CaO.SiO_2$, (ii) $4CaO.P_2O_5$ $4(CaO.SiO_2)$. This work was criticised by Hartleb,[17] who stated that the occurrence of tetraphosphate in basic slag was rare, while E. Dittler[18] was of the opinion that Blome's tetrabasic salt could not be homogeneous. The last-named author found that at high temperatures this salt broke up to give free lime and calcium phosphate. Microscopic examination of a melt composed of a mixture of tricalcium phosphate and lime, however, showed, in addition to small grains of free lime, rectangular prisms of the tetrabasic salt, with straight extinction and high refractive index. The tribasic salt has been prepared, by the cooling of a melt of appropriate composition, by J. Trenkler,[19] who found that the salt crystallised in the form of uniaxial needles with positive double refraction and high refractive index. Various compounds of lime and phosphoric anhydride have been prepared by T. Dieckmann and E. Houdremont;[20] their work will be mentioned in detail later.

C. G. T. Morison[21] was of the opinion that the phosphorus compound in the slag was a silicophosphate of iron and lime, and that its approximate composition was

$$FeO.5CaO.P_2O_5.SiO_2,$$

but Popp and his co-workers[22] reverted to the calcium salt as postulated by Carnot and Stead. The influence of the rate of cooling on the relative proportions of the phosphate and silicophosphate is discussed by E. Steinweg[23], who verified Kroll's observation[24] that slow cooling favours the formation of the latter salt.

The occurrence of crystals of *apatite*—$3Ca_3P_2O_8.CaF_2$—in slags to which large quantities of fluorspar had been added has been noted by F. Bainbridge.[25] The identification of the crystals was proved both by analysis and micro-examination. The composition of magnetic material in the slag was determined, and found to be similar to that of the feathery crystals described by Stead and Ridsdale. Slags to which fluorspar has been added have also been examined by N. Sheldon,[26] who found, in addition to the two types of crystals just mentioned, yellow-brown hexagonal plates and small angular fragments of another substance. H. Bainbridge[27] has suggested that the former is the phosphate and the latter calcium orthosilicate. M. W. Fodor[28] is stated to have separated no less than four different silicophosphates of lime, but no details regarding these are available.

Examination of the Slags. We are indebted to the various firms from whom the slags were obtained for analyses of the materials. These analyses are given in Table I, together with the molecular proportions of each oxide. Appended to the description of the microstructures are formulæ which represent the molecular composition of each slag, the sum of the " basic " oxides, lime, magnesia, and manganese and ferrous oxides being taken as unity. The sesquioxides, alumina and ferric oxide, which are separated from the other acid oxides, silica and phosphorus pentoxide,

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[15] G. Hilgenstock, Stahl und Eisen, 29, 1478, 1909.

[16] H. Blome, Stahl und Eisen, 30, 2161, 1910; Metallurgie, 7, 659, 698, 1910.

[17] Hartleb, Zeit. off. Chem., 17, 381, 1911; 18, 221, 1912.

[18] E. Dittler, Doelter's Handbuch der Mineralchemie, Dresden, 3, i, 364, 1918.

[19] J. Trenkler, *ibid.*, 3, i, 369, 1918.

[20] *Zeit. anorg. Chem.*, 120. 129, 1921.

[21] C. G. T. Morison, Journ. Agric. Sci., 3, 161, 1909.

[22] M. Popp, J. Coutzen, H. Hoffer and H. Mentz, J. Landw. Ver. Stat., 79, 229, 1913.

[23] E. Steinweg, Zeit. Ges. Hütt., 9. 28, 1912.

[24] A. Kroll, Stahl und Eisen, 31, 2020, 1911.

[25] F. Bainbridge, Trans. Faraday Soc., 16, 302, 1921; Carnegie Schol. Mem., 10, 1, 1920.

[26] N. Sheldon, Trans. Faraday Soc., 16, 310, 1921.

[27] *Loc. cit.*

[28] H. Richardson, *ibid.*, 16, 314, 1921.

constitute the acid radicles in the "spinels,"* which, as will be shown later, form a large proportion of some of the slags. This method of expressing the molecular proportions is the one usually adopted for the comparison of glazes, and, so far as the slags are concerned, we have found it very convenient, as it emphasises very well some of the essential differences between the various types.

Each slag has been examined by means of reflected light, a surface being ground and polished as in the preparation of metallic specimens. For the purpose of discriminating some of the constituents, certain microchemical tests have been utilised. For example, some of the specimens have been etched with solutions of citric acid and the dissolved material tested for phosphorus by the ammonium molybdate method. At first two per cent. solutions of citric acid were used, but later the strength of the solution was reduced to 0·2 per cent., as this gave a better result in discriminating the silicophosphate from apatite, the latter being practically unattacked in the short period the acid was allowed to act.

Hydrochloric acid may also be used to detect the presence of ferrous oxide in the free state. On etching for a very short period with a dilute solution of this reagent, it was found that the spinelloid material is practically unattacked, while the ferrous oxide is appreciably dissolved. On testing the liquid which has been used for etching no ferric iron can be detected by the potassium thiocyanate method, but on oxidising the liquid a colouration is obtained, thus showing that ferrous oxide has been dissolved but not ferric. This may be taken to indicate that the spinelloid material containing ferric oxide is not attacked, and, as the other aluminate which may be present has a very low content in ferrous oxide, that the source of the ferrous oxide is the isomorphous mixture of free oxides. In some cases the presence of silica was verified by etching the section with a mixture of dilute hydrochloric acid and malachite green, the dye being absorbed by the gelatinous silica which is set free.[29]

Thin sections of the slags have also been prepared and the material examined by transmitted light, while in some cases finely ground material was investigated in the same way. There is apparently some difference of opinion regarding the relative merits of the two methods of examination, by reflected light and by transmitted light, and it is sometimes stated that the former is much the more valuable.[30] This is certainly not our experience, and in general we think the latter method is more productive of results, although it is still better to use the one as supplementary to the other.[31] In the examination of sections by reflected light, we are restricted in the choice of criteria for identification of the various constituents. The chief criteria which are available are colour and reflecting power, habit of the crystals, and behaviour towards etching reagents. In the case of slags most of the constituents are oxides, silicates, or similar compounds, and the crystal habit is not of much value in identifying these, while etching tests are available in only a very few cases. In the examination by transmitted light, on the other hand, we have available the optical properties of these compounds; the refractive index can be determined by the Becke or Schröder van der Kolk method; the double refraction can be measured, as also can the extinction angles and so forth, while by the additional use of convergent light the crystal system can sometimes be determined. In view of the large mass of data regarding synthetic silicates, etc., such determinations are generally sufficient for the identification of the constituents.

The reflected light method, on the other hand, is much better suited for the discrimination of fine detail, as by it a higher degree of magnification can be used than in the other method, where the thickness of the section interferes to some extent with the use of high-power objectives. In this way the details of the texture of the material can be better investigated. In the case of opaque material, of course, the only possible method of examination is that by reflected light.

MICROSCOPICAL CHARACTERISTICS OF THE SLAGS.

No. 1. Examination of thin sections by transmitted light shows that the slag is not homogeneous. Even in the lumps two types can be visually distinguished. One seems to be dark in colour and of aphanitic appearance; the other is of a greenish colour and obviously crystalline. Under the microscope the former can again be resolved into two types. One is apparently composed of an aggregate of light-coloured crystals and dark material, both being very fine grained. The light crystals, which grade in size from laths which can be clearly seen with a 6 mm. objective down to very minute forms, are greenish in colour, have a high refractive index and low double refraction, and tend to occur in groups. These have the same properties as, and are identical with, the coarser pleochroic material which

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* Throughout this paper, the terms "spinel" and "spinelloid material" are used to designate the aluminates and ferrites which are found in the slags; the use of the term is not to be regarded as indicating that these compounds are necessarily true spinels. Their affinities are discussed later.

[29] cf. A. Scott, Trans. Geol. Soc. Glasgow, 16, 394, 1920.

[30] C. H. Desch, Trans. Faraday Soc., 16, 272, 1921.

[31] cf. A. Scott, Trans. Geol. Soc. Glasgow, 16, 393, 1920.

constitutes a large proportion of the phanerocrystalline type of slag. The other material present consists of minute rounded crystals which, when small, are seen to be deep-red in colour, while the larger ones are nearly opaque. The other type of aphanitic material is of a similar nature, but the grain-size of the constituent crystals is smaller, while there is also a greater proportion of the red substance which often tends to occur in groups. The boundary between the two types of slag is usually sharply delineated, but occasionally they tend to merge into each other.

The third type of slag is usually separated from the others by a band of aphanitic material which, however, is coarser in grain than the types described above. In this marginal band the greenish crystals predominate. In the main mass the greenish material itself consists of large rectangular crystals set in an apparently opaque ground-mass. The former occur as well-developed laths, which, however, are often broken. In addition to the prismatic forms, fairly well-defined pyramidal faces can sometimes be detected. There are apparently two irregular cleavages. The refractive index is high compared with that of Canada balsam, the double refraction is low, while the extinction is straight. The crystals are decidedly pleochroic, the colour varying from a characteristic greenish blue to a pale tint which is almost white. Coarser crystals separated from the slag show this phenomenon in a marked degree, the colour varying from a deep blue to a pale blue.

Examination in convergent light shows the crystals to be biaxial, with a fairly wide axial angle; this, in conjunction with the straight extinction, indicates a symmetry approaching orthorhombic. If these crystals be compared with the blue pleochroic calcium silicophosphate described by Miers,[32] the two types are seen to have the same properties. The crystals in slag No. 1, therefore, are composed of a silicophosphate of calcium in which the molecular ratio of silica to phosphoric anhydride is nearly unity.

The thin sections also show the presence of a few smaller crystals of a yellowish brown colour. They are generally found in the opaque ground-mass, and never in juxtaposition to the greenish material described above. The shape is dominantly hexagonal, most of the boundaries appearing to be the traces of pyramidal forms, although occasional lath-shaped crystals are found. The pleochroism is not very marked, the colour varying from pale yellow to a darker tint. The cleavage is fairly well developed, and orientated inclusions commonly occur. The crystals have straight extinction with reference to the greatest elongation, while some equant hexagonal grains are almost isotropic. In convergent light traces of a uniaxial figure can be observed, and it is probable that the crystals are hexagonal.

A comparison with the brown crystals of calcium silicophosphate described by Stead and Ridsdale shows that the properties of the two are practically identical, except that the latter have stronger pleochroism. This difference is probably due to the small grain-size of the crystals in our slag, those which have been available for the purposes of comparison being much thicker. The crystals, therefore, are composed of the silicophosphate of calcium in which the molecular ratio of phosphoric anhydride to silica is approximately 4 : 1. In these crystals a peculiar form of alteration can be observed; small rod-like crystallites of some secondary material tend to grow inwards from the margins of the original crystals, while in the cracks of the latter a red translucent substance is sometimes found.

A careful examination shows the apparently opaque material to be composite. Numerous red translucent crystals, which sometimes occur as rounded grains but more often in the form of dendrites, can be observed. These crystals, which are the same as those noted in the aphanitic slag, are doubly refracting, but their small size precludes a further examination of their properties. They are probably composed largely of calcium ferrite and aluminate. The material which is actually opaque is likewise composite, parts appearing to have a grey tint, by the light incident on the surface of the slide, while other parts appear dead black. Although these were not further discriminated in thin section, the results described below indicate that one consists of free oxides while the other is probably a solid solution of magnetite with calcium aluminate and ferrite.

Examination of polished surfaces by reflected light shows the presence of rectangular crystals of a dull grey colour. Where the surface is not well polished a blue-green tinge can be detected, and there is no doubt that these crystals are the silicophosphate described above. On treating with 0·2 per cent. citric acid, the crystals etch readily and show a characteristic development of etching pits. These crystals are set in a matrix which is obviously composite, and which corresponds to the opaque ground-mass seen in thin section. This matrix apparently consists of thin streaks and rounded grains of a dead-white, highly-reflecting substance, set in a light grey base which is present in predominating amount. The former, from a comparison with the slags described below, probably indicates crystals of free oxides in isomorphous admixture. The light

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[32] H. A. Miers, Journ. Chem. Soc., 52, 608, 1887.

grey base, on etching with 0·2 per cent. citric acid, is observed to be composed of scarce elongated crystals, which are easily attacked and darken in colour, and much lighter almost white crystals, which are apparently quite unattacked by the acid The former of these, from a comparison with the thin section, is the brown silicophosphate, the presence of which in thin section is masked to a large extent by the opaque base with which it is associated. The white material very probably belongs to the spinelloid material. The latter, on treatment with concentrated hydrochloric acid, reveals heterogeneity, and appears to consist of an intimate intergrowth of two types of crystals. Microchemical tests show one of these to contain ferrous oxide, which is practically absent from the other; the former is probably the magnetic "spinel" described by Stead and Ridsdale, the latter being the non-magnetic compound. The chief distinction between these two substances is the presence of traces of an octahedral cleavage in one of them; in general, however, they are difficult to discriminate.

The aphanitic parts of the slag consist of elliptical crystals of spinel set in a fine-grained matrix, which is grey in colour. From the behaviour on etching the latter seems to be composed of a minutely crystalline aggregate of the silicophosphate and either a spinelloid mineral or an isomorphous mixture of oxides. The individual crystals are too fine grained to be definitely determined.

No. 2. Examination of this slag by transmitted light shows it to consist of finely granular pale-coloured material set in an opaque groundmass. The former, which occurs as small rounded crystals without crystal form, is the greenish silicophosphate described above. Numerous much smaller brownish crystals, which occur as inclusions and in the interstices, are probably the brown silicophosphate, but their exact nature is difficult to determine on account of their small size. The opaque material is seen by reflected light to have the same three constituents as No. 1. Occasionally the deep-red "spinel" is ophitically enclosed in large plates of the greenish slicophosphate. This slag differs from No. 1 in several respects, the grain-size of the individual crystals is much smaller, and euhedral forms are rare, while the proportion of brown silicophosphate is greater.

No. 3. The microscopical appearance of this slag is rather different from that of the others. By transmitted light it appears to consist of a granular aggregate of nearly colourless equidimensional crystals, with abundant interstitial red material. The clear crystals show little sign of the development of crystal forms, and are most usually found as irregular grains. The refractive index is fairly high, but the double refraction is low, the optical properties in general being somewhat similar to those of the blue silicophosphate except for the absence of the colour and the pleochroism. The crystals have two well-defined cleavages, and in convergent light a biaxial figure is obtained. As indicated later, they probably consist of a silicophosphate in which the molecular ratio of silica to phosphoric anhydride is 3:1. A few small crystals with very different properties were also noticed. These are of prismatic habit, and intensely pleochroic, the colour varying from yellowish red to green. The refractive index and double refraction are high, and the extinction straight. It is impossible to give any indication regarding the composition of these crystals, which, however, form an inappreciable proportion of the slag as a whole. The remainder of the slag is composed of reddish material which often acts as a cementing matrix for the colourless crystals, but which is occasionally found in aggregates of spherical crystals, the latter sometimes occurring as inclusions in the colourless types. The red crystals, which vary considerably in size, have a fairly good cubic cleavage and a high refractive index. The crystal habit and other properties agree with those of the spinelloid material, and there is little doubt that they are of this nature. It must, therefore, be regarded as a mixture of the aluminates and ferrites of the bases present in the slag. Occasionally the clear crystals show sign of alteration to a darker material, which seems to be formed by a reaction with the spinelloid substance. The cementitious nature of the spinelloid compound is more apparent than real, for in many places the latter appears to be ophitically enclosed in the clear crystals, relatively large areas of which are in optical continuity. The relationship of the two resembles that of such minerals as felspar and augite in certain basalts.

The presence of this ophitic structure is verified by an examination by reflected light. When so examined the slag is seen to consist of an aggregate of grey and white crystals. The latter often occur as small circular grains with high reflecting power, and enclosed in the grey substance. The white material is undoubtedly the "spinel," and the grey the clear crystals observed by transmitted light. The grey material is not homogeneous, but seems to consist of two types which are not widely different in properties and grade sometimes into each other. On etching the surface with 0·2 per cent. citric acid, part of the grey material is attacked to a greater degree than the rest, and the surface becomes mottled and dusty. A comparison with a thin section shows this part to coincide with the alteration product, the less readily etched portion being the unaltered crystals. Etching with hydrochloric acid reveals a slight degree of heterogeneity in the white material, there being present a small proportion of free oxides.

Another section of a slag of similar composition from the same furnace shows the presence of the same constituents. In this case, however, in addition to the granular arrangement, numerous areas with a quasi-eutectic structure are present. In this the spinelloid material is arranged in the form of irregular structures often radiating from a centre.

No. 4. By transmitted light this slag is seen to consist of abundant yellowish crystals set in a dark ground-mass which appears to be homogeneous. The two types are inter-grown in well-developed radial and dendritic structures, the former probably representing transverse sections of the latter. Occasional eumorphic lath-shaped crystals of the yellow type also occur. The structure as a whole bears a strong resemblance to certain types of eutectic formation. Where the section is thin the apparently black material becomes translucent and has a red colour; it is apparently composed of an aggregate of crystals of "spinel." The yellowish material has the same properties as the alteration product referred to in the description of No. 3, while a few clear patches probably represent the unaltered crystals in the same slag.

No. 5. By transmitted light this slag is very like No. 4. The same pseudo-eutectic structure is evident, the constituent types being again the "spinels" and the yellow crystalline substance. The former of these is abundant, while the latter contains a number of clearer crystals. By reflected light, especially after etching with a 0·2 per cent. citric acid, the same structure can be seen, the dark constituent (by transmitted light) being now dead white and the yellow greyish. The white, which is probably a mixture of "spinel" and free oxides, obviously forms many-branched dendrites. The grey material, after etching, shows some heterogeneity, some portions appearing to be more soluble than others. This possibly represents various stages of alteration of the material seen in No. 3.

Nos. 6 and 7. These slags are very similar. Each consists of numerous granular crystals of the silicophosphate described above (No. 3) set in a dark ground-mass. By reflected light the latter is seen, on etching, to consist of a pseudo-eutectic aggregate of two constituents, one probably "spinel" and the other free oxides. The opaque material often forms dendritic growths of comparatively large size, but these are not generally homogeneous, as they consist of the aggregate just mentioned.

No. 8. This slag resembles Nos. 6 and 7 in structure and constituents, but the proportion of opaque material is greater, while the individual crystals are more fine grained. The silicophosphate encloses the other materials ophitically, and has often a dusty appearance owing to the presence of numerous very minute brownish crystals, which are too small for identification. The opaque material by reflected light is seen to be heterogeneous, and consists of coarse skeletal crystals of free oxides, together with two types of spinelloid material. One of the latter, which is deep red by transmitted light, occurs in the form of very delicate dendrites.

No. 9. The thin section of this slag shows the presence of relatively abundant colourless crystals with fairly well-defined crystal faces. These crystals are sometimes of large size and of a porphyritic nature; the refractive index is high and the double refraction low—considerably lower than that of the silicophosphates—while the extinction is invariably straight. In cross-section they appear to be hexagonal. These properties agree exactly with those of the mineral *apatite.* In many instances the crystals are not complete, but contain a dark core of the same shape as the apatite, the whole resembling the structures of those crystals which have so-called ghost inclusions. The section also shows a large number of smaller laths of irregular outline and yellowish in colour. These have straight extinction and double refraction much higher than that of apatite. They generally show a characteristic type of alteration, or possibly inclusion, which is practically identical with the peg-structure which is so typical of *melilite.*

The crystals cannot be melilite, however, as their double refraction is much too high, the polarisation colours being sometimes of the second order. There are two good cleavages which are inclined to each other at an angle of nearly ninety degrees. The refractive index is fairly high, the crystals show a biaxial figure in convergent light, while the extinction is apparently inclined to the direction of greatest elongation. In many cases, however, the crystals show "wavy" extinction, while in others complex twinning appears to occur. As will be seen from the discussion of the analyses, these crystals must be an impure silicate of calcium. Their properties do not agree with those of the tricalcium silicate described by Rankin and Shepherd,[33] as the double refraction is much too high. A comparison with the data given by the same authors for the dicalcium silicate, $2CaO.SiO_2$, however, shows that they probably belong to the α-form of this compound. Dicalcium silicate exists in several polymorphic

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[33] G. A. Rankin and E. S. Shepherd, *Zeit. anorg. Chem.*, 71, 19, 1911.

modifications, the α-form being stable above 1,420 degrees C., the β-form between 1,420 degrees C. and 675 degrees C., and the γ-form below 675 degrees C. The crystals in this slag are probably the α-form, because the double refraction is too high for the γ-form, while the presence of complex twinning is against its being the β-variety, which is generally untwinned. It may be noted that the presence of this compound in slags has been suggested, on chemical grounds, by Bainbridge.[34]

In this connection it may be remarked that Shepherd and Rankin have observed the formation of this substance at temperatures below the melting point of the mixtures used. The optical properties of the crystals in the slag indicate that it cannot be trisilicate.

The dark matrix consists of red sub-translucent crystals which often occur in the typical rounded form, but occasionally a dendritic habit develops. By reflected light the same constituents can be detected. No further forms are indicated on etching with 0·2 per cent. citric acid, the only effect being the solution of the impure tricalcium silicate. On etching with 2 per cent. citric acid, however, the material of dead-white colour is resolved into two constituents which are in very intimate intergrowth. One is probably a "spinel," while the other is almost certainly an isomorphous mixture of oxides of the divalent metals present.

The apatite seems to have crystallised during an early stage of the cooling of the slag, and to have developed fairly rapidly, so that portions of the mother liquid were entangled in the growing crystals. The other constituents all developed in the later stages of the cooling, and the structures observed indicate that the temperature ranges in which these have crystallised overlap to a considerable extent.

No. 10. Microscopically this slag is very similar to No. 9, and shows the same constituents. Though the apatite is apparently euhedral, it is of an almost skeletal nature, and has large inclusions of the matrix in the form of negative crystals. The yellowish crystals in this case show a tendency to occur in rounded forms rather than as laths, but they possess the same characteristic "peg-structure." Etching with 0·2 per cent. citric acid shows these crystals to contain some phosphorus pentoxide. The dark matrix is again heterogeneous, and consists of spinelloid minerals, together with free oxides of the RO. type.

No. 11. Under the microscope this slag appears to consist of a fine-grained aggregate of irregular transparent crystals, together with much opaque material. The fine-grained nature of the former is only apparent, since, between crossed nicols, considerable areas are seen to be in optical continuity. These comparatively large crystals ophitically enclose abundant opaque material which has the usual dendritic nature. The optical properties of the clear crystals indicate that they are the dicalcium silicate which has been described in No. 9. They have a similar high refractive index, while the extinction, which is often wavy, appears in general to be inclined. Twinning can also be observed in some of the crystals.

DISCUSSION OF MICRO-STRUCTURES.

Before discussing the results of the microscopical investigations in relation in the chemical analyses of the slags, it is necessary to consider the compounds described by previous workers. The pleochroic silicophosphate described by Stead and Ridsdale shows, on recalculating the analysis, that the molecular formula is approximately $RO : \cdot 18\ SiO_2 : \cdot 205\ P_2O_5$ where R is practically all calcium, that is, that the molecular proportions of silica and phosphoric anhydride are nearly equal. The data given by other investigators show analogous results, the composition, according to Carnot's analysis being $RO : \cdot 21\ SiO_2 : \cdot 22\ P_2O_5$; to Bucking and Linck's $RO : \cdot 15\ SiO_2 : \cdot 21\ P_2O_5$, and to Hilgenstock's $RO : \cdot 145\ SiO_2 : \cdot 20\ P_2O_5$. In some of the above cases the materials were possibly contaminated; nevertheless, this compound may be regarded as consisting of approximately equal molecular amounts of silica and phosphoric anhydride combined with basic oxides which are mainly calcium oxide. There is no evidence whatever as to the nature of the phosphate and silicate present in the above admixture. It has generally been suggested, mainly on the basis of the occurrence of the pure compound in certain slags, that the phosphate is present as the tetrabasic salt, and this would make the pleochroic crystals approximate to a double compound of the tetrabasic phosphate and the monobasic silicate. There is, however, as much justification in postulating a mixture of tribasic phosphate and dibasic silicate, or any other combination which fits the analyses.

The molecular form of the yellow crystalline compound described by Stead and Ridsdale is $RO : \cdot 066\ SiO_2 : \cdot 24\ P_2O_5$, which gives approximately four parts of phosphoric anhydride to one part of silica.

Bucking and Linck's analyses give almost the same result. This formula might be written—$4R_4P_2O_9 + RSiO_3$, but other forms might agree equally well with the analyses. Stead and Ridsdale's figures give the formula:

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[34] F. Bainbridge, Trans. Faraday Soc., 16, 312, 1921.

$$\left.\begin{array}{l}\cdot956\ \mathrm{CaO}\\ \cdot011\ \mathrm{MnO}\\ \cdot018\ \mathrm{FeO}\end{array}\right\}\cdot031\ \mathrm{Fe_2O_3}\left\{\begin{array}{l}\cdot065\ \mathrm{SiO_2}\\ \cdot235\ \mathrm{P_2O_5}\end{array}\right.$$

Probably the sesquioxide is present in the form of spinel; if an appropriate correction for this be made, the figures agree very well with a mixture of $R_3P_2O_8$ and R_3SiO_5. The nature of the substances which form such double compounds must be entirely conjectural.

The other silicophosphate described by Kroll has, according to the analyses, a composition ranging from $RO : \cdot09\ SiO_2 : \cdot125\ P_2O_5$ to $RO : \cdot11\ SiO_2 : \cdot105\ P_2O_5$. The ratio of silica to phosphorus pentoxide is similar to that in the first silicophosphate mentioned above, but the ratio of basic oxides to acid oxides is twice as great. Unfortunately Kroll gives no optical data respecting this compound, except that it is greenish in colour, nor did he definitely demonstrate the homogeneity of the crystalline material analysed.

Of the other crystalline materials mentioned as occurring in basic slags, the most important are the two spinelloid forms, and the "feathery" crystals described by Stead and Ridsdale. The formula of the magnetic "spinel" is given as (1) below, and that of the non-magnetic as (2):

(1)

$$\left.\begin{array}{l}\cdot809\ \mathrm{CaO}\\ \cdot131\ \mathrm{FeO}\\ \cdot022\ \mathrm{MnO}\\ \cdot038\ \mathrm{MgO}\end{array}\right\} : \left\{\begin{array}{l}\cdot247\ \mathrm{Fe_2O_3}\\ \cdot073\ \mathrm{Al_2O_3}\\ \cdot045\ \mathrm{Cr_2O_3}\end{array}\right.$$

(2)

$$\left.\begin{array}{l}\cdot955\ \mathrm{CaO}\\ \cdot028\ \mathrm{MgO}\\ \cdot017\ \mathrm{MnO}\end{array}\right\} : \left\{\begin{array}{l}\cdot282\ \mathrm{Fe_2O_3}\\ \cdot117\ \mathrm{Al_2O_3}\\ \cdot041\ \mathrm{Cr_2O_3}\end{array}\right.$$

The former therefore approximates to $RO : \cdot365\ R_2O_3$ and the latter to $RO : \cdot440\ R_2O_3$. Each is probably an isomorphous mixture of aluminates, ferrites, and chromates of the various bases present. The departure of the $RO : R_2O_3$ ratio from a simple whole number is probably to be explained by the fact that the different basic oxides present form compounds of different basicities with the various sesquioxides.

The feathery crystals described by Stead and Ridsdale have the approximate formula $RO : 0{\cdot}1R_2O_3$. It is possible that much of the sesquioxide is present in the form of impurity, though some may be in solid solution in the apparently isomorphous mass of oxides of the divalent metals. The magnetic material separated by Bainbridge is obviously a mixture of free oxides and ferrites as the molecular formula approximates to $RO : \cdot125\ R_2O_3$. As no ferrites are known in which the ratio of basic oxide to sesquioxide even approaches the figure obtained here, it is practically certain that the material includes a large proportion of free oxides.

TABLE I. ANALYSIS OF SLAGS, NOS. 1 TO 11.

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	S	P_2O_5
No. 1	7·75 ·129	— —	16·09 ·101	6.98 ·097	3·17 ·021	3·56 ·089	43·94 ·785	0·26 ·008	18·24 ·130
No. 2	5·80 ·097	2·70 ·026	5·94 ·037	10·60 ·147	6·81 ·096	3·23 ·081	44·88 ·807	0·12 ·004	19·43 ·137
No. 3	13·00 ·216	13·70 ·134	8·44 ·053	7·96 ·111	3·00 ·042	·64 ·016	41·00 ·732	0·49 —	10·9 ·077
No. 4	15·50 ·258	3·50 ·034	3·00 ·019	11·94 ·166	7·44 ·105	4·01 ·100	40·95 ·731	0·03 ·001	13·61 ·095
No. 5	17·80 ·297	2·60 ·025	4·43 ·028	14·01 ·194	8·65 ·122	4·12 ·103	37·20 ·664	0·03 ·001	11·11 ·078
No. 6	21·80 ·363	2·00 ·020	3·55 ·023	4·41 ·061	1·03 ·014	7·24 ·181	43·80 ·782	0·08 ·003	14·30 ·101
No. 7	14·35 ·239	3·21 ·031	3·55 ·023	10·32 ·143	1·03 ·018	5·96 0·149	51·10 ·912	0·19 ·006	9·81 ·070
No. 8	16·52 ·276	2·06 ·021	4·99 ·031	22·24 ·308	8·10 ·114	3·61 ·090	32·72 ·584	— —	10·04 ·07
No. 9	12·20 ·203	4·15 ·041	5·92 ·037	23·11 ·320	5·87 ·082	3·74 ·093	38·23 ·682	0·17 ·005	6·48 ·046
No. 10	14·70 ·265	4·60 ·045	5·14 ·032	10·41 ·141	8·09 ·114	4·34 ·108	39·60 ·707	0·04 ·001	13·08 ·093
No. 11	18·76 ·313	1·35 ·013	3·58 ·023	21·10 ·292	11·27 ·160	5·04 ·126	36·44 ·650	0·18 ·005	2·05 ·015

No. 1. This slag has been shown to consist mainly of the pleochroic silicophosphate, spinel, and an isomorphous mixture of free oxides, together with a small amount of brownish mineral.

On recalculating the analysis of this slag, the molecular formula which is obtained is:

$$\left.\begin{array}{l}\cdot098\ FeO\\ \cdot021\ MnO\\ \cdot090\ MgO\\ \cdot791\ CaO\end{array}\right\}\cdot102\ Fe_2O_3\left\{\begin{array}{l}\cdot131\ SiO_2\\ \cdot132\ P_2O_5\end{array}\right.$$

or approximately $RO : \cdot1\ R_2O_3 \left\{\begin{array}{l}\cdot13\ SiO_2\\ \cdot13\ P_2O_5\end{array}\right.$

The molecular ratio of silica to phosphoric anhydride is therefore unity. As the brownish material is present in very small quantity, it may be neglected for the moment; its occurrence will be discussed later. On comparing the above formula with that of Stead's green mineral, it will be noted that the ratio of silica to phosphoric anhydride is the same in the two cases; hence in such a slag as No. 1 practically the whole of the acidic oxides is found in the form of the green silicophosphate.

The presence of the brown silicophosphate indicates that locally there has been an excess of phosphoric anhydride over that required for the formation of the green compound. The coexistence of the two silicophosphates in this slag indicates that the amount of solid solution cannot be very great. The amounts of the former present will require approximately ·65 RO for the formation of these crystals, and as the spinelloid material, on the basis of Stead's analyses, will take up ·25 RO as a probable maximum, the amount of R_2O_3 being ·10, there remains at least ·09 RO, which is most likely present in the free state.

No. 2. The molecular formula of this slag is:

$$\left.\begin{array}{l}\cdot130\ \mathrm{FeO}\\ \cdot084\ \mathrm{MnO}\\ \cdot072\ \mathrm{MgO}\\ \cdot714\ \mathrm{CaO}\end{array}\right\}\begin{array}{l}\cdot023\ \mathrm{Al_2O_3}\\ \cdot033\ \mathrm{Fe_2O_3}\end{array}\left\{\begin{array}{l}\cdot085\ \mathrm{SiO_2}\\ \cdot121\ \mathrm{P_2O_5}\end{array}\right.$$

that is, approximately:

$$\mathrm{RO}:\ \cdot086\ \mathrm{R_2O_3}:\left\{\begin{array}{l}\cdot085\ \mathrm{SiO_2}\\ \cdot12\ \ \ \mathrm{P_2O_5}\end{array}\right.$$

where the ratio of phosphoric anhydride to silica approaches 3:2. This slag has been shown to contain the two silicophosphates described by Stead and Ridsdale, and a comparison of their analyses with the above indicates that the two minerals ought to be present in the ratio of about 6:1, the green form predominating. Although, on account of the grain-size of the crystals, it has not been possible to measure microscopically the amounts of the two, the green is much the more common. Hence it may be assumed that when the molecular ratio of P_2O_5 to SiO_2 is greater than unity the two acidic oxides are partitioned between these two types of crystals. A calculation similar to that made in connection with No. 1 shows that some free basic oxides must be present in addition to spinel.

No. 3. This slag is interesting, as the presence of only two constituents enables their nature to be approximately determined. The molecular formula of the slag is:

$$\left.\begin{array}{l}\cdot122\ \mathrm{FeO}\\ \cdot047\ \mathrm{MnO}\\ \cdot018\ \mathrm{MgO}\\ \cdot813\ \mathrm{CaO}\end{array}\right\}\begin{array}{l}\cdot149\ \mathrm{Al_2O_3}\\ \cdot059\ \mathrm{Fe_2O_3}\end{array}\left\{\begin{array}{l}\cdot240\ \mathrm{SiO_2}\\ \cdot085\ \mathrm{P_2O_5}\end{array}\right.$$

or approximately $\mathrm{RO}:\ \cdot21\ \mathrm{R_2O_3}\left\{\begin{array}{l}\cdot24\ \mathrm{SiO_2}\\ \cdot085\ \mathrm{P_2O_5}.\end{array}\right.$

If the spinel be assumed to approximate to that described by Stead and Ridsdale, its composition approaches $2{\cdot}4\ \mathrm{RO} : \mathrm{R_2O_3}$, and since all the sesquioxides in the slag are probably combined in the spinel, the formula and relative amount of the latter will be $\cdot5\ \mathrm{RO} : \cdot21\ \mathrm{R_2O_3}$. Deducting this from the total slag, the formula of the silicophosphate will be approximately $\cdot5\ \mathrm{RO} : \cdot24\ \mathrm{SiO_2} : \cdot085\ \mathrm{P_2O_5}$, that is, a silicophosphate in which the ratio of phosphoric anhydride to silica approaches 1:3. This compound differs radically in chemical composition from all those which have been previously described, the ratio of P_2O_5 to SiO_2 being much lower than in any of the latter. Its occurrence in Nos. 4, 5, 6, 7, and 8, as will be discussed below, indicates that it is the form of silicophosphate which separates from those slags in which the silica is present in considerable excess over the phosphoric anhydride, although the amount of the latter is still appreciable.

The apparently "ophitic" nature of the structure of this slag, and its resemblance to that of certain basalts, is probably to be explained by the fact of the syncrystallisation of two types of mixed crystals, one composed of the silicophosphate (1:3) of, say, calcium and subordinate amounts of the other oxides, and the other of aluminates and ferrites of these oxides. The analogous mixed crystals in the basalts are felspar and pyroxene.

No. 4. This slag, which is composed of the same constituents as No. 3, has the molecular formula:

$$\left.\begin{array}{l}\cdot150\ \mathrm{FeO}\\ 095\ \mathrm{MnO}\\ \cdot091\ \mathrm{MgO}\\ \cdot664\ \mathrm{CaO}\end{array}\right\}\begin{array}{l}\cdot031\ \mathrm{Al_2O_3}\\ \cdot017\ \mathrm{Fe_2O_3}\end{array}\left\{\begin{array}{l}\cdot234\ \mathrm{SiO_2}\\ \cdot086\ \mathrm{P_2O_5}\end{array}\right.$$

The ratio of silica to phosphoric anhydride is almost the same as in No. 3, and all the acidic oxides are probably in the form of the compound described above. The proportion of sesquioxides in this case is much lower, and if the appropriate amounts of the bases necessary for the formation of "spinel" be deducted from the total bases there is still an appreciable residue of the latter, which is probably present as a mixture of free oxides.

The structure in this case is not ophitic, but closely resembles certain types of eutectic structure. It cannot be a true eutectic, however, as the constituent crystals are solid solutions and not individual compounds. It probably indicates the two types of mixed crystals formed to a certain extent in the same temperature range.

No. 5. This slag resembles No. 4, both chemically and structurally. The formula calculated from the analyses is:

$$\left.\begin{array}{l}\cdot179\ \mathrm{FeO}\\ \cdot112\ \mathrm{MnO}\\ \cdot095\ \mathrm{MgO}\\ \cdot614\ \mathrm{CaO}\end{array}\right\}\begin{array}{l}\cdot23\ \mathrm{Al_2O_3}\\ \cdot26\ \mathrm{Fe_2O_3}\end{array}\left\{\begin{array}{l}\cdot274\ \mathrm{SiO_2}\\ \cdot073\ \mathrm{P_2O_3}\end{array}\right.$$

The ratio of SiO_2 to P_2O_5 is slightly greater in this instance, which may account for the more altered nature of the silicophosphate. The opaque material again includes an amount of free oxides.

Nos. 6 and 7. These slags show the same constituents as Nos. 4 and 5, but the structures are somewhat different. The molecular formulæ are:

(6)

$$\left.\begin{array}{l}\cdot059\ \mathrm{FeO}\\ \cdot014\ \mathrm{MnO}\\ \cdot174\ \mathrm{MgO}\\ \cdot753\ \mathrm{CaO}\end{array}\right\}\begin{array}{l}\cdot019\ \mathrm{Al_2O_3}\\ \cdot022\ \mathrm{Fe_2O_3}\end{array}\left\{\begin{array}{l}\cdot349\ \mathrm{SiO_2}\\ \cdot097\ \mathrm{P_2O_5}\end{array}\right.$$

(7)

$$\left.\begin{array}{l}\cdot115\ \mathrm{FeO}\\ \cdot015\ \mathrm{MnO}\\ \cdot122\ \mathrm{MgO}\\ \cdot748\ \mathrm{CaO}\end{array}\right\}\begin{array}{l}\cdot026\ \mathrm{Al_2O_3}\\ \cdot019\ \mathrm{Fe_2O_3}\end{array}\left\{\begin{array}{l}\cdot196\ \mathrm{SiO_2}\\ \cdot057\ \mathrm{P_2O_5}\end{array}\right.$$

In each case the slag has locally a granular structure so far as the silicophosphate is concerned, but the fine intergrowths of the spinel and free oxides are probably allied to the pseudo-eutectic structure mentioned above, although the complexity of each, so far as solid solution is concerned, prevents the formation of a true eutectic.

Although the ratio of silica to phosphoric anhydride is practically the same in these two slags, the total amount of these oxides is much greater in No. 6 than in No. 7, and this difference is in agreement with the greater proportion of silicophosphate visible under the microscope.

No. 8. This slag is of a similar nature to Nos. 6 and 7.

No. 9. This slag may be regarded as typical of those to which fluorspar has been added. The fluorspar combines with tricalcium phosphate to form the mineral apatite, the result being that in the present instance no silicophosphate could be detected. The identification of the hexagonal material as apatite has been verified by an examination of some crystals from the vesicles; the refractive index and double refraction of these agrees well with the data given for apatite. Several interesting points may be noted in connection with the occurrence of this compound. In the first place, the silicophosphate is apparently not formed so long as there is sufficient fluorspar to combine with the phosphoric anhydride to give apatite, which must therefore be regarded as the most stable of the phosphates which are found in these slags. Secondly, the euhedral nature of the apatite indicates its crystallisation from the molten slag at an early stage in the cooling. This is in agreement with the behaviour of this mineral in igneous rocks, where it is one of the earliest secretions from the magma.

The molecular formulæ of this slag, as calculated from the analysis, are:

$$\left.\begin{array}{l}\cdot580\ \mathrm{CaO}\\ \cdot080\ \mathrm{MgO}\\ \cdot271\ \mathrm{FeO}\\ \cdot069\ \mathrm{MnO}\end{array}\right\}\begin{array}{l}\cdot032\ \mathrm{Fe_2O_3}\\ \cdot035\ \mathrm{Al_2O_3}\end{array}\left\{\begin{array}{l}\cdot171\ \mathrm{SiO_2}\\ \cdot040\ \mathrm{P_2O_5}\end{array}\right.$$

Fluorine was not determined, but part of the calcium oxide may be regarded as replaced by calcium fluoride. The portion of this slag soluble in 2 per cent. citric acid has also been analysed, the composition being given in the first line of Table II, while the composition of the slag is given in the second line.

TABLE II.

SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	P_2O_5
11·13	0·46	—	1·92	0·79	3·60	25·29	2·22
12·20	4·15	5·92	23·11	5·87	3·74	38·23	6·48

The molecular formula of the soluble portion is:

$$\left.\begin{array}{l}\cdot387\ \mathrm{CaO}\\ \cdot076\ \mathrm{MgO}\\ \cdot022\ \mathrm{FeO}\\ \cdot009\ \mathrm{MnO}\end{array}\right\}\cdot003\ \mathrm{Al_2O_3}\left\{\begin{array}{l}\cdot159\ \mathrm{SiO_2}\\ \cdot013\ \mathrm{P_2O_5}\end{array}\right.$$

Micro-chemical tests show that the apatite is not dissolved to any extent by this acid, while the opaque material is only slightly attacked. Hence the above must be regarded as approximating to the composition of the material which has been described above as dicalcium silicate. This formula is practically $3RO.SiO_2$, where R is mainly calcium; nevertheless the silicate has been identified as $2\,CaO.SiO_2$. It is probable, however, that there is an amount of free lime in the slag, and this would go into solution in the acid. The amount of free lime may be as high as 5 per cent.,[35] and if this be deducted from the RO column, together with the amount of calcium oxide required to saturate the phosphoric anhydride and the alumina, as well as the amount of FeO and MnO, which probably represent dissolved free oxides, the formula of the calcium silicate reduces to ·315 RO: ·159 SiO_2, which is very near $2RO.SiO_2$, where R is five-sixths calcium and one-sixth magnesium.

Although the tricalcium salt, $3\,CaO.SiO_2$ has not been in the examination of the ternary system $CaO\text{-}MgO\text{-}SiO_2$, this does not mean that it cannot exist. This examination was confined to those phases stable in contact with the melt: it is, however, possible that it may form in the system at temperatures below those of the melting surface.

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[35] E. J. Russell, Trans. Faraday Soc., 16, 263, 1921.

No. 10. This slag resembles No. 9, the chief difference being that it contains a higher proportion of acidic oxides. The molecular formula is—

$$\left.\begin{array}{l}\cdot661\ \mathrm{CaO}\\ \cdot100\ \mathrm{MgO}\\ \cdot132\ \mathrm{FeO}\\ \cdot107\ \mathrm{MnO}\end{array}\right\}\begin{array}{l}\cdot042\ \mathrm{Al_2O_3}\\ \cdot033\ \mathrm{Fe_2O_3}\end{array}\left\{\begin{array}{l}\cdot247\ \mathrm{SiO_2}\\ \cdot087\ \mathrm{P_2O_5}\end{array}\right.$$

The proportion of free oxides is less than in No. 9, and this corresponds to a diminution in the amount of ferrous oxide. In the above formula, part of the calcium oxide is to be regarded as replaced by calcium fluoride. From the micro-examination it appears that practically all the phosphorus is present as apatite, the silica being in the form of dicalcium silicate.

No. 11. This slag differs from the others in its very low content in phosphoric anhydride. The molecular formula is—

$$\left.\begin{array}{l}\mathrm{CaO}\ \cdot529\\ \mathrm{MgO}\ \cdot102\\ \mathrm{FeO}\ \cdot239\\ \mathrm{MnO}\ \cdot130\end{array}\right\}\begin{array}{l}\cdot011\ \mathrm{Al_2O_3}\\ \cdot019\ \mathrm{Fe_2O_3}\end{array}\left\{\begin{array}{l}\mathrm{SiO_2}\ \cdot255\\ \mathrm{P_2O_5}\ \cdot012\end{array}\right.$$

Apart from the small proportion of the phosphorus bearing compounds, the constituents present resemble those of the fluorspar slags. The chief silicate is the dicalcium salt, probably containing part of the magnesia in solid solution as the orthosilicate. The proportion of spinel is not great, as there is comparatively a small amount of sesquioxide present. Most of the opaque material is, therefore, of the nature of free oxide. This slag is interesting, in so far as it throws some light on the effect of the presence of phosphorus pentoxide; in other cases, in forming silicophosphates where fluorides are absent and apatite where they are present. It indicates that if the phosphorus be absent from the melt, or if be removed, say, as apatite, the normal residual silicate is the dibasic salt. In the presence of phosphorus pentoxide, on the other hand, the normal constituents are the silicophosphates, the particular crystals which form depending on the composition of the melt.

The physical chemistry of the complex group of compounds which are found in basic slag constitutes a practically untouched field. The data with reference to the equilibria between the various oxides are exceedingly scanty and of little use in elucidating the behaviour of the molten slag on cooling. The most important oxides with which we are essentially concerned, and which form the components of basic slag, are lime, magnesia, the oxides of iron and manganese, silica and phosphorus pentoxide, while fluorides and to a lesser extent sulphides also appear. Obviously such a "system" is too complex for laboratory investigation at the present time; at any rate, most of those hitherto investigated having consisted of two, three, or in rare instances, four components.

In the absence of a complete physics-chemical investigation of the problem, however, there is no doubt that much useful information would be obtained from an examination of simpler complexes, say of three of the components. Thus the problems regarding the nature of the silicophosphates could probably be partly solved by the elucidation of the equilibria existing in the system CaO-SiO_2-P_2O_5, as they are the oxides which form a large proportion of the slags. From the evidence already to hand, it is apparent that the chief basic element in these compounds is calcium, as the iron and manganese seem to occur mainly in the form of "spinels" or free oxides. There is, of course, the possibility that the presence of the latter have an effect on the equilibrium of the various silicophosphates, but in the absence of any direct information it may be assumed that their main function is concerned with the alteration of the temperatures of consolidation, compared with those in the system CaO-SiO_2-P_2O_5. It is true that calcium enters into the spinels, but in view of the fact that there is generally an excess of basic oxides present, there should be little disturbance of the silicophosphates in consequence.

So far as we are aware, few investigations of the system CaO-SiO_2-P_2O_5 have been made. In addition to the work to which reference has been made earlier, the only other effort with which we are acquainted with that of Nielsen,[36] who explored part of this ternary system.

In addition to an examination of the three binary system concerned, he determined the melting points of a series of mixtures of tricalcium phosphate and silica. Maxima occur at the points represented by $Ca_3P_2O_8.2SiO_2$ and $Ca_3P_2O_8.3SiO_2$, while he states that the last-named point is a definite maximum on the melting point surface of the ternary system. Unfortunately, no optical data referring to this compound are available, its existence being apparently deduced from the occurrence of the maximum melting point. Hence it is impossible to say whether this is the compound which is found in some of the slags described above, and in which the $SiO_2 : P_2O_5$ ratio is approximately 3:1. If the two be identical, then the proportion of calcium oxide in this compound is much lower than in the other silicophosphates. This point is expected to be elucidated in an investigation of the ternary system, on which one of us is at present engaged.

Little assistance is to be gained from analogies with other types of slags, such as those from "acid" furnaces.

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[36] O. Nielsen, Ferrum, 10, 97, 1913; cf K. Huttner, *Zeit.* anorg. Chem., 59, 716, 1908.

As mentioned earlier, the system CaO-P_2O_5 has also been examined by T. Dieckmann and E. Houdremont,[37] who have determined the melting point of the following calcium compounds:—Tetraphosphate (1,630 degrees); oxyapatite (1,540 degrees); triphosphate (1,670 degrees); pyrophosphate (1,230 degrees); metaphosphate (970-980 degrees); silicophosphates (1,760 degrees); fluorapatite (1,630 degrees). They conclude that Carnot's silicophosphate is composed of tribasic calcium-phosphate and calcium orthosilicate, and not as Hilgenstock and others have suggested of the tetraphosphate and the metasilicate of calcium. Each of the compounds mentioned above gives a cooling curve with a fairly definite arrest at the melting point, and in most cases a certain degree of under-cooling as well. As no examination of mixtures with compositions between those of the various compounds was made, the results are not of great value from the physico-chemical point of view; the further discussion by these authors, on the application of the results to basic slags, is based mainly on the results of solubility tests.

In general, in basic slags, the phosphorus plays such an important role in the formation of the constituents that the latter are totally different from those found in acid slags. Thus in the material under investigation there is no trace of the existence of the orthosilicates of iron and manganese, fayalite and tephroite,[38] nor of the metasilicates such as rhodonite and others,[39] which are so common in acid slags.

If those slags, to which fluorspar has been added, be disregarded for the moment, it may be stated that basic slags consist essentially of three types of compounds, silicophosphates, spinelloid compounds, and free oxides. So far as the first of these is concerned, at least four compounds of this type have been described.

(a) The brown crystals described by Stead and Ridsdale, and having the $SiO_2 : P_2O_5$ ratio 1:4.

(b) The pleochroic crystals described by the same authors, the $SiO_2 : P_2O_5$ ratio being unity.

(c) The new silicophosphate described in the present paper, with the ratio $SiO_2 : P_2O_5$ approximately 3:1.

(d) The "octobasic" compound described by Kroll, with $SiO_2 : P_2O_5$ ratio as unity.

The last of these has not been observed in any of the material investigated in the present instance, nor is much information available regarding the type of slag in which it occurs. As suggested earlier, the evidence for the homogeneity of the crystals is not very satisfactory, as some apparently homogeneous crystals show heterogeneity on microscopic examination. An example of this will be discussed later. The remaining three compounds, however, occur in the slags described above, though not more than two co-exist in any one slag. On the assumption that the constituents of these crystals are tetracalcium phosphate—$Ca_4P_2O_9$—and calcium metasilicate—$CaSiO_3$—the three compounds may be regarded, on the basis of the analytical results, as composed of these two salts in the molecular proportions 4:1, 1:1, and 1:3 respectively, but, as there is no evidence as to the mode of partition of the calcium oxide, it is probably better to consider them as ternary compounds existing in the system CaO-P_2O_5-SiO_2. The assumption that the silicophosphate (c) is a double salt composed of the two compounds mentioned above is certainly not valid if (c) is identical with the compound mentioned by Nielsen. The available data suggest that the factor which determines the occurrence of these compounds in a slag is the chemical composition; a slag in which the ratio $SiO_2 : P_2O_5$ is approximately unity will give on cooling the green compound; if the amount of phosphorus be greater than unity there will be a tendency for the brown compound to develop as well, while in those slags with a lower phosphorus content the compound (c) will be found. It is probable that the amount of solid solution between these compounds is relatively slight, and that they separate from the molten material in a comparatively pure state.

In the case of the compound (b) the analytical results indicate that these may be an appreciable excess of the phosphate over that required for the formula with unit proportions of the two salts, and this excess may be accounted for by the assumption of a certain amount of solid solution; in part, however, the difficulty in obtaining uncontaminated crystals may be responsible.

These silicophosphates have calcium as their most important basic element, but there is probably a certain amount of other bases in solid solution with the calcium. The available analyses, however, indicate that the amount of such basic oxides cannot be very great. The optical properties of each of these salts are generally sufficient for their discrimination.

In none of the slags described above has the pure calcium tetraphosphate been observed. It is possible that it may occur as a constituent of the vesicles in some cases, as these have not been minutely examined, the investigations being in

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[37] T. Dieckmann and E. Houdremont, *Zeit. anorg. Chem.*, 120, 129, 1921.

[38] cf. J. H. L. Vogt, Die Silikatschmelzlösungen, Kristiania, 1903.

[39] cf. J. H. Whiteley and A. F. Hallimond, Journ. Iron Steel Inst., i, 199, 1919.

general confined to the " solid " material of the slag in each instance. Just as in the case of igneous rocks, the crystals which appear in the vesicles cannot always be regarded as typical of the general mass, as their development often occurs at a late stage in the cooling of the material and under conditions which are different from those obtaining in the main body of slag, especially with reference to the viscosity of the medium in which crystallisation occurs and the proportion of gaseous constituents. So far as our observations go, tetracalcium phosphate is not a visible constituent of slags of the types examined, and hence no further light on its occurrence is available.

Although in this paper the terms " spinel " and " spinelloid " mineral have been generally used for the aluminates and ferrites of calcium, magnesium, iron, and manganese which are found in the slags, it is not by any means certain that these salts are true spinels. As there is in basic slag practically always an excess of basic oxides over that required to saturate the various acidic oxides present, it is probably only necessary to take into consideration the more basic aluminates or ferrites in each instance. Several synthetic investigations of these compounds have been made, and the more important results may be indicated.

According to Shepherd and Rankin,[40] calcium oxide forms four compounds with alumina, the most basic which is stable at high temperatures being tricalcium aluminate, $3CaO.Al_2O_3$. This compound in the pure condition dissociated near 1,600 degrees C., at a temperature below its melting point, with the formation of $5CaO.3Al_2O_3$ and free CaO. Both $3CaO : Al_2O_3$ and $5CaO.3Al_2O_3$ form crystals belonging to the cubic system. The investigations of S. Hilpert and E. J. Kohlmeyer[41] indicate the existence of five compounds in the system $CaO\text{-}Fe_2O_3$, the most basic being $3CaO.Fe_2O_3$. Sosman and Merwin,[42] on the other hand, find only two ferrites of calcium, $2CaO.Fe_2O_3$ and $CaO.Fe_2O_3$, neither of which is cubic. Magnesia forms only one compound with alumina, spinel, the composition of which is represented by $MgO.Al_2O_3$, while only one ferrite, $MgO.Fe_2O_3$, has been described. Ferrous oxide forms an aluminate, $FeO.Al_2O_3$, which is found naturally as the mineral hercynite, while the corresponding ferrite is magnetite, Fe_3O_4. The analyses of the naturally occurring spinels indicate that the aluminates and ferrites of magnesium and iron form solid solutions to a wide extent, but the corresponding calcium salts are apparently not isomorphous with the former. The system $CaO\text{-}MgO\text{-}Al_2O_3$ has been examined by Rankin and Merwin,[43] who find that there is practically no formation of solid solution between spinel, $MgAl_2O_4$, and the calcium aluminates. The possibility of isomorphism between the calcium aluminates and ferrites does not seem to have been investigated, but its existence has been suggested in connection with the constitution of Portland cement clinkers. There is likewise no experimental evidence regarding the relationship between the calcium ferrites and the magnesium, manganese, and ferrous salts. The analyses of Stead and Ridsdale show that two minerals of this nature exist in slags—one a mixture of calcium and ferrous oxides, with subordinate amounts of manganese and magnesia, combined with the sesquioxides of iron, aluminium, and chromium, and the other a compound of a similar nature but without ferrous oxide. The former seems to be a form of magnetite with a preponderating admixture of the calcium and other compounds, while the latter is the calcium compounds with subordinate amounts of the magnesium and manganese salts. In the present investigation no method of discriminating these microscopically has been found, and the " spinelloid " minerals which occur in the slags appear to be homogeneous both when examined optically and also when subjected to etching.

The way in which the basic oxides are partitioned between the silicophosphates and the " spinelloid " material is interesting. In all of the former calcium oxide is the chief base and magnesia is the only other one of importance, the amounts of manganese and ferrous oxides being almost negigibly small. In the spinelloid crystals, on the other hand, the amount of magnesia is low, the important bases being lime and ferrous oxide in the one case and lime alone in the other. The excess of basic oxides seems to crystallise out in the uncombined form not as individual oxides but as isomorphous mixture. Several methods of etching this oxide material have been tried, but none have revealed any trace of heterogeneity; hence it must be assumed that a complex group of solid solutions exists. It is in this that the greater proportion of the ferrous and manganese oxides are found. The analyses of the dendrites by Stead and Ridsdale show a fairly high proportion of lime, but they also show a certain amount of sesquioxides. The latter are probably present as calcium aluminate in the free

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[40] E. S. Shepherd and G. A. Rankin, Amer. Journ. Sci., 28, 293, 1909; *Zeit. anorg. chem.*, 71, 19, 1911; G. A. Rankin, Journ. Ind. Eng. Chem., 7, 466, 1915; G. A. Rankin and F. E. Wright, Amer. Journ. Sci., 39, 1, 1915.

[41] S. Hilpert and E. J. Kohlmeyer, Ber., 42, 4581, 1909.

[42] R. B. Sosman and H. E. Merwin, Journ. Washington Acad. Sci., 6, 532, 1916; E. S. Shepherd and G. A. Rankin, Amer. Journ. Sci., 28, 293, 1909.

[43] G. A. Rankin and H. E. Merwin, Journ. Amer. Chem. Soc., 38, 568, 1916.

condition and not isomorphously admixed; hence the amount of free lime is probably rather low. The heterogeneity of the dendritic material can be observed microscopically, and in several of the slags described above etching tests showed the presence of numerous minute inclusions of "spinelloid" material arranged in a pseudo-eutectic fashion in the branches of the dendrites.

It is apparent then that, of the chief bases present, the calcium oxide is mainly found in the silicophosphate and the "spinelloid" mineral, only the excess occurring in the free form; the ferrous oxide is largely free, although a certain amount occurs in the ferrites or aluminates, while the manganese oxide is for the most part uncombined.

In those slags to which fluorspar has been added during the manufacture of the steel the equilibrium is decidedly different to that in the slags discussed above. The calcium fluoride combines with three molecules of tricalcium phosphate to form the mineral apatite, and in the cold slag a large proportion of the phosphorus and, presumably, all the fluorine is present in this form. The natural mineral apatite is a mixture of this compound, fluoapatite, and the corresponding chlorine compound, chlorapatite, but in the slags it is probably the former which is present. According to Nacken,[44] who has investigated the ternary system, CaF_2-$CaCl_2$-$Ca_3P_2O_8$, calcium fluoride and tricalcium phosphate form only one compound, $CaF_2.3Ca_3P_2O_8$, with a melting point of 1,650 degrees C.; this forms a simple eutectiferous series with CaF_2, the eutectic temperatures being 1,205 degrees C. Numerous earlier syntheses of fluoapatite are on record,[45] and there is little doubt but that it is the stable form which crystallises from a melt containing its components.

Although the published analyses of natural apatites[46] show that certain amounts of other basic oxides may be present, there is little information available with reference to the possibilities of solid solution. No analogous magnesium compound is known, but the natural mineral, wagnerite, corresponds to the formula $MgF_2.Ca_3P_2O_8$; it has also been synthesised by Winter,[47] who finds that its melting point is 1,253 degrees C. It is, however, improbable that this compound enters into solid solution in apatite, especially as it crystallises in the monoclinic system while apatite is hexagonal. Certain naturally occurring analogues of apatite in which the calcium fluoride is replaced by other radicles have been described. Thus dahllite[48] has the composition $CaCO_3.3Ca_3P_2O_8$ and voelckerite[49] $CaO.3Ca_3P_2O_8$. The former is not likely to be stable at high temperatures, while the latter, if it resembles, as seems likely, apatite in its optical properties, has not been observed in slags; hence it is improbable that it is stable under furnace conditions.

If the amount of fluorspar which has been added is sufficient to "saturate" all the calcium phosphate and so form apatite, the silica is found as dicalcium silicate, $2CaO.SiO_2$. It is probable that this silicate, as found in slags, contains some magnesium replacing the calcium. Although Rankin and Wright[50] found that tricalcium silicate, $3CaO.SiO_2$, was one of the phases in the binary system, $CaO - SiO_2$, this substance was not found by Ferguson and Merwin[51] in their elaborate investigation of the ternary system, $CaO - MgO - SiO_2$. Although experimental difficulties prevented a detailed examination of that portion of the ternary system very rich in calcium oxide, sufficient evidence was obtained to show that, on the fusion point surface, the field of free CaO is contiguous with that of $\alpha - 2CaO.SiO_2$. The latter compound apparently did not form solid solutions with either the former or the double salt monticellite $CaO.MgO.SiO_2$. If in each of the fluorspar slags described above the bases other than lime and magnesia be ignored for the moment, then the points representing the relative amounts of CaO, MgO, and SiO_2 would be either in the α-$2CaO.SiO_2$ field or in the CaO field. In the latter case consolidation would result in the crystallisation of free CaO, free MgO, and $2CaO.SiO_2$; in the former monticellite might develop if the content of magnesia were sufficiently high, but this is very improbable in such slags, especially as monticellite has not been detected in them. At present it is not known whether the dicalcium silicate holds any of the magnesium salt in solid solution; the fact that α-$2CaO.SiO_2$ has none does not preclude the possibility of some solid solution in the β-form, into which the α is transformed at 1,420 degrees C.

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[44] R. Nacken, Cent. Min., 545, 1912.

[45] cf. e.g. N. S. Manross, Liebig's Ann., 82, 353, 1852; H. Briegleb, *ibid.*, 97, 95, 1836; H. St. C. Deville, Compt. Rend., 47, 985, 1858; F. K. Cameron and W. J. M'Caughey, Journ. Phys. Chem., 15, 464, 1911.

[46] E. S. Dana, System of Mineralogy, 6th ed., 764, 1887; J. A. Voelcker, Ber., 16, 2460, 1883.

[47] H. Winter, Versuche zur Bildung von Apatiten und Wagneritähnlichen Verbindungen, Dissertation, Leipzig, 1913.

[48] W. Tschirwinsky, Cent. Min., 379, 1907; W. T. Schaller, Amer. Journ. Sci. (4), 30, 309, 1910.

[49] A. F. Rogers, Amer. Journ. Sci. (4), 33, 475, 1912.

[50] G. A. Rankin and F. E. Wright, Amer. Journ. Sci. (4), 39, 1, 1915; cf. G. A. Rankin and H. E. Merwin, Journ. Amer. Chem. Soc., 38, 568, 1916.

[51] J. B. Ferguson and H. E. Merwin, Proc. Nat. Acad. Sci., 5, 16, 1919; Amer. Journ. Sci. (4), 48, 81, 1919.

The evidence adduced in the discussion of slag No. 9 is in favour of the magnesia being in solid solution in the calcium salt. Although it has been suggested[52] that a glassy ground mass is often present in basic slags, owing to the tendency of mixtures of calcium orthosilicate and other silicates to undercool, we have never observed any glass in those slags which contain the compound $2CaO.SiO_2$. This is in agreement with the results of Ferguson and Merwin,[53] the mixture richest in lime which they examined showing crystals of CaO and $2CaO.SiO_2$, but no glass.

So far as the spinelloid material and the free oxides are concerned, there is no evidence that the introduction of fluorspar causes the equilibrium between these to differ from that in the fluorspar-free slags. The most important effect of the addition of fluorspar is the formation of apatite, which is the first compound to crystallise from the melt, the amount formed varying with the fluorine content, is that an excess of the latter element results in all the phosphorus going into the apatite. The silica then is found in the form of dicalcium silicate, while the partition of the other oxides between the various constituents is very similar to that discussed in connectin with the fluorspar-free slags.

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[52] cf. C. H. Desch, Trans. Faraday Soc., 16, 272, 1921.

[53] J. B. Ferguson and H. E. Merwin, *loc. cit.*, p. 96.

DISCUSSION

The Chairman said he was afraid the authors had packed too much into this most interesting paper of theirs for most of them to digest; but he had no doubt that in the future this paper would be looked upon as a classic on the subject of the constitution of basic slag. While Dr. Scott had not told them a great deal that was of practical application metallurgically, yet there was no doubt that what he had done was to lay the foundation for future work in that direction. The paper was now open for discussion.

Mr. Andrew McCance, D.Sc., said that he could only echo the Chairman's remarks with regard to the paper. He thought it a most original and striking contribution to the subject, and he had no doubt that in the future the Journal of the Institute would often be referred to by those who were dealing with this question. He regretted that, because of the great amount of detail information which Dr. Scott had given, he had not yet had time to study the paper properly; but there were one or two questions he should like to ask. One was with regard to the presence of free FeO in the slag. What means, he would ask, had the authors taken to identify the presence of that free ferrous oxide? Metallurgically that was an important point, because he thought everyone would agree that the phosphorus in the steel was oxidised by the FeO to P_2O_5, which united with the free lime present to form calcium phosphate. He should like to know the particular means taken to identify that FeO.

It seemed rather extraordinary that there should be so many silico-phosphates present in those slags. Compounds of that nature were not as a rule very stable, and the fact that a whole series of such compounds existed led him to question very much whether they were actual entities or merely solid solutions of one in the other. There was a further question raised that in a solid solution of that nature there must be one dominant crystal, and in the case of these numerous double compounds being solid solutions, there must be some definite change point at which one dominant crystal system changes to the other; and he had not read the paper sufficiently to be able to know whether the definite crystalline optical properties belonged to the two ends of the series, or whether the intermediate members all possessed definite crystalline optical properties.

There was a rather important point in connection with the state of the ferric oxide. Dr. Scott apparently assumed that that was present as calcium ferrate, and he did not think there was any doubt that this was so, because lime and ferric oxide would unite to form a slag if heated up in the absence of any other material. The work was mentioned that had been done on that subject by Hilpert, who had noted that there were five or six such calcium ferrates present in the series. He himself remembered reading Hilpert's paper; but the evidence which he adduced for the presence of these compounds was really very inconclusive, and he thought that was another case where, instead of half a dozen compounds existing, there was only perhaps one or at most two. The number of eutectics which were present in those slags that Dr. Scott showed were not very definite, and it seemed that Dr. Scott was of the opinion that the presence of such eutectics was very doubtful. But there was not necessarily the one type of eutectic, and the fact that one element was crystallised around another might be sufficient to justify it being called a eutectic in certain cases. He was of the opinion from the slides shown that quite a number of the structures in these slags really belonged to the eutectoid type, especially the structure of the silico-phosphate and the brown phosphate. He was afraid he could not add anything very definite to the discussion, because there was really so much matter in the paper that it would take some considerable time to study it properly, but he hoped to amplify his remarks in writing after he had had an opportunity of reading the paper through in its entirety.

Professor J. H. Andrew, D.Sc., said that he would like, in the first place, to associate himself with the remarks made by Dr. McCance as to the extreme value of the paper. With regard to the number of compounds that Dr. Scott had referred to, he thought it was a great mistake to make things any more complex than necessary, and that, instead of giving a particular formula for every composition, it would be better to bring things down to the simplest form, and to consider the fact that they might be dealing with solid solutions. With regard to the dicalcium silicate that Dr. Scott referred to, he had always understood that when the calcium ran as high as that it disintegrated on cooling. With regard to the question of the liquidus curves of slags, of which there was a model on the table, when they took the melting point of a series of slags, usually the slags solidified as a glassy mass, could they then regard these liquidus curves as representing the true state as it existed in the cold; in other words, how did they regard the liquid state in the case of the slag? He should like to know whether Dr. Scott regarded the liquid slag as consisting of the numerous compounds met with as such in the cold, or whether he regarded the liquid state as consisting of dissociated oxides or silicates. With regard to the question of the eutectics which Dr. McCance had also referred to, was he not right in assuming that examination by reflected light would show a laminated eutectic property pretty clearly, though by transmitted light the eutectic would rather give a homogenous mass, owing to the banded structure acting like a diffraction grating? He observed that the authors had not made any reference at all to the conditions under which the slags were taken. As was well known, many of these silicate minerals underwent numerous changes during cooling down to atmospheric temperature. It would be interesting, therefore, if Dr. Scott could give them some idea of the conditions under which the slags were taken, as to the rate of cooling, etc., and also whether such slags cooled normally would be glassy or crystalline. He should like to associate himself with all the kind remarks made by others interested in the paper; at the same time he certainly thought the authors would agree with him when he said that, metallurgically speaking, it was but a step in the direction in which they must go. There was not very much they could apply directly to metallurgical problems, but it would be of enormous use to anyone else about to carry on investigations on similar lines

Mr. F. Lesley Robertson said that there were few subjects on which more had been written with less of help to the steelmaker than on the composition of slags. If the information obtained by the authorities and set forth in this paper will help to throw more light on the constituents as distinct from ultimate composition of molten slags, the steelmaker may at last begin to associate intelligently the composition of his slag with rapid working condition, and obtain ideas which may help him to cheapen his process. Merely comparing ultimate analyses with working condition has proved very barren.

The field the authors' methods open is full of possibility, and it is difficult to discuss their work until we are more familiar with it. A few points suggest themselves for query:—

(1) Was it fair to assume that the constituents present in the cold solid slag were there, as such, in the molten condition?

(2) With what constituent did the authors think the sulphur associated itself?

(3) In the preparation of their specimen for examination by reflected light, how did the authors effect their final polishing?

(4) Would the presence of apatite in the molten slag render the phosphorus less liable to reduction?

Mr. J. F. Wilson said that he thought Messrs. McArthur and Scott were very much to be congratulated for the manner in which they had dealt with this subject, more especially with regard to the slag phosphates. Undoubtedly their paper made a distinct step in regard to the study of phosphates. He had been particularly interested to hear the remarks as to the formation of apatite. As he understood it, by adding fluorspar to basic slag the silica was thrown out of direct combination with the phosphates. Now fluorspar conferred fluidity on the slag, and brought it, in the terms of the smelter, into condition; this fluidity was also conferred when no phosphate was present in the slag. Considering the relatively high melting point of apatite, he should suggest that fluorspar took some other important action besides the formation of apatite. Regarding the tetrabasic phosphate, he should have liked if Dr. Scott had been able to put before them the results of the examination of such a slag as that which contained an analysis of, say, silica 10 per cent., and phosphoric acid about 24 per cent. He noted the authors' comments on the two methods of examination by reflected light and by transmitted light. As far as he could gather, there was something could be got from each, and he should think the best was—both. The authors stated, "As there is in basic slag practically always an excess of basic oxides over that required to saturate the various acidic oxides present, it is probably only necessary to take into consideration the more basic aluminates or ferrites in each instance." He, however, could not say that he agreed with that attitude. Was there not the great possibility that what they called excess basic oxides, or the spinelloid material, were really the material means by which the purification of the steel was carried out? If that were so, were not these oxides deserving the most attention? He suggested that a better knowledge of the purifying effect exerted on slags could be gained by studying these excess basic oxides. Regarding free lime iron oxide, etc., a slag low in iron oxide melted lime with difficulty; but the reverse was the case when the iron oxide was higher. Take, for instance, a furness being in a condition to tap, but being prevented from doing so by some breakdown. The slag would not go on dissolving lime practically indefinitely. They could not say that the slag had been satisfied, and the great amount they had put in afterwards was, say, existing in the free state. He thought that slags were given credit for more free lime and free iron oxides than what they really contained. As had been mentioned before, he took it that the various minerals separating out during solidfication and cooling were the assumed constituents of the liquid slag.

Dr. Scott—It did not say so in the paper.

Mr. Wilson—Reading papers on this subject, one would take it that that assumption was a general one. Was it really so?

Mr. A. J. K. Honeyman said that he should like to thank Messrs. Scott and McArthur for their most interesting paper. There were two points which he would refer to briefly. Firstly, Dr. Scott had indicated when fluorspar had been added to the melt and when omitted. If he could also supply a complete history of the melts, including the analysis and quantity of the charges and additions of ore, etc., the value of the paper would be greatly enhanced from the metallurgical point of view. This would be the more evident when the results obtained in the present paper were applied to the investigation of the use of basic slag in agriculture and in the ceramic industry.

Secondly, he was not quite sure if the slag had been properly sampled. The micro-photographs exhibited had shown that in some cases the primary crystals of the slag were remarkably well developed, and that occasionally these crystals were broken across. It would appear, therefore, that these crystals had separated from the melt while the matrix was still in a very fluid state, the fractures being caused by subsequent pouring or dumping of the still fluid slag. These crystals would tend to rise or fall in the slag according to density, and in this way its composition might vary from place to place. He should like to know how the authors had met this possibility.

Dr. Tyrrell said that he had been asked by the Secretary to take part in the discussion, but he was afraid that he could not contribute anything very illuminating to the subject from the point of view of the metallurgist; his side was rather the geological. Perhaps he might be allowed to express his pleasure at finding an assemblage of business and practical men listening with pleasure to this subject of the constitution of basic slag. There were one or two points on which Dr. Scott had certainly thrown much light—that was on the relation of igneous rocks to slags. One point that occurred to him was, while the mineral composition of these slags indicated the high temperature at which the slag could be crystalilsed, it did not by any means follow that igneous rocks of the same or similar compositions crystallised at the same high temperatures as these slags. There were, of course, some igneous rocks fairly close to those slags that Dr. Scott had referred to. Another point mentioned by Dr. Scott was the fact that the so-called eutectic structure had been produced in the case of some igneous rocks and slags. As Dr. Scott had pointed out, the actual intergrowth merely meant that the two minerals had crystallised simultaneously, and it might or might not have the composition appropriate to the eutectic. The final point was one of technique. It was most interesting to hear Dr. Scott's opinion as to the relative merits of the two methods of investigation by reflected light and transmitted light. He himself had not had much to do with the method involving reflected light. The same thing as described by Dr. Scott could be done quite well with thin sections of rocks and slags by leaving them uncovered and then applying the refractive media.

The Chairman said that he would ask Dr. Scott to reply to what part of the discussion he chose, and any further discussion or reply could be carried on by means of correspondence.

Mr. J. H. Whiteley wrote: The authors are to be congratulated for having collated so much valuable information upon a very difficult subject, and a paper of this kind is sure to be of great use to future investigators in the study of basic slags.

The elucidation of the structure of basic slags is difficult on account both of the wide range of composition possible and also the numerous forms in which silicates of calcium and magnesium can exist. Like the authors, I have not yet encountered a basic slag containing either fayalite or rhodonite—minerals which are so common in acid slags. A striking feature in basic slags is that so large a proportion of the iron can exist as ferric oxide. This is well shown in the authors' table, and I have commonly seen finishing slags containing not more than 6·0 per cent. of iron with at least one-third of that amount in the form of ferric oxide. In acid slags this is never to be observed; even when the iron content is 25·0 per cent. or more, and the carbon content of the bath under 0·15 per cent., the ferric oxide content seldom exceeds 3·0 per cent., which is equivalent to $\frac{1}{12}$ of the iron content. It thus seems reasonable to conclude that the FeO in molten acid slags is in a more stable condition than in basic slags—in other words, the ratio of free iron oxide to the total amount present in a basic slag is much higher than in an acid. This is also seen in the oxidising capacity of the two slags, for a basic slag with, say, 6·0 per cent. of iron will cause the carbon to be removed from the bath quite as rapidly as an acid slag containing 25 per cent. of iron. This difference in behaviour is undoubtedly due to the nature of the compounds present, and the study of the constitution of basic slags, as undertaken by the authors, should eventually prove of great value in this direction.

Mr. J. E. Fletcher wrote: The authors are to be congratulated on their very valuable work and for the clearly enunciated introduction to their subject. Definite conclusions concerning the liquid composition of basic slags drawn from the evidence of the micro-structure of the cooled slags are very difficult to arrive at owing to the many variables involved.

The collection of slags investigated, though interesting from the point of view of variety, is not quite so likely to yield fruitful results as would a series of slags taken progressively from a representative basic steel heat. There the changes from a weakly acid condition to a strongly basic one furnish means for comparing the transitional crystalline products which result from the cooling down of the more stable phosphates, silicates, ferrates, and aluminates which probably exist in the molten slag.

The writer would refer to several pertinent remarks in the paper on the stability of the most basic members of the slag groups examined by research workers in the domain of furnace slags.

Rankin and Shepherd (33) have shown the stability of the dicalcic silicate $2CaO.SiO_2$ to be greater than that of the monosilicate $CaO.SiO_2$. There is evidence that on cooling from high temperatures the former can, in the presence of available free silica, crystallise out as the monosilicate. Certain blast-furname slags also reveal a break up of the disilicate, the monosilicate with free lime being the products when quickly cooled.

It would seem that the disilicate $2CaO.SiO_2$ is the stable form in the molten slags at sufficiently high temperatures.

Again, the work of Kroll (14), Blome (16), and Morrison (21) is suggestive of phosphates richer in lime than the tetra form at the higher temperatures, and it does not appear improbable that the molten slag may contain a stable neutral phosphate of the composition $5\ CaO.P_2O_5$, which on cooling may yield the tetraphosphate $4\ CaO\ P_2O_5$, liberating free lime all ready for combining with the acid oxides available (SiO_2, Al_2O_3, and Fe_2O_3). It may be that the transition period following the initial breakdown of the stable silicate and phosphate is the nascent stage associated with the formation of the less stable silicophosphates.

Further, Shepherd and Rankin (40) refer to the stability of the lime aluminate of neutral character $3\ CaO.Al_2O_3$ at high temperatures, and again the writer believes this fact an important one as connected with the composition of the molten slags. Hilpert and Kohlmeyer (41) appear to confirm this view.

The writer has evidence of the presence in certain soaking pit slags of the presence of the ferrate $3\ FeO.Fe_2O_3$, which appears to be stable at high temperatures.

From these researches it would not appear improbable that generally, in molten basic slags, one may expect compounds of the type $3\ RO.Al_2O_3$ or $3\ RO.Fe_2O_3$ to be present.

The writer suggests, therefore, that the authors' work, defining the structure of the cooled basic slags, supports the view he has held for some years that in the liquid condition at high temperatures basic slags during the working cycle of steelmaking tend towards the neutral condition (acid oxygen % = basic oxygen %).

With this point in view, an examination of your ten slags will show the ratio $\frac{\text{basic oxygen \%}}{\text{acid oxygen \%}}$ of Nos. 1 to 10, taken in order, is ·85, 1·07, ·65, ·97, ·95, ·72, 1·24, 1·04, 1·36, ·91.

The writer takes the view that when the aluminates and ferrates are formed the Al_2O_3 and the Fe_2O_3 act as acid constituents to the basic oxides CaO, MnO, MgO, and FeO. He has used this hypothesis when estimating the oxygen ratios above expressed.

H. H. Campbell (Manufacture of Iron and Steel) refers to the fact that when the sum of the silica and phosphorus anhydride contents in a basic slag exceed 25 per cent. phosphorus passes back into the metal, such action being doubtless brought about by a decomposition of the phosphate, free lime being liberated. The writer has found a similar limit in the ferrous phosphate slags of the puddling process.

Slags of the type cited by the authors are bordering on the 25 per cent. ($SiO_2 + P_2O_5$) critical composition, with the exception of Nos. 3, 7, and 9. No. 9 is strongly basic and dephosphorising. No. 3 is an abnormal slag from its high alumina content, and No. 1 similarly abnormally high in ferric oxide—which two slags illustrate the spinel type containing the $RO_n.Al_2O_3$ and $RO_n.Fe_2O_3$ constituents.

The remarks of the authors confirming the research of Stead and Ridsdale on these constituents are very interesting, and there seems little doubt that in the molten slags the more basic aluminates and ferrates occur, these probably splitting up into more acid types as cooling proceeds, with the freeing of the excess RO bases.

As bearing upon this point, the writer would refer to the progressive change in the $FeO\text{-}Fe_2O_3$ ratio which takes place during the working of a steel charge where the working slag was a mixture of ferric oxide and a relatively small proportion of lime and silica.

Shortly after the slag became perfectly liquid the ratio indicated the $3\,FeO\text{-}Fe_2O_3$ condition. An hour afterwards the ferric oxide had fallen to about 3 per cent. in a slag whose composition was:—FeO 60·6, SiO_2 4·5, Fe_2O_3 2·9, CaO 30·6, MnO 2·4 per cent.

It is notorious that basic slags of this nature are far from homogeneous, and generally this is true of most basic slags. It is not strange, therefore, to hear of the evidence of such non-homogeneity in the authors' slags Nos. 1 and 3 (in the cooled slags).

The preparation of synthetic slags of the character cited by the authors is most difficult, but it does appear to the writer that if representative basic slags could be heated up to, say, 1,700° C., and samples quenched or rapidly cooled to show the effects of quick cooling in fixing the constituents, together with very slowly cooled samples, the cold slags would then give opportunities for determining the mechanism of the crystalline growths much more satisfactorily.

The writer's hypothesis that the molten basic slags are mixtures of the constituents $5\,CaO.P_2O_5$, $2\,CaO.SiO_2$, and the $3\,RO.R_2O_3$ oxides, with excess RO or SiO_2 as solutes, is shown graphically in the diagrams A and B. In graph A the analyses are plotted, and in B the composition of the slags is shown on the hypothesis that in the molten condition the phosphate, silicates, ferrate, and aluminate are present in the inert or neutral forms, containing basic and acid oxygen in equal molecular proportions.

The authors' slags Nos. 2, 4, 5, 7, 8, 9, and 10 are graphed, Nos. 1, 3, and 6 being omitted because these are of abnormal analysis.

The writer recognises the extreme value of the authors' conclusions as deduced from the micro-examination and chemical analysis of the slags, and quite agrees with the mineralogical references, especially those referring to the analogy with the phosphate and spinel types of crystals discovered by Stead and Ridsdale. It is specially interesting to note the authors' discovery of the brown silicophosphate with the ratio 3 : 1.

The practical value of such research will be further proved when, from the examination of the cold slags, it will be possible to deduce with accuracy the true composition of the slag when in the molten state. Obviously a great deal of work remains to be done before this is possible, but, just as it is now almost certainly proved that carbon exists in molten iron and steel as the tricarbide Fe_3C, from careful research on heat-treated specimens, so it should be eventually possible to arrive at the composition of the phosphates, etc., in molten basic slags by examination of slags heated and cooled in known fashion. It is certain from the authors' research that the type of crystals revealed in the cold slags points to the fact that these are the transition products of molten constituents of very different composition.

As an illustration of a representative basic slag of inert composition, the following is given:—

ANALYSIS.

SiO_2	9·9 %
P_2O_5	14·2 %
CaO	49·8 %
MgO	2·0 %
MnO	2·0 %
FeO	10·1 %
Fe_2O_3	9·8 %
Al_2O_3	2·2 %
	100·0

CONSTITUTIONAL COMPOSITION.

5 CaO . P_2O_5	42·00 %	
2 CaO . SiO_2	28·30 %	
3 CaO . Al_2O_3	5·90 %	3 RO
3 FeO Fe_2O_3		R_2O_3
MnO	23·80 %	
MgO		
	100·00 %	

Such a slag is similar to the sample taken just before adding the last lime to a mild steel charge.

Dr. SCOTT's reply to discussion:—With reference to Dr. McCance's question about free ferrous oxide, methods used for the detection of the latter under the microscope are indicated in the paper. In addition, one of us had already had some experience in identifying this material in certain types of bricks and refractory materials, and in some cases its presence was verified by comparing sections of slag with sections of brick. With regard to the possibility of some of the silicophosphates being of the nature of eutectics, there are several strong arguments against this. In the first place, microscopic and optical examination shows that each of the three silicophosphates is apparently homogeneous, the quasi-eutectic structure which appears in some of the slides being due in certain cases to the presence of cleavage. In each case the optical properties are sufficient to diagnose the particular compound present, while the fact that the silicophosphates crystallise in different systems is also strongly in favour of the view that they are different compounds. Another argument is that in some of the slides two of the silicophosphates are found in close contiguity. As there is no doubt that in this case they both crystallise from the same melt, in fact from the same small part of the melt, there is no doubt that if solid solution were possible it would have occurred in this particular case. With reference to the view that such complex compounds should be unstable at high temperatures, there is an abundance of analogous evidence against this. For example, fluorapatite is stable up to its melting point somewhere in the region of 1,650 degrees C. In addition, such compounds as chlorapatite, in which calcium fluoride has been replaced by calcium chloride, are likewise stable, while oxyapatite, and possibly also carbonatoapatite, have recently been shown to be likewise stable. Similarly we find that certain felspathoid minerals composed of alkaline silicates, combined with sodium sulphate, sodium chloride, and so forth, are also stable at high temperatures; hence there is no reason for assuming that the silicophosphates are likewise unstable. At present one of us has further work on hand regarding the ranges of these various silicophosphates. In the meantime we must reiterate the view that at least three definite silicophosphates exist, and that these do not form solid solutions with each other to any extent. With reference to calcium ferrite, although Hilpert had found a large number of calcium ferrites, it is very probable that only one or two are really stable compounds.

The question of heating and cooling curves—that is the ordinary method of thermal analysis with reference to slag—has also been raised. We have found, both with regard to this work and with regard to other work, that this method is quite hopeless at temperatures above the range of the platinum, platinum-rhodium thermocouple, and in the case of many silicates even below that range. Silicates in general give comparatively small heat effects, while there is, in addition, generally an appreciable lag in both melting and solidification. Hence it is almost impossible to get definite arrests or accurate measurement of melting points by this method. The most reliable method is to prepare a glass with the appropriate composition, anneal this at different temperatures, and note the temperature at which crystals develop. By then similarly treating the crystalline material and noting the temperature at which vitrification—that is the transition to the glassy form—occurs, determinations of the melting point or solidification point can then be made.

Some of Dr. Andrew's questions have already been answered in the above reply. So far as solidification to a glassy mass is concerned, we have absolutely no evidence whatever that glass is present in these slags. The question of the determination of the nature of the compounds present in the molten condition is extremely difficult. The existence of compounds in the solid condition is determined by means of certain phenomena, which can be noted on the melting point or similar curves. For example, the maximum on the melting point curve is usually held to denote the compounds. On the other hand, when we come to the fluid condition, the higher temperature of working precludes accurate observations of such physical properties as may be likely to indicate definite compounds. A certain amount of work has been carried out by Field on the calcium aluminium silicates, and he has determined the viscosities of the mixtures present in certain ratio of the tenary system $CaO-Al_2O_3-SiO_3$. It has been found that the maxima on the viscosity surface do not correspond to the compounds which form when these melts solidified, and it is quite possible that in certain cases the compounds which form on solidification break up when the material is in the molten condition. There is some evidence in the case of certain calcium magnesium silicates in favour of this. On the other hand, in many cases it seems almost certain that the compounds which solidify from the melt are likewise present to some extent in the molten condition. Until we know more about the properties of molten silicates and similar material at high temperatures, very little definitely can be said regarding the compounds which are present in the molten state.

With regard to Mr. Robertson's question regarding the liability of the phosphorus in the apatite to reduction, we are afraid we cannot say much about this point, except to indicate the great stability of apatite under various conditions. Mr. Robertson's model of the ternary system is exceedingly interesting, and there is no doubt that we should know more about basic slags if a similar model for the system $CaO\ SiO_2\ P_2O_5$ were available. We hope that such a model will be available shortly, based on the results of some work which is at present in progress. Mr. Robertson's remark about the high melting point of dicalcium silicate is scarcely valid, because in the case of igneous rocks many compounds develop from melts at temperatures much below the melting point of the former. Hence the fact that dicalcium silicate has a very high melting point does not preclude the possibility of its formation at temperatures below that melting point.

With reference to Mr. Wilson's remarks, we have no doubt that the addition of fluorspar to a slag does result in the formation of fluorapatite in place of fluorsilicate. At the same time fluorspar undoubtedly has effects of a physical nature. In phosphorus free slags obviously we get an increase in fluidity, and it is also possible that in certain cases the same thing may occur in phosphate slags. We have made it very clear in the paper that both methods of optical examination should be used, and all through we have utilised both as far as we possibly could. We do not deny the existence of the tetraphosphate, for it possibly exists in a great many slags; but in those we have examined, and these were taken from ten or twelve works in this country, we have never come across this particular compound.

With reference to the effect of phosphorus, we have some work in hand on this at the moment, but so far we have not obtained sufficient result to say much about it. We agree with Mr. Tyrrell that slags are analogous to igneous rocks, but we think they are much more analogous than he has suggested, because in the slags we have always a certain proportion of constituents which correspond to the mineralisers in the rocks, and the effect of these gases is very much the same as the effect of the mineralisers. We have tried the method suggested by Mr. Tyrrell; owing to the tendency for the thin sections to be damaged we have found it more convenient to work with samples of the powder.

With reference to Mr. Whiteley's remark regarding the relative proportions of ferrous and ferric oxide in acid and basic slags, we think that there is little doubt that the greater tendency for the formation of ferric oxide in basic slags is probably due to the chemical conditions. By that we mean that in the acid slag there is a much greater tendency for the formation of complex ferrous silicates, and it is possibly the formation of these compounds which inhibits the oxidation to ferric oxide.

Regarding Mr. Fletcher's interesting remarks, we are inclined to agree with him regarding the constitution of the aluminates and ferrites. There is little doubt that the compounds of this nature which are found in slags are generally tribasic, although we have not actually met one of the composition $3\ FeO,\ Fe_2O_3$ in the slags which we have examined. With reference to the possibility of the existence of such a substance at high temperatures, and also the possibility of pentabasic phosphates under similar conditions, there is, of course, very little evidence available, and in the absence of such evidence their existence can only be postulated. The approximation to unity of the oxygen ratio in the slags which we have examined suggests that there may be something in the view that the working cycle tends towards this particular condition. As mentioned above, work involving the examination of samples of slag taken at short intervals throughout the run of a steel furnace is at present in progress, but sufficient results have not yet been obtained for any discussion.

The deduction of the constitution of the molten slag from examination of the cold material would undoubtedly be exceedingly useful, but, as we have already suggested, much more experimental work will be required before such deductions can be made with any degree of certainty. The method indicated above—that is annealing samples at various temperatures and then quenching as rapidly as possible—may possibly lead to some results, and it is feasible to assume that in some cases transitions to lower temperature forms can be inhibited, providing the quenching is sufficiently rapid. In this way probably some idea can be obtained regarding the equilibrium forms at high temperatures, whether or not these equilibrium forms become unstable as the temperature falls.

The CHAIRMAN said that he understood Mr. McArthur had something to tell them about the fertilising properties of slag.

Mr. D. N. MCARTHUR said that the adoption of the basic Bessemer process in steel making had furnished agriculturists with a material of great value, and the subsequent introduction of the basic open hearth process had resulted in the production of slags which also could be used as fertilisers. But, according to one method of testing, these slags—slags prepared by the open hearth process, and especially those to which fluorspar had been added—were liable to be rejected on account of the low solubility of the phosphates.

With regard to the application of this work, he hoped in the future to apply the results to problems arising in the utilisation of slags.

He agreed with Dr. Scott in saying that very little actual free lime, as calcium oxide, did exist in slag.

A great deal had yet to be done in using slags of known constitution, as, at the present time, it was somewhat difficult to correlate the results of the application of slags to the soil owing to the different constitutions of the slags used. Another point, to which he was paying attention, was the value of the other constituents which were present in addition to the phosphates, with special reference to the calcium compounds.

The CHAIRMAN said that he thought they would all agree with him that Dr. Scott and Mr. McArthur had furnished them with a very excellent paper, which had put the cap on the work of the session. He would ask them to accord both gentlemen a very hearty vote of thanks for the work they had done in connection with this subject of basic slags, and for coming forward and presenting it to them.

The vote of thanks was most cordially given.

Dr. SCOTT briefly thanked them.

This concluded the proceedings.

OBITUARY NOTICE.

Walter MacFarlane, F.I.C., of Kelvin, Hollis Drive, Wednesbury, died 26th November, 1921, aged 67 years.

An original member of this Institute, he was Emeritus Principal of the County Technical College, Wednesbury, having held office for twenty-five years, and had only recently retired, and was looking forward to a little leisure in his later life. Born in Strathendrick, Stirlingshire, he came to Glasgow in infancy, and was educated there. Leaving a business career he applied himself to technical education at Anderson's College, now the Royal Technical College, where he gained the Stevenson Bursary of £150 for three years. In 1882 he was appointed chemist and metallurgist to the Monkbridge Iron Co. Leeds, and six years later was offered and accepted the position of chief chemist to the Glengarnock Iron and Steel Co., ultimately becoming manager of the Siemens department. With that firm he remained till he removed to Staffordshire, in 1896, to take up an appointment under the Staffordshire Technical Institute Committee, which led up to the Principalship of the College. His record as a teacher and lecturer was very high, and calls came to him from all parts of the kingdom. He carried out much research work, notably on blast furnace gases, on which he was a recognised authority. He devised much special apparatus, and his gas analysis apparatus is well known and widely used. He has written many contributions to technical literature, and his books have met with great acceptance wherever the working of iron and steel is known.

He was a member of the Iron and Steel Institute, The Staffordshire Iron and Steel Institute, of which he was a past president. He was a vice-president of our Institute, after serving several periods on the Council, and a contributor of several papers. Latterly he was elected an honorary member. He was one of the original members of the Society of Chemical Industry, and a Fellow of the Institute of Chemistry.

In commenting on his passing, the local papers in Staffordshire said "he was one of the finest men who has lived in the district for generations, and will be greatly missed by many friends and associates in our institutes, and by friends and students the world over."

g. 1

Fig. 2

g. 3

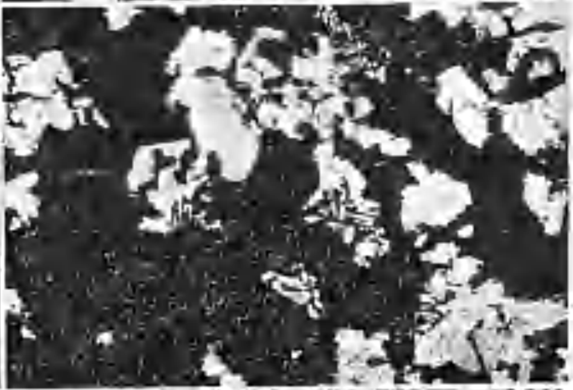


Fig. 4

g. 5

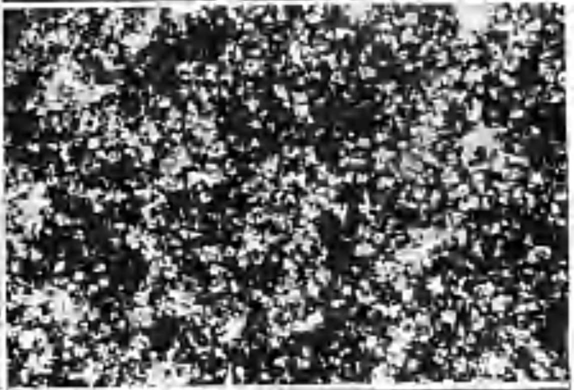


Fig. 6

g. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

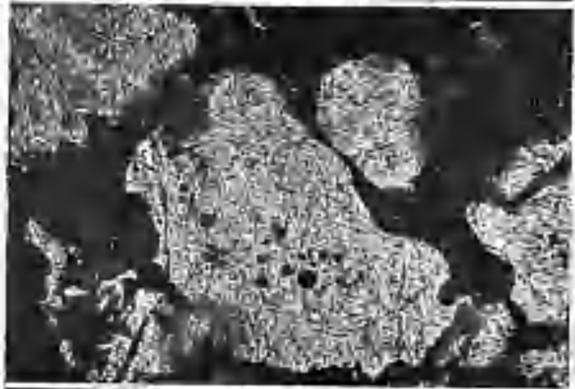
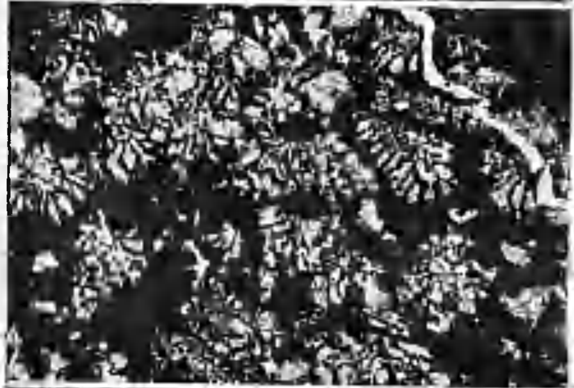


Fig. 12

Fig. 13



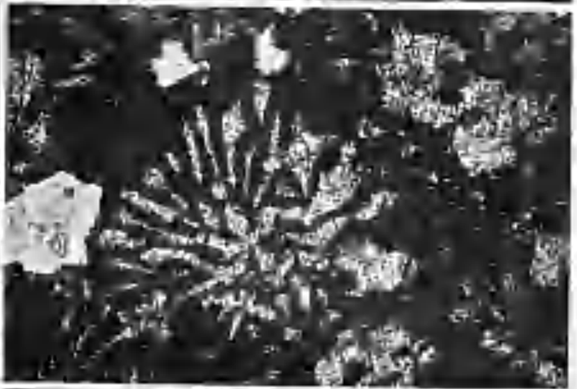


Fig. 14

Fig. 15

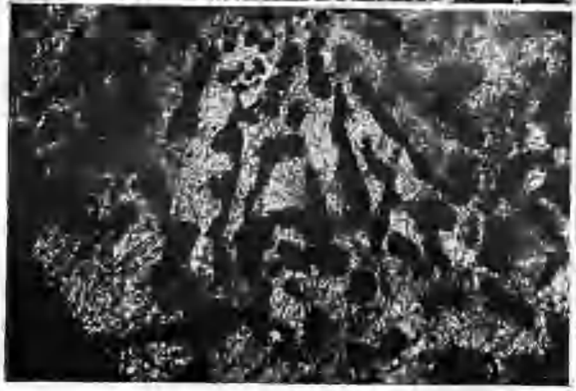
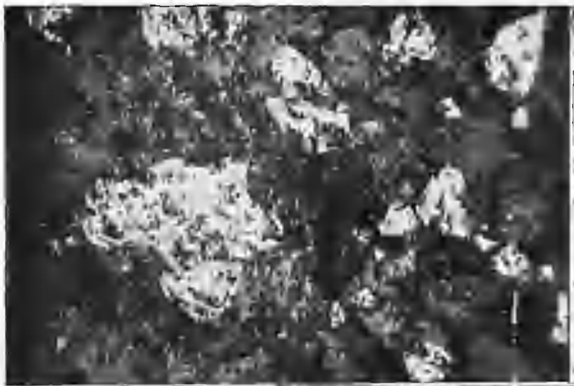


Fig 16

Fig. 17



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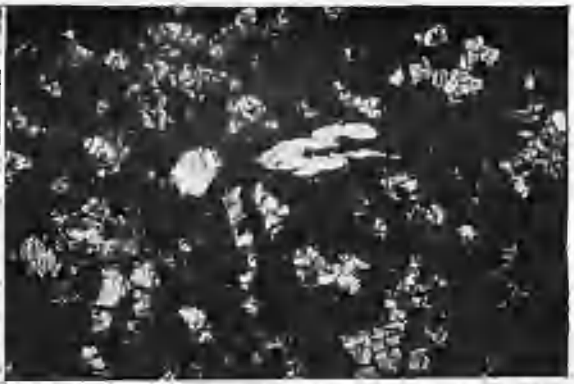


Fig. 19

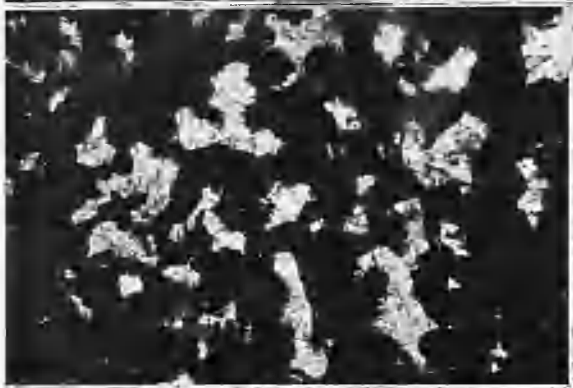


Fig. 20

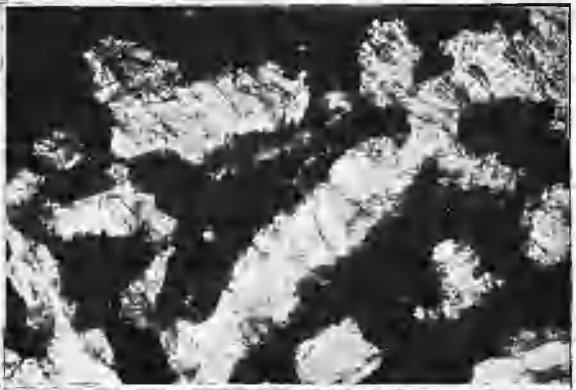


Fig. 21

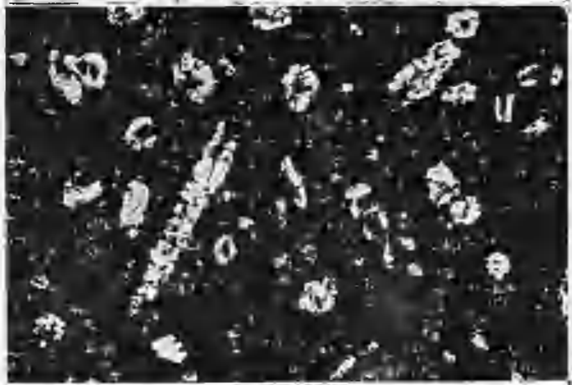


Fig. 22

Fig. 23

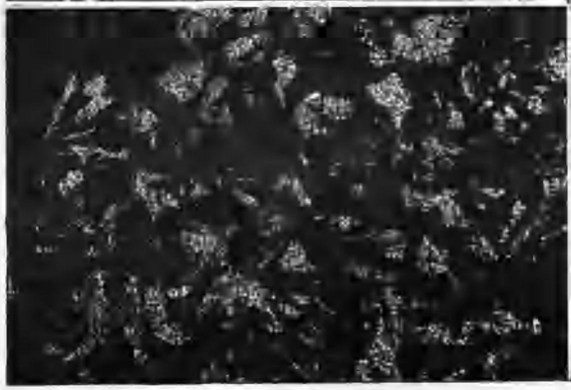


Fig. 24

DESCRIPTION OF FIGURES

Fig. 1. Slag. No. 1. By transmitted light. Showing abundant crystals of pleochroic silicophosphate (1:1) in opaque ground-mass. × 45.

Fig. 2. Slag. No. 1. Transmitted light. Showing euhedral crystal of pleochroic silicophosphate (1:1) with inclusions of ground-mass. × 320.

Fig. 3. Slag No. 1. Transmitted light. Showing euhedral twinned crystal of brown silicophosphate (1:4) in opaque matrix. × 320.

Fig. 4. Slag No. 1. Transmitted light. Show-skeletal intergrowths of spinelloid material and green silicophosphate (1:1). × 140.

Fig. 5. Slag No. 1. Reflected light. Showing spinelloid material in composite matrix. Dead-white material is free oxides, while matrix is partly " spinel " and partly silicophosphate (1:1). × 360.

Fig. 6. Slag No. 2. Transmitted light. Showing fine-grained aggregates of green silicophosphate (1:1) in opaque matrix. × 45.

Fig. 7. Slag No. 2. Transmitted light. Showing granular arrangement of silicophosphate (1:1). × 320.

Fig. 8. Slag No. 2. Reflected light. Dead-white material is mixture of free oxides, dull-white is mixture of aluminates and ferrites, while grey is silicophosphate (1:1). Black areas are pits on the surface. × 300.

Fig. 9. Slag similar No. 2 (not analysed). White areas represent sections of skeletal crystals of free oxides, while grey are " spinel," the darker patches being silicophosphate (1:1). × 360.

Fig. 10. Slag No. 3. Transmitted light. Showing crystals of silicophosphate (3:1) in ground-mass of spinel. × 45.

Fig. 11. Slag No. 3. Transmitted light. Showing crystal of silicophosphate (3:1) under high magnification. × 320.

Fig. 12. Slag No. 3. Reflected light. White material is " spinel," while grey is silicophosphate (3:1). Surface highly polished. × 400.

Fig. 13. Slag No. 4. Transmitted light. Showing radial arrangement of silicophosphate (3:1) and opaque matrix. × 45.

Fig. 14. Slag No. 4. Transmitted light. Radial crystal of silicophosphate (3:1). × 180.

Fig. 15. Slag No. 5. Transmitted light. Showing section of irregular radial skeleton of spinel (opaque) in silicophosphate (grey). × 250.

Fig. 16. Slag No. 5. Reflected light. White areas represent sections of radial crystals of spinel in grey silicophosphate (3:1) matrix. × 360.

Fig. 17. Slag No. 8. Reflected light. Showing coarse spinelloid material, mainly free oxides, in silicophosphate (3:1) matrix. × 360.

Fig. 18. Slag No. 9. Transmitted light. The large white crystals are apatite, the grey are dicalcium silicate, the black matrix being spinel. × 45.

Fig. 19. Slag No. 9. Transmitted light. The transparent crystals are dicalcium silicate. × 60.

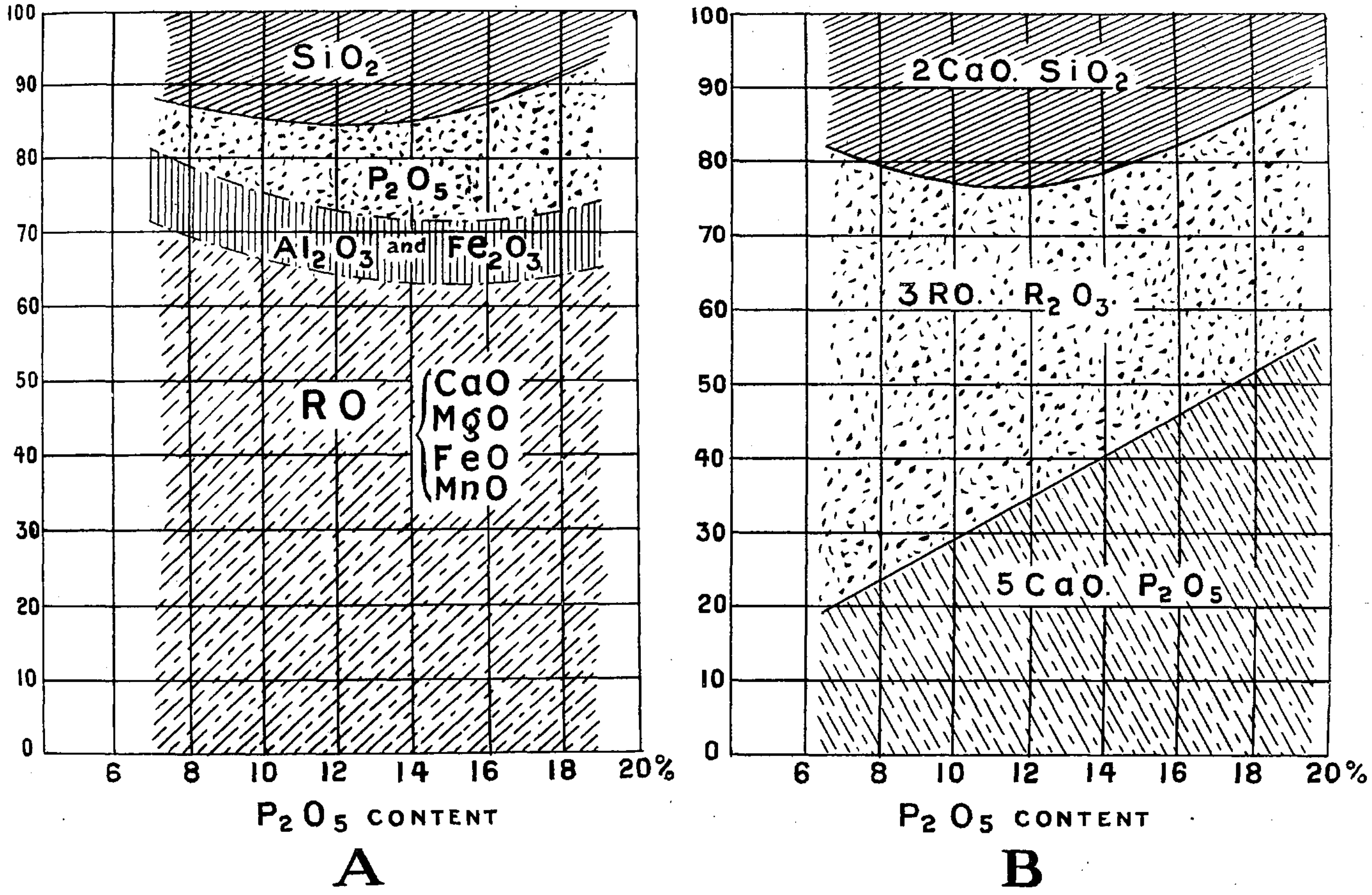
Fig. 20. Slag No. 9. Transmitted light. Showing crystal of dicalcium silicate in opaque matrix. × 240.

Fig. 21. Slag No. 10. Transmitted light. The porphyritic crystals are apatite, showing inclusions, while the small indistinct ones in the matrix are dicalcium silicate. × 45.

Fig. 22. Slag No. 10. Reflected light. Showing white spinelloid crystals in matrix of apatite and dicalcium silicate. × 300.

Fig. 23. Slag No. 11. Transmitted light. Showing crystals of dicalcium silicate in opaque matrix. × 120.

Fig. 24. Slag No. 11. Reflected light. Showing white " spinel " in dark matrix of dicalcium silicate. × 360.



Illustrating Mr. Fletcher's Remarks.