THE BENEFICIATION AND PROCESSING

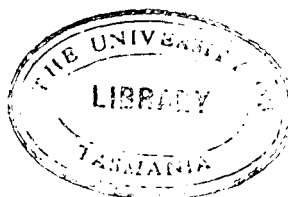## OF

SOUTH AUSTRALIAN GRAPHITE

AND A

STUDY OF ITS LAMELLAR COMPOUNDS

BY

R. C. CROFT.

I N D E X

3.

4.

SUMMARY.

The impurities present in South Australian graphite
concentrates and various chemical methods for the removal of
these have been examined.   It was found that the best of
these methods could be combined to give a process for the
complete beneficiation of high grade concentrates.   On
examination, the economic aspects of the proposed process
indicate that it is capable of being profitably operated on
an industrial scale.   The results of this work support the
claim that the purity achieved by application of the propos-
ed process is higher than that obtained by other methods of
purification.   The claims that chemical beneficiation
methods reduce graphite flake size and that appreciable
amounts of reagents are adsorbed on graphite during process-
ing have been disproved.

1. INTRODUCTION

The difficulty experienced in Australia in obtaining graphite for industrial purposes during the recent war was due partly to the restriction of imports from Ceylon, Madagascar and the U.S.A., which normally supplied almost all the Australian requirements, and also to the inability of small local production to satisfy the resulting high demand. This position emphasized the desirability of further development of domestic resources and drew attention to the need for an examination of the suitability of Australian graphite for various industrial uses.

Graphite has been found in many places in Australia, but as far as is known only three deposits are large enough to be of commercial interest. These occur on Eyre Peninsula in South Australia, at Munglinup and Kendenup in Western Australia, and at Collinsville, Queensland. Graphite from the last-named deposit is erroneously described as "amorphous" because it lacks the lustre and well developed flake form of samples from the other two sources. Although the sizes of these three deposits have not been proven, the South Australian one is known to be large. Attempts were made to develop it in 1917, but these were abortive. Mining was recommenced in 1941 and Uley and Koppio mines are now producing concentrates for the Australian market. Present production from West Australian and Queensland deposits is small.

Concentrates produced by the South Australian mines
mentioned above, usually contain 60 to 80 per cent. graphite.
A product of this quality is unsuitable for many uses and is
unlikely to compete successfully with most imported concen-
trates in peace-time.

The aims of this investigation, therefore, were to
assist the industry in satisfying the special requirements of
various consumers, and to increase the variety and purity of
products for post-war trade. It was realised that competition
in the marketing of high grade products would be keen, because
Madagascar and Ceylon possess very large graphite reserves
from which concentrates valued for their purity and flake size
are produced. Graphite manufactured in U.S.A. by the electro-
thermal process is also sought on account of its purity.
However there appeared to be a sufficient margin between the
cost of imported material and that produced locally to permit
economic processing for higher purity.

A brief survey of the industrial uses of graphite
and the nature of material required for each of these is given
in Table I. It shows that many industries use finely ground
graphite of high purity. Hence work on this project was largely
directed towards the complete beneficiation of graphite concen-
trates by chemical methods and the fine grinding of high grade
concentrates. It will be seen that the major consumer of this
grade in Australia is the dry cell industry, which received a

TABLE I

Grades of Graphite used in Industry

Product	Purity	Particle Size
1. Foundry Facings.	40-70% carbon	Finely ground.
2. Boiler compounds Polishes Clutch facings etc.	varied	Finely ground.
3. Crucibles	90% carbon	20-90 mesh, chip or flake.
4. Battery graphite	85% carbon, but highest purity desirable.	80% minus 200 mesh.
5. Pencils Pigments.	As pure as possible and free of gritty material such as silica.	minus 200 mesh.
6. Carbon brushes Electrodes Carburisers Powder metallurgy Electro typing.	Very pure - less than 1% of impurities.	minus 200 mesh.
7. Lubricants	99.9% carbon	(a) Colloidal (b) Powdered flake.

great impetus during the war because of the heavy demand for portable power units. The attention which has recently been paid in other countries to the processing of high grade natural graphite has added further interest to the investigation. American industry has been foremost in this field and has developed colloidal natural graphite lubricants and other products which compete successfully with those produced artificially.

Part I of this paper deals with the chemical beneficiation of 60 to 80 per cent. South Australian concentrates to produce purer materials suitable for use in dry cells and for the manufacture of lubricants, pigments, and electrical equipment, such as carbon brushes and electrodes. Investigation of methods for grinding pure graphite to the finenesses required by the above uses is described in Part II. The testing in dry cells of graphite samples prepared by purification and grinding methods described in the previous sections is treated in Part III. Work on interlamellar compounds of carbon, which are being investigated in connection with both the fundamental problem of the structure of South Australian graphite and new uses for this material, is reported in Part IV.

II. ORIGIN AND NATURE OF RAW MATERIALS

The sources of raw material selected for this investigation were the Uley and Koppio deposits, the ores from which contain 15 - 35 per cent. of graphite carbon.

Stilwell[25] found that Koppio ore consists essentially of graphite and quartz, the graphite flakes varying in size from 0.5 to 2 mm. and often enclosing quartz grains. Occasionally quartz encloses small grains of graphite. Smaller amounts of iron-stained biotite and chlorite, and a kaolinite mineral are also present. In order to obtain further information about the nature of the gangue minerals of both ores, petrographic, X-ray diffraction, and chemical analyses were done. The effects caused by slow heating over a wide temperature range were observed with the same object. The amounts of free ferric oxide contained in ores, concentrates, and gangue were also determined. The results of analyses are given below.

(i) Petrographic analysis:-

Thin sections were prepared from the ores and the presence of minerals mentioned above was confirmed. Calcite was added to the list.

The photo micrographs illustrate the intimacy of graphite and gangue and also the manner in which calcite serves as a bonding agent in these aggregates.

Photomicrographs of thin sections of South Australian
graphite ores:-   (Magnification 30X).

Key to lettering.

        C = Calcite   F = Hematite
        G = Graphite   Q = Quartz.

In the photomicrographs, these minerals appear grey,
black, dark grey, and white respectively.
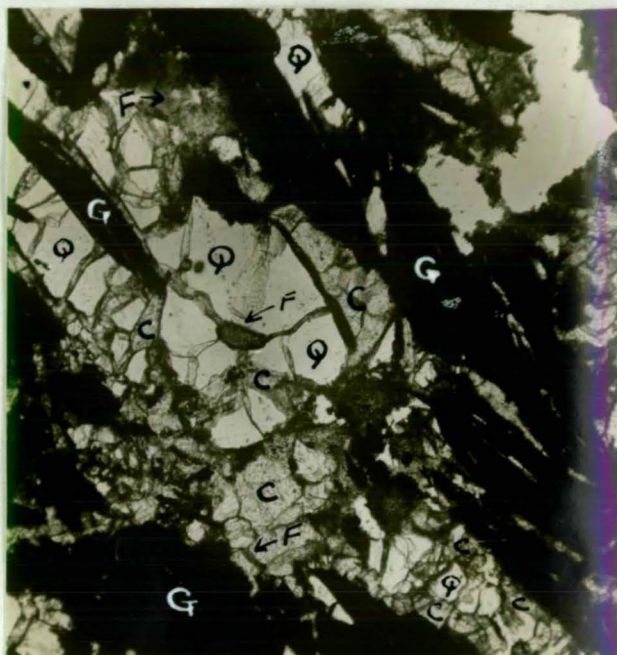
No. 1. Uley Schist.

No. 2. Koppio Ore.
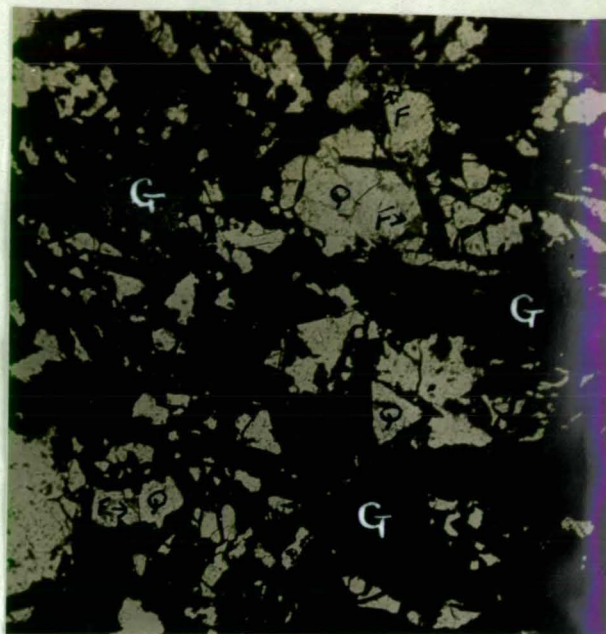
No. 3.   Uley open cut ore.

No. 4.   Koppio Ore –
surface capping.

(11)   X-ray diffraction analysis[*]:-

An X-ray examination of tailings obtained by flotation of Uley ore was performed and detected the following minerals.

α-quartz (coarse) γ-FeO.OH (Lepidocrocite),
                                                                    faint trace.
α-Fe$_2$O$_3$ (Hematite)   Montmorillonites

α-FeO.OH (Goethite)   Kaolins

                                                    Micas.

(111)   Chemical analysis :-

The compositions of Uley and Kopplo ores determined by chemical analyses are given in Table 2.   A notable feature of these ores is that they contain no sulphides. Pyrite (FeS$_2$) is often found in ores mined in other countries and Shapiro and Veselovsky[23] report its occurrence in Kureisk[+] graphite.

(iv)   Effects of heat on gangue minerals:-

The mineral composition of gangue separated from Uley graphite ore by flotation methods was examined by observing variations in Q[#] and losses of water of constitution caused by slowly heating this material from 100° to 700°C.   Experimentally determined values of Q and percentage-losses in sample weight due to dehydration[#] are plotted against temperature in Figs. 1 and 2 respectively.   These data are discussed below.

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[*]   These analyses were conducted by Mr. J. Cowley.

[+]   Russia.

[#]   Ratio of inductance to ohmic resistance.

[#]   These were determined by Mr. A. J. Gaskin.

TABLE 2[*]

Chemical Composition of Uley and Koppio Ores

Constituent	Koppio Ore	Uley Ore
SiO_2	58.56	28.88
TiO_2	0.07	0.07
Al_2O_3	1.76	4.21
Fe_2O_3	4.76	11.10
FeO	0.08	0.03
MnO	0.01	0.03
CaO	0.66	20.09
MgO	0.13	1.01
Na_2O	0.06	0.11
K_2O	0.18	0.25
P_2O_5	-	-
H_2O +	0.82	1.54
H_2O -	0.27	0.92
CO_2	0.74	16.67
SO_3	0.11	0.38
C (by combustion).	35.60	18.30
	103.81	103.59

[*] Results of analyses conducted by Mr. J. Corbett.
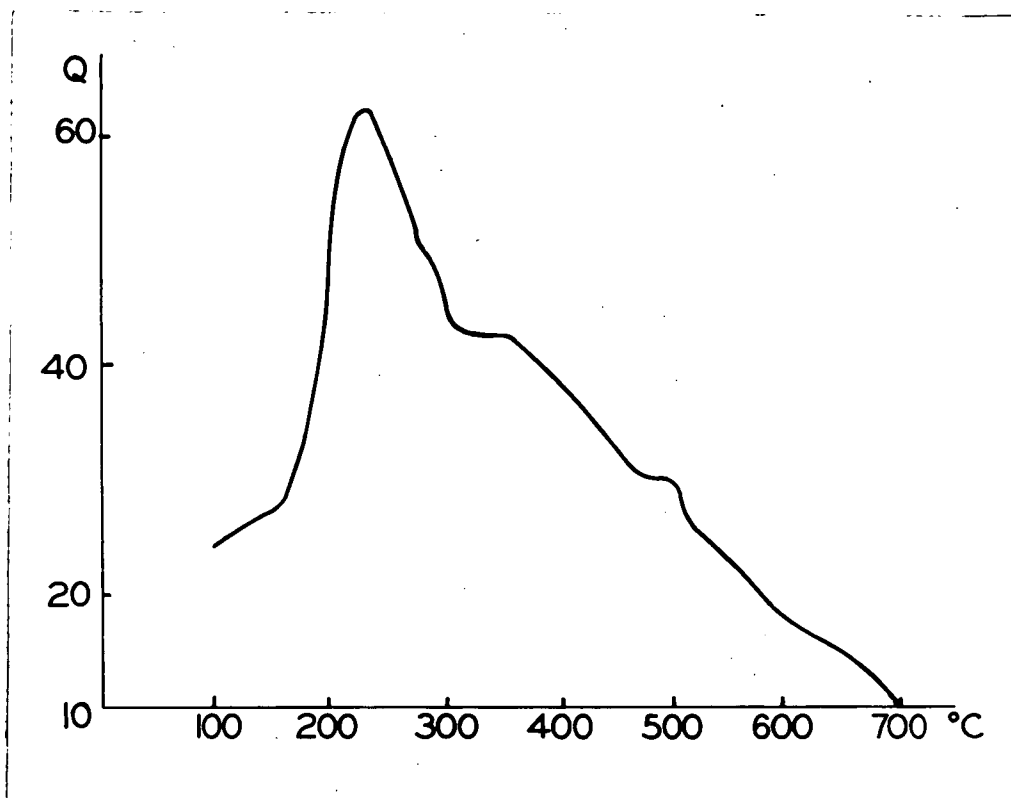
Fig. 1. Variation in the Q value of Iley gangue caused by heating the latter from 100 to 700°C.
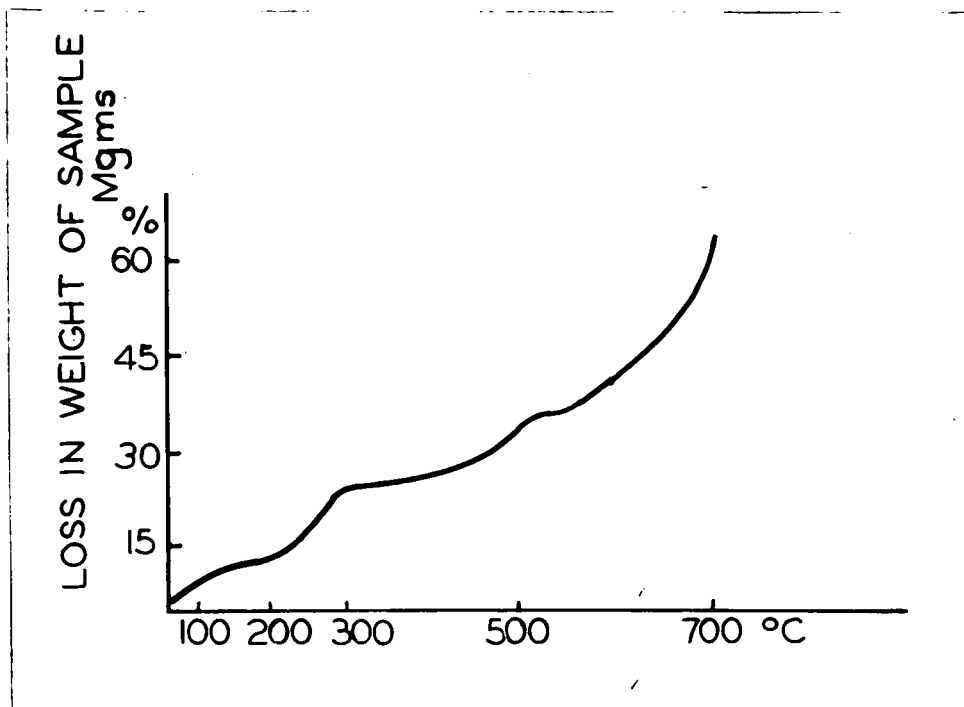
Fig. 2. Loss of water of constitution from minerals in Iley gangue caused by heating the letter from 100 to 700°C.

The inflection of curve 1 at $230^{\circ}C$ also occurs in curve 2 and is presumed to be due to the loss of water from gibbsite since curve 2 may be matched with that for pre-cipitated $Al(OH)_3$ which gives "shoulders" at $200-250^{\circ}C$ and at $500^{\circ}C$. The continued loss from $250-300^{\circ}C$ shown in curve 2 is considered to represent dehydration of limonite and of goethite, which was detected by X-ray analysis. Since the inflection in curve 1 at 325 to $360^{\circ}C$ does not occur in curve 2, it is probably due to a phase change in some form of ferric oxide, possibly goethite to hematite which is known to occur in the range $325-400^{\circ}C$. Inflections in both curves at $500^{\circ}C$ are attributed to loss of remaining water from aluminous minerals. The absence of any large inflections in curve 2 is taken as indicating the extreme fineness of the gangue minerals in the sample tested. Smoothness of the loss curve in the range $550-700^{\circ}C$ indicates "amorphous" hydrous material i.e. the absence of any definite hydrates. Curve 2 shows no montmorillonite is present; indications for kaolin are slight and doubtful. Both these minerals were found in small quantities by X-ray diffraction analysis.

(v) Analysis for free ferric oxide:-

The amounts of free ferric oxide in South Australian graphite ores, concentrates, and gangue were determined by a biological method (see p.[33]). The materials examined and the percentages of free ferric oxide they were found to contain are shown in Table 3.

TABLE 3

Amounts of Free Ferric Oxide found in South Australian Graphite Ores, Concentrates, and Gangue, by the Biological Method

Sample	Percentage Weight of Free Ferric Oxide found in Sample.
Uley Concentrate	16.1
Uley Ore	22.9
Gangue from Uley Ore[*]	48.7
Koppio Concentrate	29.7
Koppio Ore	42.7

* This material was prepared by repeated floating of tailings obtained during the preparation of concentrates from Uley ore by flotation methods.

III.   CHEMICAL BENEFICIATION.

The recovery of graphite from Australian ores by
various ore dressing methods such as tabling and flotation
after grinding has been studied by Blaskett and Gartrell[3],
Dunkin and Hart[7], and Plante[19] who found that it was
possible to produce concentrates containing 80-90 per cent
graphitic carbon. Plante succeeded in preparing concentrates
containing 92 per cent carbon, with recoveries of 86 per cent
by flotation methods, but found that to achieve this it was
necessary to dissolve calcite partially in the ores by adding
a little dilute hydrochloric acid to the flotation cell. This
process is therefore considered to owe its success partly to
chemical aid. The results of these investigators have been
quoted to indicate the limits of physical methods of enrich-
ment. Concentrates containing 97.5 per cent carbon have been
prepared by physical methods but at the expense of recovery,
and the flake size of the graphite which is greatly reduced by
the prolonged grinding necessary to liberate this mineral.

It is evident therefore that other methods than
those mentioned above must be used to raise the grade of
concentrates from 90 to 99.9 per cent.   These methods were
sought by studying chemical treatments designed to react
with and dissolve out the remaining mineral impurities.

Shapiro and Veselovsky[23] appear to be the only
investigators who have conducted extensive tests on the en-
richment of graphite with the aid of chemical reagents.

The Kurelsk graphite which they tested contains the same impurities as are found in South Australian ores as well as pyrite (Fe_2). Their researches revealed that roasting in air decomposed pyrite and silicates and resulted in more efficient removal of impurities by subsequent hydrochloric acid digestion. They also found hydrochloric acid to be superior to sulphuric for the purpose of gangue extraction. These investigators reported caustic soda and ammonium sulphate as being inefficient reagents for removal of gangue and did not find hydrofluoric acid particularly effective for this purpose.

Several undesirable features of chemical beneficiation have been suggested. Stilwell and Edwards[25] expressed the view that chemical treatment, besides being costly, would result in reduction of the flake size of graphite which enveloped gangue. A further objection, voiced by Shapiro and Veselovsky[23] and others was the adsorption of chemical reagents on graphite. Evidence in reply to these criticisms will be found in the results of this investigation.

(1)   Outline of Experimental Work.

The results of preliminary examination showed that the gangue constituents of graphite ores and concentrates may be classified according to their acid-solubility as follows:-

(a) Calcite, iron oxides, alumina, micas, and clay minerals.

(b) Quartz and a small amount of some refractory silicates.

Solution and removal of members of group (a) were attempted by acid digestion. Samples of Uley and Koppio concentrates were refluxed with hydrochloric and sulphuric acids and the effects of varying acid concentration and duration of digestion studied.

Pretreatment of concentrates to raise the acid solubility of iron and aluminium compounds was investigated by roasting samples in air and also in a reducing atmosphere. The relation of acid-solubility to roasting temperature was determined.

Removal of group (a) impurities by solution or volatilisation was also sought by heating with the solid reagents, ammonium bisulphate, ammonium bifluoride, and ammonium chloride.

Methods employed for the removal of silica were, refluxing, or autoclaving of concentrate samples with strong aqueous caustic soda, fusions with solid caustic soda and sodium carbonate, and evaporation of concentrates with hydrofluoric acid.

More exacting methods for preparing concentrates containing less than 1 per cent of impurities were also tested and were based on data obtained from the work outlined above. They included combined acid digestion and caustic autoclaving methods, and also treatment with hydrochloric and hydrofluoric acids. An active interest was also taken in the high temperature chlorination method developed by McTaggart[14].

Reference has been made to the suggestion that
chemical beneficiation methods reduce the flake size of
graphite in treated concentrates. This point was investigated
by studying the size distribution data of acid treated and
untreated concentrates.

Adsorption of reagents on finely ground graphite,
which was also suggested as an undesirable feature of chemical
treatment was investigated by determining the amount of
chlorine present in the very fine pure product produced by
high temperature chlorination, and the amounts of ferric
chloride and chloride ions retained by finely ground concen-
trate which had been digested with hydrochloric acid and then
well washed.

(2) Experimental.

(i) Analyses of materials.

Analyses were performed on Uley and Koppio concen-
trates and Uley flotation tailings which were the materials
selected for experimental work. Table 4 contains the results
of these analyses.

(ii) Removal of calcite.

The calcite present in Uley concentrate and Uley
flotation tailings, 29 and 56 per cent respectively was found
to react readily with cold dilute hydrochloric acid and was
completely removed by stirring with an equivalent amount of
cold 10 per cent acid.

TABLE 4[#]

Composition of Materials used in Tests

Constituent	Uley Concentrate	Koppio Concentrate	Uley Flotation Tailings
SiO_2	11.32	21.22	22.4
TiO_2	0.03	0.06	-
Al_2O_3	4.23	1.75	4.6
Fe_2O_3	7.09	2.30	} 16.9
FeO	0.08	0.22	}
MnO	0.03	0.01	-
CaO	14.97	0.76	31.6
MgO	0.40	0.07	-
Na_2O	0.05	0.06	-
K_2O	0.09	0.10	-
P_2O_5	-	-	-
$H_2O +$	0.74	0.70	-
$H_2O -$	0.71	0.23	-
CO_2	13.15	0.62	24.8
SO_3	0.29	0.09	-
C	48.32	73.40	< 1.0
	101.50	101.59	95.3

[#] Analyses conducted by Mr. J. Corbett.

(iii) <u>Acid digestion</u>.

(a) <u>Variation of acid strength</u>:- Digestion of Uley and Koppio samples was performed under reflux using various strengths of hydrochloric and sulphuric acids given below.

HCl — 1.4 N (approx. 5%), 1.7 N, 2.9 N, 4.3 N, 6N.

H_2SO_4 — 0.8 N, 1.7 N, 3.3 N, 6.6 N, 13.3 N, 26.5 N.

Seventy-five mls. of digestion acid were used for each 10 gms of sample digested. This ratio allowed at least 100 per cent excess of reagent. The high calcite content of Uley concentrate (29%) necessitated adding sufficiently concentrated acid in the case of hydrochloric acid digestions to react with the calcite and have a residual acid concentration of one of the above values. When sulphuric acid was used for digestion, calcite was first removed from the sample by separate treatment with an equivalent amount of 10 per cent hydrochloric acid. Such measures were not necessary with Koppio concentrate since the calcite content is only approximately 1 per cent.

Digestions were of half hour duration. After this period the hot digests were filtered, washed with hot 2 per cent digestion acid, hot water, and then dried at $110^{\circ}C$. Carbon, iron oxide, alumina, and silica, were determined in the dried samples. From the results of these analyses and the composition of the original sample, the percentage loss of each constituent due to treatment, was determined. These data are summarized in Figs. 3 and 4.
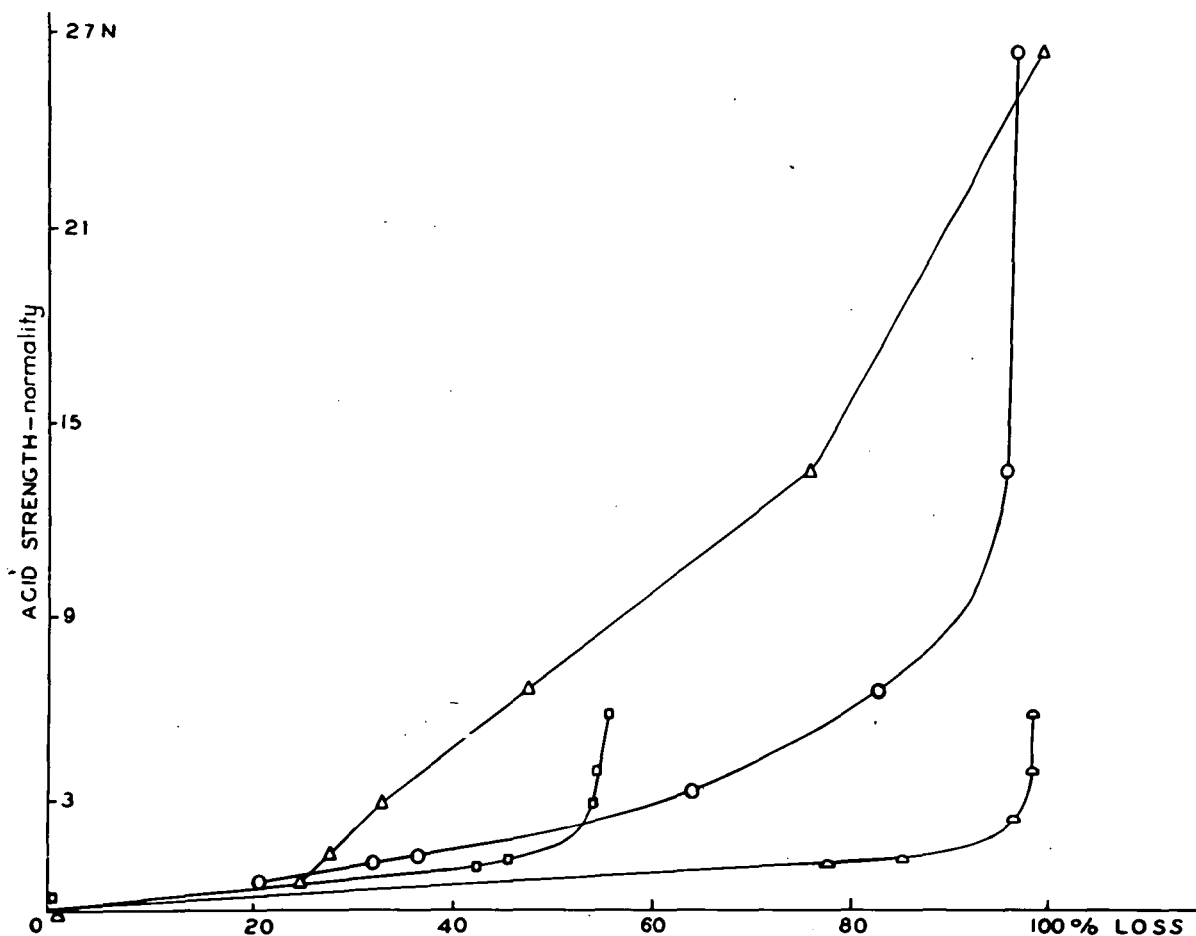
Fig. 3. Showing losses of ferric oxide and alumina from
Wlay concentrate caused by ½ hr. digestions with
different concentrations of hydrochloric and
sulphuric acids.

O — Ferric oxide loss, Sulphuric acid digestion.

○ — " " " , Hydrochloric acid digestion.

△ — Alumina " , Sulphuric " "
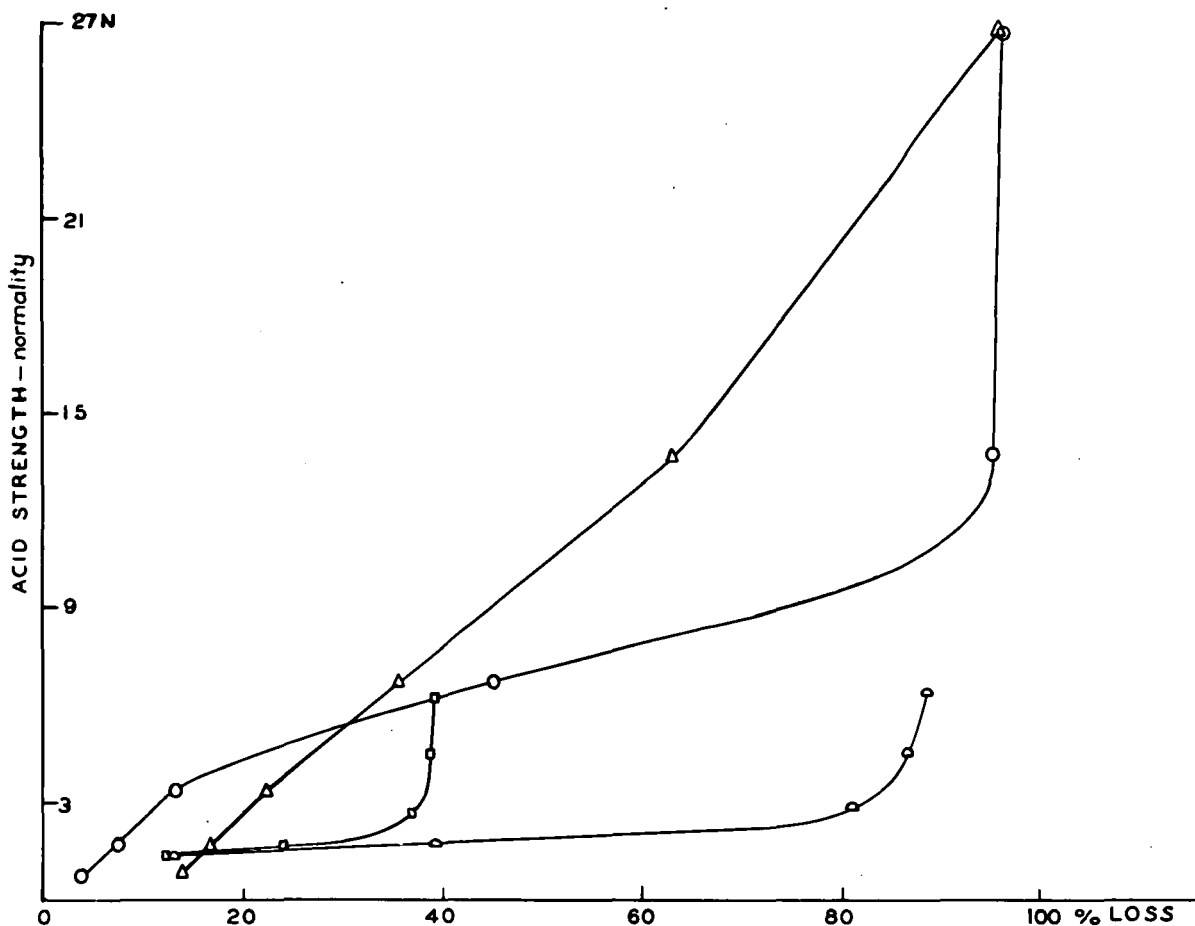
□ — " " , Hydrochloric " "

Fig. 4. Losses of ferric oxide and alumina from ferric concentrate caused by 1 hr. digestions with hydrochloric, and sulphuric acids of various strengths.

O — Ferric oxide loss, Sulphuric acid digestion.

◠ — " " " , Hydrochloric acid digestion.

△ — Alumina " , Sulphuric " "

◻ — " " , Hydrochloric " "

Discussion of half-hour digestion results:-

The conclusions drawn from data are:-

1. Iron-containing minerals in Uley and Koppio concentrates are more readily removed by hydrochloric than by sulphuric acid of the same strength.

2. Hydrochloric acid is also superior in its ability to remove up to 50 per cent of the total alumina. The remainder responds to treatment with strong (27 normal) sulphuric acid.

3. Although hydrochloric is more effective than sulphuric acid of the same normality the total loss of iron and alumina caused by digestion is greater when the latter is used at high concentrations.

4. The similarity of shape and slope of the curves suggests similar mineral constituents in the gangues of both concentrates. The digestion data for both acids show that the gangue of Koppio concentrate is slightly less soluble than that of Uley concentrate.

(b) Effect of time on acid digestion efficiency:-

In this series of tests, fixed acid concentrations were employed and the effects of varying digestion periods were examined. Separate samples of both concentrates were digested for ½, 2, and 4 hour periods, and percentage losses of gangue

impurities were determined from results of analysis performed
on residues. These data are given in Table 5.

It is evident that prolonging the period of digestion
caused substantial gains in the efficiency of extraction in all
cases. The percentage loss figures for the digestion of Uley
concentrate with 6 N hydrochloric acid for half an hour were
ferric oxide, 98.7 per cent loss and alumina 57 per cent loss.
These figures are similar to those achieved by digestion with
1.4 N hydrochloric acid and for 4 hours. The dependence of
extraction efficiency on time is particularly noticeable in
the case of Kopolo digestions.

(iv) Roasting of concentrates.

Pre-roasting as a means of increasing the acid-
solubilities of ferric oxide and alumina in graphite concen-
trates was used by Shapiro and Veselovsky[23]. It was also
studied by Tilley, Millar and Ralston[27] in their work on
the acid extraction of alumina from bauxite and other alumin-
ous materials. The latter investigators were able to show
that calcination of clay at temperatures of 500-900°C increased
the rate at which alumina was dissolved by acids, and also
noted that the solubility of ferric oxide rose to a maximum
about 550°C then fell as the roasting temperature increased.
McLeish[13] found that the chemical reactivity of the ferric
oxide used in towns gas purification increased slightly with
roasting temperatures between 325 and 375°C and fell rapidly
when the temperature of roasting exceeded 460°C. Mellor[15]
states that if ferric oxide is roasted above a certain

TABLE 5

Effect of Time on the Efficiency of
Extraction of Gangue Minerals by
Acid Digestion

Concentrate and Digestion Acid.	Digestion Period.	Percentage Losses *		
		SiO_2	Fe_2O_3	Al_2O_3
Uley 1.4 N HCl	½ hr.	0	54.0	30.8
	2 hrs.	0	92.2	51.2
	4 hrs.	0	96.3	55.0
1.4 N H_2SO_4	½ hr.	0	36.3	27.9
	2 hrs.	0	43.0	44.2
	4 hrs.	0	52.6	−
Koppio 1.4 N HCl	½ hr.	0	13.5	3.7
	2 hrs.	0	69.6	24.7
	4 hrs.	0	92.6	32.7
1.4 N H_2SO_4	½ hr.	0	6.9	−
	2 hrs.	0	27.0	6.7
	4 hrs.	0	50.6	20.6

* Difference between the weight of a constituent found in the product of treatment and the amount originally present in the untreated sample of concentrate, expressed as a percentage of the latter weight.

temperature it caloresces and becomes less acid soluble.
He notes that this temperature depends on the previous
history of the sample and usually lies in the range 400-535°C.,
although it may be as low as 325°C.   With respect to the
effect of heat on silicates, Mellor and Scott[18] found that
kaolinite is completely dehydrated at 500°C., and Mellor and
Bragg[4] showed that this resulted in the loss of crystalline
form and the appearance of a substance considered to be a form
of free alumina. However, Gerber[9] suggests that an easily
acid soluble alumino-silicate remains after the loss of water
of constitution.

The foregoing information indicates that the roast-
ing temperatures which correspond to the optimum acid
solubilities of ferric oxide and alumina do not coincide.
Therefore information was sought concerning the effects of
reducing conditions during roasting with the hope that the
solubility of ferric oxide might be increased at temperatures
which caused the greatest increase in the acid solubility of
alumina.

According to Mellor, reduction of haematite by
hydrogen is complete at 500°C., and more rapid at 600°C.
Thereafter there is little change in the rate of reduction.
The fact that ferric oxide is closely associated with graphite
in concentrates suggests that some reduction by carbon might
occur when these are roasted. A survey of information on this
point indicates that in the absence of oxygen, which would be
the case in a reducing roast, ferric oxide may be reduced to

ferrosic oxide ($Fe_3 O_4$) by heating with carbon in the temperature range 400-650°C. Ferrous oxide is produced when roasting temperatures lie between 750 and 850°C. However, these limits may vary with the condition of the ferric oxide. Reduction of ferric oxide by carbon monoxide is claimed to begin at 200°C. and to be favoured by the presence of hydrogen which also lessens the tendency of carbon to separate.

It was clear from the above information that the conditions of roasting which give the most satisfactory results vary with different materials and therefore require to be determined for each particular case.

The experimental determination of the effects of air roasts and reducing-roasts on the gangue of Uley and Koppio graphite concentrates is described below.

(a) Reducing-roast :- The materials roasted were Uley concentrate from which calcite had been quantitatively removed with 10 per cent. hydrochloric acid and Koppio concentrate. Stainless steel boats each containing 35 g. of concentrate were heated in 2 in. diameter drawn steel tubes in an electric muffle, at the temperatures given below. In order to compare the effects of roasting on Uley and Koppio concentrates, samples of both were roasted at the same time in the same tube. All roasts continued for 4 hours after the pre-selected temperature was reached. Towns gas, direct from the mains, was used as a reducing atmosphere and had the following composition -

H_2 73.6 %

CO   16.7 "

CO_2 4.4 "

O_2 1.3 "

CnHn   4.0 "

The temperatures selected for roasting were, 300°, 400°, 500°, 700°, and 800^oC., controlled to within $\pm 10^oC$. of the required value. The acids used in digesting roasted concentrates were 0.8 N sulphuric acid and 1.4 N hydrochloric acid.

After a sample had been roasted it was air-washed several times in a vacuum desiccator. A 10 gm. sub sample was then refluxed with dilute acid for half an hour. The acid insoluble residues remaining after digestion were washed with 400 mls. of hot dilute (2 per cent.) digestion acid then hot distilled water. These residues were analysed and percentage losses of the gangue constituents computed. These data are presented graphically in Figs. 5 to 7. The amount of reduction of ferric compounds at certain roasting temperatures was determined by analysis for ferrous iron. The results are given in Table 6.

(b) <u>Roasting in air</u> :- These tests differed from those just described only in the respect that samples of the same original materials were roasted in open silica dishes in an electric muffle. An additional roast was done at 600^oC. and the roast at 800^oC. was omitted because appreciable
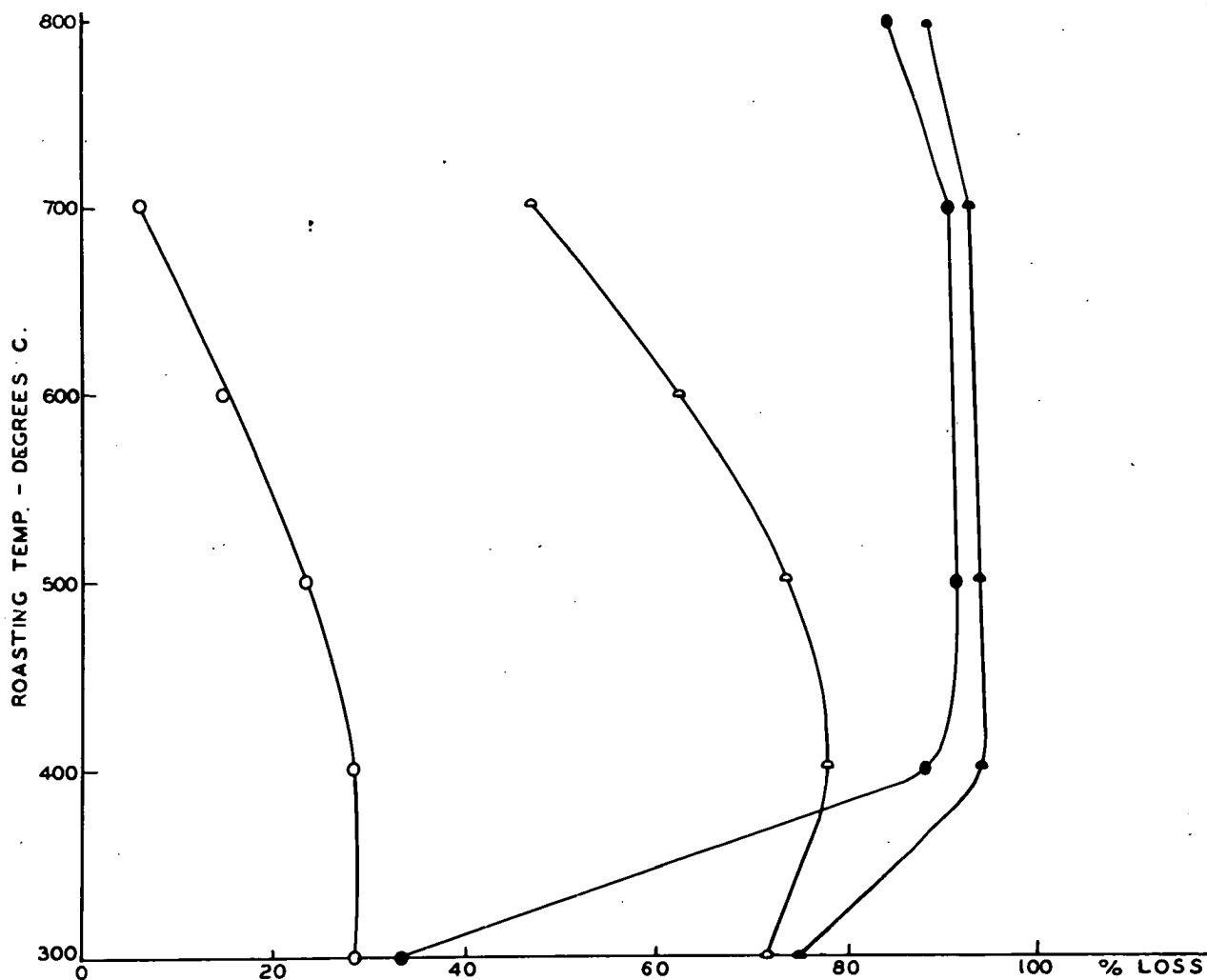
Fig. 5. Losses of ferric oxide from Iley concentrate
         achieved by roasting at various temperatures
         and subsequent acid digestion.

         O - Air roast, Sulphuric acid digestion.

         □ - "   " , Hydrochloric acid digestion.

         ● - Reducing roast, Sulphuric acid digestion.

         ▲ - "   " , Hydrochloric acid digestion.
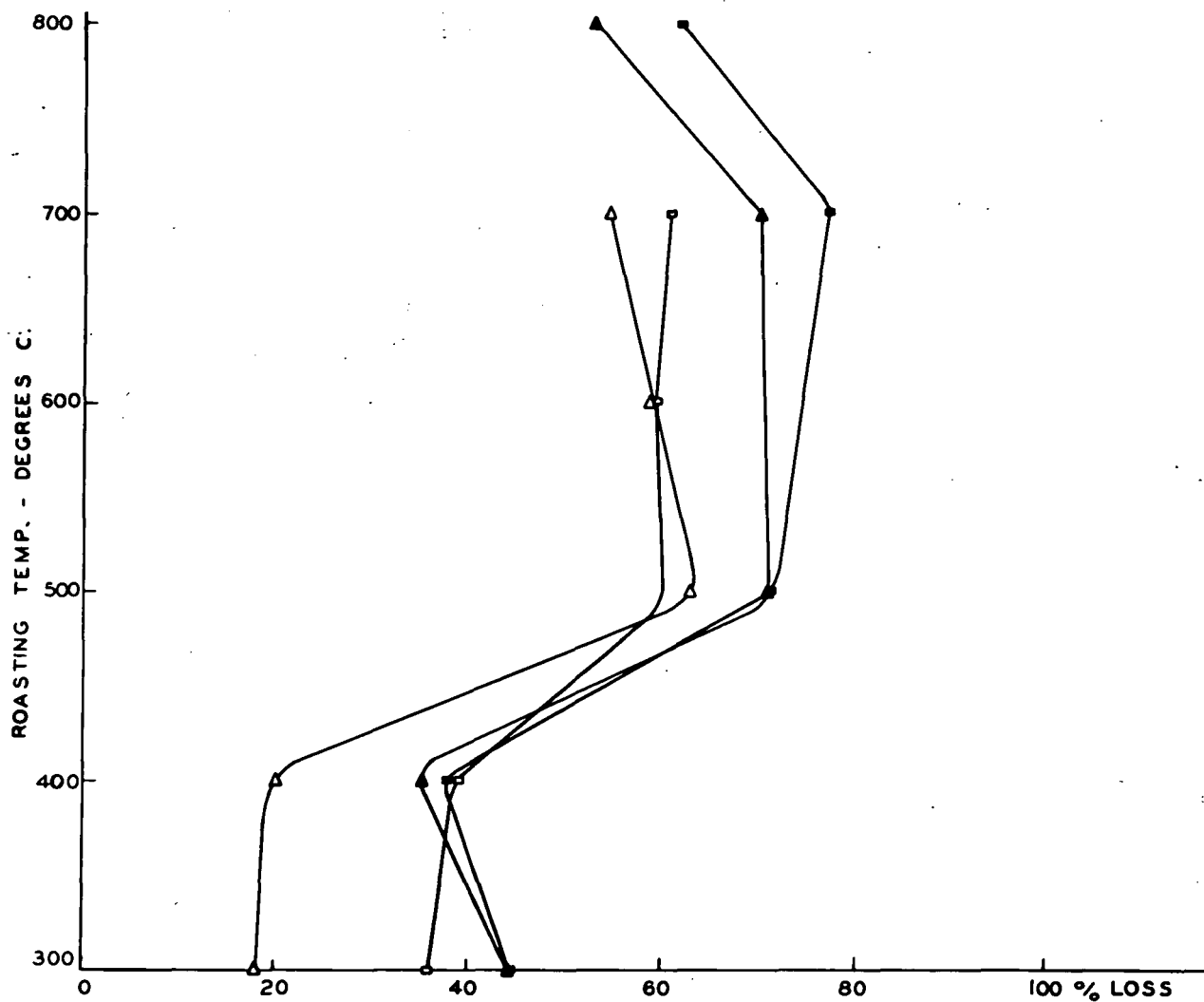
Fig. 6. Alumina losses from Iley concentrate effected by roasting at various temperatures and acid digesting the product.

△ – Air roast, Sulphuric acid digestion.

▢ – "   "   Hydrochloric acid digestion.

▲ – Reducing roast, Sulphuric acid digestion.

▬ – "   "   Hydrochloric acid digestion.
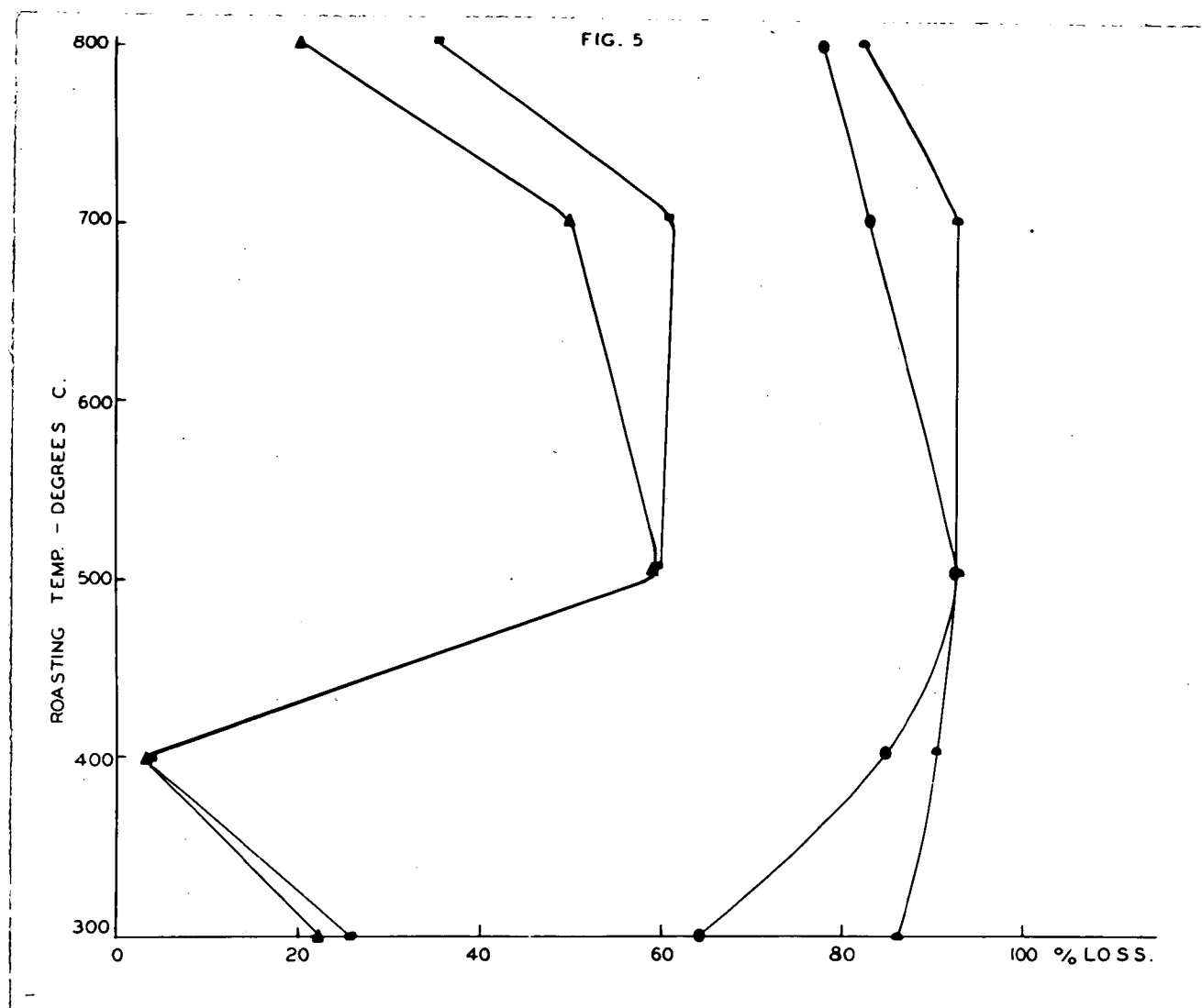
Fig. 7. Losses of ferric oxide and alumina from Ilmenic concentrate caused by roasting at various temperatures in a reducing atmosphere and acid digesting the product.

● – Ferric oxide loss, Sulphuric acid digestion.
◼ – " " " , Hydrochloric acid digestion.
▲ – Alumina " , Sulphuric " "
◼ – " " , Hydrochloric " "

TABLE 6

Reduction of Ferric Compounds present in Concentrate Causes caused by roasting samples in towns gas at Various Temperatures.

Concentrate and Roasting Temperature	Percentage of total original Fe_2O_3 reduced to FeO
Uley conc. (calcite free)	
500°C	77.6
700°C	100.5
800°C	99.5
Koppio conc.	
500°C	98.6
700°C	99.6
800°C	100.1

N.B.   Before roasting Uley concentrate (calcite-free)
       contained 0.08 per cent. FeO and Koppio concen-
       trate 0.?? per cent. FeO.

combustion of graphite occurs at this temperature. Results of these tests are also shown in Figs. 5 to 7.

The data in Table 7, showing losses of ferric oxide and alumina which occurred when unroasted concentrates were digested with the same digestion acids as used on roasted concentrates, are given to indicate the effect of roasting on the acid-solubilities of the above compounds.

Discussion of Roasting Tests:

The curves in Figs. 5 to 7, which indicate the relation of roasting temperature to acid-solubility, show that the temperature causing the maximum acid-solubility of iron-containing compounds in both concentrates lies in the range $400-500^{\circ}C$. Although air roasting effects an increase in the solubility of iron-containing compounds, the gain obtained by a reducing roast is much greater. Increasing the roasting temperature above $500^{\circ}C$. causes a decrease in acid-solubility of these compounds. This is true for both reducing and air roasts, but the decrease is greater in the case of the latter. Both types of roast raised the acid solubility of alumina in each concentrate and a maximum effect was achieved when roasting temperatures were in the range $500-600^{\circ}C$.

Inflexions between 400 and $500^{\circ}C$. in all curves showing alumina losses are thought to indicate the decomposition of silicates. This view is supported by the fact that filtration and washing of residues remaining after acid digestion of roasted concentrates were very much faster than when the concentrates had not been roasted. It is presumed

TABLE 7

Losses of Ferric Oxide and Alumina which occurred when unroasted concentrates were digested with dilute acids

Concentrate	Digestion Period	Digestion Acid	Percentage Losses Fe_2O_3	Al_2O_3
Uley conc. (calcite free)	$\frac{1}{2}$ hr.	1.4N HCl	54.0	30.8
"	"	0.8N H_2SO_4	20.5	25.0
Koppio conc.	"	1.4N HCl	13.5	15.0
"	"	0.8N H_2SO_4	3.4	13.3

that the slow filtration rate in the latter case was due to colloidal silica resulting from decomposition of silicates by the digestion acid. The slightly higher acid solubility of alumina after a reducing roast compared with that resulting from an air roast suggests that the higher solubility of iron-containing compounds in the former case permitted freer acid attack of alumina.

In general the experimental data show that roasting in a reducing atmosphere offers the following advantages.

1. The optimum acid-solubilities of both ferric oxide and alumina are achieved at the same roasting temperature.

2. The time required for acid digestion to effect high losses of ferric oxide and alumina is reduced, and a greater percentage extraction of alumina is obtained by digestion with dilute acids than by any means other than by digestion with strong sulphuric acid.

3. The time required for filtration and washing of acid digested residues is greatly reduced.

4. Sulphuric acid which is less expensive and more easily handled becomes as efficient as hydrochloric acid in the extraction of both ferric oxide and alumina.

Air roasting offers two advantages, namely the decomposition of silicates and the increasing of the acid solubility of alumina, but its small effect on iron-containing minerals makes it inferior to roasting in a reducing atmosphere.

Note on the determination of optimum roasting temperatures :-

The technique of thermal analysis, as described in recent literature[24], might be of value in determining the roasting temperatures at which gangue minerals undergo changes profitable to subsequent acid extraction. Analysis of concentrate gangue by methods used to observe variations in the value of Q (ratio of inductance to ohmic resistance) and losses of water of constitution which occur when the temperature of the gangue is steadily increased, may also be useful in indicating the temperatures at which these changes occur. Data obtained by application of these methods to gangue separated from Uley graphite ore by flotation have been discussed already in the section dealing with the nature of gangue minerals (p. 52). These results are of interest because they show that there is little difference between the temperatures at which changes in the structure or composition of gangue minerals occur and the roasting temperature found to cause maximum increase in acid-solubility of iron-containing minerals and alumina. The difference of approximately 50^{0}C. between the temperatures relating to iron-containing minerals is attributed to the use of large temperature intervals in the roasting tests which were conducted more than a year before apparatus became available for examination of gangue minerals by the methods mentioned above.

The mineral composition of gangue, determined by X-ray analysis, can also give an approximate indication of optimum roasting temperature, providing the temperatures of

change or decomposition of the identified minerals and the relative chemical reactivities of these and their thermal decomposition products are known. Thus, the presence of goethite, kaolins, and micas, detected in the gangue of Cley ore by X-ray analysis suggested that the optimum roasting temperature for Cley concentrate lay between 400° and 500°C. This was found to be the case.

(v) Heating with Salts.

The treatment of concentrates with salts and acid salts to remove impurities was suggested by the process devised by Buchner[6] and the experimental work of Hess[10] and others, all of whom were concerned with methods of separating ferric oxide from alumina in the treatment of bauxites and clays. These investigators studied the solution of sesquioxides in ammonium bisulphate and their results show that this can be readily achieved by autoclaving at 200°C. under pressure. The removal of iron impurities by volatilising them as ferric chloride has also received much attention from investigators seeking to produce pure alumina. Their methods have been discussed by Edwards, Frary and Jeffries[8].

Experimental :-

(a) Samples of calcite-free Cley concentrate were heated to 500°C. with each of the solid reagents, ammonium sulphate, ammonium bifluoride and ammonium chloride, in the ratio of 1 concentrate to 2 of reagent by weight, until all the reagent had been fumed off. Products obtained from these

treatments were digested with 1.4 N hydrochloric acid and 1.4 N sulphuric acid for ½ an hour. The percentage losses of gangue constituents caused by the combined treatments described above are shown in Table 8.

(b) Ammonium bisulphate was also tested, but within the temperature range 260-280°C.

Two tests were performed using mixtures of calcite-free Uley concentrate, ammonium sulphate, and sulphuric acid. In the first, a mixture was heated for one hour and then the melt was digested with 1.4 N sulphuric acid for one hour. Treatment in the second test was the same as in the first except that the mixture was allowed to stand 65 hours at room temperature before heating. The effect of ageing the mixture before heating was examined because Hess[10] states that the extraction of alumina from clay is greater if curing is allowed. Details of both tests and the results of ash determinations done on the washed and dried products from each are summarized in Table 9.

Attempts were made to heat mixtures containing ammonium bisulphate (prepared by heating ammonium sulphate below 170°C.) and calcite-free Uley concentrate in sealed tubes, but were discontinued owing to the difficulty of obtaining tubing which would withstand the pressures produced.

Discussion :-

Comparison of the data given in Table 7 with that in Table 8 shows that the acid-solubility of alumina present in calcite-free Uley concentrate was increased slightly by heating

TABLE 8

Losses of Gangue Constituents from calcite-free Uley concentrate caused by heating the latter with ammonium chloride, ammonium sulphate, and ammonium bifluoride and digesting the products with dilute acids. The loss of iron by volatilization as chloride, which occurred when the concentrate was heated with ammonium chloride is also shown.

Treatments	Percentage losses of		
	SiO_2	Fe_2O_3	Al_2O_3
1. Heating with Ammonium chloride	0	19.8	0
2. Product from heating with ammonium chloride digested with			
(a) 1.4 N HCl	0	30.9	50.9
(b) 1.4 N H_2SO_4	0	23.3	44.2
3. Product from heating with ammonium sulphate digested with			
(a) 1.4 N HCl	0	38.9	43.0
(b) 1.4 N H_2SO_4	0	23.9	38.7
4. Product from heating with ammonium bifluoride digested with			
(a) 1.4 N HCl	N.D.*	47.2	58.0
(b) 1.4 N H_2SO_4	N.D.*	41.6	60.6

* The silica content (15.6 per cent. in the original concentrate) of these two products was (a) 0.33% and (b) 0.31%. The percentage loss of silica could not be calculated from the carbon content, owing to the combustion of some graphite during the heating process.

TABLE 9

Losses of sesquioxides which occurred when samples
of calcite-free Uley concentrate were heated with
ammonium bisulphate (a mixture of equivalent quan-
tities of ammonium sulphate and conc. sulphuric
acid) and the melts then digested with dilute
sulphuric acid.   The effect on loss of ageing a
mixture before heating is also shown.

Test No.	Composition of mixtures (weight ratio)	Period of Ageing	Ash content of Products	Sesquioxide losses*
	Concentrate : $(NH_4)_2SO_4$: H_2SO_4		%	%
1) 2)	1 : 2 : 1.3	0 hrs	25.7	53.0
		65 "	23.5	65.0

* Calculated from ash data and the composition of the
original concentrate.

the latter with ammonium chloride, ammonium sulphate, or
ammonium bifluoride. The test results also show that ammonium
bifluoride removed most of the silica from a concentrate
originally containing 15.6 per cent. of this impurity. This
is worthy of note, because, if silica has to be removed from
concentrates by volatilization, ammonium bifluoride can be
used more conveniently than hydrofluoric acid for this purpose.
Since the small loss of ferric oxide as volatile chloride
obtained by heating the concentrate with ammonium chloride
could have been achieved more easily by a dilute acid digestion,
this method of removing iron compounds is considered unsatis-
factory.

The difference between the sesquioxide loss figures
shown in Table 9 indicates that ageing mixtures before heating
is beneficial. However, the results show that treatment with
ammonium bisulphate as described in tests is not a very
efficient method of removing ferric oxide and alumina.

(vi) Treatment with aqueous caustic soda.

The following tests were designed primarily to remove
silica as soluble sodium silicate in a manner similar to that
used in the industrial preparation of the latter as described by
Martin[11], Thorpe[26] and Vail[23].

An accompanying solution of alumina to yield sodium
aluminate was expected since conditions of treatment were
similar to those of the Bayer process for the production of
alumina. However, it was realised that the high silica content
of the gangue might lead to the formation of insoluble sodium
alumino-silicate as it does in that process.

In some of the tests described below, attempts were made to dissolve silica from Uley concentrate and gangue by digesting or autoclaving them with strong caustic soda solution. In others, these treatments were combined in various ways with dilute hydrochloric acid digestions to take advantage of any increases in the solubility of gangue constituents in one reagent caused by previous treatment with the other. The "tailings gangue" used in tests was obtained by repeated flotation of Uley tailings and contained very little graphite. It was used because the effects of treatment could be easily seen and were not obscured by graphite as was the case when concentrate was being treated. A comparison of the main constituents of tailings gangue with those of concentrate gangue is shown below.

Constituent	Tailings gangue	Concentrate gangue
$CaCO_3$	56.4	40.2
SiO_2	22.4	43.7
Fe_2O_3	16.9	10.6
Al_2O_3	4.6	3.9
	100.3	98.2

Details of Tests.

Digestions with aqueous caustic soda, conducted at atmospheric pressure, were of 1 hour's duration. The period of refluxing with dilute hydrochloric acid was $\frac{1}{2}$ an hour in all cases.

Samples of Uley concentrate were treated as follows -

Treatment 1.

A 20 g. sample of Uley concentrate was boiled under reflux with 40 mls. of 50 per cent. (w/v) aqueous sodium hydroxide (B.P. 130°C.). The mixture was filtered hot and washed with 2 per cent. NaOH, and then with water and finally with a little dilute hydrochloric acid to remove excess sodium hydroxide.

Treatment 2.

A sample prepared as described under Treatment 1 was boiled under reflux with 5 per cent. hydrochloric acid, filtered, washed and dried as before.

Treatment 3.

The two digestions were as described above, but the acid treatment was applied first.

Treatment 4.

The product of Treatment 3 was refluxed with 5 per cent. hydrochloric acid.

Treatment 5.

A sample of Uley concentrate from which calcite had been removed by acid treatment, was autoclaved with 50 per cent. sodium hydroxide for 2 hours at 165°C. (70 lbs./sq.in.). The digest was filtered, and the material in the filter washed as before. The cake on the filter was then divided into two layers - the top two-thirds (Sample 5) and the bottom one-third

(Sample 6). This separation was made because a
previous experiment showed a marked segregation of
high ash material next to the paper.

Treatment 6.

Samples 5 and 6 were digested with 5 per cent.
hydrochloric acid.

The products of the six treatments described were
analysed and the percentage losses of silica, ferric oxide,
and alumina resulting from these treatments calculated. The
losses are given in Table 10.

Samples of tailings gangue were treated by methods
similar to those described above. The treatments and the
losses of constituents caused by them are shown in Table 11.

Discussion.

Data obtained from tests conducted on both the
concentrate and tailings gangue show that autoclaving with
caustic soda under 70 lbs. pressure was more effective in
dissolving silica than digestion at atmospheric pressure.
Although digestion of the concentrate with caustic soda
(Treatment 1, Table 10) caused only small mineral losses,
it is evident that there was an appreciable amount of attack,
because subsequent acid treatment removed much more silica and
alumina than did the same acid treatment of the original sample.
(The gains in acid solubility of the mineral constituents of
concentrate gangue caused by this treatment are shown in
Table 12). Vail[28] claims that insoluble silicates and

TABLE 10

Losses of Oxides from Uley Concentrate caused by various Caustic Soda Treatments

Treatment	Percentage Losses		
	SiO_2	Fe_2O_3	Al_2O_3
1. 50% NaOH[*]	12.9	0	1.8
2. 50% NaOH[*], 5% HCl	40.0	73.0	85.3
3. 5% HCl, 50% NaOH[*]	34.0	75.5	69.5
4. 5% HCl, 50% NaOH[*], 5% HCl	38.8	82.3	93.2
5. 5% HCl, 50% NaOH (autoclaved) top 2/3 of cake	62.0	83.0	42.8
bottom 1/3 of cake	66.4	83.7	+ 6.0 (gain)
6. Sample 5 digested with 5% HCl	65.0	86.7	93.8
Sample 6 digested with 5% HCl	72.2	88.2	92.0

[*] Digestion at atmospheric pressure.

TABLE 11

Losses of Oxides from Uley Tailings Gangue caused by various caustic soda treatments

Treatments	Percentage Losses		
	SiO_2	Fe_2O_3	Al_2O_3
1. 5% HCl	0.0	39.8	23.3
2. 5% HCl, 50% NaOH[*]	14.4	61.0	43.4
3. 5% HCl, 50% NaOH[*], 5% HCl	-	-	-
4. 5% HCl, 50% NaOH (autoclaved)	66.7	45.6	46.5
5. 5% HCl, 50% NaOH (autoclaved twice)	83.0	46.4	52.0
6. 5% HCl, 50% NaOH (autoclaved), 5% HCl	74.0	60.2	87.0

[*] Digestions at atmospheric pressure.

TABLE 12

Increases in the acid solubilities of oxides contained in Ulav concentrate, caused by caustic soda digestion of the latter.

Treatments etc.	Percentage losses		
	SiO_2	Fe_2O_3	Al_2O_3
1. 50% NaOH digestion for 1 hr.	12.9	0	1.8
2. Product of 1 digested for ½ hr. with 5% HCl	40.0	73.0	85.3
(A) Losses caused by acid digestion in 2.	27.1	73.0	83.5
(B) Losses caused by ½ hr. digestion of original concentrate with 5% HCl	0	54.0	30.8
Increase in percentage amounts of oxides dissolved by 5% HCl after 50% caustic soda digestion (A) − (B)	27.1	19.0	52.7

aluminates are liable to be formed when lime is used as a
settling agent in the manufacture of sodium silicate. Hence
it is presumed that the large amount of calcite present in
Wley concentrate favoured the formation of these insoluble
compounds during caustic soda digestion and that they were
dissolved by subsequent acid treatment. Similarly, the
marked increase in acid solubility of alumina present in both
the concentrate and tailings gangue, after all caustic soda
treatments was thought to be due to the formation of sodium
alumino-silicate which is insoluble in caustic soda solution
but is readily decomposed by acids. This view, if correct,
also explains why silica was dissolved or peptized when the
products of alkali treatments were digested with hydrochloric
acid. The gain in alumina in Sample 6 (Table 10) was probably
due to hydrolysis of sodium aluminate during washing which
caused deposition of alumina in the lower part of the filter.

Some increase in the acid solubility of iron-
containing minerals resulted from caustic soda treatment, but
this was not as great as was expected. Mellor's information[16]
and the work of McLeish[13] on the activation of ferric oxide
by digestion with aqueous caustic soda suggest that the
increase should have been more substantial.

The results of Treatment 5 (Table 11) show that
considerably more silica was dissolved from tailings gangue by
a second autoclaving. Literature ([11, 26, 28] describing the
manufacture of sodium silicate indicates that this was more

probably a time effect than a consequence of adding fresh
reagent.

Test data show that the treatment in which samples
were subjected to acid digestion before and after autoclaving,
was the most effective of those tested and that it caused
satisfactory mineral losses from Uley concentrate. However,
since its application to a low grade concentrate would probably
result in appreciable losses of caustic soda owing to the
formation of insoluble compounds such as sodium alumino-
silicate, it seemed desirable that this treatment should be
used in the final purification of high grade concentrates
(95 per cent. graphite) where it might satisfactorily replace
a less desirable hydrofluoric acid process.

(vii) <u>Treatments with solid sodium hydroxide and
sodium carbonate.</u>

Samples of calcite-free Uley concentrate were mixed
with either solid sodium hydroxide, or solid sodium carbonate,
or with solid sodium carbonate plus borax glass (3 : 1) in the
ratio of 2 parts of reagent to 1 part concentrate by weight and
the mixtures were each heated for one hour at a temperature
above the melting point of the reagent. After cooling, the
melts were extracted with hot water and analyses were done on
the washed and dried residues. Sub-samples of these residues
were digested for half an hour with dilute acids and data for
computing percentage losses of gangue were obtained by analysing
the washed and dried digestion residues. Table 13 is a
summary of treatments and the gangue losses which they caused.

TABLE 13

Losses of Oxides from Calcite-free Uley
concentrate caused by heating the latter
with solid caustic soda, or solid sodium
carbonate.   Additional losses caused by
acid digestion of the products of these
treatments are also shown.

Treatments	Percentage losses of		
	SiO_2	Fe_2O_3	Al_2O_3
1. Fusion with NaOH at 450°C. for one hour	78.2	0.8	58.7
2. Fusion with Na_2CO_3 at 900°C. for one hour.	41.0	7.4	-
3. Fusion with Na_2CO_3 + borax (3 : 1) at 900°C. for one hour.	52.4	2.1	12.2
4. Product of Treatment No. 1 digested for ½ hour with			
(a) 1.4 N HCl	98.8	99.7	99.1
(b) 1.4 N H_2SO_4	99.5	96.7	98.9
5. Product of Treatment No. 2 digested for ½ hour with 1.4 N HCl.	71.2	99.6	99.2
6. Product of Treatment No. 3 digested for ½ hour with 1.4 N HCl.	94.2	99.7	99.6

Discussion.

The losses of ferric oxide and alumina caused by fusion treatments were small compared with those achieved by digesting or autoclaving acid treated Uley concentrate with aqueous caustic soda. The silica losses were slightly better than those caused by autoclaving only when caustic soda was used as the solid reagent. However, larger losses of all oxides were effected by acid digestion of the products of fusion treatments than were obtained by acid digestion of autoclaved concentrate. Approximately 20 per cent. more silica was peptized by the former digestion.

The fluidity of the melts is thought to have had some influence on the effectiveness of the solid reagents used. Comparison of the action of the sodium carbonate plus borax melt with that of the sodium carbonate alone, which was more viscous, supports this view. The caustic soda fusion was the most effective and also gave the most fluid melt.

(viii) High purity graphite.

The methods used to obtain samples of graphite containing less than 1% of impurities were —

(a) Combined acid treatments, in which samples were alternately acid digested with strong hydrochloric acid and evaporated with hydrofluoric acid.

(b) Alternate digestion of samples with strong hydrochloric acid and autoclaving with strong aqueous caustic soda.

Results of a high temperature chlorination process are included for comparison.

(a) <u>Hydrofluoric acid treatment</u> :- Samples selected for purification by use of this reagent were -

Koppio ore.

Koppio concentrate.

Uley concentrate.

Madagascar flake concentrate.

The method of treatment was to digest samples with an excess of strong hydrochloric acid twice, and evaporate the digestion residue twice with hydrofluoric acid. The product from this last step was again digested with strong hydrochloric acid, then filtered and washed thoroughly. The volumes and strengths of reagents used in this treatment are shown in Table 14. Evaporations were performed in large platinum dishes. A Dowmetal container was also used in several runs, after preliminary tests had been conducted on this alloy to determine its suitability for the purpose. The corrosion resistance of Dowmetal was tested by placing discs of the alloy in platinum basins with hydrofluoric acid and evaporating off the acid. It was necessary to separate the discs from the basins by setting them on bakelite rings, in order to avoid the hastening of corrosion by galvanic action. The acid strengths used, and percentage losses in weight of the discs are given in Table 15.

The purity of products obtained by acid treating samples in the manner described above was determined by ashing. The ash contents of samples, determined before and after acid treatment, are shown in Table 16.

TABLE 14

Volumes and strengths of reagents used
in the combined hydrochloric acid/hydro-
fluoric acid treatment of Uley concen-
trate

Hydrochloric acid digestions	Hydrofluoric acid evaporations
1. Acid Strength – 20% (w/w) 2. Vol. of acid per 100 gms. of sample – 200 mls. 3. Duration of Digestion – 1 hour.	1. Volume of acid per 100 gms. of sample – 200 mls. 2. One ml. of 1 : 1 sulphuric acid added to each 100 mls. of HF to be evaporated. 3. 40% HF (A.R.) used in treatment of samples 1, 2 and 3* 65% HF (Technical grade) used for samples 4 and 5.

* See Table 16.

TABLE 15

Corrosion of Dowmetal by hydrofluoric acid, gauged by loss in weight of discs after treatment with this acid.

Test No.	Strength of hydrofluoric acid	Average percentage loss in weight of Dowmetal discs
1	65%	0.1
2	26%	0.01
3	30%	0.01
4	39% plus 1 ml. conc. H_2SO_4	+ 0.06 (gain)
5	39% plus 1 ml. conc. H_2SO_4 plus Koppic concentrate.	+ 0.06 (gain)

TABLE 16

Percentage ash in various graphite ores
and concentrates before and after com-
bined hydrochloric acid/hydrofluoric
acid treatment.

Test No.	Sample	Percentage ash	
		Before Treatment	After Treatment
1.	Koppio ore	64.4	0.2
2.	Koppio concentrate	26.6	0.1
3.	Uley concentrate	31.5	0.5
4.	Madagascar flake concentrate	5.0	0.21
5.	" "	5.0	0.24

Discussion of Dowmetal tests :-

The results of these tests shown in Table 15 were confirmed by the fact that the Dowmetal container used in the purification of samples was quite satisfactory, except for one spot where pitting became noticeable after it had been in contact with 40% HF (plus H_2SO_4) for five days.

(b) Combined acid digestion and autoclaving treatment:- Tests to determine the effectiveness of this treatment were done on a high grade Uley concentrate which contained,

$CaCO_3$ 4.3 per cent.

SiO_2 5.6 "   "

Fe_2O_3 2.0 "   "

Al_2O_3 0.5 "   "

Samples of this material were digested for 1 hour with either hydrochloric or sulphuric acid, calcite being first quantitatively removed before digestion with the latter. The digested material was filtered, washed with water and then autoclaved with 50 per cent. aqueous caustic soda, after which it was again filtered and washed with water. The final stage of treatment consisted of an acid digestion similar to that which had been performed prior to autoclaving, and was followed by thorough washing with water.

Details of the treatments and ash contents of products are shown in Table 17.

High temperature chlorination.

This process, which has been described by McTaggart[14] is based on the fact that the oxides of iron, aluminium and

TABLE 17

Combined acid digestion and
autoclaving treatments applied
to a high grade Uley concen-
trate. The Purity of Products
is also shown.

Treatment No.	Digestion Acid	Autoclaving conditions			Per cent Ash in Product
		Duration	Temp.	Pressure lbs./sq.in.	
1	20% HCl	2 hrs.	165°C	75	0.5
2	" "	"	180	95	0.3
3*	" "	"	"	"	1.2
4	10% H_2SO_4	"	"	"	0.5
5**	" "	"	"	"	0.2
6	" "	6 hrs.	"	"	0.06

*   This sample was all minus 200 B.S.S. mesh.

** Part of the product from test No. 4 was
   again autoclaved and digested.

silicon form volatile chlorides when they are heated at high temperatures under reducing conditions in the presence of chlorine.

These conditions for formation of volatile chlorides are obtained when a sample of graphite concentrate is heated in a stream of chlorine. The highest temperature required is for the formation of silicon tetrachloride and was found by McTaggart[14] to be 1300-1400°C for a satisfactory reaction rate. However, in order to reduce the impurities of a Uley concentrate from 15 per cent. to 0.15 per cent. heating had to be continued for 12 hours.

The purest samples which this process produced contained 0.12% to 0.7% of impurities, mostly silica.

The writer took an active interest in this process and prepared a number of the Uley concentrate samples to which it was applied. The process offers an attractive alternative to hydrofluoric acid treatment, but appears to suffer from the necessities of using high temperatures and of protecting the solid graphite sample-container from atmospheric oxidation.

Discussion of methods.

Since all three methods give products containing 0.2 - 0.5% of impurities, a comparison between them is necessarily based on their cost and convenience.

Hydrofluoric acid is a source of danger to personnel. Furthermore, apart from platinum, there are no materials, except Dowmetal perhaps, in which it may be handled without corrosion problems arising. It is also an expensive reagent, of which the recovery, although possible, is difficult.

High temperature chlorination has two drawbacks.
The first of these is the large amount of energy required to
produce and maintain temperatures of 1300-1400°C in an
industrial furnace, the second is the necessity to operate
this furnace in an inert atmosphere. Again the solid graphite
containers in which samples are heated, crumble with use and
are too fragile for industrial handling.

The acid treatment and autoclaving method presents
little difficulty. It employs robust standard equipment and
consumes only a reasonable amount of energy in heating.
Another advantage of this process is that caustic soda used
in autoclaving may be readily regenerated. Furthermore the
test data shew that it is capable of yielding the purest
products.

(ix) <u>Summary and discussion of chemical beneficiation
data</u>.

In order to obtain a ready comparison, the highest
percentage extractions of gangue constituents achieved by
various methods of beneficiation are given in Table 18. Some
general conclusions drawn from these data are:-

1. Prolonged digestion time or high concentration were
required for the extraction of substantial amounts of gangue
from both Uley and Koppio concentrates by acid digestion methods.
Even then, only high concentrations of sulphuric acid removed
more than 50 per cent. of the alumina in either concentrate.

2. Pretreating concentrates by roasting them in a
reducing atmosphere enabled dilute acids to effect gangue

TABLE 18.

Summary of the highest percentage extractions of gangue constituents
from Uley and Kepple concentrates achieved by various methods of beneficiation.

Methods of beneficiation	Percentage losses					
	Uley conc.			Kepple conc.		
	SiO_2	Fe_2O_3	Al_2O_3	SiO_2	Fe_2O_3	Al_2O_3
1. Acid digestion — (a) ½ hr. digestion with (i) 6.4 N. HCl	0	98.0	54.6	0	89.2	39.3
(ii) 26.5 N. H_2SO_4	0	97.0	93.4	0	96.5	96.0
(b) 4 hr. digestion with (i) 1.4 N. HCl	0	96.3	55.0	0	92.6	32.7
(ii) 1.4 N. H_2SO_4	0	52.6	35.5	0	50.6	20.6
2. Reducing roast at 500°C. and ½ hr. digestion of the product with (i) 1.4 N. HCl	0	94.0	72.5	0	93.0	60.0
(ii) 1.4 N. H_2SO_4	0	92.0	71.5	0	93.0	60.0
3. Heating with NH_4F·HF; product digested with (i) 1.4 N. HCl	99.5	47.2	58.0	–	–	–
(ii) 1.4 N. H_2SO_4	99.5	41.6	60.6	–	–	–
4. One hr. digestion with 10% H_2SO_4/6 hrs. autoclaving with 50% aqueous NaOH at 180°C/1 hr. digestion with 10% H_2SO_4. Applied to an 87.6% concentrate.	99.0	99.0	99.4	–	–	–
Impurities reduced to 0.06%						
5. Fusion with solid NaOH; product digested with (i) 1.4 N. HCl	99.8	99.7	99.1	–	–	–
(ii) 1.4 N. H_2SO_4	99.5	96.7	98.9	–	–	–

losses comparable with, and in some cases better than, losses
caused by treatment of the original concentrates with strong
acids, or by prolonged dilute acid digestions.

3.   Removal of silica by combined autoclaving with strong
caustic soda and acid digestion was less efficient than by
fusion with solid caustic soda. The latter also resulted in
higher losses of ferric oxide and alumina by subsequent acid
digestion. However, when the former method was applied to
concentrates containing approximately 10 per cent. of impurities
instead of 30 per cent., and when the concentration of digestion
acid and temperature of autoclaving were raised, it appeared to
be very effective, especially when the period of autoclaving
was also increased.

4.   Sulphuric acid was equal to hydrochloric acid in its
ability to remove gangue from concentrates which had been either
roasted in a reducing atmosphere or subjected to the caustic
soda treatments described above.

(x) Reduction of flake size by chemical treatment.

The following tests were performed to ascertain
whether removal of gangue from Uley concentrate by chemical
treatment would reduce the size of graphite flakes enclosing
gangue minerals.

Sizing tests were done on the untreated concentrate
and on a sample of the same concentrate, which had been digested
with 10 per cent. hydrochloric acid, treated with hydrofluoric
acid to remove silica then digested with more 10 per cent.
hydrochloric acid and finally washed.

Table 19 contains distribution data obtained from the results of these tests.

Discussion :-

Reference to Fig. 8 shows that the carbon distribution graphs for both treated and untreated samples of the concentrate were almost identical in shape, and, although not coincident, displacement of the graph of treated material to the left, that is towards smaller particle size, was small.

Since the distribution curve of graphite in the treated sample is situated in a region of finer sizes compared with that of graphite in the untreated sample, it seems that flake size has been reduced. It should be noted however that in the case of the untreated sample, composite particles of graphite and gangue are retained on the screens. As the graphite flakes are smaller than the composite particles they will pass through the screen mesh when composite particles are broken up by acid treatment. The difference of "percentage minus fraction" shown by distance between curves at the same particle size therefore indicates the maximum reduction of flake size. Since composite particles are known to exist in abundance, reduction of flake size must be very small in spite of the drastic treatment.

(xi) Adsorption of reagents on graphite.

Shapiro and Veselovsky[23] claim that graphite adsorbed reagents and salts from solution during the treatment of concentrates and ores, was investigated by the methods described below.

TABLE 19

Size distribution of graphite in Uley concentrate before and after acid treatment.

Screen size		Percentage weights of graphite passing a given screen	
Screen B.S.S.	Aperture mm.	Untreated conc.	Treated conc.
25	0.600	96.0	96.7
52	0.294	67.8	74.8
72	0.211	53.1	60.8
100	0.153	29.4	37.3
150	0.104	19.2	27.2
200	0.076	9.8	14.4
300	0.053	4.6	6.6

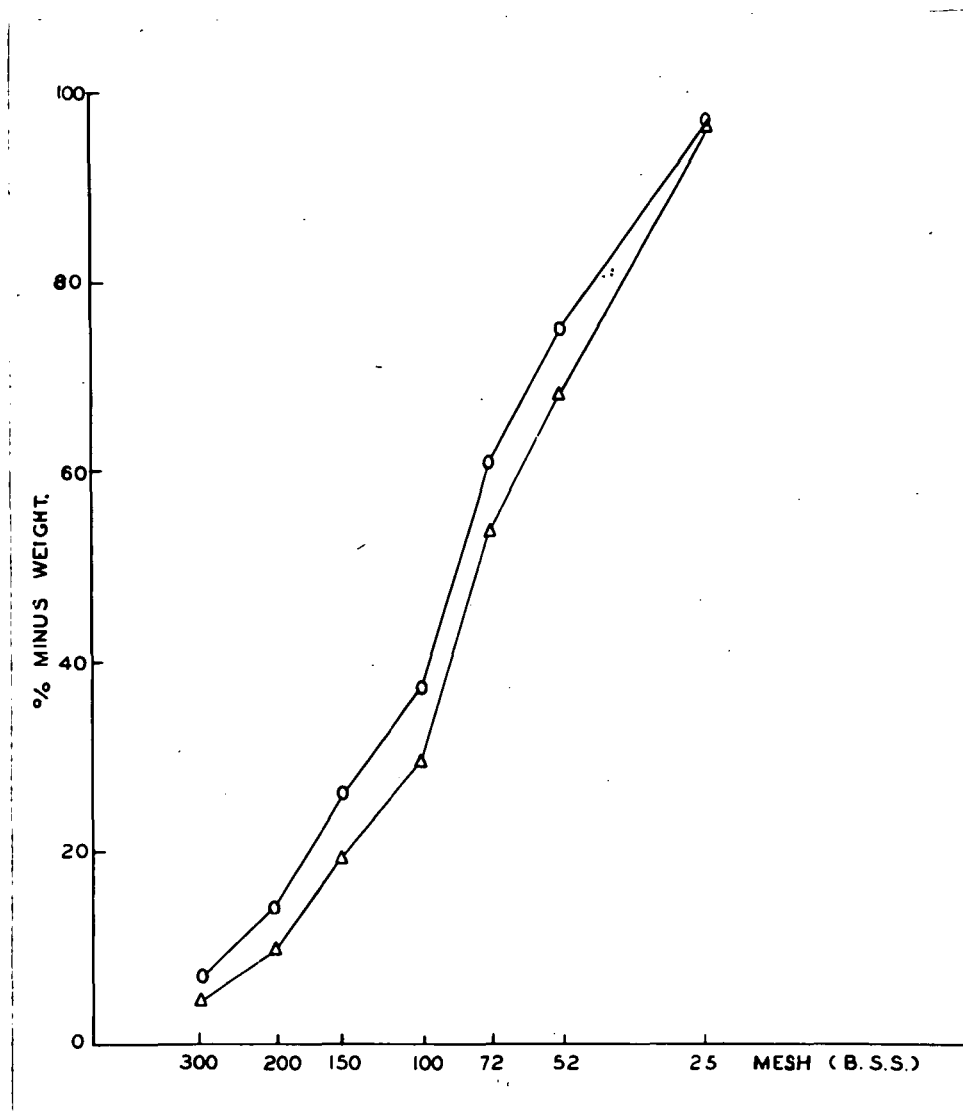* Graphite distribution data was obtained from results of ash determinations done on each screen fraction.

Fig. 8. Showing distribution of graphitic carbon in

Δ— (a) Untreated Uley concentrate.

o— (b) Hydrofluoric treated sample of (a)
Curves show cumulative percentage minus
size fraction.

A sample of finely ground Uley concentrate was digested with an acid mixture which previous tests had shown to be capable of effecting the complete solution of iron-containing gangue minerals. The digest was filtered and washed thoroughly and iron dissolved in the combined filtrates and washings was determined. A sample of ash, obtained from another portion of the same concentrate, was acid treated and analysed by the same methods. It was argued that, if the amounts of iron determined by both analyses were not equal when expressed as percentages of the sample weights of concentrate used in each case, then some dissolved iron must have been adsorbed and retained by graphite when the first acid digest was filtered and washed.

Graphite residues obtained from Uley concentrate by the acid treatment described above, were tested to see if they had adsorbed chloride ions during digestion and retained these during washing.

Samples of a finely ground graphite concentrate which had been purified by high temperature chlorination were also tested to determine how much chlorine this material may have adsorbed during treatment.

Details of these investigations are given below.

(a) Adsorption of ferric ions:- Three samples which had been prepared from Uley concentrate were ground until 90 per cent. of each passed through a 200 mesh B.S.S. screen, and were then digested with a mixture of reagents given below. Quantities indicate the amounts used in the treatment of 5 g. concentrate samples.

Hydrochloric acid	6N	50 mls.
Stannous Chloride (40 gms tin/l.)		1 ml.
Ammonium fluoride (30% aqueous solution)		2 mls.

The last two reagents were included to ensure the release of iron from silicates and the rapid solution of slowly soluble ferric oxide.

After digestion for 1 hour at boiling point residues were filtered off and washed alternately with hot 2N hydrochloric acid and hot distilled water until 500 mls. of the former and one and a half litres of the latter had been consumed in the process. Iron in the combined filtrates and washings was determined volumetrically. A similar set of samples were analysed for iron according to the standard procedure for silicate rocks after the removal of carbon by ashing. The same method and reagents were used to determine iron in both sets of determinations. (See section on analytical procedures).

Table 20 contains the results of this test.

These data indicate that, if adsorption of ferric or ferrous ions occurs, it is undetectable by the methods employed and therefore must be small.

(b) Adsorption of chloride ions:- Samples of the washed residues mentioned in the section above were agitated with hot 1N sodium hydroxide and with hot distilled water for 24 hours after which the residues were filtered off and the filtrates tested for chloride by the addition of silver nitrate and nitric acid. The result in each case was a very faint

TABLE 20

Adsorption of ferric ions by graphite during acid treatment of Uley concentrate.

Sample	Iron (Fe_2O_3) found in filtrate and washings, expressed as a percentage of original sample.	Percentage of Fe_2O_3 in original sample.
1	0.32	0.31
1 (triplicate)	0.30	0.31
2	2.90	2.89
3	1.52	1.51

opalescence. Nephelometric apparatus was not available so that the amounts of chloride were not determined, but it was evident that these amounts were very small.

(c) Adsorption of chlorine gas:- The amount of chlorine adsorbed on finely ground graphite was also determined. These samples had been prepared by McTaggart[14] from Uley concentrate ground to 50 per cent. minus 200 mesh, during the development of the high temperature chlorination technique. A modification of Pregl's[21] semi-micro method for the determination of chlorine in organic compounds was used to determine the adsorbed chlorine. The method was standardised, using twice recrystallised 2:4 dichlor-benzoic acid. Results from a number of runs showed that amounts of chlorine between 10 and 30 mg. could be determined with an average error of 2% or less. Samples of chlorinated concentrate which had been washed with nitrogen at about $1000^{o}C$ were found to contain 0.19 per cent. of adsorbed chlorine. Unwashed samples contained 0.7 per cent. Chlorine in the gas washed sample could not be removed by agitating the material with hot caustic soda solution for 24 hours. This tenacity of chlorine to a carbon surface has been reported by McBain[12].

The stability of adsorbed chlorine to alkalis referred to above is important because McTaggart's process aimed to produce graphite suitable for lubricants in which the presence of free chlorine is most undesirable.
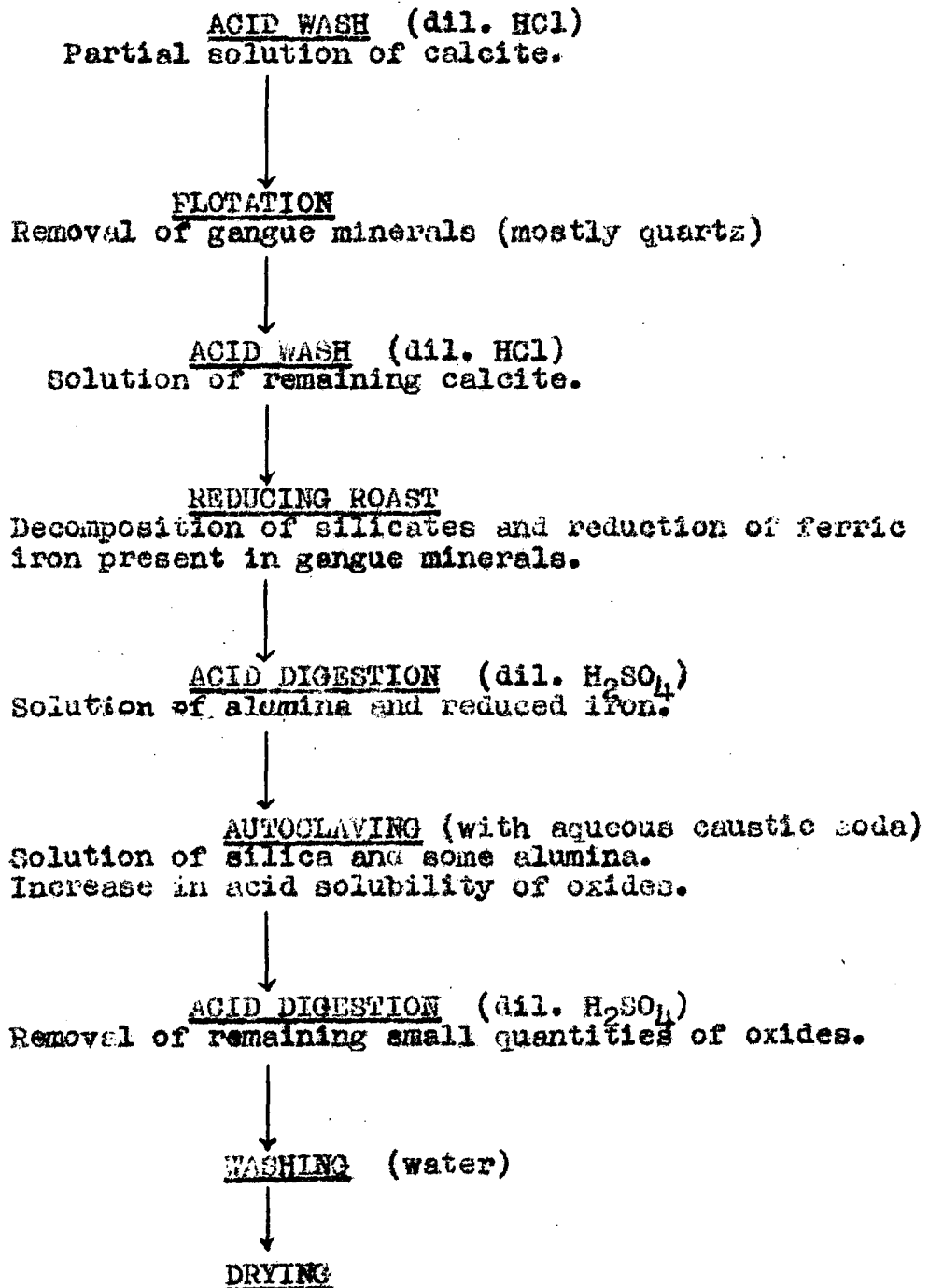
(3) A PROCESS FOR COMPLETE BENEFICIATION

A process for the complete removal of impurities from Uley ore based on the most successful of the treatments mentioned in Table 18, and combined with the most recent flotation data, is outlined below. Armstrong's[2] description of metallurgical practice at the Uley mine records that concentrates containing 60 per cent. and 80 per cent. graphitic carbon can be readily obtained from Uley ore by grinding and flotation. The scheme is designed to treat a concentrate obtained from this source. The successive operations of the proposed process are, acid wash, flotation, reducing roast, acid digestion, autoclaving with aqueous caustic soda, and acid digestion. They are shown diagrammatically in Fig. 9. Each operation is discussed below in order to show how the amounts of each mineral impurity present in a low grade concentrate is successively reduced.

1. Calcite is removed by leaching with cold dilute hydrochloric acid and the calcite free concentrate floated in an acid medium. Plante[19] obtained concentrates containing 92 per cent. carbon with 86 per cent. recoveries by this method. The purpose of including this step is primarily to reduce the silica content to a quantity which can be removed in one more operation.

2. A reducing roast and acid digestion performed on the concentrate from this second flotation results in the loss of 90 per cent. of the ferric oxide and 70 per cent. of the alumina.

FIGURE 9

OUTLINE OF PROPOSED BENEFICIATION PROCESS

ACID WASH (dil. HCl)
Partial solution of calcite.

↓

FLOTATION
Removal of gangue minerals (mostly quartz)

↓

ACID WASH (dil. HCl)
Solution of remaining calcite.

↓

REDUCING ROAST
Decomposition of silicates and reduction of ferric
iron present in gangue minerals.

↓

ACID DIGESTION (dil. H_2SO_4)
Solution of alumina and reduced iron.

↓

AUTOCLAVING (with aqueous caustic soda)
Solution of silica and some alumina.
Increase in acid solubility of oxides.

↓

ACID DIGESTION (dil. H_2SO_4)
Removal of remaining small quantities of oxides.

↓

WASHING (water)

↓

DRYING

3.   The combined acid digestion and autoclaving procedure has been shown to be capable of causing a 99.0 per cent. loss of silica, a 99.0 per cent. loss of ferric oxide, and a 99.4 per cent. loss of alumina from a high grade concentrate.

Thus all of the original calcite is removed in step 1 and 99.0 per cent. of the silica present in the product of this treatment is removed in step 3. The 10 per cent. of original ferric oxide and the 30 per cent. of original alumina remaining in the product of step 2 are reduced to 0.1 per cent. and 0.2 per cent. respectively by step 3. The final product therefore contains the following amounts of gangue constituents expressed as percentages of the respective amounts of each present in the original concentrate

$CaCO_3$	SiO_2	Fe_2O_3	Al_2O_3
0%	1%	0.1%	0.2%

Analyses of samples prepared by the above process show that the following figures are typical of the percentages of original gangue constituents retained in products.

$CaCO_3$	SiO_2	Fe_2O_3	Al_2O_3
0.00%	0.85%	0.12%	0.00%

These figures show that the process described is capable of yielding very pure graphite and are confirmed by the fact that samples prepared by it contained as little as 0.06% of impurities.

(4) Cost of Production of Pure Graphite

It is not possible to state an accurate cost figure
for the large scale production of pure graphite by the process
described above without the experience of operating the latter
industrially. However current local prices of various grades
of both imported and Australian concentrates are quoted below
to indicate that a considerable price difference exists between
high grade imports and relatively lower grade Australian
concentrates. These differences will be shown to be greater in
amount than an estimated cost of chemical processing calculated
from pilot plant data.

The prices for imported concentrates, similar in grade
to Australian products, are also quoted because they provide
useful data for examining the economics of the present South
Australian graphite industry and also show that the lower prices
of local concentrates increase the margin of cost available to
cover the expense of complete beneficiation.

Price data are shown in Tables 21 to 24 of which the
first two refer to Australian products and third and fourth to
imported concentrates. All prices for imports were obtained
from local dealers, agents and manufacturers.

The approximate cost of production per ton of Uley
concentrate, assaying 60-80 per cent. graphite has been
calculated from the data of H. Armstrong's report[?] to be £20.
The figure for Koppio concentrate was similarly found to be £34.

The erratic nature of prices given in Tables 23 and
24 is illustrated in Fig. 10 which is a plot of price against

TABLE 21

Price quotations per ton for Uley concentrates[*]

Grade [∅]	Price [+] (1944)		
	£	s	d
60 per cent	22	6	6
70 " "	27	1	6
75 " "	28	19	6
80 " "	33	14	6
85 " "	37	5	9

[*] Taken from "Mineral Resources of Australia" Summary Report No. 5 "Graphite".

[∅] Concentrates unground and unsized.

[+] Price F.O.B. Port Lincoln, S.Aus., less agent's commission.

TABLE 22

Prices paid per ton for Koppio concentrates[*]

Grade [#]	Price [+] 1944-45		
	£	s	d
40-50	11	2	-
75	43	0	3
80	51	-	-
85	56	-	-
90	64	15	-

[*] Taken from "Mineral Resources of Australia, Summary Report No. 5 "Graphite"".

[+] Price F.O.B. Port Lincoln, S.A., less agent's commission.

[#] Concentrates unground and unsized.

TABLE 23

Summary of prices paid on the Australian
market for imported concentrates contain-
ing up to 99 per cent. graphite.

No.	Carbon Content %	Description	How sold	Price/Ton (1946-47)		
				£	s	d
1.	75	Flake	per ton	45	—	—
2.	80	Powdered	71/- cwt.	71	—	—
3.	88	"	per ton	72	—	—
4.	90	Crucible	" "	67	1	—
5.	90	Powdered	" "	53	10	—
6.	90	Flake	" "	80	—	—
7.	90	Finely ground	5 ton lots	125	8	—
8.	90	"Silvery" - 200 mesh	2-5 ton lots	68	4	—
9.	90	Fine flake	per ton	105	—	—
10.	90-92	Powdered	" "	62	5	6
11.	90-95	"	" "	49	11	9
12.	93	—	" "	68	4	—
13.	93-94	300 mesh	" "	94	1	—
14.	93-95	120 mesh	" "	88	—	—
15.	95	Large flake	2/6 per pound	280	—	—
16.	over 95	Powdered	per ton	85	—	—
17.	95-97	—	5 ton lots	55	2	—
18.	97	Flake	3/9 per lb.	420	—	—
19.	97	Powdered	4/6 " "	504	—	—
20.	97-98	Lump	per ton	49	8	—
21.	97-98	—	5 ton lots	88	3	—
22.	98	Powdered	92/- per cwt.	92	—	—
23.	98	—	1/- per pound	112	—	—
24.	98	—	2/7 " "	289	6	8
25.	98-99	Lump, 200-300 mesh	1/6 " "	168	—	—

TABLE 24

Prices paid on the Australian market for imported graphite containing less than 1 per cent. of impurities

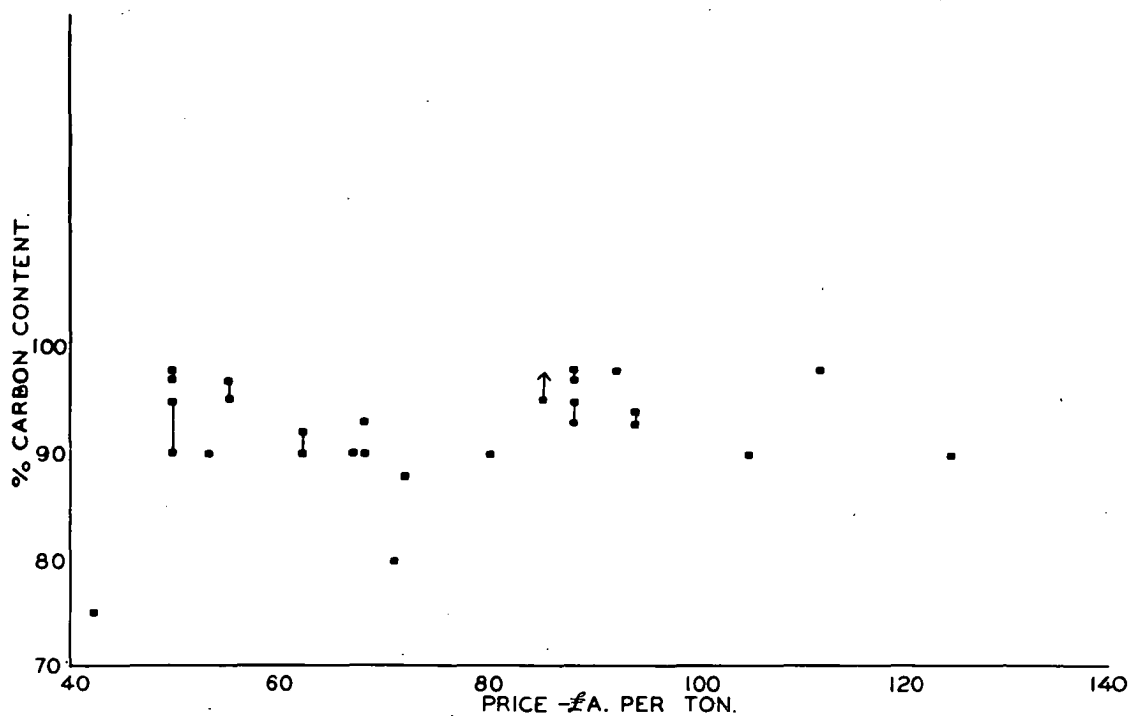| No.	Carbon Content %	Description	Price per lb. (1946-47)	Price per ton		
				£	s	d
26	99.9	Powdered	3/6	392	–	–
27	"	Flake	4/11	550	3	–
28	"	Flake – extra pure	7/6	840	–	–
29	"	Flake	4/9	532	–	–
30	"	Micronised flake	9/–	1008	–	–
31	99.7	Acetylene black	1/10	93	7	–

Fig. 10. Illustrating the lack of relation between
the prices of imported concentrates and
their carbon contents.

carbon content. These variations are partly due to inconsistency of grade which some of our analyses have shown and partly to the particular requirements of different consumers discussed below.

Crucible manufacturers require that concentrates shall contain large flakes which are capable of self-orientation during moulding, and therefore price is according to flake size. Purity is of secondary importance although limits are specified. Manufacturers of dry batteries place importance on both the fineness and purity of graphite, but the lower limit for carbon content may be as low as 80 per cent. When concentrates are to be used in the preparation of lubricants, paints, pencils, and electrical accessories, purity is of prime importance and commands very high prices.

The differences in the requirements of the different industries, however, are quite insufficient to explain the large differences in price. The claim that chemical beneficiation is economically possible is based on the high prices paid for very pure imported graphites. Some of these prices are shown in Table 24.

It is realised that the prices per ton shown in this table and obtained from price per pound data may not represent the true cost in bulk. However it is assumed that high grade Australian products would also be sold in small lots. Acetylene black has been included in the table because work on dry cell ingredients has shown that it has similar properties to finely-divided pure graphite.

The differences between prices of imported concentrates listed in Tables 23 and 24 and the average retail price of an Australian concentrate containing 86 per cent. carbon, which is taken as £40 per ton, are considerable and are still large when compared with an approximate estimated cost of producing 99.9 per cent.graphite from 85 per cent. concentrate by the process proposed above. This estimate was obtained by calculating the erection and operating costs of a plant designed from pilot plant data.[*]

The following data were assumed for the purpose of calculation.

1. **Raw material**:-

A Uley concentrate, costing £40 per ton was selected for treatment and was assumed to contain,

85.0%	Graphitic carbon
4.5%	Calcite
7.0%	Silica
3.0%	Ferric oxide
0.5%	Alumina.

This composition, which is typical for such concentrates, was taken as a basis for computing daily consumption of reagents and the necessary capacities of various items of equipment.

2. **Output**:-

The plant was designed to produce 440 lb. of 99.9 per cent. graphite daily. Assuming 250 working days per year, this becomes 50 tons per annum.

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[*] Costing of process done by Mr. I. Brown.

3.   Current local costs of labour, reagents, power, and equipment were used in costing calculations.

The complete estimate, which must be regarded as approximate, is given below.

Cost of Plant.

including 15% for contingencies £8,300. 0. 0

Cost of Production,

per ton of 99.9 per cent. graphite produced £180. 0. 0[*]

Analysis of Production Cost:-

Capital cost, including interest on capital at 5%, maintenance,
and depreciation   25.9%

Wages   35.7%

Reagents   3.5%

Raw material   30.7%

Services   4.2%
                                          100.0

The data given in Table 24 show that a comfortable margin exists between the cost of production of 99.9 per cent. graphite by the proposed process and the market prices obtainable for this grade. The cost of packaging, marketing, and similar sundries has not been allowed for above. However, the available information on these items suggests that their total cost would not exceed 5 per cent. of production cost.

---

* The figure £180. 0. 0 per ton represents a maximum, because
if units were made larger and were operated say 6 days out of
the 10 suggested, costs would be reduced. Furthermore, if
this process were to be operated as an adjunct to some larger
industry, labour costs could be reduced.

As yet no reference has been made to the Australian demand for high grade graphite. Information concerning this demand is meagre and is mostly collected in the Minerals Resources of Australia, Summary Report No.5, from which the following facts have been taken.

1. The manufacture of lubricants consumes about 50 tons annually. This graphite is all high grade, (that is 98 per cent. graphite and better) and is imported from Ceylon. Some high purity flake and colloidal products are also imported from other sources. The latter use for graphite is said to be increasing.

2. All prepared graphite articles such as electrodes, electrolytic cell plates, and brushes are imported.

The information given above indicates that markets could probably be found in Australia to absorb 50 tons of high grade Australian concentrate annually. Consumption might be increased by developing and supplying industries engaged in the manufacture of articles (such as carbon brushes) which are produced from graphite of the highest purity and which are at present being imported. Several such industries are operating in Melbourne and Sydney, but their present production capacity is small.

(5)   Analytical Methods.

The methods which were employed in this investigation
for the determination of graphitic carbon, silica, calcite, and
the oxides of iron and aluminium, are briefly described below.
For the most part they were standard procedures, but in some
cases more suitable modifications were developed. Descriptions
of these are given.   The methods used to determine variations
of the Q values of samples with temperature and the biological
method of determining free ferric oxide are also described.

(a) Graphitic Carbon:-   Preliminary analysis of ores
and concentrates for non-graphitic carbon (volatile carbon)
showed that this constituent did not exceed 1 per cent.   Also,
the total amounts of alkali metals, whose compounds are volatile
at high temperatures were present in quantities less than 0.25
per cent.   Therefore the loss in weight of samples containing
graphite after being heated in air at 875-900°C for 12-14 hours
was taken as being equivalent to their graphitic carbon content.
The quantity of graphite which remained after this treatment was
so small that it could not be detected after dissolution of the
ash in hydrofluoric acid.

The temperature of ashing was critical because the
rate of combustion of graphite below 850°C is much slower than
above this temperature.   When samples contained calcite, this
had to be determined and a correction made for the loss of CO_2
during ignition.   e.g. when a concentrate having the following
composition,

graphite	61.0 per cent.
SiO_2	16.0 " "
Fe_2O_3	5.5 " "
Al_2O_3	0.5 " "
$CaCO_3$	21.0 " "

was burned, the percentage weight of ash obtained was 29.0 per cent. This result was corrected by adding to it the weight of carbon dioxide combined in the percentage weight of calcium carbonate found by analysis of the concentrate. The corrected result and the total percentage weight of mineral impurities found in the concentrate by analyses had values of 38.2 and 38.0 per cent. respectively. The good agreement shown between these figures was usual in other cases.

(b) Calcite:- The calcite present in ores and concentrates was totally soluble in cold dilute hydrochloric acid. Less than 1% of magnesium carbonate was present in these materials, so that it was possible to use a rapid method, similar to that used in soil analysis for determination of total carbonate.

The method used consisted of adding 50 mls of N hydrochloric acid to a sample of graphite concentrate of from 0.5 to 10.0 g. according to the percentage of carbonate thought to be present, and after standing for an hour with occasional shaking, a 20 ml. aliquot was withdrawn by means of a pipette and titrated with $\frac{N}{2}$ caustic soda. The indicator used was 0.1% bromthymol blue (pH 6.0-7.6). From the difference between this titre and a blank, the carbonate content was

calculated and reported as $CaCO_3$. The method is only an approximate one, but has proved quite adequate for routine control purposes.

The method devised by Hutchinson and McLennan and described by Piper[20] was used when more accurate determinations were required.

Table 25 gives results obtained by the two methods performed on the same samples. These data show that the rapid method gives results $\frac{1}{2}$ - 1 per cent. higher than those of the more precise method.

(c) Silica:- This constituent was determined in the usual manner by double evaporation with hydrofluoric acid plus sulphuric acid.

On occasions the residue remaining after this treatment amounted to 20-60 mg., and since this residue was weighed as oxide before evaporation it was desirable to know if strong heating after removal of silica left oxides or basic sulphates. This point was checked by igniting two 0.1 g. samples of concentrate ash, rich in ferric oxide and alumina (40% R_2O_3) then sulphating, fuming off sulphur trioxide and igniting them again for 10 minutes over a Meker burner. The differences in weight after the first and second ignitions were 0.0000 and 0.0002 gms. Thus the error due to incomplete decomposition of sulphates is negligible.

(d) Alumina:- This was determined by difference ($R_2O_3 - Fe_2O_3$).

TABLE 25

**Values for the calcite content of samples
determined by the rapid method and the
Hutchinson and McLennan method.**

Method	Percentage of calcite found in samples				
	1.	2.	3.	4.	5.
1. Rapid	6.6	1.4	4.3	2.4	6.0
2. Hutchinson and McLennan	5.80	0.95	4.13	2.02	5.60

(e) Ferric Oxide:- The determination of ferric oxide in ores and concentrates was difficult, because complete solution could not be effected by boiling with strong acids. However, a satisfactory procedure was developed, in which samples (0.5 - 5.0 g.) were digested with a mixture of 20 mls. concentrated hydrochloric acid, 2 mls. stannous chloride (40 gms. tin/litre) and 2 mls. of 30% ammonium fluoride. After 30-40 minutes gentle boiling, solution was complete, the flask was cooled a little below boiling, and hydrogen peroxide was then added dropwise until the faint yellow tint of ferric chloride became permanent. Excess hydrogen peroxide was then destroyed by boiling.

Iron in solution was determined after reduction with stannous chloride by titration with either $\frac{N}{10}$ or $\frac{N}{100}$ potassium dichromate. A sharper endpoint was obtained by adding excess of this reagent and back titrating with ferrous ammonium sulphate solution. The method has been described in detail by Sarver and Kolthoff[22]. Platinum dissolved during potassium bisulphate fusion of ignited sesquioxides reduced the sharpness of the end point. However in such instances it was readily removed by reprecipitating and washing the oxides. The hydrochloric acid solution of the reprecipitated oxides could then be titrated without any trouble.

(f) Determination of Q (ratio of inductance to ohmic resistance):- The values of Q used in plotting the curve in Fig. 1, which shows variations in the value of this ratio with temperature for Uley gangue, were determined as follows.

A tablet, 1½ in. square and ¼ in. thick was prepared from gangue by pressing the latter in a die. This was placed symmetrically on a 1½ in. square of platinum foil lying on the floor of an electric muffle and was covered with another piece of foil of the same size as the first. A piece of clean firebrick was placed on top of this assembly to prevent movement and to ensure good contact between the sample and the platinum squares. The latter were connected to the terminals of a "Q-meter" (Type A50589) made by Amalgamated Wireless of Australasia Ltd. Readings were taken on this instrument after each $10^\circ C$ rise in muffle temperature which was read by means of a chromel-alumel thermocouple and indicator. A satisfactory rate of heating was obtained by switching the muffle on at room-temperature and allowing it to reach $700^\circ C$ in its own time which was 2 hours 15 min.

(g) Free Ferric Oxide:- The biological method used to determine free ferric oxide in graphite ores, concentrates, and gangue, was based on the work of Allison and Scarseth[1] and made use of the fact that soil bacteria produce reducing conditions in anaerobic fermentation of sucrose. Determinations were made as follows. Samples were added to 250 ml. conical flasks containing 200 mls. of distilled water in which sucrose equal to 5 per cent. of the sample weight was dissolved. Each flask was innoculated with 5 mls. of supernatant liquid from a soil culture and sealed with stoppers fitted with glass tubes bent to dip under the surface of the water in a thermostat in which they were left to incubate at $25^\circ C$. for varying periods.

The soil culture from which other flasks were inoculated was prepared by adding 2 gms. sucrose dissolved in 200 mls. of distilled water, to 20 grams of clean garden soil. After anaerobic incubation for 12 days the supernatant liquid of this culture was ready for use.

Cultures were filtered after incubation which usually continued for 29 days. The residues from filtration were dispersed in about 300 mls. of distilled water and the pH of the suspensions adjusted to pH 3 with 2N hydrochloric acid, using bromphenol blue as the indicator. The acidified suspensions were stirred on a water bath for one hour and then filtered. All filtrates were prepared for analysis by evaporating to a small bulk and digesting with a mixture of perchloric, nitric, and sulphuric acids in the manner described by Walkley[29]. Iron found in the culture filtrates was assumed to have been obtained by the reduction and solution of ferric compounds during incubation. That found in hydrochloric acid extracts of residues was assumed to be iron which had been reduced but not dissolved. The total weight of reduced iron found in a culture, expressed as ferric oxide, was taken to represent the amount of free ferric oxide contained in the original sample.

It is claimed that the above method does not determine iron present in silicates. Examination of cultures during incubation showed that the pH of these fell as incubation time increased. The lowest pH value recorded was 3. However, the fact that slightly greater amounts of iron were dissolved when the pH of cultures was maintained above 5.7 by the addition of

an excess of calcite, than when cultures contained no calcite, confirms the view that solution of iron was caused by reduction and not by high acidity.

NOTE: Unless otherwise stated, all analytical data reported in this paper are mean values of results obtained from duplicate analyses.

6.   CONCLUSIONS

The following conclusions are drawn from the results of the investigation described above.

1.   The main impurities found in South Australian graphite ores were, calcite, ferric oxide, alumina, and silica.

2.   Chemical methods found most successful in removing the above impurities did not resort to the use of high acid strengths and the use of hydrofluoric acid was avoided. They were,

> (a) dilute hydrochloric acid wash for removal of calcite,
>
> (b) reducing roast followed by dilute sulphuric acid digestion for removal of ferric oxide and the greater part of alumina,
>
> (c) autoclaving with strong aqueous caustic soda preceded and followed by dilute sulphuric acid digestions for removal of silica and alumina.

3.   The successive application of the above methods to an 87.6 per cent. graphite concentrate increased the purity of this material to 99.94 per cent.

4.   An examination of the economic aspects of a process in which the above methods were combined with flotation methods showed that the cost of producing pure graphite by this process was smaller than the cost of less pure imported graphite.

5.   The adsorption of reagents by graphite during chemical treatment was negligible.

6.   Chemical treatments did not reduce the flake size of graphite.

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PART II.

FINE GRINDING

OF

SOUTH AUSTRALIAN GRAPHITE CONCENTRATES.

I N D E X

SUMMARY

Fine grinding of South Australian Graphite concentrates by ball mill, pulverizer, Eagle Mill, and a chemical method, has been investigated.

Both the Eagle mill and pulverizer were found to be satisfactory. Although the power consumption of the former was slightly greater than that of the latter, its products suffered negligible contamination compared with those of the pulverizer. Ball-milling consumed more power and contaminated the products seriously.

I. INTRODUCTION.

The highest grade graphite concentrates used in industry
are generally required in a finely ground state.   Table I,
Part I, shows that material used in the manufacture of pencils,
pigments, electrical materials etc. must all pass a 200 mesh
Tyler screen. Hence the work described below was concerned
with investigating methods for fine grinding. As finely
ground low-grade graphite concentrate is difficult to purify
by chemical methods because of dusting during kiln roasting
and the difficulty of wetting and filtering fine graphite,
it was necessary to grind high purity concentrate by a method
which does not contaminate the product.

The peculiar properties of graphite and their relation
to various grinding methods are reviewed below to afford
better understanding of the problem which industry has long
regarded as both difficult and costly.

In general, grinding is a process in which a substance
is subjected to the action of forces greater than those
maintaining its crystalline form. This treatment causes
fracture and consequent reduction of particle size. Thus,
the type of crystalline structure in graphite shown in Fig. 1
and the forces maintaining it are of particular importance.
The well known use of graphite as a lubricant illustrates the
weakness of those forces which hold together the parallel
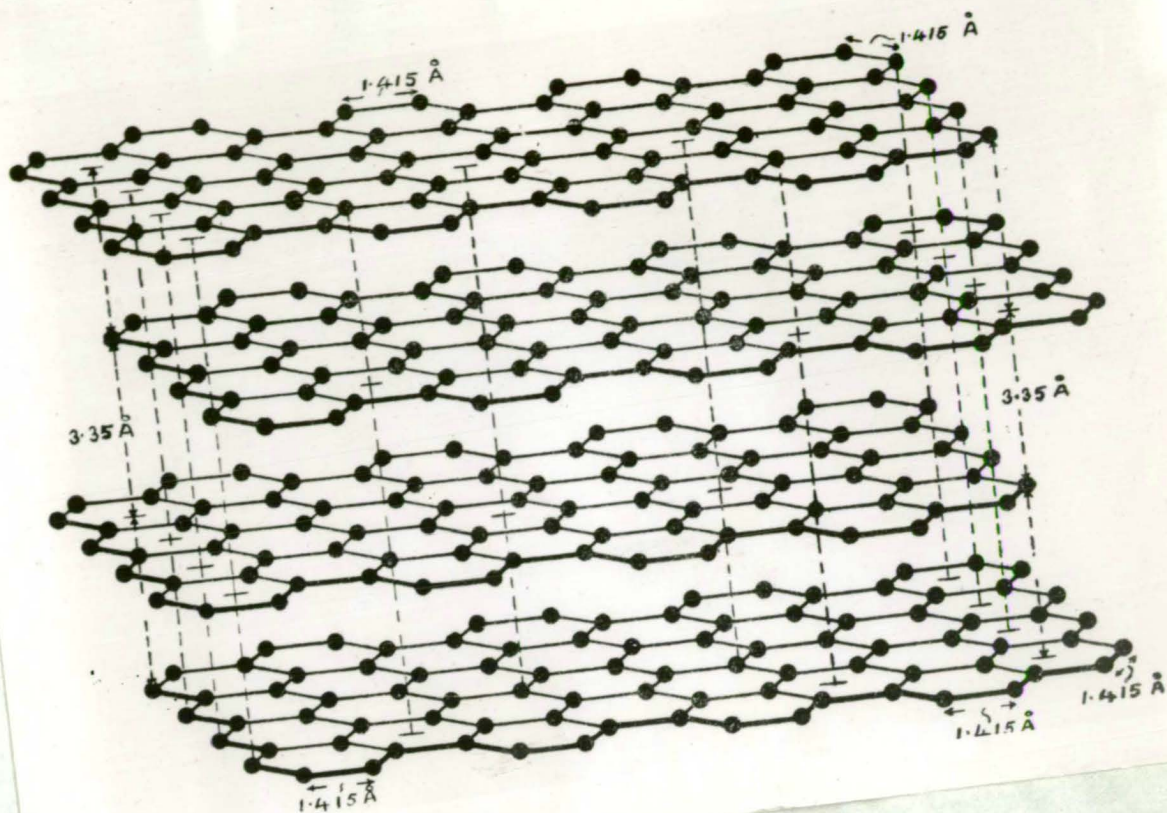planes of carbon atoms linked together in a network of hexagon

FIG. 1.

The Crystalline Structure of Graphite

(Reproduced from Riley)

rings. When a flake of graphite is subjected to strain, these planes slide over each other with considerable ease. It is evident therefore that grinding machines such as rolls and colloid mills would be of little use in grinding this material.

The lubricant property mentioned above and the ability of graphite to adhere tenaciously to the surfaces of other materials greatly reduce the efficiency of the ball mill (and rod mill). Balls and liners become coated with a film of graphite which reduces friction between them, with the result that the former are no longer carried to a point where they will cascade and cause grinding. The force necessary to fracture the hexagon ring surface is regarded as being very high. Ryschkewitsch[6] has calculated from heat of vaporisation data that twice as much work must be done to grind graphite, as would be required to grind an equal weight of quartz having the same original size to a product of the same particle size. He contends that forces great enough to disrupt this hexagon ring surface are rarely attained in grinding practice. The success of shearing mills, described below, suggests that this view refers to the ball mill.

Although graphite is flexible, it is inelastic. Thus it is possible for the fast moving hammers of a pulveriser (swing-hammer mill) to shear graphite flakes when only a part of the flake surface is struck. The "microniser" achieves the same effect by causing flakes to move at high speed round a circular

path, into which air or steam is blown under high pressure
from radially placed jets. The turbulence thus created causes
fast-moving flakes to strike each other with considerable
force. The Eagle or "micron" mill is also believed to owe
its success to a shearing effect. This mill consists of a
long pipe through which graphite is blown by steam or
compressed air. Grinding is thought to be due to the shearing
effect of a flow velocity gradient from the wall to the centre
of the pipe through which the charge is carried.

Various other methods and artifices have been used to
grind graphite, but most of them have not passed into common
practice. Some of these are discussed below.

Explosive shattering consists of subjecting a mineral to
considerable steam pressure until all capillaries and minute
cracks have been penetrated, when the pressure is suddenly
released. Expansion of steam trapped in cracks results in
fracture of the mineral. American investigators[2,3] have
applied this method to graphite ores, but their results
indicated that it was no better than mechanical methods,
although the differential crushing effect with respect to
graphite and associated gangue was greater.

Chemical methods have been used on a limited scale for
the preparation of colloidal lubricating graphite. In these,
natural graphite is oxidised by strong oxidising agents to
give graphite oxide, which when heated, decomposes to leave
finely divided graphite. However most of these procedures
are both expensive and hazardous.

The use of dispersing agents in wet ball-milling has been recommended by Russian workers[4], but little is known of this method.

The addition of hard but readily grindable material to graphite facilitates ball-mill grinding[3]. The added material maintains sufficient friction between the balls and mill-liner to permit normal functioning of the mill. Only materials which may be readily and completely removed from the mill product are suitable for addition.

A novel form of mill has been described recently and claims are made for its effectiveness as a fine grinding machine. This mill consists of a metal cylinder which is filled with steel balls, a liquid medium, and the material to be ground. The bottom of the container is vibrated rapidly by means of a supersonic generator. The vibratory motion is passed on to the contents and results in the charge being ground by impact as the balls jostle and strike each other.

II. EXPERIMENTAL

The mills used in fine grinding tests were,

(a) Porcelain ball mill.

(b) Raymond pulverizer.

(c) Eagle (or Micron) mill.

Information concerning the effects of varying size of feed, weight of charge, and grinding time, on the rate of production of fine sizes was obtained. Contamination of products as a result of mill wear was also determined in each case. An accurate comparison of grinding efficiencies in terms of new surface produced per unit of power consumed has not been made. However approximate data have been obtained from power consumption figures for the various mills. All screen analyses were done mechanically on a Ro-tap shaker using Tyler screens.

(1) Porcelain Ball Mill.

The mill used in these tests was 17 cms. deep and had an internal diameter of 18 cms. It was charged with 1486 g. of porcelain balls (average diameter 2.3 cms.) which occupied 3500 ccs. of its total volume of 4200 ccs. The mill was driven at a constant speed of 91 R.P.M.

Experiments to determine the effects of purity of graphite, charge weight, and grinding time on

grinding efficiency[*] are described below.

(i)   Effect of purity of concentrate:-

A quantity of South Australian graphite concentrate
(ash, 31 per cent.) was purified chemically to reduce
impurities to 0.5 per cent.   Samples of the original and
purified concentrate, each weighing 250 grams were ground
separately for one hour.   The products of each grind were then
mechanically sized and the fractions weighed and ashed.

Size distribution data computed from these results are
plotted in Figs. 2(a) and 2(b) in which curves showing the size
composition of the original unground samples are also plotted.
The curves show that both graphite and gangue are more readily
ground in the case of the less pure concentrate.

The ash content of the minus 270 mesh fraction obtained
by grinding the 99.5 per cent. concentrate increased by 23%
as a result of mill wear compared with less than 1 per cent.
increase for the 69 per cent. concentrate.

---

[*] Throughout this paper, "grinding efficiency" is indicated by
the rate of production of particles smaller than a specified
maximum size and is expressed in terms of the percentage
weight of the mill charge reduced to this size per hour.
This interpretation proved satisfactory in evaluating the
performance of any one mill under various conditions.
Comparisons of the performances of different mills were
based on the amounts of power they consumed in producing
the same weight of product of the same fineness and on the
degree of contamination of their products.

FIG. 2(a)

Effect of Concentrate Purity on Ball-mill Grinding
of Graphite Concentrates.

Graphs showing size distribution of graphite and
gangue in a 69 per cent. South Australian concen-
trate before and after grinding.   Curves (1) and
(2) show the size distribution of graphite and gangue
in unground concentrate and (3) and (4) the distri-
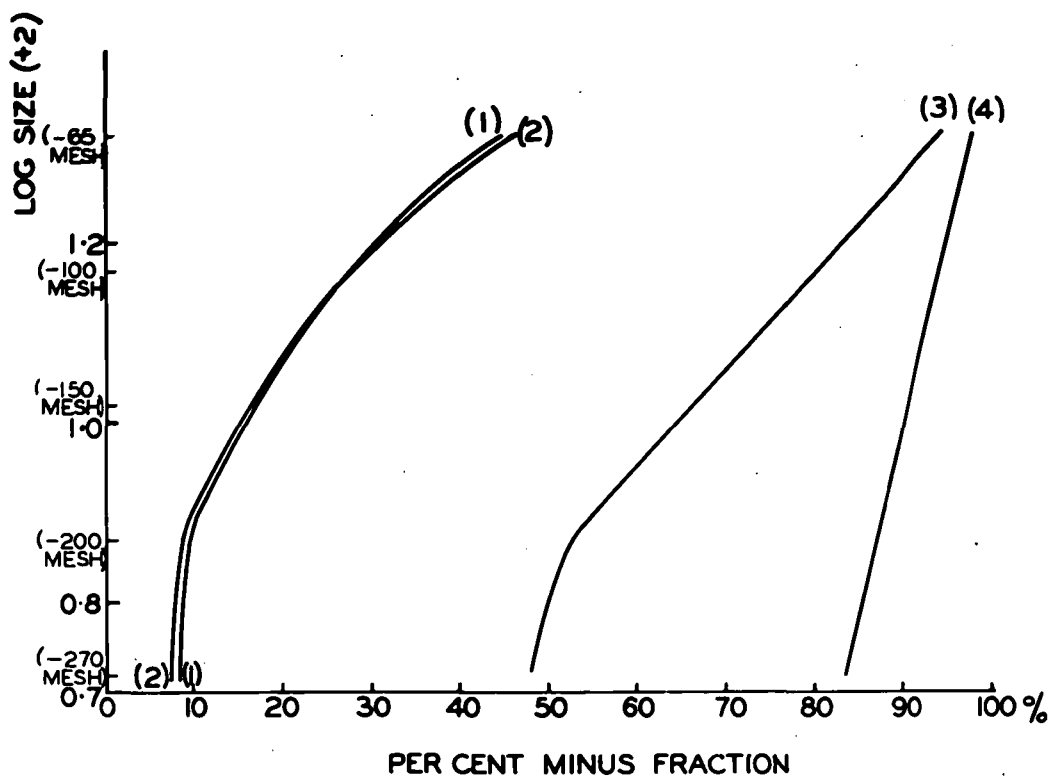bution of graphite and gangue in ground concentrate.

FIG. 2(b)

Effect of Concentrate Purity on Ball-mill Grinding
of Graphite Concentrates.

Graphs showing size distribution of graphite and
gangue in a 99.5 per cent. South Australian concen-
trate before and after grinding.   Curves (1) and
(3) show the size distribution of graphite and gangue
in unground concentrate and (2) and (4) the distri-
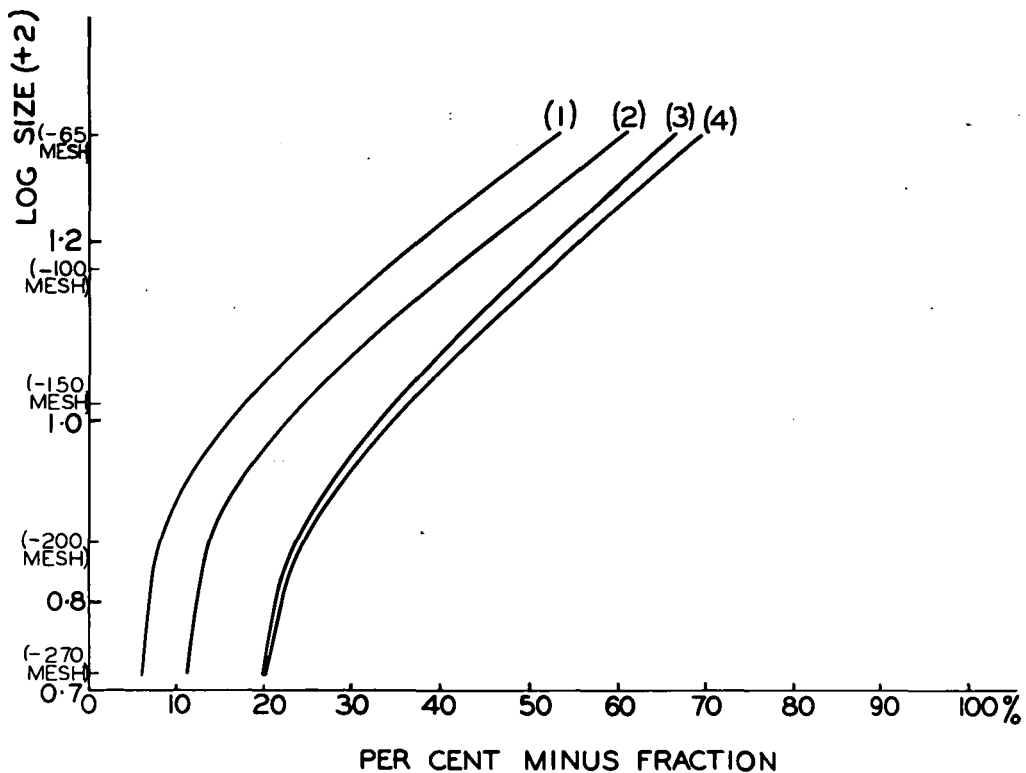bution of graphite and gangue in ground concentrate.

(ii)   Effect of varying charge weight:-

Various charges, weighing 100, 200, 400, and 600 g., of a South Australian concentrate containing 87.6 per cent. carbon were ground for one hour. The products from each grind were sized and ash determinations done on each fraction. The rates of production of minus 270 mesh material, in per cent. per hour for each run have been plotted against charge weight in Fig. 3.   These curves show that grinding efficiency increased with decreasing charge weight.

(iii)   Variation of grinding time:-

In these tests a 250 g. sample of an 87.6 per cent. concentrate was ground for a maximum period of 7 hours. Size analyses were done after 1, 3, 5, and 7 hours of grinding. The ash contents of size fractions were also determined.

A quartz sample, 250 g., having the same size composition as the original graphite was ground in the same mill (after careful cleaning of the latter) for a maximum period of $1\frac{1}{2}$ hours. Size analyses were done on the charge after $\frac{1}{2}$, $\frac{3}{4}$, 1, $1\frac{1}{4}$ and $1\frac{1}{2}$ hours grinding.

The rates of production of minus 270 mesh particles of graphite, gangue, and quartz computed from analytical data are plotted against time in Fig. 4. These graphs show that the rate of size reduction is constant for quartz, but that it decreases rapidly for graphite.

(iv)   Power consumption tests:-

The power consumed in grinding time tests was measured
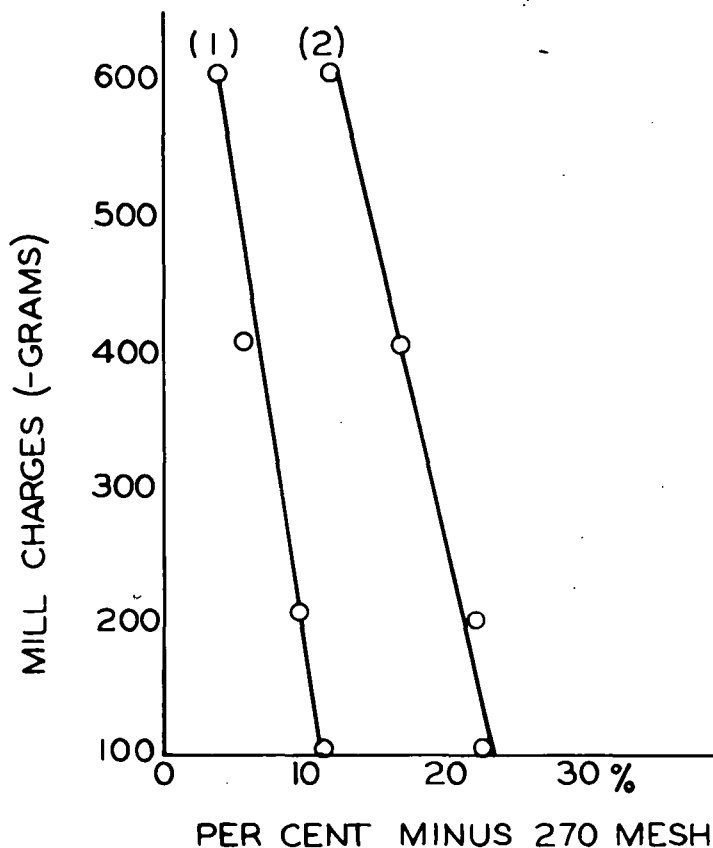
FIG. 3.

Effect of Charge Weight on Ball-mill
Grinding of Graphite Concentrate.

Graphs showing the effect of charge
weight on the rates of production of
minus 270 mesh (Tyler) material from
an 87.6 per cent. South Australian con-
centrate. Graph (1) refers to graphite
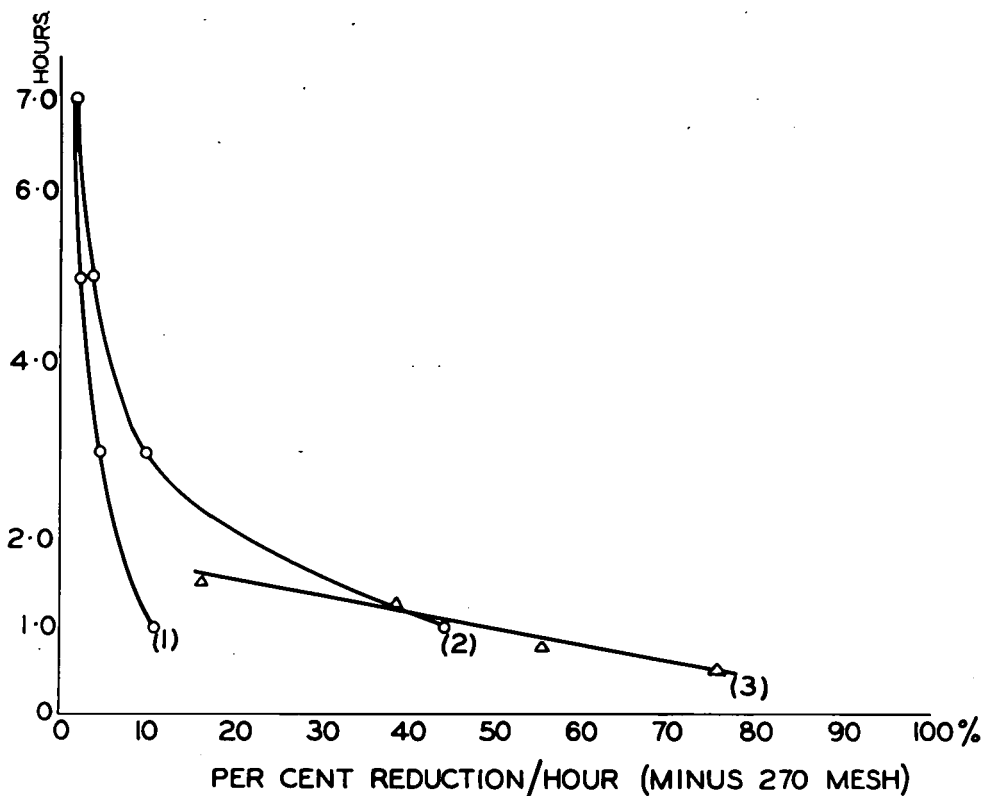and (2) to gangue.

FIG. 4.

Effect of Time on Ball-mill Grinding of Graphite Concentrate.

Curves (1) and (2) show the effects of increasing grinding time on the rates of production of minus 270 mesh (Tyler) graphite and gangue from an 67.6 per cent. South Australian concentrate. Graph (3) gives similar information for quartz ground under the same conditions.

by a watt-hour meter to which a special dial had been fitted
to enable readings to be read accurately to 10 watt hours.
Readings were taken every hour in the graphite grinding test
and every quarter hour in the case of the quartz test.
Similar data were obtained for the ball mill containing balls
but no charge. As meter readings showed power consumption
per unit time to be nearly constant in all cases, therefore
results were averaged. The average values are shown below.
Power consumed in driving mill

	Kilowatt hours.
(a) no charge	0.122
(b) containing 250 grams of 87.6 per cent. graphite concentrate	0.210
(c) containing 250 grams quartz	0.128

Discussion of results:-

(1) Purity of concentrate.

The curves in Figs. 1(a) and 1(b) clearly indicate the
loss in mill efficiency with increased purity of the charge.
It is presumed that in the case of the purer concentrate,
balls were well lubricated and slid about in the bottom of the
mill, where they abraded an appreciable quantity of material
from the mill surface and did little useful grinding. The
gangue of the less pure concentrate ensured sufficient
friction between balls and mill to make cascading of the
former possible. Thus a reasonable amount of grinding by
impact occurred. This view is confirmed by the relatively

larger increase in ash content of the minus 270 mesh material obtained by grinding the purer concentrate over that for the same size fraction from the 69 per cent. concentrate.

Results for both concentrates show that gangue is more readily ground than graphite, this is in accordance with Ryschewitsch's calculations. This differential effect which is greater for the less pure than for the pure concentrate has led several workers to suggest that graphite ores and concentrates might be partially beneficiated by grinding and screening. The data presented in Table I show the higher purity of fractions obtained from a 95 per cent. flake graphite concentrate (+ 100 mesh, B.S.S.) by ball milling and sizing.

(ii) Charge weight.

Since the curves in Fig. 3 showed that the rates of grinding of graphite increased linearly with decrease in charge weight, there was no optimum value for the latter. Thus the mill has a very low capacity when grinding at a reasonable rate.

(iii) Grinding time.

The curves for graphite and gangue in Fig. 4 suggest that for a short while after starting the mill, grinding is mainly effected by impact. However after a time (3 hours in this case) the rate of production of minus 270 mesh particles has almost reached a steady value, and any further grinding is thought to be due to attrition.

TABLE I.

Purity of fractions obtained from a
95 per cent. flake (+ 100 mesh B.S.S.)
graphite concentrate by ball milling
and sizing.

Size Fraction	Percentage Ash Content of Fraction	Percentage Weight of Fraction in Ball mill Product
+ 100 mesh, B.S.S.	4.55	4.81
53 to 76 microns	2.72	11.17
20 " 53 "	3.42	43.31
10 " 20 "	5.00	32.99
5 " 10 "	12.20	2.41
less than 5 "	18.65	4.12

The view that this decrease of grinding efficiency in the case of graphite is due to lubrication of balls and mill and not primarily to an accumulation of finer sizes is supported by the linear relation of size reduction rate to grinding time in the case of quartz. Therefore it is doubtful whether continuous classification of the mill charge would result in more efficient grinding of the graphite.

(iv) Power consumed in grinding.

From power consumption data and from the maximum grinding rate determined in grinding time tests (10 per cent. per hour at 1 hour), it has been calculated that 3,550 kilowatt hours would be required to produce one ton of minus 270 mesh material from an 87.6 per cent. graphite concentrate. At a rate of one penny per kilowatt hour, this represents a total power cost of £15.

Similar calculations for quartz, using the rate of grinding at one hour (47.5 per cent. per hour) which is not a maximum value, gave 51 kilowatt hours for the power required and 4/3 for total power cost.

Thus, if Ryschkewitsch's calculation that twice as much energy is required to grind graphite as is required to grind quartz is correct, the ratio of power quantities given above would suggest that mill efficiency in grinding graphite is much lower than in grinding quartz.

Conclusions:-

Graphite prevents the ball-mill from functioning correctly. The mill has a low grinding capacity and the

charge, if initially a high grade concentrate, is seriously contaminated.

(2) Pulverizer.

This machine was a swing-hammer type mill made by the Raymond Pulverizer Division, Combustion Engineering Co. Inc. Chicago Ill. who describe it as a Raymond Laboratory mill. The effect of purity of charge on mill performance, and contamination of the ground product were investigated. Material passed through the mill too quickly for accurate measurement of power consumption or for studying the effect of varying rate of feed.

Two concentrates, one 87.6 per cent. and the other 97.2 per cent. graphite were used. In all tests a 500 g. charge of concentrate was fed through the mill four times and a screen analysis done on the final product. Screen fractions were returned to the ground sample after weighing. This procedure was performed four times, thus the original sample went through the mill sixteen times in all.

Screen analysis data for the 87.6 per cent. concentrate are given in Table 2. Increase in percentage minus size of graphite calculated from these are plotted against number of runs through the mill in Fig. 5. Similar data for the 97 per cent. concentrate are presented in Table 3 and Fig. 6.

The ash contents of final unscreened products obtained from the 87.6 and 97.2 per cent. concentrates were found to be

TABLE 2.

Results of screen analyses conducted on
an 87.6 per cent. concentrate after var-
ious numbers of runs through the pulverizer.

Screen Fraction (Tyler)	Per cent. weight of Graphite found in Screen Fractions				
	Times through mill				
	0	4	8	12	16
+48	38.0	-	-	-	-
+65 -48	27.0	-	-	-	-
+100 - 65	15.5	0.5	-	-	-
+150 -100	9.0	2.0	0.5	-	-
+200 -150	5.5	14.5	6.5	2.0	0.5
+270 -200	1.0	9.5	18.0	14.0	4.0
-270	4.0	73.5	75.0	84.0	95.0

FIG. 5.

Relation between the rates of production of minus 200 and
270 mesh (Tyler) graphite from an 87.6 per cent. South
Australian concentrate and the number of times a charge
of this material went through the Pulverizer. Curve (1)
indicates the relation for rates of production of minus
200 mesh graphite. Curve (2) gives similar information
for minus 270 mesh graphite.

TABLE 3.

Results of screen analyses conducted on a 97.2 per cent. concentrate after various numbers of runs through the pulverizer.

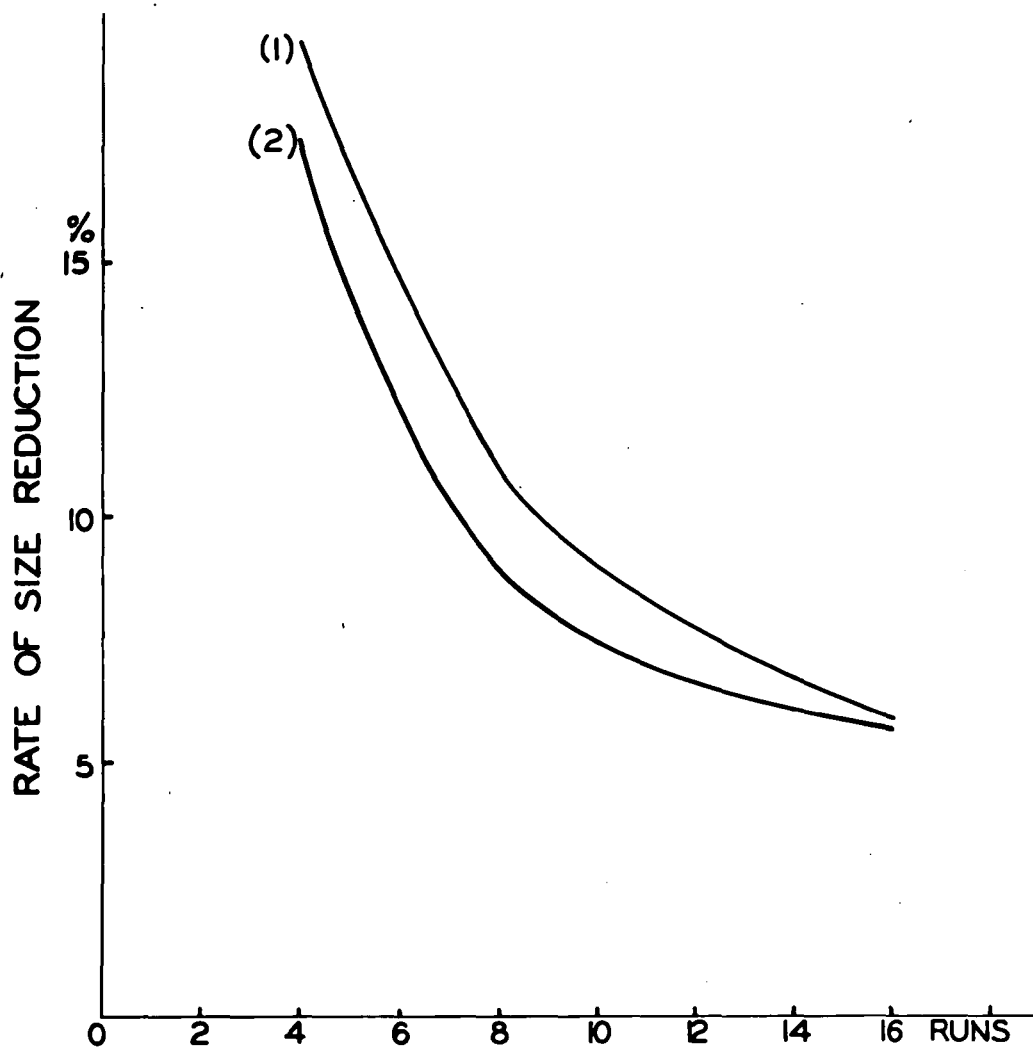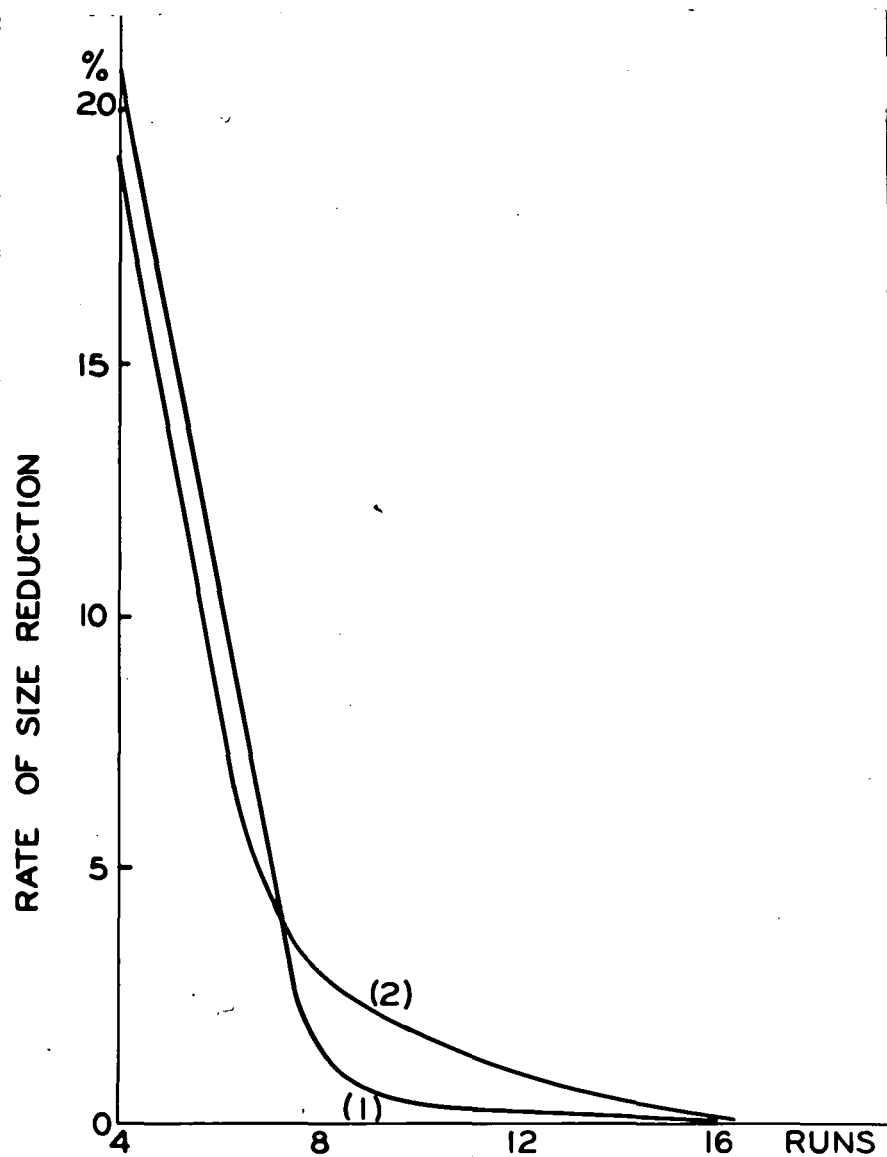| Screen Fraction (Tyler)	Per cent. weight of Graphite found in Screen Fractions				
	Times through mill				
	0	4	8	12	16
+ 100	69.0	-	-	-	-
+150 -100	14.3	0.6	-	-	-
+200 -150	6.8	5.9	0.7	-	-
+270 -200	2.7	10.2	3.7	0.5	-
-270	7.7	83.5	95.5	99.5	100
-325	-	-	-	88.0	90.0

FIG. 6.

Relation between the rates of production of minus 200 and 270 mesh (Tyler) graphite from a 97 per cent. South Australian concentrate and the number of times a charge of this material went through the Pulverizer. Curve (1) shows the relation for minus 200 mesh graphite and curve (2) for minus 270 mesh graphite.

14.9 and 3.1 per cent. respectively. The respective increases
in ash content calculated from these figures were 20.2 and 10.7
per cent.

Discussion of Results:-

Test results show that the pulveriser was very effective
in grinding graphite concentrate. The rate of reduction of
particle size does not appear to be greatly influenced by
purity of the concentrate, but Figs. 5 and 6 indicate that it
depended on average particle size in the feed; coarse
concentrate ground faster than fine. Ash figures indicate
that slight contamination occurred in the grinding of both
concentrates. However, although the increase is small it
must be regarded as a disadvantage when it is remembered that
the chemical beneficiation employed in this work aims at
producing concentrates containing less than one per cent. of
impurities. Use of an approximate figure of 0.01 kilowatt
hours for the 16 runs gave 5.3 K.W.H. as the power required
to produce one ton of -200 mesh material. Assuming the cost
of one penny per kilowatt hour, this represents a cost of 5½d.

(3) Eagle (or Micron) mill.

This mill was developed by the Eagle Pencil Co., New York,
and has been described in detail by Barry[1]. Briefly, it
consists of a long pipe through which material to be ground is
blown by a stream of air. Flow rates as low as 8 - 10 ft. per
second are used. The pipe is fitted with special valves which

—16—

permit continuous addition of fresh charge, classification of
the ground product, and return of oversize to the circuit.
The mill may be operated at pressures greater than atmospheric
and inert gases or steam may be used instead of air.

The mill used in tests described below was designed
before the appearance of Berry's paper[1] and was built mainly
with the object of preparing graphite samples for various
purposes. It differed from the Eagle mill in that it was not
continuous and was not fitted with the ejector system which
is incorporated in the latter to assist circulation of charge
and to provide the additional volume of air necessary for
continuous size classification. The ejector is claimed to
increase grinding rate. The writer's mill is shown
diagrammatically in Fig. 7. It consisted of 225 ft. of black
iron piping, 2 in internal diameter, arranged in two parallel
85 ft. lengths connected at each end by semicircular sections,
approximately 11 ft. in diameter. A centrifugal blower (D),
driven by a 1 H.P. electric motor, was connected into one of
the straight sections at 8 ft. from the beginning of the bend.
Outlet, circuit, and feed valves were situated two feet from
the intake side of the blower. These valves could be opened
or closed by a 90 degree turn and all had a bore of 2 in.

The mill was charged by feeding into valve C, which was
set vertically, with the blower running. Valve A was closed
and valve B open during this operation. After charging,
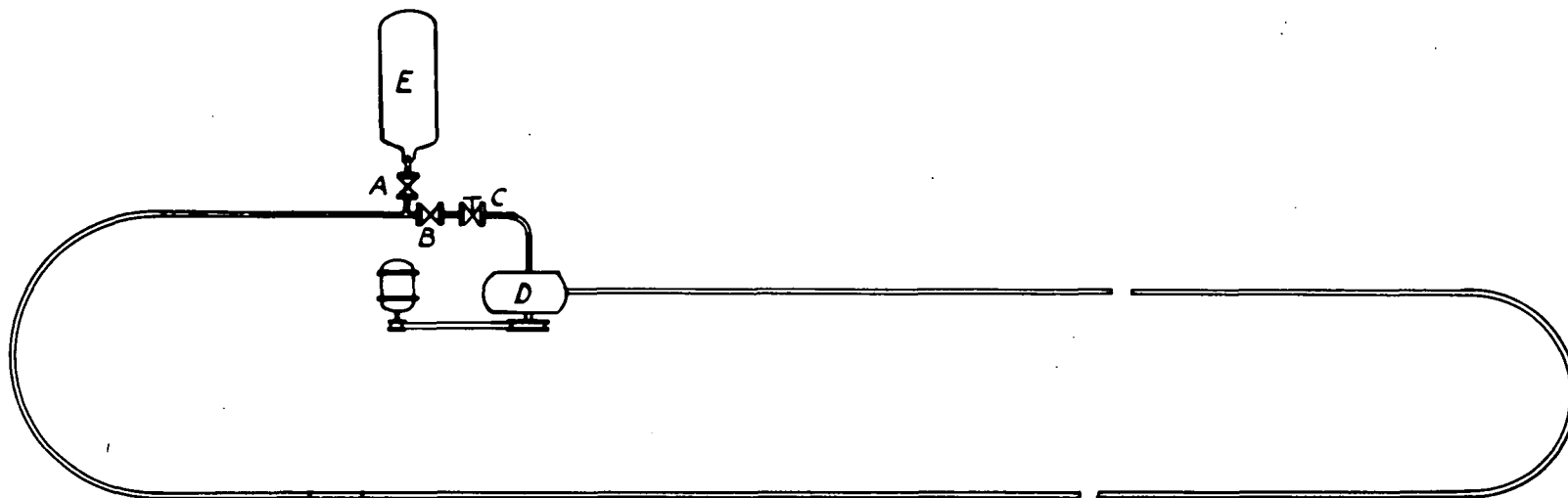
FIG. 7.

Diagram of modified Eagle mill used for grinding
South Australian graphite concentrates.
Key   A, B, C, - Full bore, 90° turn, valves
                D, - Centrifugal blower
                E, - Collecting bag.

valve C was closed and the mill left running. Grinding occurred as the charge was blown round the circuit. After the grinding period had elapsed a light-weight japara silk bag 4 ft. long and 2 ft. 6 in. in diameter was fitted to the outlet of valve A. Valves A and C were then opened and valve B closed. Ground material collected in the bag. It was found necessary to open and close valve B occasionally because, although valves A and B were set as close to each other as possible, some material collected in the dead space between them. Opening valve B blew this material round the circuit again.

A series of tests were conducted to investigate the effects of varying charge weight, grinding time, and particle size of feed, on grinding rate. These are described below, together with other tests in which the grinding of high grade concentrates was examined. Mill design did not permit determination of the effect of classification during grinding.

Details of tests:-

The rate of flow of material in the mill was 20 ft. per sec. for all tests.

(1) Charge weight.

Charges of an 87.6 per cent. -48 + 100 mesh concentrate weighing 1000, 500, and 250 g., here numbered 1, 2, and 3, respectively, were ground for 30 hours. Screen analyses were done on the products of these runs and ash contents of the fractions determined.

(ii) Grinding time.

In tests 4 and 5, the products of Nos. 1 and 2 were ground for additional periods of 44 and 37 hours respectively. Test No. 6 was similar to No. 2 except that the grinding period was increased from 30 to 96 hours.   In Test No. 7, the product of No. 6 was ground for an additional period of 104 hours.

(iii) Particle size of feed.

Test No. 8 was a repeat of No. 2, but the charge used was all -100 + 150 mesh, whereas charges used in Tests 1 to 7 were all -48 + 100 mesh.

(iv) Purity of Concentrates.

A 1300 g. sample containing 96.9 per cent. graphite was ground until it was all minus 200 mesh. The product was screened to obtain -200 + 325 mesh and -325 mesh fractions. The weight and ash contents of these were determined. A 99.4 per cent. concentrate was also ground until it all passed a 200 mesh screen. The ash content of the product was determined.

(v) The power consumed in Tests 1, 2, and 3 was determined by measuring the current flowing across one of the three phase leads. The ammeter used gave readings accurate to the second decimal place. This figure was multiplied by 3 to obtain total current. Similar control measurements were made with the mill uncharged.

Values obtained for current flowing across one phase lead after 4 hours running are shown below -

		Current in one phase lead.
(a) Mill empty		0.83 amps.
(b) Mill grinding 1000 g. charge		0.84 amps.
(c) " " 500 g. "		0.83-0.84 amps.
(d) " " 250 g. "		—

Thus, the total power consumed in grinding was

$$0.01 \text{ amp.} \times \sqrt{3} \times 415 \text{ volts} \times \frac{60}{100} = 4.3 \text{ watts}$$

where $\frac{60}{100}$ represents motor efficiency.

Results:-

Details of Tests 1 to 8 are given in Table 4, together with results of screen analyses and ash determinations done on the products of each run. Grinding rates calculated from these data are shown in Table 5. The results of tests conducted to determine the effect of concentrate purity on grinding efficiency are presented in Table 6.

Discussion of Tests 1 to 8.

The results of Nos. 1, 2 and 3 indicate that rate of production of -200 mesh material increased with decrease of charge weight. Comparison of data for tests No. 2 and No. 8 showed that size composition of the charge influenced this rate. Coarser concentrate ground more rapidly. Ash data contained in Table 4 show that concentrate gangue has been ground a little more readily than graphite.

TABLE 4

**Effects of varying charge weight, particle size of feed,
and time, on the grinding efficiency of the ungle mill.**

Test No.	Weight of Charge* (grams)		Screen Analysis of Product Per cent weight on Tyler Screens.						Duration of run (hours)	Percentage Ash Contents of Screen Fractions				
	In	Out	+48	-48 +100	-100 +150	-150 +200	-200	-325		+48	-48 +100	-100 +150	-150 +200	-200
1	1000	945	0.5	53.0	10.5	7.0	29.0	-	30	10.9	10.4	11.9	13.7	16.0
2	500	446	-	39.0	11.0	11.0	39.0	-	30	-	-	-	-	-
3	250	-	-	22.0	15.5	14.0	48.5	-	30	-	10.3	10.3	10.8	14.1
4	845*	-	0.5	33.0	11.5	8.5	46.5	-	74	-	9.2	9.6	12.3	15.4
5	346*	-	-	8.0	7.5	11.5	73.0	-	67	-	9.5	11.8	12.2	13.6
6	500	430	-	-	-	-	69.0	52.0	96	-	-	-	-	-
7	430*	-	-	-	-	21.0	79.0	63.0	200	-	-	-	-	-
8	500 (-100 +150 mesh)	450	-	-	15.0	22.0	63.0	-	30	-	-	-	-	-

* Charge was -48 + 100 mesh except in case of No. 8 which was -100 + 150 mesh.

* Product of one run returned to mill for further grinding; 100 g. of product removed for sizing and ash determinations.

TABLE 5.

Eagle mill grinding rates calculated from data in Table 3.

Test No.	Charge Weight (grams.)	Wt. of - 200 mesh material expressed as a percentage of charge wt. (a)	Duration of Run (hours) (b)	Percentage weight of -200 mesh produced per hour $(\frac{a}{b})$
1	1000	29.0	30	0.97)
4	845	46.5	74	0.63)
*			44	0.40)
3	250	48.5	30	1.62
2	500	39.0	30	1.30)
5	346	73.0	67	1.19)
*			37	0.92)
8	500	63.0	30	2.10
6	500	69.0	96	0.72)
7	428	79.0	200	0.39)
*			104	0.10)

* Data for latter part or total run obtained by difference.

TABLE 6.

Results of grinding 96.9 and 99.4 per cent.
concentrates in the Eagle mill.

		Concentrate	
		96.9 per cent.	99.4 per cent.
1.	Charge weight (grams)		
	in	1300	400
	out	1225	-
2.	Ash Content of original charge	3.1%	0.6%
3.	Screen Analyses of Products		
	-200 mesh (Tyler)	100%	100%
	-200 + 325 mesh (Tyler)	38.8%	-
	-325 mesh (")	61.2%	-
4.	Ash Content of size fractions		
	-200 mesh (Tyler)	-	0.6%
	-200 + 325 mesh (Tyler)	3.0(6)%	-
	-325 mesh (")	3.1(5)%	-
5.	Ash Content of product calculated from ash content of screen fractions.	3.1%	0.6%
6.	Increase in ash content of product with respect to original ash content of charge.	0	0

Data obtained from Tests 1 and 4, 2 and 5, 6 and 7 showed that, when a mill product was sized and returned to the mill for a further period of grinding, the average rate of production of -200 mesh material was less for the total run than for the first stage of grinding. The rate for the latter part of the run was less than the average value for the total run. These observations suggest that continuous removal of fine material as produced would ensure a constant maximum grinding rate and higher mill capacity.

The results of grinding tests conducted on concentrates containing 3.1 and 0.6 per cent. ash indicate clearly that these charges were not contaminated during grinding. They also show a slight preferential grinding of concentrate gangue.

The power required to produce one ton of -200 mesh material in this mill has been calculated from power consumption data and the maximum grinding rate which occurred in Test No.3, to be 276 kilowatt hours. At the rate of one penny per kilowatt hour, this represents a total power cost of £1. 3. 0.

Investigation of the Eagle mill is incomplete. The effects of continuous classification, variation of flow rate and of air pressure during grinding, remain to be studied.

(4) Size Reduction by Chemical Treatment.

Briefly, this method consisted of oxidising graphite by Standenmaier's method to graphite oxide which was decomposed by gentle heating.

Details of treatment:-

A 25 g. sample of a 98.8 per cent. concentrate (100 per cent. + 150 mesh) was stirred into a mixture of 1 l. of concentrated sulphuric acid and 500 mls. of concentrated nitric acid. A total of 450 g. of potassium chlorate was added in small quantities, being stirred in at intervals spaced so that evolution of gas ceased before adding the next portion. The temperature of the mixture was kept below $50^{\circ}C$. and stirring was continued for 24 hours. The residue obtained by filtering was oxidised further with potassium permanganate acidified with sulphuric acid. The product resulting after 8 hours of this treatment was lemon yellow in colour and preserved the flakiness of the graphite from which it was prepared.

Portions of this material which had been dried by washing first with alcohol then with ether were decomposed by heating to $200^{\circ}C$. The decomposition product was very voluminous, and was similar to acetylene black in appearance and bulk density. The results of a size analysis, done by the sedimentation method, are presented in Table 7. They show that chemical treatment of graphite produces a greater proportion of material much finer than can be obtained by mechanical methods of grinding.

Examinations of this "graphite oxide black" have been conducted by Ruess and Ruston[6] who proved its graphitic structure by X-ray and electron diffraction methods. It disperses very readily in both water and oils.

TABLE Z.

Size analysis of "graphite oxide black"
prepared by chemical treatment of +150
mesh concentrate.

Size fraction	Percentage weight of sample in size fraction.
10 - 20 microns	15.4 %
5 - 10 microns	30.3 %
less than 5 microns	54.2 %

III. CONCLUSION.

It is evident from the results of the investigations reported above that production of fine graphite by ball milling is inefficient and unsatisfactory because of serious contamination of the product.

The pulveriser comes close to being the best of the grinding machines tested because of its low power requirement and rapid rate of grinding. However it contaminates the charge sufficiently to make it unsuitable for grinding very pure concentrates. It is also a noisy and dusty machine.

The Eagle mill has shown itself to be efficient with respect to power consumption and superior to other machines in that it does not contaminate products. It is also quiet and dust free and requires very little attention during operation. If continuous classification of the charge during grinding improves its performance, this mill will offer an attractive means of grinding.

Although chemical treatment is capable of almost completely converting coarse graphite into a product as fine as acetylene black, the method would certainly be too costly and hazardous for industrial use. It might have limited application in the preparation of graphite of special fineness.

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PART III.

INVESTIGATION OF THE SUITABILITY OF SOUTH AUSTRALIAN GRAPHITE FOR USE IN DRY CELLS.

I N D E X

S u m m a r y

South Australian graphite has been tested as a dry cell ingredient. It was found to be at least as satisfactory for this use as the Ceylon graphite selected by the Eveready Co. (Aus.) as their standard.

The iron-containing minerals and silica in South Australian graphite concentrates had no detrimental effect on cells. Calcium and magnesium carbonates which might also be present in concentrates shortened cell life slightly, and claims that calcite causes "gassing" in cells by reacting with electrolyte were confirmed. Pyrite, which might yet be found in South Australian graphite ores also shortened cell life.

Cell performance improved as the mean particle size of graphite below 76 microns was decreased. Finely-ground South Australian graphite gave results almost as good as those for acetylene black which sets the highest standard.

I. INTRODUCTION.

It was noted in the general introduction of this paper that the shortage of overseas supplies necessitated testing the suitability of Australian graphite concentrates for use in dry cells. A preliminary survey of specifications (1) and other information (6) suggested that suitability of battery grade graphite might be determined by the following,

(a) Purity - (i.e. graphitic carbon content of concentrates.)

(b) Nature of impurities present in concentrates.

(c) Particle size of graphite.

These were investigated by preparing graphite concentrates of different purity, composition, and fineness, and testing cells containing them as ingredients.

The Eveready Co. (Aus.) specifies the following maximum limits for impurities in battery graphite.

Ash	20.0%	Co + Ni	0.03%
Fe	2.5%	As + Sb	0.03%
Cu	0.03%		

This company also claims that calcite causes "gassing" (excessive evolution of gases within cells both during storage and discharge) which results in mechanical damage to cells.

Tables 2 and 3, Part I showed that, with the exception of iron, Australian ores and concentrates contained less than the specified limits of the above impurities. Calcite contents are often high.

The effects of calcite and ferric oxide on cell performances were studied both by testing concentrates containing appreciable amounts of these impurities, and by testing pure concentrates to which impurities had been added.   Some of the added impurities were reagent grade chemicals, others were materials isolated from the gangue of graphite ores. The influence of particle size of graphite was investigated by testing a finely ground Australian concentrate and comparing its performance with those of several imported materials.

II.   EXPERIMENTAL.

(1)   Effect of Concentrate Purity on Cell Performance.

Eleven samples of graphite concentrates prepared from South Australian low-grade bulk concentrates and ores were submitted to the Eveready Co. (Aus.), Sydney, for testing in dry cells.   Brief details of methods of preparation and analytical data for these samples are given in Tables I (a) and I (b).   The results of an analysis of a Ceylon graphite taken as a standard by the Eveready Co. are included.   The test results for cells containing these samples are shown in Table 2.

The Eveready Co. stated that control of cell quality was difficult when cells were prepared by hand-mixing and hand-pressing methods.   The detection of uncontrolled variables by analysis of test results confirmed this.   However, Walkley[7], who examined their test data by statistical methods was able to show that cells containing South Australian graphite were not inferior to those produced from Standard Ceylon graphite, and also that gangue minerals, irrespective of composition, acted merely as inert diluents.   No definite indication of the effect of concentrate purity on cell performance could be obtained from the test data.

(2)   Effects Dependent on Chemical Nature of Impurities.

Results obtained in tests described above were regarded as being too variable to indicate clearly any relation between chemical composition of impurities present in concentrates and cell performance.   Subsequent to these tests, a method

TABLE I(a).

Analyses of samples tested by the Eveready Co.

Sample No.	Screen analysis (B.S.S.)		% ash (corrected)	(a) % C (by difference)	(b) % CaCO₃	(c) % SiO₂	(d) % Fe₂O₃	(e) % Al₂O₃	Total a+b+c+d+e
	-200	-300							
E1	100%	98%	21.9	78.1	0.00	19.50	0.31	1.78	99.7
E2	96	86	14.3	85.7	0.23	8.00	3.55	2.31	99.8
E3	97	92	22.0	78.0	0.00	18.95	0.55	2.42	99.9
E4	90	78	27.7	72.3	1.24	22.50	2.89	2.01	100.9
E5	91	82	25.6	74.4	0.00	22.55	1.51	1.51	100.0
E6	91	86	24.4	75.6	0.00	23.35	0.13	0.79	99.9
E7	92	74	18.6	81.4	5.80	5.96	3.80	2.55	99.5
E8	88	75	10.4	89.6	0.95	3.92	3.28	1.96	99.7
E9	96	92	18.2	81.8	4.13	9.09	3.39	1.60	100.0
E10	90	82	13.5	86.5	2.02	7.20	2.88	1.30	99.9
E11	80	60	22.1	77.9	5.60	9.78	4.84	1.80	99.9
G11	98	86	18.4	81.6	0.09	10.80	3.46	3.82	99.8

TABLE I(b).

Preparation of samples tested by the Eveready Co.

Sample No.	Method of preparation.
E1	Uley bulk conc. ground in flint ball mill, digested with 20% HCl (w/w) for ½ hr.
E2	Flotation conc. prepared by Prof. Cartrell from Uley ore.
E3	Uley bulk conc. ground in flint ball mill (calcite removed) then digested with boiling 5% HCl (e/e) for ½ hr.
E4	Koppio bulk concentrate ground in flint ball mill, prepared by tabling.
E5	Prepared from E4 by digestion with boiling 10% H_2SO_4 (w/w) for ½ hr.
E6	Prepared from E4 by digestion with boiling 50% H_2SO_4 (w/w) for ½ hr.
E7	Uley ore ground in flint ball mill, one rougher and one cleaner float.
E8	Uley ore ground in flint ball mill, one rougher and two cleaner floats.
E9	Koppio ore ground in flint ball mill, one rougher and one cleaner float.
E10	Koppio ore ground in flint ball mill, one rougher and two cleaner floats.
E11	Koppio ore ground in steel ball mill (otherwise same as E9). One rougher and one cleaner float.
C11	Ceylon graphite supplied by Eveready and used by them as a standard for comparing the above graphites.

TABLE 2.

Test data obtained by the Eveready Co. for
cells containing prepared graphite samples.
(On a percentage basis, Ceylon C11 = 100)

Sample No.	Method of Preparation	Ash (Corrected) %	CaCO₃ %	4 Ohm Continuous		Light Industrial		Current Production	
				Initial	Shelf 3 mths.	Initial	Shelf 3 mths.	Initial	Shelf 3 mths.
E1	acid treatment	21.9	0.00	124	109	115	108	107	108
E2	flotation	14.3	0.23	98	95	95	112	117	114
E3	acid treatment	22.0	0.00	88	111	122	116	96	95
E4	tabling	27.7	1.24	100	154	109	107	86	102
E5	acid treatment	25.6	0.00	95	130	121	111	104	107
E6	acid treatment	24.4	0.00	93	149	116	112	90	100
E7	flotation	18.6	5.80	91	100	98	93	109	115
E8	"	10.4	0.95	95	100	90	97	116	122
E9	"	18.2	4.13	97	101	103	101	106	110
E10	"	13.5	2.02	97	102	100	92	109	117
E11	"	22.1	5.60	96	89	98	96	96	95
C11	?	18.4	0.09	100	100	100	100	100	100
Means (excluding C11 standard)				97.6	112.7	106.9	104.6	103.3	107.7

of cell manufacture which permitted much better control and
a greater uniformity of product was developed by Skewes[9].
Advantage of this was taken to investigate the effects of
impurities more fully.

As mentioned previously it was found that South Australian
graphite has a low content of heavy metals but might contain
up to 15 per cent. ferric oxide and 30 per cent. calcite.
Attention was directed therefore to examining the effects of
the two latter components. Tests were also conducted to
determine the effect of pyrite since it is possible that this
might be found in less weathered ore taken deep in the mine.
The effects of synthetic iron oxide minerals and reagent grade
calcium and magnesium carbonates were also determined for
comparison.

(1) Methods of Cell Testing

The two tests used in assessing cell quality were the
Four Ohm Continuous Test and the Light Industrial Test. In
the former, a cell was discharged through a resistance of 4
ohms and readings of closed circuit voltage were taken across
cell terminals at frequent intervals. These readings were
plotted against time and the cell lives in minutes to 1.0 volt
and to 0.75 volts were read from the graph. The Light
Industrial Test consisted of discharging a cell through a 4
ohm resistance for 4 minutes at hourly intervals for 8 hours
per day. The closed circuit voltage of the cell was read
at the end of each 4 minute discharge period and plotted
against total period of discharge to the time when the reading

was taken. All discharge tests were conducted at the storage temperature (21°C). Initial tests were those done after a week's storage, this being sufficient time to allow the open circuit voltage of freshly made cells to reach a steady value. Further tests were also conducted after storage periods of three months or more, six months being usual. The object of these delayed tests (also called "Shelf Tests") was to detect any slow reaction between cell constituents and impurities.

(ii) Preparation of Impurities. (See Table 3).

Synthetic Iron Oxides:-

In order to determine the maximum effect which ferric oxide might have on cell performance, a sample of the most chemically active form of this substance was included for testing.

Weiser[8] quotes Hüttig and Garside who found that ferric oxide was most active when combined in equal molar proportions with water. Mono-hydrated a-ferric oxide (a-FeOOH) is identical with the mineral goethite. A sample of the latter was prepared by following the method of Fricke and Ackerman[2] and Fricke and Keefer[3]. The product was found to have a water content which agreed with that quoted by these workers, and an X-ray analysis showed its composition to be over 99 per cent. a-FeOOH.

The partially dehydrated sample used in Test No. 3 was prepared from this material by heating it for 2 hours at 240°C. at a pressure of 0.1 mm. of mercury. X-ray analysis[*] showed

* Analyses done by Mr. J. Cowley.

TABLE 3

Substances used in testing for a
relation between chemical compo-
sition of impurities and their
effect on cell performance.

Test No.	Impurity
1.	Control - no impurities.
2.	Goethite.
3.	Goethite, partially dehydrated.
4.	Hematite.
5.	Ferric oxide, obtained from Uley flotation tailings.
6.	Magnesium carbonate, obtained from Uley ore.
7.	Pyrite (FeS_2).
8.	Mica.
9.	Precipitated silica.
10.	Calcium carbonate ("Analytical Reagent" grade)
11.	Magnesium carbonate (" " ")
12.	Ferric oxide (same as No. 5) plus A.R. Calcium carbonate in equal amounts.
13.	Azurite ($2CuCO_3.Cu(OH)_2$).

that the product consisted of approximately equal quantities of $a-Fe_2O_3$ (hematite) and $a-FeOOH$.

Hematite used in Test No. 4 was prepared by heating the synthetic goethite in air at $600^{\circ}C$. for two hours.

Mineral samples:-

Impure ferric oxide used in Tests No. 5 and 12 was prepared from Uley flotation tailings by separating a magnetic fraction from these and concentrating it further by water sedimentation. The product contained 28 per cent. ferric oxide which was shown by X-ray analysis to be a mixture of $a-Fe_2O_3$ and $a-FeOOH$ in which the latter predominated, contaminated with silica.

Magnesium carbonate, used in Test No. 6 was gouged from lumps of Koppio ore. It contained approximately 60 per cent. magnesium carbonate, the remaining 40 per cent. consisting of graphite, silica, and clay minerals.

(iii). Testing of Cells Containing Impurities.

Impurities listed in Table 3 were added to graphite which had been acid treated to free it from iron oxide and calcite. This graphite contained 7.5% ash which was mainly silica. In each case 5 g. of impurity were mixed with 95 g. of graphite. A Gold Coast pyrolusite, which the Eveready Co. take as standard, was used in all tests in the ratio of 80 parts pyrolusite to 20 parts graphite mixed with "impurity".

The lives of cells prepared from these materials were determined by 4 Ohm. Continuous and Light Industrial Tests. Results obtained for cells which had been allowed to reach

equilibrium voltage at several temperatures and also for cells
which had been stored at these temperatures are summarized in
Tables 4, 5, and 6.

(iv) The Solubilities of Iron-containing Impurities in Cell
      Electrolyte.

     These were studied in order to correlate solubility data
with the effects of impurities on cell performance.   Flasks
containing mixtures of impurity and electrolyte were stored
in the same cabinet with test cells mentioned above for 6
months and were shaken daily.   An identical set of mixtures
was prepared.   These were boiled under reflux for 3 hours in
lieu of storage.   The ratio of quantities used in test mix-
tures was the same as that calculated to exist in the bobbins
of test cells and was 1 g. of impurity to 3.4 g. zinc chloride,
12.7 g. ammonium chloride, and 10.0 g. of water.

     The amounts of iron dissolved in each test are shown in
Table 7.

(v) The Reaction between Calcite and Cell Electrolyte.

     This reaction was investigated because manufacturers
claimed that calcite caused excessive evolution of gases in
dry cells.

     In tests, 2 g. samples of E7. (see Table I) containing
5.8 per cent. of calcite were mixed with 4 mls. of electrolyte,
made up as follows -

                 Water   1 l.
              Ammonium chloride 450 g.
              Zinc chloride   235 g.

TABLE 4

Impurity Tests - All lives in minutes to cut-off voltages, determined by 4-Ohm Continuous and Light Industrial tests. These are also shown as percentages of the mean life of control cells. (Life data given are means of lives of duplicate cells.)

Test No. and Impurity	4 - Ohm Continuous Test								Light Industrial Test	
	Initial 21°C		6 months' delay 21°C		6 months' delay 30°C		1 month's delay 55°C		6 months' delay 21°C	
	Life in min. to 0.75 V.	Life as per cent of control	Life in min. to 0.75 V.	Life as per cent of control	Life in min. to 0.75 V.	Life as per cent of control	Life in min. to 0.75 V.	Life as per cent of control	Life in min. to 0.9 V.	Life as per cent of control
1 - Control	575	100	495	100	460	100	N.D.		410	100
2 - Goethite	595	103	485	98	480	104	275		380	93
3 - " (heated 200°C)	570	99	485	98	470	102	440		380	93
4 - Hematite	560	97	490	99	480	104	300		380	93
5 - Ferric Oxide (tailings)	575	100	495	100	515	112	430		390	95
6 - Mag. Carb. (Uley ore)	565	98	485	98	460	100	355		360	88
7 - Pyrite	505	88	420	85	310	67	265		290	71
8 - Mica	610	106	495	100	460	100	265		380	93
9 - Silica (pptd.)	565	98	495	100	475	103	220		430	105
10 - Calc. Carb. (A.R.)	570	99	465	94	410	89	350		360	88
11 - Mag. Carb. (A.R.)	570	99	485	98	440	96	205		360	88
12 - No. 5 + No. 10	565	98	480	97	430	94	275		380	93
13 - Amarite	550	96	NIL	0	NIL	0	N.D.		N.D.	-

TABLE 5

Impurity Tests — Percentage deviations of test cell lives, shown in Table 4, from mean life of control cells.

| Test No. and Impurity | Per Cent Deviation from Control of lives determined by, | | | | Total of Percentage Deviations |
| | 4-Ohm Continuous Test | | | Light Industrial Test | |
	Initial $21^{\circ}C$	6 months $21^{\circ}C$	delay $30^{\circ}C$	6 months delay $21^{\circ}C$	
2. Goethite	+3	-2	+4	-7	-2
3. " (heated to $200^{\circ}C$)	-1	-2	+4	-7	-8
4. Hematite	-3	-1	+4	-7	-7
5. Ferric Oxide (tailings)	0	0	+12	-5	+7
6. Mag. Carb. (Uley ore)	-2	-2	0	-12	-16
7. Pyrite	-12	-15	-33	-29	-89
8. Mica	+6	0	0	-7	-1
9. Silica (pptd.)	-2	0	+3	+5	+6
10. Calc. Carb. (A.R.)	-1	-6	-11	-12	-30
11. Mag. Carb. (A.R.)	-1	-2	-4	-12	-19
12. No. 5 + No. 10	-2	-3	-6	-7	-18
13. Azurite	-4	-100	-100	—	—

TABLE 6

Impurity Tests - Variation of open circuit voltage (O.C.V.), initial closed circuit voltage (I.C.C.V.) and initial internal resistance (I.I.R.) of cells of 13 tests with storage.

Test No.	Initial			1 month at 55°C.			6 months at 21°C.			6 months at 30°C.		
	OCV	ICCV	IIR	OCV	ICCV	IIR	OCV	ICCV	IIR	OCV	ICCV	IIR.
1.	1.63	1.55	0.21	-	-	-	1.565	1.46	0.18	1.56	1.44	0.20
2.	1.64	1.54	0.25	1.57	1.38	0.34	1.565	1.45	0.21	1.56	1.42	0.19
3.	1.64	1.55	0.27	1.57	1.37	0.36	1.565	1.44	0.22	1.55	1.42	0.22
4.	1.64	1.56	0.28	1.57	1.38	0.37	1.565	1.45	0.21	1.56	1.42	0.19
5.	1.65	1.56	0.31	1.57	1.36	0.39	1.565	1.45	0.20	1.56	1.42	0.22
6.	1.62	1.53	0.29	1.58	1.37	0.41	1.565	1.45	0.17	1.56	1.42	0.21
7.	1.61	1.50	0.25	1.57	1.38	0.26	1.565	1.40	0.18	1.54	1.38	0.20
8.	1.64	1.56	0.25	1.57	1.37	0.37	1.565	1.44	0.21	1.56	1.41	0.20
9.	1.65	1.56	0.29	1.56	1.36	0.42	1.565	1.44	0.20	1.56	1.42	0.20
10.	1.60	1.50	0.33	1.57	1.36	0.43	1.565	1.43	0.22	1.55	1.41	0.23
11.	1.60	1.51	0.32	1.56	1.36	0.39	1.565	1.43	0.20	1.55	1.40	0.22
12.	1.61	1.52	0.31	1.55	1.37	0.40	1.565	1.44	0.21	1.55	1.41	0.20
13.	1.58	1.52	0.12	-	-	-	1.2	0.0	10.00	0.0	0.0	10.00

TABLE 7

Amounts of iron dissolved from iron-containing
impurities by cell electrolyte

Impurity	Per cent. of iron dissolved*	
	6 mths. storage at 21°C.	digestion
1. Goethite	0.08	0.09
2. Goethite, partially dehydrated	0.08	0.07
3. Hematite prepared from goethite	0.07	0.09
4. Ferric oxide, separated from Uley flotation tailings.	0.08	0.29
5. Pyrite (FeS_2)	13.10	11.80

* expressed as ferric oxide.

The volume used contained an amount of ammonium chloride 1400 per cent. in excess of the amount equivalent to the total calcium carbonate in the graphite sample

The mixes, contained in 125 ml. conical flasks, were immersed without agitation in a thermostat for times and temperatures shown in Table 8, and when withdrawn the contents were rapidly filtered and washed with cold distilled water. Calcium carbonate was determined on the washed residue using the Hutchinson and McLennan method, and the loss due to reaction was calculated by difference. Table 8 gives times and temperatures used in the tests, together with percentage of calcium carbonate remaining in residues, and percentage loss of carbonate.

(vi) Results of Impurity Tests.

The lives of test cells varied with nature of impurity, significant decreases occurring at all times and temperatures with azurite and pyrite and as storage time and temperature increased for carbonates.

Cells containing azurite behaved fairly normally during initial tests, but the zinc cans were almost completely corroded (metallic copper, originally contained in the azurite was deposited on the zinc can, which was then dissolved by galvanic action) after 6 months storage. This breakdown was expected and the cells were included only as a guide to the degree of failure possible.

In Test No. 7, cells showed a decrease in life shortly after preparation. This reduction continued with time and test results for cells stored at $30^{\circ}C$. indicated that the effect of pyrite increased with temperature.

Results for Tests No. 6, 10, 11 and 12 indicated that carbonates tend to shorten useful cell life, and that calcium carbonate has a greater effect than magnesium carbonate. The effect due to calcium carbonate was increased slightly by raising the storage temperature from 21 to $30^{\circ}C$. No "gassing" occurred at either temperature.

The results of tests in which cells were stored at $55^{\circ}C$. are not regarded as significant, because, although this test is used to determine suitability of cells for tropical use, it causes purely mechanical damage.

If the results contained in Table 6 are considered together with the cell test data discussed above, it appears that iron oxide impurities have little effect on cell performance because of their low solubilities in cell electrolyte. The pyrite test affords an outstanding example of the effect of iron in solution. The results suggest that solubilities obtained from digestion tests may be regarded as equilibrium concentrations which are not exceeded during long storage periods at lower temperatures. Thus digestion tests afford a rapid means of determining the probable effect of other iron-containing impurities (e.g. iron containing minerals in the gangue of a new graphite concentrate) on cell performance.

Tests, independent of those reported above have shown that

the following reaction proceeds to completion when calcium
carbonate is boiled with aqueous ammonium chloride.

$$2NH_4Cl + CaCO_3 = CaCl_2 + CO_2 + 2NH_3 + H_2O$$
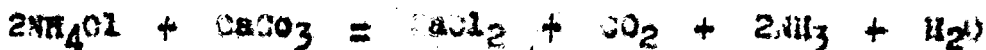
Data given in Table 8 indicate that equilibrium was
readily reached at lower temperatures. Increase in tempera-
ture to 70°C. resulted in a marked increase in reaction rate,
10 minutes at 70°C. corresponding to about 6 hours at 35°C.
No evolution of gases from mixes was observed at 25°C., but
it was quite evident at 70°C. The occurrence of a reaction
between calcite and cell electrolyte was confirmed by the
fact that filtrates, obtained by filtering the mixes, deposited
a fine crystalline precipitate which proved to be a carbonate.

(3)   Effect of Particle Size on Cell Performance.

The fineness usually specified for dry cell graphite in
Australia is 80 per cent. minus 200 mesh (B.S.S.). This
specification takes no account of possible effects resulting
from variation in distribution of material in the particle
size range below 76 microns. The high standard of perform-
ance of cells containing acetylene black suggested that cell
qualities might be improved by the use of finer graphites.
Hence a sample of finely divided South Australian graphite and
a number of imported materials including acetylene black were
tested in cells. The results obtained were compared with
each other and with those for a Ceylon graphite which the
Eveready Co. take as standard. Several different samples of
manganese dioxide were used to extend the range of test
conditions.

TABLE 8

Reaction between calcite and cell electrolyte.

Test No.	Duration of Digestion	Digestion Temperature	Per cent. calcium carbonate found in residue	Percentage loss* of Calcium Carbonate
1	2 hrs.	25°C.	4.39	25.0
2	6 hrs.	"	4.15	29.0
3	16 hrs.	"	3.93	32.8
4	24 hrs.	"	3.85	34.2
5	10 mins.	70°C.	4.10	30.0
6	30 mins.	"	3.79	35.2

* Percentage loss is the difference between calcite
content of the residue and of the original sample
expressed as a percentage of the latter.

Materials Used in Tests.

Graphites.

(a) South Australian concentrate (S.A.G.39). This material contained 92.5 per cent. carbon. The remaining 7.5 per cent. was mostly silica.

(b) "Dixon's Micronized" graphite. This was an imported sample manufactured by the Joseph Dixon Crucible Co., New Jersey, U.S.A. It is a processed natural graphite of extreme fineness and contains 2.4 per cent. ash.

(c) Acetylene Black. The sample used was imported and is sold under the name of "Shawinigan Black". An ash determination showed this material to contain less than 1 per cent. of impurities.

(d) Ceylon Graphite (G11). This was a finely ground concentrate with an ash content of 18.1 per cent.

Size analyses were done on these samples by screening and by the Andreasen pipette method (5). Their water-holding capacities and bulk densities were determined by Skewes (10) and surface areas by Hergt[4]. The purpose of measuring the last three properties was to provide alternative indices of fineness. Results of these analyses are presented in Tables 9 and 10.

TABLE 9

Distribution below 74 microns of graphite
in concentrates used to test the effect of
particle size on cell performance (micron $=\mu$).

Concentrate Sample	Percentage wt. of graphite in sample minus					
	74μ (200 mesh*)	43μ (325 mesh*)	30μ	20μ	10μ	5μ
Ceylon graphite (C11)	98.2	81.2	7.5	4.0	2.8	0.6
South Australian graphite (S.A.G. 39)	96.0	88.6	-	7.4	6.2	5.7
Dixons "Micronized" graphite	100	100	-	-	-	-
"Shawinigan Black" (acetylene black)	100	100	-	-	-	-

* Tyler Screens.

TABLE 10

Properties of concentrates used in testing
the effect of particle size of graphite on
cell performance.

Sample	Water-holding capacity (g. water/g. carbon)	Bulk Density (g./ml.after 100 taps)	Surface Area (sq.m./g.)
Ceylon graphite (C11)	34.4	0.71	5.8
South Australian graphite (SA939)	51.5	0.34	26.1
Dixons "Micronized" graphite	92.1	0.21	14.1
"Shawinigan Black" (acetylene black)	184	0.20	65.2

TESTS *

Skewes[11] found that useful cell life was critically determined by the ratio of carbon to manganese dioxide used in cell depolarizing mixtures and that the value of this ratio corresponding to maximum cell life varied for different samples of these ingredients. Hence, in order to compare the relative efficiencies of the graphites and acetylene black listed above, it was necessary to determine the maximum lives of cells containing them. This was done by preparing series of cells in which the ratio of carbon to manganese dioxide in the depolarizing mixtures was varied. The useful lives of these cells, determined after a week's storage at 21°C. by the 4 Ohm Continuous Test were plotted against values of the carbon to manganese dioxide ratio. Maximum cell lives and corresponding ratio values read from the graphs are given in Table II.

Results.

Table II contains life data for cells in which Gold Coast pyrolusite was used. Ratios of manganese dioxide to carbon corresponding to the maximum life figures listed are also shown.

Similar data are recorded in Table 12. These refer to experiments in which the relative efficiencies of mixtures of acetylene black and South Australian graphite with various manganese dioxides were determined.

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* The preparation and testing of cells was conducted by Mr. H. R. Skewes.

TABLE 11

Particle Size Tests — Maximum lives and corresponding depolariser ratios of cells in which graphite concentrates of varying fineness and acetylene black were tested.

Sample	Life to 1 volt (minutes)	Manganese dioxide/carbon ratio	Life to 0.75 volts (minutes)	Manganese dioxide/carbon ratio
Ceylon graphite (C11)	460	50/50	470	77/23
Dixons "Micronized" graphite	480	28/72	480	80/20
South Australian graphite (SAG 39)	540	47/53	540	87/13
"Shawinigan Black" (Acetylene black)	610	43/57	610	90/10

TABLE 12.

Particle Size Tests - Variations in performance of cells containing acetylene black (A.Black) and finely ground South Australian Graphite (S.A.G.), caused by use of different samples of manganese dioxide.

Materials used in Depolarizing Mixture		Life^z in minutes to 1 volt	Manganese Dioxide/ Carbon Ratio	Life^x in minutes to 0.75 volts	Manganese Dioxide/ Carbon Ratio
Manganese Dioxide	Carbon				
"Artificial A"	A.Black	410	50/50	420	75/25
	S.A.G.	430	50/50	440	60/40
"Artificial B"	A.Black	390	20/80	400	82/18
	S.A.G.	380	42/58	390	84/16
"Anode Mud"	A.Black	430	56/44	430	86/14
	S.A.G.	410	57/43	420	84/16
"Martins Well"	A.Black	350	50/50	350	87/13
	S.A.G.	290	39/61	300	75/25

z Cell life determined by 4 Ohm Continuous Test mean life of duplicate cells quoted.

Discussion of Results:-

Data contained in Table II indicate that South Australian graphite gave better results than all samples excepting acetylene black. Cells containing it had longer lives than those containing Ceylon graphite, the differences being 17.4 per cent. above to 1 volt and 14.9 per cent. above to 0.75 volt.

Exact correlation of cell life variations with fineness of graphite was not possible because of the anomalous results for cells containing Dixon's "Micronized" graphite. The obvious fineness of this material is confirmed by the figures for its water-holding capacity and bulk density shown in Table 9. However the conflicting value for surface area and the fact that it could not be dispersed by any of several methods which are used to prepare samples for sedimentation analysis suggest that some chemical process which may have been used in its preparation caused a conditioning of the surface. This might account for the poorer performance of cells containing it and its readiness to form a floc in water. However, in spite of the behaviour of this sample, there appears to be a direct relation between cell performance and bulk density. This property is regarded as being a more reliable index of fineness than the results of surface area and water-holding capacity measurements. Size analysis data obtained by the pipette method confirms the fact that better cell performance results from the use of finer graphite.

The results contained in Table II show that cells containing South Australian graphite performed nearly as well as

those containing acetylene black both with respect to life and quantities used in cells. The poorer performance of cells in which Martins Well manganese ore was used as a depolariser suggests that the particle size effect of graphite may be modified by the nature of the depolarising substance.

Since acetylene black is much finer[*] than South Australian graphite used in the above tests, the results suggest that, either little improvement in cell performance is to be gained by reducing particle size below some critical size or that full benefit of the extreme fineness of acetylene black was not obtained in these tests. Many workers investigating the suitability of carbon blacks for incorporation in rubber have observed that the platelets comprising acetylene black form aggregates which are not readily broken down by mechanical treatment or dispersing agents. This suggests that the similarity of performance of cells containing acetylene black and South Australian graphite was due to the average size of aggregates in the former being comparable with the mean size of particles in the latter. If acetylene black did retain its aggregate form in the depolarising mixtures of the test cells as

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[*] Measurements from electron micrographs taken by Mr. Warrant show that it consists of hexagonal platelets 500 $\overset{o}{A}$ in diameter and about 50 $\overset{o}{A}$ thick. The platelets are often linked together in chains but are mostly collected together in relatively large aggregates.

III. DISCUSSION.

Although tests conducted by the Eveready Co. showed that South Australian graphite was as suitable for use in dry cells as Ceylon graphite, their results were too approximate to show clearly the effect of concentrate purity on cell performance. However, the following considerations indicate that high purity is desirable.   Thus, if a standard formula ignoring concentrate grade is used in preparing cell depolarizing mixtures, it is evident that variations in purity will alter the graphite to manganese dioxide ratio which is known to be a critical factor in determining cell life.   Alternatively, if the amounts of concentrates used in mixtures are corrected to contain a constant weight of graphite, then the total weight of depolarizer which can be added to a cell will decrease as concentrate purity decreases.   Thus, the impurities behave as diluents and reduce the life of a cell by limiting the quantity of active ingredients in it.

Impurity tests showed that, of all gangue minerals which have been found in South Australian graphite ores, only calcium and magnesium carbonates had detrimental effects on cell performance.   However, since reductions of cell life caused by these two impurities were small, the presence of less than 5 per cent. of either in concentrates is not considered to decrease the quality of the latter for use in dry cells.   Investigation of the reaction between calcite and cell electrolyte showed that although this proceeded more rapidly as temperature was raised, evolution of gas was just evident at a temperature of 70°C.

Presumably the high solubility of carbon dioxide in cell electrolyte was responsible for equilibrium being readily attained at lower temperatures. This suggests that "gassing" in dry cells occurs when the solubility of carbon dioxide in cell electrolyte is exceeded. The use of concentrates containing a high percentage of carbonates and storage of cells at relatively high temperatures (over $30^{\circ}C$.) both favour this condition and have been observed to cause "gassing".

Since freshly precipitated goethite, which is an extremely chemically active form of ferric oxide, was found to have no effect on cell performance, it is concluded that local battery graphite specifications refer to metallic iron. The grinding of concentrates in steel ball mills is common in industry, and would account for the presence of this impurity.

The improvement in cell performance which resulted from a decrease in the mean particle size of graphite below 74 microns, shows the advantage of using battery graphites finer than those conforming with local specifications.

During the recent war, the demand for cells containing acetylene black was high because these were regarded as the best available. Since the performance of cells containing finely ground South Australian graphite approached that of cells containing acetylene black, it can be seen that these Australian cells were of high quality.

IV.   CONCLUSION.

The results of investigations which have been described above, lead to the following conclusions.

1.   The useful lives of cells containing South Australian graphite were at least equal to those of cells containing Ceylon graphite.   This was true for both fresh cells and others stored for 6 months at $21^{\circ}C$.

2.   Impurities introduced into cells by South Australian concentrates acted mainly as inert diluents.

3.   Ferric oxide in an extremely active form chemically (freshly precipitated goethite) had no appreciable effect on cell performance.   Pyrite (FeS_2) caused considerable decrease in cell life when cells were stored at average temperatures. This effect increased with temperature.   The solubility of ferric oxide in cell electrolyte is small while that of pyrite is relatively much greater.

4.   Both calcium and magnesium carbonates reduced cell life slightly.   The former caused a greater decrease than the latter.   The effects of both carbonates increased with storage time and temperature.

5.   Calcite was found to react with cell electrolyte.   This reaction proceeded to completion when the mixture was boiled, but equilibrium was reached at lower temperatures, owing to the appreciable solubility of carbon dioxide.   The rate of this reaction increased rapidly with rise in temperature and evolution of gas was evident at $70^{\circ}C$.

6.   Cell performance improved as the mean particle size of graphite below 76 microns was decreased.   This was true for both South Australian and imported concentrates.

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PART IV.

STUDIES ON THE CRYSTAL STRUCTURE

and

LAMELLAR COMPOUNDS

of

SOUTH AUSTRALIAN GRAPHITE.

I N D E X

SUMMARY

The crystalline nature of South Australian graphite was examined by preparing lamellar compounds from this material and comparing the yields and properties of these with similar data quoted for compounds prepared from Ceylon graphite. It was concluded, from the results of studies on graphite oxide and graphite-ferric chloride compounds, that South Australian graphite contains approximately the same total amount of graphitic structures as does Ceylon graphite. The fact, too, that the local graphite intumesces considerably when moistened with fuming nitric acid and then heated, indicates a similarity between the macro-lamellar structures of the two graphites.

Graphite oxide and graphite oxide black, obtained from the oxide by thermal decomposition, were examined under the electron microscope. Electron micrographs of both materials confirmed the lamellar structure of South Australian graphite and also showed the remarkably finely-divided state of both these substances.

Samples of South Australian graphite were partially converted to graphite oxide by anodic oxidation in a nitric acid electrolyte.

It was shown that anhydrous aluminium and beryllium chlorides do not form lamellar compounds with South Australian graphite, and also that, because of this, the

separation of anhydrous ferric chloride from mixtures
containing these chlorides is possible by heating the
mixtures with graphite.   A ready reaction between
anhydrous aluminium chloride and ferric oxide was found
to occur above 192°C. and was used in developing methods
for the separation of aluminium and beryllium, and the
separation of ferric oxide from ferruginous bauxite.
Ferric chloride was produced in both these separations and
was removed by heating reaction products with graphite.

I. INTRODUCTION

Although the crystal structure of graphite has been the subject of many studies since the beginning of this century, it has not yet been fully elucidated. Bernal[3], after examining a wide variety of graphites by the X-ray diffraction method, proposed the first acceptable structure in 1924. According to him, the graphite crystal consists of flat layer planes of carbon atoms linked together in a honeycomb-like network of hexagonal rings (see Fig. 1, Part II). These layer planes are arranged parallel and equidistant to each other so that the atoms in alternate planes are normally above one another and half the atoms in adjacent planes are normally above half the carbon atoms in the plane below, while the other half lie normally above the centres of the hexagon rings in the layer beneath. This structure was criticised by Laidler and Taylor[13] in 1940, because it does not account for some faint lines which they and also Finch and Wilman[8] observed in the X-ray powder photographs of natural and artificial graphites. Lipson and Stokes[17] attempted to explain this discrepancy by suggesting that most graphites have a composite structure consisting of about 80 per cent. of the Bernal structure, 6 per cent. of a disordered structure, and 14 per cent. of a structure which Debye and Scherrer[7] originally suggested as being the main crystal form of graphite. Then the results obtained by Laidler and Taylor[13] for artificial

graphites and graphites from Ceylon, Bavaria, Korea, and Travancore were reconsidered in the light of this explanation, it was found that these graphites all contained a small percentage of the Debye-Scherrer structure. Although it is not stated whether these graphites were found to contain any disordered structures, the results of investigations on the thermal recrystallisation of carbon, reported by Riley[21], suggest that they probably do. Riley notes that complete graphitisation of carbon obtained by pyrolysis of carbonaceous materials can be effected only by heating at high temperatures for long periods. He believes that the slowness of this process is due to the time required for carbon atoms to form hexagon ring planes and the time necessary for these planes to orientate themselves from random positions to a turbostratic arrangement (in which they are parallel, but otherwise stacked in a random fashion) and then to a state such as in the Bernal structure. Accepting the general view that natural graphites were formed by thermal recrystallisation, it is evident that they would contain intermediate structures if the process had been stopped before completion.

Reviewing the information given above, it is clear that the composite structure of graphite permits the possibility of structural variation in samples of this material obtained from various natural sources. It is also evident that, because of probable differences in the conditions and completeness of their formation, natural

graphites may contain varying proportions of intermediate
nongraphitic structures such as the turbostratic and three
dimensional cross linked forms suggested by Riley[21].
This view receives support from the fact, discovered by
Acheson[1], that both the rate and completeness of thermal
recrystallisation of carbon to graphite are influenced
considerably by the presence and nature of mineral impurities
in the original carbon.

It is evident that X-ray methods would be the most
convenient for detecting and measuring variations in the
crystal structure of graphites.   Inability to interpret
fully the results obtained by these methods, however,
indicates the desirability of obtaining confirmatory data
by other means.   An alternative method of examination is
suggested by the fact that graphite forms lamellar compounds
in which the atoms and molecules of substances intercalated
in the graphite crystal are arranged in an orderly manner.
Thus, because of the structural regularity of these compounds,
it seems likely that imperfections or irregularities in the
graphite crystal structure might influence not only the
yield of a lamellar compound from a given graphite, but also
its rate of formation.   The study of these aspects of
lamellar compound formation, therefore, should offer a means
of comparing graphites.   Ceylon graphite which has been
examined in detail by X-ray and chemical methods provides
a good standard for the purpose of this comparison.

Although the work of Laidler and Tayler[13] indicates that the above method would be of little use in determining the amount of Debye-Scherrer structure present, owing to the fact that this structure is converted to the Bernal form during lamellar compound formation, the results of Selvig and Ratliff[26], Riley[21] and others suggest that it might be useful in determining the total amounts of graphitic carbon present in samples.   This method of examination has an advantage over the X-ray diffraction method in that it differentiates between graphites which do or do not intumesce when they are treated with strong oxidising agents such as fuming nitric acid and then heated.   Riley[22] has collected evidence to show that the extent to which this swelling occurs indicates the degree of crystal development of a graphite, intumescence being most pronounced with graphites containing well developed crystals.

The first lamellar compound of carbon was discovered in 1841 by Schafhäutl[25] who found that graphite could be converted into a blue irridescent solid by boiling it with concentrated sulphuric acid containing a little concentrated nitric acid.   Brodie[5] confirmed this reaction in 1859 and discovered also that graphite could be oxidised to a yellow solid by treating it with a mixture of potassium chlorate and fuming nitric acid.   Since these early discoveries, it has been found that graphite forms compounds when heated with anhydrous ferric chloride,

potassium, rubidium, caesium, and fluorine.   Graphite
nitrate, perchlorate, biselenate, phosphate, pyrophosphate,
and arsenate have also been prepared.   It has been shown
by X-ray and chemical methods that these compounds, like
the graphite oxide discovered by Brodie, are formed by the
intercalation of atoms and molecules of the above substances
in the interlamellar spaces of the graphite crystal.   The
preparation, properties, and structure of the lamellar com-
pounds of carbon have been described in detail by Riley[22].

The investigation described below was prompted
by the fact that Mellor[18] describes South Australian
graphite as a graphitite, that is a graphite which does not
swell when moistened with fuming nitric acid and heated
over a naked flame.   Since this description suggested that
the local graphite might differ either structurally or in
other ways from natural graphites found elsewhere, it was
decided to attempt the detection of any such differences by
studying the readiness of formation, yields, and properties
of the lamellar compounds of South Australian graphite.
These data are to be correlated with the results of X-ray
diffraction analyses of the same graphite when these are
obtained.   The fact that little effort appears to have
been made by other workers to find uses for the lamellar
compounds of carbon also encouraged the study of these un-
usual complexes.   Since the work on this project is still
in progress, the following paper is an account of incomplete
studies on graphite oxide and graphite-ferric chloride
compounds prepared from South Australian graphite.

II.   EXPERIMENTAL

Outline of Experimental Work.

As stated above, studies of the lamellar compounds of
South Australian graphite were undertaken in the hope that
the data obtained might, when compared with similar data
for other natural graphites, reveal any differences between
them.   The information sought for this comparison was,
firstly the yields and secondly the properties of lamellar
compounds prepared from South Australian graphite.   Since
it appeared from Riley's paper[22] that graphite oxide and
the graphite-ferric chloride compounds have been studied
in more detail than the other lamellar compounds of carbon,
it was decided to prepare and examine these first.   Before
doing this, however, the claim[18] that South Australian
graphite does not intumesce when it was moistened with
fuming nitric acid then heated, was investigated.

Graphite oxide was prepared from pure South
Australian graphite by Staudenmaier's method[28] in which
graphite is oxidised with a mixture containing concentrated
sulphuric and nitric acids and potassium chlorate.
Samples of oxide were also prepared by electrolytic oxidation
of graphite anodes according to the method described by
Brown and Storey[6].   The properties of oxides prepared
by each method were examined.   The chemically prepared
oxide and an extremely finely divided form of carbon
(graphite oxide black) obtained from it by thermal decomposi-
tion were both examined under the electron microscope.

Graphite-ferric chloride compounds were prepared
by heating pure South Australian graphite with an excess of
anhydrous ferric chloride in sealed tubes at various tempera-
tures. The chemical properties of these compounds and the
amounts of ferric chloride which they contained were
determined.

Attempts to find uses for the lamellar compounds
of carbon have been confined , so far, to the graphite-ferric
chloride compound. Mixtures containing the anhydrous
chlorides of iron and aluminium were heated with graphite
with the object of separating the ferric chloride as a
lamellar compound. Discovery, during the course of the
work, of the ready reaction which occurs when ferric oxide
is heated with aluminium chloride, presented further
opportunities for a similar use of graphite. The removal
of ferric oxide from ferruginous bauxite was attempted by
heating the latter with anhydrous aluminium chloride and
graphite. This treatment was designed to decompose ferric
oxide by reaction with aluminium chloride and to separate
the ferric chloride thus formed by combining it with graphite.
A similar method of removing free ferric chloride formed
during reaction was employed in experiments in which the
separation of beryllium from aluminium was attempted. In
these tests a synthetic mixture of the anhydrous chlorides
of aluminium and beryllium were heated in sealed tubes with
pure ferric oxide and graphite. Separation of the three
metals from each other depended on the fact that ferric

oxide reacted more rapidly with aluminium chloride than with beryllium chloride, and on the ability of graphite to combine with the ferric chloride produced during this reaction.   After heating, therefore, the sealed tubes were supposed to contain unchanged beryllium chloride, alumina obtained from aluminium chloride by reaction with ferric oxide, and a graphite-ferric chloride compound formed by combination of graphite with the ferric chloride produced by the above reaction.   Tube contents were extracted with an organic solvent to dissolve the beryllium chloride and separate it from alumina and ferric chloride which is insoluble when combined with graphite as a lamellar compound.

The same graphite was used in all the above tests. It was obtained from the Uley mine, Eyre Peninsula, South Australia. (See p.14 Part I).

(1)   Intumescence of South Australian Graphite.

The intumescence which some graphites may be made to exhibit has been explained by Riley[22] in the following way.   When graphite is treated with certain reagents, part or all of the latter may be intercalated in spaces between the carbon layer-planes of the former.   On heating, those intercalated substances are expelled.   If, however, occluded gases or gaseous products generated by heating cannot escape freely from the interlamellar spaces, they force the lamellae apart into the shape of lenticular pouches and cause the graphite crystals to expand in the

direction of their c axes.   Riley argues that, because
the neighboring lamellae in well formed graphite crystals
are equally developed, their edges may be superimposed.
This condition, he says, results in stronger bonding of
lamellae at the periphery and therefore accounts for the
restricted escape of gases and the formation of the lenticular
pouches mentioned above.   According to this theory, non-
intumescing graphites have poorly developed macro-lamellar
structures in which neighboring lamellae may be of different
sizes and therefore not congruent.   Thus, the unsaturated
carbon atoms in the edges of these lamellae would not all
be in positions where their free valency forces could form
a strong bond between them.   This lack of strong bonding
at the edges of lamellae, it is claimed, would permit the
free escape of gases from the interlamellar spaces of
graphite crystals and the latter therefore would not swell.

The following tests were conducted to see if
South Australian graphite could be made to intumesce.   The
graphite used in these tests contained 1.2 per cent. ash
and was in the form of flakes averaging 1 mm. across.
Several small samples of this material (approx. 0.2 g.) were
placed in silica crucibles and just covered with fuming
nitric acid.   After standing thus for 15 minutes, the
samples were washed with cold water by decantation, then
dried carefully over a naked flame.   On stronger heating,
the dried product intumesced very actively and to a consider-
able extent.   Swelling was, as far as could be seen,

entirely in the direction of the c axis, that is, normal to the flat surface of the graphite flake. The increase in volume was estimated to be at least 150 times the original volume of the sample.

(2)   graphite Oxide.

This compound was first prepared by Brodie[5] in 1859 by oxidising Ceylon graphite with a mixture of solid potassium chlorate and fuming nitric acid. Five or more such treatments, each lasting 4 to 6 days, were necessary to effect complete oxidation. Staudenmaier[28] shortened this procedure by first oxidising the graphite once with Brodie's mixture and then treating the product with an acid solution of potassium permangnate. Both methods yield a yellow solid in the form of flakes which have been shown to be pseudomorphs of the original graphite flakes. Many attempts have been made to determine the structure of this compound and to establish a uniform stoichiometric composition for it, but these have met with little success in either case. Riley[22] notes that Thiele and Hofmann have both devoted considerable time to these problems and have confirmed that the above oxidation treatments bring about the intercalation of oxygen and water in the graphite crystal and do not disrupt the hexagon layer planes of the latter but merely increase the distance between them. He also notes that Hofmann and co-workers have obtained evidence from X-ray and chemical

analyses to show that the intercalated oxygen is combined
with carbon atoms in the hexagon layer planes by means of
ethylene oxide type linkages.   Ruess[23] examined graphite
oxide in the light of conclusions reached by Thiele and
Hofmann and found much evidence to support the view that it
is an oxide of definite composition, which may be hydrated
in varying degrees to hydroxide.   This picture agrees with
the suggestion offered by Hofmann that the intercalated
oxygen atoms in graphite oxide behave as hydrophilic centres
which may absorb water to such an extent that the 3 dimen-
sional structure is dispersed as 2 dimensional macro-
molecules.   Although the structure of graphite oxide is
still uncertain, the evidence available so far does indicate
that graphite oxide, like the other lamellar compounds of
carbon, is an orderly structure and that it is formed by the
intercalation of oxygen atoms into regularly arranged
positions in the interlamellar spaces of the graphite
crystal.

Many interesting properties of graphite oxide,
revealed by numerous investigators, have been described in
detail by Riley[22].

The preparation of graphite oxide from Uley
graphite by Staudenmaier's[28] chemical method and by
Brown and Storey's[6] electrolytic method, and the properties
of oxides obtained by each method, are described below.

(a) Graphite oxide - Prepared chemically.

A 30 g. sample of minus 200 mesh graphite (1.2 per cent ash) was oxidised by stirring it with a mixture which contained 1 l. of concentrated sulphuric acid 500 ml. of nitric acid (S.G. 1.4) and to which 450 g. of potassium chlorate was slowly added. Addition of the latter reagent took 6 to 8 hours because time had to be allowed for the evolution of gas from one addition to cease before the next portion of reagent was added. The mixture was kept below 50° C. and was stirred for a total time of 24 hrs. At the end of this period, solid matter was allowed to settle and clear supernatant liquid was decanted. The residue was washed several times with cold water by decantation, then twice on a vacuum filter. The washed filter cake was dispersed in a solution made up of 2 l. of saturated aqueous potassium permanganate and 500 ml. of 10 per cent. sulphuric acid, This second oxidation was conducted at 70-80°C. with continuous stirring and was considered to be complete when a water washed sample of solid material became light yellow on treatment with hydrogen peroxide. The potassium permanganate treatment lasted 7-8 hours. The product was washed with water by decantation, then freed of remaining potassium permanganate by treating it with an excess of hydrogen peroxide, and finally washed with dilute nitric acid and water. The final product was washed with absolute alcohol then ether and dried at 90°C. for 1 hour. The weight of dried oxide was 49.5 g.

Graphite oxide obtained by the above method was a pale lemon colour before oven drying which changed it to a light buff colour. The colour before drying was found to vary with the degree of hydration which it was observed could be very large. Dispersion also caused marked variations in colour. Continued washing with water caused the oxide to swell and disperse until it assumed the appearance of a light orange coloured jelly. Alcohol and acetone effected this change even more readily than water. These dispersions when dried out in an oven at $90^{\circ}C$. shrank and formed a material which resembled cardboard in appearance and texture and could not be ground. Products of this type were obtained in the first attempts to prepare graphite oxide, and it was not until the importance of thorough washing with alcohol and ether was realised that the oxide was prepared in the powder form. Samples of the dried oxide were rapidly peptised to a viscous caramel brown sol by dilute ammonia. Graphite mirrors were made by dipping glass slides into this sol and baking them at approximately $130^{\circ}C$. for about 2 hours. The thickness of the mirror film could be increased by repeating the above process.

It was found that graphite oxide readily oxidised stannous chloride in acid solution. Its oxidising action on ferrous sulphate in 2N sulphuric acid, however, was not so ready, and no reaction occurred with oxalic acid dissolved in aqueous sulphuric acid. The "available

oxygen" content of dried graphite oxide was determined by boiling a weighed sample of the latter with a 20 ml. aliquot of an $\frac{N}{2}$ solution of ferrous sulphate in 6N sulphuric acid for one hour. The ferrous sulphate remaining after this time was titrated with $\frac{N}{10}$ potassium permanganate; the "Available oxygen" figure was calculated from the titre. Results obtained in this way agreed to within 1 per cent. and gave a figure of 17 per cent.[*] for graphite oxide which had been washed with alcohol and ether and dried at 90°C. for 1 hour. It was obvious, however, that this figure did not represent the total oxygen content of the oxide because dried residues from the above determination could be further decomposed by heating to above 200°C.

The reactions noted above illustrate both the chemical stability and the oxidising properties of graphite oxide. Samples of this material which have been stored for 3 months in clear glass bottles have not changed in appearance except that slight darkening has occurred in the region next to the glass. Hence it appears that the oxide is slowly decomposed by light.

Heating the oxide to approximately 200°C. caused it to decompose in a spectacular manner. The production of a voluminous material, closely resembling acetylene black, was accompanied by deflagration and scintillations. This

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[*] Brown and Storey[6] quote 17-18% for an oxide prepared from Ceylon graphite.

material was found to contain 0.15 per cent of "available
oxygen", and also to be readily wetted and dispersed by
water.   Its extreme fineness has been noted in Part II,
and illustrated with size analysis data in Table 7 of that
section.

Both the oxide and the black prepared from it by
thermal decomposition were examined under the electron
microscope, Fig. 1, which is an electron micrograph of the
oxide after dispersion with dilute aqueous ammonia and
shadow casting with gold, shows the flake-like structure of
this material and the smallness of its dispersed particles.
Measurements taken from Fig. 1 indicate that the smallest
of these particles was 25Å thick by 250-500Å across.   The
folding of lamellae also shown in this figure suggests that
intercalation of foreign atoms in the original graphite
crystals affected the rigidity of the carbon layer-planes
of the latter in some way, perhaps by weakening the inter-
lamellar forces, or perhaps, as suggested by Riley[22],
by causing some change in the spatial distribution of
carbon valencies.   It is hoped that this suggestion may be
confirmed by dispersing the original graphite as flakes,
comparable in size with the oxide particles, and observing
whether they also fold.   The electron micrograph of graphite
oxide black (Fig. 2) shows that this material consists of
very thin continuous sheets of carbon.   The maximum thick-
ness of these sheets was calculated from the width of fold
shadows, which were assumed to be wider than the sheets in

FIG. 1.   Electron-micrograph of Graphite Oxide
(prepared chemically) after dispersion with dilute
aqueous ammonia and shadow-casting with gold.
(Magnification, 50,000 X).

FIG. 2.   Electron-micrograph of Graphite Oxide Black
which was prepared by heating yellow Graphite Oxide
(Magnification, 75,000 X).

which the folds occur, to be approximately 50Å. The
transparency of the sheets, however, suggests that they
are probably much thinner than this. The structures
shown in both electron micrographs confirm the lamellar
structure of South Australian graphite.

(b) Graphite oxide - Prepared electrolytically.

Graphite anodes were prepared from the same graphite
as used in (a) by impregnating this material with paraffin
wax and then pressing it round a dry cell carbon rod. A
pressure of 400 lb./ sq. in. was employed. The bobbin
press used in manufacturing dry cells for testing purposes
was found satisfactory for the above operation. Anodes were
oxidised electrolytically in nitric acid (3 acid, S.G. 1.4:
1 water) to which potassium chlorate was added in one experi-
ment and potassium dichromate in another. Electrolyses were
conducted at room temperature ($<25^\circ$C.) using a current
density of 1 amp./sq. decimetre. The voltage across the
cell was 1.3-1.5 volts and exceeded the polarization voltage
by 0.4-0.6 volts. Dry cell carbons were used as cathodes.
The electrolyte was agitated with a gentle stream of com-
pressed air.

During electrolysis the surface of the anode
swelled, crumbled away and collected as a sludge in the
bottom of the electrolyte container. An anode weighing
17 g. was $\frac{3}{4}$ consumed in 3-4 hours. The sludge which had
collected after this time was washed thoroughly with hot
water and dried for 1 hour at 90°C. It was then analysed

for "available oxygen" by the method used for the chemically prepared oxide.

Oxides obtained by the above method were black, but less lustrous than the original graphite from which they were prepared. They swelled rapidly to 2-3 times the original volume when heated, but did not decompose with the violence shown by the yellow oxide. The oxide prepared by using an electrolyte containing 15 g. potassium chlorate in 1 l. of 3:1 nitric acid, contained 0.5 per cent. "available oxygen". That obtained by electrolysis in a 3:1 nitric acid solution in which potassium dichromate was dissolved in the proportion of 10 g. per litre, contained 0.54 per cent. "available oxygen".

Attempts were made to increase the "available oxygen" figures quoted above by reoxidation. Anodes were prepared from electrolytic oxides by the same method used for the original graphite and were oxidised under the same conditions as used for the latter. By repeating this procedure twice, that is three oxidation treatments in all, the "available oxygen" content was raised to 1.5 per cent. A modification of the above procedure gave better results. In this, the oxide from one electrolysis was expanded by heating for 10 minutes, at 600°C. and mixed with 43 per cent. of its weight of original graphite. (The addition of raw graphite was necessary because of the lower electrical conductivity of the expanded graphite.) Anodes prepared from this mixture were oxidised electrolytically under the

same conditions as described above. The oxide obtained
by repeating this procedure three times, contained 2.4 per
cent. "available oxygen" and expanded to 7 times its
original volume when heated to 600°C. for 10 minutes.
Comparison of these results with those from the experiment
above in which products were not expanded before reoxidation,
suggests that penetration of oxygen into the graphite crystal
was facilitated by the separation of lamellae which occurred
when products were expanded.

The low "available oxygen" content of electrolyti-
cally prepared graphite oxide is thought to be due partly
to its low electrical conductivity, which became evident in
reoxidation experiments. Assuming that complete oxidation
of graphite particles depends on continuation of electrode
reactions on their surfaces, it is evident that this will
not occur when other particles of higher conductivity are
accessible to the electrolyte. Thus, if the anode is
porous or if only little swelling of graphite flakes
on oxidation is necessary to dislodge them from its surface,
oxides low in oxygen will be formed because fresh unattacked
particles are continually becoming available for partial
oxidation. These possibilities were guarded against in the
above experiments by using high anode moulding pressures and
by ensuring that anodes were saturated with paraffin wax.
The value of these precautions was confirmed by the fact
that anodes pressed at 400 lb/sq. in. corroded more evenly
than those pressed at 250 lb/sq. in. It was also found

that corrosion was more effectively confined to the surfaces
of anodes by saturating them with wax or by wetting them
with carbon tetrachloride. Agitation of the electrolyte
during electrolysis was found to influence the quality of
the oxide obtained. It had to be as gentle as possible in
order to avoid mechanical removal of oxide from the anode
before the former had reached a stage where swelling would
cause it to fall off. The "available oxygen" content of an
oxide removed by strong agitation was 0.9 per cent. whereas
an oxide which had been allowed to fall from an identical
anode through swelling alone, contained 2.4 per cent.

Although the electrolytic method of oxidising
graphite was not as effective as the chemical method, it
is regarded as being worthy of further investigation,
because, since Brown and Storey[6] have shown that the
nitric acid electrolyte can be continuously reoxidised by
atmospheric oxygen in a spray tower, the process amounts to
the electrolytic fixation of atmospheric oxygen in graphite.

(3)   <u>Graphite - Ferric Chloride Compounds.</u>

The following introductory notes are taken from
Riley's detailed summary[22] of results of investigations
into the nature of graphite-ferric chloride compounds.

When graphite and anhydrous ferric chloride are
heated together in a sealed tube at temperatures between
180 and 400°C. they combine. Only free ferric chloride
which remains if an excess of this substance was used, may

be recovered by solvent extraction.   Combination is
accompanied by expansion of the graphite in direction of
the C axis and the results of X-ray analyses show that this
is caused by intercalation of ferric chloride in the graphite
crystal where its molecules are arranged in an orderly
manner in the interlamellar spaces of the latter.

When mixtures of graphite with an excess of ferric
chloride are heated at temperatures below 309°C., the solvent-
extracted product contains 56-57 per cent. ferric chloride.
The compound prepared at temperatures between 309 and 409°C.
contains 31-37 per cent. ferric chloride after solvent ex-
traction.   Both compounds are very stable chemically, but
may be decomposed by heating.   Decomposition occurs in a
stepwise manner which indicates that the ferric chloride is
chemically combined with the graphite and not merely absorbed
by it.   If the compound formed at temperatures below 309°C.
is heated above this temperature, but below 409°C., ferric
chloride vapour is evolved and the ferric chloride content
falls to 31 to 37 per cent.   Heating between 409 and 509°C.
yields a product containing 5 per cent. ferric chloride
which is completely expelled by heating at temperatures
above 500°C.

In the work described below, compounds were pre-
pared at 230 and 350°C. and their stability to various re-
agents was examined.

(a) **Graphite-ferric chloride compound prepared at 230°C.**

This compound was prepared by mixing a sample of minus 200 mesh graphite containing 1.2% ash with 3 times its own weight of anhydrous ferric chloride and heating the mixture in a sealed tube at 230°C. for 40 hours. A sample of flake graphite (-25 + 100 mesh) of 99.5 per cent. purity was treated similarly. Free ferric chloride was removed from both products by boiling these with 6N hydrochloric acid for 6 hours. Several lots of acid were used in each case. Both residues were finally washed with a large volume of hot water until wash water was free of chloride ions, and then dried at 110°C. The dried products were analysed as follows. Weighed samples were heated at 600°C. for 20 mins. to remove ferric chloride by volatilisation. The residues were digested with 1:1 hydrochloric acid containing stannous chloride, to remove ferric oxide which forms when part of the ferric chloride evolved during heating in the first step is oxidised by atmospheric oxygen. The final residues were washed with hot dilute hydrochloric acid, then hot water, and were then dried at 110°C. and weighed. The percentage losses in weight were taken as the ferric chloride contents of the original samples. By this method of analysis, the compound produced from flake graphite was found to contain 42.7 per cent. ferric chloride and that prepared from the fine graphite, 57.4 per cent. Attempts to remove ferric chloride from the latter compound by digesting it with dilute and concentrated acids were unsuccessful except in

the case of concentrated sulphuric acid which caused swell-
ing and liberation of hydrogen chloride.   The ferric
chloride content was reduced to 9.6 per cent. by the action
of this reagent.   Hot concentrated nitric acid caused slow
decomposition.   Boiling aqueous solutions of ammonium and
sodium hydroxides and stannous chloride dissolved in 6N
hydrochloric acid had no appreciable effect on the composi-
tion of the compound even after 12 hours boiling.   It was
hoped that the action of some of the reagents mentioned
above might have caused defoliation of the compound and thus
have yielded a finer graphite than that originally used in
preparing the compound.   Defoliation, however, was effected
only by heating above 500°C. and size analyses performed
on the product so obtained showed that little reduction in
particle size had been achieved.   Defoliation was accompanied
by an increase in volume of approximately 150 per cent.

(b) <u>Graphite-ferric chloride compound prepared at 350°C.</u>

This compound was prepared from the same fine
graphite and by the same method as used in (a) above.
Removal of free ferric chloride from the product by digestion
with 6N hydrochloric acid was slower than in the case of the
230°C. compound and it was found necessary to boil for
several days with about 20 changes of acid.   Analysis of
the acid extracted product showed that it contained 35 per
cent. ferric chloride.   This compound behaved similarly to
that prepared at 230°C. towards reagents used in attempts
to decompose the latter.   It also decomposed when heated

above 50°C. Like the 230°C. compound, it was indistinguishable from pure graphite.

(4) **Applications of the Reaction between Graphite and Ferric Chloride.**

The stability and high ferric chloride contents of the compounds described above suggested that the reaction between ferric chloride and graphite might be used to separate ferric chloride from other chlorides which do not form lamellar compounds with carbon. The account of investigations given below describes how the above reaction was used to separate ferric chloride from anhydrous aluminium chloride and also from anhydrous beryllium chloride. This account also describes the separation of aluminium and beryllium and the removal of ferric oxide from ferruginous bauxite. Both of these processes were based on the ready reaction between aluminium chloride and ferric oxide and the ability of graphite to combine with the ferric chloride formed by this reaction.

(a) **Separation of the anhydrous chlorides of iron and aluminium.**

(i) Sealed tube experiments.

The claim[22] that aluminium chloride does not form a lamellar compound with graphite was confirmed experimentally as follows. A 5 g. sample of flake graphite (0.5 per cent. ash) was heated with 0.331 g. of anhydrous aluminium chloride in a sealed tube for 60

hours at 230°C.   After heating, the tube contents were
digested with 6N hydrochloric acid for 2 hours.
Analysis of the filtrate from this digest showed that
98 per cent. of the original weight of aluminium
chloride had been recovered.

The test described above was repeated using 1.013 g.
of anhydrous ferric chloride in place of aluminium
chloride.   Analysis revealed that 84 per cent. of the
former had combined with the graphite.   The test was
repeated a third time, using 5 g. of graphite, 0.536 g.
of anhydrous aluminium chloride and 2.702 g. of
anhydrous ferric chloride.   Acid digestion of tube
contents after heating, recovered 96 per cent. of the
original weight of aluminium chloride taken and 4.3 per
cent. of the original weight of ferric chloride added.
Thus the ratio of ferric chloride to aluminium chloride
was reduced from 5.05:1 in the original mixture to
0.22:1 in the acid extract.

The results of the tests in which ferric chloride
was used, suggest that the aluminium chloride present
in the second of these tests aided the diffusion of
ferric chloride into the graphite.

(ii)   Packed tube experiment.

In these experiments a mixture of iron and aluminium
chlorides, obtained by chlorinating a ferruginous bauxite
was passed through a tube packed with graphite.   The
temperature of the packed tube was kept at a temperature

which ensured that the chlorides would remain in the vapour state.

A sample of finely ground bauxite containing 40 per cent. ferric oxide and 30 per cent. alumina was bonded with charcoal and chlorinated at 600-700°C. Part of the tube in which this was performed was packed with 50 g. of 98.8 per cent. graphite (-100 + 200 mesh.) and maintained at 290-300°C. Chlorination products and chlorine passed through this packing into a cooled vessel where volatile chlorides were condensed. The chlorine rate was approximately 120 mls. per minute. Analysis of the chloride mixture which had collected in the condensation vessel after a 3 hour run showed that the ratio of ferric oxide to aluminium oxide had been reduced from 1.35:1 in the bauxite to 0.15:1 in the product of this experiment. The graphite packing was analysed to ensure that the above separation was not due to purely physical condensation of the ferric chloride. Sections of the packing were boiled with 6N hydrochloric acid for 2 hours and were then analysed for combined ferric chloride. This was found to range from 8 to 14 per cent. in various sections. These results confirm theclaim that separation of ferric chloride from aluminium chloride was achieved by combining the former with graphite.

(b) **Separation of ferric chloride formed during the**
reaction of aluminium chloride with ferric oxide.

The possibility that the anhydrous chlorides of
iron and aluminium used in the sealed tube experiments des-
cribed above may have been partially hydrolysed during fill-
ing, directed attention not only to the technique of charging
tubes, but also to reactions likely to occur between oxides
and chlorides of iron and aluminium. Indications of the
feasibility of such reactions were obtained by calculating
equilibrium constants from the thermodynamic data in Table 4
(Appendix). These calculations showed that the reaction

$$Fe_2O_3 + Al_2Cl_{6(g)} = 2FeCl_3 + Al_2O_3$$

had a large equilibrium constant, viz. 5×10^{40} at $192^{o}C$.
($465^{o}K$), and was therefore favourable. Since it was thought
that this reaction might have useful applications, the
possibility of removing the free ferric chloride by combining
it with graphite was considered worthy of examination.
This possibility was investigated experimentally by heating
mixtures of anhydrous aluminium chloride, ferric oxide, and
graphite in sealed glass tubes. These tests which were
conducted at 230 and 350 C. are described below.

In the test conducted at $230^{o}C$., a mixture contain-
ing 1.040 g. aluminium chloride, 0.625 g. ferric oxide
(equivalent to the weight of aluminium chloride taken), and
5 g. flake graphite (0.5 per cent. ash) was heated for 60
hours. After heating, the tube contents were digested for
half an hour with 6N hydrochloric acid. The amount of iron

found by analysis in the filtrate of this digest showed
that a quantity of ferric chloride equivalent to 89 per cent.
of the ferric oxide originally present, had formed a lamellar
compound with the graphite.   The possibility that this re-
sult was due to a decrease in acid solubility of the ferric
oxide caused by heating was checked by repeating the above
test with a tube containing only ferric oxide and graphite.
This test showed that 99.5 per cent. of the ferric oxide was
extracted by boiling 6N hydrochloric acid in less than 7
minutes.   Hence, it is evident that at least 89 per cent.
of the aluminium chloride reacted with ferric oxide in the
first test and that graphite combined with most of the
ferric chloride produced by this reaction.

Tests conducted at $350^\circ C.$ were designed to deter-
mine approximately the rate at which ferric oxide and
aluminium chloride react at this temperature and also to
discover if graphite combines with ferric chloride suffi-
ciently rapidly to remove the latter as it is produced by the
above reaction.   The tests were performed as follows.
Tubes containing anhydrous aluminium chloride (1.5 g.),
ferric oxide (0.9 g.), and graphite (4.0 g.) in equivalent
quantities * were heated for various periods at $350^\circ C.$
After heating, the tube contents were agitated with water
and filtered.   Ferric chloride not combined with graphite

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* The equivalent weight of graphite was calculated to be
2.23 g. per gram ferric chloride by assuming the stable
graphite-ferric chloride compound prepared at $350^\circ C.$ to
contain 31 per cent. ferric chloride.

was dissolved and was collected in the filtrate. Some
hydrolysis occurred, but the peptised ferric hydroxide
was quite easily washed through the filter. Iron was
determined in the filtrate and also in the 6N hydrochloric
extract of the residue. The results of these analyses
were used to calculate the percentages of aluminium chloride
which had reacted with ferric oxide, and the amounts of
ferric chloride, expressed as percentages, of the total
quantities of ferric chloride formed, which combined with
graphite. These results are presented graphically in
Fig. 3. They indicate that more than 9½ per cent. of the
aluminium chloride had reacted with ferric oxide after 2
hours heating and that 8½ per cent. of the ferric chloride
formed after this period, combined with graphite.

(e)   <u>Removal of ferric oxide from ferruginous bauxite.</u>

The ready reaction between ferric oxide and
aluminium chloride and the ability of graphite to combine
with the greater part of the ferric chloride formed, noted
above, suggested that ferric oxide might be removed from
ferruginous aluminium ores by heating them with aluminium
chloride in the presence of graphite. The separation of
iron and aluminium chlorides achieved by heating a mixture
of these with graphite, also described, further suggested
that the aluminium chloride to be used in the above treatment
could be obtained by chlorinating similar ores and heating
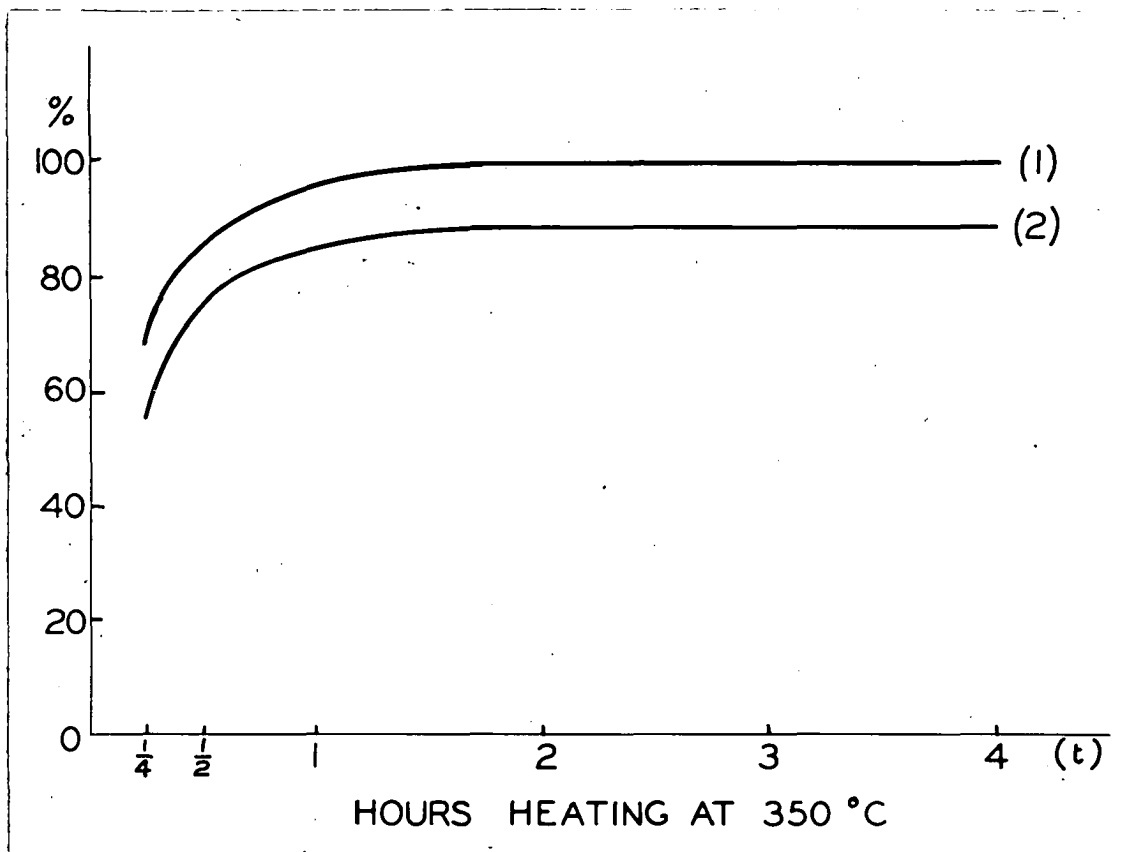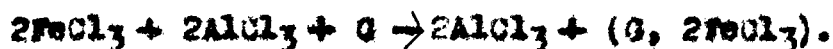the products with graphite. The following scheme shows the

FIG. 3. Curves showing (a) the rate of decomposition of aluminium chloride when this compound is heated with ferric oxide at 350°C, and (b) the rate at which ferric chloride formed by this reaction combines with graphite when it is also present.

reactions involved and the manner in which they might be combined for the treatment of bauxite.

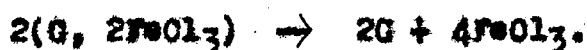1. Chlorination of bauxite (Fe_2O_3, Al_2O_3).

$(Fe_2O_3, Al_2O_3) + 6C + 12Cl_2 \rightarrow 2FeCl_3 + 2AlCl_3 + 6CO.$
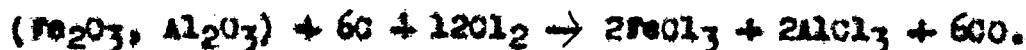
2. Separation of chlorides by heating with graphite (G)

$2FeCl_3 + 2AlCl_3 + G \rightarrow 2AlCl_3 + (G, 2FeCl_3).$

3. Heating bauxite with $AlCl_3$ and graphite.

$(Fe_2O_3, Al_2O_3) + 2AlCl_3 + G \rightarrow 3Al_2O_3 + (G, 2FeCl_3).$

4. Recovery of graphite from graphite-ferric-chloride compound by heating.

$2(G, 2FeCl_3) \rightarrow 2G + 4FeCl_3.$

5. Oxidation of $FeCl_3$ to recover chlorine

$4FeCl_3 + 6O_2 \rightarrow 2Fe_2O_3 + 12Cl_2.$

Steps 4 and 5 have been included in the above scheme to indicate the possibility of making this a cyclic process. The complete removal of ferric chloride from graphite by heating has been confirmed, but only qualitative observations of the oxidation of ferric chloride have been made. However information from the literature[29] indicates that this reaction occurs readily.

It was thought that if the above scheme were practicable, it would offer the following advantages. Only a portion of the bauxite need be treated by direct chlorination, the remainder could be beneficiated by use of aluminium chloride which must be decomposed to the oxide in any case for the recovery of chlorine. Chlorine could be recovered by treating only one reaction product viz. ferric chloride.

It is evident that, when the ferric oxide content of the bauxite is low, only a relatively small amount of the latter need be chlorinated if it is beneficiated by the above methods.

The following tests were done to confirm the reaction bet-een aluminium chloride and ferric oxide present in bauxite. Samples of bauxite were mixed with quantities of aluminium chloride equivalent to the ferric oxide they contained and with weights of graphite equivalent to the amounts of ferric chloride which would be formed by complete reaction between the aluminium chloride and ferric oxide present. These mixtures were sealed in evacuated glass tubes. One tube was heated at 250°C., but the remainder were all heated at 350°C. Some tubes were heated for 2 hours and others for 6 hours. The bauxite used in these tests contained 42 per cent. ferric oxide and 32 per cent. alumina. Flake graphite (+48 mesh, 0.5% ash) was used in some tubes and fine graphite (-200 mesh, 0.5% ash) in others.

After heating, tube contents were extracted with absolute alcohol in a soxhlet extractor until free of uncombined ferric chloride. The residues were then treated by either of the following methods. Residues from tubes in which flake graphite was used were washed with water on a 100 mesh screen until the wash water was clear. Residues containing fine graphite were agitated with water and suspended alumina was decanted from settled graphite. Ferric oxide and alumina determinations were done on alcohol extracts, screen washings and material obtained by decantation. The

extent of reaction between aluminium chloride and ferric
oxide present in the bauxite, the purity of alumina obtained,
and the amounts of original ferric oxide removed as graphite-
ferric chloride compound were calculated from the results of
these analyses.   Calculated data are shown in Table 1.
These data show that the reaction between aluminium chloride
and ferric oxide present in the bauxite was slower at 250°C.
than at 350°C.   Results for tubes 4 and 5 show that this
reaction was almost complete after 6 hours heating at 350°C.
and also that flake and fine graphites were equally effective
in combining with ferric chloride.   The incompleteness of
the aluminium chloride reaction in tube 2 is believed to have
been due to the tube being too full.   Quantities of un-
attacked bauxite could be seen between the tube wall and the
bottom of the graphite layer which had swelled and filled the
tube in this region.   This swelling may also have isolated
some graphite thus hindering reaction of the latter with
ferric chloride.   Although the reaction between aluminium
chloride and the ferric oxide in bauxite samples was almost
complete in tests 4 and 5, the amounts of ferric chloride
which combined with graphite were smaller than in tests in
which pure ferric oxide was used instead of bauxite.   A
possible explanation for this is that ferric chloride may
have been confined in the porous alumina produced by removal
of ferric oxide from bauxite, by alumina formed during reaction
of aluminium chloride with ferric oxide.

TABLE 1.
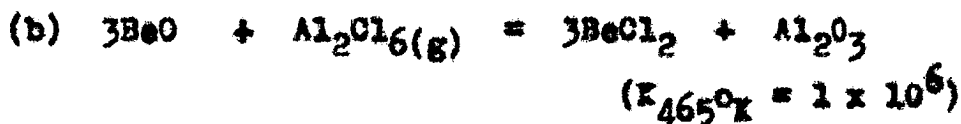
Removal of Ferric Oxide from Bauxite

Tube No.	1	2	3	4	5
Graphite used.	flake	flake	fine	flake	fine
Period of heating - hrs.	2	2	2	6	6
Temperature - $^{\circ}C$.	250	350	350	350	350
Percentage of Fe_2O_3 (present in bauxite sample) which reacted with $AlCl_3$.	74.8	90.4	96.0	98.0	98.0
Percentage of the $FeCl_3$ formed which combined with graphite	24.6	43.0	55.0	63.6	64.0
Percentage of original Fe_2O_3 removed as graphite-ferric chloride compound	18.4	39.0	53.0	62.4	62.6
Percentage of Fe_2O_3 in alumina concentrates separated from residues obtained by alcohol extraction of tube contents after heating.	-	7.0	2.60	1.30	1.31

The recovery of alumina was approximately 90 per cent. in all tests. The remaining 10 per cent. was not recovered because some alumina formed by decomposition of aluminium chloride was in the form of flakes which could neither be washed through a 100 mesh screen nor decanted from settled graphite. The possibility of ferruginous minerals being separated from alumina by the decantation method of recovering alumina concentrate from alcohol extracted tube residues was tested as follows. Two tubes similar to Tube 4 were heated for 6 hours, their contents were then alcohol extracted and alumina was recovered from the residue of one by washing on a 100 mesh screen and by decantation from the other residue. The two alumina concentrates were analysed. Since analytical results agreed closely, it was concluded that no separation of iron minerals from alumina occurred when the decantation method was employed. This conclusion confirms that the low ferric oxide contents of alumina concentrates shown in Table I were due to almost complete attack of the ferric oxide in bauxite by aluminium chloride and not to experimental method.

(d) Separation of aluminium and beryllium.

The reaction between ferric oxide and aluminium chloride discussed above, appeared to offer a method of separating the latter from other chlorides which react less readily or not at all with ferric oxide under the conditions quoted. Thus, it was considered possible that heating a

mixture of anhydrous chlorides with ferric oxide and graphite would result in aluminium chloride being decomposed to alumina, while other chlorides remained unchanged. Providing the latter did not react with alumina, they could be separated from the insoluble alumina and graphite-ferric chloride compound by solvent extraction. The separation of aluminium and beryllium chlorides was attempted in accordance with this plan. Equilibrium constants for the following reactions at $192^{o}C$. were calculated from thermodynamic data in Table 4 (Appendix).

(a) $Fe_2O_3 + 3BeCl_2 = 3BeO + 2FeCl_3$

$$(K_{465^oK} = 3 \times 10^{34})$$

(b) $3BeO + Al_2Cl_{6(g)} = 3BeCl_2 + Al_2O_3$

$$(K_{465^oK} = 1 \times 10^6)$$

Calculation of constants for higher temperatures was not possible owing to insufficient data being available. However, the values of constants given above indicated that beryllium chloride should react with ferric oxide as readily as does aluminium chloride. The second equation forecast that interaction between alumina and beryllium chloride would be negligible. Since the calculated values of the equilibrium constants for the reactions of aluminium and beryllium chlorides with ferric oxide were similar, it was evident that successful separation depended on there being a substantial difference between the rates of these reactions. It seemed probable that, if these rates were dependent on the respective

vapour pressures of the chlorides, then aluminium chloride
would react more rapidly with ferric oxide than beryllium
chloride would, because the vapour pressure of the former
at $192^{\circ}C$. is 96.0 cm. mercury whereas beryllium chloride has
a vapour pressure of only 0.9 cm. mercury at $340^{\circ}C$.[9].

Before the separation proposed above could be
tested, it was necessary to determine whether beryllium
chloride formed a lamellar compound with graphite.   If this
occurred, complete recovery of the chloride after it had been
heated in the presence of graphite might not have been possible
by solvent extraction.   To check this point, a sealed tube
containing 0.735 g. of beryllium chloride and 5 g. of graphite
was heated at $230^{\circ}C$. for 60 hours.   Since the extraction of
tube contents with absolute ethyl alcohol (a saturated solu-
tion of $BeCl_2$ in C_2H_5OH contains 151 g. $BeCl_2/l$. at $20^{\circ}C$.)
recovered 96 per cent. of the beryllium chloride originally
added, it was concluded that no lamellar compound was formed.

Attempts to separate aluminium and beryllium were
made by heating the anhydrous chlorides of these metals with
ferric oxide and graphite in sealed glass tubes, using tem-
peratures of 230 and 350 C.   In a test conducted at the
former temperature, a tube containing 0.319 g. beryllium
chloride, 1.620 g. aluminium chloride, 1.249 g. ferric oxide
and 5 g. of flake graphite (0.5 per cent ash) was heated for
60 hours.   After heating, the tube contents were extracted
with absolute alcohol for 2 hours in a Soxhlet apparatus.
The residue from extraction was digested with 6N hydrochloric

acid for 2 hours and the digest filtered.   Both the alcohol
extract and the acid filtrate were analysed for aluminium
and beryllium.   Distribution data calculated from the re-
sults of these analyses are given in Table 2.   These figures
show that the reaction between aluminium chloride and ferric
oxide reported above is unaffected by the presence of beryl-
lium chloride.   Since the ferric oxide originally added to
the tube was 30 per cent. in excess of the amount equivalent
to the weight of aluminium chloride taken, and analytical
results showed that beryllium chloride reacted with only 42
per cent. of this excess, it is evident that this reaction
was slow.   The concentration of beryllium chloride achieved
in the above separation is shown by the decrease in the ratio
of aluminium chloride to beryllium chloride.   This ratio was
3.24:1 in the original mixture and 0.07:1 in the alcohol
extract.

The separation of aluminium and beryllium effected
in the test done at 230°C. was confirmed by conducting a
similar test at 350°C.   In this experiment, the amount of
ferric oxide added was 13 per cent. in excess of that equiva-
lent to the weight of aluminium chloride present and graphite
was 22.5 per cent. in excess of that calculated to be equiva-
lent to the ferric chloride formed by complete decomposition
of aluminium chloride.   The ratio of aluminium chloride to
beryllium chloride was 14.4:1 before heating.   After 2 hours
heating at 350°C., the tube contents were rapidly transferred
to a thimble and extracted with absolute alcohol for 2 hours

TABLE 2

Data showing the distribution of
Aluminium and Beryllium between
extracts obtained in the separa-
tion of these metals conducted
at $230^\circ C$.

Extract	Percentages of original chlorides found in extracts	
	$AlCl_3$	$BeCl_2$
Ethyl alcohol	1.29	56.00
6N hydrochloric acid	96.70	43.00

in a Soxhlet apparatus. The residue from extraction was digested for 2 hours with boiling 6N hydrochloric acid. The digest was then filtered and washed. Both the alcohol extract and the filtrate from acid digestion were analysed for iron, aluminium and beryllium. The results of these analyses were used to calculate the distribution data presented in Table 3. These data show that an almost complete separation of aluminium from beryllium was achieved in the above test. They also show that decomposition of aluminium chloride to alumina was 99 per cent. complete in 2 hours. Since the same period was required for the same degree of decomposition when beryllium chloride was absent, the latter appears to have had no effect on the rate of this decomposition. The incomplete recovery of beryllium chloride by solvent extraction is believed to have been due to hydrolysis caused by water present in the absolute alcohol. A slight increase in the temperature of the tube contents, observed during the transfer of these to the Soxhlet thimble, indicated that some hydrolysis was also caused by absorption of atmosphere moisture. It is evident that no beryllium chloride was lost as a result of reaction with ferric oxide because the amount recovered was greater by 8.6 per cent. than that extracted from a simple mixture of beryllium chloride and graphite which had been heated for 2 hours at 350°C. This increase in recovery may have been due to rechlorination of a part of the hydrolysed beryllium chloride by decomposition of aluminium chloride. It is concluded from the above

TABLE 3

Separation of Aluminium from Beryllium,
conducted at 350°C.

	$AlCl_3$	$BeCl_2$	$FeCl_3$
(a) Percentages of original chlorides found in extracts			
(i) Ethyl alcohol extract	0.14	89.60	7.84[*]
(ii) 6N Hydrochloric acid extract	98.50	10.00	-

(b) Ratio of $AlCl_3$ to $BeCl_2$

(i) In original mixture before heating   14.4 : 1
(ii) In ethyl alcohol extract   0.02 : 1

(c) Percentage of the FeCl3 formed which combined with graphite   78.3

[*] Weight of ferric chloride found by analysis expressed as a percentage of total weight of ferric chloride formed.

observations that the recovery of beryllium chloride is
dependent on choice of extraction solvent and experimental
technique and not on the chemical principles of the method
of separation described.

The application of the above method to effect the
separation of beryllium chloride from the chlorination pro-
ducts of beryl ($3BeO \cdot Al_2O_3 \cdot 6SiO_2$) is being investigated at
present.   This problem is of interest because McTaggart[20]
and other workers whom he quotes were unable to separate pure
beryllium chloride from the mixture of iron, aluminium,
silicon, and beryllium chlorides which they obtained by
chlorinating intimate mixtures of beryl and carbon.   Investi-
gations reported above show that separation from iron and
aluminium chlorides is possible, but no results are available
yet to indicate how silicon tetrachloride would behave in
this separation.   It is considered probable, however, that
this compound would react more readily with ferric oxide than
aluminium chloride does because it has a greater vapour
pressure (76 cm. of mercury at $56°C$. c.f. $AlCl_3$, 76 cm. of
mercury at $192°C$.) and also a greater calculated equilibrium
constant ($K_{192°C.} = 6 \times 10^{79}$, c.f. Al_2Cl_6 reaction, $K_{192°C.} = 5 \times 10^{40}$) for the similar reaction.

$$3SiCl_4 + 2Fe_2O_3 = 3SiO_2 + 4FeCl_3.$$
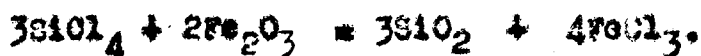
In calculating equilibrium constants for the
various reactions noted above, no account was taken of the
effect of graphite on these reactions.   The fact, however,
that the latter proceeded in fair accord with calculation
suggests that they were not influenced greatly by the
presence of graphite.

III.   DISCUSSION.

Results obtained from the investigation described
above show that graphite oxide and graphite ferric chloride
complexes may be readily prepared from South Australian
graphite.   They also show that the properties of these
lamellar compounds agree closely with those of similar com-
plexes prepared from highly crystalline graphites found else-
where.   The fact that the yield of oxide obtained from the
local graphite was 97 per cent. of the yield quoted by Riley[21]
for an oxide prepared from Ceylon graphite, suggests that
both graphites contain approximately the same total amounts
of well developed crystal structures, such as the Bernal and
Debye-Scherrer structures discussed earlier.   This suggestion
is also supported by the fact that South Australian graphite
was found to combine with ferric chloride in the same propor-
tions as have been noted [22] for well crystallised graphites
from Ceylon and other sources.   The considerable intumescence
which occurs when South Australian graphite is moistened with
fuming nitric acid then heated, indicates that the macro-
lamellar or miscellar structure of this material is also well
developed.

The electron micrographs of graphite oxide (Fig. 1.)
and graphite oxide black (Fig. 2.) both indicate the lamellar
structure of South Australian graphite.   Fig. 1 is of
interest partly because it confirms Riley's suggestion[22]
that graphite oxide may be completely dispersed in the form
of 2 demensional macro-molecules and partly because it is

believed to be the first electron micrograph of graphite
oxide which has been published.   The electron micrograph
of graphite oxide black shows very clearly the structure
which Ruess and Huston[24] deduced from X-ray diffraction and
electrical conductivity data.   The electron micrograph
published by these workers, however, does not show the struc-
ture they suggest.

The attempts which have been made, so far, to find
uses for the lamellar compounds of carbon have been few.   It
has been shown, however, that graphite oxide prepared from
South Australian graphite, like that prepared from Ceylon
graphite, can be used to prepare an extremely finely divided
form of graphitic carbon, and also graphite mirrors which
may be used as high electrical resistances.   Although no
attempt has yet been made to find uses for the graphite-
ferric chloride compounds, it has been shown that graphite
may be used to separate anhydrous ferric chloride from mix-
tures or to remove this compound as it is produced during
reaction.   This discovery drew attention to reactions between
anhydrous metal chlorides and ferric oxide, which, it is
thought, may have wider application than indicated by the
illustrations given in this paper.   The separation of rare
earth chlorides is suggested as another possible application.

The separation of aluminium and beryllium which has
been described above, is of interest because, if applicable
to the chlorination products of beryl, it avoids the high
temperature fusion and lengthy recrystallisation techniques

which are employed in the present method of extraction and separation described by Welch[30]. Any comment on the probable merit of the process for removing ferric oxide from bauxite, outlined in this paper, would be unjustifiable at present, because the investigation of the problem is incomplete. It does appear, however, that the process is somewhat simpler than those[29] which overseas countries are at present applying to clays and other low grade aluminium ores.

IV.   CONCLUSION.

The following conclusions have been drawn from the investigation described above.

1.   South Australian graphite was oxidised by Staudenmaier's method to yellow graphite oxide.   This compound was readily dispersed by water, alcohol, acetone, and dilute aqueous ammonia.   It decomposed readily on heating to give a finely divided form of graphitic carbon.   The percentage yield (97 per cent. of that quoted[21] for Ceylon graphite), "available oxygen" content (17 per cent) and other properties of this oxide agreed closely with similar information given by Riley[22] for graphite oxide prepared from Ceylon graphite.   Electron micrographs of the oxide prepared from South Australian graphite showed that this substance could be dispersed as flake-like particles measuring less than 25 Å thick by 250-500 Å across.   Graphite oxide black obtained by thermal decomposition of this oxide was also examined under the electron microscope and was found to consist of very thin (less than 50 Å thick) continuous sheets of carbon.

2.   Electrolytic oxidation of South Australian graphite anodes yielded samples of graphite containing small amounts of graphite oxide.   The "available oxygen" content of these samples was increased from 0.5 to 2.4 per cent. by heating the latter and re-electrolysing the expanded material so obtained.

3. Heating South Australian graphite with anhydrous ferric chloride in sealed tubes resulted in the formation of graphite-ferric chloride compounds. The compound obtained by heating at $230^{\circ}C$. contained 57.4 per cent. ferric chloride after extraction with boiling 6N hydrochloric acid. The corresponding figure for the compound formed at $350^{\circ}C$. was 35 per cent. Both compounds were very stable chemically and were only decomposed by heating to above $500^{\circ}C$. and by boiling for long periods (days) with either concentrated sulphuric or concentrated nitric acid.

4. South Australian graphite did not form a lamellar compound with anhydrous aluminium chloride.

5. Seperation of the anhydrous chlorides of iron and aluminium was effected by heating a mixture of these with South Australian graphite at $230^{\circ}C$.

6. Anhydrous aluminium chloride reacted readily with ferric oxide at 230 and $350^{\circ}C$. Most of the ferric chloride (88 per cent. after 2 hours heating at $350^{\circ}C$.) produced by this reaction, combined with South Australian graphite when this was also present. The reaction between equivalent quantities of ferric oxide and aluminium chloride was 99 per cent. complete after 2 hours heating at $350^{\circ}C$.

7. The ferric oxide contained in a sample of ferruginous bauxite (42 per cent. Fe_2O_3) reacted with anhydrous aluminium chloride almost as completely (98 per cent.)

as did pure ferric oxide.   When South Australian graphite was present, it combined with 62.6 per cent. of the ferric oxide produced by the above reaction.

8. Anhydrous beryllium chloride did not form a lamellar compound when heated with South Australian graphite.

9. Beryllium was separated from aluminium by heating a mixture of the anhydrous chlorides of these metals with pure ferric oxide and South Australian graphite for 2 hours at $350^\circ C$.   Unchanged beryllium chloride (89.6 per cent. of original weight) was dissolved from the reaction products by extraction with ethyl alcohol. The separation was made possible by the fact that aluminium chloride reacted with ferric oxide at a much greater rate than did beryllium chloride.   The graphite combined with 78.3 per cent. of the ferric chloride produced by this reaction.

APPENDIX TO PART IV.

Calculation of Standard Free Energies and
Equilibrium Constants of Reactions between
the Oxides and anhydrous Chlorides of Iron,
Aluminium, Beryllium, and Silicon.

V.   APPENDIX.

The equilibrium constants quoted in Sections 4 (b), (c) and
(d) to indicate the feasibility of reactions between ferric
oxide and various anhydrous chlorides were calculated from
selected thermodynamic data by means of the following
equations[16]

(i) $G = H - TS$

(ii) $-RT\ln K = \Delta G^0 = \sum G^0 \text{ (Products)} - \sum G^0 \text{ (reactants)}$

(iii) $\ln \dfrac{K_1}{K_2} = \dfrac{\Delta H^0}{R}\left(\dfrac{T_1 - T_2}{T_1 \times T_2}\right)$

Equation (i) which relates the free energy G of a substance
to its heat content H and its entropy S, was used to find the
free energy change ΔG^0 of each reaction.   Equilibrium constants
were obtained by substituting these values of ΔG^0 in equation
(ii) which shows the relation of the equilibrium constant K
of a reaction to the free energies of the reactants and pro-
ducts of the reaction.   Equation (iii) which is an integrated
form of the Van't Hoff isochore, was used to obtain values of
the equilibrium constants at temperatures above that to
which the available heat content and entropy data referred.
Because no heat capacity data was available for a number of
the substances (solid $BeCl_2$ and $FeCl_3$, and gaseous Al_2Cl_6)
appearing in the above reactions, it was necessary to assume
that ΔH^0 in equation (iii) was independent of temperature.

The heat of formation and entropy data given in
Table 4 were used in deriving equilibrium constants.   These
data were selected from what are considered to be the most

TABLE 4

Data used in calculating equilibrium constants
for reactions between ferric oxide and anhydrous
chlorides.

Compound	Heat of formation at 25°C.		Entropy at 25°C.	
	$\triangle H^{\theta}$ k cal./mole.	Ref.	S^{θ} cal./deg./mole.	Ref.
Al_2O_3 (α)	-399.0	2	12.5	10
Al_2Cl_6 (g)	-306.2	4	(117.0 (110.9	2 calc (12)
Fe_2O_3 (α)	-198.5	4	21.5	10
$FeCl_3$(s)	-102.3	4	(42.0 (42.8	calc (15) " (12)
BeO(s)	-135.0	4	3.4	11
$BeCl_2$(s)	-112.6	4	(24.0 (22.4	calc (15) " (12)
SiO_2(s)	-203.3	4	10.2	14
$SiCl_4$(g)	-142.5	4	79.2	14

reliable sources.   In several instances, viz. solid

$BeCl_2$ and $FeCl_3$, and gaseous Al_2Cl_6, lack of published

data made it necessary to calculate entropies by empirical

methods.   Examples of these calculations are given below.

Calculation of Entropies:-

(a)   Latimer's method[15]

This method is based on the claim that the differ-

ence of entropy of two solid substances having the same

formula and melting points, is largely due to a mass effect.

Latimer expressed this quantitatively in the relation

$$S_{AX} - S_{BX} = \frac{3}{2}\ R\ln\left(\frac{at.\ wt.\ A}{at.\ wt.\ B}\right)$$

where S_{AX} and S_{BX} are the entropies of two similar compounds

AX and BX.   The entropy of solid ferric chloride was calculat-

ed from the entropy of bismuth trichloride ($S_{298.1} = 46.0$

cal./deg./ mole[14]) by means of this equation.   Bismuth

trichloride was selected because its melting point viz. 230-

$232^{\circ}C$. is closer to that of ferric chloride ($280^{\circ}C$.) than the

melting point of any other similar compound.   Solution of

the equation,

$$S_{FeCl_3} - S_{BiCl_3} = \frac{3}{2}\ R\ln\left(\frac{at.\ wt.\ Fe}{at.\ wt.\ Bi}\right)$$

$$S_{FeCl_3} = \frac{3}{2}\ \times 1.99 \times 2.3 \log\frac{56}{209}\ + 46$$

gave the entropy of solid ferric chloride at $298.1^{\circ}K$ as

42.0 cal./deg./mole.   The entropies of solid aluminium

chloride and beryllium chloride at $298.1^{\circ}K$ were similarly

determined to be 39.9 and 24.0 cal./deg./mole respectively.

(b) **Kireev's method**[12]

This method of calculation is based on Kireev's observation that the entropy of formation of a crystalline compound from its elements in the hypothetical state of a monatomic ideal gas at the same temperature and pressure (p = 1 atm.) is principally determined by the number of atoms in a molecule of the compound. This type of entropy which has been called "atomic entropy of formation" (ΔS_f^a) is un-affected by differences in the state of aggregation of elements. Another property of compounds which is still more completely determined by the number of atoms in the molecule of a compound, was also defined by Kireev. This quantity which he called "ideal entropy of formation" (ΔS_f^i) refers to the formation of compounds in the hypothetical state of an ideal gas from free atoms of elements in the same state. It is evident that the state of aggregation of compounds under normal conditions has no effect on the ideal entropy of formation. Kireev has derived equations to relate the above quantities and has also tabulated atomic and ideal entropy data which may be used in these equations to calculate standard entropies. Methods used in calculating the standard entropies of solid ferric chloride, beryllium chloride, and gaseous aluminium chloride are shown below.

(1) Entropies of solid chlorides,

According to Kireev, the entropy of formation of a crystalline compound is related to its atomic entropy of formation and the entropy of vaporisation (under standard

conditions) of the elements of which it is composed, as in
the equation

$$\Delta S_f = \Delta S_f^b - (\sum \nu_k S_k - \sum \nu_k S_k^\downarrow) \quad \ldots \ldots (iv)$$

(ν_k represents the stoichiometric coefficients of the
k elementary reactants).

Values found by means of equation (iv) for entropy of forma-
tion under standard conditions are substituted in the
equation,

$$\Delta S_f + \sum \nu_k S_k = S_D \quad \ldots \ldots \ldots (v)$$

where S_D is the standard entropy of the substance.   The
standard entropies of ferric chloride and beryllium chloride
both in the crystalline state, were found by substituting the
following data in equation (iv) and (v).

Ferric chloride:-

$\Delta S_f^a = -120$ cal./deg./mole for molecules containing 4 atoms

($S_k^\downarrow - S_k$) for Fe $= 36.6$ cal./deg./g. atom.

" " " Cl $= 12.8$ " " "

By equation (iv), ΔS_f was found to be -45 cal./deg./mole.
Using this figure and the following entropies per gram atom
of iron and chlorine in the solid state,

$S_{Fe} = 6.5$ cal./deg./g. atom (14)

$S_{Cl} = 27.1$ " " " "

in equation (v) gave $S_{298.1} = 42.8$ cal./deg./mole ferric
chloride.   This agrees with the value (42.0) found above
by Latimer's method.   The entropy of beryllium chloride
was determined similarly using the data,

$\Delta S_f^a = -90$ cal./deg./mole for molecules containing 3 atoms

$(S_k^1 - S_k)$ for Be = 30.28 cal./deg./g. atom

"   "   "   Cl = 12.8   "   "   "

ΔS_f was found by equation (iv) to be -34.12 cal./deg./mole. Substituting this value in equation (v) and using $S_{298.1} = 2.28^{(14)}$ for solid beryllium gave $S_{298.1} = 22.4$ cal./deg./mole for crystalline beryllium chloride.   Latimer's method gave 22.4 cal./deg./mole.
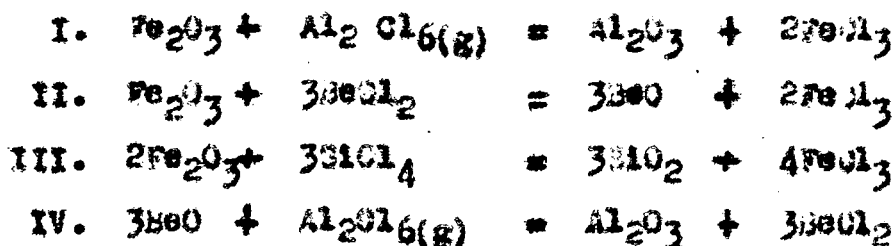
(2)   Entropy of gaseous aluminium chloride (Al_2Cl_6).

In order to determine the entropy of this substance it was necessary to find both the entropy of solid aluminium chloride and the entropy of vaporisation of this compound under standard conditions.   The former quantity was calculated by the same method as used for solid ferric chloride and was found to be 39.9 cal./deg./mole.   The latter entropy was obtained from the equation

$$(S_D - S_D^1) = \Delta S_f^a - \Delta S_f^1 \quad \ldots\ldots\ldots\ldots (vi)$$

which relates the entropy of vapourisation $(S_D - S_D^1)$ to the atomic and ideal entropies of formation.   By substituting Kireev's values of - 287.0 and - 216.0 cal./deg./mole for ΔS_f^a and ΔS_f^1 respectively, $(S_D - S_D^1)$ was found to be 71 cal./deg./mole.   Thus, the entropy of gaseous aluminium chloride was found to be 39.9 + 71 = 110.9 cal./deg./mole. which agrees reasonably well with Bayliss and Mer's[2] figure of 117 cal./deg./mole.

The data given in Table 4 and equations (i), (ii) and (iii) noted above were used to calculate equilibrium

constants at 25 and 192°C.[*] for the following reactions,

I. $Fe_2O_3 + Al_2Cl_{6(g)} = Al_2O_3 + 2FeCl_3$

II. $Fe_2O_3 + 3BeCl_2 = 3BeO + 2FeCl_3$

III. $2Fe_2O_3 + 3SiCl_4 = 3SiO_2 + 4FeCl_3$

IV. $3BeO + Al_2Cl_{6(g)} = Al_2O_3 + 3BeCl_2$

For reaction I at 298.1°C.

$\triangle H^0 = -399.0 - (2 \times 102.3) + 198.5 + 306.1$

$= -99.0$ kcal.

$\triangle S^0 = 12.5 + (2 \times 42.0) - 21.5 - 117.0$

$= -42$ cal./deg.

and the standard free energy at this temperature is

$\triangle G^0 = \triangle H^0 - T\triangle S^0 = -86.45$ k cal.

From this

$$\log_{10} K_{298.1} = \frac{-\triangle G^0}{2.3R \times 298.1} = \frac{86,450}{2.3 \times 1.99 \times 298.1} = 63.4$$

Applying equation (iii),

$$\log_{10} K_{465} = \log_{10} K_{298.1} - \frac{86,450 \times 167}{2.3 \times 1.99 \times 298.1 \times 465}$$

$$= 63.4 - 22.7 = 40.7$$

Therefore,

$$K_{465} = 5 \times 10^{40}$$

Values of $\triangle G^0$ at 298.1°K and equilibrium constants calculated as above for temperatures of 298.1 and 465°K are shown for reactions I to IV in Table 5. The large negative


TABLE 5

Standard Free Energies and
Equilibrium Constants

Reaction	$\triangle G^o$ for reaction at 25^oC. (K cal.)	K for reaction at	
		25^oC.	192^oC.
I	-86.45	2.5×10^{63}	5×10^{40}
II	-73.32	5.6×10^{53}	3×10^{34}
III	-170.05	6.3×10^{124}	6×10^{79}
IV	-13.00	3.2×10^{9}	1×10^{6}

free energy changes shown in this table for reactions I - III indicate that these reactions are thermodynamically favourable. This was supported by experimental evidence. The value of $\triangle G^0$ for reaction IV suggests that this is an almost balanced reaction. It is realised that because variations of $\triangle H^0$ with temperature were neglected in calculations, the equilibrium constants obtained for 465^0K are only approximate. It is believed, however, that the temperature range over which they were calculated was small enough to avoid the introduction of serious errors.
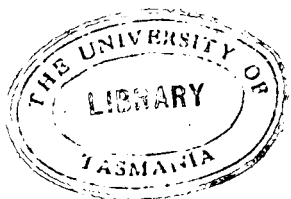
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