DENSIFICATION OF COKE

Project Report
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by

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CONTENTS

1. SUMMARY

Further work has been carried out on the densification of Stockton coke to confirm Allan's work (3), which showed that an acceptable density could be obtained by fine grinding and briquetting. The effect of particle size on this densification has now been studied.

The density of the -7 to +14 B.S. mesh fraction, from briquettes made from -350 mesh coke and heated to 1400°C for 1½ hours, exceeded 42 lb/ft^3. This was the smallest particle size tested and gave the highest density. The real specific gravity of the heated coke was found to be independent of particle size, but depended markedly on whether the sample was from heated powder or heated briquette.

2. INTRODUCTION

In this department several projects have been carried out to determine the suitability of New Zealand's West Coast coals for the manufacture of carbon electrodes. Interest in the manufacture of such electrodes in this country has arisen with the possible utilisation of some of the country's electrical resources in electrothermal and electrolytic processes; for example, the production of steel, calcium carbide or aluminium. Study has been restricted to coke produced from Stockton coal, because the very low ash content of this coal (approximately .2%) should give a coke which will easily meet the stringent ash specifications for anode carbon for aluminium production. In addition, a large supply of this coal is immediately available at low cost, as there is a ropeway from close to the coal seam to the railway at Ngakawau, and this ropeway was designed to carry thirty times its present load.

Stockton coal is a high-swelling coal, and the coke produced has a bulk density of only 21-22 lb/ft^3. For this coke to compare favourably with the petroleum coke usually used, its bulk density should be similar, that is about 44 lb/ft^3. Work has therefore been carried out on methods of increasing the density of Stockton coke. Previous workers (1,2,3) have tested a number of methods of densifying coke, and the method showing most promise was in Allen's report (3). This method is to produce dense coke chips by fine grinding the original coke, briquetting, heating to 1400°C, and crushing the briquettes to give chips of the sizes required for the manufacture of the electrodes. The object of the experimental work in this project was to determine the sources of this increase in bulk density, and to find the relationship between the density obtained by this process and the fineness to which the coke was ground.

The bulk density of a coke sample is taken as the bulk density of the -7 to +14 B.S. mesh fraction as is measured by tapping to constant volume in a measuring cylinder. The factors influencing the bulk density, as measured in this standard manner, may be:

1. The size of the sample in the measuring cylinder.
2. The amount the cylinder is tapped.
3. The ratio of cylinder diameter to particle diameter.
4. The shape of the chips from the briquettes.

5. The apparent density of the briquette crushed which is the apparent density of the chips.

No. 5 will depend on

6. Percent of pitch, pressure, and temperature of briquetting.
7. The bulk density of the powder forming the briquettes.

No. 7 will depend on

8. Real density of coke forming the particles.
9. The number and size of voids in the particles.
10. The size of the particles of powder.
11. The calcining temperature.

The first factor was investigated by Packer and Fleming (1,2) and in this work a 50 ml sample was tapped to constant volume in a standard 50 ml glass measuring cylinder, so the bulk density obtained should be close to that of a very large sample. The first section of the experimental work gives details of the preparation of samples. In the second section the bulk density of the coke powder, before and after heating, was measured for fine coke powders. Results from this part of the work thus give the dependence of particle size on the factor numbered 7 above. In the third section of the experimental work (section 3.3) the dependence of the powder size used to form the briquette on the -7 to +14 mesh bulk density of the heated and crushed briquette is given, for constant briquetting conditions. The briquetting pressure chosen, 2000 psi, is approximately the pressure developed in commercial continuous briquetting rolls. Yeow (6) has found the dependence of briquetting conditions on apparent density of briquettes. In section 3 an examination of the chip shapes and structure was made. This section thus investigates points 4 and 5 of the original list. In the last section of the experimental work the real density of the various coke powders is measured in water.

3. EXPERIMENTAL

3.1 Preparation of Samples

3.1.1 Coke :

A quantity of coke, prepared in the Ranglora gasworks from Stockton coal - drive A, for Palmer (4), was passed through the laboratory jaw crusher to $\frac{3}{8}$" size, and the resulting crushed coke was mixed in a drum to give a uniform sample. This coke was used for all the experimental work detailed in this report.

A 300 gm sample of coke was sieved for 10 min. and the oversize material ground for 1½ min. in the laboratory end runner mill and then sieved again. This procedure was repeated until the whole sample was -10 mesh, then -30 mesh, and finally -52 mesh. The material was then stored as the -52 mesh sample. A similar procedure gave three other samples with particles below the mesh sizes given in table I.

Table I

Actual Sieve Sizes

B.S.S. mesh No.	in.	microns
52	.0116	295
100	.0060	152
200	.0030	72
350	.0018	45

The samples were produced with no lower limit to the particle size because

(i) particles of similar size pack poorly compared with particles of greatly differing size,

(ii) any commercial process will involve grinding under size rather than between sizes, and

(iii) particles of differing size may be structurally or chemically different.

To avoid any of these differences causing a difference between samples, a portion of the bulk lot was taken and all of this sample was ground to the required size. It was observed that the first portion of powder

was very black and clung together like lamp-black or soot, while the latter portion of the sample, produced from breaking the harder parts of the original coke, was a dark-gray free-flowing powder. The contrast was quite marked until all the samples were mixed thoroughly before use.

Although no lower size limit was set, frequent sieving and light grinding were used to produce coke with a high proportion of particles just under the stated maximum size. A size analysis of the -100 mesh sample is given in table II.

Table II

Size Analysis of -100 Mesh Sample

-100 B.S. mesh	100 wt %
-200 "	20 "
-350 "	5 "

All coke samples were dried overnight in an oven at 110°C before use.

3.1.2 Pitch:

For the manufacture of briquettes, coal tar pitch of softening point 75°C was used. This pitch was obtained by Palmer from the Christchurch Gas Company for his work (4) and for this work it was reground by passing it once through the laboratory hammer mill. 95% then passed through the 350 B.S. sieve.

3.2 Powder Results

3.2.1 Treatment:

To examine the effect of heating on the bulk density of the coke powder, 15 gm of powder of each sample size were placed in an alumina crucible and all four crucibles heated together to 1400°C in the laboratory muffle furnace. The crucibles were placed in the cold furnace and the

temperature was then raised to 1400°C in two hours. The temperature was held at 1400°C for one hour, and then the furnace was allowed to cool overnight with the crucibles still in position.

3.2.2 Change in tapped bulk density of powder on heating:

The top ¼" layer of coke in each crucible was rejected as this may have been contaminated by oxidation in the furnace. The remainder of the sample was poured into a standard 25 ml measuring cylinder and the volume noted after tapping until no further decrease in level was observed. The density was computed from the mass of the sample and the tapped volume. The bulk densities of the unheated samples were also found, using the same sample size as the final sample to aid comparison.

The densities obtained are plotted on graph I, and show a slight increase in density for decreasing particle size, but no significant change on heating. The sample size was 9 ml.

3.2.3 Pressed density of powder:

The densities of the powders were measured by placing a weighed sample (about 5 gm) in the die of the press that was later used for briquetting. With a pressure of 2000 psi on the powder, the length the plunger projected from the top of the die was measured, using an internal gauge and a micrometer. From this length and the dimensions of the die, the volume was calculated. The densities found are given in table III and graph II.

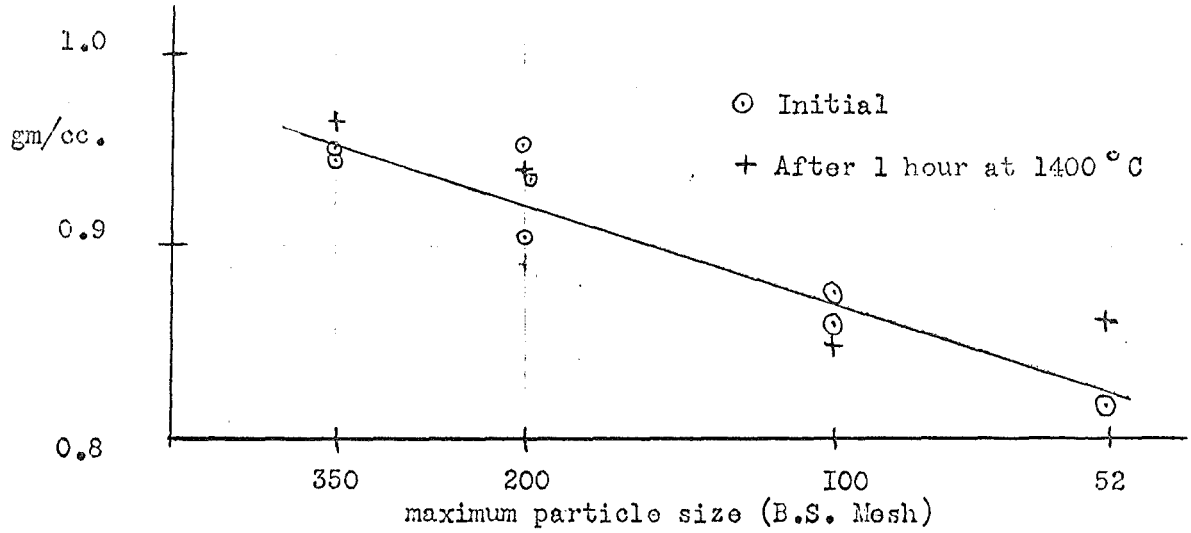
Table III

Powder Density at 2000 psi

mean particle size B.S. mesh	density unheated	density after heating
-50	.964	1.09
-100	.992	1.110
-200	1.084 .996	1.190
-350	1.115 1.108	1.247

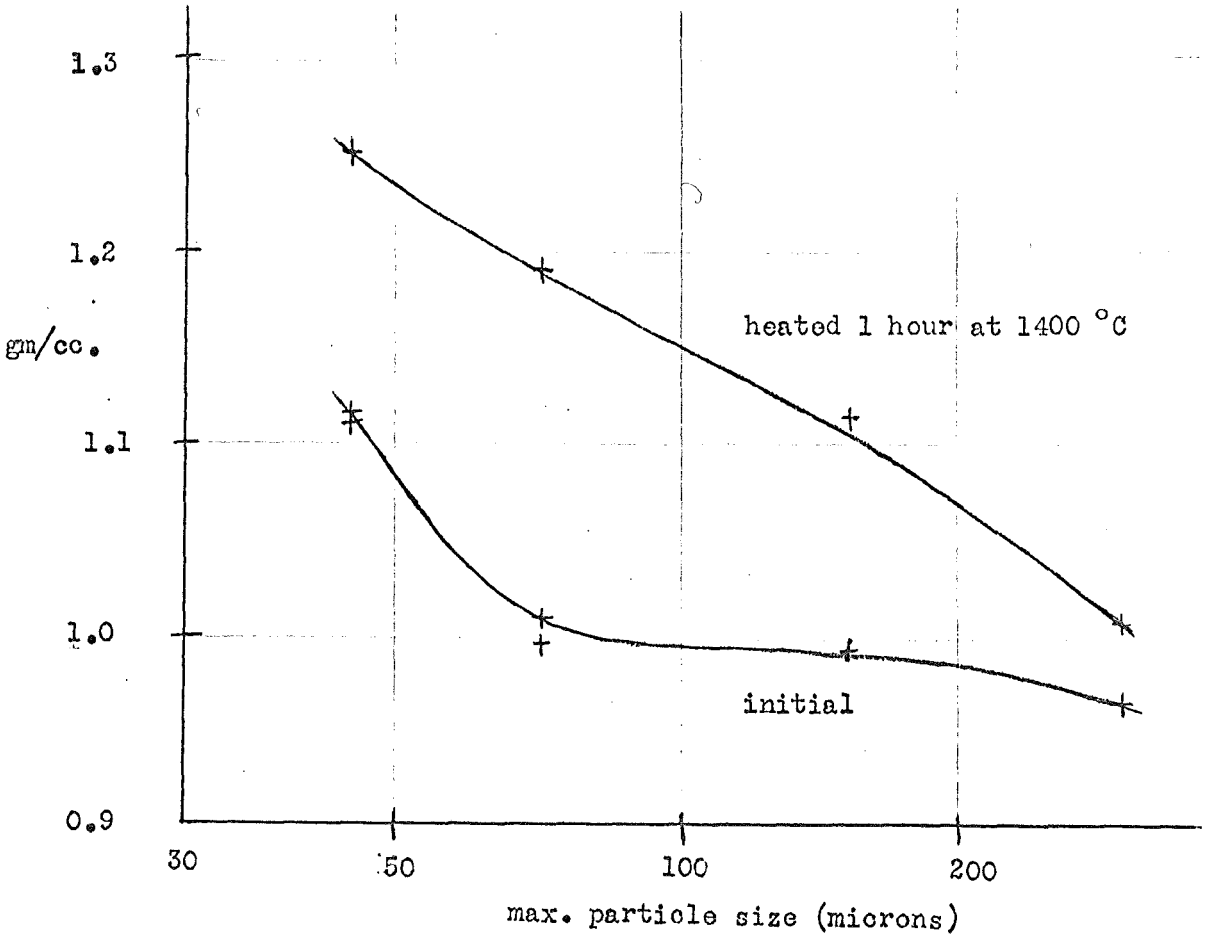
GRAPH 1

TAPPED BULK DENSITY OF POWDER



GRAPH 2

BULK DENSITY OF POWDER AT 2000 p.s.i.



In contrast to the results for tapped density, these results show an increase in density on heating as well as an increase for small sized fractions. The results from after heating show a smooth curve while those from before heating show little change in density for sizes down to 200 mesh, and a large change after this. The pressed density of the two samples was redetermined, using a different part of the powder sample and a different die. Both values are plotted on the graph. This repeat gives an indication of the accuracy of the method and confirms the occurrence of high density for the -350 mesh sample.

3.3 Briquette Results

3.3.1 Briquetting Conditions:

All briquettes were manufactured by mixing one part of pitch with nine parts (by weight) of coke powder with a mortar and pestle to give a free-flowing mixture without lumps. A new die was made to fit in the hydraulic press used by previous workers (3,4). About 12 gm of mixture was inserted in this and the die heated to 150°C, while the pressure was held at 2000 psi. The temperature and pressure were held constant for at least five minutes. The die was then allowed to cool, still under pressure. The temperature was measured using a thermocouple inserted in a hole in the plunger of the die to within ¼" of the charge.

The earlier briquettes were ejected from the dies at 50°C while the latter were ejected at 100-120°C when the briquette was quite plastic, as this temperature is above the softening point of the pitch (75°C). The effect of ejection temperature on the diameter of the briquettes is given in table IV. The internal diameter of the die was 1.023".

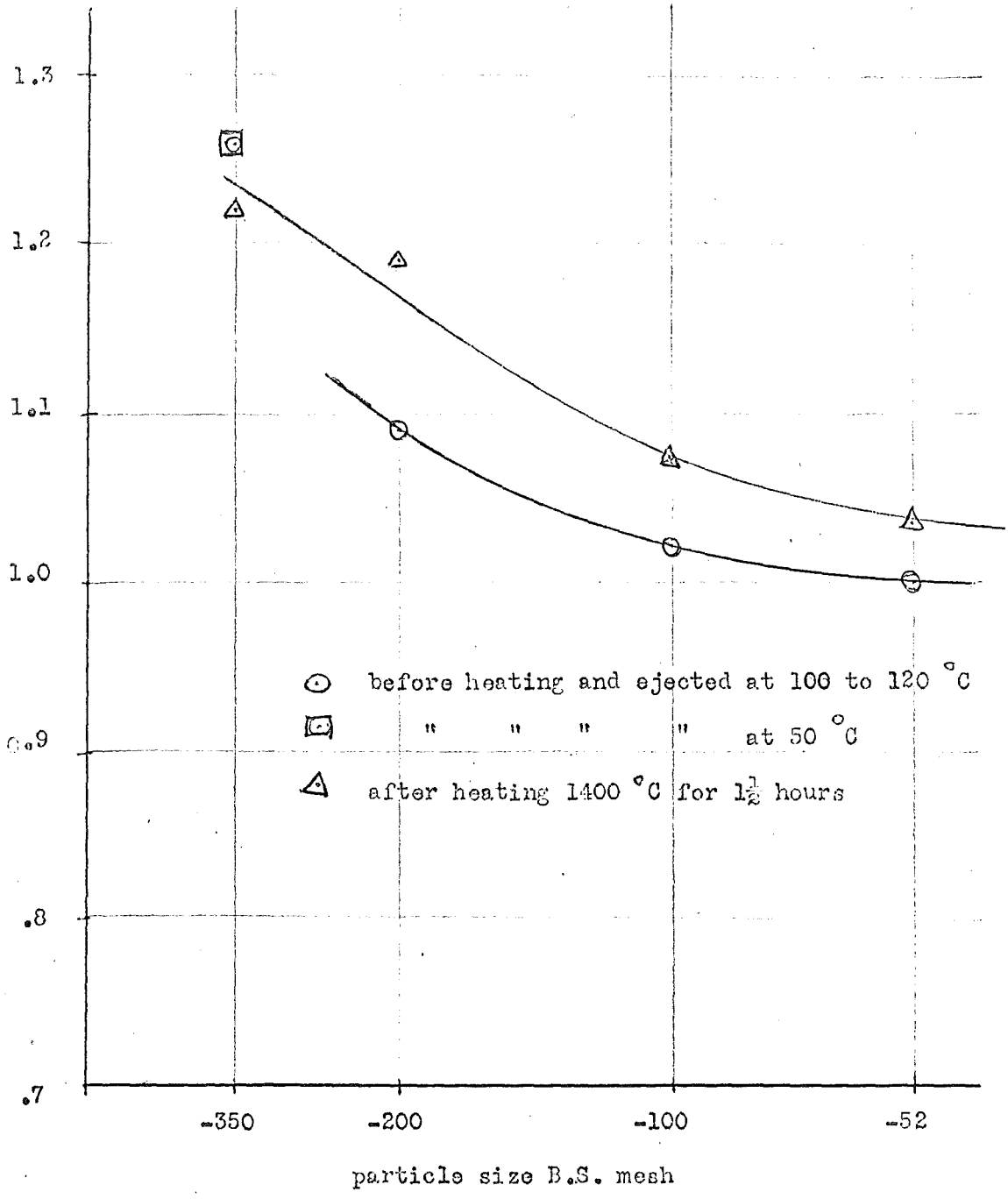
Table IV

Temp. at which briquette ejected	Diameter	Increase in diameter from die
50°C	1.026"	.003"
110°C	1.029"	.006"

In both cases the briquette tended to stick to the parallel faces of the die. When cold, the briquettes formed were too hard to be

GRAPH 3

APPARENT DENSITY OF BRIQUETTES



scratched with a fingernail. No trace of the pitch binder could be seen on examining them under a microscope.

3.3.2 Effect of heating on briquette dimensions and weight:

The briquettes were heated for an hour and a half at 1400°C in crucibles packed with powdered coke. During this treatment the briquettes retained their shape and became much harder. The briquettes decreased in weight by between 7.5 and 8.2%. They also decreased in length and in diameter by 4-6% so that the decrease in volume was about 12%. It was desired to measure the change in density during heating, but the large decreases in both volume and weight were of the same order, so that the density change lost significance when compared with them. However, the densities of some of the briquettes are plotted in graph 3.

3.3.3 Standard bulk density determinations:

Sixty grams of briquettes of particles from each size range were made and heated at 1400°C for 1½ hours. The briquettes were crushed with a hammer and the fraction -7 to +14 mesh screened out. The bulk density of this fraction was determined in a 50 ml measuring cylinder. 60 gm of briquettes gave approximately 25 gm of this size fraction which after being tapped occupied a volume of about 45 ml. The results for each size range are given in table V and plotted in graph 4.

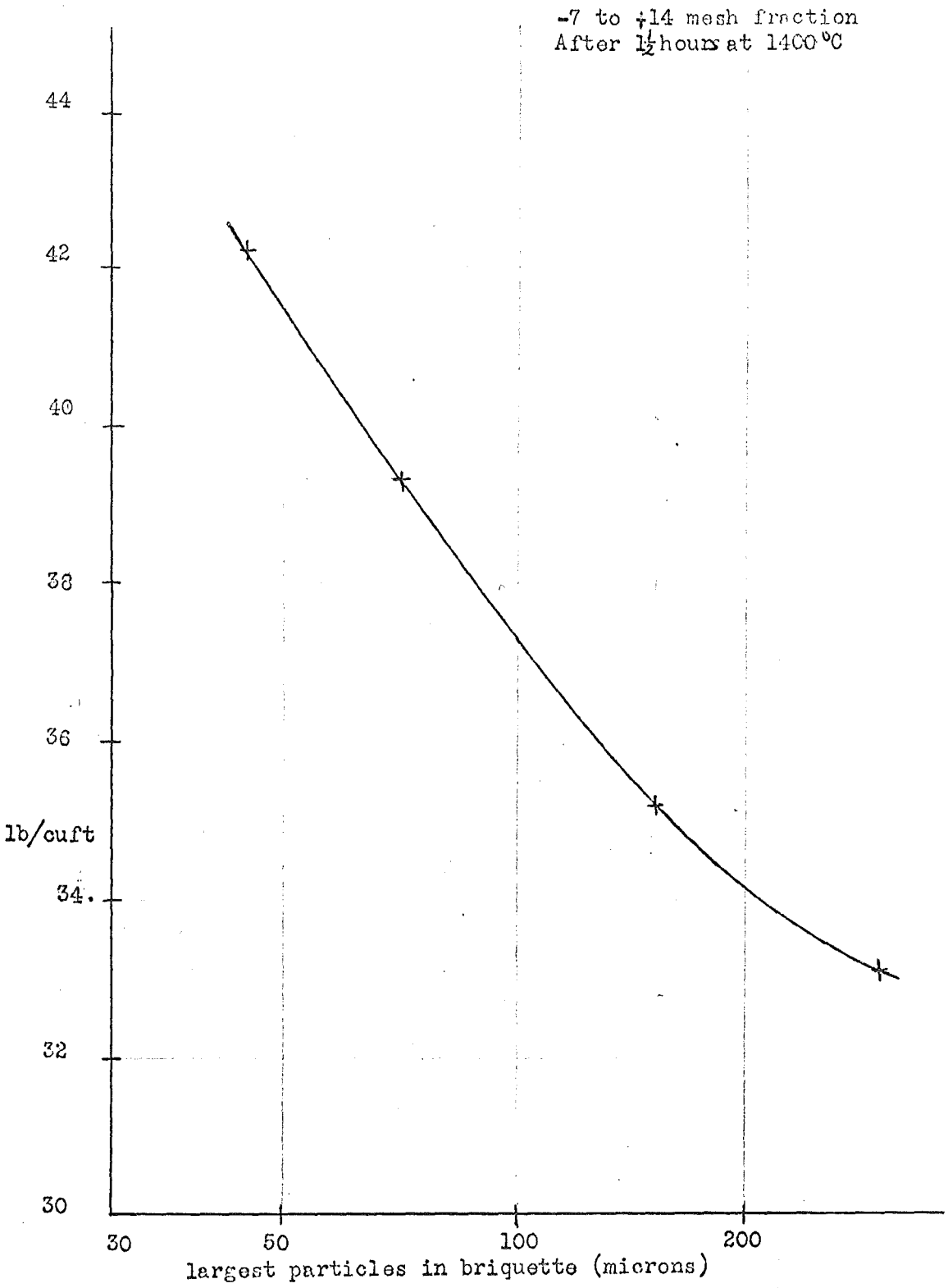
Table V

Tapped bulk density of -7 to +14 mesh material

From briquette of max. particle size	Density gm/cc	Density lb/cu.ft
-50 B.S. mesh	.53	33.0
-100	.56	35.0
-200	.65	39.3
-350	.68	42.2
Original coke	.35	20.6

GRAPH 4

BULK DENSITY OF CRUSHED BRIQUETTES



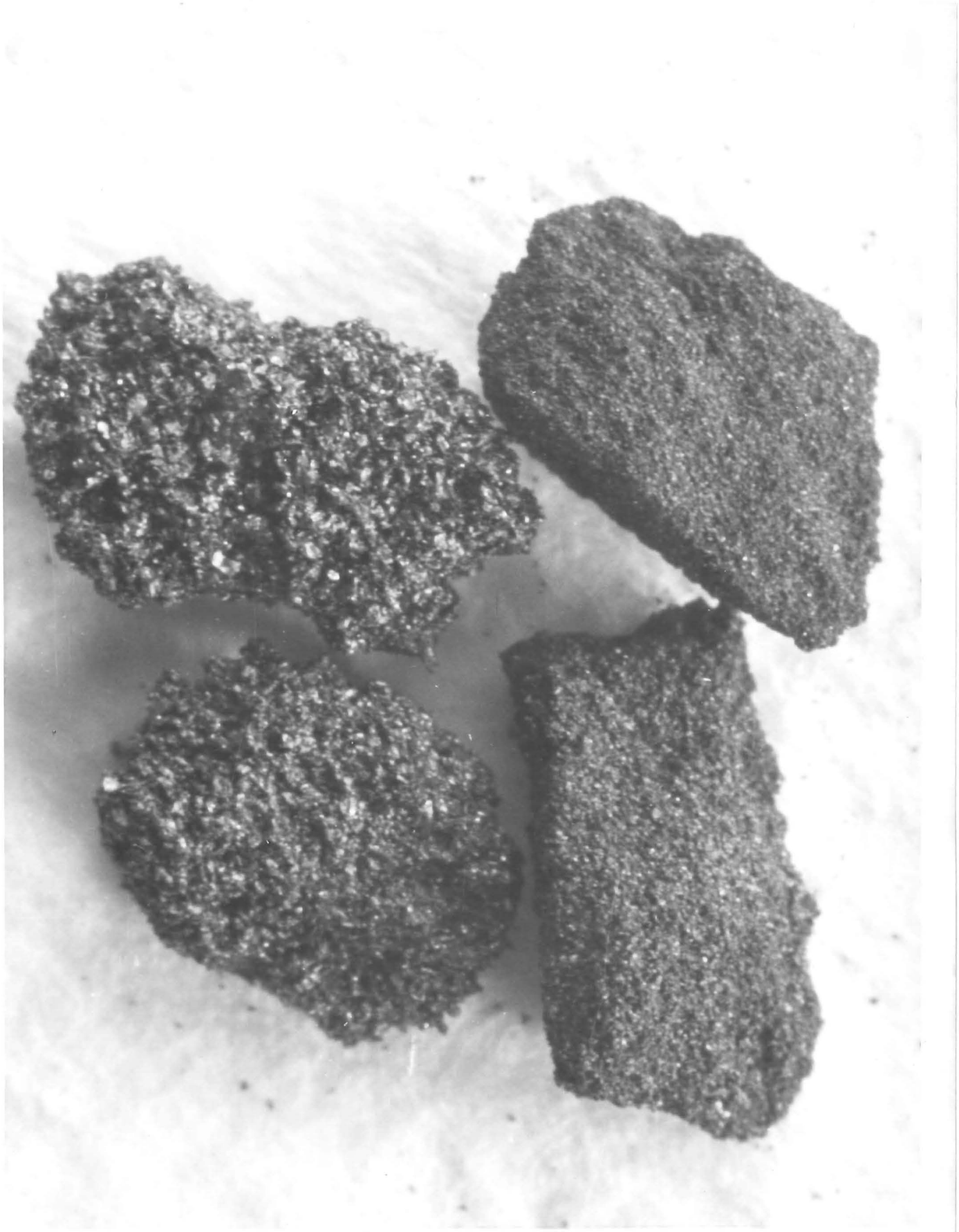
These results show a smooth increase in density as the coke is ground progressively finer before briquetting and heating.

3.3.4 Examination of briquette structure:

The briquettes were examined under a metallurgical microscope at various magnifications. No sign of the pitch binder could be seen in the briquettes. No noticeable changes in the shape or size of the particles or in their arrangement in the briquettes were observed by examining heated and unheated briquettes.

The -7 to +14 mesh chips from the briquettes after crushing were examined at low magnification. The photographs on the next two pages are of such particles. One chip from the briquettes of each powder is shown in each photograph. The photographs are both to the same scale which is given from the mm rule as 23 times. They were taken with a Pentax camera and a bellows extension.

In the photographs of the pieces of broken briquette of the -7 to +14 mesh fraction the individual particles may clearly be seen. These photographs show the tendency of particles of the larger size to form nuggety agglomerates giving the particle a rough outline compared with the particles made from the smaller sized material. This may be due to a higher proportion of pitch in some parts of the briquette giving a higher local strength. The effect of this roughness of the larger particles would be to give a lower bulk density when these -7 to +14 mesh particles were tapped in a measuring cylinder.



3.4 Real Specific Gravity of Samples

3.4.1 Method:

The real specific gravity of the coke was determined by the displacement of water. The procedure used was similar to that obtained from Comalco by Fleming (1) and to B.S. 1016.

The method is as follows.

(1) Clean a 50 ml S.G. bottle, fill with distilled water and immerse in a water bath at 20°C for one hour.

(2) Weigh bottle filled with distilled water at 20°C, empty and add 2 gm of oven-dried coke (ground to -60 B.S. mesh if the sample was not already less than this).

(3) Add 25 ml of distilled water, and couple to the bottle by means of a short piece of rubber tube, an air condenser 2 ft long and the same diameter as the bottle neck.

(4) Reflux in a glycerene bath for 30 min., then wash any scum back into the bottle with distilled water.

(5) Immerse in a water bath for one hour and weigh.

(6) The weight of water displaced by the coke then is

wt of sample + wt of bottle and water initially - wt of bottle, sample and water finally = W' (say)

Then the real specific gravity $= \frac{\text{Wt of sample (W)}}{\text{Wt of water displaced}}$

$= \frac{W}{W'}$ at 20°C.

3.4.2 Results of real specific gravity determinations:

(a) On initial coke samples

Powder size	Real specific gravity	
-52 B.S. mesh	1.74,	1.76
-100 "	1.80,	1.79
-200 "	1.87,	1.89
-350 "	1.85,	1.83

These results show a slight increase in specific gravity from the -50 to the -200 sample, then a slight drop to the -350 sample. Real specific gravity determinations appear to be repeatable to within 2%.

(b) On samples after being heated 1 hour at 1400°C as powder

Powder size	Real specific gravity
-52 B.S. mesh	2.05
-100 "	2.08
-200 "	2.08
-350 "	2.05

These results show the final real specific gravity to be independent of the particle size heated and to have increased during heating from about 1.85 to 2.06.

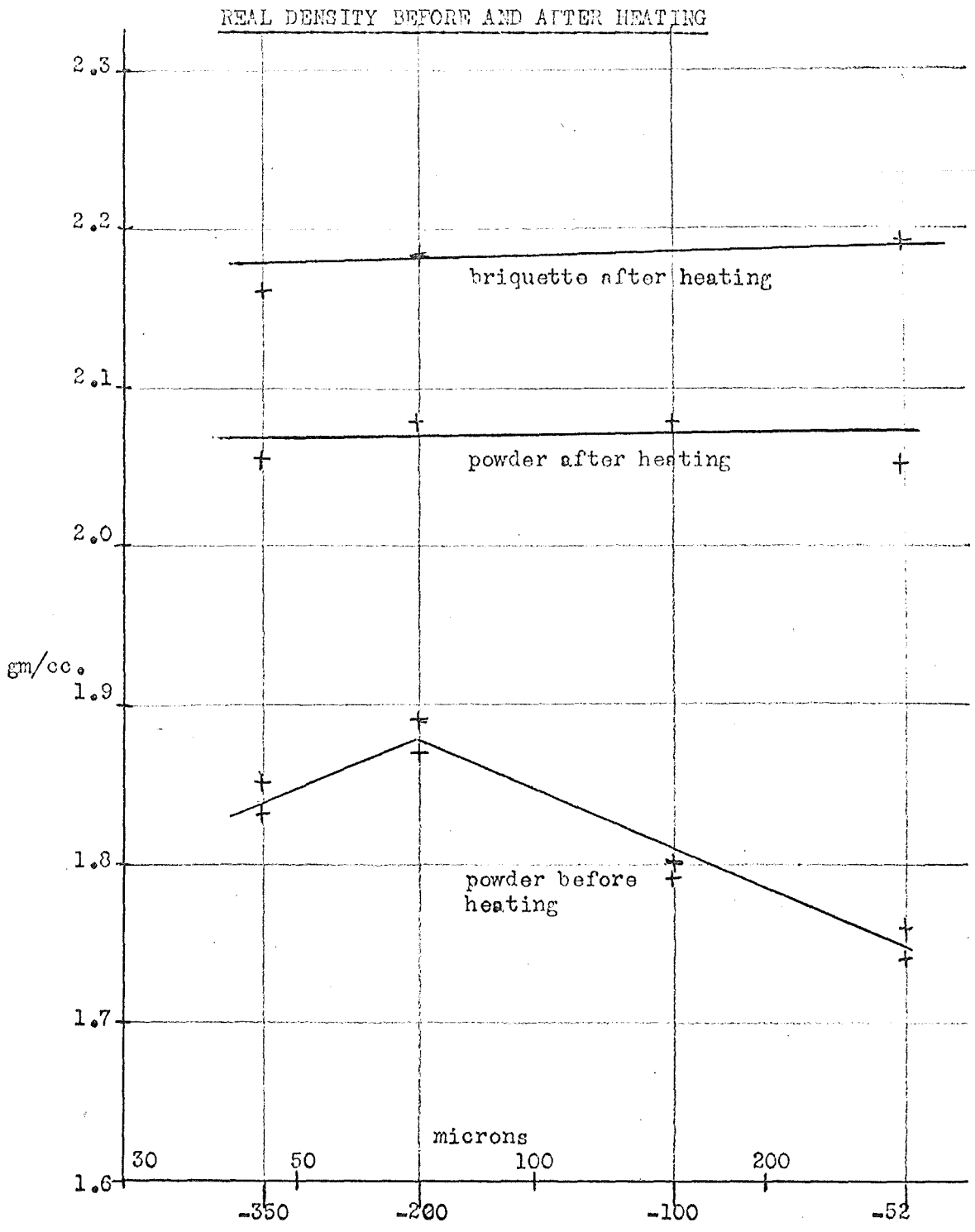
(c) On samples after being heated 1½ hours at 1400°C as briquettes

Powder size in briquettes	Briquette ground to	Real specific gravity
-52 B.S. mesh	-60 B.S. mesh	2.19
-200 "	-60 "	2.18
-350 "	-100 "	2.15

Heating for 1½ hours in this case as compared with 1 hour in case (b) was considered to have no effect on the final real specific gravity obtained. The heating time was increased for the briquettes because larger crucibles were used and the time for the centre portion of them to reach the required temperature would therefore be greater. The results show that a greater real specific gravity was obtained by briquetting the powder and heating, than by heating the powder not briquetted.

The real specific gravities are plotted on graph 5.

GRAPH 5


REAL DENSITY BEFORE AND AFTER HEATING
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
gm/cc.
briquette after heating
powder after heating
powder before heating
microns
30
50
100
200
-350
-200
-100
-52
particle size B.S.mesh

4. DISCUSSION

4.1 Real Specific Gravity

The real specific gravity determinations were repeatable to within 2% with the experimental technique used. The main limitation on the method was that some of the coke powder always floated on the water surface and consequently it was difficult to get the density bottle completely full of water without losing any of this suspended coke. As there was only 2 gm of coke in the density bottle, the loss of a small amount would result in large errors in the value for the final density.

The average value for the real specific gravity of the heated powder of 2.06 is in agreement with Fleming's results and with those of Dr Stott at the School of Mines, for the temperature used. It has also been found at the School of Mines that the specific gravity obtained by heating this coke is independent of the time at the final temperature for times up to several hours. Thus the higher values of specific gravity obtained from the crushed briquettes could not arise from the slightly longer heating time. This increase in density must, therefore, arise from the briquetting of the coke before it was heated. Pitch is less dense than the carbon forming the coke so that the only way for the pitch to increase the real density is for it to fill cavities not filled with water in real density determinations. This implies that the pitch diffuses into cavities that are sealed to water or that pitch "wets" coke particles much better than water and is consequently filling smaller cavities than the water was able to. This could also explain why no pitch was observed coating the particles of the briquette when they were examined under a microscope before and after heating. With good "wetting" of the coke surface, particles would be stuck at the points of contact rather than buried in a layer of pitch. This effect of increased real density on briquetting may be controlled by the temperature at which the briquette is formed.

From graph 5 it can be seen that the real specific gravity obtained is independent of the particle size heated. As the real specific gravity is a measure of the density of the micro-structure of the coke it follows that the micro-structure does not become any more dense when

heating small particles than when heating larger ones to the same temperature. Consequently any increase in the bulk density of small particles is greater than the increase of larger particles for the same final temperature is not due to differences in the micro-structure between the two sets of particles.

4.2 Discussion of Bulk Density of Powders

An increase in the real density of the powder particles does not necessarily give a corresponding increase in the bulk density of the powder, although it may do so. The density of the micro-structure may be increased by increasing the size of the larger pores and this would give no increase in bulk density. Alternatively some of the pores may collapse on heating to give a much greater increase in bulk density than expected from real density increases. However, the results for bulk density measured in the die (graph 2) all show an increase. The curve from after heating is much straighter than the original and thus the density gain from -200 to -350 mesh particles is not so marked.

Allan (3) showed that the tapped and pressed bulk densities are similar for 7 to 14 mesh particles. This report shows, in graphs 1 and 2, that for fine powders very different results are obtained. The pressed densities are 10% higher than the tapped densities. This may be because of the small sample size used. From graph 1 it can be seen that no increase in density on heating was measured by tapped densities, even though the same sample size was used for the determination of tapped density before and after heating. The sample size used was small, because the small crucibles used limited the amount of coke that could be heated in one run. This gave quite large errors in the determination of density, but repeats of the determinations were sufficiently close to original values to conclude that the density increase, measured in the die, did not occur when measuring the tapped bulk density. Because of this, two other suggestions of the cause of this increase in density are made. These are:

(1) Heating makes the particles more graphite-like in structure and this gives better lubrication between particles and thus they pack better.

(2) Heating causes the particles to become more brittle and thus under pressure small protuberances are brushed off the particles.

4.3 Discussion of Briquette Results

The decrease in volume of a briquette was found to be of the same magnitude as the decrease in volume of a large piece of coke formed at 900°C and heated to 1400°C in an inert atmosphere. This volume change was therefore considered to be from the usual densification process that occurs on heating coke. That this volume change depends on the coke particles is confirmed by Yeow who found no change in volume on heating briquettes to this temperature of 1400°C when his briquettes were made from coke previously heated to 1400°C, then ground. Yeow found that the loss in weight on heating a briquette was 4% for a range of particle sizes and proportions of pitch. The loss in weight in the experiments in section 3.3 was 8%, and so the additional 4% must result from volatiles being driven from the coke. This shows the initial coke contained a high proportion of tar.

The briquettes formed in these experiments were strong. This is in contrast to Allan's report where he stated his briquettes were soft and could easily be scratched with a fingernail (3, p.12). The only difference in procedure which could account for this hardness is that in this work the briquetting temperature was 150-160°C while Allan used 100-105°C. It is suggested that the strength of briquettes formed at different temperatures be studied, as strong briquettes will give greater strength to the final electrodes. It was found that slight oxidation during heating produced soft briquettes as this occurred in one furnace run and the affected briquettes were rejected. The most satisfactory method of crushing the briquettes was to place them in a steel tray and pound them with a three-pound hammer. Frequent sieving sorted the -7 mesh fraction for bulk density determinations. The briquettes were not damaged by being dropped on the floor.

Graph 4, the graph of standard bulk density, shows a smooth increase in the density of the -7 to +14 mesh fraction with decreasing particle size in the briquette. The particle size is plotted on a log scale.

The curve shows no sign of tending to a maximum density for small particle sizes. This shows that in the size range considered there is no critical size below which further densification does not occur. The final value of 42 lb/cu.ft for -350 mesh coke is higher than the value of 40 lb/ft obtained by Allen, perhaps because the briquettes crushed in this case were some 3% more dense than his. A slightly larger sample size was also used. The lower end of graph 4 appears to tend to Fleming's value of 30 lb/cu.ft from briquettes made of -7 mesh Stockton coke.

The experiments carried out show the main densification of the coke in the process investigated occurred during the fine grinding and briquetting. This density increase is greater for smaller particles. Heating the coke produced an increase in real density which gave less increase in the apparent briquette density. This in turn gave an increase in the -7 to +14 mesh bulk density. This increase in density for heating is almost independent of particle size. It is not completely independent, probably because of the influence of heating on particle packing through particle shape and lubrication.

5. CONCLUSIONS

It has been confirmed that high density coke may be produced by the fine grinding, briquetting and heating of coke from Stockton No. 2 - drive A coal. The relationship between the particle size and the final bulk density produced has been shown to be a smooth curve reaching 42 lb/cu.ft for -350 mesh coke powder and with no sign of an upper limit to bulk density for particles of smaller sizes.

It was also found that the briquettes produced with 10% pitch were extraordinarily strong. The real specific gravity of the coke was found to be independent of the particle size heated. However, the real specific gravity obtained after heating the briquettes was greater than that obtained after heating the powdered coke to the same temperature. The reason for this effect is not known. The bulk density of coke powder has been found to increase with decreasing particle size as well as during heating at high temperatures , when measured at pressure in a die.

Projects Carried Out in the Chemical Engineering Department on Stockton Coal

1. A. K. Fleming, "Electrode Carbon from Stockton No. 2 Coal", 1962.
2. G.J.K. Packer, "Investigation of Properties of Stockton Coal, for use in electrodes for the aluminium industry", 1963.
3. R. A. Allan, "The Bulk Density of Coke from Stockton No. 2 Block Coal", 1963.
4. E. R. Palmer, "Graphite from Stockton No. 2 Coal by High-temperature treatment", 1964.
5. J. G. Foulds, "Pitch Binding of Electrodes for Aluminium Production", 1964.
6. Y. L. Yeow, "Effect of Pitch Concentration and Coke Particle Size on the Quality of Anode Carbon Briquette from Stockton Coal", 1965.