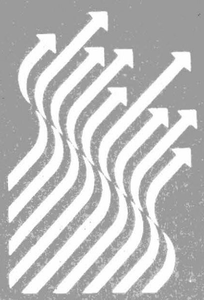
Commission of the European Communities

technical coal research

THE HIGH TEMPERATURE PROPERTIES OF COKE



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THE HIGH TEMPERATURE PROPERTIES OF COKE

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CONTENTS

Page

SUMMARY

INTRODUCTION 1

RELEVANT RESEARCH CONTENTS SUPPORTED BY THE ECSC 3

1. STUDIES OF THE RESISTANCE OF COKE TO CHEMICAL THERMAL AND MECHANICAL ATTACK 5
    1.1 General survey 5
    1.2 The effect of chemical and thermal attack on coke at temperatures below 1000°C on its subsequent resistance to mechanical stress 6
    1.2.1 Measurement of the threshold gasification temperature of coke 7
    1.3 The effect of chemical and thermal attack on coke at temperatures of 1000°C and above on its subsequent resistance to mechanical stress 9
    1.3.1 The effect of thermal treatment 11
    1.3.2 Tests involving gasification at temperatures above 1000°C 13
    1.4 General conclusions from the studies of the behaviour of cokes under chemical thermal and mechanical effects 14
2. THE INFLUENCE OF ALKALIS ON THE GASIFICATION BEHAVIOUR AND THE STRENGTH OF COKE AT HIGH TEMPERATURES 17
    2.1 General survey 17
    2.2 The effect of alkalis on the macro properties of coke 18
    2.3 The effect of alkalis on the micro and structural properties of coke 21
    2.4 The chemistry of alkali absorption 24

Page

3. RELATIONSHIPS BETWEEN FUNDAMENTAL AND HIGH TEMPERATURE COKE PROPERTIES 28
  3.1 General survey 28
  3.2 The tensile strength of blast-furnace coke 28
  3.2.1 Tensile strength of coke at high temperatures 29
  3.3 Compressive strength of coke at high temperature 30
  3.4 The effect of coke structure on fundamental strength properties 31
  3.5 Changes in strength and structural properties after partial gasification 32
  3.5.1 Tensile strength of cokes after partial gasification 32
  3.5.1.1 Tensile strength of cokes recovered from blast-furnace tuyeres 33
  3.5.2 Compressive strength of cokes recovered from blast-furnace tuyeres 34
  3.5.3 Changes in the structural properties of cokes at high temperature 34
  3.5.4 Changes in the isotropic and anisotropic structures of coke with temperature 35
  3.5.5 Structural changes in inert atmospheres at high temperature 37

4. COKE REACTIVITY 39
  4.1 General survey 39
  4.2 Relationships between various reactivity tests 40
  4.3 Consideration of various abrasion measurements after gasification or reactivity tests 41

5. PRACTICAL IMPLICATIONS OF THE RESEARCH PROJECTS 44
  5.1 Methods of preparation of coke of low threshold gasification temperature 44
  5.2 Practical considerations in the manufacture of conventional, strong metallurgical cokes of high thermal stability 47
  5.3 Production of a high quality coke for furnace use 50

Page

6. RELEVANT RESEARCH WORK CARRIED OUT OUTSIDE THE ECSC 53

7. CONCLUSIONS 56

8. RECOMMENDATIONS FOR FUTURE STUDIES 60

9. REFERENCES 62

TABLES 1 - 11 67

FIGURES 1a, 1b. 79

SUMMARY

Investigations of properties of coke which influence its behaviour at high temperatures, using tests which in part simulate conditions at the blast-furnace bosh and tuyeres, have been undertaken in a number of research projects carried out with financial assistance from the Coal and Steel Directorates of the ECSC. The reports of these studies are considered in this synoptic report.

The principal features studied in relation to the behaviour of coke at high temperatures have been the resistance to thermal shock, resistance to attack by oxidizing gases, the influence of alkali and the effect of these parameters on the resistance of coke to mechanical stress. In the majority of the work, changes in the mechanical resistance of coke have been considered after subjecting it to the effect of the various parameters. The scale of the tests has varied from the examination of coke of similar size to that used in practice, to bench scale work on small samples of small particle size.

In a number of the projects, the condition of the coke resembled that of coke which had passed down the blast-furnace shaft and comparisons of such coke could be made with coke which had been withdrawn from furnace tuyeres.

Up to temperatures of about 1400°C (the maximum generally achieved) cokes are slightly weakened by thermal effects rendering them somewhat more susceptible to subsequent breakdown by mechanical forces. Effects of oxidizing gases considerably increase this tendency.

Investigations were made of the effect of absorbed or circulating alkali in the vapour form upon the high temperature properties of coke. It was demonstrated that alkali effects considerable penetration into the coke structure, strongly increases its rate of reaction with oxidizing gases and enhances coke degradation. The effects of other forms of stress on the coke

are largely swamped by the effects of alkali, which, at present, can only be controlled by changes in blast-furnace burdening and by slag chemistry and slag volume.

Studies were made of changes in the fundamental properties of coke after the various methods of attack. In particular, compressive strength, tensile strength, pore and pore wall configuration and the mosaic structures of cokes were examined. The greatest changes in these properties were again noted after chemical attack or gasification of the cokes, and the influence of alkalis was also observed.

A survey was made of the various reactivity tests used in different projects and comparisons between the results of these tests were established. It was shown that the tests had a general tendency to place a series of cokes in the same order of reactivity, irrespective of the extent of attack on them.

Tests which involved a measurement of the loss in mechanical strength after reaction, were found to provide a more meaningful guideline to the behaviour of coke in practice.

An evaluation of the practical significance of the work was made and it was shown that some of the findings are restricted in their application under present conditions of coke making.

Due to the limited amount of available evidence, little progress has been made in relating high temperature coke properties to the nature of the parent coal.

Recommendations for future work have been suggested.

INTRODUCTION

It remains true, in 1984, that throughout the world, by far the largest proportion of pig-iron production is by the traditional blast-furnace process, where a ferruginous burden is reduced with metallurgical coke at a high temperature.

The blast-furnace process, which began in Coalbrookdale in Shropshire in 1709, when Abraham Darby produced pig-iron at the rate of three tons per day, using about 4 tons of coke per ton of pig-iron(1) has grown to a vast world wide undertaking, where furnaces are now in operation which are capable of producing at least 10,000t of pig-iron in 24h, using approximately 430-450 kg of coke to produce each tonne of hot metal.

The last twenty-five years have witnessed the most rapid developments in blast-furnace technology and in iron making.

The size of blast-furnaces has increased from 700 m^3, a typical size twenty-five years ago to well in excess of 4000 m^3 for example in many furnaces in Japan and Europe, whilst in the U.S.S.R. the blast-furnace at Krivoi Rog is reported to have a working volume in excess of 5000 m^3. The use of high top pressures, continuous charging by distributing devices such as the Paul Wurth top and higher blast temperatures have all contributed to more efficient performance and to a reduction in coke requirements.

But, perhaps one of the most significant developments has been the gradual realisation of the importance of the condition of the furnace burden. In 1960, it was still common practice to charge furnaces with a mixture of roughly screened rubble ore and coke of a wide size range and under these conditions, in smaller, less efficient furnaces, coke rates of 700-750 kg/tonne of hot metal were not uncommon. At the present time the size and quality of both the ferruginous material and the coke are carefully controlled and the benefits from this procedure are manifestly apparent.

In the lower parts of the furnace, coke remains as the only solid material present at temperatures over approximately 1400°C. The furnace permeability, and its smooth operation are thereby to a large extent controlled by the condition of the coke in the lower part of the furnace. In particular, the size, size distribution and strength of the coke are of great importance in the bosh and the melting zone of the furnace and higher up the blast-furnace shaft, the chemical reactions taking place between coke and oxidizing gases and the influence of alkalis present in the furnace affect the condition of the coke when it reaches the lower furnace regions.

It is because of this increasing awareness of the importance of coke in furnace operation and of the high proportion of the overall cost of iron-making attributable to the cost of the coke, that considerable work in recent years has been directed towards a study of those properties of coke which influence its behaviour in practice.

From such studies, it has become apparent that investigations of coke properties at ambient temperatures do not provide the complete data to explain the factors which govern the behaviour of coke at high temperatures. Attempts to relate to blast-furnace performance, those properties of coke, such as strength and size, which can be readily measured at normal temperatures have enjoyed limited success, often within restricted circumstances. It is because of this situation that considerable attention has been directed, in more recent years, to studying the behaviour of coke at high temperatures under conditions which attempt to simulate, as far as possible, some of the conditions which exist in furnace operation.

Several research projects within this general field of the study of the high-temperature properties of coke have been supported in recent years by funding from both the Coal and Steel Directorates of the ECSC. A majority of these studies are now complete and it is the purpose of this synoptic report to review this work, to attempt to establish conclusions from it, to consider the technological and economic implications of these conclusions and to point out where appropriate, areas where there is reason or need for further investigation.

RELEVANT RESEARCH CONTRACTS SUPPORTED BY THE ECSC

The subject matter of the individual research contracts may be conveniently divided into a number of groups, where similar topics have been examined by various research organizations. These groups, and the individual topics of research work within each group, are listed below.

1. STUDIES OF THE RESISTANCE OF COKE TO CHEMICAL, THERMAL AND MECHANICAL ATTACK.

1. Research project 7220-EB/113. Bergbauforschung GmbH. The estimation of coke strength after reaction with carbon dioxide. (2)
2. Research project 7220-EB/121. Bergbauforschung GmbH. The strength properties of coke under simulated blast-furnace conditions. (3)
3. Research project 7220-EB/304. Cerchar. Manufacture of a special coke with a low threshold of reactivity. (4)
4. Research project 7220-EB/305. Cerchar. Characteristics and features of formed coke. (5)
5. Research project 7220-EB/314. Cerchar. Characterisation of blast-furnace cokes (classical and formed cokes). (6)
6. Research project 7220-EB/407. CSM. Evaluation of the properties of coke at high temperature in relation to its behaviour in the blast-furnace. (7)
7. Research project 722-EB/811. NCB. Thermal stability of metallurgical coke. (8)
8. Research project 7220-EB/816. NCB. Bulk reactivity of coke. (9)
9. Research project 7220-EB/818. BCRA. Studies of the mechanical and chemical properties of coke at high temperatures. (10)

2. THE INFLUENCE OF ALKALIS.

1. Research project 7220-AA/307. Irsid. The influence of metal alkalis on the mechanical properties of coke at high temperatures under blast-furnace conditions. (11)
2. Research projects 7220-EB/815 and 7220-EB/821. The University of Newcastle-upon-Tyne. Fundamental studies of the formation, structure and reactivity of cokes as related to blast-furnace operation. (12) (13)

3. Research project 7220-EB/822. NCB. The influence of alkalis on the thermomechanical size stability of coke. (14)
4. Research projects 7220-AA/801 and 7220-AA/802. BSC/BCRA. The degradation of coke in the blast-furnace. (15)

3. RELATIONSHIPS BETWEEN FUNDAMENTAL AND HIGH-TEMPERATURE PROPERTIES OF COKE.

1. Research project 7220-EB/807. The University of Newcastle-upon-Tyne. The formation, structure and gasification of metallurgical coke. (16)

See also references 6,8,10,11,12,13, and 15.

4. COKE REACTIVITY.

See references 6,9,10 and 15.

5. PRACTICAL IMPLICATIONS OF THE RESEARCH PROJECTS.

See references 4,5,6,7,8,10, and 15.

1. STUDIES OF THE RESISTANCE OF COKE TO CHEMICAL, THERMAL AND MECHANICAL ATTACK

1.1 General survey

In blast-furnace operation, there are two principal regions in which coke reacts with oxidising gases. One is at the tuyeres where coke is combusted with preheated air at temperatures generally considered to be of the order of 75% of the flame temperature(14) i.e. between about 1500 and 1600°C. In this region, composition and chemical properties of coke play an insignificant role in the combustion behaviour, since mass transfer effects predominate(17) and coke size is the parameter of greatest importance in relation to the conversion of coke to carbon oxides.

The second region in the blast-furnace where coke reacts with oxidising gases, is in the part of the shaft above the region in which the final reduction of iron oxides takes place. Here, regeneration of CO_2 takes place and reacts at moderate temperatures, not generally greater thanabout 1100°C with coke descending the upper part of the blast-furnace shaft to give a further, but smaller loss of carbon through the so-called solution action. This vexed question of solution loss and its implied relationship to the measurement of coke reactivity by a multitude of various laboratory tests has been the subject of a plethora of discussion over many years. In the light of more recent work(18) it may be suggested that any loss of carbon due to reaction with CO_2 at relatively low temperatures influences coke consumption in the furnace by virtue of the weakening of the coke structure, resulting in a reduced resistance of the coke to mechanical breakdown and a concentration of smaller coke in front of the tuyeres. This feature is recognised in those reactivity tests, such as the Japanese NSC reactivity test, where reaction of the coke with CO_2 is followed by an examination of the strength of the coke after reaction.

From the standpoint of its thermal behaviour in the blast-furnace coke must therefore have the ideal properties of minimum solution loss at low temperatures and high reactivity at high temperatures; two conflicting requirements. In another context almost fifty years ago Hodsman remarked that "the desirable properties of coke are mutually incompatible"(19) and this statement still holds in the present context.

The research projects surveyed in this section have had, as their principal objectives, a study of the behaviour of coke at moderate and high temperatures with the object of identifying the parameters which have the greatest influence on such behaviour, the dependence of these properties on the nature and type of coal from which the coke was made, and the significance of the results in predicting and explaining the behaviour of coke under furnace conditions. These results are considered in the following sections.

1.2 The effect of chemical and thermal attack on coke at temperatures below 1000°C on its subsequent resistance to mechanical stress.

The relevant reports of work considered within this category are to be found under references 4, 5, and 6.

The work described in these reports adopts a different approach from the other work to be considered. The underlying philosophy of the work is based on the results of blast-furnace trials and on information obtained from model studies and laboratory scale trials.(20)

These studies have drawn attention to two factors of importance in operation, namely the temperature of the thermal reserve zone and the mechanical restance of the coke at the tuyeres. It is considered that the temperature of the thermal reserve zone is controlled by the temperature at which the reaction $CO_2+C \rightarrow 2CO$ begins (the threshold gasification temperature), this temperature being dependent on the properties of the coke. Evidence was quoted from blast-furnace trials using sinter of high reducibility, that improved performance, accompanied by a reduction in the coke rate, was achieved when the temperature of the thermal reserve zone was reduced from 950-850°C.

This philosophy therefore differs from the traditional conceptionthat consumption of coke by the so called solution loss should be as low as possible and that this situation is best achieved by using a coke of low reactivity where consumption of carbon does not begin until much higher temperatures, of the order of 1000°C or above. Hence the use of temperatures of 1000-1100°C commonly employed in various coke gasification and reactivity tests.

The principal objective of the work described(4)(5)(6) has therefore been to prepare fuels of low threshold gasification temperature and to devise a test at which gasification rates become significant at the temperature where loss of weight from the coke is first detected. The rate of reaction at 1200°C is also measured. At this point it is considered that the coke has been gasified to a similar extent to that when coke reaches the furnace tuyeres and a strength test is then undertaken on the partially gasified coke.

1.2.1 Measurement of the threshold gasification temperature of coke.

The apparatus is illustrated in Figs. 1-4 of the report(5). It consists of an electric furnace capable of attaining a temperature of 1450°C, equipment for gas mixture control and a thermal balance. The temperature was controlled by a thermocouple and the balance, mounted centrally on top of the furnace, had two ranges for measurement of weight loss. These were up to 100 g with an accuracy of ±10 mg and up to 1000 g with an accuracy of ±100 mg. Continuous recording of weight loss was possible.

400 g of coke of particle size 20-30 mm was heated in an atmosphere of nitrogen to 650°C. Heating from 650-1200°C was continued at a heating rate of 200°C/h in an atmosphere of 10% CO_2 20% CO, 10% H_2 and 60% N_2, the final temperature of 1200°C in the coke being attained with a furnace temperature of 1220°C. Under these conditions all cokes attained the same temperature at the end of the test which was terminated when the weight loss reached 25% and was independent of the speed of reaction. The threshold gasification temperature could be measured to within ±10°C.

The rate of gasification of the coke was determined from the gradient of the weight loss temperature curve at the end of the test in the isothermal zone at 1200°C. On completion of the test some 300 g of coke remained, and 200 g of this material was transferred to a small abrasion drum, 500 mm in diameter and 150 mm wide perforated with 3 mm holes, where it was subjected to 500 revolutions at a rate of 50 r.p.m. at room temperature. The strength of the coke was expressed in terms of the amount of material -3 mm in size.

A considerable effort was directed towards the standardization of the parameters influencing the performance of the test, such as temperature, uniformity of heating and gas composition. The results of initial trials indicated that conventional high quality metallurgical cokes had similar values of the threshold gasification temperature which were much higher than the levels of 850-950°C considered to be desirable. This observation initiated a considerable research effort in which many parameters, for example carbonizing conditions, blend composition, preheating and the use of additives were investigated in an attempt to establish conditions for the preparation of fuels whose characteristics satisfied the required levels of threshold gasification temperature and strength after reaction at 1200°C.

Cokes with a suitable threshold gasification temperature could be prepared in many ways using long established methods of blending such as the addition of low rank coals, chars, breeze or by adjusting carbonizing conditions. Not surprisingly, history repeated itself(21) and whilst the combustion properties of such cokes satisfied requirements, physical properties were inadequate and environmental conditions arising from the discharge of low-temperature cokes were unacceptable.

The results of the abrasion tests carried out on the partially gasified cokes showed that cokes of similar characteristics at ambient temperatures had small scale abrasion indices which differed widely after gasification.

Values of the threshold gasification temperature were shown to coincide with temperatures of the thermal reserve zone and it was therefore considered that the test method simulated the gasification behaviour in the furnace and produced a material for abrasion testing of similar condition to that of coke at the tuyere level.

Difficulties were experienced when using materials carbonized at low temperatures since weight losses occurred due to the release of volatile matter between 700 and 900°C. This effect was surmounted by carrying out a blank determination in nitrogen and subtracting this weight loss from that determined in the normal test.

Evidence from the gasification of cokes prepared from blends indicated that selective attack took place where the coke had been formed from high-volatile coals and a recommendation was made that this observation should be pursued by microscopic examination as suggested by other workers(22).

1.3. The effect of chemical and thermal attack on coke at temperatures of 1000°C and above on its subsequent resistance to mechanical stress.

The research projects considered within this section are listed under references 2,7,9 where coke was subjected to chemical and thermal attack. In the work described in references 8,10 and 15 a separate study was made of thermal effects alone.

The basis of the work carried out within the various projects is similar in that there is agreement that the principal factors affecting coke degradation are gasification by reaction with oxidising gases, mechanical breakdown due to fracture under load and degradation from thermal effects. Superimposed on these factors are the catalytic effects arising from alkali circulation.

Some, or all of these factors have been simulated by the test conditions in each series of experiments. The results are considered in the following sections.

A comparison of the principal features of the methods used in the various projects is presented in Table 1. The corresponding methods of expressing the results of the work are given in Table 2. It will be noted, from Table 1, that coke particle size, sample mass, the operating temperature and the duration of the tests vary widely. In the work considered in four reports(2)(3)(8)(15) and in one method used in another laboratory(7) the coke particle size resembled that generally used in furnace practice whereas an intermediate size of graded coke was used in other work(10) and small coke of 10-20 mm in size was used in another test series(7). Sample mass varied from 0.2 to 70 kg and operating temperatures from 1000°C(8) to 1350°C(10) and 1400°C in the tests where no chemical attack was involved(8).

There was less variation in the composition of the oxidising gas, all laboratories using 100% carbon dioxide with one exception in their second series of trials where a gas mixture of 60% of of nitrogen and 40% of carbon dioxide was used(2). The duration of the tests was between 1 and 30 hours.

In preliminary trials(2) the strength of coke at ambient temperature was assessed after rotating coke at 1100°C in a micum drum but significant losses of fine material due to distortion of the drum-lid led to the abandonment of this approach. In other experiments(10) the treated coke was rotated in a refractory drum at temperatures exceeding 1300°C without serious experimental problems and a similar test method was used at temperatures of 1100°C(7). Alternatively, coke was heated in a rectangular pilot-scale oven or furnace and tested in a micum-type drum after cooling(2)(8)(15).

In an attempt to rationalise the variation in the experimental parameters a ratio, E, has been calculated. This expresses the extent of chemical attack in terms of unit weight of reaction gas (carbon dioxide), reacting with unit weight of coke in unit time (g.gas/g.coke/min). It will be observed that this ratio varies widely from 0.47×10^{-4} in some drum tests(2) to 16.4×10^{-2} in other tests(7) where 200 g of 10-20 mm coke was used. Between these extremes, values of E of 0.07×10^{-2} (8), 0.37×10^{-2} for larger scale tests(7) and 2.4×10^{-2} (10) may be calculated.

Weight losses by gasification of the coke also varied in the individual experiments. The larger scale experiments(2)(8) were prolonged until the loss of weight by gasification was approximately 20 per cent, corresponding to the general loss of carbon by gasification in the blast-furnace shaft. In passing, it may also be noted that after determination of the threshold gasification temperature(4)(5)(6) the tests also involved a similar weight loss.

In another project(7) the tests generally involved a weight loss of 12-16 per cent by gasification, though in the later stages of the campaign after a change in composition of the coal blend weight losses were about 20 per cent. Tests of a shorter duration(10) than others(2)(8) were associated with a lower weight loss ranging from 9 to 15 per cent. These values are not too dissimilar from those reported elsewhere(7) where gasification was also carried out under dynamic conditions for a relatively short period.

In each of the experimental programmes the degree of resistance of the coke to attack was determined by some form of drum test, either on the hot coke during the test, or on the coke after cooling, followed by a size analysis. Tables 1 and 2 show the variations of the basic type of test which were employed. The particle size of the coke used to measure residual strength was largely conditioned by the particle size of the original material. Such strength (or abrasion) indices varied over a wide range from those of the conventional Micum test (+40 mm and -10 mm)(2), similar indices from a small Micum-type drum(10), an index based on +10 mm coke and calculation of the harmonic mean size(8), +6.35 mm in small scale tests(7) and +20 mm in the larger scale tests also carried out in the same laboratory(7). Degradation was assessed by change in the micum slope in other work(15).

1.3.1. The effects of thermal treatment

The effects of thermal treatment without gasification were studied in three exercises(8)(10)(15). In the former report(8) bulk samples of coke were reheated to 1400°C in an inert atmosphere and measurements made of the change in coke size and the loss in weight due to reheating. In another of the projects(15) a similar approach was initially used, but subsequently the heating rate of the coke was modified to eliminate weakening due to shock heating, and the coke was charged gently to the oven to minimise mechanical breakage. Additionally, the coke was stabilised by breakage tests to bring its condition to that approaching stockline coke.

In the third exercise(10) cokes of smaller size (30-40 mm) were reheated, also in an inert atmosphere, to temperatures of 1300°C and corresponding changes in coke size and mass were determined.

Although the scales of operation were different the cokes behaved similarly in each test series. Small losses in weight were noted, partially due to the removal of volatile matter, oxygen and hydrogen, at heat treatment temperatures above the maximum coke carbonizing temperature. Decreases in ash and sulphur content were also observed, the latter being unlikely to occur at temperatures below 1200°C where the decomposition of iron sulphides begins(23). Increases in density and porosity and changes in tensile strength were recorded and the micum slope of the cokes was shown to change(15) by an amount which generally corresponded to the strength change between feed and tuyere coke in furnaces where no alkali attack occured.

Small reductions in coke size were observed and it was shown that these were influenced by the particle size of the coke(8). Expressed as a percentage of the original coke size, 60-80 mm coke was reduced in size by almost 20% and 40-60 mm coke by 10% after thermal treatment. It was considered that size reduction by the disintegration of large lumps resulting from thermal stresses would not be an important mechanism(15).

A summary of the data showing the effects of heat treatment on coke properties, is given in Table 3.

One important difference in the test procedures was that the mechanical treatment of the coke was carried out at the high test temperature in one exercise(10) and after cooling the coke in the other work. From the data it was therefore possible to make an estimate of the coke degradation forthcoming from the individual effects of mechanical and thermal processes, and from these results mechanical effects appeared to contribute rather more than thermal effects to reductions in coke strength. Thermal effects were responsible for small mass losses, of the order of 1.5 to 4.0 per cent. These losses were greater, the greater the difference between the maximum carbonizing temperature and the test or reheat temperature.

Tests carried out after reheating and cooling the coke(15) suggested that thermal treatment weakened the coke and made it more susceptible to subsequent breakage by mechanical treatment. The apparent difference between the results from the two test series(10)(15) may be a consequence of the differences in temperature at which mechanical forces were applied to the coke, or of the difference in the size of coke used.

1.3.2. Tests involving gasification at temperatures above 1000°C.

The work described in two reports(2)(9) is very similar, a mass of lump coke of a size comparable to that used in blast-furnace practice being subjected to gasification at 1000-1050°C in a pilot scale oven until at least 20% weight loss had been attained. After cooling in nitrogen, the cokes were subjected to testing in a conventional drum at room temperature. This approach provided information on the effect of chemical and mechanical attack on coke which, after reaction, simulated that reaching the tuyeres.

A comparison of the results from the two projects is not possible since information from one report is limited, the results presented being essentially a statement of the establishment and proving of test conditions and different cokes were used in each laboratory.

Certain similarities are also shown by the test procedures carried out in other work(7)(10). In each test a relatively small mass of coke varying between 2.5 and 7.5 kg was heated to 1050-1100°C in a drum in the presence of carbon dioxide and, by rotating the drum at the test temperature, subjected to mechanical stresses.

After allowing the coke to cool in an inert atmosphere, physical tests were carried out to enable changes in size and mass of the coke to be measured. Under one set of experimental conditions(10), work could be carried out at temperatures approaching 1400°C, but the lower temperature of 1050°C was eventually adopted, this being a similar level to that used in many other reactivity tests.

The extent of gasification of the coke under these conditions was less than that of the tests carried out on bulk samples of coke. It varied from 8-14 per cent (10) to 10-16 per cent(7). A few trials made at 1300°C (10) enabled a weight loss of about 23% to be achieved.

Cokes used in one series of tests(7) were all high quality metallurgical cokes. Others(10) included one domestic coke of low strength and a foundry coke. A comparison of the effects of gasification combined with mechanical treatment at high temperature is presented in Table 4.

Where comparisons are possible, the similarity of the results is noteworthy. Sixteen cokes were examined in one hot drum(7), using samples of 30-70 mm in size and weighing 7.5 kg. The mean weight loss after gasification and mechanical treatment was 14.1% and the average amount of coke greater than 20 mm in size after the test was 82.7 per cent. Using 2.5 kg of coke between 30-40 mm in size a mean weight loss, for 11 cokes, of 11.8 per cent was reported and 82.5 per cent of the coke remained above 20 mm in size after testing(10). The results from the two laboratories are therefore very similar. Bearing in mind the differences in extent of gasification and the scale of each test, mean changes in size are also not dissimilar(9)(10).

1.4 General conclusions from the studies of the behaviour of cokes under chemical, thermal and mechanical effects.

Studies concerned with the measurement of the thermal gasification temperature of coke and of the significance of this parameter upon the behaviour of coke in the thermal reserve zone of the blast-furnace were largely devoted towards establishing a reliable and reproducible test method and a consideration of methods by which the thermal gasification temperature could be reduced to the desired level of approximately 850°C, from the higher levels of 950-1050°C of conventional high quality metallurgical cokes.

The test provided new information which complemented that derived from normal physical tests and indicated that the mechanism of thermal breakage of gasified coke was largely dependent on the composition of the parent coal charge. Attention was drawn to the variable behaviour of the different structural types present in the coke matrix and to the importance of other structural parameters such as pore diameter and pore-wall dimensions.

A recommendation that a more detailed investigation should be made to establish the effect of blend composition, carbonizing conditions, the use of formed coke and unconventional methods of coke preparation was followed in later work(6). The results of these studies showed that cokes with a suitably low threshold gasification temperature could be prepared by briquetting blends of low-rank coals, wood charcoal and pitch.

Recognising that the mechanical properties of such cokes were poor, it was postulated, from the results of laboratory tests, that because subsequent loss of strength on gasification was not too severe, the reactive materials could be mixed with normal coke to initiate gasification at lower temperatures in the thermal reserve zone. Having accomplished this task, the conventional coke would remain to carry out its normal functions in the lower part of the furnace. However, it was shown that a significant quantity of the reactive coke was required to produce the desired reduction in threshold gasification temperature. It may be remarked that the considerable difficulties of uniformly mixing large quantities of two types of coke in reasonable precise amounts do not appear to have been considered either on practical or economic grounds.

The work described in the five reports(2)(7)(8)(9)(10) dealing with the measurement of the properties of cokes at temperatures up to 1400°C showed many similarities. This is not surprising, since it was universally recognised that coke degradation in the blast-furnace is the result of a combinationof thermal, mechanical and chemical attack upon the coke.

The well established effects of blend composition and carbonizing conditions on the coke properties at ambient temperature were shown to influence the high temperature properties of coke. Reaction rates with oxidizing gases were shown to be temperature dependent and effects on gasification behaviour due to the presence of mineral constituents were also shown to conform with previous evidence. Strength after gasification was not necessarily related to strength before gasification, another feature previously demonstrated in earlier work.

Irrespective of the scale of testing which varied from tests carried out on 200 g of coke, 10-20 mm in size to 70-80 kg of coke between 20 and 100 mm in size, the results of each individual project showed that the principal factor influencing coke degradation at high temperatures was that due to attack by oxidizing gases. Thermal effects alone accounted for very little coke breakage. Mechanical forces, whilst causing more breakage than thermal effects, did not reduce the strength and size of coke to the same extent as attack by oxidizing gases. These effects were size dependent.

One series of tests indicated that about 85 per cent of total weight loss could be attributed to oxidation, approximately 11 per cent to thermal effects including loss of volatile matter, moisture and sulphurous gases, and the residue of about 4 per cent was attributed to mechanical effects.

The influence of alkalis, though recognised, was not considered in the above work.

2. THE INFLUENCE OF ALKALIS ON THE GASIFICATION BEHAVIOUR AND THE STRENGTH OF COKE AT HIGH TEMPERATURES

2.1. General survey

The catalytic effects of alkalis upon the ignition, combustion and gasification of coke have been recognised for many years. A British patent dealing with the improvement in the combustibility of fuels arising from the addition of saltpetre and nitre appeared almost one hundred and fifty years ago(24), and early scientific contributions relating to the activation of coke were published some sixty years ago(25).

Activated coke was produced in the U.K. on a commercial scale prior to the Second World War and further successful commercial ventures were carried out until the demand for reactive coke declined following the widespread utilization of North Sea gas.

The principal objective was to produce a material of enhanced reactivity to oxygen at relatively low temperatures (400-500°C) and little attention was given to effects of alkali on carboxyreactivity at higher temperatures, although the effects were recognised. It is only in relatively recent years that the importance of the catalytic properties of alkalis in relation to blast-furnace operation, where the conversion of carbon to carbon oxides is fundamental to the process, have been comprehensively investigated, although Bunsen recognised the presence of alkali cyanides in furnace gases in the mid 19th century.

The basic reduction reaction $CO_2+C \rightarrow 2CO$, (in its simplest terms) is strongly endothermic and it has long been recognised in blast-furnace operation that the extent of the reaction must be controlled to prevent the excessive consumption of coke in order to maintain furnace temperatures. Hence the general requirement for coke of conventional low reactivity, as measured in laboratory tests operating at temperatures of 1000-1100°C. Low reactivity of coke is most frequently associated with cokes of high physical quality (assessed by conventional tests at ambient temperature) but evidence has been accumulated in recent years of high quality cokes performing unsatisfactorily in blast-furnaces for reasons which could not be identified with certainty.

Furnace permeability is a further factor of extreme importance in operation and the poor performance of high quality cokes was quite frequently associated with the presence of excessive amounts of small coke in the lower part of the furnace. Such an observation was made in some early tuyere sampling exercises(26), where a high quality coke of mean size approximately 55 mm, when charged produced a large amount of -25 mm material at the tuyeres. Conversely, in another exercise, a relatively poor quality coke, charged to a furnace at about 60 mm size, was found to have undergone little size reduction at the tuyeres. This difference was believed to be due to the high alkali content of the burden in the furnace operating with the strong coke. This observation indicated that the presence of alkali increased coke consumption and reduced coke size and strength.

The work considered in the various research projects has been principally directed towards an examination of the effect of deposited alkali on coke size and strength, simulating, as far as possible, the cyclic devolatilisation and condensation of alkali in furnace practice.

2.2. The effect of alkalis on the macro properties of coke.

The projects considered are found under references 7,14 and 15. They were essentially concerned with the impregnation of coke by alkali followed by a study of the resistance of the treated cokes to mechanical stress with or without heat treatment. The scale of the tests ranged from experiments carried out on coke charged to and recovered from blast-furnaces, through others using several kilograms of lump coke, to some using coke cylinders. Impregnation was carried out by absorbtion of alkali from solution or by allowing coke to react with alkali vapour at high temperature.

In one series of tests(14) lump coke was impregnated by boiling under reflux with an alkali salt and drying to produce coke of a known alkali content of up to 5 per cent of sodium or potassium. The treated coke was reheated in nitrogen for 8h. at 1050°C and a study made of its size, size distribution and resistance to mechanical breakage. As noted by earlier workers(27) the effect of the potassium was dependent on the anion with which it was combined in the alkali salt, potassium carbonate or hydroxide being more effective than potassium phosphate.

Weakening of the cokes was noted when the potassium content exceeded about 1.5 per cent; the extent of the attack being dependent on coke size, larger particles being less resistant. The extent to which alkali impregnation reduced the resistance of the coke to breakdown varied with the type of the parent coal, but no systematic relationship between coal rank and increased liability to breakdown of the corresponding coke following alkali impregnation could be established.

The weakening of the coke was attributed to two principal breakage mechanisms; an increased tendency for the coke to fracture under impact to produce an increased quantity of relatively large coke particles and a decrease in its resistance to abrasion. The abrasion product differed in its size distribution from that of the untreated coke as it contained a much larger proportion of fragmented material within the size range of 10 to 0.5 mm, but dust produced by surface abrasion alone was not significantly increased in quantity.

The reduction in coke strength due to alkali impregnation from solution was dependent not only on the anion present in the solution but also on the cation. It was shown that the effect of potassium hydroxide and potassium carbonate became more noticeable when the K^+ content exceeded about 1.5 per cent, but about 4% of Na^+ was required to produce a similar effect. It was suggested that the initial absorbtion of the alkali took place by preferential reaction with mineral matter and that this action generally accounted for the absorbtion of about 1.5% K. Above this level, the potassium reacted with the coke carbon to produce the observed effects on coke size and strength.

To test this hypothesis cokes were prepared from blends of a strongly coking coal and a high volatile caking coal containing additions of various inert materials. Three per cent of silica, kaolin, calcium carbonate and washery discard were incorporated in individual coal charges and the effect of four per cent addition of breeze was also examined. Each coke was impregnated with various amounts of potassium up to about 3 per cent and then subjected to the standard heat treatment and physical test procedure.

The incorporation of the additives in the blends prepared from the type 433 coal had little effect on mean size; indeed, such tendencies as were observed suggested that the presence of the additives, particularly kaolin, slightly increased the resistance of the coke to fracture. Cokes prepared from the high volatile coal showed no significant change in their percentage size reduction, except where the blend contained breeze and the coke was weaker.

From this evidence it was concluded that the effects of additional mineral matter did not support the contention that the threshold value of about 1.5 per cent potassium represented a level below which mineral matter preferentially reacted with potassium and above which the reaction was with the coke carbon.

These observations are interesting, but are not necessarily representative of behaviour in practice, where the mineral substances are not present as discrete entities, in a more or less pure form, but exist principally as clay minerals which are converted into silicate glasses and quartz in coke(15). In relation to blast-furnace operation, account must also be taken of effects of slag chemistry in relation to the release and recirculation of alkali.

Nevertheless, experiments described in two reports(14)(15) have shown that the alkali in impregnated cokes can be separated into a free and a fixed form. In one case(15), experiments were conducted on cokes extracted from tuyeres, where the free alkali was defined as that associated with the coke carbon and the fixed alkali as that incorporated in the coke mineral matter. In the other case(14) where vapour impregnated coke cylinders were reheated to 1400°C before analysis of the various forms of potassium, a distinction was made between extractable alkali and that combined with carbon and mineral matter.

From the evidence(15) it was demonstrated that the change in abrasive properties between feed cokes and tuyere cokes, assessed by the increase in the micum slope of the tuyere cokes was generally related to the alkali associated with the coke carbon. Vapour impregnated cokes exhibited a general weakening of their structures at temperatures above 1000°C when release of alkali could be detected, but there was no evidence to suggest that the alkali reacted preferentially with coke carbon.

A further report dealing with the studies of the effect of alkali on the macro properties of coke(7) used graded coke, 9.5-11.2 mm in size. 300 g of coke was heated in a metal box, subdivided so that the vapours from a mixture of potassium carbonate and graphite could pass through the bed of coke at 1000°C. After 60 min treatment the contents of the box were cooled by a nitrogen stream and the treated coke was subjected to a grinding process whereby the energy required to crush 1 g of coke was measured. The particle size of the ground coke is not stated.

It was shown that the mean value of the energy required to crush 1 g of coke containing about 1.1% of potassium was reduced from 32.1 to 31.0 J/g. All cokes examined behaved in the same way and the results clearly indicated that absorbtion of the alkali vapour resulted in a weakening of the coke.

2.3 The effect of alkalis on the micro and structural properties of coke.

Reports considered in this context are as detailed in 2.2 with the addition of references 11,12 and 13.

A comprehensive study of the effects of alkali on the gasification behaviour and the mechanical properties of coke has been made(11). The coke samples used were in the form of cylinders, usually 15 mm in length and 10-15 mm in diameter, prepared by drilling representative coke samples. To minimise the spread of results, arising from the heterogeneity of the coke, gasification experiments and strength tests were carried out on between 40 and 70 coke cylinders. The conditions of the gasification experiments closely resembled those in work reported earlier(4-6), the coke being heated to temperatures varying between 950 and 1200°C in a gas mixture consisting of CO, CO_2, N_2 and H_2. Impregnation of the cokes was by means of potassium vapour produced from a mixture of potassium carbonate and graphite, at temperatures of 1000-1400°C.

The method of measuring coke strength partially followed that previously described(22)(28). The coke artefacts were subjected to both diametral and axial compression after cooling. Measurements of the elastic modules were also made.

The results of preliminary work indicated that in the presence of potassium at a level of about 1.5%, the speed of the gasification reaction was increased at a given temperature and the temperature of initial gasification was reduced by about 100-150°C. Strength measurements and small scale abrasion tests carried out on the treated coke after gasification to about 30% weight loss indicated that the surface of the coke was weakened by potassium impregnation resulting in a considerable increase in the amount of -2 mm fines produced in the small drum test. Compressive strength was also reduced, but was less affected than abrasion resistance.

Potassium was shown to react with the coke mineral matter and two types of ash, both generally having the characteristics of kaolinite were shown to readily absorb potassium.

Some evidence was presented indicating that potassium was preferentially taken up by the isotropic form of carbon in the coke.

From the results of this work, it was considered that the undesirable effect of potassium on the mechanical properties of coke after gasification appeared to be an indirect consequence of the increased speed of gasification rather than the result of specific and direct action of potassium on the coke structure. The implication of these views in relation to blast-furnace practice was considered to be related to an increased production of fines at lower temperatures and a possible increase of breakage at high temperatures due to the relief of internal stresses produced in the coke by absorbed potassium.

However, there is considerable evidence from other work which indicates that potassium penetrates the coke structure. In some experiments carried out on cokes recovered from blast-furnace tuyeres(29), it was shown that the potassium content of one coke (average value 1.80 per cent), varied from 1.50% at the outer surface, to 1.92% in the centre with a maximum value of 2.11% about 35 mm from the edge of a 50 mm particle. For a second coke, where the lump was approximately 70 mm in diameter, the corresponding values were 2.28% (average) 3.24% outer surface, and 1.26% in the centre, with a maximum value of 3.35%. In this case, the penetration was not complete, but as the potassium content of the original coke was only 0.3%, the values represented a substantial degree of attack.

Confirmatory evidence of penetration of alkali throughout a coke particle is also available from the examination of other tuyere cokes(15). Using an abrasion drum to progressively remove the surface of the cokes it was possible to show that free and fixed alkali distribution was relatively uniform throughout the coke particle.

The measurement of the tensile strength of coke artefacts has been widely adopted as a more fundamental basis for the assessment of the strength of coke structure, and the technique was employed to compare the strength of alkali impregnated coke specimens which were subsequently submitted to heat treatment, with the corresponding strength of the untreated specimens. The actual level of tensile strength of the artefact is a function of its density and its dimensions, hence the levels of tensile strength quoted for samples examined in different projects vary widely, principally due to dimensional differences, as the densities of most metallurgical cokes are similar.

Table 5 compares values of coke tensile strength measured in different laboratories for cokes impregnated with alkali, heated and cooled before testing. The results are expressed in terms of the percentage reduction in tensile strength.

The results are difficult to compare, since the conditions of impregnation, particularly the time, temperature and potassium content of the treated cokes vary over a wide range. Heat treatment temperature after impregnation is also an influential factor.

However, the results do show, quite unequivocally, that absorption of potassium into the coke structure brings about a general weakening of the material. There is some evidence that the effects are also dependent on the type of coke, and therefore on the nature of the parent coal, for example(11) where examination of impregnated coke by the scanning electron microscope has shown that the potassium vapour penetrates to the centre of the sample and attacks certain carbon textures and the interface between different textures, leading to selective breakage and loss of cohesion in the coke. Similar evidence is forthcoming from the work described in other reports(12)(13)(14) which also show the effect of mineral particles as crack initiators when subjected to the effects of alkali vapours.

Fundamental studies of the attack on coke structure by potassium have indicated the formation of intercalation compounds of potassium and carbon(13) and that the formation of such compounds also leads to a weakening of the material(30).

The general conclusion from the studies of the effect of absorbed alkali is that it results in a relatively complete penetration and weakening of the structure. The effect of absorbed alkali may be offset to some extent in laboratory tests by heat treatment, where the alkali which is vapourised is free to escape, but in practice where alkali circulates in the system it appears that the weakening effect on the coke can only be modified by changes in blast-furnace chemistry and particularly by slag chemistry.

There is no doubt that in practice, high concentrations of alkali result in the production of excessive amounts of small coke in the lower part of the furnace and an impairment of permeability.

2.4 The chemistry of alkali absorption (General conclusions)

The comparative ease with which alkali can be absorbed by lump or powdered coke, either through impregnation in vapour form or from solution, has been noted.

It has been suggested that alkali may react both with coke carbon and with mineral matter, particularly with the acid constituents of the mineral matter such as silicates. The results of earlier work(27) indicated that when coals were carbonized in the presence of alkali, (sodium carbonate), the reactivity of the coke was reduced when the ash content of the coal increased. However, this work was mainly concerned with the low-temperature oxygen-carbon reaction where rapid surface combustion was of paramount importance and coke strength was unimportant.

The hypotheses relating to the mode of reaction of alkali with coke have been tested in some of the work considered(14) and from these results it appears that no preferential absorption of potassium vapour can be detected.

An extensive survey(15) of the mineralogy of coal blends and the corresponding samples of coke, charged to and recovered from, blast-furnaces indicated, firstly that during carbonization the clay minerals present in the coal are converted into semi-refractory minerals and secondly, that the alkalis combined with aluminosilicate minerals were readily released at moderate temperatures during the conversion of the aluminosilicates to glass-type materials. This decomposition cycle was considered to initiate the reactions between ash and alkalis under furnace conditions. These observations have resulted in examination of the various forms of alkali present in the coke in an attempt to establish the nature and type of alkali responsible for the physical degradation of the coke. Alkali in impregnated cokes and in blast-furnace feed cokes has been considered to be present in free and fixed forms, the latter type being sub-divided into alkali combined with coke carbon and that combined with coke mineral matter.

The results from one series of experiments(14) in which coke was impregnated with potassium vapour at 1000°C appeared to indicate that approximately twice as much potassium was combined with the coke carbon as was combined with the mineral matter and it was concluded that no preferential action with mineral matter could be established. Results from other experiments indicated a ratio of carbon alkali to mineral matter alkali of about 1:1. From this data it was assumed that the initial reaction during impregnation took place with the mineral matter. However, this appears to be an isolated result and the general concensus of the data is that the attack by the alkali vapour is not preferentially directed towards the mineral matter.

An interesting observation was that cokes prepared from high rank coals appeared to undergo greater disintegration after alkali impregnation than cokes from lower rank coals(14). This observation is supported by the results of other work(12), where the larger anisotropic mosaics, present in cokes prepared from high rank coals, appeared to be more susceptible to alkali attack than smaller mosaic units present in cokes prepared from coking coals of lower rank.

A comparison of the mineralogy of vapour impregnated samples with coke samples extracted from tuyeres indicated that both materials retained high levels of alkali combined with carbon after being subjected to temperatures of approximately 1450°C(15). The examination of residues after various drum tests and "peeling" tests also indicated uniform distribution of potassium throughout coke particles recovered from tuyeres. It may therefore be considered that potassium vapour reacts with coke carbon at high temperatures in a similar way to the reactions which take place between potassium and graphite at high temperatures.

The results of further work(13) have conclusively demonstrated that chemical combination takes place between coke carbon and potassium. The exposure of finely ground coke to potassium vapour at a temperature of 800°C, or to potassium vapour produced by reaction between potassium carbonate and graphite at 910°C resulted in the formation of intercalation compounds of carbon and potassium. The metal penetrated the coke material to a considerable extent, diffusion through the porous structure being considered to play an important part in the reaction. An interesting observation was that the intercalation compounds did not form when the reactions were carried out in an atmosphere of carbon dioxide rather than nitrogen. The possibility of the reaction depending on the formation of an intermediate cyanide complex may be considered in this context.

Whilst it has been pointed out that the small scale tests involving the impregnation of coke by potassium vapour and the subsequent heat and mechanical treatment of such samples does not entirely simulate blast-furnace conditions, there appears to be no doubt that alkali effects considerable, if not complete penetration of coke at high temperatures; that this leads to the formation of carbon-potassium compounds and that these promote coke breakdown leading to the formation of excessive amounts of small coke and consequent difficulties in furnace operation.

3. RELATIONSHIPS BETWEEN FUNDAMENTAL AND HIGH TEMPERATURE COKE PROPERTIES

Results of work carried out under references 6,8,10,11,12,13, 15 and 16 are considered in this section.

3.1 General survey

Because of the lack of incisiveness and discrimination of the conventional macro-strength indices and their inability to completely characterise the behaviour of coke in use, much attention has been directed in recent years towards the examination of the structural properties of coke. The availability of sophisticated equipment has facilitated such examinations(22)(28).

It has also been possible to provide fundamental measurements of the strength of the coke substance, in particular measurements of tensile and compressive strengths.

The general principles of these methods are well documented and numerous reports of such work are available. The present report is concerned with a consideration of such measurements in relation to the behaviour of coke at high temperatures.

3.2 The tensile strength of blast-furnace coke

The levels of tensile strength of the generally high-quality metallurgical cokes studied(10)(11)(15)varied within the range of 3.7 to 6.5 MN/m^2 with an average of slightly below5MN/m^2. Corresponding values of the M_{40} and M_{10} indices were 73.8 to 91.8 and 4.8 to 8.2 respectively but only three cokes out of forty-one tested had values of M_{40} below 80 and only 5 had values of M_{10} greater than 7.0(10) (15).

The level of the results of tensile strength measured by the diametral compression test is influenced by the size and shape of the artefacts. It is usual to use cylindrical specimens and many results were obtained using 1cm x 1 cm disc specimens, the values reported being the mean of 40 to 50 individual test results.

The test measures the strength of coke free from major fissures, and this is of importance in relation to the condition of coke when it reaches the furnace stockline when it has been considerably stabilized by crushing and screening.

There is a broad general relationship between tensile strength and coke porosity, strength decreasing with increasing porosity. Changes in carbonization practice which affect porosity therefore influence tensile strength. For example, an increase in bulk density will reduce porosity and affect tensile strength. This statement is of a very general nature and somewhat over-simplified. More precise relationships between porosity and tensile strength are only found when the effect of other coke structural properties are taken into account(31).

3.2.1. Tensile strength of coke at high temperatures

In one study(10) two techniques were used to establish the effect of thermal treatment on coke tensile strength. One involved heating the cokes to a given temperature and cooling before making the measurements and in the other, tensile strength was measured at about 1200°C.

Using the first procedure, cokes were heated at the rate of 10 or 30 K/min to a temperature of 1450°C in an argon atmosphere and maintained at this temperature before cooling and testing. In other tests(8) the tensile strength of three cokes was measured after reheating to 1400°C.

Considerable experimental difficulties were encountered when attempting to measure tensile strength at high temperatures(10) but a satisfactory method was developed enabling measurements to be made at 1200°C. At higher temperatures, melting of the coke mineral matter sometimes occured and the specimens were difficult to handle. Nevertheless some tests were successfully completed at 1390°C.

The results of these experiments are collected in Table 6. From the results of one series of tests(8) it can be seen that an average increase in tensile strength of almost 10% was noted after reheating cokes to 1400°C. In other work(10) the results were more dispersed, both increases and decreases in tensile strength being noted. It was pointed out that size, heating rate and heat treatment temperature were factors which affected the results and the statistical uncertainity of the determination was such that only a small proportion of the differences between tensile strength at ambient and at high temperatures were significant(10). It was suggested that the weakening of coke at high temperatures arises from differential expansion and contraction taking place in different regions of the coke with the resultant formation of further micro-cracking and centres of weakness(32). An increase in micro cracks following heat treatment has also been shown in other work(16).

3.3. Compressive strength of coke at high temperatures

There are a number of reports in the earlier literature of experimental attempts to measure the compressive strength of coke at high temperatures. These results were inconclusive, some suggesting that the compressive strength of coke decreased with increasing temperature(33), whilst other data(34), indicated the opposite effect.

The results of later work(35) indicated that the compressive strength of coke at 1650°C was higher than at ambient temperature.

Work considered within the scope of this report(11), carried out under reliable experimental conditions, has provided data for the compressive strength of two blast-furnace cokes and two samples of the same cokes recovered from the tuyeres. Measurements were made at temperatures of 1500-1510°C.

Between 20 and 25 cylindrical samples, 23 mm high x 15 mm diameter were heated in an argon/carbon monoxide atmosphere, (40% CO), to the operating temperature and subjected to uniaxial compression at that temperature. A further test was carried out on one sample only in which the coke was cooled prior to the application of compression. The results of these tests are given in Table 7.

For the two cokes tested, an increase in compressive strength after heat treatment to slightly over 1500°C was noted. This behaviour was accompanied by a reduction in the elastic modulus for one coke only and a decrease in Young's modulus has also been reported for three cokes reheated to 1400°C(8).

3.4. The effect of coke structure on fundamental strength properties

It is well known that polished sections of coke, when examined by polarised light microscopy display optical heterogeneity. Regions of coke having similar optical properties in all directions and which display a uniform colour under the microscope are termed isotropic. Other regions, having optical properties which vary according to the direction of light transmission at the surface, display different colours or tints as the polished surface is turned in its own plane of polarised light and are termed anisotropic.

Anisotropic material may be further sub-divided according to the appearance and grain size into areas known as mosaics. These materials are developed from the vitrain of the coal during heat treatment or carbonization and the nature and type of the mosaics are a function of carbonizing conditions and coal rank, the molecular composition of the vitrain being a prime factor in their development.

Changes during carbonization in reflectance and crystallographic properties can be interpreted in terms of increasing molecular order and size and correspond to the gradation from fine grain mosaic anisotropy to flow-type anisotropy.

Between these two extremes of anisotropic types two further groups are generally recognised, medium grain mosaic and coarse grain mosaic, though further sub-division is possible. The development of these mosaic types is restricted to coals within the range of volatile matter of 16-36% d.m.m.f. (ECE classification 322/3 - 723/33). Coals of higher rank show only an intensification of basic anisotropy and coals of lower rank remain isotropic.

Therefore, in fully carbonized cokes, individual particles are an heterogeneous agglomerate of different structural forms and the properties of these entities vary. It has been established(6) that the strength of different structural forms of coke varies, for example, strength was shown to increase as the size of the mosaics decreased and the specific surface area of the mosaics increased. Micro-crack formation also decreased in size and intensity in the region of fine grain mosaics(16).

There does not appear to be any available evidence to show that coke tensile strength at high temperatures is influenced by the mosaic structures, and were this information available it is difficult to see how it could be applied under the normal conditions of practical coal carbonization.

3.5. Changes in strength and structural properties after partial gasification

3.5.1. Tensile strength of cokes after partial gasification

The same series of cokes used to study the dependence of tensile strength on test temperature(10) were subjected to partial gasification at a temperature of 970°C. To obtain different levels of gasification, two oxidising atmospheres, containing 10 and 100 per cent of CO_2 respectively were used for each coke examined. The time of gasification was generally 4 h. and the extent of gasification, measured by the loss in mass of the specimens, varied from about 5-8 per cent, using 10 per cent CO_2, to 13-20% with pure CO_2. The results of these tests are shown in Table 8. With one exception, the cokes were of lower tensile strength after gasification. The reason for this anomaly was satisfactorily explained. What is more difficult to understand is the lack of agreement between the extent of gasification of different cokes and the change in tensile strength, for example, coke 4 at a gasification level of 7.2 per cent showed a decrease in strength of 25.5 per cent, whereas coke 8 at a gasification level of 5.1 % lost only 3.4 per cent in tensile strength.

These differences could not be explained by examination of the porous structure of the coke and the coal blends used to prepare the cokes were similar. Catalysis by mineral matter of the gasification reaction could have influenced the behaviour of the cokes. Similar evidence of a reduction in tensile strength following gasification was observed in other experiments(9) and these data are also included in Table 8.

No compressive strength tests appear to have been carried out on partially gasified cokes(16), but drum tests carried out on cokes gasified at 1200°C to a 25 per cent weight loss(6) indicated that the rate of gasification was related to the texture of the coke and the strength or cohesion of partially gasified coke broke down when the size of the coal petrographic constituents was increased or the total surface was reduced. This is an interesting observation since it relates the nature of the coal substance to the size of the mosaic entities.

The results of a small-scale abrasion test(36)(16) indicated that the micro-strength of cokes prepared from a coal extract, the coke texture being of a small size, remained approximately constant to 15 per cent weight loss by gasification, before decreasing at higher levels of burn-off. From this observation it was tentatively suggested that metallurgical cokes of small sized optical texture may be more resistant to loss of strength than cokes of larger sized texture.

3.5.1.1. Tensile strength of cokes recovered from blast-furnace tuyeres

Gasification tests attempt to simulate the conditions to which coke is subjected in the blast-furnace. Such tests cannot exactly reproduce furnace conditions, but one common feature of many of them is that the loss of weight by gasification is controlled to about 25 per cent, a level recognised as the amount of coke carbon normally required for direct reduction. A mean value of 24.5 per cent, based on data for forty blast-furnaces, was reported(15).

Some of the cokes recovered from furnace tuyeres(15) were examined to determine their tensile strength. Sample preparation was difficult due to the presence of mineral inclusions in the specimens which inhibited the polishing but it was possible to compare the tensile strength of nine feed and tuyere coke samples. It will be noted from the results in Table 9 that the tensile strength of the tuyere cokes was generally higher than that of the feed cokes, this observation again supporting the view that the high temperatures to which the coke was subjected caused an increase in graphitization of the coke. The interior of the particles, from which the tensile strength specimens were obtained, therefore become stronger and retain their strength for a longer period of time.

Obviously, if the process continued indefinitely, all the coke would be consumed, but it was interesting to note that briquettes charged to a furnace had shrunk, but maintained their shape and strength when recovered from the tuyeres(37).

3.5.2. Compressive strength of cokes recovered from blast-furnace tuyeres

Compressive strength tests carried out on two cokes recovered from tuyeres(11) indicated that they were stronger than at ambient temperature and that there were only small differences in the strength of feed cokes and tuyere cokes when tested at higher temperatures. The differences, although small, appeared to be greater in the case of the coke prepared from a blend containing a higher proportion of high-volatile coal. The deformation of the tuyere cokes before rupture was also higher compared with the deformation at ambient temperature.

3.5.3. Changes in the structural properties of cokes at high temperatures

At present, it is not possible to make an examination of structural properties of coke such as porosity and pore and pore-wall dimensions at high temperatures. Some comparisons were made between various structural and textural properties of cokes at ambient temperature, after reheating, after gasification tests, and of cokes recovered from furnaces.

There was a general indication that reheating of cokes up to 1400-1450°C resulted in slight increases in real density of up to 5 per cent(10). There was little difference in the apparent density of coke, and therefore the calculated value of porosity (from density measurements) of reheated cokes was higher than at ambient temperature(8). Tuyere cokes were also higher in density than feed cokes(11)(15) but part of this increase could be attributed to the presence of ash and mineral inclusions.

After gasification, a general increase was noted in apparent density, with little change in real density(9) and therefore a marked increase in porosity was noted. Similar behaviour was shown by cokes recovered from furnace tuyeres(7) where increases in porosity of up to 7 per cent were recorded and in other experiments(11) the corresponding increases in porosity varied from zero to 5-7 per cent.

A comparison of the pore-wall thicknesses of feed and tuyere cokes(11) indicated that they were reduced by about 15 per cent and the average pore diameter of the tuyere cokes was about 2 per cent greater. The porous nature of the coke is related to its tensile strength(22), and it was noteworthy that the changes in pore and pore-wall dimensions, although relatively small, appeared to be accompanied by a slight increase in tensile strength, as already noted.

The comparatively small increase in pore diameter therefore appears to compensate for the relatively greater reduction in wall thickness and thereby promotes an overall strengthening effect.

3.5.4. Changes in the isotropic and anisotropic structures of coke with temperature

In one report(7), a comparison was made between the mosaic structures of feed and tuyere cokes. During the test period, the coal blend was of a generally uniform quality (V.M. 26.1-26.9 per cent d.m.m.f., R_0 1.20-1.30). Amounts of the individual mosaic types in the feed coke did not vary greatly, but the amount of medium grain mosaic material was highest in the coke produced from the blend of highest rank.

No systematic pattern could be detected in the changes which occured in the amounts of each mosaic type in the feed and tuyere cokes. In three cases out of five there was a decrease in the amount of isotropic and fine-grain mosaic material and for four cokes an increase in coarse granular mosaic type was reported. Changes in the other types of anisotropic material were haphazard and could not be related to coal blend properties or carbonizing conditions. Not surprisingly, all cokes recovered from the tuyeres were slightly higher in mineral matter than the feed cokes.

Generally, the lower the rank of the parent coal, the greater the amount of isotropic material present in the coke. As coal rank increases so does the amount of medium grain mosaic material, culminating, in cokes prepared from high rank coking coal of V.M. less than approximately 23 per cent, by an increase in flow-type anisotropy. These progressive changes affect the gasification behaviour of the coke(6) which tends to occur preferentially in the isotropic material. For high quality metallurgical cokes, produced from higher rank coals, the behaviour of the individual mosaics on combustion and gasification is less well defined. This may be accounted for by the size of the grains of the anisotropic material, for if the structural units are smaller than about 0.5 μm in size, it is difficult to distinguish between the behaviour of such material, which has a very low degree of three-dimensional ordering and isotropic material(38).

In other work(16), five cokes of similar optical texture, categorised as isotropic interspersed with fine mosaic (<3 μm), medium mosaic (about 5 μm) and flow-type material (5-20 μm) were examined by the scanning electron microscope after gasification. Evidence of extensive surface gasification showed that fissures developed according to the size and orientation of the optical structure and were constrained in size by the structural units of the material controlling the optical texture. There was preferential oxidation between the boundary of the inerts and the surrounding material.

In general terms, it may be concluded that isotropic and inert regions of coke are preferentially gasified and that the rate of gasification of anisotropic material is slower and decreases as the size of the anisotropic regions increase, flow-type anisotropy being most resistant to gasification.

This is another way of restating the well established concept that cokes prepared from high-rank coals are more resistant to solution loss and therefore degradation in the blast-furnace (they are less reactive) than cokes prepared from coal of lower rank or from blends containing a high proportion of low rank coal.

3.5.5. Structural changes in inert atmospheres at high temperatures

Temperature has little effect upon the coke mosaics until subjected to very high temperatures of the order of 2000°C. Some slight improvements in reactivity have been noted(38) probably due to the removal of hydrogen and sulphur from the coke and an increased level of gasification and structural ordering.

It was observed(16) that at heat treatment temperatures of slightly over 2000°C two individual cokes displayed shrinkage fissures in the smaller sized areas of optical texture, these fissures being from 5-10 μm in length and from 0.2-2.0 μm in width. It was also noted, from electron microscopy, that subjecting the coke to such intense temperatures appeared to bring about an agglomeration of the small mosaics into spheroids of 0.5-1.0 μm in size. It was suggested that the spaces between these units could act as stress absorbers and limit the extent of fissuring. Shrinkage fissures appeared to follow the lines of the stacking planes of the heat-treated coke and cease at a discontinuity. As already observed, the suggestion was made on the basis of these results, that cokes of small mosaic structure may be more resistant to breakdown.

Whilst of considerable interest, the relevance of these observations to the formation and behaviour of coke in practice must be considered. It was shown(15) that the maximum temperature to which coke is subjected in the raceway was about 1600°C. Such values have been generally confirmed by the results of Ultra high temperature dilatometer measurements made on cokes recovered from a substantial number of tuyeres which indicated that maximum temperatures of about 1550°C had been experienced by the cokes. The difficulty of controlling the mosaic structure of coke during production would also pose considerable problems and at the present time would again revert to blending of high and low rank coals technically suitable for carbonization and economically viable with little precise control over the amount or distribution of the coke mosaics.

It may therefore be concluded that in relation to the use of coke in practice, temperature alone has little or no effect on the structural properties of coke as recognised by optical examination.

4. COKE REACTIVITY

4.1. General survey

Coke reactivity is a loosely defined term which is commonly understood to refer to the rate at which coke is consumed when reacted with typical oxidizing gases such as air, carbon dioxide, oxygen or steam. The term has no precise meaning except possibly when used as an index of the results of gasification experiments generally undertaken on a laboratory scale. The reactivity of coke is, therefore, not so much a characteristic of the fuel as an implied behaviour and it is dependent on the properties of the fuel and the manner in which it is utilised in practice. However, coke reactivity has been frequently cited as a property of coke of importance in metallurgical processes, in particular the dependence upon reactivity of the loss of carbon in the blast-furnace shaft by reaction with carbon dioxide.

Many tests have been developed to measure coke reactivity and a large and diffuse literature is available on the subject. The principal obstacle to the development of a meaningful reactivity test from the point of view of iron-making has been, in the past, the lack of evidence from the results of such tests to demonstrate that they can be related to the performance of coke in industrial practice. When one considers the disparity between the conditions under which laboratory reactivity tests are made and the conditions prevailing in a blast-furnace, such lack of correlation is not surprising.

However, there has been in recent years a renewal of interest in the relationship between coke reactivity and blast-furnace performance, arising from the successful operation of large capacity blast-furnaces in Japan and elsewhere. As pointed out in a more recent contribution(18), one important way in which the significance of coke reactivity in relation to furnace performance now differs from previously held views is that the combustion of coke is now related to simultaneous changes which take place in the strength of coke. Loss of carbon during a reactivity test has been shown to result in a weakening of the coke and such behaviour has been postulated in practice, potentially capable of producing a concentration of small weak coke in the lower part of the furnaces, and the well known consequences in terms of effects on production.

In the framework of the work under consideration, several laboratories have made reactivity tests on cokes, and some comparisons of the results have been made with those from the test which has become prominent as a means of determining coke reactivity in conjunction with a measurement of strength loss, namely the N.S.C. Reactivity and Post-reaction strength test for coke(39).

In the following section the results of reactivity tests utilised in various ECSC research projects(6)(9)(10)(15) are compared with each other and where possible with results obtained from the NSC test.

4.2. Relationships between various reactivity tests

A comparison of the results of three reactivity tests was made in one laboratory(9). The scale of the tests varied considerably. In the bulk reactivity test 25 kg of +20 mm coke was reacted with carbon dioxide at 1000°C until approximately 25% of the coke was gasified. The lump reactivity test was carried out on 30-40 g of coke cylinders, 38 mm in height x 38 mm in diameter for 3 h at 975°C in carbon dioxide. Each method reported the result of the test in terms of weight loss per hour. Abrasion tests were carried out on the lump samples after gasification.

The third test considered was carried out on the micro-scale using 0.1 g of coke sized between 125 and 212 µm. The operating temperature was again 975°C, the reacting gas carbon dioxide and the reactivity index was expressed as the reciprocal of the time required for a 20 per cent weight loss.

Despite the differences in test parameters, the results of the three reactivity tests were shown to have a good statistical relationship with each other, the cokes, with a few exceptions being placed in the same order of reactivity by each test.

It is not the purpose of this report to compare the merits or demerits of various reactivity tests or to recommend any one test as being superior to others. However, because of the widespread adoption of the Japanese NSC reactivity test as a parameter for the control of coke quality for blast-furnace operation and bearing in mind the claims which have been made for the practical significance of the results of this test(40), it is considered appropriate to compare, where possible, the results of coke reactivity and post-reaction strength measured by the NSC test, with the results of other reactivity tests and of measurements of coke strength after partial gasification.

Such comparisons are available from data presented in four reports(6)(9)(10)(15). In two cases(6)(9) a direct comparison may be made between reactivity results. These comparisons are shown in Tables 10a and 10b.

From these data and from Figs 1a and 1b it is apparent that with one anomaly in each case, there is a good measure of agreement of the results of other reactivity and gasification tests and the Japanese test results. The outlying results appear to relate to more reactive cokes and it has been pointed out that for such cokes, reactivity values are subject to the influence of the mineral constituents of the coke to a greater extent than are cokes of lower reactivity.

Therefore, in agreement with earlier experience, there is a general tendency of all reactivity tests carried out in carbon dioxide at temperatures of the order of 1000°C to place cokes in a similar order.

4.3. Consideration of various abrasion measurements after gasification or reactivity tests

Test methods which involve a combustion or gasification process followed by an examination of the strength of the residual material attempt to simulate the condition of the coke when it arrives at the melting-zone of the blast-furnace. Therefore, in laboratory tests, the extent of abrasion after gasification is significant.

Measurements of coke strength or abrasion after gasification have been carried out in several ways. Where bulk samples were available, a conventional type of Micum test was used(2)(3)(4) and where small samples were tested, small scale drum tests were generally employed(7)(10).

Small coke specimens have also been examined by tensile strength measurements(10), compressive strength measurements(11), the NSC reactivity and post-reaction strength test(6)(10)(15) and by the micro strength test(16)(36).

Regardless of the scale of operation the results of each type of test, with one exception(16), indicated that cokes were less resistant to abrasion after gasification. The attack on the coke was largely restricted to the external surface and was partially particle-size dependent. The exception to this general pattern of behaviour was shown from micro-strength test measurements, where two cokes appeared to increase in resistance to breakdown after gasification. However, it is known that the results of this test are affected by the number of revolutions to which the coke is subjected and that the standard number of 800 revolutions is not always the correct number to enable an adequate differentiation to be made between the properties of different cokes.

Following a similar approach to that used in comparing the results of reactivity tests, a comparison was made of the results of mechanical tests carried out on coke after gasification. Only two comparisons were possible, each involving a comparison of the NSC post-reaction strength (PRS) with, in one case(6), the amount of -3 mm material generated, and in the other(10) with the amount of -10 mm coke produced after gasification in a drum, the test being carried out at high temperature.

These results are given in Table 11. It is apparent that no highly significant correlation holds between the results, but as in the reactivity tests, there is a general tendency for the ordering of the results to be similar, cokes having high and low abrasion indices being found at the extremes of the ranges of the results, particularly when the -3 mm abrasion index is compared with PRS.

Similar inferences may be made from other results(15) where a reasonable correlation between micum slope and reactivity and therefore with post-reaction strength is reported.

Bearing in mind the differences in the methods of coke gasification, the variations in coke size and the different techniques used to measure post-gasification abrasion properties, it is not surprising that highly significant correlations between the results of the tests are not found. As in the measurement of reactivity, each abrasion test tends to show a series of cokes in a similar order of mechanical properties and the tests made under any one set of conditions are valid in particular circumstances.

The practical significance of the results of reactivity and post-reaction strength tests will only be established when further reliable data can be obtained from operational practice, where changes in coke properties and their effect on furnace performance can be monitored under steady conditions over long periods.

5. PRACTICAL IMPLICATIONS OF THE RESEARCH PROJECTS

The principal objective of all the research work considered in this survey is to devise means of producing coke which will satisfy conditions enabling the blast-furnace to operate efficiently and economically. It is apparent that to meet these requirements, a blast-furnace must be supplied with a coke of uniform quality, capable of resisting the mechanical and thermal forces imposed upon it to such an extent that it reaches the melting zone and tuyeres in a condition where furnace permeability is maintained, coke strength is adequate to meet raceway conditions, a minimum amount of fine material is produced and alkali absorption is at a minimum. In addition, certain work has been directed to the examination of the importance of the initial gasification temperature, or reaction threshold of the coke in the thermal reserve zone. Whilst the importance of this work must not be underestimated, it is difficult to reconcile some of the underlying concepts in relation to coke quality with traditionally accepted beliefs.

5.1 Methods of preparation of a coke of low threshold gasification temperature

The preparation of a coke which will gasify at a reduced temperature has concerned the carbonization industry for decades and a vast literature exists on this subject. Initially, such work was invariably directed towards the production of a so-called 'reactive coke' intended for domestic consumption, where low ignition temperatures were sought to enable coke prepared in coke ovens to be easily ignited in simple domestic appliances.

The means available to the coke maker to enable such coke to be produced are relatively limited. Reduction of the final carbonization temperature is effective, but is not now practised because of environmental considerations. Increasing the proportion of low rank coal in the blend and coarser crushing of the coals have frequently been adopted, but there are limits to which these measures can be taken from considerations of coke formation and oven pushing. Activation of the coke by incorporation of alkali in the charge or by treatment of the coke with various alkaline or alkaline earth substances is an old method of producing a more easily ignitable material. Probably the most significant breakthrough in this field was made in the late 1960's, when it was shown that small amounts of certain inorganic additives could materially reduce the ignition temperature of high-temperature coke and the process was successfully exploited on a commercial scale in The United Kingdom for several years(27)(41). Briquetting of the charge, or a portion of the low-rank material in the charge, has also been attempted.

It must be pointed out that all of this work was designed to produce a coke of low ignition temperature and was concerned with the activity of coke towards oxygen and not with oxides of carbon at somewhat higher temperatures, although this reaction did play a part in the slow combustion of coke in closed appliances.

However, the restrictions imposed on the coke maker in preparing a fuel of improved combustion properties apply whether the carbon-oxygen reaction or the carbon-carbon monoxide-carbon dioxide reaction is involved.

The work described(4)(5)(6) has highlighted the limitations and restrictions outlined above in the manufacture of coke of reduced gasification temperatures. The methods adopted in attempting to produce such coke were traditional and not surprisingly, it was shown that the dominant factors were carbonizing rate, final carbonizing temperature and blend composition. The well established relationship between the reactivity of the coke and the position of the coke in the oven was also restated.

In attempting to reduce the gasification temperature by the methods outlined it was found that the physical properties of under carbonized cokes were not adequate for metallurgical use and that the discharge of such cokes posed practical and environmental problems. This approach was abandoned.

Variation of blend composition within the normal range of blends suitable for the manufacture of coke of satisfactory physical properties was shown to lead to only small changes in gasification threshold temperatures and the incorporation of oxidised coals, charcoal, sawdust, lignite and washery fines was also of little practical value. Only in the case of a coke prepared from a blend containing 30 % of lignite was any significant reduction in gasification threshold temperature achieved, from 950°C (base coal) to 890°C (blend) but coke quality was extremely poor.

Briquetting of high and medium volatile coals, using pitch as a binder and in certain cases incorporating oxidised coal and high inertinite coal into the blends enabled cokes to be produced at carbonizing temperatures of 800-1050°C with threshold gasification temperatures of 850-920°C. At a carbonizing temperature of 1050°C the inclusion of 30 % of wood charcoal in the blend enabled cokes to be produced with a threshold gasification temperature of 830°C. However, mechanical properties of all cokes produced from the briquetted blends were again unsatisfactory. Increasing the pitch content from 8-12 % improved mechanical properties but impaired gasification behaviour.

A reactive coke was produced by carbonizing lump coal (6-18 mm in size) in a rotary kiln at 800-900°C. When this material was reheated in a normal coke oven at a higher temperature the threshold gasification temperature was not raised. Briquettes treated under similar conditions were too weak for furnace use.

The general conclusion from these studies showed that cokes with a suitably low threshold gasification temperature could be prepared by briquetting blends of low rank coals, wood charcoal and pitch. Recognising that the mechanical properties of such cokes were poor, it was postulated, from the results of laboratory tests that because subsequent loss of strength on gasification was not too severe, the reactive materials could be mixed with normal coke to initiate gasification in the thermal reserve zone of the blast-furnace. The conventional coke would then remain to carry out its normal functions in the lower part of the furnace.

There are limitations to the use of such a technique in practice. Firstly, a significant quanitiy of the reactive coke (25-35 %) was shown to be required to produce the desired reduction in threshold gasification temperature.

Secondly, the most effective reactive coke was of small size, and to homogeneously mix large quantities of such a material (e.g. in a blast-furnace consuming 4500 t of coke per day, some 800-1000 t of reactive coke would be needed) with normal coke of much larger size, would present considerable practical problems.

A large plant would have to be constructed reasonably close to the normal coke ovens and blast-furnaces of an integrated plant and the economics of the production of the reactive coke would require careful consideration. Transport and handling of the relatively weak material would also pose problems.

Finally, the concept of promoting the reactivity of normal coke by mixing with reactive material met with little success when applied to the combustion of coke in domestic appliances.

5.2. Practical considerations in the manufacture of conventional strong metallurgical cokes of high thermal stability

Conclusions are available from a number of reports indicating the quality of coke required to enable it to withstand rigorous blast-furnace operating conditions. There is a general concensus of agreement that normal coke quality tests carried out at ambient temperature provide incomplete information on the behaviour of cokes at high temperatures and tests at high temperature are important in assessing coke quality.

When coke is subjected to high temperature testing a general deterioration in its strength and abrasion properties is observed, the onset of this behaviour being noted when testing temperatures are greater than the temperature at which the coke has been manufactured.

Carbonizing temperature, coking time, carbonizing rate and soaking time are important practical considerations in relation to the high-temperature properties of coke, since all these parameters influence the extent of graphitization and the consolidation of the structure of the coke and its subsequent degree of breakdown at high temperatures.

The extent to which these parameters can be varied is limited in conventional coke production. Given that a specified tonnage of coke must be produced to satisfy furnace requirements, the carbonizing time and temperature can only be varied within relatively narrow limits. Under normal conditions, carbonizing times of about 16-24 hours and final coke temperatures of up to 1150°C are the approximate limits available to the coke-maker.

Changing the carbonizing time and therefore the rate of carbonization of blends of medium and high-volatile coals, whilst maintaining the final carbonization temperature at a constant level of 1020-1040°C, was shown to increase coke mean size as the rate of carbonization decreased from about 30 to 22 mm/h, and the increased coke size was maintained after reheating to 1400°C followed by mechanical testing. Abrasion indices were unaffected by changes in carbonizing rate.

An increase in the final coke temperature from approximately 900-1130°C at a constant carbonizing rate had little effect on coke size when tested at ambient temperature, but markedly increased the resistance of coke to breakage after reheating at 1400°C(3).

Limited data from a further source(7) gave general support to this observation, although in this case a slight change in the composition of the coal blend may have had some influence on high-temperature properties of the coke.

Increasing the soaking time of cokes at final temperatures of 900°C and 1000°C improved thermal size stability, but this effect was not noticeable when the final charge temperature was increased to 1100°C.

Other processes known to affect the properties of coke at ambient temperature are preheating of the charge, densification and dry cooling.

Preheating is known to result in a general improvement in coke quality; exemplified by a more uniform coke structure, a generally reduced mean size and size distribution and improved resistance to breakage and abrasion(42). Preheating a charge of high volatile coal to temperatures within the range of 180-230°C resulted in a slight improvement of the high-temperature properties of coke, particularly of their resistance to abrasion(8). Supporting evidence is available, from a comparison of the high-temperature properties of cokes prepared from two identical coal charges, one wet and one preheated, both carbonized in a 6.5 m oven(10). The coke prepared from the preheated charge was superior to that from the wet charge in respect of its resistance to abrasion at temperatures up to 1500°C and in its resistance to the attack of oxidising gases at 1050°C.

Densification, or increasing the bulk density of the charge, is a well established means of improving the macro-strength properties of coke at ambient temperatures. In practice, bulk density can be increased by coarser crushing of the coal thereby increasing the charge weight in the oven; by preheating, partial briquetting of the charge, or stamp charging. There are limits to which these practices can be taken and the extent to which they can be applied depends on coal type.

The effects of some of these parameters on the properties of corresponding cokes were examined after reheating to 1400°C. A significant improvement in M_{10} and I_{10} indices was shown by coke prepared from a blend containing 40% of briquetted material and 3.2 per cent of coal-tar pitch and the thermal stability was slightly improved.

No comparisons are available between the high temperature properties of stamp charged cokes and top-charged cokes, but it was noted(15) that the porosity and tensile strength of one coke prepared from a stamped charge was similar to that of cokes used with apparent success in large Japanese furnaces.

There have been many statements made to the effect that the mechanical properties of coke, and particularly the abrasion resistance are improved by dry-quenching(43). Only limited evidence on this subject is available from the ECSC reports under consideration(6)(8).

Using one coal blend containing 60% of coal of volatile matter above 30% and a blend volatile matter content of 27.9%, no significant difference could be found in the high-temperature properties of wet and dry-quenched cokes prepared from this blend(8).

Results of other work(5) indicated that dry quenching improved the abrasion resistance of coke when the amount of high volatile coal in the blend exceeded 20%. After gasification, the resistance to abrasion of the dry-quenched coke was superior to that of the wet-quenched coke when the proportion of high-volatile coal exceeded 40% of the blend.

5.3. Production of a high quality coke for furnace use

Means by which coke quality can be affected by varying coal charge properties and carbonizing conditions within the limits of practice have been outlined. A consideration of these studies indicates that the high temperature properties of coke can be improved by increasing the final carbonizing temperature, by soaking the coke before discharge and by increasing charge bulk density, either by preheating, partial briquetting or stamp charging. Under certain conditions, dry cooling may also be beneficial and the case made(44) for a combination of preheating and dry cooling should not be overlooked.

A judicious combination of some of these factors, often based on the results of relatively small scale blending and carbonization tests and frequently limited in scope by technical and economic considerations, is the usual means adopted to prepare a coke which may perform satisfactorily in a blast-furnace under relatively constant operating conditions.

The comprehensive data derived from the sampling of feed-coke and tuyere coke at over forty blast-furnaces(15) enabled a broader view to be taken of the relation between coke quality and furnace operation. After stabilisation of the cokes by cutting, screening and sizing, all feed cokes were of high conventional quality with M_{40} values generally in excess of 80 and M_{10} values below 7. The resistance of such cokes to thermal and mechanical degradation at temperatures up to 1300°C was also shown to be very similar(10), mass losses varying from only 1.9 to 2.5 per cent in an inert atmosphere and from 7.8 to 10.4 per cent in an oxidising atmosphere at 1050°C being recorded.

Despite the generally similar properties of these high-quality cokes, size reduction in the furnaces varied considerably, from 3.3 to 24.0 mm, these values, on average, accounting for about 70% of the total size change.

No significant relationships were found between feed coke properties and size reduction in the furnace and from the overall data it was not possible to determine any systematic relationship between coke size reduction and furnace operation, largely because of the great differences in the operations considered. It was apparent that for efficient furnace operation the size range of the coke in the bosh must be such as to ensure adequate furnace permeability and that this size distribution should be maintained when the coke reaches the raceway but it was not possible to quantify the relationship between tuyere coke size and permeability. The effect of the properties of the remainder of the burden, and particularly of alkali, have an overriding effect on the behaviour of the coke in the lower regions of the furnace.

It may therefore be concluded that the well established methods of manufacturing a coke of good properties will guarantee a firm basis for the production of a coke which will display reasonable resistance to thermal and mechanical attack and will not deteriorate greatly in size. An adequate proportion of high rank coals, the maintenance of a certain level of blend fluidity or dilatation, the correct balance of inerts in the blend and controlled crushing are essential precursors. Stabilisation of the coke before charging is influential in further improving the suitability of coke for furnace operation.

Carefully controlled carbonizing conditions, densification, pre-heating and dry cooling can be utilized to effect further improvements in coke strength and combustion properties. Such high-quality cokes have been shown to maintain, or even improve their basic strength characteristics such as tensile strength at the furnace tuyeres(15)(45).

However, the important effects of alkali cannot be ignored and it is extremely difficult to conceive any means by which the resistance of coke to alkali attack can be increased, particularly bearing in mind the practical limitations imposed upon altering the structural properties of coke. Research into this field could be highly rewarding.

6. RELEVANT RESEARCH CARRIED OUT OUTSIDE THE ECSC

The first significant investigations of the high temperature properties of lump coke were carried out by Echterhoff(46) and by Bradshaw and Wilkinson(47).

Evidence from these studies provided the first indication that conventional coke strength parameters were generally unaffected by temperatures below that of the maximum carbonizing temperature. Above that temperature a general deterioration in coke strength, not necessarily directly related to the physical quality of coke at ambient temperature, was observed.

No account was taken in this work of the effect of gasification or partial burn-off of the coke. Studies which took account of these effects were carried out by a number of Japanese workers and have been widely recognised in the ECSC reports considered.

The significant features of the Japanese work were an examination of blast-furnace burdens which had been quenched in situ and the development, from the results of these examinations, of relationships between furnace operation and changes in coke quality and of laboratory tests which measured coke quality after gasification(40)(48)(49). Evidence was presented which related these test results to furnace permeability and productivity and efforts were made to correlate the data with those of the Japanese drum test carried out at ambient temperatures(40).

The various data showed that general relationships existed between the above parameters. It was noteworthy that quite small changes in the level of conventional strength indices were reflected in much larger changes in levels of reactivity and post-reaction strength, providing further support for the view that control of furnace operation could not be fulfilled on the basis of physical test data obtained on coke at ambient temperatures.

In one report(50) it was noted that the size reduction experienced by coke in its descent from furnace stockline to tuyeres was equivalent to that produced by 82-573 drum revolutions (JIS drum) on cokes of the same size distribution as those charged to a number of furnaces. Making use of the best evidence available(51) these values of JIS drum revolutions correspond to approximately 310-2000 micum drum revolutions and values within this range were found for the majority of cokes examined during the tuyere raking exercises within the ECSC(15).

As a consequence of the Japanese work, the NSC reactivity and post-reaction strength test became an additional parameter for the specification of coke quality for use in large blast-furnaces. The need for this data appears to be greater where cokes are prepared from coal blends covering a wide range of individual coals and the test has therefore been adopted for quality control at certain plants in The United Kingdom. Elsewhere, within the ECSC the test does not appear to be used to the same extent.

The practical significance of the reactivity and post-reaction strength test has been extended by further work carried out on furnaces about to be shut down. An examination of raceway conditions(52) indicated that the amount of -5 mm coke in the raceway was directly related to the reactivity of the coke charged to the furnace, but from this work it could not be concluded whether the post-reaction strength of the coke, or the initial cold strength of the coke was the dominant factor.

Further blast-furnace trials were made in which cokes were used of the same cold strength but differing in post-reaction strength. The required coke properties were achieved by controlling coal blend composition, principally on the basis of blend fluidity and inerts content.

The results of a comprehensive test programme(53) indicated that the post-reaction strength of the coke had a definite influence on furnace performance. In particular, it was shown that below a certain level of PRS there was an abrupt rise in furnace permeability and an increase in slipping. To counteract this behaviour, fuel rate had to be increased and the extent of this increase could also be related to post-reaction strength.

The relationship between post-reaction strength and the amount of small coke at the tuyere level was not clearly defined, but the amount of small coke in the region of the deadman decreased as post-reaction strength increased. It was also stated that at the tuyere level, post-reaction strength, K_2O content of the coke and coke temperature were not related to the feed coke properties.

In overall terms, blast-furnace operation was shown to be significantly affected by the amount of fine coke produced by breakdown at the belly level of the furnace and the fall of belly coke to tuyere level, a process accelerated by the presence of alkali. The extent of coke breakdown correlated with post-reaction strength.

From this work, there appears to be no doubt that high quality cokes are required for good furnace operation. In Japanese practice, cokes with a post-reaction strength of 58-62 are found to have cold strength values (DI^{150}_{15}) of at least 85, a level roughly equivalent to an M_{40} index above 90.

Whatever the merits of cold strength test indices and the actual significance of such values, the coke required for satisfactory operation is obviously very strong in conventional terms.

No techniques other than those in well-established use were employed to make the high quality coke. Careful blending on the basis of the parameters already noted (fluidity and inerts ratio) appeared to be the normal technique. Densification, by preheating and briquetting, has been applied.

The significance of coal fluidity and its relationship to other coal parameters and properties of the corresponding cokes, including fundamental strength and structural properties, reactivity and post-reaction strength, was considered in other work(54). Relationships were developed between these parameters and it appeared that a possibility existed of forecasting coke properties of significance in furnace operation from a knowledge of coal properties such as carbon and oxygen content and coal fluidity.

Apart from work within the ECSC and that carried out by Japanese workers, little other recent information on the high-temperature properties of coke appears to be available.

7. CONCLUSIONS

7.1. The high temperature properties of coke are dependent in practice upon its resistance to the combined effects of mechanical and thermal stresses and chemical attack.

7.2. In an inert atmosphere, the mechanical properties of coke are largely unaffected by an increase in temperature until the maximum carbonization temperature of the coke is exceeded. Above this level, further increase in temperature results in some weakening of the coke. This effect is greater the larger the initial size of the coke and is also influenced by the rank of the coals used.

7.3. The superimposition of mechanical forces upon coke at high temperature results in a further increase in the breakage initiated by temperature effects and stress removal.

7.4. The extent of coke degradation arising from mechanical action and thermal effects cannot be forecasted from conventional physical tests carried out on coke at ambient temperatures.

7.5. In a reactive atmosphere, the extent of coke degradation is greatly increased by reaction with oxidizing gases. Such action is largely confined to the external surface of the coke, resulting in a greater susceptibility to abrasion.

7.6. There appears to be a tendency for isotropic coke, produced from lower rank coals, to be more susceptible to chemical attack and gasification than anisotropic coke produced from higher rank coals. The extent of gasification of anisotropic material appears to be dependent upon the type and size of the mosaic structure of the anisotropic coke.

7.7. Studies of the influence of the structure and texture of coke upon its high temperature properties have included the examination of the porous structure and microstructure and the measurement of tensile and compressive strength. Under inert conditions, temperature has little effect on the coke structure, but tensile and compressive strength appear to improve with increasing temperature, probably due to the increased ordering of the structure that occurs.

7.8. Where gasification or combustion takes place there is a general increase in coke porosity, resulting from a reduction in the thickness of the pore walls and a consequent enlargement of the pores. These factors contribute towards a reduction in coke tensile and compressive strength, but the effect does not normally penetrate to the interior of the coke particles. The strength of the interior of coke particles recovered from blast-furnace tuyeres is frequently greater than that of the coke fed to the furnace.

7.9. Alkali circulating in the blast-furnace has a profound effect upon the high temperature properties of coke. Apart from the known catalytic effect of alkalis on the reaction between carbon and oxidizing gases which results in an increased level of carbon consumption at lower temperatures, it has been demonstrated, on a laboratory scale, that alkali metal vapour combines with carbon to form intercalation compounds which increase physical weakening of the coke.

7.10. The nature of the compounds formed between alkali and coke during blast-furnace operation is not entirely understood. Intercalation compounds were not detected in tuyere coke and the mineralogy of tuyere cokes was distinctly different from that of heat treated feed cokes. It is believed that in practice, alkali reaction with coke carbon is strongly influenced by the nature and composition of the ash and slag in the lower bosh.

7.11. Whatever the mechanism of the alkali carbon reaction and the nature of the compounds formed in practice, there is no doubt that the presence of alkali results in a weakening of the coke, and an increased tendency to produce small coke in the lower part of the furnace.

7.12. The various reactivity tests used to measure the effect of reaction of oxidizing gases with coke at temperatures around 900-1100°C will generally place a series of cokes in a similar order. The results do not necessarily indicate the degree of solution loss of cokes in practice, since test conditions differ radically from practical conditions. However, when combined with a post-reaction strength test, the results are indicative of coke size changes in the furnace.

7.13. Strength tests carried out on partially gasified cokes compare their resistance to abrasion in a manner analagous to that in which gasification behaviour is compared by a reactivity test.

7.14. In furnace operation it is essential to ensure satisfactory bosh permeability. The coke present in the lower part of the furnace should therefore maintain an adequate size at the bosh. Because of the wide variety of blast-furnace practice, it is impossible to specify a universally acceptable coke size.

7.15. To maintain bosh coke size at a suitable level, the size and strength of the feed coke must be adequate. Size can be controlled by coal blending, carbonizing conditions, and coke stabilisation, e.g. by cutting. Strength is largely a function of the properties of the initial coal blend.

7.16. Little evidence has been advanced to indicate new developments in relation to methods of improving coke quality. The well-known effects of coal blend properties, carbonizing conditions, and addition of inert materials on coke quality have been substantiated.

7.17. The effect of blend preheating has been shown to produce some improvement in the high temperature properties of coke, particularly in resistance to mechanical abrasion. On the other hand, the tensile strength of cokes at high temperature and their rate of gasification did not appear to be improved by charge preheating.

7.18. Reactive cokes, of low initial gasification temperature, can be produced by well established carbonization and blending techniques. It is not clear whether the use of such cokes in furnace practice is a viable or practical proposition.

8. RECOMMENDATIONS FOR FUTURE STUDIES

8.1. In relation to the significance of the high temperature properties of coke in current practices of coke and ironmaking, it is considered that there is no further requirement to continue studies into methods of coke manufacture or to study the mechanical properties of coke in inert atmospheres below temperatures at which the coke was produced. Ample general information is already available on these subjects. There may be requirements for further work in limited areas, e.g. where un-familiar coals may have to be used for coke making.

8.2. Increasing test temperatures in oxidizing atmospheres to the levels attained by coke at the tuyeres and in the raceway, may provide an indication of changes in the extent of coke breakdown arising from increased graphitization of cokes and a greater degree of ordering of the coke structure.

In this context, a study of the behaviour of the isotropic and anisotropic mosaic structures of coke may provide information relevant to the selection of coals from which the coke structural entities are derived.

8.3. The behaviour of coke at temperatures up to 1700°C should be studied in relation to the effects of humidity and hydrogen content of the reactive gases. (Japanese information indicates that temperatures up to 2000°C may be attained). The effect of coal or oil injection could be considered in this context.

8.4. The development of a coke or formed coke resistant to alkali attack would represent a major advance. The difficulties of such a development are not underestimated. Some progress may be made by extending knowledge of the reactions taking place between alkali and carbon, and further work of a fundamental nature may elucidate these problems. Preferential attack of alkali on different coke structures and textures should be considered.

8.5. Evidence should be sought of the influence of ash content and composition on the high temperature properties of coke. In this context, it would be advantageous to develop methods and equipment to enable the structural and textural properties of cokes to be studied at high temperatures.

8.6. A reliable method or methods of predicting the high temperature properties of coke from the properties of coals or coal blends would be a useful development.

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TABLES 1 - 11

Table 1.

Comparison of methods of examining coke strength at high temperature

Parameter	Reference								
	2,3		8,9		15	10	7		4,5,6
Coke particle size mm	>60	>60	>20	>20	54-67*	30-40	10-20	30-70	20-30
Mass of sample kg	50	70	70	25	25	2.5	0.2	7.5	0.4
Type of reaction unit	R	S	S	S	S	R	S	R	S
Principal dimensions									
Length mm	1000	910	660	660		228	200	900	170(Height)
Diameter mm	1000	+	++	++		456	130	280	
Mechanical treatment									
Drum revolutions	100(a)	100(a)	100/500(a)	100/500(a)	900	100(h)		700	500
r.p.m.	25	25	25	25	25	25		10	10
Duration min	4	4	4/20	4/20	36	4		70	50
Thermal treatment									
Temperature °C	1100	1050	1400	1000		1050-1300	1050	1100	1200
Duration h	1.5-3	10-30	2	7.3-14.3		2	1	1.2	1.2-3.3
Chemical treatment									
Reaction gas (CO_2)	100%	60%	-	100%	-	100%	100%	100%	CO_2 10% CO 20% H_2 10%
Rate of flow l/h	72	22000	-	5400	-	1800	1000	3000	2000
Total volume l	108-324	$2.75-8.25x10^5$	-	$4-7.7x10^4$	-	3600	1000	3500	2330-6700
Gasification level %	About 20		-	20	-	9-15	12-20		25
E	$0.47x10^{-4}$	$0.37x10^{-2}$	-	$0.07x10^{-2}$	-	$2.4x10^{-2}$	$16.4x10^{-2}$	$1.3x10^{-2}$	$1.6x10^{-2}$

(a) Ambient temperature

(h) High temperature

\+ Rectangular cross-section Height 680 mm Width 380 mm

++ Rectangular cross-section Height 660 mm Width 280 mm

* Arithmetic mean size

R Rotating S Static

Table 2.

Comparison of methods of expressing the high-temperature test results

Parameter	Reference					
	2,3	8,9	15	10	7	4,5,6
Total weight loss	*	*		*	*	
% Weight loss		*	*	*		*
% Coke remaining						
>6.35 mm					*	
>10.0 mm	*	*		*		
>20.0 mm				*		
>40.0 mm	*			>30 mm	*	
<10.0 mm	*			*		
<3.0 mm						*
Size analysis	*	(HMS)	(AMS)	(AMS)		
Micum slope			*			
Permeability		*				

* Test carried out

Table 3.

The effect of heat treatment in an inert atmosphere on coke properties

Parameter	Reference			
	8	15		10
Coke size mm	20-100	-	53-67	30-40
Test temperature °C	1400	1400	1400	1300
Weight loss %	3.8	-	-	1.7
Mean change in size %	6.5	-	2.5	1.3
Mean change in slope	-	0.29	0.27	-
Cokes tested	3	14+	6	10

+ Shock heating

Table 4.

A comparison of the combined effects of gasification, heat treatment and mechanical treatment

Parameter	Reference		
	7	10	9
Coke size mm	30-70	30-40	>20
Test temperature °C	1050	1050	1000
Mean weight loss %	14.1	11.8	20
Mean change in size %	-	16.5	23.8
%>20 mm coke after test	82.7	82.5	-
Cokes tested	16	11	4

Table 5.

The effect of alkali impregnation on coke tensile strength
(After heating and cooling)

Reference	Nature of sample	Method of impregnation	Heat-treatment conditions			K content of coke %	Decrease in tensile strength %
			Atmosphere	Temp. °C	Duration (h)		
9	Cylinders 10x5 mm	Boiling alkaline solution	N_2 CO_2	1000 1000	8.0 -	2 2	Increase Impregnated cokes stronger than untreated cokes after gasification
15	Cylinders 15x10 mm	Boiling alkaline solution	A	900 900 1200 1200 1450 1450	0.5 2.0 0.5 2.0 0.5 2.0	2.7 2.8 2.8 2.4 2.1 1.5	10.0 5.6 21.4 22.6 15.4 15.4
14	Cylinders 10x5 mm	Vapour 1000°C	N_2	-	-	3.2-9.7	11.4-38.9
15	Cylinders 15x10 mm	Vapour 980°C	A	980 1200 1450	- - -	5.8-10.4 5.8- 3.8 3.9-7.2	8.1-18.2 28.8-64.5 42.2-63.7
11	Cylinders 15x10 mm	Vapour 1100-1200°C	70% N_2 30% CO	-	-	2.5	30.8 (Breakage limit Uniaxial Compression)

Table 6.

Comparison of coke tensile strength at ambient temperature and after reheating

Reference	Coke	Tensile strength MN/m^2 at($^\circ$C)		
		15	1400	1450
10	1	4.65		3.63
	2	3.84		3.70
	3	4.44		4.38
	4	3.11		2.58
	7	3.99		4.44
	8	3.52		3.81
	9	4.07		3.89
	10*	3.17		4.19
	11	4.73		4.22
	12	4.72		4.75
	13	5.00		4.69
	15	4.79		4.59
8	2	3.3	3.6	3.6
	12Pd	4.6	5.2	
	10	5.5	5.9	

* Under carbonized coke

Table 7.

Comparison of the compressive strength of coke at different temperatures

Reference	Coke	Mean compressive strength MN/m^2	
		15°C	1506°C
11	B	23.8	27.3
	E	16.1	19.7

Table 3.

Influence of partial gasification in CO_2 on the tensile strength of coke

Reference	Coke	Gas composition (% CO_2)	Tensile Strength MN/m^2		Loss in tensile strength	
			Before gasification	After gasification	%	Rate %/h
10	1	100 10	4.65	2.38 3.96	48.8 14.8	10.5 3.2
	2	100 10	3.34	2.05 3.17	40.6 17.4	10.0 3.7
	3	100 10	4.44	2.04 3.58	54.0 19.4	11.6 4.1
	4	100 10	3.06	1.77 2.28	42.2 25.5	9.0 5.5
	7	100 10	3.99	2.65 3.76	33.6 5.8	8.4 1.5
	8	100 10	3.52	2.39 3.40	32.1 3.4	8.0 0.9
	9	100 10	4.07	2.67 3.63	34.4 10.8	8.6 2.7
	10	100 10	3.17	3.09 3.87	0.3 -22.1	0.1 -5.5
	11	100 10	4.73	2.79 4.21	41.0 11.0	12.0 3.8
	12	100 10	4.72	3.31 4.70	29.9 0.0	7.5 0.0
	13	100 10	5.00	3.28 4.62	34.4 7.6	8.6 1.9
	15	100 10	4.79	2.55 3.68	46.8 23.2	11.7 5.8
9*	VII	100	5.2	3.8	26.9	8.9
	IX	100	6.0	4.6	23.3	7.8

* The results are given for a level of gasification of 15% (VII) and 22% (IX) which corresponds to the general level of 13-21% for the cokes of Ref. 10.

Table 9.

Comparison of the tensile strength of feed cokes and tuyere cokes

Coke	Mean Tensile Strength MN/m^2	
	Feed coke	Tuyere coke
H4	3.7	4.1
M1	4.0	4.4
L6	4.8	5.0
L4	4.9	5.2
K1	4.9	5.0
J2	5.1	4.9
H1	5.2	5.5
I3	6.0	5.6
L5	6.5	6.8
Average	5.0	5.2

Table 10a.

Comparison of the results of various reactivity tests

Reference	Coke	Reactivity Test				
		Wt. loss/h		micro	N.S.C.	
		Bulk	lump	$^1/T$ for 20% loss	R*	P.R.S
8	20	1.4	2.3	0.8	16	71
	26	1.9	2.5	1.3	22	63.5
	21	2.2	2.6	1.5	26	58
	25	2.2	3.2	1.5	27	55
	28	2.1	3.1	1.1	31.5	48.5
	27	3.6	4.3	1.7	36	42
	24	5.6	8.1	3.2	59	16
	23	3.8	5.6	1.8	37.5	43
	22	2.7	3.5	1.8	30	51

* Estimated from Fig. 25, reference 8.

Table 10b.

Comparison of the results of various reactivity tests

Reference	Coke	Reactivity Test		
		Speed of reaction g/min.	N.S.C.	
			R	P.R.S.
6	3	0.79	37.9	46.0
	2	0.70	34.8	50.7
	8	0.69	42.6	43.0
	4	0.68	31.1	49.5
	1	0.58	28.4	57.9
	5	0.56	29.1	49.6
	7	0.49	25.7	60.6
	6	0.47	23.4	64.0

Table 11.

Comparison between the results of post-gasification abrasion tests

Reference	Coke	Percentage of undersize coke after test		P.R.S.
		-3 mm	-10 mm	
6	1	19.6	-	57.9
	2	19.6	-	60.6
	3	20.7	-	64.0
	4	21.7	-	43.0
	5	23.1	-	50.7
	6	24.2	-	49.6
	7	24.3	-	49.5
	8	27.9	-	43.0
10	11	-	9.6	60.2
	7	-	9.6	70.9
	10	-	11.0	72.4
	13	-	11.9	59.5
	8	-	12.3	47.1
	9	-	12.5	60.9
	4	-	14.2	38.0
	3	-	14.6	54.2
	16	-	17.3	52.7
	12	-	18.7	53.6

FIGURES 1a, 1b

Fig. 1a Comparison between C.R.E. Bulk Reactivity and N.S.C. test results.

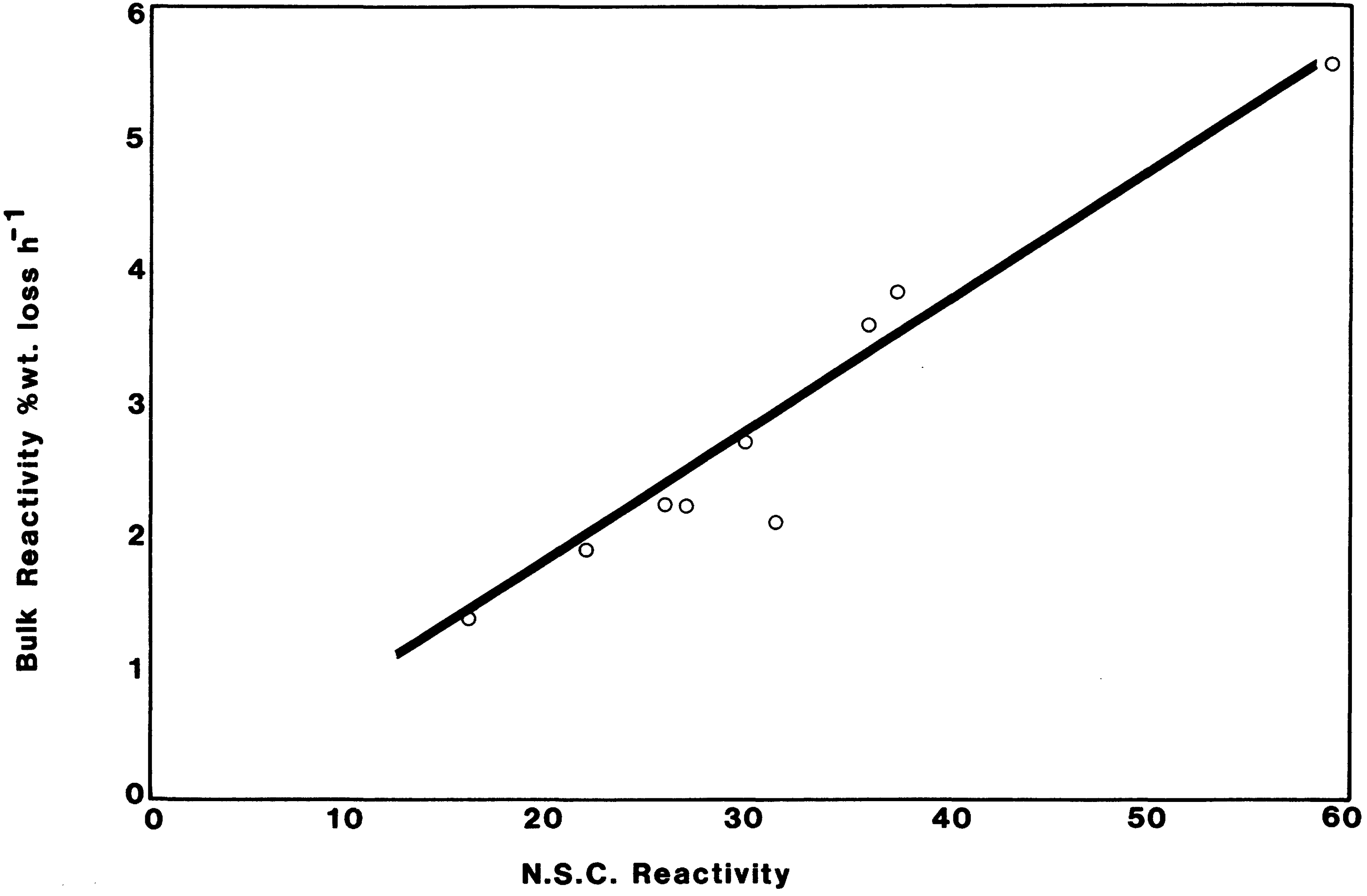

Fig. 1b Comparison between Cerchar gasification test results and N.S.C. test results.