

The influence of potassium on the reactivity and strength of coke, with special reference to the role of coke ash

by W.H. VAN NIEKERK*, R.J. DIPPENAAR†, and D.A. KOTZET‡

SYNOPSIS

It is generally accepted that alkalis attack and degrade the carbon fraction of coke in a blast furnace. Because South African cokes contain relatively high amounts of ash, the influence of alkalis on the ash fraction was investigated, the carbon and ash fractions being separated and studied separately.

Potassium engenders the formation of liquid, with a resultant expansion of volume and a decrease in the strength of the coke ash. However, the ash did not play a significant part in the degradation of the coke, and it was found that the catalytic effect of potassium on the Boudouard reaction was the overriding factor in the coke-degradation process.

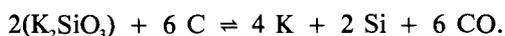
SAMEVATTING

Daar word oor die algemeen aanvaar dat alkalië die koolstoffraksie van kooks in die hoogoond aanval. Suid-Afrikaanse kookse het 'n relatief hoë asinhoud en die invloed van alkalië op die asfraksie is bestudeer. Die koolstof- en asfraksies van 'n spesifieke kooksmengsel is geskei en toe apart ondersoek.

Kalium veroorsaak by hoë temperature vloeistofvorming in die as en gevolglik sit die as uit en neem die sterkte daarvan af. Die as het egter geen noemenswaardige rol in kooksopbreking gespeel nie en daar is gevind dat die katalitiese effek van kalium op die Boudouard-reaksie 'n oorheersende rol in die kooksdegradering speel.

Introduction

South African blast-furnace practice is characterized by higher coke rates than in the rest of the world. These abnormally high coke rates can be attributed mainly to the low quality of local coking coals. Another factor contributing to this undesirable situation is the accumulation of alkalis in the shaft of the blast furnace¹. The alkalis enter the furnace as complex silicates in the charge and are released through the following type of reaction²:



Alkali attack on coke has been studied extensively in the past³⁻⁶. Gol'dshtein *et al.*³, for example, investigated coke taken from the tuyère level of a blast furnace. This coke, which was rich in alkalis, had a much higher reactivity (rate of Boudouard reaction: $\text{C} + \text{CO}_2 \rightarrow 2 \text{CO}$) than the coke normally charged to a furnace. X-ray-diffraction analysis showed a broadening and lowering of the graphite peak, implying intercalation of the carbon layers by alkalis.

Marshall and Radley⁴, investigating the effect of potassium on coke reactivity, came to the conclusion that the increase in reactivity is due to the catalytic effect of potassium on the Boudouard reaction.

The work of Kondoh *et al.*⁵ on the potassium-coke

interaction confirmed both the intercalation and the catalytic theories.

Chow and Lu⁶, in a study of the effect of potassium impregnation on coke strength, found that the tensile strength of coke decreases with the absorption of potassium. They attributed this to the development of cracks as a result of the expansion of the impregnated coke.

In all these studies, it was considered that the deterioration of coke properties is due to alkali attack on the carbon, rather than to the ash fraction, of metallurgical coke. The carbon fraction is normally considered prone to degradation by alkalis because the ash content is fairly low (typically 9 per cent) and the ash is very finely dispersed through the coke matrix. Kondoh *et al.*⁵ showed recently that the ash is too finely dispersed in the carbon matrix to affect coke properties seriously. However, South African metallurgical coke has a significantly higher ash content (typically 15 per cent) than its overseas counterparts and, since the ash portion of the coke contains a much larger fraction of absorbed alkalis⁵, the contribution of the ash fraction of South African cokes to coke degradation may well be different from that of the cokes investigated by other workers³⁻⁶.

The present study showed that alkalis, mainly potassium, influence the coke ash in two important ways.

- (1) The melting point of the ash is lowered, resulting in a larger fraction of liquid at a specific temperature below the liquidus temperature.
- (2) There is a significant volume expansion of the ash when the liquid forms, and this expansion may well result in the formation and propagation of cracks

* M. Sc. Student.

† Professor in the Iscor Chair.

Both the above of the Department of Materials Science and Metallurgical Engineering, University of Pretoria, Hillcrest, Pretoria 0002.

‡ Director, MOH-9 Products (Pty) Ltd, Pretoria North.

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within the coke structure, thereby effectively enlarging the specific surface area of the coke available for reaction with carbon dioxide.

In the present investigation, an attempt was made to analyse, on a quantitative basis, the influence of potassium on the ash, as well as on the carbon fraction of South African cokes.

Experimental Route

So that the influence of alkalis on the carbon and ash fractions of metallurgical coke could be studied, these fractions were separated and investigated separately. Potassium was used as the alkali because it has a more pronounced effect on coke properties than sodium² has.

The schematic diagram in Fig. 1 summarizes the experimental work.

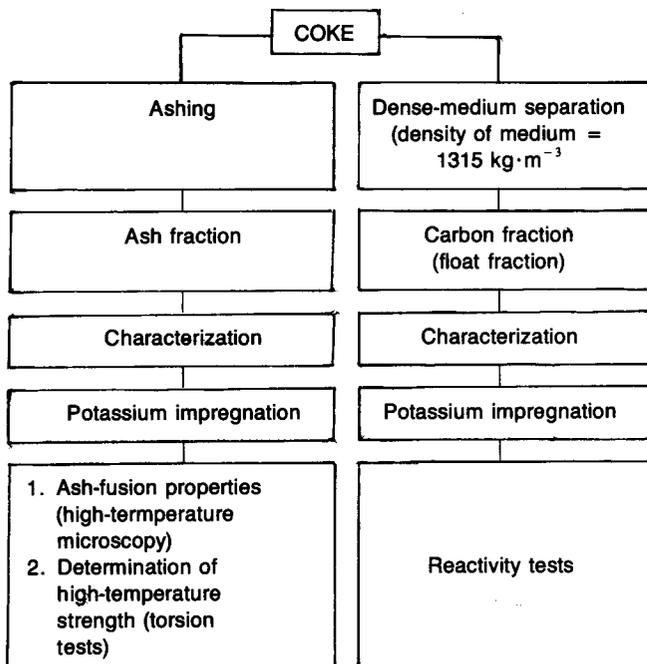


Fig. 1—Flow diagram of experimental route

Experimental Procedure

The influence of coke ash on the behaviour of metallurgical coke was studied in two types of coke prepared from the same coal mixture, namely a 'standard' coke and an 'ash-free' coke.

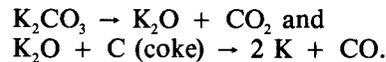
In the preparation of the ash-free coke, the coal mixture was crushed to minus 425 μm , and the ash was separated from the carbonaceous fraction with a $\text{ZnCl}_2\text{-H}_2\text{O}$ solution at a density of $1315 \text{ kg}\cdot\text{m}^{-3}$ by means of a dense-medium separation technique. The 'de-ashed' carbonaceous fraction was subsequently coked in a 7 kg experimental coking furnace at 1100°C for 4,5 hours. The standard coke was prepared from the as-received coal blend under the same conditions.

The final products were two cokes with ash contents of 14,6 per cent (standard coke) and 5,4 per cent (ash-free coke). Petrographic analyses and determinations of

specific surface areas confirmed that the cokes were virtually identical except for their ash contents.

Effect of K_2O on the Carbonaceous Fraction

Both types of coke were impregnated with potassium by the soaking of 2,4 to 4,5 mm particles of the coke in an aqueous solution of K_2CO_3 , drying at 40°C , and firing at 1000°C in an argon atmosphere for 90 minutes. The impregnation reactions involved are



The degree of impregnation by potassium was varied by changes in the concentration of the potassium carbonate solution, the percentage of K_2O absorbed being determined gravimetrically (Table I). Before the K_2O was added, the standard coke contained 0,22 per cent K_2O , and the ash-free coke approximately 0,07 per cent K_2O . These values were obtained from the ash analysis (Table II) and the respective ash contents of the two cokes.

TABLE I
THE AMOUNT OF K_2O ADDED AND THE TOTAL AMOUNT OF K_2O IN THE COKE

K_2O addition, %		Total K_2O in coke, %	
Standard	Ash-free	Standard	Ash-free
0	0	0,22	0,07
5,2	5,3	5,42	5,37
9,7	10,9	9,92	10,97

TABLE II
CHEMICAL ANALYSIS OF ASH PRIOR TO POTASSIUM IMPREGNATION

Oxide	% (by mass)
SiO_2	55,7
Al_2O_3	27,1
Fe_2O_3	6,5
CaO	4,3
K_2O	1,5
Others	4,6

The reactivities of the different cokes were determined by a thermo-gravimetric method of analysis (Fig. 2) after various tests had been carried out to establish the accuracy and reproducibility of the apparatus. In this method, 8 g of the coke sample is suspended from a balance arm and is heated in a stream of argon. When the desired temperature has been attained, carbon dioxide is introduced and the balance zeroed. The coke reactivity is defined as the time required by the coke to lose 1 g in mass (owing to the reaction of carbon with carbon dioxide).

According to the change in activation energy shown on the Arrhenius diagram⁴ (Fig. 3), the Boudouard reaction is assumed to be topochemically controlled at lower

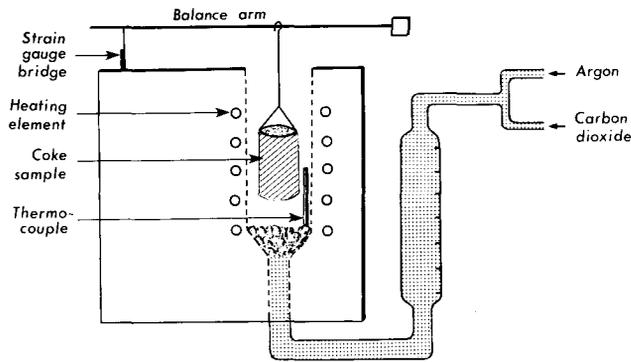


Fig. 2—Schematic representation of the thermo-gravimetric apparatus

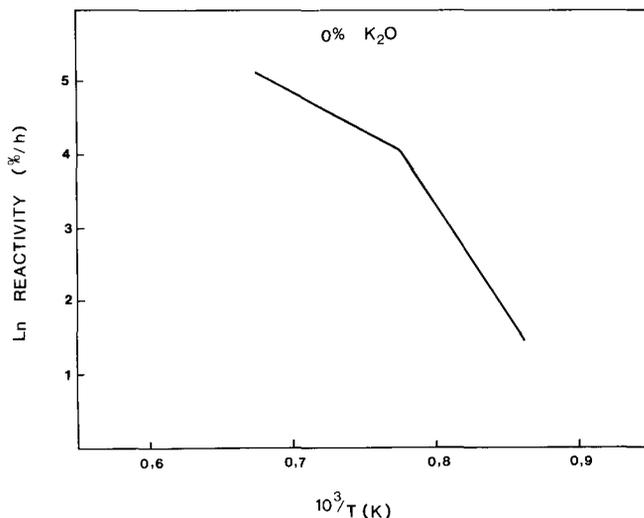


Fig. 3—Arrhenius diagram for the standard coke

temperatures. It is desirable for the reaction to be under topochemical control so that there are only two variables: concentration of reacted gas (can be kept constant) and specific surface area of the coke. The morphology of the coke structure becomes important only when the reaction becomes diffusion-controlled.

According to Fig. 3, the change from topochemical control to diffusion control takes place at approximately 1100°C. The tests were therefore carried out at 1000°C, which would ensure that the reaction was under topochemical control.

Effect of K₂O on the Ash Fraction

The ash fraction was obtained by ashing of the coal blend in an oxidizing atmosphere at 900°C. The ash was analysed by means of an X-ray fluorescence technique (Table II).

The ash fraction obtained was impregnated with potassium by being sintered with K₂CO₃ at temperatures ranging from 1250 to 1400°C, depending on the desired potassium content of the mixture. After sintering, the ash was ground to a powder, and the final percentage of K₂O in the ash was determined by X-ray fluorescence (Table III).

TABLE III
K₂O IN THE ASH FRACTION OF THE COKE

Target analysis %	K ₂ O added %	Total K ₂ O in ash %
0	0	1,5
5	4,5	6,1
6	5,4	6,9
10	8,5	10,1

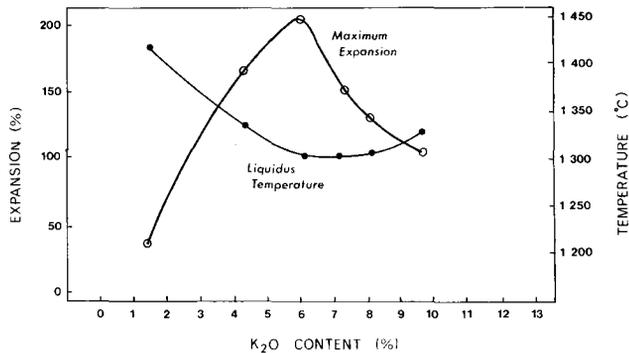


Fig. 4—Analysis by use of the high-temperature microscope

The volume expansion and fusion properties of the various coke ashes were determined with a high-temperature microscope by the photographing of pressed ash samples (about 1,5 mm in diameter) at various temperatures while heating at a constant rate. Typical results are shown in Fig. 4.

The mechanical strength of the ash fraction was evaluated in high-temperature torsion tests. A presintered ash sample, prepared by a slip-casting technique, was subjected to a constant torsional load while the temperature was increased slowly. The tests were terminated either when a temperature of 1400°C was reached, or when a 20° deflection was obtained. Typical results of the high-temperature creep properties of potassium-containing ash are shown in Fig. 5.

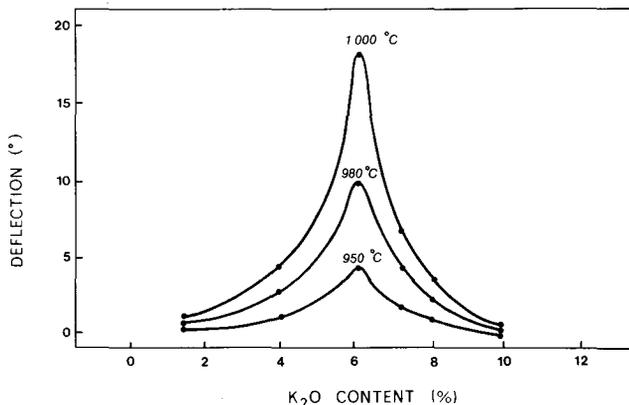


Fig. 5—Results of rising-temperature torsion test

Discussion

Coke ash containing approximately 7 per cent K_2O has a liquidus temperature of $1300^\circ C$, the lowest being in the range between 0 and 10 per cent K_2O (see Fig. 4). It is also evident that the expansion of potassium-containing ash when heated shows a maximum at a K_2O content of approximately 7 per cent.

The high-temperature torsional-creep tests were designed to confirm the results of the high-temperature microscopical investigation quantitatively. A comparison of Figs. 4 and 5 shows that the qualitative predictions based on high-temperature microscopy were indeed confirmed by the carefully controlled creep tests. As in the microscopical investigation, the torsional-creep tests reveal most distortion in ash specimens with an approximate K_2O content of 7 per cent.

The expansion of the ash specimens at high temperatures as measured microscopically and the creep as measured by hot-torsion tests are due to the formation of a liquid. The results of these experiments show clearly that the maximum amount of liquid is formed in an ash with an approximate K_2O content of 7 per cent. The same conclusion can be drawn from an analysis of the phase diagram for the system $K_2O-Al_2O_3-SiO_2$ (Fig. 6).

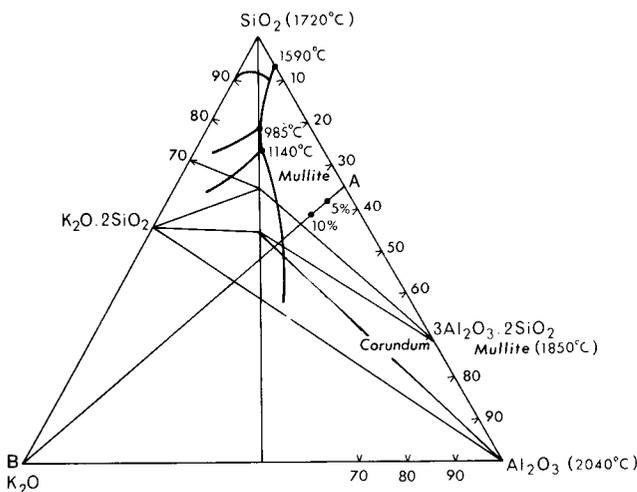


Fig. 6—Phase diagram for the system $K_2O-Al_2O_3-SiO_2$

An assumed ash composition of 65 per cent SiO_2 and 35 per cent Al_2O_3 is shown at A (Fig. 6). An increase in K_2O content will cause the ash composition to change along line A-B. Ashes with K_2O contents of 5 and 10 per cent are shown on line A-B in the mullite primary-phase field. Fig. 7 was derived from calculations of the amount of liquid present at different temperatures for given K_2O contents.

It is evident from Fig. 7 that the maximum percentage of liquid present at temperatures above the liquidus temperature in the mullite primary-phase field will also occur at approximately 7 per cent K_2O . Clearly, the coke ash with its complex composition cannot be compared directly with the simple three-component ternary system, but at least such a comparison confirms the deduction that the distortion in the ash specimens is due to the formation of a liquid.

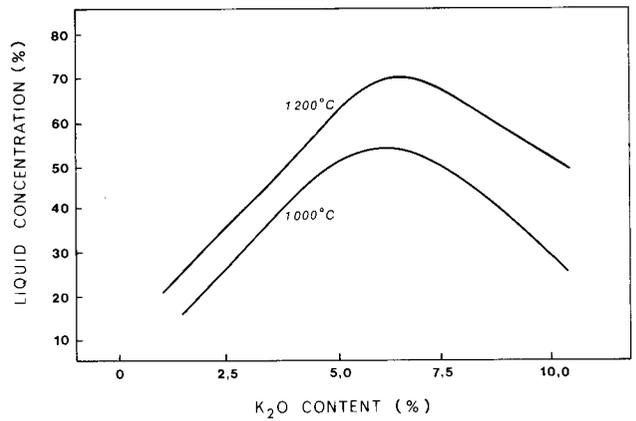


Fig. 7—Theoretical plot of the concentration of liquid phase at increasing K_2O concentration, as determined from the $K_2O-Al_2O_3-SiO_2$ phase diagram

When the results summarized in Figs. 4 and 5 are applied to the behaviour of coke ash in a blast furnace, the following deductions are made.

- When alkalis are absorbed, the ash in lumpy coke expands significantly as a result of the formation of a liquid at high temperature.
- This expansion is greatest in coke ash with a K_2O content of approximately 7 per cent.
- The excessive expansion may result in the initiation and propagation of cracks in lumpy coke, with a maximum effect probably at a K_2O content in the ash of 7 per cent. It is evident from Fig. 4 that very little potassium is needed to cause a dramatic expansion of the ash fraction of coke.

If cracks initiate and propagate owing to expansion caused by the formation of a liquid, it is expected that the reactivity of coke will also increase since degradation of the coke would yield a larger specific surface area available for the Boudouard reaction. It is to be expected that South African cokes with their high ash content would be especially susceptible to degradation as a result of alkali impregnation, should the effect of volume expansion with the resulting crack initiation and propagation be of importance. As a test of this hypothesis, reactivity studies were conducted on the standard and ash-free cokes. The results are shown in Fig. 8.

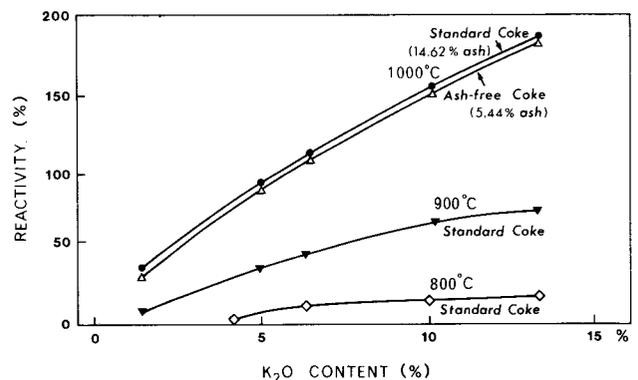


Fig. 8—Comparison of the reactivity curves for ash-free and standard coke

There was very little difference between the activities of the two types of coke. (The small difference that is shown can be attributed to the difference in specific surface area, namely $17,92 \text{ m}^2 \cdot \text{g}^{-1}$ for the standard coke as opposed to $10,37 \text{ m}^2 \cdot \text{g}^{-1}$ for the ash-free coke.)

Furthermore, there is no distinct peak in the increase in reactivity rate at 7 per cent K_2O or at lower K_2O contents, not even for the standard coke (14,6 per cent ash). It can therefore be concluded that a large expansion in the ash fraction owing to the absorption of alkalis did not break down the structure of the lumpy coke with a consequent increase in specific area. This does not mean that no expansion of the ash took place, but only that the coke structure accommodated this expansion without cracking.

The experimental findings shown in Fig. 8 can be explained if the coke is porous and if the ash particles are finely dispersed throughout the coke matrix. Both these conditions are fulfilled in the structure of the coke under consideration and explain why the ash impregnated with K_2O did not cause deterioration of the coke. That the structure of coke is porous is common knowledge, and it has been confirmed in analyses by optical and scanning electron microscope that the ash fraction in coke is indeed very finely dispersed. Although cracks were occasionally observed, no evidence was found that the initiation of cracks was associated with ash particles. However, more cracks were found in regions rich in potassium than in other regions. It was evident from the microscopical investigation that the volume expansion of the potassium-containing ash particles was accommodated in the porous coke structure at the temperatures concerned. Kondoh *et al.*⁵ reached a similar conclusion.

The conclusion to be drawn from the experimental investigation is that the ash fraction of metallurgical coke does not play a significant role in its degradation, or in increasing its reactivity as a result of potassium impregnation—not even in South African cokes with their high ash contents.

It is evident from Fig. 8 that the Boudouard reaction in the impregnated coke took place at temperatures as low as 800°C ; the unimpregnated coke started reacting only at approximately 900°C . Consequently, the main reason for the decrease in strength of alkali-impregnated

coke seems to be the accelerated Boudouard reaction, and not distortion of the coke matrix due to the volume expansion of ash.

Summary

- (1) Potassium causes the formation of a liquid phase in coke, with a resultant increase in volume and a decrease in the strength of the coke ash. However, these changes in the characteristics of the ash do not play a significant role in the degradation of the coke, and do not significantly influence its reactivity through an increase in the specific surface area available for the Boudouard reaction.
- (2) The absorption of potassium may cause cracks to form in the coke structure as a result of volume expansion, but the influence of the cracks on the strength of the coke is insignificant compared with the catalytic effect of potassium on the Boudouard reaction. Consequently, the degradation of coke by the Boudouard reaction is far more dominant than the formation of cracks as a result of alkali absorption.

Acknowledgements

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