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HIGH-TEMPERATURE BEHAVIOUR OF BLAST FURNACE COKE – A REVIEW

D.A. Reeve, J.T. Price and J.F. Gransden

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HIGH-TEMPERATURE BEHAVIOUR OF BLAST FURNACE COKE — A REVIEW

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D.A. Reeve*, J.T. Price** and J.F. Gransden**

ABSTRACT

Metallurgical coke serves as reductant in the iron blast furnace. It must be strong to maintain a suitable coke particle size distribution so that the blast furnace gases can pass easily and uniformly through the burden. Studies of tuyère coke and coke samples taken from quenched blast furnaces have shown that cokes degrade primarily by chemical reaction with alkalis and CO_2 at temperatures above 900°C , rather than by physical abrasion. Methods designed to evaluate coke at temperatures and reactive conditions similar to the blast furnace are required. Methods reviewed include: simulation of coke oxidation at the tuyères; hot strength of cokes at 1300 and 1500°C ; reactivity of coke to CO_2 at 1100°C ; and cold coke strength (after reaction with CO_2 at 1100°C). Coke strength was found to be lower at high temperatures than at room temperature. No correlation existed between hot- and cold-strength tests. Mosaic structures of coke were less reactive to CO_2 than coke particles derived from inert coal macerals.

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LE COMPORTEMENT DU COKE DE HAUT-FOURNEAU A HAUTE
TEMPERATURE — UNE REVUE

par

D.A. Reeve*, J.T. Price** et J.F. Gransden**

RESUME

Le coke métallurgique agit en tant qu'agent réducteur dans le haut-fourneau. Il doit être assez résistant pour maintenir la granulométrie du coke d'une distribution adéquate qui permettra aux gaz du fourneau de passer facilement et uniformément à travers le lit de fusion. Les études effectuées sur le coke de tuyères et les échantillons de coke prélevés des hauts-fourneaux de trempage ont démontré que les cokes se désagrègent principalement à la suite de réactions chimiques avec les alcalis et le CO_2 à des températures de plus de 900°C , plutôt que par l'abrasion physique. Il faudrait des méthodes conçues pour évaluer le coke à des températures et des conditions de réaction semblables à celles des hauts-fourneaux. Les différentes méthodes examinées sont: la simulation de l'oxygénation du coke de tuyères; la résistance à la chaleur du coke à des températures de 1300 et 1500°C ; la réactivité du coke au CO_2 à 1100°C ; et la résistance du coke à froid (après la réaction avec le CO_2 à 1100°C). La résistance du coke est plus basse à haute température qu'à la température ambiante. Il n'existe aucune relation entre les essais à froid et à chaud. Les structures mosaïques du coke réagissent moins au CO_2 que les particules de coke dérivées des macéraux de charbon inerte.

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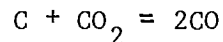
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INTRODUCTION

Coke, made by carbonizing blends of metallurgical coal, is used as a source of energy and reductant for iron oxides in the iron-making blast furnace. It also governs the burden permeability and hence the production rate, especially in the lower parts of the blast furnace where it may be the only solid material present. Blast furnace coke is characterized by size consist, tumble test index, permeability, reactivity, and chemical analysis; its breakdown during descent in the furnace has been considered to be a function of coke size, and ability to withstand abrasion.

This breakdown in the blast furnace is the subject of the present review. Recent literature confirms that breakdown is also affected by the chemistry of the blast furnace process, in particular, gas-solid interactions with alkali compounds, as well as with other catalysts such as iron and manganese of the solution loss reaction:



Improvements in the blast furnace operating performance were previously obtained by changing the nature of the iron oxide portion of the burden, particularly by introducing closely-sized pellets made from high-grade concentrates.

The importance of the role of coke in blast furnace productivity has been underlined in recent years with the increase in inner working volume of blast furnaces from 500 - 2000 m³ to at least 4000 m³ and with production rates up to 2.4 metric tons/m³/day. The No. 2 blast furnace of the Oita Works of Nippon Steel Corporation has an inner volume of 5070 m³ and the No. 9 blast furnace at Krivoi Rog in the Soviet Union has an inner

volume of 5026 m³. Early studies on the breakdown of coke during its descent involved developing hot-test procedures, but any relationship between the breakdown indices from these tests and blast furnace performance was entirely fortuitous. Also, it has been established that cold breakdown indices bear no distinct relationship to hot strength.

To establish the mechanism of coke breakdown, it is necessary to obtain coke samples from operating blast furnaces, this normally being done at the tuyeres. In Japan, advantage has been taken of the closing down of relatively small furnaces with inner volumes of less than 2000-m³, to quench the furnaces and obtain samples of coke at different points between the stockline and tuyeres. Such samples showed that the important factor relating to coke breakdown is the weakening effect of chemical attack on the coke structure, especially in the bosh region. Apparent strengthening of coke close to the tuyeres may also take place, possibly because of ferruginous material in the pore structure and the formation of compounds such as silicon carbide from the reduction of silicon monoxide.

This report reviews work done to establish hot strength tests. It also summarizes and comments on information obtained from tuyere coke and quenched blast furnaces in order to propose a meaningful laboratory research program for studying the high temperature behaviour of coke. However, first the role of coke in the blast furnace will be elucidated.

ROLE OF COKE IN THE BLAST FURNACE

Coke is transported from the underbin screens to the charging bell at the top of the blast furnace. Dropping from the bell to the stockline results in some physical breakdown. Coke moves down through the blast furnace and any remaining coke which has not been completely gasified is

eventually burned at the tuyeres. Residence time is about 14 hours for a 1500-m³ furnace. Abrasion occurs in the stack at temperatures below 1100°C and a portion of the coke is gasified by the solution loss reaction. High furnace productivity is achieved by maximizing the rate at which air is blown through the tuyeres, resulting in maximum iron oxide reduction, but may be limited by resistance of the burden to the passage of gas. This resistance in the stack is largely governed by the total amount of fines produced from coke abrasion and from low-temperature disintegration of iron oxides.

In the bosh region, coke is the only solid material present, liquid iron and slag percolating counter-current to the ascending gases. Thus bosh coke size distribution is important as it controls the bulk permeability of the bed. Blowing can be interrupted, and hence productivity diminished by the loading of interstices between the coke pieces with liquid iron and slag, ultimately flooding into the hearth when sufficient liquid has built up. Giedroyc and Hyslop have reported that UK blast furnaces operate at above 80 per cent of the flooding regime (1). However, the susceptibility of blast furnaces to loading and flooding is governed by:

- slag volume and viscosity
- blast pressure and volume
- gas velocity in the bosh
- specific surface area of the coke
- voidage of the coke bed in the bosh.

The last two factors cannot be controlled by the blast furnace operator and hence it would be useful to know the expected changes in coke size as it passes through the bosh. Increasing the coke lump size and decreasing its size range, as evidenced by blast furnace formed coke trials, assist in

optimizing the last two of the above parameters, but it remains to be established why and to what extent coke decreases in size during passage through the bosh.

Gibson and Goleczka have examined the mechanical properties of coke in relation to its bulk permeability, which affects the blowing rate in the furnace (2). They maintain that coke will continue to break down in the furnace because of the presence of cracks and fissures formed during contraction in the post-plastic period of carbonization. Although it is more likely that chemical attack by alkalis etc., produces greater breakdown, Gibson and Goleczka's work confirms that a change in harmonic mean size as the coke descends in the blast furnace is pertinent to blast furnace performance. The resistance to flow of the ascending gases increases rapidly when the harmonic mean size falls below 40 mm so that small changes in blast furnace mean coke size in this range would be expected to have a great effect on pressure drop.

In summary, the most important role of coke in the blast furnace is to ensure sufficient permeability of the burden; charging sequences constrain the coke so that it descends in layers and ensures burden permeability during the softening and fusing of intermediate ore layers. Iron oxide reduction in the various furnace zones would also be expected to influence coke strength and degradation; Hyslop and Wilkinson note that change in coke strength and abrasability is tied to the solution of carbon, in that total solution is controlled primarily by oxygen release at temperatures above 850°C and can be equated to the amount of direct reduction of the burden or about 34 percent of total reduction (3).

Coke of larger initial size, of high lump strength and abrasion resistance is required for larger blast furnaces.

HOT-STRENGTH TESTS AND COKE REACTIVITY

The possibility of changes in coke degradation at blast furnace temperatures, from those at ambient temperature had led to developing various methods for the high-temperature testing of coke. However, as already noted, any relationship between results from these tests and blast furnace performance is generally regarded as fortuitous. Literature on testing at elevated temperatures was recently reviewed in June 1976 and only general conclusions are reported here (4). The techniques employed included use of compression testers (the best known work perhaps being that of Holowaty and Squarcy (5) at 1650^oC), using ballistic apparatus, and rotating drums. The general conclusions were as follows (4):

1. Coke Strength is lower at high temperature than at room temperature.
2. There is no correlation between cold- and hot-strength tests.
3. Hot strength is diminished when the test temperature is higher than the carbonization temperature.
4. Extending the coking time improves hot strength.
5. Cokes had maximum abrasability in an oxidizing atmosphere and minimum in a reducing atmosphere.
6. The higher the porosity, the lower the compressive hot strength.
7. Compressive strength was increased by a decrease in ash content or an increase in the melting point of the ash.
8. The higher the cold Micum value, the smaller the reduction in hot strength due to temperature.

The literature survey referred to above does not mention the work of Bruk and Leibovich who studies the effect on strength of cracks in the coke (6) at 1300^oC. If there were no cracks before heating, strength increased

by a factor of five but diminished if cracks were present because they became longer. A hot test under an applied load of 1.85 kg/cm^2 showed that the largest fractions, 80 mm, had the lowest strength, indicating the importance of carefully screened coke for blast furnace use. However, the applied load was not realistic in terms of furnace operation, the burden generally being considered to exert a loading of 0.5 to 0.8 kg/cm^2 at the top of the bosh.

The temperatures employed in these techniques refer to the bosh region but testing is also done on the reactivity of coke to carbon dioxide at temperatures found in the lower part of the stack (1000°C). The kinetics of the solution loss reaction are limited by chemical considerations up to about 1100°C , by gas diffusion in the pore structure between 1100 and 1450°C , and by boundary layer diffusion at higher temperatures.

It has been reasoned since coke is being gasified in the solution loss reaction and not all of the carbon monoxide is required for indirect reduction of the iron oxide, coke reactivity should be related directly to coke rate. In fact, early work in Germany found this to be true, suggesting carbon solution loss in the stack was undesirable because it reduced heat that would otherwise be generated by combustion of the carbon at the tuyeres (7). However, Dartnell has suggested that with modern blast furnace practices using hot blast and highly reducible ores, the coke rates have been reduced to such low levels that insufficient carbon monoxide for indirect reduction is generated at the tuyeres and must be generated by the carbon solution reaction (8). Although 32 per cent of coke may be consumed by solution loss, the importance of this reaction lies not in the extent or rate of reaction but its contribution (along with thermal fissuring and decomposition of mineral matter in coke) to the deterioration of the coke quality. Indeed,

Gol'Dshtein et al. have reported that the attack of alkalis causes the carbon crystal structure and physico-chemical properties of different cokes to become similar (9). If this is true, then skip coke reactivity changes cannot directly influence blast furnace coke rate except when change in reactivity is accompanied by change in the mechanical strength of the coke.

In an attempt to combine chemical and mechanical breakdown, the Nippon Steel Corporation now employs a strength-after-reaction test in which the 200-g, 20 ± 1 -mm sample is reacted with carbon dioxide at the rate of 5ℓ/min at 1100°C for 2 hours in a Gakushin-type iron ore reducibility test retort having an internal diameter of 75 mm (10). The weight loss is reported and the coke is transferred to a 130-x 700-mm I drum and tumbled for 30 min at 20 rpm. The strength-after-reaction is reported as the percentage of +10-mm material after tumbling. The strength-after-reaction requirement for NSC Oita No. 1 blast furnace (4158 m^3 , coke strength DI_{15}^{30} 93.5, and mean size 47-50 mm) is given as 45-52 per cent (11). No relation was found between strength-after-reaction and room-temperature strength, but a good correlation exists with coke reactivity as measured by reaction percentage. There appeared to be some correlation with blast furnace permeability and fuel consumption. If there is a relationship between reaction percentage and strength after reaction, it may be possible to relate this to carbonization parameters since these govern reactivity to a large extent. Such a relationship would be significant; the ultimate goal of any hot test is to control high-temperature coke degradation (and hence bosh permeability with its attendant effect on blowing rate and furnace productivity) by adjusting carbonization parameters and coal blend composition.

In the NSC test, a high reactivity was associated with the quantity and nature of inert macerals in the coke. A strong relationship between ash content (percentage of $\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO}$) and reactivity was also found, again showing how coke contributes to its own breakdown. The relative effects of the chemical compounds in coke ash and those, perhaps from the iron ores, circulating or refluxing within the blast furnace on coke breakdown, are of interest.

A modification of the NSC test has also been used at Italsider (12). Conditions were: coke 15 ± 1 mm, 1000°C , CO_2 at 2ℓ/min for 120 min, tumble at 30 rpm for 90 min; strength-after-reaction was reported as the amount of -3-mm material. Again, a relationship was found between strength-after-reaction and reactivity but it was not linear, as reported by Murakami et al (10).

The effect of inerts on high-temperature degradation has also been established in the test developed at Nippon Kokan KK (13). Five kg of 50 - 75 mm coke is heated to 1500°C in 4.5 h in a silicon carbide drum. After maintaining temperature for 30 min the drum is rotated at 20 rpm, differences between cokes being detected by changes in the signal:noise ratio. Cokes which underwent considerable strength degradation had high inert contents. The NKK test has recently been proposed to the International Organization for Standardization Technical Committee 27, Solid Mineral Fuels, and was originally developed to evaluate formed coke (14). Until more is known about the mechanism of high-temperature breakdown, it is unlikely that any evaluation procedure can be standardized especially in view of the fact that tuyere coke analysis, described in the next section, indicates that test parameters may need to be tailored to the needs of individual blast furnaces.

Balon et al. developed a cyclone apparatus to assess the high temperature properties of metallurgical cokes under rotary circulation conditions that simulate modern blast furnace raceways (15). Six-to 10-mm coke was introduced and forced to circulate in the cyclone at 1100°C by the combustion products from air and natural gas. Residual sample weight after 3 min of testing was related to coke reactivity and initial coke strength. Depending on its chemical and structural properties, 6 - 10-mm coke was completely gasified between 5 and 8 min.

Thompson and Benedict, in their work on the effect of coal structure on coke quality, found that coke reactivity is related to carbon types in the coke structure, confirming that carbon types from the inert macerals in coal are preferentially attacked by carbon dioxide (16). However, these forms can reduce coke reactivity if protected from CO₂ attack by being thoroughly incorporated into the coke cell walls. This may explain why NSC found the nature of the inerts to be important and indicates the importance of breakdown of cell wall structure by the solution loss reaction on coke strength in the blast furnace. Thompson and Benedict have also observed that semi-inert macerals, such as pseudovitrinite only partially react with CO₂ after coking, forming a pore structure within themselves. Thus as well as altering the structure of the resultant coke, significant percentages of pseudovitrinite will produce an amorphous carbon which is more reactive to CO₂ than those from other macerals. Cell wall structure development during carbonization obviously may have a bearing on hot strength. Medium volatile coals with petrographic reflectance >1.2 per cent produce the strongest cokes when coked alone, but unless the cell wall structure is sufficiently well-developed, it does not necessarily follow that the reduction in mean size in the lower regions of the furnace will be least for these cokes.

Fukuyama et al. measured the changes in properties in the temperature range 1200-2000°C of cokes of 5-10 mm prepared from single coals in a 250-kg oven (17). The cokes, weighing 60-75 g, were heated at 10°C/min to 1350°C and 5°C/min above 1350°C; oxidation was prevented by maintaining a vacuum of 10⁻⁴ mm Hg in the furnace. Reactivity, measured at 950°C, decreased at treatment temperatures to 1500°C and increased again above 1700°C; iron reduced during the high-temperature treatment catalyzed the solution loss reaction. Microstrength increased at temperatures above 1700°C, when ash and sulphur also vaporized.

In summary, high-temperature physical tests have not yielded much information on blast furnace behaviour but a test which measures strength after reaction with CO₂ has indicated some relevance to blast furnace operation. However, the effect of chemical attack on coke cell wall structure and its relation to reactivity and strength needs further elucidation.

COKE DEGRADATION IN THE BLAST FURNACE AND THE EFFECT OF ALKALIS

Mechanical coke degradation during its descent in the blast furnace using extended Micum tumble tests has been studied in the U.K. (1, 3, 18). Coke samples ranging from 150 to 250 kg were removed from the tuyeres of five blast furnaces having inner volumes of 570, 762, 1345, 1500 and 1550-m³, immediately after the furnaces had been taken off blast, i.e., after the coke had been subjected to all chemical and physical effects in the stack and bosh, but not to combustion in the tuyere zone. Degradation in the stack could be divided into two components, (i), between the skip sampling point and the stockline and (ii), during descent in the shaft. The former was simulated by a number of 2-m drops and the latter by tumbling for sufficient revolutions to simulate the degradation. It was found that simulation of stack degradation

for skip coke required a different number of revolutions for each blast furnace (i.e. the test could not be standardized) and size distribution of fines in the tuyere coke was attributed to combustion in the furnace. The differences in size distribution became larger as the amount of work done on the coke increased, i.e., as the number of revolutions required to simulate the tuyere coke degradation increased. The skip coke required 89 revolutions for the 570-m³ furnace and 393 for the 1500-m³ furnace. A plot of the reduction ratio of the mean coke size at a scale of 0 to 1 against the logarithm of the number of revolutions showed a marked discontinuity at about 150 revolutions, indicating a change in the coke breakage pattern and after which small changes in the mean size gave relatively large changes in equivalent revolutions (Fig. 1).

Testing of skip and tuyere cokes indicated that the ability of the coke to withstand abrasion (M10) was reduced by its passage through the furnace, probably because of carbon solution at 900 - 1100°C. The proportion of coke sizes down to 40 mm was all reduced, giving correspondingly increased proportions of >40 mm material. Reduction in coke mean size increased with the size of blast furnace, being 22.0 per cent for the first 2 furnaces and 43.7 for the last three yielding a deterioration in the M40 index. There appeared to be no relationship between the M40 to M10 coke quality indices of skip coke and the size reduction ratio of tuyere coke. Nor could reactivity of skip coke, as measured under laboratory conditions be related to the strength of tuyere coke. Slopes of extended Micum graphs in which $1/S^2 \times 10^4$ are plotted against the number of revolutions of the tumble drum to 900, where S is the mean coke size, increased for tuyere coke and was related to the size reduction ratio of coke after passage from stockline to tuyere (Fig. 2). Thus, inherent coke strength is reduced by the thermal and chemical occurrences in the blast

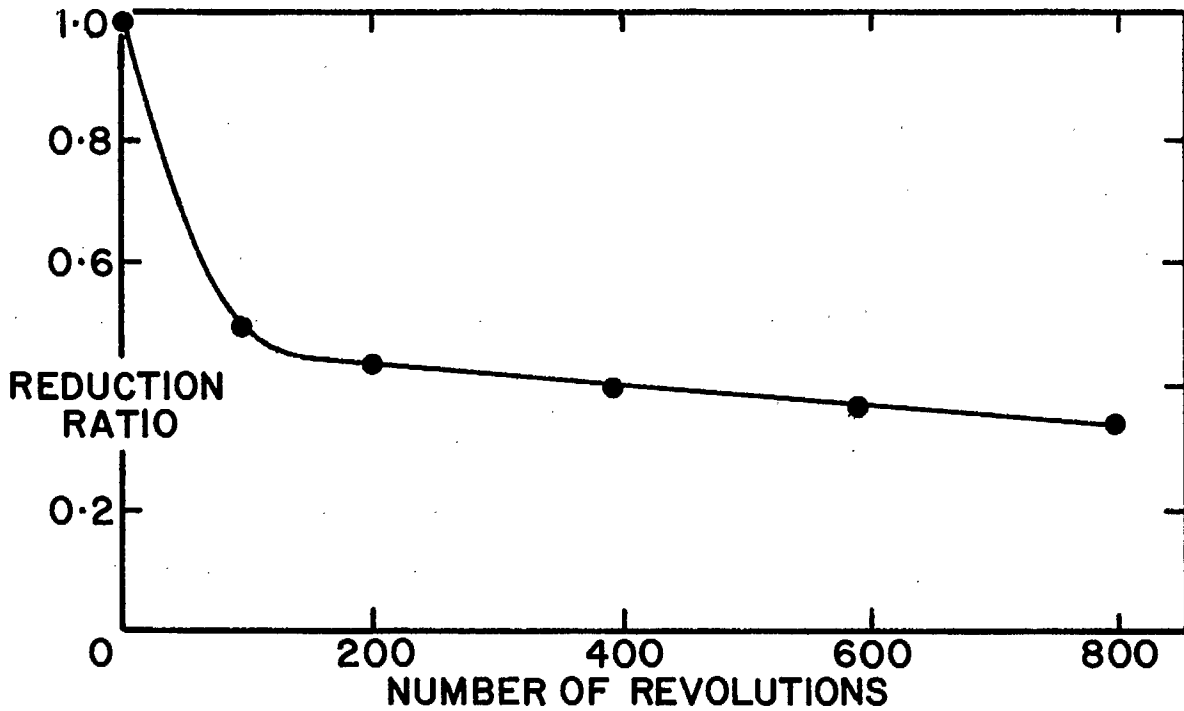


Figure 1. Reduction ratio after extended 1/5-Micum tests on skip coke(3). (After Hyslop and Wilkinson)

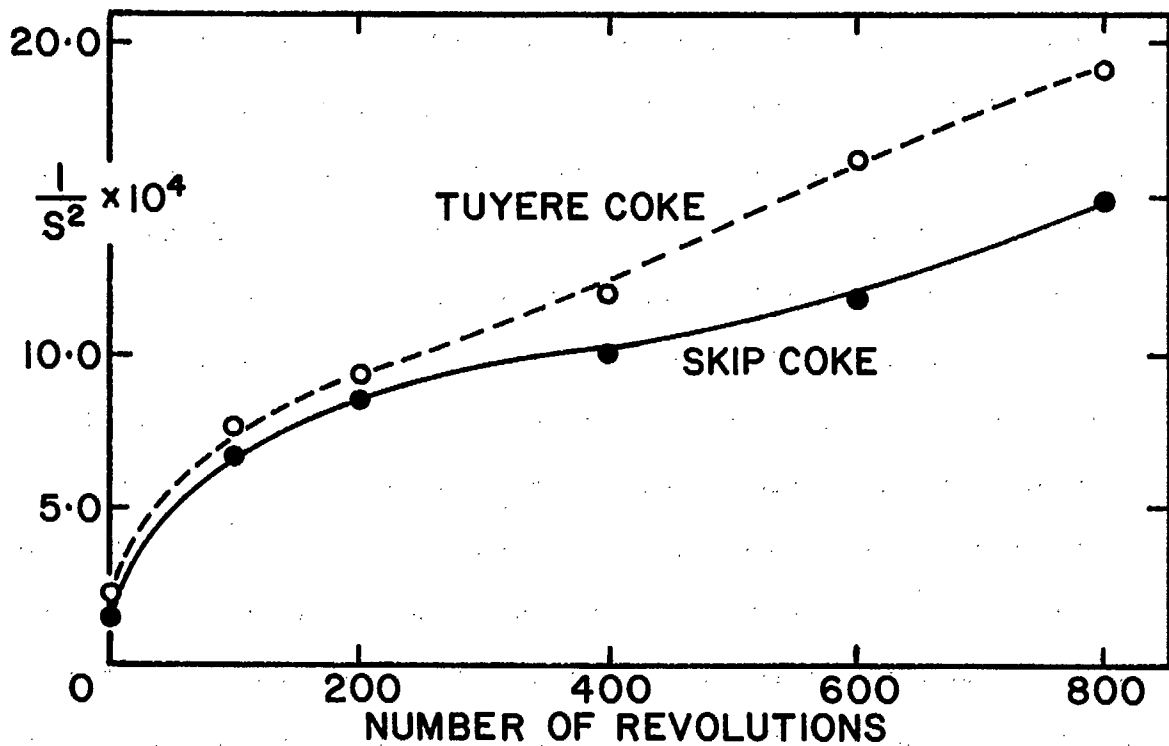


Figure 2. Extended 1/5-Micum tests on skip and tuyère cokes(3). (After Hyslop and Wilkinson)

furnace. This was confirmed by cell wall structure examination which showed up to 25 per cent internal erosion of cell walls. The mosaic structure was attacked leaving the inerts untouched, indicating high-temperature carbon solution action. Comparison of skip and tuyere cokes also showed an average bulk density increase of 13.9 per cent and an average decrease in apparent relative density of 3.5 per cent. Tuyere coke was higher in ash, iron and alkali than skip coke. Alkali contents in the tuyere cokes are summarized in Table I.

TABLE I

Alkali Contents of Skip and Tuyere Cokes
from Two Japanese Blast Furnaces

Coke Type	Furnace Inner Volume (m ³)			
	1345		1500	
	Na%	K%	Na%	K%
Skip coke	0.02	0.05	0.06	0.04
Tuyere coke	0.18	0.37	0.48	0.59

From these studies it is evident that the existing Micum test at +60 mm and 100 revolutions does not give a meaningful assessment of either wharf-stockline or stockline-tuyere coke breakdown, especially for large furnaces. Coke for larger furnaces must be more resistant to size degradation and have larger initial size. Statistical correlations indicate that important factors affecting stockline-tuyere degradation are hearth diameter and coke rate, but solution loss from the coke structure affects deterioration in mechanical properties.

Because of an unexpected increase in coke rate at ash contents above 8.5 per cent for cokes of the same strength, Italsider sampled coke at blast furnace tuyeres and found a strong relationship ($\alpha = 0.985$) between

the decrease in mean coke size and fraction of coke +20 mm as well as a statistical relationship between coke rate, per cent -20 mm material at tuyeres, and ash content (12). As mentioned previously, use of a modified version of the NSC test established a relationship between reactivity to CO₂ and strength-after-reaction. This relationship implies a direct effect of coke ash on degradation during descent in the furnace because of the relationship between coke rate and ash content. Partial melting of the ash in the bosh region may also be expected to contribute towards the degradation.

Kinzer and Kusner note that coke ash is the principal source of alkali input and have examined tuyere cokes from Republic Steel's furnaces (19). Reactivity increased by 3.5 times as alkalis increased from 0.25 per cent in the skip coke to 1.24 per cent in the tuyere coke and mean coke size decreased from 51.5 to 29.9 mm. Furnace productivity increased when the mean tuyere coke size increased. ASTM stability factor dropped from 50.9 to 38.2.

Filonenko et al. examined tuyere samples from the 2000-m³ inner working volume No. 3 furnace at Norvo-Lipetsk Iron and Steel Works in the USSR and studied changes in structure as coke descended in the furnace (20, 21, 22). The skip coke specifications were 6.9 per cent +80 mm, 14.8 per cent -40 mm, 10.44 per cent ash, and 1.33 per cent sulphur. The parameters measured were changes in porosity, pore diameter, cell wall thickness and gasification rate. The increase in tuyere coke porosity was related to an increase in the amount of pores >0.35 mm diameter. The decrease in pore diameter and increase in amount of cell walls with thickness <0.1 mm was related to the speed of gasification, this being a maximum at the top of the bosh and diminishing at lower levels because of

inner surface area reduction by liquids entering the pores. Thus, coke with high initial inner surface area would be expected to show greater decrease in strength characteristics in blast furnaces because of greater changes in micro-structural characteristics. Denser coke would be expected to behave better in the furnace because the depth of carbon solution would be less although this would not be so when the solution loss reaction is diffusion controlled. In the foregoing tests, 32 per cent porosity coke was consumed to a depth of 3-4 mm and 45 per cent to 12 mm when exposed to CO_2 for 20 min at 1000°C . Unfortunately these studies did not include an investigation of changes in the different carbon forms in the tuyere coke structure.

Bagnall and Hart have examined the micro- and meso-structural changes of Australian cokes in the blast furnaces (23). Tuyere coke showed a gradation of oxidized features from its interior toward its surface. At lower stack temperatures, carbon solution occurred within the coke causing a thinning of cell walls. At higher temperatures, carbon solution occurred primarily at the surface of the coke. Inerts particularly fusinite, in tuyeres cokes had preferentially reacted with CO_2 but lower order (isotopic and fine grain) mosaics had also reacted extensively. X-ray diffraction and scanning electron microscopic examination indicated silicon carbide began to form in coke at temperatures of 900°C . Needle-like crystals were associated with the coke mosaic while granular silicon carbide formed with inert particles. Large blocky crystals of silicon carbide were also associated with the cokes' original mineral components.

Gol'Dshtein et al. also examined coke taken from the tuyeres and slag notch of a blast furnace at the Magnitogorsk Combine, USSR (9). Skip coke was mixed with potassium carbonate and heated to 1000°C

in 5 hr to give it the same reactivity to CO_2 as tuyere coke. The coke was then de-ashed by leaching with HCl and HF but only half of the alkalis - K_2O and Na_2O were removed, indicating that the remainder was associated with crystal-lattice carbon. It was concluded that the catalytic effect of the alkalis on the solution loss reaction was due to distortion of interbasal spaces. On the other hand, exposure to high temperature during descent in the blast furnace increased the degree of coke graphitization, the coke growing along the a- and c- axes, and hence decreased the reactivity. X-ray diffraction analysis of skip coke and coke treated with K_2CO_3 after being held for 6 hr at 1500°C in a reducing atmosphere, indicated that potassium compounds have an effect on the disordering of the crystal structure, thus increasing reactivity. A study of the effect of alkalis and other compounds on the kinetics of coke graphitization at blast furnace temperatures and residence times would be a useful addition to these Russian studies.

In reported cases of quenched blast furnaces in Japan, coke degradation during descent was associated with the effect of alkalis. The No. 4 (922 m^3) blast furnace at Keihin Works of Nippon Kokan KK was quenched in 1972, while their No. 2 (1148 m^3) and No. 3 (936 m^3) were quenched in 1974. Prior to shut-down, No. 2 was charged with relatively weak coke having DI_{15}^{30} of 89.4 and 55 mm square pieces of refractory brick; coke at a strength DI_{15}^{30} of 92 was used in No. 3 and No. 4 furnaces.

Comparison of the high and low strength cokes from No. 3 and No. 2 blast furnaces indicated thermal treatment in the upper stack initially improved the DI_{15}^{30} strengths of the weaker coke to 92.0 and the stronger coke to 92.2. After reacting these cokes with CO_2 at 1000°C , their DI_{15}^{30} indices were 87.4 and 89.9 for the weaker and stronger cokes respectively, indicating the importance of the solution loss reaction. Reaction with CO_2

increased coke porosity below 1100°C but not at higher temperatures, indicating that solution loss does not affect coke strength above 1100°C.

During the descent in No. 2 furnace, wear on the refractory cubes was slight and only 10 revolutions of the JIS drum or 30 of the ASTM were required to simulate this wear. However, 100 revolutions of the JIS drum or 240 for ASTM were required to simulate coke degradation from a mean size of 65 to 40-45 mm caused by fissures and indicated that degradation due to abrasion was small and chemical effects had greater influence on strength. Coke degradation increased sharply in all furnaces about 4 m above the tuyeres. For the No. 4 blast furnace charged with good quality coke, the decrease in coke strength corresponded to 15 JIS drum revolutions; 4 - 8 for solution loss, and above 1000°C, 2 - 4 for thermal degradation and 3 - 4 for chemical attack by alkalis etc. The alkali in the coke in No. 2 blast furnace remained constant below 1100°C and increased markedly above this temperature.

A similar pattern of coke alkali adsorption has been found from other quenched experimental blast furnaces (27-30). Shimoura has estimated that 13.1 kg of K_2O and Na_2O per ton of hot metal was gasified at the tuyeres. Figure 3 shows that potassium content increased to a greater extent than sodium and alkali-coke compounds (28), similar to those suggested by Gol'Dshtein (9), have been postulated. Sodium and potassium behaviour differs in that the sodium tends to be concentrated around pores while potassium tends to be disseminated throughout the structure. compounds may cause weaknesses in the coke as it passes through the bosh and may be the cause of the chemical attack on coke in the NKK No.2 blast furnace. These conclusions are significant in that they assign a more important role to alkalis in the blast furnace than as mere catalysts of the solution loss reaction.

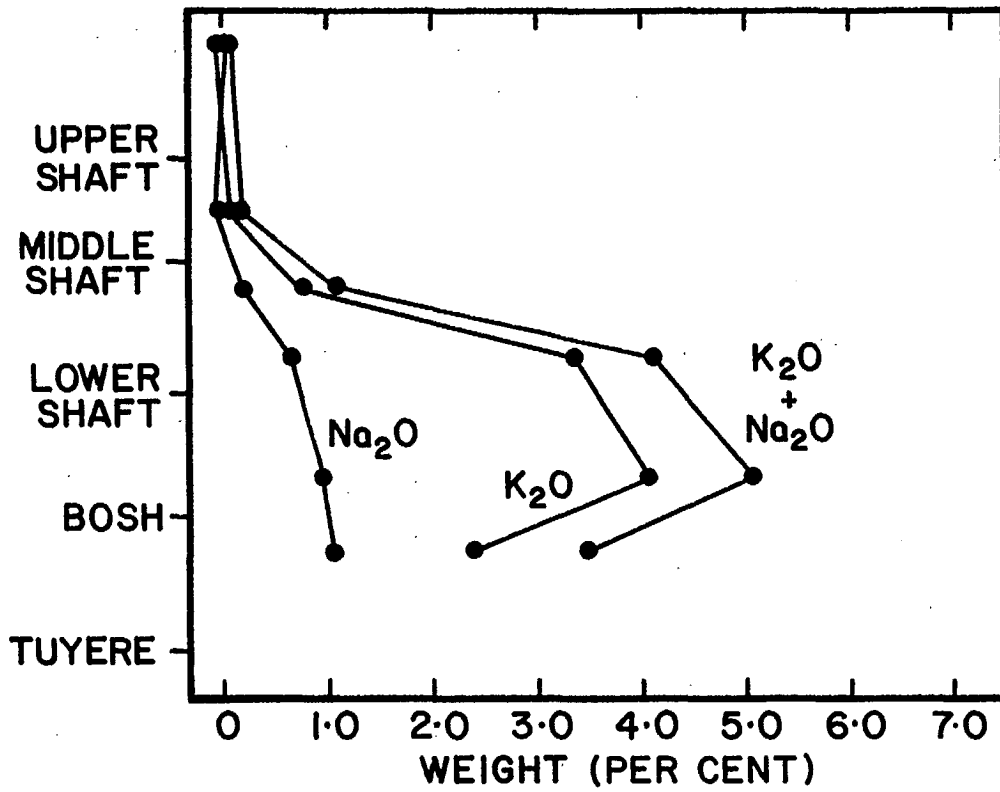


Figure 3. Absorption of alkalis on cokes in experimental blast furnace(28).
(After Tate et al)

Kawasaki Steel has also studied the problem of alkali absorption on coke using bench-scale experiments(31). Potassium vapour, generated by heating a mixture of potassium carbonate and carbon at $10^{\circ}\text{C}/\text{h}$ and maintaining 1000°C for 1 h, was absorbed into a piece of coke hanging from a quartz spring. Maximum absorption was achieved after 1 h and the potassium was found to be absorbed into both the ash and carbon. The compound $(\text{KAl}(\text{SO}_4)_2)$ was identified in the ash and the X-ray diffraction peak for graphite formation in the carbon was lowered. The potassium was absorbed in the inner pores and after absorption microcracks appeared which caused "peeling" when the coke surface was knocked.

Coke sampled from 16 levels of the quenched Hirohata No. 1 blast furnace and also the Shigashida No. 5 of NSC showed a greater decline in strength properties around the walls in the lower part of the furnace than in the middle (32). Cell wall thickness decreased down the shaft because of gasification, but reactivity increased in the neighbourhood of the tuyeres. The highest alkali concentrations were found in the high-temperatures regions of the furnace centre. As reported by other workers, the mosaic part of the coke structure resisted chemical reaction more than the coke carbon forms from the coal inert macerals. Similar results were found from the examination of cokes from the quenched NSC Kukioka No. 4 furnace (33). In the lower shaft, porosity increased to a depth of 3-mm because of solution loss. Deterioration in the bosh resulted from structural weakening caused by formation of pores in cell walls.

Coke was also sampled from 16 levels of the quenched Kokura No. 2 furnace of Sumitomo Metal Industries (34). Maximum alkali content was found at the top of the bosh, 3.5-m above the tuyeres where per cent K_2O changed from 1.9 to 11.6 and per cent Na_2O from 1.2 to 3.5. Reactivity increased to the top of the bosh and then decreased, in contrast to NSC's findings.

SUMMARY

As coke descends in the blast furnace, its mean size decreases. This degradation results in an unknown coke size distribution in the furnace bosh. An abnormal degradation can have a deleterious effect on furnace productivity because bulk permeability in the bosh region, where coke is the only solid present, is related to stability of the wind rate.

Hot-strength tests have been developed to characterize the behaviour of cokes in the blast furnace, but such tests have met with little success. Cold tumble tests give no indication of high-temperature breakdown. Mechanical degradation between tuyere and stockline can be simulated by an extended tumble test, but the number of revolutions required is a function of the particular furnace. Reactivity tests do not relate to blast furnace performance unless their results can be correlated with changes in coke strength.

As coke descends in the blast furnace it becomes weaker principally because of chemical attack on its structure, rather than by physical abrasion. Gasification in the lower stack increases pore diameter and decreases cell wall thickness. It has been conclusively established that alkalis, especially potassium, play an important role in coke degradation. They catalyze the solution loss reaction in the lower stack and also cause weakening of the coke structure, perhaps by the formation of alkali-carbon compounds, in the direct reduction zone of the upper bosh where their concentration is high. Source of alkalis is twofold: from the coke ash, hence coke contributes to its own disintegration; and from the iron ore. Alkalis can reflux in the furnace and cause swelling of iron oxide pellets during reduction, also possibly affecting their softening-under-load characteristics leading

to another source of deterioration in furnace performance. The relative effects of alkalis from these two sources is unknown and an answer to this question is required, possibly by using the counter-current reactor to simulate conditions in the blast furnace stack.

It has been recognized that solution loss occurs preferentially within coke pores at carbon sites originating from the inert coal macerals rather than at sites from the reactive macerals. High-temperature degradation has been found to be greater for cokes containing large amounts of carbon sites originating from inert macerals. Again, the effect of alkalis and other compounds on the morphology of coke structure degradation has not been elucidated and studies are required of reacted coke samples using the Quantimet 720 image-analysis system. This technique has already been adopted in the UK (35) and Australia (36). The effect on coke textural parameters of high-temperature treatment in the presence of alkalis and other compounds should be examined, using cokes made from coals with different reactive:inert maceral ratios and hence having textures from isotropic through fine mosaic to fibrous.

The ultimate objective of studying the high-temperature disintegration behaviour of cokes is to understand how changes in coke structure caused by chemical interactions in the blast furnace relate to changes in coke strength and size distribution. Relating structure to strength should allow the optimum coke for a particular furnace practice to be obtained by the tailoring of both coke oven coal-blend composition and carbonization factors.

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