

Influence of Geology on CSR (Coke Strength After Reaction With CO₂)

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ABSTRACT

Although drum strength has historically been the coke quality parameter, more recently, coke reactivity and strength after reaction with CO₂ have become the principal criteria by which coals are selected to make blast furnace coke. Typical western Canadian medium volatile, Inertinite-rich coking coals produce cokes that are among the world's best in this test. Vitrinite reflectances of 1.0 to 1.6%, inertinite contents of >30%, alkalinity indices of <1.0, high ash-fusion temperatures >2700°F, 1500°C, and low fluidity, all appear to be contributing agents. As yet however, there is no universally applicable prediction formula.

INTRODUCTION

CSR, or coke strength after reaction with CO₂, has become the more important means of evaluating the quality of coking coal and of controlling blast furnace performance within Pacific rim steel-producing countries, and is now a principal criterion by which coals are selected to make blast furnace coke. The purpose of this paper is to describe the various methods used to predict CSR and from them determine the geological factors which appear to influence CSR values.

In the late 1960's, Nippon Steel Corporation deliberately cooled and dissected three blast furnaces in an attempt to better understand the physical and chemical changes that take place in the thermal transformation of coke during its passage through the furnace. On this journey, coke undergoes a reduction in size caused by mechanical and thermal stresses, and gasification by CO₂ and H₂O. There is at the same time a decrease in drum strength, and an increase in reactivity. Cokes which have high reactivity to CO₂ have low CSR'S, and vice versa. Cokes that have inherently higher drum strengths and lower reactivity to CO₂ are therefore desirable (Figure 1), and it has been demonstrated by NSC that to maintain trouble-free operation at large blast furnaces, CSR's should be maintained above 57 (Ishikawa, 1982).

A relationship between coal rank and the reactivity of coke to CO₂ (measured by weight loss), has been documented in studies using small numbers of samples (Schapiro & Gray, 1963; British Carbonization Research Assoc. 1978). These studies showed that

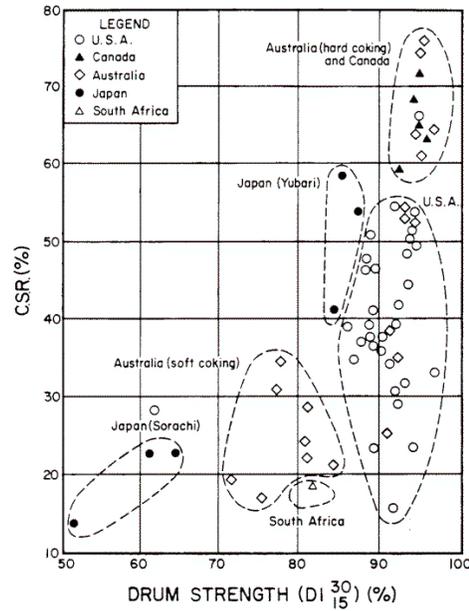


Figure 1.
Relationship between CSR and Drum strength D30/15 (Ishikawa, 1982)

coke from high volatile- and low volatile-coals suffered greatest weight loss, and that those from medium volatile coals were the least reactive. Subsequent coke microscopy studies have correlated the reactivity to the texture of the coke; fine mosaic carbons (from high volatile coals) and ribbon-like carbons (from low volatile coals) are more reactive than coarse-mosaic carbon forms (from medium volatile coal). Although a correlation between coke reactivity and coal rank had been established for a number of years prior to the advent of strength tests on reacted coke, a rigorous investigation of the geological factors which affect coke reactivity and strength from the perspective of the parent coals was not done until the 1980's.

COKE REACTIVITY & STRENGTH TEST

In the Nippon Steel Corporation (NSC) CSR test, 240 kg of wharf coke is reduced to 10 kg which is then crushed and screened

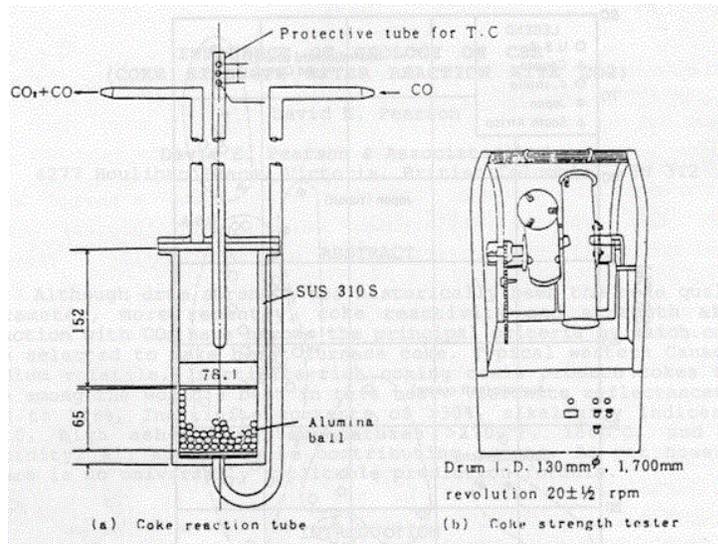


Figure 2.
Schematic of CSR apparatus.

to 20 ± 1 mm. A 200 g sample of this coke is placed in the reaction tube, and after heating to $1,100^\circ\text{C}$ in N_2 gas flow, a switch-over to CO_2 is made. The reaction is sustained for two hours. After cooling and weighing the reacted coke to determine reactivity (CRI), a strength test is performed in an I-shaped drum. After 30 minutes at 20 rpm in the I-shaped drum, the coke is screened on a 9.52mm sieve and the weight of the material remaining on the sieve is measured for CSR. The apparatus is shown diagrammatically in Figure 2.

The following values are quoted:

$$\text{CSR} = (\text{Weight of residue on sieve after reaction} * 100) / \text{Weight of material after reaction}$$

$$\text{CRI} = (\text{Amount of weight change} * 100) / \text{Weight of material}$$

The Kobe Steel method for determining coke reactivity is precisely the same as NSC'S. However, for the strength test, Kobe Steel uses an I-shaped drum that is only 700mm in length (versus 1700mm), in which the reacted coke is tumbled for 20 minutes at 30 rpm and then screened on a 10mm sieve. As a result of the modified equipment, Kobe Steel's Reaction Strength Index (RSI) is slightly different from NSC's CSR value. To obtain the equivalent RSI, add 10 units to a CSR value ($\text{RSI} = \text{CSR} + 10$).

CSR PREDICTION TECHNIQUES

Because determination of coke reactivity (CRI) and CSR (or RSI), is an expensive, time-consuming, two-stage procedure, in which the coal must first be carbonized, and the resulting coke tested, several prediction techniques have been developed using characteristics of the parent coals. However, the usefulness of these prediction methods has been questioned (Valia 1989), and as yet, there is not a universally acceptable prediction technique.

NIPPON STEEL CORPORATION METHOD

In 1980, NSC published a model for predicting CSR (Hara et al.), based on vitrinite reflectance and Inertinite content (Figure 3). The NSC diagram shows that CSR increases with increasing reflectance up to a value of about 1.4%, and that for

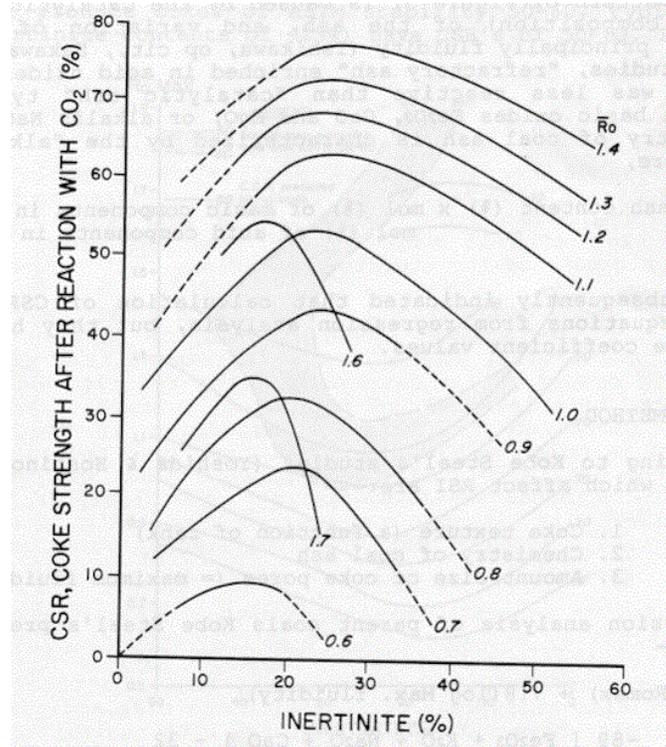


Figure 3.
NSC's 1980, CRS-prediction model.

each reflectance level, the highest CSR's are obtained at an optimum inertinite content. It also shows that with increasing values of vitrinite reflectance, the resulting cokes will have lower CSRs.

Although this diagram suggests that Western Canadian coking coals produce high-CSR cokes, it also implies that at any reflectance level the optimum CSR values would be produced by coals with inertinite contents of 15-25%, typical of Pennsylvanian-age coals.

Careful study of the diagram using a variety of coals of different rank and provenance confirms that it cannot correctly predict the CSR of cokes based only on petrographic data. For example, the Australian coal, Blackwater, from south Queensland, has a vitrinite reflectance of 1.04%, and an inertinite content of 39.0%. According to the NSC prediction such a coal should produce a coke with a CSR of about 50. The actual value of CSR for this coal is 32 (NSC, 1982).

Later studies by NSC have suggested that deviation from the predicted pattern of Figure 3, is caused by the catalytic nature (chemical composition) of the ash, and variation of coking properties, principally fluidity (Ishikawa, op cit., Sakawa 1982). In these studies, "refractory ash" enriched in acid oxides, Al_2O_3 and SiO_2 , was less reactive than "catalytic ash" typically enhanced in basic oxides Fe_2O_3 , CaO and MgO , or alkalis NaO & K_2O . The chemistry of coal ash is characterized by the "alkalinity index", where,

A.I. = ash content (%) * [(mol(%) of basic components in ash) / (mol(%) of acid components in ash)]

KOBE STEEL METHOD

According to Kobe Steel's studies (Yoshida & Hoshino 1984), the factors which affect RSI are:

1. Coke texture (a function of rank)
2. Chemistry of coal ash (= maximum fluidity)
3. Amount/size of coke pores

From regression analysis of parent coals Kobe Steel's prediction formula is:

$$RSI = 70.9(Romax) + 7.8(\log \text{ max. fluidity}) - 89[(Fe_2 + K_2O + Na_2O + CaO) / (SiO_2 + Al_2O_3)] - 32$$

BHP AUSTRALIA

Despite the Japanese studies, Australian researchers at BHP have produced another regression equation better suited to Queensland and New South Wales coals (Coin, Pers. Comm., 1985). The following equation of predicted-CSR versus measured-CSR on 52 coals and cokes has a correlation coefficient of 0.92.

$$CSR = 133.8 - 15.56 * BI - 3.1 * VM + 8.5 * LMF + 0.22 * INERTS$$

where, BI the Basicity Index, is = $(Fe_2 + K_2O + Na_2O + CaO) / (SiO_2 + Al_2O_3)$

DISCUSSION

Data from the NSC prediction technique has been redrawn in Figure 4, with CSR as the independent variable, in a diagram that includes ASTM coke strength data. This figure shows that among coals that produce cokes of ASTM stability 50-60, typical U.S. coals (Inertinite contents of <25%) have CSR's of 50-63. In marked

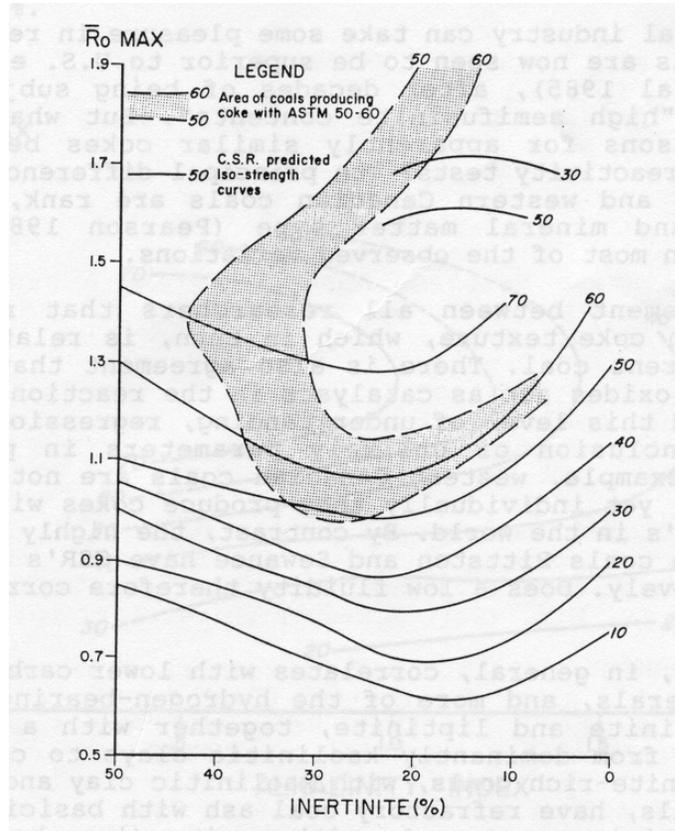


Figure 4.
CRS Prediction compared with coke strength data.

contrast however, typical western Canadian coals (Inertinite contents of >30%) that produce the same strength cokes, have CSR's of 50-70+. In addition, coals strongly enriched in Inertinite (>45%), with vitrinite reflectances of 1.2% to 1.4%, and typically referred to as "weak coking" coals, have predicted CSR's equivalent to those from U.S. premium medium volatile coals. The figure also shows that the once-premium Pocahontas low volatile coals have CSR's of 30-50, some 20 points lower than low-volatile Canadian equivalents.

Ishikawa's 1982 plot of CSR versus Drum Strength D130/15 (Figure 1.) confirms this interpretation. From his figure it can be seen that, U.S. coals with D130/15's of >92 have CSR's of 15-55. In marked contrast, all western Canadian and some Australian coals with similar D130/15's are shown to have CSR's of >59. The diagram confirms that for a blend of coking coals designed to produce a CSR in excess of 57, high-CSR Canadian and Australian coals will form the principal component, to which will be added small amounts of the lower-CSR coals. The so-called "weak coking coals" although individually very rich in Inertinite with low D130/15's (<90), have good CSR'S, and from the perspective of blending are superior to coals of higher D130/15 but with low CSR'S.

The Canadian coal industry can take some pleasure in reading that our coking coals are now seen to be superior to U.S. equivalents (Goscinski et al 1985), after decades of being subjugated by misunderstood "high semifusinite contents". But what are the underlying reasons for apparently similar cokes behaving so differently in reactivity tests? The principal differences between the U.S. coals and western Canadian coals are rank, maceral composition, and mineral matter type (Pearson 1980), which together explain most of the observed variations.

There is agreement between all researchers that reactivity correlates with coke texture, which in turn, is related to the rank of the parent coal. There is also agreement that elevated levels of base oxides act as catalysts in the reaction with CO₂. However, beyond this level of understanding, regression analyses dictate the inclusion of unlikely parameters in prediction formulae. For example, western Canadian coals are notorious for low fluidities, yet individually they produce cokes with some of the highest CSR's in the world. By contrast, the highly fluid U.S. medium volatile coals Pittston and Sewanee have CSR's of only 45 and 49 respectively. Does a low fluidity therefore correlate with a high CSR?

Higher fluidity, in general, correlates with lower carbon-bearing inertinite macerals, and more of the hydrogen-bearing reactive macerals, vitrinite and liptinite, together with a change of mineral matter from dominantly kaolinitic clays to calcite and pyrite. Inertinite-rich coals, with kaolinitic clay and quartz as dominant minerals, have refractory coal ash with basicity indices of <=0.1. Inertinite-poor coals with pyrite (iron-bearing) and calcite (calcium-bearing) mineralogy, are enriched in the basic oxides, and have basicity indices of >=0.35. Typically, Inertinite-rich coals have such an excess of refractory acidic oxides that high ash fusion temperatures are common (>2700°F, 1500°C). Among Inertinite-poor coals, there are sufficient basic oxides that ash fusion temperature are reduced (<2570°F, 1400°C). These observations show that fluidity, to some extent, correlates with an increase in the base/acid ratio (or basicity index).

Because NSC have shown that the amount of ash, as well as its chemistry, is significant, the alkalinity index is probably a better measure of the catalytic effect of coal ash than the basicity index. Figure 5. shows a contoured scattergram of twenty five Canadian and Australian coals plotted in terms of vitrinite reflectance and alkalinity index, where, A.I. = Ash (%) x B.I., or,

$$A.I. = \text{ash content (\%)} \times (\text{wt (\%)} \text{ of basic components in ash}) / (\text{wt (\%)} \text{ of acid components in ash})$$

Despite the limited data available, the diagram is an improvement over the original NSC diagram. It is reasonably accurate for inertinite-rich coals with alkalinity indices (AI's) of <=1.0, but with only fair reliability for coals with AI's >=1.0 and Rols <1.3%.

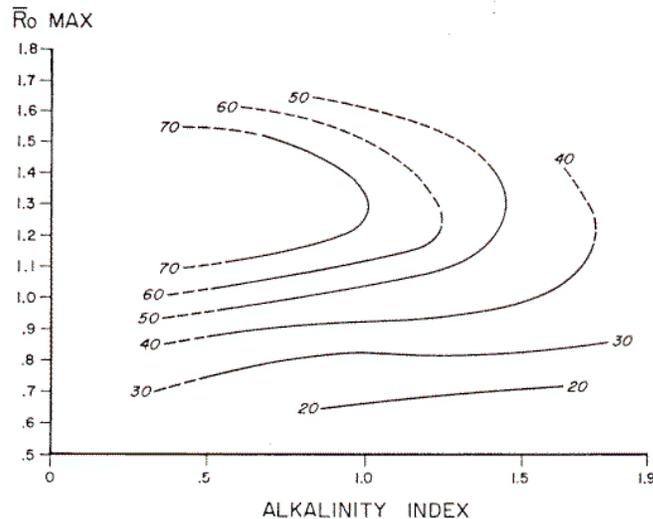


Figure 5.
CSR prediction by RoMax, alkalinity index & ash.

Since the chemistry of the peatswamp environment, which ultimately controls the coalseam mineralogy and the hydrous nature of coals, is a function of pH, future research into CSR prediction may focus on a predictive technique using vitrinite reflectance, ash content, and a

proxy for pH. The pH proxy could be, for example, the Hydrogen Index (or hydrocarbon generative capacity) of a coal, derived from RockEval analyses.

CONCLUSIONS

1. correlations exist between coal rank and coke reactivity, and in a general way this can be used to predict CSR.
2. Coal mineralogy, and specifically the alkalinity index of ash provides information on the catalytic or refractory nature of chemical constituents in the ash, and can dramatically change a rank-only prediction of CSR.
3. A negative correlation may exist with Gieseler fluidity, such that reduced fluidity imparts higher CSR's. Why this should be so is not fully understood.

ACKNOWLEDGEMENTS

Dr. W.R. Leeder is thanked for reviewing an early draft of the manuscript

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