Small Scale Determination of Metallurgical Coke CSR

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ABSTRACT

Coke Strength after Reaction (CSR) and the concomitant Coke Reactivity Index (CRI) are useful parameters for assessing the behaviour of coke in blast furnace. CanmetENERGY has developed a procedure for producing coke to allow CSR measurement involving relatively small amounts of coal sample (~15 kg). The procedure involves producing semi-coke using the Sole Heated Oven in accordance with ASTM standard D2014-97(2004). The resulting semi-coke is quenched (either wet or dry) and subsequently reheated to 1100^{0}C under nitrogen for 1 hour. CSR and CRI are measured using the coke produced using this procedure.

To demonstrate the validity of CSR and CRI measured using this approach, identical coal blends were carbonized concurrently using the CanmetENERGY pilot scale moveable wall oven (460 mm wide, 350 kg capacity) and the procedures mentioned above. CSR and CRI of the cokes produced by these two approaches were compared. Statistical analysis and coke textual analysis were performed to demonstrate the applicability of this novel approach on CSR determination with limited amount of coke sample.

Keywords: Coke, Cokemaking, CSR, CRI, Carbon Forms

Introduction

Current world-wide ironmaking capacity is dominated by blast furnace technology. In 2009, this technology accounted for 94% of global hot metal production, 912.2 Mt [1]. In comparison, direct reduced iron (DRI) production was limited to only 53.1 Mt [2]. The performance and efficiency of blast furnace ironmaking technology is continuously improving. One of the factors contributing to the success of blast furnace ironmaking is the continued amelioration in coke quality.

Metallurgical coke is the major source of carbon in the operation of the blast furnace. Besides being responsible for producing reducing gas, coke also supports the descending burden and provides passages/voids through it for distributing reducing gas in the furnace. Moreover, the combustion of coke in the lower hearth by the injected blast generates heat for melting of the hot metal. Because of the numerous functions of coke in the blast furnace, stringent requirement on its physical and chemical properties are needed to ensure smooth operation of high productivity modern blast furnaces [3].

In the lower hearth of the blast furnace, coke is the only solid material present to support the entire weight of the burden above. Coke, possessing high mechanical strength in extremely hot and dynamic environments, is required to cope with the increase in throughput of large sized blast furnaces. Prior to its descent to the lower hearth, coke reacts with CO_2 produced from the reduction of iron ore to generate CO to replenish the source of this reducing gas required for reduction of iron ore in the upper portion of the furnace. Therefore, the coke charged into the blast furnace must be capable of generating CO by reacting with CO_2 while simultaneously maintaining its physical strength after reaction.

Among the important indicators for assessing the quality of coke for blast furnace application are Coke Reactivity Index (CRI) and Coke Strength after Reaction (CSR) developed by Nippon Steel Corporation in the early 1970's [4].

To estimate the quality of coke produced from specific coal blends in terms of CSR and CRI, the most economical way is by carrying out carbonization in a pilot-scale coke oven having known and proven capability of producing industrial grade coke.

CanmetENERGY currently operates two pilot-scale slot-type coke ovens (460 mm wide and 350 kg capacity). The pilot-scale coke oven used in this investigation is depicted in Figure 1.

Figure 1. CanmetENERGY Pilot-Scale Coke Oven

The cokes produced in either of these ovens have been shown over time to be of similar quality to industrial coke via benchmarking against industrial ovens [5].

The pilot scale oven test requires a specific amount of coal to ensure the coke produced is appropriate for CSR evaluation. In such instances where the amount of coal available is insufficient to perform a pilot-scale test, as for the case of an exploration bore hole sample, CSR and CRI normally cannot be measured.

In an effort to broaden the ability to measure CSR and CRI with limited amounts of coal sample, a novel procedure for producing coke involving carbonization using a sole-heated oven was developed at CanmetENERGY. The sole-heated oven used in this study is shown in Figure 2.

Figure 2. CanmetENERGY Sole-Heated Oven

To validate this new approach for producing coke for CSR and CRI evaluation, concurrent carbonization tests of identical coal blends using sole-heated oven and pilot-scale moveable wall oven were performed. CSR and CRI of the cokes produced using both carbonization routes were compared.

Besides comparing sole-heated oven and pilot-scale oven cokes for their CSR and CRI, these were also evaluated for their Apparent Specific Gravity (ASG), the ratio of the mass of a volume of dry coke to the mass of an equal volume of water. Coke ASG varies with the rank and ash content of the coal carbonized, the bulk density of the coal charge in the oven, the carbonization temperature and the coking time [6].

Furthermore, microscopic analysis of the textures was performed on the sole-heated and pilot-scale oven cokes to compare them for their carbon forms. As discussed later, this technique is, among numerous advantages, extremely useful for understanding the behaviour of coal during coking and for interpreting pilot movable wall oven results including pressure generation and coke quality results.

Experimental

Coke Preparation by Sole-Heated Oven

The preparation of a coke sample for CSR evaluation using a coal sample of limited quantity involves two steps, namely semi-coke preparation and heat treatment. For preparation of semi-coke, the sole-heated oven was employed in accordance with the ASTM D2014-97(2010) Standard for expansion or contraction of coal.

A total of 12 kg of sample (coal or blends) is divided equally and each half-charged into chambers approximately 280 mm in width, length and depth of a double-chambered oven. A weighted piston applies a constant load of 15.17 ± 0.35 kPa on the surface of the coal in each of the chambers throughout the test. The coal bed is heated from below by the sole plate initially set at 554 °C and gradually ramped up to 950 °C according to a prescribed temperature program. The test is considered complete when the temperature at the top of the coal bed reaches 500 °C after a period of 6-7 hours. Following completion of the test, the coke is pushed from the oven, quenched in water, drained and oven dried overnight at 120 °C. In cases where expansion/contraction values are reported, the measured expansion or contraction of the sample is converted to a reference base of 833 kg/m^3 and 2% moisture.

For heat treatment, the dried semi-coke (8-9 kg) is subsequently introduced in pieces (50 x 175 mm) into a stainless steel holding box hermetically sealed on top with 3 mm thick section of stainless steel with a 1 cm exit hole in the centre for venting the hot coke gases. The holding box is connected to N_2 gas for continually flushing the semi-coke (5-10 L/min flowrate) to prevent its combustion. The holding box with the semi-coke inside is then heated in a Muffle Furnace from ambient to 1100 °C in 2-3 h at the rate of 5-10 °C/min. Upon attaining 1100 °C, the coke is soaked for an additional hour. Then, cooling is allowed to take place to approximately 100 °C. The entire heating and cooling cycle is carried out in a continuous flow of N_2 and requires about 15 hrs to complete. The average weight loss of coke during the heat-treatment process has been measured to be 5 ± 2%.

CSR, CRI and ASG Determination

After the heat treatment, the coke sample produced was prepared and tested for CSR and CRI measurement as per specifications in the ASTM D5341-99(2010) Standard. By definition, the CRI is the percent weight loss of the coke sample after reaction in CO_2 at 1100^oC for 2 hours. The cooled, reacted coke is then tumbled in an I-drum for 600 revolutions at 20 rpm. The cumulative percent of +9.5 mm coke after tumbling is denoted as the CSR. The repeatability limit (r) of this method for CRI is 2.4 and for CSR is 5.4; the reproducibility limit (R) of this method for cokes in CRI range 20-28 is between 5 and 7 and that for cokes in CSR range 55-70 (acceptable grade for ironmaking) is also between 5 and 7. ASG of cokes were determined following a method developed at CanmetENERGY and related to the ASTM D167-93(2004) and ISO 1014:1985 Standards.

Coke Texture Analysis

Carbon form analysis in this study was carried out as per a combination of the US Steel method [7] and the CanmetENERGY method. A single point count is made for each measured field of view. For each field, the stage is rotated in order to determine the possible highest rank carbon form. Normally 500 point counts are performed on a sample. Each carbon form is derived from an assumed parent coal V-type. From the coke texture analysis, one can determine the 'effective coal reflectance (%Ro)' and also the percentages of low-, medium- and high-volatile parent coals used in the blend.

The CMSI [8] is the coke mosaic size index defined as:

$$CMSI= \frac{\{(\%Incipient)+2(\%CF+\%CM)+3(\%CC+\%LF+\%LM)+4(\%LC+\%RF)+5(\%RM+\%RC)\}}{(100 - \%Isotropic - \%Total\ Inerts)} \quad (i)$$

This is a mathematical method to summarize the carbon form analysis. The formula used in this work is an adaptation of Coin's method. The higher the CMSI, the higher the rank based on carbon forms measured.

Results

The primary objective of this work is to validate and compare the measurement of CSR and CRI of cokes produced in the sole-heated oven to those generated in a pilot-scale oven. To achieve this goal, nineteen (19) coal blends were thus carbonized concurrently in both types of ovens at CanmetENERGY.

As described earlier, the CSR test has repeatability and reproducibility limits of 5 and 7, respectively (ASTM D5341-99(2010). The sole heated oven procedure produces coke for CSR testing that is within these limits for comparing to pilot-scale oven results.

Table 1 compares CSR's and CRI's of cokes produced by the two types of ovens. CSR range of the cokes examined was between 42 and 65. CRI range of the cokes examined was between 23 and 37. The difference in CSR and CRI, expressed as percentage, between cokes produced by the two ovens are also listed in this table.

Table 1. Comparison of CSR and CRI of Pilot Scale Oven and Sole Heated Oven Cokes

CSR			CRI		
Pilot Scale Oven	**Sole Heated Oven**	**% Difference**	**Pilot Scale Oven**	**Sole Heated Oven**	**% Difference**
61.9	62.4	0.8	22.7	23.9	5.3
60.5	60.8	0.5	25.1	25.1	0.0
60.3	63.9	6.0	26.9	24.9	-7.4
60.3	61.8	2.5	25.3	25.0	-1.2
58.0	54.7	-5.7	28.1	29.1	3.6
65.0	63.2	-2.8	22.5	24.2	7.6
51.3	50.9	-0.8	31.0	29.9	-3.5
60.5	51.4	1.5	25.3	25.8	2.0
60.6	61.5	1.5	25.6	26.2	2.3
62.7	51.4	-2.1	25.9	25.8	-0.4
59.9	56.7	-5.3	26.6	28.0	5.3
42.8	41.5	-3.0	35.9	37.2	3.6
60.9	60.2	-1.2	26.0	26.9	3.5
50.6	51.8	2.4	32.0	30.8	-3.8
60.3	61.7	2.3	27.6	25.9	-6.2
57.1	55.6	-2.6	28.8	30.3	5.2
54.5	59.0	8.3	30.1	27.0	-10.3
52.1	52.4	0.6	31.5	32.8	4.1
57.9	55.6	-4.0	26.1	29.0	11.1

Figure 3 shows the scatter plot between the CSR obtained for the sole heated oven coke and that for the pilot scale oven coke. A strong linear relationship was observed. In the same graph, a straight line passing through origin with unit slope (i.e. y=x plot) was superimposed for comparison. As can be seen, the data points are evenly distributed on both sides of the superimposed line, which indicating that there is no bias due to the coke preparation method with respect to the y=x plot. Furthermore, the deviations of the experimental data from the superimposed y=x plot were within the expected repeatability and reproducibility of CSR measurement. This indicates that CSR's of the coke samples produced using both methods are statistically identical.

The observed differences in the data points arise from the accumulated random error in coal handling, coke preparation and CSR measurement, etc. A more detailed analysis of the difference in CSR measured between the two preparation methods reveals that the average of the difference in CSR among the measurements is -0.06% and the standard deviation is 3.6%. The calculated 95% confidence interval is 1.6%. As shown in this error analysis, the CSR measured using sole-heated coke is within ± 2% of the pilot oven CSR value.

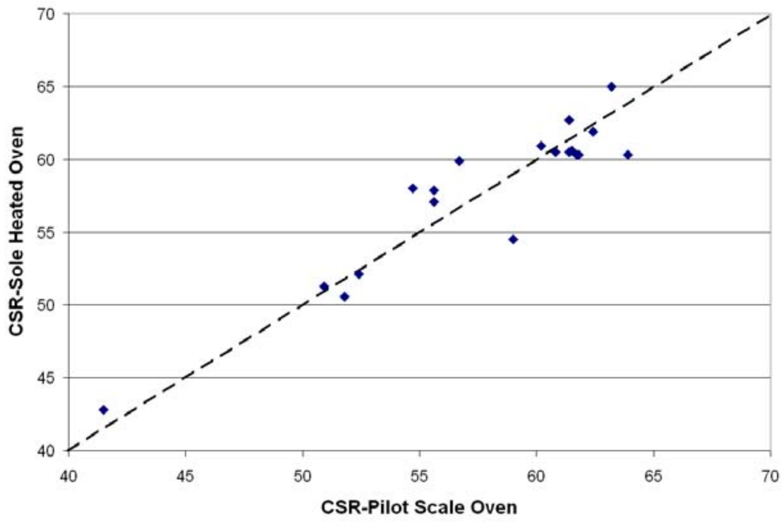

Figure 3. CSR Relationship between Sole-Heated Oven and Pilot Scale Oven

Similar to the CSR analysis, Figure 4 shows the scatter plot between the CRI obtained for the sole heated oven coke and that for the pilot scale oven coke. A strong linear relationship was observed. As can be seen, the data points are evenly distributed on both sides of the superimposed line y=x plot, which indicating that there is no bias due to the coke preparation method. Furthermore, the deviations of the experimental data from the superimposed y=x plot were within the expected repeatability and reproducibility of CRI measurement. This indicates that CRI's of the coke samples produced using both methods are statistically identical.

The average of the difference in CRI between the two coke preparation methods is 1.1% and the standard deviation is 5.4%. The calculated 95% confidence interval is 2.4%. Hence, the CRI measured using sole-heated coke is within ± 3% of the pilot oven CRI value.

To develop a better understanding of the influence of different carbonization methods on the properties of the resulting coke, an analysis of coke ASG was also performed.

As indicated in Table 2, ASG of sole-heated oven cokes are consistently higher than that of pilot oven cokes. In fact for the nineteen (19) cokes examined, ASG of sole-heated oven coke is, on average, about 6% higher than ASG of pilot oven cokes. This finding is mainly attributed to the fact that sole-heated oven cokes are produced under a constant load of 15.2 kPa, which is higher than the pressure exerted on the coal during carbonization in the pilot scale oven, ~8 kPa. Figure 5 shows the scatter plot between ASG measured on sole-heated oven coke and pilot oven coke and compared with the superimposed y=x plot.

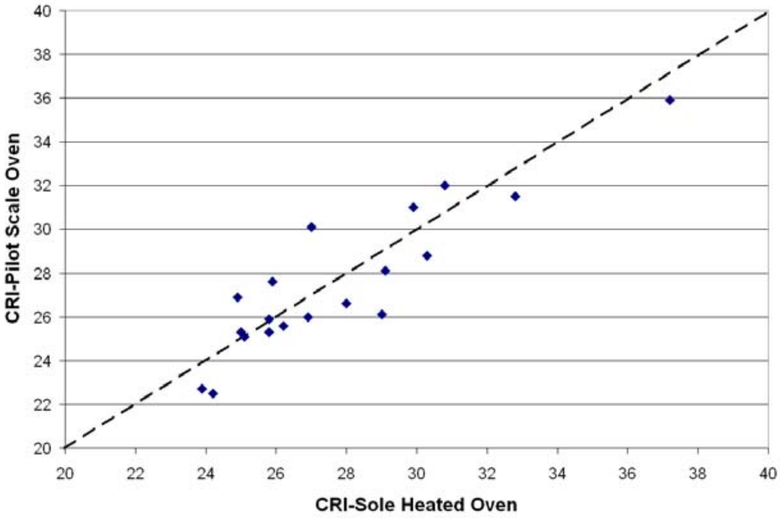

Figure 4. CRI Relationship between Sole-Heated Oven and Pilot Scale Oven

Table 2. Comparison of ASG in Pilot Scale and Sole-Heated Ovens

Pilot Scale Oven	Sole Heated Oven	% Difference
0.935	0.991	6.00%
0.921	0.977	6.11%
0.944	0.994	5.21%
0.921	0.979	6.28%
0.930	0.966	3.88%
0.920	0.967	5.11%
0.918	0.987	7.54%
0.954	1.018	6.70%
0.953	1.001	4.96%
0.953	1.009	5.87%
0.931	0.957	2.81%
0.951	1.016	6.75%
0.930	0.971	4.42%
0.922	0.994	7.89%
0.942	1.012	7.39%
0.956	1.009	5.59%
0.925	0.989	6.95%
0.946	1.002	5.93%
0.927	0.987	6.45%

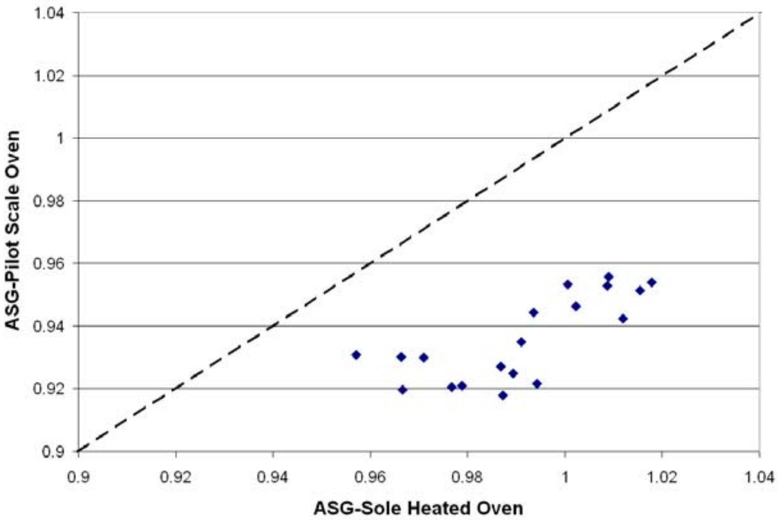

Figure 5. ASG Relationship between Sole-Heated Oven and Pilot Scale Oven

Carbon form analysis was performed on seven coke samples from both the pilot-scale movable wall oven (A-G) and the corresponding sole-heated oven (A'-G'). A summary of the carbon form analysis results is given in Table 3. The data in this table shows the total of each category based on size of the carbon form itself, i.e., fine, medium and coarse. Inerts (filler phase), are also classified by subgroups such as fusinite, semi-fusinite, and unidentified inerts along with other inerts, which are summed up in the table. As shown, similar results were obtained from both the pilot-scale movable wall test oven and the sole heated oven in terms of percent binder phase (reactive) and filler (inert) phase.

Table 3 Carbon Form Analysis Results on Selected Cokes from the Pilot Scale Oven and Sole-Heated Oven

Total Binder%		Total Filler%		CMSI		Blend Ro	
Pilot Scale Oven	**Sole Heated Oven**	**Pilot Scale Oven**	**Sole Heated Oven**	**Pilot Scale Oven**	**Sole Heated Oven**	**Pilot Scale Oven**	**Sole Heated Oven**
81.79	82.06	18.21	17.94	2.77	2.71	1.12	1.13
76.12	78.48	23.88	21.52	2.87	2.84	1.15	1.14
80.45	82.43	19.55	17.57	2.71	2.69	1.12	1.12
67.13	73.15	32.87	26.85	2.73	2.70	1.11	1.11
75.21	74.23	24.79	25.77	2.95	2.90	1.17	1.17
72.66	69.25	27.34	30.75	2.87	2.90	1.16	1.16
72.70	72.06	27.30	27.94	2.80	2.76	1.13	1.14

A good linear relationship between percent binder phase present in sole-heated and pilot scale oven cokes was observed, Figure 6. Also, the sole-heated and pilot scale oven cokes show excellent linear relationship for 'effective coal blend reflectance, Ro' as presented in Figure 7. This further denotes the similarity of the cokes produced in both types of ovens.

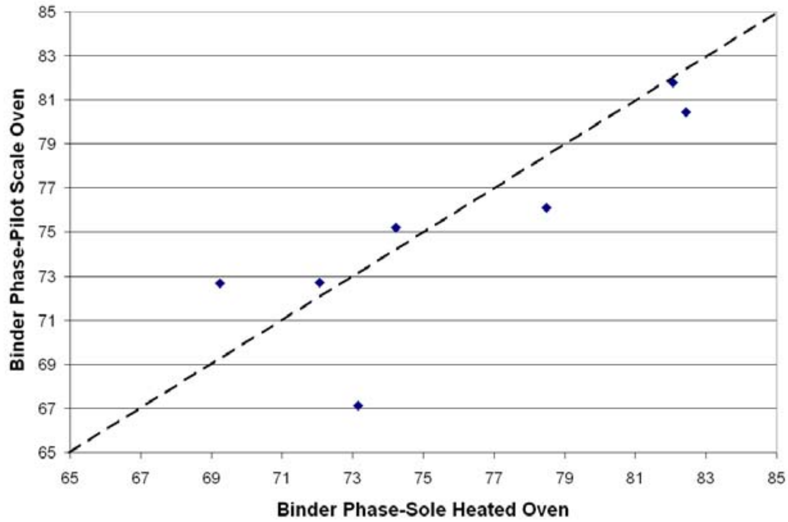

Figure 6. Binder Phase (Reactive) Relationship between Sole-Heated Oven and Pilot Scale Oven Cokes

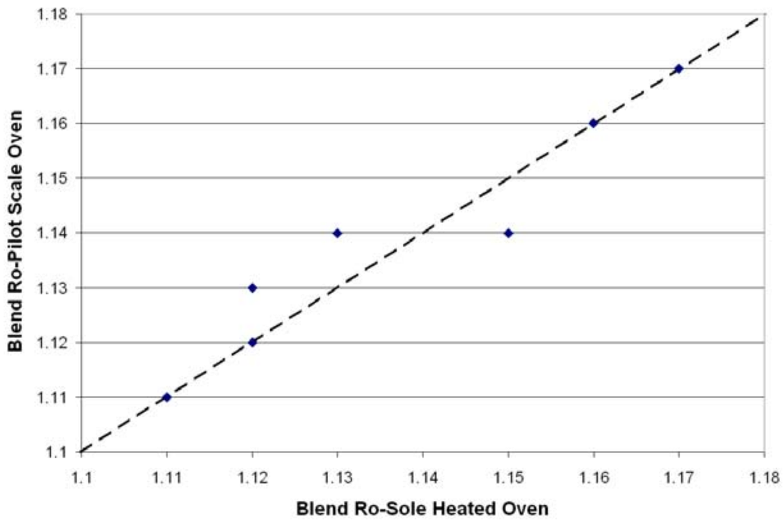

Figure 7. Effective Coal Blend Ro Relationship between Sole-Heated Oven and Pilot Scale Oven Cokes

Conclusions

This paper describes the development of a novel procedure at CanmetENERGY for the evaluation of coke CSR using a small-scale carbonization oven – the sole-heated oven.
A comparison between cokes produced in a sole-heated oven using the method developed in this work and those formed in a pilot-scale coke oven found the following:

1. CSR's and CRI's determined are statistically identical.
2. ASG's for sole-heated oven cokes are higher on account of the higher pressure (load) applied on the coal bed.

2. Carbon forms expressed as binder phase (reactive) and filler phase (inert) are similar.

3. This procedure finds useful applications as a preliminary evaluation method and a reliable screening tool in both the cokemaking and coal mining industry as it provides relevant information on (i) Coking potential/ability of coal/coal blends (ii) CSR evaluation (iii) Carbon form development prior to designing and running pilot oven trials.

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