THE IMPORTANCE OF COAL- AND COKE PROPERTIES IN THE PRODUCTION OF HIGH SILICON ALLOYS

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ABSTRACT

In the production of high silicon alloys, carbonaceous materials like coal, coke, charcoal and woodchips are utilized as reducing agents. Primarily based on historical prices of charcoal compared to fossil reduction materials, the Norwegian Ferroalloy Industry has mostly been using coal and coke (char) as carbon source. The most important role of the carbonaceous material is to react with the SiO gas to produce SiC. The ability of the reduction materials to bind SiO gas can be measured and the value is recognised as the reactivity of the carbon source. This reactivity is one of the most important parameters in the smelting process in order to obtain a high yield of metal.

The reactivity of the carbon materials is directly correlated to the material properties. It is known that the rank of the coal influences the SiO reactivity where low rank is beneficial. Coals of the same rank have however proven to have varying reactivity.

In order to investigate how the micro-constituents of coal influence the reactivity towards SiO gas, three single seam unwashed coals of different origin which fulfil the requirements of the Norwegian Ferroalloy producers have been chosen. As the structure in the carbonized product is a function of petrographic constitution and carbonization parameters, the coals have been separated into different density fractions. The various density fractions of the same coals proved to have significantly different petrographic composition. The coals were carbonized according to a procedure simulating the conditions the coals experience when charged to an industrial furnace. Chemical-, physical- and petrographical properties of both the coals and the resultant chars have been thoroughly examined and correlated towards the SiO reactivity.

1. INTRODUCTION

The most economically feasible way to produce Ferrosilicon and Silicon as commodity materials is still by carbothermic reduction of quartz in an electric submerged arc furnace.

The chemical reactions in the production are complex, but the overall reaction can be expressed in an idealized form as:

$$SiO_{2\,(s)} + 2\,C_{(s)} = Si_{(l)} + 2\,CO_{(g)} \tag{1}$$

According to Schei et al. [1], the resources of silicon in the form of quartz and silicates are almost unlimited as the Earth's crust consists of about 28 % silicon. The resources of reduction materials are more limited. The most common reduction materials are:

(i) Coal
(ii) Coke / char
(iii) Woodchips
(iv) Biocarbon in the form of charcoal

The specification of the product purity limits the number of coal types that can be used. In addition the process requires coals of a certain reactivity.

According to Videm [2], the cost of reduction materials constitute about 35 – 40% of the total materials and energy cost in the production of respectively 75% Ferrosilicon and Silicon. In this respect it is essential to gain further insight into the characteristics of the reduction materials, and their behaviour in the furnace.

1.2 Reactivity of Carbon Materials

The term reactivity is used to describe a critical property or behaviour during reaction or conversion in a chemical or a metallurgical process [3]. In the case of production of Silicon and Ferrosilicon, the reactivity of the reduction materials can be categorised by the ability carbon has to react with SiO according to the reaction:

$$SiO_{(g)} + 2\,C_{(s)} = SiC_{(s)} + CO_{(g)} \qquad (2)$$

This reaction is essential in two aspects:

(i) Minimize loss of Si (in the form of SiO) and thereby increase the Silicon yield
(ii) As SiO (g) is an energy carrier in the process, it is important to sustain this compound in the process in order to have tolerable energy efficiency. (90% of the energy is used to reduce SiO_2 to SiO, and energy is sustained in the process by reaction 2 and condensation: $2\,SiO_{(g)} = Si_{(l)} + SiO_{2\,(s)}$)

The most acknowledged reactivity test for reduction materials in the production of Ferrosilicon and Silicon was developed by Tuset and Raaness [4]. This test is called the SINTEF reactivity test.

The basis for the SiO reactivity test is that a gas mixture of 13.5% of SiO and 4.5% CO is passed through a coke bed with Argon as a carrier gas at temperature of 1650 ^{0}C. When the gas mixture comes in contact with the coke, more or less of the SiO will react with the coke to SiC according to reaction (2). The exit gas from the apparatus is passed through an infrared gas-analyzer, and the CO content in the off gas is recorded continuously as a measure of transformation. The SiO reactivity number is given as the amount of SiO gas that has passed through the coke bed unreacted before the CO content in the exit gas drops below 10%.

The SINTEF SiO reactivity test has recently been improved and automated. The modifications to the test can be seen in Lindstad et al [5]. After more than 20 years of reactivity testing, it has been found that coals with apparently identical chemical composition and volatile matter can exhibit totally different properties in terms of SiO reactivity [6]. This fact is also confirmed by industrial experience.

Raaness and Gray [6] investigated eight different coals ranging in rank from High Volatile Bituminous (HVB) ($R_0 = 0.66\%$) to Medium Volatile Bituminous (MVB) ($R_0 = 1.35\%$). The most noticeable results were that the reactivity decreased with increasing rank and that the binder phase in the char / coke was more reactive than the filler phase.

Another method for testing the reactivity of carbonaceous materials is presented by Videm [2]. Nine cokes were tested in this apparatus, and Videm et al.[7] came to the conclusion that low volume weight, high amount of binder phase and low amount of filler phase in the coke was beneficial for the SiO reactivity.

By investigating reacted samples of fossil carbon material, both Raaness and Gray [6] and Myrhaug [8] have identified a sharp borderline between reactive and unreactive carbon forms.

2. COAL SAMPLES

In order to investigate how the microstructure in coals of different origin and rank influence the reactivity towards SiO, three Run Of Mine (ROM) coal samples have been acquired for studies in this work:

(i) Blue Gem, Appalachian Basin, USA, (HVB)
(ii) Peak Downs, Bowen Basin, Australia, (MVB)
(iii) Staszic, Upper Silesian Basin, Poland, (HVB)

The as received samples were air dried for three days before the samples were mixed and split using a riffle. To avoid any oxidation, the samples were stored in air sealed containers.

3. RESULTS AND DISCUSSION

The most important properties of the carbonaceous materials in the production of silicon and ferrosilicon are:

(i) High reactivity
(ii) High conversion
(iii) Low amount of impurities

High reactivity and conversion are believed to depend on the pore size distribution of the material – which is affecting the effective diffusivity. The porosity of the char is a function of the composition of the coal and the carbonization condition. Thus information on coal properties, carbonization procedure and analyses of the resulting chars are important. Silicon for use in the production of solar cells and electrical purposes demands a very low level of impurities [1].

3.1 Chemical Properties of the Coals

The run of mine (ROM) coals were sent to an externally accredited laboratory for proximate- and ultimate analyses. The results are shown in Table 1.

Table 1: Proximate- and ultimate analysis of the ROM coals and the main components in the ash

		Blue Gem	*Peak Downs*	*Staszic*
Proximate Analysis [wt%]				
Moisture	W^a	2.4	0.9	2.5
Ash	A^a	1.5	11.6	5.9
Volatile matter	V^a	36.14	19.8	31.76
	V^{daf}	37.61	22.63	34.67
Fix C	Fix C^a	59.96	67.7	59.84
Ultimate Analysis [wt%]				
Carbon	C_t^a	80.5	77.1	75.8
Sulfur	S_t^a	0.73	0.58	0.47
Hydrogen	H_t^a	5.29	4.34	4.74
Nitrogen	N^a	1.98	1.68	1.27
Oxygen	O^a	10	4.7	11.82
Phosphorous	P^a	0.003	0.057	0.029
Ash composition [wt%]				
SiO_2		31.24	53.23	30.44
Al_2O_3		22.96	30.98	24.16
Fe_2O_3		17.41	9.03	16.26

daf = Dry Ash Free, a = As received, t = total

3.2 Petrographic analyses of the coals

During the petrographic analysis of the ROM coals, the constituents were only separated into the macerals believed to influence the reactivity the greatest. The petrographic constitutions for the ROM coals are shown in Table 2.

Table 2: Petrographic constitution of the ROM coals

Maceral Constitution [%]	*Blue Gem*	*Peak Downs*	*Staszic*
Vitrinite	77	68	51
Liptinite	13	-	13
Fusinite	2	5	7
Semifusinite	1	10	14
Inertinite	5	6	9
Mineral Matter	1	10	7

Even though Blue Gem and Staszic are of the same rank, there are large differences in the petrographic constitution. The sum of inertinites and mineral matter is less than 10 % in Blue Gem, while the relative amount in Staszic is 36 %. The composition of the coals is one of the most important parameters deciding the properties of the resulting char. Schapiro and Gray [9] defines reactive macerals as vitrinite, liptinite and a varying percentage of the semifusinite depending on the origin of the coal. Reactive macerals will form the binder phase in the carbonized product, while inert macerals will be relatively unchanged during carbonization and make up the filler phase.

The vitrinite reflectance was measured on polished pellets of the coal samples and the results are presented in Table 3.

Table 3: Vitrinite reflectance and V-Types of the coal samples

Vitrinoid V – Types	*Vitrinite Reflectance*	*Blue Gem*	*Peak Downs*	*Staszic*
V 4	0.40 – 0.49	-	-	0.3
V 5	0.50 – 0.59	-	-	2.0
V 6	0.60 – 0.69	14.4	-	22.9
V 7	0.70 – 0.79	51.1	-	61.6
V 8	0.80 – 0.89	31.9	-	12.7
V 9	0.90 – 0.99	2.6	-	0.6
V 10	1.00 – 1.09	-	-	-
V 11	1.10 – 1.19	-	-	-
V 12	1.20 – 1.29	-	8.0	-
V 13	1.30 – 1.39	-	32.0	-
V 14	1.40 – 1.49	-	43.3	-
V 15	1.50 – 1.59	-	14.3	-
V 16	1.60 – 1.69	-	2.3	
Reflectance, R_o		0.77	1.32	0.74

Gray and Devanney [10] claims that the carbon forms in the binder phase of the coke or char are based on the rank determined by the vitrinite reflectance. The classifications of these carbon forms can be seen elsewhere [11]. The original correlation between vitrinite reflectance and carbon forms in the resulting coke / char was based on mean – max reflectance, while random reflectance was used to measure the coals selected for our work. There exist several correlations between random- and mean – max reflectance, and Price [12] states that this relationship is given by equation 3. Komorek and Morga [13] have tested 189 coal samples from the Upper Silesian Basin in Poland, and have come to a relationship given in equation 4.

$$R_{max} = 1.061 \cdot R_o \tag{3}$$

$$R_{max} = 1.090 \cdot R_o - 0.052 \tag{4}$$

These relationships should enable us to evaluate the carbon forms in the resulting char even though a different basis for reporting the reflectance values is used. The vitrinite reflectance is the most acknowledged measure of rank, and puts Staszic and Blue Gem into the category as high volatile bituminous coals while Peak Downs is grouped as a medium volatile bituminous coal.

In order to have samples of the same coal with different maceral composition, the unwashed coals were separated into different density fractions by the traditional sink - float procedure [14]. The petrographic constitutions of the different density fractions were examined and are listed together with the yield of the washing in Table 4. The purpose of the washing procedure was twofold:

(i) Separation of the coal samples into density fractions with different petrographic compositions

(ii) To concentrate the mineral matter in the highest specific density fraction

According to theory, the density of the components in bituminous coals increases in the order: liptinite < vitrinite < inertinite < mineral matter [15]. In all of the coal samples it is evident that the mineral matter is increasing with higher specific density. There is also a clear trend that both vitrinite and liptinites are present to a larger extent in the lower density fractions. Coal macerals that are unchanged during carbonization, are concentrated in the second highest density fraction.

Table 4: Petrographic constitution of washed coals and yield of washing

Coals		*Specific gravity solution [g/cm³]*			
		< 1.25	*1.25 – 1.33*	*1.33 – 1.50*	*> 1.50*
Blue Gem	Vitrinite	77.6	85.9	-	17.6
	Liptinite	15.3	10.2	-	0.3
	Inertinite	2.4	2.0	-	0.1
	Fusinite	1.7	0.8	-	0.0
	Mineral Matter	3.0	1.2	-	82.0
	Yield [%]	19.6	73.1	0.0	7.3
Peak Downs	Vitrinite	93.0	81.7	74.5	49.1
	Liptinite	0.0	0.0	0.0	0.0
	Inertinite	2.0	8.1	9.6	6.9
	Fusinite	1.5	6.3	9.6	5.8
	Mineral Matter	3.5	3.9	6.2	38.2
	Yield [%]	5.1	43.6	44.3	7.1
Staszic	Vitrinite	-	70.6	61.6	30.3
	Liptinite	-	12.6	8.3	2.2
	Inertinite	-	7.9	13.1	4.0
	Fusinite	-	6.6	10.5	8.5
	Mineral Matter	-	2.3	6.7	55.0
	Yield [%]	0.0	48.6	47.8	3.7

As a supplement to the maceral analysis and the reflectance measurements, Gray [16, 17] has proposed a non-maceral analysis. This analysis was developed in order to produce petrographic data that can be used in the utilization of coal. The non-maceral analysis includes important materials that are not included in a standard maceral analysis. Simply put the non-maceral analysis divides the microstructures in coal into normal coal, pseudovitrinite, fines, oxidation, microbrecciation, mineral matter and miscellaneous. The relative amount of these microstructures will have an effect upon the utilization of coal, whether it is to be used for coke making or directly in the production of ferro-alloys as a reduction material.

The results from the non-maceral analysis are given in Table 5. From Table 5 it is evident that the Staszic coal is relatively dull compared to Blue Gem and Peak Downs. This implies that the macerals are well mixed in the coal structure, and might give an indication that it is hard to separate the macerals using a washing procedure. In addition we also see that the Peak Downs coal contains a lot more fines than the other coals. This is an expected result as the amount of fines increases with the rank. If we compare the different density fractions, there is the expected concentration of the dull structure in Peak Downs and Staszic as well as an increase in the amount of fusinite and semifusinite with increasing density. The Blue Gem coal is actually showing the opposite trend. One reason for this is probably that the Appalachian coal contains a very low amount of fusinite and semifusinite. In addition there might be less difference between the two lowest density fractions that are used to analyze Blue Gem compared to the two middle fractions for Peak Downs and Staszic. All the coals show an increase in the amount of fines and minerals in the highest density fraction.

Table 5: Non-maceral analysis for the density fractions with high enough yields to make char

	Blue Gem		*Peak Downs*		*Staszic*	
	< 1.25	*1.25 – 1.33*	*1.25 – 1.33*	*1.33 – 1.50*	*1.25 – 1.33*	*1.33 – 1.50*
Normal Coal						
Vitrinite	4.2	1.2	5.4	3.1	2.4	1.0
Semi	0.6	0.9	5.8	11.6	10.8	11.2
Fusinite	1.2	0.5	3.8	8.8	1.2	6.2
Bright	38.8	40.8	40.0	25.4	30.6	14.8
Intermediate	18.4	20.1	14.0	12.2	22.2	16.4
Dull	13	10.3	10.2	15.5	25.8	39.6
Pseudo	22	23.8	13.0	5.2	4.2	5.2
Fines	1.4	2.2	4.2	10.3	1.6	3.0
Oxidized	0.2	-	0.2	0.6	-	0.4
Microbrecciation	0.2	-	3.0	3.6	0.2	0.2
Minerals	-	0.1	-	3.8	0.6	2.0
Micellaneous	-	-	0.4	-	0.4	-

3.3 Carbonization

Based on the yield from the washing process, the fractions with sufficient amount of coal (>300 g) were carbonized using the SINTEF procedure. In the subsequent figures that are presented, the density fractions are denoted as High Density (HD) and Low Density (LD) for each of the coals / chars referring to the two fractions with highest yield from Table 4.

3.4 Physical Properties

The main physical properties of the carbonaceous material determining the reactivity towards SiO gas are porosity, pore size distribution, density, surface area and degree of crystallization. These properties have been examined by using image analysis [18, 19], pycnometer, Hg-intrusion and X-ray diffraction [20], and are listed in Table 6.

Table 6: Physical properties of the chars

	Blue Gem		*Peak Downs*		*Staszic*	
	< 1.25	*1.25 – 1.33*	*1.25 – 1.33*	*1.33 – 1.50*	*1.25 – 1.33*	*1.33 – 1.50*
Pycnometer						
Total Porosity [%]	50.9	48.9	45.8	47.0	47.3	46.4
Absolute Density [g/cm^3]	1.78	1.79	1.89	1.94	1.79	1.82
Surface Area [m^2/g]	0.67	0.69	0.65	0.96	1.79	1.21
Image Analysis						
Open Porosity [%]	11.6	13.1	19.4	17.2	13.3	12.2
Closed Porosity [%]	14.8	13.7	12.0	11.6	8.7	9.5
Total Porosity [%]	26.4	26.8	31.4	28.8	22.0	21.7
Hg-Intrusion						
Total Porosity [cm^3/g]	168	203	92	104	145	139
X-Ray diffraction						
d_{002} [Å]	3.466	3.465	3.447	3.427	3.473	3.469
Lc [Å]	19.6	19.0	21.4	22.7	17.7	15.3

According to the IUPAC classification, pores with a diameter larger than 50 nm are macropores [21]. As most of the pores measured in the calcined material are larger than 50 nm, we will use the pore size classification for cokes, suggested by Price [12].

(i) Coarse Pores: > 20 μm
(ii) Macropores: 10 nm – 20 μm
(iii) Micropores: < 10 nm (Typically 0.5 nm)

Coarse pores are created by gas bubbles trapped in the semi coke as it is formed, and are dependant upon coal properties like rank, type, size, fluidity and viscosity during the fluid phase and on carbonization parameters like heating rate, maximum temperature and atmosphere. The image analysis appear to be particularly well suited for measuring coarse pores and the pore size distributions for pores larger than 4 μm are given in Figure 1 b.

The macropores generally denotes pores that are available to gases for diffusion into the carbonaceous structure and will thus be very important for the reactivity towards SiO gas and the effective diffusivity in the material. The pore size distributions for macropores are measured by Hg-intrusion, and are illustrated in Figure 1 a.

Based on Figure 1 a, we can conclude that the two low rank coals both have a higher macroporosity than Peak Downs. The image analysis however shows the opposite trend for coarse pores. As it is believed that macroporosity contributes greater to the reactivity than coarse pores, the two low rank coals should, based on Figure 1, show the highest reactivity towards SiO gas.

Due to the preparation of the samples for image analysis, two types of pores are evaluated. Open pores which are filled with fluorescent epoxy and closed pores which are not. The open pores will be green and the closed pores will be dark in the pictures for analysis. Especially the closed pores will be vulnerable to errors as flaws during preparation like relief and scratches also will appear dark.

Figure 1 reveals that the most of the coarse pores in all the chars appear in the range between 10 – 50 µm while most of the macropores are in the range 0.1 – 5 µm. The area under the graphs will denote the total porosity. Caution should be made in directly comparing the porosity measurements from the different methods as the values for porosity are reported in different units. Referring to Table 6, the porosity from the image analysis (IA) is consistently lower than the results obtained with a pycnometer. The main reason for this is that pores less than 4 µm are not included in the IA. One of the most interesting results from Table 6 is the high specific surface area of the Staszic char which is about twice the value of Blue Gem. This result may imply that there is more carbon available for reaction with SiO which again can lead to a highly reactive material. It is believed that a high amount of pores and a high specific surface area are among the most important characteristics of the char related to a high reactivity towards SiO gas.

The X-ray results are consistent with theory as the coal with highest rank has the lowest interlayer spacing and highest stack height – i.e. the most graphitic structure.

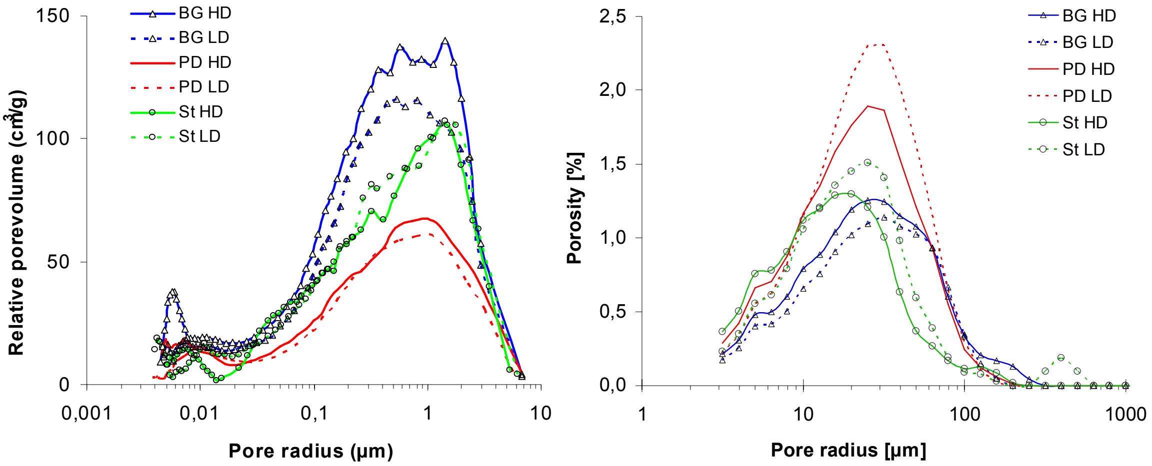

Figure 1: Pore size distribution. a): Hg-intrusion, b): Image analysis of open pores

An optical microscopic examination of coke or char displays microstructures and microtextures. The two are somewhat related. Microstructures consist of various configurations of coke walls and pores.

Table 7: Results from coke petrography with binder phase, filler phase and miscellaneous

	Blue Gem		*Peak Downs*		*Staszic*	
	< 1.25	*1.25 – 1.33*	*1.25 – 1.33*	*1.33 – 1.50*	*1.25 – 1.33*	*1.33 – 1.50*
Binder Phase						
Isotropic	12.1	10.3	-	-	18.6	34.9
Incipient	49.3	45.4	-	-	48.1	40.9
Fine Circular	36.3	41.7	-	-	31.0	18.1
Medium Circular	2.3	2.6	-	-	2.3	4.8
Coarse Circular	-	-	-	-	-	1.2
Fine Lenticular	-	-	2.7	0.8	-	-
Medium Lenticular	-	-	57.9	61.4	-	-
Coarse Lenticular	-	-	39.1	36.6	-	-
Fine Ribbon	-	-	0.4	1.2	-	-
Total	100	100	100	100	100	100

Contd...

Table 7: Results from coke petrography with binder phase, filler phase and miscellaneous (Continued)

Filler Phase						
Binder Phase	95.1	87.1	73.7	59.0	65.1	55.7
Fine Inerts	1.9	2.8	8.3	8.4	14.0	11.4
Coarse Inerts	1.9	8.2	12.4	16.9	17.5	16.5
Fine Minerals	0.2	0.2	2.6	7.5	1.7	6.6
Coarse Minerals	0.4	1.2	3.0	6.0	1.7	9.3
Pyritic Minerals	-	0.2	-	2.0	-	0.5
Miscellaneous Inerts	0.6	0.2	-	0.2	-	-
Total	100	100	100	100	100	100
Miscellaneous						
Normal Coke	85.3	80.9	96.4	96.3	93.8	97.5
Pyrolytic	6.8	8.5	3.1	3.1	4.4	2.1
Spherulitic	7.9	10.6	0.5	0.6	1.7	0.3
Total	100	100	100	100	100	100

Microtextures are the carbon forms that make up the walls. The microtextures in coke are primarily determined by the rank and type of coal used to produce the coke. The petrographic procedure for microtexture analysis consists of determining, in polarized light, the quantities of carbon forms that display different anisotropic domain sizes and shapes ranging from optically isotropic to anisotropic. The standard test method for microscopically determination of volume percent of textural components in metallurgical coke is covered by an ASTM standard [22]. These data can be used to predict coke strength and reactivity to CO_2 and SiO**.**

Based on the reflectance data given in Table 3, we would expect the binder phase in the American and European coals to consist mainly of isotropic, incipient and circular domains while lenticular carbon forms should be dominant in the binder phase in the higher rank Australian coal. The results given in Table 7 confirm these predictions. Former studies conclude that a high amount of binder phase and low degree of anisotropy is favourable in order to have a high reactivity towards SiO gas [6] and [7]. Table 7 reveals that Blue Gem contains the highest amount of binder phase and that this phase is composed of carbon forms with relatively low degree of ordering. The European char has the most isotropic binder phase, but the amount of filler phase is the highest of the tested materials. The most striking observation from Table 7 is the high amount of depositional carbon (i.e. pyrolytic and spherulitic) in the Blue Gem char. These carbons are created by escaping volatiles that crack and deposit on pore walls and the periphery of the particle. The Staszic coal contains about the same amount of volatiles as the American coal, but it is believed that due to the dull structure of this coal the volatile compounds have a greater possibility to escape the coal particle during heating hence not creating the same amount of depositional carbons.

Reactivity Results

The output from the SITEF SiO reactivity test is a graph showing the relationship between the measured CO concentration at the outlet of the reactor and the time. Based on this graph, reactivity parameters can be calculated. Historically the R10 reactivity measure has been reported. This parameter is a measure of the volume of SiO gas that escapes the reactor un-reacted before the CO level drops below 10 %. As it has been discovered that some of the CO gas will react with liquid silicon in the condensation chamber according to equation 5, a corrected CO versus time profile has been suggested by Lindstad et al [5]

$$CO_{(g)} + 2\,Si_{(l)} = SiC_{(s)} + SiO_{(g)} \qquad (5)$$

The corrected CO versus time profiles for the calcined coals are presented in figure 2.

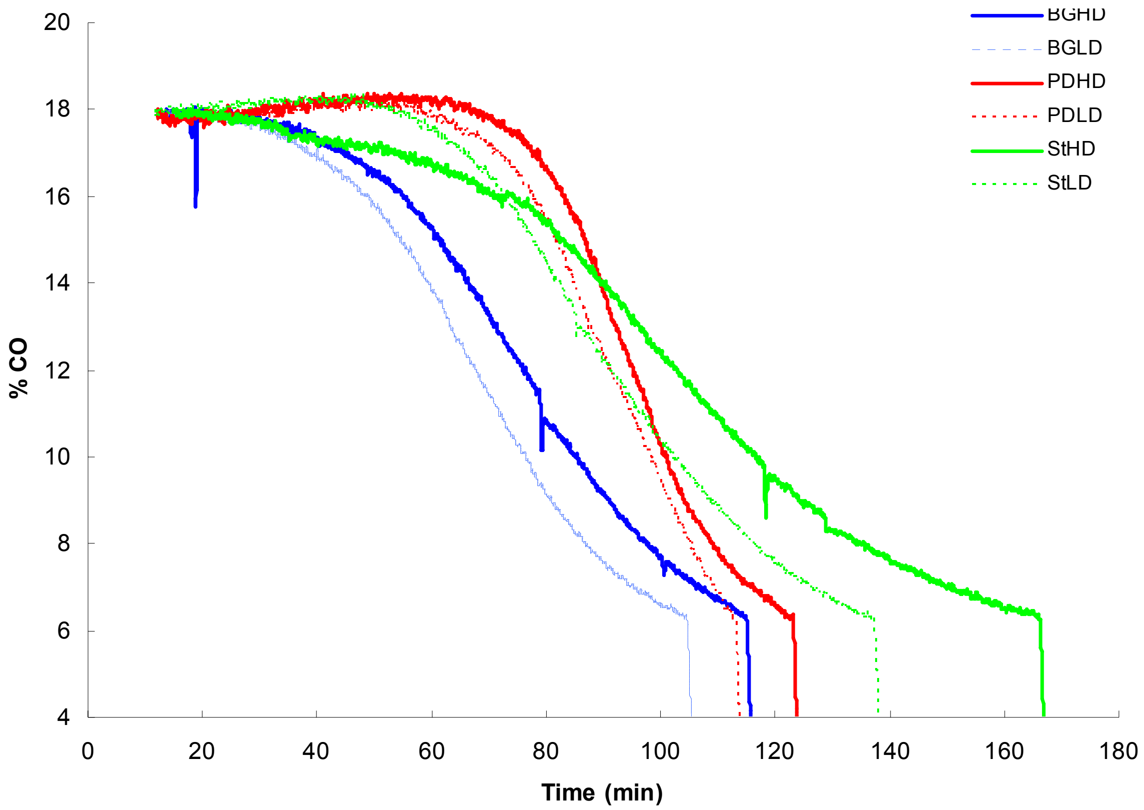

Figure 2: Corrected CO versus time profiles for the calcined coals. LD and HD are respectively the Low Density and High Density fractions used for preparing the chars

Reactivity results given as traditional R10 values and the reactivity parameter based on the corrected curves, R10 corr, can be seen in table 8.

Table 8: Reactivity parameters based on the SINTEF SiO reactivity test

	Blue Gem		Peak Downs		Staszic	
	<1.25	1.25 – 1.33	1.25 – 1.33	1.33 – 1.50	1.25 – 1.33	1.33 – 1.50
R 10 [ml SiO]	765	842	797	749	854	1229
R 10 corr [ml SiO]	708	781	523	451	754	1158

The Peak Downs coal is showing an exceptionally high reactivity and conversion with respect to its rank. An explanation for this behaviour is that the Australian coal contains a lot of inherent clastic quartz in the coal structure. Based on the information given in Table 1, more than 5 % of the total weight of the Australian coal is Si-containing minerals. The major part of this amount is clastic quartz inclusions. As these inclusions are inherent, i.e. embedded in the coal structure, they are very hard to remove using a normal washing procedure. During the course of reaction the temperature in the reactor reaches about 1650 ^{0}C, which will cause the clastic quartz inclusions to react with the surrounding carbon. In his dr.ing thesis, Wiik [23] investigated the reaction between quartz and carbon, and the reaction has significant rates above 1400 ^{0}C. The quartz will react with carbon according to equation 6.

$$SiO_{2\ (s,l)} + C_{\ (s)} = SiO_{\ (g)} + CO_{\ (g)} \qquad (6)$$

The SiO gas that is produced will successively react with the carbon matrix described by equation 2. The local porosity in the material will also increase as the quartz inclusions are consumed. Figure 1 reveals that the Peak Downs coal has the lowest amount of micropores of the three investigated coals. A petrographic examination of reacted samples of the material does however show that there are plenty of very small pores. Figure 3 illustrates the clastic quartz inclusions in the Peak Downs coal, the carbon forms in the calcined material and the pore structure in the reacted sample.

Of the three investigated coal samples – the Blue Gem coal was believed to have the most beneficial properties for a high reactivity towards SiO due to its low rank and high amount of binder phase in the calcined coal. Even though the Blue Gem coal has a low R10 value, we can see from table 7 that both density fractions of the carbonized coal contain a very high amount of depositional carbon. Depositional carbon has a very dense structure and is believed to have a low reactivity. This type of carbon will most likely act as a seal for the reacting gases as it is formed on the pore walls and on the particle edges.

Blue Gem and Staszic are coals of similar rank, but the reactivity tests show completely different results. Based on the amount of volatile matter, it was expected to see a comparable amount of depositional carbon in the two coals. The Staszic coal does however contain far less depositional carbon than Blue Gem, and still shows a lower reactivity towards SiO. The low reactivity of the Polish coal can be explained by the high quantity of inert particles in the coal – thus leading to a substantially higher amount of filler phase in the calcined coal. The difference in reactivity of the two density fractions is also designated to the difference in the amount of binder phase in the coals (see table 7). From table 4 we can also see that the low reactive macerals seem to concentrate in the 1.33 – 1.50 density fraction.

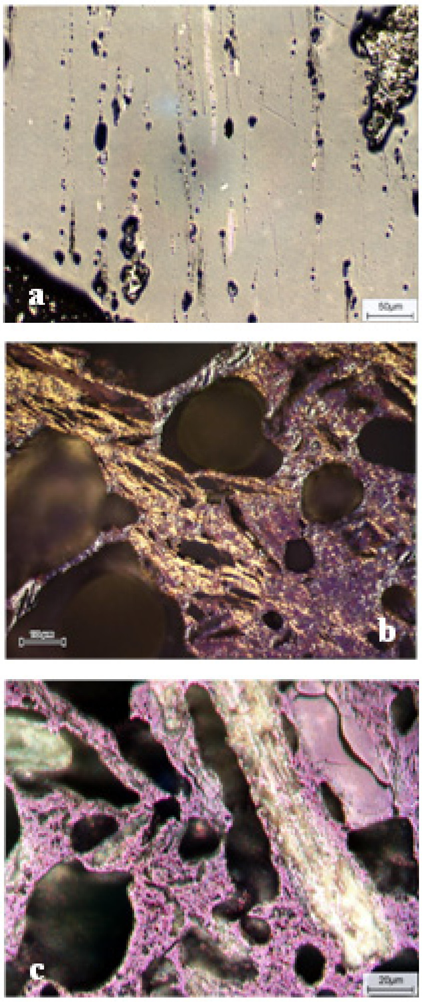

Figure 3: a) Clastic quartz inclusions (black droplets) in the vitrinite matrix of the Peak Downs coal b) Carbon forms in the char and c) The network of micro pores in the reacted sample

4. CONCLUSIONS

Based on former studies, the reactivity of carbon towards SiO gas should mainly depend on the rank of the coal and the distribution of binder and filler phase in the carbonized product. In this work two coals of similar rank and one higher rank coal have been used. In order to have the same coal with different maceral composition, the coals were separated into different density fractions. The main conclusion is that no single parameter can predict the SiO reactivity. It is however evident that a high amount of inert particles in the coal, i.e. a high amount of filler phase in the calcined coal, will give a lower reactivity towards SiO. Based on the coal samples used in this work, it is hard to evaluate the rank parameter as our high rank coal had a lot of inherent clastic quartz grains in the coal matrix. These inclusions will increase the reactivity and cause the carbon to react from the inside as well as with the SiO gas produced in the gas generator thus giving a very high conversion. The petrographic examination of the calcined coals also proves that there is a lot of depositional carbon in the Blue Gem coal. The depositional carbon is believed to seal the pore walls and periphery of the grains thus retarding the reaction towards SiO gas. The petrographic methods used in this work are valuable tools to examine both coal, calcined material and reacted samples.

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