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COAL IN THE PRODUCTION OF SILICON RICH ALLOYS

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ABSTRACT

Eight coals that are acknowledged as suitable for the manufacture of silicon and silicon-rich ferroalloys in the electric furnace were included in this study. These coals were characterized in terms of their proximate and sulphur analyses and their petrographic maceral and vitrinite reflectance analysis. Chars/cokes were prepared from each of the coals and characterized for their microstructures. The chars were tested for reactivity to silicon monoxide at 1650°C, Chars partly reacted to SiC were studied using the SEM and optical microscope to trace the gas diffusion paths of SiO gas and the formation of silicon carbide. In general the reactivity towards SiO gas increases as the coal rank or vitrinite reflection decreases for bituminous coals. Coarse inertinite of pyrofusinite increases the reactivity to SiO gas. The liptinite macerals appear to increase reactivity by increasing connected pore development in the chars. The silicon carbide formation is of topochemical nature and is controlled by pore diffusion. If the impact of coal ranks and maceral composition on coke microstructure development and availability to SiO gas diffusion is established, fundamental data on coals may be utilized in a more efficient selection of suitable coals and coke chars for use in the production of silicon and silicon-rich ferroalloys.

INTRODUCTION

Coal as a raw material in the production of silicon metal and silicon rich alloys have mainly been selected on the basis of the chemical composition, free swelling index and in some cases by SiO reactivity tests /1/,
The properties of the coals, or more correct the chars produced from the coals through the exposure of coals to high temperatures in the electric reduction furnace, are of vital importance for the operation of the process. Beside acting as a reductant these chars have two functions to perform in the furnace;

a) Conserve the intermediate SiO gas in the process by acting as a "gas filter" in the furnace and in this manner preserve matter and energy in the process

b) Influence on the electrical resistance of the furnace and thereby the operation of the furnace

The different abilities of carbon phases in chars to react with SiO gas has been reported earlier/2,3/. In this paper we will try to explain the different properties of chars in view of their structure as derived from the petrographic properties of the coals.

THE REDUCTION PROCESS

Coal, coke and quartz are the major raw materials in the production of silicon and silicon-rich ferroalloys. M.B. Mûller et al. /5/ and A. Schei /6/ have described the reactions taking place in the different temperature zones of the process.
The reduction of silica occurs through the formation of the intermediate SiO gas phase .A typical first step of the silica reduction processes would be the following reactions:

$$SiO_2(l) + Si(l) \rightarrow 2SiO(g) \quad 1$$
$$2SiO_2(l) + SiC(s) \rightarrow 3SiO(g) + CO(g) \quad 2$$

This reduction of the quartz mainly takes place in the high temperature - or crater- zone of the furnace.
The metal forming reaction in the crater area proceeds as a reaction between the SiO gas and siliconcarbide reacts to produce silicon

$$SiC(s) + SiO(g) \rightarrow 2\,Si(l) + CO(g) \quad 3$$

It is assumed that this reaction proceeds until the chemical equilibria is established/3/. Excess SiO then passes further up into the cooler parts of the furnace where it reacts with the carbon in coke and char (Eq 4) to silicon carbide, or some of it may condense to a glassy phase (Eq5). If the carbon in the char is not completely reacted to SiC before it reaches the crater area it will react with SiO (g) and form SiC and more CO (g). Unreacted carbon to the crater area is considered as unfavourable as it leads to an increased production of CO (g) and thereby an increased CO/SiO ratio in the crater zone. Since we belive that the silicon metal production according to equation 3 is determined by the chemical equlibrium this will lead to reduced production and excess circulation of SiO in the burden.
About 80-90 % of the electrical energy consumed in the process is used for the formation of siliconmonoxide gas from silica. It is therefore of vital importance that as much as possible of the SiO gas are preserved within the process in order to achieve acceptable yield on raw materials and energy. The reduction materials virtually acts as a"gas filter" in the upper part of the furnace burden according to the following reaction:

$$SiO(g) + 2C(s) \rightarrow SiC(s) + CO(g) \quad 4$$
$$2SiO(g) \rightarrow SiO_2(s) + Si(l) \quad 5$$

Tuset et al /1/ suggested that the effective inter diffusion coefficient of SiO(g) and CO(g) in the pore structure of the chars and cokes determines the reaction rate between the carbon in the burden and the SiO gas.

SiO REACTIVITY

In order to be able to distinguish between the different types of chars and cokes a "SiO reactivity" test was developed /1/. This test give information on how effective carbon materials are in filtering off SiO gas from a gas stream through the reaction to SiC, an ability thought to be crucial in the industrial process.

Through 20 years of SiO reactivity testing, we have recognized that coals with apparently identical chemical composition and volatile matter could exhibit totally different properties in terms of SiO reactivity, The same has been experienced in industrial testing of the materials. This clearly shows that the standard analyses normally used for coals are inadequate in selecting optimum coals for the silicon production or siliconrich-ferroalloys production. We believe that the properties of coal with respect to their structure and SiO reactivity is determined by the ranks of the coals and their petrographic properties determining the thermoplastic properties.

Shapiro and Gray /7,8,9/ published how different coal macerals would influence on coke properties and CO_2 reactivities with reference to cokes for the blast furnace. We believe that the same principles to a certain degree can be applied for the electric smelting furnace.

SELECTION OF TEST MATERIAL

8 types of coals all well recognized as coals with varying properties for the production of silicon metal or 75% ferrosilicon, were selected. The test materials were selected to give a variation of both coal rank and maceral composition.

CARBONIZING PROCEDURE

It is well known from coke production that the heating rate for coals determines the coke properties.

Heating rate through the plastic temperature region will together with the rank and petrographic composition determine the pore structure and the type of the coal char.

In order to be able to heat treat coal samples in a similar manner as coals will experience when charged on top of the burden of a silicon - or ferrosilicon - furnace heating rates were measured at a 24 MW FeSi furnace at Elkem Thamshavn a/s and a 32 MW FeSi furnace at Holla Smelteverk a/s.

These data were applied in the laboratory to establish a method which gave similar heating/time curves as the coal samples would experience on the surface of an industrial furnace.

"SiO TAGGING" OF CHARS

In order to study the diffusion path of SiO gas in the different char structures 15 mm large char samples from selected coal samples were exposed to SiO gas for 20 minutes at 1650°C.

The partly reacted char lumps were prepared to be studied in the electron-microscope. The lumps were embedded in epoxy and cut through the centre and polished.

The study of the SiC-carbon structures in the chars were done in a Jeol JXA 8900M microprobe.

CHEMICAL ANALYSIS

The proximate analysis and sulphur content for the coals were determined at Coal Petrographic Association using specified ASTM procedures , D-3174 for ash analysis, D-3175 for volatile matter and D-3177 for total sulphur. The proximate analysis and total sulphur content of the coal samples tested is shown in table 1

The coals are all bituminous and range from 41% dry ash free (daf.) volatile matter to 24% volatile matter (daf.). The sulphur are relatively low and range from 0.4% to 0.9%. The ash values are also low for the selected coals and range from a low of 1.2% to a high of 5.8%.

Table 1 Proximate analysis and sulphur content of coal samples

Sample	Volatile Matter (DAF)	Proximate Analysis Wt.% (dry) Vol. matter	Fix Carbon	Ash	Total Sulphur
Couloumbian coal	40.83	40.06	58.05	1.89	0.49
Blue Gem low ash	41.04	40.57	58.28	1.15	0.83
Wawel	37.06	35.33	60.01	4.66	0.68
Pokoj	33.90	32.88	64.10	3.02	0.42
Slask	35.27	33.79	62.01	4.20	0.49
Monizia	23.2	22.0	72.8	5.2	
Sewell Stoker	31.14	30.44	67.31	2.25	0.75
Jewell low vol.	23.75	22.37	71.82	5.81	0.86

COAL TYPES

Bituminous coals are classified according to their content of volatile matter. A low volatile bituminous coal has between 14 and 22% volatile matter, and a medium volatile bituminous coal has between 22 and 31% volatile matter. A volatile matter content above 31% is denoted as a high volatile bituminous coal. The Columbian coal is high volatile bituminous B in rank with a dry-ash-free (daf) volatile matter of 40.83%.

The Blue Gem high volatile bituminous coal samples are unusual low in ash. The Blue Gem coal for Silicon metal production is a low ash sample The ash in the Blue Gem coal samples are mostly from disseminated clay and pyrite minerals.

The Wawel coal is a medium/high volatile FeSi coal from Poland, with a volatile content of 33.18% daf. The ash is mostly from clay and carbonates with a small amount of pyrite.

The Slask is a high volatile coal from Poland with a volatile content of 33.8 (daf).The Pokoj coal is high volatile bituminous A in rank with 33.9% (daf) volatile matter.

The Sewell Stoker coal with 31.14% daf volatile is borderline medium to high volatile coal. Clay and pyrite accounts for most of the ash.

The Monizia low volatile FeSi coal from Poland is low bituminous coal with excellent cooking properties 23.2% (daf) volatiles. The coal ash originates mostly from clay with some pyrite and a significant amount of carbonates including both calcite and siderite.

The Jewell low volatile FeSi coal is medium volatile 23.75% daf volatile. It is near the 22% medium/low volatile boundary. The ash comes mainly from clay with some pyrite and also some siderite.

PETROGRAPHIC ANALYSIS

The coal samples were prepared for microscopic analysis according to the procedure described in ASTM D2797. The microscopic analysis was conducted using a Leitz Orthoplan microscope equipped with a vertical illuminator for reflected light observations. The procedure is described in ASTM D2799.

MACERALS IN COALS

Coals are bioclastic sedimentary solid fuels of plant origin that consist of macerals, minerals, water and gas. They vary in rank or maturity, in type or maceral composition and in grade or purity. Petrographic analysis of coal has become important as a worldwide tool in selecting coals for development, utilization and marketing.

ASTM 2799 contains the "Megascopic Description of coal, coal seams and the "Microscopical Determination of Volume Percent of Physical Components of Coal". The ASTM standard D2796 defines the terms used in the microscopical description and analysis of coal. The microscopic constituents of coals in terms of groups with similar properties are as follows:

MACERAL GROUP	MACERAL	SUB GROUP
VITRINITE	VITRINITE	TELINITE
		COLINITE
LIPTINITE OR (EXINITE)	ALGNITE	
	CUTINITE	
	RESINITE	
	SPORINITE	
INTERTINITE		
	FUSINITE	
	INERTODETRINITE	
	MACRINITE	
	MICRINITE	
	SCLEROTINITE	
	SEMIFUSINITE	

Some of the maceral encountered in the current coals are shown in pictures 1 through 6. Vitrinite is the maceral group that forms from mummification of woody parts of plants which are the parts rich in lignin and cellulose. It is commonly the most abundant coal maceral and can be divided into two categories: telinite with cellular plant structure and collinite without optically discernable cell structure. Pseudovitrinite is a form of vitrinite that tends to be massive with distinct fusiform cracks and higher reflectance than the more attrital (finer size) form. As coals mature or metamorphase, the vitrinite loses moisture and volatile matter and it increases in aromaticity and optical reflectance. In bituminous coals vitrinite forms the bulk of coke structures during carbonization.
Liptinite is the maceral group derived from hydrogen rich and decay resistant plant parts

such as algae, leaf cuticle, resinous bodies, spores and pollen. They are lowest in reflectance and commonly have distinct forms. They are incorporated into the coal forming plant mass. They become optically less distinct as coals mature, and they become difficult to identify past medium volatile bituminous coals. Liptinite in high volatile coals reacts when heated to form tar, light oils and gas with some minor amount of carbon residue.
Inertinite group macerals are carbon rich, high reflecting (bright) macerals that undergo little change with increased coalification or even carbonization. They are formed by fusinitization which involves chemical and/or thermal oxidation. They are essentially precoalified macerals that are incorporated with vitrinite precursors in coal formation. Micrinite is the smallest particle form of inertinite and is commonly granular and less than 5 micron. Macrinite is coarser than micrinite (+ 50 microns) and it is angular and probably contains fragments of semifusinite and fusinite. Fusinite is fossil charcoal with distinct cellular structure from wood. Semifusinite is lower reflecting than fusinite and transitional between vitrinite and fusinite in its physical and optical properties.The common minerals in coals are clays, quartz, pyrite and carbonates.
The reflectance of vitrinite is used by petrographers as an indicator of coal rank since it increases as rank or maturity increases. Time and temperature are also factors since as "time at temperature" increases devolatilization and reflectance increases. Reflectance, as described in ASTM D2796, is a quantifiable characteristic of coal macerals. To determine reflectance, a microscope is fitted with a photometer, and the intensity of reflected light is measured with reference to that of a known reflectance standards.

MACERAL COMPOSITION OF COAL SAMPLES

The petrographic analyses from the coal-macerals vitrinite reflectance measurements are listed in Table II and III. The maceral listing is the tool which is commonly used for calculating coke stability for metallurgical grade coals. The vitrinite reflectances are listed as vitrinoid-type in which each V-type spans 0.1% reflectance. Thus V-type 8 includes all vitrinite with a reflectance of 0.80 through 0.89% mean-maximum in green light and in oil. In these analyses the micrinite includes micrinite, macrinite and inertodetrinite. Sclerotinite is included in semifusinite and extinite includes alginite, sporinite and cutinite.
The Columbian coal is low rank bituminous with a vitrinite reflectance of 0.66%. The coal is rich in reactive macerals which total 80.9% with 19.1% of inerts.
The Blue Gem coal is dominantly reactive macerals with 87.7%. The principal vitrinoids type is V8 and the inerts including mineral matter totals 12.3%. Coals with high exinite content tend to be hard to crush and contain attrital vitrinite. Micrinite content is 9.3% and this is the principal inert. It is mostly fine in size and associated with the exinite.
The Wavel FeSi coal is a high volatile coal with mostly vitrinoid types V8 and V9. The reactives ads up to total 70.2% with 29.8% inerts. The exinite and resinite ads up to total 15.4%. The semifusinite is content very high with 16.2%, and the amount of micrinite is also very high with 30.8%.The fusinite content is 3.6%.This coal is a hard attrital dull coal.
The Slask coal is a high volatile coal with a vitrinite reflectance of 0.90% with mostly vitrinite types of V7 and V8. The amount of reactive macerals is only 52.4%, and 13.5% of this is liptinite
The Pokoj coal is high volatile A bitumineous coal with a vitrinite reflectance of 0.98%. The coal has 54.7% of reactive macerals and 45.3% of inerts.

The Sewell coal is significantly higher rank than the preceding coals and has mostly vitrinoid types V10 and V11. The reactives constitutes total 78.1%, and the inerts are 21.9%. The amount of exinite and resinite ads up to 6.1%. The micrinite content is 11.2%. This coal has 6.6% of semifusinite and 4.9% of fusinite both of which constitute the coarser size inerts. The coal is mostly attrital.
The Monizia coal is medium volatile coal with a vitrinite reflectance of 1.25%. The coal has a content of 50.7% of reactive macerals and 49.3% of inerts.
The Jewell low volatile is a medium volatile in rank with mostly vitrionid V-types 12, 13 and 14. The coal is high enough in rank that the exenite and resinite are mostly optically indistinct though some are distinguishable.The reactives ads to only 61.2% with 38.8% of inerts. The semifusinites content are 13.8% with 19.4% of micrinite and 6.8% of fusinite. This is a very attrital stoker coal.

Table II Petrographic Analysis of Coal Samples

Maceral category	Coloumbian	Blue Gem	Wawel	Slask	Monizia	Pokoj	Jewell	Sewell
Vitrinite	59.3	52.2	36.2	26.1	43.3	29.0	46.4	56.7
Pseudovitr.	13.6	22.5	23.9	5.5	4.1	8.1	7.6	13
Exinite	3.0	8.7	14.6	12.9	10.5	9.4	1.6	4.8
Cutinite	1.1	1.2	0.1	0.1	0.1	0.5	0.1	0.2
Dark Resinte	1.6	0.7	0.9	0.5	0.3	1.1	-	0.2
Light Resinite	0.5	1.8	1.6	1.9	1.8	1.0	0.9	0.9
Semifuisinit	5.4	1.7	8.7	16,2	11.5	17.0	13.8	6.6
Inetodetrinit	5.0	1.0	6.8	12.3	6.2	7.4	6.2	3.5
Micrinite	2.7	7.6	5.2	8.7	6.2	6.9	8.7	6.7
Macrinite	1.3	0.7	4.9	.8	9.6	6.9	4.5	1.0
Fusinite	5.4	1.1	4.4	3.6	4.5	9.5	6.8	4.9
Pyrite	-	0.2	0.2	0.4	0.1	8.4	0.3	0.4
Clay and	1.1	0.6	2.1	1.4	1.3	0.1	3.0	1.1
Quartz			0.4	0.6	0.5	1.1	0.1	-
Carbonate	-	-				0,5		
Total	100	100.0	100.0	100.0	100.0	100.0	100	100.0
Oxidation	1.0	1.3	1.1	1.4		1.2	0.8	0.8
Brecciation	-	-	-	-		0.1	0.2	0.2
Char	-	-	-	-		0.9	-	-

Table III .Vitrinite reflectance for coal samples.

Vitrinoid V-types	Vitrinite reflectance	Colum-bian	Blue Gem	Wawel	Slask	Mon-iza	Pokoj	Sewell	Jewell
V 5	0.50-0.59	9	-	-	-	-	-	-	-
V 6	0.60-0.69	70	-	-	-	5	-	-	-
V 7	0.70-0.79	19	4	3	1	9	-	-	-
V 8	0.80-0.89	2	56	51	52	24	6	-	-
V 9	0.9-0.99	-	40	44	43	37	65	3	-
V 10	1.00-1.09	-	-	-	1	5	27	48	1
V 11	1.10-1.19	-	-	-	-	11	2	37	7
V 12	1.20-1.29	-	-	-	-	7	-	11	23
V 13	1.30-1.39	-	-	-	-	2	-	1	35
V 14	1.40-1.49	-	-	-	-	-	-	-	30
V 15	1.50-1.59	-	-	-	-	-	-	-	4
Reflec-tance	....	0.66	0.89	0.89	0.90	0.95	0.98	1.11	1.35

TEXTURAL ANALYSIS ON CHARS

PETROGRAPHY OF CHARS

The eight char or coke derived from the coal samples were analyzed petrographically. Particles of the uncrushed char were mounted in an epoxy plastic in a cylindrical ring mount. The samples were ground and polished for microscopic analysis as described in ASTM D2797. In addition a riffle-split from each was crushed to minus 8 mesh and mounted and ground and polished for microscopic analysis on carbon forms. Photomicrography were prepared to illustrate the macrostructure (not shown in this paper) and the microstructure of the coke chars.
ASTM is currently working on a standard procedure for the "Microscopical Determination of Volume Percent of Textural Components in Metallurgical Coke". The procedure is based on the work of R.J. Gray and K.F. DeVanney /6/. In this Classification, the coke textural components fall into three major categories; Binder Phase, Filler Phase and Miscellaneous Materials. The different textural components in chars from coals as classified by Gray /6/ are shown in table IV.

MACERALS AND BINDER PHASE COKE

Bituminous coals of different rank produce distinctly different carbon forms from the various vitrinites which produces most of the binder phase. The various carbons forms are distinguishable under a microscope according to their degree of anisotropism, carbon domain size , morphology and colour of the isochromatic domains. Carbons from the reactive macerals in coal constitute the binder phase in cokes. The filler phase in cokes comes from organic inerts and minerals. In addition to the binder and filler phases in cokes there are miscellaneous materials such as depositional carbons. (ref. table 4)
Coke or char textural analyses are used to characterize cokes for comparing their

Table IV : Classification of coke textural components based on R. Gray et. al /6/

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	Domain Dimensions			
	Width (µm)	**Length to width relations**	**Parent coal Vitrinite type**	**Bituminous coal (Volatility)**
Binder Phase				
Isotropic	0.0	None	6.7	High
Incipient (Anisotropic)	0.5	l = V	8	High
Circular (Anisotropic)				
FIne Circular	0.5 -1.0	L = V	9	High
Medium Circular	1.0 - 1.5	L = V	10	High
Coarse Circular	1.5 - 2.0	L < V	11	High to Medium
Lenticular (Anisotropic)				
Fine Lenticular	1.0 3.0	L≥2W, L<4W	12	High to Medium
Medium Lenticular	3.0 - 8.0	L<2W, L<4W	13	Medium
Coarse Lenticular	8.0 - 12.0	L<2W, L≤4W	14	Medium to Low
Ribbon (Ansiotropic)				
Fine Ribbon	2.0 - 12.0	L > 4W	15	Medium to Low
Medium Ribbon	12.0 - 25.0	L > 4W	16	Low
Coarse Ribbon	25.0 +	L > 4W	17, 18	Low
Filler Phase	**Size (in microns)**	**Precursor Material**		
Organic Inerts				
Fine	< 50	Micrinite, Macrinite, Inerttodetrinite		
Coarse	≥ 50	Semifusinite, Fusinite, Macrinite		
Miscellaneous Inerts				
Oxidized coal (Coke)		Oxidized Coal		
Brecciated Coal (Coke)		Brecciated Coal		
Noncoking Vitrinite (Coke)		Vitrinite too high or low in rank		
Inorganic Inerts		Various Types of Mineral Matter		
Fine	< 50	Coal Mineral Matter and Bone Coal		
Coarse	≥ 50	Coal Mineral Matter and Bone Coal		
Miscellaneous Materials		**Description**		
Depositional Carbon		Sooty Carbon (combustion black)		
		Spherulitic Carbon (thermal black)		
		Pyrolytic Carbon		
Additive Carbons				
Miscellaneous Observations				

utilization properties. The technique is normally used in determining blend proportioning by point count analysis. The coke texture analyses are useful in promoting a better understanding of coke reactivity, and when studying the relationship between coal petrography and the conversion of macerals to various coke carbon forms.

Two separate analyses were conducted on each of the granular char samples. Table V show petrographic composition and amounts of binder and filler phases in the coal char samples. Table VI show the amount of different coke carbon forms originating from the reactive macerals measured and classified under polarized light.

The binder phase carbons from high volatile coals are from vitrinoid or V-types 6 through 11 ranging from isotropic through incipient to fine, medium and coarse circular with anisotropic domains of 0.5 to 2.0 microns as indicated in Table V.

The binder carbons from medium volatile coals are lenticular in shape, ranging in widths from 1 to 12.0 microns with length (L) to width (W) ratio of $L \geq 2W$ to $L \leq 4W$. They are produced from vitrinoid V-types 12,13 and 14. The binder phase carbons from low-volatile coals have ribbonlike domains with widths of 2 to greater than 25 microns and length to width ratios of $L > 4W$. They are from vitrinoid-types 15, 16 and 17 plus. The interference colours range from red through yellow to blue. This will be illustrated later.

The vitrinite reflectance distributions and V-types for the coal samples that have been studied are shown in Table III The V-type range from V 5 for the Columbian coal through V 15 for the Jewell coal.

The chars were analyzed by point counting 500 binder phase carbon in each sample and the results of the analysis are shown in Table VI. In general the anisotropism and anisotropic domain size increases as follows: Columbian, Blue Gem, Wawel, Slask, Pokoj, Monizia Sewell and Jewell. The coke or char carbon forms are approximately those that would be expected from the vitrinite reflectance data.

In general, the more isotropic carbons and those with smaller anisotropic domains produce weaker cokes and cokes that are more reactive to CO_2 at elevated temperatures. The lenticular carbons from medium volatile coals produce the strongest cokes and cokes that are low in CO_2 reactivity. In general, lower volatile coals have intermediate strength and reactivity properties.

MACERALS AND FILLER PHASE COKE

The filler phase carbons are counted separately. A total of 500 points were identified per sample in these analyses. The results are given in table IV. Filler phase carbons are counted into various size groups of organic and inorganic. This gives an indication of the types and grades of coals used to make the cokes. This is a separate count from the blend proportioning count.

In addition, the carbons from oxidized and brecciated coals and depositional carbons are counted to give additional information on the coals used in coke production.

The current char samples have more depositional carbon, such as pyrolytic and spherulitic, than found in byproduct coke oven cokes. The reason for this being the rapid heating during carbonizing.

The reactive macerals in a coal produces a coke binder phase whose texture changes with rank, while the organic inert produce isotropic filler phase carbons. Table II lists the pertinent petrographic and chemical data for the subject coals. During coking, the vitrinite

softens and devolatilizes, and then resolidifies as coke binder carbon. The exinite and to a less extent the resinite produces the most tars and gases during carbonization, and they leave the least coke residue.
The fusinite however, leaves the highest residue during coking since it is essentially a charcoal from the beginning. Semifusinites also leave a high yield of coke residue. Both fusinite and semifusinite come through the carbonization process with only minor changes in structure and optical appearance. Micrinites are fine size inerts that act like fusinite and semifusinite, but are more easily incorporated into the coke structure. They tend to add to the coke walls thickness and increase the strength.
The mineral matter such as clays loose OH groups and carbonates produces CO_2, while pyrites loose about half of the sulphur where as the quartz remains as SiO_2. The petrographic analysis in Table II should predict the coke composition shown in Table IV The vitrinite reflectance, as shown in Table III should and does predict the coke binder-carbon forms as shown in table VI.
Table V .Petrographic composition of binder and filler phases in coal chars.

Binder & Filler Phase Carbon Forms	**Colum -bian**	**Blue Gem**	**Wawel**	**Slask**	**Moniza**	**Pokoj**	**Sewell**	**Jewell**
Binderphase	78.6	94.4	62.0	53.4	59.4	53.2	69.4	59.6
Filler phase Organic inerts: Fine < 10μm	5.6	2.8	7.0	13.8	12.6	12.4	9.5	15.6
Medium +10-50μm	4.0	1.2	5.2	7.6	7.4	7.0	3.6	4.4
Coarse > 50μm	10.2	1.0	20.8	21.0	19.2	26.0	13.8	15.0
Inorganic inerts (Mineral matter) Fine < 50μm	1.4	0.6	4.4	1.8	1.2	1.2	2.6	4.4
Coarse > 50μm	0.2	-	0.6	2.2	0.2	0.2	1.0	1.0
Pyrolytic carbon	1.8	3.1	2.1	3.5	3.7	4.4	4.1	3.0
Spherulitic carbon	0.6	1.0	1.9	2.6	4.4	3.5	6.4	2.4

The pore and wall size distribution in addition to carbon forms are important in characterizing coke. High volatile bituminous coals tend to produce the most byproducts. They have the lowest coke yields, and they make porous and fissured cokes. The pores tend to be rounded with smooth walls. Medium volatile bituminous coals are usually the best coking coals, and they produce moderate porosities with a tendency towards elongate pores and thick and irregular coke walls. Low volatile coals have the highest coke yields, and these coals tend to be variable in pore size and shape. In addition the walls in carbon from low, volatile coals tend to have open areas of cracks, that are parallel to the anisotropic domains. Coke pores and wall sizes are also effected by the coal size, the heating rate and the bulk density.

Coke porosities were not measured in this study, but a series of photomicrographs of polished samples were taken to illustrate the porosity and carbon forms in the char samples.

Picture 7 shows the char structure of the relative low rank Couloumbian coal sample. The Char deriving from fusinite is virtually more or less unchanged from what is found in the coals. The structure in the middle of the picture with medium size rounded shaped pores derives from reactive macerals. The Columbian high volatile coal is the lowest rank coal in the group being studied. It has a vitrinite reflectance of 0.66%. It produces an

Table VI. Petrographic composition of coke carbon forms from reactive coal macerals in coal char samples.

Binder Phase Coke Carbon Forms	Colum-bian	Blue Gem	Wavel	Slask	Moniza	Pokoj	Sewell	Jewell
High Volatilecoal Carbons								
Isotropic	28,9	3,3	11,7	2,7	4,3	2,0	-	-
Incipient	48,7	24,3	30,3	17,3	9,0	5,0	0,3	-
Fine Circular	20,7	61,8	34,7	38,7	12,6	20,9	1,0	-
Medium Circular	1,7	10,3	18,7	26,3	16,2	41,2	3,3	-
Coarse Circular	-	0,3	3,3	11,0	20,4	18,6	24,4	0,7
Medium Volatilatile Coal Carbons								
Fine Lenticular	-	-	0,3	2,3	20,2	5,3	50,3	6,0
Medium Lenticular	-	-	-	1,7	13,5	5,0	16,0	56,3
Coarse Lenticular	-	-	0,7	-	3,1	2,0	4,0	31,0
Low Volatile Coal Carbons								
Fine Ribbon	-	-	-	-	0,7	-	0,7	5,7
Medium Ribbon	-	-	0,3	-	-	-	-	0,3
Coarse Ribbon	-	-	-	-	-	-	-	-

abundance of isotropic and incipient carbon forms. It is relatively high, 80.9%, in reactive macerals. It has an abundance of fine size rounded pores with some coarse pores in the char. This is shown in picture 11 in polarized light with a gypsum plate.

The Blue Gem coal is high volatile A rank bituminous, It has a vitrinite reflectance of 0.89%. It is the highest in reactive macerals with 87.7%. It produces coke with mostly incipient and circular anisotropic carbon forms. It has an abundance of small rounded pores and a moderate amount of coarse pores.This is illustrated in picture 8 The smaller pores occur in the thick walls around larger pores. An example of the circular anisotropic carbon domains in the Blue Gem char is shown in picture 12 in polarized light with a gypsum plate.

The Wawel coal is similar in rank to the Blue Gem with a vitrinite reflectance of .89%. It has 70.2% reactives. It is significantly higher in liptinite and micrinite and other inert than the Blue Gem. It produced char with a relatively abundance of incipient and fine circular carbon forms. The char structure is extremely variable as shown in picture 9

The Slask coal is similar to Wawel in rank with a vitrinite reflectance of 0.90%. The Slask coal has only 52.4% of reactive macerals and 13.0% of this is liptinite. It has the highest micrinite content of the coals examined. The char contains mostly fine and medium circular anisotropic carbon forms. The char is relatively dense but variable with distinct areas that are rich in inert. The pore walls are very irregular and elongated. An example of this char structure is given in picture 10. The structure shows incipient carbon as well as lenticular carbon and isotropic inert carbon in polarized light.

The Pokoj coal is higher in rank than the Columbian. Blue Gem, Wawel or Slask. It has a vitrinite reflectance of 0.98%. It has only 54,7% or reactives with 9.9% of liptinite. It has the highest fusinite and second highest semifusinite content of the coals. These are coarse inert and they report to the coke with very little change in microstructure. The char has areas of large irregular pores and areas of dense char rich in coarse inert. Picture 13 show the microstructure of fusinite after coking and areas with fine lenticular anisotropic carbon in polarized light.

The Sewell coal is in the borderline between high and medium-volatile coals with a vitrinite reflectance of 1.11% and 78.1% total reactives. It produces char with mostly coarse circular and fine lenticular anisotropic coke carbon domains. The char has mostly irregular medium size pores that are fairly uniform in distribution as shown i Picture 14.

The Monizia coal has a vitrinite reflectance of 1.25% and 50.7% reactive macerals. The fusinite and semifusinite content total 25.4% which is the same amount that is in the Pokoj. However, the semifusinite content is greater in the Monizia. It should produce carbon forms similar to the Jewell coal.

The Jewell coal is medium volatile bituminous with a vitrinite reflectance of 1.35% and 61.2% of reactive coal macerals. It is relatively high in fusinite and semifusinite which collectively total 20.6%. It produces mostly medium and coarse lenticular coke carbon forms as seen in Picture 15. The coke has mostly irregular and medium size pores fairly well distributed and with thick walls.

THE REACTION BETWEEN SiO GAS AND CHAR

As mentioned earlier coarse lenticular coke has low reactivity versus carbon dioxide, and similar phenomena has been observed in the reaction between carbon and silicon monoxide gas.

It was observed in the electron microscope that some of the binder phase coke structures developed in the chars does not react to silicon carbide when they are exposed to silicon monoxide. When these SiO tagged char samples were observed in polarized light in the microscope, the unreacted carbon structures consisted of high anisotropic optical materials. Coarse circular and coarse and medium lenticular structures appears to have a structure with very low effective diffusion coefficients for SiO gas. Figure 16 is taken in the electron microscope (in BEI mode) and show a partly reacted sample of Sewell char.

White areas are completely reacted to SiC. Entrapped in the SiC we can observe unreacted carbon structures. It is suggested that they are areas with anisotropic coarse low reactive carbon forms probably in the form of coarse lenticular carbon. The sharp borderline between reactive carbon which is completely reacted to SiC and low reactive carbon forms which does not contain silicon at all is illustrated in Picture 17 (3000X). One of the implications in using coal types that forms unreactive carbon forms in the coke matrix is that this carbon is transported into the high temperature crater area of the reduction furnace where as mentioned earlier in reduces the silicon metal formation and thus increases the transport of SiO away from the metal producing zone.
Picture 18 shows the reaction pattern in char from Moniza coal. Black or dark brown (gray) areas are pores, light brown (gray) areas are unreacted char and white areas are SiC. The picture reveals that char deriving from fusinite or semifusinite is completely reacted to SiC. In areas with pore walls deriving from reactive macerals, the topochemical reaction with SiO gas proceeds from the surface and through open pores into the carbon matrix.

SiO REACTIVITY OF CHARS

Table VII show the results from the SiO Reactivity tests on the char samples.Chars produced from coal samples carbonized under the conditions to be found on top of a low shaft electric furnace producing silicon metal or ferrosilicon would normally lie between 700ml SiO to 2300ml SiO. One should remember that high reactive materials is recognized by low "loss volumes" of SiO gas. In Scandinavia producers would avoid to use large amounts of coals that produces chars with reactivity figures above 1400-1500ml SiO(g).Figure 1 show the standard SiO-Reactivity scale used to characterize reductants.
Low reactive chars have normally been characterized by either poor developed pore structure, or a micropore structure which is clogged by SiC when the material is reacted with SiO gas. However, in this work we have tried to focus on the importance of the microstructural components in the chars deriving from the different macerals and maceral blends in coals.
The relative low reactivity of the Jewell sample for example can be explained by the coarse anisotropic lenticular structure partly present in the char produced. Even for the other samples which exhibits some degree of anisotropic appearance these cokes appears to be the least reactive coke structures in the coal chars.
Knowing the coke textural elements beeing formed from the various types of coals (table V), and then observing the reaction pattern of different coke structures with SiO gas at 1650°C, SiO- reactivities of different coals are more easily understood.
If SiO-reactivity is plotted versus rank of these selected coals, as shown in figure 2, it can be seen that increasing rank leads to decreasing reactivity for these low to medium rank coals. We would however, warn the reader from using rank only as a basis for selecting between coal types for the production of silicon or silicon rich ferroalloys since the test material represents well recognized reduction materials for this type of production!
Many researchers find that the porous structure of chars and cokes are strongly affected by the fluid and swelling properties during carbonizing of the coals. The amount , size and extent of the pore development and the pore connection in chars and cokes are related to the rehologic properties of each coal and will influence gas transport properties.

Table VII :SiO reactivities of coal chars

Coal samples	ml SiO
Monizia low. vol. FeSi coal	935
Slask mid/high vol. FeSi coal	918
Wawel mid/high vol. FeSi coal	953
Pokoj 4-14 mm	1165
Jewell 1 x 3/8 Stoker Coal	1116
Columbian coal 3-12mm	704
Blue Gem coal, ref.May10th1994	921
Jewell low vol. FeSi coal	1599
Sewell Si/FeSi coal	1089

Tuset et. al. /1/ have found as earlier mentioned that SiO reactivity to a large extent is related to the effective gas diffusion coeffisient of SiO in the pores. Since both CO_2 and SiO are related to gas transport phenomena the similarity between SiO reactivity and CO_2 reactivity is evident. The reaction between CO_2 and carbon leads to an increase of pore dimensions, however, will the reaction to SiC lead to a decrease of dimensions in open pores which means that they can not be interchanged. This means that similarity applies only in the initial stage of conversion.

SUMMARY

In summary coals included in the current work are low to moderate in ash content and range from high volatile B through medium volatile coals. The Columbian and Blue Gem coals produce the most isotropic, incipient and fine circular carbon forms which are characteristics of low-rank marginal coking coals. These coals are also high in reactive macerals which produce a porous coke carbon that is very reactive to CO_2 at elevated temperatures and is high in electrical resistivity at room temperatures. The Wawel coal is the one Polish coal that is closest to the Columbian and Blue Gem in all these characteristics but is much higher in euxenite and micrinite which increase the hardness of coals. The Slask coal is similar in rank to the Wawel but even higher in micrinite and semifusinite. The inerts inparticularl semifusinite and fusinite, produce isotropic carbons which are known to react differently during coking and combustion than reactive coal macerals.The Pokoj coal is a dull hard coal like the Slask and is also high in organic inert. The Pokoj has the highest fusinite content. The Pokoj is higher in rank than Wawel or Slask and produces more medium and coarse circular anisotropic carbons than any of the lower rank coals. The Sewell coal is borderline high to medium volatile bituminous in rank. It is high in total reactive macerals, produces mostly fine lenticular coke carbons which are physically strong and low in CO_2 reactivity. The pore structure of the Sewell coke is very uniform with irregular pore walls and elongated pores. The Jewell is medium volatile bituminous coal that is relatively high in inert. It is a strongly coking coal. It produces mostly medium lenticular anisotropic carbon. The walls of the coke are thick and the pores are elongate with irregular wall surfaces. Most inert are incorporated in the coke walls.There is a clear connection between the rank of the coals in the region tested and the SiO reactivity as seen in figure 2

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LITERATURE

1 J.Kr.Tuset and O.Raaness Reactivity of reduction materials in the production of silicon, silicon-rich ferroalloys and silicon carbide AIME El.Furnace Conf. St.Louis, Miss. 7-10 Dec. 1976

2 O.Raaness" Specific properties of different types of reduction materials" (in Norweigan) Kursdagene NTH 1983

3 O.Raaness "The role of reactivity in the production of silicon-carbide sillicon and sillicon rich ferroalloys NIF Gol Norway April 1990. Lecture notes Sintef report STF 34 A90092

4 M.B.Müller, S.E.Olsen and J.Kr. Tuset. "Heat and Mass Transfer in the ferrosilicon process Scand. Journ of Met. vol.1 1972 pp 145-155

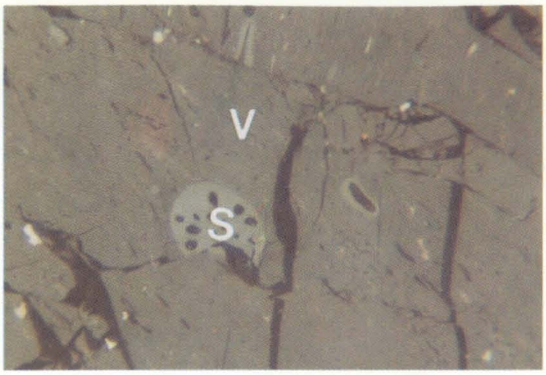
5 A.Skei and K.Larsen A stokiometric model of the ferrosilicon process. Electric Furnace Conf. Proceedings ISS/AIME vol. 39 ,1981, pp301-309.

6 R.J. Gray and K.F. DeVanney "Coke carbon forms: microscopic classification and industrial applications" International Journal of Coal Geology, vol. 6 1986 pp 277-297.

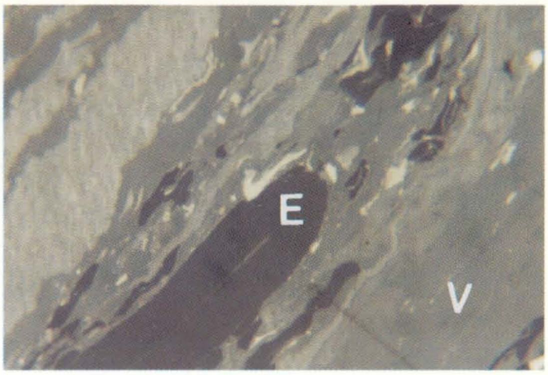
7 N.Shapiro, R.J. Gray and G.R. Euser "Recent developments in coal petrography" Proceedings of Blast Furnace, Coke Oven and Raw Materials Comitee. AIME vol. 20, pp 89-112

8 N.Shapiro and R.J. Gray "Relation of coke structur to reactivity" Blast Furnace and Steel Plant 1963 vol. 51 pp 273-280

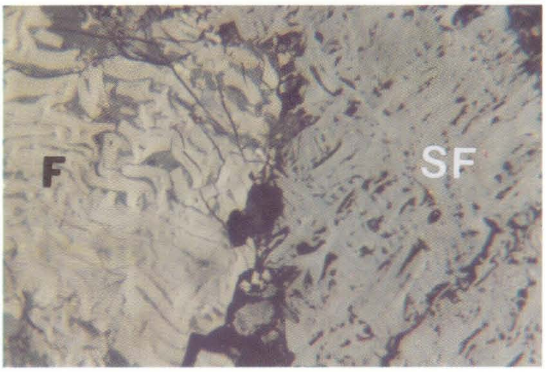
9 N.Shapiro and R.J. Gray "The use of coal petrography in cokemaking." Journal of the Inst. of Fuel vol. XI no.30 pp234-242



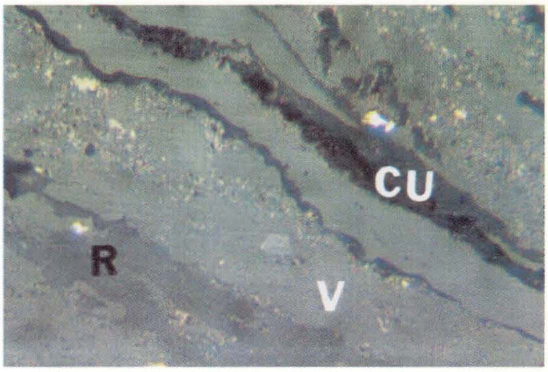
Picture 1 Polished coal sample in oil of Couloumbian Coal showing macerals: (V) Vitrinite, (S) Scleratia. Magn. X 450 in light microscope.



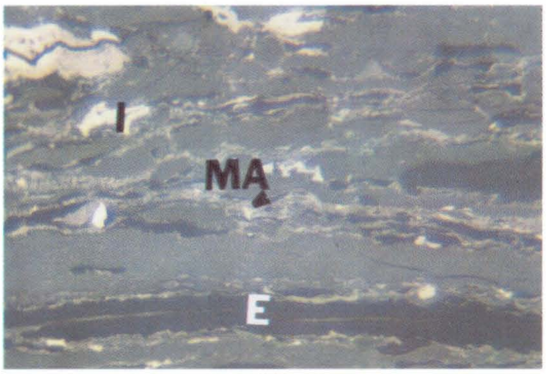
Picture 2 Polished Pokoj coal sample in oil showing (V) Vitrinite, and (E) Exinite. Magn. X 450 in light microscope.



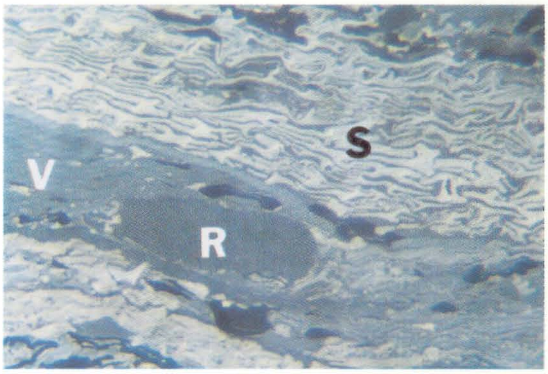
Picture 3 Polished Pokoj coal sample showing the characteristic structure of (F) fusinite and (SF) semifusinite. Magn. X 450 in light microscope.



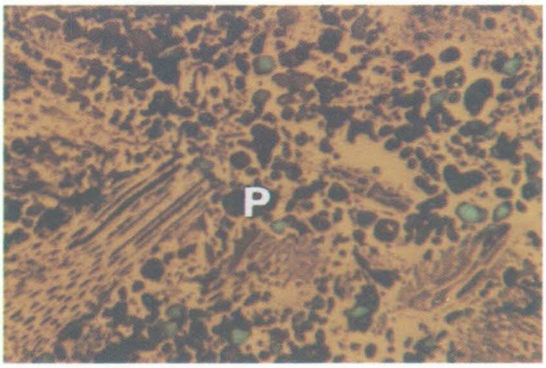
Picture 4 Polished sample of Blue Gem showing (CU) Cutinite (leaf cuticle) (V) vitrinite and (R) Resinite. Magn. X450 in light microscope.



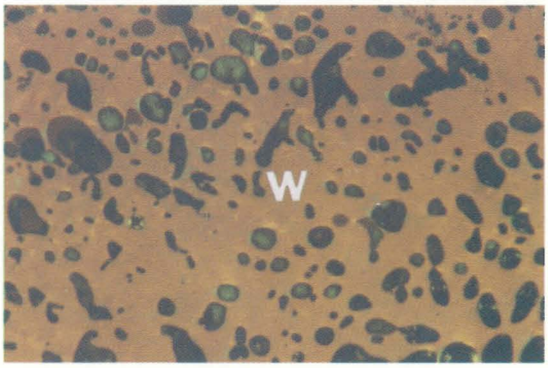
Picture 5 Sewell coal sample showing (I) Inderdotrinite, (MA) Macrinite and (E) Sporinite. Magn. X 450 in light microscope.



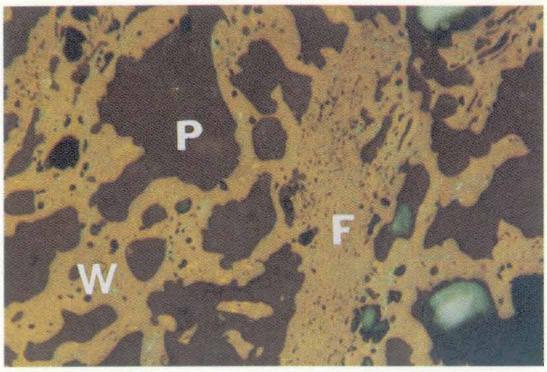
Picture 6 Photomicrograph of Slask coal showing (V) Vitrinite, (R) Resinite and (S) Semifusinite. Magn. X 450 in light microscope.



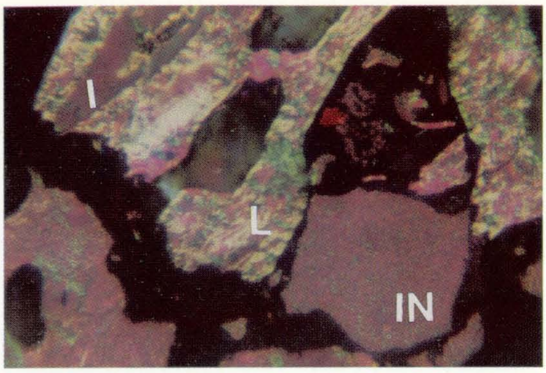
Picture 7 shows the char structure from the Couloumbian coal sample. (P) Pores. Taken in polarized light. Magn 160X



Picture 8 shows char structure from Blue Gem coal which has a high content of reactive macerals. Taken in polarized light. Magn. 160X

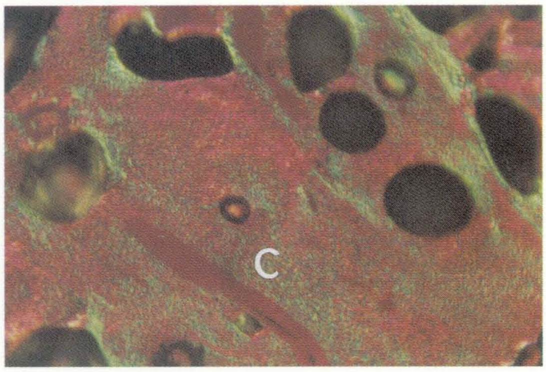


Picture 9 shows char from Wawel coal. The structure is extremely variable (W) Walls,(F) Fusinite.Taken in polarized light. Magn. 160X

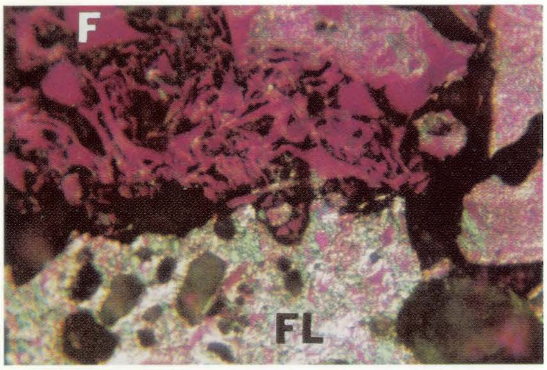


Picture 10 Char from Slask coal sample. The pore walls are very irregular and elongated. (I) Isotropic inerts, (L) Lenticular Carbon, (IN) Incipient Carbon Taken in polarized light with gypsum plate Magn. 160X

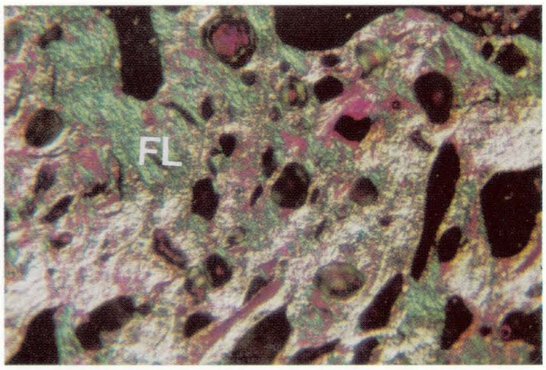
Picture 11 Isotropic carbon domains in the Blue Gem char. (I) Isotropic carbon.Taken in polarized light with gypsum plate Magn. 160X



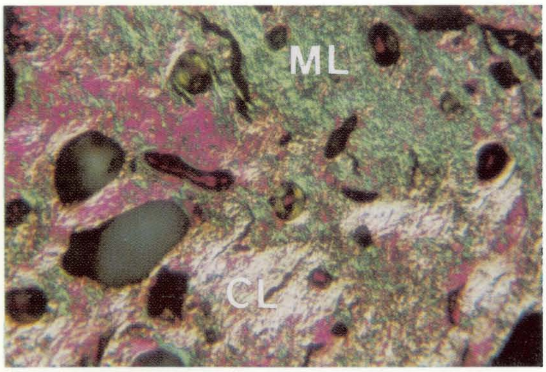
Picturure 12 An example of the circular anisotropic carbon domains in the Blue Gem char. (C) Circular anisotropic carbon domains. Taken in polarized light with gypsum plate Magn. 1000X in oil



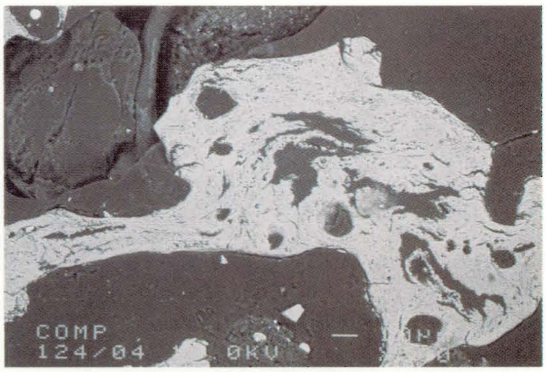
Picture 13 show the microstructure of fusinite after coking and areas with (FL) fine lenticular anisotropic carbon in char from Pokoj coal. Taken in polarized light with gypsum plate Magn. 450X in oil



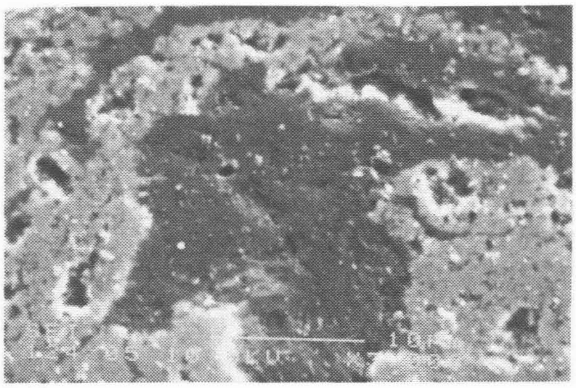
Picture14 The Sewell char has mostly irregular medium size pores that are fairly uniform in distribution. (FL) Fine size lenticular anisotopism. Taken in polarized light with gypsum plate Magn. 450X in oil



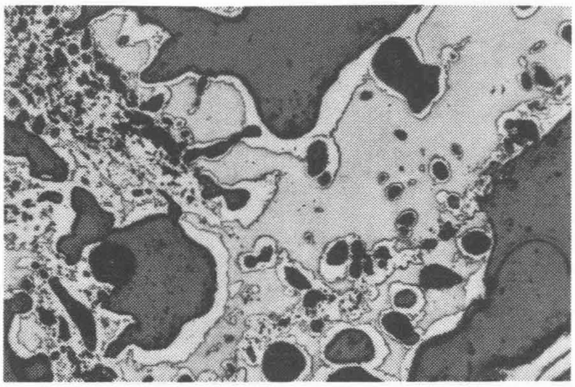
Picture 15 Jewell coal produces mostly medium and coarse lenticular coke carbon forms. (ML) Medium lenticular, (CL) Coarse lenticular. Taken in polarized light with gypsum plate Magn. 450X in oil



Picture 16 taken in an electron microscope (BEI) shows char from Jewell coal partly reacted to SiC. Light gray areas are SiC and dark entrapped areas unreacted carbon. Magn.500X



Picture 17 is a section of picture 16 and reveals the sharp borderline between reactive and unreactive carbon forms. Magn. 3000X



Picture 18 Partly reacted char of Moniza coal Black or dark brown areas are pores, light brown are unreacted char and white areas are SiC. Taken in polarized light. Magn. 160X

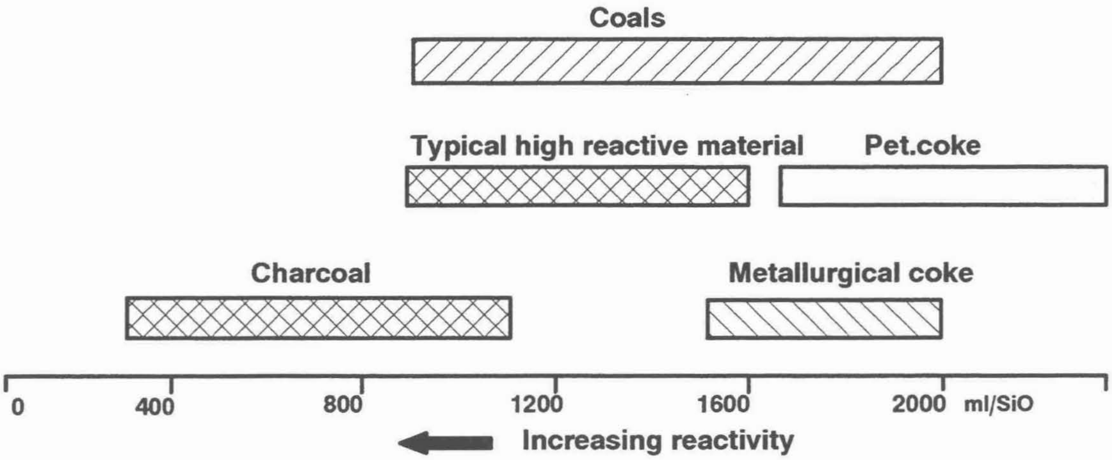


Figure 1. Shows where on the reactivity scale to expect different reduction materials

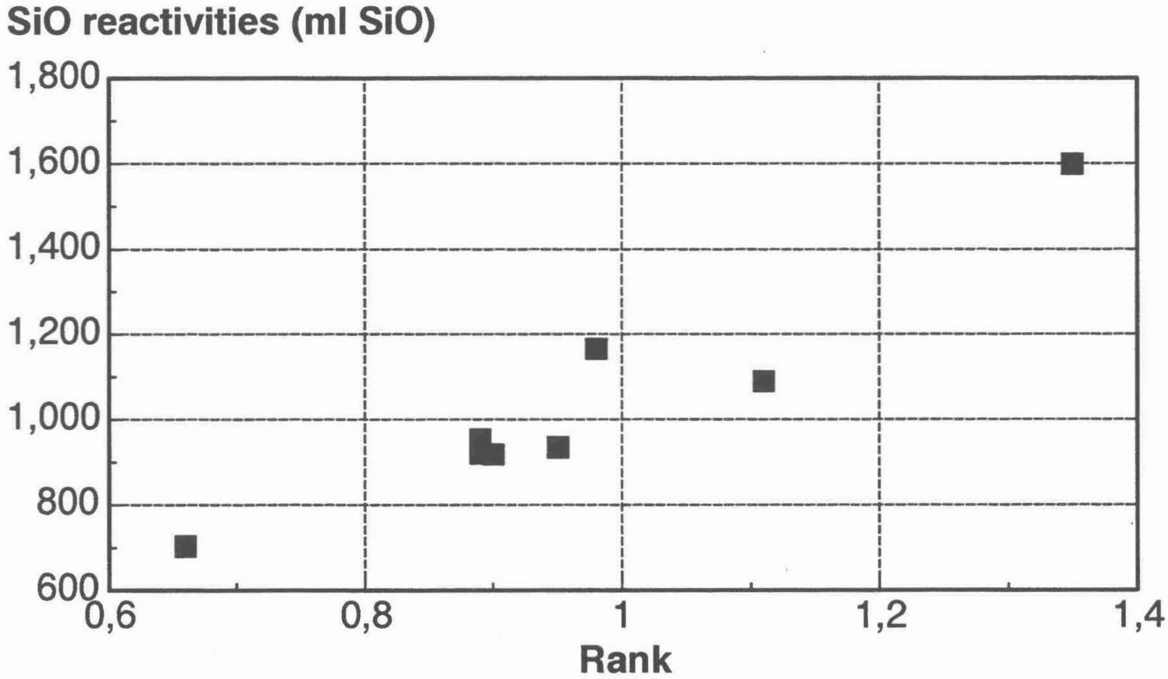


Figure 2. SiO reactivities versus rank on coal