Statistical Analysis of Properties for Coals Used in the Production of Silicon Rich Alloys

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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, are of vital importance for the operation of the process. Besides 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 have been reported earlier [2,3,4]. In this paper we will try to explain by multivariate analysis the different properties of coals as derived from the petrographic properties.

PETROGRAPHIC DATA AND MACERAL GROUPS IN COALS

Thirty five coals of different types and origin, some of them being acknowledged as suitable for the manufacture of silicon and silicon-rich ferroalloys in the electric furnace, have been studied and characterized by their petrographic maceral and vitrinite reflectance properties. ASTM standard D 2797 and D 2798 describes how to prepare and measure mean maximum reflectance of a coal sample.

In comparing petrographic data from both coals and chars the information on each sample cannot be handled as independent variables since they have a certain degree of covariation. In practice this causes problems when trying to apply standard statistical methods and such methods do not present the full information hidden in the measured data.

Coals can be seen as a material constantly undergoing a chemical process. This ageing process or maturing process will continuously alter the properties of the coals. It results in increasing carbon content and reduced hydrogen content. This process alters the thermoplastic behaviour of the coal when heated during a carbonising process.

Petrographic analysis of coal is an important tool for selecting proper coal for different marked segments. ASTM standard D-2799 defines the "Microscopical Determination of Volume Percent of Physical Components in Coal".

The most important microscopic constituents of coal in terms of groups are as follows:

Maceral Group	Maceral	Sub Group
Vitrinite	Vitrinite	Telenite
		Collinite
Liptinite or Exinite	Alginite	
	Cutinite	
	Resinite	
	Sporinite	
Inertinite	Fusinite	
	Interdotrinite	
	Macrinite	
	Micrinite	
	Sclerotonite	
	Semifusinite	

Table 1 Main groups of macerals in bituminous coals

Vitrinite is the main maceral in coals and is mainly formed from mummification of wooden parts of wood rich in cellulose and lignin, and it is divided into Telenite with a cellular plant structure and Collinite without distinct optical structure.In this work we have tested coals ranging from 17% volatile to 76% volatile matter and max.mean vitrinite reflectance ranging from 1,7% to 0,3%.

The coal can be regarded as a mineral aggregate where each of the minerals having different properties. The coal minerals or macerals as they are denoted as in coal petrography have different behaviour, and are precursors for different carbon forms produced upon heating. The amount of vitrinites in the coal samples has varied from 27% to 78% (sum vitr). Exinite, resinite and reactive semifusinite together with the vitrinites the reactive macerals (total react) that produces the binder phase in the char produced upon heating of coals. The remaining components as rest of semi fusinite, fusinite micrinite and minerals form the filler phase in the char.

In silicon and ferrosilicon production only fix carbon will be utilised in the reduction of the quartz. Table 2 show the carbon yield for coal types of different rank (R. Patalsky /8/) during production of coke.Carbon forms or coke textural components and their precursors in the coal has been described by R.Gray /4/. A certain span of the vitrinite reflectance scale will produce carbon forms with a certain ability to transport and react with silicon

monoxide gas. He distinguishes between the binder phase that builds the pore walls and the filler phase embedded in the pore walls.

Table 2 Carbon yields and carbon forms from coals with different rank

Carbon form	Yield of coke	Vitrinite (V) Types
High Volatile Coals		
Isotropic	61,4	6&7
Incipient (anisotropic)	64,9	8
Fine circular anisotropic	68,8	9
Medium circular anisotropic	69,3	10
Coarse circular anisotropic	71,7	11
Medium Vol. Coals		
Fine lenticular	73,7	12
Medium lenticular	75,5	13
Coarse lenticular	77,3	14
Low Vol. Coals		
Fine ribbon	79,1	15
Medium ribbon	80,8	16
Coarse ribbon	82,6	17&18

SiO REACTIVITY

The SiO reactivity test /9/ is a standard method for selecting reduction materials for the production of silicon metal, silicon rich ferroalloys and silicon carbide. This method describes the ability of a reductant to react with gaseous silicon-monoxide at 1650°C to form silicon-carbide.

$$SiO(g) + 2C(s) \rightarrow SiC + CO(g)$$

Loss of SiO gas in these reduction processes is a major reason for low yield of raw materials and high consumption of electric energy per ton finished product.

The SiO reactivity number is given in millilitre SiO gas and expresses how much gas passes unreacted though a coke bed under defined conditions. It is in fact a loss figure, and a low figure hence represents a reactive material.

We have tested a set of coals in 5 ferroalloys plants, and found that their performance in the furnace are close connected to the petrographic properties for the coals in the same way as found for SiO reactivity. We are therefore quite confident in applying SiO reactivity as a measure for suitability of a coal in the reduction process.

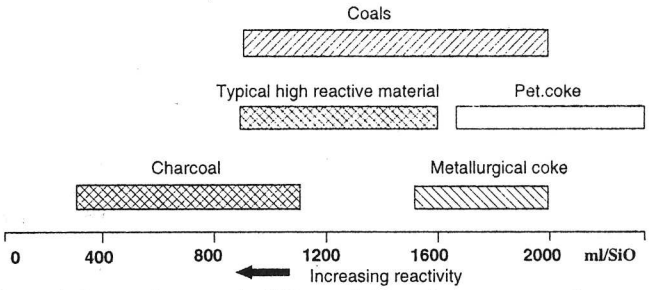

Figure 1 shows where on the SiO reactivity scale to expect various reduction materials.

MULTIVARIAT ANALYSIS OF EXPERIMENTAL DATA

The general problem may be stated as wanting to establish a model that describes the connection between a set of X-variables, often called the independent variables, and a set of (dependent) Y-variables:

$$\mathbf{Y} = f(\mathbf{X}) \qquad (1)$$

where:

$$\mathbf{Y} = \begin{bmatrix} y_{1,1} & y_{1,1} & .. & y_{1,J} \\ y_{2,1} & y_{2,2} & .. & y_{2,J} \\ . & . & .. & . \\ y_{I,1} & y_{I,2} & .. & y_{I,J} \end{bmatrix} \text{ and } \mathbf{X} = \begin{bmatrix} x_{1,1} & x_{1,1} & .. & x_{1,K} \\ x_{2,1} & x_{2,2} & .. & x_{2,K} \\ . & . & .. & . \\ x_{I,1} & x_{I,2} & .. & x_{I,K} \end{bmatrix} \qquad (2)$$

I are the number of objects (experiments, sets of X/Y-data), J and K are the number of Y- and X-variables respectively.
The X-variables in our case are the results from petrographic analysis, and the Y-variables are SiO-reactivities.

Choice of method

The alternative often chosen in situations like this will be a method belonging to the Multiple Linear Regression (MLR) "family". In this case these methods will be impeded by the fact that many of the X-variables of interest will be more or less linearly dependent on each other. Such methods rely on the transpose and inverse of **X**, or rather the construction $(\mathbf{X}^T\mathbf{X})^{-1}$, collinearity in **X** may have a detrimental effect on the stability of the "b-coefficients" and render them useless for causal interpretation. By employment of Principal Component Regression (PCR) or Partial Least Squares Regression (PLS) collinearity between X-variables represents a stabilising advantage rather than a problem. Such methods are discussed by Martens and Næs [6] and are also described in the Unscrambler User Guide [7]. To make an Unscrambler model a set of data (**X**- and **Y**-matrices for a set of objects) is needed, and the user determines some strategies. Such strategies include the choice of "validation method" to test the prediction ability of the model. In this project we have used "cross validation", that is; a small number of objects (subset) are kept out in the calibration procedure and are later used to test (validate) the model. Series of calibrations are run automatically with different subsets of the objects used for validation until all the objects have served as validation objects.
In each of these runs the program determines the first PC by decomposing the matrices containing data from all objects except those of the validation subset. The first PC gets a "direction" such e that it will describe the largest variation in the data set.

The next step is to determine the next PC on basis of the remaining, unexplained variation in the data set and so on until a maximum number of PCs has been reached. For each validation subset th prediction error is computed for all model orders, and these are combined when all the runs are completed. This prediction error will in general have a minimum for a certain model order (number of PCs included) since a low order is associated with a high calibration error (still unexplained variation in the data) while a high order is associated with random noise being included in the model.

General Comments

he most obvious advantage with this method is its ability to cope with collinearity in the X-variables. Equally important is that we get values for the explained or still unexplained variance in the data of each variable as a function of model order (number of PCs in the model). These variance data can be examined for modelling (calibration) and prediction (validation) separately. The model can also be studied in the form of a **b**-matrix, well known from the MLR methods. In this way it is relatively easy to get an understanding of how the variables influence on each other and whether the model includes theoretically probable causalities or not.

MODELING RESULTS

Figure 2 is a two-dimensional scatter plot or map of *scores* for two specified components, PC1 and PC2 from PLS. The plot gives information about patterns in the samples. The component 1 versus component 2 score plot is especially useful, since these two components summarise more variation in the data than any other pair of components.

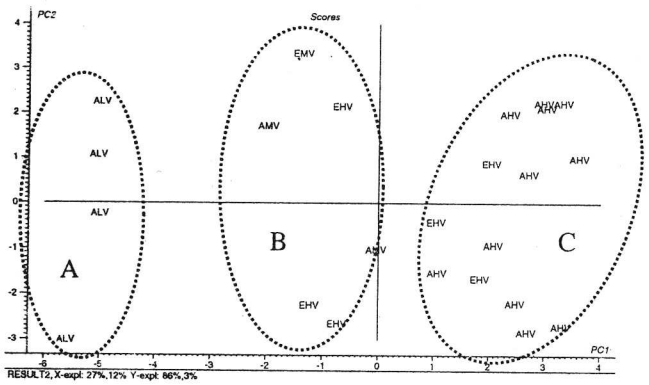

Figure 2 is a two-dimensional scatter plot or map of *scores* for two specified components, PC1 and PC2 from PLS. A or E are abbreviation for American or European coals. HV, MV or LV stands for High Volatile, Medium Volatile or Low Volatile coals.

The closer the samples are in the score plot, the more similar they are with respect to the two components concerned. Conversely, samples far away from each other are different from each other. Note the three groups indicated (A, B and C).The plot can be used to interpret differences and similarities among samples. Look at the present plot together with the corresponding *loading* plot in figure 3 for the same two components. This helps to determine which variables are responsible for differences between samples. For example, samples to the right of the score plot will usually have a large value for variables to the right of the loading plot, and a small value for variables to the left of the loading plot.

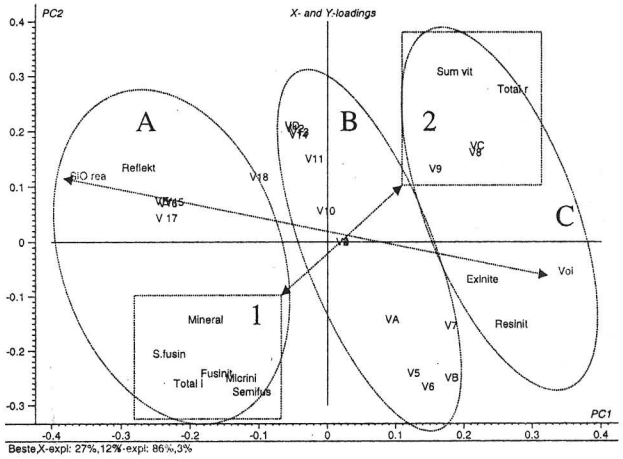

Figure 3 is a 2D-scatter plot of X- and Y-loadings for two specified components (PC1 and PC") from PLS2. It is used to detect important variables and to understand the relationships between X- and Y-variables.

The plot is most useful for interpreting component 1 versus component 2 as shown, since these two usually represent the most important part of variability of the data. The plot shows the importance of the different variables for the two components specified.

Variables close to each other in the loading plot will have high positive correlation if the two components explain a large part of the variance of X and Y. A similar correlation applies for variables in the same quadrant lying close to a straight line through the origin. Variables in diagonally opposed quadrants will have a tendency to be negatively correlated. Variables in orthogonal directions (right angle) will have low correlation. Here we see as expected that the variables **SiO-reactivity** and **Volatiles** are negatively correlated and this is also the case for the two groups of variables contained in the squares marked 1 and 2 on the plot. We also see that these last variables in general will have a low correlation to the y-variables **SiO-reactivity** and **Volatiles**. In the present case, however, the variation in the direction represented by PC2 is of very little importance for explaining the variations in the y-variables. PC2 accounts for 3% of the explanation of the variation in y-variables while PC1 accounts for 86%. Consequently, we will use only one component, PC1, in the following.

In figure 4 the measured values of **SiO-reactivity** and **Volatiles** are plotted versus predicted values. We can still recognise the groups A, B and C. As we see the different coal types are "printed twice" in these plots.

This is due to the fact that predicted values from the *calibration* (fitting of model to the measured values) as well as from the *validation* (testing the model for ability to predict new y-values on basis of x-data not included in the calibration). See also 2.1 Choice of method. The two types of predicted values should ideally be identical and, of course, we would like that they were close to the measured values as well. This is as we can see not the case, but the model presented in figure 4a and 4b shows good agreement between the two types of predicted values, but lesser agreement

with the measured ones. The correlation between measurement and prediction is, however, not bad, approximately 90% and 87% (calibration and validation respectively) for **SiO-reactivity** and 97% and 96% for **Volatiles**. This means that there is a certain difference between the actual measurements and the information contained in the model.

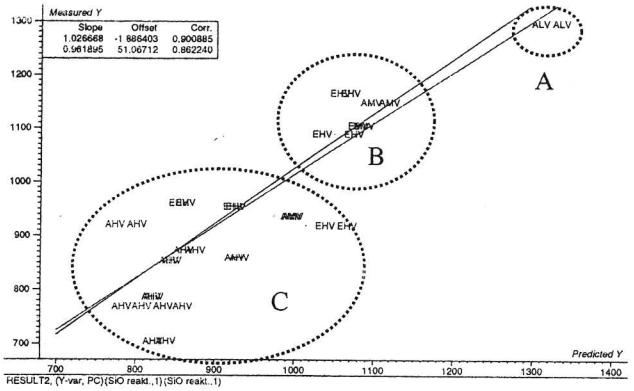

Figure 4a show predicted and validated SiO reactivity values versus measured SiO reactivity. The double printing show respectively validated and predicted SiO reactivity versus measured reactivity. A or E are abbreviation for American or European coals. HV, MV or LV stands for High Volatile, Medium Volatile or Low Volatile coals.

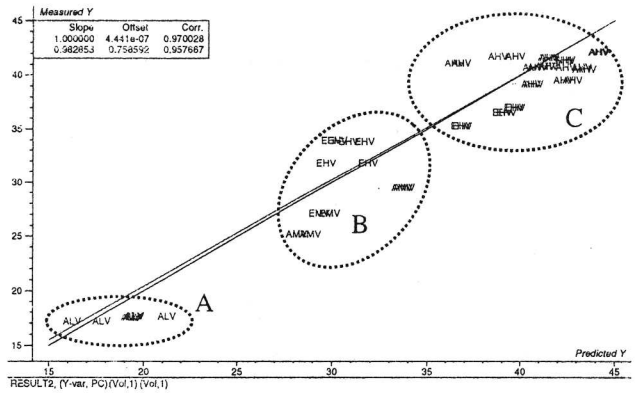

Figure 4b show predicted and validated volatile content in the coal versus measured. The double printing show respectively validated and predicted volatile content versus measured volatile content. A or E are abbreviation for American or European coals. HV, MV or LV stands for High Volatile, Medium Volatile or Low Volatile coals.

However, the prediction capabilities of the model are very good relative to the fitted model. This means that the model contains very little of the unstructured information (noise) present in the data.
The data used in the computations are all "weighted" by a factor inversely proportional to the *standard deviation* of the data for each variable and this means in practice that all the variables have an equal *variance*, in fact it is 1.0. In practice this means that the relative importance of the variables included, can be studied by looking at the set of *weighted* ***b-coefficients***.

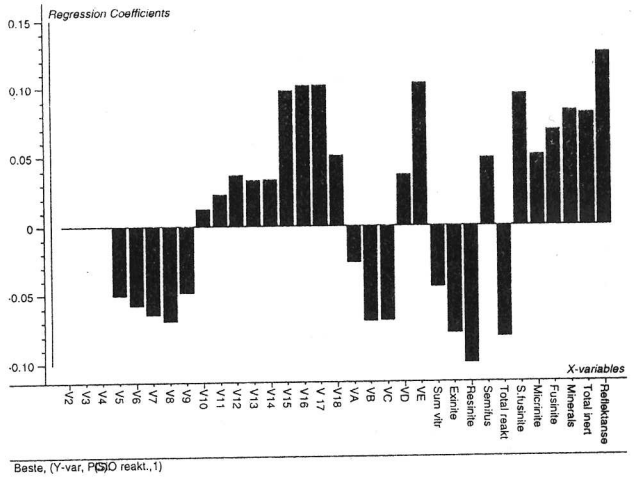

Figure 5 shows b coefficients in a regression equation indicating direction and relative importance of the X-variables on the SiO-reactivity.

A model of this type may later on be used in estimation on basis of new measured and even "artificial" data. Thus it forms the basis for prediction of how different coals, or even cokes, would perform in the electric reduction furnace, and help to select proper materials for the process.
The production managers at the ferrosilicon plants of FESIL gave characters to the performance of different coals included in this work ranging from excellent to poor.
A similar prediction model was developed to predict and validate these characters. Excellent and good performance characters were coals with high SiO reactivities , and high amounts of the VB and VC vitrinite groups.

CONCLUSIONS

Based on multivariate statistical methods on petrographic data from coals we have been able to develop a model on how various factors influences the SiO-reactivity on cokes produced from coals.Table 3 summarizes the results from the multivariate analysis of coal petrograpic data.
As we can see from figure 5 and table 3 a prediction model for prediction of coal properties in the production of silicon or ferrosilicon should contain the following elements:

- Distribution and amounts of V(itrinite) types in the coals or amount of carbon forms precursors (VA-VE)
- Reflektance, rank
- Amount and distribution in reactive macerals
- Amount and distribution of inert macerals

Coals deposited on different pre historic super continents contain according to petrographers different types and distribution of plant material.
The depositional conditions will also vary. European and Eastern American coals may be predicted with the same model . However, they do not necessary apply for coals from India, Australia or South Africa which have been formed under different conditions

X Var.	Description of Coal Parameter.	Effect on Y Var. SiO Reactivity*
V2,V3	Young low reflecting vitrinites macerals with max, mean reflectance 0,2%-0,39%	Not included
V4,-V9	Vitrinite macerals classes with max, mean reflectance 0,4%-0,99%	Increases SiO reactivity (lowering the figure)
V10 - V18	Vitrinite macerals classes with max, mean reflectance 1,00%-1,89%	Decreasing SiO reactivity (increasing the figure)
VA	Amount of V2+V3+V4	Increasing the SiO reactivity
VB	Amount of V5+V6+V7+V8 These V classes are precursors to isotropic or incipient carbon forms in the coke	Increasing the SiO reactivity due to reactive carbon forms
VC	Amount of V9+V10 will produce fine or medium circular (ansisotropic) carbon forms in the coke	Increasing the SiO reactivity due to reactive carbon forms
VD	Amount of V11+V12+V13+ V14 producing coarse circular and Lenticular (fine,medium and coarse)carbon forms	Reducing the SiO reactivity slightly
VE	Amount of V15+V16+ V17+ V18 producing ribbon formed (fine, medium and course) carbon forms	Strong negative effect on SiO reactivity
Sum vitr	Amount of vitrinite	Depending on major V type
Exinite Resinite	Macerals producing binder phase carbon in the coke	Increasing the SiO reactivity due to reactive carbon forms
Semifus	Maceral in binder phase	Reducing SiO reactivity
Total react	Amount of binder phase macerals	Increasing the SiO reactivity due to reactive carbon forms. Large amounts of VD and VE vitrinites are negative
Total inert	Macerals as semi fusinite, micrinite fusinite and mineral matter are inert materials acting as filler materials in pore walls	Negative influence on SiO reactivity
Reflectance	Total vitrinite reflectance gives the rank of the coal. Increasing rank with increasing reflectance	Influences strongly on SiO reactivity. High reflectance (rank) produces low reactive carbon forms and low reflectance reactive carbon forms

Table3 The table shows how different petrographic coal data influences on the SiO reactivity of cokes produced from these coals based on the prediction model.

*When considering the SiO reactivity figures which are given in ml SiO gas they represent the amount of SiO which passes unreacted through a coke bed. A low figure is a reactive coke and a high figure represents a low reactive coke.

4. AKNOWLEDGEMENT

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