IMPROVED SINTEF SIO-REACTIVITY TEST

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ABSTRACT

The SINTEF SiO-reactivity test, developed by Tuset and Raaness in the 1970's, is a recognised method of characterising the "reactivity" of carbonaceous reactants, used in the ferrosilicon and silicon metal industries. Recently, the test has been updated, which has resulted in the development of an extended and improved SINTEF SiO reactivity test. This has included updating the test reactor, control system, data-logging, handling and preparation of carbonaceous materials to be tested and measurement procedure. The scientific basis has been re-assessed, resulting in a new interpretation of the test results. The repeatability of the test has improved significantly, especially through system automation.

In the "old" test, the kinetics of the reaction: SiO(g) + 2C(s) = SiC(s) + CO(g) for a specific carbonaceous material was characterised solely by the "R10" parameter, the volume of SiO(g) which passes un-reacted through the coke-bed as the concentration of CO in the outlet gas decreases from 18 to 10%. As both the kinetics and obtainable conversion of SiO to SiC for a reductant is of importance to the ferroalloy producer, the new SINTEF SiO reactivity test ranks carbon materials both according to degree of conversion and reaction rate.

From research carried out on the test in the past couple of years at SINTEF and NTNU, it has also become clear that some of the reactions taking place in the test reactor are more complex than previously assumed. As an example, it was previously assumed that the condensation reaction of SiO gas in the condensation chamber of the test reactor can be described as: 2 SiO(g) = Si(l,s) + SiO₂(s). However, it has been established that the side-reaction: CO(g) + 2Si(l) = SiC(s) + SiO(g) causes approximately 10% of the total volume of CO to react to SiC and SiO₂ in the condensation chamber. This means that some back-reaction i.e., the reverse SiO-generator reaction 3SiO(g) + CO(g) = 2SiO₂ + SiC also takes place in the condensation chamber. In the new SINTEF test, the %CO versus time curves are therefore corrected in order to describe the effect of the reaction between SiO(g) and C(s) studied i.e., SiO(g) + 2C(s) = SiC(s) + CO(g). A correction-formula for this purpose is presented.

1. INTRODUCTION

The SINTEF SiO Reactivity Test, developed in 1974 [1], has been in continuous use as a means of selecting suitable reduction materials for the production of silicon metal. The test is used to rank different reductants in order of their reactivity with SiO gas, in order to ensure that the process can be operated at maximum efficiency. Over this time there have been incremental developments, leading to minor improvements. Originally the test was designed for coke and charcoal. When ferrosilicon and silicon-metal producers started to use coal in their furnaces, it became necessary to calcine the material before the SiO-test to remove volatile matter. Recently, SINTEF has embarked upon a complete revision of the test equipment and procedure, in order to take advantage of new materials and equipment that simply did not exist 30 years ago. In conjunction with this the reactions occurring within the SiO reactivity furnace have also been re-examined.

2. EXPERIMENTAL

2.1 Equipment

The SINTEF SiO reactivity test is conducted within a vacuum graphite tube resistance furnace, as shown in Figure 1:. Within the furnace is held the 'reactor', which is comprised of three separate sections, held together with a graphite helix.

Generator – The generator contains SiO_2 and SiC powder mixed together and pelletised, which when heated to the correct temperature react to produce 4.5% CO and 13.5% SiO.

1. Reaction chamber – The gases produced in the generator pass through the reaction chamber, which holds the carbon sample to be tested. The chamber has a volume of 20 mL.

Top supporter leading effluent gas out of the furnace

Top support plug

Condencing chamber filled with alumina tubes

Graphite heating element

Graphite helix

Reaction chamber

Gas distributor

Furnace controlling thermocouple

Thermocouple

SiO generator

Inlet for carrier gas
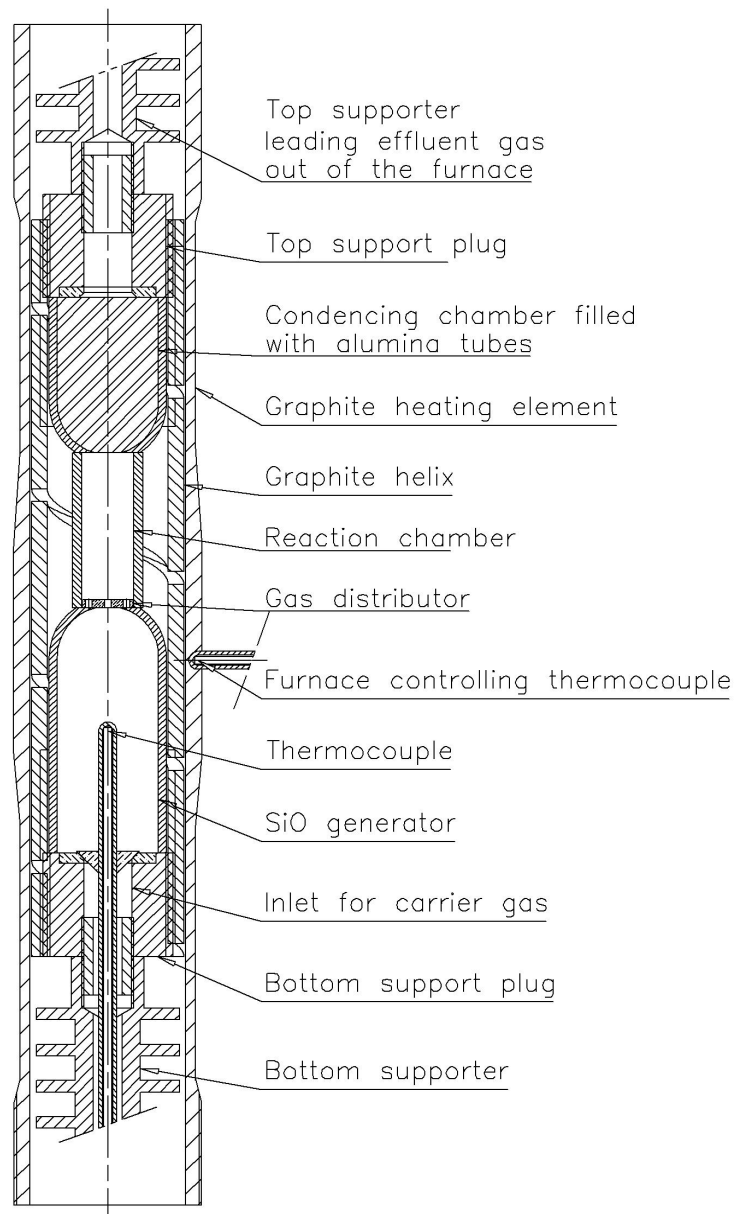
Bottom support plug

Bottom supporter

Figure 1: SiO reactor

2. Condensator – After the gases have passed through the sample they enter the condensator, where they are cooled. The condensator is filled with alumina tubes, which provide surface area to cool the gas, and for any un-reacted SiO gas to be condensed to form SiO_2.

All of these parts are constructed of re-crystallised alumina, with graphite support plugs on each end connecting the components to the helix. All of the internal alumina parts of the furnace are joined with alumina cement, while the graphite supports are sealed to the alumina using gaskets made from graphite paper, which are compressed and aligned by the graphite helix. The graphite supporters are also used as inlet and outlet tubes for the transport of Ar and Ar + CO, respectively. The temperature in the centre of the generator is measured with a type B thermocouple, which is inserted through the base of the furnace. The temperature of the sample is not measured directly; however the temperature profile is frequently checked to ensure that the sample temperature is slightly higher than the generator. A thermocouple placed close to the heating element is used to control the furnace.

Argon enters the bottom of the furnace at 320 ml/min, where it passes through the generator and carries the CO and SiO through a gas distributor to the test sample. After the gas has passed through the reaction chamber, it enters the condensator where it is cooled, allowing any remaining SiO to be converted to SiO_2. Finally, after passing through a series of filters, the gas is analysed for CO in an infrared analyser.

The improvements in the equipment have been incremental, such as the use of graphite paper as a gasket (minimising the possibility of gas bypassing the sample), streamlining the gas path through the furnace to the CO analyser (to improve the response time) and optimisation of the temperature profile within the furnace (providing more uniform sample temperature, while allowing the gas to be quickly quenched in the condensator).

2.2 Test Procedure

The test begins with the selection and preparation of the sample. Initially, a representative sample of approximately 1 kg is taken from the bulk material source. The sample is then dried, crushed and sieved to +4.0-9.5mm, then calcined at 1200°C for 20 minutes, and finally crushed and sieved again to a particle size of +4.0–6.3 mm according to a defined procedure. The calcined sample is then placed within the reaction chamber, where it is reacted with a gas mixture of 13.5% SiO, 4.5% CO and 82%Ar, which corresponds to equilibrium at 1650°C. The concentration of CO in the outlet is analysed and recorded as a function of time. The test is stopped when the concentration of CO equals 5.2% corresponding to the maximum obtainable conversion of C to SiC. Un-reacted and reacted coke is analysed for total and free carbon and the SiO-reactivity parameters are calculated in order to determine the extent and rate of carbon conversion to SiC.

The basis of the procedure is identical to the original test, with several incremental improvements that have enhanced the repeatability. The major improvements in the test have been in automating the test procedure. All operator interaction with the test that may in some way influence the result has been automated. Once the sample is sealed in the furnace, and the test is ready to commence, a LabView program is initiated and the operator simply monitors the test.

Firstly, the software sends a program to the Eurotherm controller to heat the furnace with a predefined program until the sample temperature is 1500 °C, where it is held until the concentration of CO in the outlet gas drops below 5%. This allows the maximum amount of ash in the sample to be reduced, without any formation of SiO in the generator chamber. After this criterion is met, the temperature is held an additional 10 minutes and then rapidly heated to the test temperature of 1650 °C. At this stage the test has just commenced and it is necessary to achieve 18% CO in the outlet gas as rapidly as possible, however, this is complicated by the possible further reduction of higher oxides in the ash. Cascade control of the furnace using the %CO as an input to the furnace temperature was unstable, while the more common PID control loop was too slow. Instead, a simple step control regime was implemented. The LabView program simply waits 40 seconds (the dead time in measuring the %CO), then waits for a stable gas concentration. Once this is achieved, the deviation from 18% is calculated and a set point change applied to the furnace controller. It was found that the %CO is ex-

tremely sensitive to temperature, with only 5 °C required to increase the concentration of CO in the outlet gas from 17% to 18%. This sequence is then repeated until the %CO is stable at 18% or 10 minutes has passed. It is necessary to apply a time limit that is less than that required for a reactive sample to experience break through, i.e. the time at which SiO gas can be expected to pass un-reacted through the sample. This procedure to acquire 18% CO in the off gas has been much more successful than the previous manual adjustment of furnace temperature, which tended to depend upon operator experience.

The furnace then remains at the required temperature until the outlet gas contains 5.2% CO, which is designated as the end point. The raw data is then imported to EXCEL, where a macro is used to automatically calculate the reactivity parameters.

2. BACKGROUND AND THEORY

The reaction between SiO(g) and carbon in the upper part of the furnace is extremely important in the ferrosilicon and silicon metal process [2].

$$SiO(g) + 2\ C(s) = SiC(s) + CO\ (g) \tag{1}$$

If free carbon is not available in sufficient amounts or does not react fast enough, SiO will be lost by the reaction

$$2\ SiO(g) = SiO_2(s) + Si(l) \tag{2}$$

or other side reactions.

The metallurgist operating a furnace knows from experience that some carbon materials reacts fast and gives high silicon-yield, while others have low reactivity. The SINTEF SiO reactivity test developed in the 1970's by Tuset and Raaness [1] made it possible to quantify the SiO reactivity. It has been found to be a valuable tool, based on the vast numbers of tests carried out for the smelting industry and the coal and coke suppliers. Originally the test was developed for coke, but with the increasing use of coal charged at the top of the burden of the furnace, it was necessary to adapt the method. Thus the coal samples are heated at a rate similar to the heating rates in an industrial ferrosilicon or silicon-metal furnace, producing a char for the SiO-test [3].

3.1 Basic principles

The main reactions and gas streams within the test apparatus are shown in Figure 2:. At equilibrium, the gas produced in the SiO-generator at 1650 °C contains 13.5 % SiO and 4.5 % CO, with the remainder Ar. The equilibrium calculation has recently being checked with the newest data in FactSage by Myrhaug [4], giving 13.615 % SiO and 4.539 % CO. This deviation is very small compared to measuring errors and shall not change any numbers used in the test. The argon stream is kept constant at 19.2 l/h (1 bar and 20 °C)

The concentration of CO in the gas leaving the condensation chamber is continuously measured during the test, producing a plot of %CO versus time. Previously the reactivity has been calculated solely from this curve, where the reactivity is the volume (ml) of SiO which passed through the coke bed in the time which the concentration of CO fell from 18% to 10 %, as calculated from the equation:

$$R10 = \sum_{18 \to 10} \frac{Q_{Ar}\,(18 - pctCO)}{82 - 0.82.pctCO} . \Delta t \tag{3}$$

But the test has always been run until the concentration of CO in the outlet gas had fallen to 5.2 %, giving additional information such as the possibility to calculate a R5.2 reactivity (down to 5.2 % CO in the outlet gas).

Ar   CO   SiO

Q_{Ar} (100-pct.CO)% Q_{CO}* (pct.CO)%

Condensation-chamber

Condensation: 2 SiO(g) = Si(l,s) + SiO₂(s)
Condenser reaction: CO(g) + 2 Si(l) = SiC(s) + SiO(g)

Q_{Ar} 82% Q_{CO}* (18-x)% Q_{SiO}* x%

Reaction-chamber

Reaction: SiO(g) + 2C(s) = SiC(s) + CO(g)

Q_{Ar} 82% Q_{CO} 4,5% Q_{SiO} 13,5%

SiO generator

SiO-formation: 2SiO₂ + SiC = 3SiO(g) + CO(g)

Q_{Ar} 100%

Figure 2: Reactions, gas-streams Q (ml/min) and gas composition (vol %) passing the 3 main units in the SiO reactivity apparatus

3.2 Conversion

Some chars, even those with a high reactivity as measured by the R10 value, do not always fully convert to SiC. To fully understand the potential of a particular carbonaceous reductant we should also measure the degree of conversion of carbon to SiC.

The free carbon in the tested sample ($C_{2,free}$) and the total carbon in both the calcined ($C_{1,total}$) and tested ($C_{2,total}$) sample are determined as part of the current test procedure, which, combined with the sample weight before (m_1) and after the test (m_2), can be used in Equation 4 to calculate the degree of conversion (X):

$$X = \frac{2.(C_{2,total} - C_{2,free}).m_2}{C_{1,total}.m_1}.100\%$$ (4)

Where m is mass of sample, 1 and 2 refer to before and after the test, respectively. Carbon contents are given in %.

The free carbon as a percentage of the total carbon in the sample before the test is calculated by:

$$free\ carbon = \frac{C_{2,free}.m_2}{C_{1,total}.m_1}.100\%$$ (5)

The carbon loss is then calculated by:

$$carbon\ loss = 100\% - X - free\ carbon$$ (6)

3.3 Reactivity

The reactivity is calculated by performing a numerical integration of the concentration of CO with respect to time, which is then used to determine the volume of SiO gas that did not react with the sample. Figure 3: is an example of two parallel runs of an Australian coal. The reactivity has generally been expressed by the parameter R10, which has units of ml SiO(g) (at NTP) which has passed through the sample until the concentration of CO in the outgas has fallen to 10%, as defined in Equation 3..
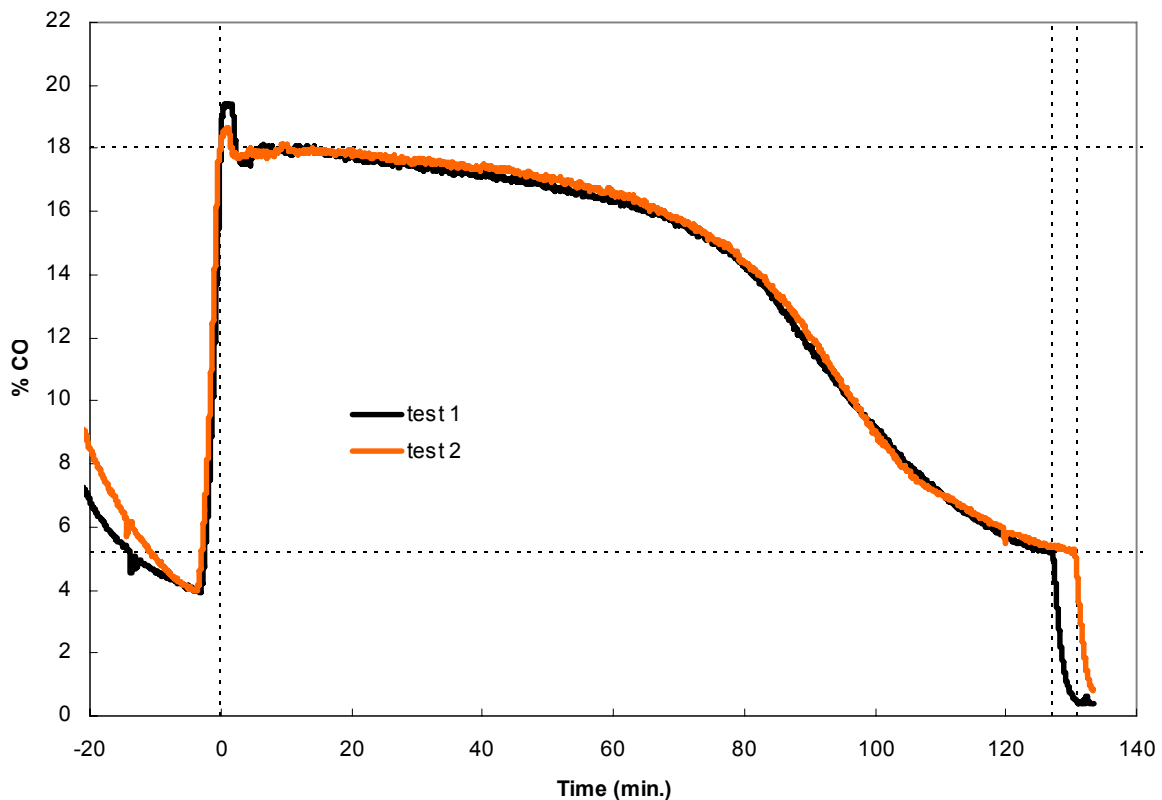

Figure 3: An example of the %CO vs time from reactivity tests for an Australian coal, showing the repeatability

From the recorded data it is possible to also calculate a similar reactivity for any concentration of CO, e.g. R5.2 represents the quantity of SiO that has passed through the sample until the concentration of CO has reached 5.2%. A high R10 indicates a low reactivity, while a low value indicates high reactivity.

Since the volume of the test sample is fixed by the volume of the reactor chamber, the parameters generated so far express the reactivity per volume of the reducing material, while the mass flow [kg/s] is the input variable for a ferroalloy furnace. The mass of carbon in the test sample is also determined, making it possible to also calculate a mass-based reactivity parameter, such as the current R10 divided by the mass of carbon in the sample ($R10/m_c$), which would provide a comparison on a mass basis. From the test data it is possible to calculate a vast number of parameters, all of which will be useful under specific conditions and in different processes.

4. REACTIONS IN CONDENSATION CHAMBER

As the gas leaves the reaction chamber it is cooled in the condensation chamber, where all SiO present will react by condensation reactions forming SiO_2 and SiC [2]. The quantity of condensed SiO can be calculated from the amount of SiO produced in the gas generator (calculated from the weight loss in the gas generator) less the amount of SiO consumed to produce SiC (calculated from the degree of conversion of carbon to SiC *(X)*, which is determined in section 0)

$$\Delta m_{SiO,condensor} = -\Delta m_{SiO,Generator} \cdot MF_{SiO} - \Delta m_{sample} \left(\frac{M.W._{SiO}}{M.W._{SiC} - 2*M.W._{C}} \right) \qquad (9)$$

Where $M.W._x$ = the molecular weight of species *x*
         m = mass

The amount of CO produced in the gas generator and in the reaction chamber is then calculated by corresponding equations:

$$\Delta m_{CO, formed} = -\Delta m_{SiO-generator} \cdot MF_{CO} + \Delta m_{sample} \left(\frac{M.W._{CO}}{M.W._{SiC} - 2*M.W._{C}} \right) \qquad (10)$$

Where MF_{CO} and MF_{SiO} are the mass fraction of SiO and CO in the gas produced in the generator chamber, which are 0.825 and 0.175, respectively. The total amount of CO consumed in the condenser reaction can then be calculated from a mass balance of the condensation chamber and by analysing the concentration of carbon in the condensate.

$$\Delta m_{CO,condensator} = \left(\frac{\%C_{condensator}}{100} \right) \cdot \Delta m_{condensator} \cdot \frac{M.W._{CO}}{M.W._{C}} \qquad (11)$$

Where $\Delta m_{CO,condensator}$ = the weight of CO consumed within the condensation chamber (g)

         $\%C_{condensator}$ = the concentration of carbon measured in the condensation chamber (%)

         $\Delta m_{condensator}$ = the change in weight of the condensator

The total amount of CO in the gas leaving the furnace ($\Delta m_{CO,analysed}$) is calculated by numerical integration of the concentration of CO with respect to time. The amount of CO consumed in the condensator can also be calculated from the following mass balance:

$$\Delta m_{CO,condensator} = \Delta m_{CO,analysed} - \Delta m_{CO,generator} - \Delta m_{CO,reactor} \tag{12}$$

Where $\quad \Delta m_{CO,condensator}$ = mass of CO consumed in the condensator (g)

$\quad\quad\quad \Delta m_{CO,analysed}$ = mass of CO analysed (g)

$\quad\quad\quad \Delta m_{CO,generator}$ = mass of CO formed in the generator (g)

$\quad\quad\quad \Delta m_{CO,reactor}$ = mass of CO produced in the reactor (g)

An investigation of the condensation reactor after repeating SiO tests for three different materials is shown in Table 1:. The table shows the concentration of carbon in the condensate (%$C_{condensator}$) (if there was no back reaction then there should be no carbon present), the weight of CO consumed in the condensator (CO$_{condensed}$) and the total amount of CO produced by both the pellets and sample (CO$_{pellet+sample}$). It can be seen that the amount of CO consumed in the condensation chamber is a significant proportion of the total CO. Variations in the quantities are largely due to different test times.

Table 1: Condensation chamber mass balance

Coal	%$C_{condensator}$ (%)	CO$_{condensed}$ (g) [1)	CO$_{pellet+sample}$ (g) [2)	%CO$_{consumed}$
European	4.2	0.49	7.3	6.7 %
European	7.0	0.53	6.9	7.7 %
Appalachian	5.1	0.47	5.7	8.2 %
Appalachian	4.3	0.44	6.0	7.3 %
Australian	3.1	0.74	8.1	9.1 %
Australian	4.7	0.78	6.6	11.8 %

[1) Results from the same materials reported in Table 2

[2) Calculated from the mass loss of the generator and the mass change and analysis of the sample

4.1 Correction for condensation

The condensation reaction occurs when silicon is formed in the condensation chamber, which results in the concentration of CO falling below 18 % through reaction 2. By assuming that the condensation reaction increases linearly with time, it is possible to correct the concentration of CO using equation 13. This is a reasonable assumption, as the quantity of silicon metal formed in the condensation chamber is proportional to the amount of SiO, which will increase with time.

$$\%CO_{corrected} = \left[1 + k_1\left(\frac{t - t_{18\%}}{t_{end} - t_{18\%}}\right)\right] * (\%CO_{analysed}) \tag{13}$$

Where $\quad t_{18\%}$ = time at which the %CO falls below 18%

$\quad\quad\quad t_{end}$ = time when the test ends, CO = 5.2%

$\quad\quad\quad k_1$ = rate constant, found experimentally to be 0.21.

5. VALIDATION

Figure 4:shows the measured and corrected curves for a test with char made from Australian coal. To validate the improved method parallel tests have been carried out on a large number of carbon materials. The results from three tests with chars and one test with coke are summarized in Table 2.
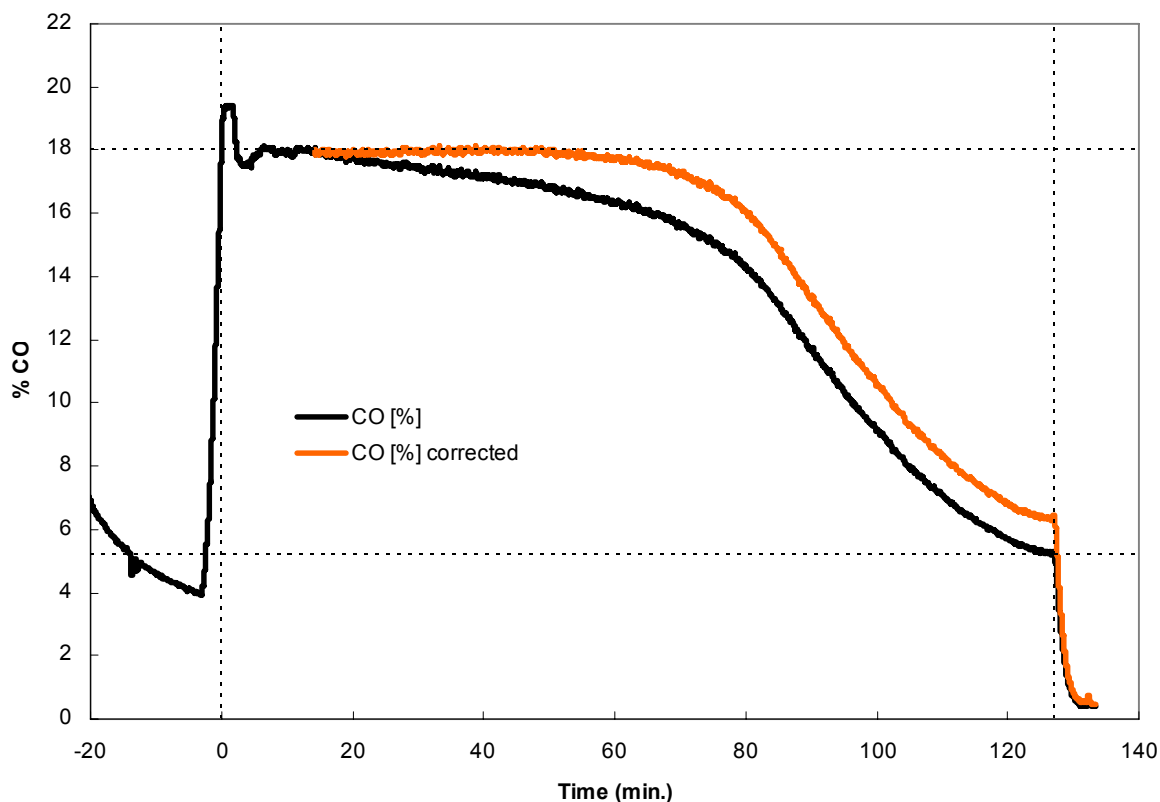

Figure 4: %CO vs. time curves for Australian coal

Table 2: Repeatability of SiO-reactivity test

Test material	m_C [g]	% Conversion (X)	R10	R10corr	R10corr/m_C
Australian	5.3	95	817	580	109
Australian	5.2	100	757	519	100
Appalachian	4.7	84	697	606	129
Appalachian	5.2	79	722	567	109
European	4.8	90	701	562	117
European	5.1	94	823	636	125
Coke	7.1	76	936	985	139
Coke	7.2	72	1019	1033	143

m_C is mass of carbon in test sample.

The average difference between parallel tests was 8.7 % for R10corr. The conclusion, which is also confirmed by recent tests of coal samples from silicon and ferro-silicon producers is that the average difference between parallel tests is less than 10 %. The average difference in the conversion (X) was about 5 %, relative.

6. CONCLUSION

The SiO reactivity test has recently been revised. All equipment and procedures have been assessed, with improved materials not initially available and the automation of the testing process. The reproducibility of the test is now better than 10% for all samples, ranging from highly reactive charcoals to relatively inert cokes.

A side reaction has also been identified in the condensator chamber, where CO reacts with condensed silicon metal to reduce the concentration of CO measured in the outlet gas. This can be corrected by accounting for the average rate of CO consumed before break through of the SiO gas occurs. By correcting the results in this way, it is possible to provide more repeatable results.

The SINTEF SiO reactivity test is a useful tool to help select suitable reduction materials, which is becoming more critical with the increasing variation and reduced supply currently experienced.

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