What happens when cold CH$_4$ (g) meets hot SiO (g)?

*Based on a paper by B. Monsen, L. Kolbeinsen, S. Prytz, V. Myrvågnes, and K. Tang presented at the INFACON conference in Kazakhstan June 2013*

The possibilities for using natural gas are investigated in a Norwegian competence building project KMB - GasFerroSil. The overall objective of the project is to reduce energy consumption and CO$_2$ emissions in the Ferroalloy, Silicon and Titania slag industry. Silicon carbide is an important intermediate in silicon production, and is formed above 1512 °C from hot SiO gas and solid carbon according to reaction (1). One basic idea in GasFerroSil regarding Si- and FeSi-processes is to utilize natural gas in the production of silicon carbide, according to reaction (2).

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

$$\text{SiO} \, (g) + 2\text{CH}_4 = \text{SiC} \, (s) + \text{CO} \, (g) + 4\text{H}_2 \quad (2)$$

Enabling hot SiO gas to meet cold CH$_4$ before it cracks into C and H$_2$, a special water-cooled injection lance was constructed and inserted directly into a reaction chamber at 1600-1650 °C where hot SiO gas is flowing.

The production of silicon (Si) and ferrosilicon (FeSi) is conducted in semi-closed furnaces allowing air to enter the furnace just above the charge. The oxygen in air sustains the combustion of CO gas from the reduction process as well as oxidation of the gaseous bi-product, SiO. Heat generated from these reactions forms the basis for subsequent energy recovery and the fine silica dust is collected in bag filters and sold. Most of the SiO gas generated in the lower part of the furnace reacts with carbon in the charge to form silicon carbide, which in turn reacts with quartz to form silicon, SiO and CO. Hot SiO gas and solid carbon react and form silicon carbide as an important intermediate product in silicon production, according to reaction (1) above 1512 °C.

In GASFERROSIL we have had a closer look at the options available if the off gases are combined with natural gas, but new processes for silicon production have also been considered. A common challenge for all the examples of possible industrial usage of natural gas has been that cold natural gas must meet hot SiO gas. This challenge has been addressed in the present work together with thermodynamic calculations using FactSage. The main question was: "Is it possible to experimentally investigate what happens when cold CH$_4$ (g) meets hot SiO (g), or will the methane crack on its way into the furnace and plug the equipment?" A lot is known about how SiO reacts with carbon materials and how it will decompose into silicon and silica at temperatures lower than ~1100°C, but little is known about possible reactions with methane. Methane, on the other hand, decomposes easily to carbon and hydrogen during heating, starting at around 400 °C while the conversion should be complete at 1000°C, according to thermodynamic calculations by Wærnes et al [1]. In order to enable hot SiO gas to meet cold natural gas before it decomposes to carbon and hydrogen, a special water-cooled injection lance was constructed. The lance was inserted directly into a reaction chamber at 1600-1650 °C where hot SiO gas was flowing.

**EXPERIMENTAL**

The furnace and most of the experimental set-up is the same as normally used for the SiO-reactivity test at SINTEF [2, 3]. A water-cooled lance with 10 mm outer diameter was made for CH$_4$-injection. Cold CH$_4$ will meet hot SiO gas in the reaction chamber (red colour) in Figure 1. The lance tip is positioned in the middle of the reaction chamber in most experiments. The SiO-gas generator (blue chamber) is filled with pellets from which SiO and CO is formed according to equation (5) and Argon (19.2 l/h) is used as carrier gas, as in the SiO test. The hot SiO gas is formed around 1650 °C and flows into the reaction chamber. The weight of pellets before and after each experiment was registered. The amount of SiO gas generated can be calculated from the pellets weight loss or by measuring the CO-level in the off-gas without methane injection.

The reaction chamber (red chamber) is a little wider than the one used in SiO-reactivity tests in order to get enough space for both the water cooled lance and products. The inner tube diameter is 28 mm and the height is 60 mm. Here will cold methane meet hot SiO gas and the reactions (2) and (3) can be studied by measuring the off-gas CO-level and by and analysing excavated products.
The condensation chamber (green chamber) is not filled with alumina Raschig rings, as in the SiO reactivity test. Condensation takes place on the cold lance, mainly on the part inside the reaction chamber according to reactions (4) or (6).

Condensation chamber, and on the lance:

\[
2 \text{SiO (g)} = \text{SiO}_2 (s) + \text{Si (s)} \tag{4}
\]

\[
3 \text{SiO (g)} + \text{CO (g)} = 2 \text{SiO}_2 (s) + \text{SiC (s)} \tag{6}
\]

Reaction chamber

\[
\text{SiO (g)} + 2 \text{CH}_4 (g) = \text{SiC (s)} + \text{CO (g)} + 4 \text{H}_2 (g) \tag{2}
\]

\[
\text{CH}_4 (g) = \text{C (s)} + 2 \text{H}_2 (g) \tag{3}
\]

SiO generator (SiO formation chamber)

\[
2 \text{SiO}_2 (s) + \text{SiC (s)} = 3 \text{SiO (g)} + \text{CO (g)} \tag{5}
\]

Figure 1 Experimental principle for cold CH\textsubscript{4} to meet hot SiO.

The temperature was measured in the middle of the SiO generator (T\textsubscript{SiO}) as in the SiO-test. Both the reaction chamber and the surface of the SiO-pellets may be cooled down by the water cooled lance. Therefore, T\textsubscript{SiO} was kept stable in the range 1644-1651 °C during methane injection while the temperature in the SiO-test usually is around 1630–1640°C.

Experimental procedure: The basis of the SiO-reactivity test is that a gas mixture containing 13.5 % SiO and 4.5 % CO is passed through a coke-bed with argon (19.2 l/h) as a carrier gas at around 1650 °C. In the present set-up there is no coke-bed, but a product-bed did build up during methane injection and consequently the pressure increased a little. Methane injection was started when the temperature in the SiO chamber had reached 1555-1625°C and lasted for 60 minutes in most experiments. The furnace was turned off after the injection was stopped.

Off-gas measurements: The CO-level in the off-gas was measured by a CO gas analyser, which was calibrated before the start of each experiment. A µ-GC was used in some experiments in order to measure hydrogen, CO, CO\textsubscript{2}, unconverted CH\textsubscript{4}, and to see if other species were formed.

Chemical analyses of products were carried out by MOLAB. These analyses were total carbon (combustion, IR), free carbon (temperature controlled combustion) according to ISO 9286:1997 chemical analysis of silicon carbide, and silicon that was determined by titration according to Fedorov’s method.

Identification of phases was done by XRD (X-ray diffraction analyses). Semi-quantitative XRD were carried out at NTNU, with a User D8 ADVANCE using a DIFFRAC\textsuperscript{plus} SEARCH software and quantitative XRD was carried out using mathematical modelling.

REACTION EQUILIBRIA BETWEEN CH\textsubscript{4} AND SiO

The reaction equilibria between streams of SiO (g) at 1650 °C and CH\textsubscript{4} (g) at 25 °C at arbitrary pressure (1 bar) have been simulated for various molar ratio of CH\textsubscript{4} to SiO at adiabatic condition (no heat added) as shown in Figure 2 using thermochemical data from the FACT databases [4]. Increasing the CH\textsubscript{4}/SiO ratio results in lower adiabatic temperature because the carbon black producing reaction (3) is endothermic. An optimal SiC production occurs at a molar ratio of CH\textsubscript{4}/SiO \sim 1.26 for which 0.75 mole SiC is formed at a temperature close to 1380 °C. It is well known that the lowest temperature for SiC production by reacting SiO gas with carbon is around
1512 °C. The gas mixture produced in the SiO generator is close to the 3SiO-CO mixture. Therefore reaction equilibria at fixed temperatures in the range 1200 - 2000°C were also simulated for various molar ratios of CH₄ (g) and streams with 0.75SiO (g) + 0.25CO (g) as seen in Figure 3.

Figure 2 Thermodynamic calculations in the system Si-O-C-H for reactions between cold methane (CH₄ at 25°C) and hot silicon monoxide (SiO at 1650°C) for various molar ratios of CH₄/SiO. No energy added, adiabatic temperature, product species (left) and partial pressures (right) calculated.

Figure 3 Equilibrium SiC (mole SiC) contours at left and energy changes (ΔH, kJ) of isothermal reactions at right, both as a function of the CH₄/(0.75SiO+0.25CO) mole ratio at 1200-2000°C.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 4 Production rates on a molar basis (at left) and product composition (wt %) at right. Molar ratio with SiO-generation is based on pellet weight loss in each experiment.
Figure  shows the production rates (moles/h) for SiC, SiO$_2$ to the left, C and Si, while at the right the product composition (wt %) is shown for various molar ratios of CH$_4$/SiO. The generation of SiO gas is based on the SiO-pellets weight loss in each experiment. The experimentally determined SiC production rate in Figure resembles the thermodynamic calculated equilibrium at adiabatic conditions shown in Figure 2. The curves and relative amounts of SiC, SiO$_2$ and C are very similar at high molar ratios of CH$_4$/SiO. At low ratios the experimentally determined SiO$_2$ is higher, probably due to the cooling effect of the lance.

CONCLUSIONS

The reaction equilibria between hot SiO-gas (1650 °C) and cold CH$_4$ (25 °C) were simulated for various molar ratio of CH$_4$ to SiO at adiabatic condition. Thermodynamic calculations show that maximum SiC production occurs at CH$_4$/SiO~1.3 at 1380°C, while the lowest temperature for SiC production by reacting SiO-gas with C is around 1512 °C. Consequently, SiC can be produced at a lower temperature by reacting CH$_4$ with SiO. This is due to the high carbon activity when methane reaches the hot zone which can be of great technical significance for a new SiC or Si process. Excess natural gas will crack to carbon and hydrogen while the temperature drops. In this way natural gas can also act as a cooling agent, while carbon and hydrogen are produced. The efficiency of silicon carbide formation at these temperatures was verified experimentally for various molar ratios of CH$_4$/SiO. A water-cooled lance for CH$_4$ injection was inserted directly into a reaction chamber at 1600-1650 °C where hot SiO gas was flowing. In this way it was avoided that methane cracks on its way into the furnace and plugs the equipment. Hence, it was possible to experimentally investigate what happened. SiC was formed to a large extent, confirmed by chemical analyses, and verified by XRD analyses. Maximum SiC was formed close to CH$_4$/SiO = 1.5. The CO flow rate provides a continuous method for monitoring the process. Experimental and thermodynamic results are in close agreement.

REFERENCES


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