A Thermodynamic Model for Silicon Furnace.

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ABSTRACT

A model for the silicon furnace has been carried out, considering that a thermodynamic equilibrium is achieved in the inner zone of the furnace. The calculation is made by minimising Gibbs free energy in this zone. According to this model, when the ratio C/SiO_2 increases, the silicon recovery raises to a maximum, then lowers. The maximum silicon recovery varies according to the furnace parameters: the reactivity of reducing agents, the temperature in the inner zone, the gas temperature and the moisture of raw materials. We have tested also the undercoking condition with SiC recovery in the crucible, and the segregation in the mix.

INTRODUCTION

Some models have already been made to increase the understanding of the silicon process.

We have created our own model that is somewhat different from the previous ones.

As with other known models, this model is very simplified, and ignores the presence of minor elements such as Ca and Al.

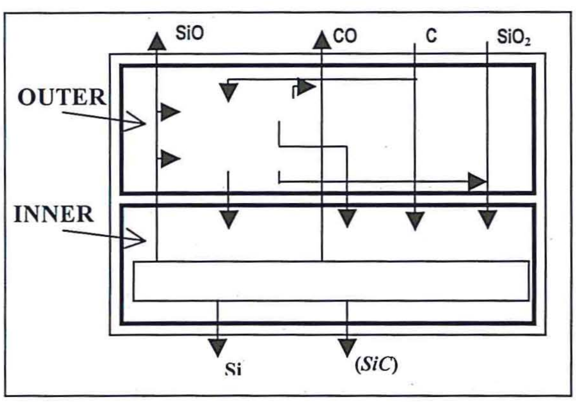

Figure 1 : model of the furnace

We have used the classical division of the furnace in 2 zones :

- An outer zone where SiO is consumed by two main reactions :

$$SiO + 2C \rightarrow SiC + CO$$

$$2\ SiO \rightarrow SiO2 + Si$$

- An inner zone, where the thermodynamic equilibrium is achieved, and the products of reactions (condensed and gas) are determined by the minimum Gibbs free energy. So, we need no hypothesis on the crucible gas composition, neither on the chemical reactions which take place in the inner zone of the furnace.

HYPOTHESIS

The thermal balance of the outer zone is achieved, which allows the calculation of the rate of condensed SiO, according to the temperature in the crucible, the temperature of the gas, the heat of reactions and the water evaporation.

The pressure in the crucible is calculated assuming that the gas leaving the furnace is at atmospheric pressure. As the gas goes upwards, the temperature decreases, there is a great loss of gas by SiO condensation and reaction with carbon, resulting in the production of CO and water vapour . The volume being constant, the pressure decreases, and so we can calculate the pressure in the inner zone.

PARAMETERS

Before starting a run, we have to set up the following parameters :

- Ratio Carbon/Silica in the raw materials,

- Crucible temperature,

will use this situation as a reference to compare with further calculations with changed parameters.

Crucible Temprature(°C)	2000	Reactivity number	75.0%
Gas temperature (°C)	600	SiC consumed in crucible	0.10
H_2O/C	0.80	**Si recovery max**	**84.5%**

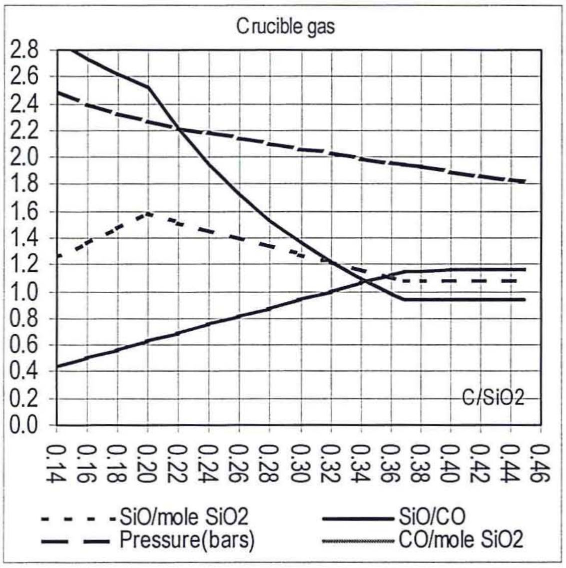

Figure 4 : gas composition and pressure in the crucible

Now, we are able to see the variation in this maximum silicon recovery when we change one parameter of the model. We are going to show the changes on graphics between the reference case (thin lines) and the new situation (thick lines).

EFFECT OF THE REACTIVITY NUMBER

We recall that it is the fraction of the carbon that can react in the outer zone, forming SiC and SiO.
We have tested a decrease of this number from 75% to 70% (see fig.5).

Under these conditions we find a maximum silicon recovery of 79.5% : decreasing the reactivity number by 5%, we have dropped the silicon recovery by 5%. This explains the fact that a little amount of very low reactivity coke can impact dramatically on the performance of a furnace.
Another remark : electrodes are carbon that reaches the bottom of the furnace unreacted. Therefore we can guess that a high rate of electrode consumption would affect negatively the results of the furnace.

Crucible temprature(°C)	2000	Reactivity number	70.0%
Gas temperature (°C)	600	SiC consumed in crucible	0.00
H_2O/C	0.80	**Si recovery max**	**79.5%**

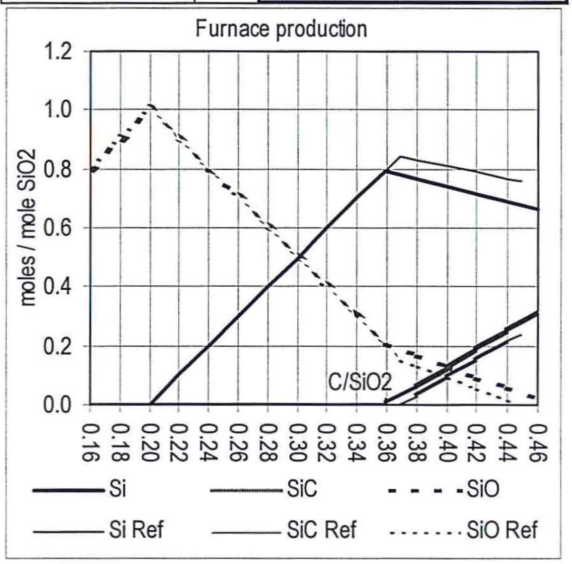

Figure 5 : lower reactivity of reducing agents

EFFECT OF THE CRUCIBLE TEMPERATURE.

We have tested a crucible temperature of 1950°, while returning the reactivity number to standard condition : 75%.

Crucible temprature(°C)	1950	Reactivity number	75.0%
Gas temperature (°C)	600	SiC consumed in crucible	0.00
H_2O/C	0.80	**Si recovery max**	**65.1%**

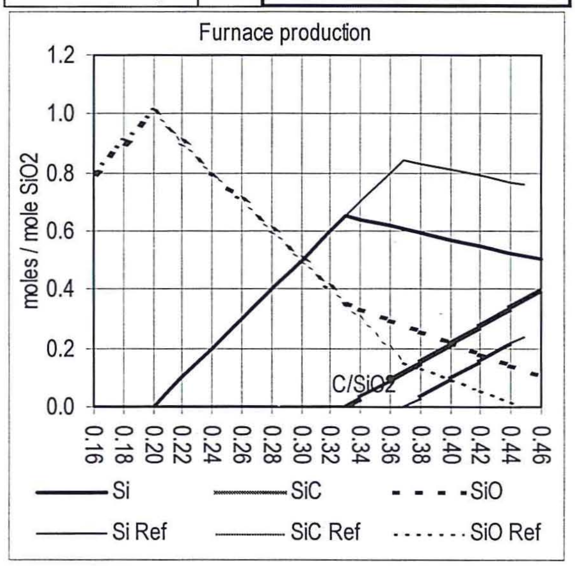

Figure 6 : lower temperature in the crucible

Thus, a drop in the crucible temperature of 50°C strongly decreases (-19.4%) the maximum silicon recovery, with an optimum C/SiO2 ratio very low (0.330 electrodes included). In fact, we are not able to control this temperature. But in poor thermal conditions, after a long stop for example, the average temperature in the crucible is probably lower than in normal operation. Then, in this case, it is necessary to drop the ratio C/SiO2, in order to produce a minimal amount of SiC.
In fact, the crucible temperature is not the same across the bottom of the furnace: this can explain the SiC formation in the sides of the crucible, normally colder than the center.

EFFECT OF THE GAS TEMPERATURE

After returning to standard conditions, we have increased the gas temperature from 600 to 700°C. Surprisingly, the results have improved (see fig 7), with a maximum silicon recovery of 87.5% versus 84.5% in the standard conditions (+3%). Considering the heat balance of the outer zone the refreshing of the gas is an exothermic process that compete with condensation reaction: if the temperature difference between the crucible and the surface is lower, the SiO condensation rate (and thus the SiO consumption in the outer part)will increase.

Crucible temprature(°C)	2000	Reactivity number	75.0%
Gas temperature (°C)	700	SiC consumed in crucible	0.00
H_2O/C	0.80	**Si recovery max**	**87.5%**

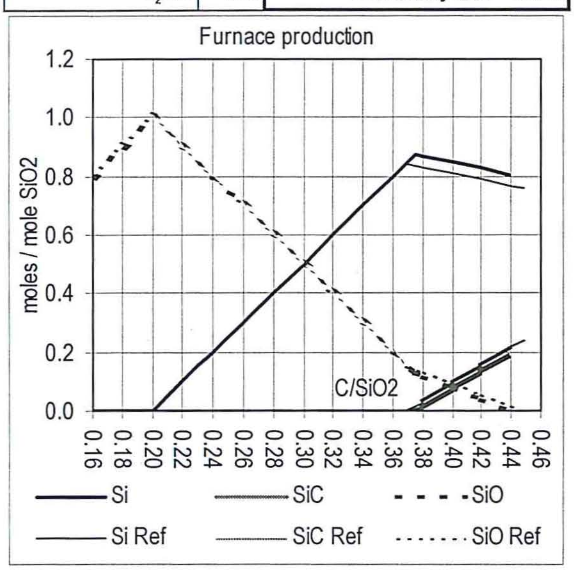

Figure 7 : effect of gas temperature

EFFECT OF MOISTURE IN REDUCING AGENTS

After returning to standard conditions, we have increased the ratio H2O/C from 80 to 90% (see fig. 8). The maximum silicon yield increases from 84.5% to 86.8% (+2,3%). The explanation is found again in the heat balance of the outer zone : water evaporation needs heat, which is provided by the condensation reaction. More SiO is consumed, and then the silicon yield increases.

From practical experience, the effect of moisture content of the mix is negligible.

We think that, when the water content in reductants increases, as the water evaporates in the very upper part of the mix, the gas temperature will decrease, and the effect on the silicon recovery will be compensated.

Crucible temprature(°C)	2000	Reactivity number	75.0%
Gas temperature (°C)	600	SiC consumed in crucible	0.00
H_2O/C	0.90	**Si recovery max**	**86.8%**

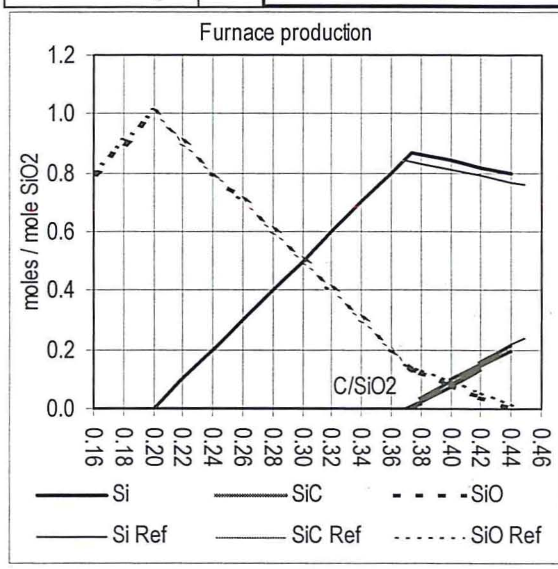

Figure 8 : effect of the moisture of reducing agents.

CASE OF SIC RECOVERING IN THE FURNACE

In some case, when we have some SiC in the bottom of the furnace, we decrease the C/SiO2 ratio to try to recover this SiC. In our model, we have introduced some SiC directly in the inner zone of the furnace. The amount is 10% molar of the quartz fed in the furnace (which is a lot, in practical, we would have to use the quantity able to react, which is generally low).

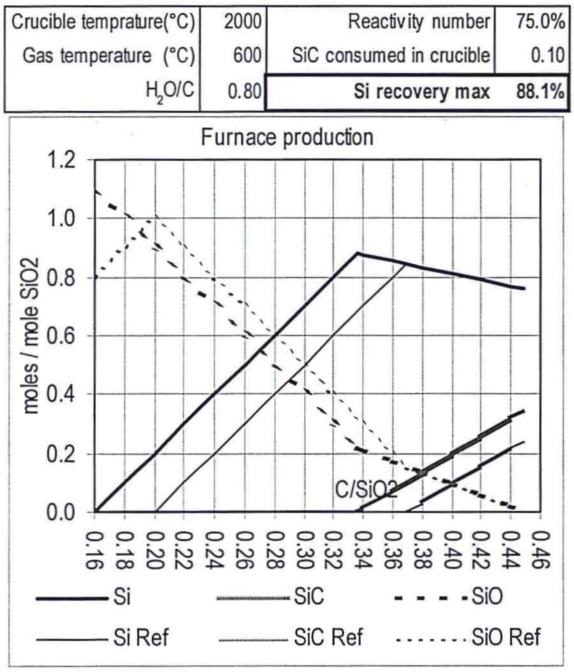

Figure 9 : undercoking with SiC recovery in the crucible

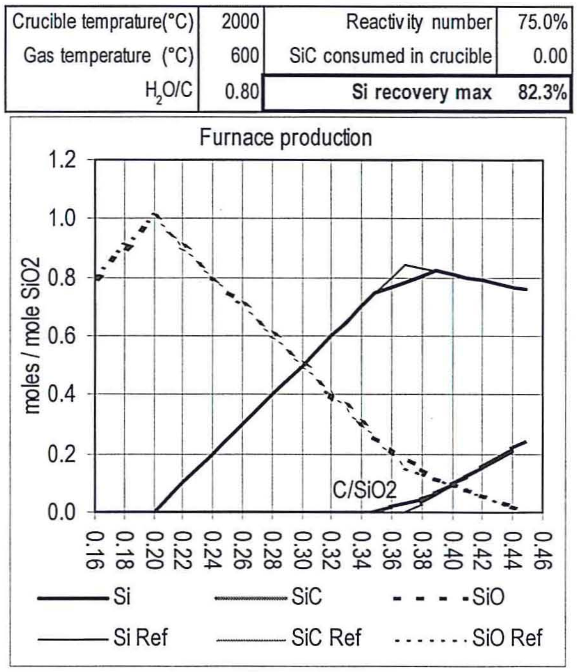

Figure 10 : segregation in the mix

In that case, the optimum C/SiO2 ratio is much lower (from 0.369 to 0.336), and the maximum silicon recovery is higher from 84.5 to 88.1 (+3.6%) than in standard case. The curves are translated to the left.

EFFECT OF MIX SEGREGATION

In some furnaces there may be a problem with the homogeneity of the mix. In some cases, the ratio Carbon/silica will be higher than the average value in the mix, and in other cases, this ratio will be lower.

We have made a simulation with half of the mix with a C/SiO2 ratio 0,02 higher than the specified value, and half of the mix with a C/SiO2 ratio 0,02 lower than the specified value.

Then, the maximum silicon recovery is lower than in a furnace without segregation (from 84.5% to 82.3%). To reach this value, we must increase the ratio C/SiO2 from 0.369 to 0.389, but SiC deposit begins at C/SiO2= 0.349, with only 74.5% of silicon recovery. In the case of segregation in the mix, the furnace is difficult to run, the silicon recovery varies slowly when we change the C/SiO2 ratio, and remains lower than in a furnace without this problem. For a standard value of C/SiO2, we get some SiC inside the furnace.

DISCUSSION

Theoretically, this model allows a silicon recovery of 100% by increasing the temperature in the crucible. In fact, we cannot increase this temperature at will, if we could do so, the reactions will progress faster, consuming more heat, which will lower the temperature (without change in energy input).
We have observed that with the same kWh/t consumption, some furnaces have a high silicon recovery, but poor quartz/MWh consumption, and other furnaces have a poor silicon recovery, but higher quartz/MWh consumption. But unfortunately, we have not found a furnace with both high silicon recovery and high quartz/MWh consumption. We explain this fact thus : if the reactions in the furnace progress quickly, the quartz consumption will be high, but the temperature will be low, and then according to our model, the silicon recovery will be rather low.
The model shows that a temperature much higher than the minimum temperature allowing Si production is necessary to reach the silicon recovery observed in the furnaces.

In this model, we assume that the whole current reaches the electrode tips, so that there is no Joule effect in the mix. In real furnace, this is not true, and some heat provided by the current affects the heat balance in the mix. So, the SiO condensation must be lower. This current does not reach the inner zone, which may affect its temperature. Both items tend to lower the silicon recovery. Then, the current repartition in the furnace is very important to get good results on a silicon furnace.

CONCLUSION

We hope this model contributes to silicon furnace understanding, by pointing out the importance of some parameters, and by quantifying their effects. But it is still far from a description of the total reality which is extremely complex.

This model is used in Pechiney Electrometallurgie and Invensil in the training of metallurgical engineers to give them the good reflexes in running silicon furnaces. This model will allow the metallurgical engineers to make the most of the tools used as a standard in Pechiney Electrometallurgie and Invensil :

- standard method to run the silicon and ferro-silicon furnaces based on visual parameters, on mass balance and on electrical data of the furnace allowing the engineers team to decide the actions to be carried out.
- automatic algorithm based on a few measured parameters giving a diagnostic of the state of the furnace. The engineers team compare both results before taking their decision.

This model will help the metallurgical engineers to decrease the process variations, and thus to improve both the efficiency of the process, and the quality of the products.

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