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SILISIUM PRODUKSJONSPROSESS. ENERGI OG EKSERGI ANALYSE FOR HOLLA SILISIUM SMELTEVERK.

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SILICON PRODUCTION PROCESS

ENERGY AND EXERGY ANALYSIS FOR HOLLA

SILICON PLANT

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Department of Chemistry
Norwegian University off Science and Technology

Declaration

I declare that the work presented in this thesis has been accomplished independently.

Trondheim, July 2, 2012

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Summary

The metallurgical industry is trying to unite quality of raw materials with the relatively low in cost power and the best technology. The exergy method makes possible to find and quantify the capability of improving thermal and chemical processes. Although exergy application has a significant potential to improving efficiencies, is still not common in industry.

The objective of this study is to look at the energy and exergy distribution in the silicon processes at Holla plant. The production of silicon metal is technically well established. Cost reduction is one of a new process modification. Holla plant has achieved reduced cost by using cheaper raw materials. In 2006, Holla stopped to use charcoal in mixture of raw materials. Since then charcoal has been used occasionally.

Two analyses has been established using data from furnace #4 at Holla plant. First one with data collected from 2006 where charcoal was included in raw materials. The second one from 2011 where charcoal has not been component of raw materials.

The energy analysis reveals big energy losses ,which goes to the environment as waste heat. Only 28.7 MW of 80.4 MW in the first analysis and 30.13 MW of 82 MW in the second analysis energy delivered to the silicon process is got back as a chemical energy in the product in analysis .

The production of silicon involves large exergy destruction, approximately 39.2 MW in both analyses.

Sammendrag

Metallurgisk industri prøver å forene kvalitet av rå varer med relativt lav pris og den beste teknologien. Eksergi gjør det mulig å finne og kvantifisere evnen til forbedring av termiske og kjemiske prosesser. Selve eksergi applikasjonen har en betydelig rolle i å forbedre effektivitet, dette er ennå ikke vanlig i industrien.

Målet med denne studien er å se på energi og eksergi fordeling i silisium prosessen ved Holla-anlegget. Produksjon av silisium metall er teknisk godt etablert. Kostnadsreduksjon er et nytt grep i modernifiseringen. Anlegget ved Holla har oppnådd reduserte kostnader ved å bruke biligere råvarer. I 2006 sluttet Holla å bruke trekull i blandingen av råvarer. Siden da har trekull bare vært brukt av og til.

To analyser har blitt etablert med data fra ovn #4 ved anlegget. Den første med data samlet inn fra 2006, der trekull var inkludert i råvaren. Den andre med data fra 2001 der trekull ikke var en del av råvaren.

Energi analysen avdekker store energitap som går som tapt varme. Bare 28.7 MW av 80.4 MW in den første analysen og 30.13 MW av 82 MW av energien ble levert til silisium-prosessen, kom tilbake som en kjemisk energi i produktet.

Produksjon av silisium innebærer store eksergi ødeleggelse, omtrent 39,2 MW i begge analyser.

PREFACE

Thesis is submitted to the Department of Chemistry, Faculty of Natural Sciences and Technology at NTNU.

Thesis work was carried out between January 2012 and Mai 2012 . The focus of the project was Holla silicon plant, where silicon is a major product.

This work is a part of project carried out by Marit Takla. Takla is presenting an exergy analysis of the theoretical silicon production process and silicon industrial process.

Acknowledgements

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Notation

C	Velocity
E,e	Energy, specific energy
G,g	Gibbs function, specific Gibbs function
ΔG_0	Gibbs function of reaction
g_e	Acceleration due to gravity
H,h	Enthalpy, specific enthalpy
P	Thermodynamic pressure
m	Mass
Q,q	Heat transfer, heat transfer per mass
$\dot{Q}_A$	Heat flux
S, s	Entropy, specific entropy
T	Thermodynamic absolute temperature
W,w	Work ,specific work $\dot{Q}_A$
$\dot{W}_x$	Shaft power
$\dot{W}_{el}$	Electrical power
x_i	Variable parameter

Greek symbols

E , ε	Exergy, specific exergy
E_{ph}, ε_{ph}	Physical exergy, specific physical exergy
E_0, ε_0	Chemical exergy, specific chemical exergy
E_k, ε_k	Kinetic exergy, specific kinetic exergy
E_p, ε_p	Potential exergy, specific potential exergy
$E^{\Delta P}, \varepsilon^{\Delta P}$	Pressure component of exergy and of specific exergy
$E^{\Delta T}, \varepsilon^{\Delta T}$	Thernal component of exergy and of specific exergy
E^Q, ε^Q	Thermal exergy, specific thermal exergy, in open system
μ	Chemical potential

Subscripts

CR	Control region
e	Exit from the control region
i	Property off the i-th component off the a mixture: i-th item
i	Inlet to the control region
IN	Entering the control region:input
j	j-th co-reactant
0	Environmental state
00	Dead state
OUT	Leaving the control region;output
P	Product, constant pressure
R	Reactant
ΔP	Pressure component
ΔT	Thermal component

1. Introduction

World energy resources are limited but demands are increasing with growing population and living standards [32].

The metallurgical industry is known for high energy and natural resources usage [9]. Large use of natural, non-renewable resources by industrial sector caused the alert among researchers and scientist. The pollution due to wide use of natural resources started to be seen as major difficulty for human future and existence. That is why it is so important to create quantity path to aim energy security and environmental worries [3,9,10,15,25,32].

Thermodynamics is in general showed as the science of energy. Today, thermodynamics includes all aspects of energy and energy transformations [10].

Two fundamental laws are establishing the thermodynamic scientific discipline [1,3,4,13,20,24]. The First Law describes the principle of conservations of energy. The Second Law describes the quality of energy and material, degradation of energy [1,13]. Thermodynamics plays very important role in devices and systems with energy transformation and transfer [1,13,18].

The use of energy as a tool for understanding and improving of energy systems however can be confusing [24].

In 1953 the term exergy is introduced by Rant. He described exergy as "*technical working capacity*" [18].

Exergy analysis of a process as it is functioned today is a first step towards a resource efficient process [25]. The exergy is an important factor of thermodynamics, which can be used to estimate and improve the efficiencies energy system [10,24]. Exergy can be used as tool, which supple more useful information than energy provides due to the losses in energy system [10,12,24].

Exergy is defined as the maximum theoretical work obtained from a given form of energy, using the environment as e reference state [1,3,4,13,18].The concept of exergy is focusing on the combination of the two laws of thermodynamic and balance of masses [13,17,18,20].

If all processes of the system and environment are reversible the exergy is conserved[20]. Irreversible process is destroying exergy [20].

Each type energy transfer has a corresponding exergy transfer [3,4,10,12].

Industrial processes is acting unwanted upon the natural environment. The unwanted effects can be divided into two groups: depletion of limited non-renewable resources and rejection of harmful substances [10,16].
In 1974 the International Federation of Institutes for Advances Study in the Energy Analysis Workshop on Methodology and Conventions presented the use of exergy analysis according to the depletion of natural resources. The most known person promoting the use of exergy was Jan Szargut [3,4,10,18].
The concept of sustainable development supposed to be the answer to the issues described above[10,16,18].

The important question is explanation why exergy can be used as a general environmental indicator and tool used to improve efficiencies energy systems [10]. Exergy balance joins both mass and energy flows. Secondly, makes able to analyse automatically the First and the Second Law of Thermodynamics. The advantage for exergy maintaining is possibility of comparative evaluation of different kinds of material [3,10]. This can be done not only in mass terms, but in the terms of available energy "saved". Available energy "saved" is described as energy, which is not needed for separation and purification from the average structure of the environment [3,4,10,16,18].

The project is executed at the silicon plant of Holla Wacker in Kyrksæterøra town in South Trøndelag. Figure 1 displays a picture of the Holla silicon plant.
The plant has been in operation since 1964 [7,21]. The company was sold from Fesil AS to German company Wacker Chemie AG in 2010 [7,21]. Silicon is one of Wacker`s most important raw material and is needed for the production of silicones and hyperpure polysilicon [7,21].

Figure.1. Holla plant [21].

Silicon is the second-most abundant element in the earth`s crust after oxygen [2]. Natural form of silicon is combined with oxygen as fairly pure silicon dioxide and silicate. Silicon was recognized as element in the early nineteenth century. On the end of nineteenth century silicon is produced on industrial scale as element or on alloys [2]

The production capacity of Holla plant is around 50,000 metric tons of silicon per year, which corresponds to about one third of Wacker`s current annual needs [7,21].

The production of silicon has not changed significantly during the twentieth century. The only progress is seen with larger and more sophisticated equipment [2,6].

The industrial process for the production of silicon involves reduction of silicon dioxide (SiO_2) with carbon in an electrical arc furnace [2,6,17,19].This is an intensive energy process. Requiring temperatures are above 1800 °C. These temperatures are achieved by adding large amounts of electric energy [2].

This thesis is focusing on the energy and exergy analysis from data collected at the plant. The analysis was performed on furnace #4. Holla furnace #4 produces about 3 tons of silicon per hour. The process is running 24 hours a day unless there are problems with operation or maintenance is required. This requires about 5500 kg reactive carbon (Fix-C) and 7500 kg quartz to be delivered to the furnace every hour [2,6,11].

1.1. Silicon marked

The Norwegian Governments´s involvement in the mineral industry remained high. Norway has a long coastline with many ports. This is giving opportunities for producing and exporting many industrial minerals. Opening of the mineral industry to foreign investors is ensuring a steady growth of industrial mineral output [8,9].

Silicon is used by the chemical industries into great number industrial products. The marked for silicon is growing as a response of demands from markeds [27]. It is consider that the need for silicon metal will proceed to increase at annual average growth rate of approximately 10 % in the next 2-3 years. Europe stays the major markedplace for the material. China has appeared as the fastest developing silicon industry and major destination for silicon production [8,9,27].

China provides around 67 % of total volume. From the Figure.2. we see that Russia takes the second place with 8,8% marked share. Norway is on the third place [8,27].

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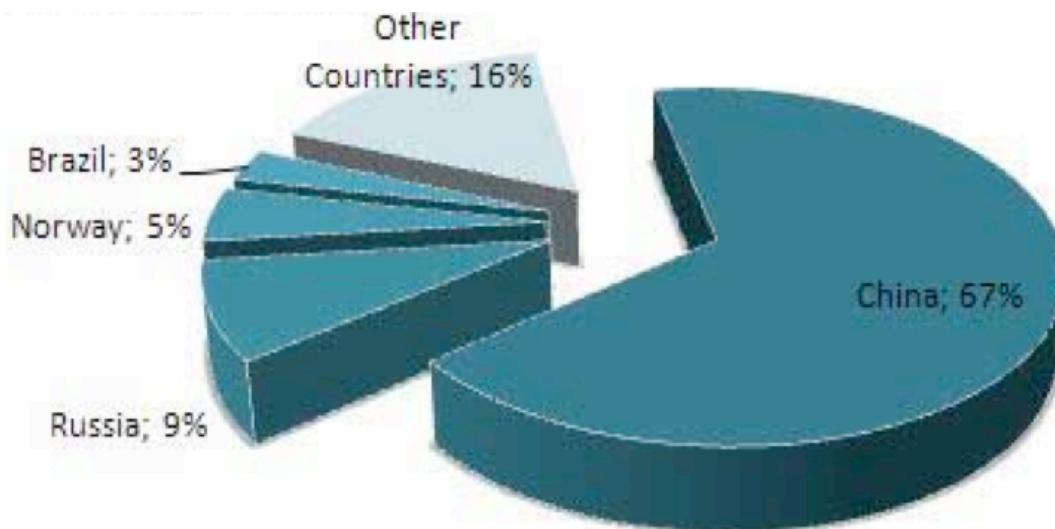
Figure 2. World silicon metal marked [8].

1.2. Silicon application

Silicon usage is explored all the time. The main applications for silicon are [2]:

- desoxidation and alloying of steel and cast iron (mainly ferrosilicon)
- alloying of other metals, especially aluminium (mainly silicon metal)
- raw material in the chemical industry (mainly silicon metal, some high silicon ferrosilicon)
- raw material for the semiconductor industry like electronic devices and photovoltaic cell

The ability of silicon to improve the strength of aluminium alloys has far reaching consequences for the transport industry [35]. Aluminum alloys, which are light, substitute heavier cast iron components [35]. Cylinder heads, car wheels and engine blocks are produced from aluminium alloys [35].

The basis of modern computing and electronic are silicon chips. The silicon used in production of semiconductor chips must be ultra pure [35].

Silicon is used to produce optical glass as well. Optical glass is used to produce liquid crystal displays and optical fibre [35].

Other application for silicon finds place in photovoltaic industries. Photovoltaic industries is a new method of generating electrical power by converting solar radiation into direct current electricity. Semiconductors are used during this operation. Photovoltaic power generation uses solar panels, which are made from silicon [35].

1.3. Project objectives and outline

The aim for this project is energy and exergy analysis for industrial silicon process.

There have been done two analyses. First data set has been amassing from week 36 in 2006 second one has been collected from week 52 in 2011. The factor differing both analyses is composition of raw materials. The first analysis do not contain charcoal as a component of raw materials, the second one does. Exclusion of charcoal from raw materials was motivated by the cost reduction.

The structure of the thesis is as follow:

Chapter 2 gives theoretical introduction to energy and exergy analysis as outlined by Kotas and Szargut.

Chapter 3 describes the silicon process at Holla plant. The first part of the chapter describes process operation and chemistry of the process. The second part presents raw materials used in silicon process. Appendix A and B is a part of this Chapter.

Chapter 4 presents results of an energy and exergy analysis studies of furnace #4.

Chapter 4 is a part based on measurements and data analysis that is explained in details in Appendix C.

Finally, Chapter 5 discuss the results of the energy and exergy analysis done for furnace #4 at Holla plant.

Unfortunately, there was no time for thermo-ecological cost analysis. However some conclusion are drawn.

2. Theory

Before starting analyzing the silicon process for furnace #4 at Holla plant, the terms energy and exergy will be explain. Presented principles are based on the theory of exergy as outlined in [1,3,10,13,14,18].

2.1 Energy analysis

The energy balance for a control volume when reaction is in steady- flow system is defined as:

$$0 = \dot{Q}_{CV} + \dot{W}_{CV} + \sum_i m_i h_i - \sum_e m_e h_e \qquad [2.1.1]$$

The kinetic and potential energy contribution is neglected. The right side of Eq.2.1.1. is as follow , $\dot{Q}_{CV}$ - heat and $\dot{W}_{CV}$ - work added to the control volume. Terms h describes enthalpy and m is material stream. Subscripts i and e refers to inlet and outlet streams.

2.2 Exergy analysis

Short description of exergy has been presented in Chapter 1 Introduction. Chapter 2.2 is introducing the exergy concept, which is used to estimate the useful part of energy.

Exergy is a measure of quality of energy. It is defined as the maximum work, which can be obtained from a given form of energy, using the environment as a reference state. A reference state is so called dead state. A dead state is in thermodynamics equilibrium with its surroundings [1,3,4,13].

Riekert proposed another very convenient version of exergy, which follows [18]:
Exergy expresses the amount of mechanical work necessary to produce a material in its specified state from components common in the natural environment, in a reversible way, heat being exchanged only with the environment.

In comparison to energy, which is a function of the state of the considered matter only, exergy is a function of the state of the considered matter and of the common components of the environment [3,24].

The exergy analysis method combines the First and the Second Law. The exergy balance is similar to energy balance. The fundamental difference is a statement of the law. The exergy balance may be looked upon as a statement of law of degradation of energy while energy balance is a statement of law of conservation of energy. Degradation of energy is equivalent to the irretrievable loss of exergy due to all real processes being irreversible [1,3,4,13].

The time rate of change of the exergy in a control volume is given by the following expression [1,13]:

$$\frac{dE_{CV}}{dt} = \sum_j \left(1 - \frac{T_0}{T_j}\right)\dot{Q}_j - \left(\dot{W}_{CV} - p_0\frac{dV_{CV}}{dt}\right) + \sum_i m_i e_i - \sum_e m_e e_e - \dot{E}_d \qquad [2.2.1]$$

where $\dfrac{dE_{CV}}{dt}$ is the time rate off change of exergy in a control region. Subscripts i and e refers to inlet and exit streams, respectively The term $\sum_j \left(1 - \dfrac{T_0}{T_J}\right)\dot{Q}_J$ can be interpreted as exergy accompanying transfer of thermal energy. Second term in the Eq.2.2.1 $(\dot{W}_{CV} - p_0\dfrac{dV_{CV}}{dt})$ can be described as exergy accompanying work.

The last term in Eq. 2.2.1 refers for destruction of exergy or equivalently the lost work within the system.

$$\dot{E}_d = \dot{w}_{lost} \qquad [2.2.2]$$

Eq. 2.2.1 for a steady state, non expanding system reduces to :

$$0 = \sum_j \left(1 - \frac{T_0}{T_J}\right)\dot{Q}_j - \dot{W}_{CV} + \sum_i m_i e_i - \sum_e m_e e_e - \dot{w}_{lost} \qquad [2.2.3]$$

The lost work, $\dot{w}_{lost}$ will be written

$$\dot{w}_{lost} = \sum_j \left(1 - \frac{T_0}{T_J}\right)\dot{Q}_J - \dot{W}_{CV} + \sum_i m_i e_i - \sum_e m_e e_e = \dot{E}_{in} - \dot{E}_{out} \qquad [2.2.4]$$

Term in Eq. 2.2.4 $\dot{E}_{in} - \dot{E}_{out}$ represents the total exergy entering and leaving the control volume [1].

Exergy of a stream of matter can be divided into components [1]:

$$\dot{E} = \dot{E}_k + \dot{E}_P + \dot{E}_{ph} + \dot{E}_0 \qquad [2.2.5]$$

where $\dot{E}_k$ is kinetic exergy, $\dot{E}_P$ is potential exergy , $\dot{E}_{ph}$ is physical exergy and $\dot{E}_0$ is chemical exergy.

Kinetic and Potential exergy

Below Eq.2.2.6 and 2.2.7 are defining the kinetic and potential exergy:

$$\dot{E}_k = \dot{m}\frac{C_0^2}{2} \qquad [2.2.6]$$

$$\dot{E}_P = \dot{m}\, g_E\, Z_0 \qquad [2.2.7]$$

where C_0, (m/s) is velocity, g_E (m^2/s) is gravitional acceleartion, considered as a constant, m is the mass flow rate off the fluid stream and Z_O altitude off the stream above the sea level [1].

Physical exergy

The physical exergy is equal to the maximum amount of work obtained when the stream of substance is brought from its initial state to the environmental state defined by P_0 and T_0 by physical processes involving only thermal interaction with the environment. Physical exergy can be divided into a part depending on pressure and temperature [1].

The temperature - dependent part of the physical exergy is always positive and equals zero at an environmental temperature.

The pressure- dependent part increases with pressure and is negative when the pressure is lower than the ambient one [1].

Clearly, physical exergy of a stream of substance can be expresses as a two - component function [1].

$$\varepsilon_{ph} = \varepsilon^{\Delta T} + \varepsilon^{\Delta P} \qquad [2.2.8]$$

where $\varepsilon^{\Delta T} = \left[-\int_{T_1}^{T_0} \frac{T - T_0}{T} \right]$ is thermal component of physical exergy

and $\varepsilon^{\Delta P} = T_0 \left(s_0 - s_i \right) - \left(h_0 - h_i \right)$ which is pressure component of physical exergy.

Here, h and s are enthalpy and entropy of the stream. Dead state presents h_0, s_0 and T_0 which is enthalpy, entropy and temperature.

Chemical exergy

Chemical exergy expresses the exergy content of the substance at environmental temperature and pressure [1,3,4].

The chemical exergy is equal to the maximum amount of work obtainable when the substance under consideration is brought from the environmental state to the dead state by the processes involving heat transfer and exchange of substance only with the environment [1,4].

To assess the chemical exergy of a material stream the properties of the elements comprising the stream must be referred to the properties of a set of selected substances in the environment as agreed upon in the community, the reference substances [1,3,13]. Standard chemical exergy values based on a standard exergy environment is tabulated and can be found in text books, e.g. Szargut.

In case when the chemical exergy of a substance is unknown, the value of chemical exergies can be determined from Eq.2.2.9

$$\varepsilon_0 = -\Delta G_0 + \sum_P n\varepsilon - \sum_R n\varepsilon \qquad [2.2.9]$$

where ΔG_0 is the change in the Gibbs energy for the reaction forming a substance from the reference substances at temperature T_0 and pressure p_0, n is the moles off reactants and products per mole off the substances whose exergy is being evaluated [1,4].

In many important applications the working medium consist of a mixture of gasses. The chemical exergy is determined then from:

$$\varepsilon_{0,mix} = \sum x_i \varepsilon_{0i} + RT_0 \sum_i x_i \ln x_i \qquad [2.2.10]$$

where x_i is the mole fraction of component i in the solution and R is the universal gas constant [1].

Table 1 presents short summary of energy and exergy concepts.

Table 1. Energy and exergy comparison [20].

ENERGY	EXERGY
• is depended on the parameters of matter or energy flow only, and independent of the environment parameters • has the values different from zero • is motion or ability to produce motion • is always conserved in a process, so can neither be destroyed or produced • is a measure of quantity only	• is depended both on the parameters of matter or energy flow and on the environment parameters • is equal to zero • is work or ability to produce work • is always conserved in a reversible process, but is always consumed in a irreversible process • is a measure of quanity and quality due to entropy

3. Case studies

The industrial process is a 35 MW furnace operated at Holla silicon plant. We collected data from measurements to established energy and exergy balance for furnace #4.

Results presented by Takla for an exergy analysis [25] of the theoretical silicon process production [25] can be used as a reference case for the silicon production process. The exergy analysis for the case of the silicon production process with pure components is the first such analysis done.

This part of the project is supporting on project outlined by Marit Takla [25,29]. The theoretical silicon production [25] gives a basis for exergy analysis of a real process done at Holla plant.

3.1. The theoretical silicon production process

The exergy analysis for the pure components is performed on the basis of 1MT silicon. Silicon is produced in the pure Si-O-C system as described in book *Production of High Silicon Alloys* [2].

The process is divided into three subsystems, which are areas during the silicon process [25]:

- gas treatment section, where the combustion of gas from the furnace by adding air take place
- submerged arc furnace section, where reduction of quartz take place and the upper part of the furnace where heat exchange between the electrode, cold raw material and the furnace gas take place
- product treatment section, where solidification and cooling of the metal take place

Figure 3 presents the schematic diagram of the silicon process.
This schematic diagram shows the material and energy flows in the system.
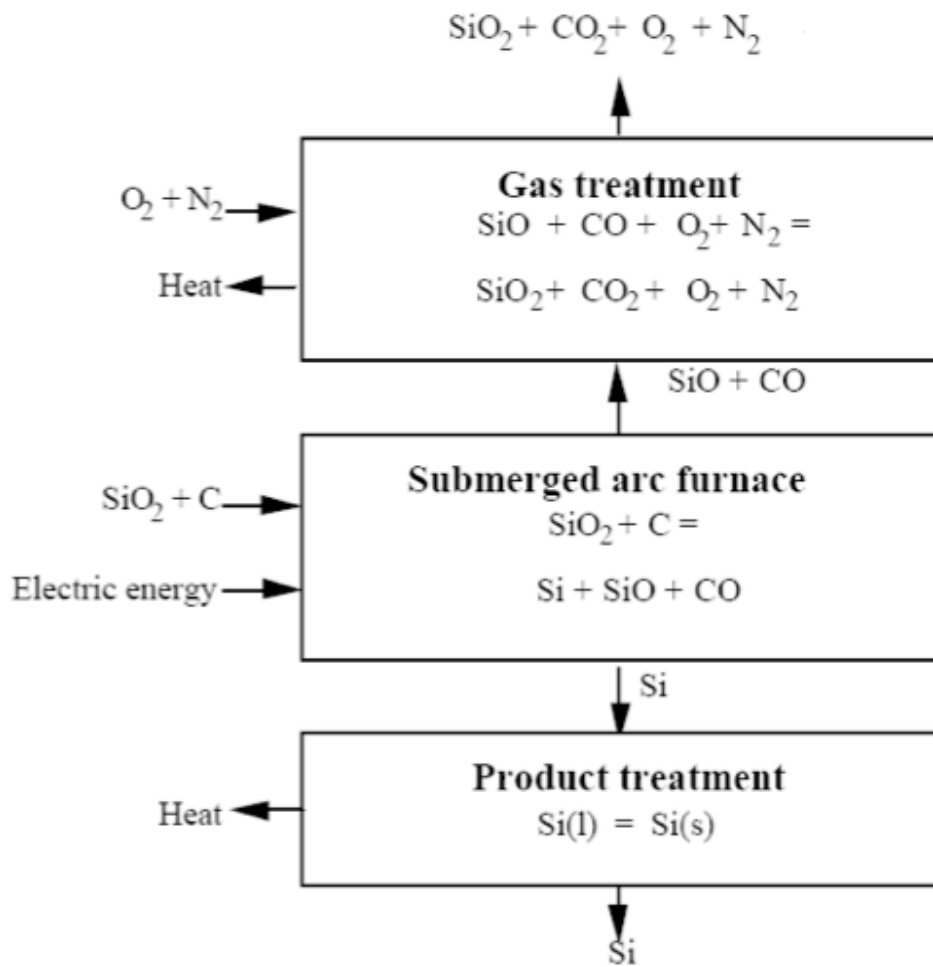
Figure.3. A schematic diagram of the production of silicon [31].

THE SUBMERGED ARC FURNACE

We assume that pure SiO_2 and carbon are at the environmental state of temperature $T_0 = 25$ $^\circ$ C and pressure $p_0 = 1$ atm. Pure silicon dioxide and carbon are added to the furnace together with electrical energy [25,29]. The furnace reaction is endothermic. The reaction can be described by following equation:

$$(1+x) \, SiO_2 + (2+x) \, C \rightarrow Si + xSiO + (2+x) \, CO \qquad [2.2.11]$$
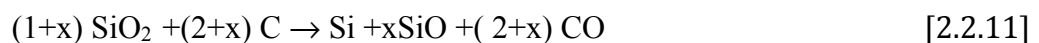
The silicon yield R is calculated as a function of the reaction parameter x and is in interval of $0 \leq R \leq 1$.

$$R = \frac{1}{1+x} \qquad \text{[2.2.12]}$$

The entropy and enthalpy of reaction describes by Eq. 2.2.12 is positive. The amount of electrical energy delivered to the furnace is referred to as the furnace load. It is important to emphasize that there are no losses in the electric supply system or thermal losses from the furnace to the surroundings [25].

The gas is leaving the top of furnace .The leaving gas consist of SiO and CO has measured temperature of 1400 ° C. We assume that the gas is ideal. At a temperature around 1600° C liquid silicon leaves the bottom of the furnace [25,29].

GAS TREATMENT SECTION

The reaction in the gas treatment section is described by reaction:

$$xSiO + (2+x)CO + mO_2 + 4mN_2 \rightarrow xSiO_2 + (2+x)CO_2 + (m-x-1)O_2 + 4mN_2 \qquad \text{[2.2.13]}$$
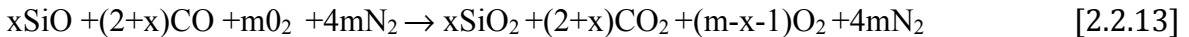
The gas leaving the top of the furnace enters the gas treatment section. In the gas treatment section gas is mixed with excess of air and burned [25].

In Eq. 2.2.13 subscript m is the amount of oxygen introduced with air. Excess of oxygen and nitrogen in the air are heated to the temperature of the gas leaving the gas treatment section at a temperature of T= 150° C and $p = p_0$.

PRODUCT TREATMENT SECTION

In this section, liquid silicon is solidified and cooled down from 1600° C to 25° C. Silicon leaves the process at $p=p_0$ and $T_0 = 25$ ° C [25].

3.2. The silicon process operation at the Holla plant.

To be able to present results achieved from the silicon process from furnace #4 at Holla plant is necessary to know the process and chemistry of the process. The following Chapter and Appendix A gives a description of silicon industrial process.

A silicon plant can be divided into four main groups [6];

- The handling of raw materials
- The furnace including the electrical supply system
- The system for the cleaning of waste gas including energy recovery
- The metal product processing system

The handling of raw materials includes transport, storage, weighing and mixing. Chapter 3.2.2 presents description of raw materials.

All raw materials, except woodchips, are imported to Holla plant in ships. The storage of raw materials is out door in special rooms. It is important to avoid moisture.
The raw materials are transported to "day bins" where the process of weighing and mixing starts [6,11].
Figure 4 presents the typical commercial silicon production in furnace. The Figure 4 includes raw material, power supply system, off-gas and tapping, casting and crushing.
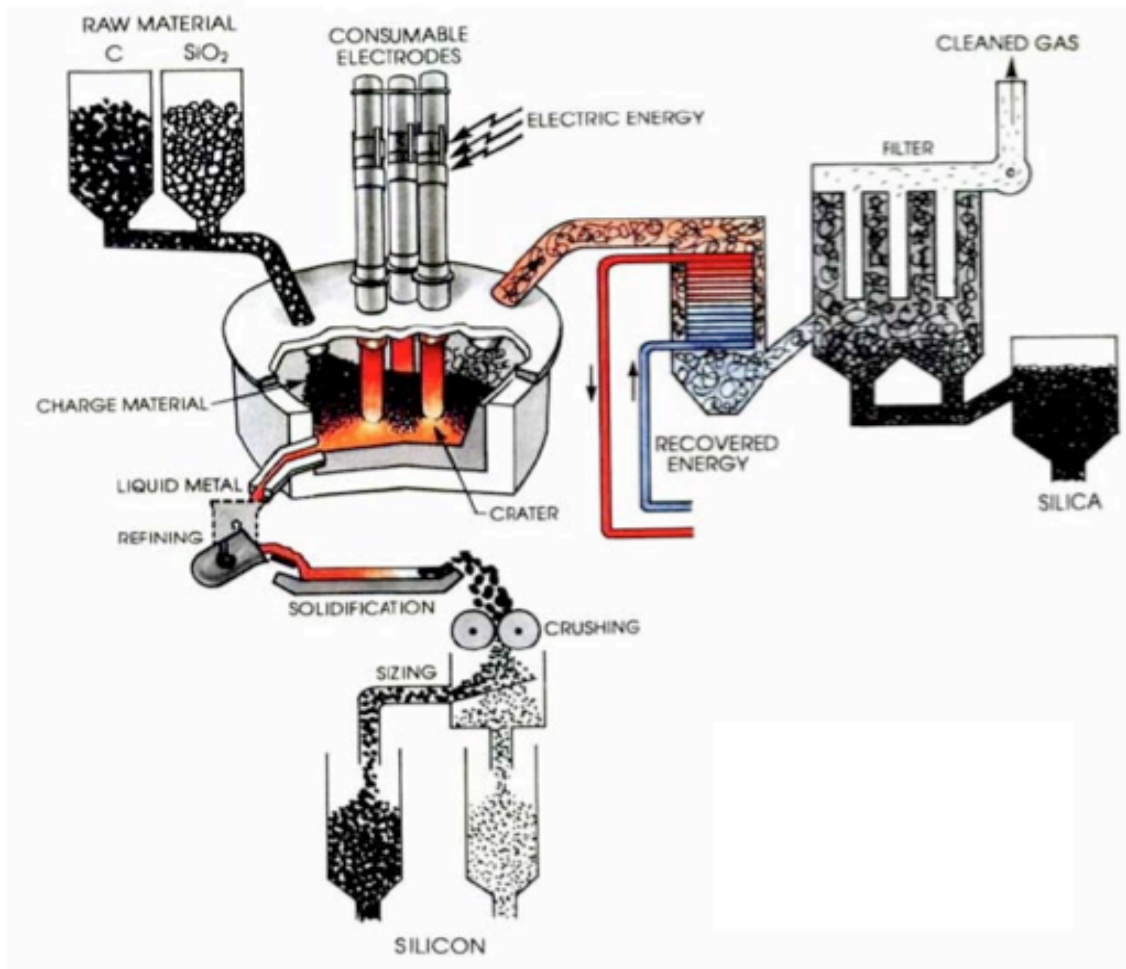
Figure.4.The commercial silicon production [2].

The raw materials (called charge materials as well) are delivered to a furnace at the top. The furnace, which is a heart of the plant includes [2,6,11]:

- electricity supply consisting of electric grid, transformers, bus bars and the electrodes
- equipment for adding raw materials
- a furnace shaft consisting of shell and a lining that can resist extremely high temperatures and attack by chemicals
- equipment for tapping the alloy from the lower part of the furnace body

Hood and the body are forming a typical furnace, which is about 10 m in diameter.   The size of the furnace is characterized by electrical power needed, which can be in the range from less than 10 MW to 45 MW [25].

The hood is water -cooled and is the upper part of the furnace [6].

The liquid silicon is tapped through holes in the side close to the bottom of the furnace. The silicon is normally refined during the tapping by purging oxygen and air through the metal and adding fluxes to adjust the refining slag. The main goal is to reduce the calcium and aluminium content to desired levels [6].

The liquid silicon is poured into suitable moulds, allowed to cool down. After solidification process silicon is crushed to the desired particle size (see Figure A.4. and A.5.)

The off-gas from the furnace reaction (SiO +CO) is mixed with excess air under the furnace hood and burned. Next, is captured into the gas –cleaning system and filtered [8,11,25].

The excess of air is controlling the off-gas temperature. The dust in the filter consist mainly of SiO_2 particle.

3.2.1.Chemistry of the process

Silicon production is based on the submerged arc furnace (SAF). In this section carbonaceous reduction materials are mixed with quartz to form silicon [2]. The main input to the process is one or more quartz types and carbon materials [21]. Figure .A.1 presents the mixed raw materials, which are delivered to the furnace where the rock-hard quartz starts to melt.

Silicon production is basically to use carbon and energy to remove oxygen from quartz. The most important ability for carbon materials is to react fast with SiO gas. It is so-called SiO-reactivity [6].

Since the chemical industry have different requirements so the production processes is optimized in different ways [6].

Segregation of raw materials is a major challenge. It includes how raw materials were storage and transported and charged to the furnace [6].

The raw material strength may be divided into mechanical and thermal strength. The mechanical strength is important to prevent from too high size reduction of the raw materials and generations of fines that are brought in to the furnace [6]. The thermal strength is significant for preventing the raw materials from disintegrate and produce fines as a result of high temperatures inside the furnace during process[2,5,6,11].

The size of particles is important. Small particles need less time to be fully converted to SiC. The flow of SiO-gas can be affected negatively by too big amount of fines. Any fines will fill the gas volume between large particles in the charge and obstruct the gas-permeability in the furnace [2]. Further, SiO gas will be blocked from reacting with C to produce SiC [6]. This stage of creating SiC is an important partial reaction. This will cause losses of SiO gas from the furnace and reduced productivity [6].

To achieve best reaction between carbon- materials with SiO gas in furnace carbon materials are mixed [6].

Eq. 3.2.1.1 presents reaction taking place inside furnace.

$$SiO_2 + 2C + energy \rightarrow Si + 2CO_{(g)}$$
[3.2.1.1]

However, in practice the process in not so simple. Quartz (SiO_2) has a high stability. This is caused of existence of very strong bonds between silicon and oxygen in quartz.

Transition states in silicon production, like Eq. 3.2.1.2 and 3.2.1.3 requires large quantities of energy and high process temperatures, since quartz, SiO_2 is very stable.

$$SiO_{2(s)} \rightarrow SiO_{2(l)} \qquad\qquad [3.2.1.2]$$

$$SiO_2 + C \rightarrow SiO_{(g)} + CO_{(g)} \qquad\qquad [3.2.1.3]$$

Eq. 3.2.1.1 and 3.2.1.3 define the silicon recovery by their relation. The silicon recovery is the molar fraction of Si from raw materials retained in the silicon. Silicon recovery is very important for the energy consumption.

The Figure 5 shows the circulation of silicon through the intermediate products SiC and $SiO_{(g)}$.

C
(coal/coke)

SiO₂
(quartz)

SiO₂
(microsilica)

CO₂

Surface

$2SiO+O_2=2SiO_2$
$2CO+O_2=2CO_2$

O₂
(air)

$SiO_{(g)}+2C$
$=SiC+CO_{(g)}$

Charge

$SiO_{(g)}$
$CO_{(g)}$

SiC

$2SiO_{(g)}=$
SiO_2+Si

Inner reduction zone

$SiO_2 + C + SiC =$
$Si + SiO_{(g)} + CO_{(g)}$

SiO₍g₎

SiO_2+Si
$=SiO_{(g)}$
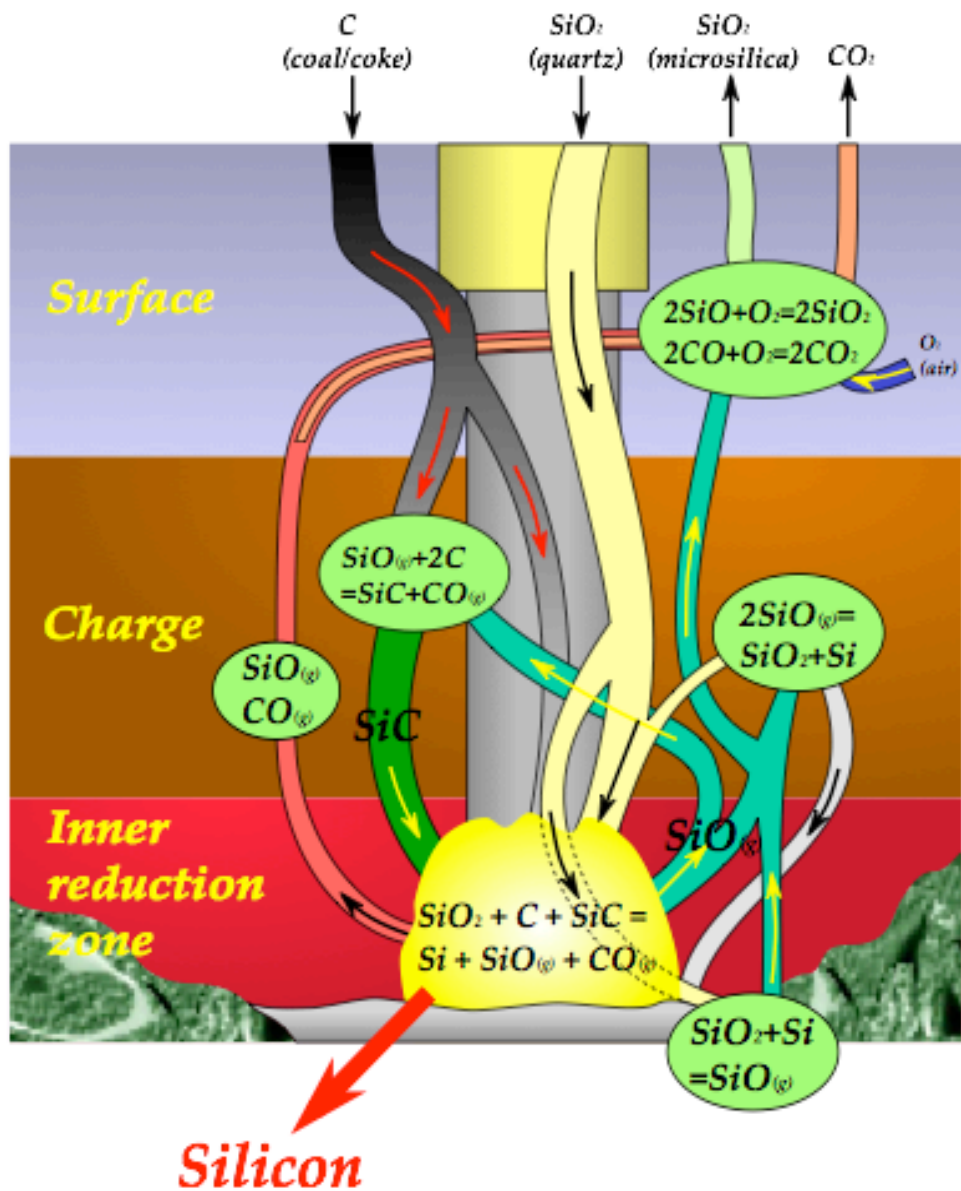
Silicon

Figure 5.Chemistry of the silicon process inside the furnace. The addition of raw materials and the formation of silicon and microsilica is illustrated [30,32].

Since in real process it is several reactions, which take place in the different regions of the furnace, the furnace can be divided into regions. It is common to split the furnace in an upper and outer zone with mostly moderate temperatures and a high temperature inner/ lower zone surrounding the gas filled cavity around the electrode tips.

The silicon production is much more complicated than Eq.3.2.1.1 describes.

Eq. 3.2.1.4 and 3.2.1.5 presents two main reactions.

$$SiO_{(g)} + 2C \rightarrow SiC + CO_{(g)} \qquad\qquad [3.2.1.4]$$

$$SiO_2 + SiC \rightarrow Si + SiO_{(g)} + CO_{(g)} \qquad\qquad [3.2.1.5]$$

SiC is formed in the upper / outer zone (charge region) of the furnace (see Eq. 3.2.1.4). How Eq. 3.2.1.5 shows SiC from Eq. 3.2.1.4 is used for the formation of Si and $SiO_{(g)}$ in the inner high temperature region. The silica SiO_2 dust will be formed above the charge region by burning $SiO_{(g)}$ with atmospheric oxygen.

Chemical reactions in the upper/outer zone

The carbon reacts with $SiO_{(g)}$ from the hot zone to $SiC_{(s)}$ and $CO_{(g)}$ according to Eq. 3.2.1.4 .

This slightly endothermic reaction describes the first of two important ways of catching / recovering $SiO_{(g)}$ in the upper part of the furnace [6]. The size of a carbon particle remains fairly constant as reaction progresses in and around pores in the material [6]. This is resulting in a carbon rich core surrounded by an SiC rich layer[6]. The layer is growing slower as the diffusion length increases with time. This results that even small enough carbon particles will be fully converted to SiC before entering the hot zone.

So-called condensation which takes place in the upper/outer zone is presented by Eq. 3.2.1.6

$$2SiO_{(g)} \rightarrow Si + SiO_2 + \text{a lot of heat} \qquad\qquad [3.2.1.6]$$

This reaction takes place on sufficiently cold surfaces in the charge [6]. This results in the sticky, glassy condensate consisting of an intimate mixture of $Si_{(s,l)}$ and $SiO_{2(s,l)}$.

The silicon in the condensate probably gathers to silicone droplets and may leak out of the condensate as the temperature increases close to the cavity walls [6]. This means that the condensate when it comes down to the hot zone may have almost the same properties as molten quartz [6].

The Eq. 3.2.1.6 above helps to recover $SiO_{(g)}$ from the hot zone and contributes to the overall silicon production as well [6].

However it can form a glassy "lid" in certain depths of the charge. This will keep a good gas from distribution and the down wards flow of solid and liquid materials [6]. The silicon yield, which is the fraction of Si in the raw materials that ends up in silicon will suffer. Sometimes temperatures are so high that condensation reaction stops. This is causing fall of silicon yield. That is why it is important that $SiO_{(g)}$ reacts as much as possible with carbon according to Eq. 3.2.1.4.

Chemical reactions in the lower/ inner zone

In the lower / inner high temperature zone are important the following reactions [6]:

$$Si_{(l)} + SiO_2 \rightarrow 2SiO_{(g)} \qquad\qquad [3.2.1.7]$$

$$SiC_{(s)} + 2SiO_{2(l)} \rightarrow 3SiO_{(g)} + CO_{(g)} \qquad\qquad [3.2.1.8]$$

Eq. 3.2.1.7 shows that $SiO_{(g)}$ is produced .
Eq.3. 2.1.7 is the reverse of Eq. 3.2.1.6. Silicon is produced by

$$SiC_{(s)} + SiO_{(g)} \rightarrow 2Si_{(l)} + CO_{(g)} \qquad\qquad [3.2.1.9]$$

There are other reactions which may also take place in the hot zone. Any unreacted carbon will first react to SiC according to Eq. 3.2.1.4. or by

$$Si_{(g,l)} + C_{(s)} \rightarrow SiC_{(s)} \qquad [3.2.1.10]$$

By having a high temperature in the hot zone and by reducing the amount of carbon entering the hot zone it is possible to increase silicon yield [6] .

The temperature factor in the hot zone is an important factor since the equilibrium $SiO_{(g)}$ to $CO_{(g)}$ ratio decreases with temperature. The high temperature in the hot zone reduces the amount of $SiO_{(g)}$ to the upper zone.

It is important to remove as much oxygen as possible from quartz and SiO outside the hot zone. Then the less carbon enters the hot zone without changing the carbon balance [6].

There are two possibilities to minimize the amount of carbon to the hot zone [6].

First is to avoid too much carbon in the raw material mix. The other possibility is to have as much carbon as possible to react with $SiO_{(g)}$ according to Eq. 3.2.1.4 . If we achieve process where all carbon in the raw materials reacts according to Eq.3.2.1.4 in the low temperature zone, the half of it will leave the furnace as $CO_{(g)}$. This means that this part will not enter the hot zone [6]. The important issue is un reacted carbon entering the hot zone. It is seen as the "poison" for the process [6]. Here we see why the SiO-reactivity and sizing of the carbon materials are very important. It is important for a good gas distribution to make sure that all carbon meets enough $SiO_{(g.)}$ [6].

In a well operated furnace it is rational to consider that about 10 % of the carbon enters the hot zone un reacted [6] .

$SiO_{(g)}$ from the hot zone must be recovered before it leaves the furnace. If the process does not take place the $SiO_{(g)}$ from the hot zone burn in air to silica fume in the furnace hoots or off-gas system according to Eq.3.2.1.11.

$$SiO_{(g)} + 1/2\ O_{2(g)} \rightarrow SiO_{2(s,l)} \qquad [3.2.1.11]$$

From the metallurgical point of view the reaction with carbon is the preferred reaction to recover $SiO_{(g)}$. It is slightly endothermic and reduces SiO production in the hot zone [6]. The condensation reaction described earlier provided unwanted sticky charge and strong heating of the charge [6].

To make the furnace less sensitive to a good gas distribution the materials are mixing with high and low reactivity. How experience showed some carbon materials can react high up in the furnace while others recover SiO further down [6].

3.2.2. The raw materials

Properties of raw materials are an important part of the process [2,6,17]. Following chapter presents description of raw materials used in silicon process.

The main input to the process is one or more quartz types. Coal, coke woodchips and charcoal are carbon materials [2,6]. Raw materials has a crucial influence on the chemistry silicon process how presented in Chapter 2.1.

All raw materials are quality controlled. Samples are taken from the raw materials from shipping to the furnace locations. Metal samples are taken during tapping, refining, solidification, crushing and packing process. Sample control allows for adjusting the raw materials mix, furnace operation and refining [6,11].

Quartz

The starting material for silicon production, quartz gravel is shipped to Holla from mines in Egypt, Spain and Norway [11]. The quartz /quartzite is chosen based on the following characteristics [5,22]:

- high purity and low level of contamination as Fe_2O_3, Al_2O_3, TiO_2, P_2O_5 and other trace elements
- high mechanical strength against impact and size degradation
- high thermo-mechanical strength
- high point of softening and melting
- low cost of extraction, handling, sizing and transport

Three main quartz types have been defined [22]:
- River gravel, usually is a pebbles mix of quartz and quartzite (Q1)
- Massive rock of quartzite (Q2) or quartz (Q3)

Carbon- volatile compounds

Coke, coal, charcoal and woodchips are the usual carbon sources used in silicon process.

The amount of fixed carbon (Fix- C) in the reduction agents is important for silicon process [2,6]. Coke and coal are introducing other elements than carbon as well. Extra chemical energy is added by the volatile hydrocarbons to the input to the process [2]. Coke has low content of volatile hydrocarbons. Coke may contain up to 35-40 % of volatile hydrocarbons. The volatile hydrocarbons will increase the amount of energy in the off-gas system [2]. The volatile hydrocarbons will burn together with the CO-gas from the process [2].

In the silicon process the non-pure carbon is used. This is changing the process in several ways [2]:

- accompanying volatile hydrocarbons add extra chemical energy
- carbon materials contain ash with oxides such as aluminium oxide and calcium oxide which requires energy to be reduced
- water content has to be driven off

- the accompanying extra mass may be beneficial to SiO- condensation

Table 2 shows broad variations on the Fix-C (fixed carbon) and volatile content in carbon sources used in silicon process[2].

Coke and coal has much higher energy content in volatiles then woodchips. This is according to the higher content oxygen in the woodchips [2].

Table.2. Example of carbon materials on a wet basis [2].

Type	Fixed Carbon (%)	Volatile (%)	Moisture (%)	Ash (%)	Energy content volatile* (kWh/kg)	Sulphur (%)
Coke	75	4	16	4	10.6	0.33
Coal	51	35	12	2	10.6	0.15
Charcoal	46	8	39	6	10.6	0.023
Woodchips	12	35	52	1	4.3	0.02

* estimated values SINTEF.

 Woodchips

The woodchips are added to the feed mix in a proportion typically 0,45 to 0,60 of the weight of the quartz. Woodchips have an important role in the silicone metal production.

The benefits of using woodchips in the silicon process are[6,11,21]:

- increasing burden permeability
- increasing charge resistivity
- offering great reactive carbon surfaces for the reduction of SiO to SiC
- keeping the top of the charge cool because of the heat consumed for water evaporation

Charcoal

Charcoal is an interesting reducing agent, which does not contribute to global warming. Charcoal is produced from growing wood and is renewable.

There are major differences between charcoal and the most common metallurgical type of cokes used today[6]. Usually charcoal has a lower fixed carbon content and much higher content of volatile matters, while ash is rather low with composition strongly dependent on soil and use of fertilisers. Charcoal volume weight is low. Compared to coke industrial charcoal has higher CO_2- reactivity, lower thermal abrasive strength and higher electrical resistivity, which is decreasing with increasing temperature [6,11,22].

Carbon electrode

Electrode is a fundamental elements in the operation if arc furnace. Appendix Figure A.2. presents picture of the electrodes used in silicon process.

How mentioned before the silicon process requires a lot of electric energy. Three consumable carbon electrodes at relatively low voltage and high currents are delivering energy to the process.

The furnace #4 at the Holla plant uses Elsa electrode. The Elsa electrode is suitable for the silicon production. How Figure 5 presents below, electrode has a graphite core. An outer region of paste and its low cost in contrast with the prebaked electrode,makes it very attractive for the silicon production [34].

Elsa electrode has an ability to minimize the silicon losses during the process. Mainly, early detection gives possibilities to prevent damages to other parts of the furnace [34].

Appendix B presents structure and performance of Elsa electrode, hence operation details.

The illustration below shows the basic structure of Elsa electrode used at the Holla plant in silicon process.
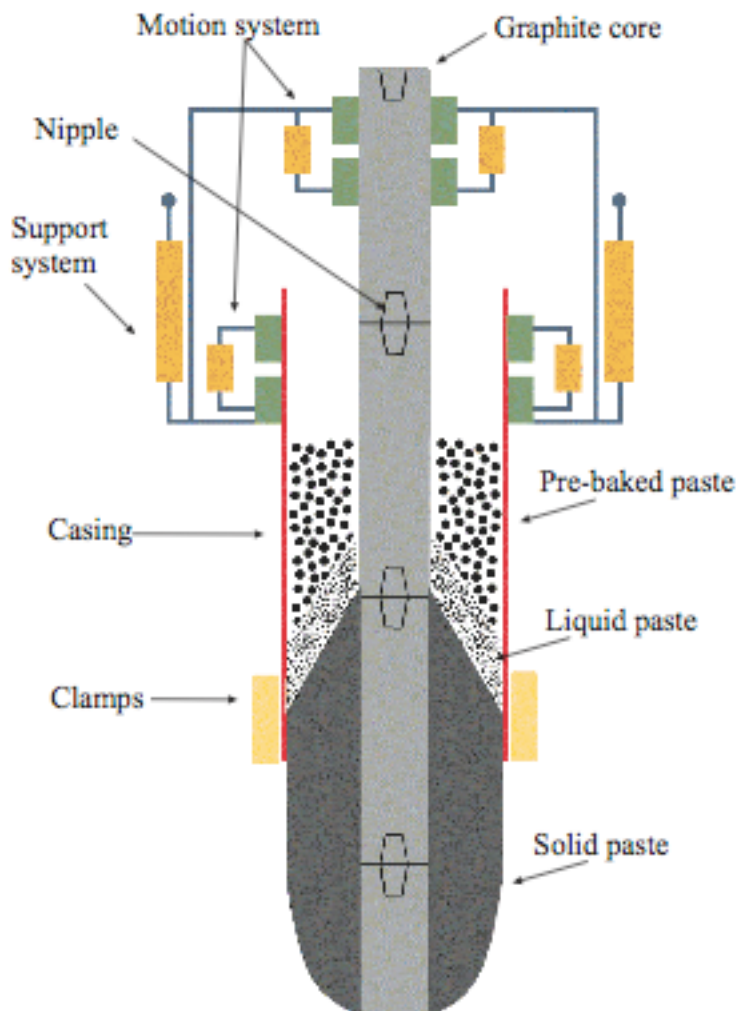
Figure.6. Elsa electrode produced by the Spanish ferroalloy company Ferroatlàntica. Nowadays, more than 25 % of the silicon produced in the world is achieved using the Elsa electrode [28].

3.2.3. Environmental aspects

Carbon is an important material for producing silicon. Carbon is needed for breaking the silicon- oxygen bond in quartz. It is very important to reduce CO_2 emission. One of the ways to reduce CO_2 emission in silicon process is to use more bio carbon materials.

Charcoal and woodchips are such materials. Other method is to run the process at higher silicone yield and better energy efficiency.

However attempts to reduce bio carbon cost by more effective pyrolysis prosses or ways to get inexpensive wood are still unsuccessful [6].

3.3. Deviation from theoretical process

The theoretical silicon process differs significantly from the real one. The main differences between theoretical and industrial process are [2]:

- energy losses from the process
- the use of non-pure carbon
- carbon losses to the off-gas system

Theoretical silicon process has not thermal losses from the furnace or losses in the electric supply system, which take place in the industrial silicon process. The carbon losses due to the off-gas system are observed in industrial process, which is caused of use non-pure raw materials.

The real process uses raw non-pure materials like coal, charcoal, woodchips and the coke. These materials include volatiles, ash, moisture and other trades elements.

Another difference not observed in theoretical process is radiation and convection from arc furnace. Presence of thermal energy cooling water is another important deviation from theoretical process.

The real process needs different types operations and limitations, which increasing heat recovery and make more valuable products.

It is very important to achieve continuous operation in industrial process. Continuous operation is the important part of heat recovery. Since stable operation gives higher average gas temperatures.

4.Energy and exergy analysis for silicon process

In this chapter will be described the real silicon process which took place at Holla plant. The focus was on furnace # 4. Data from Holla plant are used to the energy and exergy analysis.

There has been done to analyses for silicon process. The input data from 2006 and 2011 has been used.

Input data from 2006 include charcoal in carbon material fed to the furnace. Input data from 2011 exclude charcoal.

4.1. Calculation details

Data presented in thesis were collected from furnace #4 at Holla plant.

The following assumptions precede calculations were made:

- kinetic and potential energy of materials going into the furnace and coming out is neglected
- kinetic and potential exergy of materials going into the furnace and coming out of the furnace are neglected
- the total mass of metal set to 1tonn
- the silicon recovery as molar fraction of input in the metal is set to 0,9
- the factor for oxygen from air relative to stoichiometric combustion is set to 5
- full capacity of the furnace is 35 MW, however the recommended value of 33MW has been used as the average set point
- the environmental temperature and pressure are taken to be $T_0 = 25°C$ and $p_0 = 1$ atm
- the temperatures associated with the mass flow are considered as follow:
    1. inputs ,25 ºC
    2. output , metal, 1600º C
    3. the process gas leaving the furnace is considered as 1300º C, this results in a gas and silica dust temperature of approximately 800º C at standard parameters

- the relative distribution of fixed carbon contribution from the carbonaceous materials are set :

  in first analysis with charcoal as component of raw materials: to 25 % by coal, 25 % each coke and charcoal, 10% woodchips

  in second analysis without charcoal as component of raw materials: to 89% by coal, 7% by coke and 4% by woodchips

- furnace operation is assumed to be at steady state
- consumption of Elsa electrode during the silicon process has not been include in calculation
- air is considered to be composed of 24 % O_2 and 76% N_2
- chemical reactions are considered to complete fully
- quartz considered to be pure
- many of the trace elements and compounds , NO_x and CH_4 were assumed to have negligible contributions to the heat balance
- the Exergy Calculator has been used to calculate the chemical exergy for compounds [16].
- the chemical exergy of Si has been calculated from Eq.2.2.9
- value for the enthalpy, entropy and Gibbs energy necessary to calculate the physical exergies were determined from HSC Chemistry ® [36].

4.2 Energy analysis

The energy process is based on the chemical model presented in Chapter 3 and data collected from Holla plant.
The analysis is based on measurements and calculations explained and presented in Appendix C.

4.2.1. Energy input

The carbon materials fed to furnace #4 are charcoal, coal, coke and woodchips. The chemical analysis of the material was used to estimate the amount of carbon, volatiles and moisture supplied to the furnace (see Appendix C) [11].

The mean silicon yield was R= 90 %

The relative distribution of fixed carbon contribution from the carbonaceous materials are set to 25 % by coal, 25 % each coke and charcoal, 10% woodchips.

Tabel.3. Estimated energy delivered to furnace. Raw materials include charcoal.

ENERGY TYPE	ENERGY INTO THE PROCESS [MW]	Part [%]
Electric Energy	32.2	40
Chemical Energy Fix Carbon	29.5	36
Chemical Energy Volatiles	18.7	24
Total	80.4	100

Table 3 presents data collected in 2006. Raw materials do not include charcoal.

Table 4 presents data collected in 2011. Raw materials do not include charcoal.
The relative distribution of fixed carbon contribution from the carbonaceous materials are set to 89 % by coal, 7 % by coke and 4% by woodchips.

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Tabel.4. Estimated energy delivered to furnace. Raw materials do not include charcoal.

ENERGY TYPE	ENERGY INTO THE PROCESS [MW]	Part [%]
Electric Energy	33.3	41
Chemical Energy Fix Carbon	28.2	34
Chemical Energy Volatiles	20.5	25
Total	82	100

4.2.2. Energy output

The result from the estimated energy output is presented below.

Table.5.Estimated energy from furnace. Raw materials include charcoal.

ENERGY TYPE	ENERGY FROM THE PROCESS[MW]	PART[%]
Chemical Energy in Product	28.7	36
Heat in Product	1.95	3,5
Energy in Off-Gas	36.7	44.5
Cooling System *	13.05	16
Total	80,4	100

* Estimated energy from the cooling system was calculated by supporting on report from Spets [11].

From the total 80.4 MW of energy supplied to the furnace only 28.7 MW is returned as chemical energy in the product.

Measurements were performed at the same loads in a period of one week.

Table 6 presents estimated energy output from furnace #4. The raw materials do not include charcoal.

Table.6. Estimated energy from furnace. Raw materials do not include charcoal.

ENERGY TYPE	ENERGY FROM THE PROCESS[MW]	PART[%]
Chemical Energy Product	30.13	37
Heat in Product	1.65	2
Energy in Off-Gas	42	51
Cooling System	8.22	10
Total	82	100

Estimated energy from cooling system was calculated by using output data from Holla plant.

It can be seen that furnace gas contains most of the heat.
From the total 82 MW of energy supplied to the furnace only 30.13 MW is returned as chemical energy in the product.

An energy balance for submerged arc furnace operated at a silicon Holla plant presented below shows the distribution of energy among the inputs and outputs of the process.
After consultation [11,12] it was recommended to present collected dataset for both balances on the same diagrams.

Since data presented in Chapter 4.2.1 and 4.2.2 do not show significant differences Figure 7 presents energy diagram for both dataset collected from Holla silicon plant.
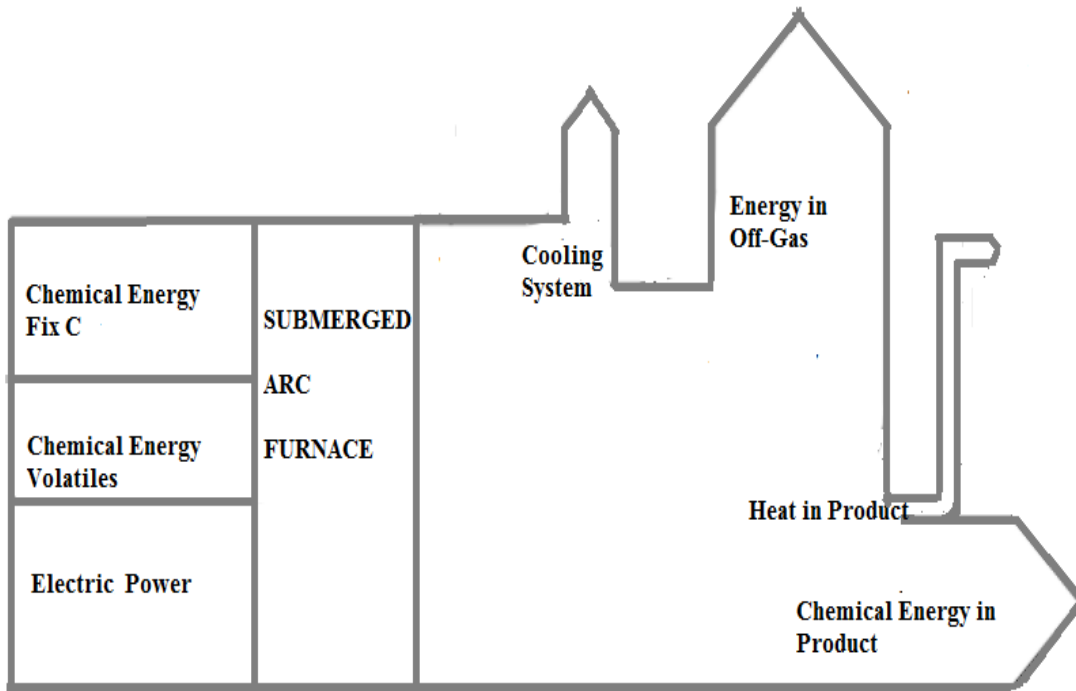
Figure.7. Energy balance for submerged arc furnace operated at a Holla silicon plant .Energy balance is established using data presented in Table 3,4,5,6,.

4.3. Exergy analysis

 According to [1,16] the standard chemical exergy of the raw materials was used. All streams entering and outgoing were calculated separately.

The air is considered to have zero exergy as it is part of the environment.

4.3.1 Exergy input

Table 7. Estimated exergy delivered to furnace 4 at Holla. Raw materials include charcoal.

Exergy Type	E_{ph} [MW]	E_0 [MW]	$E_{ph} + E_0$ [MW]	Part[%]
Electric Energy	32.2	0	32.2	40
Raw Material	0	48.2	48.2	60
Air	0	0	0	0

Table.7. presents results for raw materials which do not include charcoal. Results obtained without charcoal are introduced in Table 8.

Table.8.Estimated exergy delivered to furnace 4 at Holla. Raw materials do not include charcoal

Exergy Type	E_{ph} [MW]	E_0 [MW]	$E_{ph} + E_0$ [MW]	Part[%]
Electric Energy	33.3	0	33.3	40
Raw Material	0	48.7	48.7	60
Air	0	0	0	0

4.3.2. Exergy output

Tabel .9. Estimated exergy from the furnace 4 at Holla. Raw material include charcoal

Exergy Type	E_{ph}[MW]	E_0 [MW]	E_{ph} + E_0 [MW]	Part[%]
Exergy in Product	1.9	23,7	26.9	65
Exergy in Off-Gas	12,7	0.9	13.6	33
Cooling System	0,8	0	0,8	2
Total			41,2	100

How we see from Table 9 and 10 the quality of the energy from the cooling system is quite low.

Tabel .10. Estimated exergy from the furnace 4 at Holla. Raw materials do not include charcoal

Exergy Type	E_{ph}[MW]	E_0 [MW]	E_{ph} + E_0 [MW]	Part[%]
Exergy in Product	2,1	25,6	27.7	64
Exergy in Off-Gas	13,7	1,2	14,9	34.5
Cooling System	0,6	0	0,3	1.5
Total			42.9	100

Figure 8 gives illustration of the exergy flow for the silicon process. The Grassman diagram represents exergy flows for both datasets. The width of the streams represents the amount of exergy in the stream.
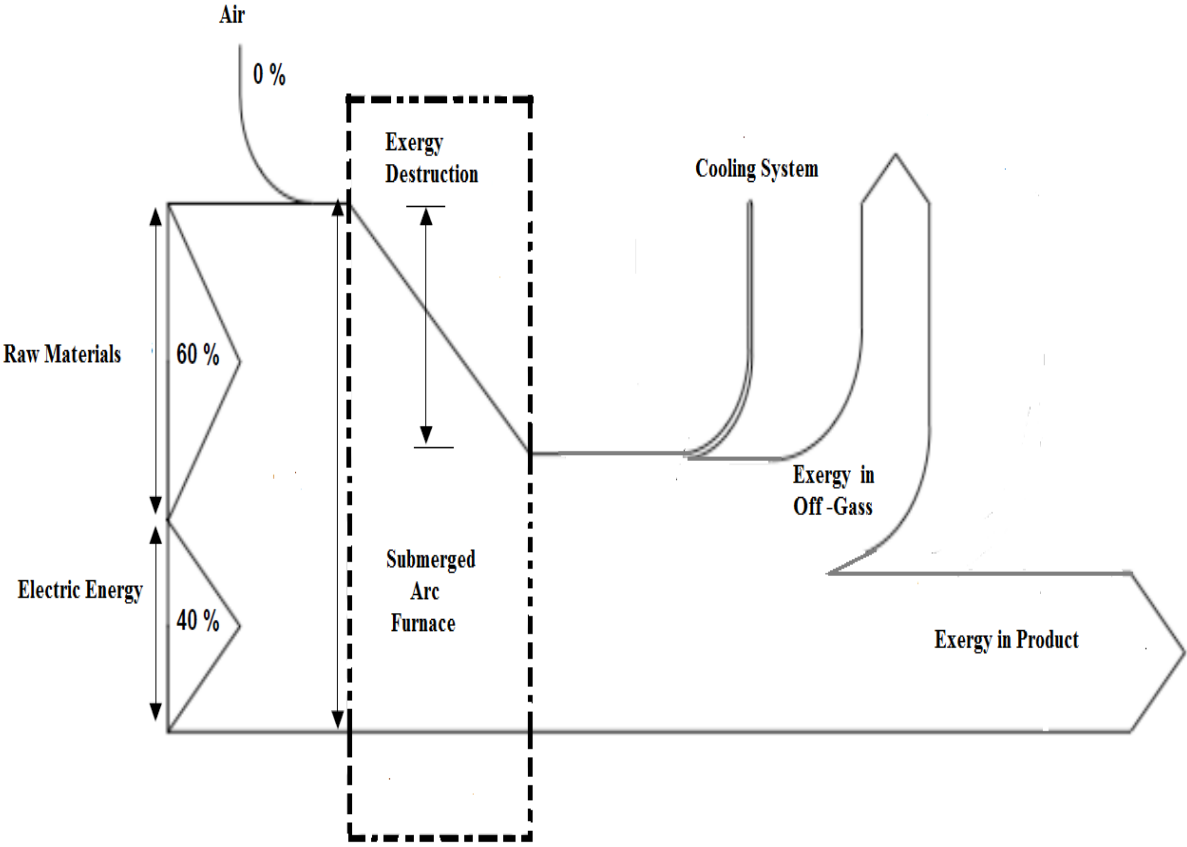

Figure.8. Grassman diagram illustrating exergy flow. The width of the stream presents the amount of exergy in the stream.

Exgery destruction in first analysis is about 39,2 MW and the second one 39.1 MW.

5. Discussion

The production of silicon metal is technically well established [2]. However how we read in *Production of High Silicon Alloys " a new modification is not a gadget that can solve all technical problems*"[2]. One failure may result in poor operation.

Cost reduction of the process is a reason for process modification. This can be accomplished by [2] :

- increased silicon recovery
- lower heat loss
- cheaper raw materials
- cheaper equipment, lower investment per tonne/ year production capacity
- less labour
- lower environmental costs, costs connected to pollutants
- higher value of by-products. the SiO_2 dust recovered from smoke, heat value of exhaust gas
- process more adaptable for control

Until 2006 Holla plant was using charcoal as one of the raw materials component. How ever the last input of raw materials including charcoal took place at week 36 in 2006.
To expensive transport was the decisive factor, which stopped using charcoal. It was as well a step forward new process modifications. How result presented in Chapter 4, this decision did not show any significant deviations or result in poor silicon operation

The real process is involving many energy losses not seen in the theoretical process [25]. The Figure 9 below represents input and output of the silicon process.
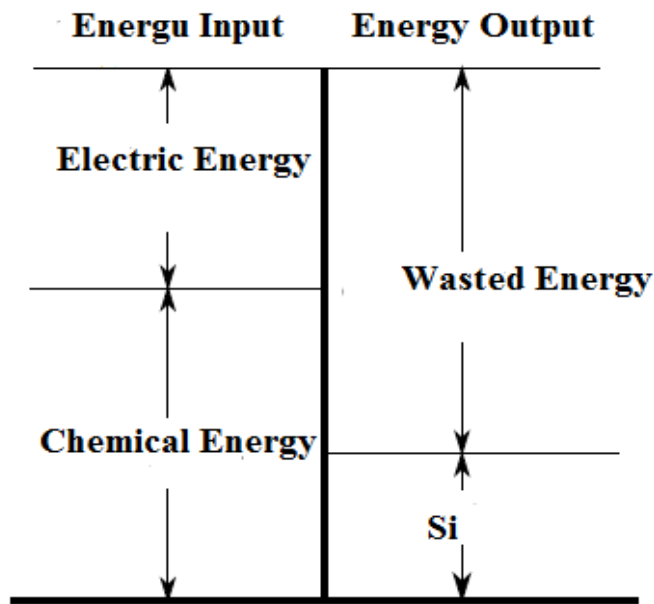
Figure. 9. Sketch of the total energy input and output to the silicon process.

Electrical energy in a 10 MW arc furnace considers for about 45 % of the total energy delivered to the process and chemical energy from raw materials. About 70 % of all energy provided to the process is wasted as a heat into surroundings [2,25].

Available energy is dissipated as thermal energy in the off-gas, in the cooling water by radiation and convection from the furnace and from the cooling process of the liquid silicon [2,25,33]. The heat content leaving the process is equivalent to about 50 % of the total energy input to the process for a 10 MW furnace [33].

In Chapter 5 we will discuss achieved results. Due to results the energy efficiency for silicon process at Holla plant and energy recovery system will be consider.

5.1.A. Energy analysis

Chapter 4 presents estimated input and output energy. It is clearly, that lack of charcoal in raw materials do not affects significantly silicon process. The differences seen in estimated energy from furnace # at Holla are caused by differ load. The measurements were performed at different time and had diverse relative distribution of fixed carbon contribution from the carbonaceous materials.

According to the Tables 5 and 6 we see that furnace gas include most of the heat. Energy consumption is very important factor of the silicon process. Silicon recovery has decisive impact on the energy consumption and exergy how presented in the base case done for theoretical process by Takla. Takla demonstrated results where for a silicon yield of 1, approximately 52,5 % of the total exergy into the process is lost. The total exergy losses increases to 63,6 % for a silicon yield of 0.7 [25].

The total load is 80.4 MW (measurements 2006) and 82MW (measurements 2011) of energy delivered to the furnace. How results shows , only 28.7 MW (measurements 2006) and 30.13 MW (measurements 2011) is returned as chemical energy in the product.
How mentioned early, energy goes off as waste heat. The waste heat is wasted to the environment. However, the wasted heat can be recovered. Chapter 5.3 describes utilization methods.

We see that quality of energy from the cooling system is low. The enthalpy in the cooling water is determined from measured values of flow and the difference between inlet and outlet temperature. How calculations showed it should be consider a different kind of cooling system [11,19].

Possibility to produce silicon at silicon yield 100% is desirable, however only possible in theoretical process. Holla plant is operating at silicon yield 90 %. It is possible to increase silicon yield from 2 to 4% [11]. The most important factor stopping this action is economic factor. Increasing silicon yield will involve extra cost of raw materials. By increasing silicon yield with 1 % the expenses of raw materials will increased about 0,1 %. [11]. Increased silicon recovery will result in need of reduction of silicon losses by using carbonaceous materials with a high reactivity to the $SiO_{(g)}$ [11].

Figure 10 presents example of carbon materials with different SiO reactivity.
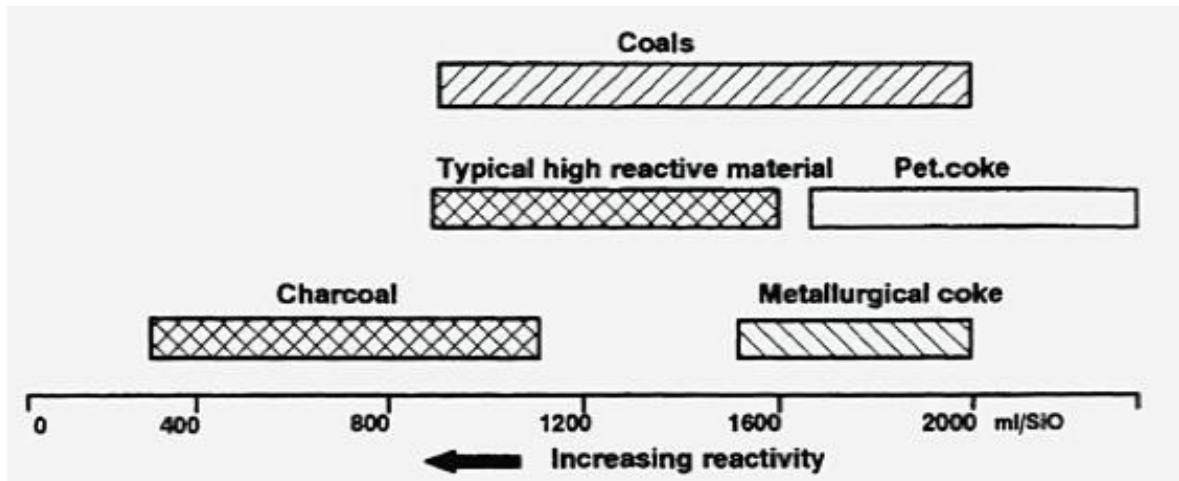
Figure.10. Example of carbon materials with different SiO reactivity. A low number indicates high reactivity in the carbon [2].

Reduced silicon yield will cause following reactions in the real process:

- more energy will be used to produce silica dust
- amount of quartz used in silicon process will increase
- economic consequences

Second important factor in silicon process is the air addition factor. The air addition factor is the factor of ambient oxygen addition relative to stoichiometric requirements. The lowest air addition factor is 1, the highest 20. With the lowest air factor is understand 1 time more oxygen in added air than required for stoichiometric combustion.

Assumptions made, could have influence on the presented results.
Energy losses and inaccuracies have not been taken separately into account. It has not been considered separately in energy balance the lost heat during the tapping and solidification process as well.

The high temperature near furnace is caused by heat convection through the furnace body and due to heat radiation from the furnace top. The heat convection has not been considered in calculations [11].

5.1.B. Exergy analysis

Production of silicon is very energy intensive. Significant amount of electrical energy are requite[14]. Intensive Research and Development (R &D) tried to find compatible solutions for waste minimisation and utilization [15].

The analysis of exergy losses is giving possibilities for improving industrial processes. It is obvious that the amount of useful exergy decreases because of unavoidable irreversibilities [3,10].

The total exergy into the process is due to the electric work and carbon materials delivered to the furnace. The losses in the furnace will be due to chemical reactions and lack of homogeneity of composition in the reaction mixture and temperature gradients in the mass of reactants and products [25,29].

Exergy in the metal leaving the furnace is independent on the silicon yield. However, the exergy flow is depended upon the silicon yield and off –gas temperature [25,29].

The exergy in the gas exiting the furnace will be increasing with decreasing silicon yield. This is according to increasing amount of the gas species CO and SiO. CO and SiO have a high chemical exergy value [25,29].

Combustion is irreversible and spontaneous process, that is why a big fractions of the exergy in the gas treatment section is destroyed [3,10].

The gases leaving the gas treatment section and its thermal exergy are determined by temperature, which is adjusted by the excess of air inlet [25].

The off-gas exergy gives possibility to the potential power production [25]. Power production can be achieved by installation of energy recovery apparatus in the off-gas

system [25]. By increasing the off-gas temperature raises the potential for increasing the overall resource utilization [2, 25,19].

 The width of the stream is illustrating amount of exergy in flows (see Figure 8). Exergy content in the gas and product streams are large. Which agrees with result presented in [25]. Deviation of the width of the exergy streams of the product entering and exiting seen in Figure 8 are due to the thermal exergy loss from product during cooling and solidification. There is heat transfer from the liquid silicon to environment.

Table 7 and 8 presents exergy delivered into the furnace # 4. From Table 9 and 10 which presents all streams exiting the furnace can be notice that exergy from the cooling system is low, approximately 2% of the output. It shows that there is a potential to get higher grade energy from the cooling system [19].

The exergy destruction in the furnace #4 for the first analysis is 39.2 MW and the second one 39.1 MW.

Large exergy destruction shows that it is important to investigate the silicon process to get more reliable results. With regard to thermodynamic analysis, the thermo- ecological cost should be investigated further.

The quality of raw materials used at Holla plant should be characterized in terms of their exergy. Szargut presents the concept of thermo-ecological cost. The thermo-ecological cost are expressing cumulative consumption of the non-renewable exergy per unit of any product considered useful [3,10,16].

There are two groups of unfavourable industrial effects. Mainly, depletion of limited non-renewable resources and rejection of harmful substances [3,10,16]. The depletion of non-renewable resources should be minimised to keep them for future humankind. Exergy can be applied as a measure of the quality of natural resources. The influence of human activities on the depletion of natural resources can be evaluated by means of cumulative exergy calculus [3,10,16].

The following problems can be solved by use the thermo- ecological cost analysis [16]:

- influence of the operational parameters of energy and technological systems upon the depletion of non-renewable natural resources
- selection of the kind of technology that ensures minimal consumption of non-renewable natural resources
- evaluation of harmful impacts of waste products
- optimisation of design and operational parameters to ensure minimum depletion of natural resources
- comparison of sustainably of different useful products

How we see exergy analysis done at Holla plant can be used to thermo-ecological costs analysis. The thermo-ecological cost analysis can result in better operation system by helping with silicon process modification.

However because of lack of the time the thermo-ecological cost for Holla plant has not been done.

Irreversibility

Combustion is a typical irreversible phenomenon. By reducing the thermodynamic irreversibility of chemical reactions gives opportunity to reduce exergy losses [3,37]. By design is possible to run not complete chemical reaction, which will give reduction of exergy losses. However such design require an exergy expenditure to separate and recycle the reagents.

Economic marked is decisive factor is chemical industry. Design is the solution. However it acquires costs [11].

Szargut described every exergy loss as a cause of decreasing in the useful effect of a given process or increased consumption of the means that drive it. Szargut, in one of many publications demonstrate that 65-90% of the exergy losses are due to the thermodynamic irreversibility of chemical reactions. In the separation stages there is only 10-20% exergy losses [3,16].

5.2. Utilization

How Table 5 and 6 shows approximately 64% of the total energy supplied to the silicon process disappear as heat into the surroundings.

Accessible energy is missed as thermal energy in the cooling water and in off-gases. Losses of available energy occurs by radiation and convection from the furnace and solidification process of the liquid process.

No system from recovering the energy lost from solidification process in the casting area at the silicon plant is reported in literature so far [25]. Large exergy destruction shows that it is important to install energy recovery system.

Energy recovery system is a way of increasing the energy efficiency. The available functions for heat recovery are [19]:

- steam generation
- produce electricity: Rankine cycle
- hot water for district heating
- direct use

How Chapter 4 presents the temperatures in the off-gas are high. This make the thermal energy in off-gases qualified for electric energy conversion. Electric energy conversion will occure by usage a steam turbine and generator system.

To convert heat to work, the heat engine is needed. There is theoretical possibility for the furnace gas to be led through a Brayton-Cycle or the Rankine cycle [12].

The difference between Brayton and Rankine is "inside" the engine. In a Brayton cycle, the working fluid is a gas all the time; in a Rankine it changes phase. But in both cases the working fluid receives heat from the furnace gas in a heat exchanger. Gas is contaminated. Thus the dirty gas is a problem for Brayton, as well for Rankine [12].

However the purity of the gases is mainly not relevant for the comparison between Brayton

and Rankine. A small reservation is that the material temperature of the heat-exchanger for a gas/gas heat exchanger (i.e. Brayton) will be higher than for a gas/liquid heat exchanger (evaporator inn Rankine), and then the material might be more vulnerable for erosion (particles in furnace gas) and corrosion [12].

In any coal-fired power plant, the power cycle (usually Rankine) will receive heat from dusty and corrosive flue gas. Cleaning of the flue gas is usually at the end, after the heat exchangers. However this solution is impossible at Holla plant [12].

From thermodynamic point of view the best way to recovery heat is to utilize it for heating purposes like [19]:

- agriculture
- fish farming
- heat for greenhouse
- steam generation for industry
- hot water generation for district heating

The heat from the cooling system can be used to utilize the heat from the furnace. The heat from cooling system will preheat the water and then a heat exchanger with the furnace gas to heat the water up to the temperature needed. Figure 11 presents a schematic setup.
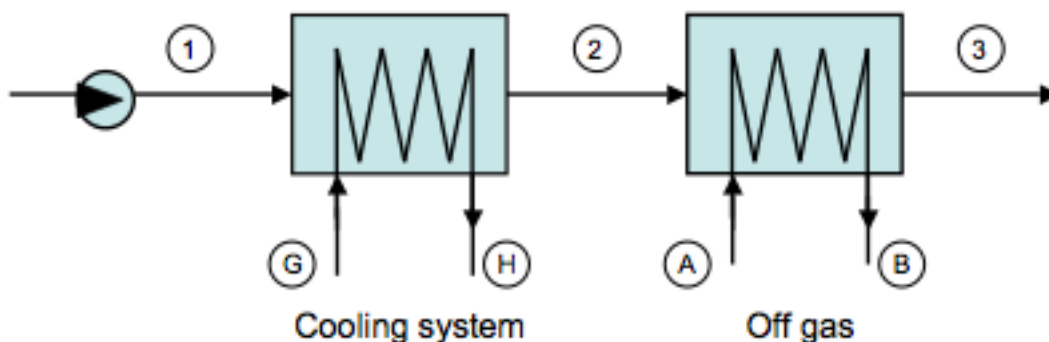

Figure.11. Schematic setup of steam and hot water production[19].

Solution presented above and in [19] are simple solutions. However economy factor has a decisive impact.

6.3. Calculation errors

The energy and exergy analysis contain errors. The data collect from Holla plant differ on many factors:

- data collected to first analysis are from 2006 and include charcoal, data to the second analyse are collected from 2011 do not include charcoal

According to mass, energy and exergy balance many factors during the silicon process could have influence on results. Some of them are enumerate below [11].:

- there was different input of air in both process
- the supplied electrical energy is variable
- chemical energy of the carbonaceous materials will be in a small degree different due to inconsistencies in the supply
- temperature and off gas composition will also vary due to changing conditions
- required maintenance
- operation problems
- inhomogeneity of raw materials used in the process is difficult to track. Undetected variations in the water content can give operational problems. The important ratio between quartz and chemically active free carbon (Fix-C) can be missed out [2,6].

The main errors come from incomplete data measurements. Another affecting analyse factor is varying process conditions. The heat content of the gases might easily change. The analysis of silicon process should be performed a longer time period. This can provide to more accurate data.

CONCLUSION

The main focus of this master thesis is energy and exergy analyse of the Holla silicon plant.

We use word energy for the different kinds of energy characterized with a high quality. The quality of energy is defined by means of exergy, exempt from the law of conservation. For the reduction of exergy losses it should be reached the limits of economic profitability and technological possibilities. The exergy knowledge gives possibility of improvement in the design of energy process [3].

The energy analysis presented in this study shows that much of the energy used in the silicone process leaves out to the environment as waste heat.
Result shows that approximately 37% of the energy supplied to the process is getting back as chemical energy in the product. Which means at rest of the heat is wasted.

The analyses of silicon metal production involves large energy destruction which is approximately 39.2 MW , which is 50 % of exergy supplied. This thesis showed that the largest exergy losses are in the gas treatment section.
How expected it can be beneficial to recover thermal exergy in the off-gas.

By exergy analyzing each component in a silicon process it can be possible to find out where the main focus on improving the system should be put. This can help to make correct design decision. Exergy studies are answering for the question where the system and process can be more efficient. By this we do understand determining the types and locations of losses and waste [10,12].

Appendix A

<u>SILICON PRODUCTION AT HOLLA PLANT</u>
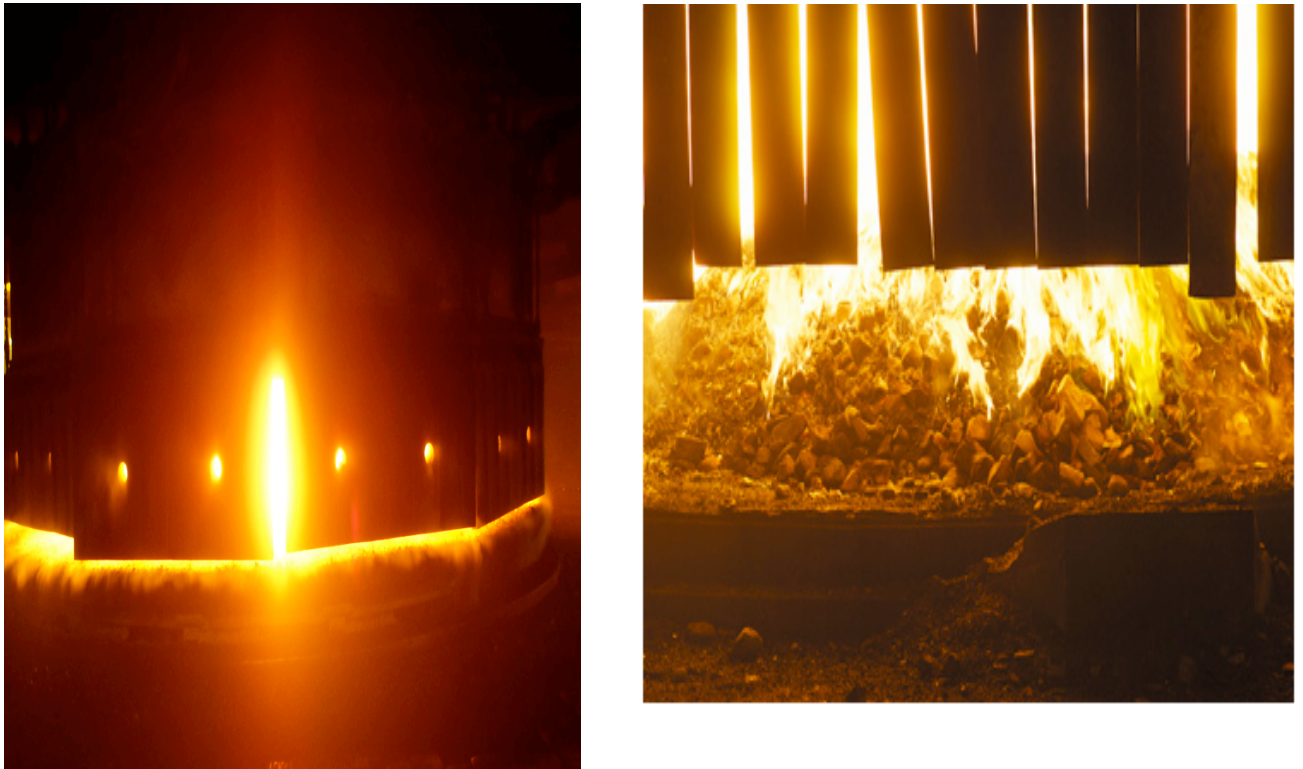
Figure A.1.   The mixed raw materials are delivered to the furnace where the rock-hard quartz starts to melt. The main input to the process is one or more quartz types and carbon materials [21].
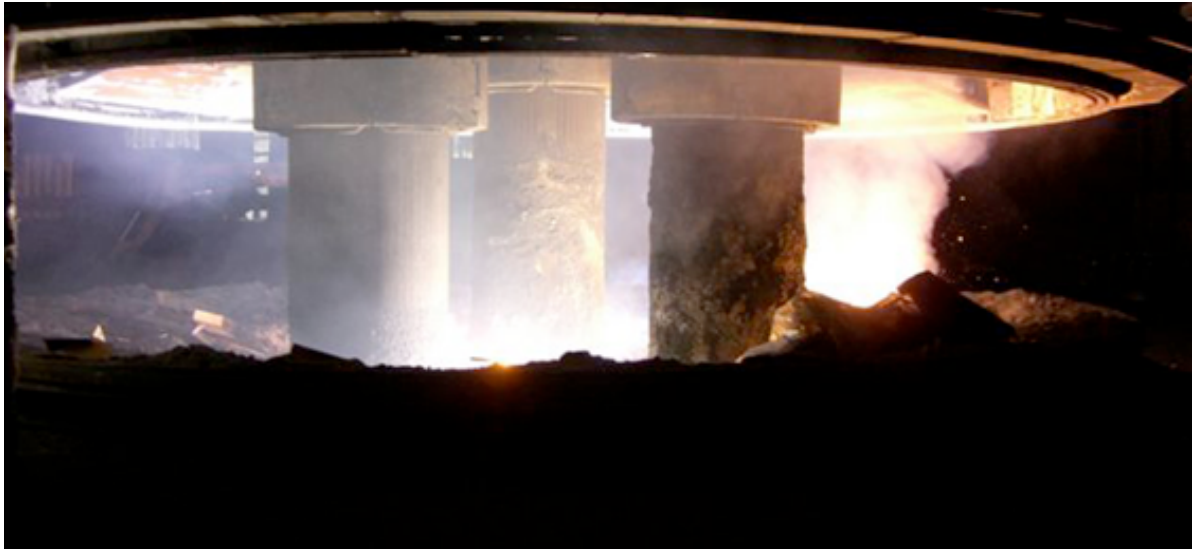
Figure.A.2. Electrode used during silicon process [21].

Figure.A.3. The carbon in the coal removes the two oxygen atoms from the quartz-leaving liquid metallurgical-grade silicon [21].

Figure.A.4. Liquid silicon metal flows out of ladles onto a bed of silicon sand, where it can cool and solidify [21].

Figure. A.5. Liquid silicon, which after cooling will be taken to the crusher [21].

Appendix B

Elsa electrode

The main quality, which differs Elsa electrode from other types of electrode is a structure. The structure let a detailed analysis of the breakages to be carry out.

The Elsa electrode is compound electrode how mentioned in Chapter 2.1 A satisfactory furnace operation depends on a proper electrode performance. Schematic drawing below is illustrating a two-dimensional model for Elsa electrode.
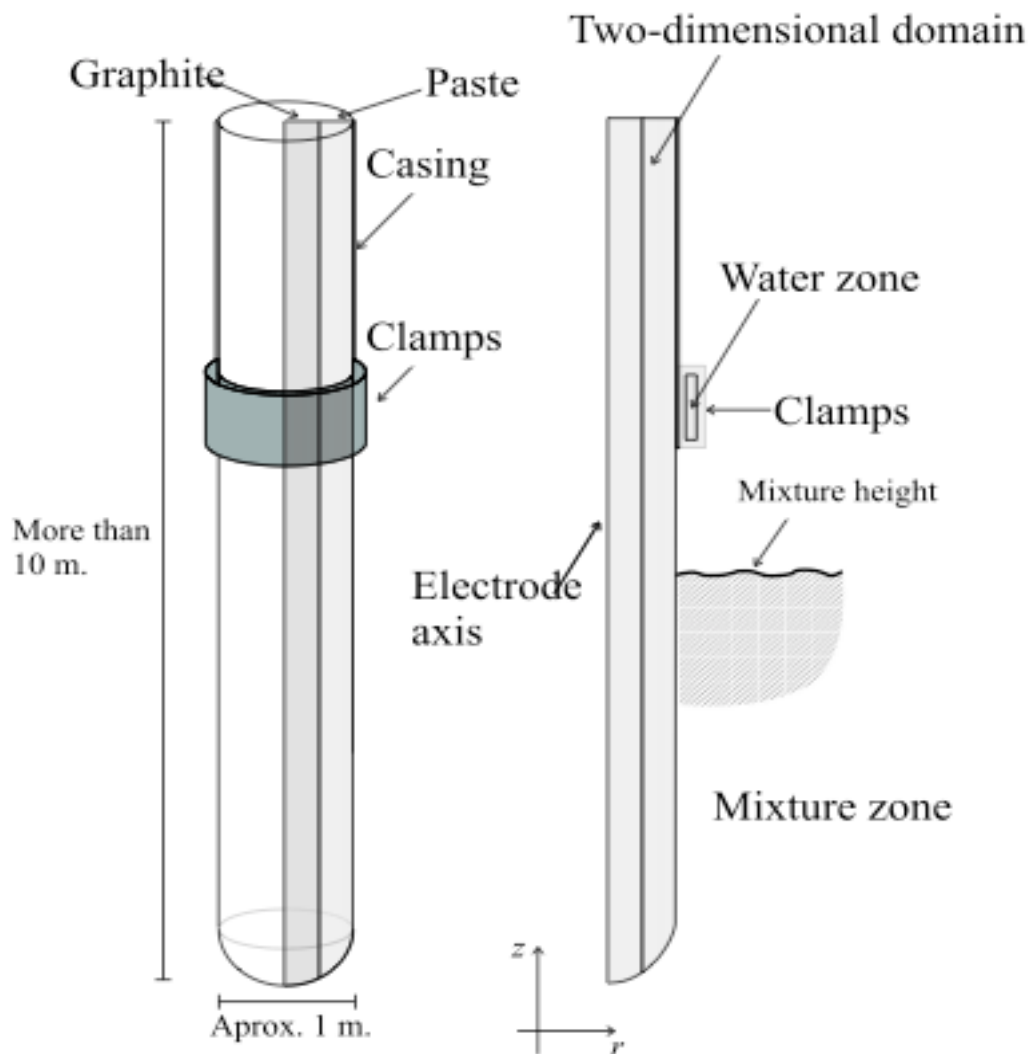
Figure.B.1. Sketch of the two-dimensjonal model for Elsa electrode [34].

The paste is baked in the contact clamps zone. The paste baking should be a continuous process for successful operation. The paste is baked in the contact clamps (see Figure). The temperature of the process is between 100°C and 500°C. In clamps zone the paste will suffer several changes of state. The baking of the paste is closely related to the electrode current and slipping rate [34].

The electrode has to be moved smoothly downwards to counterbalance its consumption on the tip. The movement of the electrode has to be done in small increments. It is important to avoid breakages in the soft paste [34]. The figure below shows schematically normal operation. The baking zone is stabilized within the lower part of the holder [34].
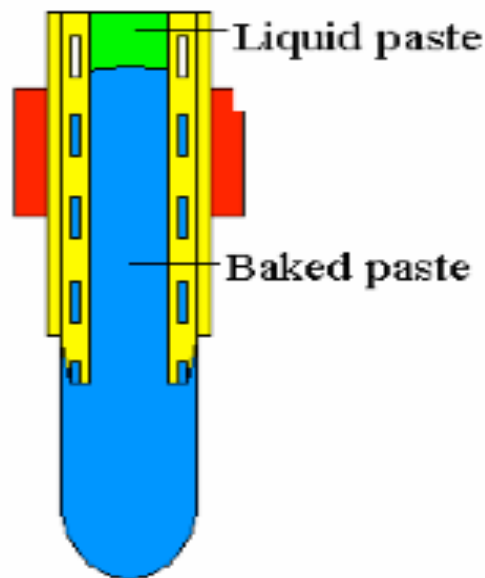
Figure.B.2. The illustration presents "normal situation" during the silicon process. Position of the baking paste is not affected [29].

If the baking paste comes below the clamps it can cause a leakage of soft paste [34]. The leakage of the paste will cause movement of the lower part of the electrode into the furnace pot. This will result volatiles and paste will catch the fire.

That is why relation between the electric current and the slipping ratio should be known. The other parameters like temperature in the surroundings, of the cooling water, properties of paste should be known [34].

APPENDIX C

<u>**Measurements**</u>

 Appendix C   presents calculation done on data collected from Holla plant.

Silicon process flow can be divided into three main parts described in Chapter 4.

The commercial silicon production is based on the submerged arc furnace (SAF)

The calculation used in energy and exergy analyse are based on reaction presented below.

$$SiO_2 + 2C \rightarrow Si + 2CO_{(g)} \qquad\qquad\qquad\qquad [C\text{-}1]$$

$$SiO_2 + C \rightarrow SiO_{(g)} + CO_{(g)} \qquad\qquad\qquad\qquad [C\text{-}2]$$

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO_{(g)} \qquad\qquad\qquad\qquad [C\text{-}3]$$

$$Al_2O_3 + 3C \rightarrow 2Al + 3CO_{(g)} \qquad\qquad\qquad\qquad [C\text{-}4]$$

$$CaO + C \rightarrow Ca + CO_{(g)} \qquad\qquad\qquad\qquad [C\text{-}5]$$

$$TiO_2 + 2C \rightarrow Ti + 2CO_{(g)} \qquad\qquad\qquad\qquad [C\text{-}6]$$
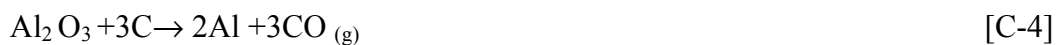
The thermodynamic model in HSC will represent each process. This will provide a large number of energy distribution.

 Eq. C.1-2 are primary reactions for the silicon process. The other oxides, which are in the process as ash in carbon materials or lime stone are considered to be reduced according to Eq. C.3-C.6. within the furnace.

 The fractions of elements, which do not end up in the metal, are considered to be oxidized back to the original oxides with atmospheric oxygen. Oxidation take place above the furnace charge[11, 31].

Raw materials go inside the furnace. However carbonaceous volatiles go directly to combustion at the surface. It is necessary to define the composition of volatiles due to HSC calculation [11,31].

The elemental analysis described [30] is used as basis to define the elemental make up. This is described in the model as Vol C (the carbon content), $H_{2(g)}$, $O_{2(g)}$, $N_{2(g)}$ and S.

Using the silicon recovery, the amount of quartz required can be calculated. By relating with the relative contribution of fixed carbon, the stoichiometric amount of carbon required for Eq. C-1 through C-6 is defined [11,31].

So the furnace gas composition is calculated as the remainder of all elements/compounds not part of the metal.

The elements/compounds of the process gas and volatiles are combusted according to Eq. C-7 through C-14, whereas nitrogen and argon are considered inert.

$$2SiO_{(g)} + O_{2(g)} \rightarrow 2SiO_2 \qquad\qquad [C\text{-}7]$$

$$4Fe + 3O_{2(g)} \rightarrow 2Fe_2O_3 \qquad\qquad [C\text{-}8]$$

$$4Al + 3O_{2(g)} \rightarrow 2Al_2O_3 \qquad\qquad [C\text{-}9]$$

$$2Ca + O_{2(g)} \rightarrow 2CaO \qquad\qquad [C\text{-}10]$$

$$Ti + O_{2(g)} \rightarrow TiO_2 \qquad\qquad [C\text{-}11]$$

$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)} \qquad\qquad [C\text{-}12]$$

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O \qquad\qquad [C\text{-}13]$$

$$S + O_{2(g)} \rightarrow SO_2 \qquad\qquad [C\text{-}14]$$
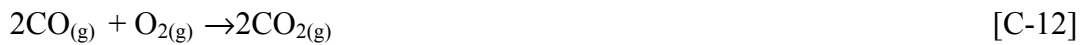
The Table 11 presents composition calculated for input and output for silicon process. Data are collected from week 36 in 2006. This was the last time Holla plant used a charcoal as one of the components of raw materials. At that time Holla used coke, coal, charcoal and woodchips, which are carbon source in composition 25 % each.

 How mentioned in Chapter 4 one of the process modification is cost reduction. One of the process modifications done at Holla plant was decision of buying cheaper raw materials. That is why charcoal has been stopped use in 2006. However the charcoal is used occasionally by Holla plant.

Table.11. Composition calculated, which is a base for further calculations. Raw materials include charcoal. Data are collected from week 36 in 2006.

	QUARTZ	COKE	CHARCOAL	COAL	WOODCHIPS	LIME-STONE	AIR	METAL	DUST	GAS
									OUTPUT	
H_2O		10	50	10	100					3,14
FixC		91.26	77.76	59.23	12.59					
VolC		4.43	11.2	24.6	38.01					
H_2		0.45	0.93	5	6.18					
O_2		0.97	5.59	4.9	43		24			18.64
N_2		0.83	2.65	1.3	0.06		76			73.65
S		1	0	3.25	0.02					
Fe_2O_3		0.296	0.56	0.28	0.08				0.12	
Al_2O_3		0.5	2.18	0.34	0.01	10			0.643	
CaO		0.07	0.34	0.15	0.035	50.43			8.54	
TiO_2		0.021	0.08	0.02	0.01				0.023	
SiO_2	100								90.67	
Si								98.29		
Fe								0.286		
Al								0.689		
Ca								0.7		
Ti								0.035		
CO										7.35
CO_2						39.57				
Ar										1.32
SO_2										0.05

Table 12 presents data from week 52 (year 2011) collected from Holla plant . Charcoal is not included in raw materials. The percentage division is as follow: 4 % of woodchips, 7% coke and the rest 89 % coal. This percentage division is speciality of Holla plant.

 After consultation with Holla personnel the data presented in Table12 for limestone and woodchips are the same as in Table 11.

How said earlier the contribution from electrode is not included. After consultation it was decided that contribution from electrode has not decisive influence on energy and exergy analysis.

Table.12. Composition calculated, which is a base for further calculations. Raw materials do not include charcoal. Data are collected in week 52

		INPUT					OUTPUT		
	QUARTZ	COKE	COAL	WOODCHIPS	LIME-STONE	AIR	METAL	DUST	GAS
H_2O		11	12	100					3,11
FixC		89.56	59.78	12.59					
VolC		4.36	25.4	38.01					
H_2		0.43	5	6.18					
O_2		0.98	4.8	43		24			17.96
N_2		0.88	1.1	0.06		76			71.65
S		1	0.38	0.02					
Fe_2O_3		0.13	0.135	0.08				0.08	
Al_2O_3		0.11	0.31	0.01	10			0.94	
CaO		0.78	0.1	0.035	50.43			8.61	
TiO_2		0.012	0.0.012	0.01				0.02	
SiO_2	100							92.67	
Si							98.39		
Fe							0.296		
Al							0.689		
Ca							0.6		
Ti							0.025		
CO									8.35
CO_2					39.57				
Ar									1.37
SO_2									0.06

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